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Luminescence modulation by cation- π interaction in a lanthanide assembly: implications for potassium detection

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Herein luminescent lanthanide supramolecular assemblies were constructed via coordination of the crown-connected bisterpyridine (L_1) and Ln^{3^+} ions, which can self-assembly to form homogeneous spherical nanoparticles with an average diameter of 700 nm on silicon plate surface upon slow evaporation of solvents. Potassium ions are shown to give rise to obvious enhancement in luminescence of Ln^{3^+} (Ln=Eu, Tb) ions in the lanthanide assemblies. The changes are the consequence of the capture of the cations by the crown moieties through cation- π interactions, increasing the triplet excited energy level of L_1 and thus favoring the population of Lanthanide's excited state from the antenna triplet state by means of an energy transfer. Besides, energy transfer from Tb³⁺ to Eu³⁺ was observed in the luminescent Eu³⁺/Tb³⁺ bimetallic assemblies (**Eu/Tb'L**₁) and the efficiency can be tuned by potassium concentration. Thus, **Eu/Tb'L**₁ can serve as self-calibrating sensor, which can selectively and quantitatively detect potassium by linearly correlating the K⁺ concentration to the emission intensity ratio of ${}^5D_4 \rightarrow {}^7F_5$ transition (Tb³⁺) to ${}^5D_0 \rightarrow {}^7F_2$ transition (Eu³⁺).

Introduction

Functional supramolecular assembly triggered by metal-ligand (M-L) coordination interactions are highly important for developing optical switches/devices, catalysis, sensors, drug and bioapplications.¹ Among the various carriers. supramolecular systems, trivalent lanthanide (Ln³⁺)-directed M-L assemblies are being increasingly explored in the design of advanced materials owing to their unique optical properties, such as sharp emission lines, high luminescent efficiency and long-lived excited states.^{1b, 2} These properties make them ideal and highly desirable candidates for the integration into luminescent supramolecular assemblies where the emission signals can be modulated by external stimulus, including small molecules,³ ions,⁴ pH,⁵ temperature,⁶ vapors,⁷ etc. As one of the most components in constructing the assembly, the organic linkers (ligands) are playing very important roles in constructing supramolecular compounds flexibly by selfassembly coordination $\mathsf{process}^8$ and in sensitizing the Ln^{3^+} emission via the so-called "antenna effect" as well as in shielding the Ln³⁺ ions from deleterious quenching interactions.9 Therefore, the design and synthesis of novel organic linkers are highly significant for developing new Ln³⁺directed supramolecular systems having excellent luminescent properties of Ln³⁺ and extra functionalities such as sensing abilities, which still remains a great challenge.

We report herein the formation, physical analysis and

sensing ability for K^* of Ln^{3*} -based supramolecular assembly $(Ln^*L_1, Ln=Eu, Tb \text{ or } Eu/Tb$ with Eu to Tb molar ratio being one) formed by self-assembly the ligand (L_1) that consists of an 18-crown-6 (18C6) connected to two 2,2':6',2''-terpyridyl (tpy) moieties (Scheme 1). The tpy moieties can coordinate to Ln^{3+} ions to form luminescent supramolecular structure since they can harvest light and sensitize the Ln^{3+} emission via "antenna effect", while the 18C6 moiety can effectively modulate the luminescence behavior through the binding of alkaline cations via cation- π interactions, especially, potassium ion,¹⁰ which enables Ln^*L_1 to be used as potential luminescence sensor for selective and quantitative detection for potassium. Interestingly, the emission intensity ratio of ${}^5D_4 \rightarrow {}^7F_5$ transition (Tb³⁺) to ${}^5D_0 \rightarrow {}^7F_2$ transition (Eu³⁺) of the bimetallic Eu³⁺/Tb³⁺ assembly can be linearly related to K⁺ concentration.

Results and discussion

The organic linker L_1 was synthesized by the reaction of 4'-(4-(Bromomethyl)-phenyl)-2,2':6',2"-terpyridine (L₂) with 4,13-diaza-18-crown-6-ether (D-18C6) in approximately 84% yield and the structure is presented in Figure 1. The purity and chemical structure of the L₁ was verified using nuclear magnetic resonance (NMR) spectroscopy, electrospray ionization mass spectroscopy (Figure S1, Supporting Information) and elemental S2. analysis characterization. The ¹H NMR spectrum shows the presence of the tpy protons as sharp singlets from δ = 7.25 ppm to δ = 8.75 ppm,¹¹ indicative of the C_2 symmetry of L_1 . Coordination of L_1 to $LnCl_3 \cdot 6H_2O$ (the added molar ratio kept as 1:1) in the mixture of dichloromethane and ethanol leads to Ln L1. The complexation of Ln^{3+} to L_1 via nitrogen atoms is obviously evidenced by the shift of the absorption bands at 1602, 1585, 1567, and 1543 cm⁻¹ assigned

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 $= Eu^{3+}$ $= Tb^{3+}$ $= K^{+}$ $= L_1$

Scheme 1. Graphical representation of the formation of Ln·L₁ and the schematic illustration of self-calibrating detection for K⁺.



