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A Reversible Luminescent Lanthanide Switch Based on a Dibenzo[24]-Crown-8−Dipicolinic Acid Conjugate

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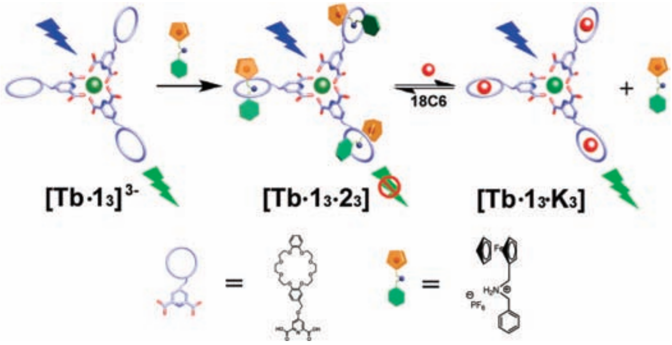
ABSTRACT



A novel host molecule H_21 bearing a dibenzo[24]-crown-8 moiety and a dipicolinic acid group was synthesized, and its Tb^{3+} complex displayed a satisfactory luminescent emission. The tris[2]pseudorotaxane formed from $[Tb{\cdot}1_3]^{3-}$ and ferrocene derivative 2 reveals excellent reversible luminescent lanthanide behavior.

The construction of multicomponent supramolecular assemblies by weak, noncovalent interactions is attracting increasing interest in artificial systems due to their multifunctionality.[1,2] Among the various artificial devices and machines, lanthanide luminescent-based devices[3] are a well-developed field owing to their unique luminescence properties, such as long-lived excited states, long wavelength emission, large Stokes shift, and sharp linelike emission bands. The luminescence mechanism of the lanthanide complexes[4] has been examined in detail, and many lanthanide luminescent-based devices have been developed. They show exciting applications on fluorescence imaging,[5] light-emitting materials,[6] and sensing devices.[3b,7] However, the reversible modulation of the luminescent intensity of lanthanide complexes remains challenging.

The lanthanide f−f transitions are Laporte-forbidden and very weak;[8] therefore, luminescence is only observed at high concentrations or when excited directly by lasers. This problem can be resolved by using a sensitized process which

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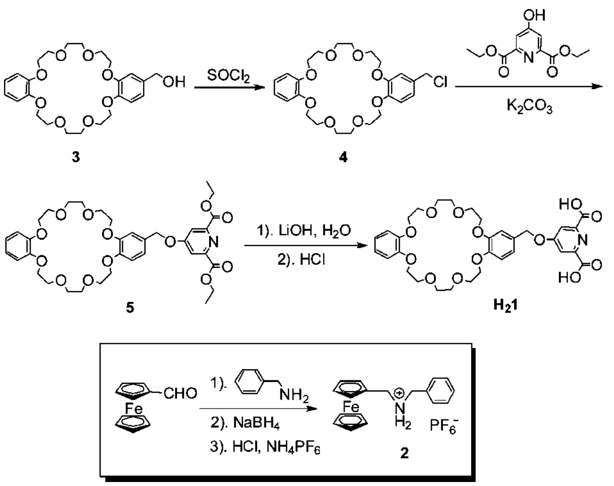
Scheme 1. Synthetic Routes for H_2**1** and **2**



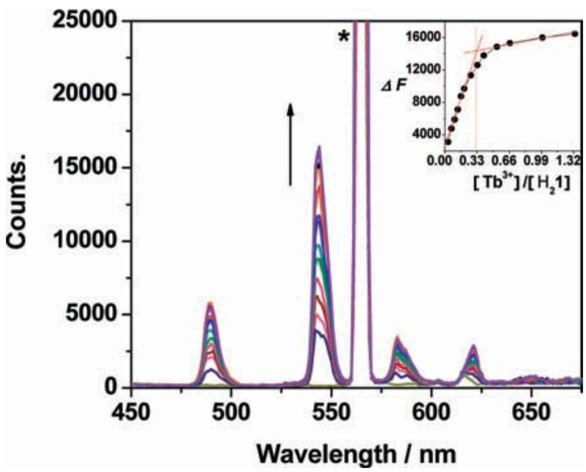


Figure 1. Emission spectra of H_2**1** (1.5×10^{-5} M) upon addition of Tb^{3+} in $CH_3CN/CHCl_3$ solution (1:1) at 298 K. $\lambda_{exe} = 282$ nm, and the * peak corresponds to the $2\lambda_{exe}$ signal.

involves incorporating a sensitizing chromophore, often termed as "antenna", into the lanthanide-coordinating ligand, allowing indirect excitation of the lanthanide ion through an intramolecular energy transfer process. Photoinduced electron transfer (PET) mechanism in donor−acceptor systems is an effective approach to tune the excited-state emission, and it has been examined in detail that the lanthanide luminescence can be controlled by intramolecular PET within the ligands.[7c] Herein, we design a ligand which consists of two moieties: pyridine-2,6-dicarboxylic acid (DPA) as an excellent chelator and antenna for Tb^{3+} and dibenzo-24-crown-8 (DB24C8) as a luminescent on/off switch via the binding of the guest molecule containing dialkylammonium salts.[9] The complex of the ligand with Tb^{3+} is a highly emissive lanthanide complex, and its luminescence can be modulated by the guest molecules. To the best of our knowledge, this is the first example of a reversible luminescent lanthanide switch based on noncovalent interactions.

