Dendrimer container for anion-responsive lanthanide complexation and "on–off" switchable near-infrared luminescence

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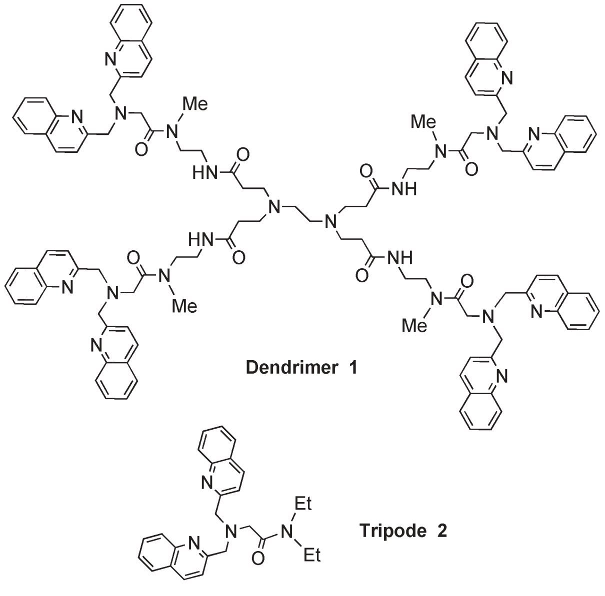
A new dendrimer-type ligand dynamically switched the lanthanide complexation and luminescence profiles in response to external anions.

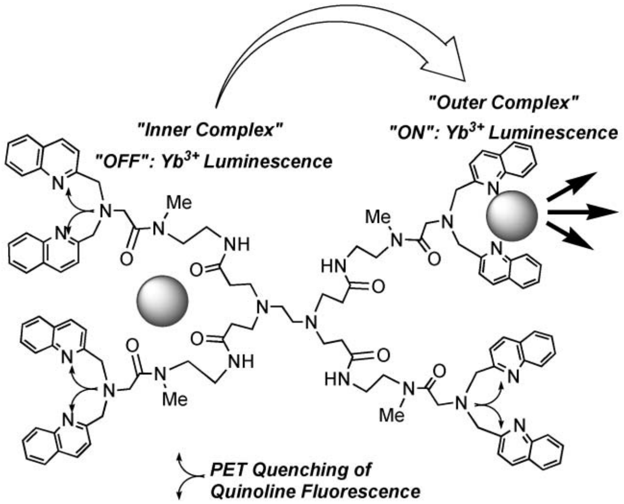
Lanthanide complexes have received recent attention as specific catalysts, effective MRI reagents, and other functional devices based on unique chemical and physical properties.[1] Among them, luminescent lanthanide complexes offered further applications in anion sensing, genomic and proteomic screening, and biological imaging.[2] In addition to long-lived, highly intense, and line-shaped luminescence, they have a wide variety of coordination numbers and versatile coordination structures. Several lanthanide complexes have already been demonstrated to alter their structures and stoichiometry upon highly coordinated complexation with co-existing anions, solvents, and other environmental species.[3] Tris(2-pyridylmethyl)amine derivatives typically formed 1 : 1 complexes with lanthanide chlorides and nitrates, but yielded mixtures of several complexes with lanthanide triflates.[4] Such an anion-dependent lanthanide complexation process was often coupled with the luminescence process. Dendrimer ligands provide high functionalization of lanthanide complexes.[5,6] They simultaneously incorporate several lanthanide cations in the restricted domains and form various types of highly coordinated complexes with co-existing species. Vögtle and co-workers prepared dendrimer-Nd^{3+} complexes to give intense near infrared luminescence,[6b] and Petoud *et al.* developed the highly densed Eu^{3+} complexes on the dendrimer periphery as an effective emitter.[6c]

We report that dendrimer-type ligand **1** functions as a lanthanide container exhibiting "on–off" switchable luminescence (Fig. 1). The employed dendrimer **1** is composed of two different kinds of coordination sites for the lanthanide cations at inner and outer spheres. Each tripod unit on the dendrimer periphery includes two quinoline nitrogen, tertiary nitrogen, and amide oxygen donor atoms for tetradentate coordination. Its parent tripod **2** formed stable 1 : 1 complexes with Eu^{3+} nitrate and gave intense luminescence upon irradiation of its quinoline chromophore.[7] The polyamidoamine core moiety provides multidentate coordination for the lanthanide cations.[6] Since the quinoline chromophores stand apart from the bound lanthanide center in this type of inner complex, photo-induced electron transfer (PET) quenching with neighboring tertiary nitrogen atom readily occurs and energy transfer for lanthanide luminescence is effectively prevented. Thus, the present dendrimer can exhibit two different binding modes exhibiting "on–off" lanthanide luminescence (Scheme 1): "outer" complexation at the tetradentate tripod site offers the "on" luminescence state upon quinoline excitation; and "inner" complexation at the multidentate core site gives the "off" luminescence state. We found that the nature of external anion


