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

(11) **EP 1 501 337 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
12.12.2012 Bulletin 2012/50

(21) Application number: **03725696.3**

(22) Date of filing: **28.04.2003**

(51) Int Cl.:
H01L 51/50 $^{(2006.01)}$

(86) International application number:
PCT/JP2003/005437

(87) International publication number:
WO 2003/094578 (13.11.2003 Gazette 2003/46)

(54) **ORGANIC ELECTROLUMINESCENCE DEVICE AND MATERIAL THEREOF**

ORGANISCHES ELEKTROLUMINESZENZBAUELEMENT UND MATERIAL DAFÜR

DISPOSITIF D’ELECTROLUMINESCENCE ORGANIQUE ET MATERIAU ASSOCIE

(84) Designated Contracting States:
DE FR GB

(30) Priority: **01.05.2002 JP 2002129608**

(43) Date of publication of application:
26.01.2005 Bulletin 2005/04

(73) Proprietor: **Nissan Chemical Industries, Ltd.**
Chiyoda-ku,
Tokyo 101-0054 (JP)

(72) Inventors:
- **YAMADA,Tomohisa,**
  c/o Electronic Materials Research Laboratories,
  Funabashi-shi,
  Chiba 274-8507, (JP)
- **YOSHIMOTO,Takuji**
  c/o Electronic Materials Research Laboratories,
  Funabashi-shi,
  Chiba 274-8507, (JP)

(74) Representative: **Stoner, Gerard Patrick et al**
Mewburn Ellis LLP
33 Gutter Lane
London
EC2V 8AS (GB)

(56) References cited:

WO-A-01/72926	**WO-A-93/05077**
DE-A1- 2 425 193	**DE-A1- 2 425 194**
JP-A- 2001 244 079	**JP-A- 2001 244 079**
JP-A- 2002 056 985	**JP-A- 2003 068 464**

- **TATSUO ERABI ET AL: "2,6-Dimethoxyphenyl-kio yusuru ikutsuka no antei carbenium-en no cyclic voltammetry" ELECTRO ORGANIC CHEMISTRY - TORONKAI KOEN YOSHISHU, XX, XX, 18 June 2001 (2001-06-18), pages 35-36, XP002969583**
- **TATSUO ERABI ET AL.: ’2,6-Dimethoxyphenyl-kio yusuru ikutsuka no antei carbenium-en no cyclic voltammetry’ DAI 25 KAI ELECTRO ORGANIC CHEMISTRY TORONKAI KOEN YOSHISHU 18 June 2001, pages 35 - 36, XP002969583**

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Printed by Jouve, 75001 PARIS (FR)

Description

TECHNICAL FIELD

[0001] The present invention relates to an organic electroluminescence device and a material thereof. More particularly, the present invention relates to an organic electroluminescence device that emits light upon application of voltage to its emission layer of an organic compound and relates also to a charge transport material incorporated thereinto.

BACKGROUND ART

[0002] An organic electroluminescence device capable of emission with a luminance of about 1000 cd/m^2 at a driving voltage equal to or lower than 10 V was reported by Tang et al. of Eastman Kodak in 1987. See Appl. Phys. Lett., vol. 51, p. 913, 1987.

[0003] Tang et al. searched for the optimal electrode and organic compound that would increase the emission efficiency of the device. They prepared an organic electroluminescence device in which the hole transport layer is an aromatic amine compound and the electron transport emission layer is an aluminum complex of 8-hydoxyquinoline. This device emits light when it has DC voltage applied across its electrodes. The DC voltage injects holes through the anode and electrons through the cathode, so that they undergo recombination in the emission layer to emit light.

[0004] Among the known hole transport materials are aromatic diamine derivatives (disclosed in Japanese Patent Laid-open Nos. Hei 8-20771, Hei 8-40995, and Hei 8-40997) and aromatic amine-containing polymers (disclosed in Japanese Patent Laid-open Nos. Hei 11-283750 and 2000-36390).

[0005] Among the known hole injection materials are phthalocyanine derivatives and aromatic triamines of starburst type (disclosed in Japanese Patent Laid-open Nos. Sho 63-295695 and Hei 4-308688).

[0006] The existing organic electroluminescence devices have some problems to be addressed. That is, they need to have a longer life, to work at a lower driving voltage, and to work with a constant current without voltage increase and luminance decrease. Although no elucidation has been made yet, the performance of the device seems to depend on the properties (such as glass transition temperature and melting point) of the organic materials constituting the device. The device made of an organic material poor in heat resistance tends to break during continuous operation.

[0007] Any device with a short life or a high driving voltage poses a problem when used as the light source for facsimile, copying machine, and back light of liquid crystal display, particularly, the device is not desirable for display.

[0008] It is an object of the present invention to provide an organic electroluminescence device capable of high luminance emission at a low driving voltage (for a longer life) and a material used for the device.

[0009] WO 01/72926 describes trityl-type compounds having three aryl groups bound to a central carbon atom in which one of the aryl groups is a fluorophore in which the compound can exist in a non-ionized state or in an ionized state.

[0010] WO 93/05077 describes low bandgap polymers having a fused bithiophene structure.

[0011] Electroorganic Chemistry - Toronkai Koen Yoshishu, 18 June 2001, pages 35 and 36, Tatsuo Erabi et al. describes some substituted tri-aryl carbenium salts and some of their cyclic voltammetry and spectroscopic properties.

[0012] JP 2001 244079 describes an organic electroluminescent element and the effect of changing the thickness of a chemical doped layer (comprising a Lewis acid component) on the light emitted from the element.

[0013] DE 24 25 194 A1 and DE 24 25 193 A1 also describe some triarylmethanol compounds.

DISCLOSURE OF INVENTION

[0014] The present inventors conducted a series of researches to tackle the above-mentioned problems. As a result, they found the organic electroluminescence device and the material to be used therefor, which are defined in the present invention.

[0015] It is an object of the present invention to provide an organic electroluminescence device as defined in claim 1, of the type having one or more than one emission layer in the form of thin film of an organic compound between paired electrodes (anode and cathode), which includes at least one layer containing a compound with carbenium ions represented by formula (1) below.

[0016] As used herein, the term "layer containing a compound with carbenium ions" shall mean a charge transport layer, which includes, for example, electron injection layer, electron transport layer, hole transport layer, and hole injection layer.

[0017] It is another object of the present invention to provide a material as defined in any one of claims 6 to 10 containing a compound with carbenium ions, which is used for the organic electroluminescence device. This material is a charge transfer material that forms the above-mentioned layers. It includes, for example, electron injection material, electron transport material, hole injection material, and hole transport material. The one for hole transport and hole injection is preferable.

BRIEF DESCRIPTION OF DRAWINGS

[0018]

Fig. 1 is a schematic sectional view showing one embodiment of the organic electroluminescence device according to the present invention.

Fig. 2 is a schematic sectional view showing another embodiment of the organic electroluminescence device according to the present invention.

Fig. 3 is a schematic sectional view showing another embodiment of the organic electroluminescence device according to the present invention.

Fig. 4 is a schematic sectional view showing another embodiment of the organic electroluminescence device according to the present invention.

Fig. 5 is a schematic sectional view showing another embodiment of the organic electroluminescence device according to the present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

[0019] The organic electroluminescence device according to the present invention is one which has one or more than one emission layer in the form of thin film of an organic compound between paired electrodes. It is characterized in having at least one layer containing a compound with carbenium ions. This layer may be a hole transport layer, hole injection layer, electron transport layer, or electron injection layer, for example.

[0020] The embodiments of the organic electroluminescence device according to the present invention will be described below with reference to Figs. 1 to 5, which are schematic diagrams illustrating the structure of the device and are not intended to restrict the scope of the present invention.

