Tuning the photoluminescence of condensed-phase cyclic trinuclear Au(I) complexes through control of their aggregated structures by external stimuli

Kaori Fujisawa*, Shigeyuki Yamada, Yukihiro Yanagi, Yasunori Yoshioka, Ayumi Kiyohara & Osamu Tsutsumi

Department of Applied Chemistry, College of Life Sciences, Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu 525-8577, Japan.

A series of new cyclic trinuclear Au(I) complexes with alkoxy side chains of various lengths were synthesized as photoluminescence materials. None of the complexes emitted luminescence in solution; however, some showed photoluminescence in the crystalline phase. Single crystal X-ray structural analyses revealed that an intermolecular interaction between two Au atoms (aurophilic interaction) existed only in the emissive complexes, which formed molecular aggregates in the crystal. Because isolated molecules show no luminescence in the present system, we conclude that only molecules aggregated via aurophilic interactions can luminesce. We demonstrated that luminescence properties, such as colour and intensity, were very sensitive to the aggregated structure of the molecules. We also found that such luminescence properties can be controlled by a change in the aggregated structure induced by external stimuli, such as heat, solvent, and mechanical stress.

Highly luminescent materials are of great interest for light-emitting devices[1]. However, the luminescence intensity of most organic molecules is abruptly reduced in concentrated solutions or condensed phases owing to concentration quenching or aggregation-caused quenching. Recently, some types of organic molecules have shown strong photoluminescence in the condensed phase, where aggregation enhanced the photoluminescence through a phenomenon called aggregation-induced emission (AIE)[2–6]. The luminescence of AIE materials is strongly affected by the structure of the molecular aggregates as well as the molecular structure[7].

Recent advances in the chemistry of Au(I) complexes have proved that an isolated molecule of the complex in dilute solution does not emit. However, aggregates of the complex are emissive owing to intermolecular interactions between Au atoms (aurophilic interactions)[8–11]. Since the aggregated molecules emit, the luminescence properties of Au complexes could potentially be tuned by controlling the structure of the molecular aggregates. In fact, Balch and co-workers first reported that cyclic trinuclear Au complexes containing a nitrogen ligand, $Au_3(MeN=COMe)_3$, constructed columnar structures and displayed an interesting phenomenon in which the luminescence intensity of the complex was strongly enhanced by contact with a good solvent after UV irradiation[12]. Moreover, the Fackler group described the electronic properties of the cyclic trinuclear Au complexes by means of density functional theory (DFT) calculations[13,14]. Very recently, Omary and co-workers reported the crystal structures, luminescence properties, and conductive behaviour of similar carbeniate trinuclear Au complexes[15].

In previous reports, we also developed novel Au complexes and demonstrated that the luminescent behaviour can be precisely modified by changing their aggregated structure[16–20]. In our extensive efforts towards the development of new photoluminescent Au complexes, we also found that cyclic trinuclear Au complexes (Figure 1a) showed intriguing luminescence properties in the crystalline phase. In addition, the luminescence properties of the Au complexes can be switched by external stimuli, such as heat, solvent, and mechanical stress, where a significant change in luminescent intensity and colour result from a stimuli-induced change in the aggregated structure. In this paper, we report the synthesis and characterization of a series of new cyclic trinuclear Au complexes **1**–**6**, four of which luminesce in the solid phase, and discuss the relationship between their aggregated structures and photophysical properties.
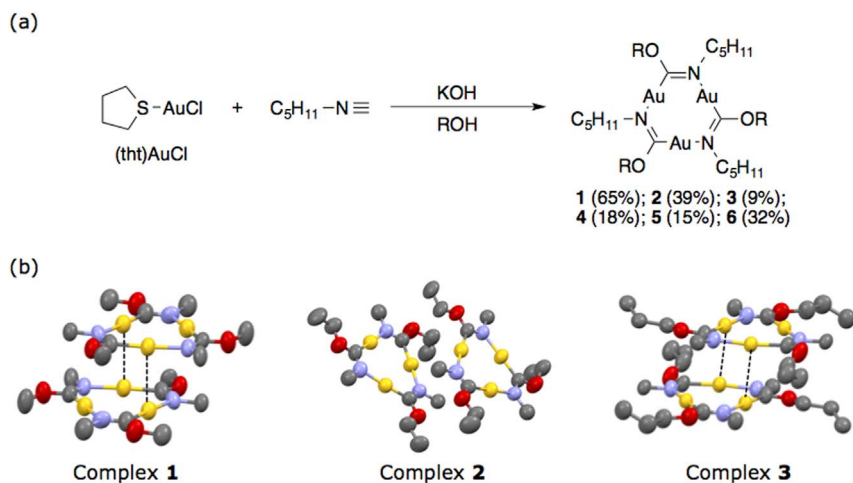
Figure 1 | (a) Molecular structures and synthesis of cyclic trinuclear Au(I) complexes: **1**, R = CH_3; **2**, R = C_2H_5; **3**, R = C_3H_7; **4**, R = C_5H_{11}; **5**, R = C_6H_{13}; **6**, R = C_7H_{15}. (b) Crystal structures of the Au complexes at room temperature. The existence of an intermolecular Au···Au interaction is indicated with black broken lines. For clarity, only the major components are shown: hydrogen atoms and alkyl groups are omitted. Grey atoms represent C, purple represent N, red represent O, and yellow represent Au.

Results and Discussion

Synthesis and structural characterization. The synthesis and characterization of a cyclic trinuclear Au complex with methoxy group side chains, **1**, have been previously reported by Balch and co-workers[21]. The additional complexes in this work, **2–6**, were synthesized according to the same procedure (Figure 1a).

Briefly, (tht)AuCl (tht = tetrahydrothiophene) was mixed with *n*-pentyl isocyanide in the presence of potassium hydroxide in the corresponding alcohol solvent to obtain the desired complexes in 9–65% yields. The complexes were purified by recrystallization from a mixture of benzene and heptane, and were well characterized by ^{1}H NMR and mass spectrometry, as described in the Methods section. The ^{1}H NMR spectra of the final products showed that all complexes were sufficiently pure for studies of photoluminescence behaviour (Figure S1–S6 in Electronic Supplementary Information).

