(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 128 159 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
16.08.2017 Bulletin 2017/33

(21) Application number: **08722028.1**

(22) Date of filing: **13.03.2008**

(51) Int Cl.:
C09K 11/06 $^{(2006.01)}$ ***C07D 471/04*** $^{(2006.01)}$
H01L 51/50 $^{(2006.01)}$

(86) International application number:
PCT/JP2008/054624

(87) International publication number:
WO 2008/114690 (25.09.2008 Gazette 2008/39)

(54) COMPOUND WHEREIN SUBSTITUTED BIPYRIDYL GROUP IS CONNECTED WITH PYRIDOINDOLE RING STRUCTURE THROUGH PHENYLENE GROUP, AND ORGANIC ELECTROLUMINESCENT DEVICE

VERBINDUNG, BEI DER EINE SUBSTITUIERTE BIPYRIDYLGRUPPE ÜBER EINE PHENYLENGRUPPE AN EINE PYRIDOINDOLRINGSTRUKTUR GEBUNDEN IST, UND ORGANISCHES ELEKTROLUMINESZENTES GERÄT

COMPOSÉ DANS LEQUEL UN GROUPE BIPYRIDYLE SUBSTITUÉ EST RELIÉ À UNE STRUCTURE DE NOYAU PYRIDOINDOLE PAR L'INTERMÉDIAIRE D'UN GROUPE PHÉNYLÈNE, ET DISPOSITIF ÉLECTROLUMINESCENT ORGANIQUE

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MT NL NO PL PT RO SE SI SK TR

(30) Priority: **15.03.2007 JP 2007066214**

(43) Date of publication of application:
02.12.2009 Bulletin 2009/49

(73) Proprietor: **Hodogaya Chemical Co., Ltd.**
Tokyo 104-0028 (JP)

(72) Inventors:
- **YOKOYAMA, Norimasa**
  Tokyo 104-0028 (JP)
- **HAYASHI, Shuichi**
  Tokyo 104-0028 (JP)
- **KUSANO, Shigeru**
  Tokyo 104-0028 (JP)
- **NAGAOKA, Makoto**
  Tokyo 104-0028 (JP)

(74) Representative: **Müller-Boré & Partner**
Patentanwälte PartG mbB
Friedenheimer Brücke 21
80639 München (DE)

(56) References cited:

EP-A1- 1 571 193	**WO-A1-2004/053019**
WO-A1-2007/029696	**JP-A- 2006 032 599**
US-A1- 2005 249 970	**US-A1- 2006 251 918**

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Description

[0001] The present invention relates to a compound suitable for an organic electroluminescence (EL) device which is a self-luminescent device suitable for various displaying devices and a device. More specifically, it relates to a compound having a substituted bipyridyl group and a pyridoindole ring structure connected with each other through a phenylene group and to an organic EL device using the compound.

[0002] Since organic EL devices are self-luminescent devices, they are bright and excellent in visibility as compared with liquid-crystalline devices and capable of giving clear display, so that the organic EL devices have been actively studied.

[0003] In 1987, C. W. Tang et al. of Eastman Kodak Company put an organic EL device using organic materials into practical use by developing a device having a multilayered structure wherein various roles are assigned to respective materials. They formed a lamination of a fluorescent material capable of transporting electrons and an organic material capable of transporting holes, so that both charges are injected into the layer of the fluorescent material to emit light, thereby achieving a high luminance of 1000 cd/m^2 or more at a voltage of 10 V or lower (see e.g., Patent Documents 1 and 2).

[0004]

Patent Document 1: JP-A-8-48656
Patent Document 2: Japanese Patent No. 3194657

[0005] To date, many improvements have been performed for practical utilization of the organic EL devices, and high efficiency and durability have been achieved by an electroluminescent device wherein an anode, a hole-injecting layer, a hole-transporting layer, an emitting layer, an electron-transporting layer, an electron-injecting layer, and a cathode are sequentially provided on a substrate, to further segmentalize various roles (see e.g., Non-Patent Document 1).

[0006] Non-Patent Document 1: Japan Society of Applied Physics Ninth Workshop Preprint, pp. 55-61 (2001)

[0007] Moreover, for the purpose of further improvement of luminous efficiency, utilization of triplet exciton has been attempted and utilization of a phosphorescent material has been investigated (see e.g., Non-Patent Document 2).

[0008] Non-Patent Document 2: Japan Society of Applied Physics Ninth Workshop Preprint, pp. 23-31 (2001)

[0009] The emitting layer can be also prepared by doping a charge-transporting compound, generally called a host material, with a fluorescent material or a phosphorescent material. As described in the above-mentioned Workshop Preprints, the choice of the organic materials in organic EL devices remarkably affects various properties such as efficiency and durability of the devices.

[0010] In the organic EL devices, the charges injected from the both electrode are recombined in the emitting layer to attain light emission. However, since the mobility of holes is higher than the mobility of electrons, a problem of reduction in efficiency caused by a part of the holes passing through the emitting layer arises. Therefore, it is required to develop an electron-transporting material in which the mobility of electrons is high.

[0011] A representative light-emitting material, tris(8-hydroxyquinoline)aluminum (hereinafter referred to as Alq3) is commonly used also as an electron-transporting material but it cannot be considered that the material has hole-blocking capability.

[0012] As a technique to prevent the passing of a part of holes through the emitting layer and to improve probability of charge recombination in the emitting layer, there is a method of inserting a hole-blocking layer. As hole-blocking materials, there have been hitherto proposed triazole derivatives (see e.g., Patent Document 3), bathocuproine (hereinafter referred to as BCP), a mixed ligand complex of aluminum (BAlq) (see e.g., Non-Patent Document 2), and the like.

[0013] For example, as an electron-transporting material excellent in hole-blocking ability, there is proposed 3-(4-biphenylyl)-4-phenyl-5-(4-t-butylphenyl)-1,2,4-triazole (hereinafter referred to as TAZ) (see e.g., Patent Document 3).

[0014] Patent Document 3: Japanese Patent No. 2734341

[0015] Since TAZ has a work function as large as 6.6 eV and thus exhibits a high hole-blocking ability, it is used as an electron-transporting hole-blocking layer to be laminated onto the cathode side of a fluorescence-emitting layer or phosphorescence-emitting layer prepared by vacuum deposition, coating or the like, and contributes to increase the efficiency of organic EL devices (see e.g., Non-Patent Document 3).

[0016] Non-Patent Document 3: Fiftieth Meeting of Japan Society of Applied Physics and Related Societies, 28p-A-6 Lecture Preprint, p. 1413 (2003)

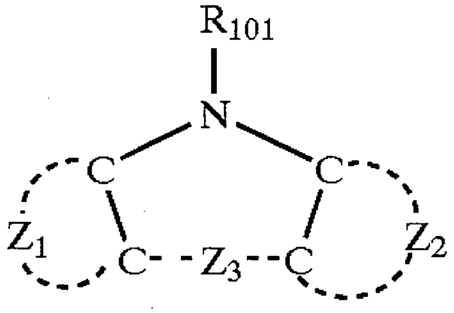
[0017] However, TAZ has a great problem of having low electron transport property, and it is necessary to prepare an organic EL device in combination with an electron-transporting material having a higher electron transport property (see e.g., Non-Patent Document 4).

[0018] Non-Patent Document 4: Japan Society of Applied Physics, Journal of Organic Molecules/Bioelectronics Section, Vol. 11, No. 1, pp. 13-19 (2000)

[0019] Further, BCP has a work function as large as 6.7 eV and a high hole-blocking ability, but has a low glass transition point (Tg) which is 83°C, so that it is poor in thin-film stability and thus it cannot be considered that it sufficiently functions as a hole-blocking layer.

[0020] All the materials are insufficient in film stability or are insufficient in the function of blocking holes. In order to improve characteristic properties of the organic EL devices, it is desired to develop an organic compound which is excellent in electron-injection/transport performances and hole-blocking ability and is highly stable in a thin-film state.

[0021] US 2005/0249970 A1 discloses an organic electroluminescent element which contains a pair of electrodes having therebetween at least one constituting layer containing a phosphorescent light emitting layer, wherein one of the constituting layer contains a compound represented by the following formula:



wherein Z1 represents an aromatic heterocylic ring which may have a substituent; Z2 represents an aromatic heterocylic ring or an aromatic hydrocarbon ring both of which may have a substituent; Z3 represents a divalent linking group or a single bond; and R101 represents a hydrogen atom or a substituent.

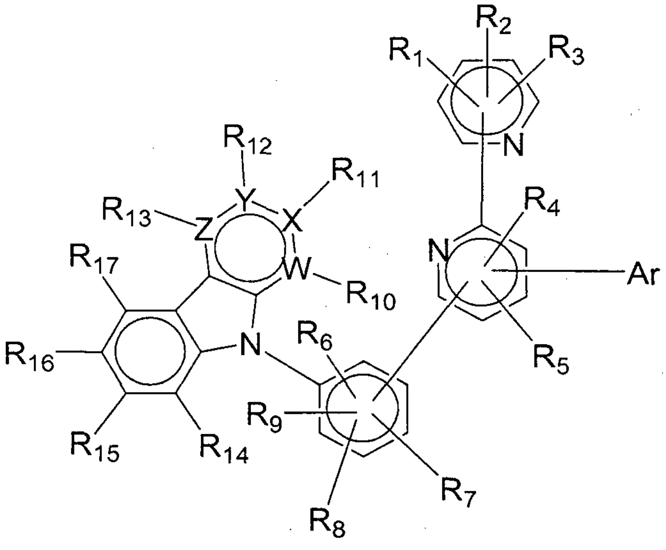
[0022] Objects of the present invention are to provide an organic compound having excellent properties, which is excellent in electron-injection/transport performances, has hole-blocking ability and is highly stable in a thin-film state, as a material for an organic electroluminescence device having a high efficiency and a high durability, and to provide an organic electroluminescence device having a high efficiency and a high durability using the compound.

[0023] As physical properties of the organic compound to be provided by the invention, there may be mentioned (1) good electron injection characteristic, (2) high electron mobility, (3) excellent hole-blocking ability, (4) good stability in a thin-film state, and (5) excellent thermal resistance. In addition, as physical properties of the organic EL device to be provided by the invention, there may be mentioned (1) high luminous efficiency, (2) low emission initiation voltage, (3) low practical driving voltage, and (4) high maximum emission luminance.

[0024] Thus, in order to achieve the above objects, the present inventors have designed and chemically synthesized compounds having a substituted bipyridyl group and a pyridoindole ring structure connected with each other through a phenylene group, with focusing on the fact that the nitrogen atom of the pyridine ring which exhibits affinity to an electron has an ability of coordinating to a metal and is excellent in thermal resistance. The present inventors have experimentally produced various organic EL devices using the compounds, and have extensively performed property evaluation of the devices. As a result, they have accomplished the invention.

