

Tunable and white luminescence from mixed lanthanide with aza-macrocycles through multistimuli responses

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ABSTRACT

In this work, two aza-macrocycles (**1** and **2**) were designedly synthesized as hosts for sensitizing lanthanide luminescence in aqueous solution to explore new light emitting material. It is expected that macrocycle molecules can encapsulate lanthanide centers into their cavity to form new lanthanide fluorescent materials based on their excellent host–guest binding abilities. In addition, macrocycle molecules are blue emitters, so it will be possible to construct white light-emitting and color-tunable materials through the doping of both Tb³⁺ ions and Eu³⁺ ions into aza-macrocycle hosts with an appropriate molar ratio. All of experimental results verify that aza-macrocycle based lanthanide materials realized tunable luminescence and white light emissions through changing relative concentration (Tb/Eu = 1:0, 1:1, 1:2, 1:4, 1:6, 1:8, 0:1) of the constituent Ln³⁺ ions and the excitation wavelength from 351 nm to 395 nm. As far as we know, it is very rare that the color-tunable and white-light emission can be controlled by two types of strategies and on the basis of macrocycle hosts.

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1. Introduction

Over the past several decades, enormous research interest and significant effort have been directed and dedicated towards the development of new lanthanide materials due to their remarking photophysical properties including large Stokes shifts, wide lifetime range, and characteristic narrow line-like emission bands, therefore they as one of the most important classes of luminescent materials attain a special status [1–17]. Among them, multicolored photoluminescence tuning in a single-phase material exhibits invaluable potential in display and security applications including light emitting devices, panel display systems, molecular logic gates, optical memory devices, color-tunable phosphors and so on [18–29]. Generally, color-tunable luminescent performance can be realized through co-doping multi-color emitting activator ions into matrices, then changing the relative amount of different light emitters. However, the realization of such fluorescent modulation materials based on direct lanthanide(III) codoped method depends on a key factor, which is suitable matrices. Matrices as host are able to stabilize multiple luminescent dopants and control

the energy transfer processes, because physical blending may cause an inhomogeneous dispersion of the dopant and thermodynamically unstable composite, resulting in self-quenching and low luminescence efficiency. In order to overcome the mixing problem, it is an important task to develop appropriate matrices as host, which can efficiently sensitize the Ln³⁺ ions via an “antenna effect”. Wang et al. synthesized a poly(acrylic acid)/silica hydrogel nanofiber as adsorbent to capture the Ln³⁺ ion under water circumstance, successfully sensitizing their emission with good photoluminescent performance and tunable emission color [35]. Rao et al. selected a metal–organic framework material (ZJU-1) as a host [46] to construct Ln³⁺-codoped ZJU-1 (ZJU-1: Tb, Eu), which offers a possibility to tune the luminescence color via varying the doping stoichiometric ratio of Tb³⁺/Eu³⁺. Among the reported luminescent materials [30–52], Eu(III) and Tb(III) as typical optical ions were adopted extensively, since they can emit intense red and green characteristic fluorescence, respectively. By adjusting the relative amounts of co-doping Eu and Tb components in a host framework, a multiple emission color can be accomplished. It is well known that the luminescence of Tb³⁺ is much easier than Eu³⁺ ions in the same matrices. That is due to the lower excited resonance level of Tb³⁺, locating at 20500 cm⁻¹ for ⁵D₄. Therefore Tb³⁺ ions display obviously superior match with the energy state of the ligand through ligand to metal energy transfer

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process, comparing with 19000 cm^{-1} for 5D_1 of Eu^{3+} . Fortunately, Tb^{3+} ion acting as an energy transfer acceptor can improve the weak luminescence of $\text{Eu}(\text{III})$ in a mixed Eu/Tb framework because of energy transfer from Tb^{3+} to Eu^{3+} . In other words, multiple colours can be realized by controlling different energy transfer processes, such as the extra excitation wavelength [53–55].

