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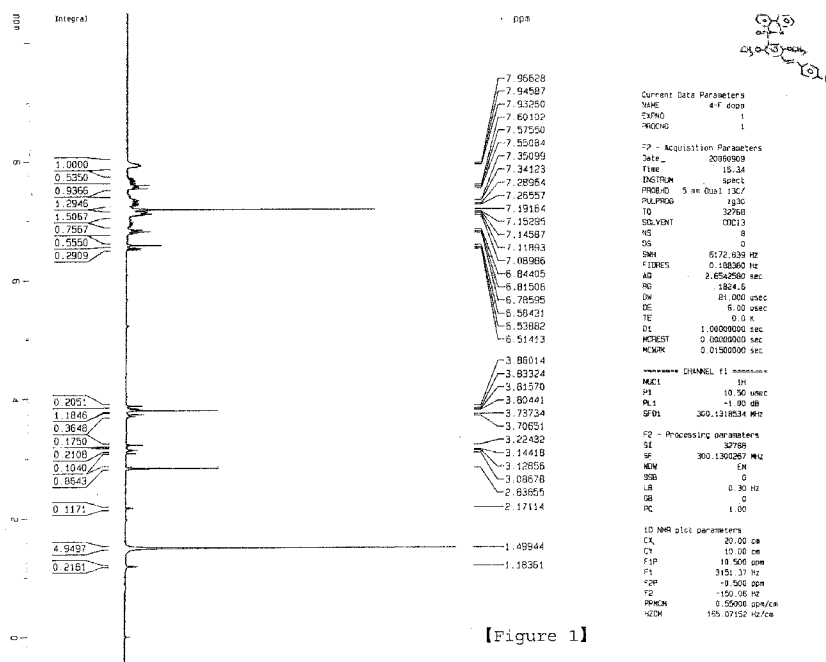
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(54) Title: PHOSPHAPHENANTHRENE COMPOUNDS AND ORGANIC LIGHT EMITTING DIODE USING THE SAME



[Figure 1]

(57) Abstract: The present invention relates to new phosphaphenanthrene compounds with excellent light emitting property and an organic light emitting diode (OLED) using the same.



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【DESCRIPTION】**【Invention Title】**

PHOSPHAPHENANTHRENE COMPOUNDS AND ORGANIC LIGHT EMITTING
DIODE USING THE SAME

5

【Technical Field】

The present invention relates to phosphaphenanthrene
compounds being phosphorous compounds with light emitting
property and an organic light emitting diode (hereinafter,
10 referred to as OLED) with excellent light emitting property
using the same.

【Background Art】

An OLED, which is a self-light emitting display, has
15 several advantages of wide viewing angle, rapid response speed,
low voltage driving, etc. and has currently been used as a
next-generation flat panel display.

A general OLED is basically configured of a multi-layer
thin film structure made of organic compounds, such as a hole
20 transporting layer, a light emitting layer, an electron
transporting layer, and a hole transporting layer between a
cathode and an anode of the OLED, etc. The OLED uses a
principle that when electricity is applied between both
electrodes, recombines electrons with holes at the light

emitting layer by the injection of electrons from the cathode and the injection of holes from the anode and emits light during the drop of energy level from an excited state to a ground state.

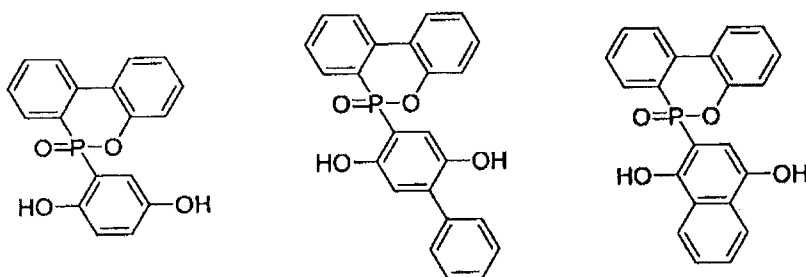
5 Since it has been announced that the OLED using aromatic diamine and Alq3 as materials for forming the light emitting layer is first developed by Eastman Kodak Co. (USA) on 1987 (Appl. Phys. Lett. p913, (1987)), a study intending to improve performance of naphthyldiamine-based light emitting materials
10 (US patent publication No. 6549345), fluorescent-type light emitting materials (US patent publication No. 6803121) such as anthracene-based materials, and phosphor-type light emitting materials such as light emitting materials using iridium complex with more excellent efficiency (US patent publication
15 No. 6858327) has been progressed. Today, the OLED has actually been applied to a small flat panel display, such as a mobile phone, etc.