Dendrimer 1

Tripode 2

Fig. 1 Dendrimer ligand **1** and parent tripod **2**.



Scheme 1 On–off switchable dendrimer container for luminescent Yb^{3+} cations. (Possible mechanism).

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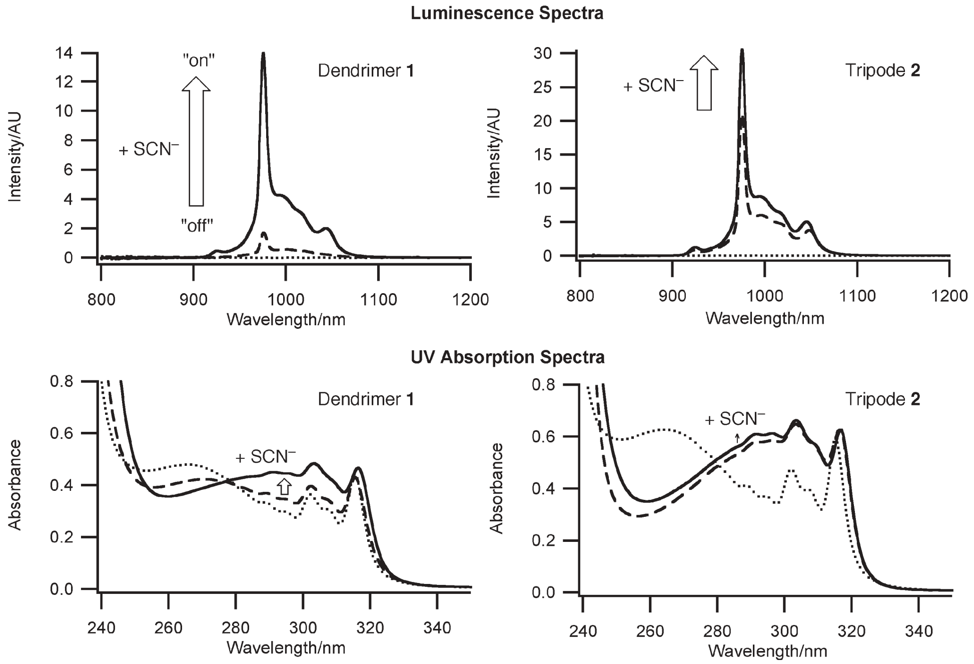

Fig. 2 UV and luminescence spectral changes of Yb^{3+} complexation with dendrimer **1** and tripod **2**. Black line, ligand + Yb^{3+} + SCN^-; broken line, ligand + Yb^{3+}; dotted line, ligand only. Conditions: [dendrimer **1**] = 2.0 × 10^{-5} M, [tripod **2**] = 8.0 × 10^{-5} M, [$Yb(CF_3SO_3)_3$] = 1.2 × 10^{-4} M, [$n Bu_4N(SCN)$] = 3.6 × 10^{-4} M, excitation at 318 nm, solvent; DMSO–CH_3CN (0.2 : 99.8, v/v).

significantly controlled the structure of the highly coordinated complex property between dendrimer ligand, lanthanide center, and anion. Since some anions dramatically changed the lanthanide coordination modes, the present dendrimer dynamically switched the ytterbium luminescence in response to external anions.

