A Novel Class of Emitting Amorphous Molecular Materials with Bipolar Character for Electroluminescence

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A novel class of color-tunable emitting amorphous molecular materials with desired bipolar character, 4-dimesitylboryl-*N*,*N*-bis(9,9-dimethylfluoren-2-yl)aniline (FlAMB-0T), 2-{4-[bis-(9,9-dimethylfluoren-2-yl)amino]phenyl}-5-(dimesitylboryl)thiophene (FlAMB-1T), 2-{4-[bis-(9,9-dimethylfluoren-2-yl)amino]phenyl}-2′-dimesitylboryl-5,5′-bithiophene (FlAMB-2T), and 5-{4-[bis(9,9-dimethylfluoren-2-yl)amino]phenyl}-5″-dimesitylboryl-2,2′:5′,2″-terthiophene (FlAMB-3T), have been designed and synthesized. This novel class of compounds is characterized by reversible anodic oxidation and cathodic reduction, intense fluorescence emission, and ready formation of stable amorphous glasses with high glass-transition temperatures above 120 °C. They function as excellent emitting materials for organic electroluminescent (EL) devices, emitting multicolor light including white. They also serve as good host materials for emissive dopants in organic EL devices, permitting color tuning and leading to higher performance.

Introduction

Small organic molecules generally tend to crystallize very readily; however, it has been revealed that they can also form stable amorphous glasses if their molecular structures are properly designed. In recent years, the amorphous glasses of small molecules, i.e., amorphous molecular materials, have been receiving a great deal of attention as a new class of functional organic materials, and such studies have been opening up a new field of organic materials science that deals with molecular glasses which are in the thermodynamically nonequilibrium state. The amorphous glasses are attractive as materials because of their isotropic properties, homogeneous properties due to the absence of grain boundaries, and ease of uniform film formation. We have performed a series of studies on the creation of amorphous molecular materials and investigated their structures, reactions, properties, and applications.[1] We have proposed several new concepts for photo- and electroactive amorphous molecular materials, which include electrically conducting amorphous molecular materials,[1c,2] photochromic amorphous molecular materials,[3] molecular resists for nanolithography,[4] and materials for photovoltaic devices[1a,5] and organic electroluminescent (EL) devices.[6] Amorphous molecular materials, which are characterized by well-defined glass-transition phenomena and ready formation of uniform amorphous films by vapor deposition and/or spin coating from solution, have demonstrated their suitability and versatility for use in optoelectronic and photonic devices, in particular, organic EL devices.[1d,7,8]

Organic EL devices have been the subject of recent extensive studies in view of both academic interest and application for displays and lightning.[1d,7−11] The development of high-performance materials is a key issue for the fabrication of high-performance organic EL devices. We report here the synthesis and properties of a novel class of high-performance emitting amorphous molecular materials for electroluminescence based on a new molecular design concept.

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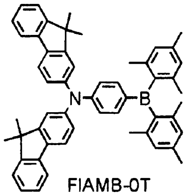
In any type of organic EL device consisting of a single emitting layer and multilayers using additional charge-transport layers, the emitting layer functions as the recombination center for the holes and electrons injected from the anode and cathode. The generated electronically excited-state molecule of the emitting layer either emits luminescence or serves as a host that transfers its excitation energy to a luminescent dopant. Therefore, materials for use in the emitting layer should meet the requirements of energy level matching for charge carrier injection and acceptance of both holes and electrons, and should desirably possess bipolar character, i.e., both electron-donating and electron-accepting properties, to permit the formation of both stable cation and anion radicals. In addition, the emitting materials should form homogeneous thin films with morphological and thermal stability and exhibit intense fluorescence.

Among a number of reported materials for use in the emitting layer in organic EL devices, tris(8-quinolinolato)aluminum (Alq$_3$) has been most widely used as a green emitter or a host material for luminescent dopants.[9] However, its anodic oxidation is irreversible,[12] and the instability of the Alq$_3$ cation radical is thought to lead to a long-term degradation of Alq$_3$-based organic EL devices, causing a significant decrease in the efficiency of luminescence.[13] Other emitting materials, including only scarce examples of materials with bipolar character, e.g., compounds having an 1,3,4-oxadiazole moiety, have also been reported.[14−20] However, the redox properties of most of the reported materials have not been studied in detail, with some materials undergoing irreversible oxidation or reduction. Ruthenium(II) complexes have bipolar character,[19] but do not form uniform thin films by themselves.

On the basis of the concepts described above for materials for use in the emitting layer in organic EL devices, we have designed and synthesized a novel class of compounds that form amorphous glasses, 4-dimesitylboryl-*N*,*N*-bis(9,9-dimethylfluoren-2-yl)aniline (FlAMB-0T), 2-{4-[bis(9,9-dimethylfluoren-2-yl)amino]phenyl}-5-(dimesitylboryl)thiophene (FlAMB-1T), 2-{4-[bis(9,9-dimethylfluoren-2-yl)amino]phenyl}-2′-dimesitylboryl-5,5′-bithiophene (FlAMB-2T), and 5-{4-[bis(9,9-dimethylfluoren-2-yl)amino]phenyl}-5″-dimesitylboryl-2,2′:5′,2″-terthiophene (FlAMB-3T), and investigated their properties and application as materials in organic EL devices. It was expected that the variation of the π-conjugation length of the central thiophene unit would affect the energy levels of both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of FlAMB-*n*T (n = 0, 1, 2, and 3), leading to the tuning of the emission color.[6c] Organic EL devices using oligothiophenes and oligothiophene-based polymers as emitters have been reported.[21] As it will be shown below, the present novel class of amorphous molecular materials, FlAMB-*n*T (n = 0, 1, 2, and 3), function not only as excellent color-tunable emitting materials but also as host materials for emissive dopants in organic EL devices. To the best of our knowledge, FlAMB-*n*T (n = 0, 1, 2, and 3) are the first definite examples of emitting amorphous molecular materials that fulfill all the requirements described above. A part of the present work on FlAMB-1T has been reported as a communication.[6e]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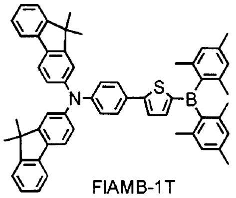
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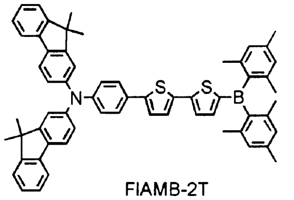
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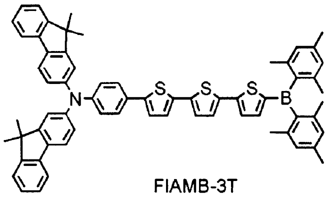
FlAMB-3T

Experimental Section

Materials. Fluorene was purchased from Tokyo Chemical Industry Co., Ltd. and purified by recrystallization from ethanol. Aniline was purchased from Wako Pure Chemical Industries Ltd. and purified by distillation immediately before use. 2-Thiopheneboronic acid and dimesitylboron fluoride were purchased from Lancaster and Aldrich, respectively, and used without further purification. 4,4′,4″-Tris[3-methylphenyl(phenyl)amino]triphenylamine (*m*-MTDATA) was prepared according to our previous publication.[1a] Alq$_3$ was obtained from Shin-Nittetsu Chemical Co., Ltd. 5,5′-Bis(dimesitylboryl)-2,2′-bithiophene (BMB-2T) was prepared as described in our previous paper.[6c] Gel permeation chromatography was performed by using an LC-908 recycling preparative HPLC (Japan Analytical Industry Co., Ltd.) with two columns for the separation of low-molecular-weight organic compounds, JAIGEL-1H and JAIGEL-2H (a kind of styrene polymer gel).

