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Chiroptical Properties of Nonanuclear Tb(III) Clusters with Chiral Champhor Derivative Ligands*

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The chiroptical properties of nonanuclear Tb(III) clusters are reported. The nonanuclear Tb(III) clusters are composed of nine Tb(III) ions, ten μ-OH parts, and sixteen chiral organic ligands, (±)-bornyl salicylate. Their chiroptical properties were estimated by circular dichroism (CD) and circularly polarized luminescence (CPL). Their electronic structures were calculated using TD-DFT (B3LYP/6-31G(d)) method.
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Keywords: Lanthanides; Photoluminescence; Chirality; Circularly polarized luminecnece; Visible/ultraviolet absorption spectroscopy

I. INTRODUCTION

Luminescence of metal complexes composed of metal ions and organic ligands has attracted wide interest for applications that include optical materials [1], organic light-emitting diodes [2, 3], and fluorescent sensors[4, 5]. The luminescent properties of these complexes strongly depend on the combination of the metal center and the organic ligands. The luminescence properties of transition-metal complexes are derived from the d–d and metal-to-ligand charge-transfer (MLCT) transitions based on the outer d-orbitals of the complexes [6]. These characteristics are strongly dominated by the orbital interactions between the transition-metal ion and the organic ligands [6]. The design of the organic ligands can give controllable luminescent wavelength and intensity based on the d–d and the MLCT transitions.

On the other hand, lanthanide ions have the inner $4f$ orbitals, which induce different luminescence properties from those of transition-metal ions. Compared to transition-metal complexes, lanthanide complexes provide specific narrow emission band because of their inner $4f$ orbitals [7, 8]. They also exhibit long emission lifetime based on the $4f$–$4f$ forbidden transitions. Here, organic ligands can play an important role in the intense lanthanide luminescence. The organic ligands perform as efficient light harvesting systems for photosensitized luminescence of the lanthanide complexes. The organic ligands also enhance the radiative rate by introducing an asymmetric geometry around the lanthanide ion, effectively [9–12]. Based on their two strategies for design of the ligands, various types of strong luminescent lanthanide complexes with asymmetric structures have been reported [13, 14].

Luminescent complexes with chiral ligands show circularly polarized luminescence (CPL) [15]. This is based on the differential emission intensity of left- and right-handed circular polarized light according to the chirality of the emitter, and is often used as an indicator of chirality in a metal ion center [16–18]. The CPL property is expected to be useful for applications such as future three-dimensional displays, security paints, and optical telecommunications. The magnitude of CPL is represented by the dissymmetry factor g_{CPL} [15]. At the present stage, a large number of scientific researches on mononuclear chiral lanthanide complexes with large g_{CPL} values have been performed [19–21].

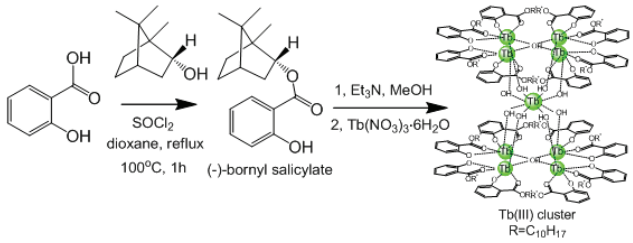


FIG. 1. Synthetic scheme of a (−)-bornyl salicylate ligand and a nonanuclear Tb(III) cluster.

Recently, polynuclear lanthanide clusters with chiral ligands have attracted attention for their CPL with characteristic structure [22, 23]. For example, Gunnlaugsson reported large CPL of dinuclear Eu(III) complexes using triple-stranded helical ligands [24]. Mazzanti reported the changeable g_{CPL} of polynuclear Eu(III) clusters depending on their several types of self-assembly structures [25]. In contrast, chiroptical lanthanide clusters composed of lanthanide ions and bridged oxygens, Ln-O-Ln lattices, have never been reported yet. In this study, we report the chiroptical properties of novel nonanuclear Tb(III) clusters for the first time. These clusters are constructed by nine Tb(III) ions, ten μ-OH parts, and sixteen chiral salicylic acid esters, bornyl salicylates, (±)-bor (Fig. 1) [26]. These ligands are champhor derivatives for enhancement of g_{CPL} according to the previous report [27]. We have demonstrated the intense CPL and electronic structures of Tb(III) clusters with bornyl salicylates, Tb-(±)-bor.