The synthetic pathways of host molecule H_2**1** and guest molecule **2** are shown in Scheme 1. The alkylation of 4-hydroxy-pyridine-2,6-dicarboxylic acid diethyl ester with 4-chloromethyl-dibenzo-24-crown-8 affords **5** in 85% yield. Subsequent hydrolyzation of **5** with lithium hydroxyl produces the target compound H_2**1** in 97% yield. Compound **2** is obtained by condensation of ferrocene−carboxaldehyde with primary amines followed by $NaBH_4$ reduction of the formed imines and then by treatment with HCl(aq) and NH_4PF_6.

Due to the high association constants between DPA and the lanthanide ions,[10] the ligand can form a stable 3:1 luminescent complex with Tb^{3+}. In the present investigation, the complex $[Tb\cdot\mathbf{1}_3]^{3-}$ was synthesized with a yield of 60% by treating H_2**1** with $Tb(NO_3)_3\cdot 6H_2O$ in MeOH (Supporting Information). The coordination stoichiometry between H_2**1** and Tb^{3+} was also obtained by the molar ratio method using fluorescence spectrometry. As seen in Figure 1 (inset), the curve of ΔF vs $[Tb^{3+}]/[H_2\mathbf{1}]$ molar ratio shows an inflection point at a molar ratio of 0.33, corresponding to a 3:1 $H_2\mathbf{1}/Tb^{3+}$ coordination complex. The result is consistent with our previous observation.[11] Benefiting from the fascinating luminescence property of Tb^{3+}, the complex displays a satisfactory luminescent emission in solution. When excited at 282 nm, the complex shows four emission peaks at 491

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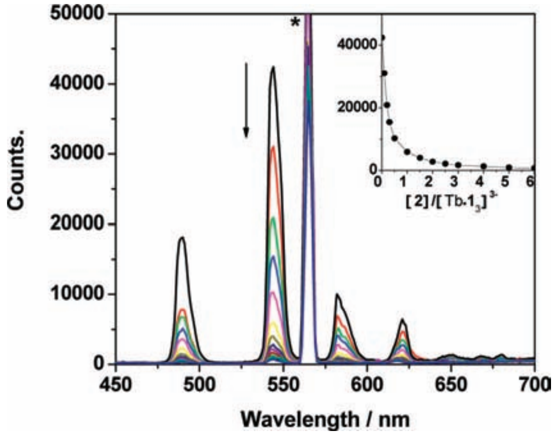

Figure 2. Emission spectra of the complex $[Tb·\mathbf{1}_3]^{3-}$ (5×10^{-6} M) and the emission changes at 544 nm (inset) upon addition of **2** in $CH_3CN/CHCl_3$ solution (1:1) at 298 K. $\lambda_{exe} = 282$ nm, and the * peak corresponds to the $2\lambda_{exe}$ signal.

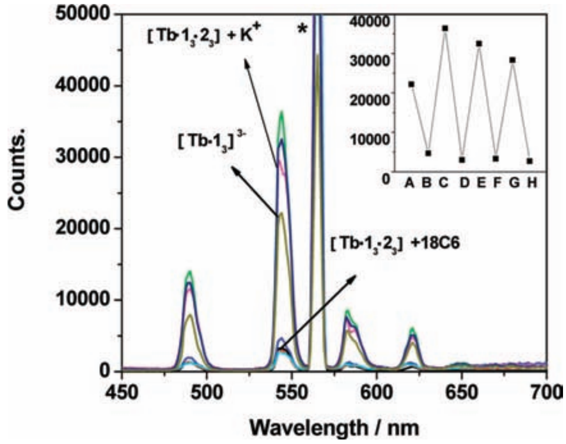

Figure 3. Emission spectral changes observed for $[Tb·\mathbf{1}_3]^{3-}$, $[Tb·\mathbf{1}_3·\mathbf{2}_3] + K^+$, $[Tb·\mathbf{1}_3·\mathbf{2}_3]$ + 18-crown-6, and the emission changes of $[Tb·\mathbf{1}_3]^{3-}$ at 544 nm (inset) in the absence (A) and in the presence (B) of **2** and added KPF_6 (C, E, G) and 18-crown-6 (D, F, H) in $CH_3CN/CHCl_3$ solution (1:1).

nm ($^5D_4 \rightarrow {}^7F_6$), 544 nm ($^5D_4 \rightarrow {}^7F_5$), 586 nm ($^5D_4 \rightarrow {}^7F_4$), and 622 nm ($^5D_4 \rightarrow {}^7F_3$) with a quantum yield of 0.046.

