

Spectroscopic Study on the Photophysical Properties of Lanthanide Complexes with 2, 2'-Bipyridine-*N*, *N'*-dioxide

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Five novel lanthanide (Eu^{3+} , Tb^{3+} , Gd^{3+} , Sm^{3+} and Dy^{3+}) complexes with 2, 2'-bipyridine-*N*, *N'*-dioxide (bipyO₂) were synthesized and characterized by elemental analysis, IR spectrum. The triplet state energy of bipy O₂ was determined to be 22275 cm⁻¹ with the phosphorescence spectrum of bipy O₂ and its gadolinium complex. The photophysical properties of these complexes indicated that the triplet state energy of the ligand is suitable for the sensitization of the luminescence of Eu^{3+} , Tb^{3+} , Sm^{3+} and Dy^{3+} , especially of Tb^{3+} .

KEY WORDS: lanthanide complexes; 2, 2'-bipyridine-*N*, *N'*-dioxide; photophysical property; energy transfer; fluorescence.

INTRODUCTION

Much research have been performed on the lanthanide complexes with heterocyclic ligands, such as 1,10-phenanthroline, or 2,2'-bipyridine because these complexes can exhibit strong luminescence which have a lot of potential applications for the fluorescence probes or labels in biological immunoassay and active central species in photoluminescent materials [1–6]. Besides this, these compounds also act as the second assistant ligands for some lanthanide complexes of carboxylates or β -diketonates to replace the water molecules in coordination sphere, which can decrease the nonradiative energy loss to obtain high luminescence [7–12]. 2,2'-Bipyridine can be chemically modified to form the substituted heterocyclic ligands bipyNO or bipyO₂ [13,14]. A few studies on the synthesis and characterization of their lanthanide complexes with bipyNO were reported [15,16]. Little has been found in the literature on the photophysical properties of lanthanide complexes with bipyO₂ except for using them as the structural ligands [18–19]. In this paper, we

synthesized the corresponding complexes with luminescent lanthanide ions (Eu^{3+} , Tb^{3+} , Gd^{3+} , Sm^{3+} and Dy^{3+}). The photophysical properties of these complexes were discussed in detail using ultraviolet absorption spectra, phosphorescence spectrum, fluorescence excitation and emission spectra.

EXPERIMENTAL

Synthesis of Lanthanide Complexes

Lanthanide oxides (Eu_2O_3 , Tb_4O_7 , Gd_2O_3 , Sm_2O_3 , Dy_2O_3) were converted to their nitrates by treatment with concentrated nitric acid. BipyO₂ was synthesized according to the ref [13]. The corresponding lanthanide complexes with this ligand were prepared by homogeneous precipitation. Aqueous solution of lanthanide nitrates were added very slowly to the aqueous solutions of bipyO₂. Then white precipitates appeared and were filtered off, washed with ethanol or water, dried and stored over silica gel. The compositions of the complex systems were confirmed by elemental analysis: $\text{Ln}(\text{bipyO}_2)_2(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$, Ln = Eu, Tb, Sm, Dy, Gd. Anal. Calcd. for $\text{C}_{20}\text{H}_{20}\text{EuN}_7\text{O}_{15}$: C, 32.01; H, 2.69; N, 13.07; Found: C 31.79; H, 2.40; N, 12.74. For

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$C_{20}H_{20}TbN_7O_{15}$: C, 31.72; H, 2.66; N, 12.95; Found: C, 32.05; H, 2.41; N, 12.68. For $C_{20}H_{20}SmN_7O_{15}$: C, 32.08; H, 2.69; N, 13.09; Found: C, 32.39; H, 2.42; N, 12.77. For $C_{20}H_{20}DyN_7O_{15}$: C, 31.57; H, 2.65; N, 12.89; Found: C, 31.85; H, 2.37; N, 12.61. For $C_{20}H_{20}GdN_7O_{15}$: C, 31.79; H, 2.67; N, 12.97; Found: C, 31.55; H, 2.41; N, 12.73.

