Aggregation-enhanced direct $S_0$–$T_n$ transitions and room-temperature phosphorescence in gold(I)-complex single crystals

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Abstract
The design of efficient aggregation-induced emission materials requires an improved understanding of photophysical processes in aggregated materials. Herein, the photophysical behavior of an Au(I) complex (R6) that exhibits intense room-temperature phosphorescence (RTP) in crystals is described. In addition, the photophysical processes related to RTP are discussed based on the structure of the molecular aggregates and the primary structure of the molecule. An extremely efficient $S_0$–$T_n$ direct transition is found to occur in the R6 crystal. Furthermore, intermolecular Au–Au interactions and the internal/external heavy-atom effects of Au atoms are demonstrated to enhance the electronic transitions involving intersystem crossing, namely, direct $S_0$–$T_n$ excitation, radiative $T_1$–$S_0$ transition (phosphorescence), and $S_1$–$T_n$ intersystem crossing. Because of the dense molecular packing, both Au–Au interactions and heavy-atom effects play important roles in the crystals. As a result, R6 shows more efficient RTP in crystals than in solution. These insights into the mechanism of highly efficient RTP in Au(I)-complex crystals are expected to advance the development of new luminogens for a variety of sensing and imaging applications.

KEYWORDS
aggregation-induced emission, aurophilic interaction, gold(I) complex, phosphorescence, spin-forbidden transition

1 | INTRODUCTION
The phenomenon whereby molecules show enhanced luminescence through aggregation in condensed phases is called aggregation-induced emission (AIE).$^{[1–3]}$ AIE-active luminogens (AIEgens), which were first reported in 2001 by Tang and co-workers,$^{[4]}$ have attracted much attention because they exhibit efficient luminescence in condensed phases, whereas conventional organic materials have no or weak luminescence owing to aggregation-caused quenching effects.$^{[4–7]}$ The typical working mechanism of AIE involves the suppression of internal molecular motion (i.e., vibrations and rotations that promote the nonradiative deactivation of excited states) through the aggregation of molecules.$^{[1]}$ Inspired by pioneering research, various types of AIEgens have been developed with potential applications in biological imaging, chemical sensing, optoelectronic systems, and related fields.$^{[8–13]}$

Organometallic complexes containing d$^{10}$ transition metals (e.g., Pt(II), Ag(I), and Au(I)) exhibit AIE phenomena through a different mechanism that involves metallophilic interaction.$^{[14]}$ In the last decade, numerous d$^{10}$ transition-metal complexes have been developed as AIEgens that demonstrate interesting photophysical properties.$^{[14]}$ In particular, Au(I) complexes have gained attention because many examples have been reported wherein luminescence behavior is tuned by controlling the distance between Au atoms.$^{[15–19]}$ For example, some Au complexes show luminescence mechanochromism, whereby their luminescence color changes in response to mechanical stimuli.$^{[20]}$ We have developed a series of Au complexes as a new type of AIEgen with strong luminescence in condensed phases.$^{[21–26]}$ For
example, an Au complex with an isocyanide ligand (R6; Figure 1) shows strong room-temperature phosphorescence (RTP) in crystals in the presence of air, with a phosphorescence quantum yield of more than 50%.\[26\]

A detailed understanding of photophysical processes in aggregated materials and the working mechanism of AIE is required to design AIE materials. However, because photophysical investigations of aggregated materials are generally complicated, the photophysical processes and mechanisms involved in the highly efficient RTP of Au-complex crystals are not yet completely understood. In this study, we investigated the luminescence of R6 crystals and determined the dependence of the photophysical behavior on both the primary structure of the molecule and the structure of the molecular aggregates in crystals. By preparing an extraordinarily large, high-quality single crystal of R6, we were able to obtain detailed structural and spectroscopic information about the luminescence processes in R6 crystals. In particular, we found that a direct transition from the singlet ground state (S0) to a triplet excited state (T1) occurs in R6 crystals. In addition, we demonstrated that electron transitions involving intersystem crossing (direct S0→T1 excitation, phosphorescence, and S1→T2 intersystem crossing) are enhanced by both intermolecular interactions between Au atoms (aurophilic interactions) and the internal/external heavy-atom effects of the Au atoms, which result in the R6 crystals exhibiting a high RTP quantum yield (ΦRTP).