Au complexes **1–3** furnished single crystals suitable for X-ray crystallography; however, appropriate single crystals of complexes **4–6** could not be obtained for structural analysis. Thus, X-ray crystallography was conducted for complexes **1–3** at room temperature,

and their crystal structures are shown in Figure 1b. The crystallographic data is also summarized in Table 1.

Balch and co-workers have previously revealed the crystal structure of complex **1** by recrystallization from diethyl ether to obtain needles of an orthorhombic polymorph along with blocks of a triclinic crystal system[21]. In this study, however, recrystallization from a mixed solvent system of benzene and heptane gave a crystal with a *P-1(#2)* triclinic space group. In Table 1, the Au···Au distances between neighbouring molecules estimated from the X-ray crystallography are listed for complexes **1–3**. Another important difference between our present data and that of the previous report are the Au···Au interatomic distances; in the present crystal of **1**, the Au···Au distance between neighbouring molecules was 3.38 Å (Table 1), whereas it was 3.62 Å in the previously reported crystal[21]. Taking into account the sum of the van der Waals radii of the two Au atoms (3.8 Å)[22], an intermolecular aurophilic interaction can be considered to exist in the crystal when the Au···Au distance is shorter than 3.8 Å. Because of the shorter Au···Au distances, stron-

Table 1	Crystallographic data for complexes **1–3**		
	1	2	3
Empirical Formula	$C_{21}H_{42}Au_3N_3O_3$	$C_{24}H_{48}Au_3N_3O_3$	$C_{27}H_{54}Au_3N_3O_3$
Formula Weight	975.48	1017.56	1059.64
Temperature [°C]	25	20	20
Crystal Colour/Habit	Colourless/Block	Colourless/Plate	Colourless/Plate
Crystal Size [mm]	$0.17 \times 0.14 \times 0.070$	$0.68 \times 0.15 \times 0.050$	$0.42 \times 0.32 \times 0.040$
Crystal System	Triclinic	Monoclinic	Triclinic
Space group	*P-1 (#2)*	*P2₁/a*	*P-1*
a [Å]	12.1436(5)	11.1362(19)	9.464(4)
b [Å]	15.6745(7)	17.4766(18)	12.701(4)
c [Å]	16.6002(7)	16.6988(14)	14.882(5)
α [°]	65.7069(9)	--	78.852(2)
β [°]	78.6727(7)	107.302(10)	76.34(3)
γ [°]	80.3615(9)	--	88.23(3)
V [Å³]	2810.6(2)	3102.9(7)	1705.2(11)
Z	4	4	2
R[F² > 2σ(F²)]]ᵃ	0.0493	0.0550	0.0811
wR(F²)ᵇ	0.1465	0.1760	0.2349
Au···Auᶜ [Å]	3.38	3.92	3.35

ᵃR = Σ||F_o| − |F_c||/Σ|F_o|.
ᵇwR = {[Σw(|F_o| − |F_c|)]/Σw|F_o|}$^{1/2}$.
ᶜAu···Au interatomic distances between neighbouring molecules in crystals.

ger aurophilic interactions exist in the present crystal compared with those in the previously reported crystal. Thus, we conclude that the molecules aggregated into a dimer in the crystal via aurophilic interactions, as shown in Figure 1b.

Au complex **3** crystallized in the triclinic *P-1* space group (Table 1) with a Au⋯Au distance of 3.35 Å, meaning that dimer aggregation via intermolecular aurophilic interactions occurred in this crystal. In both complexes **1** and **3**, the aurophilic interaction existed at two sites in each molecular pair. In the crystal of complex **2**, however, an aurophilic interaction was not observed. Instead, this complex crystallized in the monoclinic *P2₁/a* space group with Au⋯Au distances between neighbouring molecules longer than 3.8 Å.

Photophysical properties of the complexes. By measuring the UV absorption of the complexes in dilute solutions, we confirmed that all complexes had absorption maxima around 260 nm (the molar extinction coefficients (ε) were *ca.* 2×10^4 L mol^{-1} cm^{-1}), which can likely be assigned as the absorption band based on metal-to-ligand charge transfer, as mentioned in ref. 23. All materials were completely transparent at wavelengths longer than 300 nm. From a practical viewpoint, this transparency is favourable for luminescent materials.

In dilute solutions of Au complexes **1–6**, no emission was observed for concentrations between 10^{-6} and 10^{-3} mol L^{-1} (excitation wavelength (λ_{ex}) = 260 nm). Interestingly, complexes **1**, **3**, **4**, and **5** exhibited photoluminescence in the crystalline phase when excited at 260 nm at room temperature with quantum yields of 2–3% (Figure 2); however, complexes **2** and **6** did not emit in the crystalline phase. As the length of the alkoxy side chain was the only difference in the molecular structures of the emissive and non-emissive complexes, the distinct photoluminescence behaviour is likely caused by the structure of the molecular aggregates in the crystal. Unlike emissive complexes **1** and **3** (Figure 1b and Table 1), intermolecular aurophilic interactions were not observed in the crystal of the non-emissive complex **2** (Au⋯Au distance = 3.92 Å). The photoluminescence results for the complexes both in solution and the crystalline phase suggests that the intermolecular aurophilic interaction, *i.e.* aggregation of molecules into a dimer, plays a crucial role in the luminescence of the present gold complexes. Thus, we conclude the luminescence arises from the molecular aggregates formed via aurophilic interactions.

As shown in Figure 2, the luminescent wavelength, *i.e.* the colour, of the crystals also depends on the length of the alkoxy side chain.

Complexes with shorter alkoxy groups (**1** and **3**) emitted purple luminescence with a major emission band at ~400 nm and a minor band at ~680 nm, whereas complexes with longer side chains (**4** and **5**) emitted red luminescence with only one significant emission band at ~680 nm.

