

A Novel Greenish Blue-emitting Amorphous Molecular Material: 2,5-Bis{4-[2-naphthyl(phenyl)amino]phenyl}thiophene

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A novel greenish blue-emitting amorphous molecular material, 2,5-bis{4-[2-naphthyl(phenyl)amino]phenyl}thiophene (BNpA-1T), was designed and synthesized. Its molecular properties, glass-forming property, and application to an organic EL device were investigated.

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

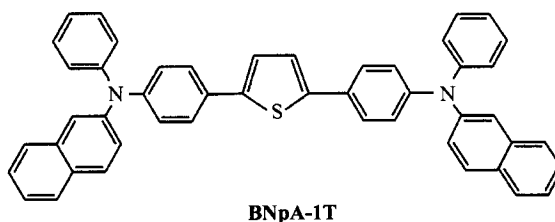
Introduction

In general, low molecular-weight organic compounds tend to crystallize. For example, oligothiophenes tend to crystallize readily because of their planar molecular structure. In fact, the films of oligothiophenes prepared by vacuum deposition or spin-coating have been reported to be polycrystalline.^{1,2} The use of polycrystalline film of oligothiophenes for devices, *e. g.*, organic electroluminescent (EL) devices, is not preferable because grain boundaries may cause carrier traps or short circuit, and the fluorescence quantum efficiencies of oligothiophenes in the polycrystalline film are much lower than in the solutions and single crystals.³⁻⁵

Amorphous molecular materials formed by low molecular-weight organic compounds are pure materials with well-defined molecular structures and definite molecular weights without any distribution. Amorphous molecular materials are promising candidates for use in organic EL devices. They permit the formation of smooth, uniform amorphous thin films by vacuum deposition or by coating from solution.

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.^{6,7} 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.

With regard to low molecular-weight emitting materials, tris(8-quinolinolato) aluminum (Alq₃) has been used most extensively as green-emitting material with electron transporting properties. Blue or greenish blue-emitting materials for organic EL devices have also been reported, including amongst others, oxadiazole derivatives,⁸ distyrylene derivatives,⁹ triazole derivative,¹⁰ spiro-linked compounds¹¹ and tri(*p*-terphenyl-4-yl)-amine.¹² Organic EL devices using these emitting materials have been reported to exhibit brightness of approximately 1,000 cd/m². Blue- or greenish blue-emitting materials with high performance still remain to be developed.



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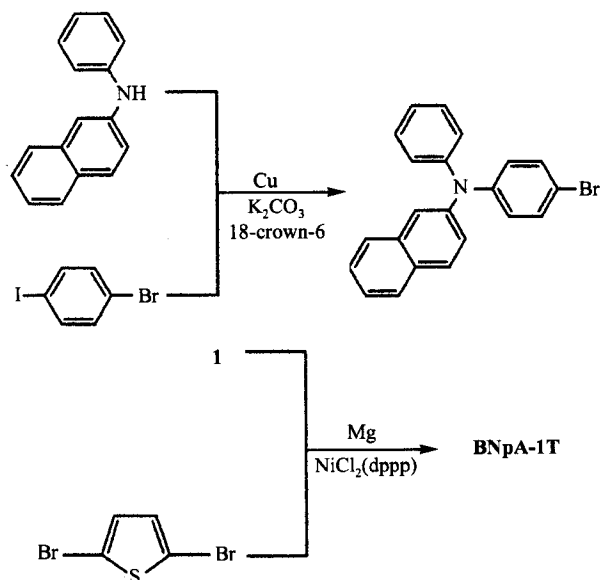
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We report here a novel greenish blue-emitting amorphous molecular material, 2,5-bis{4-[2-naphthyl-(phenyl)amino]phenyl}thiophene (**BNpA-1T**). Its glass-forming property, molecular properties, and application to an organic EL device were investigated.

Results and discussion

BNpA-1T was synthesized by the Grignard coupling reaction of *N*-(4-bromophenyl)-*N*-phenyl-2-naphthylamine (**1**) with 2,5-dibromothiophene in the presence of 1,3-bis(diphenylphosphino)propane nickel(II) chloride in tetrahydrofuran. Compound **1** was prepared by the Ullmann reaction of *N*-phenyl-2-naphthylamine with 4-bromoiodobenzene in the presence of copper powder, potassium carbonate, and 18-crown-6. **BNpA-1T** was purified by silica-gel column chromatography using toluene/hexane (1:4) as an eluent, followed by recrystallization from toluene/hexane (Scheme 1).

Scheme 1



BNpA-1T was found to readily form a stable amorphous glass with high glass-transition temperature (T_g) of 91 °C, as determined by differential scanning calorimetry (DSC). It also forms a uniform amorphous film by vacuum deposition. Fig. 1 shows DSC curve of **BNpA-1T**. When the sample was heated, well-defined glass-transition phenomenon was observed at 91 °C. On further heating, any other phase transformation was ob-

served. The result indicates that the amorphous glass of **BNpA-1T** was quite stable.

