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Chiral tripode approach toward multiple anion sensing with lanthanide complexes

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ABSTRACT

A chiral tripodal ligand was demonstrated to form a series of lanthanide complexes exhibiting multiple anion-sensing profiles, which incorporated a fluorescent quinoline and a stereo-controlled substituent in a tetradentate skeleton. This mainly gave 1:2 (lanthanide cation/ligand) complexes with lanthanide triflates but 1:1 complexes with lanthanide nitrates. Since addition of external guest anion dynamically changed the preferred stoichiometry, the chiral lanthanide complexes exhibited anion-responsive fluorescence, luminescence, and circular dichroism spectral characteristics as multiple anion-sensing probes.

1. Introduction

Fluorescent chemo-sensing of specific targets is an attractive subject in organic, inorganic, analytical, and biological chemistry.[1] A variety of fluorescent probes have been successfully developed in monitoring the specific targets via photoinduced electron transfer (PET), coordination-enhanced fluorescence (CEF), and other photochemical mechanisms. In addition to several structural optimization of the probes, Canary et al. presented double cation sensing based on fluorescence and circular dichroism (CD) methods, in which asymmetrically substituted ligands remarkably offered the Zn^{2+} selective sensing.[2] Some lanthanide complexes were recently recognized as effective luminescent probes,[3] because they formed highly coordinated complexes with several guest species to exhibit guest-dependent lanthanide-based luminescence. Faulkner et al. developed a water-soluble octadentate cyclen ligand to form luminescent Tb^{3+} complex, which targeted macrophage-monocyte linkage cells.[3e] Sculimbrene and Imperiali also employed luminescent Tb^{3+} complex in LRET detection of the protein targets.[3g] Ponce et al. developed macrocyclic ligand for Tb^{3+}-luminescence detection of a particular biomarker.[3h] We report here that a series of chiral tripode **1**–lanthanide complexes offer multiple anion sensing. Since tripode **1** incorporated both a fluorescent quinoline and a stereo-controlled $-CH_3$ substituent, its lanthanide complexes exhibited ligand-fluorescence, ligand-CD, and lanthanide-luminescence signals in response to the specific anions. As illustrated in Figure 1, the tripodal ligand provides the vacant coordination sites on the lanthanide center available for incoming guests, and its lanthanide

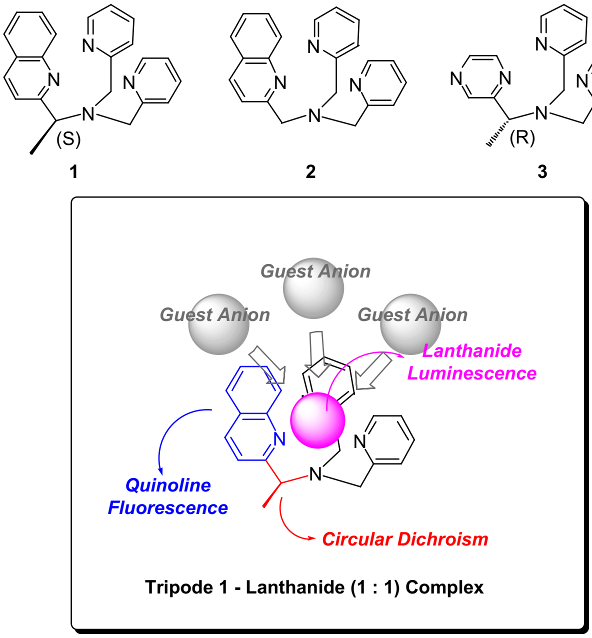

Figure 1. Tripode ligands for anion-responsive lanthanide complexes.

