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(54) **FLUORENE COMPOUND AND ORGANIC LUMINESCENT DEVICE USING THE SAME**

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H01L 51/54 (2006.01)
C09K 11/06 (2006.01)
C07C 13/567 (2006.01)

(52) **U.S. Cl.** **428/690**; 428/917; 313/504; 313/506; 257/40; 257/E51.049; 257/E51.051; 585/27

(58) **Field of Classification Search** .... None
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,539,507 A	9/1985	VanSlyke et al.	....	313/504
4,720,432 A	1/1988	VanSlyke et al.	....	428/457
4,885,211 A	12/1989	Tang et al.	....	428/457
5,130,603 A	7/1992	Tokailin et al.	....	313/504
5,151,629 A	9/1992	VanSlyke	....	313/504
5,227,252 A	7/1993	Murayama et al.	....	428/690
5,247,190 A	9/1993	Friend et al.	....	257/40
5,317,169 A	5/1994	Nakano et al.	....	257/40
5,382,477 A	1/1995	Saito et al.	....	428/690
5,409,783 A	4/1995	Tang et al.	....	428/690
5,514,878 A	5/1996	Holmes et al.	....	257/40
5,672,678 A	9/1997	Holmes et al.	....	528/373
5,726,457 A	3/1998	Nakano et al.	....	257/40
6,093,864 A	7/2000	Tokailin et al.	....	585/25
6,652,997 B2	11/2003	Suzuki et al.	....	428/690
6,929,870 B2	8/2005	Ishida et al.	....	428/690
2003/0039838 A1*	2/2003	Chen et al.	....	428/411.1
2003/0087126 A1	5/2003	Ishida et al.	....	428/690
2003/0235713 A1	12/2003	Suzuki et al.	....	428/690
2005/0106414 A1*	5/2005	Saitoh et al.	....	428/690

FOREIGN PATENT DOCUMENTS

EP	1 221 434	7/2002
JP	58-128328	7/1983
JP	2-247278	10/1990
JP	3-255190	11/1991
JP	4-145192	5/1992
JP	5-202356	8/1993
JP	5-247460	9/1993
JP	9-202878	8/1997
JP	9-227576	9/1997
JP	11-111460	4/1999
JP	11-167991 A *	6/1999
JP	2001-039933	2/2001
JP	2002-154993	5/2002
JP	2003-128651	5/2003

(Continued)

OTHER PUBLICATIONS

M.A. Baldo, et al., "Highly Efficient Phosphorescent Emission from Organic Electroluminescent Devices", Nature, vol. 395, pp. 151-153 (1998).

(Continued)

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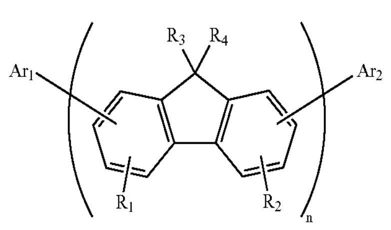
(57) **ABSTRACT**

A fluorene compound represented by the following general formula [1]:

[I]



is used to provide an organic luminescent device. Such a device has an optical output exhibiting a high luminance with an extremely high efficiency, and has an extremely high durability.

11 Claims, 3 Drawing Sheets

FOREIGN PATENT DOCUMENTS

JP	2003-229273	8/2003
JP	2004-042485	2/2004
JP	2004-043349	2/2004
WO	02/14244	2/2002

OTHER PUBLICATIONS

S. Ghosal, et al., "Formation of 1,3-Diynes and Biphenyls via the Copper (11) Nitrate Mediated Coupling of Organotin Compounds", J. Org. Chem., vol. 52, pp. 4296-4298 (1987).

C.W. Tang, et al., "Organic Electroluminescent Diodes", Appl. Phys. Lett., vol. 51, pp. 913-915.

T. Yamamoto, et al., "A Novel Type of Polycondensation Utilizing Transition Metal-Catalyzed C-C Coupling", Bull. Chem. Soc. Jap., vol. 51, pp. 2091-2097 (1978).

J.H. Burroughes, et al., "Light-Emitting Diodes Based on Conjugated Polymers", Nature, vol. 347, pp. 539-541 (1990).

N. Miyaura, et al., "Palladium-Catalyzed Cross-Coupling Reactions of Organaboron Compounds", Chem. Reviews, vol. 95, pp. 2457-2483 (1978).

Tokito, S., et al.; "Acene Containing Polyfluorenes for Red, Green and Blue Emission in Organic Light-Emitting Diodes"; PROC. SPIE, vol. 4105, pp. 69-74 (2001).

* cited by examiner

FIG. 1

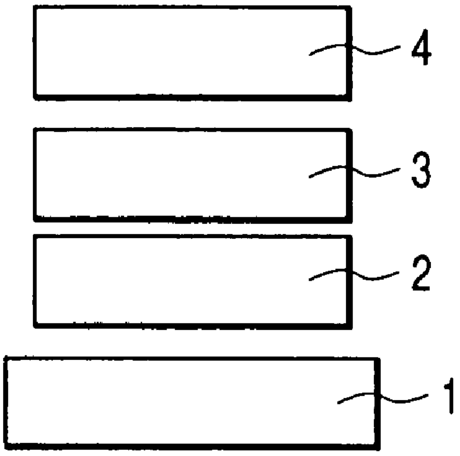


FIG. 2

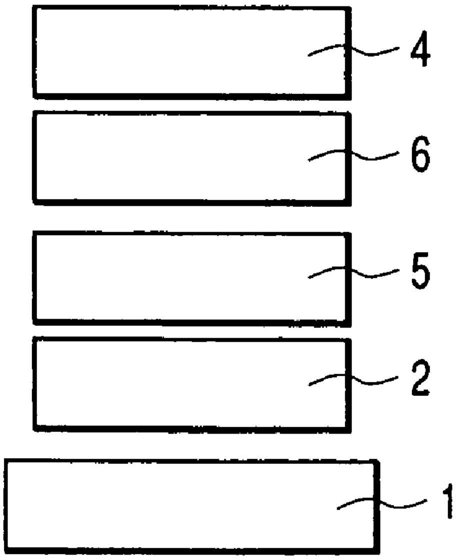


FIG. 3

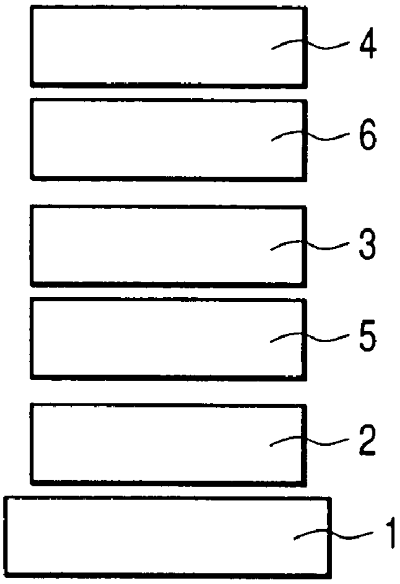


FIG. 4

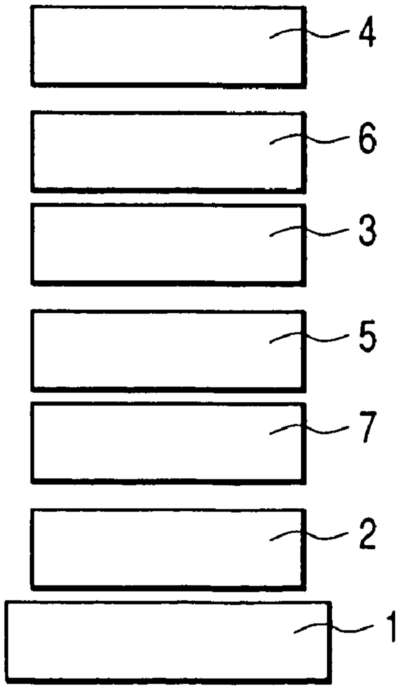


FIG. 5

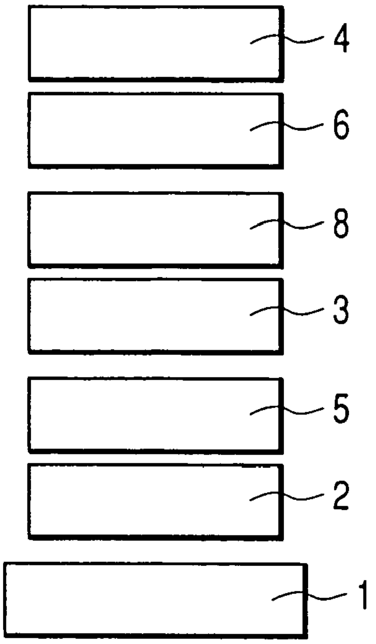
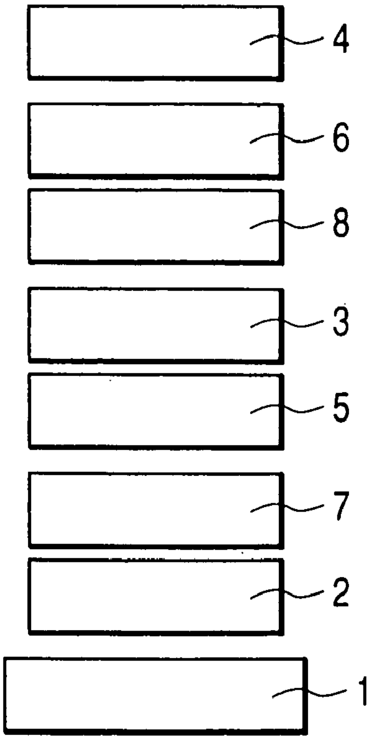


FIG. 6



FLUORENE COMPOUND AND ORGANIC LUMINESCENT DEVICE USING THE SAME

This is a national stage of PCT/JP03/10259 filed Aug. 12, 2003.

TECHNICAL FIELD

The present invention relates to a novel organic compound and an organic luminescent device using the same.

BACKGROUND ART

An organic luminescent device is a device where a thin film containing a fluorescent organic compound or a phosphorescent organic compound is sandwiched between an anode and a cathode; an electron and a hole injected from the respective electrodes generate an exciton of the fluorescent compound or the phosphorescent compound; and light emitted when the exciton returns to a ground state is utilized.

According to a study of Kodak company in 1987 (Appl. Phys. Lett. 51, 913 (1987)), there has been reported a luminescence of approximately 1000 cd/m^2 at an applied voltage of approximately 10 V in a device having a separated-function type two-layer structure using ITO as an anode, a magnesium-silver alloy as a cathode, an aluminum quinolinol complex as an electron transport material and a luminescent material, and a triphenyl amine derivative as a hole transport material. The related patents include U.S. Pat. Nos. 4,539,507, 4,720,432, 4,885,211, and so on.

In addition, it is possible to generate a luminescence from ultraviolet to infrared ones by changing the kinds of the fluorescent organic compound, and in recent years, extensive studies have been made on various kinds of compounds. For instance, such compounds are disclosed in U.S. Pat. Nos. 5,151,629, 5,409,783 and 5,382,477, Japanese Patent Application Laid-Open Nos. 2-247278, 3-255190, 5-202356, 9-202878, 9-227576, and so on.

In recent years, many studies have been made on an application of energy in a triplet state to an EL using phosphorescent compounds as luminescent materials. A high luminous efficiency exhibited by an organic luminescent device using an iridium complex as a luminescent material has been reported by a group at Princeton University (Nature 395, 151 (1998)).

Furthermore, in addition to the organic luminescent device using a low molecular weight material as mentioned above, an organic luminescent device using a conjugated polymer has been reported by a group at Cambridge University (Nature, 347, 539 (1990)). In this report, a luminescence from a single layer is confirmed through film formation of polyphenylene vinylene (PPV) using a coating system.

The related patents of the organic luminescent device using the conjugated polymer include U.S. Pat. Nos. 5,247,190, 5,514,878, 5,672,678, Japanese Patent Application Laid-Open Nos. 4-145192 and 5-247460, and so on.

In this way, a recent progress in the organic luminescent device is remarkable, and characteristics thereof suggest a possibility of applications for various purposes, which enable the luminescent device with a high luminance even at a low applied voltage, a wide variety of luminous wavelengths, a high-speed response, and a thin and lightweight form.

However, an optical output with a higher luminance or higher conversion efficiency is required under the present conditions. In addition, many problems still remain to be solved regarding a durability against a change with time due to a long-term use, deterioration caused by an atmospheric gas containing oxygen, moisture, or the like. Furthermore, it is not still insufficient for solving problems related to the needs for luminescences of blue, green, and red having high color purity when considering the applications to a full color display and the like.

DISCLOSURE OF THE INVENTION

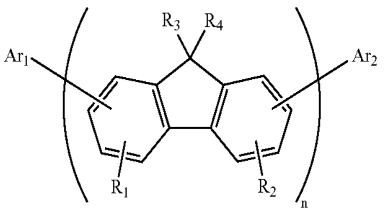
An object of the present invention is to provide a novel fluorene compound.

Also, another object of the present invention is to provide an organic luminescent device using a specific fluorene compound, which has an optical output with an extremely high efficiency and a high luminance.

In addition, another object of the present invention is to provide an organic luminescent device having an extremely high durability.

Furthermore, another object of the present invention is to provide an organic luminescent device that can be easily produced at relatively low costs.

Accordingly, a fluorene compound according to the present invention is represented by the following general formula [1]:



[I]

(wherein R_1 and R_2 represent a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted heterocyclic group, a substituted amino group, a cyano group, or a halogen atom, in which R_1 themselves or R_2 themselves which are bonded to different fluorene groups may be identical to or different from each other and R_1 and R_2 which are bonded to the same fluorene group may be identical to or different from each other; R_3 and R_4 represent a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group, in which R_3 themselves or R_4 themselves which are bonded to different fluorene groups may be identical to or different from each other and R_3 and R_4 which are bonded to the same fluorene group may be identical to or different from each other; Ar_1 and Ar_2 represent a substituted or unsubstituted fused polycyclic aromatic group having at least three benzene rings in total or a substituted or unsubstituted fused polycyclic heterocyclic group bonded to the fluorene group with a carbon atom and having at least three rings including a benzene ring and a heterocyclic ring in total, in which Ar_1 and Ar_2 may be identical to or different from each other; and n represents an integer of 1 to 10, preferably 1 to 3.)

Further, as a preferable form, an organic luminescent device according to the present invention includes at least a pair of electrodes including an anode and a cathode and one or a plurality of layers containing an organic compound sandwiched between the pair of electrodes, in which at least one of the layers containing the organic compound contains at least one of the fluorene compounds.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a cross-sectional view showing an example of the organic luminescent device in accordance with the present invention.

FIG. **2** is a cross-sectional view showing another example of the organic luminescent device in accordance with the present invention.

FIG. **3** is a cross-sectional view showing still another example of the organic luminescent device in accordance with the present invention.

FIG. **4** is a cross-sectional view showing still another example of the organic luminescent device in accordance with the present invention.

FIG. **5** is a cross-sectional view showing still another example of the organic luminescent device in accordance with the present invention.

FIG. **6** is a cross-sectional view showing still another example of the organic luminescent device in accordance with the present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

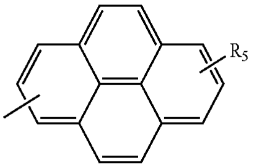
Hereinafter, the present invention will be described in detail.

First, the fluorene compound of the present invention will be described.

The fluorene compound of the present invention is represented by the above general formula [I].

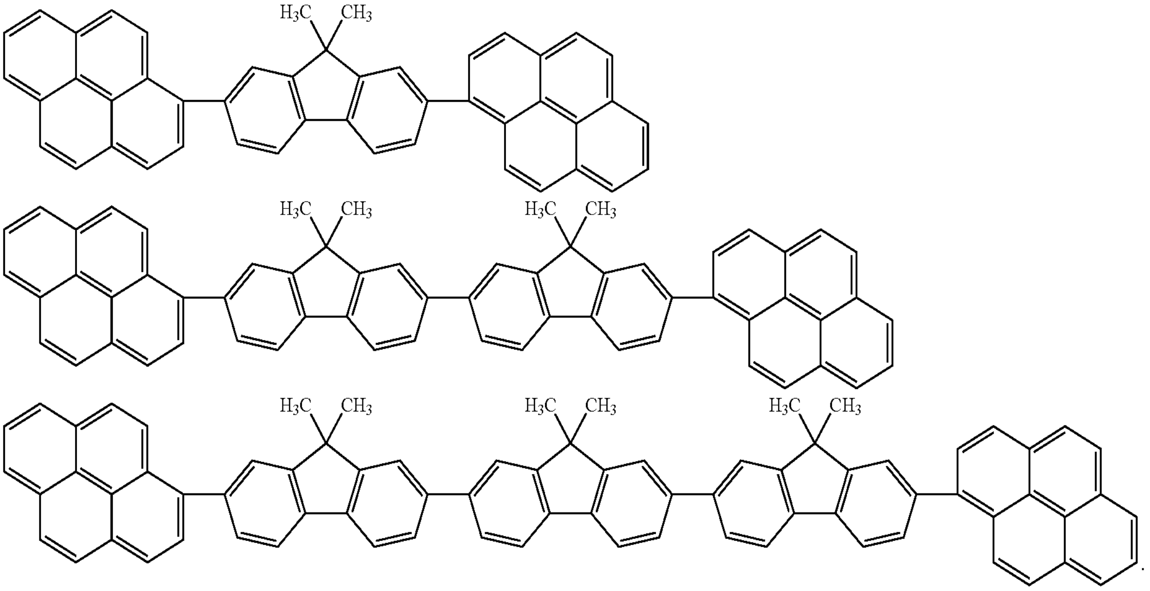
Here, at least one of Ar_1 and Ar_2 is preferably a fused polycyclic aromatic group represented by the following general formula [II]:

[II]



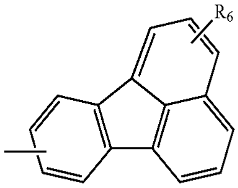
(wherein R_5 represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted heterocyclic group, a substituted amino group, a cyano group, or a halogen atom.)

Furthermore, the fluorene compound of the present invention is more preferably represented by one of the following structural formulas:



Further, at least one of Ar_1 and Ar_2 is preferably a fused polycyclic aromatic group represented by one of the following general formulae [III] to [IX]:

[III]



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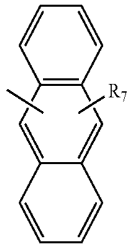
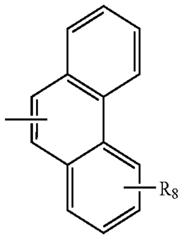
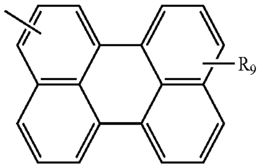
[IV]



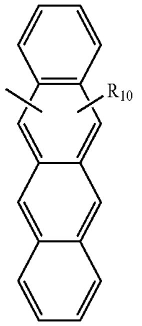
[V]



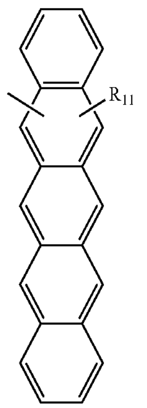
[VI]



[VII]



[VIII]



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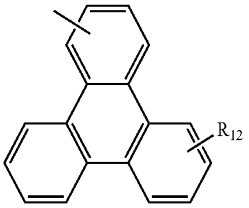
[IX]



(wherein R_6 to R_{12} represent a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted heterocyclic group, a substituted amino group, a cyano group, or a halogen atom.)

Specific examples of substituents in the above general formula [I] to the above general formula [IX] will be shown below.

As the alkyl group, a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, a tert-butyl group, an octyl group, and the like can be given.

As the aralkyl group, a benzyl group, a phenethyl group, and the like can be given.

As the aryl group, a phenyl group, a biphenyl group, a terphenyl group, and the like can be given.

As the heterocyclic group, a thienyl group, a pyrrolyl group, a pyridyl group, an oxazolyl group, an oxadiazolyl group, a thiazolyl group, a thiadiazolyl group, a terthienyl group, and the like can be given.

As the substituted amino group, a dimethylamino group, a diethylamino group, a dibenzylamino group, a diphenylamino group, a ditolylamino group, a dianisolylamino group, and the like can be given.

As the halogen atom, fluorine, chlorine, bromine, iodine, and the like can be given.

As the fused polycyclic aromatic group, a fluorenyl group, a naphthyl group, a fluoranthenyl group, an anthryl group, a phenanthryl group, a pyrenyl group, a tetracenyl group, a pentacenyl group, a triphenylenyl group, a perylenyl group, and the like can be given.

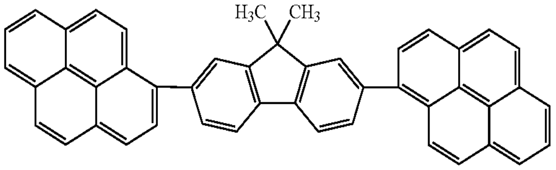
As the fused polycyclic heterocyclic group, a carbazolyl group, an acridinyl group, a phenanthrolyl group, and the like can be given.

As substituents which the above-mentioned substituents may have, alkyl groups such as a methyl group, an ethyl group, and a propyl group; aralkyl groups such as a benzyl group and a phenethyl group; aryl groups such as a phenyl group and a biphenyl group; heterocyclic groups such as a thienyl group, a pyrrolyl group, and a pyridyl group; amino groups such as a dimethylamino group, a diethylamino group, a dibenzylamino group, a diphenylamino group, a ditolylamino group, and a dianisolylamino group; alkoxyl groups such as a methoxyl group, an ethoxyl group, a propoxyl group, and a phenoxyl group; a cyano group; halogen atoms such as fluorine, chlorine, bromine, and iodine; and the like can be given.

Next, typical examples of the fluorene compound of the present invention will be hereinafter given.

However, the present invention is not limited thereto.