Dendrimer **1** was prepared by coupling of quinolylmethyl chloride with polyamidoamine precursor, which was derived from tetrakis(methoxycarbonylethyl)ethylene diamine.† Since this formed partially insoluble lanthanide complexes in MeOH or CH_3CN, we usually used DMSO–CH_3CN mixed solvent (0.2 : 99.8, v/v). Its Yb^{3+} complexation was well monitored by UV and luminescence spectral changes, but the observed spectral shapes were greatly different from those with tripod **2** (Fig. 2). The parent tripod **2** was confirmed to mainly form a 1 : 1 complex with $Yb(CF_3SO_3)_3$ exhibiting characteristic near infrared luminescence upon quinoline excitation. In contrast, dendrimer **1** gave modest UV spectral changes at the quinoline absorption band (*ca.* 305 nm) upon $Yb(CF_3SO_3)_3$ complexation. Since the resulting complex species exhibited very weak near infrared luminescence, the Yb^{3+} cations were thought to locate at the inner coordination sites and stand apart from the excited quinoline moieties.[8] The UV and luminescence titration curves obtained with dendrimer **1** and $Yb(CF_3SO_3)_3$ had bends around [$Yb(CF_3SO_3)_3$]/[dendrimer **1**] = 2, the dendrimer accommodated two Yb^{3+} cations in the presence of $CF_3SO_3^-$ anion (Fig. 3). Since sandwich-type (tripod unit : Yb^{3+} = 2 : 1) complexation and other structures were also assumed, further detailed NMR and high-resolution emission spectroscopic studies should be required.

Addition of SCN^- anion to the **1**–$Yb(CF_3SO_3)_3$ system induced large spectral changes around the quinoline absorption band, and gave a similar shape to that with tripod **2**–$Yb(CF_3SO_3)_3$ (1 : 1) complex. Since the intense Yb^{3+} luminescence appeared upon quinoline excitation, the employed SCN^- anion promoted the tripod–Yb^{3+} complexation at the outer coordination sites. The UV and luminescence titration experiments provided a possibility that dendrimer **1** accommodated four Yb^{3+} cations in the presence of excess SCN^- anion (Fig. 3). Thus, the SCN^- anion was supported to change the coordination environments around the Yb^{3+} cations

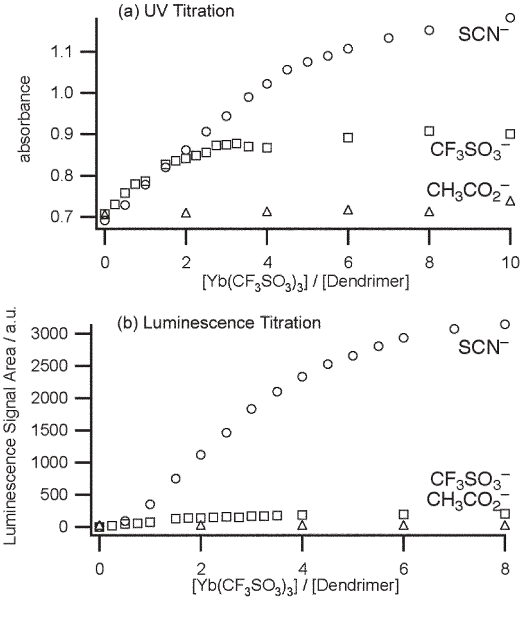

Fig. 3 UV and luminescence titration curves for dendrimer **1**–Yb^{3+} complexation, Conditions: [dendrimer **1**] = 4.0 × 10^{-5} M, [$n Bu_4NX$] = 9.6 × 10^{-4} M, 1 cm cuvette, solvent; DMSO–CH_3CN (0.2 : 99.8, v/v), (a) monitored at 299 nm, (b) excitation at 318 nm.