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II. EXPERIMENTAL

A. Materials

Salicylic acid ($C_6H_4(OH)COOH$) and 1,4-dioxane ($C_4H_8O_2$) were purchased from Wako Pure Chemical Industries, Ltd. (+)-borneol ($C_{10}H_{18}O$, 97%) and (−)-borneol ($C_{10}H_{18}O$, 97%) were purchased from Aldrich. Thionyl chloride ($SOCl_2$) was purchased from Tokyo Chemical Industry Co., Ltd. Terbium(III) nitrate hexahydrate ($Tb(NO_3)_3{\cdot}6H_2O$), and triethylamine ($(C_2H_5)_3N$) were purchased from Kanto Chemical Co., Inc.

B. Instrumental Techniques

^{1}H-NMR spectra were recorded in $CDCl_3$ on an Auto-NMR JEOL ECS 400 MHz Spectrometer; $CHCl_3$ (δ_H = 7.26 ppm) was used as an internal reference. Fast atomic bombardment mass spectrometry (FAB-MS) spectra were measured on a JEOL JMS-700TZ. Electronic absorption, circular dichroism (CD), and CPL spectra were measured with a JASCO V-670 spectrophotometer, Jasco J-1500 spectropolarimeter and Jasco CPL-200 spectrofluoropolarimeter (excitation wavelength = 380 nm), respectively.

C. Synthesis of (+)-bornyl salicylate ((+)-bor, $C_{17}H_{22}O_3$) [28]

A solution of salicylic acid (1.0 g, 7.2 mmol) and (+)-borneol (1.12 g, 7.2 mmol) in 30 mL of dioxane were refluxed with thionyl chloride (0.82 g, 6.9 mmol) for 1 h at 100°C. The mixture was extracted with $NaHCO_3$ aq. (2×20 mL) and ethyl acetate (2×20 mL). The organic layer was separated and dried with magnesium sulfate, and the solvent was evaporated. The residue was chromatographed on silica gel eluting with ethyl acetate/hexane (10/90). Yield: 0.29 g (17%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 10.9 (s, 1H, -OH), 7.87–7.89 (d, 1H, Ar), 7.44–7.48 (t, 1H, Ar), 6.97–6.99 (d, 1H, Ar), 6.88–6.92 (t, 1H, Ar), 5.10–5.14 (m, 1H, -CH), 2.07–2.51 (m, 2H), 1.75–1.77 (m, 1H), 1.12–1.47 (m, 4H), 0.97 (s, 3H, -CH_3), 0.92 (s, 6H, -CH_3).

D. Synthesis of (−)-bornyl salicylate ((−)-bor, $C_{17}H_{22}O_3$) [28]

Yield: 0.63 g (32%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 10.9 (s, 1H, -OH), 7.87–7.89 (d, 1H, Ar), 7.44–7.48 (t, 1H, Ar), 6.97–6.99 (d, 1H, Ar), 6.88–6.92 (t, 1H, Ar), 5.10–5.14 (m, 1H, -CH), 2.07-2.51 (m, 2H), 1.75–1.77 (m, 1H), 1.12–1.47 (m, 4H), 0.97 (s, 3H, -CH_3), 0.92 (s, 6H, -CH_3).

E. Synthesis of $[Tb_9(sal\text{-}(+)\text{-}bor)_{16}(\mu\text{-}OH)_{10}]^+[NO_3]^-$ (Tb-(+)-bor, $C_{272}H_{346}NO_{61}Tb_9$)

(+)-bornyl salicylate (0.10 g, 0.36 mmol) was dissolved in methanol, and triethylamine (0.036 g, 0.36 mmol) was added to this solution with stirring at 40°C. Then $Tb(NO_3)_3{\cdot}6H_2O$ (0.095 g, 0.21 mmol) in methanol was added dropwise to this solution with further stirring for 20 min. White powder, Tb-(+)-bor, $[Tb_9(sal\text{-}(+)\text{-}bor)_{16}(\mu\text{-}OH)_{10}]^+[NO_3]^-$, was obtained. Yield: 0.079 g (56%). MS (FAB) found: m/z = 5973.54, calcd for $C_{272}H_{346}NO_{61}Tb_9$: M^+, 5973.75.

F. Synthesis of $[Tb_9(sal\text{-}(-)\text{-}bor)_{16}(\mu\text{-}OH)_{10}]^+[NO_3]^-$ (Tb-(−)-bor, $C_{272}H_{346}NO_{61}Tb_9$)

(−)-bornyl salicylate (0.10 g, 0.36 mmol) was dissolved in methanol, and triethylamine (0.036 g, 0.36 mmol) was added to this solution with stirring at 40°C. Then $Tb(NO_3)_3{\cdot}6H_2O$ (0.095 g, 0.21 mmol) in methanol was added dropwise to this solution with further stirring for 20 min. White powder, Tb-(−)-bor, $[Tb_9(sal\text{-}(-)\text{-}bor)_{16}(\mu\text{-}OH)_{10}]^+[NO_3]^-$, was obtained. Yield: 0.11 g (76%). MS (FAB) found: m/z = 5973.88, calcd for $C_{272}H_{346}NO_{61}Tb_9$: M^+, 5973.75.