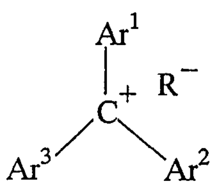
[0021] Figs. 1 to 5 are schematic diagrams illustrating the embodiments of the organic electroluminescence device according to the present invention. In these figures, there are shown a cathode 1, an emission layer 2, a hole transport layer 3, an anode 4, a substrate 5, a hole injection layer 6, an electron injection layer 7, and an electron transport layer 8.

[0022] As shown in the figures, the layer of organic compound held between paired electrodes is composed of an emission layer and at least one charge transport layer (such as electron injection layer, electron transport layer, hole transport layer, and hole injection layer). According to the present invention, at least one of the charge transport layers should contain a compound with carbenium ions.

[0023] The charge transport layer containing a compound with carbenium ions improves the efficiency of electron and hole injection into the emission layer, thereby permitting the organic electroluminescence device to emit light at a low voltage.

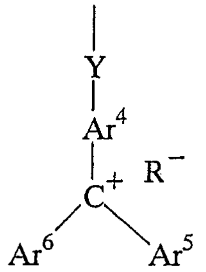
[0024] In a preferred embodiment, the layer containing a compound with carbenium ions should be used as a hole transport layer 3, so that the efficiency of hole injection into the emission layer 2 improves and the organic electroluminescence device emits light at a low voltage. In another preferred embodiment, the layer containing a compound with carbenium ions should be used as both of a hole transport layer 3 and a hole injection layer 6, or either of a hole transport layer 3 or a hole injection layer 6, as shown in Figs. 2 and 3, so that the efficiency of hole injection into the emission layer 2 improves and the organic electroluminescence device emits light at a low voltage.

[0025] According to the present invention, the compound with carbenium ions is one which is represented by the formula (1) below.



(1)

(where Ar^1 to Ar^3 denote identical or different, substituted or unsubstituted aromatic groups, or at least one of them being a monovalent substituent group represented by the formula (2) below.



(2)

where Ar^4 to Ar^6 denote substituted or unsubstituted aromatic groups which are identical with or different from Ar^1 to Ar^3, respectively; Y denotes a single bond, -O-, or a divalent organic group selected from C_{1-6} alkylene group, -COO-, -CONH-, 9H-fluorenylene group, and 9,9-dimethyl-9H-flurorenylene group; and R^- denotes an anion species.)

[0026] In the formula (1) above, Ar^1 to Ar^6 may be identical or different, substituted or unsubstituted aromatic groups. Unsubstituted aromatic groups include, for example, phenyl group, biphenyl group, triphenyl group, tetraphenyl group, naphthyl group, phenanthrenyl group, fluorenyl group, and anthranyl group.

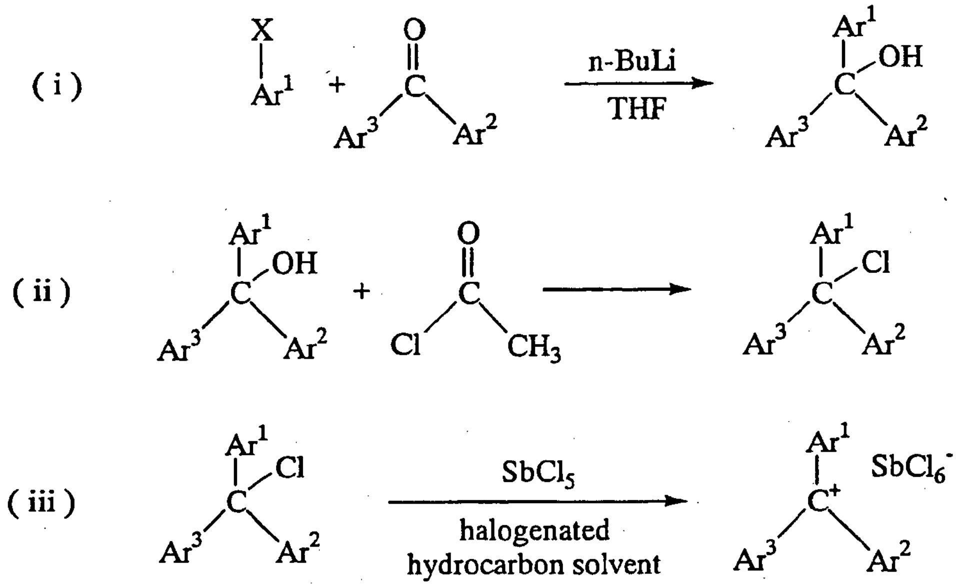
[0027] The substituted aromatic group mentioned above has any of the following substituent groups. C_{1-6} alkyl groups, C_{1-6} alkoxy groups, amino groups, C_{1-4} mono- or dialkyl substituted amino groups, C_{1-6} thioalkyl groups, and cyano groups. Preferable among these groups are electron-donating groups, which include C_{1-4} alkyl groups, such as methyl group, ethyl group, propyl group, isopropyl group, butyl group, isobutyl group, s-butyl group, and t-butyl group; C_{1-4} alkoxy groups, such as methoxy group, ethoxy group, propoxy group, isopropoxy group, butoxy group, isobutoxy group, s-butoxy group, and t-butoxy group; and amino groups, methylamino groups, dimethylamino groups, ethylamino groups, and diethylamino groups. The number of these substituent groups is usually 1 to 3.

[0028] More desirable examples of the aromatic groups Ar^1 to Ar^6 include phenyl groups, o-, m-, and p-tolyl groups, xylyl groups, o-, m-, and p-cumenyl groups, biphenyl groups, naphthyl groups, 4-methoxy-phenyl groups, 9H-fluorenyl groups, and 9,9-dimethyl-9H-flurorenyl groups.

[0029] In the formula (2) above, Y in the substituent group denotes a single bond, -O-, or a divalent organic group selected from C_{1-6} alkylene group, -COO-, -CONH-, 9H-fluorenylene group, and 9,9-dimethyl-9H-flurorenylene group. Preferable among these examples are a single bond, -O-, and a divalent organic group selected from C_{1-4} alkylene group, 9H-fluorenylene group, and 9,9-dimethyl-9H-flurorenylene group.

[0030] The carbenium cation represented in the formula (1) above has a counter ion indicated by R-. This anion includes, for example, SbX_6^-, PX_6^-, TaX_6^-, ClO_4^-, ReO_4^-, BX_4^-, AsX_6^-, and AlX_6^-. Of these examples, SbX_6^- is preferable (where X denotes a halogen atom). The halogen atom includes fluorine atom, chlorine atom, bromine atom, and iodine atom, with the former two being preferable.

[0031] The compound represented by the formula (1) may be synthesized in any way without specific restrictions. The process for synthesis may consist of the following three steps, assuming that the anion is $SbCl_6^-$ and Ar^1 is a mono-halogenated phenyl compound ($X\text{-}Ar^1$, where X is Cl, Br, or I).



[0032] Step (i): In this step, a mono-halogenated phenyl compound is dissolved in a solvent (such as THF) under a nitrogen atmosphere. The solution is cooled with dry ice to about -78°C. A lower alkyl lithium compound (such as n-butylalkyl) is added dropwise in an amount equimolar with the mono-halogenated phenyl compound. After stirring for 30 minutes to 1 hour, the solution is given dropwise a benzophenone compound (dissolved in a solvent such as THF) in an amount equimolar with the mono-halogenated phenyl compound. The solution is allowed to cool to room temperature to terminate reaction. The reaction time is usually 3 to 24 hours, depending on conditions. The reaction product is cleaned of residual n-butyllithium by washing with methanol-water mixed solvent. Upon solvent removal, there is obtained the desired triphenyl methanol compound, which is subsequently purified by column chromatography or the like.