 As blue light emitting compounds known up to now, there are distryl-based anthracene derivatives developed by
20 Idemitsu Kosan (EP 388, 768 (1990), Kyushu University (PRO, SRIE, 1910, 180(1993)), or the like. However, the blue light emitting materials have light emitting efficiency lower than light emitting bodies of other colors and should further be improved in thin film stability, heat resistance, etc.

Meanwhile, it is common to use host materials as the phosphor-type light emitting materials so as to maximize efficiency through energy transfer. For example, as low molecular phosphor hosts, there are 4,4'-N,N'-dicarbazole-biphenyl (CBP), 1,3-bis(9-carbazolyl)benzene (mCP), etc (Journal of Materials chemistry (2003) 13, 2157-2163; Journal of Materials chemistry (2005) 15, 2304-2315), as polymeric phosphor hosts, there are poly (N-vinylcarbazole)(PVK), etc. Recently, C.W. Tang group reported that an organic light emitting diode with a single layer structure and a multi-layer structure uses the polymeric polyvinylcarbazole as the phosphor host, instead of using the CBP and the mCP as the phosphor hosts (J. Appl. Phys., Vol.92, No.7, 3447). However, the organic light emitting diode has a disadvantage of deterioration of devices by driving heat generated when it is driven for a long time. In particular, since the material, such as the mCP, has low glass transition temp. -T_g, it is easily crystallized into the thin film material when the device is driven, thereby causing a large disadvantage of a change in color purity and a reduction in device lifetime by the driving heat. Therefore, in material development for the long-time and high-efficiency OLED, the heat resistance as an important variable in addition to the color purity and the efficiency has been considered as an important variable.

The inventors have developed materials with excellent light emitting property as well as heat resistance by introducing phosphaphenanthrene derivatives being phosphorous compounds as materials for the OLED from their continued efforts and have successfully performed the OLED configuration using the same.

The phosphaphenanthrene derivatives have been used as only flame retardant, etc. (KR patent publication 1993-3867), but have little example used as materials for the OLED. Polymer materials including phosphaphenanthrene compounds used as the materials for the OLED is known in US Laid-Open No. 2002-0193522 of the related art. As the phosphaphenanthrene compounds included in the polymer materials, the following three compounds are known. However, the known technology is limited to the following three compounds and is not applied to EL.



【Disclosure】

【Technical Problem】

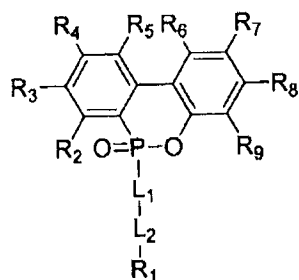
An object of the present invention provides

phosphaphenanthrene compounds with heat resistance and excellent light emitting property required for implementing a high-efficiency and long-lifetime device as described above. Another object of the present invention provides an organic light emitting diode containing prepared phosphaphenanthrene compounds as light-emitting materials.

【Technical Solution】

The present invention relates to phosphaphenanthrene compounds with excellent heat resistance and light emitting property represented by the following chemical formula 1 usable as core materials for an OLED and an organic light emitting diode including the same as light emitting materials.

[Chemical Formula 1]



[In the chemical formula 1, L_1 is chemical bond or (C_2-C_{10}) alkenylene, (C_6-C_{30}) arylene or NR_{11} , and alkenylene or arylene of the L_1 may further be substituted into at least one selected from (C_1-C_{22}) alkyl, (C_6-C_{30}) aryl, (C_2-C_{30}) heteroaryl, (C_6-C_{30}) ar or (C_1-C_{22}) alkyl, (C_1-C_{22}) alkyl (C_6-C_{30}) aryl, halogen, (C_1-C_{10})