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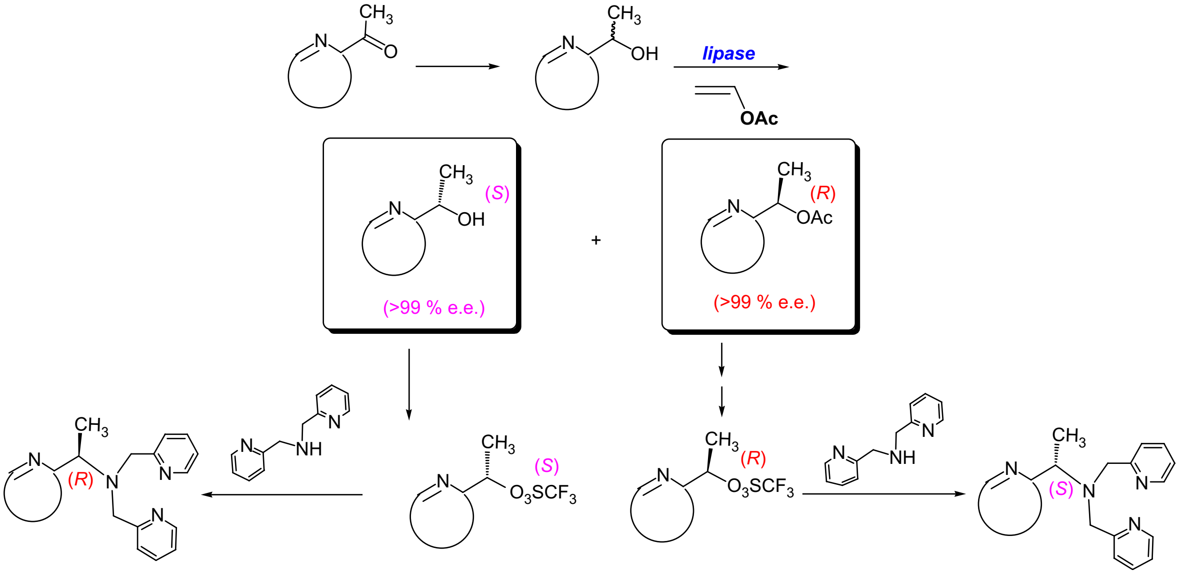

Figure 2. Synthesis of chiral tripodes.

complexes have several variations in complex stoichiometry.[4] We characterize a series of tripode–lanthanide complexes as anion receptors (Fig. 1). They were demonstrated to change the preferred stoichiometry depending on the natures of co-existing anions. Although various chiral ligands were combined with lanthanide centers in asymmetric catalytic reactions,[5] some of them can work as multiple spectroscopic probes for specific anions.

2. Results and discussion

2.1. Synthesis of chiral tripodes

Tripodes **1** and **2** have been prepared earlier and used in transition metal complexation processes.[6] Zahn and Canary synthesized chiral tripode **1** via diastereoselective crystallization of