[0033] Step (ii): In this step, the triphenyl methanol compound is stirred in excess acetyl chloride (as a solvent) so that the hydroxyl group is chlorinated. The reaction temperature ranges from room temperature to 60°C, and the reaction time ranges from 3 hours to 7 hours. After acetyl chloride has been removed, there is obtained the desired triphenylchloromethane compound.

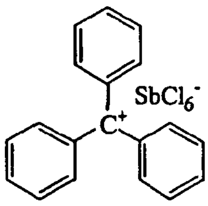
[0034] Step (iii): In this step, the triphenylchloromethane compound (which has been obtained under a nitrogen atmosphere) is dissolved in a halogenated hydrocarbon solvent. The resulting solution is given slowly dropwise a solution of halogenated hydrocarbon solvent in which is dissolved antimony pentachloride in an amount equimolar with the triphenylchloromethane compound. Precipitates (as the reaction product) are recovered by filtration, which is followed by washing (several times) with hexane-chloroform mixed solvent. Upon vacuum drying, the desired product is obtained.

[0035] Other compounds may also be synthesized in the same way as mentioned above. Incidentally, some of the triphenylchloromethane compounds are commercially available as reagents.

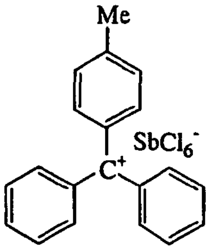
[0036] Shown below are the typical examples of the compounds represented by the formula (1). The scope of the present invention is not limited to them. Incidentally, Me denotes methyl group in the following formulas.

Compound Chemical Structure

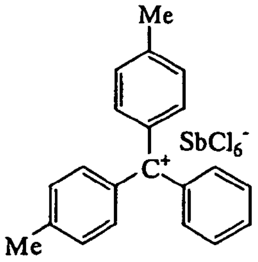
A-1:



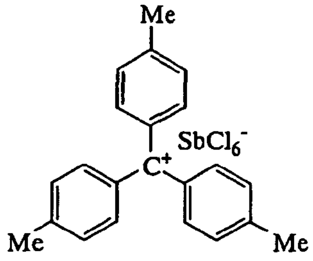
A-2:



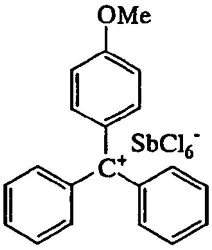
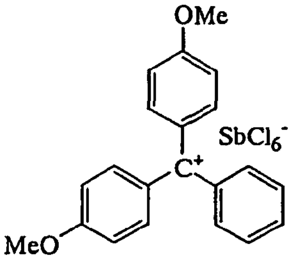
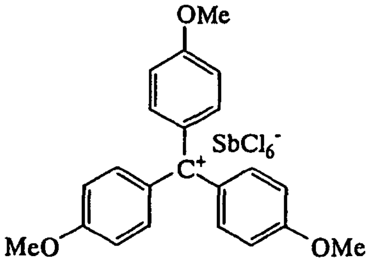
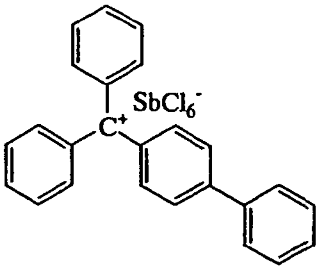
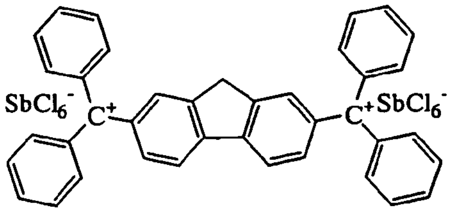
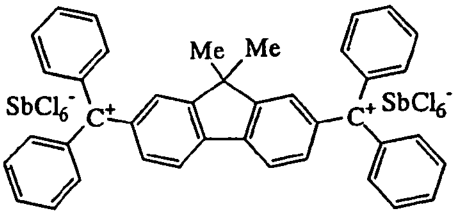
A-3:



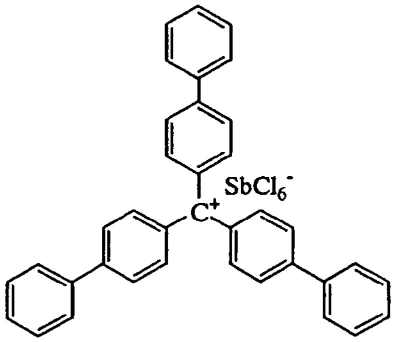
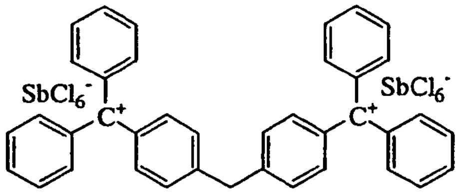
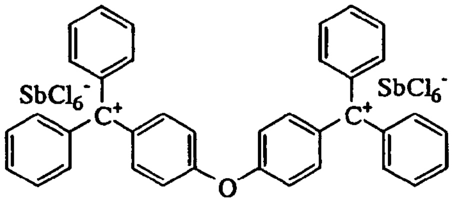
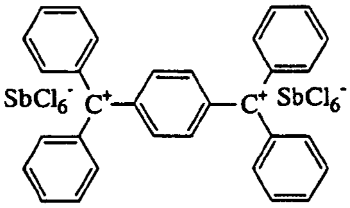
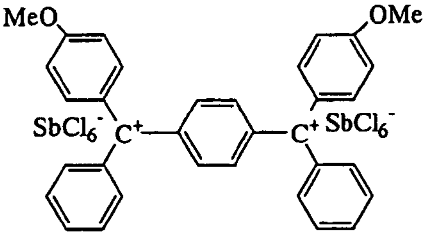
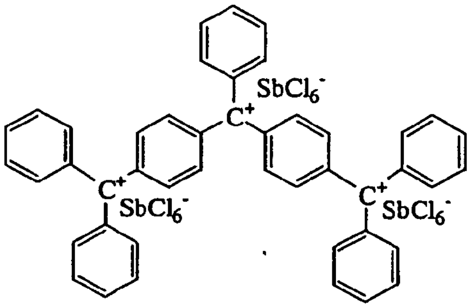
A-4:



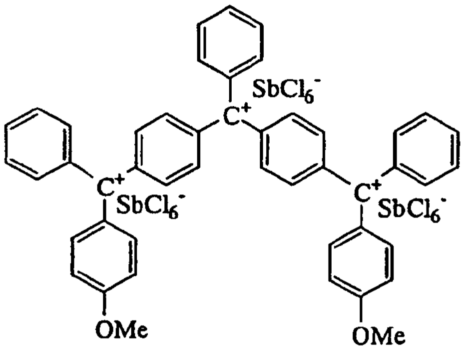
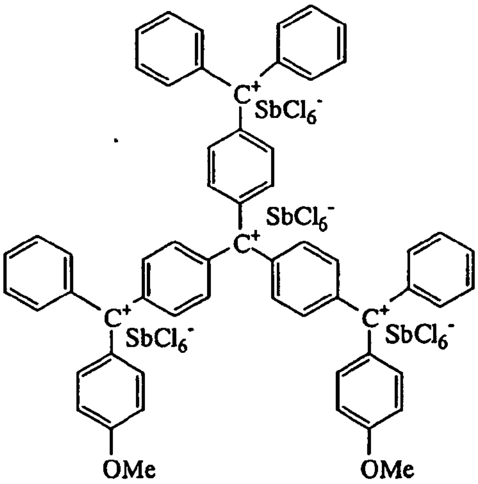
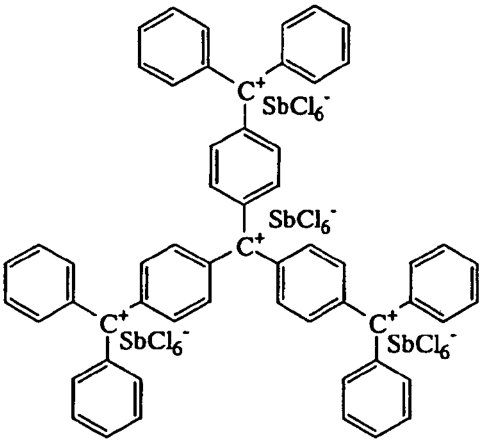
(continued)