Synthesis of 2-Iodofluorene (I). 2-Iodofluorene (**I**) was synthesized by the iodination of fluorene (100 g, 602 mmol) with iodine (80 g, 320 mmol) in the presence of ortho-periodinic acid (H$_5$IO$_6$) (20 g, 88 mmol) in 80% acetic acid aqueous solution at 80 °C for 4 h under nitrogen atmosphere. After the solution was cooled, the solvent was removed by decantation, and a brown solid was obtained. This was dissolved in toluene and washed with 5% NaHSO$_3$ aqueous solution to remove the remaining iodine. Then, the resulting solid was purified by alumina column chromatography using toluene as an eluent, followed by recrystallization from toluene. Yield: 105 g (60%), mp 131 °C.

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Synthesis of 9,9-Dimethyl-2-iodofluorene (II). 2-Iodofluorene (**I**) (60 g, 205 mmol) was dissolved in tetrahydrofuran (THF) and treated with potassium *tert*-butoxide (24 g, 214 mmol) to give red solution, followed by methylation with methyliodide (30.4 g, 214 mmol). This procedure was repeated once more to yield 9,9-dimethyl-2-iodofluorene (**II**). The compound was purified by silica gel column chromatography using hexane as an eluent, followed by vacuum distillation. Yield: 49.2 g (75%), mp 63 °C.

Synthesis of *N,N*-Bis(9,9-dimethylfluoren-2-yl)aniline (III). *N*,*N*-Bis(9,9-dimethylfluoren-2-yl)aniline (**III**) was synthesized by the Ullmann reaction of 9,9-dimethyl-2-iodofluorene (**II**) (50 g, 156 mmol) with aniline (5.5 g, 59 mmol) in mesitylene at 170 °C for 8 h in the presence of copper powder (7.5 g), potassium carbonate (35 g), and 18-crown-6-ether (1.5 g), and purified by silica gel column chromatography using toluene/hexane as an eluent, followed by recrystallization from toluene/hexane. Yield: 20 g (71%), mp 196 °C.

Synthesis of *N,N*-Bis(9,9-dimethylfluoren-2-yl)-4-bromoaniline (IV). *N*,*N*-Bis(9,9-dimethylfluoren-2-yl)-4-bromoaniline (**IV**) was synthesized by the bromination of *N*,*N*-bis(9,9-dimethylfluoren-2-yl)aniline (**III**) (10 g, 21 mmol) with *N*-bromosuccinimide (3.6 g, 21 mmol) in chloroform at room temperature for 1 h. It was purified by silica gel column chromatography using toluene as an eluent, followed by recrystallization from toluene. Yield: 11.3 g (95%), mp 189 °C.

Synthesis of 5-[2,2′-Bithiophene]boronic Acid. 2,2′-Bithiophene (5.0 g, 30 mmol) was lithiated with hexane solution of *n*-butyllithium (1.6 M, 28 mL) in THF at 0 °C under nitrogen atmosphere. Then, it was reacted with trimethylborate (6.2 g, 60 mmol), followed by hydrolysis with water to give 5-[2,2′-bithiophene]boronic acid. Yield: 5.9 g (94%).

Synthesis of 5-[2,2′;5′,2″-Terthiophene]boronic Acid. 2,2′;5′,2″-Terthiophene (10 g, 40 mmol) was lithiated with hexane solution of *n*-butyllithium (1.6 M, 37.5 mL) in THF at 0 °C under nitrogen atmosphere. Then, it was reacted with trimethylborate (8.3 g, 80 mmol), followed by hydrolysis with water to give 5-[2,2′;5′,2″-terthiophene]boronic acid. Yield: 9.8 g (84%).

Synthesis of 2-[*N,N*-Bis(9,9-dimethylfluoren-9-yl)phenyl]thiophene (VI). 2-[*N*,*N*-Bis(9,9-dimethylfluoren-2-yl)phenyl]thiophene (**VI**) was synthesized by the Suzuki coupling reaction of *N*,*N*-bis(9,9-dimethylfluoren-2-yl)-4-bromoaniline (**IV**) (4.0 g, 7.0 mmol) with 2-thiopheneboronic acid (2.0 g, 15.6 mmol) in THF/2 N potassium carbonate aqueous solution at 70 °C for 8 h under nitrogen atmosphere in the presence of tetrakis(triphenylphosphine)palladium(0) (0.8 g, 0.7 mmol). It was purified by silica gel column chromatography using toluene/hexane as an eluent, followed by recrystallization from toluene/hexane solution. Yield: 3.2 g (83%), mp 222 °C.

Synthesis of 2-[*N,N*-Bis(9,9-dimethylfluoren-2-yl)phenyl]-5,5′-bithiophene (VIII). 2-[*N*,*N*-Bis(9,9-dimethylfluoren-2-yl)phenyl]-5,5′-bithiophene (**VIII**) was synthesized by the Suzuki coupling reaction of *N*,*N*-bis(9,9-dimethylfluoren-2-yl)-4-bromoaniline (**VI**) (2.0 g, 3.5 mmol) with 5-[2,2′-bithiophene]boronic acid (2.0 g, 9.4 mmol) in THF/2 N potassium carbonate aqueous soluition at 70 °C for 8 h under nitrogen atmosphere in the presence of tetrakis(triphenylphosphine)palladium(0) (0.5 g, 0.4 mmol). It was purified by silica gel column chromatography using toluene/hexane as an eluent, followed by recrystallization from toluene/hexane solution. Yield: 1.5 g (66%), mp 220 °C.

Synthesis of 2-[*N,N*-Bis(9,9-dimethylfluoren-2-yl)phenyl]-5,2′:5′,2″-terthiophene (X). 2-[*N*,*N*-Bis(9,9-dimethylfluoren-2-yl)phenyl]-5,2′:5′,2″-terthiophene (**X**) was synthesized by the Suzuki coupling reaction of *N*,*N*-bis(9,9-dimethylfluoren-2-yl)-4-bromoaniline (**IV**) (2.0 g, 3.5 mmol) with 5-[2,2′;5′,2″-terthiophene]boronic acid (2.4 g, 8.0 mmol) in THF/2 N potassium carbonate aqueous solution at 70 °C for 8 h under nitrogen atmosphere in the presence of tetrakis(triphenylphosphine)palladium(0). It was purified by silica gel column chromatography using toluene/hexane as an eluent, followed by recrystallization from toluene/hexane solution. Yield: 2.0 g (79%), mp 256 °C.

Synthesis of FlAMB-0T. *N*,*N*-Bis(9,9-dimethylfluoren-2-yl)-4-bromoaniline (**IV**) (4.0 g, 7.2 mmol) was lithiated with a heptane solution of *tert*-butyllithium (1.6 M, 6.8 mL) in THF at −78 °C under nitrogen atmosphere. Then, THF solution of dimesitylboron fluoride (4.3 g, 16.4 mmol) was added to the lithiated *N*,*N*-bis(9,9-dimethylfluoren-2-yl)-4-bromoaniline (**V**) at −78 °C and stirred for 8 h under nitrogen atmosphere to give FlAMB-0T. It was purified by silica gel column chromatography using toluene/hexane as an eluent, followed by recrystallization from THF/ethanol solution. Yield: 2.5 g (48%). The compound was further purified by the same procedures of column chlomatography and recrystallization from solution, mp 281 °C.

MS: *m/e* 725 (M^+). ^1H NMR (600 MHz, THF-d_8) d (ppm): 7.68 (2H, d, $J = 8.2$), 7.67 (2H, d, $J = 7.5$), 7.40 (2H, d, $J = 7.3$), 7.38 (2H, d, $J = 8.9$), 7.34 (2H, s), 7.27 (2H, t, $J = 7.5$), 7.22 (2H, t, $J = 7.5$), 7.17 (2H, d, $J = 8.1$), 7.04 (2H, d, $J = 8.9$), 6.78 (4H, s), 2.25 (6H, s), 2.07 (12H, s), 1.40 (12H, s). Anal. Calcd for $C_{54}H_{52}BN$: C, 89.36; H, 7.22; N, 1.93. Found: C, 89.13; H, 7.14; N, 1.96. UV−vis (THF): λ_{max} (nm) (log ϵ) 365 (4.5), 402 (4.6). PL (THF): λ_{max} (nm) 505.