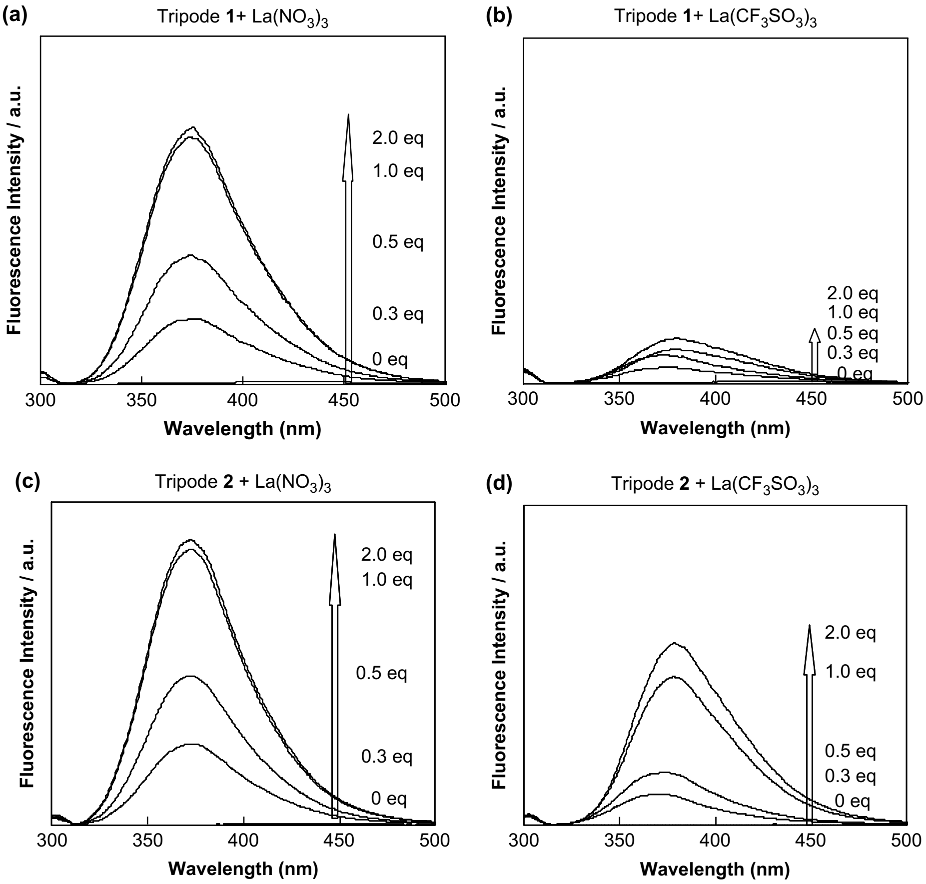

Figure 3. Fluorescence spectral changes upon tripode–La^{3+} complexation in CH_3CN. [Tripode]=1.0×10^{-4} mol/L, [$La(NO_3)_3\cdot 6H_2O$]=0–2.0×10^{-4} mol/L, [$La(CF_3SO_3)_3$]=0–2.0×10^{-4} mol/L in acetonitrile. Excitation at 302 nm. Slit widths: 10 and 3 nm.

