

The UV-visible, Infrared Spectra and Luminescence Analysis of Lanthanum(III) and Neodymium(III)- (Diphenylamino)₃-(2,2- Bipyridyl) Complexes

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Abstract

Nowadays, the study of the lanthanide complexes has drawn the attention of researcher due to its importance in the chemistry applications. These complexes have been used extensively in semiconductor, solar cell, OLED emitter, electro-phosphorescence, and bio-imaging applications. A series of lanthanides complexes were synthesized by “*in situ*” reaction method. Herein, we proposed a study of the synthesis of lanthanide(III) complexes containing ligands with N-donor atoms. The structure of complexes [Ln(III)(diphenylamine)₃(2,2 bipyridyl)] (Ln= Lanthanum(III), Neodymium(III)) was confirmed by UV-visible and FT-IR spectroscopic approaches. The luminescence properties of the complexes were measured by Nd: YAG laser. The UV-visible spectrum of the complexes revealed an effect of La(III) and Nd(III) ions towards the absorption bands of the electronic spectrum. Based on the UV-vis and FT-IR analysis, we concluded that the central lanthanide ion was coordinated to N-donor atoms from both of the diphenylamine and bipyridyl ligands.

Keywords: Luminescence, Lanthanide, Diphenylamine, 2.2-Bipyridyl.

INTRODUCTION

Recently, massive efforts have been shown in the synthesis of lanthanide complexes for various applications. They have been used for catalysis, analytical determination, pharmaceuticals ingredients and photoluminescence materials [1,2,3]. Several studies about spectral characterization and luminescence properties of lanthanide complexes have been reported [3,4,5,6]. Generally, the structure of the lanthanide complexes is determined by single crystal X-ray [3,4,7,8]. Unfortunately,

not all the lanthanide complexes are obtained in the form of crystals. Therefore, the spectroscopic analysis is important.

Previously, we reported the spectroscopic information of La(III) and Nd(III) complexes with 2,9 dimethyl-1.10 phenanthroline and piperidine dithiocarbamate ligands [6]. Accordingly, from the infrared spectral, we found that dithiocarbamate served as bidentate ligand and electronic transition complexes at 307 and 329 nm, respectively. The use of different lanthanide ions in the synthesis of such complexes may result in different electronic transition. In this current study, we extended our research on La(III) and Nd(III) with 2,2 bipyridyl and diphenylamine by simple mixture reaction. Here the first report about the spectroscopic and luminescence information of La(III) and Nd(III) with bipyridyl and diphenylamine.

EXPERIMENTAL

Both of the complexes [La(diphenylamine)₃-(Bipy)] and [Nd(diphenylamine)₃-(Bipy)] were prepared using a procedure as shown Figure 1. A solution of lanthanide(III) chloride (2 mmol) in ethanol (10 mL) was added to a solution of 2,2 bipyridyl (2 mmol) in ethanol (10 mL). The white solution was slowly added with diphenylamine (6 mmol) in ethanol (20 mL). The reaction was facilitated by stirring the mixture for 2 hours, while the products were obtained by a precipitation step. The powder was collected by filtration and was dried by allowing ambient air flow at room temperature. The spectroscopic properties of the complexes were characterized using UV-vis, FT-IR and Photoluminescence techniques. The electronic absorption spectra of the complexes were recorded on a JASCO, Japan (V-570) double beam spectrophotometer. Luminescence measurement was conducted using Nd: YAG Laser at power of 0.2 mJ.

