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First aggregation-induced emission of a Tb(III) luminophore based on modulation of ligand-ligand charge transfer bands†

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Herein the aggregation-induced emission (AIE) of a Tb(m) complex is reported for the first time. The Tb(m) complex is composed of three anionic ligands (acac: acetylacetonate) and one large hetero- π -conjugated neutral ligand (dpq: dipyrido[3,2-*f*:2',3'-*h*]quinoxaline). The formation of a crystalline J-aggregate of the Tb(m) complex (CJ-Tb(m)) was characterized by X-ray crystal structure analysis and absorption spectra. A crystalline H-aggregate (CH-Tb(m)) was also prepared using the ligand steric effect (tmh: 2,2,6,6-tetra-methyl-3,5-heptanedionate). The emission and AIE properties of CJ-Tb(m) were evaluated using emission spectra, lifetime, and quantum yields, whereas CH-Tb(m) did not emit photons. Density functional theory calculations predict that the AIE originates from the modulation of ligand-to-ligand charge transfer bands through J-aggregation.

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Introduction

Luminescent materials that exhibit aggregation-induced emission (AIE) have attracted considerable attention¹ since the discovery of the AIE effect by Tang in 2001.^{1*a*} AIE-active materials are non-emissive (or weakly emissive) in the solution state but exhibit strong luminescence in an aggregated state (*e.g.*, supramolecular systems in solution, amorphous films, and crystalline powders). The AIE phenomenon originates from restrictions to intramolecular rotation induced by aggregation. Various types of AIE-based materials for bio-applications have been reported. For example, Wen described the heavy-atomfree 1,1,4,4-tetraphenylbuta-1,3-diene exhibiting the AIE effect for photodynamic cancer therapy.² Tang demonstrated an AIEactive tetraphenylethene-based chemo-sensor for Hg²⁺ that

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shows solvatochromism and cell imaging characteristics.³ Yuan built a singlet oxygen sensor for the targeted photodynamic ablation of cancer cells using an AIE probe.⁴ However, these luminescent materials have short emission lifetimes (on the order of nanoseconds) that resemble the emission lifetimes of biomolecules such as proteins.⁵ The fabrication of AIE-active luminophores with long emission lifetimes (on the order of milliseconds) is required for their developing use in bio-applications.

Green luminescent Tb(m) complexes are promising molecular materials with narrow 4f–4f emission bands (full-width at half maximum < 5 nm) and long emission lifetimes (>1 ms).⁶ Recently, several research groups found that the ligand-to-ligand charge transfer (LLCT) band strongly affects the luminescence properties of these complexes.⁷ Control of the LLCT band in solution and crystallized states could lead to the synthesis of Tb(m) luminophores with effective AIE.

In general, crystal packing structures are classified into slipped-stacked configurations (J-aggregates) and face-to-face configurations (H-aggregates) in terms of molecular alignment.⁸ The H-aggregates of Tb(m) complexes promote the formation of quenching states such as excimers,⁹ whereas the J-aggregates induce effective red-shifts of absorption bands without the formation of a quenching state.¹⁰ In this study, we report the first observation of AIE from a Tb(m) complex.

To prepare a Tb(III) complex with LLCT-controlled states, we selected β -diketonate ligands (acac: acetylacetonate or tmh: 2,2,6,6-tetramethyl-3,5-heptanedionate) and dipyrido[3,2-f:2',3'-h]quinoxaline (dpq) as energy donating and accepting parts,

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Fig. 1 (a) Chemical structures and schematic images of Tb(III) complexes. Schematic images of (b) Tb(III) complex in solution, (c) Tb(III)-based J-aggregates, and (d) Tb(III) based H-aggregates.

respectively (Fig. 1a and b). The large π -conjugated dpq ligand is also expected to aid in building the Tb(m)-based aggregates. We prepared crystalline Tb(m)-based J-aggregates (CJ-Tb(m), Fig. 1c) and H-aggregates (CH-Tb(m), Fig. 1d) by controlling the steric structure of the β -diketonate ligands. This discovery of AIE, based on LLCT control of the Tb(acac)₃dpq complex, represents a frontier field for molecular materials chemistry, photophysical chemistry, and coordination chemistry.