[0025] Namely, the invention provides a compound having a substituted bipyridyl group and a pyridoindole ring structure connected with each other through a phenylene group, which is represented by the general formula (1). Also, the invention provides an organic EL device comprising a pair of electrodes and at least one organic layer interposed between the electrodes, wherein the compound is used as a constituent material for the at least one organic layer:

[Chem. 1]



(1)

wherein Ar represents an unsubstituted aromatic hydrocarbon group, aromatic hydrocarbon group substituted with a pyridoindolyl group, or an unsubstituted condensed polycyclic aromatic group; R1 to R17 represent a hydrogen atom; and W, X, and Z represent a carbon atom and Y is a nitrogen atom and the nitrogen atom does not have a substituent of R12, or W, X, and Y represent a carbon atom and Z is a nitrogen atom and the nitrogen atom does not have a substituent of R13.

[0026] The "aromatic hydrocarbon group" and "condensed polycyclic aromatic group" in the unsubstituted aromatic hydrocarbon group, aromatic hydrocarbon group substituted with a pyridoindolyl group, or unsubstituted condensed polycyclic aromatic group, which is represented by Ar in the general formula (1) specifically includes a phenyl group, a biphenyl group, a terphenyl group, a tetrakisphenyl group, a styryl group, a naphthyl group, an anthryl group, an acenaphthenyl group, a fluorenyl group, a phenanthryl group, an indenyl group, and a pyrenyl group.

[0027] The compound having a substituted bipyridyl group and a pyridoindole ring structure connected with each other through a phenylene group, which is represented by the general formula (1) of the invention, provides high electron mobility as compared with conventional electron-transporting materials, has an excellent hole-blocking ability, and is stable in a thin-film state.

[0028] The compound having a substituted bipyridyl group and a pyridoindole ring structure connected with each other through a phenylene group, which is represented by the general formula (1) of the invention, can be used as a constituent material for an electron-transporting layer of an organic EL device. The use of the material exhibiting a higher electron injection/mobile rate as compared with conventional materials provides effects of improving electron transport efficiency from the electron-transporting layer to an emitting layer to enhance luminous efficiency and also lowering a driving voltage to enhance durability of the organic EL device.

[0029] The compound having a substituted bipyridyl group and a pyridoindole ring structure connected with each other through a phenylene group, which is represented by the general formula (1) of the invention, can be also used as a constituent material for a hole-blocking layer of an organic EL device. The use of the material excellent in hole-blocking ability and also excellent in electron transport property as compared with conventional materials and having high stability in a thin-film state provides effects of lowering a driving voltage, improving current resistance, and enhancing maximum emission luminance of the organic EL device, while exhibiting high luminous efficiency.

[0030] The compound having a substituted bipyridyl group and a pyridoindole ring structure connected with each other through a phenylene group, which is represented by the general formula (1) of the invention, can be also used as a constituent material for an emitting layer of an organic EL device. The use of an emitting layer prepared by using the material of the invention excellent in electron transport property as compared with conventional materials and having a wide bandgap as a host material for the emitting layer and making a fluorescent material or a phosphorescent material, called a dopant, carried thereon provides an effect of realizing an organic EL device exhibiting a lowered driving voltage and having improved luminous efficiency.

[0031] According to the invention, there is provided a compound having a substituted bipyridyl group and a pyridoindole ring structure connected with each other through a phenylene group, which is useful as a constituent material for an electron-transporting layer, a hole-blocking layer, or an emitting layer of an organic EL device. Further, since the organic EL device prepared by using the compound having a substituted bipyridyl group and a pyridoindole ring structure connected with each other through a phenylene group exhibits high electron mobility as compared with conventional electron-transporting materials, has an excellent hole-blocking ability, and is stable in a thin-film state, it becomes possible to realize a high efficiency and a high durability.

[0032]

FIG. 1 is a 1H-NMR chart of the compound (Compound 36) of Invention Example 1.
FIG. 2 is a 1H-NMR chart of the compound (Compound 40) of Invention Example 2.
FIG. 3 is a 1H-NMR chart of the compound (Compound 164) of Invention Example 3.
FIG. 4 is a 1H-NMR chart of the compound (Compound 20) of Invention Example 4.
FIG. 5 is a 1H-NMR chart of the compound (Compound 24) of Invention Example 5.
FIG. 6 is a 1H-NMR chart of the compound (Compound 37) of Invention Example 6.
FIG. 7 is a 1H-NMR chart of the compound (Compound 41) of Invention Example 7.
FIG. 8 is a 1H-NMR chart of the compound (Compound 52) of Invention Example 8.
FIG. 9 is a 1H-NMR chart of the compound (Compound 72) of Invention Example 9.
FIG. 10 is a 1H-NMR chart of the compound (Compound 116) of Invention Example 10.
FIG. 11 is a 1H-NMR chart of the compound (Compound 165) of Invention Example 11.
FIG. 12 is a 1H-NMR chart of the compound (Compound 192) of Invention Example 12.
FIG. 13 is a 1H-NMR chart of the compound (Compound 193) of Invention Example 13.
FIG. 14 is a drawing showing the constitution of the EL devices of Examples 16 to 24.
FIG. 15 is a drawing showing the constitution of the EL device of Comparative Example 1.

[0033]

1: Glass substrate
2: Transparent anode
3: Hole-injecting layer
4: Hole-transporting layer
5: Emitting layer
6: Hole-blocking layer
7: Electron-transporting layer
8: Electron-injecting layer
9: Cathode

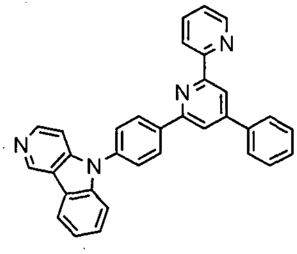
[0034] The compound having a substituted bipyridyl group and a pyridoindole ring structure connected with each other through a phenylene group according to the invention is a novel compound, and the compound can be synthesized, for example, by subjecting a corresponding halogenoanilinopyridine to a cyclization reaction with a palladium catalyst to synthesize a pyridoindol ring (see e.g., Non-Patent Document 5) and then by condensing it with one of various halogenophenylenes having a substituted bipyridyl group to synthesize a compound having a substituted bipyridyl group and a pyridoindole ring structure connected with each other through a phenylene group. Each of the various halogenophenylenes having a bipyridyl group can be synthesized by condensing a corresponding aldehyde and an acetylpyridine in the presence of a base and further reacting the resulting product with a corresponding pyridinium iodide (see e.g., Non-Patent Document 6).

[0035] Non-Patent Document 5: J. Chem. Soc., Perkin Trans. 1, p. 1505 (1999)

[0036] Non-Patent Document 6: Synthesis, 1 (1976)

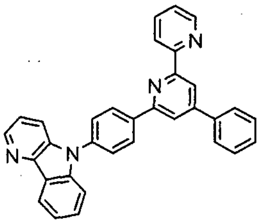
[0037] Among the compounds having a substituted bipyridyl group and a pyridoindole ring structure connected with each other through a phenylene group, which is represented by the general formula (1), specific examples of preferred compounds are shown below, but the invention is not limited to these compounds.

[Chem. 4]



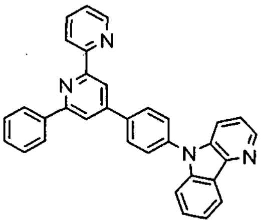
(Compound 4)

[Chem. 5]



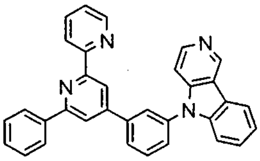
(Compound 5)

[Chem. 9]



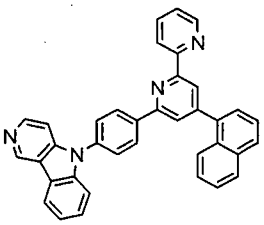
(Compound 9)

[Chem. 16]



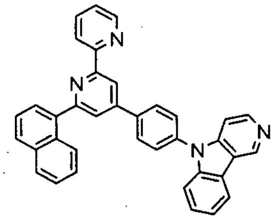
(Compound 16)

[Chem. 20]



(Compound 20)

[Chem. 24]



(Compound 24)

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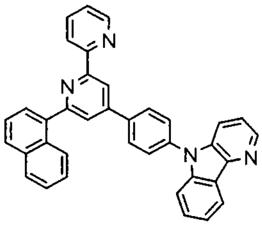

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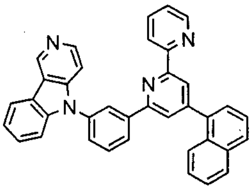
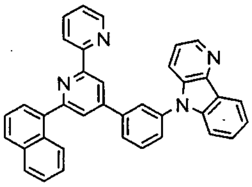
[Chem. 28]



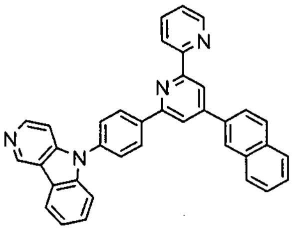
(Compound 28)

[Chem. 33]



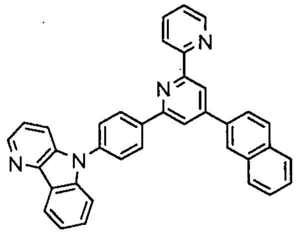
(Compound 33)

[Chem. 36]



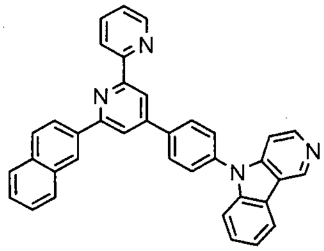
(Compound 36)

[Chem. 37]



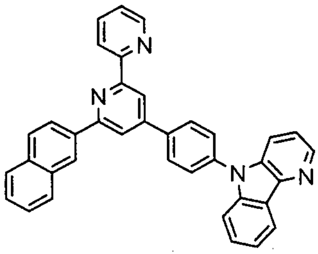
(Compound 37)

[Chem. 40]



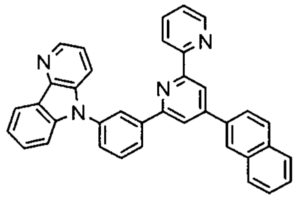
(Compound 40)

[Chem. 41]



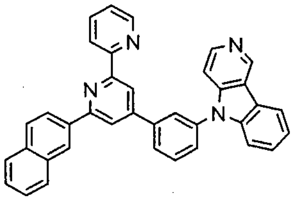
(Compound 41)

[Chem. 45]



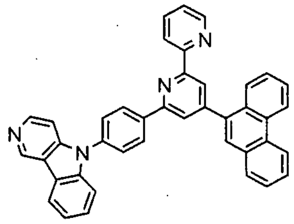
(Compound 45)

[Chem. 48]



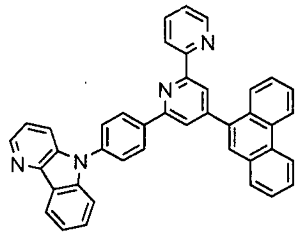
(Compound 48)

[Chem. 52]



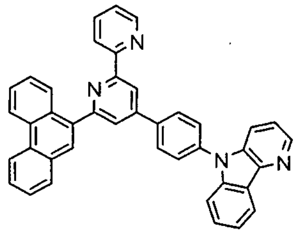
(Compound 52)