Physical Measurement

Elemental analyses (C, H, N) were carried out by the Elementar Cario EL elemental analyzer. Infrared spectroscopy with KBr pellets was performed on a Nicolet Nexus 912 AO446 model spectrophotometer in the $4000 \sim 400 \text{ cm}^{-1}$. Ultraviolet absorption spectra of bipyO₂ and its five lanthanide complexes were obtained with an Agilent 8453 spectrophotometer ($10^{-4} \text{ molL}^{-1}$ ethanol solutions). Both phosphorescence spectra of the bipyO₂ and its gadolinium complex were determined with Perkin-Elmer LS-55 spectrophotometer: excitation wavelength = 370 nm, delay time = 0.01 ms, scan speed = 1000 nm/s, the phosphorescence measurement began 100 microseconds after lamp flash and it continued 200 microseconds. The luminescence (excitation and emission) spectra for the solid complex samples were determined with Perkin-Elmer LS-55 spectrophotometer: excitation slit width = 10 nm, emission slit width = 5 nm.

RESULTS AND DISCUSSION

All the IR spectra of these lanthanide complexes show the similar features. The N—O stretch vibrational bands of 1262 cm^{-1} belong to free bipyO₂ and show some red shifts in the corresponding IR spectra of lanthanide complexes, i.e., the same value of 1242 cm^{-1} was observed for the five lanthanide (Eu, Tb, Sm, Dy and Gd) complexes. This indicates that the formation of N—O in the complexes decreases the π bond component and force constant of N—O bond for free bipyO₂. On the other hand, the distortion vibrational bands of free bipyO₂ ligand, 841 cm^{-1} , 848 cm^{-1} , 1016 cm^{-1} and 1133 cm^{-1} , all show some blue shifts in the IR spectra of its lanthanide complexes of 854 cm^{-1} , 860 cm^{-1} , 1042 cm^{-1} , 1165 cm^{-1} . This may be due to the formation of ten-chelated ring (four coordinated oxygen atoms from two bipyO₂ ligands and six coordinated oxygen atoms from three NO₃⁻) of these complexes.

Figure 1 shows ultraviolet-visible absorption spectra for the free bipyO₂ ligand and the corresponding five lanthanides (Eu, Tb, Sm, Dy, Gd) complexes. They all exhibit similar domain absorption peaks in the ultraviolet region

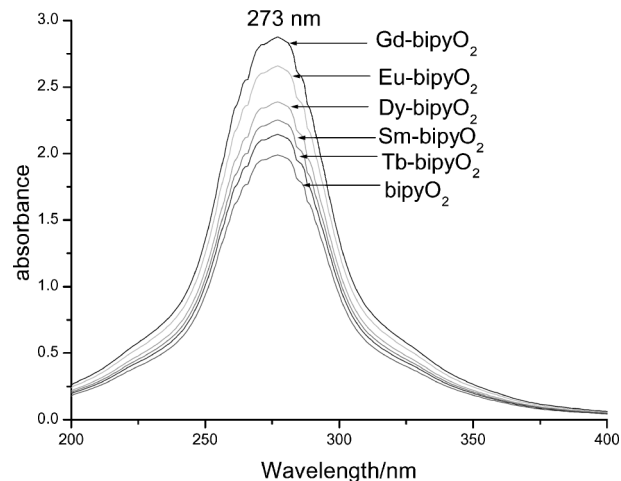


Fig. 1. Ultraviolet absorption spectra of bipyO₂ and Ln(bipyO₂)₂(NO₃)₃·2H₂O (Ln = Eu, Tb, Gd, Sm, Dy).

in the range of 200–400 nm except for a slight difference of absorption intensity, and the maximum absorption peaks are located at around 273 nm, which can be attributed to the characteristic absorption of bipyO₂ ligand. The results imply that the absorption depends mainly on the ligand and bipyO₂ is the energy donor and luminescence sensitizer of Ln³⁺ ion.

