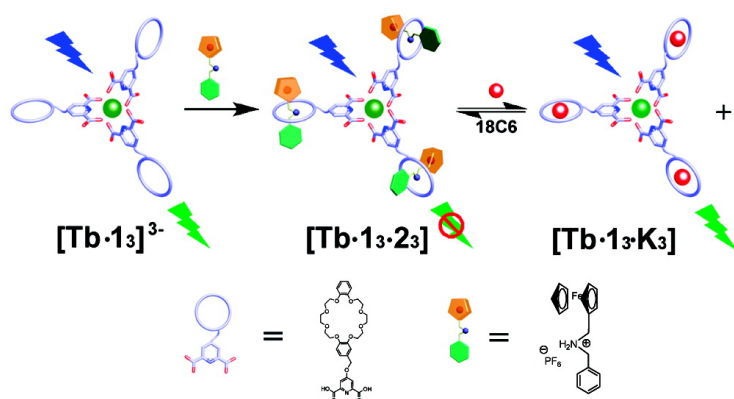


## A Reversible Luminescent Lanthanide Switch Based on a Dibenzo[24]-Crown-8#Dipicolinic Acid Conjugate

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

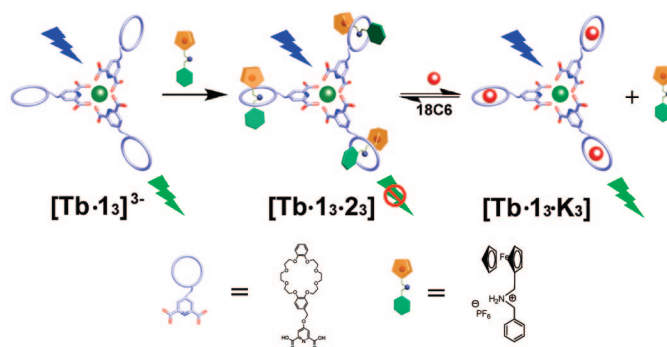
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## ABSTRACT



A novel host molecule H<sub>2</sub>1 bearing a dibenzo[24]-crown-8 moiety and a dipicolinic acid group was synthesized, and its Tb<sup>3+</sup> complex displayed a satisfactory luminescent emission. The tris[2]pseudorotaxane formed from [Tb·13]<sub>3</sub><sup>3-</sup> 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.<sup>1,2</sup> Among the various artificial devices and machines, lanthanide luminescent-based devices<sup>3</sup> 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<sup>4</sup> has been examined in detail, and many lanthanide

luminescent-based devices have been developed. They show exciting applications on fluorescence imaging,<sup>5</sup> light-emitting materials,<sup>6</sup> and sensing devices.<sup>3b,7</sup> However, the reversible modulation of the luminescent intensity of lanthanide complexes remains challenging.

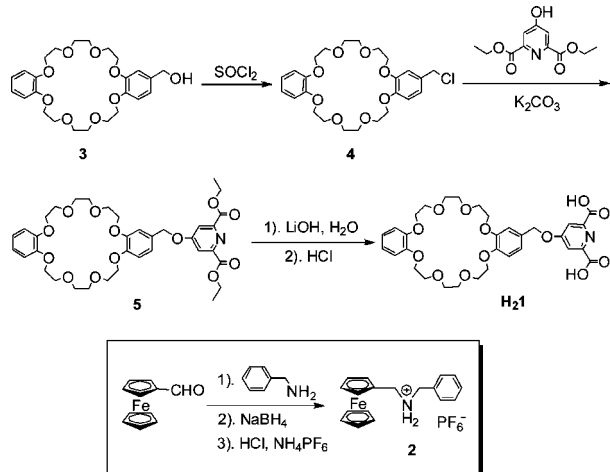
The lanthanide f–f transitions are Laporte-forbidden and very weak,<sup>8</sup> therefore, luminescence is only observed at high concentrations or when excited directly by lasers. This problem can be resolved by using a sensitized process which

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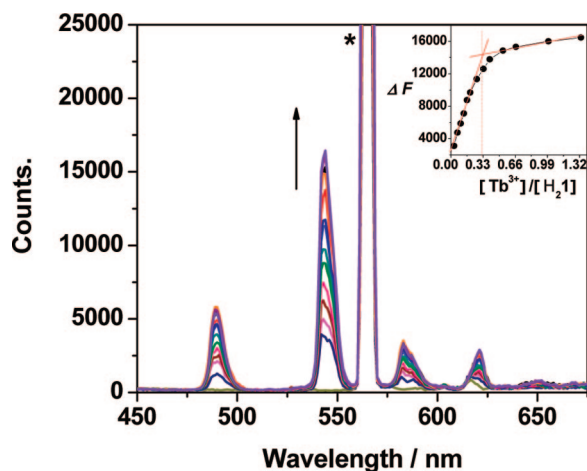
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**Scheme 1. Synthetic Routes for H<sub>2</sub>1 and 2**