Synthesis of FlAMB-1T. 2-[*N*,*N*-Bis(9,9-dimethylfluoren-2-yl)phenyl]thiophene (**VI**) (3.0 g, 5.4 mmol) was lithiated with a hexane solution of *n*-butyllithium (1.6 M, 6.7 mL) in THF at −78 °C under nitrogen atmosphere. Then, a THF solution of dimesitylboron fluoride (2.68 g, 10 mmol) was added to the lithiated 2-[*N*,*N*-bis(9,9-dimethylfluoren-2-yl)phenyl]thiophene (**VII**) at −78 °C and stirred for 8 h under nitrogen atmosphere to give FlAMB-1T. It was purified by silica gel column chromatography using toluene/hexane as an eluent, followed by recrystallization from THF/ethanol solution. Yield: 2.2 g (50%). The compound was further purified by the same procedures of column chlomatography and recrystallization from solution, mp 274 °C.

MS: *m/e* 807 (M^+). ^1H NMR (600 MHz, THF-d_8) d (ppm): 7.69−7.61 (6H, m), 7.53 (1H, d, $J = 4.0$), 7.40 (2H, d, $J = 7.3$), 7.37 (2H, d, $J = 3.7$), 7.26 (2H, t, $J = 7.3$), 7.21 (2H, t, $J = 7.3$), 7.15 (2H, d, $J = 8.6$), 7.08 (2H, d, $J = 8.3$), 6.82 (4H, s), 2.27 (6H, s), 2.15 (12H, s), 1.40 (12H, s). Anal. Calcd for $C_{58}H_{54}BNS$: C, 86.22; H, 6.74; N, 1.73; S, 3.97. Found: C, 86.27; H, 6.99; N, 1.73; S, 3.85. UV−vis (THF): λ_{max} (nm) (log ϵ) 337 (4.6), 368 (4.6), 435 (4.6). PL (THF): λ_{max} (nm) 537.

Synthesis of FlAMB-2T. 2-[*N*,*N*-Bis(9,9-dimethylfluoren-2-yl)phenyl]-5,5′-bithiophene (**VIII**) (1.3 g, 2.0 mmol) was lithiated with a hexane solution of *n*-butyllithium (1.6 M, 5.0 mL) in THF at −78 °C under nitrogen atmosphere. Then, a THF solution of dimesitylboron fluoride (2.68 g, 10 mmol) was added to the lithiated 2-[*N*,*N*-bis(9,9-dimethylfluoren-2-yl)phenyl]-5,5′-bithiophene (**IX**) at −78 °C and stirred for 8 h under nitrogen atmosphere to give FlAMB-2T. It was purified by silica gel column chromatography using toluene/hexane as an eluent, followed by recrystallization from THF/ethanol solution. Yield 460 mg (26%). The compound was further purified by column chromatography, gel permeation chromatography, and recrystallization.

MS: *m/e* 889 (M^+). ^1H NMR (750 MHz, THF-d_8) d (ppm): 7.67 (2H, d, $J = 7.5$), 7.65 (2H, d, $J = 8.2$), 7.55 (2H, d, $J = 8.8$), 7.41−7.39 (3H, m), 7.35 (2H, d, $J = 3.9$), 7.33 (2H, d, $J = 3.8$), 7.36−7.28 (6H, m), 7.26 (2H, t, $J = 7.4$), 7.21 (2H, t, $J = 7.5$), 7.19−7.15 (4H, m), 7.08 (2H, d, $J = 8.0$), 6.81 (4H, s), 2.27 (6H, s), 2.15 (12H, s), 1.40 (12H, s). Anal. Calcd for $C_{62}H_{56}BNS_2$: C, 83.66; H, 6.34; N, 1.57; S, 7.21. Found: C, 83.74; H, 6.50; N, 1.52; S, 6.98. UV−vis (THF): λ_{max} (nm) (log ϵ) 363 (4.7), 446 (4.7). PL (THF): λ_{max} (nm) 566.

Synthesis of FlAMB-3T. 2-[*N*,*N*-Bis(9,9-dimethylfluoren-2-yl)phenyl]-5,2′:5′,2″-terthiophene (**X**) (1.0 g, 1.4 mmol) was lithiated with a hexane solution of *n*-butyllithium (1.6 M, 5.0 mL) in THF at −78 °C under nitrogen atmosphere. Then, a THF solution of dimesitylboron fluoride (2.68 g, 10 mmol) was added to the lithiated 2-[*N*,*N*-bis(9,9-dimethylfluoren-2-yl)phenyl]thiophene (**XI**) at −78 °C and stirred for 8 h under nitrogen atmosphere to give FlAMB-3T. It was purified by silica gel column chromatography using toluene/hexane as an eluent, followed by recrystallization from THF/ethanol solution. Yield: 270 mg (20%). The compound was further purified by column chromatography, gel permeation chromatography, and recrystallization.

MS: *m/e* 972 (M$^+$). ^{1}H NMR (600 MHz, THF-d_8) d (ppm): 7.69−7.65 (4H, m), 7.55 (2H, d, J = 8.3), 7.42−7.39 (3H, m), 7.34 (1H, d, J = 4.0), 7.33−7.31 (3H, m), 7.29 (1H, d, J = 4.0), 7.27(2H, t, J = 7.4), 7.24−7.20 (3H, m), 7.20 (1H, d, J = 4.0), 7.16 (2H, d, J = 8.8), 7.09 (2H, d, J = 8.0), 6.82 (4H, s), 2.27 (6H, s), 2.14 (12H, s), 1.40 (12H, s). Anal. Calcd for $C_{66}H_{58}BNS_3$: C, 81.54; H, 6.01; N, 1.44; S, 9.90. Found: C, 81.26; H, 6.06; N, 1.44; S, 9.83. UV−vis (THF): λ_{max} (nm) (log ϵ) 372 (4.6), 457 (4.6). PL (THF): λ_{max} (nm) 582.

Cyclic Voltammetry. Cyclic voltammetry was performed for dichloromethane or THF solution of FlAMB-nT (1.0×10^{-3} M) containing tetra-*n*-butylammonium perchlorate (0.1 M), using a platinum disk (1.6 mm diameter) and a platinum wire as the working and counter electrodes, respectively, and Ag/AgNO$_3$ (0.01 M in acetonitrile) as the reference electrode. Scan rate was 500 mV s^{-1}.

Fabrication of Hole- and Electron-Only Devices and Organic EL Devices. Hole-only devices were fabricated by sequential vacuum deposition of organic materials onto an indium−tin-oxide (ITO)-coated glass substrate, followed by vacuum deposition of silver onto the organic layer. Electron-only devices were fabricated by vacuum deposition of aluminum onto glass substrate and sequential vacuum deposition of organic materials onto aluminum, followed by vacuum deposition of lithium fluoride and aluminum onto the organic layer. Organic EL devices were fabricated by sequential vacuum deposition of organic materials onto an ITO-coated glass substrate, followed by vacuum deposition of lithium fluoride and aluminum onto the organic layer. Vacuum deposition of organic materials was carried out at a deposition rate of 0.2−0.3 nm s^{-1} at 10^{-5} Torr. The ITO electrode (ca. 14 Ω sq^{-1}, Sanyo Vacuum Industries) was cleaned by being immersed in an ultrasonic bath of 1,1,1-trichloroethane, followed by exposure to hot acetone vapor and UV ozone immediately before use. The same cleaning procedure was also performed for the glass substrate (Matsunami micro slide glass S-111) before use.