1



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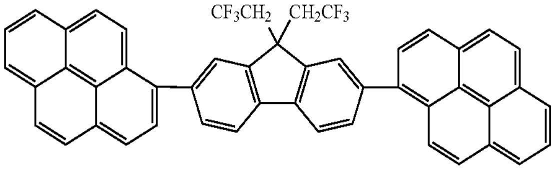

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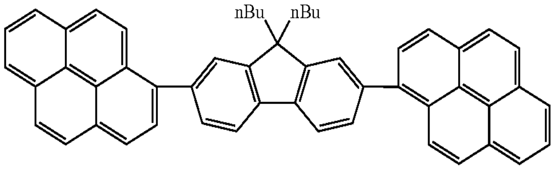

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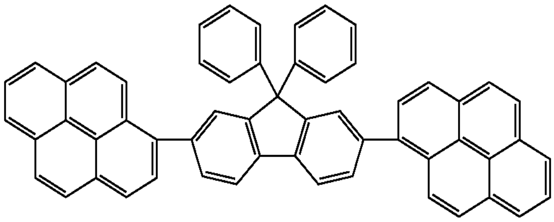

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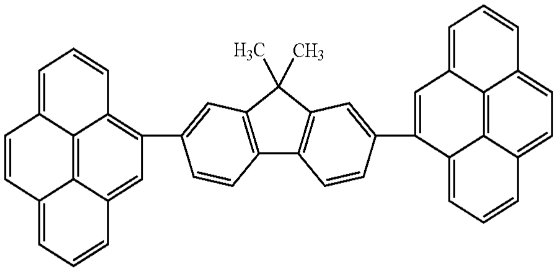

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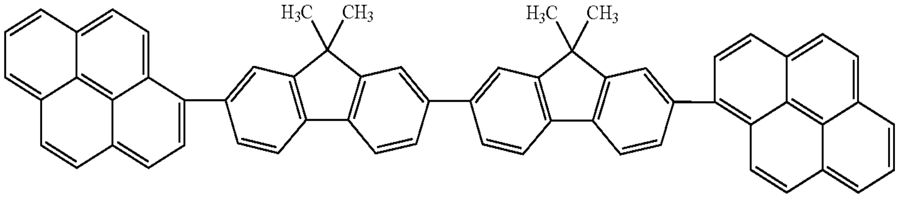

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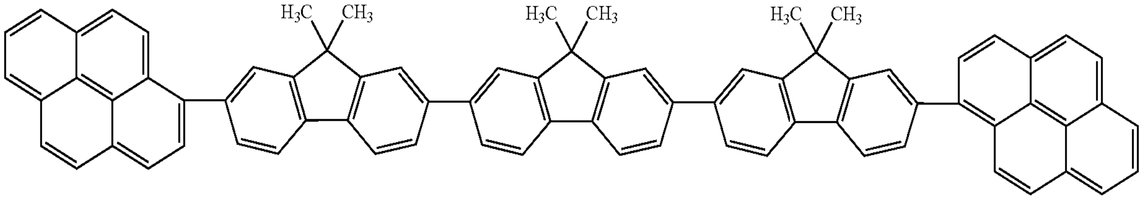

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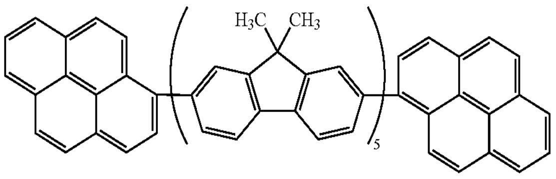

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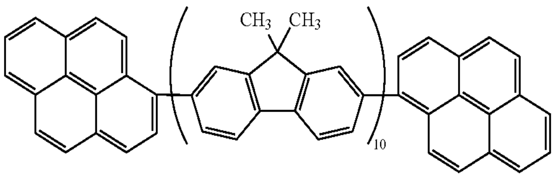

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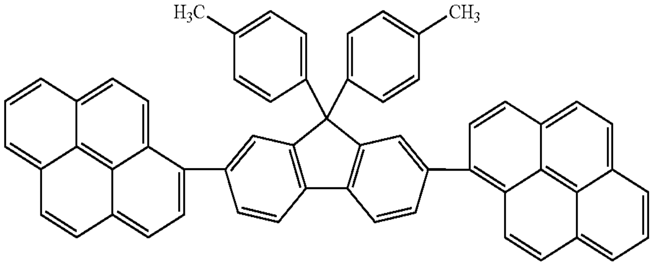

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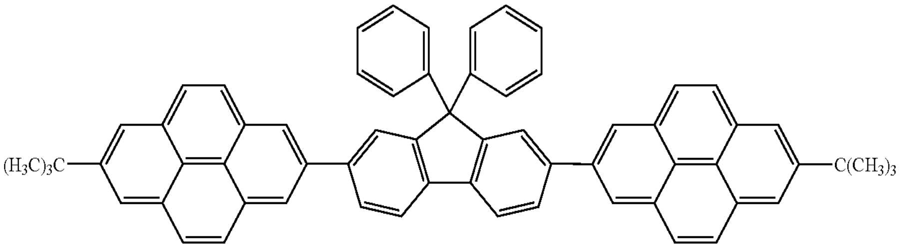

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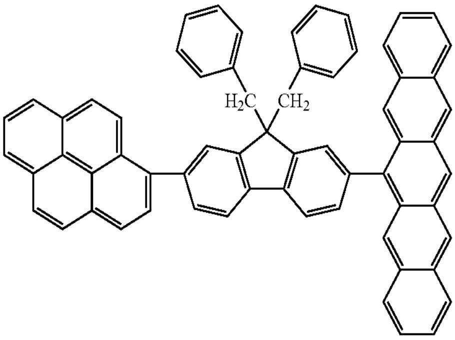

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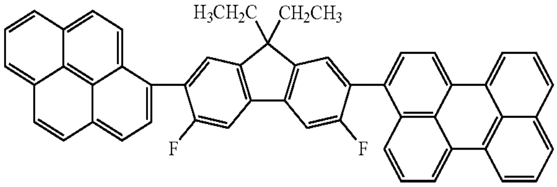

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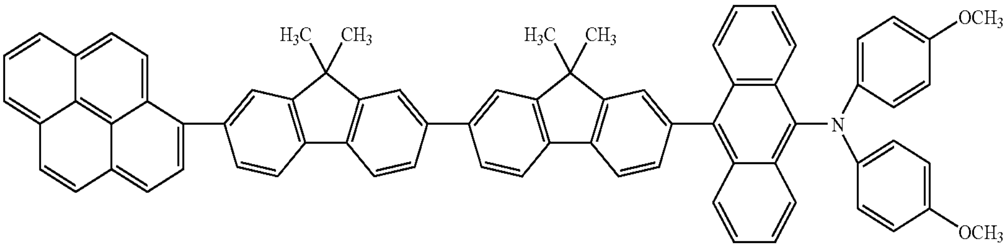

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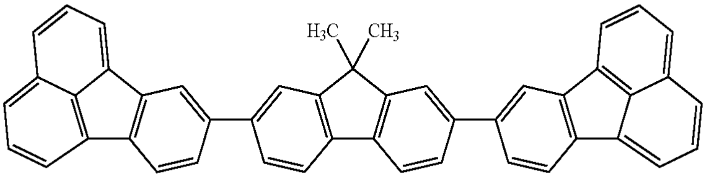

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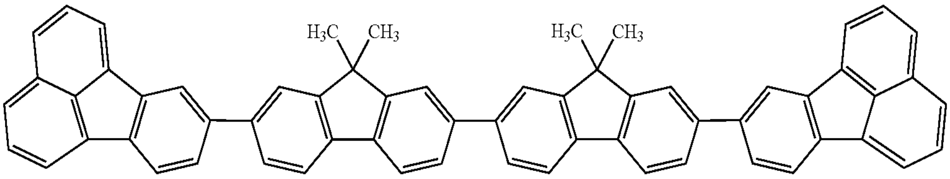

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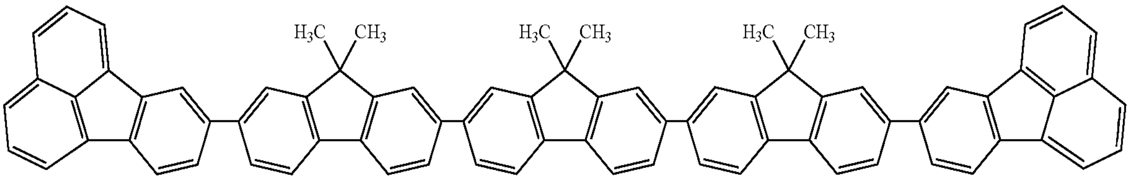

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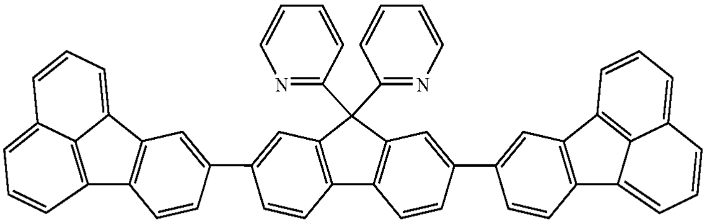

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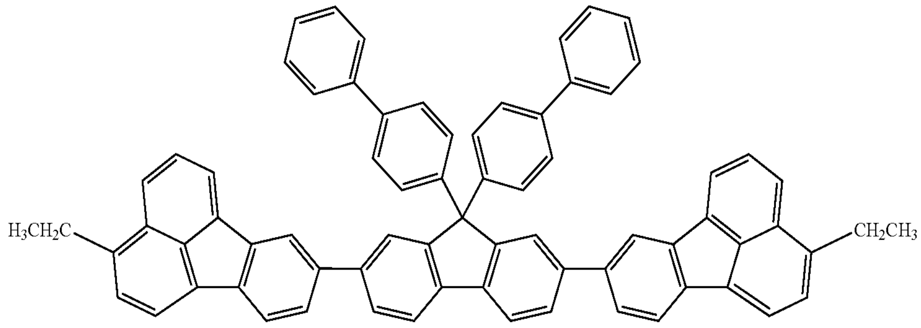

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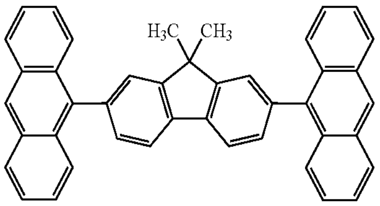

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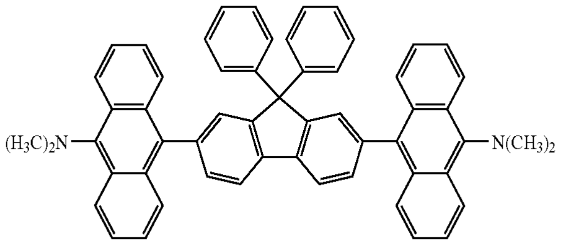

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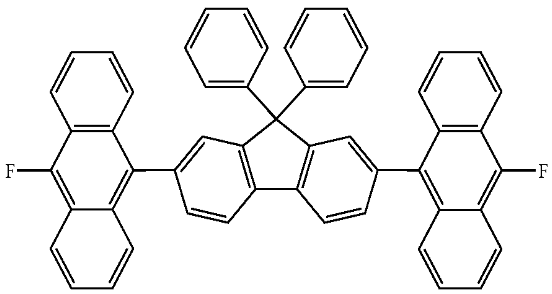

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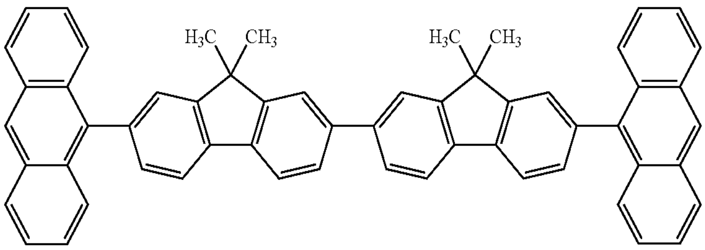

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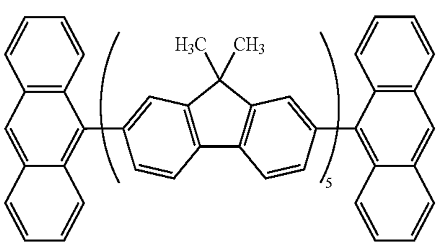

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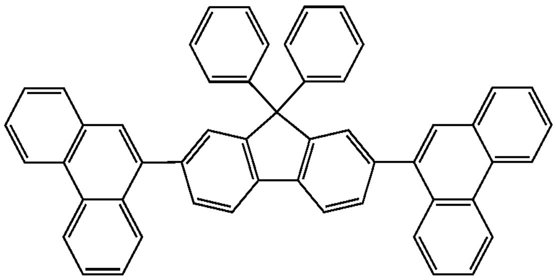

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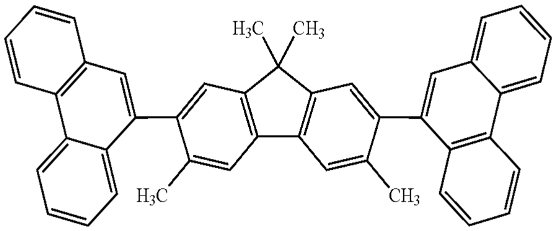

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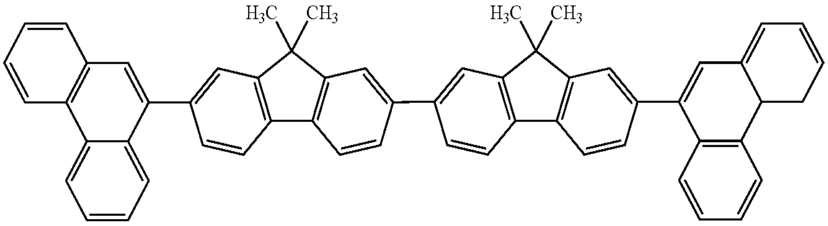

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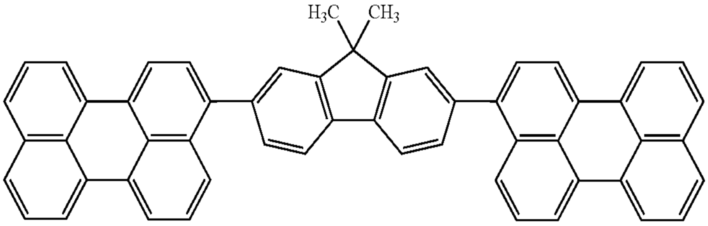

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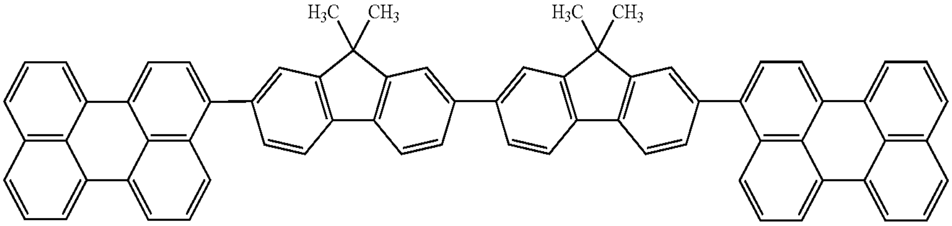

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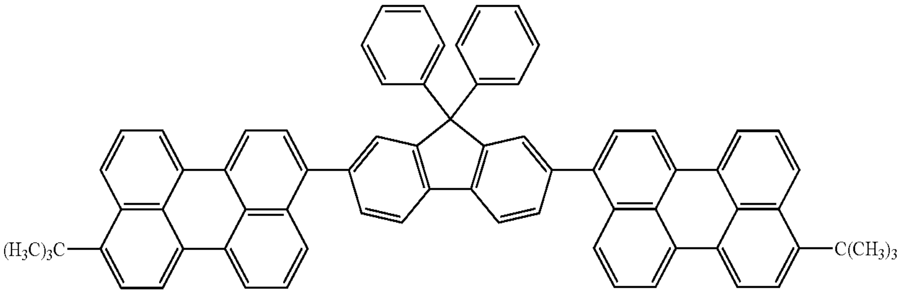

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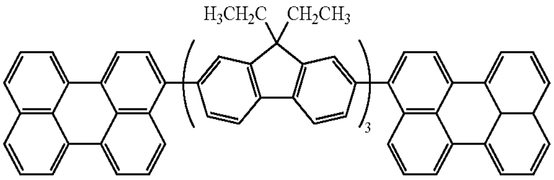

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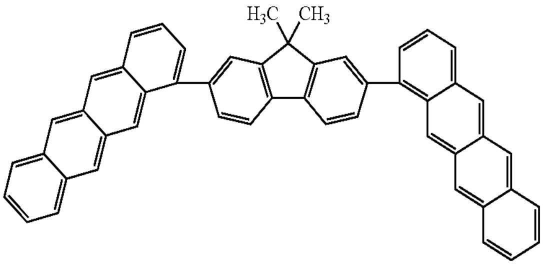

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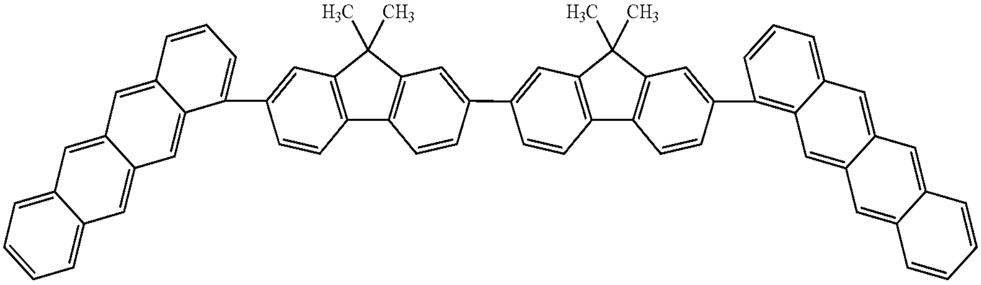

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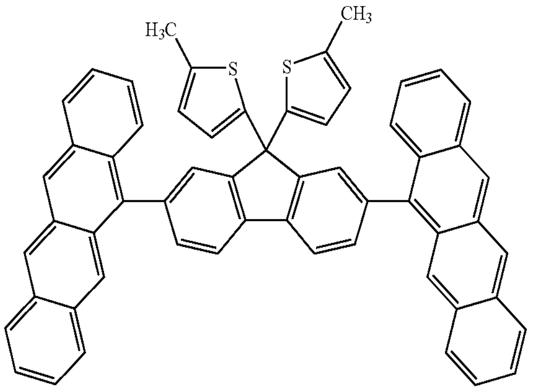

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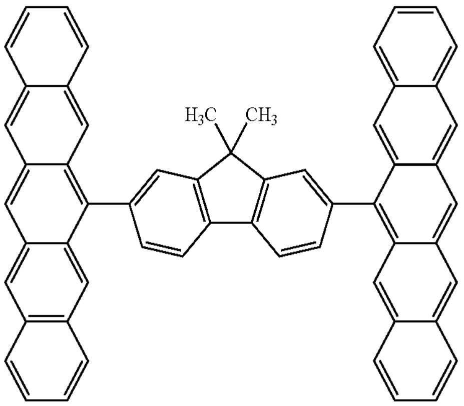

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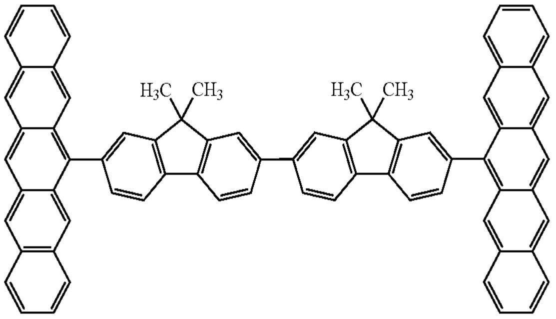

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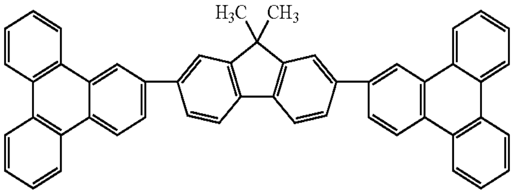

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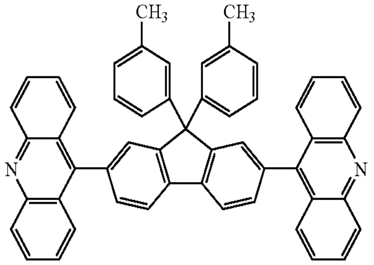

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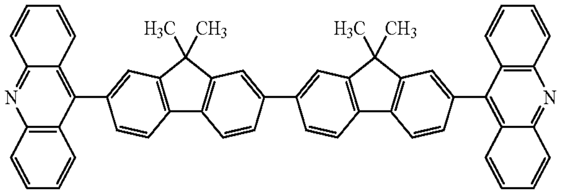


The fluorene compound of the present invention can be synthesized by a well-known method and obtained by using, for example, a synthesis method such as Suzuki coupling method (e.g., Chem. Rev. 1995, 95, 2457-2483) using a palladium catalyst, Yamamoto method (e.g., Bull. Chem. Soc. Jpn. 51, 2091, 1978) using a nickel catalyst, or a method in which a synthesis is performed by using a tin aryl compound (e.g., J. Org. Chem., 52, 4296, 1987).

The fluorene compound of the present invention is superior to the conventional compounds in electron transport property, luminescence property, and durability, which is useful for a layer containing an organic compound of an organic luminescent device, in particular, an electron transport layer and a luminescent layer, and a layer formed by a vacuum evaporation method, a solution-coating method, etc., is hard to undergo crystallization or the like and is excellent in stability with time.

Next, the organic luminescent device of the present invention will be described in detail.

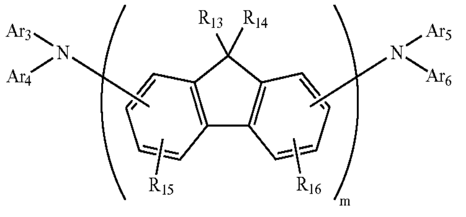
The organic luminescent device of the present invention includes at least a pair of electrodes including an anode and a cathode and one or a plurality of layers containing an organic compound sandwiched between the pair of electrodes, in which at least one of the layers containing the organic compound contains at least one of the fluorene compounds represented by the above general formula [1].

In the organic luminescent device of the present invention, it is preferable that at least an electron transport layer or a luminescent layer among the organic compound-containing layers contain at least one of the fluorene compounds.

In the organic luminescent device of the present invention, the fluorene compound represented by the above general formula [1] is formed between the anode and the cathode by the vacuum evaporation method or the solution-coating method. The organic layer is preferably formed into a thin film with a thickness of less than 10 μm, more preferably 0.5 μm or less, much more preferably 0.01 to 0.5 μm.