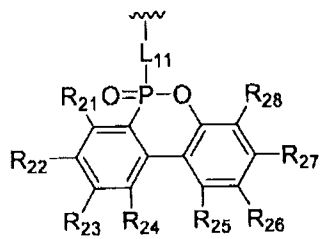
alkylsilyl, (C₆-C₃₀)arylsilyl, carboxylic acid, cyano, or OR₃₁;

L₂ is (C₂-C₁₀) alkenylene, (C₂-C₁₀) alkynylene, (C₆-C₃₀) arylene, (C₂-C₃₀) heteroarylene or -Ar₁-A- Ar₂-, and alkenylene, arylene, or heteroarylene of the L₂ may further be substituted
 5 into at least one selected from (C₁-C₂₂) alkyl, halogen, cyano, carboxylic acid, (C₁- C₁₀) alkylsilyl, (C₆-C₃₀) arylsilyl, (C₆-C₃₀) aryl, (C₂- C₃₀) heteroaryl, (C₆- C₃₀)ar (C₁- C₂₂)alkyl, (C₁-C₂₂)alkyl(C₆- C₃₀)aryl or OR₃₁;

Ar₁ and Ar₂ are independent from each other and are (C₆-
 10 C₃₀) arylene or (C₂- C₃₀) heteroarylene, and arylene or heteroarylene of the Ar₁ and Ar₂ may further be substituted into at least one selected from (C₁- C₂₂)alkyl, (C₆- C₃₀) aryl, (C₆- C₃₀) aryloxy, (C₂-C₃₀)heteroaryl, halogen, (C₁-C₁₀) alkylsilyl, (C₆-C₃₀) arylsilyl, (C₁- C₂₂)alkoxy, carboxylic acid
 15 or cyano;

A is NR₁₂, (O=)PR₁₃, SiR₁₄R₁₅, SO₂ or O;

R₁ is hydrogen, (C₁-C₂₂)alkyl, (C₆-C₃₀) aryl, (C₂-C₃₀) heteroaryl, halogen, cyano, (C₁-C₂₂)alkoxy, (C₆-C₃₀) aryloxy, (C₆-C₃₀) arylsulfonyl, mono- or di (C₁- C₁₀)alkylamino, mono- or
 20 di(C₆-C₃₀)arylamino, (C₂-C₇)alkenyloxy, (C₂-C₇) alkynyloxy, (C₂-C₇) alkenylcarbonyloxy, (C₂-C₇) alkynylcarbonyloxy, (C₁-C₁₀) alkylsilyl, (C₆-C₃₀) arylsilyl or



, and alkyl, aryl, heteroaryl, alkoxy, aryloxy, arylsulfonyl,

alkylamino, arylamino, alkenyloxy, alkynyloxy, alkylsilyl
 5 or arylsilyl of the R_1 may further be substituted into at least
 one selected from (C_1-C_{10}) alkyl, halogen, cyano, nitro,
 carboxylic acid, (C_6-C_{30}) aryl, mono- or $di(C_1-C_{10})$ alkylamino,
 mono- or $di(C_6-C_{30})$ arylamine, (C_1-C_{10}) alkylsilyl, or (C_6-C_{30})
 arylsilyl;

10 L_{11} is chemical bond or (C_2-C_{10}) alkenylene, (C_6-C_{30})
 arylene or NR_{16} , and alkenylene or arylene of the L_{11} may
 further be substituted into at least one selected from (C_1-C_{22})
 alkyl, (C_1-C_{22}) alkoxy, (C_3-C_{22}) cycloalkyl, (C_6-C_{30}) aryl, cyano,
 halogen, amino, mono- or $di(C_1-C_{10})$ alkylamino, mono- or $di(C_6-C_{30})$
 15 $C_{30})$ arylamine, nitro, or hydroxy;

R_2 to R_9 are independent from each other and are hydrogen,
 (C_1-C_{22}) alkyl, (C_1-C_{22}) alkyl including oxygen, nitrogen, or
 sulfur, (C_1-C_{22}) alkoxy, (C_3-C_{22}) cycloalkyl, (C_3-C_{22}) cycloalkyl
 (C_1-C_{22}) alkyl, (C_6-C_{30}) aryl, halogen, cyano, amino, mono- or
 20 $di(C_1-C_{10})$ alkylamine, mono- or $di(C_6-C_{30})$ arylamine, hydroxy,
 nitro, mono-or di-benzylamine, or (C_3-C_{10}) cycloalkylamine and

the R_2 to R_9 are combined with carbon of neighboring substituent by (C_3-C_5) alkylene or (C_3-C_5) alkenylene to form a fused ring, carbon of the fused ring may be substituted into heteroatoms selected from oxygen, sulfur, or nitrogen, and
5 alkyl, alkoxy, cycloalkyl, cycloalkylalkyl, aryl, or amino of the R_2 to R_9 may further be substituted into at least one selected from (C_1-C_{10}) alkyl, halogen, (C_6-C_{30}) aryl, (C_1-C_{10}) alkylsilyl, or (C_6-C_{30}) arylsilyl;