As Fig. 2 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/L).

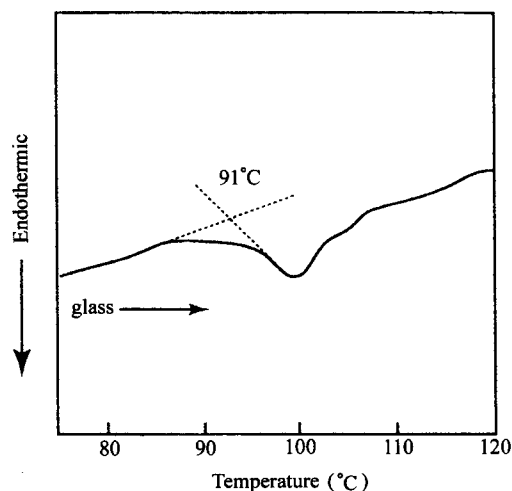


Fig. 1 DSC curve of **BNpA-1T**, heating rate: 5 °C/min.

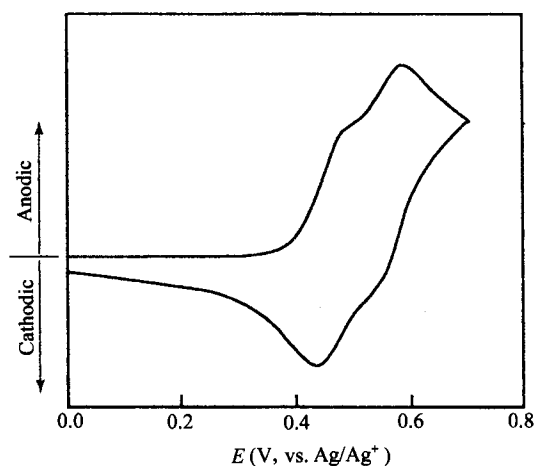


Fig. 2 Cyclic voltammogram of **BNpA-1T** (1.0×10^{-3} mol/L) in dichloromethane containing tetrabutylammonium perchlorate (0.1 mol/L), scan rate: 500 mV/s.

BNpA-1T shows intense blue fluorescence with maximum at 452 and 478 nm in tetrahydrofuran. The fluorescence quantum yield of **BNpA-1T** in tetrahydrofuran was 0.47. **BNpA-1T** in the amorphous solid film shows fluorescence spectrum bathochromic shift relative

to that of solution in appearance, emitting greenish blue light. A multilayer organic EL device using 4,4',4''-tris[3-methylphenyl(phenyl)amino]triphenylamine (*m*-MTDATA) as the hole-transport layer,^{13,14} **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 0.2–0.3 nm/s at 1.33×10^{-3} Pa, 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.

The device, ITO/*m*-MTDATA(30 nm)/**BNpA-1T**(20 nm)/Alq₃(30 nm)/MgAg, emitted bright greenish blue light when a positive voltage was applied to the ITO electrode. Fig. 3 shows the photoluminescence spectrum of **BNpA-1T** spin coated film and electroluminescence spectrum of the organic EL device, ITO/*m*-MTDATA(30 nm)/**BNpA-1T**(20 nm)/Alq₃(30 nm)/MgAg. Electroluminescence spectrum was in good agreement with the photoluminescence spectrum of spin coated **BNpA-1T** film.

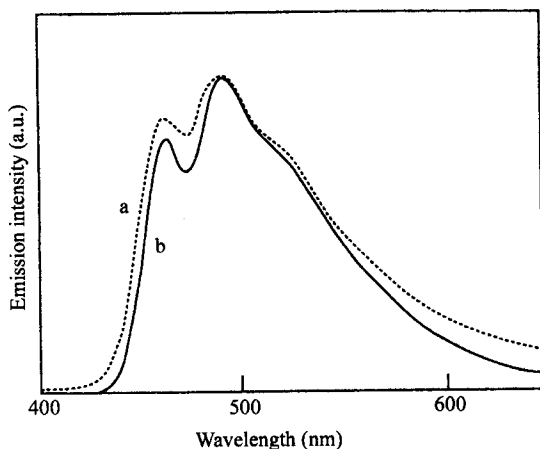


Fig. 3 Photoluminescence spectrum of an **BNpA-1T** spin coated film (a) and electroluminescence spectrum of the organic EL device, ITO/*m*-MTDATA(30 nm)/**BNpA-1T**(20 nm)/Alq₃(30 nm)/MgAg (b).

Fig. 4 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/m² at 13 V with a luminous efficiency of 0.9 lm/W at a luminance of 300 cd/m². The results show that, **BNpA-1T** may act as excellent emitting material in or-

ganic EL devices.

In conclusion, a novel 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.