According to the previous report by Balch and co-workers, crystals of complex **1** displayed red photoluminescence with an emission band around 650 nm[21]. In sharp contrast, the present crystal of **1** emitted purple luminescence. As mentioned above, luminescence should be due to molecular aggregates formed via aurophilic interactions, and we consider the luminescence properties to be affected by the aggregated structure. Because the Au⋯Au distance and space group of these crystals are different, the difference in luminescence colour was a result of the different aggregated structures.

The photoluminescence lifetimes (τ) of the emissive complexes were measured in the crystalline phase at room temperature (25°C) and are listed in Table 2. All the emissive complexes had luminescence lifetimes on the order of microseconds. Thus, we conclude that the observed photoluminescence of the Au complexes is derived from phosphorescence emitted from triplet excited states. In addition, with the exception of complex **3**, which showed a bi-exponential decay, single-exponential decays were observed for the photoluminescence of the crystals. We believe that the bi-exponential decay of complex **3** resulted from the existence of two types of excited states; at present, however, the detailed mechanism of photoluminescence in the crystal of **3** is not clear.

Effects of the aggregated structure on the photoluminescence of Au complexes. In order to explore in more detail the effects of the aggregated structure of Au complexes on the photoluminescence properties in the condensed phase, we measured luminescence spectra in various phases after applying several types of stimuli.

Figure 3 shows the photoluminescence spectra of complex **1**. The initial crystal of complex **1** obtained by recrystallization from mixed solvents (Crystal-1A) exhibited purple luminescence with two bands at 400 and 680 nm, as mentioned above. After melting the crystal at 85°C to obtain a liquid phase (Liquid-1), both emission bands disappeared, as shown in Figure 3a. Dissociation of the dimer likely occurred because of the vigorous micro-Brownian motion of the molecules and random molecular arrangement in the Liquid-1 phase. After cooling the Liquid-1 phase to obtain a crystal (Crystal-1B), only the emission band at 680 nm was recovered and red luminescence was observed (Figure 3b); the band at 400 nm did
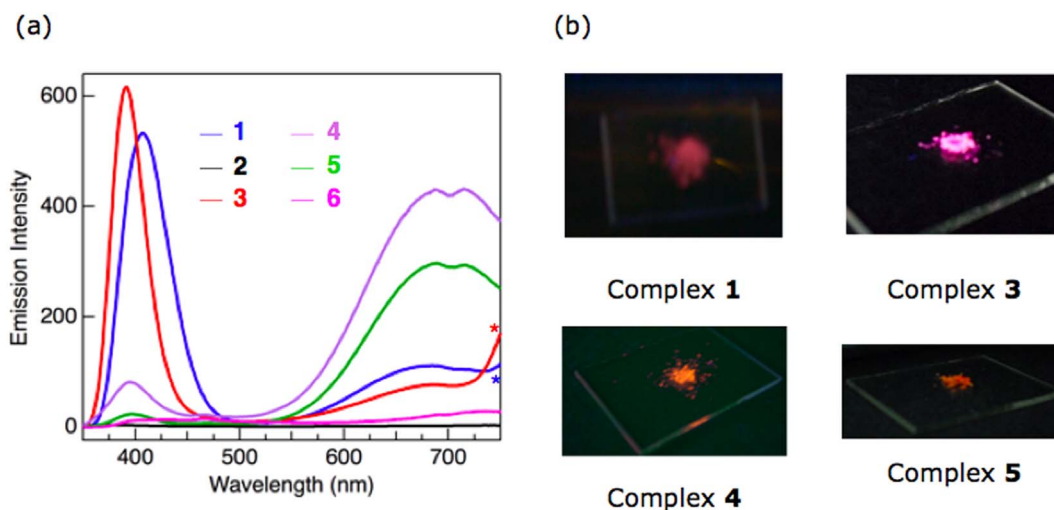

Figure 2 | (a) Corrected photoluminescence spectra of **1–6** in the crystalline phase at room temperature (λ_{ex} = 300 nm). The second order diffraction of the emission at shorter wavelengths appears at >700 nm for complexes **1** and **3**, as indicated by asterisks. (b) Photographs of emissive crystals of **1**, **3**, **4**, and **5** taken under irradiation at 254 nm.

Table 2 | Photoluminescence lifetimes (τ) of the crystals of the Au complexes at 25°C

Complex	Wavelength [nm]	Lifetime, τ [μs]
1	400	5.0
	680	5.8
3	390	1.0 (86%), 2.5 (14%)
	680	1.2 (82%), 3.5 (18%)
4	680	7.9
5	680	7.5

not appear in Crystal-1B. The spectral shape and colour of Crystal-1B was in accord with those of the crystal reported by Balch and co-workers[21]; consequently, we speculate that the aggregated structure of the molecules in Crystal-1B is the same as that in the previously reported crystal. When Crystal-1B was allowed to stand at room temperature, the spectral shape and colour of the emission did not change. However, addition of a small amount of CH_2Cl_2 to Crystal-1B, followed by drying to obtain another crystal (Crystal-1C), resulted in the restoration of both emission bands at 400 and

680 nm, and the spectral shape and emission colour of Crystal-1C (Figure 3b) was similar to that of Crystal-1A. Furthermore, mechanical grinding of Crystal-1C in a mortar produced yet another crystal (Crystal-1D), which recovered the spectral shape and colour of Crystal-1B (Figure 3b).

To understand the change in the luminescence properties of complex **1**, the stimuli-responsive behaviour of complex **1** is schematically summarized in Figure 3c along with the Commission Internationale de l'Eclairage (CIE) chromaticity diagram (Figure 3d), which illustrates the stimuli-induced colour change. Our observation of this change in luminescence properties indicates that the intensity and colour of the luminescence can be tuned by external stimuli, such as heat, solvent, and mechanical stress.

