COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Anion sensing with luminescent lanthanide complexes of tris(2-pyridylmethyl)amines: Pronounced effects of lanthanide center and ligand chirality on anion selectivity and sensitivity

Takashi Yamada, Satoshi Shinoda and Hiroshi Tsukube*
Department of Chemistry, Graduate School of Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan. E-mail: tsukube@sci.osaka-cu.ac.jp; Fax: 81 6 6605 2560; Tel: 81 6 6605 2560

Received (in Cambridge, UK) 20th March 2002, Accepted 23rd April 2002
First published as an Advance Article on the web 7th May 2002

Luminescent lanthanide complexes with tris(2-pyridylmethyl)amine ligands exhibited anion-specific sensory functions, and their anion selectivity and response sensitivity were modulated by a combination of lanthanide center and chiral ligand.

Since several inorganic anions play fundamental roles in various chemical and biological systems,[1] their specific receptors have been developed to monitor the targeted anions of biological, environmental, clinical, and industrial interests.[2] Among them, the lanthanide complexes have attracted considerable attention as promising sensory materials, because of their unique coordination chemistry and intense luminescence with long excited-state lifetimes.[3,4] Typically, Lehn *et al.* observed that the luminescence of cationic lanthanide cryptates was sensitive to added I^- and phosphate anions,[3] and Parker *et al.* presented lanthanide cyclen complexes for selective detection of bicarbonate anion.[4] We report below that Eu^{3+} complex with chiral tris(2-pyridylmethyl)amine ligand **1** acts as a luminescent receptor effective for NO_3^- anion, while corresponding Tb^{3+} complex exhibits Cl^- anion selectivity.[5] A series of tris(2-pyridylmethyl)amine ligands are recognized as potential tetradentate ligands for transition metal cations[6] and useful platforms for intelligent metal complexes.[7] They also form stable lanthanide complexes exhibiting characteristic luminescence.[8–11] Mazzanti *et al.* recently determined the crystal structure of $EuCl_3$ complex with parent tris(2-pyridylmethyl)amine **2**, in which three Cl^- anions directly coordinated with Eu^{3+} center together with four nitrogen atoms of ligand.[10] Thus, this type of lanthanide complex has outstanding features as an anion-specific luminescent receptor: three pyridine chromophores of the ligand are well arranged to act as effective photon antenna; and several vacant sites of the lanthanide coordination sphere are available for incoming anion guests.[12] Furthermore, a proper combination of lanthanide center and chiral ligand is expected to modulate the luminescent anion sensing process.[11]

Eu^{3+} complexes $[Eu\text{-}L](CF_3SO_3)_3$ (L = **1** and **2**, Fig. 1) were readily prepared by mixing stoichiometric amounts of ligand and $Eu(CF_3SO_3)_3$ in acetonitrile. UV and ESI-MS spectroscopic characterizations supported that the resulting complexes possess 1:1 stoichiometry and stability high enough to use in the solution.[13] The luminescence spectrum of $[Eu\text{-}\mathbf{1}](CF_3SO_3)_3$ was measured upon excitation of pyridine chromophores at 260 nm by the addition of tetrabutylammonium salt including I^-, Br^-, Cl^-, F^-, ClO_4^-, NO_3^-, SCN^-, $CH_3CO_2^-$, HSO_4^- or $H_2PO_4^-$ anion in acetonitrile. Fig. 2a illustrates that the addition of 3 equivalent NO_3^- anion enhanced the luminescence intensity at 618 nm by 4.9 times and significantly changed the emission spectral shapes. In contrast, Cl^- anion induced the modest enhancement (1.8 times) of luminescence intensity and $CH_3CO_2^-$ anion offered slight spectral changes. The luminescence lifetime of $[Eu\text{-}\mathbf{1}](CF_3SO_3)_3$ (0.8 ms) was increased by the addition of 3 equivalent Cl^- (1.3 ms) or NO_3^- (1.5 ms) anion, supporting that these coordinative anions replaced acetonitrile, water or $CF_3SO_3^-$ anion bound at the Eu^{3+} cation. Similar modulations of lanthanide luminescence have been reported in several anion-coordination systems.[4,12] Fig. 3a indicates the anion sensing luminescence properties of $[Eu\text{-}\mathbf{1}](CF_3SO_3)_3$. This complex was confirmed to effectively work as a NO_3^- anion-specific luminescent sensor, and rarely