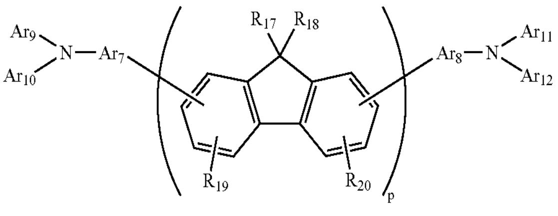
Further, according to a preferable mode of the organic luminescent device of the present invention, at least a luminescent layer among the layers containing the organic compound includes at least one of the fluorene compounds represented by the above general formula [1] and one of arylamine compounds represented by the following general formulae [X]to [XIV] and an acetylene compound represented by the following general formula [XV]:

[X]



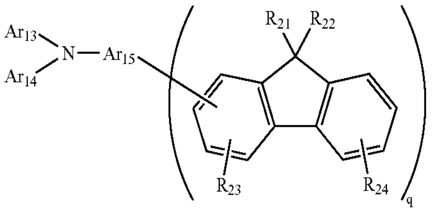
(wherein R_{13} and R_{14} represent a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group, in which R_{13} themselves or R_{14} themselves which are bonded to different fluorene groups may be identical to or different from each other and R_{13} and R_{14} which are bonded to the same fluorene group may be identical to or different from each other; R_{15} and R_{16} represent a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted heterocyclic group, a cyano group, or a halogen atom, in which R_{15} themselves or R_{16} themselves which are bonded to different fluorene groups may be identical to or different from each other and R_{15} and R_{16} which are bonded to the same fluorene group may be identical to or different from each other; Ar_3, Ar_4, Ar_5, and Ar_6 represent a substituted or unsubstituted aromatic group, a substituted or unsubstituted heterocyclic group, a substituted or unsubstituted fused polycyclic aromatic group, or a substituted or unsubstituted fused polycyclic heterocyclic group, in which Ar_3, Ar_4, Ar_5, and Ar_6 may be identical to or different from one another and Ar_3, Ar_4, Ar_5, and Ar_6 may be bonded with one another to form a ring; and m represents an integer of 1 to 10);

[XI]



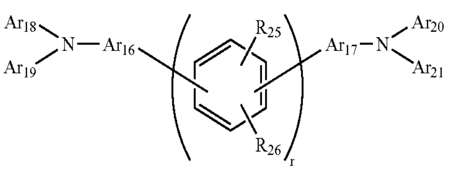
(wherein R_{17} and R_{18} represent a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group, in which R_{17} themselves or R_{18} themselves which are bonded to different fluorene groups may be identical to or different from each other and R_{17} and R_{18} which are bonded to the same fluorene group may be identical to or different from each other; R_{19} and R_{20} represent a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted heterocyclic group, a cyano group, or a halogen atom, in which R_{19} themselves or R_{20} themselves which are bonded to different fluorene groups may be identical to or different from each other and R_{19} and R_{20} which are bonded to the same fluorene group may be identical to or different from each other; Ar_7 and Ar_8 represent a divalent substituted or unsubstituted aromatic group or a substituted or unsubstituted heterocyclic group, in which Ar_7 and Ar_8 may be identical to or different from each other; Ar_9, Ar_{10}, Ar_{11}, and Ar_{12} represent a substituted or unsubstituted aromatic group, a substituted or unsubstituted heterocyclic group, a substituted or unsubstituted fused polycyclic aromatic group, or a substituted or unsubstituted fused polycyclic heterocyclic group, in which Ar_9, Ar_{10}, Ar_{11}, and Ar_{12} may be identical to or different from one another and Ar_9, Ar_{10}, Ar_{11}, and Ar_{12} may be bonded with one another to form a ring; and p represents an integer of 1 to 10);

[XII]



(wherein R_{21} and R_{22} represent a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group, in which R_{21} themselves or R_{22} themselves which are bonded to different fluorene groups may be identical to or different from each other and R_{21} and R_{22} which are bonded to the same fluorene group may be identical to or different from each other; R_{23} and R_{24} represent a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted heterocyclic group, a cyano group, or a halogen atom, in which R_{23} themselves or R_{24} themselves which are bonded to different fluorene groups may be identical to or different from each other and R_{23} and R_{24} which are bonded to the same fluorene group may be identical to or different from each other; Ar_{13} and Ar_{14} represent a substituted or unsubstituted aromatic group, a substituted or unsubstituted heterocyclic group, a substituted or unsubstituted fused polycyclic aromatic group, or a substituted or unsubstituted fused polycyclic heterocyclic group, in which Ar_{13} and Ar_{14} may be identical to or different from each other and Ar_{13} and Ar_{14} may be bonded to each other to form a ring; Ar_{15} represents a divalent substituted or unsubstituted aromatic group or a substituted or unsubstituted heterocyclic group; and q represents an integer of 1 to 10);

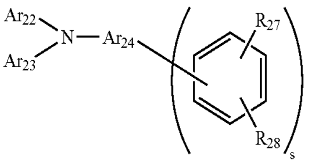
[XIII]



(wherein R_{25} and R_{26} represent a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted heterocyclic group, a cyano group, or a halogen atom, in which R_{25} themselves or

R_{26} themselves which are bonded to different phenylene groups may be identical to or different from each other and R_{25} and R_{26} which are bonded to the same phenylene group may be identical to or different from each other; Ar_{16} and Ar_{17} represent a divalent substituted or unsubstituted aromatic group or a substituted or unsubstituted heterocyclic group, in which Ar_{16} and Ar_{17} may be identical to or different from each other; Ar_{18}, Ar_{19}, Ar_{20}, and Ar_{21} represent a substituted or unsubstituted aromatic group, a substituted or unsubstituted heterocyclic group, a substituted or unsubstituted fused polycyclic aromatic group, or a substituted or unsubstituted fused polycyclic heterocyclic group, in which Ar_{18}, Ar_{19}, Ar_{20}, and Ar_{21} may be identical to or different from one another and Ar_{18}, Ar_{19}, Ar_{20}, and Ar_{21} may be bonded with one another to form a ring; and r represents an integer of 1 to 10);

[XIV]



(wherein R_{27} and R_{28} represent a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted heterocyclic group, a cyano group, or a halogen atom, in which R_{27} themselves or R_{28} themselves which are bonded to different phenylene groups may be identical to or different from each other and R_{27} and R_{28} which are bonded to the same phenylene group may be identical to or different from each other; Ar_{22} and Ar_{23} represent a substituted or unsubstituted aromatic group, a substituted or unsubstituted heterocyclic group, a substituted or unsubstituted fused polycyclic aromatic group, or a substituted or unsubstituted fused polycyclic heterocyclic group, in which Ar_{22} and Ar_{23} may be identical to or different from each other and Ar_{22} and Ar_{23} may be bonded to each other to form a ring; Ar_{24} represents a divalent substituted or unsubstituted aromatic group or a substituted or unsubstituted heterocyclic group; and s represents an integer of 1 to 10); and

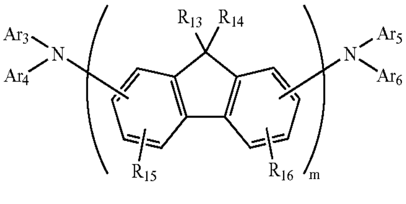
[XV]

$$Ar_{25}-\!\left(C\equiv C\right)_t\!-Ar_{26}$$

(wherein Ar_{25} and Ar_{26} represent a substituted or unsubstituted aromatic group, a substituted or unsubstituted heterocyclic group, a substituted or unsubstituted fused polycyclic aromatic group, or a substituted or unsubstituted fused polycyclic heterocyclic group, in which Ar_{25} and Ar_{26} may be identical to or different from each other; and t represents an integer of 1 to 5.)

Specific examples of substituents in the general formulae [X] to [XV] are the same as those exemplified in the above general formulae [1] to [IX]. Typical examples of the arylamine compounds represented by the general formulae [X] to [XIV] and the acetylene compound represented by the general formula [XV] will be given below, but the present invention is not limited thereto.

[X]



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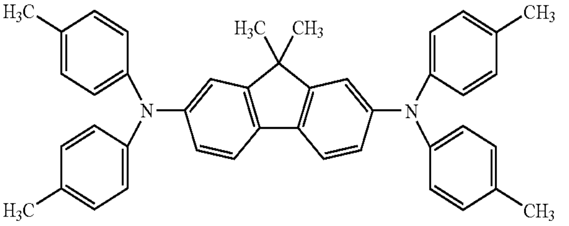

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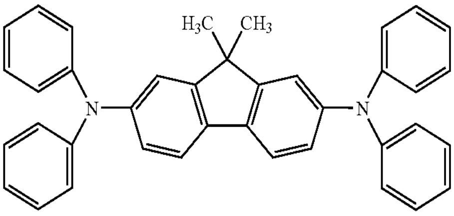

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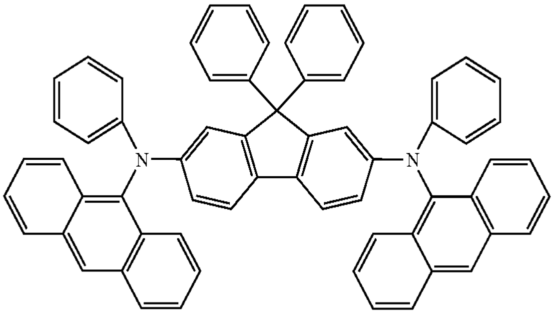

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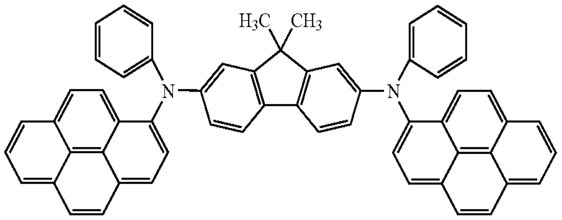

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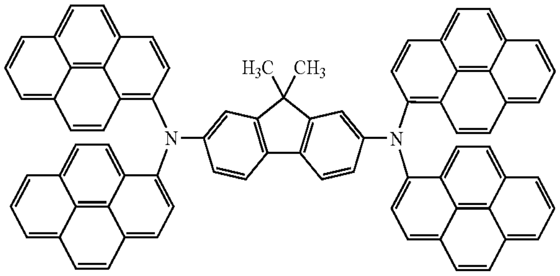

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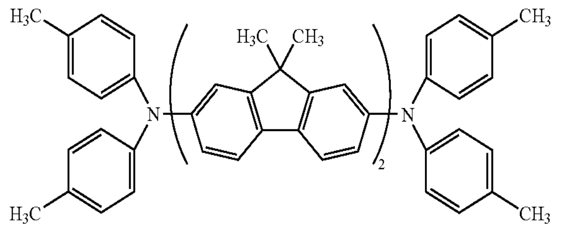

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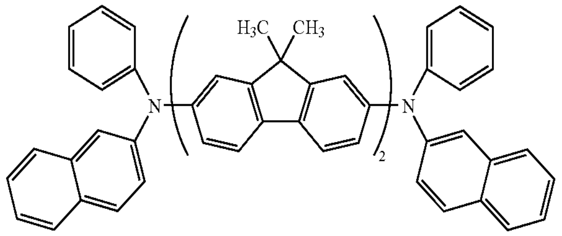

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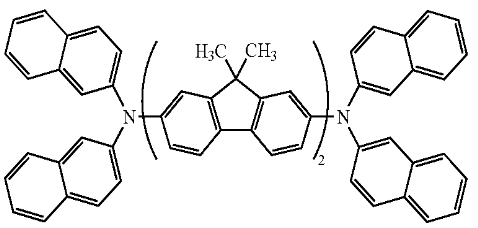

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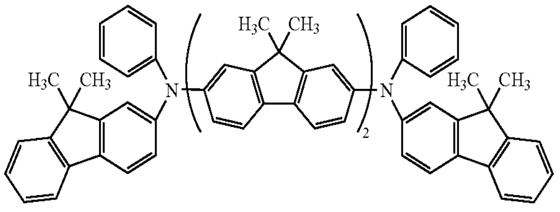

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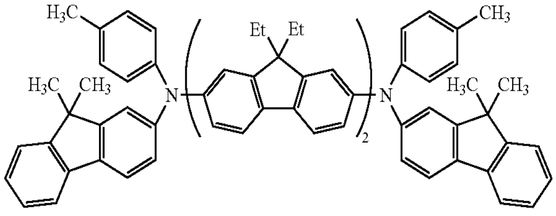

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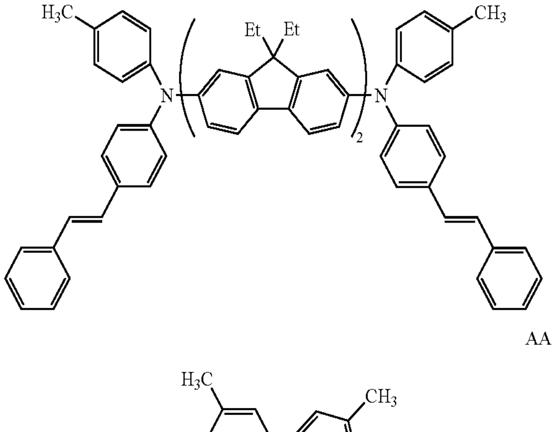

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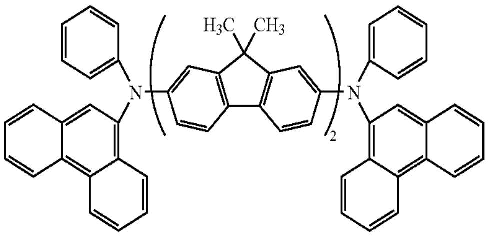

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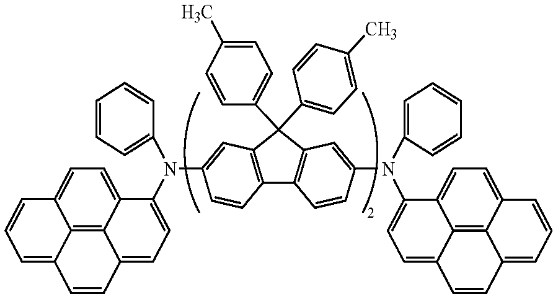

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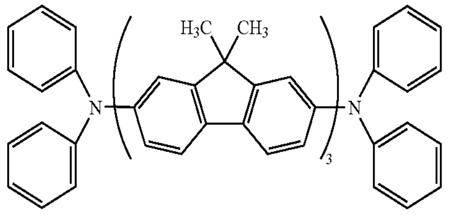

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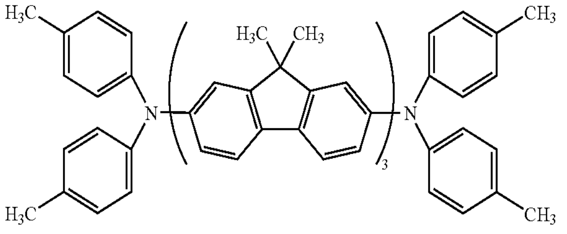

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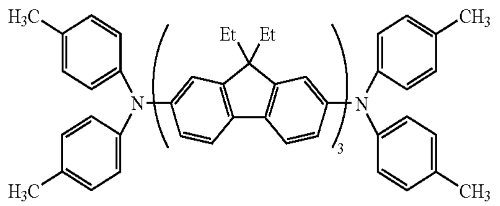

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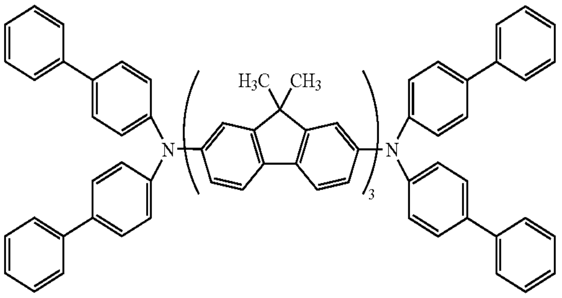

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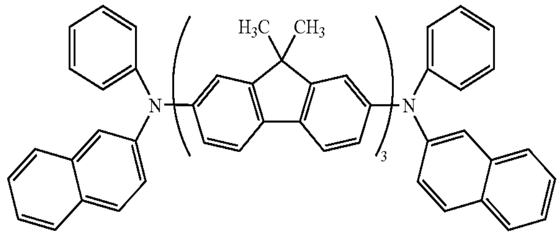

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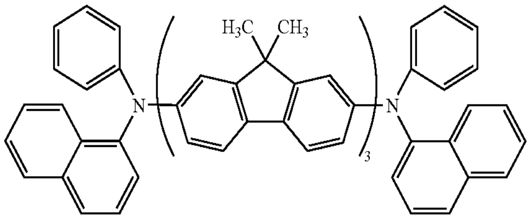

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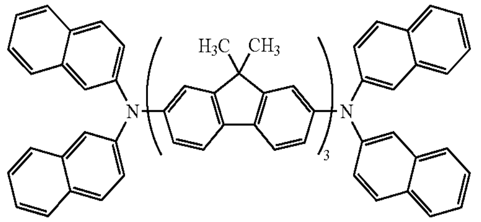

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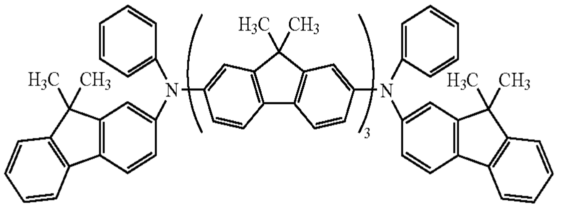

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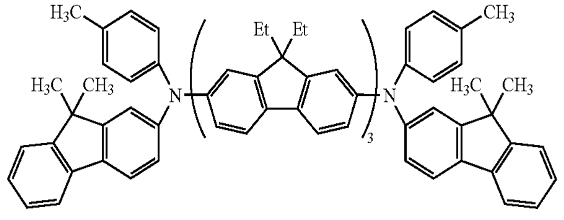

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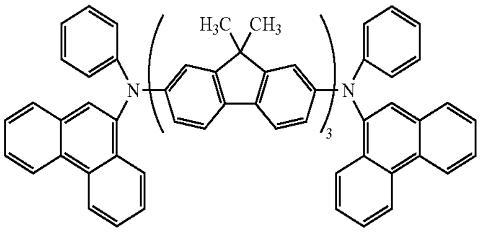

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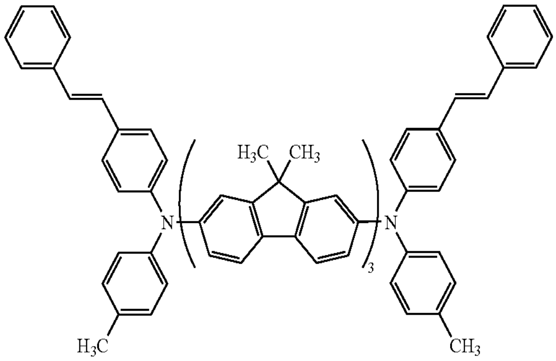

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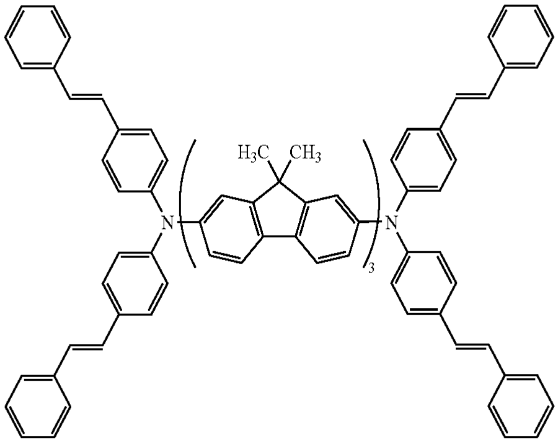

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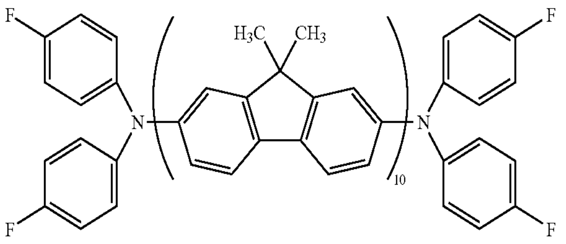
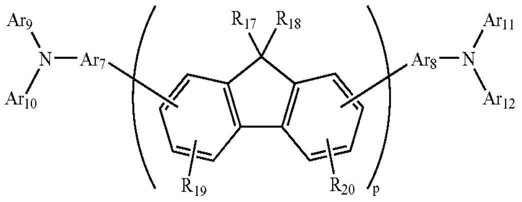


[XI]



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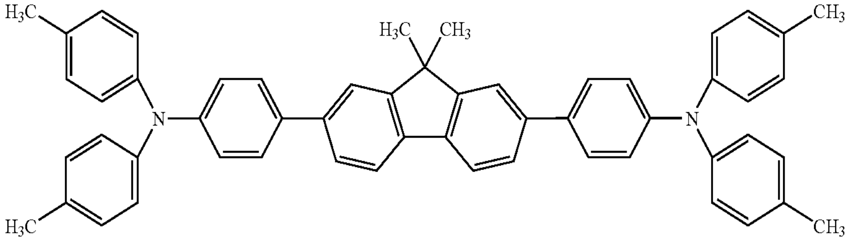

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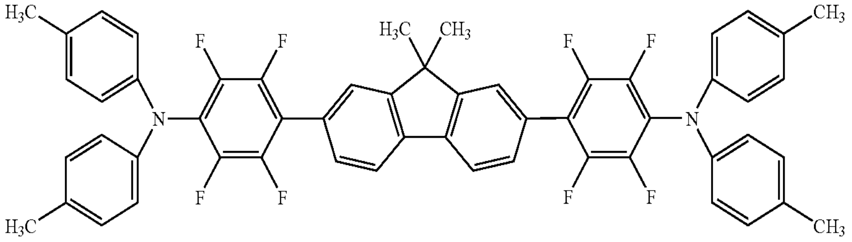

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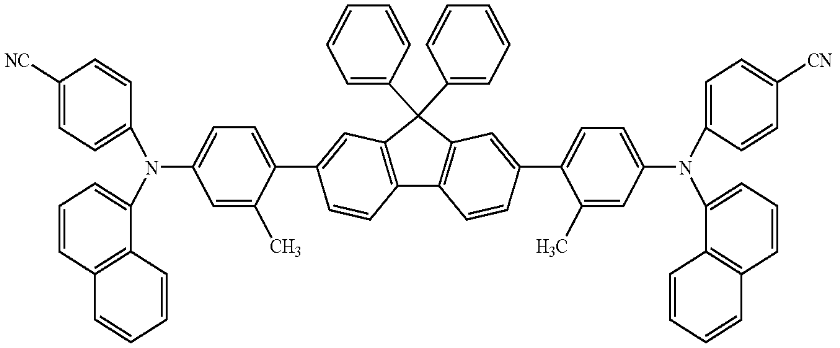

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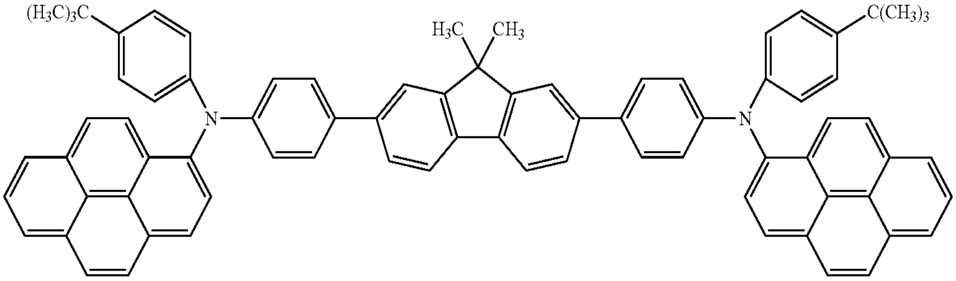

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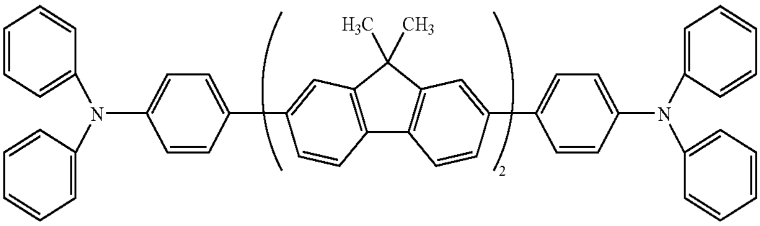

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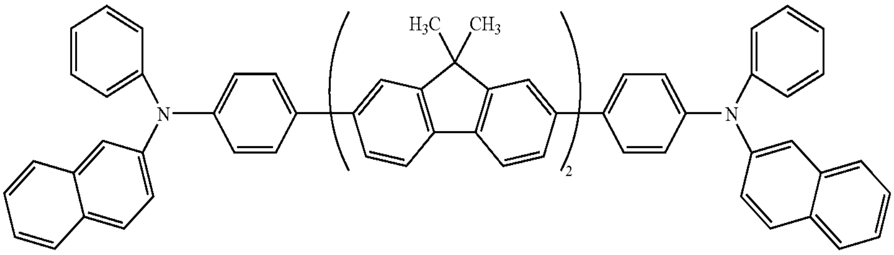