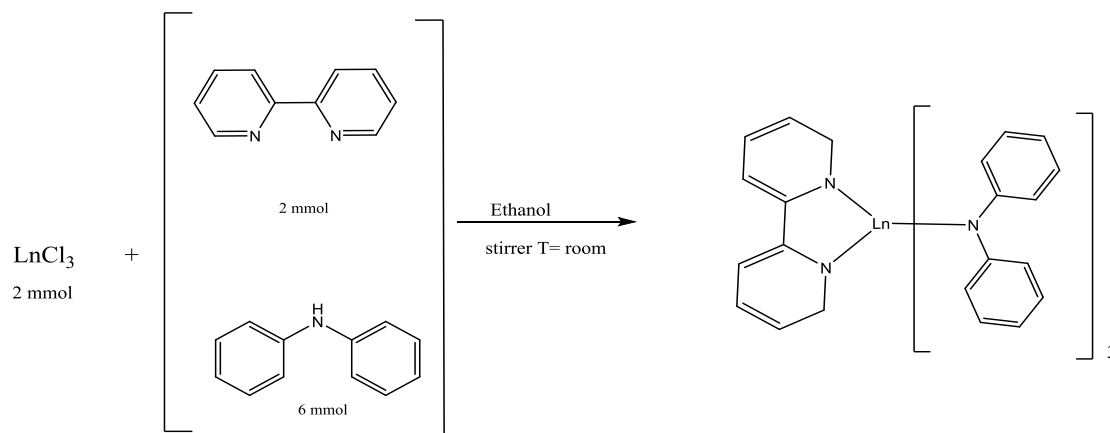


Figure 1. Preparation of the $[\text{La}(\text{diphenylamine})_3(\text{Bipy})]$ complexes, where $\text{Ln} = \text{La}(\text{III})$ and $\text{Nd}(\text{III})$.

RESULTS AND DISCUSSION

The electronic and infra red spectra of $[\text{La}(\text{diphenylamine})_3(\text{Bipy})]$ and $[\text{Nd}(\text{diphenylamine})_3(\text{Bipy})]$ were determined. The spectra of the lanthanide complexes would show their electronic. The electronic absorption spectra of $[\text{La}(\text{diphenylamine})_3(\text{Bipy})]$ and $[\text{Nd}(\text{diphenylamine})_3(\text{Bipy})]$ were shown in figure 2(a) and 2(b), respectively. The electronic absorption of ligands was characterized by two absorption bands. The strong absorption bands in the UV range of 305-322 nm were assigned to the $\pi \rightarrow \pi^*$ intra-ligand transition of the aromatic bipyridyl and diphenylamine.

A specific pattern is shown by the $[\text{La}(\text{diphenylamine})_3(\text{Bipy})]$ and $[\text{Nd}(\text{diphenylamine})_3(\text{Bipy})]$ complexes. Broad but weak

intensity absorption bands were detected on the visible region (inset in Fig. 2a) at 414 and 442 nm. They can be associated with charge transfer (CT) transition of the type $\text{L} \rightarrow \text{M}$ and $\text{M} \rightarrow \text{L}$ between $\text{La}(\text{III})$ and the ligands. Meanwhile, other weak bands that appeared in 502 and 580 nm showed the d-d transitions of $\text{La}(\text{III})$ ($2B_{1g} \rightarrow 2E_g$). On the other hand, the bands observed for the $\text{Nd}(\text{III})$ complex (inset in Fig. 2b) corresponded to the f-f transition from the ground state $^4I_{7/2}$ to the excited states of $^4G_{7/2}$, $^2G_{7/2}$ and $^4G_{5/2}$. The electronic spectrum of the complexes showed a general red-shift which can be associated with covalent bonding. The UV-vis spectroscopic parameters showed that the covalent character occurred between hard lanthanide(III) ion and the soft ligands.