Apparatuses. Electronic absorption spectra of FlAMB-*n*T (n = 0, 1, 2, and 3) were measured with a Hitachi U-3500 spectrophotometer. Cyclic voltammetry was performed using a BAS 100B. Photoluminescence (PL) and electroluminescence (EL) spectra were measured with a Hitachi model F-4500 fluorescence spectrometer. The photoluminescence lifetime was measured by a single-photon counting technique with a Horiba NAES-550 time-resolved spectrofluorometer. The current versus voltage and luminance versus voltage characteristics were measured using an Advantest TR6143 electrometer and a Minolta LS-100 photoluminance meter. Differential scanning calorimetry (DSC) was carried out with a Seiko Instruments DSC220C. Fluorescence lifetime was measured for THF solution by a single-photon counting technique with a Horiba NAES-550 time-resolved spectrofluorometer.

Results and Discussion

Design and Synthesis of FlAMB-*n*T. The molecular design of FlAMB-*n*T is based on the following considerations. To provide desired bipolar character, both electron-donating and electron-accepting moieties that undergo reversible oxidation and reduction, respectively, are introduced in the molecule through a central π-conjugated system. Thus, the incorporation of the difluorenyl(phenyl)amine and dimesitylboron moieties, which are π-conjugated through the central thiophene rings, is intended to provide both electron-donating and accepting properties, respectively, and also to facilitate formation of amorphous glasses due to their nonplanar molecular structures. The introduction of the rigid fluorenyl moiety is also expected to raise the glass-transition temperature (T_g). It is expected that the central thiophene ring controls the HOMO and LUMO energy levels depending upon its π-conjugation length and that the tuning of emission color can be performed by varying the conjugation length of the central thiophene unit.

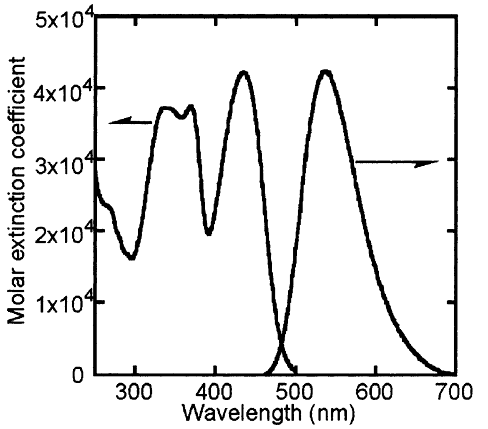


Figure 1. Electronic absorption and fluorescence spectra of FlAMB-1T in THF solution.

Table 1. Electronic Absorption Band Maxima (λ^{abs}_{max}) with Molar Extinction Coefficients (ϵ), Fluorescence Band Maxima (λ^{f}_{max}) with Fluorescence Quantum Efficiencies (Φ_f), and Fluorescence Lifetimes (τ_f) of FlAMB-*n*T (n = 0, 1, 2, and 3)

compound	λ^{abs}_{max} (nm)[a]	log ϵ	λ^{f}_{max} (nm)[a]	Φ_f[b]	τ_f (ns)[a]
FlAMB-0T	402	4.6	505	0.45	4.3
FlAMB-1T	435	4.6	537	0.50	3.7
FlAMB-2T	446	4.7	566	0.23	3.6
FlAMB-3T	457	4.6	582	0.14	1.6

[a] In THF solution. [b] Determined with reference to aqueous sulfuric acid solution of quinine sulfate.

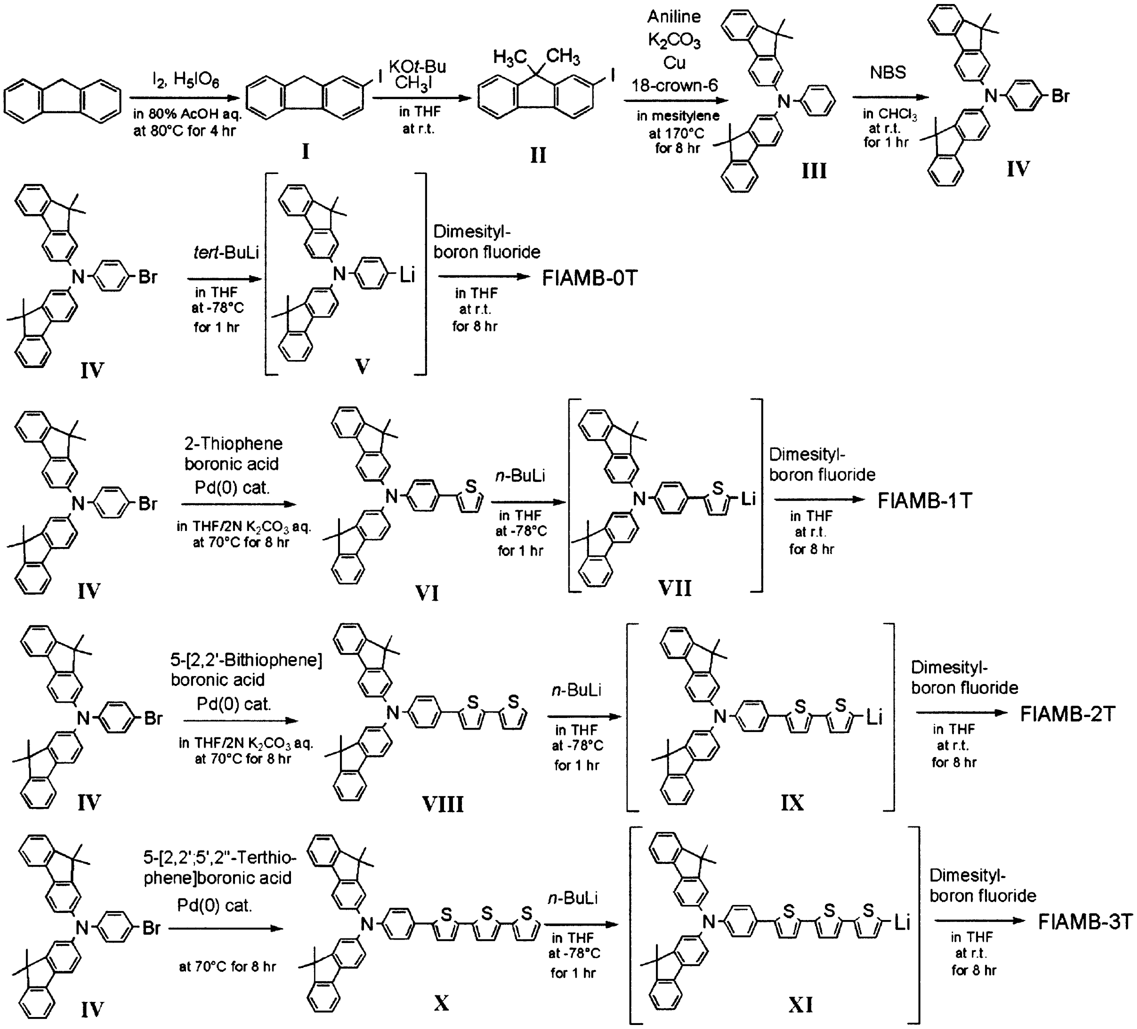
The synthetic procedures of FlAMB-*n*T are shown in Scheme 1. FlAMB-0T was synthesized by the coupling reaction of dimesitylboronfluoride with lithiated *N*,*N*-bis(9,9-dimethylfluoren-2-yl)aniline (V), which was synthesized starting from fluorene. FlAMB-*n*T (n = 1, 2, and 3) were also synthesized by the coupling reaction of dimesitylboron fluoride with lithiated [*N*,*N*-bis(9,9-dimethylfluoren-2-yl)phenyl]oligothiophenes, which were obtained by the Suzuki coupling reaction of *N*,*N*-bis-(9,9-dimethylfluoren-2-yl)-4-bromoaniline (IV) with thiophene- and oligo(bi and ter)thiophene-boronic acid.

