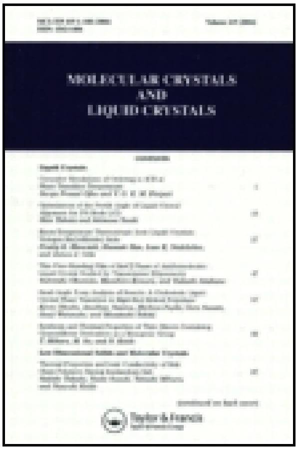

Molecular Crystals and Liquid Crystals

Characterization of New Benz-X-Azole Dye Derivatives and Metal Complexes

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Version of record first published: 22 Jul 2010

To cite this article: Young-A Son, Byung-Soon Kim, Myung-Sik Choi & Sung-Hoon Kim (2009): Characterization of New Benz-X-Azole Dye Derivatives and Metal Complexes, Molecular Crystals and Liquid Crystals, 498:1, 158-164

To link to this article: http://dx.doi.org/10.1080/15421400802615527

Mol. Cryst. Liq. Cryst., Vol. 498, pp. 158–164, 2009
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802615527

Characterization of New Benz-X-Azole Dye Derivatives and Metal Complexes

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*Novel luminescence dyes having benzoxazole **3** and benzthiazole **4** moieties were synthesized and characterized. Zinc (II) complex dyes **5** and **6** were consecutively prepared and their corresponding light emitting properties were also studied with respect to the photoluminescence (PL) functions of the dyes **3** and **4**. The strong light emitting properties and their resulting PL spectra were observed from the dyes **3** and **5**, namely dyes having benzoxazole moieties. To expect the molecular conformation, theoretical modeling calculation were performed to determine the molecular interatomic distance and dihedral angle due to the limitation of single crystal formation from polymeric dye molecules.*

Keywords: conjugated polymer; dopant/matrix system; energy transfer; Horner-Emmons condensation; light-emitting diode

INTRODUCTION

A comprehensive number of researches have been carried out to develop the potential areas of organic photo and electroluminescence (PL, EL) during the last decade. Especially, organic fluorescent or phosphorescent dyes have been used as emitting materials. Thus, these dyes can provide various emission colors in accordance with a wide selection of fluorescent dyes [1–4]. Generally, organic photoluminescence (PL)

This research was supported by the Program for the Training of Graduate Students in Regional Innovation which was conducted by the Ministry of Commerce Industry and Energy of the Korean Government.

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and electroluminescence (EL) can be expressed as the emission of light by organic molecules when they are exposed to photo irradiation and electric field [1,5]. These potential organic light emitting materials have been considered with wide application areas such as data transfer, storage and display of information and have also great potential for economic profit. In this context, it is of great importance to develop and characterize new light emitting compounds in both of academic and industrial interests.

In this work, two organic luminescence compounds having benzoxazole and benzthiazole moieties and their zinc (II) metal complexes have been synthesized and their PL spectra were determined. Using DMol^3 program, atomic distance and dihedral angle were also calculated and compared with the synthesized moiety.

EXPERIMENTAL

Synthesis

The intermediate compounds **1** and **2** were prepared by condensing *p*-aminosalicylic acid, 6.52 mmole (0.998 g), with *o*-aminophenol and *o*-aminothiophenol 6.52 mmole (0.711 g, 0.816 g) in 20 g of polyphosphoric acid (85% phophorus pentoxide) over three hours at 200°C. Other general procedures were followed by the indicated reference [6]. For next step synthesis, the dyes **3** and **4** were obtained from the prepared intermediates **1** and **2**, which previously described reference [7,8]. Terephthalaldehyde (0.1 mmole, 0.013 g) and compounds **1** and **2** (0.2 mmole, 0.045 g, 0.048 g) 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 product was filtered using benzene and dried (dyes **3** and **4**).