[Chem. 53]



(Compound 53)

[Chem. 57]



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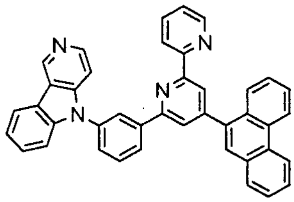
[Chem. 60]



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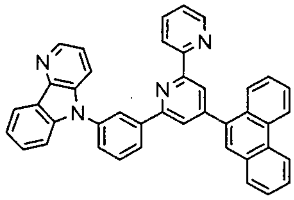
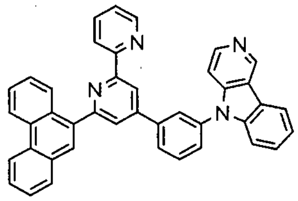
[Chem. 61]



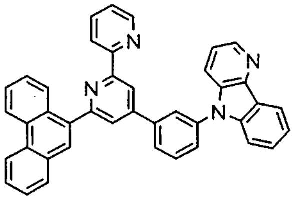
(Compound 61)

[Chem. 64]



(Compound 64)

[Chem. 65]



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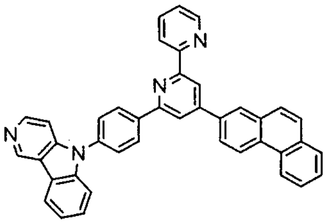
[Chem. 68]



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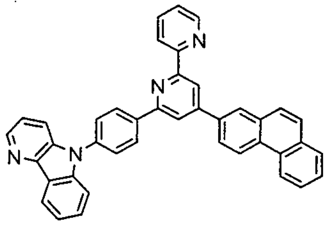
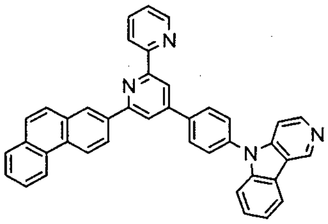
[Chem. 69]



(Compound 69)

[Chem. 72]



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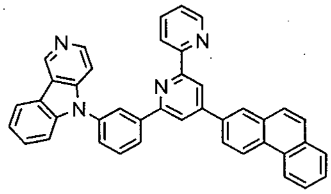
[Chem. 76]



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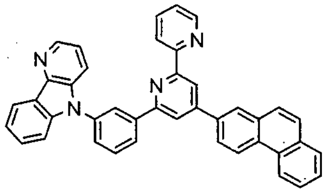
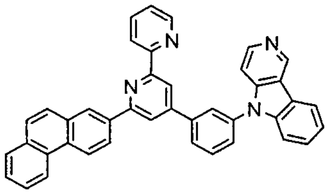
[Chem. 77]



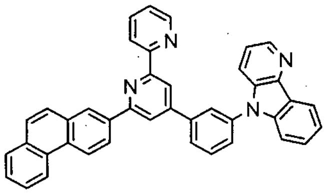
(Compound 77)

[Chem. 80]



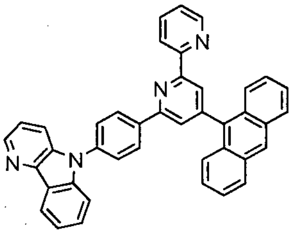
(Compound 80)

[Chem. 81]



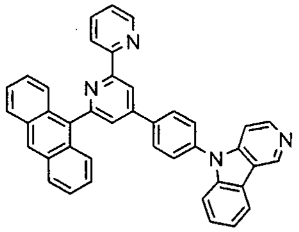
(Compound 81)

[Chem. 85]



(Compound 85)

[Chem. 88]



(Compound 88)

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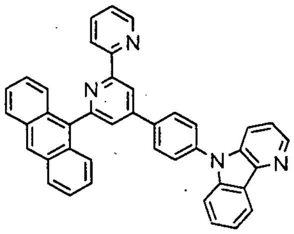

(Compound 89)

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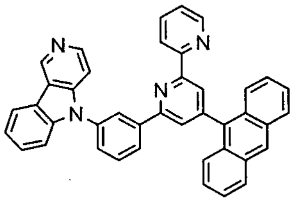
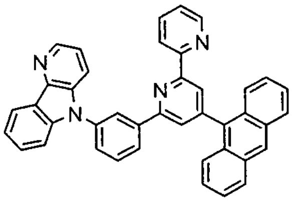


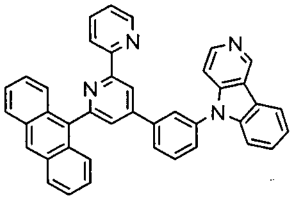
(Compound 92)

[Chem. 93]



(Compound 93)

[Chem. 96]



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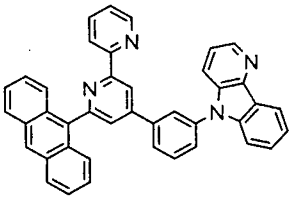

(Compound 97)

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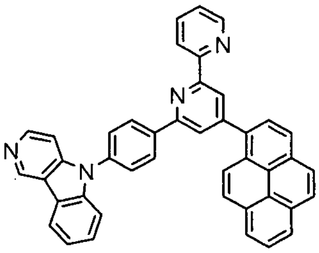

(Compound 100)

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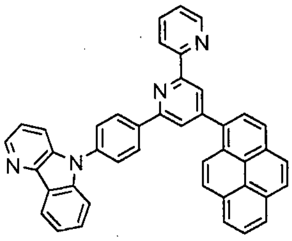

(Compound 101)

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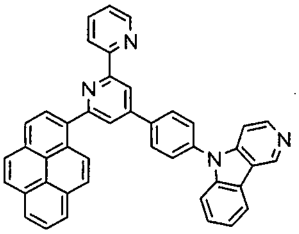

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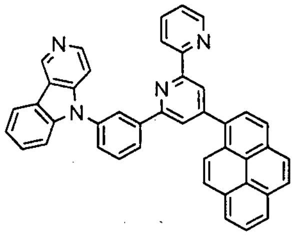

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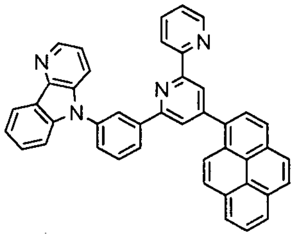

(Compound 109)

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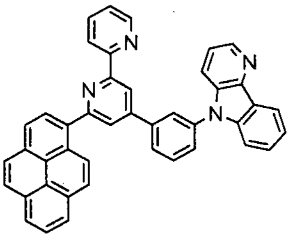

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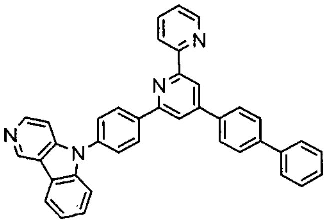

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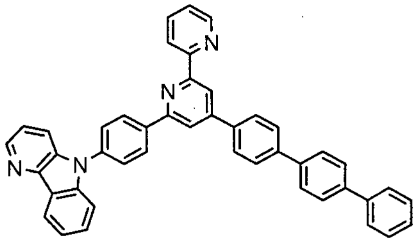

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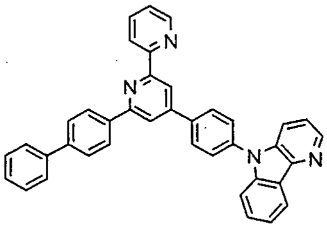

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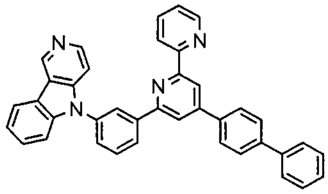

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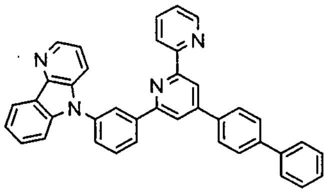

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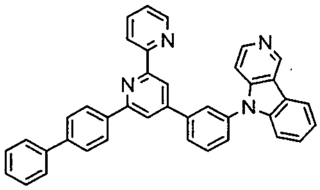
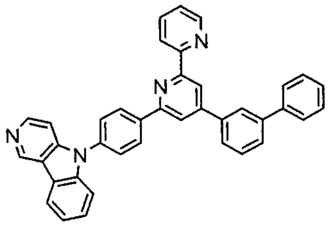


(Compound 128)

[Chem. 132]



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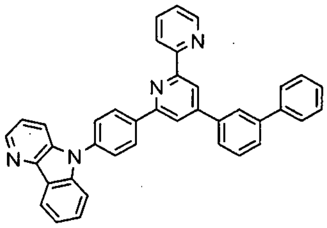

(Compound 133)

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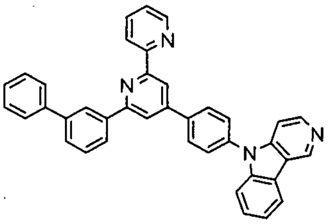

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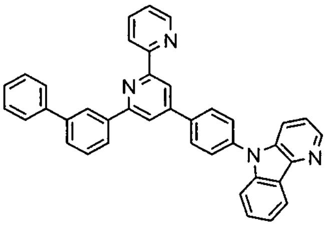
[Chem. 137]



(Compound 137)

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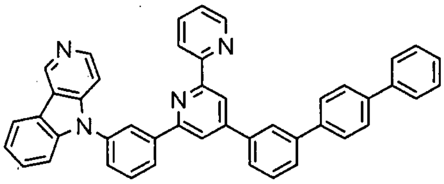

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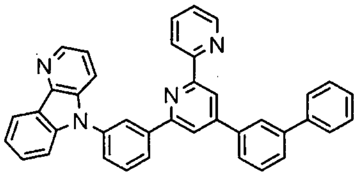

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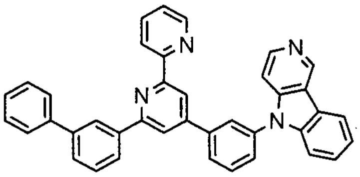

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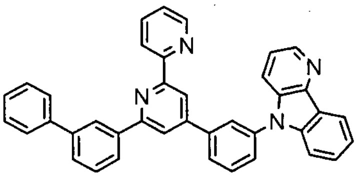

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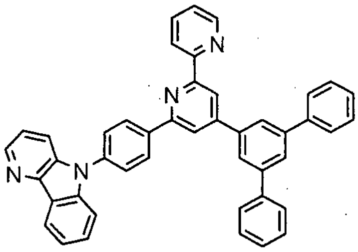
[Chem. 149]



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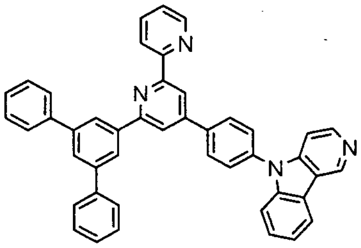
[Chem. 152]



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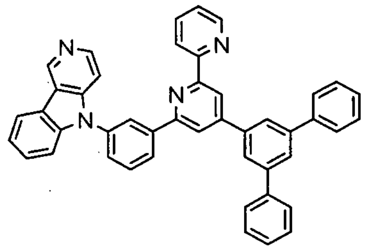