Results and discussion

Tb(m) complexes in solution states

To analyze the lowest excited triplet (T_1) levels, we prepared Gd $(acac)_3dpq$ and Gd $(tmh)_3dpq$. By using Gd(m) complexes, the T_1 levels of Tb $(acac)_3dpq$ and Tb $(tmh)_3dpq$ in CH₂Cl₂ were found to be 19 200 cm⁻¹ and 19 100 cm⁻¹, respectively (Fig. 2). These energy levels are lower than the emission level of the Tb (m) ion $({}^5D_4: 20\ 500\ cm^{-1})$, indicating the formation of quenching states for Tb(m) emission. Previous reports state the T_1



Fig. 2 Phosphorescence spectra of Gd(acac)₃dpq (black line) in CH₂Cl₂ (1.0 × 10⁻³ M, delay: 20 ms, 185 K, λ_{ex} = 350 nm) and Gd(tmh)₃dpq (red line) in CH₂Cl₂ (1.0 × 10⁻³ M, delay: 10 ms, 180 K, λ_{ex} = 350 nm).



Fig. 3 Main T₁ state configurations (>10%) of Tb(acac)₃dpq (HOMO-4 \rightarrow LUMO+1: 27%, HOMO-6 \rightarrow LUMO: 15%, HOMO-5 \rightarrow LUMO: 11%). DFT calculations were performed using Al(III) ions instead of Tb(III) ions.^{7a,15}

levels of dpq and acac (tmh) ligands as 23 500 cm⁻¹ and 25 000 (24 400) cm⁻¹,¹¹⁻¹³ respectively. Time-dependent density functional theory (TD-DFT) (CAM-B3LYP/6-31G(d), IPCM-CH₂Cl₂)¹⁴ calculations revealed that the T₁ states are mainly composed of transitions from the delocalized orbital between dpq and β -diketonate to dpq orbitals, thus inducing LLCT characteristic (Fig. 3, see the ESI† for details). This interpretation is consistent with the observed characteristically broad emission bands.¹⁶ These results suggest that Tb(acac)₃dpq and Tb (tmh)₃dpq in solution do not emit photons for quenching into the LLCT state.

Tb(m) complexes in aggregation states

Single crystals of Tb(acac)₃dpq and Tb(tmh)₃dpq (Fig. 4) were obtained by recrystallization from CH2Cl2/hexane solution. Single-crystal X-ray analysis revealed the structures of the Jand H-aggregates of $Tb(acac)_3dpq$ (CJ-Tb) and $Tb(tmh)_3dpq$ (CH-Tb), respectively (Fig. 4, Table 1). Two patterns of intermolecular dipole-dipole interactions (Fig. 4a, 1.0 nm and 1.2 nm) were observed for the Tb(acac)₃dpq crystal structure, which correspond to the slipped-stacked configuration (J-aggregation: CJ-Tb(m)). On the other hand, strong intermolecular π - π interactions (Fig. 4b, 0.3 nm) between two dpq ligands were observed for Tb(tmh)₃dpq, which correspond to the face-to-face configuration (H-aggregation: CH-Tb(III)). The strong π - π interaction induces the formation of an effective quenching state for Tb(III) emission (Fig. 5, $T_1 = 17200 \text{ cm}^{-1}$). This energy shift is thought to originate from charge resonance interactions between dpq ligands.¹⁷ The triplet level of CJ-Tb(m) was calculated via TD-DFT, and the estimated T₁



Fig. 4 X-ray crystal structures of (a) Tb(acac)₃dpq and (b) Tb(tmh)₃dpq.

Table 1 Crystallographic data of Tb(acac)₃dpq and Tb(tmh)₃dpq

	Tb(acac)₃dpq	Tb(tmh)₃dpq
Chemical formula	C ₂₉ H ₂₉ N ₄ O ₆ Tb	C47H65N4O6Tb
Formula weight	688.49	937.92
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	9.3675(2)	10.9111(2)
b/Å	9.4780(2)	12.2969(2)
c/Å	15.8705(3)	19.3981(3)
$\alpha / ^{\circ}$	100.326(2)	104.160(2)
<i>β</i> /°	92.661(2)	93.820(2)
γ/°	99.070(2)	110.125(2)
Volume/Å	1364.86(5)	2336.81(8)
Z	2	2
Density/g cm ⁻³	1.675	1.337
Temperature/°C	20	20
R^a	0.0235	0.0240
WR_2^{b}	0.0776	0.0832



Fig. 5 Phosphorescence spectrum of Gd(tmh)₃dpq in solid state (λ_{ex} = 350 nm).