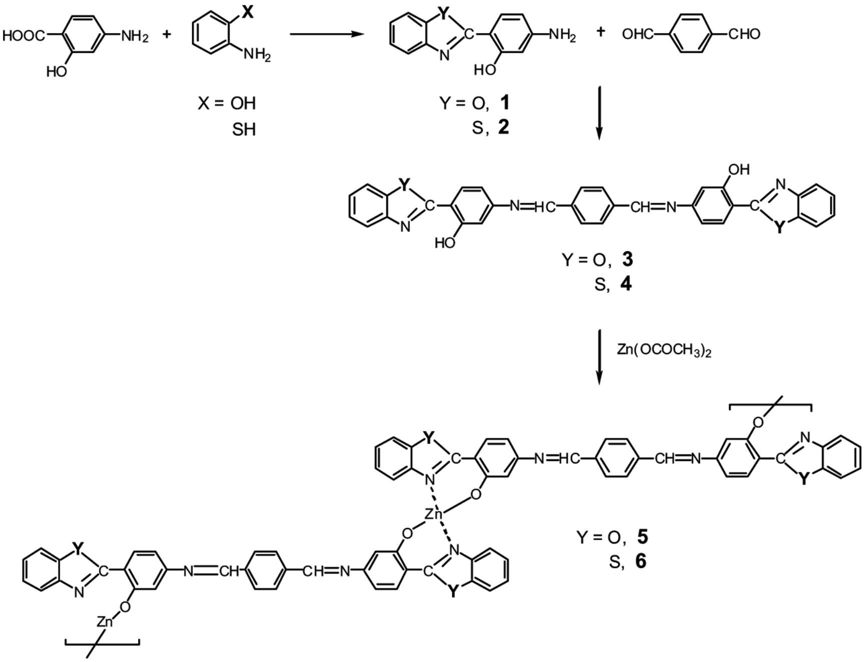
Dye **1**, Yield: 23.03% (0.340 g); calculated for $C_{13}H_{10}N_2O_2$: C, 69.02; H, 4.46; N, 12.38: found; C, 69.16; H, 4.16; N, 12.81.

Dye **2**, 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, 64.55; H, 4.03; N, 11.52; S, 12.62.

Dye **3**, Yield: 34.80% (0.019 g); calculated for $C_{34}H_{22}N_4O_4$: C, 74.17; H, 4.03; N, 10.18: found; C, 73.69; H, 4.10; N, 9.45.

Dye **4**, Yield: 33.98% (0.020 g); calculated for $C_{34}H_{22}N_4O_2S_2$: C, 70.08; H, 3.81; N, 9.62; S, 11.01: found; C, 70.09; H, 4.04; N, 9.18; S, 10.95.

The zinc (II) complexes of dyes **3** and **4** have been synthesized using $Zn(OCOCH_3)_2$ in DMF. As shown in Scheme 1, they can be readily obtained by the direct metal chelation of benz-X-azole legand. Dyes



SCHEME 1 Synthetic route of metal complexes.

3 and **4** (0.36 mmole, 0.198 g, 0.210 g) in 20 ml of DMF were dissolved at 80°C. $Zn(OCOCH_3)_2$ (0.18 mmole, 0.034 g) dissolved in 1.8 ml of methanol was added and the reaction mixture was stirred at reflux for 3 h. The mixtures were poured into methanol. The precipitate was filtered, washed with methanol and dried at 50°C (dyes **5** and **6**).

Dye **5**, Yield: 47.57% (0.108 g); calculated for $C_{70}H_{46}N_8O_8Zn$: C, 66.84; H, 3.69; N, 8.91: found; C, 65.20; H, 3.01; N, 8.63.

Dye **6**, Yield: 41.68% (0.099 g); calculated for $C_{70}H_{46}N_8O_4S_4Zn$: C, 63.59; H, 3.51; N, 8.47; S, 9.70: found; C, 63.33; H, 3.19; N, 8.48; S, 9.86.

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 determined by TGA-2050 at heating 20°C/min.

RESULTS AND DISCUSSION

For the purposes of obtaining luminescence dye intermediates, the reaction of carboxylic groups or relevant derivatives with aromatic ortho bisubstituted compounds was employed to produce benz-X-azole derivatives [6,9]. In this work, *p*-aminosalicylic acid and *o*-aminophenol (and *o*-aminothiophenol) were used to produce the benz-X-azole dye intermediates as described above. After this reaction, the prepared benz-X-azole dye intermediates **1** and **2** were reacted with dialdehyde, namely terephthalaldehyde to produce the dyes **3** and **4**. It is well known that the active amine groups can readily react with carbonyl groups, especially an aldehyde. For the light-emitting properties of the dyes, benzoxazole derivative **3** showed the photoluminescent property with solid states. In contrast, the dye **4**, benzthiazole derivative displayed lower level of photholuminescence effect (Fig. 1). Figure 1 shows the corresponding PL spectra of the benzoxazole and benzothiazole dye compounds. Strong emission with an emission peak around 500 nm and 540 nm was observed by dye **3**.