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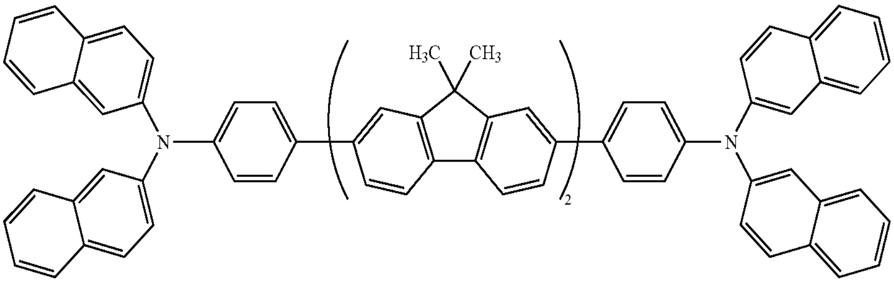

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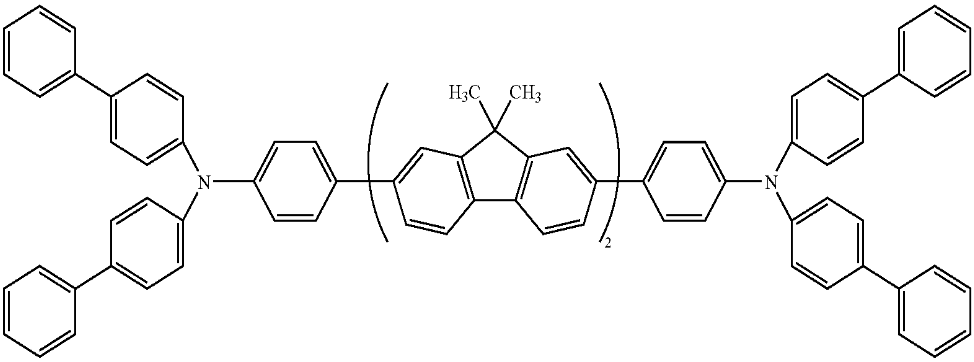

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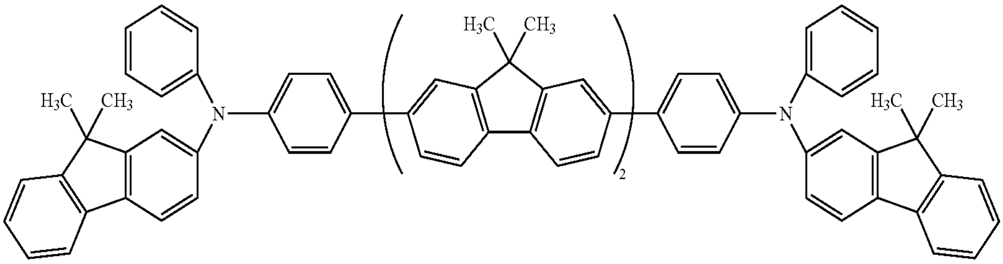

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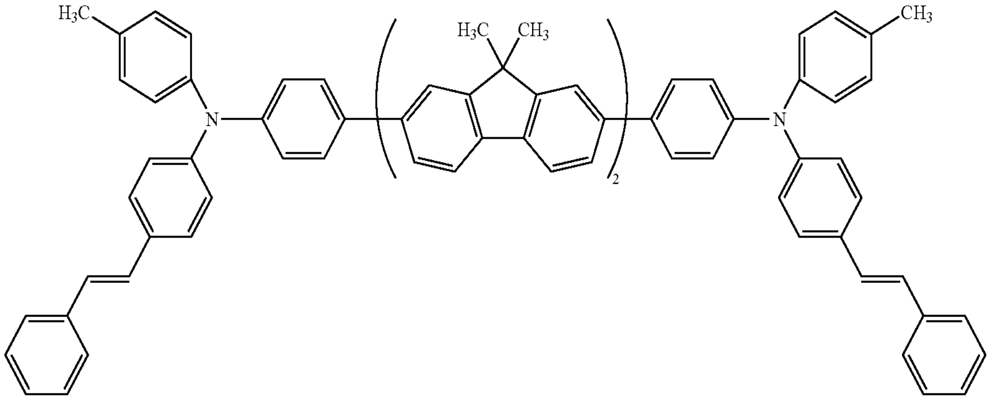

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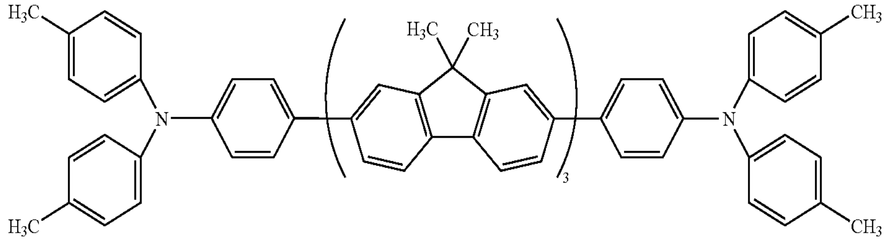

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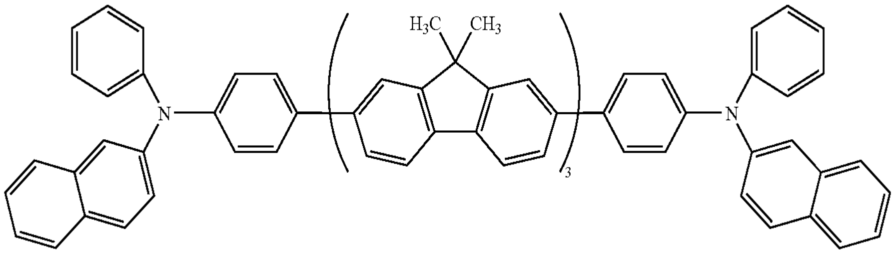

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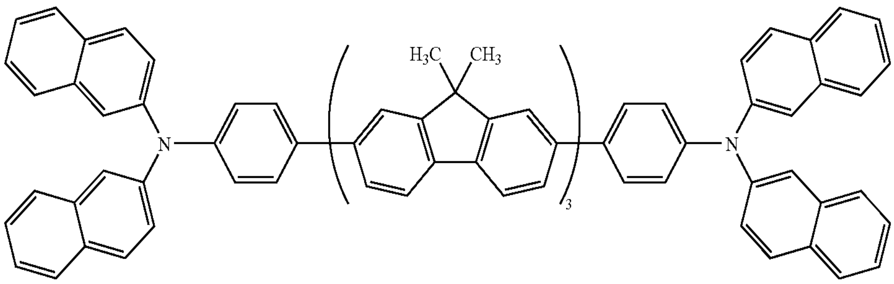

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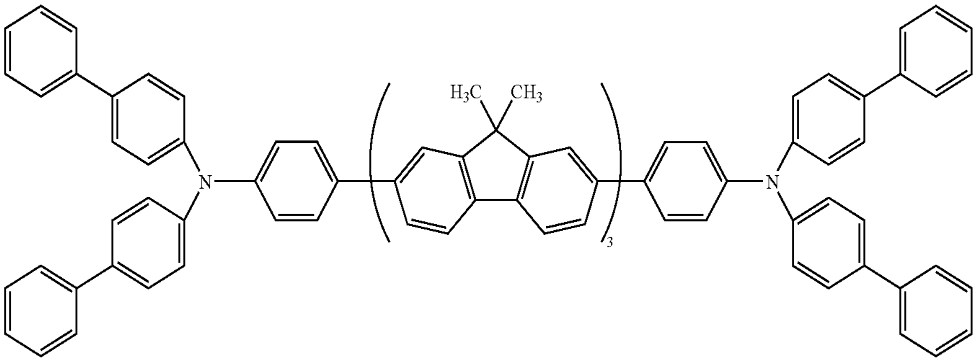

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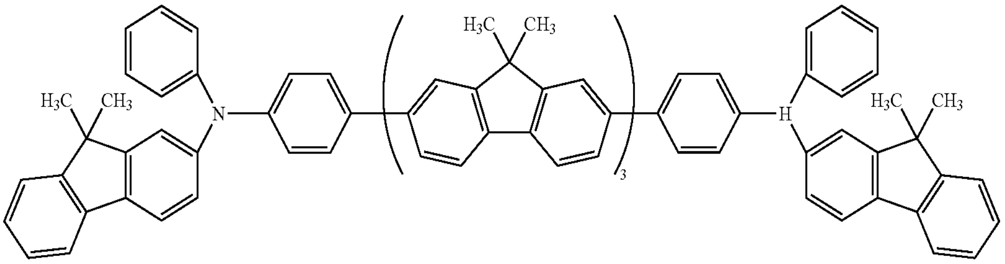

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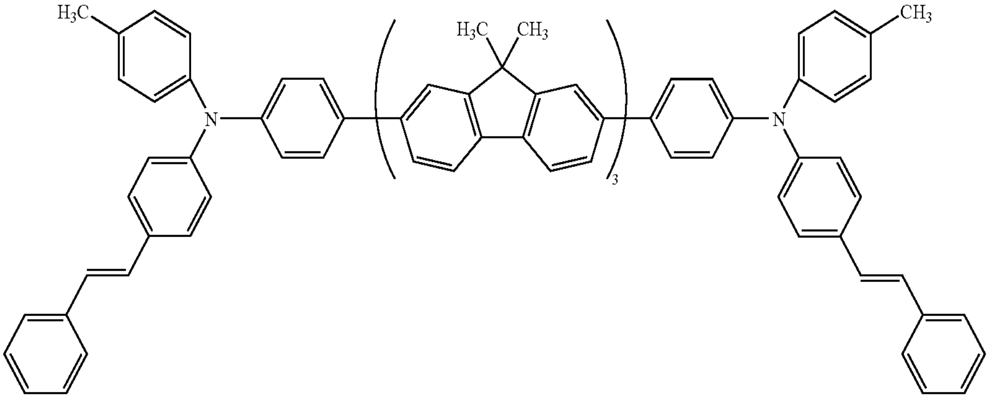

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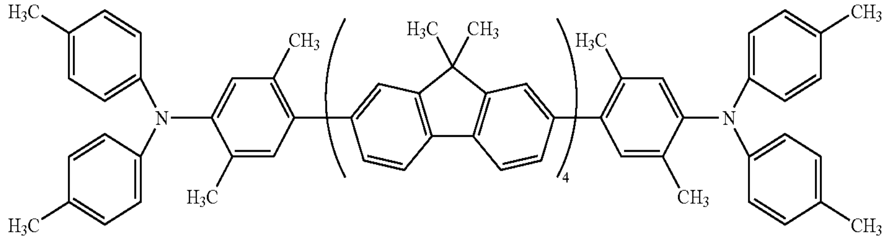

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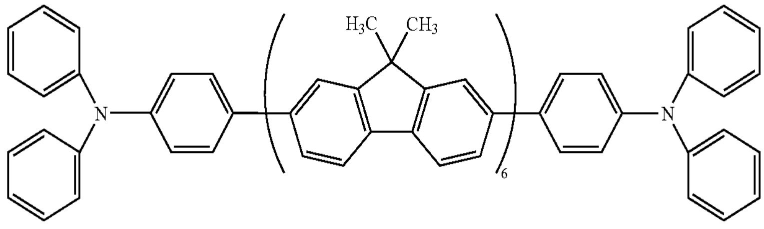

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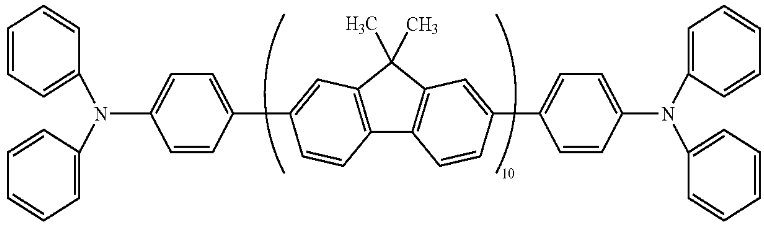

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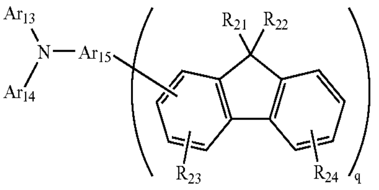

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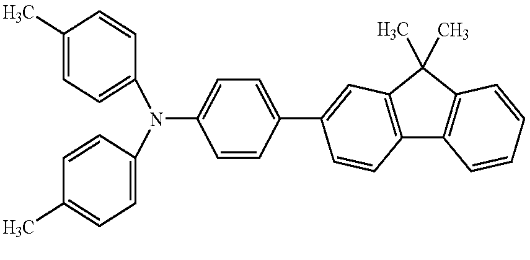

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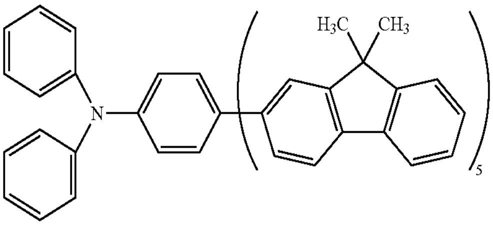

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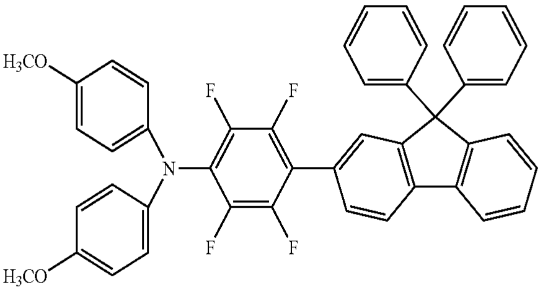

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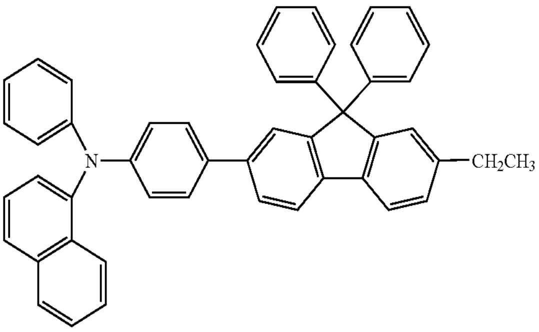

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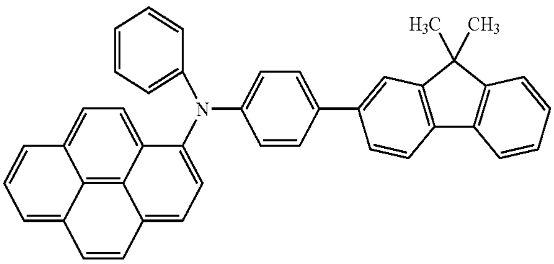

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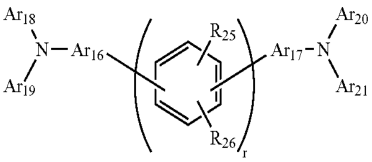

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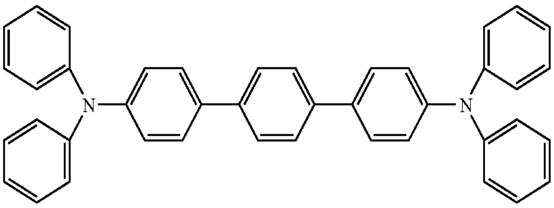

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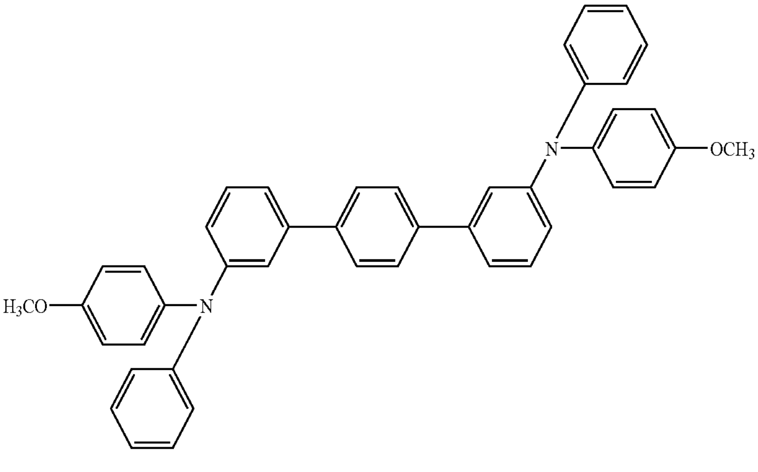

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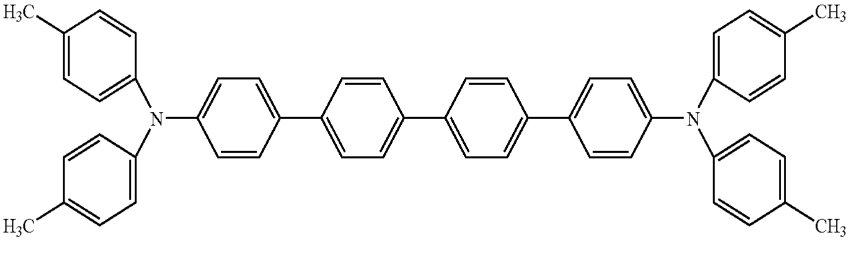

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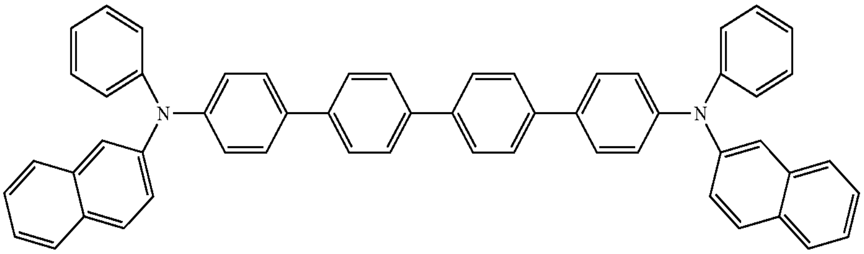

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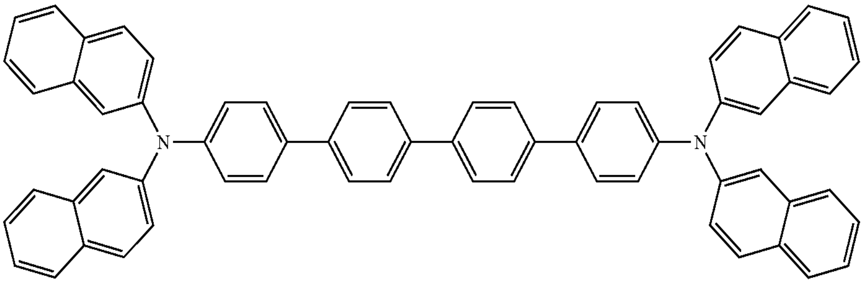

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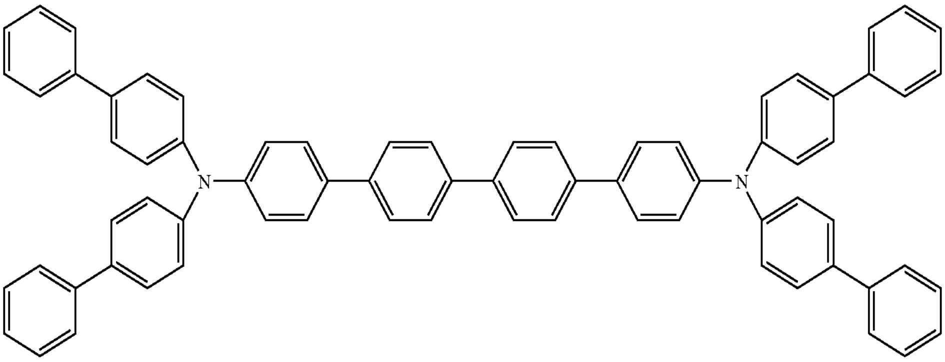

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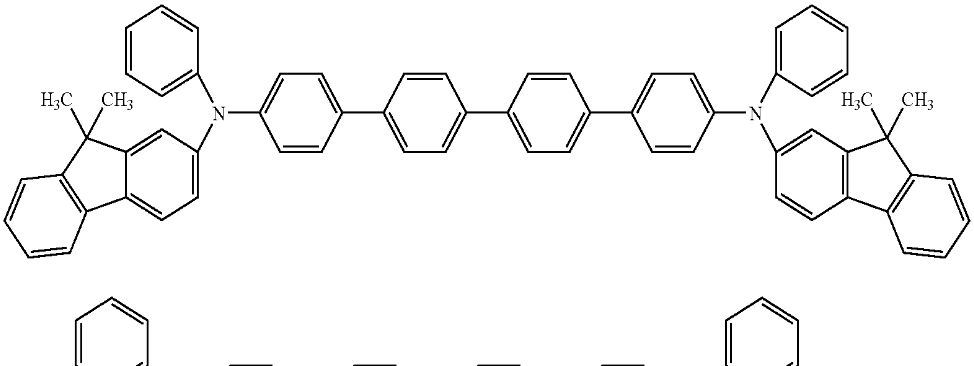

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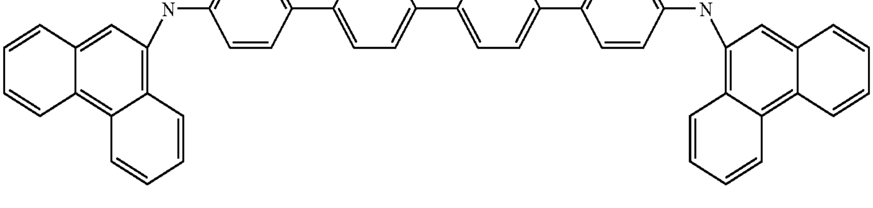

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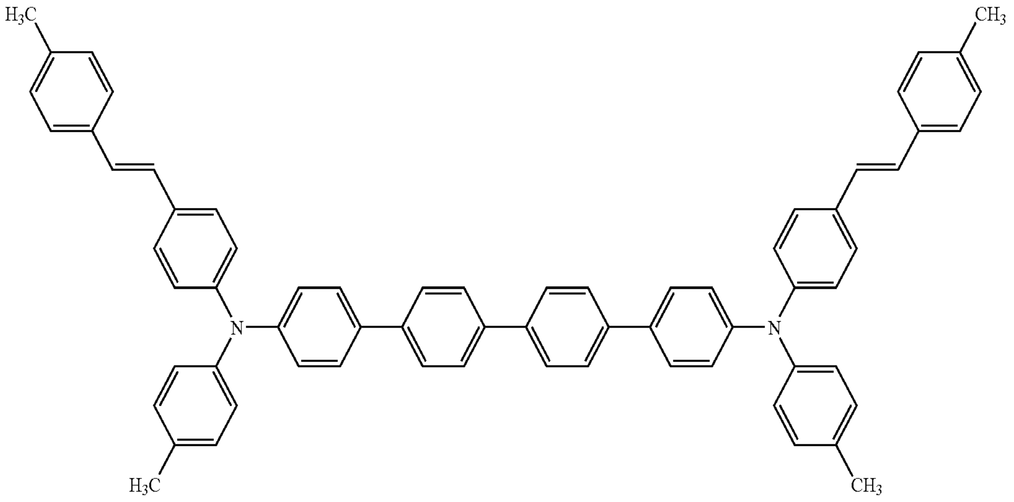