2 | RESULTS AND DISCUSSION

2.1 | Synthesis and characterization of the complex

The chemical structure of the Au(I) complex used in this study (R6) is shown in Figure 1. The alkynyl ligand was synthesized from 1-bromo-4-hexyloxybenzene by a Sonogashira coupling reaction according to a previously reported procedure.\[26\] Subsequently, the target Au complex was prepared in a one-pot reaction by alkylation of (tht)AuCl (tht: tetrahydrothiophene) followed by ligand exchange with pentyl isocyanide. Purification using column chromatography and recrystallization gave the pure complex as colorless plate crystals. The final product was fully characterized by 1H NMR spectroscopy, high-resolution mass spectrometry (HRMS), infrared (IR) spectroscopy, and elemental analyses. The analytical data, which are provided in the experimental section, confirmed that the desired Au complex had been prepared in high purity.

The slow evaporation of dichloromethane as a good solvent from a dichloromethane/hexane solution of the complex gave extraordinarily large and high-quality single plate crystals (typically 10 × 10 mm²; Figure 2A). Polarized optical microscopy revealed that these single plate crystals are homogeneous and several tens of micrometers thick (typically 50 μm). Although the recrystallization process was not always reproducible, large single crystals were frequently produced at a constant temperature below 25°C. Therefore, precisely controlling the temperature is important for producing very large high-quality single crystals, as it enables the good solvent to evaporate very slowly at a constant rate.

R6 was subjected to single-crystal X-ray structural analysis at room temperature to clarify its structure. The results obtained for the single plate crystals prepared in this study agree well with the previously reported crystallographic data for R6.\[26\] The crystal axes were assigned to each side of the parallelogram-shaped single plate crystal (Figure 2A). As previously reported, R6 crystallized in the triclinic P-1 space group with two formula units per unit cell and crystal packing that involves molecules stacked in an antiparallel orientation (Figure 2B,C).\[26\] The two Au atoms in neighboring molecules in the crystal are separated by 3.55 Å, indicating that dimers are formed through intermolecular Au–Au interactions.\[26\] As shown in Figure 2B,C, while the intermolecular Au–Au interaction operates in the crystallographic a axis direction, the phenyl ring of the phenylacetylene ligand lies on the [100] surface.

2.2 | Photophysical behavior in solution and single crystals

The absorption spectrum of the complex in a dilute tetrahydrofuran (THF) solution ([R6] = 2.3 × 10−3 mol L⁻¹) is shown in Figure 3A. An absorption peak with a molar extinction coefficient (ε) of 4 × 10³ L mol⁻¹ cm⁻¹ was observed in the ultraviolet (UV) range at 290 nm.

The photoluminescence and excitation spectra of an R6 single crystal were acquired at room temperature in the presence of air (Figure 3B). Under ambient conditions, the crystal showed intense blue luminescence with a maximum (λₘₐₓ lum) at 450 nm, whereas no luminescence was observed in solution ([R6] = 2.3 × 10⁻³ mol L⁻¹) (Figure S1A). In contrast, R6 exhibited luminescence similar to that of the crystal in a solution ([R6] = 2.3 × 10⁻³ mol L⁻¹) bubbled with Ar gas to remove dissolved oxygen (Figure S1B). However, no luminescence was observed in more dilute solutions (<10⁻⁴ mol L⁻¹), even when bubbled with Ar. We previously reported that luminescence from this complex in a crystal has a lifetime of 52 μs, which is RTP caused by aggregation.\[26\] The results obtained in the current study support this assignment and indicate that R6 is an AIE-active material. This AIE activity was further confirmed by observing the luminescence behavior in a mixed solvent system (Figure S2). The complex showed no luminescence in pure THF, which is a good solvent for R6. However, the addition of water, which is a poor solvent, at volume fractions greater than 60% induced aggregation and significantly enhanced the emission (Figure S2B), showing that R6 is an AIE-active material.