G. Computational Details

Density function theory (DFT) calculations were carried out with the Gaussian R09W B.01 employing the three-parameter hybrid functional of Becke based on the correlation functional of Lee, Yang, and Parr (B3LYP) [29, 30]. The 6-31G(d) basis set was used for all atoms.

III. RESULTS AND DISCUSSION

A. Electronic structures of the ligands and the Tb(III) clusters

The UV-vis absorption spectra of (±)-bor molecules and Tb-(±)-bor clusters are shown in Fig. 2a. The absorption bands of (±)-bor molecules and Tb-(±)-bor clusters were observed at around 307 nm and 350 nm, respectively. Their absorption bands are assigned to the π–π^* transition of (±)-bor molecules and ligands in Tb-(±)-bor clusters. The absorption coefficients of ligands in Tb-(±)-bor clusters were approximately 60,000 $M^{-1}cm^{-1}$ [31], which was 200,000 times larger than that of $4f$–$4f$ transition of Tb(III) ion. The large absorption coefficients may lead to effective photosensitized luminescence of Tb-(±)-bor clusters.

To clarify the π-electronic properties of the (±)-bor ligands, the energy level and oscillator strength of the lowest singlet excited states (S1) were calculated using the TD-DFT (B3LYP/6-31G(d)) method. According to the Tb-(±)-bor clusters, we carried out the simplified complex model, Li-(+)-bor. The oscillator strengths of a (+)-bor molecule and a Li-(+)-bor complex were calculated to be 0.116 (λ = 291.5 nm) and 0.145 (λ = 334.5 nm), respectively. These transitions are mainly dominant to HOMO→LUMO transition (Fig. 3: transition probability $TP_{HOMO\rightarrow LUMO,(+)-bor}$ = 94%, $TP_{HOMO\rightarrow LUMO,Li-(+)-bor}$ = 95%). The energy gap between HOMO and LUMO is directly linked to the absorption wavelength. The energy gaps of (+)-bor and Li-(+)-bor part are found to be 4.81 eV and 4.15 eV, respectively (Fig. 3). The magnitude of the destabilization of HOMO in Li-(±)-bor is larger than that of LUMO.

At the red-shifted intense absorption band, positive (or negative) CD signal was observed for Tb-(+)-bor (or Tb-

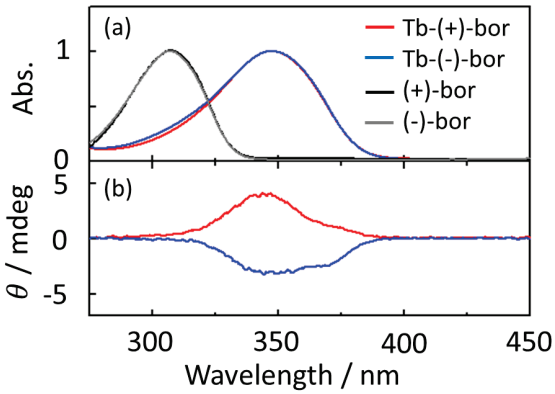


FIG. 2. UV-vis (a) and CD (b) spectra of Tb-(+)-bor (red line), Tb-(−)-bor (blue line), (+)-bor (black line), and (−)-bor (gray line) in DMF (2.0×10^{-4} M).

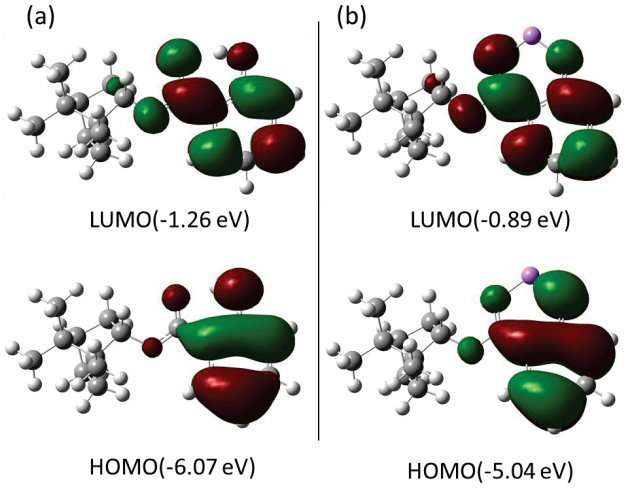


FIG. 3. Molecular orbital of (+)-bor (a) and Li-(+)-bor (b).