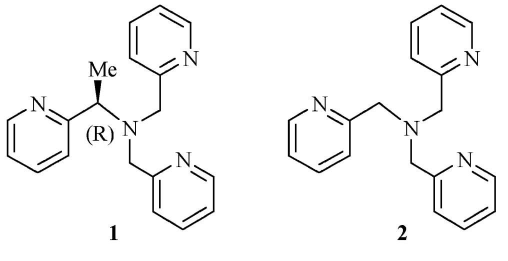

Fig. 1 Ligands **1** and **2**.

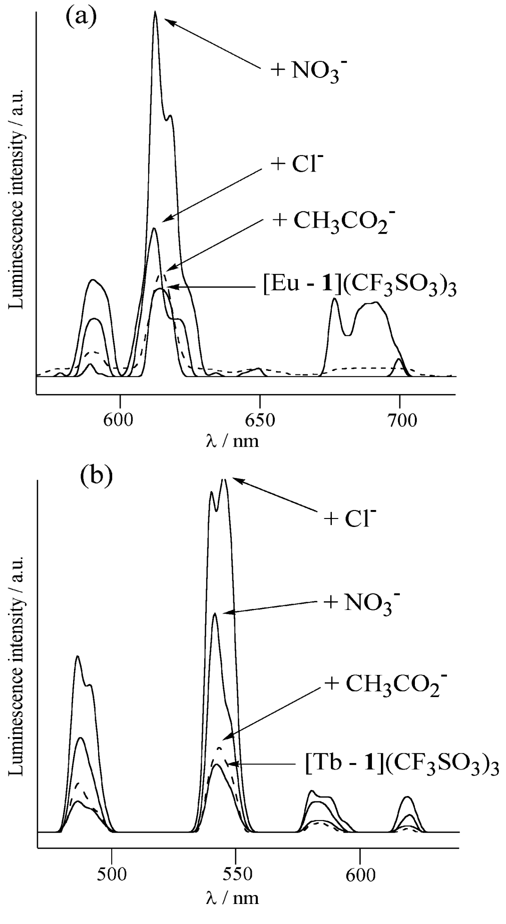

Fig. 2 Luminescence spectral changes of $[Eu - \mathbf{1}](CF_3SO_3)_3$ and $[Tb\text{-}\mathbf{1}](CF_3SO_3)_3$ by the addition of NO_3^-, Cl^- and $CH_3CO_2^-$ anions in acetonitrile. Excitation at 260 nm; Normalized based on UV absorbance at 260 nm; $[\mathbf{1}] = [Ln(CF_3SO_3)_3] = 4.80–5.20 \times 10^{-6}$ M; [Anion] = $1.45–1.55 \times 10^{-5}$ M; Slit width was adjusted as 10.0 nm for excitation and 5.0 nm for emission.