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.<sup>7c</sup> Herein, we design a ligand which consists of two moieties: pyridine-2,6-dicarboxylic acid (DPA) as an excellent chelator and antenna for Tb<sup>3+</sup> and dibenzo-24-crown-8 (DB24C8) as a luminescent on/off switch via the binding of the guest molecule containing dialkylammonium salts.<sup>9</sup> The complex of the ligand with Tb<sup>3+</sup> 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



**Figure 1.** Emission spectra of H<sub>2</sub>1 ( $1.5 \times 10^{-5}$  M) upon addition of Tb<sup>3+</sup> in CH<sub>3</sub>CN/CHCl<sub>3</sub> solution (1:1) at 298 K.  $\lambda_{\text{exc}} = 282$  nm, and the \* peak corresponds to the  $2\lambda_{\text{exc}}$  signal.

reversible luminescent lanthanide switch based on noncovalent interactions.

The synthetic pathways of host molecule H<sub>2</sub>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<sub>2</sub>1 in 97% yield. Compound 2 is obtained by condensation of ferrocene–carboxaldehyde with primary amines followed by NaBH<sub>4</sub> reduction of the formed imines and then by treatment with HCl(aq) and NH<sub>4</sub>PF<sub>6</sub>.

Due to the high association constants between DPA and the lanthanide ions,<sup>10</sup> the ligand can form a stable 3:1 luminescent complex with Tb<sup>3+</sup>. In the present investigation, the complex [Tb•1<sub>3</sub>]<sup>3-</sup> was synthesized with a yield of 60% by treating H<sub>2</sub>1 with Tb(NO<sub>3</sub>)<sub>3</sub>•6H<sub>2</sub>O in MeOH (Supporting Information). The coordination stoichiometry between H<sub>2</sub>1 and Tb<sup>3+</sup> was also obtained by the molar ratio method using fluorescence spectrometry. As seen in Figure 1 (inset), the curve of  $\Delta F$  vs [Tb<sup>3+</sup>]/[H<sub>2</sub>1] molar ratio shows an inflection point at a molar ratio of 0.33, corresponding to a 3:1 H<sub>2</sub>1/Tb<sup>3+</sup> coordination complex. The result is consistent with our previous observation.<sup>11</sup> Benefiting from the fascinating luminescence property of Tb<sup>3+</sup>, 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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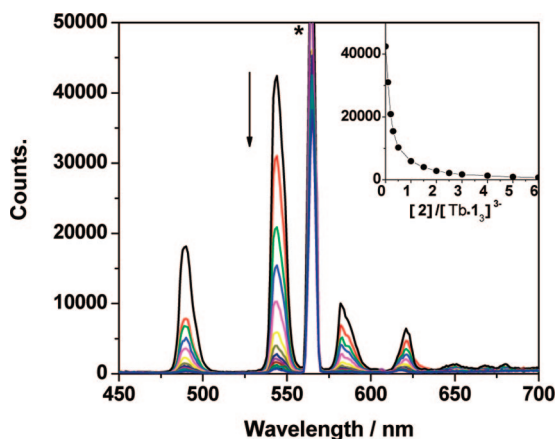
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**Figure 2.** Emission spectra of the complex  $[\text{Tb}\cdot\mathbf{1}_3]^{3-}$  ( $5 \times 10^{-6}$  M) and the emission changes at 544 nm (inset) upon addition of **2** in  $\text{CH}_3\text{CN}/\text{CHCl}_3$  solution (1:1) at 298 K.  $\lambda_{\text{exc}} = 282$  nm, and the \* peak corresponds to the  $2\lambda_{\text{exc}}$  signal.

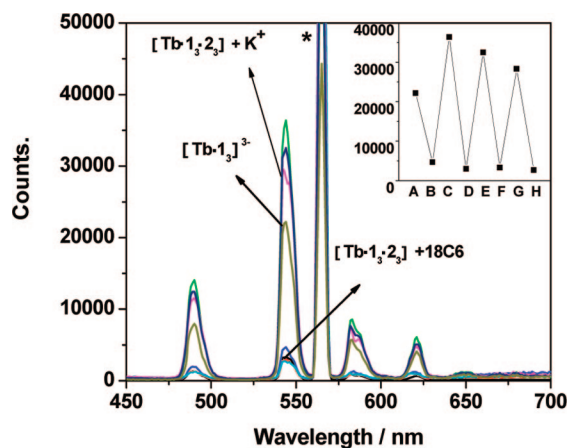
nm ( $^5\text{D}_4 \rightarrow ^7\text{F}_6$ ), 544 nm ( $^5\text{D}_4 \rightarrow ^7\text{F}_5$ ), 586 nm ( $^5\text{D}_4 \rightarrow ^7\text{F}_4$ ), and 622 nm ( $^5\text{D}_4 \rightarrow ^7\text{F}_3$ ) with a quantum yield of 0.046.

