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Characterization of Acetylacetonato-bis-(2-(4-amino-2-hydroxyphenyl)benzthiazole) Complex

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Organic luminescent materials have received great attentions due to their potential application subjects onto full color image displays such as mobile phones, PDA and etc. In the present work, we synthesized new electroluminescence material such as acetylacetonato-bis-[2-(4-amino-2-hydroxyphenyl)benzthiazole] aluminum complex fluorescent dye. The spectroscopic characteristics and the fluorescent properties of this dye molecule were characterized by UV-Vis absorption and PL spectra. In addition, the synthesized dye moiety was discussed using the theoretical molecular calculation technique in terms of the molecular interatomic distance and HOMO/LUMO levels.

Keywords: aluminum complex; benzthiazole; fluorescent; organic luminescent material; PL spectra

INTRODUCTION

Recently, organic luminescent materials have received great attentions due to their attractive characteristics and potential application areas [1–4]. Since the first reported organic light-emitting device using tris-(8-hydroxyquinoline) aluminum (Alq_3) was introduced, many efforts have been focused on the syntheses of new organic materials and have achieved great performance on EL device [5]. For the emitting material, the dye metal complex is one of the most

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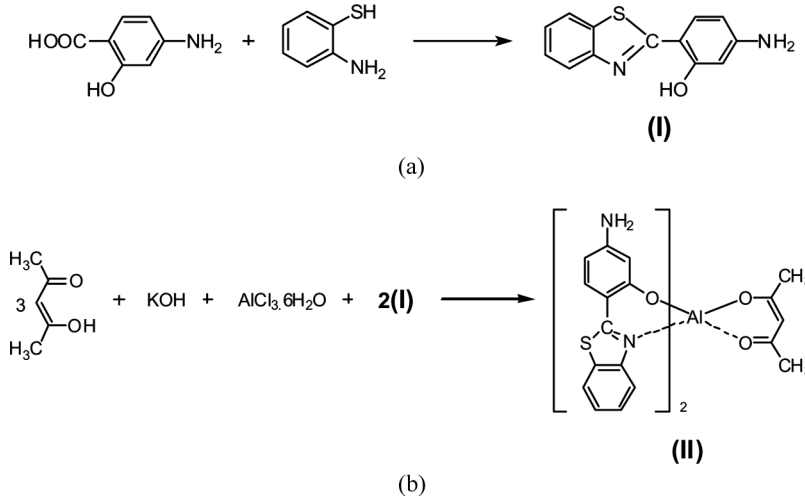
widely used subject in the light-emitting diode due to the properties of high fluorescence, thermal stability and excellent electron-transporting mobility [6–8].

In this context, we have synthesized new luminescence metal complex such as acetylacetonato-bis-[2-(4-amino-2-hydroxyphenyl)-benzthiazole] aluminum complex fluorescent dye. Using DMol^3 program, the energy level, atomic distance and absorption spectra expectation were calculated and compared with the synthesized moiety. The spectroscopic characteristics and the fluorescent properties of this dye molecule were examined and determined.

EXPERIMENTAL

Synthesis

As presented in Scheme 1(a), *p*-aminosalicylic acid (0.998 g, 6.52 mmol) and *o*-aminothiophenol (0.816 g, 6.52 mmol) added in 20 g of polyphosphoric acid was heated at 200°C with constant stirring. After 3 h, the reaction was quenched into the ice water and being stirred for 24 h. The formed precipitate solution was adjusted to the neutral pH condition using 1% sodium carbonate solution. After 3 h, the mixture was filtrated with distilled water at several times and dried in oven at 40°C. Yield 38.84% (0.614 g); calculated for $C_{13}H_{10}N_2OS$: C, 64.44; H, 4.16; N, 11.56; S, 13.23. Found: C, 64.54; H, 4.03; N, 11.52; S, 12.62.



SCHEME 1 Synthetic route of metal complex.

Synthesis of acetylacetonato-bis-[2-(4-amino-2-hydroxyphenyl) benzthiazole] aluminum complex was shown in Scheme 1(b). $A1C1_3{\cdot}6H_2O$ (0.8 g, 3.3 mmol) dissolved in 2.5 ml water was added into acetyl acetone (1 g, 9.9 mmol) and solution of potassium hydroxide (0.56 g, 9.9 mmol) in 5 ml water. Into the formed solution, 2-(4-amino-2-hydroxyphenyl) benzthiazole (I) (1.6 g, 6.6 mmol) in 75 ml benzene was dropped. The mixture was heated at reflux with constant stirring. After 2 h, the reaction was cooled to room temperature and the mixture was filtrated with benzene at several times and dried in vacuum. Yield 20.78% (0.417 g); calculated for $C_{31}H_{25}AlN_4O_4S_2$: C, 61.17; H, 4.14; N, 9.20; S, 10.54. Found: C, 58.11; H, 3.87; N, 10.19; S, 11.65.