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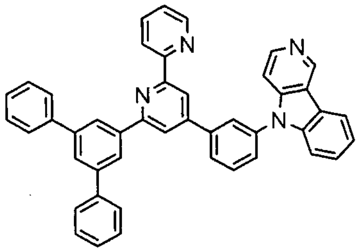

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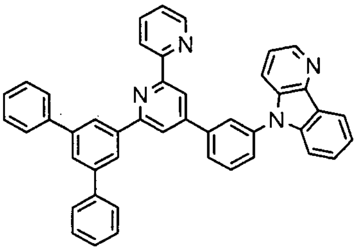

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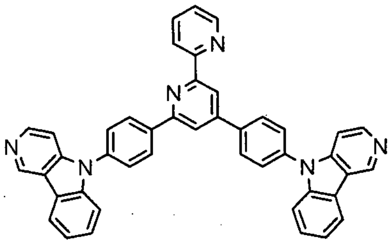

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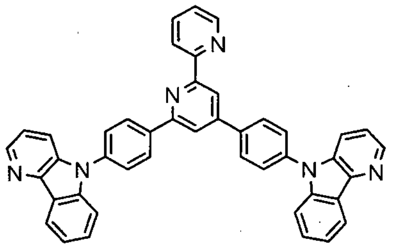

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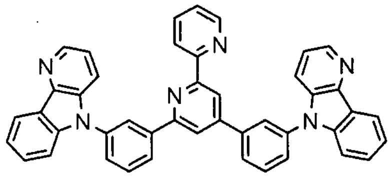

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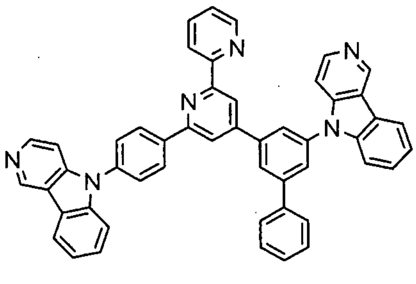

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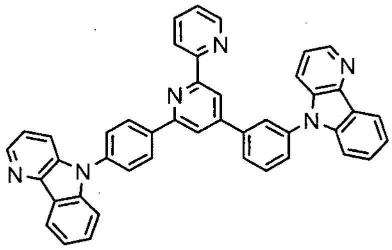

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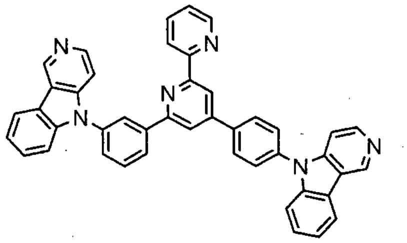

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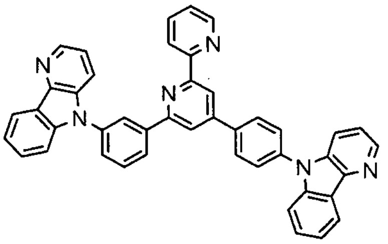

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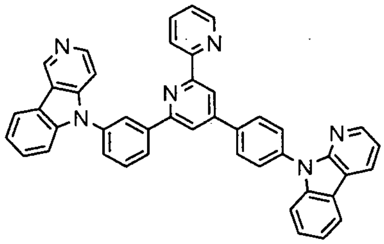

(Compound 178)

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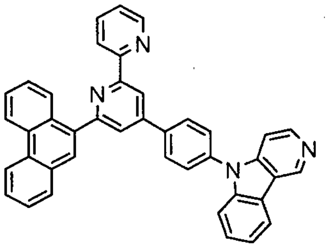

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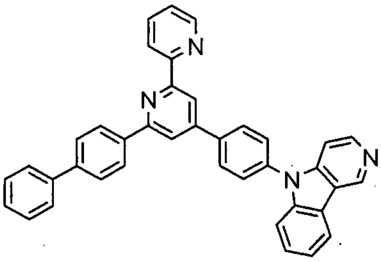

(Compound 193)

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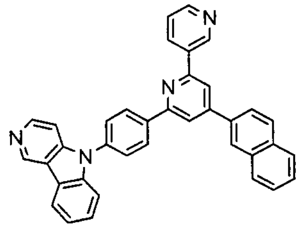

(Compound 200)

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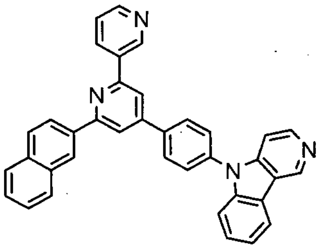

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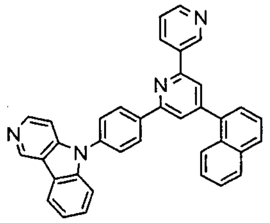

(Compound 202)

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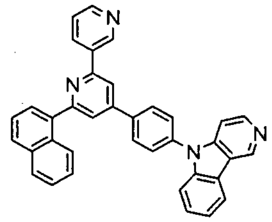

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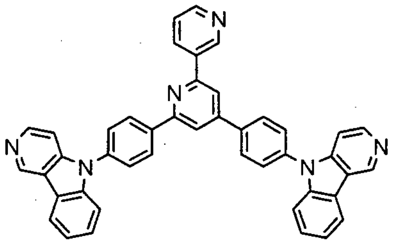

(Compound 204)

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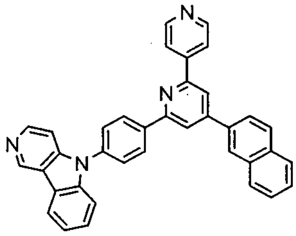

(Compound 206)

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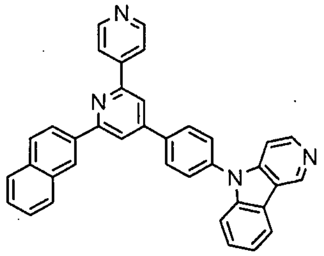

(Compound 207)

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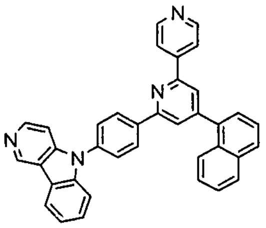

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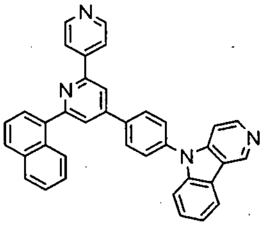

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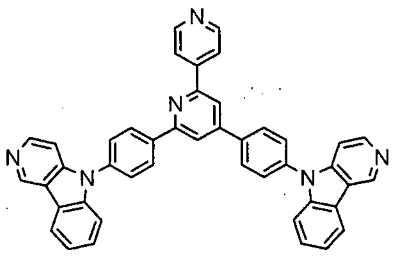


(Compound 210)

[0038] Purification of these compounds was performed by purification by column chromatography, adsorption purification, a recrystallization or crystallization method with a solvent, or the like. Identification of the compounds can be performed by NMR analysis. As physical properties, DSC measurement (Tg) and measurement of melting point were performed. The melting point serves as an index of vapor deposition properties and the glass transition point (Tg) serves as an index of stability in a thin-film state.

[0039] The melting point and the glass transition point were measured using a powder material by means of a highly sensitive differential scanning calorimeter DSC 3100S manufactured by Bruker AXS.

[0040] Further, the work function was measured by preparing a thin film of 100 nm on an ITO substrate and using a photo-electron spectroscopy in air (Model AC-3, manufactured by Riken Keiki Co., Ltd.). The work function is regarded as an indicator of hole-blocking ability.

[0041] Examples of the structure of the organic EL device of the invention include a structure having an anode, a hole-injecting layer, a hole-transporting layer, an emitting layer, a hole-blocking layer, an electron-transporting layer and a cathode in this order on a substrate, and a structure further having an electron-injecting layer between the electron-transporting layer and the cathode. In these multilayer structures, it is possible to omit several layers of the organic layers and, for example, the structure may have a constitution sequentially having an anode, a hole-transporting layer, an emitting layer, an electron-transporting layer and a cathode on a substrate.

[0042] As the anode of the organic EL device, an electrode material having a large work function, such as ITO or gold, is used. As the hole-injecting layer, besides copper phthalocyanine (hereinafter referred to as CuPc), materials such as star-burst type triphenylamine derivatives and wet-process type materials may be employed.

[0043] For the hole-transporting layer, N,N'-diphenyl-N,N'-di(m-tolyl)-benzidine (hereinafter referred to as TPD) and N,N'-diphenyl-N,N'-di(α-naphthyl)-benzidine (hereinafter referred to as NPD), various triphenylamine tetramers, and the like may be used. Further, as the hole-injecting/transporting layers, wet-process type polymer materials such as PEDOT/PSS may be employed.

[0044] As the emitting layer, hole-blocking layer, and electron-transporting layer of the organic EL device of the invention, besides the compound having a substituted bipyridyl group and a pyridoindole ring structure connected with each other through a phenylene group, aluminum complexes, thiazole derivatives, oxazole derivatives, carbazole derivatives, polydialkylfluorene derivatives, and the like may be used.

[0045] By using a conventional luminescence material such as an aluminum complex or styryl derivative for the emitting layer and using the compound having a substituted bipyridyl group and a pyridoindole ring structure connected with each other through a phenylene group as the hole-blocking layer and the electron-transporting layer, a high-performance organic EL device can be prepared. Further, a high-performance organic EL device can be prepared also by adding a dopant, for example, a fluorescent material such as quinacridone, coumarin or rubrene or a phosphorescent material such as an iridium complex of phenylpyridine, as a host material of the emitting layer.

[0046] Furthermore, the compound having a substituted bipyridyl group and a pyridoindole ring structure connected with each other through a phenylene group can be used as the electron-transporting layer through multilayering or co-deposition with conventional electron-transporting material(s).

[0047] The organic EL device of the invention may have an electron-injecting layer. As the electron-injecting layer, lithium fluoride or the like may be used. For the cathode, an electrode material having a low work function such as aluminum, or an alloy having a low work function such as aluminum magnesium is used as an electrode material.

[0048] Embodiments of the invention will be illustrated in greater detail with reference to Examples.

Example 1

(Synthesis of 6-[4-(5H-pyrido[4,3-b]indol-5-yl)phenyl]-4-(naphthalen-2-yl)-[2,2']bipyridine (Compound 36))

[0049] 10.0 g of 4'-bromoacetophenone, 12.8 g of iodine, and 80 ml of pyridine were added and the whole was heated and stirred at 100°C for 3 hours. After cooling to room temperature, 100 ml of water was added and purification by recrystallization was performed. Drying was performed under reduced pressure at 70°C for 12 hours to obtain 15.5 g (yield 76%) of 4-bromophenacylpyridinium iodide as a brown powder.

