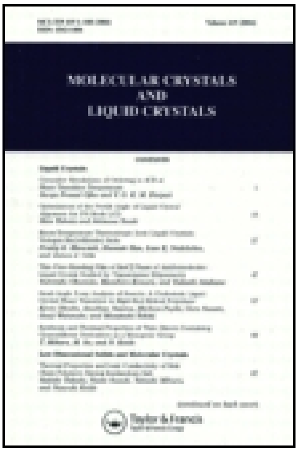

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Liquid-Crystalline Behavior and Photoluminescence Properties of Gold(I) Complex: Relationship between Aggregation Structure and Properties

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Version of record first published: 02 Aug 2012.

To cite this article: Kaori Fujisawa, Yuichi Izumi, Akira Nagamatsu, Kenjiro Uno & Osamu Tsutsumi (2012): Liquid-Crystalline Behavior and Photoluminescence Properties of Gold(I) Complex: Relationship between Aggregation Structure and Properties, Molecular Crystals and Liquid Crystals, 563:1, 50-57

To link to this article: http://dx.doi.org/10.1080/15421406.2012.688615

Mol. Cryst. Liq. Cryst., Vol. 563: pp. 50–57, 2012
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.688615

Liquid-Crystalline Behavior and Photoluminescence Properties of Gold(I) Complex: Relationship between Aggregation Structure and Properties

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*Liquid-crystalline (LC) behavior and photoluminescent properties of a gold(I) complex, **2** were investigated. It was confirmed that the complex showed enantiotropic LC phases. In addition, we found that the complex showed strong photoluminescence in the condensed phases, but no luminescence was observed in a dilute solution. The single-crystal X-ray structure analysis suggested that the complex formed dimer in the condensed phases and the dimer formation plays crucial role in both LC behavior and photoluminescent properties.*

Keywords Aggregation-induced emission; aurophilic interaction ; gold complex; liquid crystal; photoluminescence

1. Introduction

Molecules containing Au(I) atoms exhibit strong photoluminescence in condensed phases owing to the aurophilic interaction between intermolecular Au–Au atoms, and their strong luminescence is interesting in applications for photo-electronic devices, chemical sensors, and so on [1]. When the interatomic distance between Au–Au atoms is shorter than the van der Waals distance, ~3.6 Å, new bonding between these atoms are formed due to the aurophilic interaction, and their binding energies are as large as those of hydrogen bonding [1, 2]. Therefore, the aurophilic interaction was utilized for the formation of supramolecular assemblies. As mentioned above, one of the important futures of the aurophilic interaction is that they can bring about luminescence of the complexes in the condensed phases.

Because the luminescence was emitted from the molecular aggregations based on the aurophilic interaction, properties of the luminescence, such as color, intensity, polarization, and so on, from the aurophilic interaction depends on the aggregation structures. For example, reversible mechanochromic photoluminescence has been observed in $(C_6F_5Au)_2(\mu$-1,4-diisocyanobenzene) [3]. In this complex, mechanical grinding of the crystal induced a

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change in color of luminescence as well as the aggregation structures. Namely, this phenomenon suggests that the emission properties of gold complexes strongly depend on the aggregation structure.

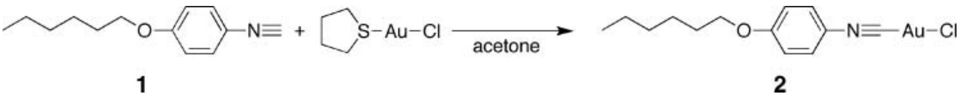
Liquid crystals (LCs) are one of the self-organized materials. The characteristics of LCs are ordered structure, fluidity, and responsivity to external stimulus (electronic field, light, and so on) [4]. Some of gold complexes having rod-like structure showed LC phase [5]. On the contrary, Coco *et al.* reported that (μ-1-isocyano-4-hexoylbenzene)AuCl, which has an asymmetric non-rod-like structure, showed smectic (Sm) LC phase [6].