We consider the stimuli-induced change in the luminescence properties of complex **1** to result from a change in the aggregated structure; thus, we measured the powder X-ray diffraction (XRD) pattern to confirm our hypothesis (Figure 4a). For comparison, an XRD pattern simulated from the single crystal structural analysis reported previously is also plotted[21]. The XRD pattern of Crystal-1A was very similar to that of Crystal-1C; similarly, the XRD pattern of Crystal-1D was similar to that simulated from the previous report.
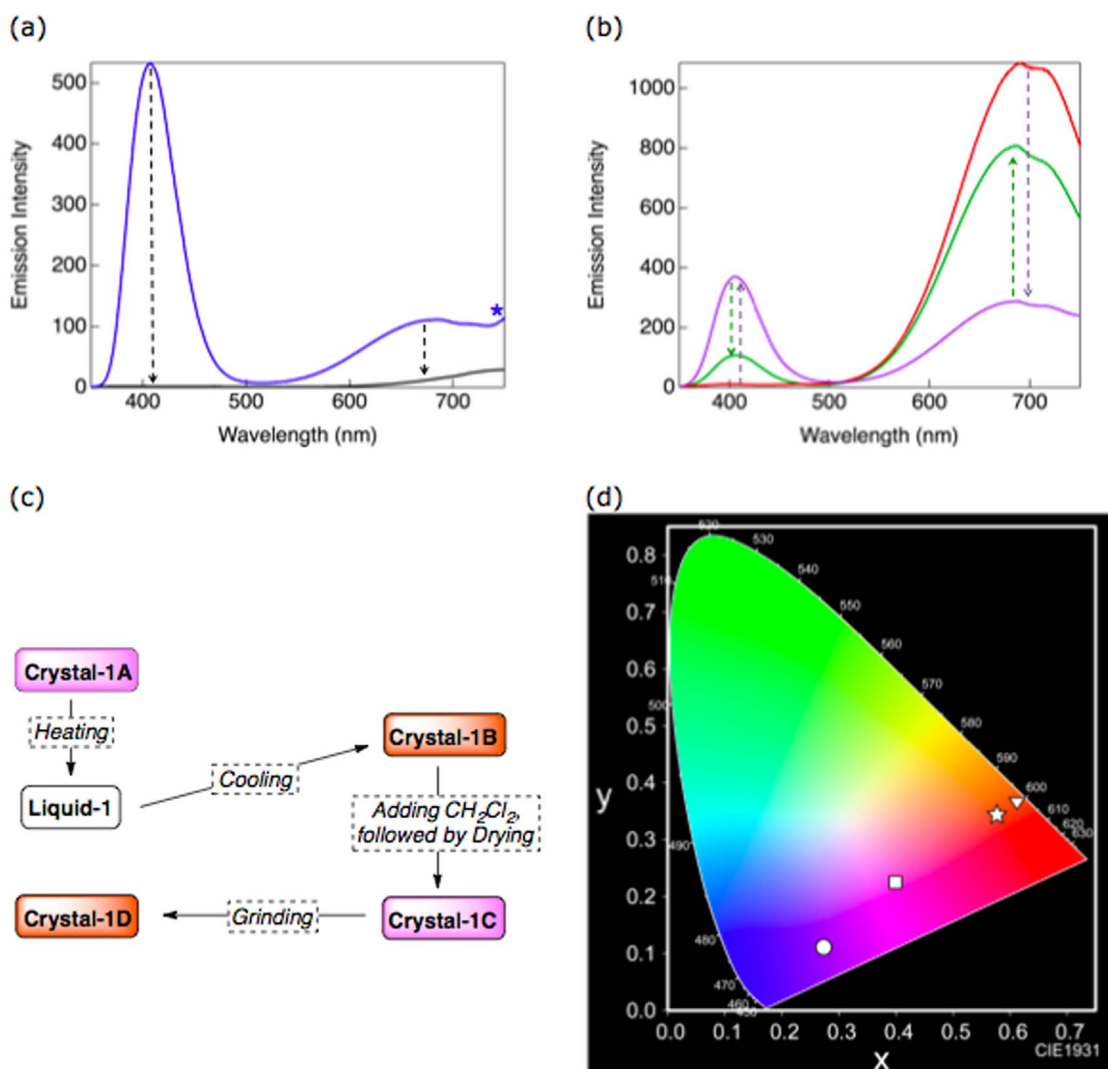

Figure 3 | Corrected photoluminescence spectra of different phases of complex **1** (λ_{ex} = 300 nm): (a) Crystal-1A at room temperature (blue) and Liquid-1 at 85°C (black), and (b) Crystal-1B (red), Crystal-1C (purple), and Crystal-1D (green). In figure (a), the second order diffraction of the emission at shorter wavelength appears at >700 nm and is indicated with an asterisk. (c) Schematic illustration of the stimuli-responsive behaviour of complex **1**. (d) CIE chromaticity diagram for the photoluminescence of complex **1** in Crystal-1A (○), Crystal-1B (▽), Crystal-1C (□), and Crystal-1D (☆).
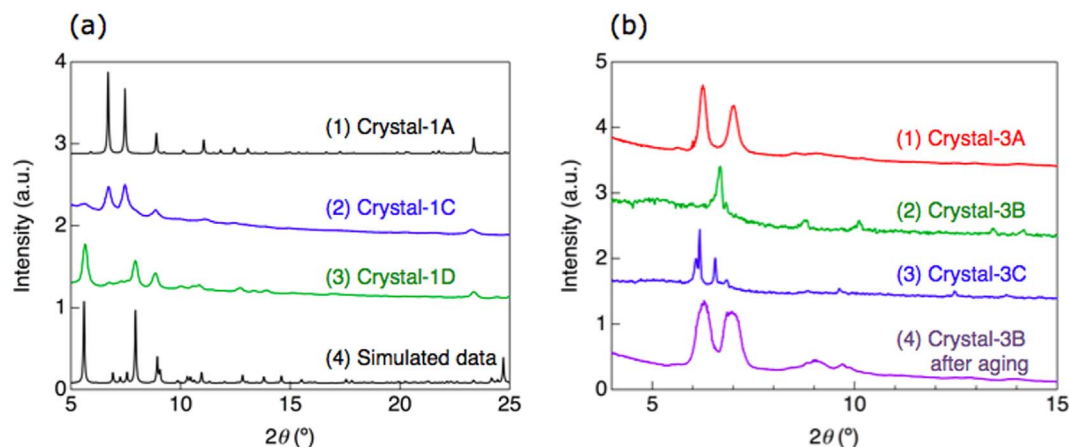
Figure 4 | X-ray diffraction patterns of 1 and 3 in various states at room temperature. (a) XRD of **1** for (1) Crystal-1A, (2) Crystal-1C, (3) Crystal-1D, and (4) simulated data reported in ref. 21. (b) XRD of **3** for (1) Crystal-3A, (2) Crystal-3B, (3) Crystal-3C, and (4) Crystal-3B after aging at 35°C for 15 h.