As described later in detail, these compounds are characterized by reversible oxidation and reduction, intense fluorescence emission, and ready formation of stable amorphous glasses with relatively high T_gs above 120 °C.

Molecular Properties of FlAMB-*n*T. Figure 1 shows the electronic absorption and fluorescence spectra of FlAMB-1T. FlAMB-*n*T (n = 0, 1, 2, and 3) exhibit intense greenish blue, green, yellow green, and yellow fluorescences for n = 0, 1, 2, and 3, respectively. Table 1 summarizes the electronic absorption band maxima together with molar extinction coefficients, the fluorescence band maxima, fluorescence quantum efficiencies, and fluorescence lifetimes of FlAMB-*n*T (n = 0, 1, 2, and 3) in THF solution.

FlAMB-*n*T (n = 0, 1, 2, and 3) were found to undergo both reversible anodic oxidation and cathodic reduction to form stable cation and anion radicals. Figure 2 shows

Scheme 1. Synthetic Routes of FlAMB-*n*T



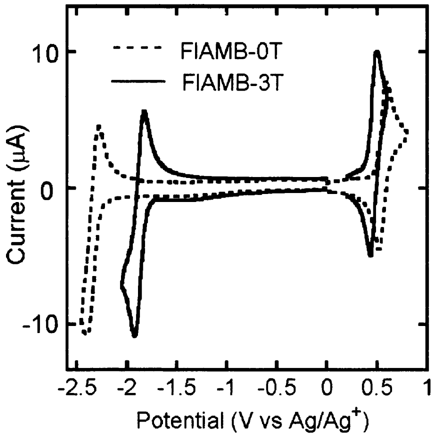


Figure 2. Cyclic voltammograms of FlAMB-0T and FlAMB-3T. Measured in dichloromethane (for oxidation) and THF (for reduction). Scan rate: 500 mV s^{-1}.

cyclic voltammograms of FlAMB-0T and FlAMB-3T. Both compounds exhibited one anodic and one cathodic wave on oxidation and reduction, respectively, together with their corresponding cathodic and anodic waves. The i_{pc}/i_{pa} calculated according to the Nicholson equation[22] was almost unity for the anodic oxidation and cathodic reduction processes for all the coumpounds. When the scan was repeated in the region between −2.4 and 0.8 V vs Ag/Ag^+ (0.01 M), the same trace was obtained. Thus, FlAMB-*n*T ($n = 0$, 1, 2, and 3) possess bipolar character, generating stable cation and anion radicals. Table 2 summarizes the half-wave oxidation and reduction potentials of FlAMB-*n*T ($n = 0$, 1, 2, and 3). The results show that the oxidation potential gradually decreases and the reduction potential becomes increasingly more positive with increasing conjugation length of the central thiophene rings, leading to the differences of 0.09 and 0.48 V, respectively, between $n = 0$ and $n = 3$. That is, the HOMO−LUMO energy gap decreases by 0.57 eV with increasing conjugation length of the thiophene unit from 0 to 3. Thus, it was revealed that the π-conjugation length of the thiophene rings finely controls the HOMO and LUMO energy gap. These electrochemical data are in agreement with the spectroscopic results that the electronic absorption and fluorescence bands of FlAMB-*n*T ($n = 0$, 1, 2, and 3) undergo red shift with increasing conjugation length of the thiophene unit. The HOMO−LUMO energy gaps determined from the oxidation and reduction potentials are in agreement with those estimated from the edges of the electronic absorption bands (Table 2).

Glass-Forming Properties of FlAMB-*n*T. FlAMB-*n*T ($n = 0$, 1, 2, and 3) were found to form stable

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[22] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods Fundamentals and Applications*; John Wiley & Sons: New York, 2001; p 240.

Table 2. Half-Wave Oxidation and Reduction Potentials ($E_{1/2}^{ox}$ and $E_{1/2}^{red}$) and HOMO−LUMO Energy Gaps for FlAMB-*n*T ($n = 0, 1, 2,$ and 3)

compound	$E_{1/2}^{ox}$ (V vs Ag/Ag$^+$)[a]	$E_{1/2}^{ox}$ (V vs Fc/Fc$^+$)[b]	$E_{1/2}^{red}$ (V vs Ag/Ag$^+$)[a]	$E_{1/2}^{red}$ (V vs Fc/Fc$^+$)[b]	HOMO−LUMO energy gap (eV)[c]
FlAMB-0T	0.56	0.36	−2.35	−2.51	2.87 (2.83)
FlAMB-1T	0.51	0.31	−2.01	−2.17	2.48 (2.60)
FlAMB-2T	0.48	0.28	−1.95	−2.11	2.39 (2.43)
FlAMB-3T	0.47	0.27	−1.87	−2.03	2.30 (2.36)

[a] Determined by cyclic voltammetry in dichloromethane (for oxidation) and THF (for reduction) with Ag/AgNO$_3$ (0.01 M) as a reference electrode. Scan rate: 500 mV s^{-1}. [b] Redox potentials vs ferrocene/ferricinium (Fc/Fc$^+$) was calibrated by the use of $E_{1/2}^{ox}$ for ferrocene (0.20 and 0.16 V vs Ag/AgNO$_3$ (0.01 M) in dichloromethane and THF, respectively). [c] Determined from oxidation and reduction potentials. The values in the parentheses were estimated from the edge of the electronic absorption band.

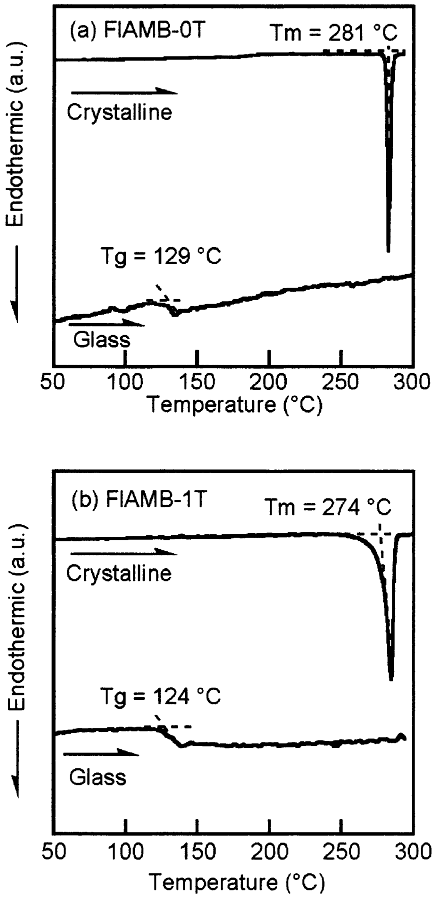

Figure 3. DSC curves of FlAMB-0T and FlAMB-1T. Heating rate: 5 °C min^{-1}.

