Synthesis and Luminescent Properties of 2-Phenyl-5-{4[2-(6-substituent-2H-benz[de]isoquinoline-1,3(2H)-dione-2-yl) polymethano-]amino-}phenyl-1,3,4-oxadiazole

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Several new derivatives of 1,8-naphthalimide, which are connected with 1,3,4-oxadiazole via a covalent bond, have been synthesized. We have investigated the electroluminescent (EL) device fabricated with these new compounds. In these compounds 1,3,4-oxadiazole moiety facilitates the electron injection from the electrode and transfers its excited energy to 1,8-naphthalimide which acts as an emitting center. Greenish yellow EL peaked at 532 nm with a maximum luminous efficiency of 0.43 lm/W was observed.

In organic electroluminescent (EL) devices, the generation of light is the consequence of the recombination of holes and electrons injected from the electrodes. Such carrier recombination in the organic emitter layer excites the emitting centers. It is well known that to achieve good performance in EL devices, the injection of electron and hole should be in balance. Electron-withdrawing oxadiazole unit is thought to have high electron affinity and be able to facilitate the electron injection. Several small organic molecules, such as 2- (4-biphenylyl)-5- (4-tert- butylphenyl) - 1, 3, 4 -oxadiazole (PBD), have been successfully used as electron-injection material to improve the balance of charge carriers injection and to increase the photon / electron quantum efficiency. [1-5] The improved performance is believed to result from the high electron affinity of oxadiazole unit in the molecules. However, an EL device with 1, 8-naphthalimides as emitter showed only luminance of 35 cd /m^2 . [1] Recently, several analogues of PBD have been synthesized and tested to be good electron injection material. [6] On the other hand, it is important to find an appropriate device structure to maximize the carrier recombination efficiency. Various types of EL devices with a multilayer or single layer structure have been reported, and various emitting colors, even white light have been obtained. [7, 8] Considering of the complication of doping in emitter layer and intermolecular excited energy transfer in EL devices, we therefore focused on developing bi- (or tri-) chromophoric compounds, in which both electron and hole transporting units were connected directly with emitting unit via covalent bonds. Thus, the possibility of developing organic EL devices without layer-layer exciton quenching is quite high. In this study, new bichromophoric compounds containing 1,3,4-oxadiazole and 1,8-naphthalimides were synthesized. We report, in this paper, on the use of a new bichromophoric fluorescent dye for the fabrication of organic EL devices.

The synthesis of 2-phenyl-5-{ 4-[(2H-benz [de] isoquinoline -1,3 (2H)-dione-2-yl-) ethyl] amino} phenyl- 1, 3, 4-oxadiazole (NIO1) was made as follows: 0.2g 1,8-naphthalic anhydride

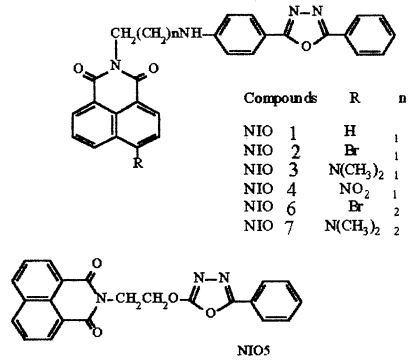

Figure 1. The structures of the compounds.

and 0.3g 2-phenyl-5-[4- (2-amino) ethyl] phenyl- 1, 3, 4-oxadiazole, which was synthesized according to the literature,[9] were added into 20 ml absolute ethanol , then stirred and heated to reflux for 1.5 h. After cooling, a yellow precipitate was obtained. It was then recrystallized by THF and acetone. Using the above method we have synthesized NIO2—NIO4, NIO6, NIO7. In synthesis of NIO5, 2-hydroxyl-5-phenyl-1,3,4-oxadiazole was synthesized according to the literature.[10] NIO5 was purified by column chromatography using petroleum ether-ethyl acetate (3:1) as eluent . ^{1}H NMR data (in d^6-DMSO): **NIO1**: 3.47(t, 2H, 13.31 Hz); 4.33 (t,2H, 13.39 Hz); 6.82 (d, 2H); 7.62 (m, 3H); 7.86 (m, 4H); 8.10 (d, 2H); 8.49 (m, 4H); **NIO2**: 3.50 (t, 2H,13.81 Hz); 4.25 (t, 2H, 13.51 Hz); 6.80 (d, 2H, 8.75 Hz); 7.62 (m, 3H); 7.84 (d, 2H, 8.70 Hz); 8.06 (m, 3H); 8.25 (d, 1H, 7.88 Hz); 8.40 (d, 1H, 7.88 Hz); 8.57 (m, 2H); **NIO3**: 3.11 (s, 6H); 3.48 (t, 2H); 4.26 (t, 2H); 6.85 (d, 2H, 8.75 Hz); 7.25 (d, 1H, 8.37 Hz); 7.60 (m, 3H); 7.80 (m, 3H, 8.69 Hz, 15.81 Hz); 8.09 (d, 2H); 8.35 (d, 1H, 8.29 Hz); 8.50 (t, 2H, 8.47 Hz, 15.9 Hz); **NIO4**: 3.57 (t, 2H); 4.26 (t, 2H); 6.85 (d, 2H, 8.71 Hz); 7.62 (m, 3H); 7.83 (d, 2H, 8.62 Hz); 8.11 (m, 3H); 8.65 (m, 4H); **NIO5**: 4.15 (t, 2H, 10.99 Hz); 4.45 (t, 2H, 11.0 Hz); 7.40 (t, 2H); 7.52 (m, 3H); 7.75 (t, 2H); 8.48 (m, 4H); **NIO6**: 1.96 (t, 2H,13.8 Hz); 3.20 (t, 2H, 14.1 Hz); 4.18 (t, 2H, 14.2 Hz); 6.71 (d, 2H, 8.8 Hz); 7.60 (m, 3H); 7.79 (d, 2H, 8.7Hz); 8.0 (d, 1H); 8.10 (d, 2H); 8.22 (d, 1H, 7.9 Hz); 8.35 (d, 1H, 7.8 Hz); 8.59 (m, 2H); **NIO7**: 1.95 (t, 2H); 3.07 (s, 6H); 3.21 (t, 2H); 4.14 (t, 2H); 6.72 (d, 2H, 8.68 Hz); 7.20 (d, 1H, 8.31 Hz); 7.64 (m, 3H); 7.72 (t, 1H); 7.79 (m, 2H, 8.66 Hz); 8.08 (d, 2H); 8.35(d, 1H,8.21Hz);8.50 (m,2H).