The XRD experiments clearly suggest that complex **1** can form two types of crystals at room temperature: one in the triclinic space group (Crystal-1A and Crystal-1C) with intermolecular Au···Au distances of 3.38 Å and one in the orthorhombic space group (Crystal-1D) with Au···Au distances of 3.62 Å[21]. We conclude that the spectral shape and colour of the photoluminescence in complex **1** is strongly related

to the aggregated structure of the molecules, *i.e.* the space group and distance between neighbouring Au atoms. The triclinic crystals (Crystal-1A and Crystal-1C) of complex **1** showed purple luminescence with two emission bands at 410 nm and 680 nm, whereas the orthorhombic crystal (Crystal-1D) exhibited red luminescence with a band at 680 nm, as reported by Balch and co-workers[21]. Both
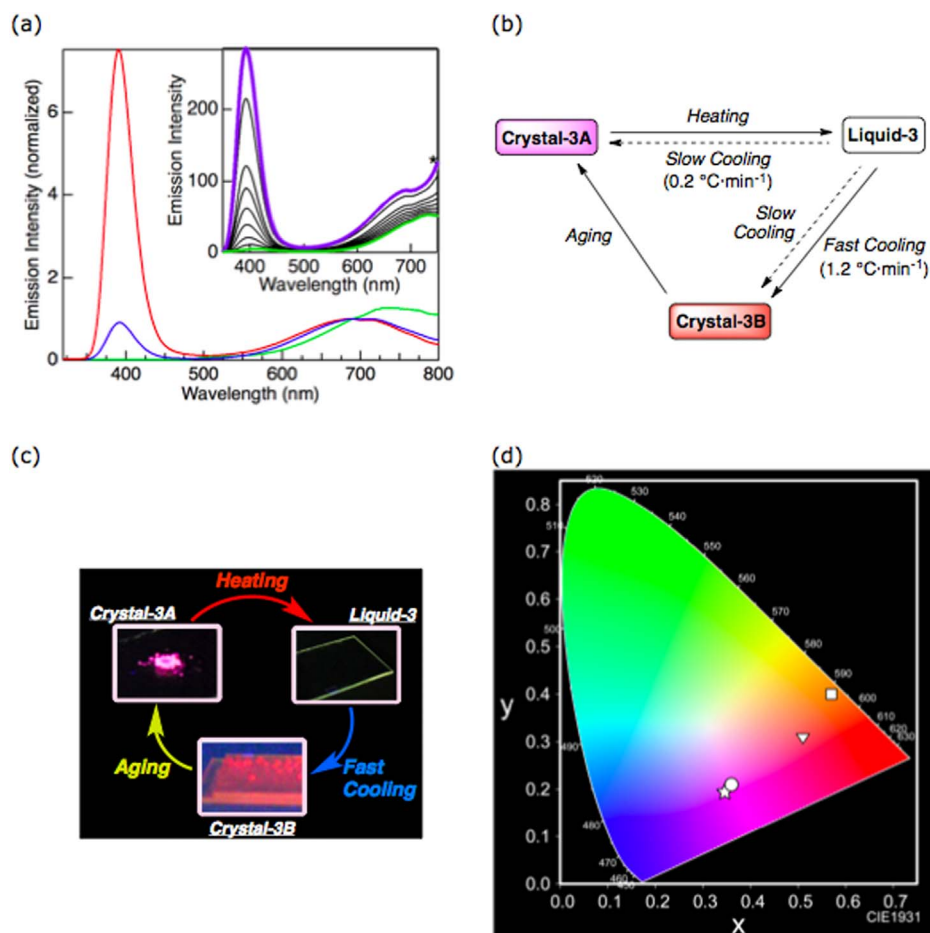

Figure 5 | (a) Corrected photoluminescence spectra of **3** at room temperature (λ_{ex} = 300 nm) for Crystal-3A (red), Crystal-3B (green), and Crystal-3C (blue); the inset shows the time evolution of the photoluminescence spectrum in Crystal-3B upon aging at 35°C for 0 h (green) to 15 h (purple). The second order diffraction of the emission at shorter wavelength appears at >700 nm and is indicated with an asterisk. (b) Schematic illustration of the stimulus-responsive behaviour of complex **3**. (c) Photographs of **3** in various states taken under irradiation at 254 nm. (d) CIE chromaticity diagram for the photoluminescence of complex **3** in Crystal-3A (☆), Crystal-3B (□), Crystal-3C (▽), and after aging at 35°C for 15 h (○).
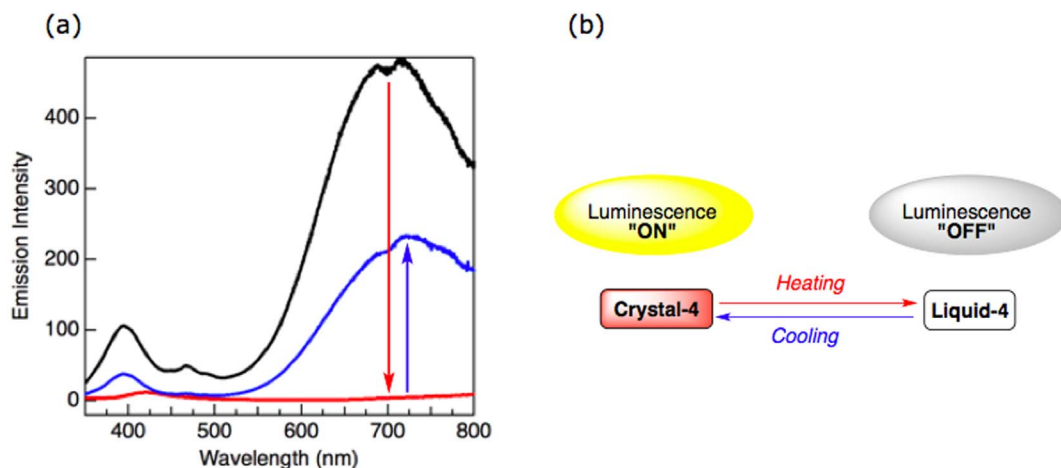
Figure 6 | (a) Corrected photoluminescence spectra of **4** (λ_{ex} = 260 nm) for crystals obtained after recrystallization (black), in the molten state (red), and after freezing from the molten state (blue). (b) Schematic illustration of the stimulus-responsive behaviour of complex **4**.