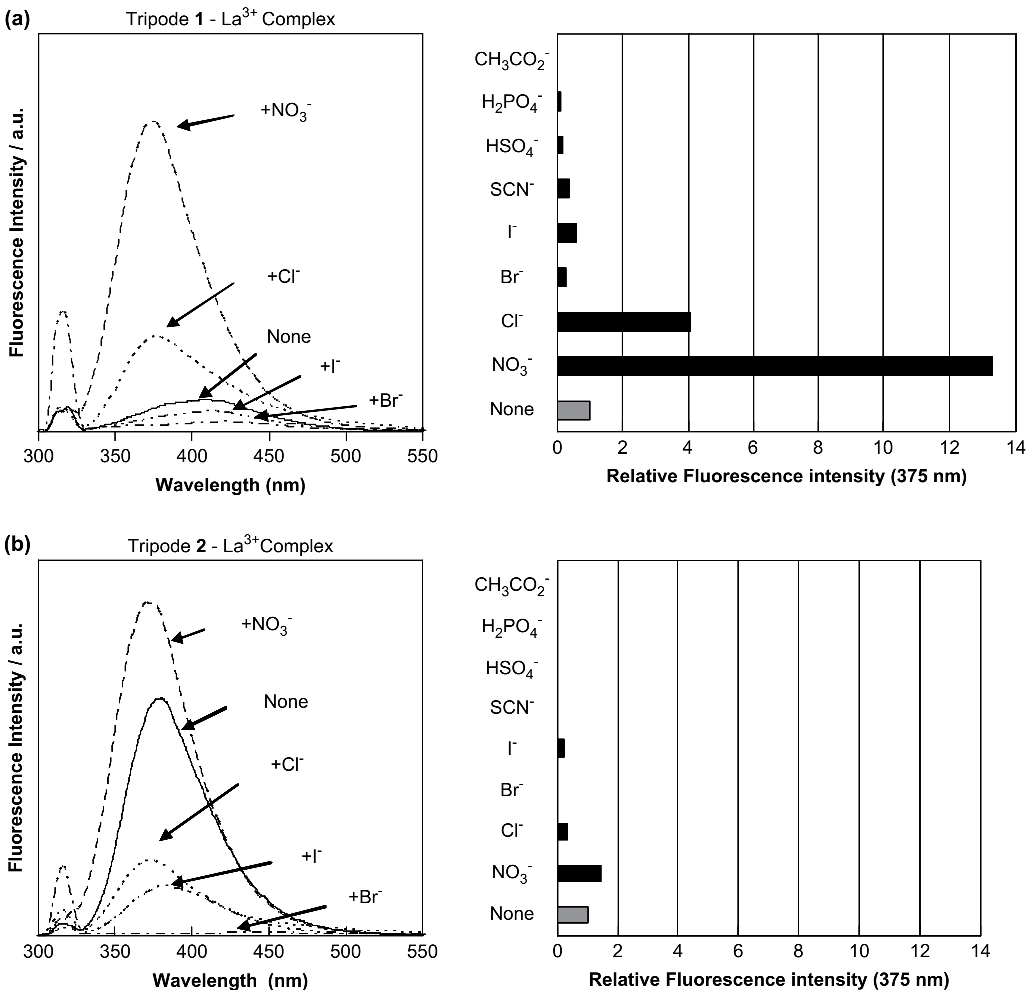

Figure 4. Fluorescence anion sensing with tripode–La^{3+} complexes. [Tripode]=1.0×10^{-4} mol/L, [$La(CF_3SO_3)_3$]=1.0×10^{-4} mol/L, [n-Bu_4NX]=6.0×10^{-4} mol/L in acetonitrile. Excitation at 316 nm. Slit widths: 10 and 3 nm.

((2-quinolyl)ethyl)amine, and characterized CD spectrum of its copper complex.[6a] As reported in the stereo-controlled synthesis of chiral tris(2-pyridylmethyl)amines,[7a,b] we prepared chiral tripodes **1** and **3** (Fig. 2), in which lipase-catalyzed optical resolution of nitrogen-aromatic precursors[7c,d] and subsequent S_N2-type coupling reaction were successfully combined. *Candida antarctica* lipase provided perfect optical resolution of racemic quinoline- and pyrazine-ethanols as well as pyridine-ethanol. Typically, racemic pyrazine-ethanol (2 g) was reacted with vinyl acetate (4 mL) in the presence of lipase (600 mg, Novozyme 435) in dried isopropyl ether (400 mL). The trans-esterification reaction automatically stopped at ca. 50% reaction conversion, and chiral HPLC analysis with Chiralcel-OB (Daicel Chem. Industry, Japan) indicated >99% ee of acetate product, and its stereochemistry was suggested to be (*R*)-configuration.[7d] The S_N2-type substitution between the corresponding mesylates and dipicolylamine was carried out according to the reported procedure.[8] We derived tripode **1** from (*R*)-acetate and tripode **3** from (*S*)-alcohol. Comparison of CD spectrum of our tripode **1** with that of reported (*S*)-derivative[6a] confirmed that both tripodes had identical stereochemistry and optical purity. When the quinoline moiety was combined with pyridine moieties in the tripodal fashion, it worked as a fluorescence signaling center, a coordinating site for lanthanide complexation, and a photo-antenna for UV excitation, while thiazole moiety provided stronger coordination.[9,10b] Achiral tripode **2** was prepared for comparison, which was derived from dipicolylamine and chloromethylquinoline. This compound was employed as an effective ligand for transition metal cations,[6b,11] but its fluorescence and lanthanide complexation properties were first characterized below.

2.2. Lanthanide complexation with tripodes

Tripodal ligands **1**–**3** formed a series of lanthanide complexes having anion-dependent stoichiometry. Their complexation behavior was monitored by UV, CD, fluorescence, or luminescence spectroscopic method. Figure 3 shows quinoline-fluorescence spectral changes of tripodes **1** and **2** upon addition of two kinds of La^{3+} salts. Since both tripodes had tertiary nitrogen atoms neighboring the quinoline chromophores, these ligands exhibited very weak quinoline-fluorescence signals due to the PET quenching mechanism. When $La(NO_3)_3$ was added to a CH_3CN solution of each tripode, the enhanced quinoline-fluorescence signal was observed at around 375 nm via the CEF mechanism (Fig. 3a and c). The observed fluorescence changes indicated that $La(NO_3)_3$ mainly formed highly fluorescent 1:1 (La^{3+}/ligand) complexes with both tripodes,[9] in which the tertiary nitrogen atoms provided effective coordination with the La^{3+} centers and were not involved in the PET quenching mechanism. Addition of $La(CF_3SO_3)_3$ had different types of influence on the quinoline fluorescences of the two tripode systems. When tripode **1** complexed $La(CF_3SO_3)_3$, the resulting complex exhibited weak fluorescence. The observed fluorescence spectral changes suggested that 1:2 complexation mainly occurred,