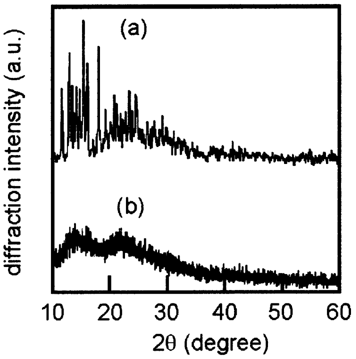

Figure 4. X-ray diffraction patterns of FlAMB-0T: (a) crystal sample and (b) glass sample.

amorphous glasses with high T_gs above 120 °C, as evidenced by polarizing microscopy, differential scanning calorimetry (DSC), and X-ray diffraction. Although FlAMB-0T and FlAMB-1T were obtained as polycrystals by recrystallization from THF/ethanol solution, FlAMB-2T and FlAMB-3T were obtained as amorphous powders despite attempted recrystallization from solution. Figure 3 shows DSC curves of FlAMB-*n*T (n = 0 and 1). The DSC measurement revealed that upon heating of the crystalline samples of FlAMB-0T and FlAMB-1T obtained by recrystallization from solution, they melted at 280 and 298 °C, respectively, to give isotropic liquids. When the isotropic liquids were cooled on standing in air, they formed transparent, stable amorphous glasses via a supercooled liquid state. When the glass samples of FlAMB-0T and FlAMB-1T were heated, glass transition took place at 129 and 124 °C, respectively. The amorphous glass samples of FlAMB-2T and FlAMB-3T showed glass-transition phenomena at 127 and 131 °C, respectively. The relatively high T_gs for FlAMB-*n*T are attributed to the incorporation of a rigid fluorene moiety. The increase of T_g by the incorporation of rigid moieties such as carbazole and fluorene has been shown for other amorphous molecular materials.[6a,23] The stability of amorphous glasses was further examined with respect to FlAMB-0T and FlAMB-1T which were obtained as crystals from solution. It was found that the amorphous glasses of FlAMB-*n*T (n = 0 and 1) did not undergo crystallization on heating above their T_gs even at a slower heating rate in DSC measurements (Figure 3), e.g., 1 °C min^{-1}, and on annealing at temperatures close to their T_gs for more than 10 h. It is suggested that the amorphous glasses of FlAMB-*n*T (n = 0, 1, 2, and 3) are very stable. Figure 4 shows the X-ray diffraction patterns of the FlAMB-0T crystal and glass samples. The amorphous glass sample showed only a broad halo in its X-ray diffraction patterns in contrast to sharp peaks characteristic of the crystal. FlAMB-*n*T (n = 0, 1, 2, and 3) form uniform amorphous films by vacuum deposition and spin coating from solution.

Hole- and Electron-Only Devices Using FlAMB-*n*T. Reversible, anodic oxidation and cathodic reduction of FlAMB-*n*T (n = 0, 1, 2, and 3) indicates that these compounds possess bipolar character. To examine whether FlAMB-*n*T can actually permit the injection of both holes and electrons from the electrodes and transport them in solid devices, hole- and electron-only devices using FlAMB-1T were fabricated, in which only holes and electrons, respectively, are injected from the electrodes: ITO/*m*-MTDATA(50 nm)/FlAMB-1T(150 nm)/Ag (device H1) and Al/FlAMB-1T(150 nm)/Alq$_3$(50 nm)/LiF(0.5 nm)/Al (device E1). For comparison, the corresponding hole- and electron-only devices using well-

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(23) (a) Okumoto, K.; Shirota, Y. *Chem. Lett.* **2000**, 1834. (b) Okumoto, K.; Noda, T.; Ohara, T.; Shirota, Y. *Synth. Met.* **2001**, *121*, 1655.

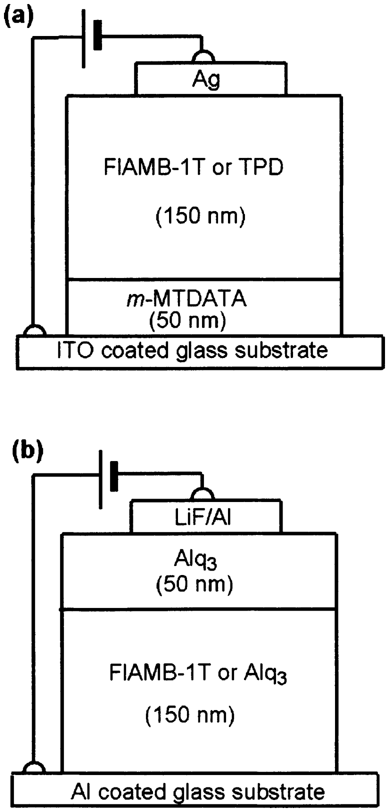

Figure 5. Side view of (a) hole-only devices: ITO/*m*-MTDATA(50 nm)/FlAMB-1T(150 nm)/Ag (device H1) and ITO/*m*-MTDATA(50 nm)/TPD(150 nm)/Ag (device H2); and (b) electron-only devices: Al/FlAMB-1T(150 nm)/Alq_3(50 nm)/LiF(0.5 nm)/Al (device E1) and Al/Alq_3(200 nm)/LiF(0.5 nm)/Al (device E2).

known hole and electron transporters, *N,N′*-bis(3-methylphenyl)-*N,N′*-diphenyl-[1,1′-biphenyl]-4,4′-diamine (TPD) and Alq_3, respectively, were also fabricated: ITO/*m*-MTDATA(50 nm)/TPD(150 nm)/Ag (device H2) and Al/Alq_3(200 nm)/LiF(0.5 nm)/Al (device E2). The side views of the fabricated hole-only and electron-only devices are shown in Figure 5. Figure 6 (a) and (b) show voltage–current density characteristics for the hole- and electron-only devices, respectively. The results show that both hole and electron currents flow for the hole- and electron-only devices using FlAMB-1T, respectively, being comparable to those for the hole- and electron-only devices using TPD and Alq_3, respectively. It is indicated that both holes and electrons are injected from the ITO and LiF/Al electrodes, respectively, into FlAMB-1T through the *m*-MTDATA or Alq_3 layer and that injected holes and electrons are transported through the FlAMB-1T layer to the counter electrodes in solid devices. On the other hand, the injected current density for the electron-only device using TPD, Al/TPD(150 nm)/Alq_3(50 nm)/LiF(0.5 nm)/Al, was approximately 2 orders of magnitude smaller than those for the electron-only devices using FlAMB-1T and Alq_3.

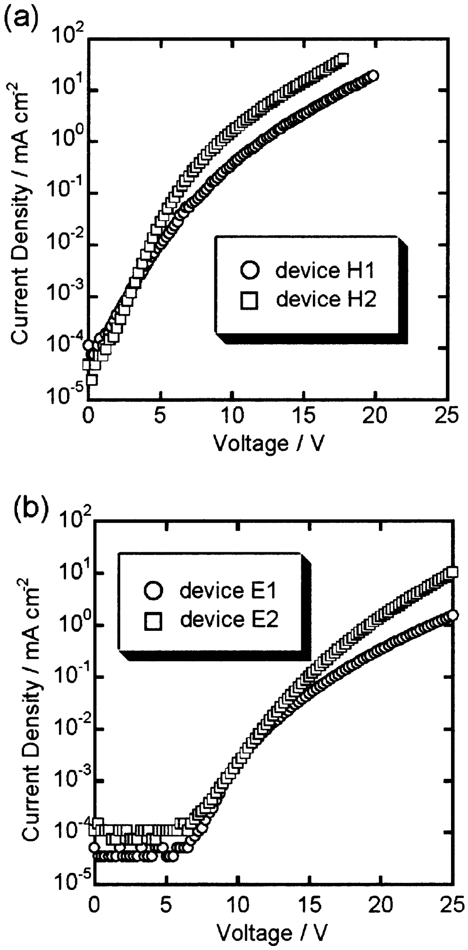

Figure 6. Voltage–current density characteristics for (a) hole-only devices: ITO/*m*-MTDATA(50 nm)/FlAMB-1T(150 nm)/Ag (device H1, circle) and ITO/*m*-MTDATA(50 nm)/TPD(150 nm)/Ag (device H2, square); and (b) electron-only devices: Al/FlAMB-1T(150 nm)/Alq_3(50 nm)/LiF(0.5 nm)/Al (device E1, circle) and Al/Alq_3(200 nm)/LiF(0.5 nm)/Al (device E2, square).