emission bands at 410 nm and 680 nm can be attributed to the intermolecular Au···Au interaction; the lower-energy luminescent band at 680 nm is caused by the aurophilic interaction between the closest pair of Au atoms (3.38 Å), and the higher-energy luminescent band at 410 nm might be due to the weak Au···Au interaction between the second-closest pair of Au atoms (3.71 Å)[24]. Using this change in photoluminescence, we can reversibly control the luminescence colour of complex **1** by changing the aggregated structure through the introduction of external stimuli, such as heat, solvent, and mechanical stress.

We observed similar changes in the photoluminescence properties of complex **3** (Figure 5). The initial crystal obtained by recrystallization (Crystal-3A) showed purple luminescence with two emission bands at 400 and 680 nm, whereas the isotropic liquid (Liquid-3) at 65°C did not show luminescence. The crystal obtained by freezing the Liquid-3 state at a cooling rate of 1.2°C (Crystal-3B) showed red luminescence at 740 nm. However, the crystal formed by slow cooling Liquid-3 at a rate of 0.2°C (Crystal-3C) exhibited purple luminescence with two emission bands, similar to Crystal-3A. In Crystal-3C, the major emission band was still the longer wavelength band; however, upon aging Crystal-3B and Crystal-3C at 35°C the intensity of the emission band at 400 nm rapidly increased and the relative intensity of this band became larger than that of the longer wavelength band. The initial luminescence spectrum was recovered after 15 h of aging at 35°C; the inset of Figure 5a shows the spectral changes in Crystal-3B over time as a typical example. In complex **3**, the luminescence colour can be controlled by thermal processes without any chemical or mechanical stress.

The XRD pattern of crystal **3** also suggests the existence of two types of crystals at room temperature (Figure 4b). The crystal structure of red-luminescent Crystal-3B, obtained by fast cooling from Liquid-3, was different from that of purple-luminescent Crystal-3A. On the other hand, the diffraction pattern in purple-luminescent Crystal-3C, obtained by slow cooling, suggests that Crystal-3C has the same crystalline phase as Crystal-3A but also contains a small amount of Crystal-3B. The luminescence spectroscopy and XRD data support the hypothesis that the luminescence behaviour of the Au complex is strongly affected by the aggregated structure of molecules. Again, we can control the luminescence colour in this complex by precise control of the thermal treatment process without using solvent.

Stimuli-responsive behaviour was also observed in complexes **4** and **5**. Figure 6 shows the photoluminescence spectra of **4** in various states as a typical example. Both complexes showed red photoluminescence, which vanished completely after melting. From the above

discussion, we can speculate that the orthorhombic crystal with Au···Au distances of 3.6 Å shows red luminescence. Thus, we consider complexes **4** and **5** to form the same type of crystal at room temperature. These complexes did not exhibit polymorphism, which accounts for their simple response to thermal stimulus.

In this study, we synthesized a series of new cyclic trinuclear Au(I) complexes **1–6** bearing alkoxy side chains of various lengths. We demonstrated that the photoluminescence properties of the Au complexes in the condensed phase are sensitive to the structure of the molecular aggregates and that luminescence properties, such as intensity and colour, can be tuned by controlling the aggregated structure with external stimuli. In complex **1**, the luminescence colour could be tuned using a combination of thermal, chemical, and mechanical stimuli. On the other hand, the luminescence colour of complex **3** could be controlled using only thermal stimulus, without chemical or mechanical stimuli. The present study suggests that it is important to consider the structure of the molecular aggregates when designing new luminescent materials and that the luminescence properties can be tuned by controlling the aggregated structures.

Methods

Synthesis of cyclic trinuclear Au(I) complexes 1–3. (tht)AuCl (0.20 g, 0.62 mmol) was suspended in 12 mL of alcohol ($C_nH_{2n+1}OH$; n = 1, 2, or 3). Potassium hydroxide (55 mg, 0.98 mmol) was added to the mixture, followed by n-pentyl isocyanide (81 µL, 0.64 mmol). The suspension was stirred at room temperature for 4 h. The solid product was removed by filtration and washed with dichloromethane. The filtrate was dried under reduced pressure, and the residue was dissolved in dichloromethane and water then added to the solution. The organic layer was extracted with dichloromethane, washed with brine, and dried over anhydrous sodium sulphate. The solvent was evaporated under reduced pressure. The residue was purified by short silica-gel column chromatography (1:1 dichloromethane:diethyl ether) and recrystallization (1:1 benzene:heptane) to afford the desired complexes **1** (0.13 g, 0.13 mmol, 65% yield), **2** (82 mg, 81 µmol, 39% yield), and **3** (20 mg, 19 µmol, 9% yield).

1: mp 78°C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.0 (s, 9H), 3.4 (t, J = 7.2 Hz, 6H), 1.7 (quint, J = 7.2 Hz, 6H), 1.3 (m, 12H), 0.9 (t, J = 6.8 Hz, 9H). ESI-MS (m/z): [M+H]$^+$ calcd. for $C_{21}H_{43}Au_3N_3O_3$, 976.2301; found, 976.23.