While the RTP spectra of the single crystal and crystalline powder of R6 both exhibit vibronic structures, the intensities of their sharp luminescence bands at 428 nm are significantly different (Figure S3). A sharp luminescence band was observed at 428 nm when the single crystal was ground into the crystalline powder. Although only a shoulder was observed at 428 nm in the spectrum of the single crystal (Figure 3B), a distinct peak is present at this wavelength in the
spectrum of the crystalline powder. This sharp peak was also observed in the deoxygenated concentrated solution (Figure S1B). Lifetime measurements of the crystalline powder that exhibited this sharp band revealed a single exponential decay with a microsecond-order lifetime; no faster nanosecond-timescale decays were observed. Therefore, we conclude that the sharp luminescence band at 428 nm corresponds to phosphorescence from molecular aggregates in the amorphous regions and/or crystal defects or grain surfaces in the crystalline powder. Similar luminescence spectra with sharp peaks have been observed for Au or Pt complexes with sharp peaks at the shortest wavelengths assigned to luminescence 0–0 bands. The reason for the observed enhancement in the intensity of the 0–0 band in concentrated solutions and the crystalline powder is currently not completely clear. The molecular packing structures of disordered states (concentrated solutions, amorphous regions, crystal defects, and grain surfaces) differ from those of ordered states (single crystals). As the packing structures are different, the potential energy surfaces of the excited states, and the Franck–Condon factors of the vibronic bands, especially for the 0–0 band, for the crystalline powder and the single crystal are expected to differ, which provides a reason for the remarkably enhanced intensity of the 0–0 band in the crystalline powder and in solution.

Second-derivative phosphorescence spectra were used to sensitively identify the positions of peaks and shoulders, which helped to further analyze the vibronic structures (Figure 4). The vibrational modes in the phosphorescence spectra were assigned by comparing the IR spectra of R6 in the single crystal and crystalline powder (Figure S6), with assignments summarized in Table S1. This analysis revealed that the vibronic bands in the phosphorescence spectra mainly originate from the vibrations of the phenyl ring and ethynyl group of the alkynyl ligand.

The excitation spectra of the single crystal and crystalline powder show similar spectral shapes (Figure S3). Two main excitation bands are evident between 350 and 430 nm (band A) and below 350 nm (band B) in the excitation spectrum of the R6 single crystal (Figure 3B). Band B was further divided into a sharp band at 340 nm (B1) and a band at around 280 nm (B2). Band B2 is also present in the absorption spectrum of the dilute solution (Figure 3A), whereas bands A and B1 are specific to the crystal. However, a very weak absorption band with vibronic structure was observed in the same wavelength region as band A (observed for the crystal) in the spectrum of
A concentrated solution ([R6] = 2.3 × 10⁻³ mol L⁻¹) (inset, Figure 3A). Assuming that all molecules form dimers in the concentrated solution, the ε value at the absorption maximum (λ\text{max}_{\text{abs}} = 375 nm) was determined to be 5 L mol⁻¹ cm⁻¹. This very small absorption band, which is observed only in spectrum of the concentrated solution, might correspond to a spin-forbidden S₀–Tₙ transition. Because the S₀–Tₙ transition is a strictly spin-forbidden process in the Born–Oppenheimer approximation (i.e., zero-order approximation), its ε value is typically 10⁶ times smaller than the value for the spin-allowed S₀–S₁ transition. [27] Recently, several studies have reported that direct S₀–Tₙ transition has been reported for conventional organic compounds without transition metal atoms. [29] Consequently, it is reasonable to conclude that this small absorption band can be assigned to the direct S₀–Tₙ transition.