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.<sup>12</sup> Many research projects have been focused on the chemical and electrochemical formation of pseudorotaxanes composed of alkyl(ferrocenylmethyl)-ammonium and dibenzo[24]-crown-8.<sup>13</sup> When 3.0 equiv of compound **2** bearing the Fc moiety was added to the solution of  $[\text{Tb}\cdot\mathbf{1}_3]^{3-}$ , 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  $[\text{Tb}\cdot\mathbf{1}_3]^{3-}$ . 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  $[\text{Tb}\cdot\mathbf{1}_3\cdot\mathbf{2}_3]$ . Instead of **2** with dibenzylammonium hexafluorophosphate, the luminescence of the complex  $[\text{Tb}\cdot\mathbf{1}_3]^{3-}$  was slightly decreased (Supporting Information), which provides further evidence for the PET process in tris[2]pseudorotaxane  $[\text{Tb}\cdot\mathbf{1}_3\cdot\mathbf{2}_3]$ .

Interestingly, when  $\text{KPF}_6$  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  $\text{K}^+$  and the intramolecular PET process from Fc to the DPA moiety is suppressed. This is reasonable because the association constant ( $K_a = 7.6 \times$

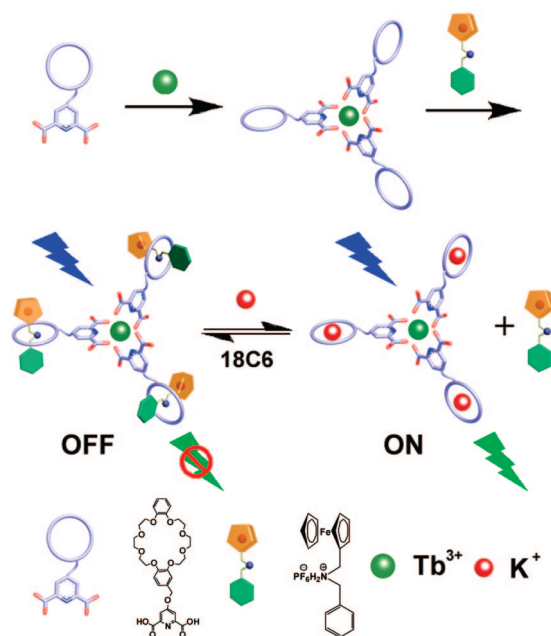
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**Figure 3.** Emission spectral changes observed for  $[\text{Tb}\cdot\mathbf{1}_3]^{3-}$ ,  $[\text{Tb}\cdot\mathbf{1}_3\cdot\mathbf{2}_3] + \text{K}^+$ ,  $[\text{Tb}\cdot\mathbf{1}_3\cdot\mathbf{2}_3] + 18\text{-crown-6}$ , and the emission changes of  $[\text{Tb}\cdot\mathbf{1}_3]^{3-}$  at 544 nm (inset) in the absence (A) and in the presence (B) of **2** and added  $\text{KPF}_6$  (C, E, G) and 18-crown-6 (D, F, H) in  $\text{CH}_3\text{CN}/\text{CHCl}_3$  solution (1:1).

$10^3 \text{ M}^{-1}$ )<sup>14</sup> between DB24C8 and  $\text{K}^+$  is larger than that of the complex  $\text{H}_2\mathbf{1}\cdot\mathbf{2}$  ( $K_a = 1.2 \times 10^3 \text{ M}^{-1}$ ).<sup>15</sup> Therefore, the consequent complexation of  $\text{K}^+$  would dissociate the previous tris[2]pseudorotaxane due to competitive binding of the dialkylammonium salts with  $\text{K}^+$ .



**Figure 4.** Schematic representation of the presumed coordination mode for the  $[\text{Tb}\cdot\mathbf{1}_3\cdot\mathbf{2}_3]$  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  $K^+$  ( $K_a = 1.3 \times 10^6 \text{ M}^{-1}$ ).<sup>16</sup> 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  $[\text{Tb}\cdot\mathbf{1}_3\cdot\mathbf{2}_3]$  system is illustrated in Figure 4, which reveals the expected luminescent lanthanide switch behavior.

In conclusion, the new host molecule  $\text{H}_2\mathbf{1}$  composed of DPA and DB24C8 as well as its  $\text{Tb}^{3+}$  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

(15) We determined the association constant ( $K_a$ ) of the complex  $\text{H}_2\mathbf{1}\cdot\mathbf{2}$  using  $^1\text{H}$  NMR spectroscopy with the single-point method.<sup>16</sup>

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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  $[\text{Tb}\cdot\mathbf{1}_3\cdot\mathbf{2}_3]$  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  $\text{H}_2\mathbf{1}$ , the complex  $[\text{Tb}\cdot\mathbf{1}_3]^{3-}$ , and the fluorescence spectra of  $[\text{Tb}\cdot\mathbf{1}_3]^{3-}$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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