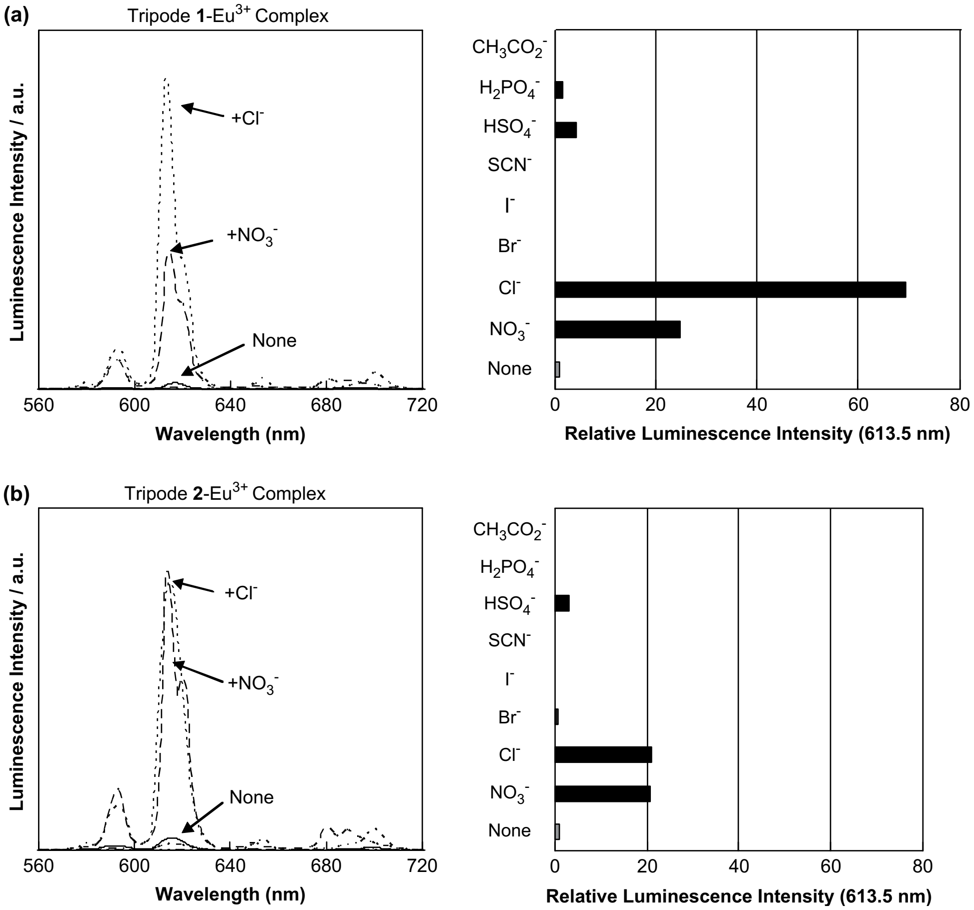

Figure 5. Luminescence anion sensing with tripode–Eu^{3+} complexes. [Tripode]=1.0×10^{-4} mol/L, [$Eu(CF_3SO_3)_3$]=1.0×10^{-4} mol/L, [*n*-Bu_4NX]=6.0×10^{-4} mol/L in acetonitrile. Excitation at 315 nm. Slit widths: 10 and 3 nm. Delay time, 0.2 ms. Gate time, 1.0 ms.

in which the tertiary nitrogen atom of tripode **1** rarely coordinated with the La^{3+} center and still caused the PET quenching. In contrast, non-substituted tripode **2** was found to primarily form fluorescent 1:1 complexes with both $La(NO_3)_3$ and $La(CF_3SO_3)_3$, indicating that the $-CH_3$ substitution on the tripodal ligand effectively offered interesting anion-dependency in the complex stoichiometry and subsequent quinoline fluorescence. We had reported that several tetradentate tripodes containing two nitrogen-aromatics and one amide moiety formed lanthanide complexes,[10] the stoichiometry of which largely depended on the natures of co-existing anions. Similar anion effects on the lanthanide complexation were confirmed, though the present type of tripodes generally exhibited lower stability. The $-CH_3$ group introduced was thought to disturb the coordination from tertiary nitrogen atom due to its stericity.

