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〈단신〉

Diheteryl-substituted triphenylamine 화합물의 합성과 형광 특성

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Synthesis and Photoluminescent Property of Diheteryl-substituted Triphenylamine Compound

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Abstract— FTriphenylamine dye compound having diheteryl moiety was synthesized and its photoluminescent property was investigated. Organic luminescent materials have received great attentions due to potential application subjects onto full color image displays. In this context, the dye (III) for light emitting materials was synthesized using 2-(4-amino-2-hydroxyphenyl)benzoxazole (I) and 4,4′-diformyltriphenylamine (II). It is well known that the amino groups of compound (I) react with carbonyl groups, especially an aldehyde, to afford azomethine linkages. The dye shows bulish-green fluorescence property, which is anticipated for the light-emitting material for display devices. In this context, our aim is to synthesize diheteryl-substituted triphenylamine fluorescent dye as an emitting material. The spectroscopic characteristics and the fluorescent properties of this dye molecule were examined and determined.

Keywords: *organic luminescent materials, benzoxazole, triphenylamine, photoluminescence, PL*

1. Introduction

Organic luminescent materials have recently attracted great attentions due to their attractive characteristics and potential application subjects onto electronic display industry[1-6]. The distinctive properties of organic luminescent materials are that they use organic fluorescent or phosphorescent dyes as an emitting materials. Comparing to the other display technologies, organic light emitting diodes have attracted great attentions due to their only advantageous such as low driven voltage, wide viewing angle, high brightness and ultra-thin[7]. Since the initial reported of the light emitting materials using of tri-(8-hydroxyquinoline) aluminum, many research efforts have been focused on the development of new organic materials with high efficiency and stability[8-11].

In this work, we have synthesized diheteryl-substituted triphenylamine fluorescent dye as an emitting material. The spectroscopic characteristics and the fluorescent properties of this dye molecule were examined and determined. The UV-Vis absorption and PL spectra were recorded with Agilent 8453 spectrophotometer and Shimadzu RF-5301 Spectrofluorophotometer, respectively.

Elemental analyses were recorded with a Carlo Elba Model 1106 analyzer.

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As presented in Fig. 1 (a), *p*-aminosalicylic acid (0.998 g, 6.52 mmol) and *o*-aminophenol (0.711 g, 6.52 mmol) added in 20 g of polyphosphoric acid was heated at 200 ℃ with constant stirring. After 3h, the reaction was quenched into the ice water and being stirred for 24h. The formed precipitate solution was adjusted to the neutral pH condition using 1 % sodium carbonate solution. After 3h, the mixture was filtrated with distilled water at several times and dried in oven at 40 ℃. Yield: 23.03 % (0.340 g); calculated for $C_{13}H_{10}N_2O_2$: C, 69.02; H, 4.46; N, 12.38: found; C, 69.16; H, 4.16; N, 12.81.

Synthesis of diheteryl-substituted triphenylamine compound was shown in Fig. 1 (b).

4,4′-diformyltriphenylamine (0.03 g, 0.1 mmol) and 2-(4-amino-2-hydroxyphenyl)benzoxazole (0.0453 g, 0.2 mmol) were mixed and stirred in 5 ml of benzene. 5~6 drops of piperidine was added dropwise during the reaction. Reflux was continued for 2 days. The reaction was cooled to room temperature and the mixture was filtrated with benzene at several times and dried in vacuum.[12] Yield 38.6 % (0.028 g); calculated for $C_{46}H_{31}N_5O_4$: C, 76.97 H, 4.35 N, 9.76. Found: C, 75.02 H, 5.69 N, 10.30.

In this work, *p*-aminosalicylic acid and *o*-aminophenol were used to produce the 2-(4-amino-2-hydroxyphenyl)benzoxazole dye intermediate.

After this reaction, the prepared 2-(4-amino-2-hydroxyphenyl)benzoxazole dye (I) reacted with dialdehyde to produce the dye(III).

It is well known that the active amine groups can readily react with carbonyl groups, especially an aldehyde, to afford azomethine linkages. The absorption and fluorescence spectra of dye (I) and diheteryl-substituted triphenylamine compound dye (III) in chloroform are shown in Fig. 2 and Fig. 3, respectively. The absorption peaks of dye (I) and dye (III) were obtained at 330 nm and 346 nm, respectively. The fluorescence spectra of dye (I) and dye (III) observed at 465 nm and 490 nm, respectively. For the π-conjugated dye molecule, it is proposed that the greater the conjugation within dye structure is, the less the emission energy is, and the maximum emission shows a red shift[13]. In comparison with dye (I), dye (III) has more conjugation system within the dye structure which leads to shift the maximum emission. The dyes show blue and bluish-green fluorescence property, respectively (Fig. 4).

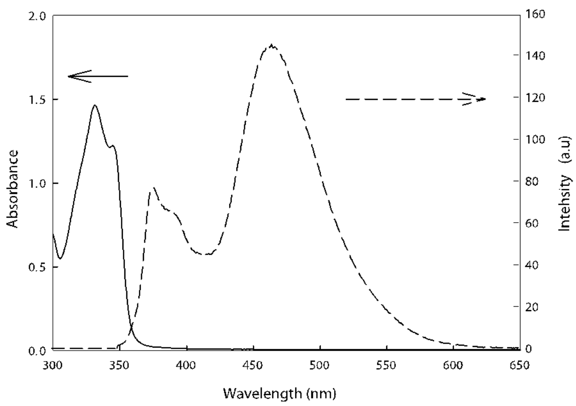

Fig. 2. The absorption and fluorescence spectra of dye (I).