R_{11} to R_{16} are independent from each other and are (C_1-C_{22})
10 alkyl, (C_3-C_{22}) cycloalkyl, (C_6-C_{30}) aryl, mono- or di (C_1-C_{10}) alkylamino, mono- or di (C_6-C_{30}) arylamino, or amino, and alkyl, cycloalkyl, or aryl of the R_{11} to R_{16} may further be substituted into at least one selected from halogen, (C_1-C_{22}) alkyl, (C_6-C_{30}) aryl, (C_1-C_{22}) alkoxy, 3-member to 7-member
15 heterocycloalkyl including at least one of oxygen, nitrogen, or sulfur, or cyano;

R_{21} to R_{28} are independent from each other and are hydrogen, (C_1-C_{22}) alkyl, (C_1-C_{22}) alkyl including oxygen, nitrogen, or sulfur, (C_1-C_{22}) alkoxy, (C_3-C_{22}) cycloalkyl, (C_3-C_{22}) cycloalkyl
20 (C_1-C_{22}) alkyl, (C_6-C_{30}) aryl, halogen, cyano, amino, mono-or di (C_1-C_{10}) alkylamino, mono-or di (C_6-C_{30}) arylamino, hydroxy, nitro, mono-or di-benzylamino, or (C_3-C_{10}) cycloalkylamino and the R_{21} to R_{28} are combined with carbon of neighboring substituent by (C_3-C_5) alkylene or (C_3-C_5) alkenylene to form a

fused ring, carbon of the fused ring may be substituted into heteroatoms selected from oxygen, sulfur, or nitrogen, and alkyl, alkoxy, cycloalkyl, cycloalkylalkyl, aryl, or amino of the R_{21} to R_{28} may further be substituted into at least one
5 selected from (C_1-C_{10}) alkyl, halogen, (C_6-C_{30}) aryl, (C_1-C_{10}) alkylsilyl, or (C_6-C_{30}) arylsilyl; and

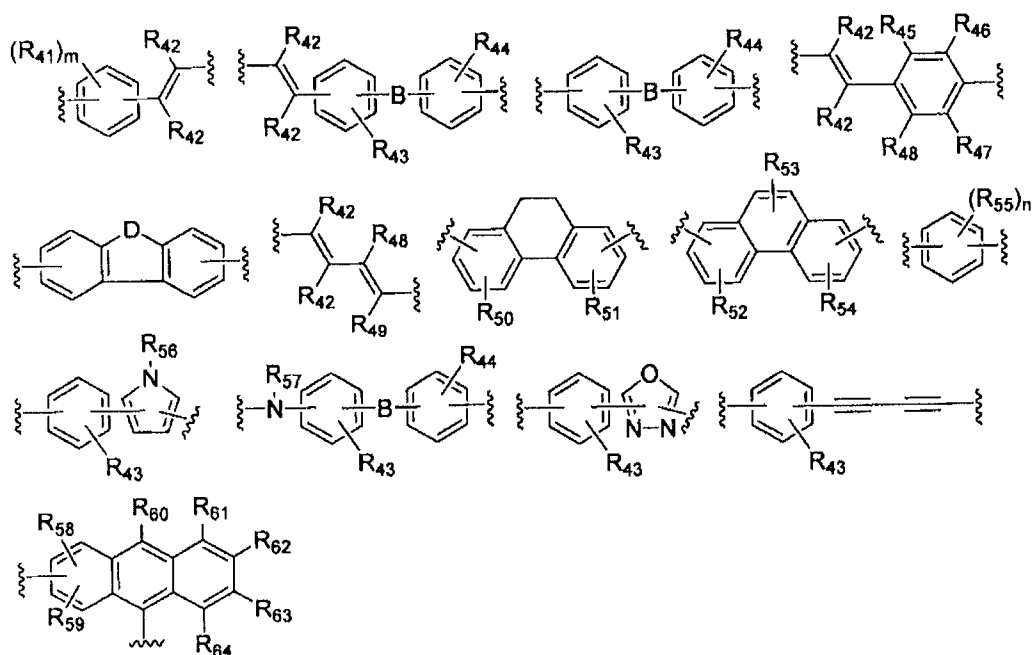
R_{31} is (C_1-C_{22}) alkyl, (C_6-C_{30}) aryl, (C_2-C_{10}) alkenyl, or (C_1-C_{22}) alkylcarbonyl and alkyl, aryl, or alkylcarbonyl of the R_{31} may further be substituted into at least one selected from
10 3-member to 5-member heterocycloalkyl including at least one from N, O, and S, (C_3-C_{22}) cycloalkyl, (C_2-C_{10}) alkynyl, (C_2-C_{10}) alkenyl, cyano, or halogen.]