To further understand the photophysical properties of R6 in the crystals, their molecular orbitals were calculated using time-dependent density functional theory (TD-DFT) employing B3LYP hybrid functionals with the SDD basis set for the Au atoms and 6–311+G(d,p) for the remaining atoms. Single-point calculations were performed for the dimer formed by the Au–Au intermolecular interaction in the single crystal using the previously reported conformation obtained by single-crystal structural analysis, [26] with the oscillator strength (f) distribution calculated for the transitions to singlet excited states shown in Figure 3B. The molecular orbitals that correspond to the electronic transitions calculated to have large f values at 345.45 nm (f = 0.6206) and 276.55 nm (f = 0.3988) are shown in Figure 5. The R6 single crystal exhibited a sharp and intense excitation band at 340 nm (band B₁). TD-DFT calculations revealed that the excitation band at 345.45 nm corresponds to a transition from S₀ to the lowest excited singlet state (S₁) and that the main contribution to this transition is a one-electron HOMO to LUMO excitation process (Table S2). Based on the coefficients of the HOMO and the LUMO, this transition occurs from the π orbital of the ethynyl benzene ligand to the Au–Au atoms and is therefore a ligand-to-metal-metal charge transfer (LMMCT) transition. In contrast, the excitation band of the crystal at 280 nm (band B₂) corresponds to a transition from S₀ to an upper excited singlet state (Sₙ). These calculations indicate that this excitation band is mainly due to the S₀–Sₙ transition (276.55 nm, f = 0.3987), which is attributable to a transition from HOMO–1 to LUMO+2 (π–π* transition). Hence, we concluded that excitation band B in the crystal is assignable to one-electron excitation processes between singlet states, including S₀–S₁ (1LMMCT) and S₀–Sₙ (π–π* transitions).

As mentioned above, band A was observed as a small absorption band in the spectrum of the concentrated solution (inset, Figure 3A) and is attributable to the direct S₀–Tₙ transition; however, this absorption band was not observed in dilute solutions ([R6] ≪ 10⁻³ mol L⁻¹). These results suggest that spin–orbit coupling (SOC), which brings about inter-system crossing, is enhanced by aggregation of the complex. To confirm this hypothesis, the effects of spin–orbit interactions on the absorption spectra of the monomer and dimer were evaluated by single-point TD-DFT calculations at the B3LYP/def2-TZVP level. To reduce calculational load, we used a model compound (R6*) in which the long alkyl chains in R6 were substituted with methyl groups (Figure S8). The conformation of the remaining compound was set to the structure previously determined by single-crystal structure analysis; [26] the results are summarized in Table S3 in the supporting information. The transition energy obtained by this calculation is in good agreement with the experimental observation. Considering the SOC effects, f was determined to be 3.6 × 10⁻⁵ for the S₀–T₁ transition in the monomer; however, a 10 times larger value (6.3 × 10⁻⁴) was obtained for the S₀–T₁ transition in the dimer. TD-DFT calculations that include SOC support our hypothesis that SOC effects are enhanced by complex aggregation.

Excitation band A in the spectrum of the crystals is also assigned to the direct S₀–Tₙ transition. The 0–0 bands of the excitation and phosphorescence spectra of the single crystal
overlap at approximately 420 nm (Figure 3B), which supports the assignment of excitation band A in the crystal to the \( S_0 \rightarrow T_\pi \) transition. According to the TD-DFT calculations, the excitation energies for the \( S_0 \rightarrow T_1 \) (HOMO \( \rightarrow \) LUMO) and \( S_0 \rightarrow T_2 \) (HOMO-1 \( \rightarrow \) LUMO) transitions are 2.95 eV (421 nm) and 2.96 eV (419 nm) for the R6 dimer, whereas that for the \( S_0 \rightarrow S_1 \) transition was determined to be 3.59 eV (345 nm) (Table S2). Thus, the excitation energy calculated for the \( S_0 \rightarrow T_\pi \) transition is consistent with the wavelength of excitation band A. Furthermore, the transitions at \( \sim 420 \) nm (HOMO \( \rightarrow \) LUMO and HOMO-1 \( \rightarrow \) LUMO) are \(^3\)LMMCT transitions based on the coefficients of the molecular orbitals.

