

Lanthanide Coordination Polymers and Their Ag⁺-Modulated Fluorescence

Weisheng Liu,* Tianquan Jiao, Yizhi Li, Quanzhong Liu, Minyu Tan,* Hong Wang, and Liufang Wang

Department of Chemistry and National Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, P.R. China

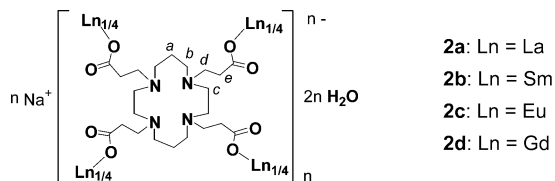
Received June 11, 2003; E-mail: liuws@lzu.edu.cn

Many lanthanide complexes are noted for their luminescence arising from f–f transitions generated via the “antenna effect”.¹ Europium-based systems are of special interest for optical excitation and emission studies because they exhibit high luminescent quantum efficiencies, and the details of Eu(III) (4f–4f) excitation and emission spectra are particularly sensitive to structural details of the coordination environment.² These features have been exploited in biological contexts, for example, in fluoroimmunoassays³ and structural probes,^{1a} and also make lanthanide chromophores the focus of new display materials.⁴ Their use has opened up a lot of opportunities in growing fields of large social and economical impact, such as luminescent material, environmental sciences, medical diagnostics, and cell biology.^{5–8}

There, however, are some knotty problems. (i) Many of the lanthanide complexes are not soluble in water, restricting their uses in biologic system. (ii) The emission band usually contains multiple peaks, which reduces the monochromaticity and measurement precision. (iii) All of the excitation wavelengths are located in or near UV range, while the UV light is nocuous for the biologic system. These largely limit their applications. Our present approach exploits the controllable modulation of lanthanide luminescence by designing special structures of complexes.

Herein, we chose and prepared a tetra(amino acid) ligand, 1,4,8,11-tetraazacyclotetradecane-1,4,8,11-tetrapropionic acid (H₄L, **1**),⁹ and synthesized four three-dimensional coordination polymers of lanthanide {Na[LnL(H₂O)₄]·2H₂O}_n (Ln = La (**2a**), Sm (**2b**), Eu (**2c**), Gd (**2d**)) (Scheme 1) by self-assembly. The complexes were

Scheme 1. Scheme for the Complexes {Na[LnL(H₂O)₄]·2H₂O}_n (Coordination H₂O Omitted for Clarity; Systematic Name of the Ligand H₄L: 1,4,8,11-Tetraazacyclotetradecane-1,4,8,11-tetrapropionic Acid (H₄L, **1**))



prepared by mixing the ligand **1** (1.0 mmol) and lanthanide nitrate (1.0 mmol) in 10 mL of 1:1 H₂O/EtOH and then adjusting the pH of the solution to ~5 by dilute NaOH solution. The resulting precipitate was filtered, washed by cold H₂O and EtOH, and dried over P₄O₁₀. The solid complexes (**2a–d**) obtained were characterized by elemental analysis and IR spectra (see Supporting Information). Slow evaporation of the water solution of the Gd(III) complex **2d** yielded a single crystal suitable for X-ray analysis after a period of ~4 weeks. The four complexes are soluble in water, and the Eu(III) complex **2c** has strong luminescence.

The crystal structure¹⁰ of **2d** is shown in Figure 1. The ligand binds to Gd³⁺ by coordination bonds, forming a 3-D network polymer polymerized along the *c*, *b* axis, and the diagonal of the *a*

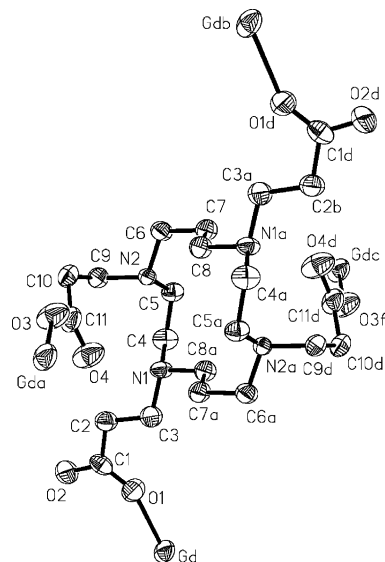


Figure 1. The crystal structure of the Gd(III) complex **2d** (only one ligand is present for clarity).

and *c* axes (Figure 2), and there are channels along these directions. Na⁺ distributes in interspaces between the channels. There is an empty coordination site in the tetraazacycle of the ligand in the complex (see Figures 1 and 2c). The four complexes **2a–2d** have similar IR spectra, of which the characteristic bands have similar shifts (see Table S3), suggesting they have a similar coordination structure.

