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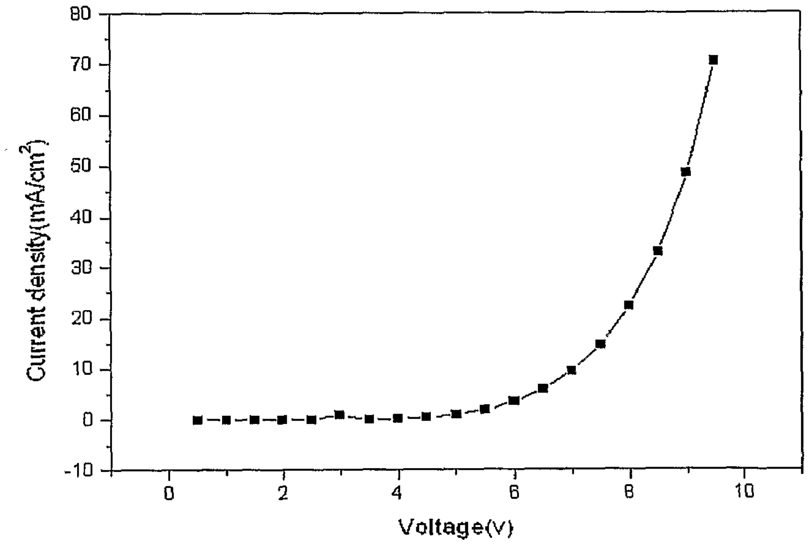
(54) Title: ELECTROLUMINESCENT COMPOUNDS COMPRISING FLUORENE GROUP AND ORGANIC ELECTROLUMINESCENT DEVICE USING THE SAME



(57) Abstract: The present invention relates to organic electroluminescent compounds represented by Chemical Formula 1 and an electroluminescent device comprising the compound in an electroluminescent layer. The electroluminescent compound according to the invention has good luminous efficiency and excellent lifetime of the material, so that an OLED device having very good operation lifetime can be prepared.

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Description

ELECTROLUMINESCENT COMPOUNDS COMPRISING FLUORENE GROUP AND ORGANIC ELECTROLUMINESCENT DEVICE USING THE SAME

Technical Field

[1] The present invention relates to an electroluminescent compound comprised of blue electroluminescent materials, which show excellent luminous property with high efficiencyand excellent lifetime, and electroluminescent devices comprising the same in the electroluminescent layer.

Background Art

[2] Among display devices, electroluminescence (EL) devices, being self-luminous type display devices, have advantages of wide visual angle, excellent contrast as well as rapid response rate. Eastman Kodak firstly developed an organic EL device employing low molecular aromatic diamine and aluminum complex as a substance for forming an electroluminescent layer, in 1987 [Appl. Phys. Lett. 51, 913, 1987].

[3] The most important factor to determine luminous efficiency, lifetime or the like in an organic EL device is electroluminescent material. Several properties required for such electroluminescent materials include that the material should have high fluorescent proton yield in solid state and high mobility of electrons and holes, is not easily decomposed during vapor-deposition in vacuo, and forms uniform and stable thin film.

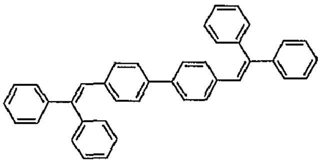
[4] Organic electroluminescent materials can be generally classified into high-molecular materials and low-molecular materials. The low-molecular materials include metal complexes and purely organic electroluminescent materials which do not contain metal, from the aspect of molecular structure. Such electroluminescent materials include chelate complexes such as tris(8-quinolinolato)aluminum complexes, coumarin derivatives, tetraphenylbutadiene derivatives, bis(styrylarylene) derivatives, oxadiazole derivatives. From those materials, it is reported that light emission of visible region from blue to red can be obtained, so that the realization of colored display device is expected.

[5] In the meanwhile, for blue materials, a number of materials have been developed and commercialized since the development of DPVBi (Chemical Formula a) by

Idemitsu-Kosan. In addition to the blue material system from Idemitsu-Kosan, dinaphthylanthracene (Chemical Formula b), tetra(t-butyl)perylene (Chemical Formula c) system or the like have been known. However, extensive research and development should be performed with respect to these materials. The distrylcompound system of Idemitsu-Kosan, which is known to have highest efficiency up to now, has 6 lm/W of power efficiency and beneficial device lifetime of more than 30,000 hr. However, when it is applied to a full-color display, owing to the reduction of color purity over driving time, the lifetime is merely several thousand hours. In case of blue light, it becomes advantageous from the aspect of the luminous efficiency, if the light emitting wavelength is shifted a little toward longer wavelength. However, it is not easy to apply the material to a display of high quality because of unsatisfactory pure blue color. In addition, the research and development of such materials are urgent because of the problems in color purity, efficiency and thermal stability.

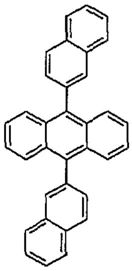
[6] [Chemical Formula a]

[7]



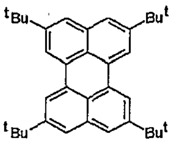
[8] [Chemical Formula b]

[9]



[10] [Chemical Formula c]

[11]



[12]

Disclosure of Invention

Technical Problem

[13] The object of the invention is to overcome and make up for the problems of those blue materials as described above, and provide electroluminescent compounds having improved luminous efficiency and lifetime of the device. Another object of the invention is to provide organic EL devices employing said electroluminescent compounds as electroluminescent material, which have high efficiency and long lifetime.

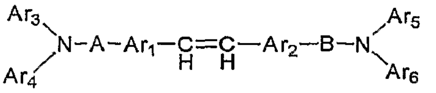
Technical Solution

[14] The present inventors have made efforts in order to solve the problems of prior art as described above, and invented novelelectroluminescent compounds to realize an organic EL device having excellent luminous efficiency and noticeably improved life time.

[15] Thus, the present invention provides novel electroluminescent materials and electroluminescent devices containing said electroluminescent materialsin the electroluminescent layer. Specifically, the electroluminescent materials according to the present invention are characterized in that they are represented by following Chemical Formula 1:

[16] [Chemical Formula 1]

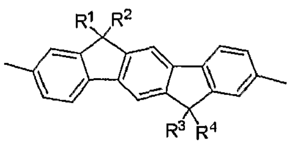
[17]

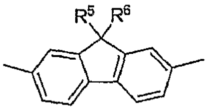


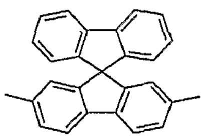
$$(Ar_3)(Ar_4)N-A-Ar_1-\underset{H}{C}=\underset{H}{C}-Ar_2-B-N(Ar_5)(Ar_6)$$

[18] In Chemical Formula 1, Ar $_1$ is a chemical bond or selected from indenofluorene, fluorene and spiro-fluorene as represented by following chemical formulas, Ar $_2$ is selected from indenofluorene, fluorine andspiro-fluorene as represented by following chemical formulas:

[19]







[20] A and B independently represent a chemical bond, or are selected from phenylene group, naphthylene group, biphenylene group, anthracenyl group, perylenylene group or pyrenylene group,but the compounds wherein both A and Ar $_1$ are chemical bonds are excluded.

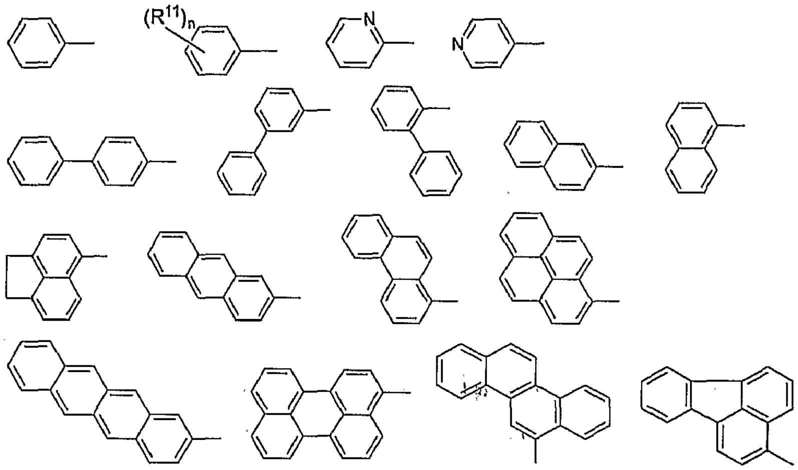
[21] R^1 through R^6 are independently selected from C_1~C_{20} alkyl, cycloalkyl, C_1~C_{20} alkyl having one or more halogen substituent(s), and phenyl or naphthyl having C_1~C_5

alkyl substituent(s), more preferably R^1 through R^6 are independently selected from C_1~C_5 alkyl, C_5-C_7 cycloalkyl, phenyl and naphthyl, and said halogen is selected from F, Cl and Br. Specifically, R^1 through $R^6$are exemplified as methyl, ethyl, propyl, butyl, amyl, cyclopentyl, cyclohexyl, phenyl and naphthyl.

[22] Ar_3 through Ar_6 are independently selected from C_5~C_{20} aromatic or multicyclic aromatic ring, and the aromatic ring may contain hetero atom(s).

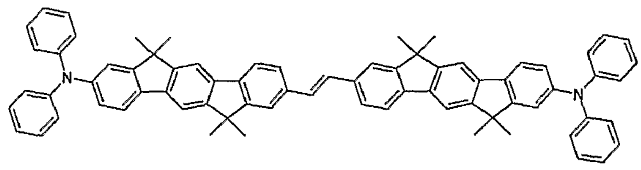
[23] Preferably, Ar_3 through Ar_6 independently represent phenyl, tolyl, xylyl, pyridyl, biphenyl, naphthyl, anthryl, phenanthryl, pyrenyl, naphthacenyl, acenaphthyl, perylenyl, chrysenyl, fluoranthenyl with or without alkyl (R^{11}) substituent(s), wherein R^{11} is selected from C_1~C_5alkyl group, and n is an integer from 1 to 5.

[24]



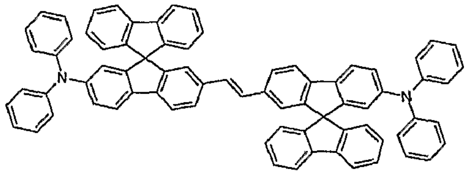
[25] The electroluminescentcompounds represented by Chemical Formula 1 according to the present invention are specifically exemplified by following compounds:

[26]



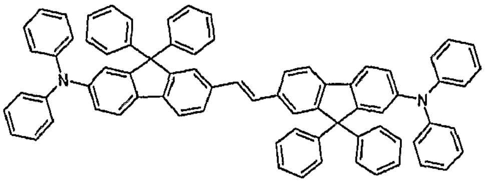
[27] DIF-1

[28]



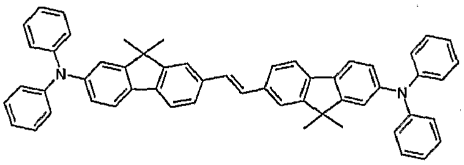
[29] DSF-1

[30]



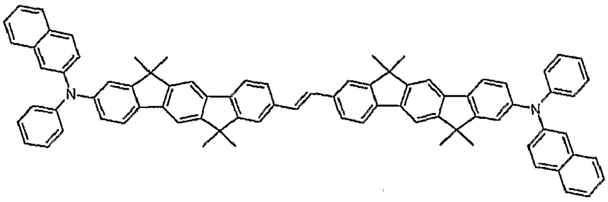
[31] DPF-1

[32]



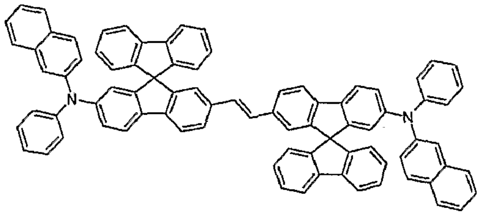
[33] DMF-1

[34]



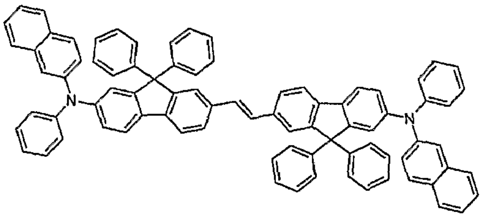
[35] DIF-2

[36]



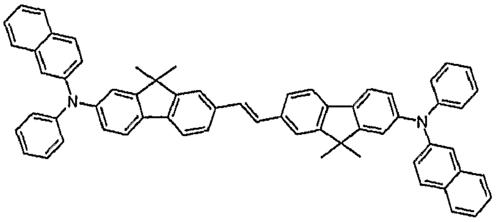
[37] DSF-2

[38]



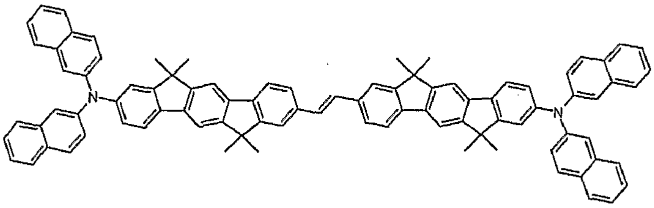
[39] DPF-2

[40]



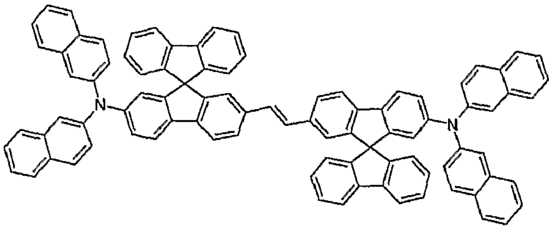
[41] DMF-2

[42]



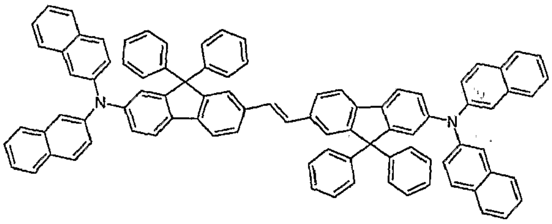
[43] DIF-3

[44]



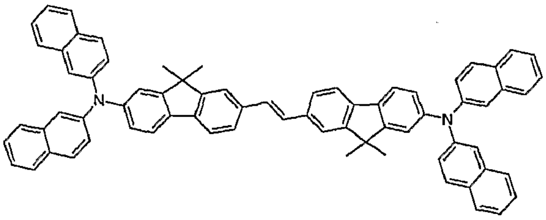
[45] DSF-3

[46]



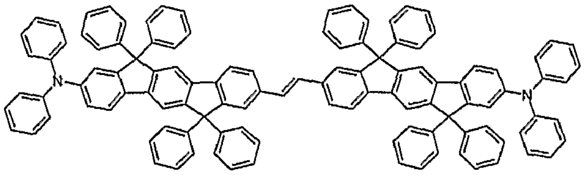
[47] DPF-3

[48]



[49] DMF-3

[50]



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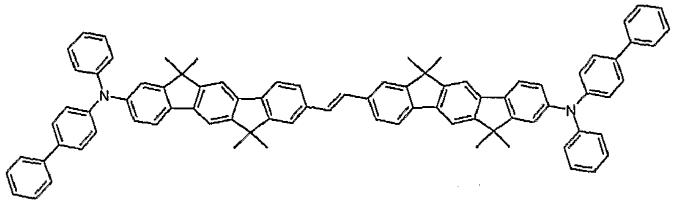
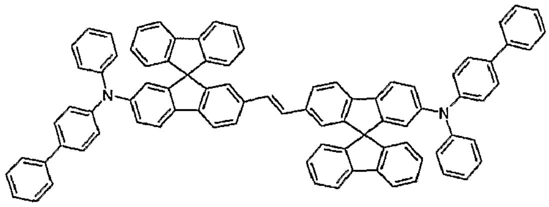
[52]



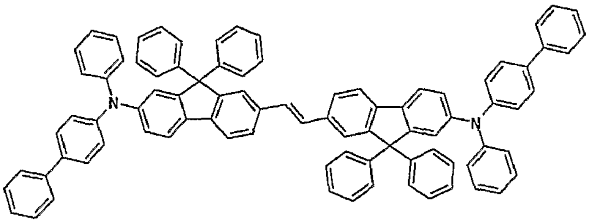
[53] DIF-4

[54]