The excitation spectra of these lanthanide complexes show that they have no effective absorption in long wavelength ultraviolet region of the range 300–400 nm. The effective energy absorption mainly takes place in the narrow ultraviolet region of 200–280 nm. Fig. 2A gives the excitation spectra of Eu(bipyO₂)₂(NO₃)₃·2H₂O and Tb(bipyO₂)₂(NO₃)₃·2H₂O. The excitation bands for Eu(bipyO₂)₂(NO₃)₃·2H₂O under the red emission of 613 nm shows four main peaks, 222.5 nm, 242 nm, 259 nm, 271.5 nm. The excitation bands for Tb(bipyO₂)₂(NO₃)₃·2H₂O under the green emission of 543 nm possess four main peaks, 235.5 nm, 251.5 nm, 266 nm and 276.5 nm, respectively. And the excitation intensity of Tb complex is stronger than that of Eu one. Figure 2B gives the excitation spectra of Sm(bipyO₂)₂(NO₃)₃·2H₂O and Dy(bipyO₂)₂(NO₃)₃·2H₂O. The excitation bands for Sm(bipyO₂)₂(NO₃)₃·2H₂O under the orange emission of 596 nm show four main peaks, 222.5 nm, 242 nm, 256 nm, 271 nm. The excitation bands for Dy(bipyO₂)₂(NO₃)₃·2H₂O under the blue emission of 484 nm exhibit three main peaks, 222.5 nm, 242 nm and 259 nm respectively. The excitation intensity of Dy complex is stronger than that of the Sm complex. We further measured the corresponding emission spectra by selective excitation with the four different excitation wavelengths,

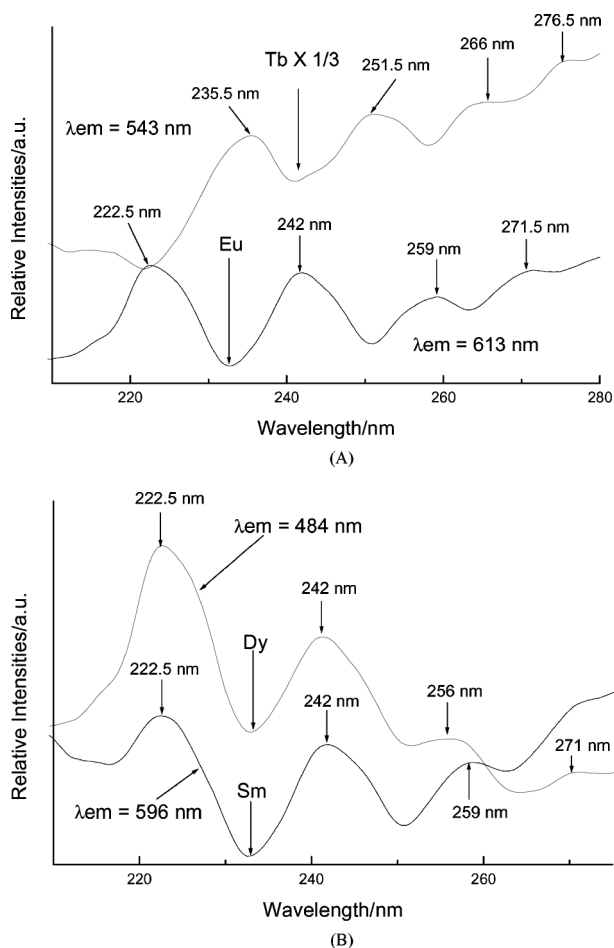


Fig. 2. Excitation spectra of $\text{Ln}(\text{bipyO}_2)_2(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$, (A): $\text{Ln} = \text{Eu}$, Tb ; (B): $\text{Ln} = \text{Sm}$, Dy .

they show the similar emission position except for different luminescent intensities. Figures 3–6 give the selected emission spectra of $\text{Eu}(\text{bipyO}_2)_2(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$, $\text{Tb}(\text{bipyO}_2)_2(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$, $\text{Sm}(\text{bipyO}_2)_2(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ and $\text{Dy}(\text{bipyO}_2)_2(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$, respectively. This indicates that the four excitation bands are all the effective energy sensitizer for the luminescence of Ln ions.

For $\text{Eu}(\text{bipyO}_2)_2(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ complex, the emission spectra show four emission peaks under the excitation of 259 nm: 581 nm, 591 nm, 613 nm, 650 nm and 700 nm, corresponded with the characteristic emission for the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ transitions ($J = 0, 1, 2, 3, 4$) of Eu^{3+} ion: where the term symbols refer to be atomic spectral term of lanthanide ions, among 5 is the spin multi which equal to be $2S + 1$ ($S = \text{spin quantum number}$), D represents the orbital quantum number, and J is the J (inner quantum number, $J = L \pm S$). Among the red luminescence intensity of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is the strongest. For $\text{Tb}(\text{bipyO}_2)_2(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ complex,

