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Synthesis of a New Family of Green Light Emitting Material Containing Both Hole and Electron Transporting Units

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Abstract: Two new molecules containing oxadiazoles and triphenylamine-stilbene moiety were synthesized. Their luminescent properties were determined, which indicated that they had strong green fluorescent properties. All the two molecules can be used as green organic electroluminescence materials.

Keywords: Synthesis, green organic electroluminescence materials, fluorescence, triphenylamine, oxadiazole.

Since Tang and Van Slyke reported the first double-layer organic electroluminescent (EL) device using Alq_3 (q = 8-hydroxyquinolinyl) in 1987[1], organic EL devices have received a great deal of attention in view of their application as full-color flat-panel displays as well as academic interest[2,3,4]. There have been extensive studies of organic EL devices directed toward achieving high brightness and multi- or full-color emission, and in particular, improving the durability and thermal stability of the devices.

Many highly fluorescent materials were developed to fulfill the need of three basic colors, red, green, and blue, for a full-color display. Among these, an efficient green emission is one of the most sought-after colors. New green-emitting materials with high performance still remain to be developed. We introduced a triphenylamine segment and 1, 3, 4-oxadiazole moiety to an emitter molecule used for organic LE device applications.

The general method for preparing **8a** and **8b**[5] is outlined in **Scheme 1**.

Results and Discussion

To obtain stable EL devices, increased thermal stability is an important factor. In EL devices, the amorphous form of organic layer was mostly used. Thus, we especially consider the stability of the amorphous state. The melting point (T_m) and glass transition temperature (T_g) of the two molecules of **8a** and **8b** are 237°C, 115°C and 235°C, 113°C, respectively. None of the materials showed a clear crystallization

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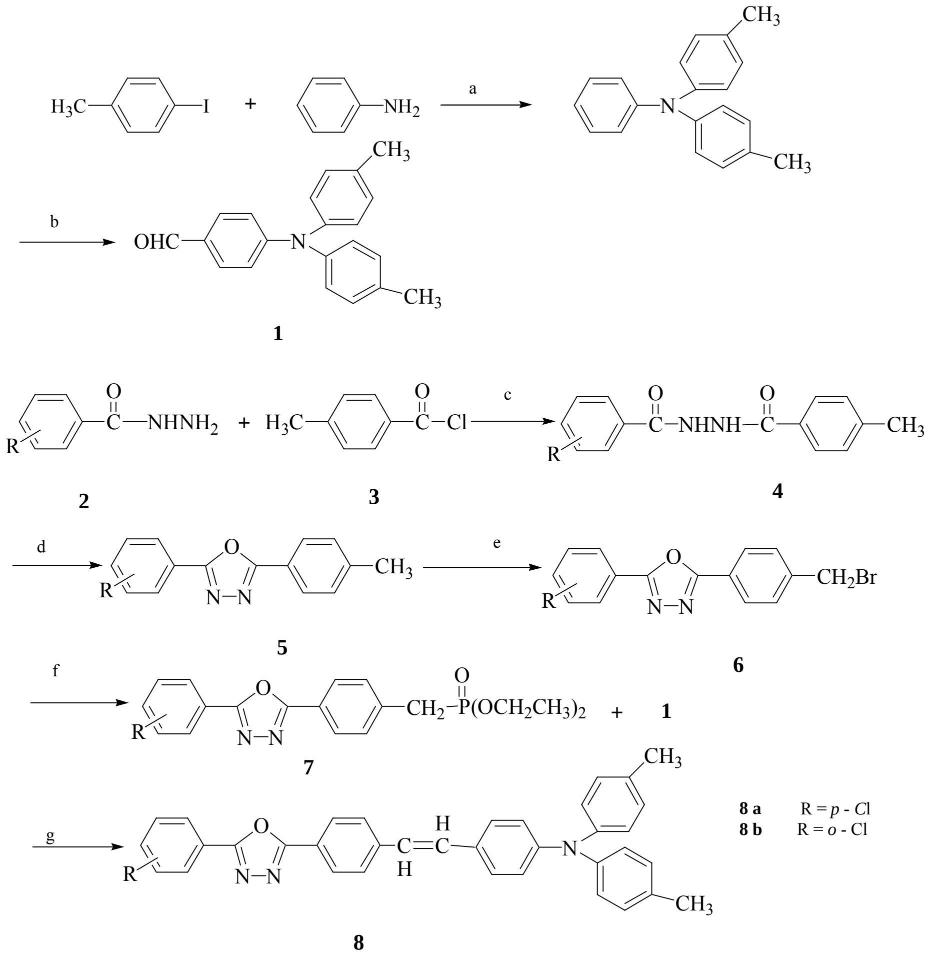
temperature (T_c). They can form desirable stable amorphous phases in a deposited film. The structure of the triphenylamine units possibly contributes to the desirable thermal properties.