DOI: 10.1039/b202822k

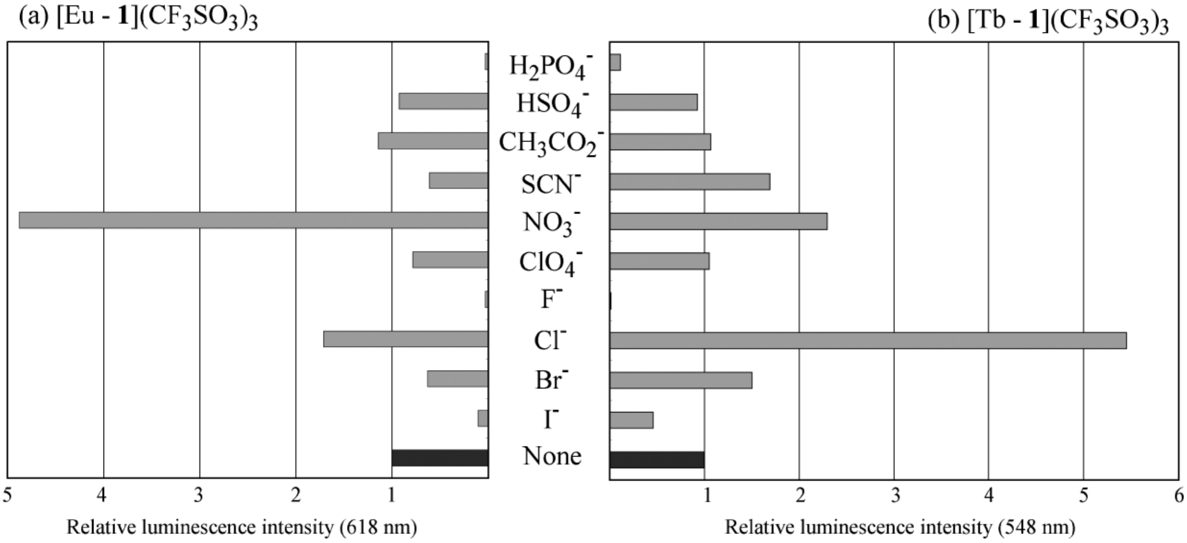

Fig. 3 Anion sensing profiles of luminescent lanthanide complexes. Conditions: see Fig. 2.

responded to I^-, Br^-, F^-, ClO_4^-, SCN^-, HSO_4^-, and $H_2PO_4^-$ anions.[14] The circular dichroism signal of [Eu-**1**](CF_3SO_3)$_3$ complex observed around 260 nm was also intensified upon addition of NO_3^- anion, indicating that the effective coordination from NO_3^- anion modified the three-dimensional arrangement of pyridine chromophores. Since the luminescence phenomenon observed upon excitation at 260 nm included a series of light absorption, ligand-to-lanthanide energy transfer and lanthanide luminescence processes, the direct excitation of Eu^{3+} cation at 397 nm was carried out to focus the effect of anion coordination on the lanthanide luminescence process.[15] The luminescence intensity observed at 618 nm of [Eu − **1**](CF_3SO_3)$_3$ was increased 8.3 times by the addition of 3 equivalent NO_3^- anion, though other anions offered little influence on the luminescence intensity upon direct excitation: 0.7 times for Br^-; 2.5 times for Cl^-; 1.2 times for ClO_4^-; and 1.0 times for SCN^-. The effective coordination from NO_3^- anion was thought to prevent the quenching of the excited Eu^{3+} cation.

Tb^{3+} complex [Tb-**1**](CF_3SO_3)$_3$ preferred Cl^- anion to NO_3^- anion and exhibited different anion selectivity in the luminescence sensing (Figs. 2b and 3b). The observed enhancements in the luminescence intensity at 548 nm upon addition of 3 equivalent anions were estimated to be 5.4 for Cl^-, 2.2 for NO_3^-, and 1.1 for $CH_3CO_2^-$, while F^- and I^- anions suppressed the emission. Its anion sensing profile indicates that the nature of lanthanide center dramatically modified anion sensing selectivity. When achiral ligand **2** was employed, its Eu^{3+} and Tb^{3+} complexes favored NO_3^- and Cl^- anions, respectively. These complexes showed similar anion sensing luminescence profiles to those of complexes with chiral ligand **1**, but exhibited relatively lower sensitivity in the luminescence anion sensing upon excitation at 260 nm: relative intensity of [Eu-**1**] to [Eu-**2**] at 618 nm was observed as 1.5 for NO_3^- anion; that of [Tb −**1**] to [Tb-**2**] at 589 nm was 1.3 for Cl^- anion. The direct excitation of Eu^{3+} cation at 397 nm offered similar chirality-enhanced luminescence: relative intensity of [Eu-**1**] to [Eu-**2**] at 618 nm was observed as 1.6 for NO_3^- anion. Since chiral ligand **1** offered higher efficiency of the lanthanide luminescence than achiral ligand **2**, further combinations of chiral chromophoric ligands and luminescent lanthanide centers promise many possibilities in the development of anion sensory systems which are applicable for various targets.