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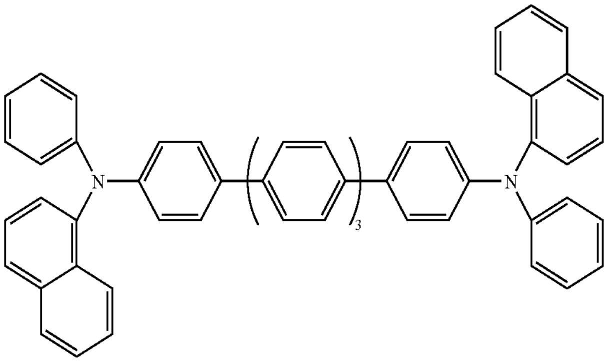

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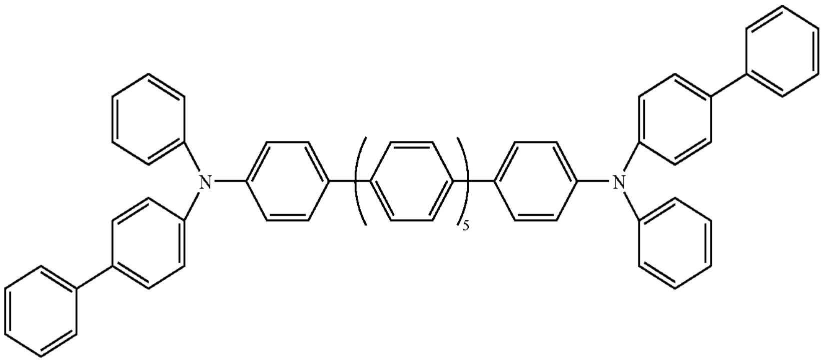

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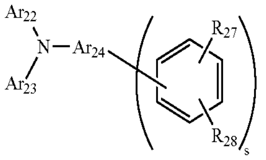

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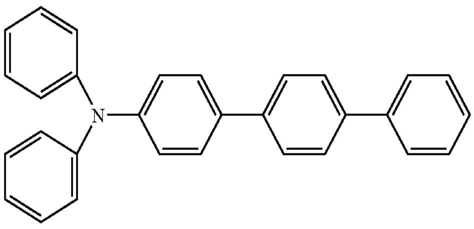

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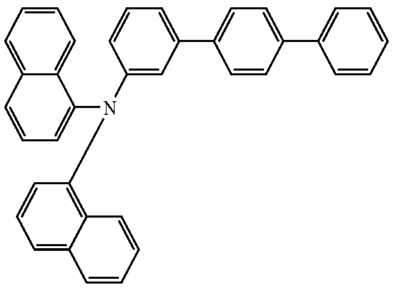

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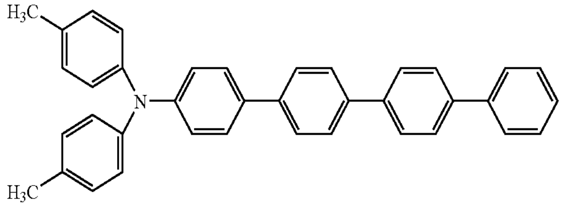

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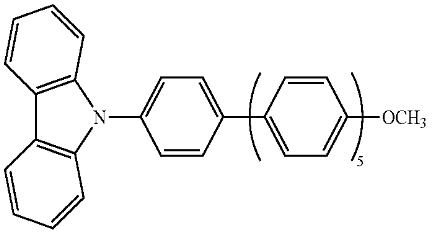

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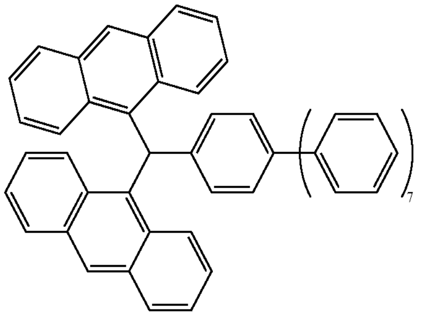
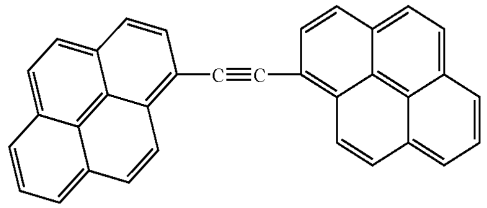


[XV]

$Ar_{25}-(C\equiv C)_t-Ar_{26}$

AC-68



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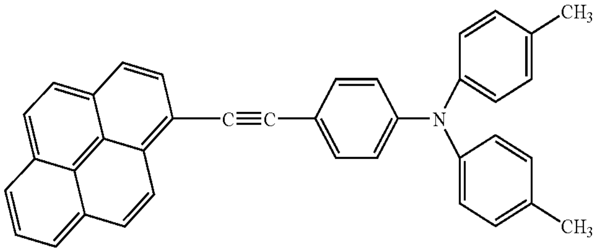

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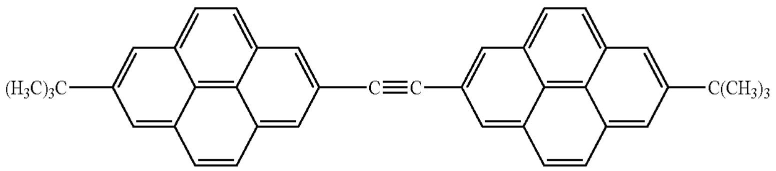

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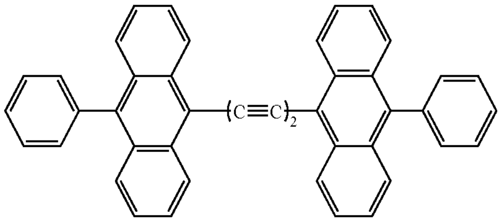

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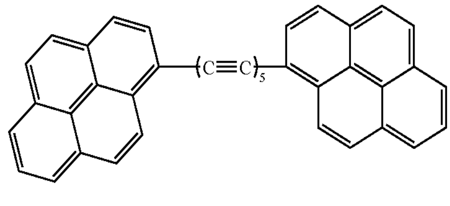


In FIGS. **1** to **6**, preferable examples of the organic luminescent device of the present invention are shown.

FIG. **1** is a cross-sectional view showing an example of the organic luminescent device of the present invention. In FIG. **1**, the device is composed of an anode **2**, a luminescent layer **3**, and a cathode **4**, which are formed on a substrate **1** in order. The luminescent device with this structure is advantageous when the luminescent material used herein has a hole-transporting ability, an electron-transporting ability, and a luminescence property in itself or when plural compounds having the respective characteristics are used as mixed.

FIG. **2** is a cross-sectional view showing another example of the organic luminescent device of the present invention. In FIG. **2**, the device is composed of an anode **2**, a hole transport layer **5**, an electron transport layer **6**, and a cathode **4**, which are formed on a substrate **1** in order. In this case, a luminescent material having either or both of a hole transport property and an electron transport property is advantageously used for the corresponding one of the layers, in combination with a hole transport material or an electron transport material having no luminescence property for the other layer. In addition, in this case, the luminescent layer **3** is composed of either the hole transport layer **5** or the electron transport layer **6**.

FIG. **3** is a cross-sectional view showing still another example of the organic luminescent device of the present invention. In FIG. **3**, the device is composed of an anode **2**, a hole transport layer **5**, a luminescent layer **3**, an electron transport layer **6**, and a cathode **4**, which are formed on a substrate **1** in order. With this arrangement, a carrier transport function and a luminescence function are separated from each other, and plural compounds respectively having a hole transport property, an electron transport property, and a luminescence property are used appropriately in combination therewith. Thus, the degree of freedom upon selecting materials extremely increases. In addition, various kinds of compounds having different luminous wavelengths can be used. Therefore, a variety of luminescence hues can be achieved. Furthermore, it also becomes possible to increase the luminous efficiency by effectively confining each carrier or exciton in the middle luminescent layer **3**.

FIG. **4** is a cross-sectional view showing still another example of the organic luminescent device of the present invention. In FIG. **4**, as compared with the example of FIG. **3**, the device is constructed such that a hole injecting layer **7** is inserted on the anode **2** side. It is effective for improving an adhesion between the anode **2** and the hole transport layer **5** or improving a hole injection property. Thus, this arrangement is effective for lowering a voltage.

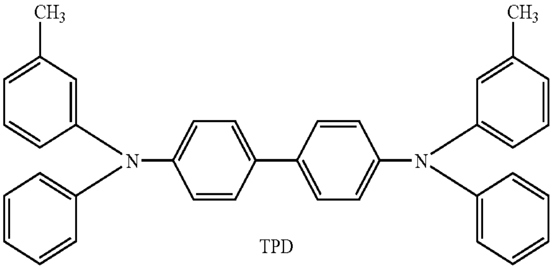
FIGS. **5** and **6** are cross-sectional views showing other examples of the organic luminescent device of the present invention, respectively. In FIGS. **5** and **6**, as compared with the examples of FIGS. **3** and **4**, the device is constructed such that a layer (a hole-blocking layer **8**) serving to prevent a hole or an exciton from passing toward the cathode **4** side is inserted between the luminescent layer **3** and the electron transport layer **6**. The use of a compound having an extremely high ionization potential for the hole-blocking layer **8** is effective for improving the luminous efficiency.

Note that, in FIGS. **1** to **6**, there are shown common basic device structures. The structure of the organic luminescent device using the compound of the present invention is not limited thereto. For example, it is possible to adopt various layer structures such as one in which an insulating layer is formed at the interface between an electrode and an organic layer, one in which an adhesive layer or an interference layer is formed, and one in which the hole transport layer is composed of two layers with different ionization potentials.

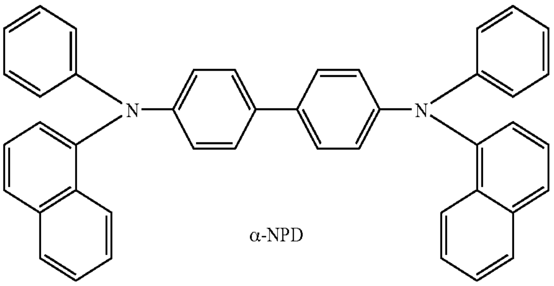
The fluorene compound represented by the general formula [I] to be used in the present invention is a compound superior to the conventional compounds in electron transport property, luminescence property, and durability, and the fluorene compound can be used in any of the modes shown in FIGS. **1** to **6**.

In the present invention, the fluorene compound represented by the general formula [I] is used as a component for the electron transport layer or the luminescent layer. However, hole transport compounds, luminescent compounds, electron transport compounds, or other such well-known compounds may be used together as needed.

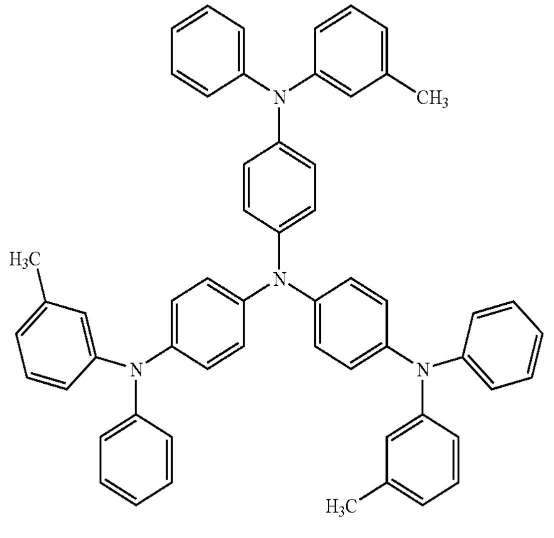
Examples of those compounds will be given below. Hole transport compound:



TPD



α-NPD



m-MTDATA

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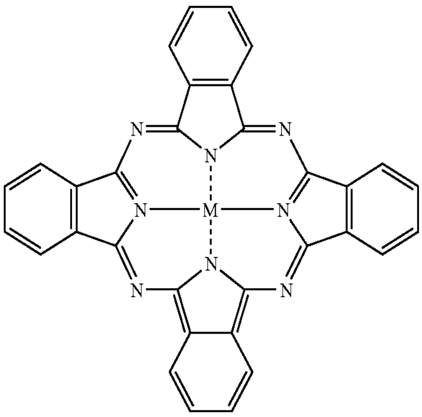
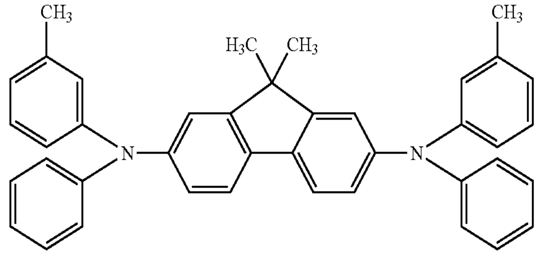
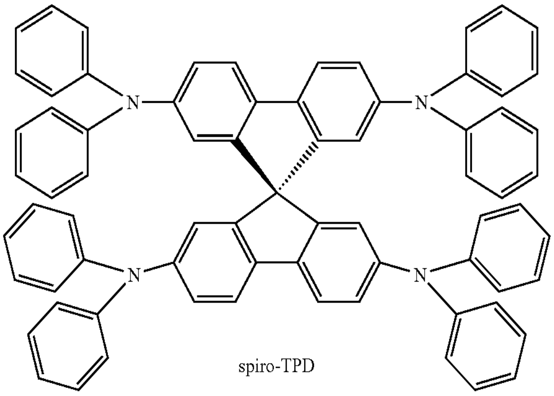


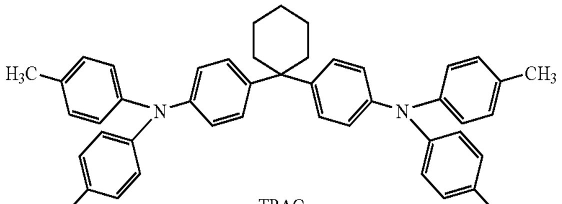
Pc—M
M: Cu, Mg, AlCl, TiO, $SiCl_2$, Zn, Sn,
MnCl, GaCl, etc



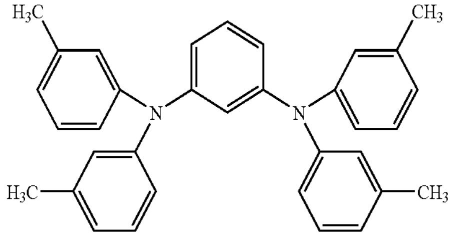
DTDPFL



spiro-TPD

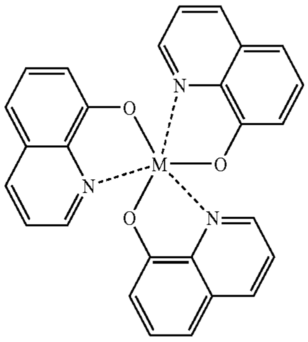


TPAC

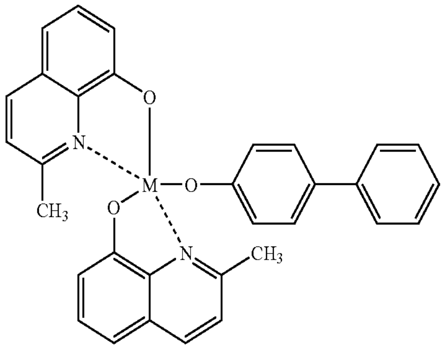


PDA

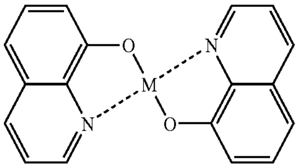
Electron Transport Luminescent Material:



M: Al, Ga



M: Al, Ga



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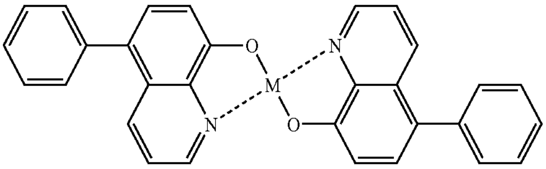
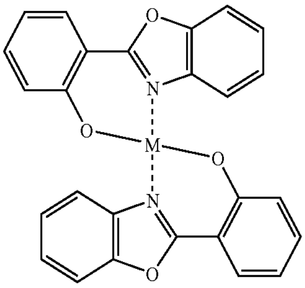


M: Zn, Mg, Be



M: Zn, Mg, Be

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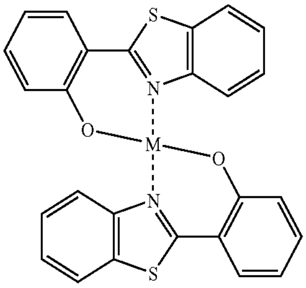

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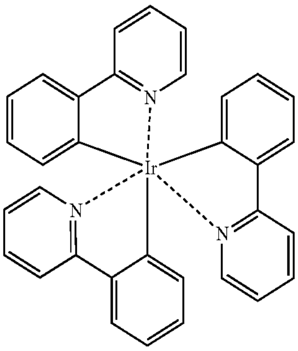

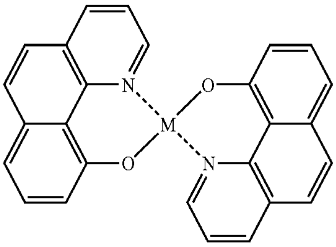

M: Zn, Mg, Be

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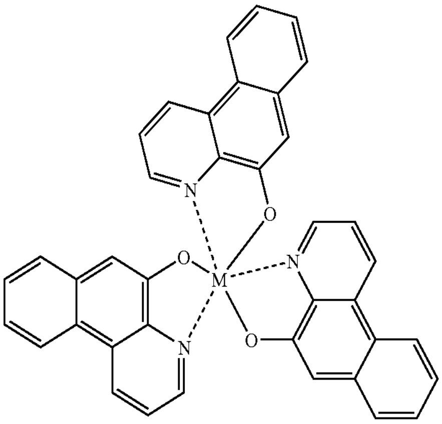
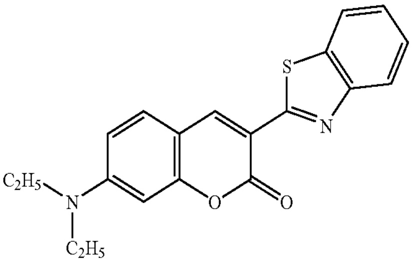
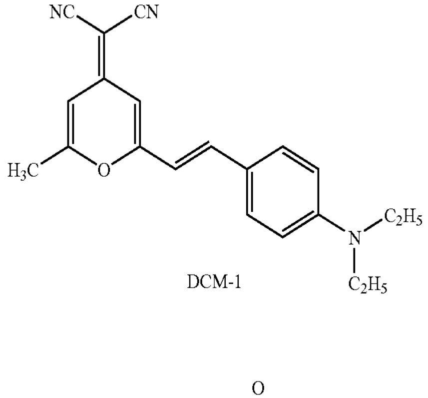


M: Al, Ga

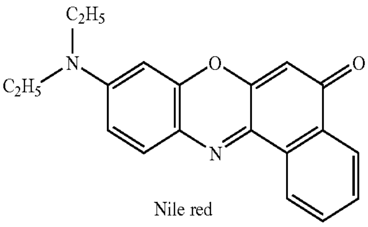
Luminescent Material:



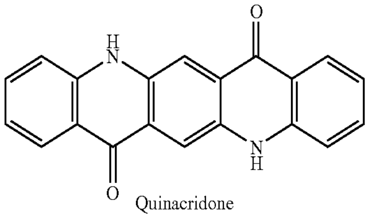
Coumarin 6



DCM-1



Nile red



Quinacridone

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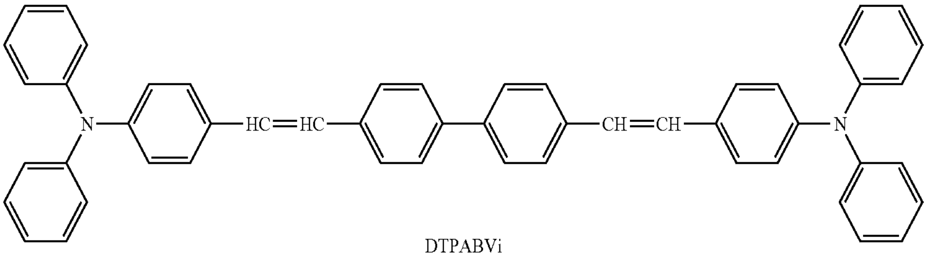
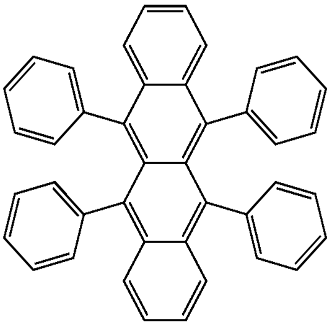
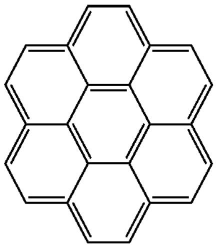


DTPABVi

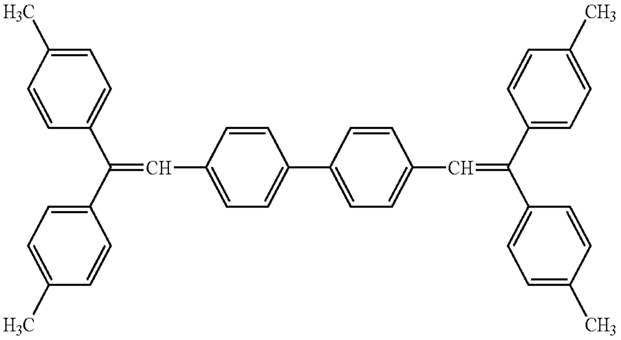


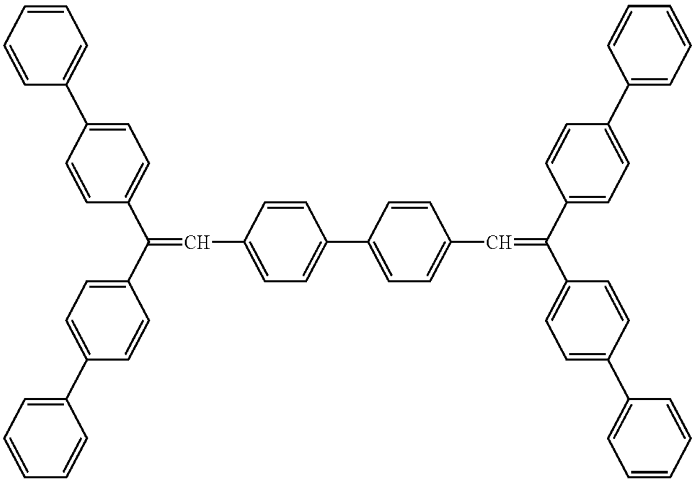
Rubrene

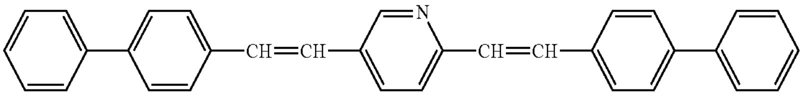


Coronene

Luminescent Layer Matrix Material and Electron Transport Material:







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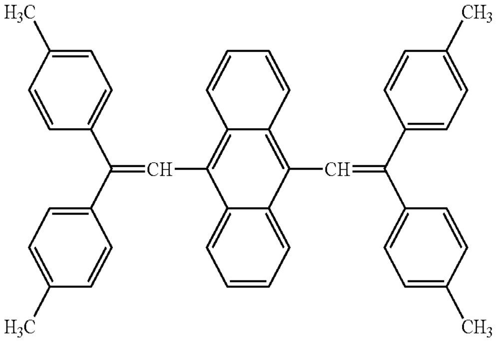
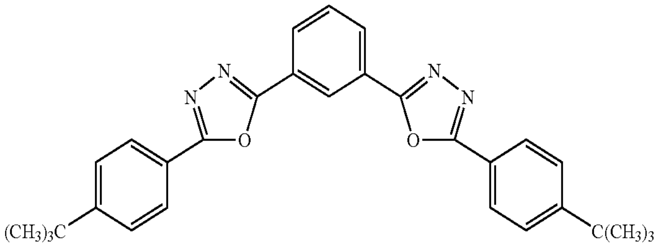

H$_3$C
CH$_3$
CH
CH
H$_3$C
CH$_3$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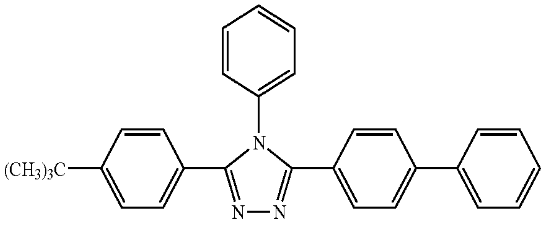
O
N
N
O
(CH$_3$)$_3$C
C(CH$_3$)$_3$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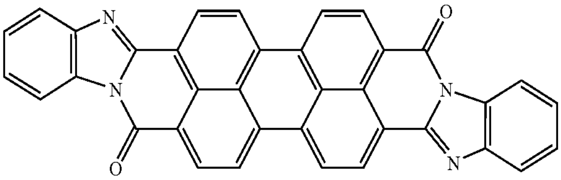
(CH$_3$)$_3$C
N
N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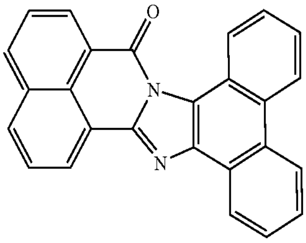
N
N
O
N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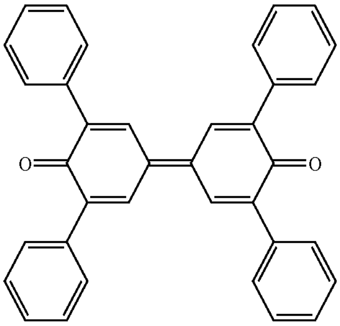
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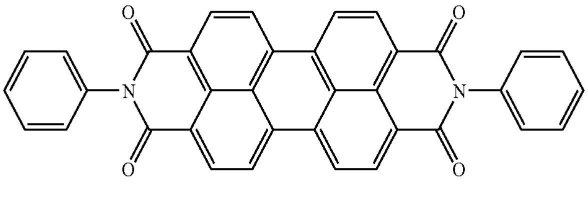
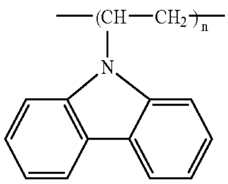
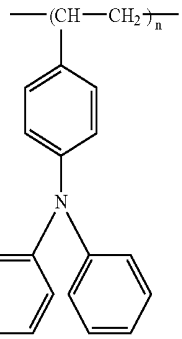
O


O
O
N
N
O
O

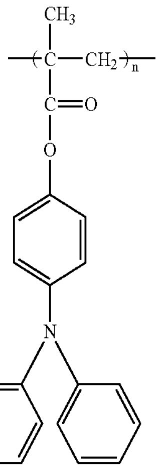
Polymeric Hole Transport Material:



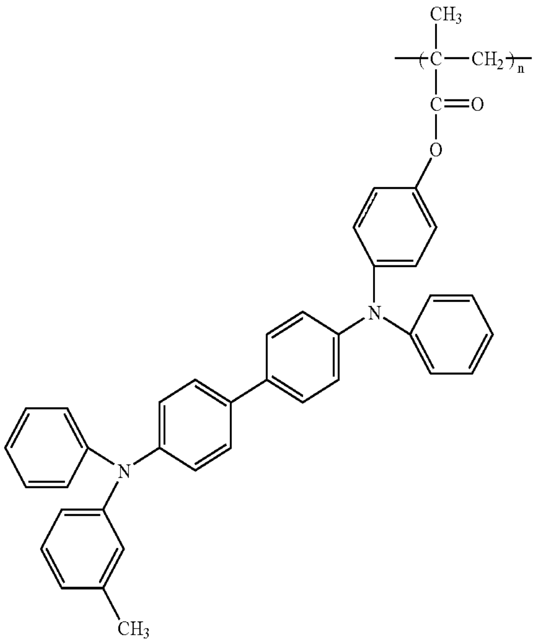
PVCz



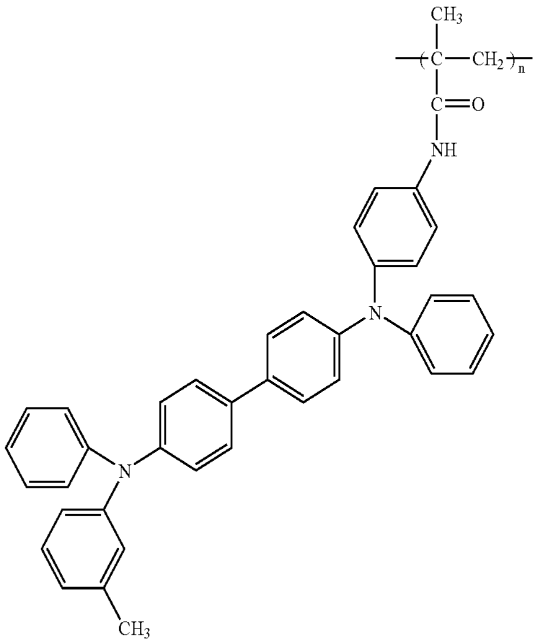
DPA-PS



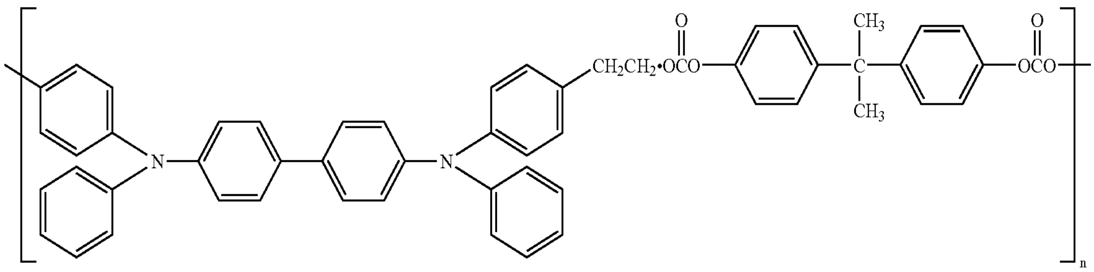
TPA-PMMA



TPD-PMMA



TPD-PMAA



TPD-PCA

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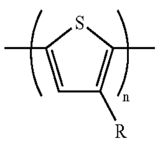
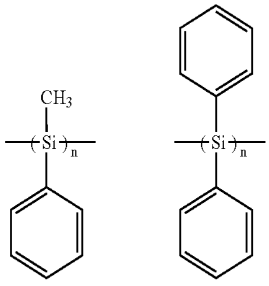


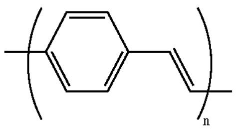
R: C_6H_{13}, C_8H_{17}, $C_{12}H_{25}$

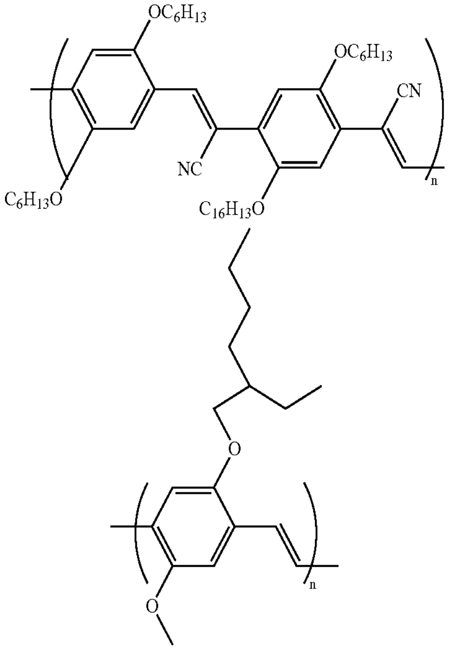
Polythiophene

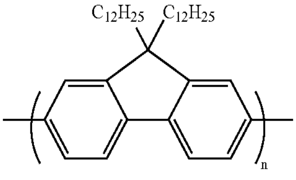


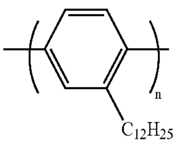
Polysilane

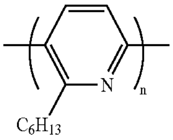
Polymeric Luminescent Material and Charge Transport Material:











In the organic luminescent device of the present invention, the layer containing the fluorene compound represented by the general formula [I] and the layer containing other organic compounds are generally formed as thin films by a vacuum evaporation method or by a coating method after being dissolved in an appropriate solvent. In particular, in the case of forming a film with the coating method, the film formation may be performed in combination with an appropriate binder resin.

The above binder resin can be selected from a wide variety of binder resins including, for example, poly(vinylcarbazole) resin, polycarbonate resin, polyester resin, polyarylate resin, polystyrene resin, acrylic resin, methacrylic resin, butyral resin, poly(vinyl acetal) resin, diallyl phthalate resin, phenolic resin, epoxy resin, silicone resin, polysulfone resin, and urea resin, although not limited thereto. In addition, one of the above resins may be used solely, or two or more such resins may be combined with each other as a copolymer.

Preferably, the anode material may have a work function that is as large as possible. For example, a simple metal substance such as gold, platinum, nickel, palladium, cobalt, selenium, or vanadium, or an alloy thereof, or a metal oxide such as tin oxide, zinc oxide, indium tin oxide (ITO), or indium zinc oxide can be used. In addition, a conductive polymer such as polyaniline, polypyrrole, polythiophene, or poly(phenylene sulfide) can be also used. Any one of those electrode materials may be used solely or the plural electrode materials may be used in combination.

On the other hand, preferably, the cathode material may have a small work function. For example, a simple metal substance such as lithium, sodium, potassium, cesium, calcium, magnesium, aluminum, indium, silver, lead, tin, or chromium, or an alloy of the plural substances can be used therefor. It is also possible to use a metal oxide such as indium tin oxide (ITO). In addition, the cathode may take either a single-layer structure or a multi-layer structure.

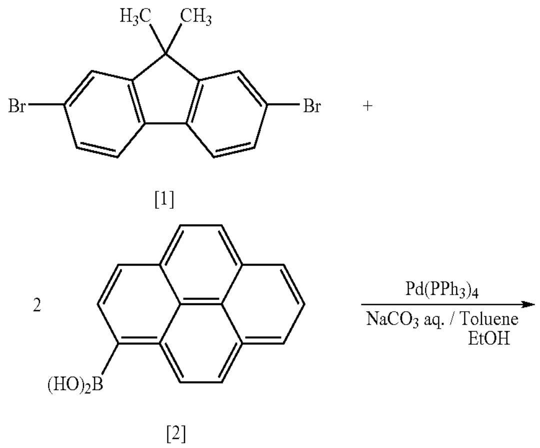
The substrate used in the present invention may be, although not particularly limited, an untransparent substrate such as a metallic substrate or a ceramic substrate, or a transparent substrate formed of glass, quartz, plastic sheet, or the like. In addition, it is also possible to control the luminescent color by using a color filter film, a fluorescent color-converting filter film, a dielectric reflection film, or the like for the substrate.

Furthermore, a protective layer or a sealing layer may be also formed on the prepared device for preventing the device from contacting oxygen, moisture, or the like. The protective layer may be a diamond thin film, a film made of an inorganic material such as a metal oxide or a metal nitride, or a polymer film made of fluoroplastics, poly(paraxylylene), polyethylene, silicone resin, polystyrene resin, or the like. In addition, a photo-curing resin or the like can be used therefor. Furthermore, it is also possible to package the device itself with an appropriate sealing resin while covering with glass, a gas-impermeable film, a metal, or the like.

Hereinafter, the present invention will be described in more detail based on examples. However, the present invention is not limited to those examples.

Synthesis Example 1

Synthesis of Exemplified Compound No. 1



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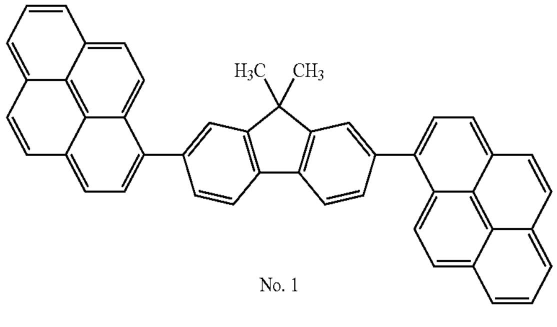
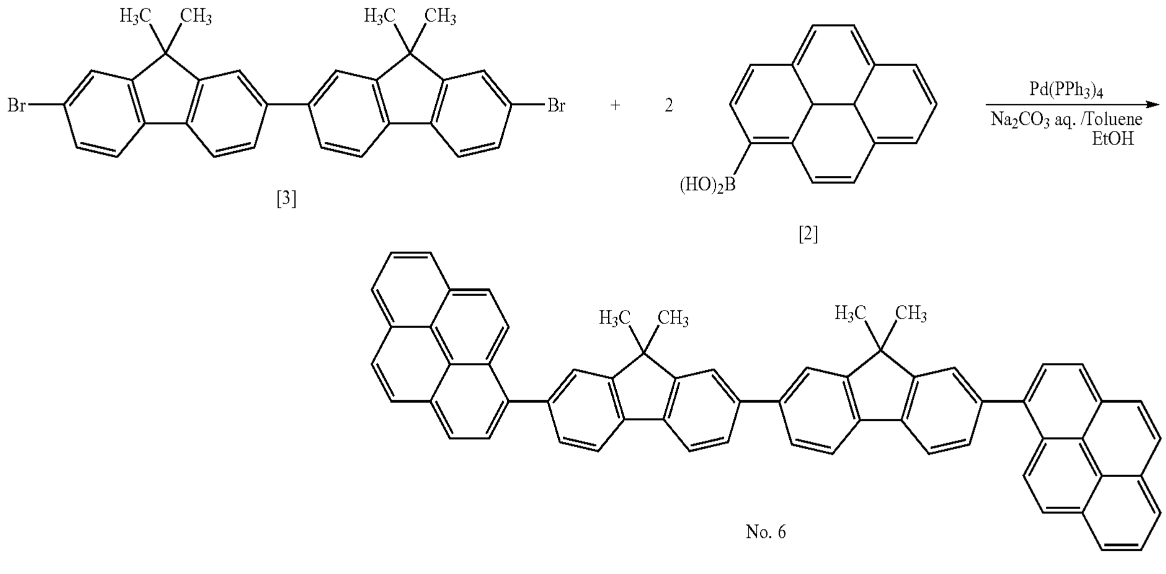


To a 500-ml three-neck flask, 2.0 g (5.68 mmol) of 2,7-dibromo-9,9-dimethylfluorene [1], 4.2 g (17.0 mmol) of pyrene-1-boronic acid [2], 120 ml of toluene, and 60 ml of ethanol were added. Then, an aqueous solution of 24 g of sodium carbonate/120 ml of water was dropped thereinto with stirring in a nitrogen atmosphere at a room temperature, followed by the addition of 0.33 g (0.28 mmol) of tetrakis (triphenylphosphine) palladium (0). After stirring the mixture for 30 minutes at a room temperature, the temperature was allowed to rise to 77° C., followed by stirring for 5 hours. After the reaction, an organic layer was extracted with chloroform and was then dried with anhydrous sodium sulfate, followed by purification with a silica gel column (hexane+toluene mixture developing solvent). Consequently, 3.0 g (89% yield) of an exemplified compound No. 1 (white crystal) was obtained.

Synthesis Example 2

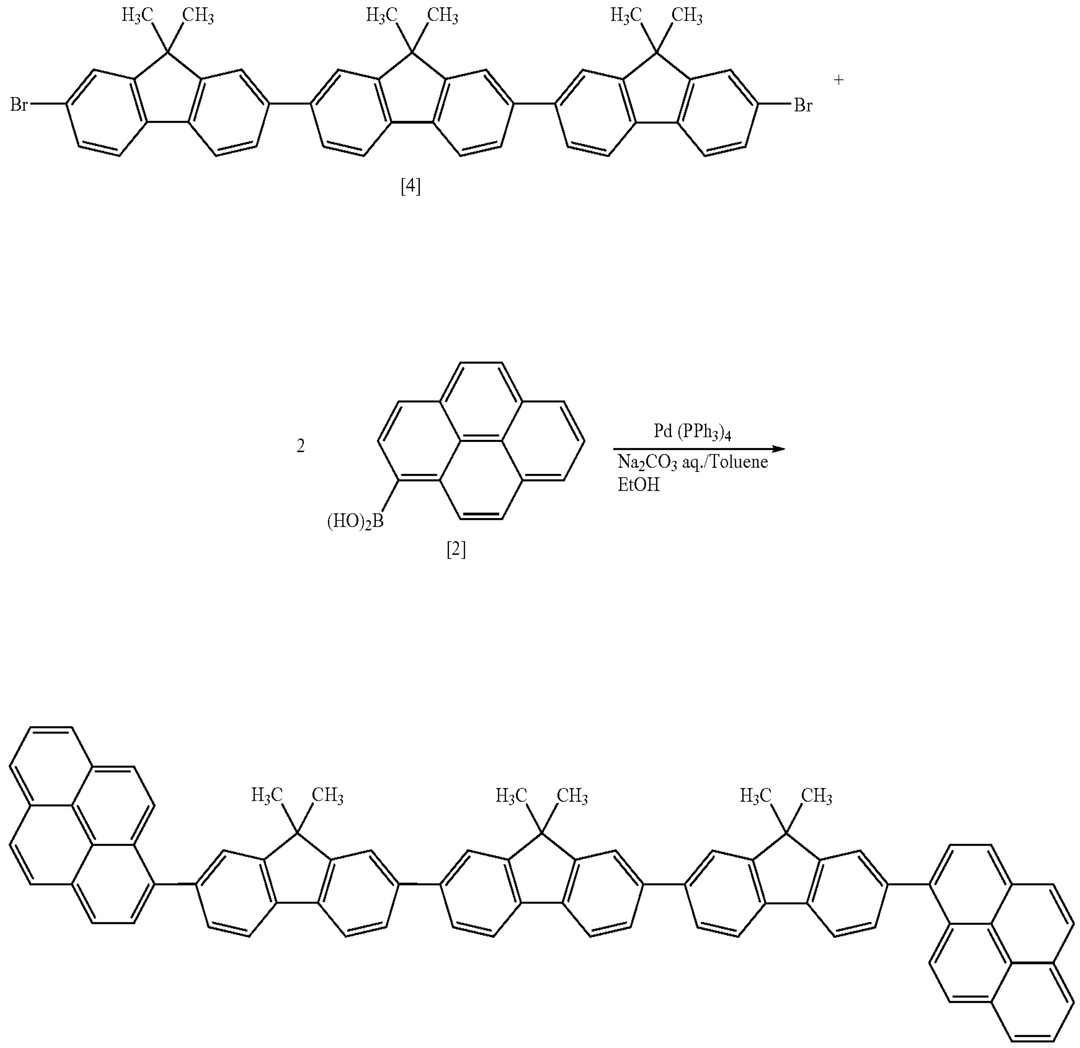
Synthesis of Exemplified Compound No. 6



To a 500-ml three-neck flask, 3.0 g (5.49 mmol) of dibromofluorene compound [3], 4.0 g (16.5 mmol) of pyrene-1-boronic acid [2], 100 ml of toluene, and 50 ml of ethanol were added. Then, an aqueous solution of 20 g of sodium carbonate/100 ml of water was dropped thereinto with stirring in a nitrogen atmosphere at a room temperature, followed by the addition of 0.33 g (0.28 mmol) of tetrakis (triphenylphosphine) palladium (0). After stirring the mixture for 30 minutes at a room temperature, the temperature was allowed to rise to 77° C., followed by stirring for 5 hours. After the reaction, an organic layer was extracted with chloroform and was then dried with anhydrous sodium sulfate, followed by purification with a silica gel column (hexane+toluene mixture developing solvent). Consequently, 3.4 g (79% yield) of an exemplified compound No. 6 (white crystal) was obtained.

Synthesis Example 3

Synthesis of Exemplified Compound No. 7

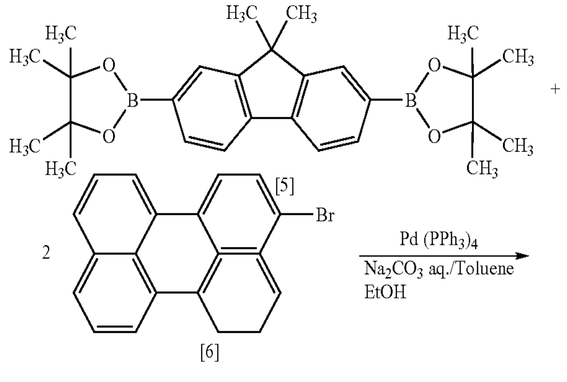


No. 7

To a 500-ml three-neck flask, 3.0 g (4.07 mmol) of dibromofluorene compound [4], 3.0 g (12.2 mmol) of pyrene-1-boronic acid [2], 100 ml of toluene, and 50 ml of ethanol were added. Then, an aqueous solution of 16 g of sodium carbonate/80 ml of water was dropped thereinto with stirring in a nitrogen atmosphere at a room temperature, followed by the addition of 0.23 g (0.20 mmol) of tetrakis (triphenylphosphine) palladium (0). After stirring the mixture for 30 minutes at a room temperature, the temperature was allowed to rise to 77° C., followed by stirring for 5 hours. After the reaction, an organic layer was extracted with chloroform and was then dried with anhydrous sodium sulfate, followed by purification with a silica gel column (hexane+toluene mixture developing solvent). Consequently, 2.7 g (68% yield) of an exemplified compound No. 7 (white crystal) was obtained.

Synthesis Example 4

Synthesis of Exemplified Compound No. 28



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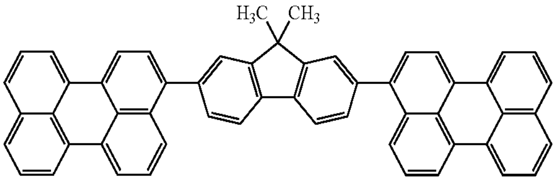


No. 28

To a 500-ml three-neck flask, 3.0 g (6.74 mmol) of diborate fluorene [5], 6.7 g (20.2 mmol) of 3-bromoperylene [6], 140 ml of toluene, and 70 ml of ethanol were added. Then, an aqueous solution of 26 g of sodium carbonate/130 ml of water was dropped thereinto with stirring at a room temperature in a nitrogen atmosphere, followed by the addition of 0.39 g (0.34 mmol) of tetrakis (triphenylphosphine) palladium (0). After stirring the mixture for 30 minutes at a room temperature, the temperature was allowed to rise to 77° C., followed by stirring for 10 hours. After the reaction, an organic layer was extracted with chloroform and was then dried with anhydrous sodium sulfate, followed by purification with a silica gel column (hexane+toluene mixture developing solvent). Consequently, 3.1 g (66% yield) of an exemplified compound No. 28 (white crystal) was obtained.