2.3. Multiple anion sensing with chiral tripode–lanthanide complexes

The lanthanide complexes with chiral tripode **1** are expected to offer multiple anion sensing, because they exhibited anion-responsive ligand-fluorescence, ligand-CD, and lanthanide-luminescence signals. Figure 4a shows the anion-responsive quinoline-fluorescence spectral changes of tripode **1**–La^{3+} complex. Addition of 6 equiv of NO_3^- anion to the solution of tripode **1**–$La(CF_3SO_3)_3$ remarkably enhanced the fluorescence signals at around 375 nm, while Cl^- and other anions had modest influence. As described above, the coordinative NO_3^- anion favored 1:1 complexation, and the preferred stoichiometry of the La^{3+} complex was dynamically altered from 1:2 (less fluorescent species) to 1:1 (intense fluorescent ones). Thus, tripode **1**–La^{3+} complex well worked as a NO_3^- anion-selective fluorophore. The La^{3+} complex with achiral tripode **2** was compared (Fig. 4b), where the addition of NO_3^- anion increased only 1.4 times the fluorescence intensity and the other anions decreased the intensity. The CH_3-substituted tripode **1** was demonstrated to form the fluorescence La^{3+} complex exhibiting excellent NO_3^- anion selectivity. When tripodes **1**–**3** formed $Eu(CF_3SO_3)_3$ complexes, they exhibited characteristic red emission based on f–f transition. Among them, tripode **1**–Eu^{3+} complex worked as the most effective anion-responsive luminescent probe. It offered 70 times luminescence enhancement for Cl^- anion and 25 times for NO_3^- anion, while other anions had only slight influence on the Eu^{3+} luminescence intensity (Fig. 5a). Since this Eu^{3+} complex exhibited the decreased quinoline-fluorescence signal, the energy transfer from the excited quinoline to the Eu^{3+} center turned the Eu^{3+} luminescence on. This Eu^{3+} complex exhibited different anion-sensing selectivity from the corresponding fluorescent La^{3+} complex: For **1**–Eu^{3+} complex, $Cl^- \gg NO_3^- \gg$ none; and for **1**–La^{3+} complex, $NO_3^- \gg Cl^- \gg$ none. This means that the additional factors probably are involved in the Eu^{3+} luminescence process. The Eu^{3+} complex with tripode **2** exhibited the enhanced luminescence for NO_3^- and Cl^- anions, but no selectivity was observed between these two anions (Fig. 5b). Tripode **3**–Eu^{3+} complex also gave red luminescence, but no anion-responsibility was observed. The proper combination of nitrogen-aromatic and stereo-controlled substituent effectively offered the highly efficient anion sensing with luminescent tripode–Eu^{3+} complex. Chiral