[0050] Subsequently, 6.0 g of 2-naphthoaldehyde, 4.7 g of 2-acetylpyridine, and 40 ml of methanol were added and the whole was cooled to -5°C under stirring. 62 ml of a 3 wt% NaOH/methanol solution was added dropwise thereto and the whole was stirred at -5°C for 2 hours. Then, the reaction was further carried out at the same temperature for 2 days. 37. 0 g of ammonium acetate, 15.5 g of the above 4-bromophenacylpyridinium iodide, and 100 ml of methanol were added to the reaction solution and the whole was stirred at 55°C for 2 days. After cooling to room temperature, the resulting crude product was collected by filtration, washed with methanol, and then dried under reduced pressure at 70°C for 12 hours to obtain 3.8 g (yield 23%) of 6-(4-bromophenyl)-4-(naphthalen-2-yl)-[2,2']bipyridine as a gray powder.

[0051] 2.5 g of the resulting 6-(4-bromophenyl)-4-(naphthalen-2-yl)-[2,2']bipyridine, 1.0 g of 5H-pyrido[4,3-b]indole, 0.2 g of copper powder, 2.4 g of potassium carbonate, 0.2 ml of dimethyl sulfoxide, and 10 ml of n-dodecane were added and the whole was stirred for 7 hours under heating and refluxing. After cooling to room temperature, 60 ml of chloroform was added thereto, insoluble solid was removed by filtration, and the filtrate was concentrated under reduced pressure to obtain a crude product. The crude product was purified by column chromatography (carrier: NH silica gel, eluent: hexane/chloroform) to obtain 1.85 g (yield 62%) of 6-[4-(5H-pyrido[4,3-b]indol-5-yl)phenyl]-4-(naphthalen-2-yl)-[2,2']bipyridine (Compound 36) as a white powder.

[0052] The structure of the resulting white powder was identified using NMR. The results of 1H-NMR measurement are shown in FIG. 1.

[0053] The following 24 hydrogen signals were detected on 1H-NMR (CDC13). δ (ppm) = 9.42 (1H), 8.85 (1H), 8.76 (2H), 8.49-8.57 (3H), 8.36 (1H), 8.20-8.25 (2H), 7.90-8.03 (5H), 7.73 (2H), 7.51-7.58 (4H), 7.38-7.42 (3H).

Example 2

(Synthesis of 4-[4-(5H-pyrido[4,3-b]indol-5-yl)phenyl]-6-(naphthalen-2-yl)-[2,2']bipyridine (Compound 40))

[0054] 4-(4-Bromophenyl)-6-(naphthalen-2-yl)-[2,2']bipyridine was synthesized in the same manner as in the above Example 1. 2.5 g of the resulting 4-(4-bromophenyl)-6-(naphthalen-2-yl)-[2,2']bip.yridine, 1.0 g of 5H-pyrido[4,3-b]indole, 0.2 g of copper powder, 2.4 g of potassium carbonate, 0.2 ml of dimethyl sulfoxide, and 10 ml of n-dodecane were added and the whole was stirred for 9 hours under heating and refluxing. After cooling to room temperature, 60 ml of chloroform was added thereto, insoluble solid was removed by filtration, and the filtrate was concentrated under reduced pressure to obtain a crude product. The crude product was purified by column chromatography (carrier: NH silica gel, eluent: hexane/chloroform) to obtain 2.17 g (yield 72%) of 4-[4-(5H-pyrido[4,3-b]indol-5-yl)phenyl]-6-(naphthalen-2-yl)-[2,2']bipyridine (Compound 40) as a yellow-white powder.

[0055] The structure of the resulting yellow-white powder was identified using NMR. The results of 1H-NMR measurement are shown in FIG. 2.

[0056] The following 24 hydrogen signals were detected on 1H-NMR (CDC13). δ (ppm) = 9.42 (1H), 8.76-8.80 (3H), 8.70 (1H), 8.57 (1H), 8.42 (1H); 8.22-8.25 (2H), 8.12 (2H), 8.03 (2H), 7.92-7.94 (2H), 7.73 (2H), 7.53-7.57 (4H), 7.38-7.43 (3H).

Example 3

(Synthesis of 4,6-bis[4-(5H-pyrido[4,3-b]indol-5-yl)phenyl]-[2,2']bipyridine (Compound 164))

[0057] 4,6-Bis(4-bromophenyl)-[2,2']bipyridine was synthesized in the same manner as in the above Example 1. 1:8 g of the resulting 4,6-bis(4-bromophenyl)-[2,2']bipyridine, 1.4 g of 5H-pyrido[4,3-b]indole, 0.2 g of copper powder, 1.6 g of potassium carbonate, 0.1 ml of dimethyl sulfoxide, and 5 ml of n-dodecane were added and the whole was stirred for 11 hours under heating and refluxing. After cooling to room temperature, 50 ml of methanol was added thereto and insoluble solid was removed by filtration. 300 ml of chloroform was added to the insoluble solid and extraction was performed. The extraction liquid was concentrated under reduced pressure to obtain a crude product. The crude product was subjected to purification using o-dichlorobenzene as a recrystallization solvent and drying was performed under reduced pressure at 70°C for 12 hours to obtain 1.45 g (yield 58%) of 4,6-bis[4-(5H-pyrido[4,3-b]indol-5-yl)phenyl]-[2,2']bipyridine (Compound 164) as a yellow-white powder.

[0058] The structure of the resulting yellow-white powder was identified using NMR. The results of 1H-NMR measurement are shown in FIG. 3.

[0059] The following 28 hydrogen signals were detected on 1H-NMR (CDC13). δ (ppm) = 9.43 (2H), 8.76-8.84 (3H), 8.52-8.59 (4H), 8.14-8.26 (5H), 7.94 (1H), 7.76 (4H), 7.52-7.57 (4H), 7.39-7.44 (5H).

Example 4

(Synthesis of 6-[4-(5H-pyrido[4,3-b]indol-5-yl)phenyl]-4-(naphthalen-1-yl)-[2,2']bipyridine (Compound 20))

[0060] 6-(4-Bromophenyl)-4-(naphthalen-1-yl)-[2,2']bipyridine was synthesized in the same manner as in the above Example 1. 2.2 g of the resulting 6-(4-bromophenyl)-4-(naphthalen-1-yl)-[2,2']bipyridine, 0.9 g of 5H-pyrido[4,3-b]indole, 0.2 g of copper powder, 2.1 g of potassium carbonate, 0.2 ml of dimethyl sulfoxide, and 10 ml of n-dodecane were added and the whole was stirred for 6 hours under heating and refluxing. After cooling to room temperature, 60 ml of chloroform was added thereto, insoluble solid was removed by filtration, and the filtrate was concentrated under reduced pressure to obtain a crude product. The crude product was purified by column chromatography (carrier: NH silica gel, eluent: hexane/chloroform) to obtain 2.02 g (yield 77%) of 6-[4-(5H-pyrido[4,3-b]indol-5-yl)phenyl]-4-(naphthalen-1-yl)-[2,2']bipyridine (Compound 20) as a brown-white powder.

[0061] The structure of the resulting brown-white powder was identified using NMR. The results of 1H-NMR measurement are shown in FIG. 4.

[0062] The following 24 hydrogen signals were detected on 1H-NMR (CDC13). δ (ppm) = 9.41 (1H), 8.77 (1H), 8.70 (1H), 8.64 (1H), 8.56 (1H), 8.48 (2H), 8.24 (1H), 8.03 (1H), 7.90-8.00 (4H), 7.71 (2H), 7.50-7.61 (6H), 7.36-7.42 (3H).

Example 5

(Synthesis of 4-[4-(5H-pyrido[4,3-b]indol-5-yl)phenyl]-6-(naphthalen-1-yl)-[2,2']bipyridine (Compound 24))

[0063] 4-(4-Bromophenyl)-6-(naphthalen-1-yl)-[2,2']bipyridine was synthesized in the same manner as in the above Example 1. 2.2 g of the resulting 4-(4-bromophenyl)-6-(naphthalen-1-yl)-[2,2']bipyridine, 0.9 g of 5H-pyrido[4,3-b]indole, 0.2 g of copper powder, 2.1 g of potassium carbonate, 0.2 ml of dimethyl sulfoxide, and 10 ml of n-dodecane were added and the whole was stirred for 5 hours under heating and refluxing. After cooling to room temperature, 60 ml of chloroform was added thereto, insoluble solid was removed by filtration, and the filtrate was concentrated under reduced pressure to obtain a crude product. The crude product was purified by column chromatography (carrier: NH silica gel, eluent: hexane/chloroform) to obtain 2.04 g (yield 77%) of 4-[4-(5H-pyrido[4,3-b]indol-5-yl)phenyl]-6-(naphthalen-1-yl)-[2,2']bipyridine (Compound 24) as a yellow-white powder.

[0064] The structure of the resulting yellow-white powder was identified using NMR. The results of 1H-NMR measurement are shown in FIG. 5.

[0065] The following 24 hydrogen signals were detected on 1H-NMR (CDC13). δ (ppm) = 9.41 (1H), 8.86 (1H), 8.76 (1H), 8.60 (1H), 8.56 (1H), 8.35 (1H), 8.23 (1H), 8.10 (2H), 7.99 (2H), 7.94 (1H), 7.80-7.85 (2H), 7.71 (2H), 7.64 (1H), 7.52-7.57 (4H), 7.36-7.43 (3H).

Example 6

(Synthesis of 6-[4-(5H-pyrido[3,2-b]indol-5-yl)phenyl]-4-(naphthalen-2-yl)-[2,2']bipyridine (Compound 37))

[0066] 6-(4-Bromophenyl)-4-(naphthalen-2-yl)-[2,2']bipyridine was synthesized in the same manner as in the above Example 1. 2.5 g of the resulting 6-(4-bromophenyl)-4-(naphthalen-2-yl)-[2,2']bipyridine, 1.0 g of 5H-pyrido[3,2-b]indole, 0.2 g of copper powder, 2.4 g of potassium carbonate, 0.2 ml of dimethyl sulfoxide, and 10 ml of n-dodecane were added and the whole was stirred for 19 hours under heating and refluxing. After cooling to room temperature, 60 ml of chloroform was added thereto, insoluble solid was removed by filtration, and the filtrate was concentrated under reduced pressure to obtain a crude product.. The crude product was subjected to purification using o-dichlorobenzene as a recrystallization solvent and drying was performed under reduced pressure at 70°C for 12 hours to obtain 1.03 g (yield 34%) of 6-[4-(5H-pyrido[3,2-b]indol-5-yl)phenyl]-4-(naphthalen-2-yl)-[2,2']bipyridine (Compound 37) as a yellow-white powder.

[0067] The structure of the resulting yellow-white powder was identified using NMR. The results of 1H-NMR measurement are shown in FIG. 6.

[0068] The following 24 hydrogen signals were detected on 1H-NMR (CDCl3). δ (ppm) = 8.85 (1H), 8.78 (1H), 8.75 (1H), 8.65 (1H), 8.48-8.50 (3H), 8.36 (1H), 8.21 (1H), 7.98-8.03 (3H), 7.90-7.94 (2H), 7.81 (1H), 7.74 (2H), 7.55-7.60 (4H), 7.36-7.43 (3H).