We investigated the effects of the ds-block cations Cu²⁺, Ag⁺, Zn²⁺, Cd²⁺, and Hg²⁺ on the fluorescence spectrum of the Eu³⁺ complex **2c** when the ds-block cation enters the empty coordination site in the azacycle of the ligand in the complex. The result indicates that the cations Cu²⁺, Zn²⁺, Cd²⁺, and Hg²⁺ quench the fluorescence of the Eu³⁺ complex, but Ag⁺ can enhance and modulate it (Figure 3). Complex **2c** exhibits three emission bands at 592, 615, and 696 nm, corresponding to the ⁵D₀ → ⁷F_J (*J* = 1, 2, 4) transitions. Among these transitions, ⁵D₀ → ⁷F₂ is the strongest. When Ag⁺ enters into the empty coordination site, the emission spectrum changed from multiple peaks to a single peak; the emission intensity of the hypersensitive (electric dipole) ⁵D₀ → ⁷F₂ transition for Eu³⁺ increased by 4.9 times, while the other ⁵D₀ → ⁷F_J (*J* = 1, 4) transitions largely decreased and were too weak to be observed (see Figure 3a). The excitation wavelength of the fluorescence moved from UV (395 nm) to visible light range (484.7 nm) (see Figure 3b). The changes of emission spectra upon addition of Ag⁺ are shown in Figure 3c, the inset of which indicates the data points obtained from the titrations of **2c** with AgNO₃, and the fit to a 1:1 binding model, in agreement with the Ag⁺ entering the empty coordination site.

We have investigated the solution structure of **2c** and the structure after addition of Ag⁺ by ¹H NMR in D₂O. Some shift accompanied

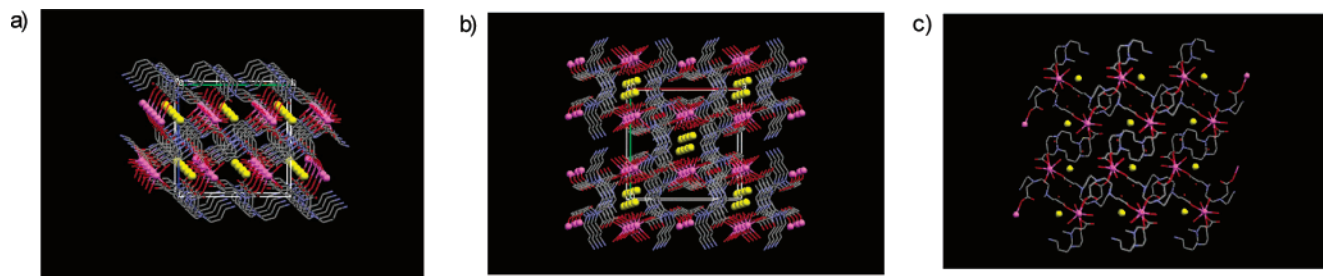


Figure 2. The 3-D network polymer viewed along *a* (a), *c* (b), and the diagonal of the *a* and *c* axes (c). Pink, Gd; yellow, Na; gray, C; blue, N; red, O.