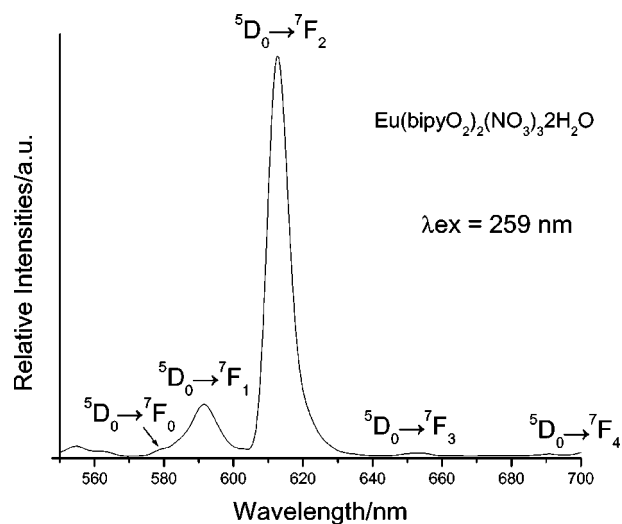


Fig. 3. Emission spectrum of $\text{Eu}(\text{bipyO}_2)_2(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$.

the emission spectra show four emission peaks under the excitation of 266 nm: 490 nm, 543 nm, 583 nm and 621 nm, attributed to be the characteristic emission for the $^5\text{D}_4 \rightarrow ^7\text{F}_J$ ($J = 6, 5, 4, 3$) transition of Tb^{3+} ion (atomic spectral term of Tb^{3+}). Among the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition exhibits the strongest green emission, and $^5\text{D}_4 \rightarrow ^7\text{F}_6$ transition shows the second strongest blue emission. For $\text{Sm}(\text{bipyO}_2)_2(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ complex, the emission spectra show four emission peaks under the excitation of 259 nm: 561 nm, 596 nm, 643 nm and 721 nm, attributed to be the characteristic emission for the $^4\text{G}_{5/2} \rightarrow ^6\text{H}_J$ ($J = 5/2, 7/2, 9/2, 11/2$) transition of Sm^{3+} ion (atomic spectral term of Sm^{3+}). For $\text{Dy}(\text{bipyO}_2)_2(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ complex, the

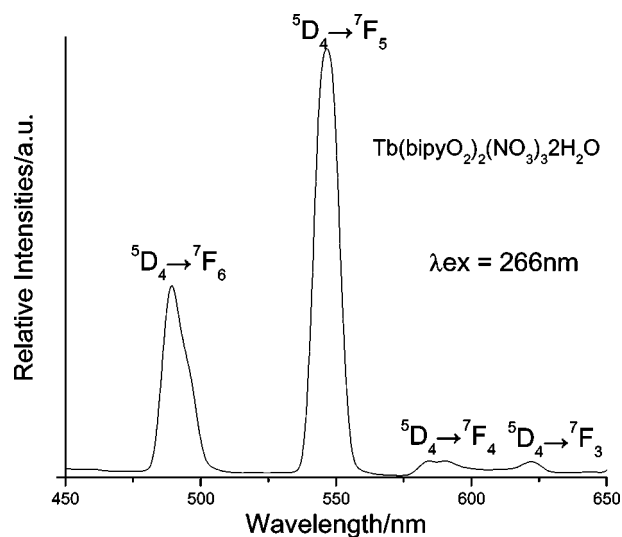


Fig. 4. Emission spectrum of $\text{Tb}(\text{bipyO}_2)_2(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$.

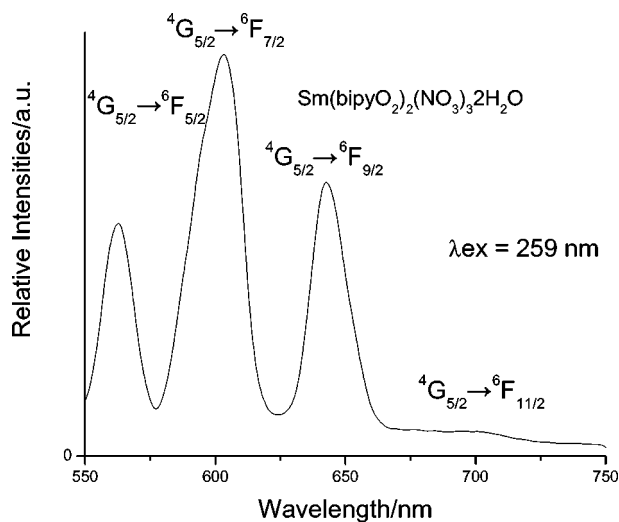


Fig. 5. Emission spectrum of $\text{Sm}(\text{bipyO}_2)_2(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$.

