Development of a New Greenish Blue-emitting Amorphous Molecular Material
2,5-Bis{4-[2-naphthyl(phenyl)amino]phenyl}thiophene

Yasuhiko Shirota*, Ping Liu, Takahiro Ohara, and Tetsuya Noda

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565-0871, Japan

Keywords: Amorphous molecular material, greenish blue-emitting material, organic electroluminescent device

Organic Electroluminescent (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. 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. Both polymers and small molecules have been studied for use in organic EL devices [1,2]. Low molecular-weight organic compounds that readily form stable amorphous glasses, namely, amorphous molecular materials, are promising candidates for use in organic EL devices [3]. They permit the formation of smooth, uniform amorphous thin films by vacuum deposition or by coating from solution.

With regard to low molecular-weight emitting materials, tris(8-quinolinolato)aluminum (Alq3) has been used most extensively as a green-emitting material with electron-transporting properties. Blue- or greenish blue-emitting materials for organic EL devices have also been reported, including oxadiazole derivatives [4], distyrylarylene derivatives [5], a triazole derivative [6], spiro-linked compounds [7] and tri(ρ-terphenyl-4-yl)amine [8]. Organic EL devices using these emitting materials have been reported to exhibit brightness of approximately 1,000 cd m⁻² except for 4,4'-bis(2,2-diphenylethenyl)biphenyl. Blue- or greenish blue-emitting materials with high performance still remain to be developed.

We report here a new greenish blue-emitting amorphous molecular material, 2,5-bis{4-[2-naphthyl(phenyl)amino]phenyl}thiophene (BNpA-1T) and the fabrication and performance of an organic EL device using BNpA-1T as the emitting material.

BNpA-1T

BNpA-1T was synthesized by the Grignard coupling reaction of N-(4-bromophenyl)-N-phenyl-2-naphthylamine with 2,5-dibromothiophene in the presence of 1,3-bis(diphenylphosphino)propane nickel(II) chloride in tetrahydrofuran (THF). N-(4-Bromophenyl)-N-phenyl-2-naphthylamine was prepared by the Ullmann reaction of N-phenyl-2-naphthylamine with 4-bromomiodobenzene in the presence of copper powder, potassium carbonate, and 18-crown-6 at 130°C for 9 hr. BNpA-1T was purified by silica-gel column chromatography using toluene/hexane (1:4) as an eluent, followed by recrystallization from toluene/hexane. It was identified by infrared absorption, electronic absorption, ¹H NMR spectroscopy, and mass spectrometry.

BNpA-1T: MS: m/e 670 (M+). ¹H NMR (THF-d₈): δ (ppm) 7.72 (4H, d), 7.58 (2H, d), 7.52 (4H, d), 7.43 (2H, s), 7.32 (2H, dd), 7.29 (2H, dd), 7.25-7.22 (8H, m), 7.10 (4H, d), 7.06 (4H, d), 7.00 (2H, t)
BNpA-1T was found to readily form a stable amorphous glass with a glass-transition temperature ($T_g$) of 91°C, as determined by differential scanning calorimetry. It also forms an uniform amorphous film by vacuum deposition. BNpA-1T shows intense blue fluorescence with band maxima at 452 nm and 478 nm in THF. The fluorescence quantum yield of BNpA-1T in THF was 0.47. BNpA-1T in the amorphous solid film shows a fluorescence spectrum red shifted relative to that of solution in appearance, emitting greenish blue. As Fig. 1 shows, BNpA-1T undergoes reversible anodic oxidation, exhibiting two sequential anodic and the corresponding cathodic waves in the cyclic voltammogram. The half-wave oxidation potential of BNpA-1T was 0.48 V vs Ag/Ag+ (0.01 mol dm$^{-3}$). This value is similar to that of a well-known hole transporter N,N'-bis(3-methylphenyl)-N,N'-diphenyl-[1,1'-biphenyl]-4,4'-diamine.

A multilayer organic EL device using 4,4',4'''-tris[3-methylphenyl(phenyl)amino]triphenylamine (m-MTDATA) as the hole-transport layer [9], BNpA-1T as the emitting layer and Alq3 as the electron-transport layer was fabricated by sequential vacuum deposition of these organic materials onto an ITO-coated glass substrate at a deposition rate of 2-3 Å s$^{-1}$ at 10$^{-5}$ Torr, followed by the codeposition of magnesium and silver (ca 10:1 in volume ratio) onto the Alq3 layer by simultaneous evaporation from two separate sources [10].

The fabricated device, ITO/m-MTDATA(300Å) /BNpA-1T(200Å)/Alq3(300Å)/MgAg, emitted bright greenish blue light when a positive voltage was applied to the ITO electrode. The electroluminescence spectrum was in good agreement with the photoluminescence spectrum of a spin coated BNpA-1T film.

Fig. 2 shows the luminance versus applied voltage and the injected current versus applied voltage characteristics for the EL device. The emission started at 3.0 V and the device exhibited a maximum luminance of 8800 cd m$^{-2}$ at 13V with a luminous efficiency of 0.9 lm W$^{-1}$ at a luminance of 300 cd m$^{-2}$.

Fig. 2. Luminance versus applied voltage and the injection current density versus applied voltage characteristics for the organic EL device.

Conclusion

A new emitting amorphous molecular material with a $T_g$ of 91°C, BNpA-1T, was developed. A multilayer organic EL device using BNpA-1T as the emitting layer emitted greenish blue light, exhibiting high performance.

References