To further clarify the photophysical processes in the R6 crystals, polarized absorption and excitation spectra were collected for a 54-\( \mu \)m thick parallelogram-shaped single crystal. We defined the direction parallel to the crystallographic a axis as 0° for the polarization plane of the incident light (Figure 6). Band A was strongly observed in the absorption spectrum of the single crystal (Figure 6A) in the 0° polarization direction; however, band A was very weak in the 90° polarization direction. Similar results were observed for the polarized excitation spectra (Figure 6B). As mentioned above, the intermolecular Au–Au interaction is almost aligned with the crystallographic a axis, with the molecular long axis orthogonal to this crystallographic axis. Therefore, the transition moment of band A is parallel to the Au–Au interaction, which suggests that the electronic transition of band A is related to this interaction (i.e., an intermolecular band), consistent with the calculations that show that band A corresponds to an LMMCT transition. We also acquired the polarized luminescence spectrum of the R6 single crystal (Figure S4). The direction parallel to the crystallographic a axis is defined as 0° for the polarization plane of the emitted light in Figure S4. As observed in the absorption spectrum, strong photoluminescence was observed in the single crystal in the 0° polarization direction; however, it was remarkably weak in the 90° polarization direction, which suggests that the electronic transition for emission is also related to the Au–Au interaction.

The \( \varepsilon \) value for the direct \( S_0 \rightarrow T_\pi \) transition in the single crystal was determined to be \( \sim 50 \) \( \text{L mol}^{-1} \text{cm}^{-1} \) at 380 nm, based on the absorbance of the \( S_0 \rightarrow T_\pi \) absorption band, the thickness of the single crystal (54 \( \mu \)m), and the molar volume of R6 obtained by X-ray crystallography.\(^{26}\) Notably, this value is substantially larger than typical \( \varepsilon \) values for \( S_0 \rightarrow T_\pi \) transitions (\( \sim 10^{-3} \) \( \text{L mol}^{-1} \text{cm}^{-1} \))\(^{27}\) As previously mentioned, an \( \varepsilon \) value of 5 \( \text{L mol}^{-1} \text{cm}^{-1} \) was determined for the \( S_0 \rightarrow T_1 \) transition of R6 in concentrated solution. Although this value is \( 10^4 \) times smaller than that for the allowed \( S_0 \rightarrow S_\pi \) (\( \pi \rightarrow \pi^* \)) transition of R6 in solution, it is still larger than \( \varepsilon \) values generally observed for organic molecules. We conclude that the internal heavy-atom effect in the formed dimers induced by the Au atom is responsible for the large \( \varepsilon \) value for the \( S_0 \rightarrow T_1 \) transition in concentrated solution. Furthermore, the external heavy-atom effect may also effectively enhance the spin-forbidden transition in the crystal because the R6 molecules are packed very densely, and the number density of Au atoms is very high. This combination of internal and external heavy-atom effects promotes spin-forbidden transitions, which enables the R6 crystal to exhibit an efficient direct \( S_0 \rightarrow T_\pi \) transition with an \( \varepsilon \) value on the order of \( 10^1 \). This synergism also influences the \( T_1 \rightarrow S_0 \) radiative transition, thereby enhancing the phosphorescence rate. As a result, the complex in the crystal showed intense RTP with a large \( \Phi_{\text{RTP}} \) of 52% and a relatively phosphorescence short lifetimes (52 \( \mu \)s), as previously reported.\(^{26}\)

2.3 RTP quantum yields of R6 crystals

Generally, phosphorescence emission from the \( T_1 \) state occurs through \( S_0 \rightarrow S_\pi \) excitation followed by intersystem crossing to \( T_\pi \) and internal conversion to \( T_1 \) because the \( S_0 \rightarrow T_1 \) direct transition is spin-forbidden. Therefore, \( \Phi_{\text{RTP}} \) is determined by the product of the quantum yields of intersystem crossing (\( \Phi_{\text{ISC}} \)) and the radiative \( T_1 \rightarrow S_0 \) transition. However, in the present complex, the direct \( S_0 \rightarrow T_\pi \) transition occurs extremely efficiently by excitation in band A; thus, \( \Phi_{\text{RTP}} \) should be higher when the crystal is excited in band A. To investigate this unusual excitation path, we measured the \( \Phi_{\text{RTP}} \) value as a function of the excitation wavelength
FIGURE 6 Polarized (A) absorption and (B) excitation spectra of an R6 single crystal. For the incident light, a polarization of 0° was defined as the direction parallel to the crystallographic a axis (see top figures).