luminescence spectra show two apparent emission peaks under the excitation of 256 nm: one is at 483 nm, the other is at 574 nm, which corresponds to the characteristic emission for the ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_J$ ($J = 15/2, 13/2$) transition of Dy^{3+} ion, respectively (atomic spectral term of Dy^{3+}).

Comparing the luminescence intensities of these complex systems under the same maximum excitation, it can be found that terbium complex shows the strongest luminescence compared to those of other lanthanide systems, and the samarium complex shows the weakest emission. The europium and dysprosium complex systems show weaker luminescence than the terbium complex but stronger than the samarium complex. Gd^{3+} complex was

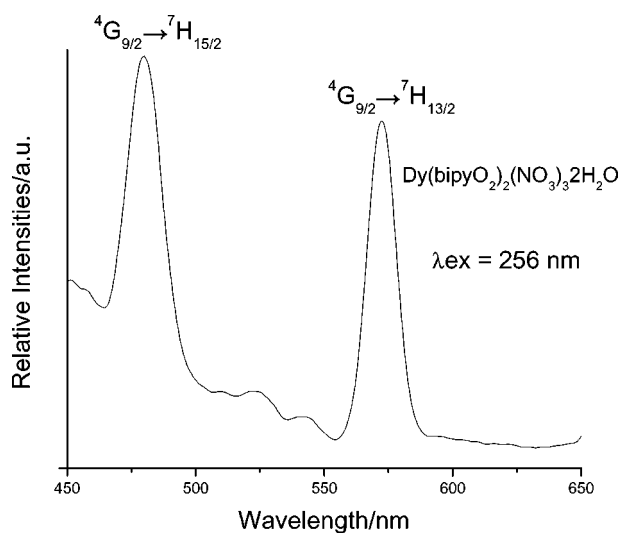


Fig. 6. Emission spectrum of $\text{Dy}(\text{bipyO}_2)_2(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$.

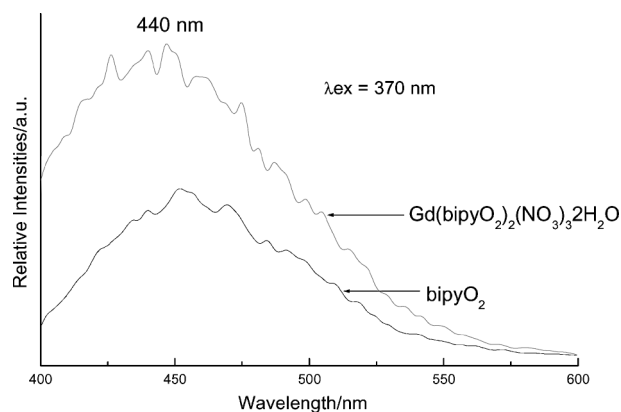


Fig. 7. Phosphorescence spectra of $\text{Gd}(\text{bipyO}_2)_2(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ and bipyO_2 ligand.

