Blue Electroluminescent 1,2,4-Triazole Derivative

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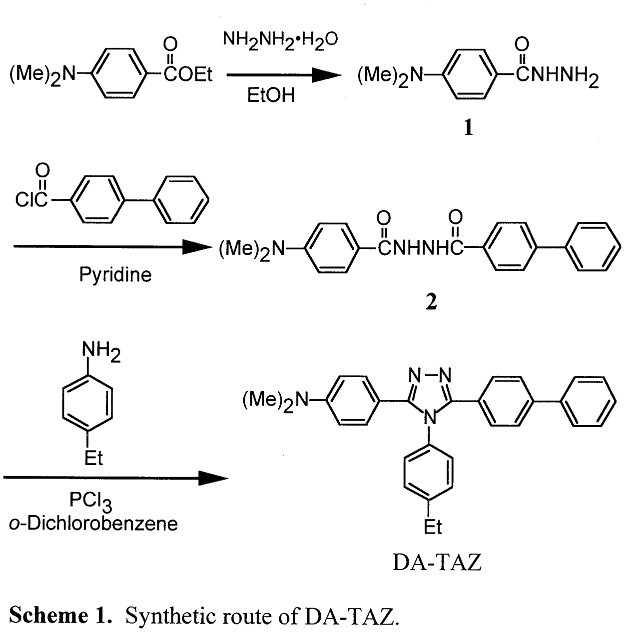
A blue fluorescent 1,2,4-triazole derivative, DA-TAZ, was synthesized and examined as an emitter layer in organic electroluminescent device. The device structure of glass substrate / indium- tin oxide / hole-transporting diamine layer / DA-TAZ layer / Mg:Ag was employed. The EL device exhibited bright blue light originating from the DA-TAZ emitter layer with a maximum luminance of 1200 cd/m^2 at 14 volt.

Electroluminescence in organic materials has been investigated by a number of researchers for practical organic electroluminescent (EL) devices.[1-16] Generation of light in such systems is the result of recombination of holes (radical cations) and electrons (radical anions) injected from the electrodes. Such recombinations in the emitter layer, then, produce the excitons (excited molecules). Such devices usually consist of a multilayer structure with a hole-transporting layer and an electron-transporting layer to confine injected carriers as well as generated excitons in the organic layers. The most widely used electron-transporting materials are 1,3,4-oxadiazoles[3-6] and 1,2,4-triazoles (TAZs).[13-16] In particular, 3-(4-biphenylyl)-5-(4-*t*-butylphenyl)-4-(4-ethyl-phenyl)-1,2,4-triazole, *p*EtTAZ, has been shown to be effective in blocking holes due to its high ionization potential (Ip) of 5.8 eV.

In this study, our objective is to design and synthesize a 1,2,4-triazole that can be used as an emitter layer in organic EL device. Because injection of holes to an electron-transporting TAZ layer is necessary to achieve hole-electron recombination in the TAZ layer, an electron-donating group (dimethylamino) was introduced to the TAZ structure in order to lower the ionization potential.

The synthesis of a dimethylamino group-containing TAZ started from 4-dimethylaminobenzoic acid methyl ester which was reacted with hydrazine monohydrate in ethanol to give 4-dimethylaminobenzohydrazide, **1** (yield 88%). Compound **1** was then reacted with 4-phenylbenzoyl chloride in pyridine to yield 1-(4-biphenylyl)-4-(4-dimethylaminophenyl)hydrazide, **2** (yield 87%). The ring closure reaction of **2** with *p*-ethylaniline in the presence of phosphorus trichloride was conducted in *o*-dichlorobenzene at reflux temperature to yield 3-(4-biphenylyl)-4-(4-ethylphenyl)-5-(4-dimethylaminophenyl)-1,2,4-triazole, DA-TAZ. DA-TAZ was purified by column chromatography using silica gel and finally by sublimation (yield 14%). mp 253.8-254.5 °C. [Elemental analysis: H 6.31 (6.35), C 80.8 (81.1), N 12.6 (12.6), ( ) Calcd]



Scheme 1. Synthetic route of DA-TAZ.