2: mp 55°C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.4 (q, J = 7.2 Hz, 6H), 3.4 (q, J = 7.2 Hz, 6H), 1.7 (quint, J = 7.2 Hz, 6H), 1.4–1.2 (m, 21H), 0.9 (m, 9H). ESI-MS (m/z): [M+H]$^+$ calcd. for $C_{24}H_{49}Au_3N_3O_3$, 1018.2770; found, 1018.28.

3: mp 60°C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.4 (t, J = 6.8 Hz, 6H), 3.4 (t, J = 7.2 Hz, 6H), 1.8–1.6 (m, 12H), 1.4–1.3 (m, 12H), 0.9 (t, J = 7.2 Hz, 9H), 0.9 (t, J = 6.8 Hz, 9H). ESI-MS (m/z): [M+H]$^+$ calcd. for $C_{27}H_{55}Au_3N_3O_3$, 1060.3240; found, 1060.32.

Synthesis of cyclic trinuclear Au(I) complexes 4–6. (tht)AuCl (0.24 g, 0.75 mmol) was suspended in 14 mL of alcohol ($C_nH_{2n+1}OH$; n = 5, 6, or 7). Potassium hydroxide (0.068 g, 1.8 mmol) was added to the mixture, followed by the addition of n-pentyl isocyanide (0.10 mL, 1.0 mmol). The suspension was stirred at room temperature for 2 h. The reaction mixture was passed though silica gel using 1 : 1 dichloromethane:ether as an eluent. The solvent was evaporated under reduced pressure. The residue was purified by reprecipitation (4 : 1 dichloromethane:methanol/water) to yield the desired complexes **4** (52 mg, 45 μmol, 18% yield), **5** (43 mg, 36 μmol, 15% yield), and **6** (97 mg, 79 μmol, 32% yield).

4: mp 32°C. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 4.4 (t, J = 6.8 Hz, 6H), 3.4 (t, J = 7.2 Hz, 6H), 1.7 (quint, J = 7.2 Hz, 12H), 1.3 (m, 24H), 0.9 (t, J = 6.8 Hz, 18H); ESI-MS (m/z): [M+H]$^+$ calcd. for C$_{33}$H$_{67}$Au$_3$N$_3$O$_3$, 1144.4179; found, 1144.42.

5: mp 32°C. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 4.4 (t, J = 7.2 Hz, 6H), 3.4 (t, J = 7.3 Hz, 6H), 1.7 (quint, J = 7.2 Hz, 12H), 1.3 (m, 30H), 0.9 (t, J = 7.0 Hz, 18H); ESI-MS (m/z): [M+H]$^+$ calcd. for C$_{36}$H$_{73}$Au$_3$N$_3$O$_3$, 1186.4648; found, 1186.46.

6: mp 26°C. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 4.4 (t, J = 7.2 Hz, 6H), 3.4 (t, J = 7.3 Hz, 6H), 1.7 (quint, J = 7.2 Hz, 12H), 1.3 (m, 36H), 0.9 (t, J = 7.0 Hz, 18H); ESI-MS (m/z): [M+H]$^+$ calcd. for C$_{39}$H$_{79}$Au$_3$N$_3$O$_3$, 1228.5118; found, 1228.51.

X-ray crystallography. Single crystals were obtained by slow evaporation from a 1 : 1 benzene:heptane solution and mounted on a glass fibre. Reflection data were measured using an ω-scan technique on a Rigaku automated four-circular-axis diffractometer (AFC-5R) with graphite monochromatized Cu Kα radiation (λ = 1.54178 Å) or a Rigaku two-circular-axis diffractometer (R-AXIS RAPID) with Mo Kα radiation (λ = 0.71075 Å) at room temperature (296 K). The initial structure in the unit cell was determined by a direct method using SIR92[25]. The structure model was refined by full-matrix least-squares methods using SHELXL97[26]. All calculations were performed on the crystallographic software package WinGX[27]. Powder X-ray diffraction measurements were carried out on an Ultima IV, XRD-DSC II (Rigaku) diffractometer with a heating stage using Ni-filtered Cu Kα radiation (λ = 1.54178 Å). The data in Table 1 have been indexed and are included in the Cambridge Crystallographic Centre (CCDC) database with the following reference numbers: CCDC 1025550 for **1**, CCDC 1025551 for **2**, and CCDC 1025552 for **3**. 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.

Photophysical properties. UV-visible absorption and steady-state photoluminescence spectra were recorded on a JASCO V-550 absorption spectrophotometer and on a Hitachi F-7000 fluorescence spectrophotometer with R928 photomultiplier tube (Hamamatsu) as a detector, respectively. The same crystals prepared for the single-crystal X-ray structure analysis were used for measurements in the crystalline and LC states. The crystals were placed between a pair of quartz plates and set on a homemade heating stage to record the spectra at a controlled temperature. Photoluminescent quantum yields were determined using a calibrated integrating sphere system (Hitachi). Photoluminescence decay profiles were measured using a N$_2$ laser (USHIO pulsed dye laser, KE160; wavelength 337 nm; pulse width 600 ps; 10 Hz). The emission profiles were recorded with a streak camera (Hamamatsu, C4334).