In this work, aza-macrocycles were selected as hosts for sensitizing lanthanide luminescence in aqueous solution to explore new light-emitting material. Macrocycles as a class of prototypical and seminal hosts play a significant role in a wide variety of chemical fields, such as the detection and recognizing of metal ions involved in biological processes, clinical diagnostics or pollution (e.g., lead, mercury, cadmium) through their excellent host–guest binding abilities [56–64]. Therefore, it is expected that they can encapsulate lanthanide centers into their cavity to form new lanthanide fluorescent materials. In addition, they can be also modified to selectively bind specific guest by hydrogen-bonding functionalities, cavity size or shape. Besides, the composites of macrocycle and lanthanide combine luminescent and adsorbed performances, that will be a practical issue from the view of environmental protection and resource utilization. Furthermore, such macrocycles are blue emitters, it will be possible to construct white light-emitting and color-tunable materials through the doping of both Tb^{3+} ions and Eu^{3+} ions with an appropriate molar ratio. Herein, two aza-macrocycle ligands as hosts synthesized can crawl selectively lanthanide ions in water environment, realizing multi-responsive tunable and white luminescent emissions through changing the relative concentration of the constituent Ln^{3+} ions and the excitation wavelength.

2. Experimental

2.1. Materials and measurements

All starting chemicals employed in the present work were obtained commercially and used without further purification. Two aza-macrocycles (**1** = 3,6,9,17,20,23-hexaazatricyclo-[23.3.1.1^{11,15}]-triaconta-1(29),11(30),12,14,25(26),27-hexaene); **2** = 3,7,10,18,22,25-hexaazatricyclo-[25.3.1.1^{12,16}]-dotriaconta-1(31),12(32),13,15,27,29-hexaene) and one cryptand ligand ZTN were synthesized according to the previously documented [65,66]. Energy Disperse Thermogravimetric and differential thermal analysis (TG-DTA) data were collected on a Thermal Analysis Instrument (SDT 2960, TA Instruments, New Castle, DE) from room temperature to $700\text{ }^\circ\text{C}$ with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under air atmosphere in the Al_2O_3 crucible. Excitation and emission spectra of the samples in the solid-state or mixed solutions were recorded on a Hitachi F-7000 spectrophotometer equipped with a 150W xenon lamp as the excitation source at room temperature. The luminescence decay curves for $\text{Tb}^{3+}@2$, $\text{Eu}^{3+}@2$, $\text{Eu}_x\text{Tb}_y@2$ ($x:y = 1:1$) were obtained using a Lecroy Wave Runner 6100 digital oscilloscope (1 GHz) with a tunable laser (pulse width = 4 ns, gate = 50 ns) as the excitation source (Continuum Sunlite OPO). The luminescence lifetimes were calculated by Origin 7.5 software package. ^1H NMR data was collected on a Bruker 500 MHz spectrometer. All ICP tests are performed on a ICP-OES (ICP 6300, Thermo Scientific, USA) instrument based on solid samples of $\text{Tb}_x\text{Eu}_y@1$ ($x:y = 1:0, 1:1, 1:2, \text{ and } 0:1$).

2.2. Fluorescence measurements

Firstly, the samples of **1**, **2**, or ZTN (10 mg) were soaked in water solutions of nitrate salts of Eu^{3+} , Tb^{3+} , Na^+ , K^+ , Ag^+ , Mg^{2+} , Ca^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} , Al^{3+} , Eu^{3+} , Tb^{3+} (3 mL, 0.01 mol L^{-1}), respectively, for 24 h at room temperature. Then, the

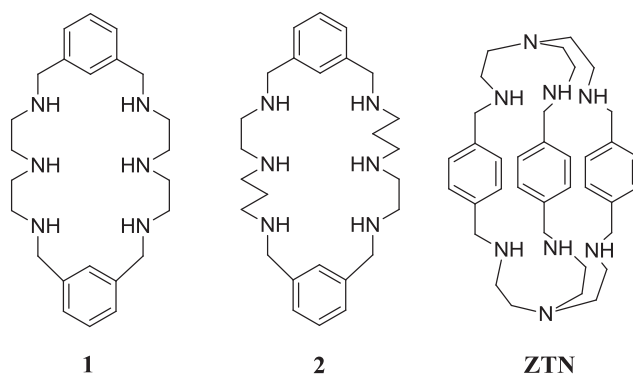
luminescent was then determined after vibrating under ultrasonic for 5 min.