energy (22 900 cm⁻¹) was sufficiently higher than the emission level of the Tb(III) ion (20 500 cm⁻¹). The T₁ states correspond to localized dpq states (Fig. S12†), indicating that the excited LLCT energy increased with the change in coordination geo-

metry from the solution to solid state. To determine the coordination geometry around the Tb(m) ion, we performed continuous shape measure calculations (Table S1, see ESI† for the detail).¹⁸ The continuous shape measure factor *S* was calculated to estimate the distortion degree of the coordination structure in the first coordination sphere based on the crystal structure data. The *S* value is given by the following equation.

$$S = \min \frac{\sum_{k}^{N} |Q_{k} - P_{k}|^{2}}{\sum_{k}^{N} |Q_{k} - Q_{0}|^{2}} \times 100$$

where Q_k is the vertices of the actual structure, Q_0 is the center of mass of the actual structure, N is the number of vertices, and P_k is the vertices of the ideal structure. Eight-coordinated lanthanide complexes exhibit a square antiprism (SAP, point group: D_{4d}), trigonal dodecahedron (TDH, point group: D_{2d}), or biaugmented trigonal prism (BTP, point group: C_{2v}) structure according to the *S* value. Based on the calculations, Tb (acac)₃dpq was categorized as SAP coordination geometries (Table S1,† *S* = 0.581). On the other hand, the *S* value of the isolated Tb(m) complex obtained by theoretical calculations was categorized as TDH coordination geometry (*S* = 4.569), indicating different coordination geometry of between Tb(m) complexes in solution and solid states. The coordination geometry changes lead to LLCT band modulation, which should induce AIE property (Fig. 6).

Aggregation-induced emission of Tb(m) luminophore

The emission photograph of Tb(acac)₃dpq in solution (CH₂Cl₂, 1.0 × 10⁻³ M) and solid states under UV-light are shown in Fig. 7a. We successfully observed the green emission of CJ-Tb (m), although Tb(acac)₃dpq in solution did not emit photons. The luminescence and excitation spectra of Tb(acac)₃dpq are shown in Fig. 7b. Sharp emission bands at 488, 545, 581, 619, and 648 nm were observed for Tb(acac)₃dpq, which are assigned to the ⁵D₄ \rightarrow ⁷F₆, ⁵D₄ \rightarrow ⁷F₅, ⁵D₄ \rightarrow ⁷F₄, ⁵D₄ \rightarrow ⁷F₃, and ⁵D₄ \rightarrow ⁷F₂ transitions of the Tb(m) ion, respectively.

The excitation spectrum has broad bands in the UV-visible region, indicating an effective energy transfer from the J-aggregate to the Tb(m) ion ($\Phi = 16\%$, $\tau = 0.47$ ms, Table 2).



Fig. 6 Schematic images of energy diagram of $Tb(acac)_3(dpq)$ in solution (a) and solid (b) states.



Fig. 7 (a) Photographs of Tb(acac)₃(dpq) in solution and solid states under UV-light. (b) Emission (solid line, $\lambda_{ex} = 350$ nm) and excitation (broken line, $\lambda_{em} = 545$ nm) spectra of Tb(acac)₃(dpq). Photographs in casting solutions of (c) Tb(acac)₃(dpq) and (d) Tb(tmh)₃(dpq) under UV-light.

The luminescence lifetime of CH-Tb(III) was much shorter ($\tau = 0.02 \text{ ms}$) due to aggregation-induced quenching of the Tb(III) ion.

The AIE behavior of CJ-Tb(m) during the solidification of the luminescent species in solution is shown in Fig. 7c. We observed green luminescence from the edge of the solution at 21 s, and then bright green luminescence at 56 s. In contrast to the AIE effect of Tb(acac)₃dpq, we did not observe green luminescence from CH-Tb(m) (Fig. 7d). We also found that the emission lifetime was strongly dependent on temperature (Fig. 8), demonstrating the potential of the AIE-active $\mbox{Tb}(\mbox{III})$ luminophore as a thermometer.

Finally, we determined the water solubility of the complex between CJ-Tb(m) and sodium dodecyl sulfate (SDS) for possible future applications. DLS measurements of the complex in SDS-water (SDS: 2.0×10^{-2} M) revealed a nano-order particle size (Fig. 9a, $d_{ave} = 196$ nm). Effective Tb(m) emission in SDS-water was also observed (Fig. 9b, $\tau = 0.38$ ms).