The aggregation structure of the LC gold complexes can be readily controlled, because the LC phase structure, namely aggregation structure, can be controlled with external stimulus. Hence, the luminescence properties of the materials might be tunable by the use of LC gold complexes. In this study, thus, we synthesized gold complexes, **2**, with isocyanide ligand, observing their LC natures and luminescence properties to discuss the relationship between aggregation structure in the condensed phase and those properties.

2. Experimental

Materials

The structure of the gold complex, **2**, used in this study is shown in Scheme 1. The scheme also shows the synthetic route for this complex. In the preparation of the complex, all solvents and reagents were of reagent quality, purchased commercially, and used without further purification, except as noted otherwise. ^{1}H NMR spectrum was recorded on a JEOL ECS-400 (400 MHz) spectrometer. The chemical shifts are reported in parts per million (ppm) using the residual proton in the NMR solvent as an internal reference. MALDI-TOF mass spectra were measured on Bruker autoflex II instruments with dithranol (Aldrich) as a matrix. Ligand **1** was synthesized according to reported procedures [6].



Scheme 1.

Synthesis of gold complex **2** [6]. Ligand **1** (90.2 mg 0.44 mmol) and (thetrahydrothiophene)AuCl (150 mg, 0.45 mmol) were suspended in 15 mL of acetone and the suspension was stirred for 2 h. The reaction mixture was filtrated and the filtrate was recrystallized from acetonitrile to give compound **2** (167 mg 0.38 mmol) in 87% yield. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.43 (d, 2H, $J = 8.7$ Hz, CH in aromatic), 6.93 (d, 2H, $J = 8.7$ Hz, CH in aromatic), 3.98 (t, 2H, $J = 6.4$ Hz, -OC$\underline{H}_2$), 1.78 (quintet, 2H, $J = 7.6$ Hz, -OCH$_2$C$\underline{H}_2$), 1.44 (m, 2H,-OCH$_2$CH$_2$C$\underline{H}_2$), 1.28–1.39 (m, 4H, -(C$\underline{H}_2$)$_2$CH$_3$), 0.89 (t, 3H, $J = 6.8$ Hz, -C$\underline{H}_3$). MALDI TOF–MS (*m/z*): $[M + H + K]^+$ calcd for $C_{13}H_{17}AuClKNO$, 474.03; found, 474.07.

Phase Transition Behavior

LC behavior of the complex was observed by polarizing microscopy (Olympus, BX51) equipped with a hot–stage (Instec, HCS302 hot-stage and mK1000 controller). Thermodynamic properties of LCs were determined with differential scanning calorimeter (DSC, Perkin Elmer, Diamond DSC) at a heating and cooling rate of 1.0°C/min. At least three scans were performed to check reproducibility. X-ray powder diffraction (XRD) experiments were carried out with Rigaku Ultima IV, XRD-DSC II.

Photophysical Property

UV-visible absorption and steady-state photoluminescence spectra were recorded on a JASCO V-550 absorption spectrophotometer and on a Hitachi F-7500 fluorescence spectrophotometer, respectively.

X-Ray Crystallography

Single crystals were obtained by slow evaporation from dichloromethane/ethyl acetate (1/2) solution. The single crystals obtained were subjected to X-ray diffraction experiment. A single crystal of **2** was mounted on a glass fiber, and reflection data were measured by ω–scan technique on a Rigaku automated four-circular-axis diffractometer AFC-5R with graphite monochromatized Cu Kα radiation ($\lambda = 1.54178$ Å). The measurement was carried out at room temperature (296 K). The initial structure of **2** in the unit cell was determined by a direct method using SIR92 [7]. The structure model was refined by full-matrix least-squares methods using SHELXL97 [8]. All calculations were performed on the crystallographic software package WinGX [9]. Obtained crystallographic data are summarized in Table 1.