FlAMB-*n*T as Color-Tunable Emitters in Organic EL Devices. The present novel class of emitting amorphous molecular materials, FlAMB-*n*T ($n = 0$, 1, 2, and 3), fulfills the requirements for materials that function as the recombination center of holes and electrons in organic EL devices. Therefore, they are expected to function as emitting materials for organic EL devices. The following four multilayer organic EL devices using *m*-MTDATA as a hole-transport layer,[6a,b] FlAMB-*n*T ($n = 0$, 1, 2, and 3) as an emitting layer, 5,5′-bis(dimesitylboryl)-2,2′-bithiophene (BMB-2T) as a hole-blocking, electron-transport layer,[6c] and Alq_3 as an electron-transport layer were fabricated, and their performance was examined: ITO/*m*-MTDATA (50 nm)/FlAMB-*n*T (20 nm)/BMB-2T (20 nm)/Alq_3 (10 nm)/LiF (0.5 nm)/Al with Device A, B, C, and D corresponding to $n = 0$, 1, 2, and 3, respectively. Figure 7 shows the side view of these devices. The EL spectra of the four devices were in good agreement with the fluorescence spectra of the films of FlAMB-*n*T ($n = 0$, 1, 2, and 3), respectively, as shown in Figure 8 and Table 3. These results indicate that the EL originates from the excited singlet state of FlAMB-*n*T ($n = 0$, 1, 2, and 3) generated by the recombination of holes and electrons injected from the ITO and Al electrodes by a stepwise process via the hole-transport and electron-transport layers, respectively, for all the devices. The devices A, B, C, and D emitted greenish-blue, green, yellowish-green, and yellow light with the CIE1931 chromaticity coordinates (*x*, *y*) of (0.13, 0.31), (0.24, 0.61), (0.36, 0.60), and (0.49, 0.59), respectively, as shown in Figure 9. The emission

Table 3. Performance Characteristics of Organic EL Devices

device[a]	emission color	peak wavelength[b] (nm)	maximum luminance (cd m^{-2})	luminous efficiency[c] (lm W^{1-})	external quantum efficiency[c]
A	greenish blue	479 (479)	13 800 (at 9.0 V)	1.8	1.6%
B	green	509 (500)	26 900 (at 12.0 V)	3.1	2.0%
C	yellowish green	535 (535)	28 200 (at 10.0 V)	2.6	1.1%
D	yellow	562 (563)	16 600 (at 10.0 V)	0.9	0.6%

[a] ITO/*m*-MTDATA (50 nm)/FlAMB-*n*T (20 nm)/BMB-2T (20 nm)/Alq$_3$ (10 nm)/LiF (0.5 nm)/Al with A, B, C, and D corresponding to *n* = 0, 1, 2 and 3, respectively. [b] The values in parentheses are the PL maxima for the films of FlAMB-*n*T. [c] At a luminance of 300 cd m^{-2}.

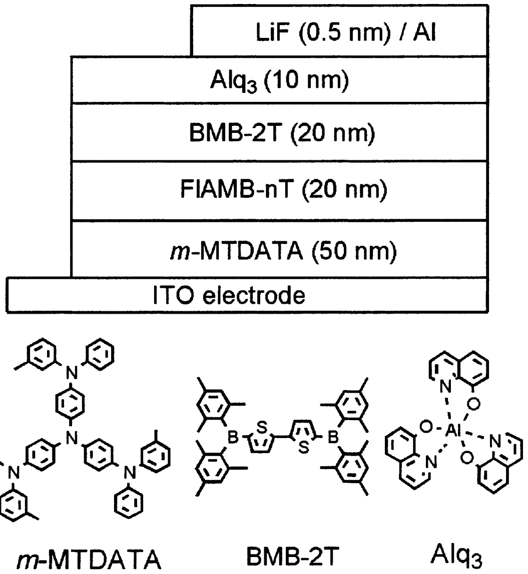

Figure 7. Side view of multilayer organic EL devices and molecular structures of the materials used.

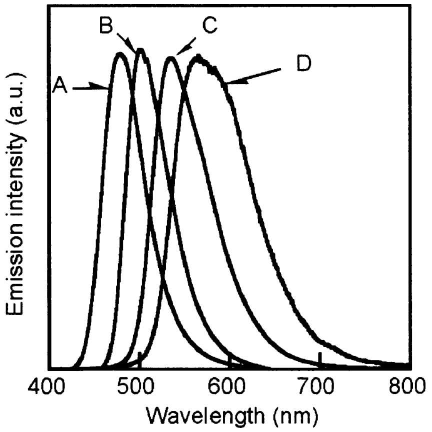

Figure 8. EL spectra of organic EL devices ITO/*m*-MTDATA (50 nm)/FlAMB-*n*T (20 nm)/BMB-2T (20 nm)/Alq$_3$ (10 nm)/LiF (0.5 nm)/Al with A, B, C, and D corresponding to *n* = 0, 1, 2 and 3, respectively.

color was tuned by varying the conjugation length of the central thiophene unit in FlAMB-*n*T (*n* = 0, 1, 2, and 3).

All the fabricated devices exhibited high performance. The emission started at a driving voltage of ca. 3 V for all the devices. Table 3 summarizes the maximum luminance, luminous, and external quantum efficiencies for the devices A, B, C, and D. The devices are characterized by high luminance and high luminous and external quantum efficiencies. In particular, the devices A, B, and C exhibit the highest level performance among undoped, fluorescence-based organic EL devices that emit light of each color.

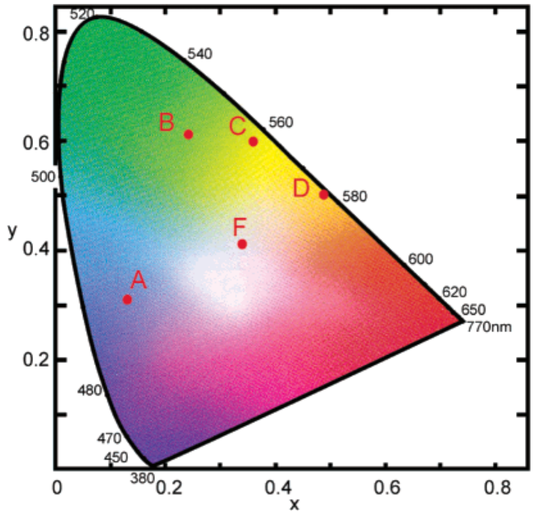

Figure 9. CIE1931 chromaticity coordinates (*x*, *y*) of devices A, B, C, D, and F.

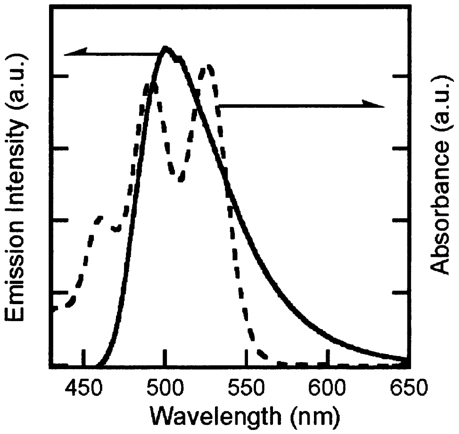

Figure 10. Fluorescence spectrum of FlAMB-1T film (solid line) and electronic absorption spectrum of rubrene in THF solution (dashed line).