Conclusions

In this paper, we reported a novel strategy to fabricate emission materials exhibiting the AIE effect by using the orientation control of ligands around the Tb(m) ion. The Tb(m) complex has the advantage of prominent luminescence with narrow emission bands and long emission lifetimes based on



Fig. 8 Temperature-dependent emission lifetime of CJ-Tb(III) (λ_{ex} = 356 nm).



Fig. 9 (a) DLS graph of Tb(acac) $_3(dpq)$ -SDS, (b) Photographs and schematic image of Tb(acac) $_3(dpq)$ -SDS in H₂O.

Table 2 Photophysical properties of Tb(III) complexes

State	Compounds	T_1/cm^{-1}	Aggregation type	Absorption edge/cm ⁻¹	${\varPhi_{ m tot}}^{b}$ /%	τ^{c}/ms
CJ-Tb(ш)	Tb(acac)₃dpq	22900^{a}	J-Aggregation	16 800	16	0.47
CH-Tb(III)	Tb(tmh) ₃ dpq	17 200	H-Aggregation	20 300	<1	0.02
Solution	Tb(acac) ₃ dpq	19 200	Monomer	_	ND	ND
Solution	Tb(tmh) ₃ dpq	19100	Monomer	_	ND	ND

^{*a*} Theoretical calculation value. ^{*b*} $\lambda_{ex} = 360$ nm. ^{*c*} $\lambda_{ex} = 355$ nm

4f-4f transition. This study provides new insights into AIE materials based on lanthanide(III) complexes.

Experimental section

General method

¹H-NMR spectra were recorded in CDCl₃ on a JEOL ECS-400 (400 MHz) spectrometer; CHCl₃ ($\delta_{\rm H}$ = 7.26 ppm) was used as the internal reference. Electrospray ionization (ESI) mass spectrometry was performed using JEOL JMS-T100 LP instrument. Elemental analyses were performed using MICRO CORDER JM10. Thermogravimetric analyses (TGA) were performed using an EXSTAR 6000 TG/DTA 6300 instrument (Seiko Instruments Inc.). UV-vis absorption spectra were measured using a JASCO V-670 spectrophotometer. Diffuse-reflection spectra was recorded with a JASCO V-670 spectrophotometer equipped with an integrating-sphere unit (JASCO ISN-723). Luminescence spectra, excitation spectra, and luminescence lifetimes for Tb(acac)₃dpq and Tb(tmh)₃dpq were measured using a Horiba FluoroLog®3 spectrofluorometer. Temperaturedependent luminescence lifetimes for Tb(acac)3dpg were measured using a Horiba FluoroLog®3 spectrofluorometer with a cryostat (Thermal Block Company, SA-SB245 T) and a temperature controller (Oxford, Instruments, ITC 502S). Luminescence quantum yields were measured using a FP-6300 spectrofluorometer with an integration sphere (ILF-533). DLS measurement was performed using nanotracWave II = UT151-SPHG.

Materials

Magnesium sulfate, anhydrous (>98.0% (titration)), methanol (guaranteed reagent), ethanol (guaranteed reagent), and chloroform-d₁ (99.8%) were purchased from Kanto Chemical Co., Inc. Dichloromethane (spectroscopic grade), chloroform (spectroscopic grade), and 1,2-dichloroethane (spectroscopic grade) were purchased from Wako Pure Chemical Industries, Ltd. 1,10-Phenanthroline-5,6-dione (>98.0%), 2,2,6,6-tetramethyl-3,5-heptanedione, and ethylenediamine anhydrous (>98.0%) were purchased from Tokyo Chemical Industry Co., Ltd. Terbium(III) acetylacetonate hydrate was purchased from Sigma-Aldrich (99.9%).

Preparation of dpq (dipyrido[3,2-*f*:2',3'-*h*]**quinoxaline**). We prepared the dpq ligand according to a previous report.^{11,19} 1,10-Phenanthroline-5,6-dione (627 mg, 2.99 mmol) and ethylenediamine (1.0 mL, 15.0 mmol) were dissolved in water (40 ml), and the mixed solution was stirred for 12 h at 60 °C. The resulting precipitate was filtrated, washed with water, and dried under vacuum to afford a cream-colored solid (yield: 559 mg, 80%).¹H-NMR (400 MHz, CDCl₃/TMS) δ /ppm = 9.52 (d, *J* = 8.4 Hz, 2H), 9.30 (d, *J* = 4.4 Hz, 2H), 9.00 (s, 2H), 7.81 (dd, *J* = 8.0, 4.0 Hz, 2H).