EXAMPLE 1

A device having the structure shown in FIG. **2** was prepared.

On a glass substrate as the substrate **1**, indium tin oxide (ITO) was deposited into a film with a thickness of 120 nm by a sputtering method to obtain the anode **2**, so that the substrate thus formed was used as a transparent conductive support substrate. The substrate was sequentially subjected to ultrasonic cleaning with acetone and with isopropyl alcohol (IPA). Following this, the substrate was washed with IPA through boiling and then dried. Furthermore, the substrate after UV/ozone cleaning was used as the transparent conductive support substrate.

On the transparent conductive support substrate, a chloroform solution of the compound represented by the following structural formula was applied to form a film of 30 nm in thickness by a spin-coating method, resulting in the hole transport layer **5**.

Furthermore, a fluorene compound represented as the exemplified compound No. 1 was deposited into a film of 50 nm in thickness by a vacuum evaporation method, resulting in the electron transport layer **6**. The film formation was performed under the conditions that the degree of vacuum at the time of evaporation was 1.0×10^{-4} Pa and the film formation rate was 0.2 to 0.3 nm/sec.

A metal layer film of 50 nm in thickness was formed on the above organic layer as the cathode **4** using an evaporation material including aluminum and lithium (lithium concentration: 1% by atom) by a vacuum evaporation method, and further an aluminum layer of 150 nm in thickness was formed by a vacuum evaporation method. The film formation was performed under the conditions that the degree of vacuum at the time of evaporation was 1.0×10^{-4} Pa and the film formation rate was 1.0 to 1.2 nm/sec.

Furthermore, the resultant structure was covered with a protective glass plate in a nitrogen atmosphere and was then sealed with an acrylic resin adhesive.

When a direct current voltage of 10 V was applied onto the device thus obtained with an ITO electrode (anode **2**) provided as a positive electrode and an Al—Li electrode (cathode **4**) provided as a negative electrode, electric current was caused to flow into the device at a current density of 12.5 mA/cm^2 and blue-colored luminescence at a luminance of 8500 cd/m^2 was observed.

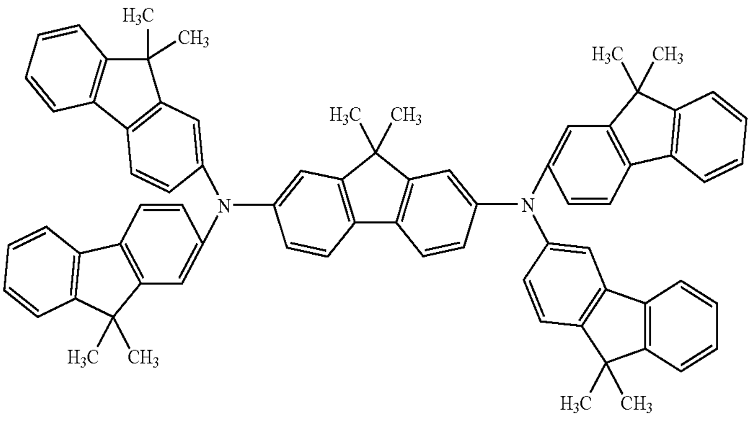
Furthermore, when the current density was kept at 10.0 mA/cm^2 and the voltage was applied for 100 hours, the deterioration of luminance was small; an initial luminance of 7200 cd/m^2 was reduced to a luminance of 6800 cd/m^2 after 100 hours.

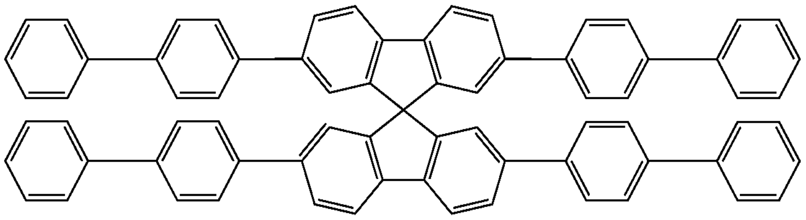
EXAMPLES 2 TO 10

Devices were prepared and evaluated in the same way as that of Example 1, except that compounds shown in Table 1 were used in place of the exemplified compound No. 1. The results are shown in Table 1.

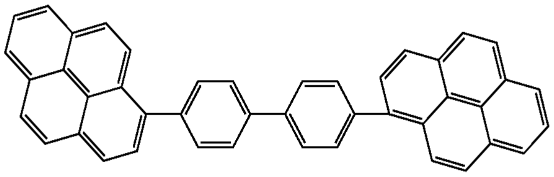
Comparative Examples 1 to 3

Devices were prepared and evaluated in the same way as that of Example 1, except that compounds represented by the following structural formulae were used in place of the exemplified compound No. 1. The results are shown in Table 1.

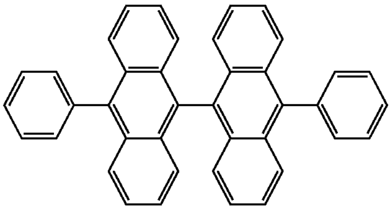




Comparative Compound No. 1



Comparative Compound No. 2



Comparative Compound No. 3

TABLE 1

		Initial stage		Durability		
Example No.	Exemplified compound No.	Applied voltage (V)	Luminance (cd/m^2)	Current density (mA/cm^2)	Initial luminance (cd/m^2)	Luminance after 100-hour (cd/m^2)
Example 1	1	10	8500	10.0	7200	6800
Example 2	6	10	8800	10.0	7900	7600
Example 3	13	10	4800	10.0	4300	4100
Example 4	15	10	8200	10.0	7000	6700
Example 5	22	10	5000	10.0	4500	4200
Example 6	27	10	7400	10.0	7200	6900
Example 7	29	10	8000	10.0	7100	6700
Example 8	32	10	6600	10.0	5700	5500
Example 9	35	10	6700	10.0	5600	5200
Example 10	39	10	4700	10.0	4300	4000
Comparative Example 1	Comparative 1	10	900	10.0	750	400
Comparative Example 2	Comparative 2	10	750	10.0	700	200
Comparative Example 3	Comparative 3	10	1400	10.0	1100	500

EXAMPLE 11

A device having the structure shown in FIG. **3** was prepared.

Similarly to Example 1, the hole transport layer **5** was formed on the transparent conductive support substrate.

Further, a fluorene compound represented as an exemplified compound No. 2 was deposited into a film of 20 nm in thickness by a vacuum evaporation method, resulting in the luminescent layer **3**. The film formation was performed under the conditions that the degree of vacuum at the time of evaporation was 1.0×10^{-4} Pa and the film formation rate was 0.2 to 0.3 nm/sec.

Furthermore, aluminum tris quinolinol was deposited into a film of 40 nm in thickness by a vacuum evaporation method, resulting in the electron transport layer **6**. The film formation was performed under the conditions that the degree of vacuum at the time of evaporation was 1.0×10^{-4} Pa and the film formation rate was 0.2 to 0.3 nm/sec.

Next, after forming the cathode **4** in the same manner as in Example 1, the resultant structure was sealed.

When a direct current voltage of 8 V was applied onto the device thus obtained with the ITO electrode (anode **2**) provided as a positive electrode and the Al—Li electrode (cathode **4**) provided as a negative electrode, electric current was caused to flow into the device at a current density of 12.0 mA/cm^2 and blue-colored luminescence at a luminance of 16000 cd/m^2 was observed.

Furthermore, when the current density was kept at 10.0 mA/cm^2 and the voltage was applied for 100 hours, the deterioration of luminance was small; an initial luminance of 14000 cd/m^2 was reduced to a luminance of 13000 cd/m^2 after 100 hours.

EXAMPLES 12 TO 22

Devices were prepared and evaluated in the same way as that of Example 11, except that compounds shown in Table 2 were used in place of the exemplified compound No. 7. The results are shown in Table 2.

Comparative Examples 4 to 6

Devices were prepared and evaluated in the same way as that of Example 11, except that comparative compounds No. 1 to No. 3 were used in place of the exemplified compound No. 7. The results are shown in Table 2.

Furthermore, aluminum tris quinolinol is deposited into a film of 40 nm in thickness by a vacuum evaporation method, resulting in the electron transport layer **6**. The film formation was performed under the conditions that the degree of vacuum at the time of evaporation was 1.0×10^{-4} Pa and the film formation rate was 0.2 to 0.3 nm/sec.

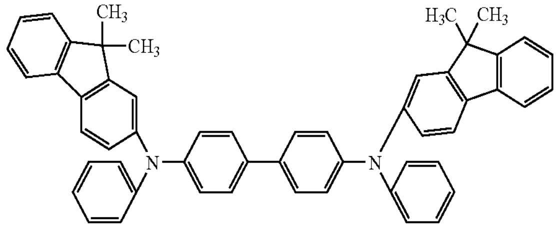
TABLE 2

		Initial stage		Durability		
Example No.	Exemplified compound No.	Applied voltage (V)	Luminance (cd/m^2)	Current density (mA/cm^2)	Initial luminance (cd/m^2)	Luminance after 100-hour (cd/m^2)
Example 11	2	8	16000	10.0	14000	13000
Example 12	5	8	10000	10.0	9000	8000
Example 13	7	8	14000	10.0	11000	9500
Example 14	9	8	12000	10.0	10000	9000
Example 15	11	8	13000	10.0	10000	8500
Example 16	16	8	10000	10.0	8000	7000
Example 17	21	8	8500	10.0	7500	7000
Example 18	26	8	9000	10.0	8000	7000
Example 19	30	8	9500	10.0	9000	8000
Example 20	33	8	10000	10.0	9000	7500
Example 21	37	8	10000	10.0	8500	8000
Example 22	38	8	9000	10.0	8000	7000
Comparative Example 4	Comparative 1	8	2000	10.0	1500	900
Comparative Example 5	Comparative 2	8	1500	10.0	1000	300
Comparative Example 6	Comparative 3	8	3000	10.0	2500	1000

EXAMPLE 23

A device having the structure shown in FIG. **3** was prepared.

On the transparent conductive support substrate similar to that in Example 1, a chloroform solution of a compound represented by the following structural formula was applied to form a film of 20 nm in thickness by a spin-coating method, resulting in the hole transport layer **5**.



Furthermore, the fluorene compound represented as the exemplified compound No. 1 and the arylamine compound represented as an exemplified compound No. AA-6 (weight ratio of 100:1) were deposited into a film with a thickness of 20 nm by a vacuum evaporation method to form the luminescent layer **3**. The film formation was performed under the conditions that the degree of vacuum at the time of evaporation was 1.0×10^{-4} Pa and the film formation rate was 0.2 to 0.3 nm/sec.

Next, after forming the cathode **4** in the same manner as in Example 1, the resultant structure was sealed. When a direct current voltage of 8 V was applied on the device thus obtained with an ITO electrode (anode **2**) provided as a positive electrode and an Al—Li electrode (cathode **4**) provided as a negative electrode, electric current was caused to flow into the device at a current density of 13.0 mA/cm^2 and blue-colored luminescence at a luminance of 32000 cd/m^2 was observed.

Furthermore, when the current density was kept at 10.0 mA/cm^2 and the voltage was applied for 100 hours, the deterioration of luminance was small; the initial luminance of 25000 cd/m^2 was reduced to a luminance of 22000 cd/m^2 after 100 hours.

EXAMPLES 24 TO 77

Devices were prepared and evaluated in the same way as that of Example 23, except that compounds shown in Tables 3 to 5 were used in place of the exemplified fluorene compound No. 1 and the exemplified arylamine compound No. AA-6, respectively. The results are shown in Tables 3 to 5.

Comparative Examples 7 to 9

Devices were prepared and evaluated in the same way as that of Example 23, except that the comparative compounds No. 1 to No. 3 were used in place of the exemplified compound No. 1. The results are shown in Table 5

TABLE 3

					Durability		
			Initial stage				Luminance
Example No.	Exemplified compound No.	Exemplified arylamine compound No.	Applied voltage (V)	Luminance (cd/m^2)	Current density (mA/cm^2)	Initial luminance (cd/m^2)	after 100-hour (cd/m^2)
Example 23	1	AA-6	8	32000	10.0	25000	22000
Example 24	1	AA-7	8	34000	10.0	28000	25000
Example 25	1	AA-10	8	35000	10.0	28000	24000
Example 26	1	AA-1	8	31000	10.0	24000	20000
Example 27	1	AA-2	8	31000	10.0	23000	20000
Example 28	8	AA-3	8	22000	10.0	19000	16000
Example 29	10	AA-4	8	24000	10.0	20000	17000
Example 30	10	AA-5	8	19000	10.0	17000	15000
Example 31	10	AA-12	8	23000	10.0	21000	17000
Example 32	12	AA-13	8	26000	10.0	22000	17000
Example 33	1	AA-14	8	32000	10.0	26000	21000
Example 34	2	AA-14	8	35000	10.0	27000	22000
Example 35	1	AA-15	8	34000	10.0	29000	25000
Example 36	1	AA-18	8	37000	10.0	31000	27000
Example 37	1	AA-21	8	35000	10.0	30000	25000
Example 38	5	AA-21	8	36000	10.0	29000	26000
Example 39	1	AA-24	8	38000	10.0	32000	28000
Example 40	14	AA-26	8	18000	10.0	17000	14000
Example 41	1	AA-27	8	30000	10.0	24000	21000

TABLE 4

			Initial stage		Durability		
Example No.	Exemplified compound No.	Exemplified arylamine compound No.	Applied voltage (V)	Luminance (cd/m^2)	Current density (mA/cm^2)	Initial luminance (cd/m^2)	Luminance after 100-hour (cd/m^2)
Example 42	10	AA-28	8	20000	10.0	18000	14000
Example 43	10	AA-29	8	16000	10.0	13000	10000
Example 44	17	AA-30	8	17000	10.0	15000	11000
Example 45	18	AA-31	8	22000	10.0	19000	17000
Example 46	1	AA-32	8	33000	10.0	27000	23000
Example 47	1	AA-33	8	34000	10.0	29000	25000
Example 48	1	AA-37	8	36000	10.0	31000	28000
Example 49	1	AA-38	8	31000	10.0	25000	21000
Example 50	1	AA-39	8	35000	10.0	30000	25000
Example 51	8	AA-44	8	23000	10.0	21000	18000
Example 52	1	AA-45	8	29000	10.0	23000	19000
Example 53	19	AA-46	8	29000	10.0	24000	19000
Example 54	1	AA-47	8	30000	10.0	24000	21000
Example 55	1	AA-48	8	27000	10.0	20000	16000
Example 56	8	AA-49	8	19000	10.0	16000	12000
Example 57	10	AA-50	8	25000	10.0	20000	15000
Example 58	10	AA-51	8	24000	10.0	20000	17000
Example 59	1	AA-52	8	30000	10.0	25000	22000
Example 60	28	AA-53	8	19000	10.0	14000	10000

TABLE 5

			Initial stage		Durability		
Example No.	Exemplified compound No.	Exemplified arylamine compound No.	Applied voltage (V)	Luminance (cd/m^2)	Current density (mA/cm^2)	Initial luminance (cd/m^2)	Luminance after 100-hour (cd/m^2)
Example 61	1	AA-54	8	31000	10.0	25000	23000
Example 62	1	AA-55	8	32000	10.0	27000	25000
Example 63	1	AA-58	8	31000	10.0	24000	22000
Example 64	2	AA-58	8	33000	10.0	27000	23000
Example 65	5	AA-55	8	30000	10.0	25000	22000
Example 66	28	AA-61	8	25000	10.0	22000	17000
Example 67	1	AA-62	8	27000	10.0	23000	20000
Example 68	1	AA-63	8	29000	10.0	23000	20000
Example 69	1	AA-64	8	27000	10.0	20000	18000
Example 70	1	AA-65	8	30000	10.0	24000	20000

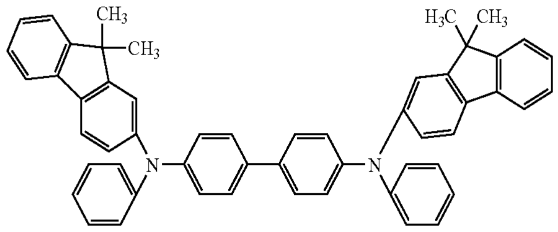
TABLE 5-continued

			Initial stage		Durability		
Example No.	Examplified compound No.	Exemplified arylamine compound No.	Applied voltage (V)	Luminance (cd/m^2)	Current density (mA/cm^2)	Initial luminance (cd/m^2)	Luminance after 100-hour (cd/m^2)
Example 71	31	AA-66	8	18000	10.0	15000	10000
Example 72	10	AA-67	8	16000	10.0	14000	9000
Example 73	1	AC-68	8	31000	10.0	26000	22000
Example 74	1	AC-69	8	28000	10.0	22000	18000
Example 75	1	AC-70	8	30000	10.0	23000	18000
Example 76	28	AC-71	8	21000	10.0	18000	14000
Example 77	28	AC-72	8	23000	10.0	20000	16000
Comparative Example 7	Comparative 1	AA-6	8	5000	10.0	4000	1500
Comparative Example 8	Comparative 2	AA-6	8	3500	10.0	2500	900
Comparative Example 9	Comparative 3	AA-6	8	6000	10.0	4000	1000

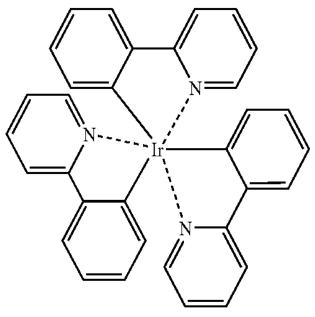
EXAMPLE 78

A device having the structure shown in FIG. **3** was prepared.

On the transparent conductive support substrate similar to that in Example 1, a chloroform solution of a compound represented by the following structural formula was applied to form a film of 20 nm in thickness by a spin-coating method, resulting in the hole transport layer **5**.



Furthermore, the fluorene compound represented as an exemplified compound No. 20 and a compound represented by the following structural formula (weight ratio of 100:5) were deposited into a film with a thickness of 20 nm by a vacuum evaporation method to form the luminescent layer **3**. The film formation was performed under the conditions that the degree of vacuum at the time of evaporation was 1.0x10^{-4} Pa and the film formation rate was 0.2 to 0.3 nm/sec.



Furthermore, bathophenanthroline (BPhen) is deposited into a film of 40 nm in thickness by a vacuum evaporation method, resulting in the electron transport layer **6**. The film formation was performed under the conditions that the degree of vacuum at the time of evaporation was 1.0x10^{-4} Pa and the film formation rate was 0.2 to 0.3 nm/sec.

Next, after forming the cathode **4** in the same manner as in Example 1, the resultant structure was sealed. When a direct current voltage of 8 V was applied on the device thus obtained with an ITO electrode (anode **2**) provided as a positive electrode and an Al—Li electrode (cathode **4**) provided as a negative electrode, electric current was caused to flow into the device at a current density of 10.0 mA/cm^2 and green-colored luminescence at a luminance of 11000 cd/m^2 was observed.

Furthermore, when the current density was kept at 7.0 mA/cm^2 and the voltage was applied for 100 hours, the deterioration of luminance was small; an initial luminance of 8000 cd/m^2 was reduced to a luminance of 6500 cd/m^2 after 100 hours.

EXAMPLES 79 TO 87

Devices were prepared and evaluated in the same way as that of Example 78, except that a compound shown in Table 6 was used in place of the exemplified compound No. 20. The results are shown in Table 6.

Comparative Examples 10 to 12

Devices were prepared and evaluated in the same way as that of Example 78, except that the comparative compounds No. 1 to No. 3 were used in place of the exemplified compound No. 20. The results are shown in Table 6.

TABLE 6

		Initial stage		Durability		
Example No.	Exemplified compound No.	Applied voltage (V)	Luminance (cd/m^2)	Current density (mA/cm^2)	Initial luminance (cd/m^2)	Luminance after 100-hour (cd/m^2)
Example 78	20	8	11000	7.0	8000	6500
Example 79	21	8	7000	7.0	6000	5000
Example 80	23	8	10000	7.0	8000	7000
Example 81	24	8	9500	7.0	7000	5500
Example 82	25	8	12000	7.0	9500	7000
Example 83	27	8	10000	7.0	7500	6500
Example 84	32	8	8000	7.0	6000	5000
Example 85	34	8	7000	7.0	6000	4500
Example 86	36	8	7500	7.0	7000	5500
Example 87	39	8	9000	7.0	8000	6500
Comparative Example 10	Comparative 1	8	3000	7.0	2000	800
Comparative Example 11	Comparative 2	8	1000	7.0	800	300
Comparative Example 12	Comparative 3	8	2000	7.0	1500	700

EXAMPLE 88

A device having the structure shown in FIG. **1** was prepared.

On a transparent conductive support substrate which was similar to that of Example 1, a solution prepared by dissolving 0.050 g of a fluorene compound represented as the exemplified compound No. 1 and 1.00 g of poly-N-vinyl carbazole (weight average molecular weight=63,000) in 80 ml of chloroform was applied to form a film of 120 nm in thickness by a spin-coating method (rotation speed=2000 rpm) to form the organic layer (luminescent layer **3**).

Next, after forming the cathode **4** in the same manner as in Example 1, the resultant structure was sealed. When a direct current voltage of 10 V was applied on the device thus obtained with an ITO electrode (anode **2**) provided as a positive electrode and an Al—Li electrode (cathode **4**) provided as a negative electrode, electric the current was caused to flow into the device at a current density of 8.5 mA/cm^2 and blue-colored luminescence at a luminance of 3200 cd/m^2 was observed.

Furthermore, when the current density was kept at 5.0 mA/cm^2 and the voltage was applied for 100 hours in the nitrogen atmosphere, the deterioration of luminance was small; the initial luminance of 2500 cd/m^2 was reduced to a luminance of 2100 cd/m^2 after 100 hours.

EXAMPLES 89 TO 92

Devices were prepared and evaluated in the same way as that of Example 88, except that a compound shown in Table 7 was used in place of the exemplified compound No. 1. The results are shown in Table 7.

Comparative Examples 13 to 15

Devices were prepared and evaluated in the same way as that of Example 88, except that the comparative compounds No. 1 to No. 3 were used in place of the exemplified compound No. 1. The results are shown in Table 7.

TABLE 7

		Initial stage		Durability		
Example No.	Exemplified compound No.	Applied voltage (V)	Luminance (cd/m^2)	Current density (mA/cm^2)	Initial luminance (cd/m^2)	Luminance after 100-hour (cd/m^2)
Example 88	1	10	3200	5.0	2500	2100
Example 89	6	10	3500	5.0	3000	2500
Example 90	7	10	3400	5.0	2800	2500
Example 91	15	10	2600	5.0	2200	1900
Example 92	28	10	2200	5.0	2000	1800
Comparative Example 13	Comparative 1	10	850	5.0	750	400
Comparative Example 14	Comparative 2	10	650	5.0	600	80
Comparative Example 15	Comparative 3	10	800	5.0	700	250

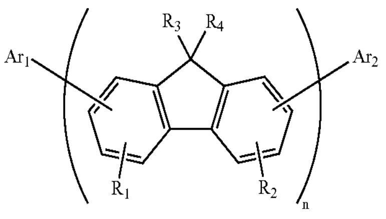
As described above with reference to the embodiments and the examples, the organic luminescent device using the fluorene compound represented by the general formula [1] provides luminescence with a high luminance by the application of a low voltage and is excellent in durability. In particular, the organic layer containing the fused polycyclic compound of the present invention is excellent as the electron transport layer and is also excellent as the luminescent layer.