Measurements

PL spectra were recorded with Shimadzu RF-5301 Spectrofluorophotometer. Elemental analyses were recorded with a Carlo Elba Model 1106 analyzer. Themogravimetric analysis (TGA) was conducted using TGA-2050 under nitrogen gas at a heating 20°C/min.

RESULTS AND DISCUSSION

The UV-Vis absorption and PL spectra of dye (I) and its aluminum complex dye (II) in chloroform are shown in Figures 1 and 2, respectively.

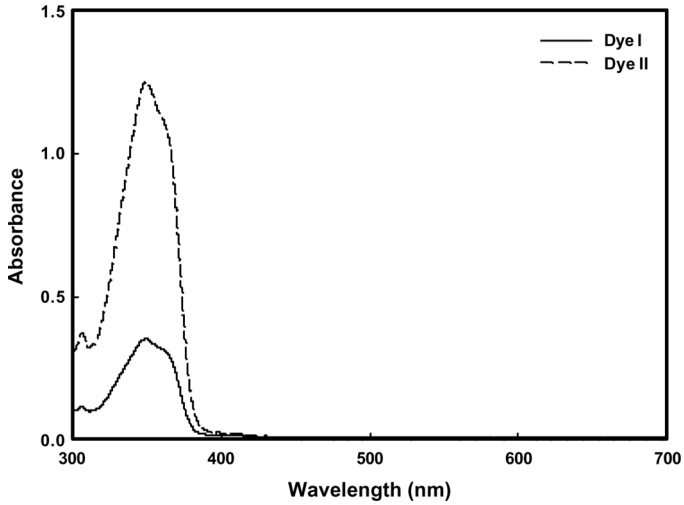


FIGURE 1 UV-Vis absorption spectra of dye (I) and its aluminum complex dye (II).

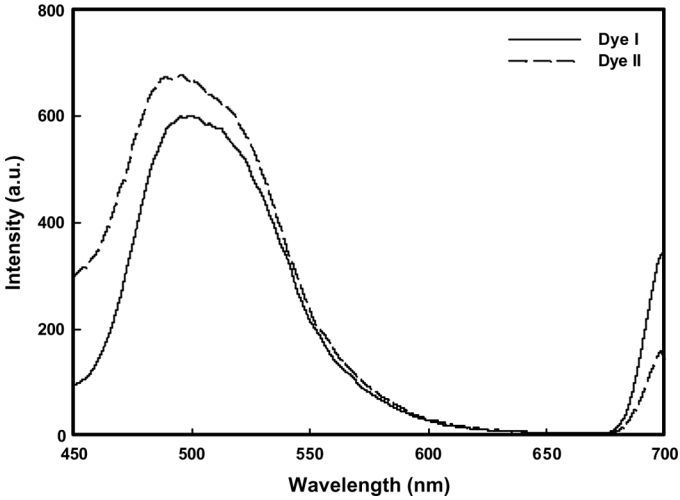


FIGURE 2 PL spectra of dye (I) and its aluminum complex dye (II).

The UV-Vis absorption peaks of dye (I) and dye (II) were obtained at 350 nm. The emission spectra of dye (I) and its aluminum complex dye (II) were observed at 500 nm and 495 nm. For the metal complex dye molecule, it is proposed that the effect of the metal ion within the dye structure is to increase conformational rigidity and decrease the π-π^* energy gap [9].

Furthermore, the molecular structural calculation and absorption spectral expectation were investigated using modeling calculation software. All the theoretical calculations were performed by Dmol^3 program in the Materials Studio 4.2 package [10,11] which was the quantum mechanical code using density functional theory and was then used for spectroscopic calculations. Perdew-Burke-Ernzerhof (PBE) function of generalized gradient approximation (GGA) level [12] with double numeric polarization basis set [10] was used to calculate the energy level of the frontier molecular orbital. The optimized molecular structure is shown in Figure 3. The molecular interatomic distances between Al and the thiazole N are 1.93 and 4.19 Å, while the distance between central Al and carbonyl O in acetylacetonate is 4.23 Å. The HOMO and LUMO levels of the dye are -4.351 and -2.815 eV, respectively. In addition, the calculated absorption wavelengths are collected in Figure 4. The calculated first transition absorption (λ_{max}:360 nm) is relatively compatible with observed absorption spectra from the finding of Figure 1. In this context, it is proposed that this theoretical calculation approach could be beneficial