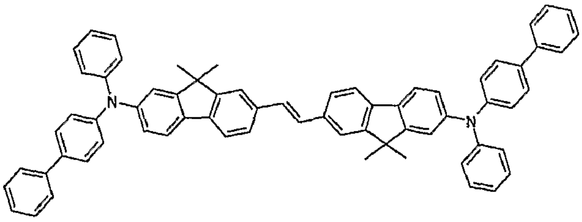
[55] DSF-4

[56]



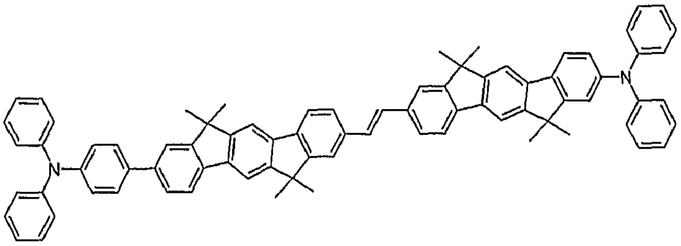
[57] DPF-4

[58]



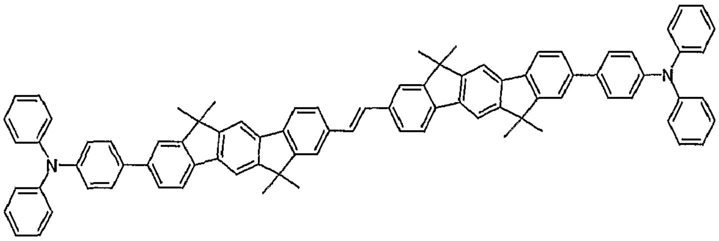
[59] DMF-4

[60]



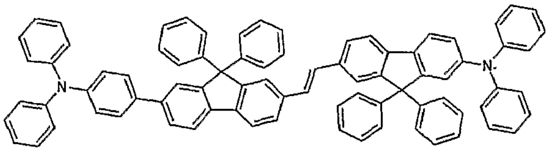
[61] DIF-11

[62]



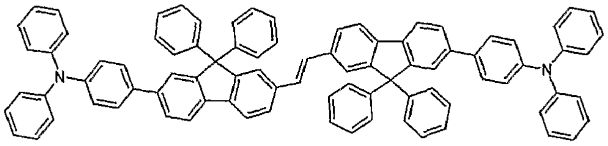
[63] DIF-12

[64]



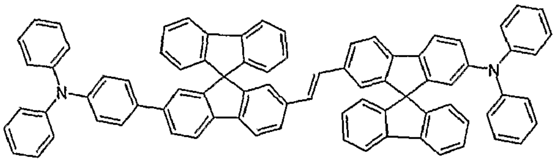
[65] DPF-11

[66]



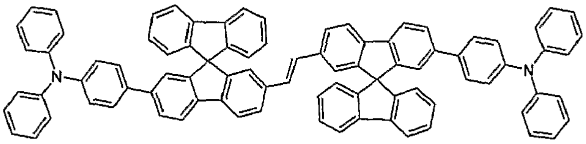
[67] DPF-12

[68]



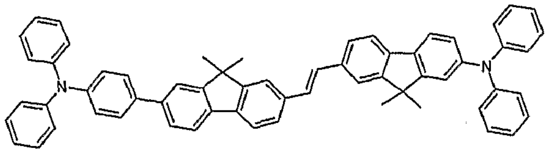
[69] DSF-11

[70]



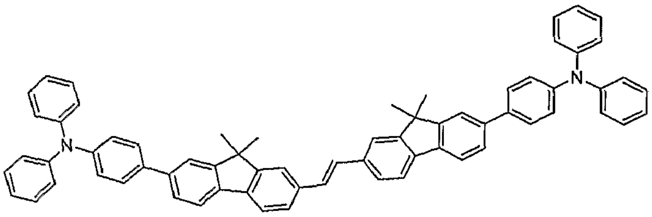
[71] DSF-12

[72]



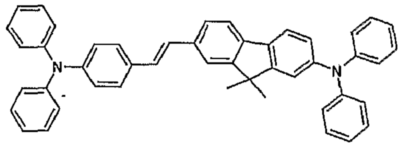
[73] DMF-11

[74]



[75] DMF-12

[76]

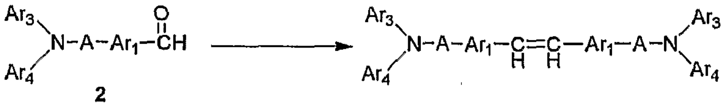


[77] DMF-21

[78] Among the electroluminescent compounds represented by Chemical Formula (1) according to the present invention, the compounds wherein Ar_1 is same as Ar_2, Ar_3 is same as Ar_5, Ar_4 is same as Ar_6, and A is same as B, that is symmetrical on the basis of the double bond, can be prepared by coupling 2 moles of aldehyde compound via MacMurry reaction, as illustrated by Reaction Scheme 1:

[79] [Reaction Scheme 1]

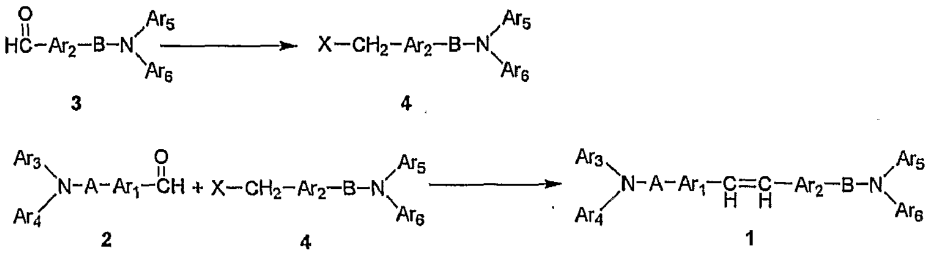
[80]



[81] Among the compounds of Chemical Formula (1), asymmetrical compounds can be prepared by reducing and halogenating the aldehyde compound of Chemical Formula (3)to obtain the compound of Chemical Formula (4), which is then coupled with the compound of Chemical Formula (2) via Wittig reaction or Wadsworth-Horner-Emmons reaction (a modification of Wittig reaction).

[82] [Reaction Scheme 2]

[83]

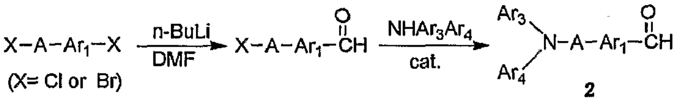


[84] [In the Reaction Scheme (2), Ar_1 through Ar_6, and A and B are defined as above, and X represents halogen, Cl or Br.]

[85] The compound represented by Chemical Formula 2, an important intermediate to prepare the compound according to the invention can be prepared by substituting the dibromoaryl compound with butyl lithium and reacting the product with DMF to prepare dibromoaldehyde compound, which is then subjected to substitution by a secondary amine in the presence of a catalyst, as illustrated by Reaction Scheme 3:

[86] [Reaction Scheme 3]

[87]



[88] The preparation of the compounds according to the present invention or intermediates thereof is not restricted to the reactions expressed by the Reaction Schemes described above, but a person having ordinary skill in the art may prepare the compounds by adopting known reactions in organic chemistry.

[89] In addition, the present invention provides an electroluminescent device comprising the electroluminescent represented by Chemical Formula (1) in the electroluminescent layer. More specifically, the invention provides an electroluminescent device employing the electroluminescent compound of Chemical Formula (1) according to the invention as a dopant together with a conventional host material in the electroluminescent layer.

Brief Description of the Drawings

[90] Fig. 1 is a schematic view showing cross-sectional structure of the OLED devices of Example 1 and Comparative Example 1;

[91] Fig. 2 shows EL spectrums of Example 1 and Comparative Example 1;

[92] Fig. 3 is a curve showing luminance property versus driving voltage of the OLED according to Example 1;

[93] Fig. 4 is a curve showing current density property versus driving voltage of the OLED of Example 1; and

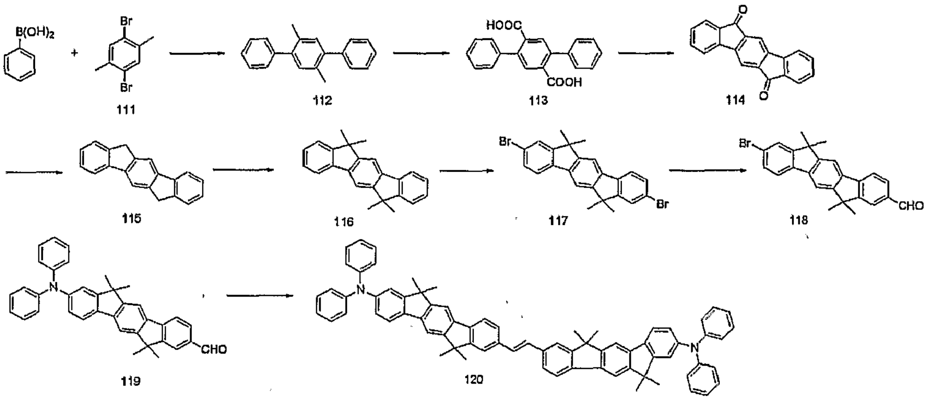
[94] Fig. 5 is a curve showing luminous efficiency propertyversus luminance of the OLED device of Example 1.

Mode for the Invention

[95] The present invention is further described with respect to the novel electroluminescent compounds according to the invention, a process for preparing the same and the electroluminescent properties of the device employing the same by referring to representative compounds according to the present invention, which are provided for illustration only but are not intended to be restrictive in any way.

[96] [Synthetic Example 1] Preparation of DIF-1 (Compound 120)

[97]



[98] Preparation of Compound (112)

[99] Compound (111), 1,4-dibromo-p-xylene (200 g, 0.76 mol) and phenyl boronic acid (204 g, 1.67 mol), $Pd(OAc)_2$ (0.34 g, 1.52 mmol), potassium carbonate (524 g, 3.79 mol) and $n\text{-}Bu_4NBr$ (490 g, 1.51 mol) were suspended in 1.9 L of distilled water, and the suspension was stirred at 70°Cfor 24 hours. After the reaction was completed, 2 L of distilled water was added to the reaction mixture, and the solid produced was filtered under reduced pressure, to obtain Compound (112) (196 g, 0.76 mol) as gray solid.

[100] Preparation of Compound (113)

[101] Compound (112) (196 g, 0.76 mol) was dissolved in pyridine (1.23 L, 15.17 mol) and H_2O (2 L), and $KMnO_4$ (420 g, 2.66 mol) was slowly added to the reaction solution by ten portions, and the resultant mixture was heated under reflux for 48 hours.

[102] Distilled water (5 L, at 50°C was added thereto, and the solid by-product was filtered off under reduced pressure. Addition of 35% HCl (3L) gave Compound (113) (174 g, 0.55 mol) as white solid.

[103] Preparation of Compound (114)

[104] Compound (113) thus prepared (174 g, 0.55 mol) was added to concentrated sulfuric acid (1.8 L), and the mixture was stirred at 25°Cfor 4 hours.

[105] After completionof the reaction, ice water (6 L) was added, and the resultant mixture was stirred for 1 hour, and filtered under reduced pressure to obtain solid. To the solid, added was a solution of potassium carbonate (200 g) dissolved in distilled water (5 L). The resultant mixture was stirred for 1 hour and filtered under reduced pressure to obtain Compound (114) (120 g, 0.43 mol) as purple solid.

[106] Preparation of Compound (115)

[107] Compound (114) thus prepared (120 g, 0.43 mol) was dissolved in diethylene glycol (1.4 L), and potassium hydroxide (240 g, 4.25 mol) and hydrazine hydrate (207 mL, 4.25 mol) were added thereto. The resultant mixture was stirred at 220°Cfor 48 hours.

[108] After cooling to ambient temperature, 20% hydrochloric acid solution (4 L) was added, and the mixture was stirred for 1 hour. Solid was obtained from the mixture by filtration under reduced pressure. To the solid, acetone and tetrahydrofurane (2 L, each) were added, and the mixture was stirred for 20 hours. Filtration under reduced pressure and drying gave Compound (115), also referred to as indenofluorene (85 g, 0.34 mol, yield: 79%), as gray solid.

[109] Preparation of Compound (116)

[110] To the solution of Compound (115) (5.2 g, 20.5 mmol) dissolved in tetrahydrofuran (50 mL), n-BuLi (1.6 M in n-hexane) (29.4 mL, 47.0 mmol) was slowly added dropwise at -78°C After 1 hour of reaction, iodomethane (7.55 mL, 53.2 mmol) was added therto, and the temperature was slowly raised to ambient temperature. Stirring was continued at the same temperature for 1 hour. Again, the temperature of the reaction mixture was dropped to -78°C n-BuLi (1.6 M in n-hexane) (37.1 mL, 59.3 mmol) was slowly added dropwise to the mixture. After1 hour of reaction, iodomethane (7.55 mL, 53.2 mmol) was added therto, and the temperature was slowly raised to ambient temperature. Stirring was continued at the same temperature for 15 hour.Then, aqueous ammonium chloride solution (20 mL) and distilled water (15 mL) were added to quench the reaction. After removal of organic layer under reduced pressure, and recrystallization from n-hexane (100 mL), Compound (116) (1.7 g, 5.48 mmol) was obtained.

[111] Preparation of Compound (117)

[112] Compound (116) (1.7 g, 4.64 mmol) and FeCl3 (11.3 mg, 0.07 mmol) were

dissolved in 30 mL of chloroform, and the temperature of the mixture was adjusted to 0°Cby using an ice-bath. Bromine (0.72 ml, 13.9 mmol) dissolved in 5 mL of chloroform was slowly added dropwise thereto, and the mixture was stirred for 24 hours. After the reaction was completed, the reaction was quenched by saturated aqueous sodium thiosulfate solution (50mL). The reaction mixture was separated, and the organic layer was removed under reduced pressure, and recrystallized from n-hexane (100 mL) to give Compound (117) (1.6 g, 3.42 mmol).

[113] Preparation of Compound (118)

[114] Compound (117) thus obtained (1.6 g, 3.42 mmol) was dissolved in tetrahydrofuran (40 mL), and n-BuLi(1.6 M in n-hexane)(4.8 mL, 3.0 mmol) was slowly added dropwise thereto at -78°C After stirring the reaction mixture for 30 minutes, N,N-dimethylformamide(0.3 mL, 4.14 mmol) was added thereto. Stirring was continued while slowly raising the temperature for 2 hours, and the reaction was quenched by adding aqueous NH_4Cl solution (20 mL) and distilled water (20 mL). The organic layerwas separated, removed under reduced pressure, and recrystallized from 100 mL of methanol:n-hexane (1/1, v/v) to obtain Compound (118) (1.1 g, 2.64 mmol).

[115] Preparation of Compound (119)

[116] The aldehyde compound (118) thus obtained (1.1 g, 2.6 mmol), diphenylamine (0.67 g, 4.0 mmol), cesium carbonate (1.29 g, 3.96 mmol) and palladium acetate ($Pd(OAc)_2$) (18 mg, 0.08 mmol) were suspended in 100 mL of toluene. To the suspension, tri(t-butyl) phosphine ($P(t\text{-}Bu)_3$)(32 mg, 0.16 mmol) was added, and the mixture was stirred at 120°Cor 4 hours. Saturated aqueous ammonium chloride solution (30 mL) was added thereto, and the mixture was extracted with ethyl acetate (50 mL), filtered, and recrystallized from methanol:n-hexane (1/1, v/v) (50 mL) to obtain Compound (119) (1.2 g, 2.4 mmol).