Example 7

(Synthesis of 4-[4-(5H-pyrido[3,2-b]indol-5-yl)phenyl]-6-(naphthalen-2-yl)-[2,2']bipyridine (Compound 41))

[0069] 4-(4-Bromophenyl)-6-(naphthalen-2-yl)-[2,2']bipyridine was synthesized in the same manner as in the above Example 1. 2.5 g of the resulting 4-(4-bromophenyl)-6-(naphthalen-2-yl)-[2,2']bipyridine, 1.1 g of 5H-pyrido[3,2-b]indole, 0.2 g of copper powder, 2.4 g of potassium carbonate, 0.2 ml of dimethyl sulfoxide, and 10 ml of n-dodecane were added and the whole was stirred for 18 hours under heating and refluxing. After cooling to room temperature, 60 ml of chloroform was added thereto, insoluble solid was removed by filtration, and the filtrate was concentrated under reduced pressure to obtain a crude product. The crude product was purified by column chromatography (carrier: NH silica gel, eluent: hexane/chloroform) to obtain 1.86 g (yield 62%) of 4-[4-(5H-pyrido[3,2-b]indol-5-yl)phenyl]-6-(naphthalen-2-yl)-[2,2']bipyridine (Compound 41) as a yellow-white powder.

[0070] The structure of the resulting yellow-white powder was identified using NMR. The results of 1H-NMR measurement are shown in FIG. 7.

[0071] The following 24 hydrogen signals were detected on 1H-NMR (CDCl3). δ (ppm) = 8.76-8.80 (3H), 8.70 (1H), 8.65 (1H), 8.48 (1H), 8.42 (1H), 8.21 (1H), 8.10 (1H), 8.02 (2H), 7.92 (2H), 7.79 (1H), 7.73 (2H), 7.55-7.57 (4H), 7.36-7.44 (3H).

Example 8

(Synthesis of 6-[4-(5H-pyrido[4,3-b]indol-5-yl)phenyl]-4-(phenanthren-9-yl)-[2,2']bipyridine (Compound 52))

[0072] 6-(4-Bromophenyl)-4-(phenanthren-9-yl)-[2,2']bipyridine was synthesized in the same manner as in the above Example 1. 2.6 g of the resulting 6-(4-bromophenyl)-4-(phenanthren-9-yl)-[2,2']bipyridine, 1.0 g of 5H-pyrido[4,3-b]indole, 0.2 g of copper powder, 2.2 g of potassium carbonate, 0.2 ml of dimethyl sulfoxide, and 10 ml of n-dodecane were added and the whole was stirred for 5 hours under heating and refluxing. After cooling to room temperature, 80 ml of chloroform was added thereto, insoluble solid was removed by filtration, and the filtrate was concentrated under reduced pressure to obtain a crude product. The crude product was purified by column chromatography (carrier: NH silica gel, eluent: toluene) to obtain 2.35 g (yield 78%) of 6-[4-(5H-pyrido[4,3-b]indol-5-yl)phenyl]-4-(phenanthren-9-yl)-[2,2']bipyridine (Compound 52) as a pale red-white powder.

[0073] The structure of the resulting pale red-white powder was identified using NMR. The results of 1H-NMR measurement are shown in FIG. 8.

[0074] The following 26 hydrogen signals were detected on 1H-NMR (CDCl3). δ (ppm) = 9.41 (1H), 8.83 (1H), 8.78 (2H), 8.70-8.72 (2H), 8.55 (1H), 8.49 (2H), 8.23 (1H), 8.08 (1H), 8.01 (1H), 7.91-7.96 (2H), 7.88 (1H), 7.71-7.75 (4H), 7.67 (1H), 7.61 (1H), 7.50-7.55 (2H), 7.37-7.41 (3H).

Example 9

(Synthesis of 4-[4-(5H-pyrido[4,3-b]indol-5-yl)phenyl]-6-(phenanthren-2-yl)-[2,2']bipyridine (Compound 72))

[0075] 4-(4-Bromophenyl)-6-(phenanthren-2-yl)-[2,2']bipyridine was synthesized in the same manner as in the above Example 1. 2.6 g of the resulting 4-(4-bromophenyl)-6-(phenanthren-2-yl)-[2,2']bipyridine, 1.0 g of 5H-pyrido[4,3-b]indole, 0.2 g of copper powder, 2.2 g of potassium carbonate, 0.2 ml of dimethyl sulfoxide, and 10 ml of n-dodecane were added and the whole was stirred for 6 hours under heating and refluxing. After cooling to room temperature, 80 ml of chloroform was added thereto, insoluble solid was removed by filtration, and the filtrate was concentrated under reduced pressure to obtain a crude product. The crude product was purified by column chromatography (carrier: NH silica gel, eluent: hexane/chloroform) to obtain 1.40 g (yield 47%) of 4-[4-(5H-pyrido[4,3-b]indol-5-yl)phenyl]-6-(phenanthren-2-yl)-[2,2']bipyridine (Compound 72) as a pale red-white powder.

[0076] The structure of the resulting pale red-white powder was identified using NMR. The results of 1H-NMR measurement are shown in FIG. 9.

[0077] The following 26 hydrogen signals were detected on 1H-NMR (CDC13). δ (ppm) = 9.42 (1H), 8.75-8.86 (6H), 8.57 (2H), 8.24 (2H), 8.12 (2H), 7.91-7.95 (3H), 7.82 (1H), 7.63-7.73 (4H), 7.54 (2H), 7.38-7.43 (3H).

Example 10

(Synthesis of 4-(biphenyl-4-yl)-6-[4-(5H-pyrido[4,3-b]indol-5-yl)phenyl]-[2,2']bipyridine (Compound 116))

[0078] 4-(Biphenyl-4-yl)-6-(4-bromophenyl)-[2,2']bipyridine was synthesized in the same manner as in the above Example 1. 2.5 g of the resulting 4-(biphenyl-4-yl)-6-(4-bromophenyl)-[2,2']bipyridine, 1.0 g of 5H-pyrido[4,3-b]indole, 0.2 g of copper powder, 2.3 g of potassium carbonate, 0.2 ml of dimethyl sulfoxide, and 10 ml of n-dodecane were added and the whole was stirred for 5 hours under heating and refluxing. After cooling to room temperature, 80 ml of chloroform was added thereto, insoluble solid was removed by filtration, and the filtrate was concentrated under reduced pressure to obtain a crude product. The crude product was purified by column chromatography (carrier: NH silica gel, eluent: toluene/ethyl acetate) to obtain 2.81 g (yield 93%) of 4-(biphenyl-4-yl)-6-[4-(5H-pyrido[4,3-b]indol-5-yl)phenyl]-[2,2']bipyridine (Compound 116) as a yellow-white powder.

[0079] The structure of the resulting yellow-white powder was identified using NMR. The results of 1H-NMR measurement are shown in FIG. 10.

[0080] The following 26 hydrogen signals were detected on 1H-NMR (CDC13). δ (ppm) = 9.41 (1H), 8.78 (1H), 8.76 (1H), 8.73 (1H), 8.56 (1H), 8.49 (2H), 8.24 (1H), 8.13 (1H), 7.96 (2H), 7.91 (1H), 7.79 (2H), 7.73 (2H), 7.69 (2H), 7.48-7.56 (4H), 7.37-7.42 (4H).

Example 11

(Synthesis of 4,6-bis[4-(5H-pyrido[3,2-b]indol-5-yl)phenyl]-[2,2']bipyridine (Compound 165))

[0081] 4,6-Bis(4-bromophenyl)-[2,2']bipyridine was synthesized in the same manner as in the above Example 1. 2.2 g of the resulting 4,6-bis(4-bromophenyl)-[2,2']bipyridine, 1.7 g of 5H-pyrido[3,2-b]indole, 0.2 g of copper powder, 2.0 g of potassium carbonate, 0.2 ml of dimethyl sulfoxide, and 10 ml of n-dodecane were added and the whole was stirred for 18 hours under heating and refluxing. After cooling to room temperature, 50 ml of chloroform was added thereto, insoluble solid was removed by filtration, and the filtrate was concentrated under reduced pressure to obtain a crude product. The crude product was purified by column chromatography (carrier: NH silica gel, eluent: hexane/chloroform) to obtain 1.50 g (yield 50%) of 4,6-bis[4-(5H-pyrido[3,2-b]indol-5-yl)phenyl]-[2,2']bipyridine (Compound 165) as a yellow-white powder.

[0082] The structure of the resulting yellow-white powder was identified using NMR. The results of 1H-NMR measurement are shown in FIG. 11.

[0083] The following 28 hydrogen signals were detected on 1H-NMR (CDC13). δ (ppm) = 8.83 (1H), 8.76-8.78 (2H), 8.66 (2H), 8.48-8.52 (4H), 8.17 (1H), 8.13 (2H), 7.94 (1H), 7.81 (2H), 7.76 (4H), 7.56-7.61 (4H), 7.36-7.44 (5H).

Example 12

(Synthesis of 4-[4-(5H-pyrido[4,3-b]indol-5-yl)phenyl]-6-(phenanthren-9-yl)-[2,2']bipyridine (Compound 192))

[0084] 4-(4-Bromophenyl)-6-(phenanthren-9-yl)-[2,2']bipyridine was synthesized in the same manner as in the above Example 1. 2.2 g of the resulting 4-(4-bromophenyl)-6-(phenanthren-9-yl)-[2,2']bipyridine, 0.8 g of 5H-pyrido[4,3-b]indole, 0.2 g of copper powder, 1.8 g of potassium carbonate, 0.2 ml of dimethyl sulfoxide, and 10 ml of n-dodecane were added and the whole was stirred for 8 hours under heating and refluxing. After cooling to room temperature, 80 ml of chloroform was added thereto, insoluble solid was removed by filtration, and the filtrate was concentrated under reduced pressure to obtain a crude product. The crude product was purified by column chromatography (carrier: NH silica gel, eluent: hexane/chloroform) to obtain 1.36 g (yield 54%) of 4-[4-(5H-pyrido[4,3-b]indol-5-yl)phenyl]-6-(phenanthren-9-yl)-[2,2']bipyridine (Compound 192) as a yellow-white powder.

[0085] The structure of the resulting yellow-white powder was identified using NMR. The results of 1H-NMR measurement are shown in FIG. 12.

[0086] The following 26 hydrogen signals were detected on 1H-NMR (CDC13). δ (ppm) = 9.40 (1H), 8.89 (1H), 8.84 (1H), 8.78 (2H), 8.61 (1H), 8.55 (1H), 8.32 (1H), 8.23 (1H), 8.12 (2H), 8.04 (1H), 7.99 (2H), 7.83 (1H), 7.71-7.74 (4H), 7.62-7.67 (2H), 7.52 (2H), 7.37-7.42 (3H).