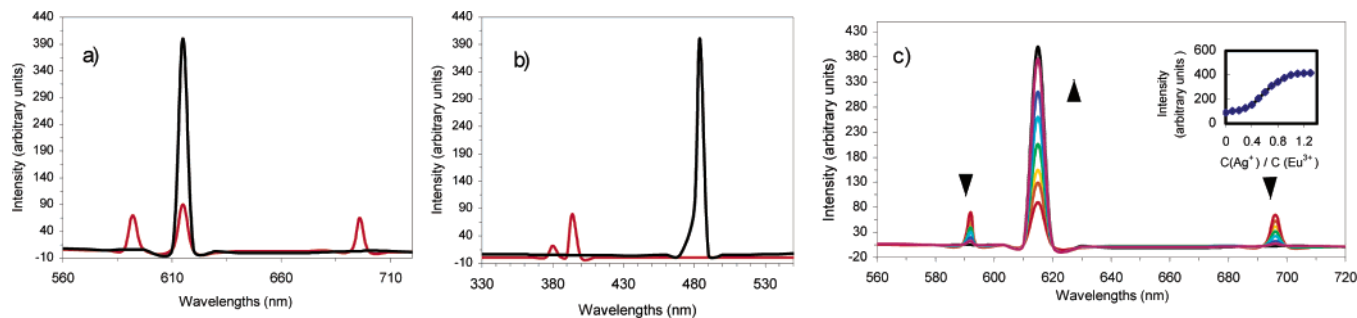


Figure 3. (a) Luminescence emission spectra of a 1.0×10^{-4} M solution of complex **2c** (red line) in H_2O and after the addition of 1.0 equiv of Ag^+ (black line), excited at 395 and 384.7 nm. (b) Excitation spectra of a 1.0×10^{-4} M solution of complex **2c** (red line) in H_2O and after the addition of 1.0 equiv of Ag^+ (black line), monitored at 615 nm. (c) Increase in luminescence intensity of a 1.0×10^{-4} M solution of complex **2c** in H_2O upon addition of Ag^+ . Inset: luminescence intensity at 615 nm, plotted against the mole concentration ratios $C(\text{Ag}^+)/C(\text{Eu}^{3+})$; the line represents the fit to a 1:1 binding model.

by a line broadening, as expected for a paramagnetic ion, is observed for **2c** (see Figure S1). The assignment of the NMR signals has been achieved by two-dimensional COSY spectra (see Figure S2). As compared to the diamagnetic complex **2a**, the CH_2 protons H_e (re. Scheme 1) nearest to the paramagnetic ion $\text{Eu}(\text{III})$ are shifted upfield and form a broad peak with H_a , suggesting the coordination structure is similar to the solid structure, to which $\text{Eu}(\text{III})$ is coordinated by the carboxy group. Upon the addition of 1 equiv of Ag^+ , the broad peak including H_b and H_d close to the azacyclic nitrogen shows a partial dissociation, while the peak including H_a and H_e which are located at the azacyclic group and the substituents, respectively, shows a full dissociation. The result indicates that Ag^+ is coordinated by the azacyclic amine group. The dissociation of H_a and H_e suggests that the coordination of Ag^+ increases the rigidity of the complex and would cause modification of the paramagnetic spin state.

To our knowledge, the fluorescence effect is without precedent and needs further investigation. These results have an important significance for developing the applicable scope of lanthanide luminescent materials and structural probes and sensors. We expect that the europium complex cluster can be used in research of new luminous materials, in medical diagnostics and cell biology, and as molecular devices for Ag^+ sensor.

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Supporting Information Available: X-ray crystallographic data in CIF format and printable tables for $\{\text{Na}[\text{GdL}(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}\}_n$, and

experimental details, elemental analysis, and spectral data for all of the compounds (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (10) Data collection on a R3M/E four-circle diffractometer with graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å). Structure solutions by standard Patterson and difference Fourier methods and refined on F^2 . Crystal data: formula $\text{C}_{11}\text{H}_{24}\text{Gd}_{0.5}\text{N}_2\text{Na}_{0.5}\text{O}_7$, crystal size $0.12 \times 0.12 \times 0.16$ mm, monoclinic, $C2/c$, $a = 15.458(3)$, $b = 14.220(3)$, $c = 14.245(3)$ Å, $V = 3085.2(11)$ Å 3 , $z = 8$, $F(000) = 1580$, $\lambda = 0.71073$ Å, $\mu(\text{Mo K}\alpha) = 2.234$ mm. Least-squares refinement based on 2342 reflections with $I > 2\sigma(I)$ gave final $R = 0.0187$ and $wR = 0.0676$.

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