3. Results and Discussion

LC Behavior of Au(I) Complex

It was observed with a polarizing optical microscope that gold complex **2** showed enantiotropic LC phases (Fig. 1): for example, a typical optical texture for smectic (Sm) phase

Table 1. Crystallographic data of **2** obtained from X-ray diffraction experiments

Empirical Formula	$C_{13}H_{17}AuClNO$
Formula Weight	435.70
Temperature	296 K
Crystal Color, Habit	Colorless, Block
Crystal Dimensions	0.69 × 0.08 × 0.06 mm
Crystal System	Monoclinic
Space Group	$P21/a$
Z	8
a (Å)	20.744 (2)
b (Å)	7.279 (3)
c (Å)	21.511 (3)
α (deg)	90
β (deg)	116.686 (8)
γ (deg)	90
V (Å^3)	2902.1 (13)
$R\ [F^2 > 2\sigma(F^2)]$	0.043
$wR(F^2)$	0.122
S	1.09

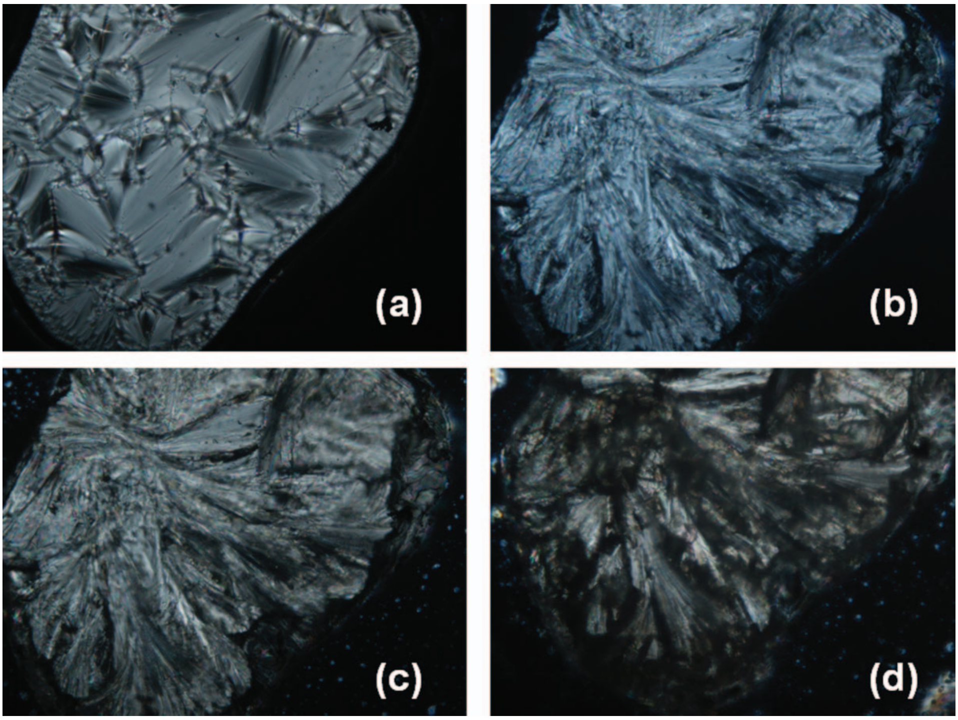


Figure 1. Polarizing optical micrographs of complex **2** observed in cooling process: (a), at 166°C; (b), at 110°C; (c), at 94°C; (d), at 41°C.

was observed at 166°C (Fig. 1a). Figure 2 shows DSC thermogram of complex **2**. In the heating process, four endothermic signals were observed in the DSC thermogram. From both results, we determined that the material showed Sm phase between 124°C and 166°C and the endothermic signal at 166°C in the DSC thermogram is attributable to the clearing

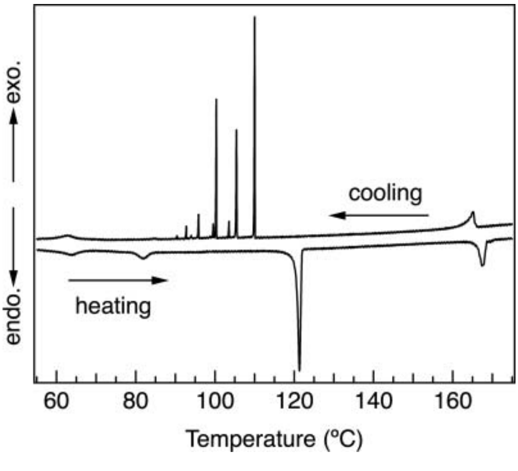


Figure 2. DSC thermogram of complex **2**. The scan rate was 1°C/min.

point. At present, however, other endothermic signals observed in the heating process of DSC cannot be assigned. In the cooling process, complex **2** showed much more complicated phase transition behavior. After the Sm phase was observed between 166°C and 117°C, a lot of unassigned exothermic peaks appeared in the thermogram.