Figure 1. a) Synthetic pathway for L_1 . b) Schematic representation of the formation of $Ln'L_1$; Photograph under near UV light illumination (365 nm) of $Eu'L_1$ (c), $Tb'L_1$ (d) as well as $Eu/Tb'L_1$ (e) in solid state and in MeOH solution (0.1 mM).



Figure 2. SEM images of Eu[·]L₁ in MeOH solution (a, b) and on silicon plate surface (c, d).

to the pyridine ring of L_1 shown in FTIR spectra (Figure S3).¹²

Furthermore, the characteristic peaks for the pyridine moieties in ¹H NMR measurements (**Figure S4**) broadened and shifted downfield, further verifying the formation of Ln⁻L₁.¹¹

To further ascertain the formation of supramolecular assembly, scanning electron microscopy (SEM) were performed. Due to the similarity in morphology of $Eu'L_1$, $Tb'L_1$ and $Eu/Tb'L_1$, herein we only take $Eu'L_1$ as an example. The SEM images shown in Figure 2a and 2b reveal that entangled nanofibers driven by the multiple M-L interactions were formed in MeOH solution when reacting Ln^{3+} ions with ligand L_1 , whereas homogeneous spherical nanoparticles with an average diameter of 700 nm (Figure 2c and 2d) were observed when the MeOH solution of $Eu'L_1$ was casting on silicon surface followed by slowly evaporating the solvent. Energy-dispersive X-ray (EDX, Figure S5) analysis reveals the formation of complex with L_1 to Eu^{3+} ratio of 1:1, which can be further confirmed by elemental analysis (EGA, Figure S6) results. The Eu^{3+}

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content in **Eu'L**₁ was determined to be 13.12%, a value roughly corresponds to a molar ratio of 1:1 between **L**₁ and Eu³⁺. In addition, TGA indicates that **Eu'L**₁ shows good thermal stability.

The interaction of L_1 with Ln^{3+} in solution can be further ascertained by UV/Vis absorption and luminescence spectroscopy titration. A band centered at approximately 280 nm assigned to $\pi \rightarrow \pi^*$ transition of tpy moieties was observed in absorption spectra of L_1 (Figure 3a). Upon the stepwise binding with Eu^{3+} , its absorbance maximum of this band was bathochromically shifted and its absorbance decreased gradually with the appearance of a shoulder at 320 nm, accompanied by an isosbestic point at approximately 300 nm, and reached the maxima with the L_1 to Eu³⁺ molar ratio being 1:1, thereby indicating the formation of Eu³⁺ complex with a 1:1 stoichiometry. The concomitant evolution in luminescent emission spectra upon excitation at 345 nm was presented in Figure 3b. A gradually increase in the emission intensity was observed upon stepwise addition of Eu³⁺, and the maximum was achieved when the molar ratio was 1:1, which slowly leveled off when an excess amount of Eu³⁺ were added. This could be explained by a ligand quenching pathway caused the C-H vibrations of some ligands.¹³ Similar phenomena were also observed for Tb'L₁ in titration experiment results (Figure S7), in accordance with previous reports on luminescent complexes between Ln³⁺ and tpy-based ligand.^{9f, 14}

 $Ln'L_1$ was found highly luminescent both in solution and in solid state irradiated with UV lamp as shown in Figure 1c, 1d and 1e. The luminescence data of $Eu'L_1$ and $Tb'L_1$ are shown in Figure 4. The excitation spectra (Figure S8) observed at 617 nm and 545 nm show a broad band in the range 250-375 nm attributed to the absorption



Figure 3. Changes in a) the absorption, b) the luminescence emission spectra (λ_{ex} =345 nm) of L₁ (0.01 mM) upon the addition of EuCl₃·6H₂O (0 \rightarrow 1.5 equivalents) in dichloro/methanol (1:1 v/v). Inset: luminescence changes of ⁵D₀ \rightarrow ⁷F₂ at 617 nm versus Eu³⁺/L₁.