(−)-bor) clusters (Fig. 2b). In general, asymmetric factor of CD signals, g_{CD}, is gained by the following equation,

$$g_{\mathrm{CD}} = 4\frac{|m|}{|\mu|}\cos\theta \qquad (1)$$

where m, μ, and θ are represented by the magnetic transition dipole moment, the electric transition dipole moment, and the angle between m and μ, respectively. Asymmetric factor g_{CD} of the cluster was 1.8×10^{-4} at 376 nm. The g_{CD} in Tb-(±)-bor clusters are the same order to those of typical chiral molecules ($g_{\mathrm{CD}} \simeq 10^{-4}$).

B. Luminescence properties of Tb(III) clusters.

Figure 4 shows photoluminescence (PL) and CPL spectra of the Tb-(±)-bor clusters. The spectral shapes of $4f$–$4f$ transitions in Tb-(+)-bor clusters agreed with that in Tb-(−)-bor clusters (Fig. 4a). These transition bands in PL spectra were contributed to $^5\mathrm{D}_4 \rightarrow {}^7\mathrm{F}_J$ (J = 6, 5, 4, 3) transitions. We also observed the CPL spectra of Tb-(±)-bor clusters (Fig. 4b). The wavelengths and g_{CPL} are summarized in table 1. Asymmetric factor of CPL, gCPL,

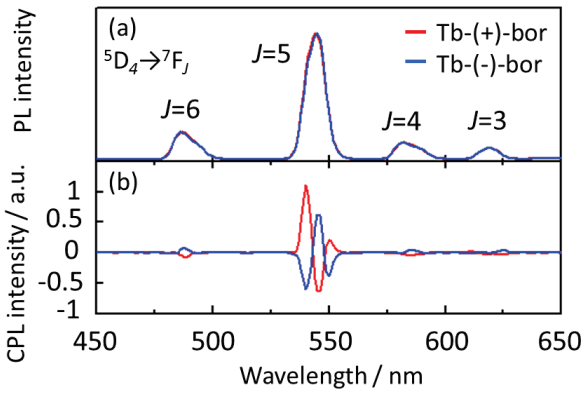


FIG. 4. CPL (a) and PL (b) spectra of Tb-(+)-bor (red line), and Tb-(−)-bor (blue line) in DMF (1.0^{-4} M).

TABLE I. Luminescent wavelengths and corresponding $|g_{\mathrm{CPL}}|$ values of Tb(III) ions.

Transition band	Wavelength/nm	$\lvert g_{\mathrm{gCPL}}\rvert$
$^5\mathrm{D}_4 \rightarrow {}^7\mathrm{F}_6$ ($\Delta J = +2$)	488	0.0056
$^5\mathrm{D}_4 \rightarrow {}^7\mathrm{F}_5$ ($\Delta J = +1$)	545	0.024
$^5\mathrm{D}_4 \rightarrow {}^7\mathrm{F}_4$ ($\Delta J = 0$)	582	0.0057
$^5\mathrm{D}_4 \rightarrow {}^7\mathrm{F}_3$ ($\Delta J = -1$)	630	0.017

is expressed by the same equation to g_{CD} [32], and g_{CD} and g_{CPL} of the magnetic dipole transition band are larger than those of electric dipole transition band. According to the luminescent properties of Eu(III) complexes, transitions for $\Delta J = \pm1$ are closely related to the magnetic dipole transition. In our experiments, g_{CPL} of $\Delta J = \pm1$ in Tb-(±)-bor clusters were the larger than those of ΔJ = 0 and ±2 in Tb-(±)-bor clusters. These g_{CPL} values ($\Delta J = 1$) are similar to those of previous chiral Tb(III) complexes, *e.g.* previous reported mononuclear Tb(III) complex ($g_{\mathrm{CPL}} = 0.04$) [16]. In this study, Tb(III) cluster composed of nine Tb(III) ions also shows effective CPL properties compared with mononuclear Tb(III) complex. This result indicates that chiroptical Tb(III) cluster with Tb-O-Tb lattices is expected to be useful for future optical materials.

IV. CONCLUSIONS

We synthesized novel nonanuclear Tb(III) clusters with chiral bornyl salicylate ligands. They emitted strongly according to the $4f$–$4f$ transitions of Tb(III) ions, and showed CPL signal corresponding to these transitions. This is the first observation of CPL using Tb(III) clusters with inorganic frameworks. Novel lanthanide cluster with CPL properties is expected to open up a frontier field to coordination chemistry, photophysical chemistry and material science.

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