Preparation of Tb(acac)₃**dpq.** Tb(acac)₃dpq was prepared according to our previous report.^{11,19} A methanol solution (20 ml) containing dpq (143 mg, 0.616 mmol) was added to a methanol solution (20 ml) containing Tb(acac)₃·nH₂O

(433 mg), and the mixed solution was refluxed for 12 h. The resulting precipitate was filtrated, washed with methanol and ethanol, and dried under vacuum to afford a cream-colored solid (yield: 349 mg).

ESI-MS: m/z calcd for $C_{29}H_{29}N_4O_6Tb$, $[M-acac]^+ = 589.09$; found: 589.07; elemental analysis calcd (%) for C 50.59, H 4.25, N 8.14; found: C 50.33, H 4.14, N 7.98.

Preparation of Tb(tmh)₃**dpq.** Tb₂(tmh)₆ was prepared according to a previous report.¹⁴ A methanol solution (50 ml) containing dpq (233 mg, 1.00 mmol) was added to a methanol solution (50 ml) containing Tb₂(tmh)₆ (710 mg, 0.501 mmol), and the mixed solution was refluxed for 12 h. The resulting precipitate was filtrated, washed with methanol and ethanol, and dried under vacuum to afford a cream-colored solid (yield: 692 mg, 74%).

ESI-MS: m/z calcd for $C_{47}H_{65}N_4O_6Tb$, $[M-tmh]^+ = 757.28$; found: 757.25; elemental analysis calcd (%) for C 59.99, H 6.96, N 5.95; found: C 59.83, H 6.96, N 5.93.

Preparation of Gd(acac)₃**dpq.** A methanol solution (40 ml) containing dpq (235 mg, 1.01 mmol) was added to a methanol solution (20 ml) containing $Gd(acac)_3 \cdot nH_2O$ (458 mg), and the mixed solution was refluxed for 12 h. The resulting precipitate was filtrated, washed with methanol and ethanol, and dried under vacuum to afford a cream-colored solid (yield: 434 mg).

ESI-MS: m/z calcd for $C_{29}H_{29}GdN_4O_6$, $[M-acac]^+ = 588.09$; found: 588.08; elemental analysis calcd (%) for C 50.71, H 4.26, N 8.16; found: C 50.27, H 4.15, N 8.05.

Preparation of Gd(tmh)₃**dpq.** $Gd_2(tmh)_6$ was prepared according to a previous report.¹⁹ A methanol solution (40 ml) containing dpq (237 mg, 1.02 mmol) was added to a methanol solution (20 ml) containing $Gd(tmh)_6$ (709 mg, 0.501 mmol), and the mixed solution was refluxed for 12 h. The resulting precipitate was filtrated, washed with methanol and ethanol, and dried under vacuum to afford a cream-colored solid (yield: 812 mg, 85%).

ESI-MS: m/z calcd for $C_{47}H_{65}GdN_4O_6$, $[M-tmh]^+ = 756.28$; found: 756.32; elemental analysis calcd (%) for C 60.10, H 6.98, N 5.96; found: C 59.39, H 6.87, N 5.82.

Single-crystal X-ray structure determination

X-ray crystal structures and crystallographic data for Tb $(acac)_3$ dpq and (for Tb $(tmh)_3$ dpq are shown in Fig. 4 and Table 1. Single crystals of the compounds were mounted on micromesh (MiTeGen M3-L19–25L) using paraffin oil. Measurements were made by using a Rigaku RAXIS RAPID imaging-plate area detector or XtaLAB AFC11 (RCD3) with graphite-monochromated Mo-K α radiation. Non-hydrogen atoms were anisotropically refined. All calculations were performed using a crystal-structure crystallographic software package. The CIF data were confirmed by the check CIF/PLATON service. CCDC 1867203 (for Tb(acac)_3dpq), 1867204 (for Tb(tmh)_3dpq), 1975471 (for Gd(acac)_3dpq), and 1911406 (for Gd(tmh)_3dpq) contain the supplementary crystallographic data for this paper.†

Conflicts of interest

There are no conflicts to declare.

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