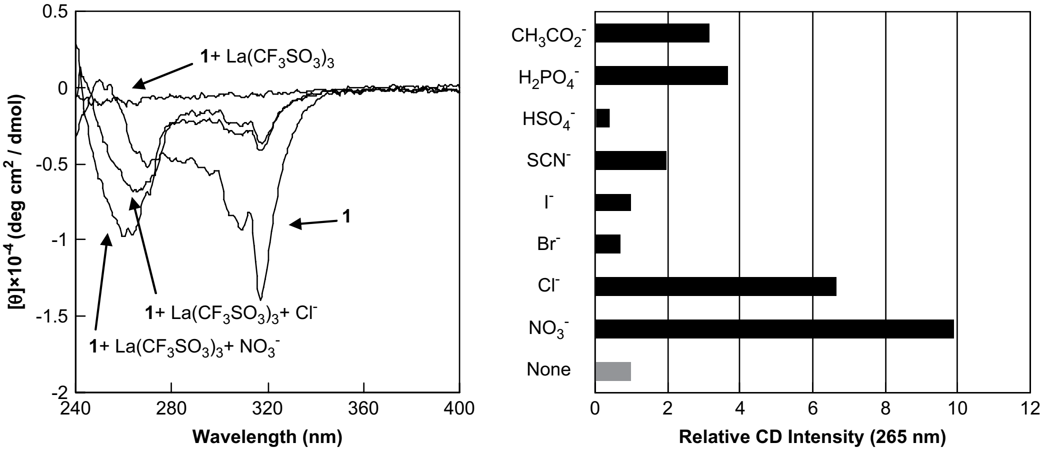

Figure 6. CD anion-sensing profiles of tripode **1**–La^{3+} complex. [Tripode]=1.0×10^{-4} mol/L, [La(CF$_3$SO$_3$)$_3$]=1.0×10^{-4} mol/L, [n-Bu$_4$NX]=6.0×10^{-4} mol/L in acetonitrile.

tripode **1** itself exhibited a characteristic CD signal at around 320 nm, and addition of equimolar La(CF$_3$SO$_3$)$_3$ to its CH$_3$CN solution remarkably decreased the CD intensity (Fig. 6). When external anions were further added to tripode **1**–La(CF$_3$SO$_3$)$_3$ complex, characteristic anion effects were observed in its CD spectrum. Among the examined anions, NO$_3^-$ and Cl$^-$ anions particularly gave intense negative CD signals at around 265 nm. This La^{3+} complex exhibited a similar NO$_3^-$ anion preference in the fluorescence sensing, but lower anion selectivity was observed in the CD sensing: peak ratio of NO$_3^-$/Cl$^-$=1.5 in CD sensing <3.3 in fluorescence sensing. Both CH$_3$CO$_2^-$ and H$_2$PO$_4^-$ anions were detectable via CD sensing, while fluorescence sensing did not allow their detection. These presented almost the same CD profiles as that of tripode itself, indicating that these anions provided much stronger coordination with the La^{3+} cation than tripode **1** to release the chiral ligand. Tripode **1**–Eu^{3+} complex also exhibited CD signals, but offered modest anion-responsive CD spectral changes. When La^{3+} complex with chiral tripode **3** was examined, no significant difference in the CD spectra was observed between NO$_3^-$ and CF$_3$SO$_3^-$ anions. Although the CD method is well recognized as a versatile tool for configuration assignments and structural evaluation of chiral molecules and complexes,[12] the present results suggest the possibility that the designed chiral ligand–lanthanide complexes can work as anion-selective CD probes.[13]

Biological importance of inorganic anions is well recognized, and a variety of anion-selective probes have been developed.[14] We demonstrated above that the proper combination of chiral tripode and lanthanide center offered multiple anion detection. Indeed, chiral tripode **1**–lanthanide complexes worked well as anion-selective fluorescence, luminescence, and CD probes. Further sophistications of chiral ligands can offer more specific anion-sensing functions.

3. Experimental section

3.1. General

^{1}H and ^{13}C NMR spectra were recorded on JEOL LA-300 and -400 spectrometers. Fluorescence and luminescence spectra were obtained on a Perkin Elmer LS-50B equipped with a Hamamatsu R-928 photomultiplier, and CD spectra were measured with a Jasco J-820 spectrometer. CH$_3$CN employed here was purchased from Nacalai Tesque, Japan (spectroscopic analysis grade). Karl Fischer water determination carried out by UBE Scientific Analysis Laboratory (Ube, Japan) indicated that the CH$_3$CN solutions contained 0.07–0.15 wt % of H$_2$O. The lanthanide salts were commercially available and used as received: La(NO$_3$)$_3$·6H$_2$O and Eu(NO$_3$)$_3$·6H$_2$O were purchased from Nacalai Tesque, and La(CF$_3$SO$_3$)$_3$ and Eu(CF$_3$SO$_3$)$_3$ were obtained from Sigma–Aldrich Japan.