Figure 4. a) Digital photos of I (**Eu**'L₁), II (**Eu**'L₂), III (**Tb**'L₁), IV (**Tb**'L₂) in MeOH solution under near UV light illumination (365 nm). The concentration of the solutions was 0.1 mM; b) luminescence emission spectra of the I (red) and II (black); c) luminescence emission spectra of the III (green) and IV (black) (λ ex = 345 nm); d) Schematic diagram of the ligand-metal energy transfer from triplet state of the L₁ and L₂ to Ln³⁺ ions.

of tpy units. The emission spectrum of Eu⁻L₁ excited at 345 nm shown in Figure 4b exhibit five sharp bands at 579, 593, 617, 649and 698 nm, assigned to the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ (J=0-4) transitions of Eu³⁺ which further confirm the coordination of tpy to Eu^{3+} ions. For **Tb**⁻L₁, excitation into the absorption of tpy at 345 nm leads to the metalcentered Tb³⁺ emission at 489, 545, 583 and 621 nm, assigned to the transitions of Tb³⁺ from the ${}^{5}D_{4}$ level to the ${}^{7}F_{J}$ levels (J= 6, 5, 4, 3). The emission spectrum of EuL₁ is dominated by the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition at 617 nm and the strongest emission line at 544 nm of **Tb**⁻**L**₁ is attributed to the ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ transition, which is responsible for the bright red emission and green emission, respectively, shown in Figure 1 and Figure 4. It is worthy to note that Eu[']L₂ and Tb[']L₂ (ligand to metal ratio being 2:1) possessing the same coordination mode and number with Eu[·]L₁ and Tb[·]L₁ while lacking the D-18C6 unit show much weaker emission intensity (Figure 4b and 4c, black line), which can be easily seen by naked eyes when the samples were irradiated with UV lamp, i.e., no obvious emission can be observed for the methanol solution of Tb⁻L₂ (Figure 4a (IV)). In addition, the decay time of $\ensuremath{\text{Eu'L}}_2$ and $\ensuremath{\text{Tb'L}}_2$ was determined to be 0.61 ms and 0.47 ms from the corresponding decay curves, respectively, a much shorter value compared with that of Eu L₁ (0.73 ms) and Tb L₁ (0.71 ms) (Figure S9). These data reveal that the D-18C6 moiety contained in L_1 can favor the population of Lanthanide's excited state from the antenna triplet state by means of an energy transfer. This can be further verified by the energy levels of the triplet state of L_1 and L_2 determined according to the method reported previously¹⁵ (Figure 4d). The value is remarkably increased from

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20790 to 22420 cm⁻¹ after the integration of D-18C6 and L₂ (Figure **S10**), enabling L₁ much more suitable for sensitizing the luminescence of both Eu³⁺ and Tb³⁺ with respect to L₂ according to Latva's empirical rule.¹⁶

Furthermore, obvious luminescence enhancement was observed upon adding potassium ions to Ln'L1 in methanol, implying that LnL_1 can be used as luminescent sensor for K^+ detection. This is very important since K⁺ is an essential ion in biological systems and its selective and sensitive detection is of great importance.¹⁷ However, luminescent K^* sensors explored until now are based on the luminescence intensity of single emissive transition and are compromised to errors due to the concentration of sensor, the drifts of the optoelectronic systems, and excitation efficiency.¹⁸ We observed herein that the Eu^{3+}/Tb^{3+} heterometallic structure **Eu/Tb**^{L_1} display a high selectivity toward K⁺ as shown in **Figure 5**. In a preliminary screening experiment, different cations were added to Eu/Tb[·]L₁ in a methanol solution. Among the cations tested, only potassium ions remarkably increase the luminescence intensity of both Eu³⁺ ions and Tb³⁺ ions, leading to 175% and 140 % of the original value for Eu^{3+} and Tb^{3+} (Figure 5b), respectively, whereas other metal such as Na⁺, Li⁺, Ca²⁺, Mg²⁺, Cr³⁺, Ni²⁺, Zn²⁺, Al³⁺ and Ag⁺ ions can quench Eu³⁺ and Tb³⁺ luminescence efficiently. The shape of the emission spectra are not perturbed by the binding of K^{\dagger} , which means no structural rearrangement occurs at the Ln³⁺ center,^{10b} indicating that **Eu/Tb** L_1 is a stable luminescent K⁺ sensor. The evolution of luminescent emission spectra $Eu/Tb^{-}L_{1}$ on the K⁺ addition is presented in Figure 6. The Tb³⁺ emission intensity at 545 nm and Eu³⁺ emission intensity at 617 nm of Eu/Tb⁻L₁ increases



Figure 5. The luminescence emission spectra (a) and histogram (b) of Eu/Tb'L₁ in MeOH solution (0.1 mM) with various metal cations (λ_{ex} =345 nm) (I, I₀ are the intensity of Eu/Tb'L₁ in 545 nm and 617 nm before and after addition of K⁺).