The zinc (II) complex dyes **5** and **6** were consecutively synthesized. As shown in the PL spectra result of the dye **3** (Fig. 1), the zinc (II) complex of the benzoxazole derivative compound (dye **5**) also showed its strong PL spectral property (Fig. 2). However, in the case of the benzthiazole zinc (II) complex dye **6**, the photoluminescence effect was weakly observed (Fig. 2). For further molecular structural study,

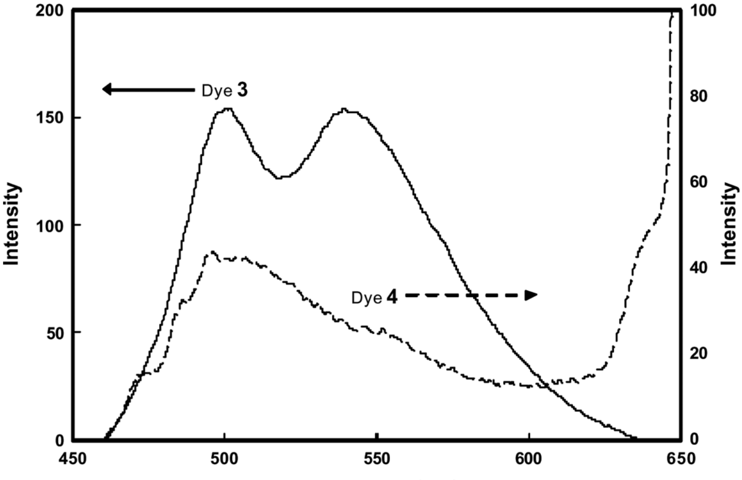


FIGURE 1 PL spectra of dye 3 and dye 4 in solid state.

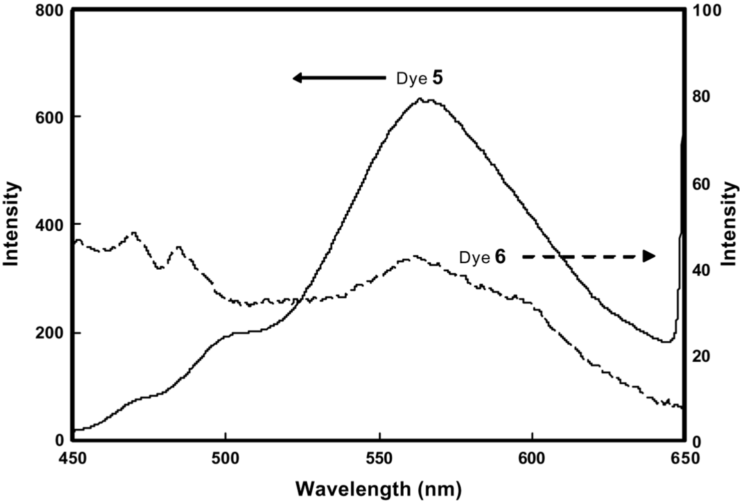


FIGURE 2 PL spectra of dye 5 and dye 6 in solid state.

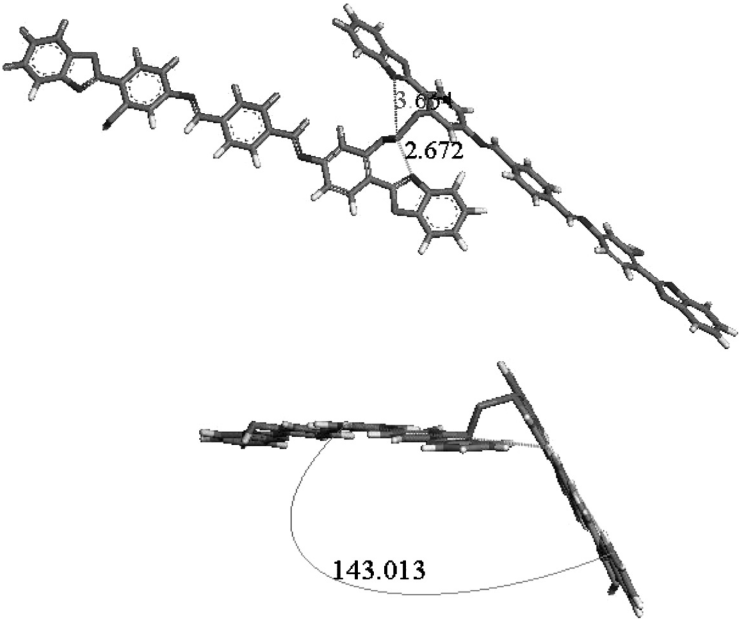


FIGURE 3 Optimized molecular conformation using DMol^3 modeling calculation.