FIGURE 7 Room-temperature phosphorescence (RTP) quantum yields of R6 crystals as functions of excitation wavelength: red, single crystal; blue, crystalline powder. For comparison, the excitation spectrum of the single crystal is also plotted (green). All measurements were performed at 296 K in the presence of air.

FIGURE 8 Jablonski diagram of the photophysical processes in the R6 single crystal.

(Figure 7). When the R6 single crystal was excited in band B, the Φ_{RTP} value was found to depend on the excitation wavelength, increasing from ~40% when excited at <320 nm (S_{0}–S_{n} transition) to 60% when excited at 340 nm (S_{0}–S_{1} transition). In contrast, excitation in band A (S_{0}–T_{n} transition) gave a constant Φ_{RTP} value of ~60%, which is consistent with Kasha’s law. Interestingly, the Φ_{RTP} value increased dramatically by directly exciting S_{0}–T_{n}.

The Φ_{RTP} values of the crystalline powder exhibited the same tendency; however, they were lower than those of the single crystal, with Φ_{RTP} values of ~30% obtained by excitation at <320 nm and ~45% by excitation at both 340 nm and in band A, suggestive of an increase in nonradiative deactivation in the crystalline powder. The Φ value of crystals crushed to less than 200 × 200 μm in size is almost the same as that of the crystalline powder, and a significantly intense 0–0 band was observed in the luminescence spectrum. In contrast, crystal grains of approximately 2 × 0.5 mm in size exhibited an intermediate Φ value between that of the large single crystal and the crystalline powder, and a small 0–0 band. Thus, we conclude that single crystals that are least several millimeters in size are required to obtain a Φ value of ~60%.

2.4 Plausible electron transition processes and quantum efficiencies in crystals

Here, we discuss and summarize the transition processes involved in RTP for the R6 crystal using the Jablonski diagram shown in Figure 8. We concluded that the excitation process depended on the excitation band (vide supra). The DFT results for the dimer suggest that absorption band B
corresponds to singlet–singlet excitation processes, including S₀–S₁ (1LMMCT at 340 nm) and S₀–S₃ (1(π–π*)) at 280–320 nm) transitions. Moreover, excitation band A corresponds to the direct transition from S₀ to Tₙ.

Excitation band A had five vibronic fine structures at 369, 380, 392, 409, and 423 nm, which were further categorized into two subgroups comprising three peaks at 369, 380, and 392 nm with peak spacings (δ) of 780 cm⁻¹ (subgroup 1), and two peaks at 409 and 423 nm (δ = 811 cm⁻¹, subgroup 2) (Figure S5A). These subgroups are considered to be vibronic structures that correspond to different electronic states.

Therefore, we conclude that absorption band A involves two transition states (i.e., T₁ and T₂) in the triplet state. A similar vibronic structure was also observed in the absorption band at 360–420 nm in the spectrum of the concentrated solution, which was assigned to the S₀–Tₚ transition (Figure S5B). As shown in Figure 6, the transition moment of band A is aligned with the Au–Au interaction, suggesting that excitation band A is related to the Au–Au interaction; therefore, the T₁ and T₂ states are assigned to be 1LMMCT excited states.

The quantum efficiency of each photophysical process was determined from the excitation wavelength dependence of Φ_RTP (Figure 7). Direct excitation to triplet states gave a Φ_RTP value of 60% for the single crystal; therefore, the quantum efficiency of the radiative relaxation from the T₁ state is 60%. In addition, the S₀–S₁ excitation (1LMMCT transition) at 340 nm led to a Φ_RTP value of 60%, suggesting that Φ_TSC for S₁–Tₚ intersystem crossing is almost 100%. Because S₁ is a 1LMMCT excited state, this effective intersystem crossing is due to the Au–Au interaction aided by strong internal and external heavy-atom effects in the single crystal. However, Φ_RTP decreased to 40% upon excitation at 320 nm and remained constant at shorter wavelengths, which implies that the quantum yield for internal conversion (Φ_IC) to S₁ is 67%. Interestingly, a direct deactivation path to S₀ that bypasses the S₁ state exists (quantum yield of 33%). Here, although the nature of the electronic state is unclear, we hypothesize a singlet excited state (Sₚ) to explain deactivation path branching.