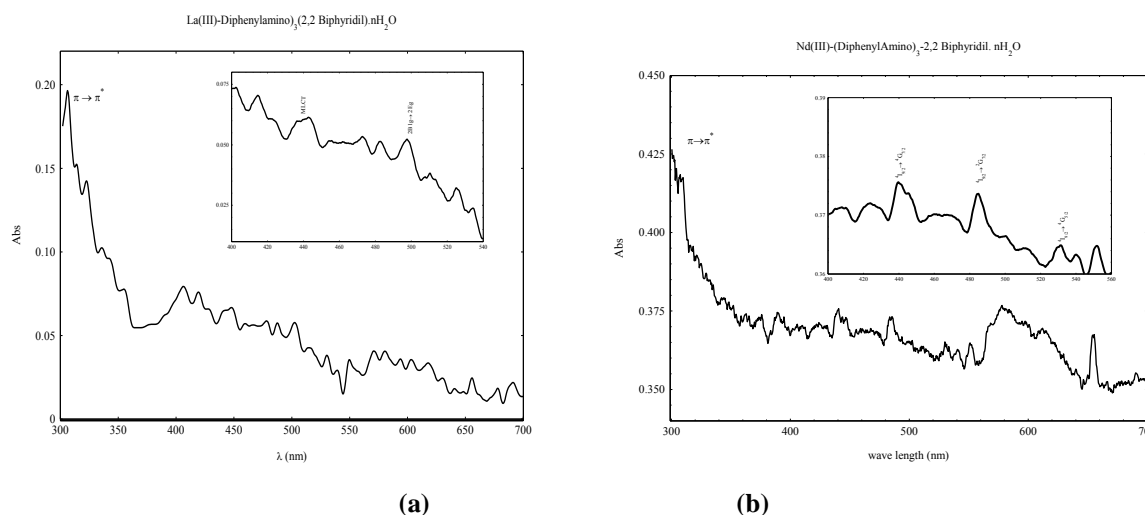


Figure 2. (a) Electronic absorption spectrum of $[\text{La}(\text{diphenylamine})_3(\text{Bipy})]$. The inset shows the d-d transition of $\text{La}(\text{III})$; (b) Electronic absorption spectrum of $[\text{Nd}(\text{diphenylamine})_3(\text{Bipy})]$. The inset shows f-f transition of $\text{Nd}(\text{III})$.

Figures 3(a) and 3(b) show the FTIR spectra for $\text{La}(\text{III})$ and $\text{Nd}(\text{III})$ complexes with both of diphenylamine and bipyridyl, respectively.

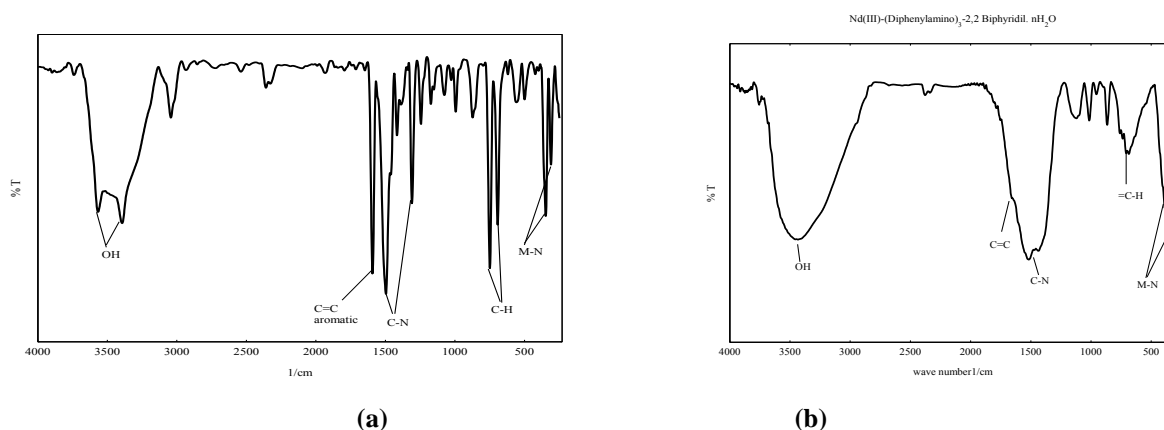


Figure 3. FT-IR spectrum of (a) [La(diphenylamine)₃(Bipy)] and (b) FT-IR spectrum of [Nd(diphenylamine)₃(Bipy)]