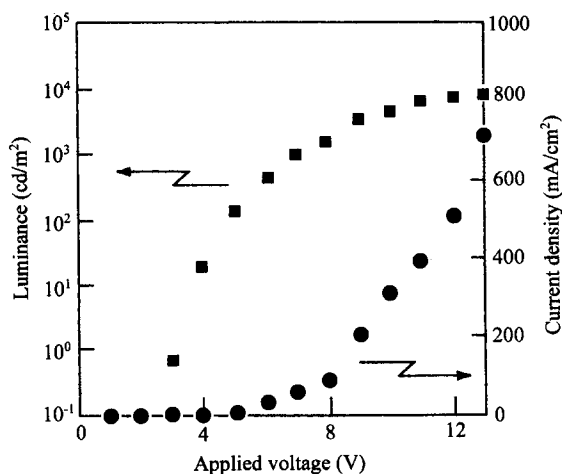


Fig. 4 Luminance versus applied voltage and the injection current density versus applied voltage characteristics for the ITO/*m*-MTDATA(30 nm)/**BNpA-1T**(20 nm)/Alq₃(30 nm)/MgAg device.

Experimental

Fluorescence spectra were measured on a Hitachi 850 fluorescence spectrophotometer. Cyclic voltammetry was carried out by Bioanalytical Systems BAS 100B/W using for dichloromethane solution containing **BNpA-1T** (1.0×10^{-3} mol/L) and tetrabutylammonium perchlorate (0.1 mol/L) using a platinum disk (1.6 mm in diameter) and a platinum wire as the working and counter electrodes, respectively, and Ag/AgNO₃ (0.01 mol/L in acetonitrile) as the reference electrode. Differential scanning calorimetry (DSC) was carried out with a Seiko DSC 6200.

Synthesis of *N*-(4-bromophenyl)-*N*-phenyl-2-naphthylamine (1)

N-Phenyl-2-naphthylamine (25 g, 0.114 mol) and 4-bromiodobenzene (64.5 g, 0.228 mol) were reacted in the presence of copper powder (7.2 g, 0.114 mol), K₂CO₃ (31.5 g, 0.228 mol), and 18-crown-6 (1.5 g,

5.7 mmol) at 130°C for 9 h under nitrogen atmosphere. The resulting solution was extracted with toluene. After the solvent was removed, the residue was purified by silica-gel column chromatography using a mixed solvent of toluene and hexane (1:5 V/V) as an eluent, followed by recrystallization from ethanol. Yield: 42%; ¹H NMR (acetone-*d*₆, 600 MHz) δ: 7.03 (d, *J* = 8.6 Hz, 2H), 7.11–7.15 (m, 3H), 7.26 (d, *J* = 8.6 Hz, 1H), 7.35 (dd, *J* = 8.6, 8.4 Hz, 2H), 7.39–7.47 (m, 5H), 7.71 (d, *J* = 8.6 Hz, 1H), 7.85 (d, *J* = 8.6 Hz, 1H), 7.85 (s, 1H); MS (EI) *m/z* (%): 373 (M⁺).

Synthesis of 2,5-bis{4-[2-naphthyl(phenyl)amino]-phenyl}thiophene (BNpA-1T)

A THF solution (30 mL) containing *N*-(4-bromophenyl)-*N*-phenyl-2-naphthylamine (**1**, 11.5 g, 31 mmol) in the presence of magnesium (0.90 g, 37 mmol) was stirred for 24 h at room temperature under nitrogen atmosphere to give the Grignard reagent. The resulting solution was added to a THF solution (20 mL) containing 2,5-dibromothiophene (1.87 g, 7.8 mmol) in the presence of NiCl₂(dppp) (84 mg, 0.15 mmol), and stirred for 24 h to give **BNpA-1T**, which was purified by silica-gel column chromatography using a mixed solvent of toluene and hexane (1:4 V/V) as an eluent, followed by reprecipitation from toluene to hexane. Yield: 14%; ¹H NMR (THF-*d*₈, 600 MHz) δ: 7.00 (t, *J* = 8.6 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 4H), 7.10 (d, *J* = 8.6 Hz, 4H), 7.22–7.24 (m, 6H), 7.25 (s, 2H), 7.29 (dd, *J* = 8.6, 8.4 Hz, 2H), 7.32 (dd, *J* = 8.6, 8.4 Hz, 2H), 7.43 (s, 2H), 7.52 (d, *J* = 8.6 Hz, 4H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.72 (d, *J* = 8.6 Hz, 4H); ¹³C NMR (THF-

*d*₈, 150 MHz) δ: 121.4, 124.0, 124.1, 124.8, 125.1, 125.3, 125.3, 126.9, 127.7, 128.2, 129.7, 129.8, 130.1, 131.3, 135.5, 143.3, 146.0, 148.1, 148.5; MS (EI) *m/z* (%): 670 (M⁺); Anal. calcd for C₄₈H₃₄N₂S: C 85.93, H 5.11, N 4.18, S, 4.78; found C 85.65, H 5.39, N 4.17, S 4.79.

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