Scheme 1



a) Cu, K_2CO_3, 18-crown-6, 75% yield; b) $POCl_3$, DMF, 70% yield; c) pyridine, 95% yield ; d) $POCl_3$, 93% yield; e) NBS, benzene, 67% yield; f) $P(OCH_2CH_3)_3$, 90% yield ; g) *t*-BuOK , DMF , 78% yield

The EL of organic materials occurs from a recombination of an anion radical and a cation radical of emitter molecules, resulting in formation of a molecular exciton and successive radiative decay of an exciton. Organic EL materials should have excellent fluorescent properties in solid state. Typically, green dopants which possess a high fluorescence quantum yield, are intramolecule charge-transfer compounds with both strong electron donor and electron acceptor groups. The emission wavelengths of these compounds can be tuned by changing the relative electron donating and accepting abilities of the donor and acceptor groups. Many researchers revealed that 1,3,4-

oxadiazole rings function well as an electron-transport moiety[6,7] for obtaining high EL performance. On the other hand, triphenylamine groups are known to possess a superior hole-transport mobility[8]. When we incorporate these units into the molecular structure of emitters, we can then expect improved bipolar character and improved EL characteristics. The triphenylamine group has three non-coplanar benzyl groups, which are beneficial for increasing the steric hindrance of the molecule. The introduction of triphenylamine group is expected to further reduce the effect of concentration quenching.

Because PL has almost the same mechanism to EL, we investigated fluorescent properties of these compounds to estimate their EL spectra. **Table 1** summarizes photoluminescent (PL) and absorption spectra of **8a** and **8b**. The absorption peaks occur between 300 and 400 nm with two major absorptions in $CHCl_3$. The two absorption peaks can therefore be attributed to the oxadiazole and the Ar_3N-stilbene moieties, respectively. The emissions of **8a** and **8b** have peaks maximum at 516 and 513 nm in the green region, respectively. Photoluminescence in hexane was also examined. The compounds exhibit strong solvatochromism. Upon UV excitation, a more polar excited state is expected. Thus, a polar solvent stabilizes the excited state more than the ground state. The fluorescence quantum yields (Φ_f) of **8a** and **8b** were 90% and 92% in chloroform, respectively, which were estimated with diphenylanthracene as a standard ($\Phi_f = 1$)[9]. The PL of the solid films are *ca.* 10 nm red-shifted relative to respective PL in $CHCl_3$. A serious concentration quenching of PL in a thin-film form was not observed in these materials.

In summary, the two compounds were found to readily form a stable amorphous glass with high glass-transition temperature. Their photoluminescence (PL) properties were studied, their strong green solid PL showed that they could be used as green organic EL material. Further study is in progress.

Table 1 Photophysical property of **8a** and **8b**

Entry	λ_{max} Abs in 0^{-5} M $CHCl_3$ solution (nm)	λ_{max} EM in 10^{-5} M $CHCl_3$ solution (nm)	λ_{max} EM in 10^{-5} M hexane solution (nm)	λ_{max} EM in solid film (nm)
8a	308, 411	516[a]	475[a]	525[c]
8b	309, 406	513[b]	473[b]	520[c]

[a] Excitation wavelength 411 nm. [b] Excitation wavelength 406 nm. [c] Excitation wavelength 300 nm

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5. 1H-NMR (200MHZ) data for **8a** (CDCl$_3$, δ ppm): 2.32 (s, 6H,CH$_3$); 7.02～8.10 (m, 22H, ArH). **8b** (CDCl$_3$, δ ppm): 2.32 (s, 6H,CH$_3$); 7.02～8.10 (m, 22H, ArH). EI-MS, *m/z* (%) for **8a**： 554(M$^+$, 100). **8b**: 554 M$^+$, 100).
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