[117] Preparation of Compound (120)

[118] Zinc dust (6.0 g, 92.4 mmol), $TiCl_4$ (31 mL, 30.8 mmol) and tetrahydrofuran (26 mL) were stirred at -10°Cunder argon atmosphere. After 4 hours, Compound (119) (1.2 g, 2.4 mmol) was added thereto, and the mixture was stirred for 24 hours. After adding 30 mL of distilled water, the mixture was stirred for 1 hour, and filtered under reduced pressure. Then, acetone (30 mL) and dichloromethane (30 mL) were added, and the mixture was stirred and filtered under reduced pressure. To the solid produced, added was N,N-dimethylformamide (50 mL), and the resultant mixture was heated under reflux with stirring for 2 hours, filtered under reduced pressure, and dried to obtain

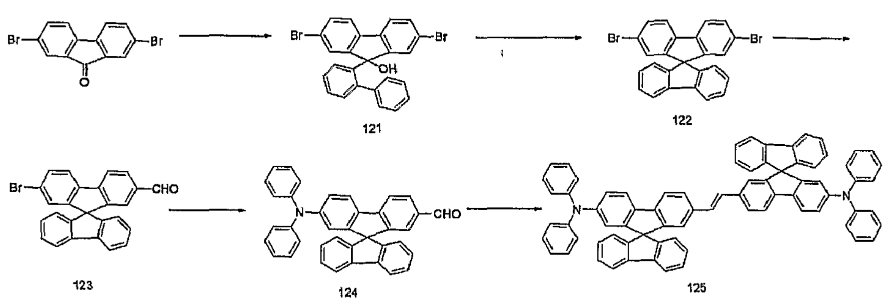
Compound (120, DIF-1) (0.93 g, 0.95 mmol, yield on the basis of Compound (118): 72%) as yellow solid.

[119] ^{1}H NMR(CDCl$_3$, 200 MHz) : δ1.67(s, 24H), 6.46(m, 8H), 6.61-6.62(m, 6H), 6.78(m, 2H), 6.99-7.01(m, 10H), 7.57(m, 2H), 7.70-7.74(m, 8H), 7.95(m, 2H)

[120] MS/FAB : 978(found) 979.30(calculated)

[121] [Synthetic Example 2] Preparation of DSF-1 (Compound 125)

[122]



[123] Preparation of Compounds (121) and (122)

[124] To 2-bromobiphenyl (6.27 g, 26.9 mmol) and magnesium powder (0.68 g, 28.2 mmol), diethyl ether (5 mL) was added, and the mixture was heated under reflux with stirring for 3 hours. To 2,7-dibromofluorenone (10 g, 29.6 mmol), diethyl ether solvent (5 mL) was added, and, after stirring, the mixture was slowly added to the reaction mixture. After stirring at 25°Cfor 24 hours, saturated aqueous ammonium chloride solution (50 mL) was placed in an ice-bath. After stirring for 1 hour, it was filtered, washed with 100 mL of distilled water, and filtered under reduced pressure to obtain crude Compound (121), which was added to glacial acetic acid (40 mL) and heated under reflux for 2 hours. To the reaction solution, 30% hydrochloric acid solution (40 mL) was slowly added to form solid, which was then filtered under reduced pressure, washed with 100 mL of distilled water, recrylstallized from 50 mL of methanol, and dried under reduced pressure to obtain Compound (122) (9.8 g, 20.7 mmol).

[125] Preparation of Compound (123)

[126] Compound (123) was obtained according to the same synthetic procedure as for Compound (118). Reaction was carried out by using Compound (122) prepared as above (9.8 g, 20.7 mmol), tetrahydrofuran (40 mL), n-BuLi (1.6 M in n-hexane) (33.6 mL, 21 mmol) and N,N-dimethylformamide (2.1 mL, 29.0 mmol). Recrystallization from 30 mL of methanol and 30 mL of n-hexane gave Compound 123 (5.23 g, 12.36 mmol).

[127] Preparation of Compound (124)

[128] Compound (124) was obtained according to the same synthetic procedure as for

Compound (119). Reaction was carried out by using the aldehyde compound (123) prepared as above (5.23 g, 12.4 mmol), diphenylamine (3.14 g, 18.5 mmol), cesium carbonate (6.04 g, 18.5 mmol), $Pd(OAc)_2$ (83 mg, 0.37 mmol), toluene (200 mL), $P(t\text{-}Bu)_3$ (150 mg, 0.74 mmol). Recrystallization from 100 mL of methanol:n-hexane (1/1, v/v) gave Compound 124 (3.8 g, 7.4 mmol).

[129] Preparation of Compound (125)

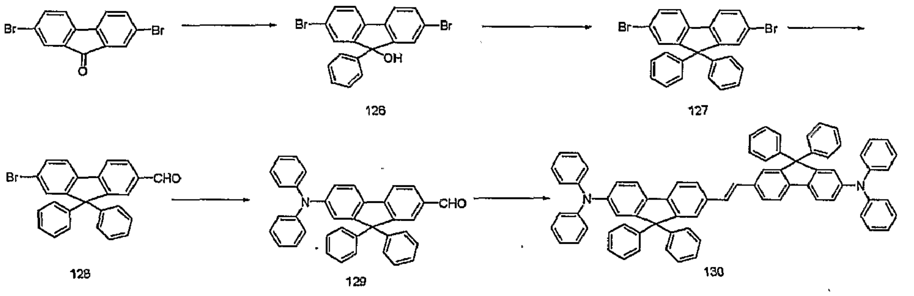
[130] Compound (125) was obtained according to the same synthetic procedure as for Compound (120). By using zinc dust (4.85 g, 74.2 mmol), $TiCl_4$ (1M solution in dichloromethane) (30 mL, 29.7 mmol), tetrahydrofuran (26 mL) and Compound (124) (3.8 g, 7.4 mmol), Compound (125, DSF-1) (2.4 g, 2.4 mmol, yield on the basis of Compound (123): 39%) was obtained as white powder.

[131] ^1H NMR($CDCl_3$, 200 MHz) : δ6.46(m, 8H), 6.58-6.62(m, 6H), 7.35(d, 2H), 6.99-7.01(m, 10H), 7.16-7.19(m, 8H), 7.35(m, 4H), 7.54-7.59(m, 4H), 7.71-7.72(m, 6H), 7.84(d, 2H)

[132] MS/FAB : 990(found) 991.22(calculated)

[133] [Synthetic Example 3] Preparation of DPF-1 (Compound 130)

[134]



[135] Preparation of Compounds (126) and (127)

[136] Diethyl ether (50 mL) was added to magnesium (4.9 g, 0.20 mol), and a solution of bromobenzene (31.4 g, 0.20 mmol) dissolved in 150 mL of diethyl ether was slowly added dropwise thereto. After heating the reaction mixture under reflux for 3 hours, a solution of 2,7-dibromofluorene (33.8 g, 0.10 mol) dissolved in 40 mL of diethyl ether was slowly added dropwise to the reaction mixture, which was then heated under reflux for 12 hours.

[137] After the reaction was completed, the precipitate generated was filtered under reduced pressure to obtain Compound (126) (41.5 g, 0.10 mmol). Compound (126) was dissolved in 145 mL of benzene, and trifluoromethanesulfonic acid (45 mL) was slowly added dropwise thereto, while raising the temperature slowly. After stirring the mixture at 100°Cor 30 minutes, the reaction solution was added to ice-water to

generate solid. The solid generated was filtered under reduced pressure, washed with 50 mL of methanol and 100 mL of diethyl ether, and dried under reduced pressure to obtain Compound (127) (27.1 g, 57.0 mmol) as pale yellow solid.

[138] Preparation of Compound (128)

[139] Compound (128) was obtained according to the same synthetic procedure as for Compound (118). By using Compound (127) (27.1 g, 56.9 mmol), tetrahydrofuran (120 mL), n-BuLi (1.6 M in n-hexane) (35.6 mL, 56.9 mmol) and N,N-dimethylformamide (6.2 mL, 79.7 mmol), Compound (128) (12.1 g, 28.4 mmol) was obtained.

[140] Preparation of Compound (129)

[141] Compound (129) was obtained according to the the same synthetic procedure as for Compound (119). By using the aldehyde compound (128) (12.1 g, 28.4 mmol), diphenylamine (7.3 g, 42.6 mmol), cesium carbonate (13.9 g, 42.6 mmol), $Pd(OAc)_2$ (192 mg, 0.85 mmol), toluene (600 mL) and $P(t\text{-}Bu)_3$ (347 mg, 1.7 mmol), Compound (129) (8.8 g, 17.1 mmol) was obtained.

[142] Preparation of Compound (130)

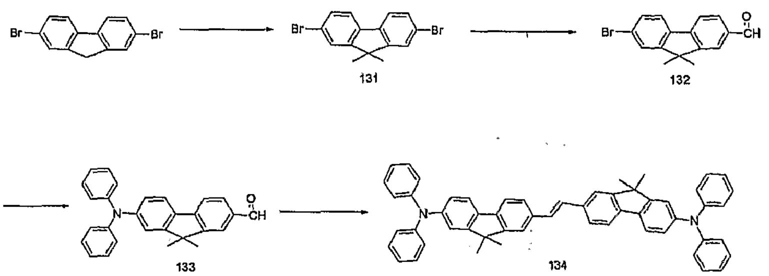
[143] Compound (130) was obtained according to the same synthetic procedure as for Compound (120). By using zinc dust (11.2 g, 171 mmol), TiCl4 (1 M solution in dichloromethane) (69 mL, 68.4 mmol), tetrahydrofuran (60 mL) and Compound (124)(8.8 g, 17.1 mmol), Compound (130, DSF-1) (5.6 g, 5.1 mmol, yield on the basis of Compound (128): 35%) was obtained as white solid.

[144] ^{1}H NMR($CDCl_3$, 200 MHz) : δ6.46(m, 8H), 6.58-6.62(m, 6H), 6.75(d, 2H), 6.99-7.17(m, 30H), 7.54-7.59(m, 4H), 7.71(d, 2H), 7.84(m, 2H)

[145] MS/FAB : 994(found) 995.26(calculated)

[146] [Synthetic Example 4] Preparation of DMF-1 (Compound 134)

[147]



[148] Preparation of Compound (131)

[149] Under nitrogen atmosphere, 2,7-dibromofluorene (50.0 g, 154.3 mmol) and potassium hydroxide (69.2 g, 1.23 mol) were dissolved in 700 mL of DMSO. The

solution was chilled to 0°C and distilled water (113 mL) was slowly added dropwise thereto, and the resultant mixture was stirred for 1 hour. Then, iodomethane (CH_3I) (38.5 mL, 0.617 mol) was slowly added, and the resultant mixture was slowly warmed to ambient temperature, and stirred at the temperature for 15 hours. The reaction was quenched by adding 200 mL of distilled water to the reaction solution, and the reaction mixture was extracted with 300 mL of dichloromethane. The organic layer obtained was concentrated under reduced pressure, and purified by silica gel column chromatography (eluent: n-hexane:dichloromethane = 20:1) to obtain Compound (131) (53.0 g, 0.15 mol).

[150] Preparation of Compound (132)

[151] Compound (132) was obtained according to the same synthetic procedure as for Compound (118). By using Compound (131) (53.0 g, 0.15 mol), tetrahydrofuran (350 mL), n-BuLi (1.6 M in n-hexane) (63.2 mL, 158 mmol) and N,N-dimethylformamide (16.3 mL, 211 mmol), Compound (132) (20.9 g, 69.4 mmol) was obtained.

[152] Preparation of Compound (133)

[153] Compound (133) was obtained according to the same synthetic procedure as for Compound (119). By using the aldehyde compound (132) (20.9 g, 69.4 mmol), diphenylamine (12.5 g, 104.1 mmol), cesium carbonate (24.1 g, 104.1 mmol), $Pd(OAc)_2$ (332 mg, 2.1 mmol), toluene (800 mL) and $P(t\text{-}Bu)_3$ (0.60 g, 4.2 mmol), Compound (133) (15.2 g, 39.0 mmol) was obtained.

[154] Preparation of Compound (134)

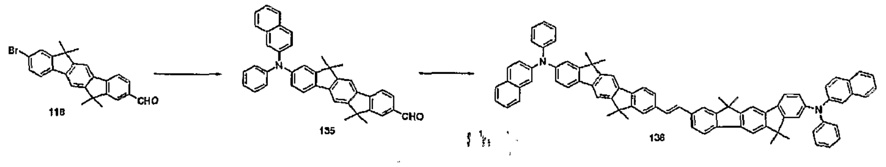
[155] Compound (134) was obtained according to the same synthetic procedure as for Compound (120). By using zinc dust (19.4 g, 390 mmol), $TiCl_4$ (1 M solution in dichloromethane) (120 mL, 156 mmol), tetrahydrofuran (104 mL) and Compound 133 (15.2 g, 39.0 mmol), Compound (134, DMF-1) (9.7 g, 12.9 mmol, yield on the basis of Compound (132): 37%) was obtained as white solid.

[156] ^{1}H NMR($CDCl_3$, 200 MHz) : δ1.67(s, 12H), 6.46(m, 8H), 6.58-6.62(m, 6H), 6.75(d, 2H), 6.99-7.01(m, 10H), 7.54-7.59(m, 4H), 7.71(d, 2H), 7.84(m, 2H)

[157] MS/FAB : 745(found) 746.98(calculated)

[158] [Synthetic Example 5] Preparation of DIF-2 (Compound 136)

[159]



[160] Preparation of Compound (135)

[161] Compound (135) was obtained according to the same synthetic procedure as for Compound (119). By using the aldehyde compound (118) (3.0 g, 7.2 mmol), N-phenylnaphthalene-2-amine (3.5 g, 10.8 mmol), cesium carbonate (1.3 g, 10.8 mmol), Pd(OAc)$_2$ (48 mg, 0.22 mmol), toluene (100 mL) and P(t-Bu)$_3$ (87 mg, 0.43 mmol), Compound (135) (2.8 g, 5.0 mmol) was obtained.

[162] Preparation of Compound (136)

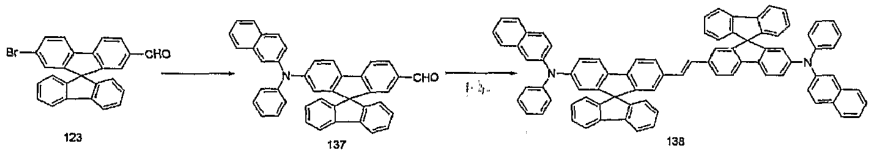
[163] Compound (136) was obtained according to the same synthetic procedure as for Compound (120). By using zinc dust (4.0 g, 60.4 mmol), TiCl$_4$ (1 M in dichloromethane) (21 mL, 20.1 mmol), tetrahydrofuran (50 mL) and Compound 135 (2.8 g, 5.0 mmol), Compound (136, DIF-2) (2.3 g, 2.1 mmol, yield: 58%) was obtained as yellow solid.

[164] ^{1}H NMR(CDCl$_3$, 200 MHz) : δ 1.67(s, 24H), 6.46(m, 4H), 6.61-6.62(m, 4H), 6.76-6.78(m, 6H), 6.99-7.09(m, 8H), 7.23(m, 2H), 7.44-7.55(m, 8H), 7.70-7.74(m, 8H), 7.95(m, 2H)

[165] MS/FAB : 1078(found) 1079.41(calculated)

[166] [Synthetic Example 6] Preparation of DSF-2 (Compound 138)

[167]



[168] Preparation of Compound (137)

[169] Compound (137) was obtained according to the same synthetic procedure as for Compound (119). By using the aldehyde compound (123) (6.8 g, 16.0 mmol), N-phenylnaphthalene-2-amine (5.3 g, 24.0 mmol), cesium carbonate (7.8 g, 24.1 mmol), Pd(OAc)$_2$ (107 mg, 0.48 mmol), toluene (150 mL) and P(t-Bu)$_3$ (194 mg, 0.96 mmol), Compound (137) (7.5 g, 13.3 mmol) was obtained.

[170] Preparation of Compound (138)

[171] Compound (138) was obtained according to the same synthetic procedure as for Compound (120). By using zinc dust (8.7 g, 133 mmol), TiCl$_4$ (1 M solution in dichloromethane) (53 mL, 53.2 mmol), tetrahydrofuran (65 mL) and Compound 137 (7.5 g, 13.3 mmol), Compound (138, DSF-2) (8.1 g, 7.5 mmol, yield: 93%) was obtained as pale gray solid.