Compound	Chemical Structure
A-5:	
A-6:	
A-7:	
A-8:	
A-9:	
A-10:	

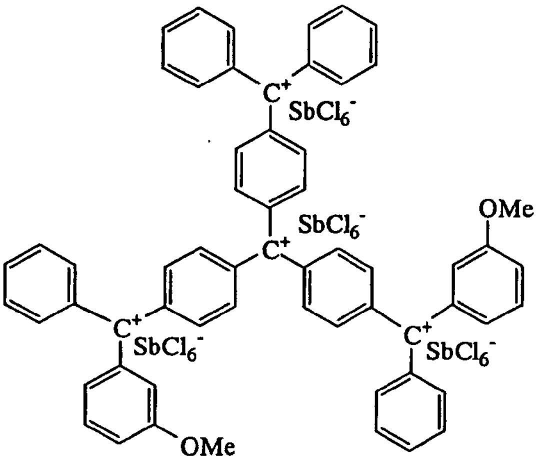
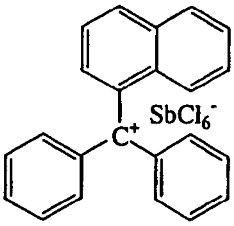
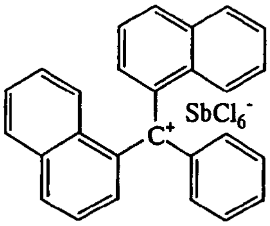
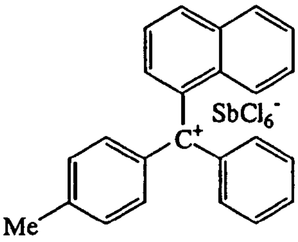
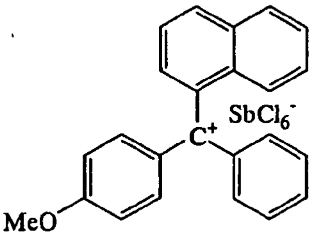
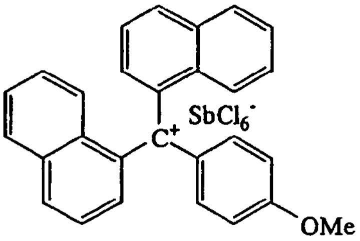
(continued)

Compound	Chemical Structure
A-11:	
A-12:	
A-13:	
A-14:	
A-15:	
A-16:	

(continued)

Compound	Chemical Structure
A-17:	
A-18:	
A-19:	

(continued)

Compound	Chemical Structure
A-20:	
A-21:	
A-22:	
A-23:	
A-24:	
A-25:	

[0037] According to the present invention, the compound with carbenium ions may be used alone as the charge transport material, or the polymer containing a compound with carbenium ions in the main chain or side chain may be used alone as the charge transport material. More than one of such compounds or polymers may be used in combination with one another. Also, the compound with carbenium ions may be mixed with any other charge transport material. Alternatively, the compound with carbenium ions may be combined with a compound capable of charge transfer to form a polymer. Such materials may be used alone or in combination with one another.

[0038] The layer containing carbenium ions may be formed by coating and ensuing drying (on a substrate or another layer) from a solvent solution containing a compound with carbenium ions. Coating may be accomplished by spin coating, printing, or the like.

[0039] The solvent used for coating includes, for example, halogenated hydrocarbon solvents (such as chloroform, dichloromethane, dichloroethane, trichloroethylene, ethylene dichloride, tetrachloroethane, and chlorobenzene), aprotic polar solvents (such as N-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF), dimethylacetamide (DMAc), and dimethylsulfoxide (DMSO)), and polar solvents (such as propylene glycol monobutyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, and other alkoxy alcohols).

[0040] The compound with carbenium ions may be used alone as the hole transport material. It may also be mixed with any other hole transport material for improvement in its characteristic properties.

[0041] Examples of other hole transport materials are listed below.

1,1-bis(4-di-p-triphenylaminophenyl)cyclohexane, which is an aromatic amine compound having a tertiary aromatic amine unit connected thereto. (Japanese Patent Laid-open No. Sho 59-194393)

4,4-bi[N-(naphthyl)-N-phenylamino]biphenyl or its analog, which is an aromatic amine compound having two or more tertiary amine groups and two or more condensed aromatic rings substituting for the nitrogen atoms. (Japanese Patent Laid-open No. Hei 5-234681)

Aromatic triamine of starburst structure, such as a derivative of trtiphenylbenzene. (USP No. 4923774)

Aromatic diamine, such as N,N'-diphenyl-N,N'-bis(3-methylphenyl)biphenyl-4,4'-diamine. (USP No. 4764625)

Triphenylamine derivative which is sterically asymmetric as the entire molecule. (Japanese Patent Laid-open No. Hei 4-129271)

A compound having more than one aromatic diamine group as substituents for the pyrenyl group. (Japanese Patent Laid-open No. Hei 4-175395)

Aromatic diamine composed of tertiary aromatic amine units connected through an ethylene group. (Japanese Patent Laid-open No. Hei 4-264189)

Aromatic diamine with a styryl structure in which aromatic tertiary amine units are connected through a thiophene group. (Japanese Patent Laid-open No. Hei 4-304466)

Aromatic triamine of starburst type. (Japanese Patent Laid-open No. Hei 4-308688)

Benzylphenyl compound (Japanese Patent Laid-open No. Hei 4-364153)

A compound composed of tertiary amines connected through a fluorene group. (Japanese Patent Laid-open No. Hei 5-25473)

Triamine compound. (Japanese Patent Laid-open No. Hei 5-239455)

These materials may be used alone or in combination with one another.

[0042] Additional examples of hole transport materials include polyvinylcarbazole, polysilane, polyphosphazene (Japanese Patent Laid-open No. Hei 5-310949), polyamide, polybiphenylamine, and polymer having a triphenylamine skeleton. These examples are not limitative. They may be used alone or in combination with one another.

[0043] A compound with carbenium ions may be used alone as an electron transfer material, or it may be used in combination with another electron transfer material for improvement in its characteristic properties.

[0044] Examples of other electron transfer materials include nitro-substituted fluorenone derivatives, nitro-substituted fluorene derivatives, thiopyran dioxide derivatives, diphenone derivatives, perylene tetracarboxyl derivatives, anthraquinodimethane derivatives, fluoronylidenemethane derivatives, perylene derivatives, oxadiazole derivative and polymers, quinoline derivatavies, triazole derivatives and polymers, and imidazole derivatives. These examples are not limitative. They may be used alone or in combination with one another.

[0045] According to the present invention, the anode 4 is a transparent electrode having a surface resistance of 1 to 50 Ω/□ and a visible ray transmittance equal to or higher than 80%. It should preferably be a transparent film formed from indium-tin oxide (ITO) or zinc oxide-aluminum in amorphous form or microcrystalline form. Alternatively, it should preferably be a transparent film of laminate structure formed on the transparent insulating substrate 1 (such as glass and plastic film) by vacuum deposition or sputtering. The transparent film of laminate structure is composed of a core layer (about 10 nm thick) of silver, chromium, copper, or copper-silver alloy (which serves to reduce resistance) and outer layers of ITO, titanium oxide, or tin oxide (in amorphous or microcrystalline form). The anode may also be a semi-transparent electrode having gold or platinum deposited thereon or a semi-transparent electrode having a polymer (such as polyaniline, polythiophene, and polypyrrole) coated thereon.