The molecular shape of complex **2** is different from those of typical LC molecules: typically the shapes of the LC molecules are rod- or disc-like, but it seems that the molecular shape of complex **2** is not the case for those shapes. To clarify the actual structure of complex **2** in the condensed phase, we performed the single crystal X-ray structural analysis. The molecular structure obtained by the single crystal X-ray diffraction experiment is shown in Fig. 3. The crystallographic data were also surmised in Table 1.

In the crystal, interatomic distance between Au–Au atoms of neighboring molecules was 3.4 Å. When the distance between Au atoms is shorter than the sum of van der Waals radii of two Au atoms, ~3.6 Å, new intermolecular bonding is formed due to aurophilic interaction [10]. Therefore, the result clearly indicates that the between those two molecules the intermolecular bonding was formed by the aurophilic interaction, namely, the molecules formed a dimer in the crystalline phase. In addition, the interatomic distance between H and Cl atoms in the neighboring molecules are also shorter than the van der Waals distance, suggesting that complex **2** formed intermolecular CH/Cl hydrogen bonding (Fig. 3b). This fact also supports the formation of the dimer in the crystalline phase. As shown in Fig. 3a, the dimer has a symmetric rod-like structure. We suppose the complex forms the same dimer structures in the LC phases, and then complex **2** showed LC phases even if the

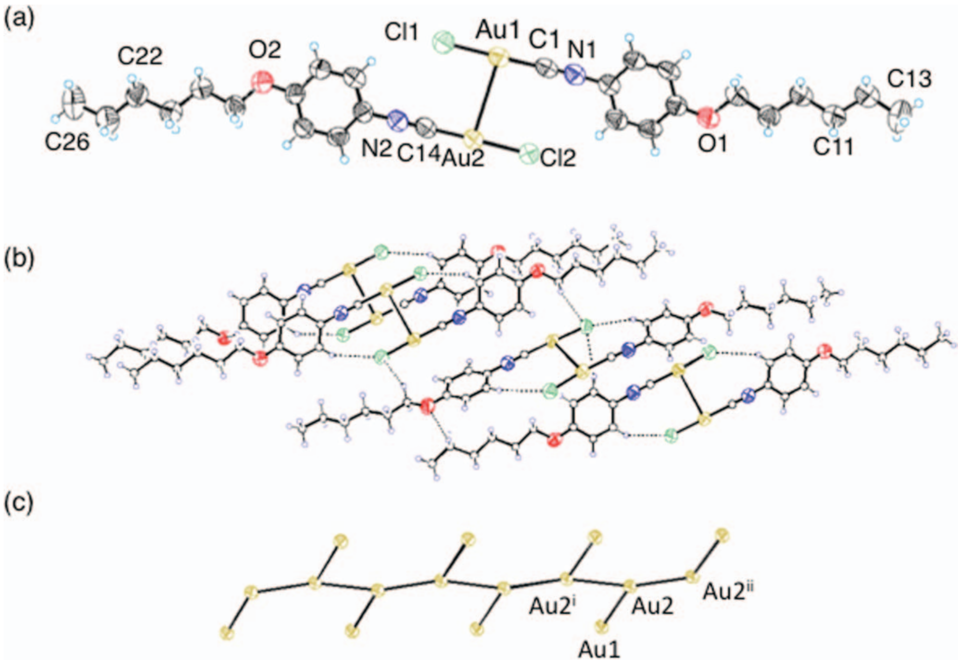


Figure 3. Structure of complex **2** determined by X-ray structure analysis. (a), ORTEP view of the dimer structure. (b), Crystal packing structure of **2**. CH/Cl hydrogen bond is indicated with dashed lines. (c) Lateral aggregation structure of **2** (only gold atoms were shown for clarity). The distance between Au–Au atoms are: Au1–Au2 = 3.3810(5), Au2–Au2$^{\mathrm{i}}$ = 3.72436(0), Au2–Au2$^{\mathrm{ii}}$ = 3.68900(0) Å, respectively.