3.2. Synthesis of tripode ligands

All the employed ligands **1**–**3** were prepared as illustrated in Figure 2. Selected data for tripodes **1** and **3** are described below.

3.2.1. *(S)-N,N-Bis((pyridin-2-yl)methyl)-1-(quinolin-2-yl) ethanamine* ***1***

Mp 91.5–94.4 °C, colorless solid (ether–hexane). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.50 (ddd, J=4.8, 1.6, 0.8 Hz, 2H, ArH), 8.11 (d, J=8.4 Hz, 1H, ArH), 8.07 (d, J=8.4 Hz, 1H, ArH), 7.78 (dd, J=8.2, 1.2 Hz, 1H, ArH), 7.70 (d, J=8.4 Hz, 1H, ArH), 7.68 (ddd, J=8.4, 7.0, 1.2 Hz, 1H, ArH), 7.62 (dt, J=7.6, 2.0 Hz, 2H, ArH), 7.55 (br d, J=8.0, 2H, ArH), 7.50 (ddd, J=8.0, 7.2, 1.2 Hz, 1H, ArH), 7.12 (ddd, J=7.2, 5.2, 1.2 Hz, 2H, ArH), 4.27 (br q, J=6.4 Hz, 1H, CH), 4.03 (d, J_{gem}=14.8 Hz, 2H, CH$_2$), 3.91 (d, J_{gem}=15.2 Hz, 2H, CH$_2$), 1.66 (d, J=6.8 Hz, 3H, CH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 162.9, 160.1, 148.6, 147.2, 136.0, 135.6, 129.2, 128.8, 127.1, 126.9, 125.7, 122.6, 121.5, 120.8, 60.9, 56.6, 13.7. IR (KBr) 3060, 3009, 2976, 2933, 2840, 1619, 1591, 1569, 1503, 1473, 1433 cm^{-1}. HRMS (EI$^+$) calcd for C$_{23}$H$_{22}$N$_4$ 354.1844, found 354.1853. Anal. Calcd for C$_{23}$H$_{22}$N$_4$: C, 77.94; H, 6.26; N, 15.81%. Found: C, 77.83; H, 6.26; N, 15.83%.

3.2.2. *(R)-1-(Pyrazin-2-yl)-N,N-bis((pyridin-2-yl)methyl) ethanamine* ***3***

Colorless oil. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.82 (d, J=1.5 Hz, 1H, ArH), 8.50 (dd, J=2.4, 1.5 Hz, 1H, ArH), 8.50 (m, 2H, ArH), 8.42 (d, J=2.4 Hz, 1H, ArH), 7.64 (dt, J=7.8, 1.7 Hz, 2H, ArH), 7.51 (d, J=7.8 Hz, 2H, ArH), 7.14 (ddd, J=6.4, 5.1, 1.2 Hz, 2H, ArH), 4.18 (q, J=6.8 Hz, 1H, CH), 3.98 (d, J_{gem}=14.6 Hz, 2H, CH$_2$), 3.81 (d, J_{gem}=14.6 Hz, 2H, CH$_2$), 1.57 (d, J=6.8 Hz, 3H, CH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 160.0, 157.8, 149.0, 145.3, 143.4, 142.7, 136.4, 122.6, 121.9, 57.7, 56.5, 12.5. IR (KBr) 3052, 3009, 2977, 2932, 2846, 1590, 1570, 1525, 1473, 1433, 1402, 1378 cm^{-1}. HRMS (EI$^+$) calcd for C$_{18}$H$_{19}$N$_5$ 305.1640, found 305.1640.

3.3. Spectroscopic experiments

The fluorescence and luminescence experiments were carried out in CH$_3$CN upon excitation of nitrogen-aromatic chromophores. Because the lanthanide complexes exhibited somewhat different UV spectra upon addition of external anions, their fluorescence and luminescence intensities were corrected using absorbance at excitation wavelengths. The concentrations of lanthanide triflate, tripodal ligand, and external anion (as a tetrabutylammonium salt) are shown in each Figure. CD experiments were similarly carried out in CH_3CN using chiral tripodes **1** and **3**. Their concentration conditions are shown in Figure 6.

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