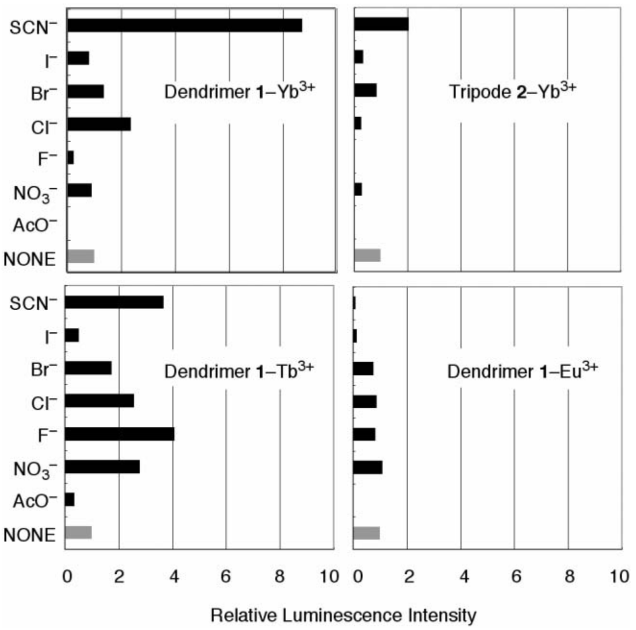

Fig. 4 Luminescence anion sensing with dendrimer **1**– and tripod **2**–Yb^{3+} complexes. Conditions: [dendrimer **1**] = 2.0 × 10^{-5} M, [tripod **2**] = 8.0 × 10^{-5} M, [$Ln(CF_3SO_3)_3$] = 1.2 × 10^{-4} M, [*n*Bu_4NX] = 3.6 × 10^{-4} M, excitation at 318 nm, solvent; DMSO–CH_3CN (0.2 : 99.8, v/v).

due to the more stable highly coordinated complexation. Such dynamic structural changes of the dendrimer **1**–Yb^{3+} complex switched the near infrared luminescence on (see Fig. 2). The SCN^- anion was often reported to provide effective coordination with the Yb^{3+} centers,[9] in which the nitrogen atom of the SCN^- anion coordinated. When more coordinative $CH_3CO_2^-$ anion was added, the dendrimer–Yb^{3+} complex was destroyed and the bound Yb^{3+} cations were released into the bulk solution.

The present dendrimer–Yb^{3+} complex acted as an anion-responsive near infrared sensing device. Fig. 4 compares luminescence intensity of the dendrimer **1**–Yb^{3+} complex upon addition of three equivalents of SCN^-, I^-, Br^-, Cl^-, F^-, NO_3^-, and $CH_3CO_2^-$ anions. When SCN^- anion was added to the dendrimer **1**–$Yb(CF_3SO_3)_3$ complex, *ca.* 9-fold luminescence intensity enhancement at around 980 nm was observed. In contrast, addition of the Cl^- anion increased the signal intensity 2.3-fold, and F^- and $CH_3CO_2^-$ anions largely decreased the luminescence due to the dendrimer complex decomposition. Since the targeted SCN^- anion is a principal metabolite of the toxic CN^- anion and exists in human serum saliva and urine,[10] our dendrimer system offered near infrared luminescence sensing of the biologically interesting anion.[11] Tripod **2**–Yb^{3+} complex also exhibited SCN^- anion-responsive near infrared emission behavior, but its luminescence enhancements were much lower. This dendrimer also accommodated luminescent Eu^{3+} and Tb^{3+} cations, but exhibited modest anion-responsive luminescence profiles. For example, its Tb^{3+} luminescence was enhanced 4-fold by the addition of F^- and SCN^-anions, while the Eu^{3+} luminescence rarely changed. Therefore, the dendrimer **1**–Yb^{3+} complex particularly worked as a near infrared luminescence anion sensor as well as a molecular switch that specifically changed near infrared Yb^{3+} luminescence in response to the external anion.

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Notes and references

† Dendrimer **1**: ^{1}H-NMR (MeOH-d_4, 400 MHz, mixture of *cis* and *trans* isomers in 1 : 2 ratio): δ 1.95–2.59 (a series of broad multiplets, 20 H, NCH_2, $COCH_2$), 2.71–2.83 (two broad multiplets, 12 H, CH_3), 3.11–3.32 (broad multiplets, 16 H), 3.48, 3.58* (two broad s, 8 H, $COCH_2N$), 4.05, 4.09* (two s, 16 H, NCH_2Ar), 7.39–7.45 (broad multiplet, 8 H, ArH), 7.57–7.74 (series of broad multiplet, 24 H, ArH), 7.87–7.90 (broad multiplet, 8 H, ArH), 8.09–8.12 ppm (broad multiplet, 8 H, ArH); ^{13}C-NMR (MeOH-d_4, 100 MHz): δ 34.02*, 34.08, 34.25*, 34.41, 35.94, 37.84, 38.38*, 48.43, 50.81, 51.76, 56.92*, 57.23, 62.09, 122.74*, 122.82, 127.59*, 127.64, 128.81, 128.88, 128.96, 130.89, 138.23, 148.20, 161.16, 161.27*, 172.33*, 172.43, 174.78 ppm (*assigned to the minor isomer); IR (KBr): 1647, 1601, 1561, 1506 cm^{-1}; HRMS(FAB): $(M + H)^+$ found (calcd.) for $C_{114}H_{125}N_{22}O_8$: 1930.0048 (1930.0051).

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