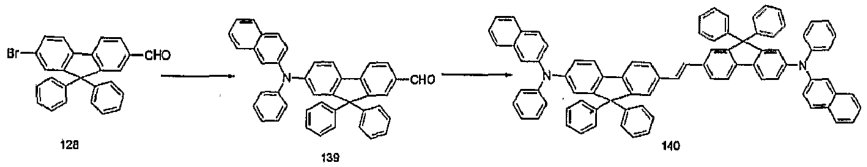
[172] ^{1}H NMR(CDCl$_3$, 200 MHz) : δ6.46(m, 4H), 6.58-6.62(m, 4H), 6.75-6.79(m, 6H),

6.99-7.23(m, 18H), 7.71(m, 4H), 7.44-7.59(m, 10H), 7.71-7.72(m, 6H), 7.84(m, 2H)

[173] MS/FAB : 1090(found) 1091.34(calculated)

[174] [Synthetic Example 7] Preparation of DPF-2 (Compound 140)

[175]



[176] Preparation of Compound (139)

[177] Compound (139) was obtained according to the same synthetic procedure as for Compound (119). By using the aldehyde compound (128) (6.8 g, 16.0 mmol), N-phenylnaphthalene-2-amine (5.3 g, 24.0 mmol), cesium carbonate (7.8 g, 24.1 mmol), $Pd(OAc)_2$ (107 mg, 0.48 mmol), toluene (150 mL) and $P(t\text{-}Bu)_3$ (194 mg, 0.96 mmol), Compound (139) (7.5 g, 13.3 mmol) was obtained.

[178] Preparation of Compound (140)

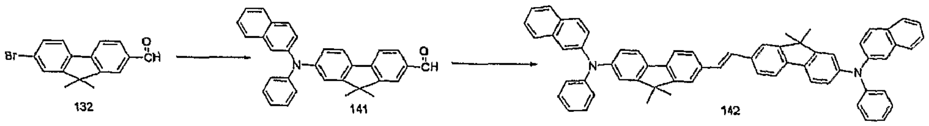
[179] Compound (140) was obtained according to the same synthetic procedure as for Compound (120). By using zinc dust (8.7 g, 133 mmol), $TiCl_4$ (1 M solution in dichloromethane) (53 mL, 53.2 mmol), tetrahydrofuran (65 mL) and Compound 139 (7.48 g, 13.3 mmol), Compound (140, DPF-2) (8.1 g, 7.5 mmol, yield: 93%) was obtained as pale gray solid.

[180] ^1H NMR($CDCl_3$, 200 MHz) : δ 6.46(m, 4H), 6.58-6.62(m, 4H), 6.75-6.79(m, 6H), 6.99-7.23(m, 30H), 7.44-7.59(m, 10H), 7.06(m, 2H), 7.84(m, 2H)

[181] MS/FAB : 1096(found) 1095.37(calculated)

[182] [Synthetic Example 8] Preparation of DMF-2 (Compound 142)

[183]



[184] Preparation of Compound (141)

[185] Compound (141) was obtained according to the same synthetic procedure as for Compound (119). By using the aldehyde compound (132) (5.3 g, 17.5 mmol), N-phenylnaphthalene-2-amine (4.1 g, 26.3 mmol), cesium carbonate (6.1 g, 26.3 mmol), $Pd(OAc)_2$ (84 mg, 0.52 mmol), toluene (117 mL) and $P(t\text{-}Bu)_3$ (152 mg, 1.1 mmol), Compound (141) (5.8 g, 13.2 mmol) was obtained.

[186] Preparation of Compound (142)

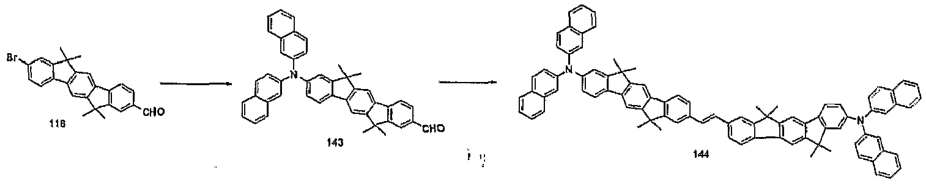
[187] Compound (142) was obtained according to the same synthetic procedure as for Compound (120). By using zinc dust (6.7 g, 68.0 mmol), TiCl$_4$ (1 M solution in dichloromethane) (41 mL, 27.2 mmol), tetrahydrofuran (50 mL) and Compound 139 (5.8 g, 6.8 mmol), Compound (142, DMF-2) (6.3 g, 7.4 mmol, yield: 84%) was obtained as pale gray solid.

[188] ^{1}H NMR(CDCl$_3$, 200 MHz) : δ 1.67(s, 12H), 6.46-6.62(m, 8H), 6.76-6.79(m, 6H), 6.99-7.09(m, 8H), 7.23(m, 2H), 7.44-7.59(m, 10H), 7.71(m, 2H), 7.84(m, 2H)

[189] MS/FAB : 846(found) 847.10(calculated)

[190] [Synthetic Example 9] Preparation of DIF-3 (Compound 144)

[191]



[192] Preparation of Compound (143)

[193] Compound (143) was obtained according to the same synthetic procedure as for Compound (119). By using the aldehyde compound (118) (5.0 g, 12.0 mmol), di(naphthalene-3-yl)amine (4.8 g, 18.0 mmol), cesium carbonate (5.9 g, 18.0 mmol), Pd(OAc)$_2$ (81 mg, 0.36 mmol), toluene (90 mL) and P(t-Bu)$_3$ (145 mg, 0.72 mmol), Compound (143) (5.7 g, 9.5 mmol) was obtained.

[194] Preparation of Compound (144)

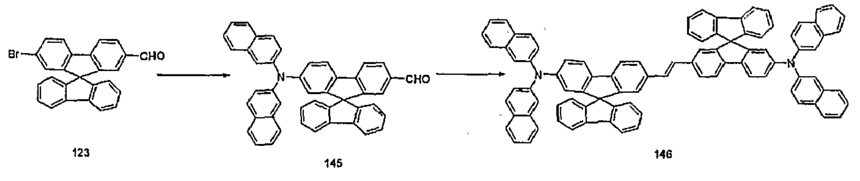
[195] Compound (144) was obtained according to the same synthetic procedure as for Compound (120). By using zinc dust (7.4 g, 0.11 mol), TiCl$_4$ (1 M in dichloromethane) (38 mL, 38 mmol), tetrahydrofuran (75 mL) and Compound (143) (5.7 g, 9.5 mmol), Compound (144, DIF-3) (4.0 g, 3.4 mmol, yield: 57%) was obtained as yellow solid.

[196] ^{1}H NMR(CDCl$_3$, 200 MHz) : δ1.67(s, 24H), 6.61-6.79(m, 12H), 6.99(d, 2H), 7.09-7.23(m, 8H), 7.44-7.57(m, 14H), 7.70-7.74(m, 8H), 7.95(m, 2H)

[197] MS/FAB : 1178(found) 1179.53(calculated)

[198] [Synthetic Example 10] Preparation of DSF-3 (Compound 146)

[199]



[200] Preparation of Compound (145)

[201] Compound (145) was obtained according to the same synthetic procedure as for Compound (119). By using the spiro-type aldehyde compound (123) (5.9 g, 13.9 mmol), di(naphthalene-3-yl)amine (4.8 g, 18.0 mmol), cesium carbonate (6.8 g, 20.9 mmol), $Pd(OAc)_2$ (93 mg, 0.42 mmol), toluene (90 mL) and $P(t\text{-}Bu)_3$ (169 mg, 0.84 mmol), Compound (145) (6.6 g, 10.7 mmol) was obtained.

[202] Preparation of Compound (146)

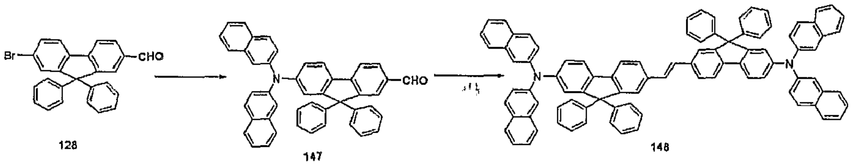
[203] Compound (146) was obtained according to the same synthetic procedure as for Compound (120). By using zinc dust (7.0g, 0.11 mol), $TiCl_4$ (1 M solution in dichloromethane) (43 mL, 43 mmol), tetrahydrofuran (65 mL) and Compound 145 (6.6 g, 10.7 mmol), Compound (146, DSF-3) (7.0 g, 5.9 mmol, yield: 84%) was obtained as gray solid.

[204] ^1H NMR($CDCl_3$, 200 MHz) : δ 6.58(m, 2H), 6.75-6.79(m, 10H), 6.99(s, 2H), 7.09-7.23(m, 16H), 7.35-7.55(m, 20H), 7.71-7.72(m, 6H), 7.84(m, 2H)

[205] MS/FAB : 1190(found) 1191.46(calculated)

[206] [Synthetic Example 11] Preparation of DPF-3 (Compound 148)

[207]



[208] Preparation of Compound (147)

[209] Compound (147) was obtained according to the same synthetic procedure as for Compound (119). By using the spiro-type aldehyde compound (128) (4.3 g, 10.1 mmol), di(naphthalene-3-yl)amine (3.5 g, 15.2 mmol), cesium carbonate (5.0 g, 15.2 mmol), $Pd(OAc)_2$ (68 mg, 0.30 mmol), toluene (66 mL) and $P(t\text{-}Bu)_3$ (123 mg, 0.61 mmol), Compound (147) (4.8 g, 7.8 mmol) was obtained.

[210] Preparation of Compound (148)

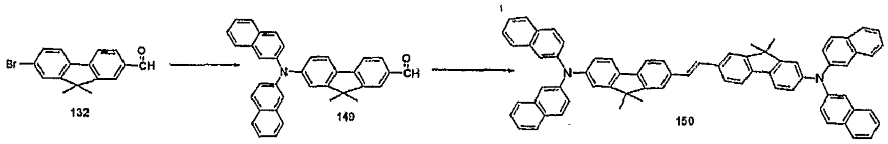
[211] Compound (148) was obtained according to the same synthetic procedure as for Compound (120). By using zinc dust (5.1 g, 78.0 mmol), $TiCl_4$ (1 M solution in dichloromethane) (31 mL, 31.2 mmol), tetrahydrofuran (47 mL) and Compound (147) (4.8 g, 7.8 mmol), Compound (148, DPF-3) (5.1 g, 4.2 mmol, yield: 83%) was obtained as gray solid.

[212] ^1H NMR($CDCl_3$, 200 MHz) : δ6.58(m, 2H), 6.75-6.79(m, 10H), 6.99-7.23(m, 30H), 7.44-7.55(m, 16H), 7.71-7.84(m, 4H)

[213] MS/FAB : 1194(found) 1195.49(calculated)

[214] [Synthetic Example 12] Preparation of DMF-3 (Compound 150)

[215]



[216] Preparation of Compound (149)

[217] Compound (149) was obtained according to the same synthetic procedure as for Compound (119). By using the spiro-type aldehyde compound (132) (5.6 g, 18.5mmol), di(naphthalene-3-yl)amine (4.6 g, 27.8 mmol), cesium carbonate (6.5 g, 27.8 mmol), Pd(OAc)$_2$ (89 mg, 0.56 mmol), toluene (86 mL) and P(t-Bu)$_3$ (160 mg, 1.11 mmol), Compound (149) (6.3 g, 12.8 mmol) was obtained.

[218] Preparation of Compound (150)

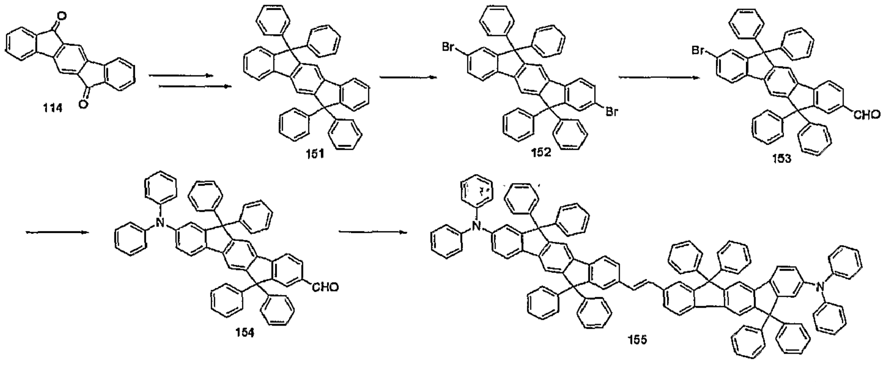
[219] Compound (150) was obtained according to the same synthetic procedure as for Compound (120). By using zinc dust (6.7 g, 0.128 mol), TiCl$_4$ (1 M solution in dichloromethane) (41 mL, 51.2 mmol), tetrahydrofuran (62 mL) and Compound (149) (6.3 g, 12.8 mmol), Compound (150, DMF-3) (7.5 g, 7.9 mmol, yield: 85%) was obtained as gray solid.

[220] ^{1}H NMR(CDCl$_3$, 200 MHz) : δ 1.67(s, 12H), 6.58(m, 2H), 6.75-6.79(m, 10H), 6.99(s, 2H), 7.09-7.23(m, 8H), 7.44-7.55(m, 16H), 7.71(m, 2H), 7.84(m, 2H)

[221] MS/FAB : 946(found) 947.21(calculated)

[222] [Synthetic Example 13] Preparation of DTPIF-1 (Compound 155)

[223]



[224] Preparation of Compound (151)

[225] Diethyl ether (59 mL) was added to magnesium (5.8 g, 0.283 mol), and bromobenzene (37.2 g, 0.283 mol) diluted in 178 mL of diethyl ether was slowly added dropwise thereto. After heating the reaction mixture under reflux for 3 hours, a solution of Compound (114) (20.0 g, 70.8 mmol) dissolved in 47 mL of diethyl ether

was slowly added dropwise to the reaction mixture, which was then heated under reflux for 12 hours. After the reaction was completed, the precipitate generated was filtered under reduced pressure to obtain intermediate product (24.6 g, 44.0 mmol). The intermediate product was dissolved in 172 mL of benzene, and the solution was slowly added dropwise to trifluoromethanesulfonic acid (53 mL), while raising the temperature slowly. After stirring the mixture at 100°Cor 30 minutes, the reaction solution was added to ice-water (200 mL) to generate solid. The solid generated was filtered under reduced pressure, washed with 59 mL of methanol and 119 mL of diethyl ether, and dried under reduced pressure to obtain Compound (151) (32.1 g, 57.4 mmol) as pale yellow solid.

[226] Preparation of Compound (152)

[227] Compound (151) (32.1 g, 57.4 mmol) and ferric chloride (56 mg) were dissolved in chloroform (338 mL). A solution of bromine (33.9 g, 121 mmol) dissolved in 56 mL of chloroform was charged to a dropping funnel, and slowly added dropwise thereto at 0°C After the addition was completed, the reaction mixture was stirred for 1 hour. The reaction was quenched by adding saturated aqueous sodium thiosulfate solution. The reaction mixture was extracted with 500 mL of dichloromethane, and the organic layer was dried, filtered and recrystallized from dichloromethane:hexane (1/1, v/v) (200 mL), to obtain Compound (152) (33.0 g, 46.0 mmol).

[228] Preparation of Compound (153)

[229] Compound (153) was obtained according to the same synthetic procedure as for Compound (118). By using Compound (152) (33.0 g, 46.0 mmol), tetrahydrofuran (146 mL), n-BuLi (1.6 M in n-hexane) (43 mL, 55.2 mmol) and N,N-dimethylformamide (6.2 mL, 64.4 mmol), Compound (153) (23.0 g, 34.5 mmol) was obtained.

[230] Preparation of Compound (154)

[231] Compound (154) was obtained according to the same synthetic procedure as for Compound (119). By using the aldehyde compound (153) (23.0 g, 34.5 mmol), diphenylamine (13.8 g, 51.8 mmol), cesium carbonate (26.4 g, 51.8mmol), $Pd(OAc)_2$ (365 mg, 1.0 mmol), toluene (1.2 L) and $P(t\text{-}Bu)_3$ (660 mg, 2.1 mmol), Compound (154) (23.4 g, 31.0 mmol) was obtained.