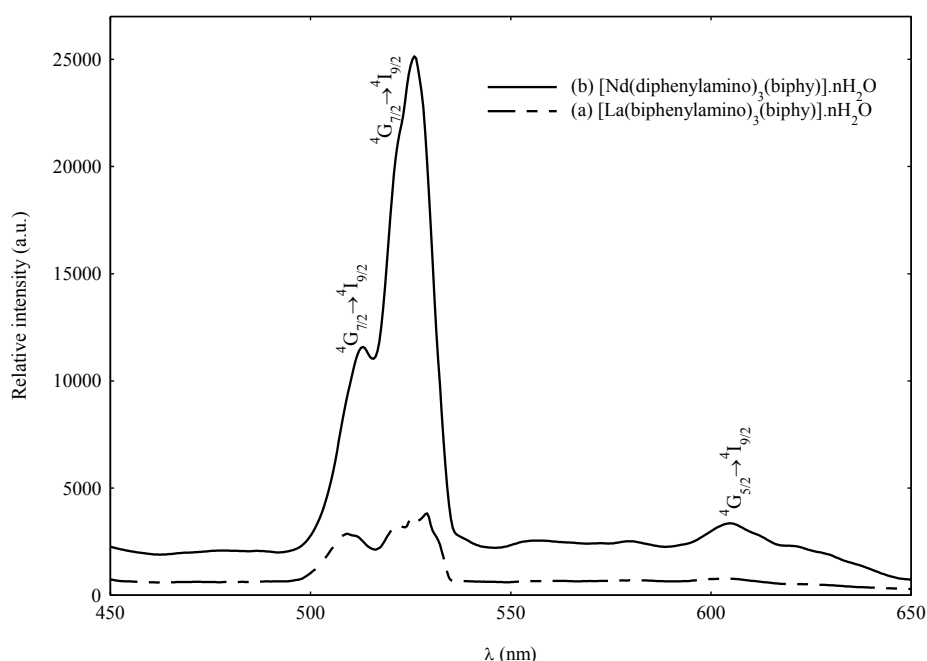


Figure 4. Emission spectra for complex (a) [La(diphenylamine)₃(Bipy)] and (b) [Nd(diphenylamine)₃(Bipy)] in the solid state at room temperature.

The infrared spectra of [La(diphenylamine)₃-(Bipy)] and [Nd(diphenylamine)₃-(Bipy)] complexes are similar. Both appeared as a single peak at 347 cm⁻¹ and 349 cm⁻¹ indicating the presence of a coordination of the nitrogenous ligands with lanthanide ions. The other important infrared peaks from both complexes are observed in the range between 1450 cm⁻¹ and 1550 cm⁻¹ which correspond to the aromatic ligands. The ν(C-N) modes appeared at 1494 cm⁻¹ and 1426 cm⁻¹ for the [La(diphenylamine)₃-(Bipy)] and [Nd(diphenylamine)₃-(Bipy)] complexes, respectively. The FTIR spectra of the complexes also shows C=C bond as can be observed at 1593 cm⁻¹ and 1531 cm⁻¹. Furthermore, there was a characteristic absorption of the hydroxyl group appeared at around 3500 cm⁻¹, indicating that the complexes contain water molecules.

The luminescence spectra of [La(diphenylamine)₃-(Bipy)] and [Nd(diphenylamine)₃-(Bipy)] complexes were investigated and the spectra are shown in Figure 4. The emission spectra of [La(diphenylamine)₃-(Bipy)] and [Nd(diphenylamine)₃-(Bipy)] complexes were measured in the solid state at room temperature. The maximum emission of both complexes are different. For complex [Nd(diphenylamine)₃(Bipy)], the emission spectra were recorded by 355 nm excitation which showed three peaks. Intense broadband emission at 513 and 526 nm were mainly from the ⁴G_{7/2} → ⁴I_{9/2} transition. It showed a dramatic change after coordination. The increasing of the luminescence could be attributed to the coordination of the ligand to the metal center. The luminous mechanism of complexes might be intra-ligand fluorescent emission (π → π*). The weak emission peak corresponding to the intra-configurational f-f transitions from the ground state of Nd(III)

is also observed at 625 nm corresponds to as a result of ${}^4G_{5/2} \rightarrow {}^4I_{9/2}$ transition. This observation was the close proximity of these three excited state to each other so that the electrons from the excitation state occurred too rapidly relaxed to the ${}^4G_{5/2}$ level [9]. For complex [La(diphenylamine)₃(Bipy)], the maximum emission was very weak compared with complex [Nd(diphenylamine)₃(Bipy)]. It can be concluded that La(III) complex with diphenylamine and bipyridyl ligands was not an excellent complex source for photoluminescence, because of the luminescence result from the aromatic ligand.

CONCLUSION

We have successfully constructed two complex compounds of [La(diphenylamine)₃(Bipy)] and [Nd(diphenylamine)₃(Bipy)] through a simple mixture reaction method. The nitrogenous ligands coordinate with lanthanide ions in bidentate and monodentate. The complexes showed intense emission in the solid state at room temperature. Comparing with the complex [Nd(diphenylamine)₃(Bipy)], the excitation and emission peaks of [La(diphenylamine)₃(Bipy)] exhibited less excellent complex as the source for photoluminescence materials.

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