Furthermore, we considered whether or not the observed luminescence in the R₆ crystal is thermally activated delayed fluorescence (TADF) [30] for which the energy gap between the singlet and triplet excited states (ΔE_ST) is the most important factor. The TD-DFT-calculated energies of the S₁ and T₁ states of R₆ are 3.589 and 2.945 eV, respectively, and ΔE_ST is 0.6432 eV, which is much larger than typical ΔE_ST values for reported TADF materials (~0.1 eV or smaller) [30]. In addition, the luminescence intensities at 80 K and room temperature are similar (Figure S7). Based on the large ΔE_ST value and the lack of enhanced luminescence at room temperature, we exclude TADF as a photophysical process involving R₆.

It should be mentioned that the luminescence efficiencies did not decrease significantly with increasing temperature, as shown in Figure S7, and the integral of the spectrum in the 400–600 nm wavelength region at 80 K was only 1.3 times larger than that at room temperature. Because molecular motions such as internal rotations and vibrations are restricted in the crystal lattice, the thermal deactivation of excited states is restricted, even at room temperature.

In the crystalline powder, Φ_IC for the S₃–S₁ internal conversion was similar to that for the single crystal (Φ_IC = 67%). The T₁–S₀ radiative transition efficiency for the crystalline powder (45%) is 15% lower than that for the single crystal. Moreover, as mentioned earlier, the crystalline powder showed sharp luminescence at 428 nm, attributable to emission from molecular aggregates in the amorphous regions, crystal defects, or grain surfaces (Figure S2B). We conclude that the luminescence efficiency of such an aggregate is lower than that of aggregates in the single crystal because the internal molecular motions are not suppressed very strongly; therefore, the crystalline powders exhibit a lower Φ_RTP value.

The current results indicate that the Au–Au interaction enhances transition efficiencies accompanied by spin flipping, namely T₁–S₀ radiative transition, S₁–Tₚ intersystem crossing, and S₀–T₁ direct excitation. Further, the phosphorescence emission is enhanced by the Au–Au interaction as well as the internal and external heavy-atom effects of the Au atoms. Thus, Au complexes show extraordinarily strong S₀–Tₚ absorption and highly efficient RTP in crystals owing to both aurophilic interactions and heavy-atom effects.

3 | CONCLUSION

In this study, we prepared a large single crystal of R₆, which enabled a detailed investigation of the photophysical processes of this Au complex in the crystals. We found that an extremely efficient direct S₁–Tₚ transition occurs in the R₆ crystal; direct excitation to the excited triplet state improved Φ_RTP by 15%. We also demonstrated that electronic transitions involving intersystem crossing (S₀–Tₚ direct excitation, T₁–S₀ radiative transition [phosphorescence], and S₁–Tₚ intersystem crossing) are enhanced by intermolecular Au–Au interaction and the internal/external heavy-atom effects of the Au atoms. Owing to these effects, the Au complex showed more efficient RTP in the crystal than in solution. We believe that these results improve our understanding of the photophysical processes of Au complexes, which will help to establish design guidelines for new luminescent materials, particularly stimuli-responsive luminescent materials.