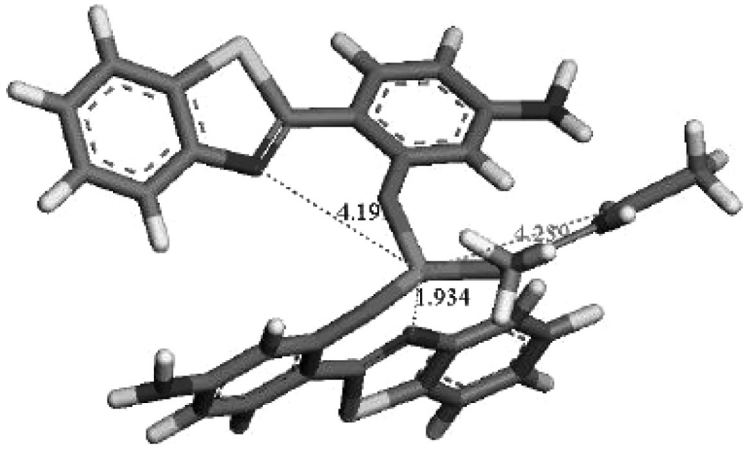


FIGURE 3 Optimized molecular conformation using DMol^3 modeling calculation.

to expect the spectral properties of the other designed organic luminescent compounds.

Thermal stability of the synthesized dye (II) was evaluated by TGA with the initial degradation temperature. The initial degradation behavior of the synthesized dye in the range of 50–700°C is shown in Figure 5. From the result, it is proposed that the degradation temperature was observed at 210–300°C with 70% of corresponding weight loss and that this aluminum complex dye (II) was stable at the temperature range of 210°C.

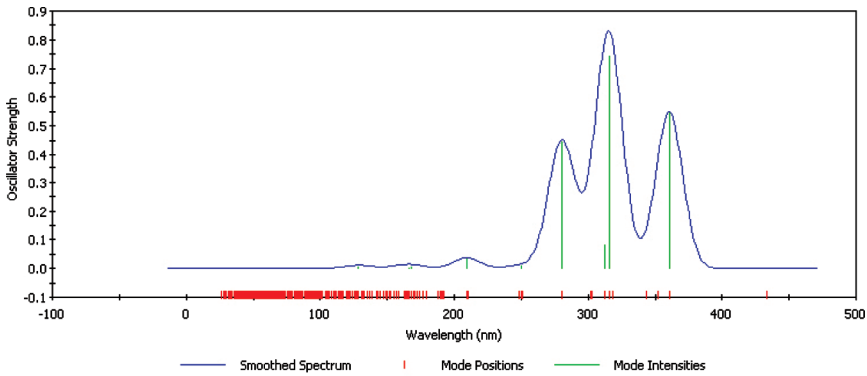


FIGURE 4 Calculated first transition absorption spectrum.

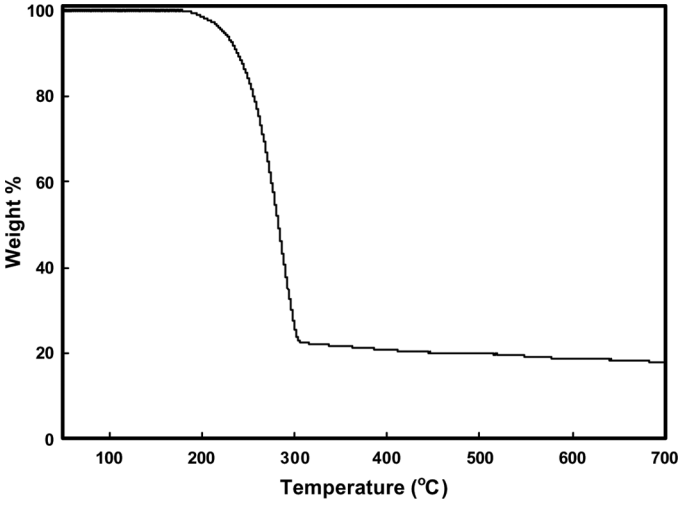


FIGURE 5 Thermal analysis for the dye (II) by TGA.

CONCLUSIONS

In this study, we have synthesized electroluminescence material, namely acetylacetonato-bis-[2-(4-amino-2-hydroxyphenyl) benzthiazole] aluminum complex fluorescent dye and have observed its PL spectra. The emission spectra of dye (I) and its aluminum complex dye (II) were obtained at 500 nm and 495 nm. Aluminum complex dye (II) compared with dye (I) showed strong fluorescence intensity. Satisfactory thermal stability of acetylacetonato-bis-[2-(4-amino-2-hydroxyphenyl) benzthiazole] aluminum complex dye was determined by TGA analysis.

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