[0046] The emission layer 2 is formed from any of aromatic amine compounds, coumarin compounds (as a laser dye), perylene derivatives, anthracene derivatives, rubrene derivatives, and tris(8-hydroxyquinoline)-aluminum metal complex.

[0047] The cathode 1 is formed from any of metal (with a small work function), alloy thereof, electrically conductive compounds, and mixtures thereof. Examples of such metals include Na, K, Mg, Li, and In. The cathode may be formed by vacuum deposition or sputtering.

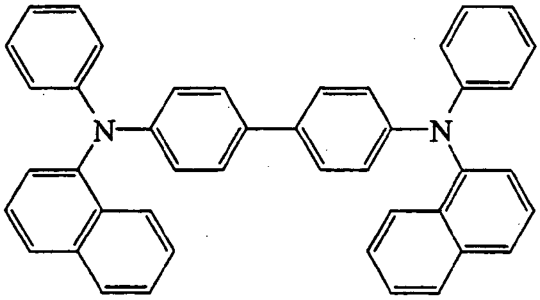
EXAMPLES AND COMPARATIVE EXAMPLES

[0048] The invention will be described in more detail with reference to the following examples and comparative examples, which are not intended to restrict the scope thereof.

Comparative Example 1

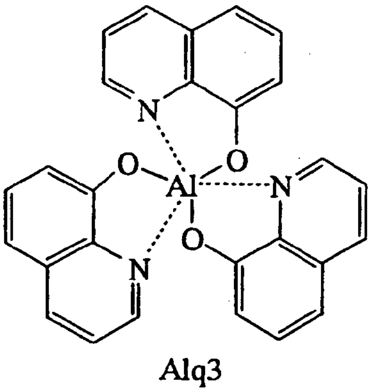
[0049] A glass substrate with ITO was cleaned with a neutral detergent and then ultrasonically washed sequentially in water, acetone, and isopropanol. It further underwent boiling in isopropanol and UV-ozone cleaning. The organic layer and cathode were formed by vacuum deposition. Thus there was obtained the desired device.

[0050] The hole transport material was commercial α-naphthylphenyldiamine (α-NPD, purified by sublimation). The vacuum deposition for the hole transport material was carried out at a degree of vacuum no higher than $8_X,0^{-4}$ Pa. The vacuum deposition was also carried out at a rate of 0.3 nm/s until the deposited film became 50 nm thick.



α-NPD

[0051] On the hole transport layer was formed the emission layer from commercial tris(8-hydroxyquinoline)aluminum (Alq3) (purified by sublimation). The vacuum deposition of the emission layer was carried out at a degree of vacuum no higher than 8×10^{-4} Pa. The vacuum deposition was also carried out at a rate of 0.3 nm/s until the deposited film became 50 nm thick.



Alq3

[0052] Further, the electron injection layer was formed from lithium fluoride (LiF). The vacuum deposition of the electron injection layer was carried out at a degree of vacuum no higher than 8×10^{-4} Pa. The vacuum deposition was also carried out at a rate of 0.01 nm/s until the deposited film became 0.5 nm thick. Finally, the cathode was formed from aluminum. The vacuum deposition of the cathode was carried out at a degree of vacuum no higher than 8×10^{-4} Pa. The vacuum deposition was also carried out at a rate of 0.2 nm/s until the deposited film became 100 nm thick. The thus obtained device has the characteristic properties shown in Table 1.

Example 1

[0053] The hole injection layer 3 was formed on the ITO substrate by spin coating under the following conditions from the compound designated as A-6 above.

[0054] Conditions of spin coating:

Solvent: chloroform
Solids: 0.2% by weight
Spinner speed: 3500 rpm
Duration of spinning: 5 seconds

[0055] On the spin-coated layer were formed the hole transport layer, emission layer, electron injection layer, and cathode in the same way as in Comparative Example 1. Thus there was obtained the desired organic electroluminescence device. It has the characteristic properties shown in Table 1. Incidentally, the compound A-6 mentioned above was synthesized in the following manner.

[0056] A 300-ml three-mouth flask was charged with 150 ml of dehydrated chloroform. In this chloroform was dissolved 5 g (0.014 mol) of 4,4'-dimethoxytrityl chloride (reagent made by Tokyo Kasei Kogyo Co. Ltd.) under a nitrogen atmosphere. To the solution was slowly (dropwise) added 5 g (0.0168 mol) of antimony pentachloride. The reactants were allowed to react at room temperature for 3 hours. After reaction, the solution was added dropwise to 1000 ml of hexane, and precipitates were recovered by filtration. Thus there was obtained 8 g (0.0126 mol) of A-6 (yields = 90%).

Example 2

[0057] The hole injection layer 3 was formed from A-6 on the ITO glass substrate by spin coating under the following conditions.

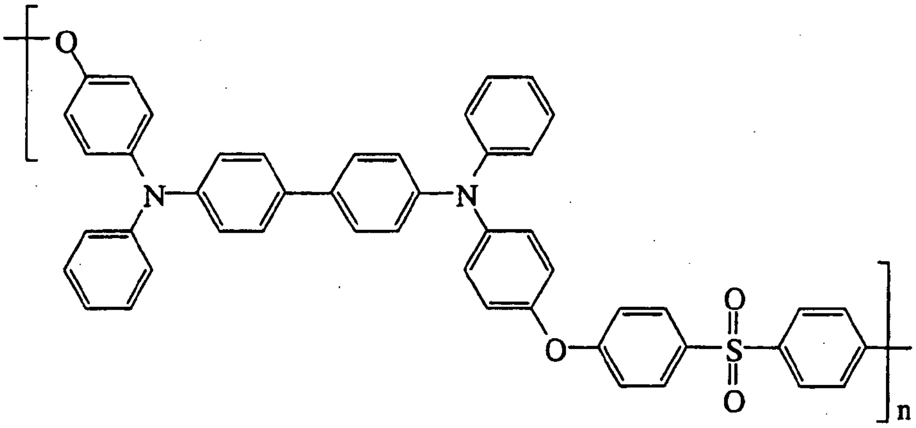
[0058] Conditions of spin coating:

Solvent: propylene glycol monomethyl ether
Concentration: 0.2% by weight
Spinner speed: 3500 rpm
Duration of spinning: 5 seconds

[0059] On the spin-coated layer were formed the hole transport layer, emission layer, electron injection layer, and cathode in the same way as in Comparative Example 1. Thus there was obtained the desired organic electroluminescence device. It has the same characteristic properties as in Example 1.

Comparative Example 2

[0060] The hole injection layer 3 was formed on the ITO glass substrate from triphenylamine-containing polyether (MW = 29000) represented by the formula below, by spin coating under the following conditions.



[0061] This compound was synthesized by the method proposed by Kido et al. (See Polymer for Advanced Technologies, vol. 7, p. 31, 1996, and Japanese Patent Laid-open No. Hei 9-188756.)

[0062] Conditions of spin coating:

Solvent: chloroform
Concentration: 0.01 g/ml
Spinner speed: 3100 rpm
Duration of spinning: 5 seconds

[0063] On the spin-coated layer were formed the hole transport layer, emission layer, electron injection layer, and cathode in the same way as in Comparative Example 1. Thus there was obtained the desired organic electroluminescence device. It has the characteristic properties shown in Table 1.