This work was supported by grants for Scientific Research (No. 13874077) from the Japan Society for Promotion of Science and for Reimei Research from the Japan Atomic Energy Research Institute

Notes and references

1 J. N. Demas and B. A. DeGraff, *Coord. Chem. Rev.*, 2001, **211**, 317; T. S. Snowden and E. V. Anslyn, *Curr. Opin. Chem. Biol.*, 1999, **3**, 740.
2 P. D. Beer and P. A. Gale, *Angew. Chem. Int. Ed.*, 2001, **40**, 486; I. Alfonso, B. Dietrich, F. Rebolledo, V. Gotor and J.-M. Lehn, *Helv. Chim, Acta*, 2001, **84**, 280; C. D. Abernathy, C. L. B. MacDonald, J. A. C. Clyburne and A. H. Cowley, *Chem. Commun.*, 2001, 61.
3 N. Sabbatini, M. Guardigli, J.-M. Lehn and C. Mathis, *J. Alloys. Comp.*, 1992, **180**, 363.
4 D. Parker, *Coord. Chem. Rev.*, 2000, **205**, 109; J. I. Bruce, R. S. Dickins, L. J. Govenlocks, T. Gunnlaugsson, S. Lopinski, M. P. Lowe, D. Parker, R. D. Peacock, J. B. Perry, S. Aime and M. Botta, *J. Am. Chem. Soc.*, 2000, **122**, 9674.
5 We presented our preliminary report at the International Conference of ‘Rare Earths’-2001’, Brazil (Abstract CP-14) on September 22–26, 2001.
6 M. Costas, K. Chen and L. Que, *Coord. Chem. Rev.*, 2000, **200–202**, 517.
7 J. W. Canary, C. S. Allen, J. M. Castagnetto and Y. Wang, *J. Am. Chem. Soc.*, 1995, **117**, 8484.
8 R. Wietzke, M. Mazzanti, J.-M. Latour, J. Pecaut, P.-Y. Cordier and C. Madic, *Inorg. Chem.*, 1998, **37**, 6690.
9 X.-P. Yang, C.-Y. Su, B.-S. Kang, X.-L. Feng, W.-L. Xiao and H.-Q. Liu, *J. Chem Soc., Dalton Trans.*, 2000, 3253.
10 R. Wietzke, M. Mazzanti, J.-M. Latour and J. Pecaut, *J. Chem. Soc., Dalton Trans.*, 2000, 4167.
11 Lanthanide complexes with chiral ligand **1**: T. Yamada, S. Shinoda, J. Uenishi and H. Tsukube, *Tetrahedron Lett.*, 2001, **42**, 9031.
12 A luminescent anion sensor was recently developed along this line, in which Eu^{3+} cation and chromophoric bis-bipyridine-phenylphosphine oxide ligand were combined. But the effects of lanthanide nature and ligand chirality on the anion sensing process were not addressed: M. Montalti, L. Prodi, N. Zaccheroni, L. Charbonniere, L. Douce and R. Ziessel, *J. Am. Chem. Soc.*, 2001, **123**, 12694.
13 The stability constant (log β) for 1:1 complexation was determined as 7.9 ± 0.4 in acetonitrile based on UV spectral titration.
14 The lanthanide luminescence is often sensitive to water contamination. Interestingly, the anion-enhanced luminescence behaviors were similarly observed even in aqueous acetonitrile solutions (H_2O / CH_3CN = 1/99, v/v), though 20–30% decreases in luminescence intensity from non-aqueous acetonirtile solutions.
15 The direct excitation experiments required much higher concentrations of Eu^{3+} complexes than those of the ligand excitation experiments: [**1** or **2**] = [Eu(CF_3SO_3)$_3$] = 5.0×10^{-3} M; [Anion] = 1.5×10^{-2} M.