Example 13

(Synthesis of 6-(biphenyl-4-yl)-4-[4-(5H-pyrido[4,3-b]indol-5-yl)phenyl]-[2,2']bipyridine (Compound 193))

[0087] 6-(Biphenyl-4-yl)-4-(4-bromophenyl)-[2,2']bipyridine was synthesized in the same manner as in the above Example 1. 2.5 g of the resulting 6-(biphenyl-4-yl)-4-(4-bromophenyl)-[2,2']bipyridine, 1.0 g of 5H-pyrido[4,3-b]indole, 0.2 g of copper powder, 2.3 g of potassium carbonate, 0.2 ml of dimethyl sulfoxide, and 10 ml of n-dodecane were added and the whole was stirred for 7 hours under heating and refluxing. After cooling to room temperature, 80 ml of chloroform was added thereto, insoluble solid was removed by filtration, and the filtrate was concentrated under reduced pressure to obtain a crude product. The crude product was purified by column chromatography (carrier: NH silica gel, eluent:

toluene/ethyl acetate) to obtain 1.96 g (yield 65%) of 6-(biphenyl-4-yl)-4-[4-(5H-pyrido[4,3-b]indol-5-yl)phenyl]-[2,2']bipyridine (Compound 193) as a white powder.

[0088] The structure of the resulting white powder was identified using NMR. The results of 1H-NMR measurement are shown in FIG. 13.

[0089] The following 26 hydrogen signals were detected on 1H-NMR (CDCl3). δ (ppm) = 9.42 (1H), 8.76 (3H), 8.57 (1H), 8.34 (2H), 8.25 (1H), 8.11 (3H), 7.91 (1H), 7.80 (2H), 7.70-7.73 (4H), 7.49-7.53 (4H), 7.38-7.43 (4H).

Example 14

[0090] For the compounds of the invention, melting point and glass transition point were determined by means of a highly sensitive differential scanning calorimeter (DSC 3100S manufactured by Bruker AXS). The results are shown in Table 1.

[Table 1]

	Melting Point	Glass Transition Point
Compound of Example 1	244°C	114°C
Compound of Example 2	253°C	117°C
Compound of Example 3	339°C	161°C
Compound of Example 4	152°C	115°C
Compound of Example 5	151°C	116°C
Compound of Example 6	218°C	108°C
Compound of Example 7	248°C	110°C
Compound of Example 8	181°C	139°C
Compound of Example 9	271°C	139°C
Compound of Example 10	150°C	112°C
Compound of Example 11	343°C	155°C
Compound of Example 12	186°C	132°C
Compound of Example 13	231°C	114°C

[0091] The compounds of the invention show a glass transition point of 100°C or higher, and thus are stable in a thin-film state.

Example 15

[0092] Using each of the compounds of the invention, a deposited film having a film thickness of 100 nm was prepared on an ITO substrate and work function was measured on a photo-electron spectroscopy in air (Model AC-3, manufactured by Riken Keiki Co., Ltd.). The results are shown in Table 2.

[Table 2]

	Work Function
Compound of Example 1	6.11 eV
Compound of Example 2	6.18 eV
Compound of Example 3	6.15 eV
Compound of Example 4	6.25 eV
Compound of Example 5	6.33 eV
Compound of Example 6	5.99 eV
Compound of Example 7	6.12 eV

(continued)

	Work Function
Compound of Example 8	6.27 eV
Compound of Example 9	6.34 eV
Compound of Example 10	6.27 eV
Compound of Example 11	6.15 eV
Compound of Example 12	6.37 eV
Compound of Example 13	6.16 eV

[0093] Thus, the compounds of the invention have values deeper than a work function of 5.4 eV possessed by common hole-transporting materials such as NPD and TPD and have a large hole-blocking ability.

Example 16

[0094] An organic EL device was prepared by depositing a hole-injecting layer 3, a hole-transporting layer 4, an emitting layer 5, a hole-blocking layer 6, an electron-transporting layer 7, an electron-injecting layer 8, and a cathode (aluminum electrode) 9 in this order on a glass substrate 1 on which an ITO electrode had been formed as a transparent anode 2 in advance, as shown in FIG. 14.

[0095] After the glass substrate 1 on which ITO having a film thickness of 150 nm had been formed was washed with an organic solvent, the surface was washed by UV ozone treatment. It was mounted in a vacuum deposition machine, which was then evacuated to 0.001 Pa or lower.

[0096] Subsequently, copper phthalocyanine was formed thereon at a deposition rate of 3.6 nm/min to a thickness of about 20 nm as the hole-injecting layer 3. NPD was formed on the hole-injecting layer 3 at a deposition rate of 3.6 nm/min to a thickness of about 40 nm as the hole-transporting layer 4. As the emitting layer 5, Alq3 was formed on the hole-transporting layer 4 at a deposition rate of 3.6 nm/min to a thickness of about 30 nm. On the emitting layer 5, the compound of invention Example 1 (Compound 36) was formed at a deposition rate of 3.6 nm/min to a thickness of about 30 nm as the hole-blocking layer-cum-electron-transporting layer 6 and 7. On the hole-blocking layer-cum-electron-transporting layer 6 and 7, lithium fluoride was formed at a deposition rate of 0.36 nm/min to a thickness of about 0.5 nm as the electron-injecting layer 8. Finally, aluminum was deposited to a thickness of about 200 nm to form the cathode 9. The prepared device was stored in a vacuum desiccator and characteristic properties were measured in the atmosphere at ordinary temperature.

[0097] The results of measuring luminescence properties when direct voltage was applied to the organic EL device prepared using the compound of invention Example 1 (Compound 36) of the invention are summarized in Table 3.

Example 17

[0098] An organic EL device was prepared under the same conditions as in Example 16 except that the material of the hole-blocking layer-cum-electron-transporting layer 6 and 7 was replaced by the compound of invention Example 2 (Compound 40), and characteristic properties thereof were investigated.

[0099] The results of measuring luminescence properties when direct voltage was applied to the organic EL device prepared using the compound of invention Example 2 (Compound 40) of the invention are summarized in Table 3.

Example 18

[0100] An organic EL device was prepared under the same conditions as in Example 16 except that the material of the hole-blocking layer-cum-electron-transporting layer 6 and 7 was replaced by the compound of invention Example 10 (Compound 116), and characteristic properties thereof were investigated.

[0101] The results of measuring luminescence properties when direct voltage was applied to the organic EL device prepared using the compound of invention Example 10 (Compound 116) of the invention are summarized in Table 3.

[Comparative Example 1]

[0102] For comparison, an organic EL device was prepared under the same conditions as in Example 16 except that the material of the hole-blocking layer-cum-electron-transporting layer 6 and 7 was replaced by Alq3 as the electron-transporting layer 7, and characteristic properties thereof were investigated. The results of measurement are shown in Tables 3 and 4.

[Table 3]

	Compound	Voltage [V] (@10mA/cm^2)	Luminance [cd/m^2] (@10mA/cm^2)	Luminous Efficiency [cd/A] (@10mA/cm^2)	Power efficiency [lm/W] (@10mA/cm^2)
Example 16	Compound 36	5.90	480	4.80	2.54
Example 17	Compound 40	6.05	460	4.60	2.38
Example 18	Compound 116	6.35	464	4.64	2.29
Comparative Example 1	Alq3	6.60	450	4.50	2.13

[0103] Thus, it was revealed that the organic EL devices of the invention are excellent in luminous efficiency and can achieve remarkable decrease in driving voltage, as compared with the devices using Alq3 which is a commonly employed general electron-transporting material.

Example 19

[0104] An organic EL device was prepared under the same conditions as in Example 16 except that the material of the hole-blocking layer-cum-electron-transporting layer 6 and 7 was replaced by the compound of invention Example 3 (Compound 164), and characteristic properties thereof were investigated.

[0105] The results of measuring luminescence properties when direct voltage was applied to the organic EL device prepared using the compound of invention Example 3 (Compound 164) of the invention are summarized in Table 4.

Example 20

[0106] An organic EL device was prepared under the same conditions as in Example 16 except that the material of the hole-blocking layer-cum-electron-transporting layer 6 and 7 was replaced by the compound of invention Example 5 (Compound 24), and characteristic properties thereof were investigated.

[0107] The results of measuring luminescence properties when direct voltage was applied to the organic EL device prepared using the compound of invention Example 5 (Compound 24) of the invention are summarized in Table 4.

Example 21

[0108] An organic EL device was prepared under the same conditions as in Example 16 except that the material of the hole-blocking layer-cum-electron-transporting layer 6 and 7 was replaced by the compound of invention Example 6 (Compound 37), and characteristic properties thereof were investigated.

[0109] The results of measuring luminescence properties when direct voltage was applied to the organic EL device prepared using the compound of invention Example 6 (Compound 37) of the invention are summarized in Table 4.

Example 22

[0110] An organic EL device was prepared under the same conditions as in Example 16 except that the material of the hole-blocking layer-cum-electron-transporting layer 6 and 7 was replaced by the compound of invention Example 7 (Compound 41), and characteristic properties thereof were investigated.

[0111] The results of measuring luminescence properties when direct voltage was applied to the organic EL device prepared using the compound of invention Example 7 (Compound 41) of the invention are summarized in Table 4.

Example 23

[0112] An organic EL device was prepared under the same conditions as in Example 16 except that the material of the hole-blocking layer-cum-electron-transporting layer 6 and 7 was replaced by the compound of invention Example 12 (Compound 192), and characteristic properties thereof were investigated.

[0113] The results of measuring luminescence properties when direct voltage was applied to the organic EL device prepared using the compound of invention Example 12 (Compound 192) of the invention are summarized in Table 4.

Example 24

[0114] An organic EL device was prepared under the same conditions as in Example 16 except that the material of the hole-blocking layer-cum-electron-transporting layer 6 and 7 was replaced by the compound of invention Example 13 (Compound 193), and characteristic properties thereof were investigated.

[0115] The results of measuring luminescence properties when direct voltage was applied to the organic EL device prepared using the compound of invention Example 13 (Compound 193) of the invention are summarized in Table 4.

[Table 4]

	Compound	Luminance [cd/m^2] (@10mA/cm^2)	Luminous Efficiency [cd/A] (@10mA/cm^2)	Power efficiency [lm/W] (@10mA/cm^2)
Example 19	Compound 164	515	5.15	2.32
Example 20	Compound 24	495	4.95	2.30
Example 21	Compound 37	485	4.85	1.81
Example 22	Compound 41	465	4.65	1.59
Example 23	Compound 192	490	4.90	2.06
Example 24	Compound 193	455	4.55	2.04
Comparative Example 1	Alq3	450	4.50	2.13

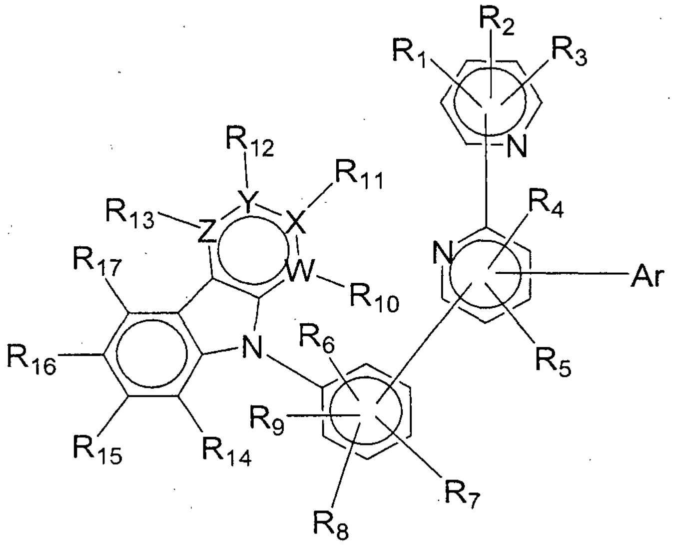
[0116] Thus, it was revealed that the organic EL devices of the invention have high luminance per unit current density and are excellent in luminous efficiency, as compared with the devices using Alq3 which is a commonly employed general electron-transporting material.