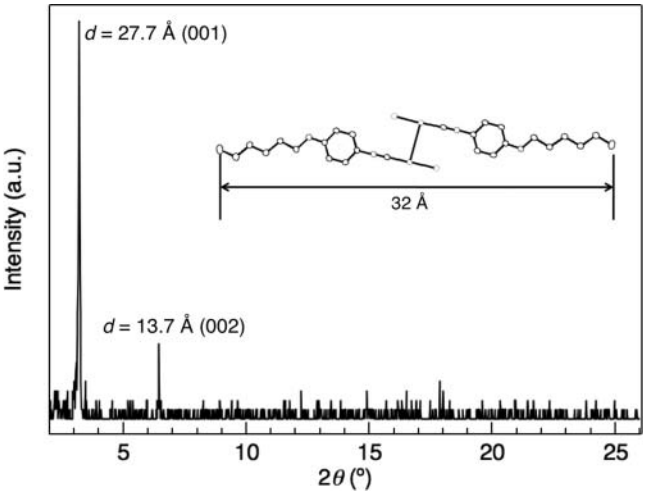


Figure 4. XRD pattern of complex **2** at 130°C in heating process. Inset in the figure shows the molecular structure of the dimer at 20°C and its molecular length obtained from the single crystal X-ray analysis.

monomer is not rod-like structure. Furthermore, the Au–Au interatomic distance between unit dimers is 3.7 Å (Fig. 3c). From this result, we consider that the lateral interaction acts between the dimers. When the lateral intermolecular interaction acts, the molecules tend to form the layer structures. We consider that this is the reason why complex **2** shows the Sm phase.

The LC phase structure was also observed by XRD, and the diffraction pattern at 130°C on heating process was shown in Fig. 4. The XRD pattern clearly indicated that the complex showed the Sm phase with the inter layer spacing (*d*) of 28 Å. A head to tail length of the dimer was 32 Å, which was obtained by single crystal X-ray structure analysis at 20°C (Fig. 5 inset). The observed *d*-spacing was roughly in agreement with the length of the dimer of the complex. We can safely conclude, therefore, that the complex **2** formed the dimer also in the LC phase and the dimer showed Sm A phase. We consider that the small difference between the *d*-spacing and the length of dimer is due to the difference in temperature.

Photophysical Property of Au(I) Complex

Figure 5 shows absorption and photoluminescence spectra of complex **2** in a dichloromethane solution and in the crystal at room temperature. In the dilute solution (10^{-4} mol/L), an absorption band appeared at ~280 nm (Fig. 5a, 1). The complex exhibited strong photoluminescence in the crystalline state (Fig. 5a, 3). As shown in Fig. 5b, however, only week photoluminescence was observed in the concentrated solution (~10^{-2} mol/L), and the complex showed no luminescence in the dilute solution (~10^{-6} mol/L). Generally, luminescent chromophore (luminophore) can emit more efficiently in dilute solutions, and the emission is quenched in concentrated solutions or in condensed phases due to the concentration quenching effect. On the other hand, complex **2** show the opposite behavior; the intensity of the emission of this complex become stronger with increasing the concentration of solutions and the strongest emission was observed in the crystalline state. In the complex containing Au(I), since the luminescence is emitted from the excitation states