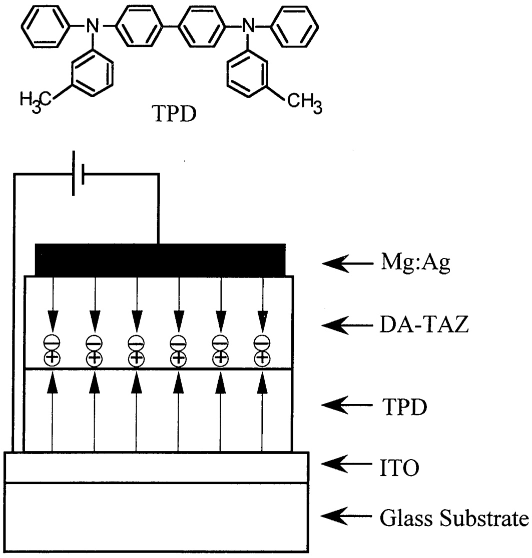


Figure 1. The molecular structures of TPD, and the sturucture of a double-layer-type EL device.

DA-TAZ was examined as an emitter layer in a double-layer-type device having a hole transport layer inserted between the anode and the emitter layer. The device structure is a glass substrate / indium-tin oxide (ITO) / *N,N*'-diphenyl-*N,N*'-(3-methyl phenyl)-1,1'-biphenyl-4,4'-diamine, TPD (500 Å) / DA-TAZ (500 Å) / Mg:Ag (10:1). The organic layers were successively deposited onto an ITO-coated glass plate at 2.0 x 10^{-5} Torr. The Mg:Ag top electrode was finally codeposited at 7.0 x 10^{-6} Torr. The emitting area was 0.5x0.5 cm^2. Luminance was measured with a Topcon BM-8 luminance meter at room temperature and Ips were measured by atmosphere ultraviolet photoelectron analysis using a Riken Keiki AC-1 under ambient atmosphere.

Bright blue light was observed from the EL device when operated in a continuous dc mode with Mg:Ag negative. The EL spectrum in Figure 2 is identical with the photoluminescence spectrum of the vacuum deposited film of DA-TAZ, indicating that electron-hole recombination occurs in the DA-TAZ layer. In contrast, a device with TPD and a TAZ having higher Ip value, such as *p*EtTAZ, exhibits emission, peaking at 410 nm, from the TPD layer.[16] Thus, the introduction of an electron-donating dimethylamino group is effective to lower Ip value, and holes are injected from the TPD (Ip=5.4 eV) layer to the DA-TAZ (Ip=5.5 eV) layer.

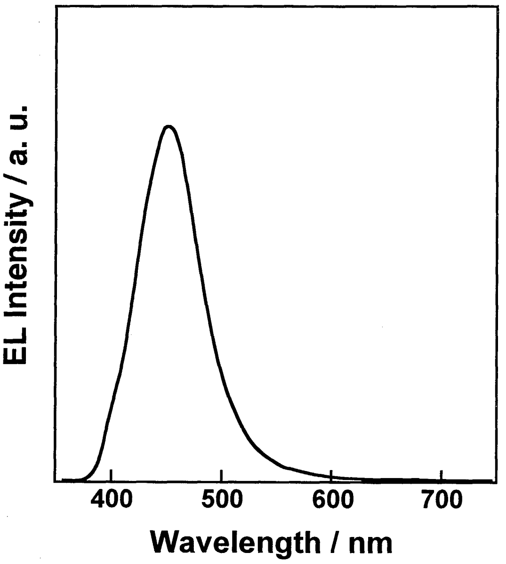


Figure 2. EL spectrum of an ITO/TPD (500 Å)/DA-TAZ (500 Å)/Mg:Ag device.