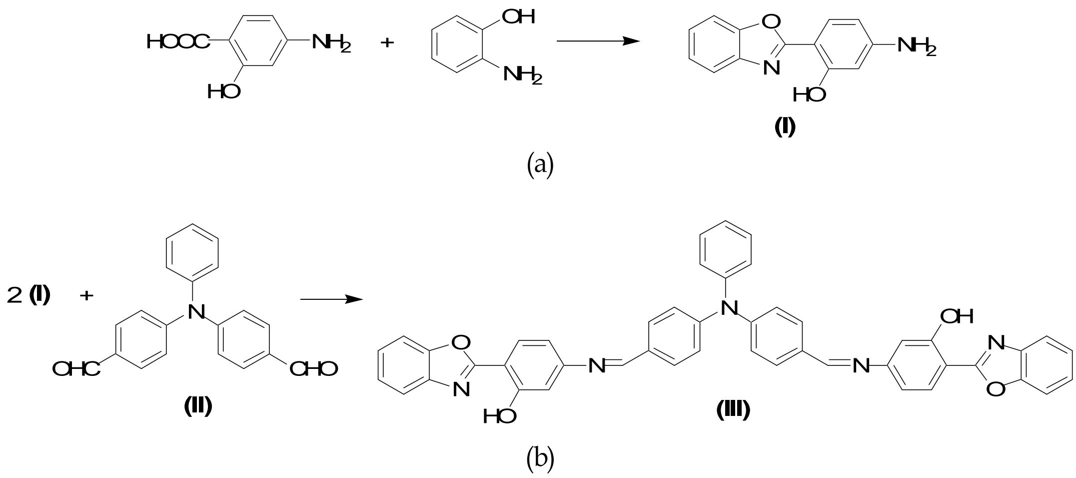

Fig. 1. Synthetic scheme of the dyes.

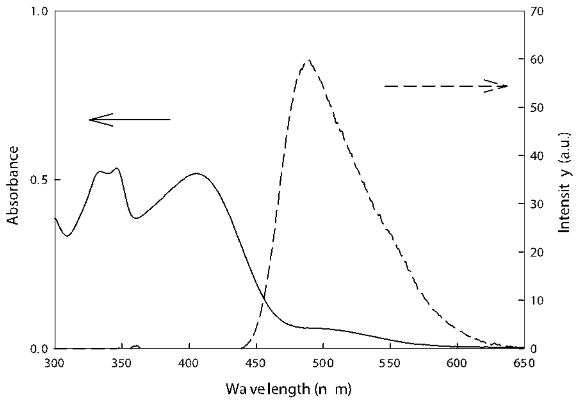

Fig. 3. The absorption and fluorescence spectra of dye (III).

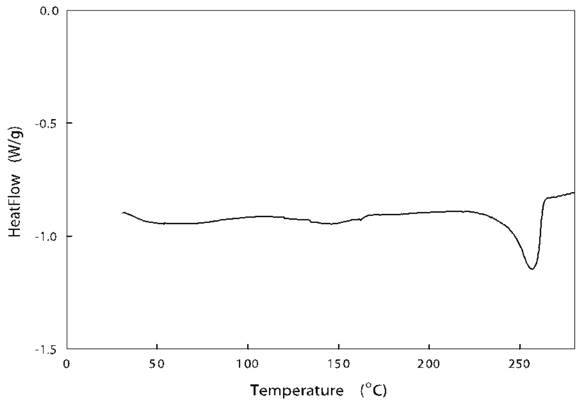

Fig. 5. Thermal analysis for the dye (III) by DSC.

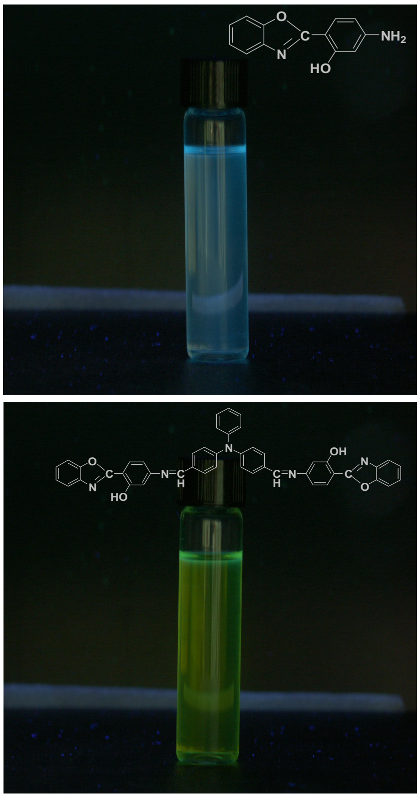

Fig. 4. Fluorescence images of dyes.

In addition, the critical factor for the optoelectronic application is thermal stability function of organic luminescence materials. Thermal stability of the synthesized dye (III) was evaluated by means of differential scanning calorimetry (DSC) in the temperature range of 30~280°C with temperature-raising rate 5°C. Form the DSC result, the synthesized dye (III) was good thermal stability at the temperature near 250°C which is fairly acceptable for the display end uses (Fig. 5).

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