In EL devices, PVK was spin-cast onto the substrates at 2500 rpm from a 1, 2-dichloroethane solution with a concentration of 4 mg/ml. Then, a layer of NIO7 was vacuum

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evaporated at a pressure below 2 x10^{-3} Pa. Finally, metal contact of aluminum were vacuum evaporated at the same pressure. EL spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer. The luminance was measured with a LS-1 portable luminance meter. All measurements were performed at room temperature in air.

Table 1. The absorption (λ_{max}^{ab}) and fluorescence maximum wavelengths (λ_{max}^{fl}) of the compounds in THF solutions

NIO	1	2	3	4	5	6	7
λ_{max}^{ab}	333	340	333	334	332	340	332
(nm)			413				411
λ_{max}^{fl}							
(nm) *	403	406	517	412	378	409	515

* λ_{max}^{fl} values were obtained at the excitation of their maximum absorption wavelengths for various compounds, respectively.

The absorption spectrum of NIO7 in thin solid film and the PL of NIO7 in THF solution, and the absorption and emission spectra of the mixture were shown in Figure 2. Another compounds show similar phenomenon. Comparing the spectra in Figure 2, the absorption of these new bichromophoric compounds is the exact sum of that of the constituent chromophores . This indicates that there is little or no interaction between chromophores, so that their individual characteristics should be maintained in the bichromophoric compounds. In these compounds the emission of oxadiazole was quenched, which means there exists an intramolecular energy transfer. [11]

Figure 3 shows that the EL device made from NIO7 has a broad luminescence spectrum which spans the range 475- 650 nm with a peak at 532 nm. The normalized EL spectra do not change with the voltage, which means the emission zone lies within the NIO7 layer when the voltage is varied. A luminance of 225 cd/m^2 at an applied voltage of 27 V was observed. The maximum luminous efficiency is 0.43 lm/W at 19 V. As seen in Figure 3, there is only the characteristic emission of the 1,8-naphthalimide moiety in the EL spectrum. That imply the energy of the excited oxadiazole moiety (Donor) transfers to the 1,8-naphthalimide moiety (Acceptor) and the EL originates from it.

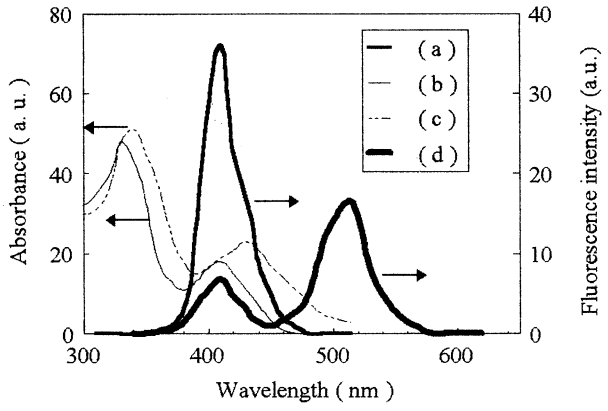

Figure 2. (a) Fluorescence spectrum of a mixture of *N*-Et-4-dimethylamino- 1, 8-naphtalimide and 2-phenyl-5-[4-(3-amino) propylamino] phenyl -1, 3, 4-oxadiazole (1:1 mol / mol) in THF solution (2.5 × 10 $^{-5}$ M, excited at 327 nm) ; (b) Absorption of the above mixture ; (c) Absorption of NIO7 in thin solid film; (d) Fluorescence spectrum of NIO7 in THF solution (2.5 × 10 $^{-5}$ M, excited at 332 nm)

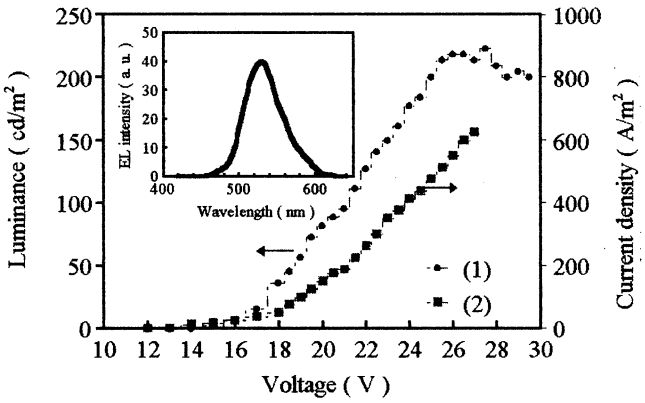

Figure 3. The current density J-V characteristics (curve 2) and Brightness -V characteristics (curve 1) of an ITO/ PVK/ NIO7/ Al device. The insert figure is EL spectrum of the device.

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