selected as model complex for the determination of the triplet state energies of the organic ligands owing to their high phosphorescence–fluorescence ratio compared to those of the other Ln^{3+} complexes and Gd^{3+} can sensitize the phosphorescence emission of ligands. The phosphorescence spectrum of the gadolinium complex with bipyO_2 and free bipyO_2 ligand were measured (as shown in Fig. 7) and the triplet state energy of bipyO_2 can be determined to be 22275 cm^{-1} based on the both maximum phosphorescence band of 440 nm and the phosphorescence emission of $\text{Gd}(\text{bipyO}_2)_2(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ is stronger than that of free bipyO_2 . The energy differences between the triplet state of bipyO_2 and the resonance energy level of Eu^{3+} (${}^5\text{D}_0$, 17265 cm^{-1}), Tb^{3+} (${}^5\text{D}_4$, 20500 cm^{-1}), Sm^{3+} (${}^4\text{G}_{5/2}$, 17900 cm^{-1}) and Dy^{3+} (${}^4\text{F}_{9/2}$, 21000 cm^{-1}) can be calculated to be 5010 cm^{-1} , 1775 cm^{-1} , 4375 cm^{-1} , and 1275 cm^{-1} , respectively. From these energy differences, it can be seen that bipyO_2 can sensitize the four lanthanide ions effectively. According to the intramolecular energy mechanism [20–22], the intramolecular energy transfer efficiency depends chiefly on two energy transfer processes: the first one leads from the triplet level of ligands to the emissive energy level of the Ln^{3+} ion by Dexter's resonant exchange interaction; the second one is just an inverse energy transfer by a thermal deactivation mechanism. Both energy transfer rate constants depend on the energy differences between the triplet level of the ligands and the resonant emissive energy of Ln^{3+} . Intramolecular energy transfer efficiency in lanthanide complexes conforms to Dexter's exchange energy transfer theory:

$$K_{\text{ET}} = (2\pi Z^2/R) \exp(-2rl) \int F_{\text{d}}(E)F_{\text{a}}(E) dE \quad (1)$$

K_{ET} is the rate constant of energy transfer, r is the intermolecular distance between the energy donor and acceptor atoms, l is the van der Waals radius, the integral

represents the overlap between the luminescence spectrum of the ligands and the absorption spectrum of Ln^{3+} ($F_d(E)$: the luminescence spectrum of energy donor (ligand), $F_a(E)$: absorption spectrum of energy acceptor (Ln^{3+}), and $2\pi Z^2/R$ is a constant relating to the mutual distance between Ln^{3+} and coordinated atom. r and l are both considered to be constant for intramolecular energy transfer processes.

From Eq. (1), K_{ET} increases with decreasing energy difference $\Delta E(\text{Tr-Ln}^{3+})$ between the triplet state energy of ligands and the resonance emission energy of Eu^{3+} and Tb^{3+} . Thus, ligands with a large energy difference can not sensitize rare earth ions effectively. On the other hand, there exists an inverse energy transfer process which affects luminescence intensity by temperature ($k(T)$: rate constant of inverse energy transfer process (thermal deactivation process), A : preexponential factor):

$$K(T) = A \exp(-\Delta E(\text{Tr-Ln}^{3+})/RT) \quad (2)$$

It can be seen that the activation energy is approximately equal to $\Delta E(\text{Tr-Ln}^{3+})$ in the inverse energy transfer process; therefore, a decreasing energy difference increases $k(T)$. Based on this evidence, the conclusion can be drawn that $\Delta E(\text{Tr-Ln}^{3+})$ is of opposite influence on the two energy transfer processes and an optimal value can be assumed to exist. So it can be predicted that the triplet state energy of bipyO₂ is more suitable for the luminescence of terbium ion than europium and dysprosium ions. Besides this, there exist a lot of internal energy levels (${}^6\text{F}_{11/2}$, ${}^6\text{F}_{9/2}$, ..., ${}^6\text{H}_{11/2}$ etc) between the first excited state ${}^4\text{G}_{5/2}$ and ground state ${}^6\text{H}_{9/2}$ of Sm^{3+} , causing readily some nonradiative energy transfer process to lose the excited energy, resulting the weakest luminescence of Sm^{3+} complex.

CONCLUSIONS

Five lanthanide (Eu, Tb, Sm, Dy, Gd) complexes with 2, 2'-bipyridine-*N*, *N'*-dioxide (bipyO₂) have been synthesized and characterized. The photophysical properties of them have been studied with ultraviolet spectra, excitation and emission spectra. The triplet state energy of bipyO₂ is determined to be 22725 cm⁻¹ with the phosphorescence spectrum of the gadolinium complex at about 440 nm. The energy transfer between bipyO₂ and lanthanide ions (Eu^{3+} , Tb^{3+} , Sm^{3+} , Dy^{3+}) has been studied to predict that the optimum energy transfer exists between the ligand and Tb^{3+} . The excitation and emission spectra for the four complexes were discussed in detail and the results indicate that terbium complex show the strongest luminescence. So the photophysical properties of lumines-

cent lanthanide complexes can be studied with all kinds of spectroscopy, especially luminescence spectroscopy.

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