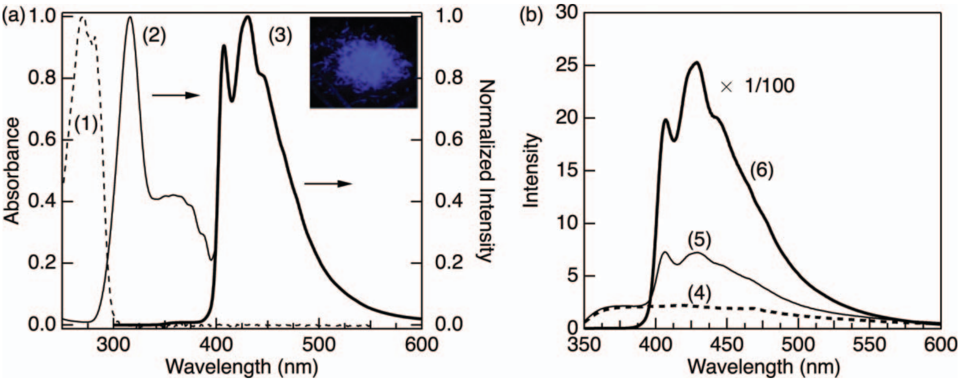


Figure 5. Absorption and photoluminescence spectra of complex **2**. (a), Absorption spectrum in dichloromethane solution (1: 2.3 × 10^{-4} mol/L), normalized excitation spectrum in crystal (2: $\lambda_{em} =$ 430 nm), and normalized photoluminescence spectrum in crystal (3: $\lambda_{ex} = 310$ nm). (b), Photoluminescence spectra ($\lambda_{ex} = 310$ nm) in dilute dichloromethane solution (4: 1.4 × 10^{-2} mol/L), in concentrated dichloromethane solution (5: 2.3 × 10^{-6} mol/L), and in crystal (6). Inset in figure (a) is photograph of crystal of complex **2** taken under illumination of a UV lamp at 254 nm.

caused by the aurophilic interaction, the intensity, *i.e.* quantum yield, of photoluminescence is much greater in the condensed phase. Complex **2** formed the dimer in the crystalline phase by the aurophilic interaction as shown in Fig. 3a, thus we conclude that the crystal of **2** emitted the photoluminescence owing to the aurophilic interaction. The shape of the luminescence spectrum of concentrated solution (~10^{-2} mol/L) was roughly the same as that in the crystalline phase (Fig. 5b). Even in the solution, the complex formed the dimer with the same structure in the crystalline phase, so that we can conclude the luminescence in the concentrated solution was also due to the aurophilic interaction. However, in the dilute solution (~10^{-6} mol/L), the concentration is too low to aggregate, and no luminescence was observed. Those results mean that the luminescence observed form complex **2** is "aggregation-induced emission" (AIE) [11]. The shape of the excitation spectra of **2** in the crystal was quite different from its absorption spectra in the dilute solution (Fig. 5a). This result also supports the luminescence was emitted from the aggregations. We also confirmed that the strong photoluminescence with the same spectral shape was also appeared in the LC phase in complex **2**.

Conclusion

In this study, we synthesized complex containing Au(I) and investigated its LC and photophysical properties. Different from conventional luminescent materials, the complex show strong photoluminescence in the condensed phases (crystalline and LC phase) owing to the aurophilic interaction. This future of complex **2** is very favorable for the practical application to luminescent devices, *e.g.* electroluminescence (EL), and so on. Because those materials should be used in the condensed phases in the devices, the materials are required to show luminescence with high quantum yields in the condensed phases. In addition, since the luminescence was based on the intermolecular interaction, we expect that the luminescence properties can be controlled by aggregation structures.

Acknowledgment

This work was supported by the Sasakawa Scientific Research Grant from the Japan Science Society (KF), a Grant-in-Aid for Young Scientists (B) from the Japan Society for the Promotion of Science (21710094, OT), A-STEP from the Japan Science and Technology Agency (AS231Z04286D and AS232Z01430C, OT), and a scientific research program from the Ritsumeikan Global Innovation Research Organization (R-GIRO). The research was also technically supported by the Kyoto-Advanced Nanotechnology Network (Nara Institute of Science and Technology). We thank Dr. Jun-ichi Mamiya and Prof. Atsushi Shishido (Tokyo Institute of Technology) for the XRD measurement.

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