[232] Preparation of Compound (155)

[233] Compound (155) was obtained according to the same synthetic procedure as for Compound (120). By using zinc dust (30.0 g, 0.31 mol), $TiCl_4$ (1 M solution in dichloromethane) (183 mL, 0.124 mol), tetrahydrofuran (160 mL) and Compound

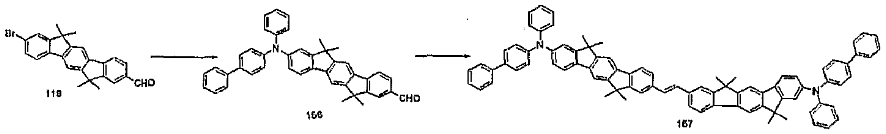
(154) (23.4 g, 31.0mmol), Compound (155, DTPIF-1) (14.9 g, 10.0 mmol, yield on the basis of Compound (153): 57%) was obtained as white powder.

[234] ^{1}H NMR(CDCl$_3$, 200 MHz) : δ 6.46(m, 8H), 6.61-6.62(m, 6H), 6.78(m, 2H), 7.01-7.14(m, 50H), 7.57(m, 2H), 7.67-7.70(m, 8H), 7.95(m, 2H)

[235] MS/FAB : 1474(found) 1475.85(calculated)

[236] [Synthetic Example 14] <u>Preparation of DIF-4 (Compound 157)</u>

[237]



[238] <u>Preparation of Compound (156)</u>

[239] Compound (156) was obtained according to the same synthetic procedure as for Compound (119). By using the aldehyde compound (118) (10.0 g, 24.0 mmol), N-phenylbiphenylamine (8.8 g, 36.0 mmol), cesium carbonate (11.7 g, 36.0 mmol), Pd(OAc)$_2$ (161 mg, 0.72 mmol), toluene (90 mL) and P(t-Bu)$_3$(291 mg, 1.44 mmol), Compound (156) (12.6 g, 21.6 mmol) was obtained.

[240] <u>Preparation of Compound (157)</u>

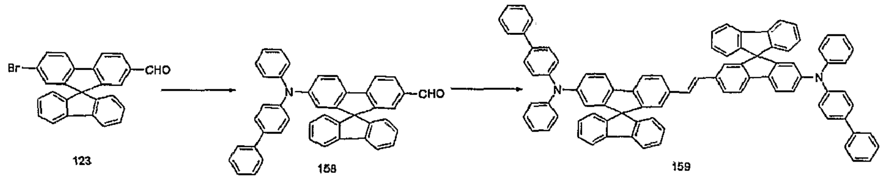
[241] Compound (157) was obtained according to the same synthetic procedure as for Compound (120). By using zinc dust (17.0 g, 0.26 mol), TiCl$_4$ (1 M in dichloromethane) (86 mL, 86 mmol), tetrahydrofuran (150 mL) and Compound (156) (12.6 g, 21.6 mmol), Compound (157, DIF-4) (5.6 g, 5.0 mmol, yield: 41%) was obtained as yellow solid.

[242] ^{1}H NMR(CDCl$_3$, 200 MHz) : δ 1.67(s, 24H), 6.46-6.62(m, 12H), 6.78(m, 2H), 6.99-7.01(m, 6H), 7.22-7.32(m, 10H), 7.48-7.57(m, 6H), 7.70-7.73(m, 8H), 7.95(m, 2H)

[243] MS/FAB : 1130(found) 1131.49(calculated)

[244] [Synthetic Example 15] <u>Preparation of DSF-4 (Compound 159)</u>

[245]



[246] <u>Preparation of Compound (158)</u>

[247] Compound (158) was obtained according to the same synthetic procedure as for Compound (119). By using the spiro-type aldehyde compound (123) (4.54 g, 10.7

mmol), N-phenylbiphenylamine (4.4 g, 18.0 mmol), cesium carbonate (5.25 g, 16.1 mmol), Pd(OAc)$_2$ (71.6mg, 0.32 mmol), toluene (75 mL) and P(t-Bu)$_3$ (130 mg, 0.65 mmol), Compound (158) (4.16 g, 7.1 mmol) was obtained.

[248] Preparation of Compound (159)

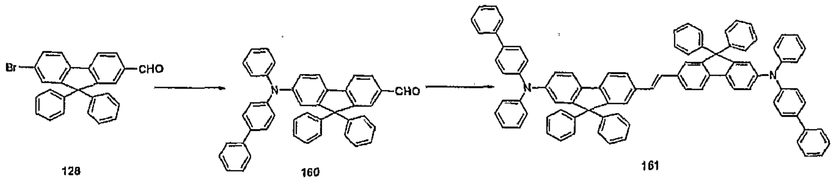
[249] Compound (159) was obtained according to the same synthetic procedure as for Compound (120). By using zinc dust (4.7 g, 70.8 mmol), TiCl$_4$ (1 M solution in dichloromethane) (29 mL, 28.3 mmol), tetrahydrofuran (40 mL) and Compound (158) (4.16 g, 7.1 mmol), Compound (159, DSF-4) (6.02 g, 5.2 mmol, yield: 97%) was obtained as gray solid.

[250] ^{1}H NMR(CDCl$_3$, 200 MHz) : δ6.46-6.58(m, 12H), 6.75(d, 2H), 6.99-7.01(m, 6H), 7.16-7.32(m, 22H), 7.48-7.59(m, 8H), 7.71-7.84(m, 8H)

[251] MS/FAB : 1142(found) 1143.42(calculated)

[252] [Synthetic Example 16] Preparation of DPF-4 (Compound 161)

[253]



[254] Preparation of Compound (160)

[255] Compound (160) was obtained according to the same synthetic procedure as for Compound (119). By using the spiro-type aldehyde compound (128) (4.0 g, 9.40 mmol), N-phenylbiphenylamine (3.9 g, 14.1 mmol), cesium carbonate (4.6 g, 14.1 mmol), Pd(OAc)$_2$ (63 mg, 0.28 mmol), toluene (66 mL) and P(t-Bu)$_3$(115 mg, 0.56 mmol), Compound (160) (3.7 g, 6.2 mmol) was obtained.

[256] Preparation of Compound (161)

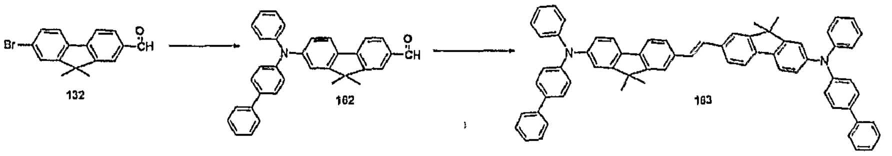
[257] Compound (161) was obtained according to the same synthetic procedure as for Compound (120). By using zinc dust (4.2 g, 62.0 mmol), TiCl$_4$ (1 M solution in dichloromethane) (26 mL, 24.8 mmol), tetrahydrofuran (36 mL) and Compound (160) (3.7 g, 6.2 mmol), Compound (161, DPF-4) (5.3 g, 4.6 mmol, yield: 98%) was obtained as gray solid.

[258] ^{1}H NMR(CDCl$_3$, 200 MHz) : δ 6.46-6.62(m, 12H), 6.75(d, 2H), 6.99-7.32(m, 36H), 7.48-7.59(m, 8H), 7.71(m, 2H), 7.84(m, 2H)

[259] MS/FAB : 1176(found) 1147.75(calculated)

[260] [Synthetic Example 17] Preparation of DMF-4 (Compound 163)

[261]



[262] Preparation of Compound (162)

[263] Compound (162) was obtained according to thesame synthetic procedure as for Compound (119). By using the aldehyde compound (132) (6.0 g, 19.9 mmol), N-phenylbiphenylamine (5.8 g, 29.9 mmol), cesium carbonate (6.9 g, 29.9 mmol), $Pd(OAc)_2$ (65 mg, 0.60 mmol), toluene (99 mL) and $P(t\text{-}Bu)_3$ (172 mg, 1.2 mmol), Compound (162) (5.5 g, 11.8 mmol) was obtained after recrystallization from 60 mL of methanol.

[264] Preparation of Compound (163)

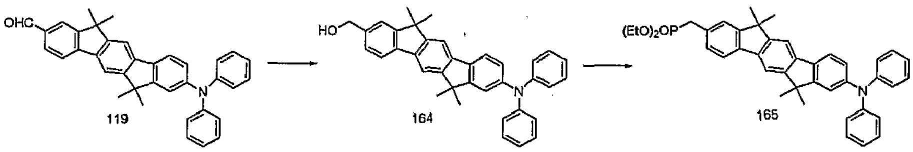
[265] Compound (163) was obtained according to the same synthetic procedure as for Compound (120). By using zinc dust (6.2 g, 118.0 mmol), $TiCl_4$ (1 M solution in dichloromethane) (38 mL, 47.2 mmol), tetrahydrofuran (53 mL) and Compound (162) (5.5 g, 11.8 mmol), Compound (163, DMF-4) (8.0 g, 8.8 mmol, yield: 88%) was obtained as gray solid.

[266] ^1H NMR($CDCl_3$, 200 MHz) : δ1.67(s, 12H), 6.46-6.62(m, 12H), 6.75(m, 2H), 6.99-7.01(m, 6H), 7.22-7.32(m, 10H), 7.48-7.59(m, 8H), 7.71-7.84(m, 4H)

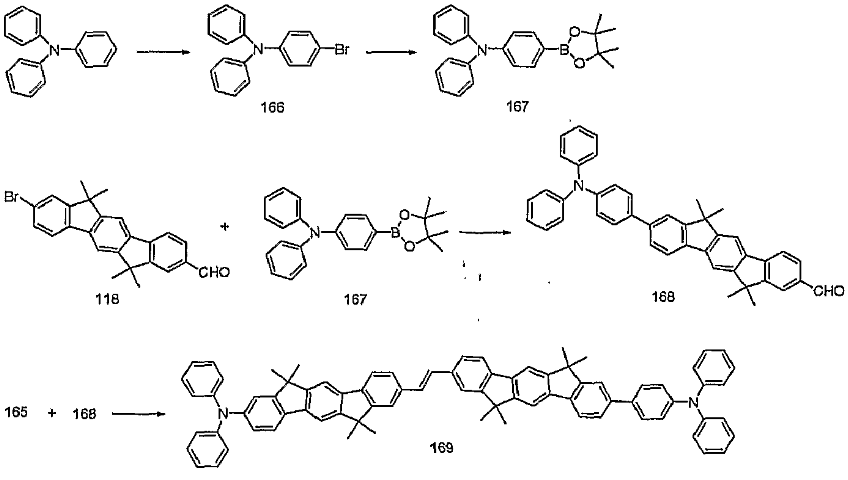
[267] MS/FAB : 888(found) 899.17(calculated)

[268] [Synthetic Example 18] Preparation of DIF-11 (Compound 169)

[269]



[270]



[271] Preparation of Compound (164)

[272] In tetrahydrofuran (20 mL), dissolved are Compound (119) (1.2 g, 2.4 mmol), $NaBH_4$ (0.1 g, 3.6 mmol). The solution was cooled to 0°C, and 10 mL of methanol was slowly added dropwise thereto. After stirring the mixture for 30 minutes, distilled water (50 mL) was added thereto to quench the reaction. The reaction mixture was extracted with ethyl acetate (30 mL), dried under reduced pressure, and purified by column chromatography (dichloromethane/hexane = 1/1) to obtain Compound (164) (0.9 g, 1.8 mmol).

[273] Preparation of Compound (165)

[274] Compound (164) (0.9 g, 1.8 mmol) was charged to a reaction vessel, and triethyl phosphite (20 mL) was added to bedissolved therein under nitrogen atmosphere. To another eaction vessel, charged was triethyl phosphite (10 mL), and iodine (0.6 g, 1.8 mmol) was added in small portions with the lid open, while stirring at 0°C for 30 minutes. The mixture containing iodine and triethyl phosphite was charged to a reaction vessel containing Compound (109). The temperature was raised to 150°C, and the mixture was stirred for 4 hours. When the reaction was completed, triethyl phosphite was removed by distillation under reduced pressure. The residue was washed with 500 mL of water, extracted with 500 mL of ethyl acetate, and driedunder reduced pressure. After purification via column chromatography (eluent: ethyl acetate/ hexane = 1/1) to obtain Compound (165) (1.1 g, 1.7 mmol).

[275] Preparation of Compound (166)

[276] Triphenylamine (5.0 g, 20.4 mmol), N-bromosuccinimide (3.6 g, 20.4 mmol) were dissolvedin 40 mL of dichloromethane under nitrogen atmosphere, and the solution was stirred at 25°C for 5 hours. Then,the reaction was quenched by adding 100 mL of distilled water. The mixture was extracted with dichloromethane (30 mL), dried under reduced pressure, and recrystallized from hexane (100 mL) to obtain the target compound (166) (5.2 g, 16.0 mmol).

[277] Preparation of Compound (167)

[278] Compound (166) (5.2 g, 16.0 mmol) thus obtained was dissolved in purified tetrahydrofuran (100 mL) under nitrogen stream, and the solution was cooled to -78°C. To the solution, n-butyl lithium (1.6M in hexane) (15.0 mL, 24.0 mmol) was slowly added dropwise, and the resultant mixture was stirred for 1 hour. Then, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(6.5 mL, 32.0 mmol) was added thereto. The temperature was slowly raised to 25°C, and the mixture wasstirred at the same temperature for 1 day. The reaction was quenched by adding 200 mL of distilled

water, and the mixture was extracted with 100 mL of ethyl acetate, dried under reduced pressure and recrystallized from tetrahydrofuran (20 mL) and methanol (200 mL), to obtain the target compound (167) (3.2 g, 8.6 mmol).

[279] Preparation of Compound (168)

[280] After previously adjusting the temperature at 120°C, Compound (118) (5.0 g, 11.9 mmol), Compound (167) (5.3 g, 14.4 mmol), tetrakis palladium triphenylphosphine ($Pd(PPh_3)_4$) (1.4 g, 1.2 mmol) and aliquat 336 (0.6 mL, 1.2 mmol) were dissolved in 100 mL of toluene. To the solution, aqueous 2M potassium carbonate solution (60 mL) was added and the mixture was heated under reflux with stirring for 4 hours. Then, the temperature was lowered to 25°C, and distilled water (150 mL) was added thereto to quench the reaction. The mixture was extracted with 100 mL of ethyl acetate, dried under reduced pressure, and recrystallized from methanol (100 mL) and tetrahydrofuran (20 mL), to obtain the target compound (168) (5.8 g, 9.9 mmol).

[281] Preparation of Compound (169)

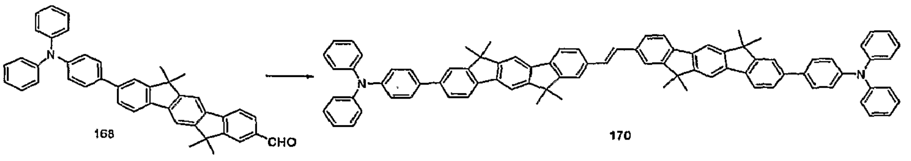
[282] Compound (165) (6.2 g, 9.9 mmol) and Compound (168) (5.8 g, 9.9 mmol) were charged to a reaction vessel, and dried under reduced pressure. After providing nitrogen atmosphere, tetrahydrofuran (200 mL) was added and dissolved therein, and the mixture was cooled to 0°C. To another vessel, potassium tert-butoxide (t-BuOK) (1.7 g, 14.8 mmol) dissolved in tetrahydrofuran (20 mL) was slowly added dropwise. After stirring at 0°Cfor 2 hours, distilled water (300 mL) was added thereto, and the resultant mixture was stirred. The solid generated was filtered under reduced pressure to obtain solidproduct, which was washed with methanol (200 mL x 3). The product was washed with ethyl acetate (50 mL) and recrystallized from tetrahydrofuran (50 mL) and methanol (300 mL) to obtain the target compound (169) (5.7 g, 5.4 mmol, yield: 55%).