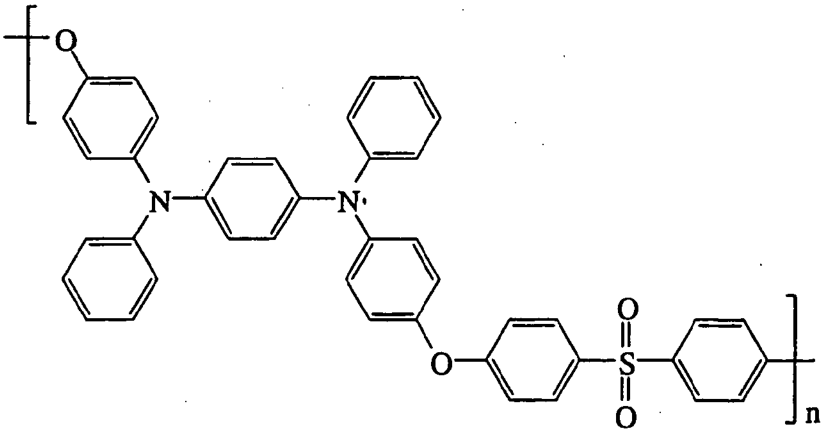
Example 3

[0064] The hole injection layer 3 was formed on the ITO glass substrate from a material composed of the triphenylamine-containing polyether (used in Comparative Example 2) and 30% by weight of A-6 (synthesized in Example 1), by spin coating under the same conditions as in Comparative Example 1.

[0065] On the spin-coated layer were formed the hole transport layer, electron transport emission layer, electron injection layer, and cathode in the same way as in Comparative Example 1. Thus there was obtained the desired organic electroluminescence device. It has the characteristic properties shown in Table 1.

Example 4

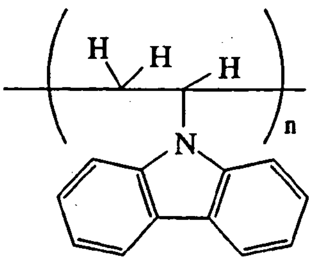
[0066] The hole injection layer 3 was formed on the ITO glass substrate from a material composed of the triphenylamine-containing polyether (MW = 12000) represented by the formula below and 30% by weight of A-6, by spin coating under the same conditions as in Comparative Example 1. The triphenylamine-containing polyether was synthesized by the above-mentioned method proposed by Kido et al.



[0067] On the spin-coated layer were formed the hole transport layer, emission layer, electron injection layer, and cathode in the same way as in Comparative Example 1. Thus there was obtained the desired organic electroluminescence device. It has the characteristic properties shown in Table 1.

Comparative Example 3

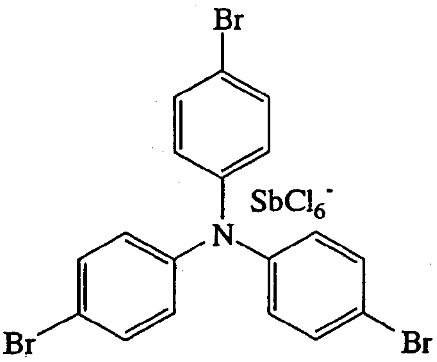
[0068] The hole injection layer 3 was formed on the ITO glass substrate from a polyvinylcarbazole (reagent made by Kanto Kagaku) represented by the formula below, by spin coating under the same conditions as in Comparative Example 1.



[0069] On the spin-coated layer were formed the hole transport layer, electron transport emission layer, electron injection layer, and cathode in the same way as in Comparative Example 1. Thus there was obtained the desired organic electroluminescence device. It has the characteristic properties shown in Table 1.

Comparative Example 4

[0070] An attempt was made to form the hole injection layer 3 from a material composed of the polyvinylcarbazole (used in Comparative Example 3) and 5% by weight of the compound represented by the formula below (disclosed in Japanese Patent Laid-open No. Hei 11-283750). The attempt was unsuccessful because gelation took place immediately after mixing.



Example 5

[0071] The hole injection layer 3 was formed on the ITO glass substrate from a material composed of the polyvinylcarbazole (used in Comparative Example 3) and 5% by weight of A-6, by spin coating under the same conditions as in Comparative Example 1.

[0072] On the spin-coated layer were formed the hole transport layer, electron transport emission layer, electron injection layer, and cathode in the same way as in Comparative Example 1. Thus there was obtained the desired organic electroluminescence device. It has the characteristic properties shown in Table 1.

Examples 6 to 8

[0073] The hole injection layer 3 was formed on the ITO glass substrate from a material composed of the triphenylamine-containing polyether (used in Comparative Example 2) and 5% by weight of A-5, A-7, and A-8, respectively, by spin coating under the same conditions as in Comparative Example 1.

[0074] On the spin-coated layer were formed the hole transport layer, electron transport emission layer, electron injection layer, and cathode in the same way as in Comparative Example 1. Thus there was obtained the desired organic electroluminescence device. It has the characteristic properties shown in Table 1.

[0075] Incidentally, A-5, A-7, and A-8 were synthesized in the same way as in Example 1.

Table 1

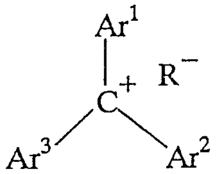
	Designation of compound	Threshold voltage for emission (V)	Voltage at 100 cd/m^2 (V)	Voltage at 500 cd/m^2 (V)
Comparative Example 1		6	10.5	11
Comparative Example 2		5	10	11.5
Comparative Example 3		10.5	16	17
Example 1	A-6	3.5	8	9.5
Example 3	A-6	3	6	8
Example 4	A-6	3	6.5	8.5
Example 5	A-6	3.5	11.5	13.5
Example 6	A-5	3	6	8
Example 7	A-7	3	6.5	9
Example 8	A-8	3	6.5	9

INDUSTRIAL APPLICABILITY

[0076] The present invention makes it possible to easily produce long-lived defect-free organic electroluminescence devices capable of intensive emission at a low voltage. The organic electroluminescence device of the present invention is suitable for displays of various apparatus.

Claims

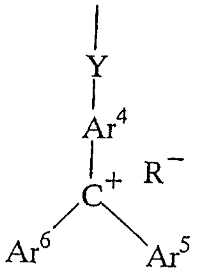
1. An organic electroluminescence device of the type having one or more than one emission layer in the form of thin film of an organic compound between paired electrodes, which includes at least one layer containing a compound with carbenium ions represented by the formula (1) below.



(1)

where Ar^1 to Ar^3 denote identical or different, substituted or unsubstituted aromatic groups, and R$^-$ denotes an anion species.

2. The organic electroluminescence device as defined in Claim 1, wherein at least one of Ar^1 to Ar^3 is a monovalent substituent group represented by the formula (2) below.



(2)

where Ar^4 to Ar^6 denote substituted or unsubstituted aromatic groups which are identical with or different from Ar^1 to Ar^3, respectively; Y denotes a single bond, -O-, or a divalent organic group selected from C_{1-6} alkylene group, -COO-, - CONH-, 9H-fluorenylene group, and 9,9-dimethyl-9H-flurorenylene group.

3. The organic electroluminescence device of claim 1 or 2, wherein one or more of the aromatic groups Ar^1 to Ar^6 are substituted with one or more groups selected from C_{1-6} alkyl groups, C_{1-6} alkoxy groups, amino groups, C_{1-4} mono- or dialkyl substituted amino groups, C_{1-6} thioalkyl groups and cyano groups.

4. The organic electroluminescence device as defined in any one of claims 1 to 3, wherein the layer containing the compound with carbenium ions is the hole transport layer.

5. The organic electroluminescence device as defined in any one of claims 1 to 3, wherein the layer containing the compound with carbenium ions is the hole injection layer.

6. The organic electroluminescence device as defined in any one of claims 1 to 3, wherein the layer containing the compound with carbenium ions is the electron transport layer.