Ferrocene (Fc) has been widely utilized in multifunctional compounds as it is a good redox and electron donor active unit with the potential to be used in material with novel light-emitting and charge-transfer properties.[12] Many research projects have been focused on the chemical and electrochemical formation of pseudorotaxanes composed of alkyl(ferrocenylmethyl)-ammmonium and dibenzo[24]-crown-8.[13] When 3.0 equiv of compound **2** bearing the Fc moiety was added to the solution of $[Tb·\mathbf{1}_3]^{3-}$, the fluorescence emission of the complex was significantly quenched, about 94% at 544 nm (Figure 2), indicating that the introduction of the ferrocenyl guest molecule completely altered the luminescent behavior of $[Tb·\mathbf{1}_3]^{3-}$. This observation should be attributed to an intramolecular PET from the Fc moiety of **2** to DPA of $\mathbf{1}^{2-}$ after the formation of tris[2]pseudorotaxane $[Tb·\mathbf{1}_3·\mathbf{2}_3]$. Instead of **2** with dibenzylammonium hexafluorophosphate, the luminescence of the complex $[Tb·\mathbf{1}_3]^{3-}$ was slightly decreased (Supporting Information), which provides further evidence for the PET process in tris[2]pseudorotaxane $[Tb·\mathbf{1}_3·\mathbf{2}_3]$.

Interestingly, when KPF_6 was added to the solution of the tris[2]pseudorotaxane, the quenched lanthanide emission was restored. This observation suggests that the dialkylammonium cation in DB24C8 is replaced by K^+ and the intramolecular PET process from Fc to the DPA moiety is suppressed. This is reasonable because the association constant ($K_a = 7.6 \times 10^3$ M^{-1})[14] between DB24C8 and K^+ is larger than that of the complex $H_2\mathbf{1}·\mathbf{2}$ ($K_a = 1.2 \times 10^3$ M^{-1}).[15] Therefore, the consequent complexation of K^+ would dissociate the previous tris[2]pseudorotaxane due to competitive binding of the dialkylammonium salts with K^+.

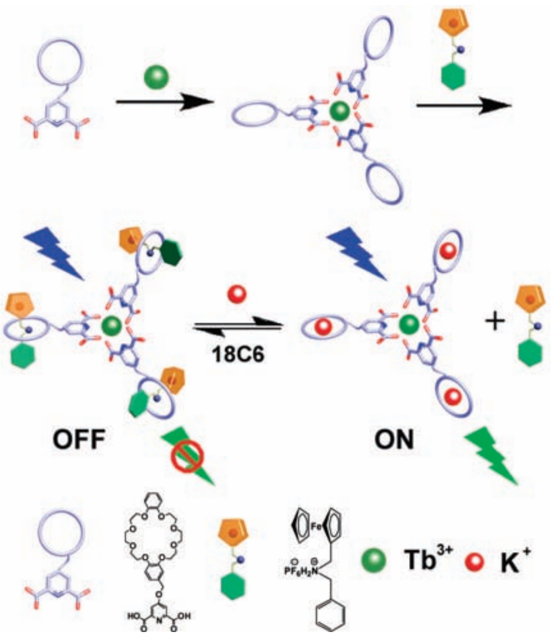

Figure 4. Schematic representation of the presumed coordination mode for the $[Tb·\mathbf{1}_3·\mathbf{2}_3]$ system.

To check the reversibility of this process, pristine 18-crown-6 was added to the solution. As shown in Figure 3,

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the luminescence quenching was reproduced again as a proof of regeneration of the tris[2]pseudorotaxane supramolecular assembly. This observation can be attributed to the strong binding ability of 18-crown-6 with K^+ ($K_a = 1.3 \times 10^6$ M^{-1}).[16] The ion-controlled binding and release of **2** could easily be performed by adding and removing K^+. That is, addition of K^+ causes the restoration of luminescence, while addition of 18-crown-6 is responsible for its quenching. The process can be repeated several times (Figure 3). The schematic representation of the switch mode for the [Tb•$\mathbf{1}_3$•$\mathbf{2}_3$] system is illustrated in Figure 4, which reveals the expected luminescent lanthanide switch behavior.

In conclusion, the new host molecule H_2**1** composed of DPA and DB24C8 as well as its Tb^{3+} complex has been synthesized, and the reversible luminescent behaviors of the complex upon addition of the ferrocenyl guest molecule **2** and K^+ have been investigated. The luminescence of the complex is quenched significantly in the presence of **2**, while its emission can be restored upon addition of K^+. The reversible luminescent process can be modulated by controlling the binding and release of the guest molecules by adding K^+ or 18C6, respectively. Significantly, this experiment demonstrates that the luminescence of the tris[2]pseudorotaxane [Tb•$\mathbf{1}_3$•$\mathbf{2}_3$] may be switched in a reversible manner by external chemical stimuli. This new synthetic strategy of a reversible luminescent lanthanide switch through electron transfer may find potential application in the construction of new molecule-based devices.

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Supporting Information Available: Experimental procedures and characterization data for host molecule H_2**1**, the complex [Tb•$\mathbf{1}_3$]$^{3-}$, and the fluorescence spectra of [Tb•$\mathbf{1}_3$]$^{3-}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) We determined the association constant (K_a) of the complex H_2**1**•**2** using ^{1}H NMR spectroscopy with the single-point method.[16]

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