[283] H NMR($CDCl_3$, 200 MHz) : δ 1.68(s, 24H), 6.46-6.62(m, 15H), 6.75(m, 1H), 6.99-7.01(m, 10H), 7.24(m, 2H), 7.54-7.69(m, 6H), 7.71-7.77(m, 4H), 8.06-8.12(m, 12H),

[284] MS/FAB : 1054(found) 1055.4(calculated)

[285] [Synthetic Example 19] Preparation of DIF-12 (Compound 170)

[286]



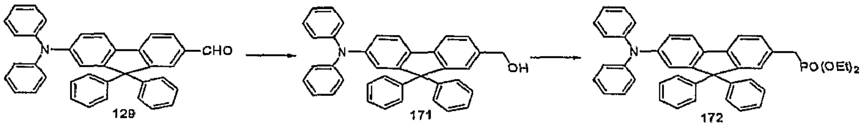
[287] The same procedure for preparing Compound (120) in Synthetic Example 1 was repeated but using Compound (168) (3.0 g, 5.1 mmol) instead of Compound (119), to obtain Compound (170) (2.8 g, 2.5 mmol, yield: 48%) as yellow solid.

[288] H NMR($CDCl_3$, 200 MHz) : δ 1.67(s, 24H), 6.45-6.52(m, 12H), 6.64(m, 4H), 6.99-7.02(m, 10H), 7.23(m, 4H), 7.57-7.63(m, 4H), 7.73-7.74(m, 6H), 7.80(m, 2H), 7.95-8.01(m, 4H)

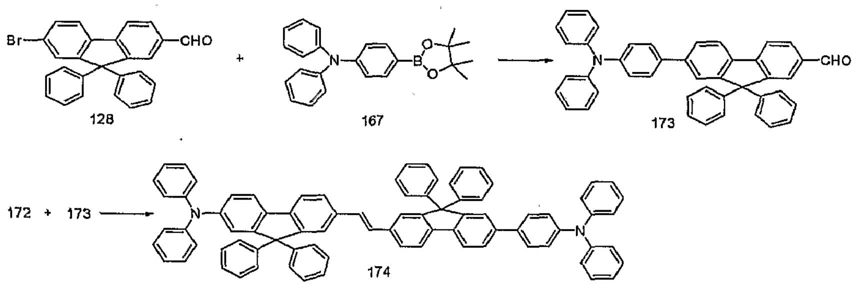
[289] MS/FAB : 1130(found) 1131.4(calculated)

[290] [Synthetic Example 20] Synthesis of DPF-11 (Compound 174)

[291]



[292]



[293] <u>Preparation of Compound (172)</u>

[294] The same procedure as Synthetic Example 18 was carried out but using Compound (129) (8.8 g, 17.1 mmol) prepared from Synthetic Example 3, to obtain the target compound (172) (7.6 g, 11.9 mmol).

[295] <u>Preparation of Compound (174)</u>

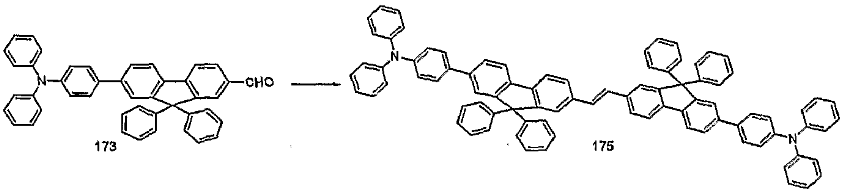
[296] The same procedure as Synthetic Example 18 was carried out from Compound (128) (12.1 g, 28.4 mmol) prepared from Synthetic Example 3, to provide Compound (173), which was then reacted with Compound (172) to obtain the target compound (174) (4.2 g, 3.9 mmol).

[297] H NMR($CDCl_3$, 200 MHz) : δ6.46-6.52(m, 12H), 6.75(m, 1H), 6.99-7.17(m, 32H), 7.54-7.60(m, 4H), 7.71(m, 2H), 7.77(m, 1H), 7.84-7.92(m, 3H)

[298] MS/FAB : 1070(found) 1071.3(calculated)

[299] [Synthetic Example 21] Preparation of DPF-12 (Compound 175)

[300]



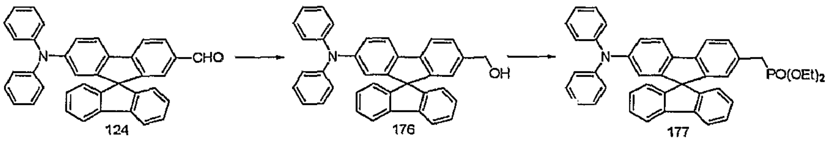
[301] The same procedure for preparing Compound (120) in Synthetic Example 1 was repeated but using Compound (173) (3.0 g, 5.1 mmol) instead of Compound (119), to obtain Compound (175) (2.5 g, 2.2 mmol, yield: 43%) as yellow solid.

[302] H NMR(CDCl$_3$, 200 MHz) : δ 6.46-6.52(m, 12H), 6.62(m, 4H), 6.99-7.23(m, 34H), 7.54-7.60(m, 4H), 7.71-7.77(m, 4H), 7.84-7.90(m, 4H)

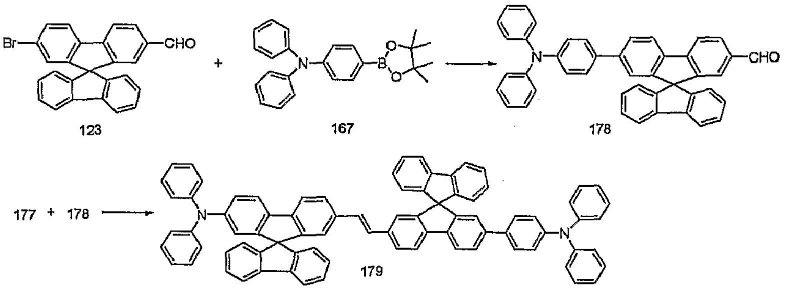
[303] MS/FAB : 1130(found) 1131.4(calculated)

[304] [Synthetic Example 22] Preparation of DSF-11 (Compound 179)

[305]



[306]



[307] Preparation of Compound (177)

[308] The same procedure as Synthetic Example 18 wascarried out but using Compound (124) (4.3 g, 8.4 mmol) prepared from Synthetic Example 2, to obtain the target compound (177) (3.6 g, 5.7 mmol).

[309] Preparation of Compound (179)

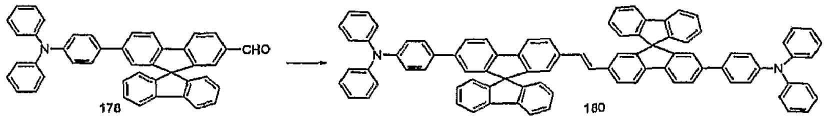
[310] The same procedure as Synthetic Example 18 was carried out from Compound (123) (5.0 g, 11.8 mmol) prepared from Synthetic Example 2, to provide Compound (178), which was then reacted with Compound (177) to obtain the target compound (179) (3.8 g, 3.6 mmol).

[311] H NMR(CDCl$_3$, 200 MHz) : δ 6.46-6.62(m, 15H), 6.75(m, 1H), 6.93-7.01(m, 10H),7.16-7.23(m, 10H), 7.35(m, 4H), 7.54-7.60(m, 4H), 7.71-7.90(m, 10H)

[312] MS/FAB : 1066(found) 1067.3(calculated)

[313] [Synthetic Example 23] Preparation of DSF-12 (Compound 180)

[314]



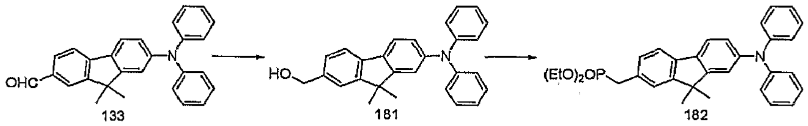
[315] The same procedure for preparing Compound (120) in Synthetic Example 1 was repeatedbut using Compound (178) (3.0 g, 5.1 mmol) instead of Compound (119), to obtain Compound (180) (3.5 g, 3.3 mmol, yield: 60%) as yellow solid.

[316] H NMR(CDCl$_3$, 200 MHz) : δ6.46-6.52(m, 12H), 6.62(m, 4H), 6.99-7.02(m, 10H), 7.16-7.23(m, 12H), 7.35(m, 4H), 7.54-7.60(m, 4H), 7.71-7.72(m, 8H), 7.84-7.91(m, 4H)

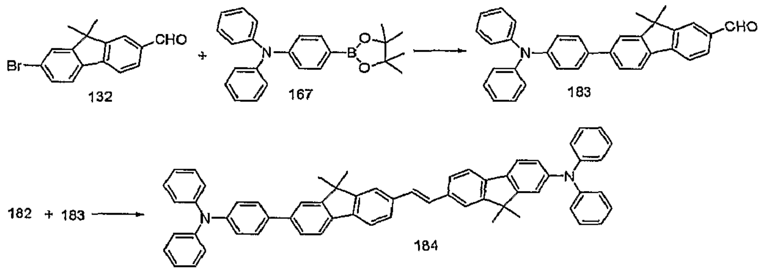
[317] MS/FAB : 1142(found) 1143.4(calculated)

[318] [Synthetic Example 24] Preparation of DMF-11 (Compound 184)

[319]



[320]



[321] Preparation of Compound (182)

[322] The same procedure as Synthetic Example 18 was carried out but using Compound (133) (5.0 g, 12.8 mmol) prepared from Synthetic Example 4, to obtain the target compound (182) (4.4 g, 8.6 mmol).

[323] Preparation of Compound (184)

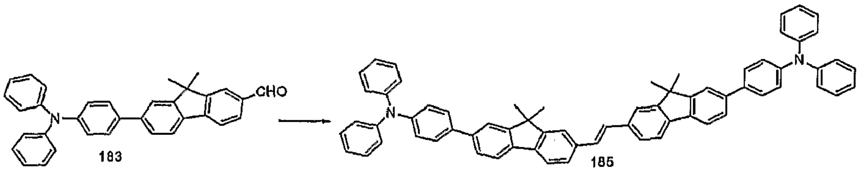
[324] The same procedure as Synthetic Example 18 was carried out from Compound (132) (5.0 g, 16.6 mmol) prepared from Synthetic Example 4, to provide Compound (183), which was then reacted with Compound (182) to obtain the target compound (184) (3.8 g, 3.6 mmol).

[325] H NMR(CDCl$_3$, 200 MHz) : δ1.67(s, 12H), 6.46-6.62(m, 15H), 6.75(d, 1H), 6.99-7.01(m, 10H), 7.23(m, 2H), 7.54-7.59(m, 4H), 7.71(m, 2H), 7.77-7.90(m, 4H)

[326] MS/FAB : 822(found) 823.1(calculated)

[327] [Synthetic Example 25] Preparation of DMF-12 (Compound 185)

[328]



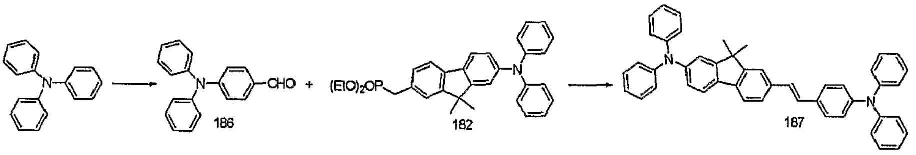
[329] The same procedure for preparing Compound (120) in Synthetic Example 1 was repeated but using Compound (183) (3.0 g, 6.4 mmol) instead of Compound (119), to obtain Compound (185) (3.4 g, 3.8 mmol, yield: 60%) as yellow solid.

[330] H NMR($CDCl_3$, 200 MHz) : δ 1.67(s, 12H), 6.46-6.52(m, 12H), 6.62(m, 4H), 6.99-7.01(m, 10H), 7.23(m, 4H), 7.54-7.60(m, 4H), 7.71-7.90(m, 8H)

[331] MS/FAB : 898(found) 899.1(calculated)

[332] [Synthetic Example 26] Preparation of DMF-21 (Compound 187)

[333]



[334] Triphenylamine (10.0 g, 40.7 mmol) was dissolved in 100 mL of N,N-dimethylformamide, and the solution was cooled to 0°C. To another vessel, N,N-dimethylformamide (32 mL, 407.6 mmol) was charged, and cooled to 0, and POCl3 was slowly added thereto.The mixture was stirred for 30 minutes, and slowly added dropwise to the vessel containing triphenylamine solution at 0°C. The resultant mixture was further stirred at 45°C for 18 hours, and saturated sodium hydroxide solution was slowly poured thereto. Then, an excessamount of water was added thereto, and the mixture stirred. The solid generated was filtered, and washed with water (twice) and methanol (twice) to obtain the target compound (186) (10.0 g, 36.6 mmol).

[335] Preparation of Compound (187)

[336] Compound (186) (2.1 g, 7.8 mmol) was reacted with Compound (182) according to the same procedure as Synthetic Example 18, to obtain the target compound (187) (3.0 g, 4.7 mmol, yield: 62%).

[337] H NMR($CDCl_3$, 200 MHz) : δ1.67(s, 6H), 6.46(m, 10H), 6.58-6.62(m, 5H), 6.75(m, 1H), 6.79-7.01(m, 10H), 7.17(m, 2H), 7.54-7.59(m, 2H), 7.71(m, 1H), 7.84(m, 1H)

[338] MS/FAB : 629(found) 630.8(calculated)

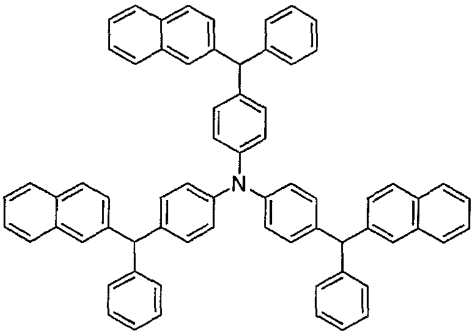
[339] [Example 1] Manufacture of OLED device

[340] An OLED device was made by using the electroluminescent material according to the present invention as a dopant, as illustrated by Fig. 1.

[341] First, a transparent electrode ITO thin film (2) (15 Ω/□ obtained from a glass for OLED (1) was subjected to ultrasonic washing withtrichloroethylene, acetone, ethanol and distilled water, subsequently, and stored in isopronanol before use.

[342] Then, an ITO substrate was equipped in a substrate folder of vacuum vapor-deposit device, and 4,4 ,4''-tris(N,N-(2-naphthyl)-phenylamino)triphenylamine (2-TNATA) represented by following structural formula was placed in a cell of the vacuum vapor-deposit device, which was then ventilated up to 10^{-6} torr of vacuum in the chamber. Electric current was applied to the cell to evaporate 2-TNATA to vapor-deposit a hole injection layer (3) having 60 nm of thickness on the ITO substrate.

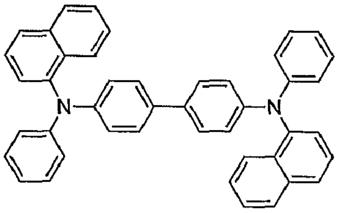
[343]



2-TNATA

[344] Then, to another cell of the vacuum vapor-deposit device, charged was N,N'-bis(α-naphthyl)-N,N'-diphenyl-4,4'-diamine (NPB) represented by following chemical formula, and electric current was applied to the cell to evaporate NPB to vapor-deposit a hole transport layer (4) having20 nm of thickness on the hole injection layer.

[345]

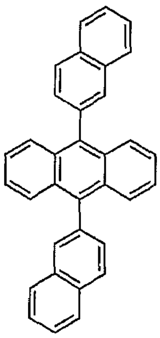


NPB

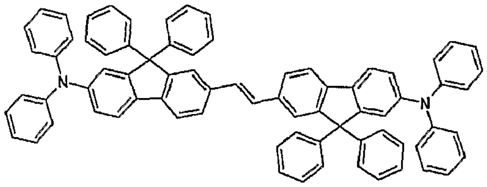
[346] After forming the hole transport layer, an electroluminescent layer (5) was vapor-deposited thereon as follows. In one cell of the vacuum vapor-deposit device, charged

was dinaphthylanthracene (DNA) represented by following chemical formula, and in another cell charged was a compound according to the present invention (e.g. Compound DPF-1) as an electroluminescent material. An electroluminescent layer was vapor-deposited on the hole transport layer by using the vapor-deposit rate of 100:1.