modeling calculation was considered to calculate the conformational data of dyes. In general, unfortunately, organic polymeric dyes such as dyes 5 and 6, do not readily provide the single crystals for X-ray structural determinations, which has severely limited to obtaining data available for exact structural characteristic studies. Thus, these theoretical calculations were performed using 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 corresponding optimized molecular structure of dye 5 is shown in Figure 3. The interatomic distances between Zn and the oxazole N are 2.672 and 3.664 Å. The calculated dihedral angle between two benzoxazole ligands is 104° for dye 5. In stead of X-ray single crystal spectroscopy, the general structural conformation of this polymeric dye molecule can be expected using molecular modeling approaches.

In addition, thermal stabilities of the synthesized dyes were evaluated by TGA using the initial degradation temperature in the temperature range of 50–800°C (Fig. 4). It was determined that the synthesized

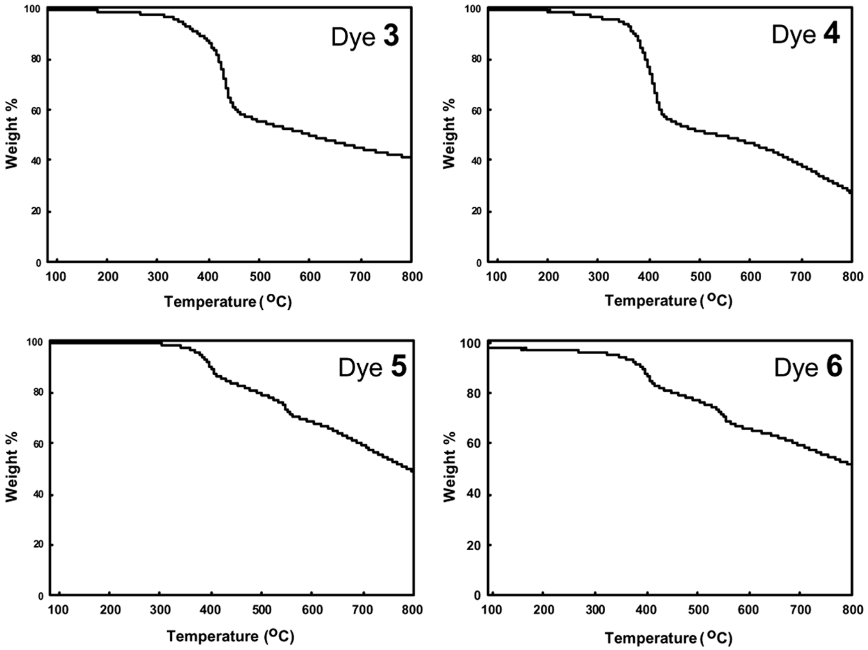


FIGURE 4 Thermal analysis for the dyes 3–6 by TGA.

four luminescence dyes were very stable at the temperature below 300°C. This finding indicates that these dyes may provide perfect thermostabiliy functions for the corresponding EL display end uses.

CONCLUSIONS

In this context, the benzoxazole dye type showing strong light emitting function can be useful for the electroluminescence (EL) materials. In addition, because the dyes **5** and **6** have two metal complex legands in the structures, these dyes can be further coordinated to zinc to form bridged multinuclear polymeric metal complexes. The emission maximum of metal complex benzoxazole dye **5** is shifted from 500 nm/540 nm (dye **3**) to 565 nm. This is due to the change in the distribution of electron density that occurs when the proton of the hydroxyl group of dye **3** is removed and the remaining oxygen anion is coordinated to metal zinc ion. In this context, since changing the distribution of the electronic density in the dye molecules affects the energy of light emitted by the molecule, it would be possible to synthesize or modify EL materials that emit light of the desired wavelength.

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