Secondly, **1** and **2** (10 mg) dissolved in water solutions (3 mL) of Tb^{3+} with different concentrations of 10^{-8} – 10^{-1} mol/L , respectively. After 12 h, all solutions were determined by luminescent instrument.

Thirdly, **1** and **2** (10 mg) dissolved in water solutions (3 mL) of lanthanide nitrate salts keeping the same concentration (0.01 mol/L) of Ln^{3+} ions with different molar ratios of $\text{Eu}^{3+}/\text{Tb}^{3+}$, respectively. After 12 h, all solutions were determined by luminescent instrument.

3. Results and discussion

Herein, two aza-macrocycles (**1** and **2**) (Scheme 1) with open nitrogenous sites as binding paws were synthesized via Mannich reaction based on isophthalaldehyde and diethylenetriamine for **1**, isophthalaldehyde and *N*-(2-aminoethyl)-1,3-propanediamine for **2**, according to the literature procedure [65,66]. Free **1** and **2** show purple emission at a wide range of 350–500 nm as shown in solid state luminescence spectra at room temperature, but their luminescent intensity obviously decreases in aqueous solutions (Fig. S2). The interesting experimental phenomenon occurred, while each 10 mg of **1** (or **2**) was added into every aqueous solution (0.01 M, 3 mL) containing different metal ions (+1: Na^+ , K^+ , Ag^+ ; +2: Mg^{2+} , Ca^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} ; +3: Al^{3+} , Eu^{3+} , Tb^{3+}) for 24 h, respectively. The luminescence properties of all solutions containing metal ions and macrocycle molecules ($\text{M}@1$ and $\text{M}@2$) were investigated and recorded in Fig. 1. As shown in Fig. 1, $\text{Tb}^{3+}@2$ material emits four typical sharp emission bands from Tb^{3+} ions in the visible spectrum under the excitation of 377 nm, corresponding to transitions from the 5D_4 state: $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$, and $^5D_4 \rightarrow ^7F_3$ ($\lambda_{\text{em}} = 490\text{ nm}$, 545 nm, 587 nm, and 623 nm, respectively), of which, $^5D_4 \rightarrow ^7F_5$ is the strongest; $\text{Eu}^{3+}@2$ shows very weak characteristic emissions from the Eu^{3+} ion at $\lambda_{\text{em}} = 593\text{ nm}$, 617 nm and 700 nm under $\lambda_{\text{ex}} = 377\text{ nm}$. Similar results can be observed for $\text{Tb}^{3+}@1$ and $\text{Eu}^{3+}@1$. Therefore, **1** and **2** as hosts are capable to successfully protect lanthanide cations with a significant enhancement turn-on luminescent response compared with non-emitters of the Tb^{3+} and Eu^{3+} in aqueous solution with aqueous quenching. Other metal ions have negligible effect on the enhancement of **1** and **2** luminescence. When the concentration of Tb^{3+} is lower than 0.01 M, the $\text{Tb}^{3+}@1$ and $\text{Tb}^{3+}@2$ emit very weak or scarcely characteristic emissions (Fig. 2). Along with the incremental concentration of Tb^{3+} and Eu^{3+} from 0.01 M to 0.1 M, the luminescent spectra of $\text{Tb}^{3+}(\text{Eu}^{3+})@1$ (or **2**) show a nearly 10-fold fluorescent enhancement (Fig. 3, Fig. S3). And the luminescence of the aqueous solution containing pure Tb^{3+} ions is very weak under similar experimental condition.



Scheme 1. The structures of aza-macrocylic ligands **1**, **2** and cryptand ligand ZTN.

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