[347]



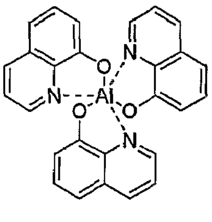
DNA



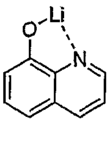
DPF-1

[348] Then, tris(8-hydroxyquinoline)aluminum (III) (Alq) represented by following structural formula was vapor-deposited as an electron transport layer (6) in a thickness of 20 nm, and lithium quinolate (Liq) represented by following structural formula was vapor-deposited as an electron injection layer (7) in a thickness from 1 to 2 nm. Thereafter, an Al cathode (8)was vapor-deposited in a thickness of 150 nm by using another vapor-deposit device,to manufacture an OLED.

[349]



Alq



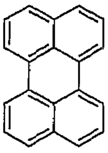
Liq

[350] Each substance employed in the OLED device was used after being purified by sublimation in vacuo at 10^{-6} torr.

[351] [Comparative Example 1] Manufacture of OLED device by using conventional electroluminescent material

[352] A hole injection layer (3) and a hole transport layer (4) were formed as in Example 1. In one cell of the vacuum vapor-deposit device, charged was dinaphthylanthracene (DNA) as a blue electroluminescent material, and in another cell charged was perylene having the structure shown below. An electroluminescent layer (5) was vapor-deposited on the hole transport layer by using the vapor-deposit rate of 100:1.

[353]



perylene

[354] According to the same procedure as in Example 1, anelectron transport layer (6) and an electron injection layer (7) were vapor-deposited, and Al cathode (8) was deposited in a thickness of 150 nm by using another vapor-deposition device, to manufacture an OLED.

[355] [Example 2] Electroluminescent properties of the OLED manufactured

[356] Luminous efficiencies of OLEDs comprising the organic electroluminescent compound according to the invention prepared from Example 1 and the conventional electroluminescent compound prepared from Comparative Example 1 were measured at 500 cd/m^2 and 2,000 cd/m^2, individually, of which the results are shown in Table 1. Since the luminescent properties in the range of lowluminance and those applied on a panel are very important in case of blue electroluminescent material, in particular, the data of luminance ofabout 2,000 cd/m^2 was established as the standard in order to reflect those properties.

[357] Table 1

No.	EL Material1	EL Material2	EL peak (nm)	Luminous Efficiency (cd/A)		Color Coordinate		Luminous Efficiency/Y
				@500cd/m²	@2,000cd/m²	X	Y	
1	DNA	DIF-1	468	10.8	10.5	0.167	0.210	50.0
2	DNA	DSF-1	464	11.5	11.8	0.165	0.207	57.0
3	DNA	DPF-1	465	11.6	12.1	0.159	0.199	60.8
4	DNA	DMF-1	466	10.2	9.8	0.167	0.215	45.6
5	DNA	DIF-2	466	10.5	10.3	0.168	0.221	46.6
6	DNA	DSF-2	466	10.8	11.3	0.163	0.214	52.8
7	DNA	DPF-2	465	11.5	11.9	0.165	0.203	58.6
8	DNA	DMF-2	468	10.6	9.7	0.167	0.220	44.1
9	DNA	DIF-3	468	9.9	9.5	0.168	0.227	41.9
10	DNA	DSF-3	469	11.2	11.3	0.169	0.230	49.1
11	DNA	DPF-3	467	12.2	12.2	0.166	0.217	56.2
12	DNA	DMF-3	468	10.0	9.3	0.164	0.218	42.7
13	DNA	DTPIF-1	460	8.7	8.2	0.157	0.189	43.4
14	DNA	DIF-4	467	9.2	9.0	0.164	0.209	43.1
15	DNA	DSF-4	468	10.2	10.4	0.167	0.223	46.6
16	DNA	DPF-4	468	11.1	11.3	0.168	0.220	51.4
17	DNA	DMF-4	465	8.9	8.9	0.166	0.212	42.0
18	DNA	DIF-11	460	8.3	8.0	0.156	0.190	42.1
19	DNA	DIF-12	456	8.0	7.8	0.155	0.184	42.4
20	DNA	DPF-11	460	8.5	8.1	0.156	0.189	42.8
21	DNA	DPF-12	456	8.2	8.0	0.155	0.183	43.7
22	DNA	DSF-11	460	8.7	8.2	0.156	0.191	42.9
23	DNA	DSF-12	456	8.3	7.8	0.154	0.183	42.6
24	DNA	DMF-11	456	8.6	8.4	0.155	0.183	45.9
25	DNA	DMF-12	456	8.5	8.2	0.155	0.186	44.1
26	DNA	DMF-21	454	7.8	7.5	0.153	0.180	41.6
Comp. 1	DNA	perylene	456,484	4.45	3.62	0.160	0.200	22.3

[358] As can be seen from Table 1, the OLED device employing the organic electroluminescent compounds according to the inventionas the electroluminescent material was compared to the OLED device of Comparative Example which employs widely known DNA:perylene as a conventional electroluminescent material, on the basis of "luminous efficiency/Y" value which shows similar tendency to proton efficiency. As the result, the OLED device employing the organic electroluminescent compound according to the present invention showed higher "luminous efficiency/Y" value than that of Comparative Example.

[359] In view of the fact that the organic electroluminescent compound according to the invention showed higher "luminous efficiency/Y"value, it is found that the organic electroluminescent compounds of the present invention is a material havinghigh proton

efficiency. In addition, it is found that the organic electroluminescent compounds of the present invention can realize higher efficiency while having the similarcolor purity as compared to conventional electroluminescent compounds. In particular, in case of the series of DPF-1,2 and 3, the "luminous efficiency/Y" value was enhanced by about 2.5 to 3-folds as compared to conventional electroluminescent compound.

[360] Thus, the organic electroluminescent compounds according to the present invention can be used as a blue electroluminescent material of high efficiency, being very advantageous in view of luminance of OLED in full-colored display, power consumption and lifetime of the device as compared to conventional devices.

[361] Fig. 2 shows EL spectrum of DPF-1 as an electroluminescent material according to the invention and that of Comparative Example 1. Figs. 3 to 5 show the current density-voltage property, luminance-voltage property and luminous efficiency-current density property of the OLED comprising DPF-1, respectively. As can be seen from Figs. 3-5, the current density-voltage property, luminance-voltage property and luminous efficiency-current density property of the OLED according to the invention were excellent.

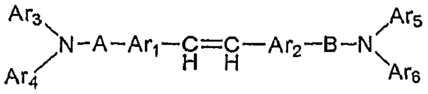
Industrial Applicability

[362] The novel organic electroluminescent compounds according to the present invention may be employed in electroluminescent layer of an electroluminescent device, and have good luminousefficiency and excellent life properties, thereby providing OLEDs having very long lifetime of operation.

Claims

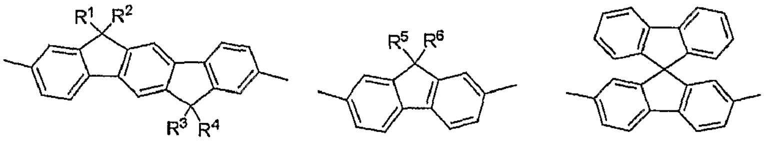
[1] An electroluminescent compound represented by following Chemical Formula 1:

[Chemical Formula 1]



$$Ar_3Ar_4N-A-Ar_1-CH=CH-Ar_2-B-NAr_5Ar_6$$

wherein, Ar_1 is a chemical bond or selected from indenofluorene, fluorene and spiro-fluorene as represented by following chemical formulas, Ar_2 is selected from indenofluorene, fluorine and spiro-fluorene as represented by following chemical formulas:



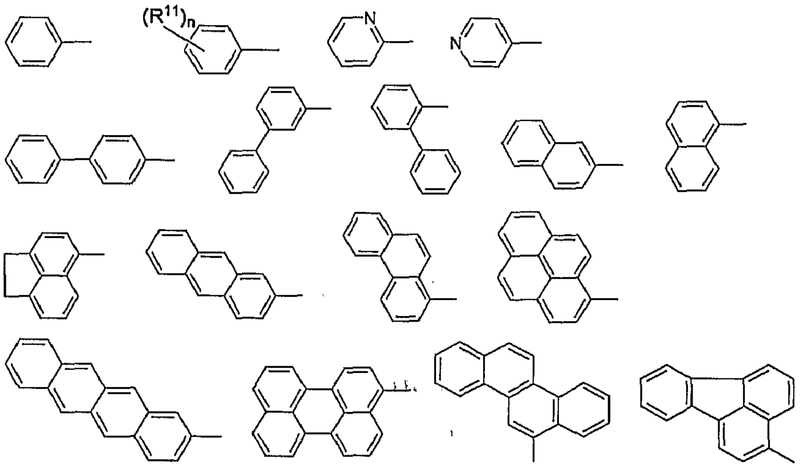
A and B independently represent a chemical bond, or are selected from phenylene group, naphthylene group, biphenylene group, anthracenyl group, perylenylene group and pyrenylene group;

R^1 through R^6 are independently selected from C_1~C_{20} alkyl, cycloalkyl, C_1~C_{20} alkyl having one or more halogen substituent(s), and phenyl or naphthyl having C_1~C_5 alkyl substituent(s);

Ar_3 through Ar_6 are independently selected from C_5~C_{20} aromatic or multicyclic aromatic ring, and the aromatic ring may contain hetero atom(s);

but the compounds wherein both A and Ar_1 are chemical bonds are excluded.

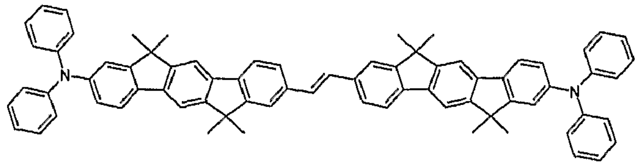
[2] An electroluminescent compound according to claim 1, wherein Ar_1 and Ar_2 are independently selected from following structures:

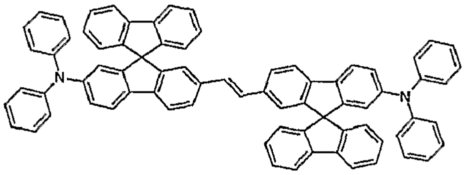


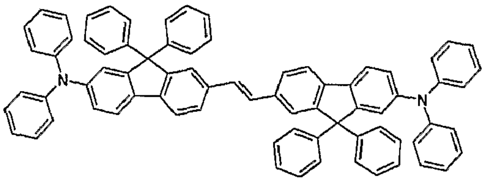
wherein, R^{11} is selected from C_1~C_5 alkyl group with or without halogen substituent(s); and n is an integer from 1 to 5.

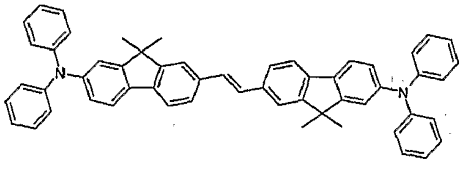
[3] An electroluminescent compound according to claim 2, wherein R^1 through R^6 are independently selected from C_1~C_5 alkyl, a C_5~C_7 cycloalkyl, phenyl and naphthyl.

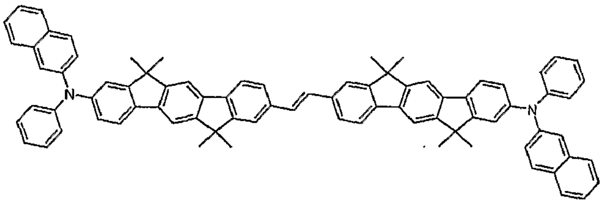
[4] An electroluminescent compound according to claim 3, wherein Ar_1 is same as Ar_2, Ar_3 is same as Ar_5, and Ar_4 is same as Ar_6.