7. The organic electroluminescence device as defined in any one of claims 1 to 3, wherein the layer containing the compound with carbenium ions is the electron injection layer.

8. Use of a compound with carbenium ions as defined in any one of claims 1 to 3, in a charge transport material.

9. Use of a compound with carbenium ions as defined in any one of claims 1 to 3, in a hole transport material.

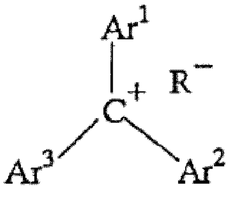
10. Use of a compound with carbenium ions as defined in any one of claims 1 to 3, in a hole injection material.

11. Use of a compound with carbenium ions as defined in any one of claims 1 to 3, in an electron transport material.

12. Use of a compound with carbenium ions as defined in any one of claims 1 to 3, in an electron injection material.

Patentansprüche

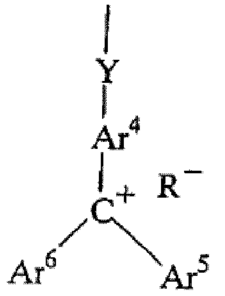
1. Organische Elektrolumineszenzvorrichtung des Typs mit einer oder mehr als einer Emissionsschicht in Form eines Dünnfilms aus einer organischen Verbindung zwischen Paarelektroden, die zumindest eine Schicht umfasst, die eine Verbindung mit Carbeniumionen der nachstehenden Formel (1) enthält:



(1)

worin Ar^1 bis Ar^3 für identische oder unterschiedliche, substituierte oder unsubstituierte aromatische Gruppen stehen und R^- für eine Anionenspezies steht.

2. Organische Elektrolumineszenzvorrichtung nach Anspruch 1, wobei zumindest eines aus Ar^1 bis Ar^3 eine einwertige Substituentengruppe der nachstehenden Formel (2) ist:



(2)

worin Ar^4 bis Ar^6 für substituierte oder unsubstituierte aromatische Gruppen stehen, die mit Ar^1 bis Ar^3 identisch sind bzw. sich von diesen unterscheiden; Y für eine Einfachbindung, -O- oder eine zweiwertige organische Gruppe, ausgewählt aus einer C_{1-6}-Alkylengruppe, -COO-, -CONH-, einer 9H-Fluorenylengruppe und einer 9,9-Dimethyl-9H-fluorenylengruppe, steht.

3. Organische Elektrolumineszenzvorrichtung nach Anspruch 1 oder 2, wobei eine oder mehrere der aromatischen Gruppen Ar^1 bis Ar^6 mit einer oder mehreren Gruppen substituiert sind, die aus C_{1-6}-Alkylgruppen, C_{1-6}-Alkoxygruppen, Aminogruppen, C_{1-4}-Mono- oder -Dialkyl-substituierten Aminogruppen, C_{1-6}-Thioalkylgruppen und Cyanogruppen ausgewählt sind.

4. Organische Elektrolumineszenzvorrichtung nach einem der Ansprüche 1 bis 3, wobei die Schicht, welche die Verbindung mit Carbeniumionen enthält, die Lochleitungsschicht ist.

5. Organische Elektrolumineszenzvorrichtung nach einem der Ansprüche 1 bis 3, wobei die Schicht, welche die Verbindung mit Carbeniumionen enthält, die Lochinjektionsschicht ist.

6. Organische Elektrolumineszenzvorrichtung nach einem der Ansprüche 1 bis 3, wobei die Schicht, welche die Verbindung mit Carbeniumionen enthält, die Elektronenleitungsschicht ist.

7. Organische Elektrolumineszenzvorrichtung nach einem der Ansprüche 1 bis 3, wobei die Schicht, welche die Verbindung mit Carbeniumionen enthält, die Elektroneninjektionsschicht ist.

8. Verwendung einer Verbindung mit Carbeniumionen nach einem der Ansprüche 1 bis 3 in einem Ladungstransportmaterial.

9. Verwendung einer Verbindung mit Carbeniumionen nach einem der Ansprüche 1 bis 3 in einem Lochtransportmaterial.

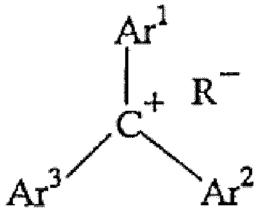
10. Verwendung einer Verbindung mit Carbeniumionen nach einem der Ansprüche 1 bis 3 in einem Lochinjektionsmaterial.

11. Verwendung einer Verbindung mit Carbeniumionen nach einem der Ansprüche 1 bis 3 in einem Elektronentransportmaterial.

12. Verwendung einer Verbindung mit Carbeniumionen nach einem der Ansprüche 1 bis 3 in einem Elektroneninjektionsmaterial.

Revendications

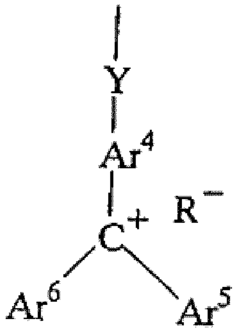
1. Dispositif électroluminescent organique du type ayant une ou plusieurs couches d’émission sous forme de film mince d’un composé organique entre des électrodes appariées, qui contient au moins une couche contenant un composé avec des ions carbénium représenté par la formule (1) ci-dessous :



(1)

dans laquelle Ar^1 à Ar^3 désignent des groupes aromatiques substitués ou non substitués, identiques ou différents, et R^- désigne une espèce anionique.

2. Dispositif électroluminescent organique selon la revendication 1, dans lequel au moins l'un de Ar^1 à Ar^3 est un groupe substituant monovalent représenté par la formule (2) ci-dessous :



(2)

dans laquelle Ar^4 à Ar^6 désignent des groupes aromatiques substitués ou non substitués qui sont identiques à ou différents de Ar^1 à Ar^3, respectivement ; Y désigne une liaison simple, -O-, ou un groupe organique divalent choisi parmi un groupe alkylène en C_1 à C_6, -COO-, -CONH-, un groupe 9H-fluorénylène, et un groupe 9,9-diméthyl-9H-fluorénylène.

3. Dispositif électroluminescent organique selon la revendication 1 ou 2, dans lequel un ou plusieurs des groupes organiques Ar^1 à Ar^6 sont substitués par un ou plusieurs groupes choisis parmi les groupes alkyle en C_1 à C_6, les groupes alcoxy en C_1 à C_6, les groupes amino, les groupes mono- ou di-(alkyl en C_1 à C_4)amino, les groupes thioalkyle en C_1 à C_6, et les groupes cyano.

4. Dispositif électroluminescent organique selon l'une quelconque des revendications 1 à 3, dans lequel la couche contenant le composé avec des ions carbénium est une couche de transport de trous.

5. Dispositif électroluminescent organique selon l'une quelconque des revendications 1 à 3, dans lequel la couche contenant le composé avec des ions carbénium est une couche d'injection de trous.

6. Dispositif électroluminescent organique selon l'une quelconque des revendications 1 à 3, dans lequel la couche contenant le composé avec des ions carbénium est une couche de transport d'électrons.

7. Dispositif électroluminescent organique selon l'une quelconque des revendications 1 à 3, dans lequel la couche contenant le composé avec des ions carbénium est une couche d'injection d'électrons.

8. Utilisation d'un composé avec des ions carbénium tel que défini dans l'une quelconque des revendications 1 à 3, dans un matériau de transport de charges.

9. Utilisation d'un composé avec des ions carbénium tel que défini dans l'une quelconque des revendications 1 à 3, dans un matériau de transport de trous.

10. Utilisation d'un composé avec des ions carbénium tel que défini dans l'une quelconque des revendications 1 à 3, dans un matériau d'injection de trous.