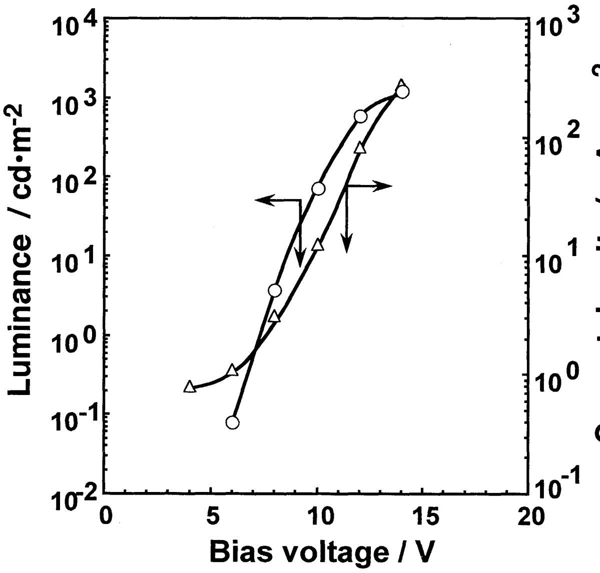


Figure 3. Luminance-current density-voltage characteristics of an ITO/TPD (500 Å)/DA-TAZ(500 Å)/Mg:Ag device.

The continuous dc current (I)-voltage (V) and luminance (B)-voltage (V) curves for the ITO / TPD / DA-TAZ / Mg:Ag device are displayed in Figure 3. Luminance increases with increasing the injection current as well as the bias voltage. The maximum luminance of 1200 cd/m^2 was achieved at 14 V. This is one of the highest luminance reported for pure blue light (λ = 450 nm) emitting organic EL devices.[17] At this drive voltage, the current density is 275 mA/cm^2.

In conclusion, we have demonstrated that 1,2,4-triazole can be an excellent blue light emitter, and are now preparing other TAZs with different substituents for EL application.

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References

1 C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, **51**, 913 (1987).
2 C. W. Tang, S. A. VanSlyke, and C. H. Chen, *J. Appl. Phys.*, **65**, 3610 (1989).
3 C. Adachi, T. Tsutsui, and S. Saito, *Appl. Phys. Lett.*, **55**, 1489 (1989).
4 C. Adachi, T. Tsutsui, and S. Saito, *Appl. Phys. Lett.*, **57**, 531 (1990).
5 Y. Hamada, C. Adachi, T. Tsutsui, and S. Saito, *Nippon Kagaku Kaishi* (*J. Chem. Soc. Jpn.*), **1991**, 1540 [in Japanese].
6 Y. Hamada, C. Adachi, T. Tsutsui, and S. Saito, *Jpn. J. Appl. Phys.*, **31**, 1812 (1992).
7 J. Kido, K. Nagai, and Y. Ohashi, *Chem. Lett.*, **1990**, 657.
8 J. Kido, K. Nagai, Y. Okamoto, and T. Skotheim, *Chem. Lett.*, **1991**, 1267.
9 J. Kido, K. Nagai, Y. Okamoto, and T. Skotheim, *Appl. Phys. Lett.*, **59**, 2760 (1991).
10 J. Kido, K. Hongawa, M. Kohda, K. Nagai, and K. Okuyama, *Jpn. J. Appl. Phys.*, **31**, L960 (1992).
12 J. Kido, Y. Guo, J. McBreen, K. Nagai, and Y. Okamoto, *Polym. Adv. Tech.*, **3**, 429 (1992).
13 J. Kido, C. Ohtaki, K. Hongawa, K. Okuyama, and K. Nagai, *Jpn. J. Appl. Phys.*, **32**, L917 (1993).
14 J. Kido, K. Hongawa, K. Okuyama, and K. Nagai, *Appl. Phys. Lett.*, **63**, 2627 (1993).
15 J. Kido, K. Hongawa, K. Okuyama, and K. Nagai, *Appl. Phys. Lett.*, **64**, 815 (1994).
16 J. Kido, M. Kimura, and K. Nagai, *Science*, **267**, 1332 (1995).
17 Y. Hamada, K. Sano, M. Fujita, T. Fujii, Y. Nishio and K. Shibata, *Nippon Kagaku Kaishi* (*J. Chem. Soc. Jpn.*), **1993**, 879 [in Japanese].