[0117] Since the compound having a substituted bipyridyl group and a pyridoindole ring structure connected with each other through a phenylene group according to the invention exhibits a good injection property of electrons and is stable in a thin-film state, the compound is excellent as a compound for organic EL devices. By preparing organic EL devices using the compound, driving voltage can be decreased and durability can be improved. For example, it becomes possible to spread the applications onto electric home appliances and illumination.

Claims

1. A compound having a substituted bipyridyl group and a pyridoindole ring structure connected with each other through a phenylene group, which is represented by the following general formula (1):

[Chem. 1]



(1)

wherein Ar represents an unsubstituted aromatic hydrocarbon group, aromatic hydrocarbon group substituted with a pyridoindolyl group, or an unsubstituted condensed polycyclic aromatic group; R1 to R17 represent a hydrogen atom; and W, X, and Z represent a carbon atom and Y is a nitrogen atom and the nitrogen atom does not have a substituent of R12, or W, X, and Y represent a carbon atom and Z is a nitrogen atom and the nitrogen atom does not have a substituent of R13.

2. An organic electroluminescence device comprising a pair of electrodes and at least one organic layer interposed between the electrodes, wherein the at least one organic layer contains the compound according to claim 1.

3. The organic electroluminescence device according to claim 2, wherein the at least one organic layer is an electron-transporting layer.

4. The organic electroluminescence device according to claim 2, wherein the at least one organic layer is a hole-blocking layer.

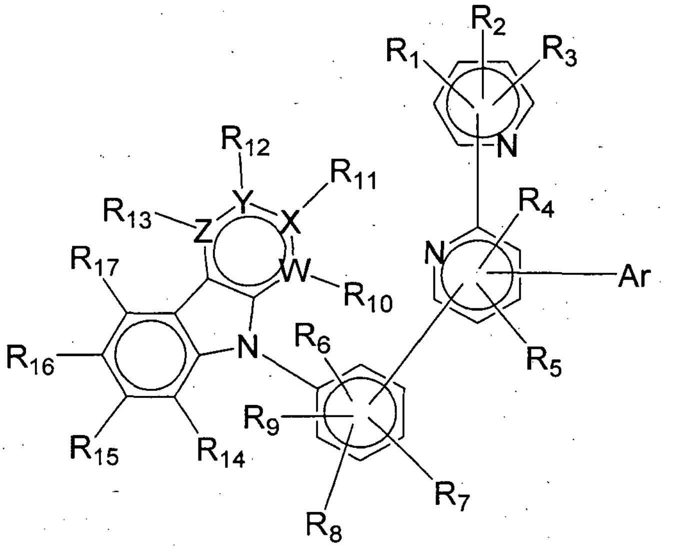
5. The organic electroluminescence device according to claim 2, wherein the at least one organic layer is an emitting layer.

6. The organic electroluminescence device according to claim 2, wherein the at least one organic layer is an electron-injecting layer.

Patentansprüche

1. Verbindung mit einer substituierten Bipyridylgruppe und einer Pyridoindolringstruktur, die miteinander über eine Phenylengruppe verbunden sind, welche durch die folgende allgemeine Formel (1) dargestellt ist:

[Chem. 1]



(1)

wobei Ar eine unsubstituierte aromatische Kohlenwasserstoffgruppe, eine aromatische Kohlenwasserstoffgruppe substituiert mit einer Pyridoindolylgruppe oder eine unsubstituierte kondensierte polycyclische aromatische Gruppe darstellt; R1 bis R17 ein Wassertoffatom darstellen; und W, X und Z ein Kohlenstoffatom darstellen und Y ein Stickstoffatom darstellt und das Stickstoffatom keinen Substituenten von R12 aufweist oder W, X und Y ein Kohlenstoffatom darstellen und Z ein Stickstoffatom darstellt und das Stickstoffatom keinen Substituenten von R13 aufweist:

2. Organisches Elektrolumineszenzgerät, umfassend ein Elektrodenpaar und mindestens eine zwischen den Elektroden eingefügte organische Schicht, wobei die mindestens eine organische Schicht die Verbindung gemäß Anspruch 1 enthält.

3. Organisches Elektrolumineszenzgerät gemäß Anspruch 2, wobei die mindestens eine organische Schicht eine elektronentransportierende Schicht ist.

4. Organisches Elektrolumineszenzgerät gemäß Anspruch 2, wobei die mindestens eine organische Schicht eine lochblockierende Schicht ist.

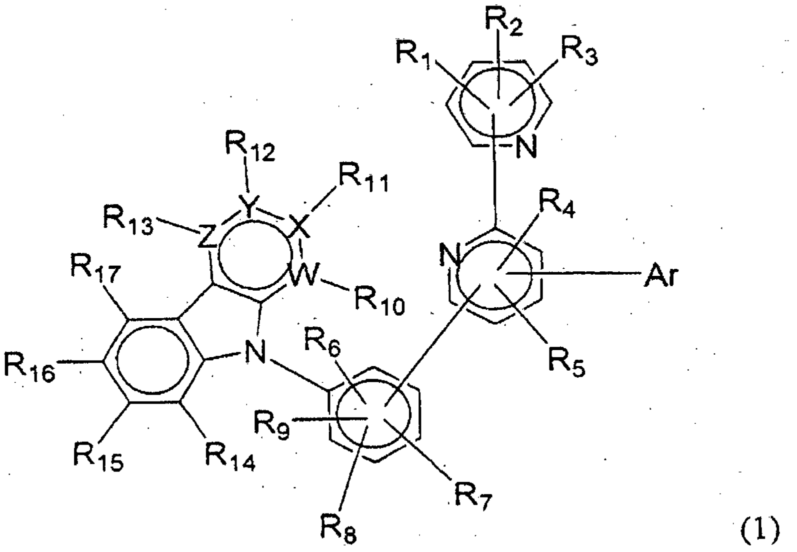
5. Organisches Elektrolumineszenzgerät gemäß Anspruch 2, wobei die mindestens eine organische Schicht eine emittierende Schicht ist.

6. Organisches Elektrolumineszenzgerät gemäß Anspruch 2, wobei die mindestens eine organische Schicht eine elektroneninjizierende Schicht ist.

Revendications

1. Composé ayant une groupe bipyridyle substitué et une structure de cycle pyridoindole raccordés l'un à l'autre par l'intermédiaire d'un groupe phénylène, qui est représenté par la formule générale (1) suivante :

[Chem. 1]



(1)

dans laquelle Ar représente un groupe hydrocarboné aromatique non substitué, un groupe hydrocarboné aromatique substitué par un groupe pyridoindolyle, ou un groupe aromatique polycyclique condensé non substitué ; R_1 à R_{17} représentent un atome d'hydrogène ; et W, X et Z représentent un atome de carbone et Y est un atome d'azote et l'atome d'azote ne comporte pas de substituant de R_{12}, ou W, X et Y représentent un atome de carbone et Z est un atome d'azote et l'atome d'azote ne comporte pas de substituant de R_{13}.

2. Dispositif électroluminescent organique comprenant une paire d'électrodes et au moins une couche organique interposée entre les électrodes, dans lequel l'au moins une couche organique contient le composé selon la revendication 1.

3. Dispositif électroluminescent organique selon la revendication 2, dans lequel l'au moins une couche organique est une couche transporteuse d'électrons.

4. Dispositif électroluminescent organique selon la revendication 2, dans lequel l'au moins une couche organique est une couche de blocage de trous.

5. Dispositif électroluminescent organique selon la revendication 2, dans lequel l'au moins une couche organique est une couche émettrice.

6. Dispositif électroluminescent organique selon la revendication 2, dans lequel l'au moins une couche organique est une couche d'injection d'électrons.

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 8048656 A **[0004]**
- JP 3194657 B **[0004]**
- JP 2734341 B **[0014]**
- US 20050249970 A1 **[0021]**

Non-patent literature cited in the description

- *Japan Society of Applied Physics Ninth Workshop Preprint,* 2001, 55-61 **[0006]**
- *Japan Society of Applied Physics Ninth Workshop Preprint,* 2001, 23-31 **[0008]**
- *Fiftieth Meeting of Japan Society of Applied Physics and Related Societies,* 2003, vol. 28, 1413 **[0016]**
- Journal of Organic Molecules/Bioelectronics Section. Japan Society of Applied Physics, 2000, vol. 11, 13-19 **[0018]**
- *J. Chem. Soc., Perkin Trans.,* 1999, vol. 1, 1505 **[0035]**
- *Synthesis,* 1976, vol. 1 **[0036]**

专利名称(译)	其中取代的联吡啶基通过亚苯基与吡啶并吲哚环结构连接的化合物和有机电致发光器件		
公开(公告)号	EP2128159B1	公开(公告)日	2017-08-16
申请号	EP2008722028	申请日	2008-03-13
[标]申请(专利权)人(译)	保土谷化学工业株式会社		
申请(专利权)人(译)	HODOGAYA化学有限公司.		
当前申请(专利权)人(译)	HODOGAYA化学有限公司.		
[标]发明人	YOKOYAMA NORIMASA HAYASHI SHUICHI KUSANO SHIGERU NAGAOKA MAKOTO		
发明人	YOKOYAMA, NORIMASA HAYASHI, SHUICHI KUSANO, SHIGERU NAGAOKA, MAKOTO		
IPC分类号	C09K11/06 C07D471/04 H01L51/50		
CPC分类号	C07D471/04 C07D519/00 C09K11/06 C09K2211/1007 C09K2211/1011 C09K2211/1029 H01L51/0067 H01L51/0072 H01L51/5048 H01L51/5072		
优先权	2007066214 2007-03-15 JP		
其他公开文献	EP2128159A1 EP2128159A4		
外部链接	Espacenet		

摘要(译)

本发明的目的是提供一种具有优异性能的有机化合物，其具有优异的电子注入/传输性能，具有空穴阻挡能力并且在薄膜状态下高度稳定，作为用于有机电致发光器件的材料具有高效率和高耐久性，并且使用该化合物提供具有高效率和高耐久性的有机电致发光器件。本发明涉及具有通过亚苯基彼此连接的取代联吡啶基和吡啶并吲哚环结构的化合物，其由通式（1）表示，和包含一对电极和至少一个的有机EL装置插入在电极之间的有机层，其中该化合物用作至少一个有机层的构成材料。