11. Utilisation d'un composé avec des ions carbénium tel que défini dans l'une quelconque des revendications 1 à 3, dans un matériau de transport d'électrons.

12. Utilisation d'un composé avec des ions carbénium tel que défini dans l'une quelconque des revendications 1 à 3, dans un matériau d'injection d'électrons.

FIG.1

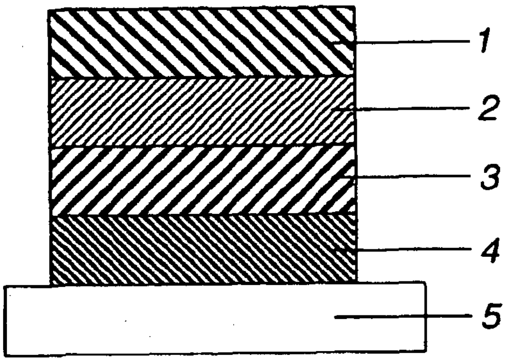


FIG.2

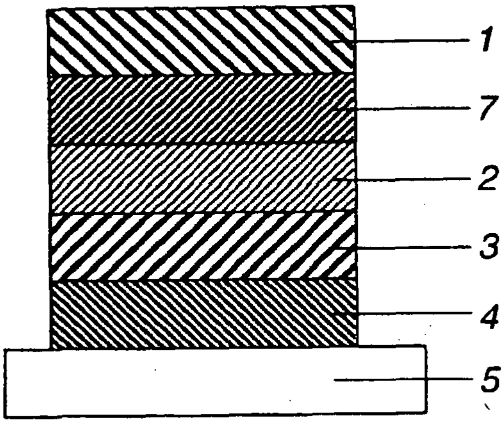


FIG.3

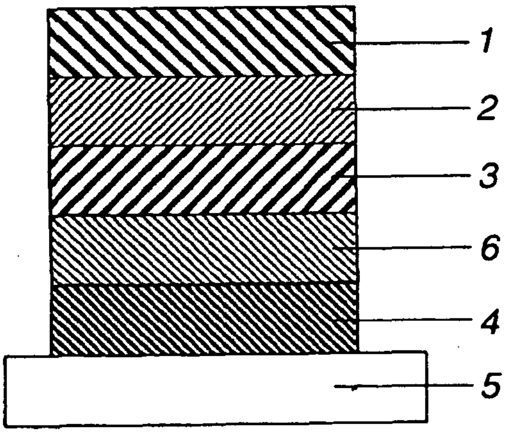


FIG.4

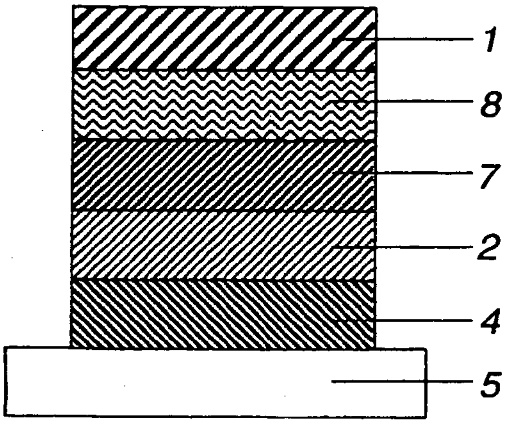
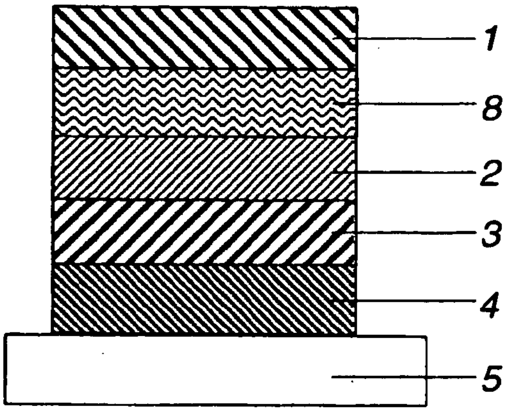


FIG.5



REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP HEI820771 B **[0004]**
- JP HEI840995 B **[0004]**
- JP HEI840997 B **[0004]**
- JP HEI11283750 B **[0004] [0070]**
- JP 2000036390 A **[0004]**
- JP SHO63295695 B **[0005]**
- JP HEI4308688 B **[0005] [0041]**
- WO 0172926 A **[0009]**
- WO 9305077 A **[0010]**
- JP 2001244079 A **[0012]**
- DE 2425194 A1 **[0013]**
- DE 2425193 A1 **[0013]**
- JP SHO59194393 B **[0041]**
- JP HEI5234681 B **[0041]**
- US 4923774 A **[0041]**
- US 4764625 A **[0041]**
- JP HEI4129271 B **[0041]**
- JP HEI4175395 B **[0041]**
- JP HEI4264189 B **[0041]**
- JP HEI4304466 B **[0041]**
- JP HEI4364153 B **[0041]**
- JP HEI525473 B **[0041]**
- JP HEI5239455 B **[0041]**
- JP HEI5310949 B **[0042]**
- JP HEI9188756 B **[0061]**

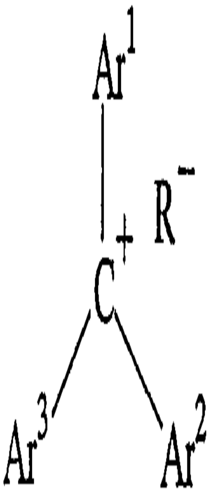
Non-patent literature cited in the description

- **TANG et al.** *Eastman Kodak,* 1987 **[0002]**
- *Appl. Phys. Lett.,* 1987, vol. 51, 913 **[0002]**
- **TATSUO ERABI.** *Electroorganic Chemistry,* June 2001, vol. 18, 35, 36 **[0011]**
- *Polymer for Advanced Technologies,* 1996, vol. 7, 31 **[0061]**

专利名称(译)	有机电致发光器件及其材料		
公开(公告)号	EP1501337B1	公开(公告)日	2012-12-12
申请号	EP2003725696	申请日	2003-04-28
[标]申请(专利权)人(译)	日产化学工业株式会社		
申请(专利权)人(译)	NISSAN CHEMICAL INDUSTRIES，LTD.		
当前申请(专利权)人(译)	NISSAN CHEMICAL INDUSTRIES，LTD.		
[标]发明人	YAMADA TOMOHISA C O ELECTRONICS MATERIALS RES LAB YOSHIMOTO TAKUJI C O ELECTRONICS MATERIALS RES LAB		
发明人	YAMADA,TOMOHISA, C/O ELECTRONIC MATERIALS RESEARCH LABORATORIES, YOSHIMOTO,TAKUJI C/O ELECTRONIC MATERIALS RESEARCH LABORATORIES,		
IPC分类号	H01L51/50 H01L51/00 H01L51/30 H01L51/40		
CPC分类号	H01L51/005 H01L51/002 H01L51/0035 H01L51/0042 H01L51/0052 H01L51/0058 H01L51/0081 H01L51/5012 H01L51/5048 H01L51/5088 H01L51/5092 H01L2251/308 Y10S428/917		
代理机构(译)	斯托纳，PATRICK GERARD		
优先权	2002129608 2002-05-01 JP		
其他公开文献	EP1501337A4 EP1501337A1		
外部链接	Espacenet		

摘要(译)

一种能够解决实现低压驱动和高亮度问题的有机电致发光器件，其对于延长其寿命是重要的，该有机电致发光器件包括由单个或多个有机化合物薄膜组成的发光层介于正极和负极之间，其特征在于，在其中配置至少一层含有具有碳鎓离子的化合物的层。和电荷传输材料（例如，用于有机电致发光器件的空穴传输材料），其特征在于其中含有具有碳鎓离子的化合物。



(1)