4 | EXPERIMENTAL SECTION

4.1 | Materials

The complex (R₆) was prepared according to a previously reported procedure [26] and purified using column chromatography and recrystallization. The structure and purity of the complex were confirmed by ¹H NMR, HRMS, IR, and elemental analyses. Unless otherwise mentioned, all the solvents and reagents were purchased from commercial suppliers and used without further purification. Column chromatography was carried out using silica gel (64–210 μm; Wakosil C-200), and thin-layer chromatography (TLC) was performed using silica gel TLC plates (Silica-gel 60 F₂₅₄; Merck). ¹H NMR spectra (ECS-400; JEOL) were recorded at 400 MHz using the NMR signal of residual undeuterated solvent as an internal reference. IR spectra were obtained using the KBr disk method (FT/IR-610; JASCO), and all the spectra were reported in wavenumber (cm⁻¹). HRMS was performed using a JEOL JMS-700 spectrometer. Elemental C, H, and N analyses were conducted using a Micro Corder analyzer (JM10; J-SCIENCE).
R6: mp 89°C; 1H NMR (400 MHz, CDCl3, δ): 7.38 (dd, J = 6.8 and 2.0 Hz, 2H, 3.5-H in benzene), 6.76 (dd, J = 6.8 and 1.8 Hz, 2H, 2.6-H in benzene), 3.92 (t, J = 6.6 Hz, 2H, OCH2), 3.61 (t, J = 6.9 Hz, 2H, NCH2), 1.87−1.71 (m, 4H, OCH2CH2, NCH2CH2), 1.46−1.27 (m, 10H, OCH2CH2(CH2)3, NCH2CH2(CH2)2), 0.94 (t, J = 7.2 Hz, 3H, N(CH2)4C), 0.89 (t, J = 7.0 Hz, 3H, O(CH2)3CH3); FTIR (KBr, cm−1): 3034, 2952, 2931, 2861, 2360, 2252, 1603, 1503, 1245; HRMS (ESI) m/z: [M + Na]+ calcd for C20H28AuNONa, 518.1734; found, 518.1735. Anal calcd for C 48.49, H 5.70, N 2.83, Au 39.76; found: C 48.32, H 5.42, N 2.83, ash 40.0.

4.2 | Preparing single crystals and X-ray crystallography

To obtain large and high-quality single crystals, the complex was recrystallized from a solution using the slow evaporation method. In a 500 ml beaker, 100 mg of the purified complex was dissolved in 10 ml of dichloromethane as a good solvent. Then, 20 ml of hexane was layered on the resultant solution as a poor solvent. The beaker was covered with aluminum foil with several (typically five) holes ~2 mm in diameter, and the solution was left to stand at 25°C for 2 days to slowly evaporate the good solvent. The precipitated crystals were collected by gentle filtration.

A single crystal was mounted on a glass fiber, and reflection data were collected using an ω-scan technique on an automated four-circular-axis diffractometer (AFC-5R; Rigaku) with graphite-monochromatized Cu Ka radiation (λ = 1.54178 Å). Experiments were performed at room temperature (296 K). The initial structure in the unit cell was determined by a direct method using SIR92. [31] The structural model was refined by full-matrix least-squares methods with SHELXL97. [31] All calculations were performed using the WinGX crystallographic software package. [31] CCDC 927045 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.3 | Photophysical properties

Absorption spectra of the complex in the crystal and in solution were recorded using an absorption spectrometer (V-550; JASCO) and fluorescence spectra were recorded using a fluorescence spectrometer (F-7000; Hitachi). Polarized absorption and excitation spectra were recorded using an absorption spectrometer (UV-3150; Shimadzu) or a fluorimeter (F-4500; Hitachi), into which the polarizer was set.

4.4 | Calculations

TD-DFT calculations were performed using the Gaussian 03 program package employing B3LYP hybrid functional with SDD (for the Au atoms) and 6−31+G(d,p) (for the other atoms) basis sets. [32] For the R6 dimer in the crystal, single-point calculations were conducted using the computational method previously determined by single-crystal structure analysis. [32] The vertical excitation energies and f values were determined for the 15 lowest transitions to excited singlet states and for the six lowest transitions to excited triplet states.

The SOC effect in each absorption spectrum was also evaluated using the Orca program package at the B3LYP/def2-TZVP level. To reduce the calculational load, we used a model compound (R6′) in which the long alkyl chains of R6 were substituted with methyl groups (Figure S6). The conformation of the remaining compound was set to that determined by single-crystal structure analysis. [32]

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest that could be perceived as prejudicing the impartiality of the research reported.

DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supplementary material of this article.

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