1. Shinar, J. & Savvateev, V. in *Organic Light-emitting Devices: A Survey* [Shinar, J. (ed.)][1–41] (Springer, 2004).
2. Zhao, Z., Lam, J. W. Y. & Tang, B. Z. Self-assembly of organic luminophores with gelation-enhanced emission characteristics. *Soft Mater.* **9**, 4564 (2013).
3. Zhao, Z., Lam, J. W. Y. & Tang, B. Z. Tetraphenylethene: a versatile AIE building block for the construction of efficient luminescent materials for organic light-emitting diodes. *J. Mater. Chem.* **22**, 23726 (2012).
4. Hong, Y., Lam, J. W. Y. & Tang, B. Z. Aggregation-induced emission. *Chem. Soc. Rev.* **40**, 5361 (2011).
5. Hong, Y., Lam, J. W. Y. & Tang, B. Z. Aggregation-induced emission: phenomenon, mechanism and applications. *Chem. Commun.* 4332 (2009).
6. An, B.-K., Kwon, S.-K., Jung, S.-D. & Park, S. Y. Enhanced emission and its switching in fluorescent organic nanoparticles. *J. Am. Chem. Soc.* **124**, 14410 (2002).
7. López-de-Luzuriaga, J. M. [Luminescence of Supramolecular Gold Containing Materials] in *Modern Supramolecular Gold Chemistry* [Laguna, A. (ed.)] (Wiley-VCH Verlag GmbH&Co. KGaA, 2009).
8. Gavara, R., Llorca, J., Lima, J. C. & Rodriguez, L. A luminescent hydrogel based on a new Au(I) complex. *Chem. Commun.* **49**, 72 (2013).
9. Baron, M. et al. Blue-Emitting Dinuclear N-heterocyclic Dicarbene Gold(I) Complex Featuring a Nearly Unit Quantum Yield. *Inorg. Chem.* **51**, 1778 (2012).
10. Rawashdeh-Omary, M. A. et al. Golden Metallopolymers with an Active T$_1$ State via Coordination of Poly(4-vinyl)pyridine to Pentahalophenyl-Gold(I) Precursors. *J. Am. Chem. Soc.* **131**, 3824 (2009).
11. Schmidbaur, H., Cronje, S., Djordjevic, B. & Schuster, O. Understanding gold chemistry through relativity. *Chem. Phys.* **311**, 151 (2005).
12. Vickery, J. C., Olmstead, M. M., Fung, E. Y. & Balch, A. L. Solvent-Stimulated Luminescence from the Supramolecular Aggregation of a Trinuclear Gold(I) Complex that Displays Extensive Intermolecular Au···Au Interactions. *Angew. Chem. Int. Ed.* **36**, 1179 (1997).
13. Burini, A., Mohamed, A. A. & Fackler Jr, J. P. Cyclic Trinuclear Gold(I) Compounds: Synthesis, Structure, and Supramolecular Acid-base π-Stacks. *Comments on Inorg. Chem.* **24**, 253 (2003).
14. Abdou, H. E. et al. Structure and properties of gold(I) complexes of interest in biochemical applications. *Coord. Chem. Rev.* **253**, 1661 (2009).
15. McDougald Jr, R. N. et al. Molecular and Electronic Structure of Cyclic Trinuclear Gold(I) Carbeniate Complexes: Insights for Structure/Luminescence/Conductivity Relationships. *Inorg. Chem.* **53**, 7485 (2014).
16. Sugmoto, N., Tamai, S., Fujisawa, K. & Tsutsumi, O. Photoluminescent Gold(I) Complex with Biphenyl Acetylene Ligand Showing Stable Nematic Liquid-Crystalline Phase. *Mol. Cryst. Liq. Cryst.* **601**, 97 (2014).
17. Rokusha, Y., Sugimoto, N., Yamada, S. & Tsutsumi, O. Synthesis, liquid-crystalline behavior, and photoluminescence properties of novel Au(I) complex with naphthalene ring in a mesogenic core. *Proc. SPIE* **9182**, 918206, DOI: 10.1117/12.2060334 (2014).
18. Fujisawa, K. et al. Reversible thermal-mode control of luminescence from liquid-crystalline gold(I) complexes. *J. Mater. Chem. C.* **2**, 3549 (2014).
19. Fujisawa, K. et al. Photoluminescent properties of liquid crystalline gold(I) isocyanide complexes with a rod-like molecular structure. *J. Mater. Chem. C.* **1**, 5359 (2013).
20. Fujisawa, K., Izumi, Y., Ngamatsu, A., Uno, K. & Tsutsumi, O. Liquid-Crystalline Behavior and Photoluminescence Properties of Gold(I) Complex: Relationship between Aggregation Structureand Properties. *Mol. Cryst. Liq. Cryst.* **563**, 50 (2012).
21. White-Morris, R. L., Olmstead, M. M., Attar, S. & Balch, A. L. Intermolecular Interactions in Polymorphs of Trinuclear Gold(I) Complexes: Insight into the Solvoluminescence of Au^i$_3$(MeN=COMe)$_3$. *Inorg. Chem.* **44**, 5021 (2005).
22. Schmibaur, H. The aurophilicity phenomenon: a decade of experimental findings, theoretical concepts and emerging applications. *Gold Bull.* **33**, 3 (2000).
23. Balch, A. L., Olmstead, M. M. & Vickery, J. C. Gold(I) Compounds without Significant Aurophilic Intermolecular Interactions: Synthesis, Structure, and Electronic Properties of Ph$_3$PAuC(O)NHMe and Au$_3$(PhCH$_2$N=COMe)$_3$: Comparative Monomeric and Trimeric Analogues of the Solvoluminescent Trimer, Au$_3$(MeN=COMee)$_3$. *Inorg. Chem.* **38**, 3494 (1999).
24. Forward, J. M., Bohmann, D., Fackler Jr, J. P. & Staples, R. J. Luminescence Studies of Gold(I) Thiolate Complexes. *Inorg. Chem.* **34**, 6330 (1995).
25. Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. Completion and refinement of crystal structures with SIR92. *J. Appl. Crystallogr.* **26**, 343 (1993).
26. Sheldrick, G. A short history of SHELX. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **64**, 112 (2008).
27. Farrugia, L. J. WinGX suite for small-molecule single-crystal crystallography. *J. Appl. Crystallogr.* **32**, 837 (1999).

Acknowledgments

Author contributions

Yu.Y., Ya.Y. and A.K. synthesized the complexes. K.F. and S.Y. performed the characterizations, structure analyses, and photophysical experiments. O.T. conceived the study. K.F., S.Y. and O.T. wrote the paper. All authors interpreted the data, discussed the results, and reviewed the manuscript.

Additional information

Supplementary information accompanies this paper at http://www.nature.com/scientificreports

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Fujisawa, K. et al. Tuning the photoluminescence of condensed-phase cyclic trinuclear Au(I) complexes through control of their aggregated structures by external stimuli. *Sci. Rep.* **5**, 7934; DOI:10.1038/srep07934 (2015).