Figure 6. (a) Luminescent emission intensity of **Eu/Tb'L**₁ in MeOH solution (0.1 mM) in the presence of various equivalents of K⁺ under excitation at 345 nm. Insets: the luminescence intensity at 617 nm and 545 nm with different equivalents of K⁺; (b) The fitted curve between I_{Tb}/I_{Eu} and various equivalents of K⁺ (0.5-6 eq).

constantly when the added K⁺ is increased from 0 to 4 equivalents, further increasing K⁺ concentration leads to an obvious drop in Tb³⁺emission intensity, whereas the emission intensity of Eu³⁺ at 617 nm displays stable enhancement (**Figure 6a**). This different K⁺-dependent emission pattern of ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ transition (Tb³⁺, I_{Tb}) and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition (Eu³⁺, I_{Eu}) in the bimetallic compound indicates that **Eu/Tb'L**₁ can be used as an excellent candidate for self-calibrating sensor, not necessarily requiring any additional calibration of luminescence intensity. Remarkably, the K⁺ equivalent (eq[K⁺]) within the range from 0.5 to 6 can be linearly related to the emission intensity ratio (I_{Tb}/I_{Eu}) of **Eu/Tb'L**₁ can also be used as an excellent luminescent sensor for the quantitative analysis of K⁺, a detection limit down to 1 μ M can be achieved, a promising value compared to those previously reported in ref.¹⁹

$$I_{Tb}/I_{Eu} = 3.5179 - 0.2514 \text{ eq}[K^{T}]$$

(1)

The 18C6 moiety is of high importance for **Eu/Tb'L₁** to realize the selective and quantitative detection of potassium ions for it can be served as a lariat to selectively capture K⁺ via selective cation- π interactions.²⁰ The binding of K⁺ can remarkably increase the triplet state energy level of the ligand L₁, e.g., it was increased from 22420 cm⁻¹ to 23400 cm⁻¹ when four equivalents of potassium ions was added to L₁, and this can explain why luminescence enhancement of Ln³⁺ can be observed for **Eu/Tb'L₁**. In addition, like other Eu³⁺/Tb³⁺ bimetallic systems,²¹ energy transfer also occurs from Tb³⁺ ions to Eu³⁺ ions in **Eu/Tb'L₁** as evidenced by the shorter lifetime of Tb³⁺⁵D₄ excited state and the longer value of Eu³⁺⁵D₀ excited state compared with that of the corresponding monometallic sample **Tb'L₁** and **Eu'L₁** shown in **Table 1**, respectively. The energy transfer

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Table 1. The luminescence decay time of ${}^{5}D_{4}$ state in MeOH solution of **Eu/Tb'L**₁ with the variation equivalents of K⁺ (excited at 345 nm).

@544 nm	Untreated	1	2	3	4	5	6
Tb'L ₁	0.71	0.74	0.76	0.78	0.82	0.82	0.81
Eu/Tb ⁻ L ₁	0.70	0.68	0.66	0.64	0.62	0.59	0.56
η _{τь-εu} /%		8.1	13.2	15.4	24.4	28.0	30.9

efficiency from Tb³⁺ ions to Eu³⁺ ions (η_{Tb-Eu}) was determined according to previously method using Equation (2)²² and was listed in **Table 1**.

 $\eta_{Tb-Eu} = 1 - \tau_1 / \tau_{Tb}$ (2)

where τ_1 and τ_{Tb} are the lifetime of the 5D_4 state in **Tb'L**₁ and **Eu/Tb'L**₁. From Table 1, we can observe that the energy transfer efficiency changes as the K⁺ concentration changes. The changes in the triplet excited energy level of L₁ and the alteration of the energy transfer efficiency from Tb³⁺ to Eu³⁺ caused by the presence of K⁺ are therefore responsible for the luminescent response of **Eu/Tb'L**₁ towards K⁺ ions.

Conclusions

In conclusion, this work reports a novel luminescent and selfcalibrating sensor for potassium ions constructed by Ln³⁺directed supramolecular self-assembly through the coordination of Eu³⁺ and Tb³⁺ with a crown-connected bisterpyridine. The crown moiety makes the bimetallic system highly attractive in the selective and quantitative detection of potassium ions since the energy transfer from the ligand to Eu³⁺ and Tb³⁺ as well as that from Tb³⁺ to Eu³⁺ can be tuned by K^{+} -crown cation- π interaction. The result is that the K^{+} concentration can be linearly correlated to the emission intensity ratio of ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ transition (Tb³⁺) to ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition (Eu³⁺), and a detect limit down to 1 μ M can be obtained. This work highlights the importance of the design and synthesis of organic linker for constructing luminescent lanthanide supramolecular assembly that show promising applications in various fields such as sensing.