FlAMB-1T as a Host Material for an Emissive Dopant in Organic EL Devices. The amorphous molecular materials, FlAMB-*n*T (*n* = 0, 1, 2, and 3), are also expected to serve as good host materials for emissive dopants, permitting color tuning and improving performance. FlAMB-1T and rubrene were chosen as the host material and the yellow-emitting dopant, respectively, because the fluorescence spectrum of FlAMB-1T and the electronic absorption spectrum of rubrene are well overlapped, as shown in Figure 10. An organic EL device using rubrene-doped FlAMB-1T as an emitting layer, ITO/*m*-MTDATA(50 nm)/5 wt % rubrene-doped FlAMB-1T (20 nm)/BMB-2T (20 nm)/Alq$_3$ (10 nm)/LiF (0.5 nm)/Al (device E), was fabricated and the performance was examined. The device emitted bright yellow light originating from rubrene, with no

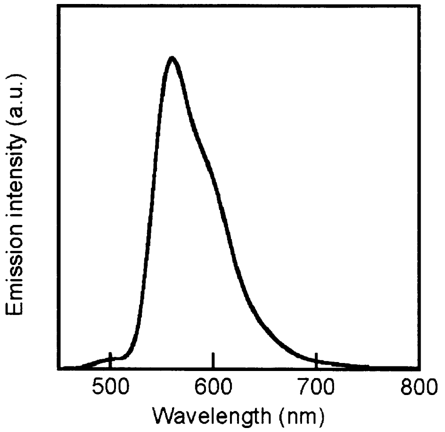

Figure 11. EL spectrum of device E, ITO/*m*-MTDATA(50 nm)/5 wt % rubrene-doped FlAMB-1T (20 nm)/BMB-2T (20 nm)/Alq$_3$ (10 nm)/LiF (0.5 nm)/Al.

green emission from FlAMB-1T being observed. Figure 11 shows the EL spectrum of this device. The EL spectrum is in good agreement with the photoluminescence spectrum of rubrene in solution. The result indicates that efficient excitation energy transfer from FlAMB-1T to rubrene took place. The device exhibited high performance with a maximum luminance of 35 740 cd m^{-2} and luminous and external quantum efficiencies of 4.3 lm W^{1-} and 2.1% at a luminance of 300 cd m^{-2}, respectively. The results show that the present novel amorphous molecular materials can function not only as emitters but also as good hosts for emissive dopants.

FlAMB-*n*T for White-Light Emission. The development of organic EL devices that emit white light is also a subject of great interest in view of their application for lighting. Doping of fluorescent or phosphorescent dyes or complexes in a host material has been used to obtain white light EL.[24] A metal complex, which exhibits luminescence with bands in the wide wavelength region, has also been reported.[25] It is expected that the creation of a series of color-tunable emitting materials leads to the production of white-light emission depending upon the combination of suitable emitting materials. With regard to the present series of color-tunable emitting amorphous molecular materials, the combination of FlAMB-0T and FlAMB-3T is expected to produce white light, as suggested from the superposition of their fluorescence spectra. A device using *m*-MTDATA as a hole-transport layer, FlAMB-0T and FlAMB-3T as emitting bilayers, 1,3,5-tris(4-fluorobiphenyl-4′-yl)benzene (F-TBB)[6f] as a hole-blocking layer, and Alq$_3$ as an electron-transport layer, ITO/*m*-MTDATA (50 nm)/FlAMB-3T (10 nm)/FlAMB-0T (10 nm)/F-TBB (20 nm)/Alq$_3$ (10 nm)/LiF (0.5 nm)/Al (device F), was fabricated. The device F emitted white light, exhibiting high performance with a maximum luminance of 16 600 cd m^{-2} at 11.0 V, luminous and external quantum efficiencies of 1.2 lm W^{-1} and 0.90% at a luminance of 300 cd m^{-2}, respectively. The EL spectrum of the device F and the CIE1931 chromaticity coordinates for this device are shown in Figure 12 and Figure 9, respectively. BMB-2T also functions as the hole-blocking layer for this device, but the device using F-TBB as the hole-blocking layer exhibited higher color purity for white light. Thus, white light EL was realized by the use of the emitting bilayers of the emitting amorphous molecular materials, FlAMB-0T and FlAMB-3T.

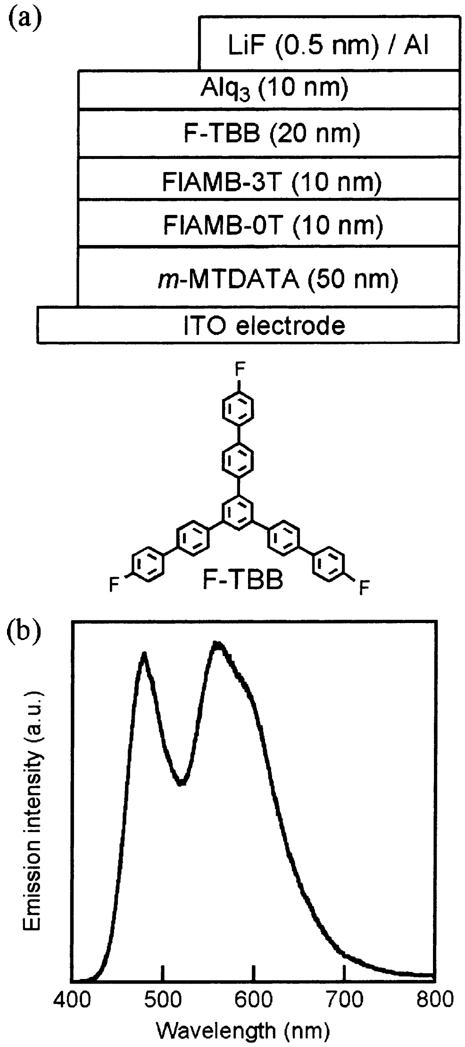

Figure 12. (a) Side view of device F, ITO/*m*-MTDATA (50 nm)/FlAMB-3T (10 nm)/FlAMB-0T (10 nm)/F-TBB (20 nm)/Alq$_3$ (10 nm)/LiF (0.5 nm)/Al and molecular structure of F-TBB. (b) EL spectrum of device F.

Conclusions

In the present study, a novel class of color-tunable emitting amorphous molecular materials with desired bipolar character, FlAMB-*n*T ($n = 0$, 1, 2, and 3), have been designed and synthesized. They are characterized by reversible electrochemical oxidation and reduction to give stable cation and anion radicals, intense fluorescence emission, and ready formation of thermally and morphologically stable amorphous glasses. It is shown that the oxidation and reduction potentials of FlAMB-*n*T ($n = 0$, 1, 2, and 3) decrease and become more positive, respectively, with increasing conjugation length of the central thiophene unit. That is, the HOMO–

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LUMO energy gaps of FlAMB-*n*T ($n = 0$, 1, 2, and 3) decrease with increasing conjugation length of the thiophene rings by 0.57 eV on going from $n = 0$ to $n = 3$. The results show that the π-conjugation length of the central thiophene rings in FlAMB-*n*T controls the fine-tuning of the emission color. FlAMB-*n*T ($n = 0$, 1, 2, and 3) function as excellent color-tunable emitting materials in organic EL devices. The fabricated organic EL devices using FlAMB-*n*T as emitting materials exhibited very high performance. FlAMB-*n*T also serve as good host materials for emissive dopants in organic EL devices, permitting color tuning and leading to higher performance. In addition, a high-performance organic EL device that emits white light was also developed by using the bilayers of FlAMB-0T and FlAMB-3T. The present study shows a new paradigm for the molecular design of emitting amorphous molecular materials with desired bipolar character, and presents the first definite examples of such materials as promising candidates for both emitting and host materials in organic EL devices. The present study is expected to pave the way for the development of a variety of further new emitting amorphous molecular materials for electroluminescence.

Supporting Information Available: Electronic absorption and fluorescence spectra of FlAMB-*n*T ($n = 0$, 2, and 3) in THF solution, cyclic voltammograms of FlAMB-1T and FlAMB-2T, and DSC curves of FlAMB-2T and FlAMB-3T glasses. These materials are available free of charge via the Internet at http://pubs.acs.org.

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