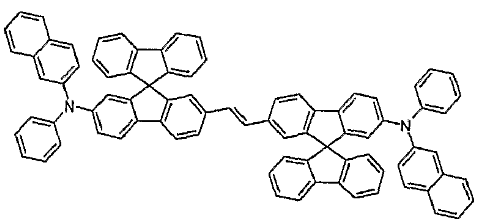


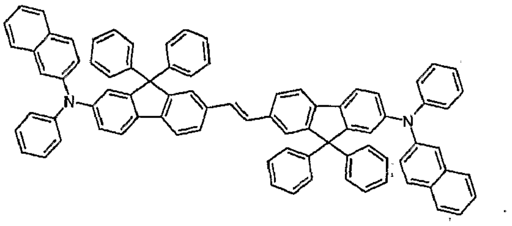


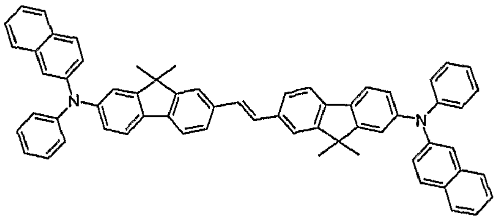


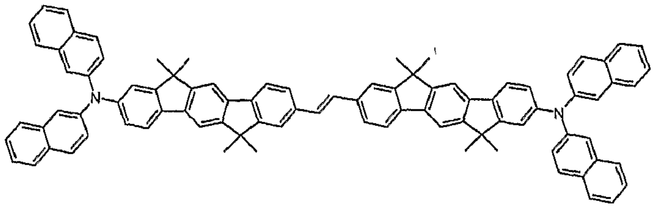


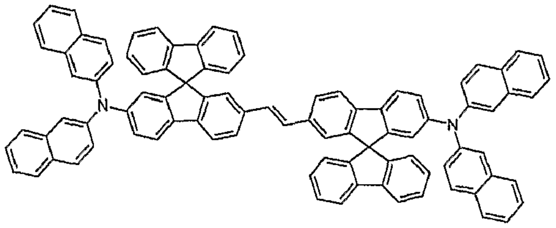


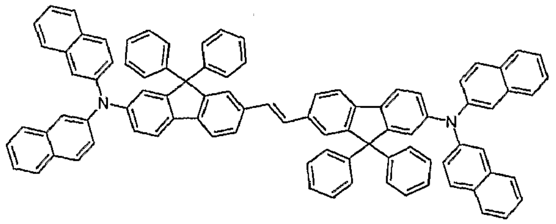


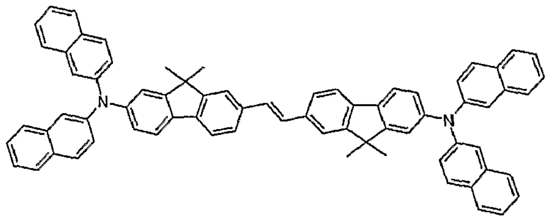


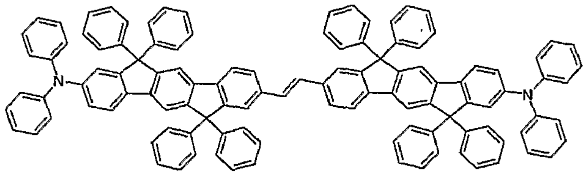


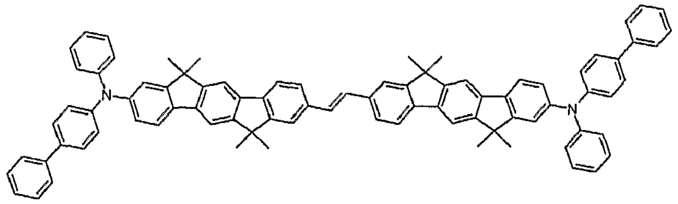


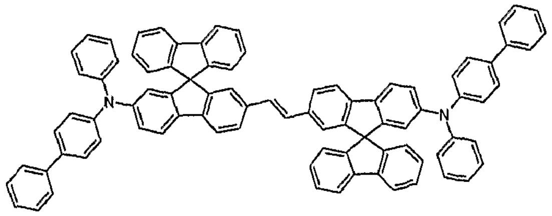


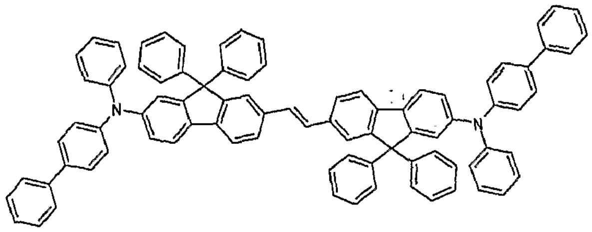


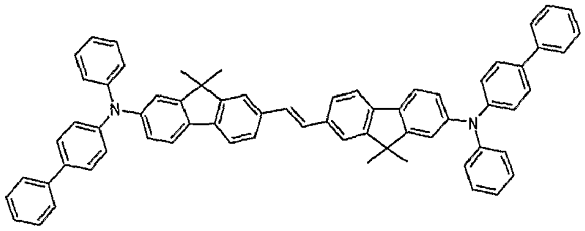


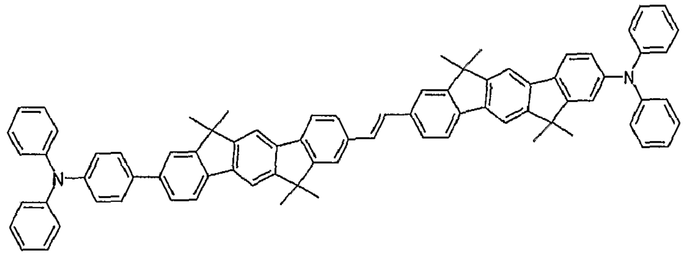


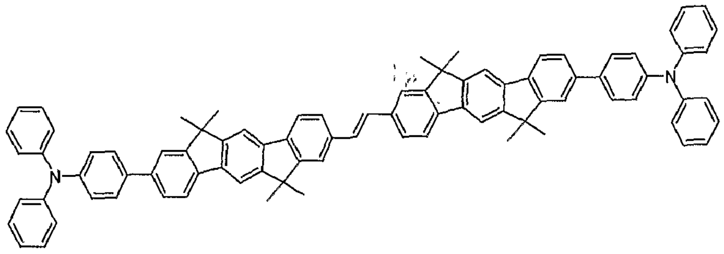


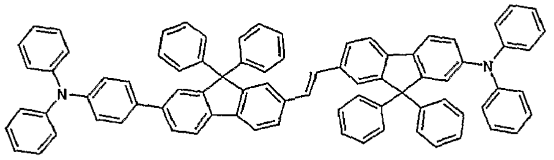


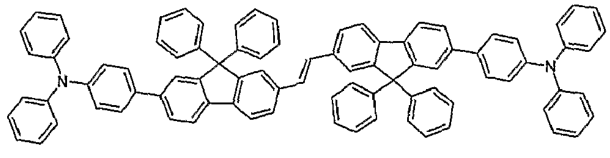


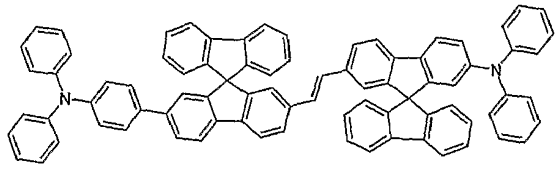


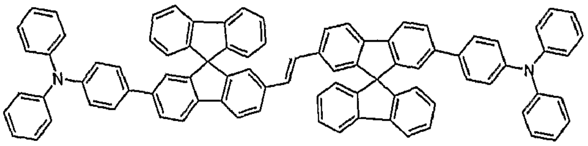


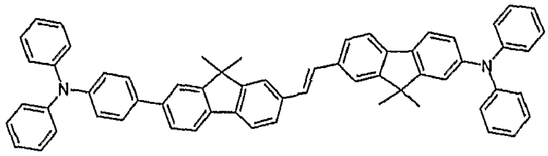


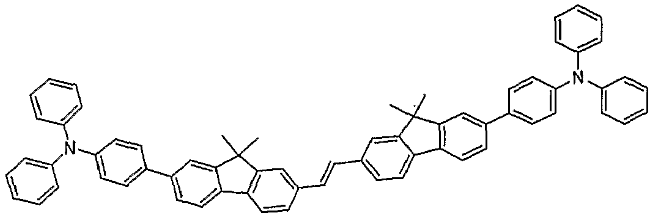


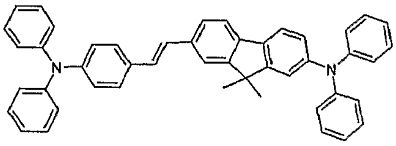








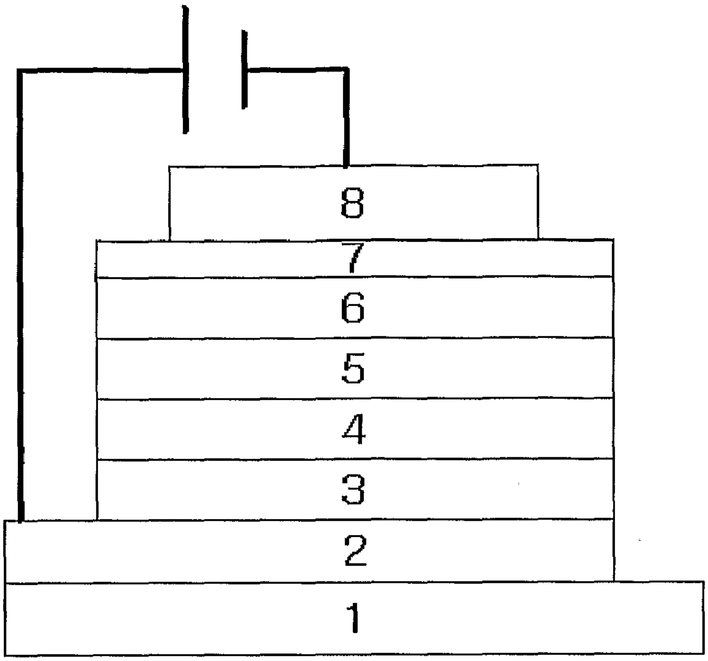




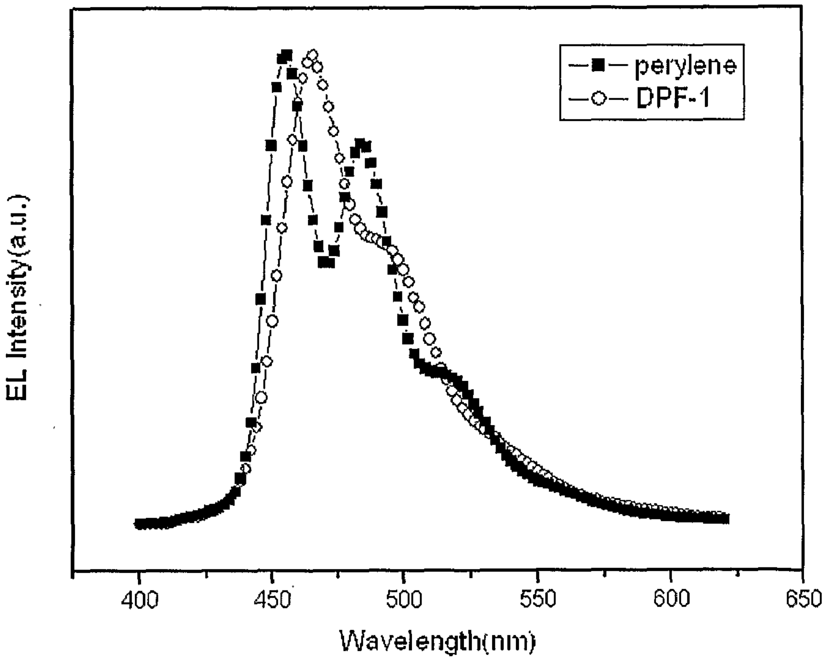
[5] An electroluminescent device comprising an electroluminescent compound according to any one of claims 1 to 5.

[6] An electroluminescent device according to claim 6, in which the electroluminescent compound is used as a dopant material in an electroluminescent layer.

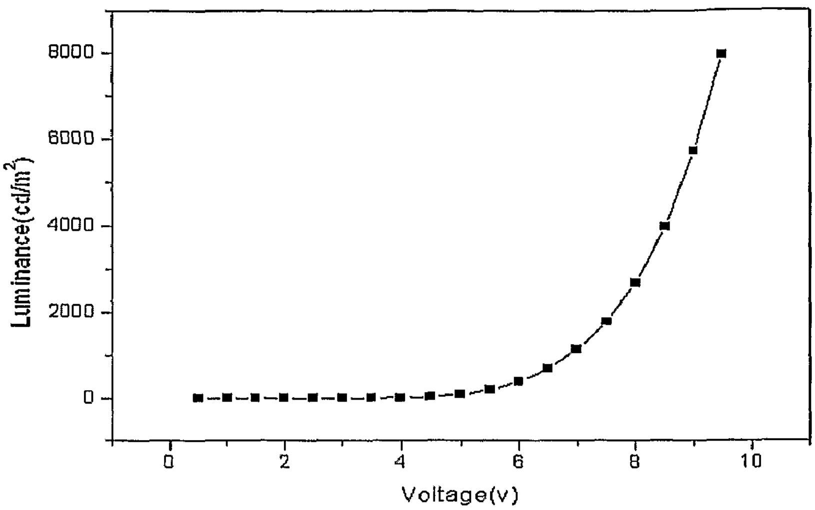
[Fig. 1]


8
7
6
5
4
3
2
1

[Fig. 2]

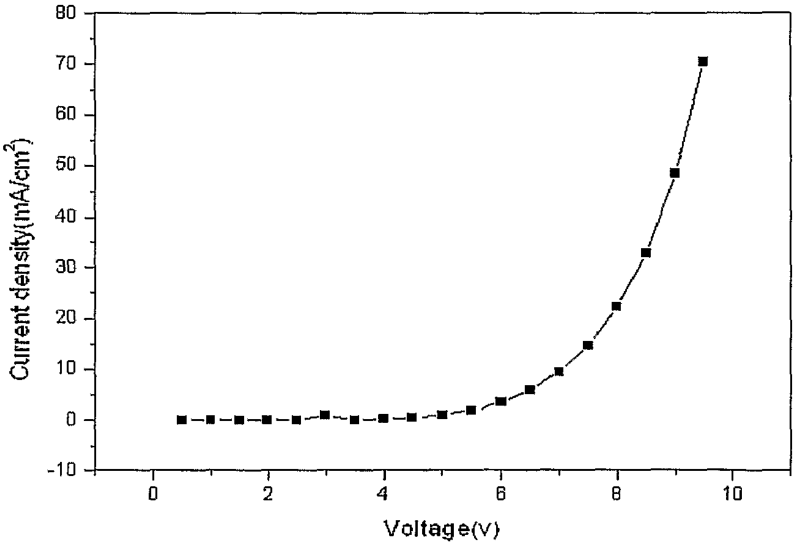

perylene
DPF-1
EL Intensity(a.u.)
400
450
500
550
600
650
Wavelength(nm)

[Fig. 3]



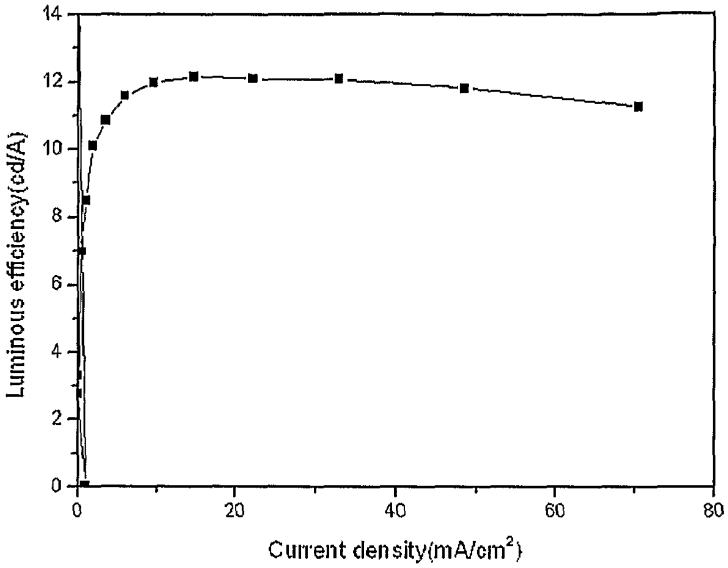
Luminance(cd/m^2)
8000
6000
4000
2000
0
0
2
4
6
8
10
Voltage(v)

[Fig. 4]



Current density(mA/cm^2)
80
70
60
50
40
30
20
10
0
-10
0
2
4
6
8
10
Voltage(V)

[Fig. 5]


Luminous efficiency(cd/A)
0
2
4
6
8
10
12
14
0
20
40
60
80
Current density(mA/cm^2)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2007/000456

A. CLASSIFICATION OF SUBJECT MATTER

C09K 11/06(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09K 11/06

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKIPASS, USPAT, PAJ, CA(STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2004-277368 A (MITSUI CHEMICALS INC) 07 October 2004 See abstract, claims, formula(1)	1-6
A	US 2003/91859 A1 (CHO et al.) 15 May 2003 See abstract, claims	1-6
A	JP 2005-119994 A (MITSUI CHEMICALS INC) 12 May 2005 See the whole document	1-6
A	JP 2005-325097 A (CANON INC) 24 November 2005 See the whole document	1-6

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

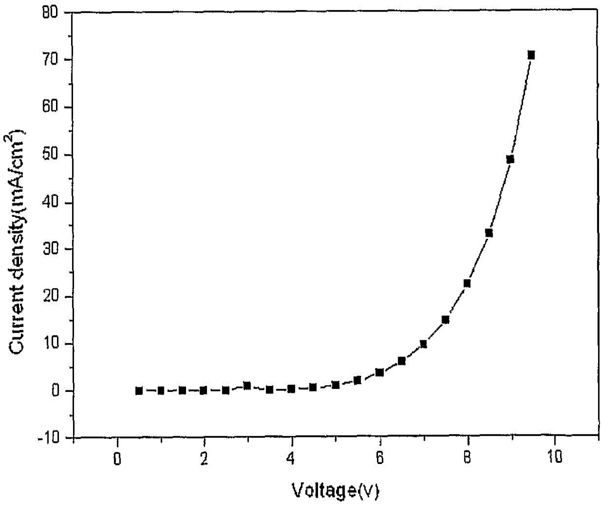
Date of the actual completion of the international search 09 MAY 2007 (09.05.2007)	Date of mailing of the international search report **09 MAY 2007 (09.05.2007)**
Name and mailing address of the ISA/KR Korean Intellectual Property Office 920 Dunsan-dong, Seo-gu, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140	Authorized officer SOHN, Chang Ho Telephone No. 82-42-481-8398

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP16277368	07.10.2004	None	
US20030091859A1	15.05.2003	JP15064003 KR1020020088937	05.03.2003 29.11.2002
JP17119994	12.05.2005	None	
JP17325097	24.11.2005	US2005236977AA	27.10.2005

专利名称(译)	包含芴基的电致发光化合物和使用其的有机电致发光器件		
公开(公告)号	EP1981951A4	公开(公告)日	2011-04-27
申请号	EP2007708617	申请日	2007-01-26
申请(专利权)人(译)	GRACEL显示增量.		
当前申请(专利权)人(译)	GRACEL显示增量.		
[标]发明人	CHOI IL WON KIM CHI SIK SHIN HYO NIM LEE MI AE SHIN HWAN SEUNG KWAK MI YOUNG KIM NAM KYUN KIM BONG OK KIM SUNG MIN CHO YOUNG JUN KWON HYUCK JOO BAEK JUNG SU		
发明人	CHOI, IL WON KIM, CHI SIK SHIN, HYO NIM LEE, MI AE SHIN, HWAN SEUNG KWAK, MI YOUNG KIM, NAM KYUN KIM, BONG OK KIM, SUNG MIN CHO, YOUNG JUN KWON, HYUCK JOO BAEK, JUNG SU		
IPC分类号	C09K11/06		
CPC分类号	C09K11/06 C09K2211/1011 C09K2211/1014 H01L51/0058 H01L51/0059 H01L51/006 H01L51/0079 H01L51/0081 H01L51/5012 H01L2251/308 H05B33/14		
优先权	1020060008840 2006-01-27 KR 1020070006082 2007-01-19 KR		
其他公开文献	EP1981951A1		
外部链接	Espacenet		

摘要(译)

本发明涉及由化学式1表示的有机电致发光化合物和在电致发光层中包含该化合物的电致发光器件。根据本发明的电致发光化合物具有良好的发光效率和优异的材料寿命，因此可以制备具有非常好的工作寿命的OLED器件。


80
70
60
50
40
30
20
10
0
-10
0
2
4
6
8
10
Current density(mA/cm^2)
Voltage(V)