Experimental

Materials: 4'-(4-(bromomethyl)phenyl)-2,2':6',2"-terpyridine (L₂) was synthesized by the modified method previously reported^{12a,23}. EuCl₃·6H₂O, TbCl₃·6H₂O (99.99%, Beijing HWRK Chem) and 4,13-diaza-18-crown 6-ether (D-18C6, 98%, J&K) were used as received. Unless otherwise stated, all manipulations were conducted under air atmosphere.

Syntesis of L_1 : D-18C6 (0.21 g, 0.8 mmol), L_2 (0.65 g, 1.6 mmol), and Cs₂CO₃ (0.65 g, 2 mmol) were refluxed at 80 °C in 120 mL of CH₃CN for 12 h under nitrogen. The reaction mixture was evaporated under reduced pressure and treated with a mixture of water and chloroform (1:2). The organic layer was separated, evaporated under reduced pressure. The crude product was purified by column chromatography over silica gel (eluent: 12:1 CH₂Cl₂/MeOH), L_1 was

obtained as brown powder in 84% yield. ¹H NMR (400 MHz, CDCl₃): δ 8.73 (dd, 4H), 8.71 (s, 4H), 8.66 (d, 4H), 7.94-7.86 (m, 8H), 7.67 (s, 4H), 7.37 (ddd, 4H), 4.13 (s, 4H), 3.80 (s, 8H), 3.63 (s, 8H), 3.17 (s, 8H). ESI-MS: m/z 905.4 ([M+H]⁺). Elemental analysis for L₁, found (calcd.): C 74.27 (74.31), H 6.29 (6.24), N 12.36 (12.38).

Synthesis of Ln'L₁: For the preparation of **Eu'L₁**, EuCl₃·6H₂O (0.1 mmol) was dissolved in EtOH (100 mL). 0.09 g of **L**₁ (0.1 mmol) in dichloromethane (100 mL) was sonicated until complete dissolution. The resulting solution was added dropwise under vigorous stirring to the solution of EuCl₃·6H₂O at room temperature. After stirring at 70 °C for 8 h, the mixture was allowed to evaporate slowly at 80 °C. The resulting powder was washed several times with dichloromethane and EtOH, and dried under vacuum overnight. Elemental analysis for **Eu'L₁**, found (calcd.): C 57.81 (57.79), H 4.91 (4.82), N 9.81 (9.63). In addition, **Tb'L₁**, **Eu/Tb'L₁** and **Gd'L₁** were also easily obtained by the same method. Elemental analysis for **Tb'L₁**, found (calcd.): C 57.65 (57.44), H 4.81 (4.79), N 9.56 (9.57); Elemental analysis for **Eu/Tb'L₁**, found (calcd.): C 57.65 (57.61), H 4.81 (4.80), N 9.54 (9.60).

Synthesis of Ln'L₂: LnCl₃·6H₂O (0.1 mmol) (Ln=Eu, Tb, Gd) was dissolved in EtOH (100 mL). 0.08 g of L₂ (0.2 mmol) in dichloromethane (100 mL) was sonicated until complete dissolution. The resulting solution was added dropwise under vigorous stirring to the solution of LnCl₃·6H₂O at room temperature. After stirring at 70 °C for 8 h, the mixture was allowed to evaporate slowly at 80 °C. The resulting powder was washed several times with dichloromethane and EtOH, and dried under vacuum overnight.

Characterization: ¹H NMR spectra was recorded at room temperature, using perpetuated solvents as internal standards. Elemental analysis was performed on an Elementar Vario El system. The TG studies were analyzed by using a SDT-TGQ 600 at a heating rate of 10 °C min⁻¹ using dried air as purging gas. SEM images were obtained from an FE-SEM (Hitachi S-4300) at an acceleration voltage of 10 kV. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded in the spectral range from 4000 to 400 cm⁻¹ with a Bruker Vector 22 spectrophotometer by using pressed KBr pellets for solid samples. A UV-visible Agilent cray100 spectrometer was used to determine the wavelength of the maximum UV absorbance peak. The luminescence measurements (excitation spectra, emission spectra, luminescence decay time) of solid state powder and solution were measured on an Edinburgh Instruments FS920P.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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