Furthermore, the device can be prepared by using a vacuum evaporation method or a casting method, so that the device having a large area can be easily prepared at a relatively low cost.

The invention claimed is:

1. A fluorene compound represented by the following general formula [I]:

[I]

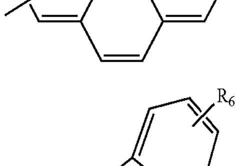


wherein R_1 and R_2 represent a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted heterocyclic group, a substituted amino group, a cyano group, or a halogen atom, in which R_1 themselves or R_2 themselves which are bonded to different fluorene groups may be identical to or different from each other and R_1 and R_2 which are bonded to the same fluorene group may be identical to or different from each other;

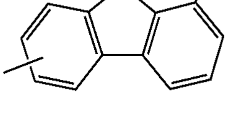
wherein R_3 and R_4 represent a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group, in which R_3 themselves or R_4 themselves which are bonded to different fluorene groups may be identical to or different from each other and R_3 and R_4 which are bonded to the same fluorene group may be identical to or different from each other;

wherein Ar_1 and Ar_2 represent a substituted or unsubstituted fused polycyclic aromatic group represented by one of the following general formulae [II], [III] and [V] through [IX]

[II]

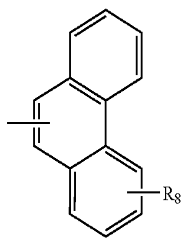


[III]

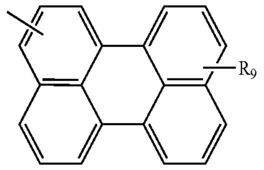


-continued

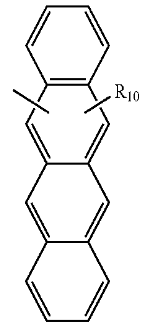
[V]



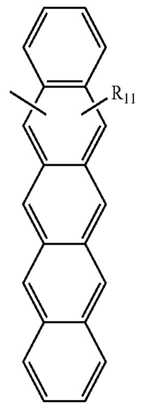
[VI]



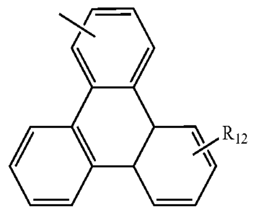
[VII]



[VIII]



[IX]



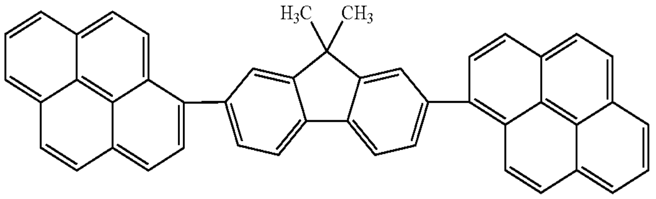
wherein R_5, R_6 and R_8 to R_{12} each represent a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted heterocyclic group, a substituted amino group, a cyano group, or a halogen atom;

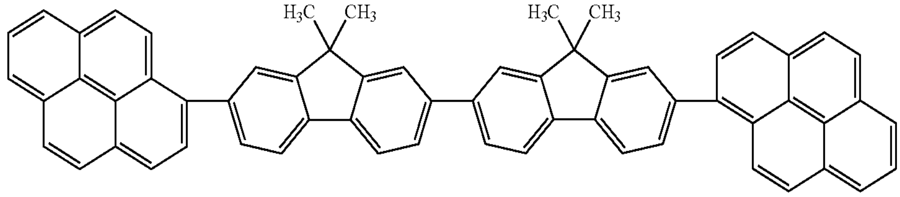
in which Ar_1 and Ar_2 may be identical to or different from each other; and

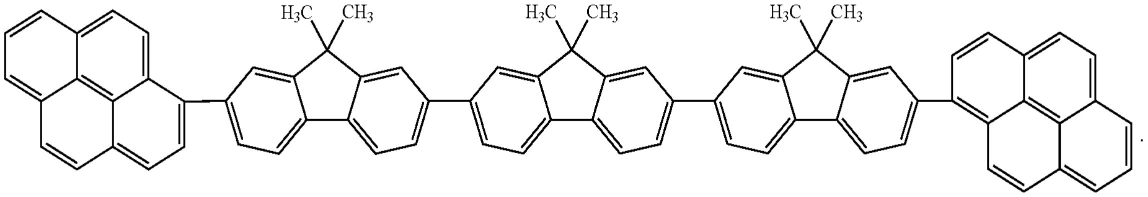
wherein n represents an integer of 1 to 10.

2. The fluorene compound according to claim **1**, wherein n is an integer of 1 to 3.

3. The fluorene compound according to claim **1**, wherein the compound is represented by one of the following structural formulas:





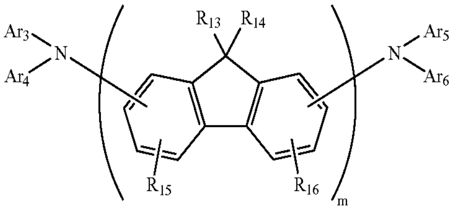


4. An organic luminescent device comprising at least a pair of electrodes including an anode and a cathode and one or a plurality of layers containing an organic compound sandwiched between the pair of electrodes, wherein at least one of the layers containing the organic compound contains at least one fluorene compound according to claim **1**.

5. The organic luminescent device according to claim **4**, wherein at least an electron transport layer or a luminescent layer among the layers containing an organic compound contains the at least one fluorene compound.

6. The organic luminescent device according to claim **4**, wherein at least a luminescent layer among the layers containing an organic compound contains the at least one fluorene compound and an arylamine compound represented by the following general formula [X]:

[X]



wherein R_{13} and R_{14} represent a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group, in which R_{13} themselves or R_{14} themselves which are bonded to different fluorene groups may be identical to or different from each other and R_{13} and R_{14} which are bonded to the same fluorene group may be identical to or different from each other;

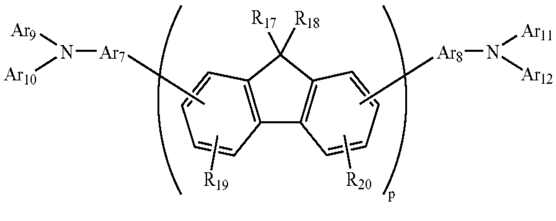
wherein R_{15} and R_{16} represent a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted heterocyclic group, a cyano group, or a halogen atom, in which R_{15} themselves or R_{16} themselves which are bonded to different fluorene groups may be identical to or different from each other and R_{15} and R_{16} which are bonded to the same fluorene group may be identical to or different from each other;

wherein Ar_3, Ar_4, Ar_5, and Ar_6 represent a substituted or unsubstituted aromatic group, a substituted or unsubstituted heterocyclic group, a substituted or unsubstituted fused polycyclic aromatic group, or a substituted or unsubstituted fused polycyclic heterocyclic group, in which Ar_3, Ar_4, Ar_5, and Ar_6 may be identical to or different from one another and Ar_3, Ar_4, Ar_5, and Ar_6 may be bonded with one another to form a ring; and

wherein m represents an integer of 1 to 10.

7. The organic luminescent device according to claim **4**, wherein at least a luminescent layer among the layers containing an organic compound contains the at least one fluorene compound and an arylamine compound represented by the following general formula [XI]:

[XI]



wherein R_{17} and R_{18} represent a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group, in which R_{17} themselves or R_{18} themselves which are bonded to different fluorene groups may be identical to or different from each other and R_{17} and R_{18} which are bonded to the same fluorene group may be identical to or different from each other;

wherein R_{19} and R_{20} represent a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted heterocyclic group, a cyano group, or a halogen atom, in which R_{19} themselves or R_{20} themselves which are bonded to different fluorene groups may be identical to or different from each other and R_{19} and R_{20} which are bonded to the same fluorene group may be identical to or different from each other;

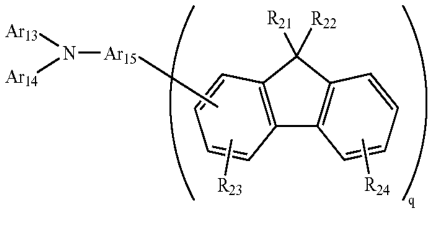
wherein Ar_7 and Ar_8 represent a divalent substituted or unsubstituted aromatic group or a substituted or unsubstituted heterocyclic group, in which Ar_7 and Ar_8 may be identical to or different from each other;

wherein Ar_9, Ar_{10}, Ar_{11}, and Ar_{12} represent a substituted or unsubstituted aromatic group, a substituted or unsubstituted heterocyclic group, a substituted or unsubstituted fused polycyclic aromatic group, or a substituted or unsubstituted fused polycyclic heterocyclic group, in which Ar_9 Ar_{10}, Ar_{11}, and Ar_{12} maybe identical to or different from one another and Ar_9, Ar_{10}, Ar_{11}, and Ar_{12} may be bonded with one another to form a ring; and

wherein p represents an integer of 1 to 10.

8. The organic luminescent device according to claim **4**, wherein at least a luminescent layer among the layers containing an organic compound contains the at least one fluorene compound and an arylamine compound represented by the following general formula [XII]:

[XII]



wherein R_{21} and R_{22} represent a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted heterocyclic group, in which R_{21} themselves or R_{22} themselves which are bonded to different fluorene groups may be identical to or different from each other and R_{21} and R_{22} which are bonded to the same fluorene group may be identical to or different from each other;

wherein R_{23} and R_{24} represent a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted heterocyclic group, a cyano group, or a halogen atom, in which R_{23} themselves or R_{24} themselves which are bonded to different fluorene groups may be identical to or different from each other and R_{23} and R_{24} which are bonded to the same fluorene group may be identical to or different from each other;

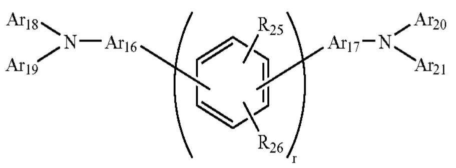
wherein Ar_{13} and Ar_{14} represent a substituted or unsubstituted aromatic group, a substituted or unsubstituted heterocyclic group, a substituted or unsubstituted fused polycyclic aromatic group, or a substituted or unsubstituted fused polycyclic heterocyclic group, in which Ar_{13} and Ar_{14} may be identical to or different from each other and Ar_{13} and Ar_{14} may be bonded to each other to form a ring;

wherein Ar_{15} represents a divalent substituted or unsubstituted aromatic group or a substituted or unsubstituted heterocyclic group; and

wherein q represents an integer of 1 to 10.

9. The organic luminescent device according to claim **4**, wherein at least a luminescent layer among the layers containing an organic compound contains the at least one fluorene compound and an arylamine compound represented by the following general formula [XIII]:

[XIII]



wherein R_{25} and R_{26} represent a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted heterocyclic group, a cyano group, or a halogen atom, in which R_{25} themselves or R_{26} themselves which are bonded to different phenylene groups may be identical to or different from each other and R_{25} and R_{26} which are bonded to the same phenylene group may be identical to or different from each other;

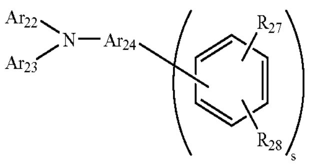
wherein Ar_{16} and Ar_{17} represent a divalent substituted or unsubstituted aromatic group or a substituted or unsubstituted heterocyclic group, in which Ar_{16} and Ar_{17} may be identical to or different from each other;

wherein Ar_{18}, Ar_{19}, Ar_{20}, and Ar_{21} represent a substituted or unsubstituted aromatic group, a substituted or unsubstituted heterocyclic group, a substituted or unsubstituted fused polycyclic aromatic group, or a substituted or unsubstituted fused polycyclic heterocyclic group, in which Ar_{18}, Ar_{19}, Ar_{20}, and Ar_{21} may be identical to or different from one another and AR_{18}, AR_{19}, Ar_{20}, and Ar_{21} may be bonded with one another to form a ring; and

wherein r represents an integer of 1 to 10.

10. The organic luminescent device according to claim **4**, wherein at least a luminescent layer among the layers containing an organic compound contains the at least one fluorene compound and an arylamine compound represented by the following general formula [XIV]:

[XIV]



wherein R_{27} and R_{28} represent a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aralkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted heterocyclic group, a cyano group, or a halogen atom, in which R_{27} themselves or R_{28} themselves which are bonded to different phenylene groups may be identical to or different from each other and R_{27} and R_{28} which are bonded to the same phenylene group may be identical to or different from each other;

wherein Ar_{22} and Ar_{23} represent a substituted or unsubstituted aromatic group, a substituted or unsubstituted heterocyclic group, a substituted or unsubstituted fused polycyclic aromatic group, or a substituted or unsubstituted fused polycyclic heterocyclic group, in which Ar_{22} and Ar_{23} may be identical to or different from each other and Ar_{22} and Ar_{23} may be bonded to each other to form a ring;

wherein Ar_{24} represents a divalent substituted or unsubstituted aromatic group or a substituted or unsubstituted heterocyclic group; and

wherein s represents an integer of 1 to 10.

11. The organic luminescent device according to claim **4**, wherein at least a luminescent layer among the layers containing an organic compound contains the at least one fluorene compound and an acetylene compound represented by the following general formula [XV]:

[XV]

$$Ar_{25}\!-\!\left(C\equiv C\right)_{t}\!-Ar_{26}$$

wherein Ar_{25} and Ar_{26} represent a substituted or unsubstituted aromatic group, a substituted or unsubstituted heterocyclic group, a substituted or unsubstituted fused polycyclic aromatic group, or a substituted or unsubstituted fused polycyclic heterocyclic group, in which Ar_{25} and Ar_{26} may be identical to or different from each other; and

wherein t represents an integer of 1 to 5.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 7,241,513 B2
APPLICATION NO. : 10/491745
DATED : July 10, 2007
INVENTOR(S) : Koichi Suzuki et al.

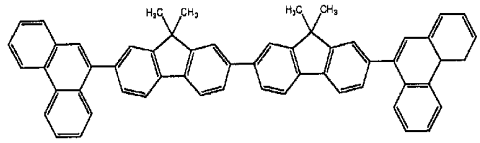
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

ON COVER PAGE AT (56) OTHER PUBLICATIONS

After “C.W. Tang, et al.,”: “pp. 913-915.” should read --pp. 913-915 (1987)--.

COLUMN 13

Ex. 27, “



27

” should read

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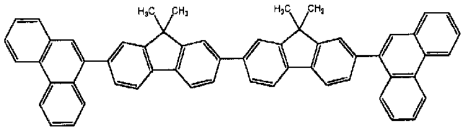
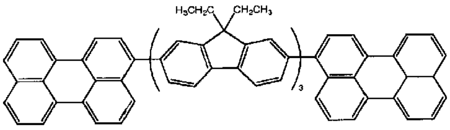


27

--; and

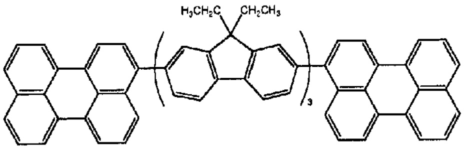
Ex. 31, “



31

” should read

--



31

--.

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

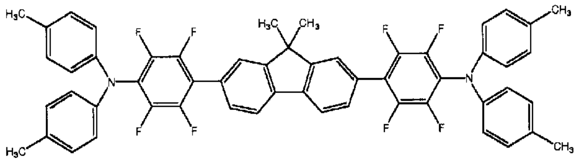
PATENT NO. : 7,241,513 B2 Page 2 of 4
APPLICATION NO. : 10/491745
DATED : July 10, 2007
INVENTOR(S) : Koichi Suzuki et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

COLUMN 25

AA-28

Ex. AA-28, "



"

should read

AA-28

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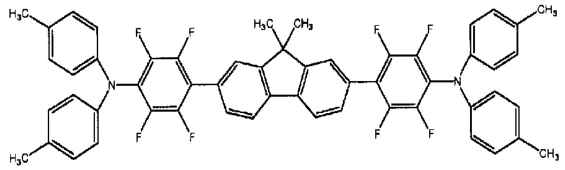
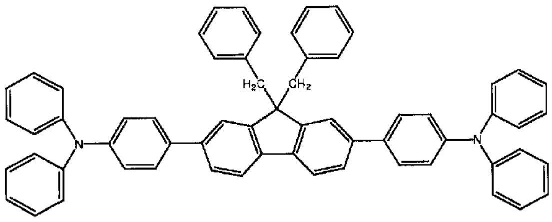


AA-29



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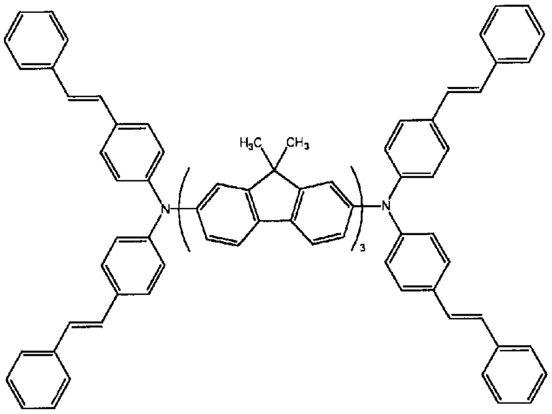
COLUMN 26

Ex. AA-25, "



"

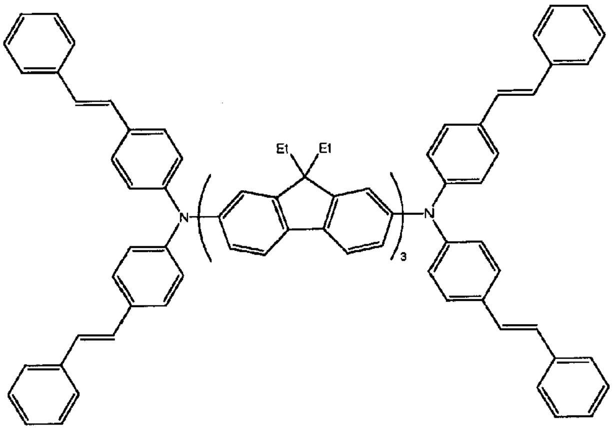
UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

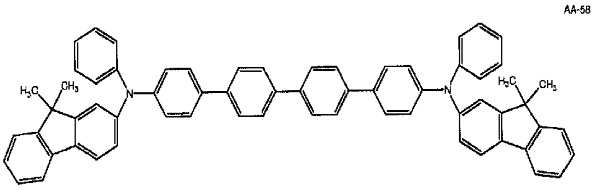
PATENT NO. : 7,241,513 B2
APPLICATION NO. : 10/491745
DATED : July 10, 2007
INVENTOR(S) : Koichi Suzuki et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

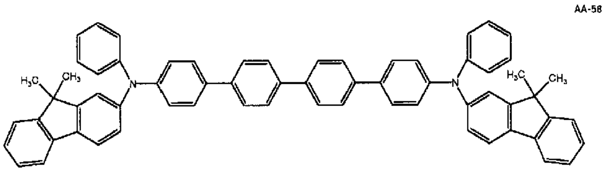
should read

--  --.

COLUMN 35

Ex. AA-58, "  "

should read

--  --.

COLUMN 55

Line 22, "$NaCO_3$ aq." should read --Na_2CO_3 aq.--.

UNITED STATES PATENT AND TRADEMARK OFFICE

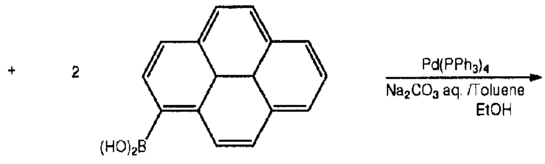
CERTIFICATE OF CORRECTION

PATENT NO. : 7,241,513 B2
APPLICATION NO. : 10/491745
DATED : July 10, 2007
INVENTOR(S) : Koichi Suzuki et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

COLUMN 56

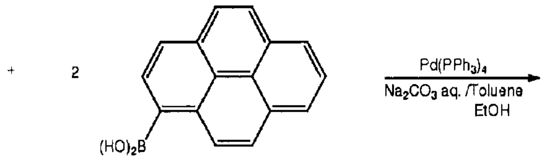
Lines 31-39, "



[2]

" should read

--



[2]

--.

COLUMN 75

Line 22, "maybe" should read --may be --.

COLUMN 76

Line 43, "AR_{18}, AR_{19}," should read --Ar_{18}, Ar_{19},--.

Signed and Sealed this

Twenty-seventh Day of May, 2008

Jon W. Dudas

JON W. DUDAS
Director of the United States Patent and Trademark Office

专利名称(译)	芴化合物和使用其的有机发光装置		
公开(公告)号	US7241513	公开(公告)日	2007-07-10
申请号	US10/491745	申请日	2003-08-12
[标]申请(专利权)人(译)	铃木KOICHI HIRAOKA MIZUHO 妹尾明弘 YAMADA NAOKI NEGISHI CHIKA 斋藤明仁 田中大作 八代RYOJI		
申请(专利权)人(译)	铃木KOICHI HIRAOKA MIZUHO 妹尾明弘 YAMADA NAOKI NEGISHI CHIKA 斋藤明仁 田中大作 八代RYOJI		
当前申请(专利权)人(译)	佳能株式会社		
[标]发明人	SUZUKI KOICHI HIRAOKA MIZUHO SENOO AKIHIRO YAMADA NAOKI NEGISHI CHIKA SAITOH AKIHITO TANAKA DAISAKU YASHIRO RYOJI		
发明人	SUZUKI, KOICHI HIRAOKA, MIZUHO SENOO, AKIHIRO YAMADA, NAOKI NEGISHI, CHIKA SAITOH, AKIHITO TANAKA, DAISAKU YASHIRO, RYOJI		
IPC分类号	H01L51/54 C07C13/567 C09K11/06 H01L51/50 C07C13/573 C07C13/62 C07C13/66 C07C22/08 C07C25/22 C07C211/61 C07C217/92 C07C255/58 C07D219/02		
CPC分类号	C07C13/567 C07C22/08 C07C25/22 C07C211/61 C07C217/92 C07C255/58 C09K11/06 C07C13/66 Y10T428/10 C07C2103/18 C07C2103/24 C07C2103/26 C07C2103/40 C07C2103/42 C07C2103/44 C07C2103/50 C07C2103/52 C09K2211/1003 C09K2211/1011 C09K2211/1014 Y10S428/917 C07C2603/18 C07C2603/24 C07C2603/26 C07C2603/40 C07C2603/42 C07C2603/44 C07C2603/50 C07C2603/52		
优先权	2002246447 2002-08-27 JP		
其他公开文献	US20040253389A1		

外部链接	Espacenet USPTO

摘要(译)

由下列通式[I]表示的芴化合物： 用于提供有机发光器件。这种装置具有显示高亮度和高效率的光输出，并且具有极高的耐久性。