The (C_6-C_{30}) aryl group is preferably (C_6-C_{18}) aryl group and more preferably (C_6-C_{12}) aryl group. A concrete example of
15 the aryl group may include an aromatic group, such as phenyl, naphthyl, biphenyl, tetrahydronaphthyl, indanyl, fluorenyl, phenanthrenyl, anthracenyl, triphenylenyl, pyrenyl, crycenyl, naphhtacenyl.

The (C_2-C_{30}) heteroaryl group is preferably (C_3-C_{18})
20 heteroaryl group and more preferably (C_3-C_{12}) heteroaryl group. The heteroaryl group may include 1 to 3 heteroatoms selected among N, O, P, or S as aromatic ring structure atoms, wherein the other aromatic ring structure atoms mean an aryl group being carbon. The hetero aryl group includes, for example, a

divalent aryl group forming N-oxide or quaternary salt by oxidizing or quartering heteroatoms in the ring. A representative example may include furyl, pyranyl, isobenzofuranyl, pyrrolyl, imidazolyl, pyrazolyl, isothiazolyl, isoxazolyl, tetrazolyl, pyridyl, pyrazinyl, pyrimidinyl, pyridazinyl, indolizinyll, isoindolyl, indolyl, indazolyl, quinolizinyll, isoquinolyl, quinolyl, carbazolyl, phenanthridinyl and N-oxide (for example, pyridyl N-oxide, quinolyl N-oxide) corresponding thereto, and quaternary salt thereof, or the like, but is not limited thereto.

In the phosphaphenanthrene compounds of the chemical formula 1 according to the present invention, $\{L_1-L_2\}$ is selected from the following structure, but is not limited thereto.



[B is chemical bond or NR_{71} , $(\text{O}=\text{})\text{PR}_{71}$, $\text{SiR}_{73}\text{R}_{74}$, SO_2 , or O;

D is $\text{CR}_{81}\text{R}_{82}$, NR_{83} , O, S, or SO_2 ;

5 R₃₁ is (C₁-C₂₂) alkyl, (C₆-C₃₀) aryl, (C₂-C₁₀) alkenyl, or
(C₁-C₂₂) alkylcarbonyl, and alkyl, alkenyl, or alkylcarbonyl of
the R₃₁ may further be substituted into at least one selected
from 3-member to 5-member heterocycloalkyl including at least
one from N, O, and S, (C₃-C₂₂)cycloalkyl, (C₂-C₁₀) alkynyl, (C₂-
10 C₁₀) alkenyl, cyano, or halogen;

R₄₁ to R₆₄ are independent from each other and are hydrogen, (C₁-C₂₂) alkyl, (C₆-C₃₀) aryl, halogen, (C₂-C₃₀) heteroaryl, cyano, carboxylic acid, (C₁-C₁₀) alkylsilyl, (C₆-C₃₀) arylsilyl, (C₆-C₃₀) ar(C₁-C₂₂) alkyl, (C₁-C₂₂)alkyl(C₆-C₃₀)aryl or OR₃₁, or R₄₅ and R₄₆ or R₄₇ and R₄₈ are coupled with (C₃-C₅) alkylene or (C₃-

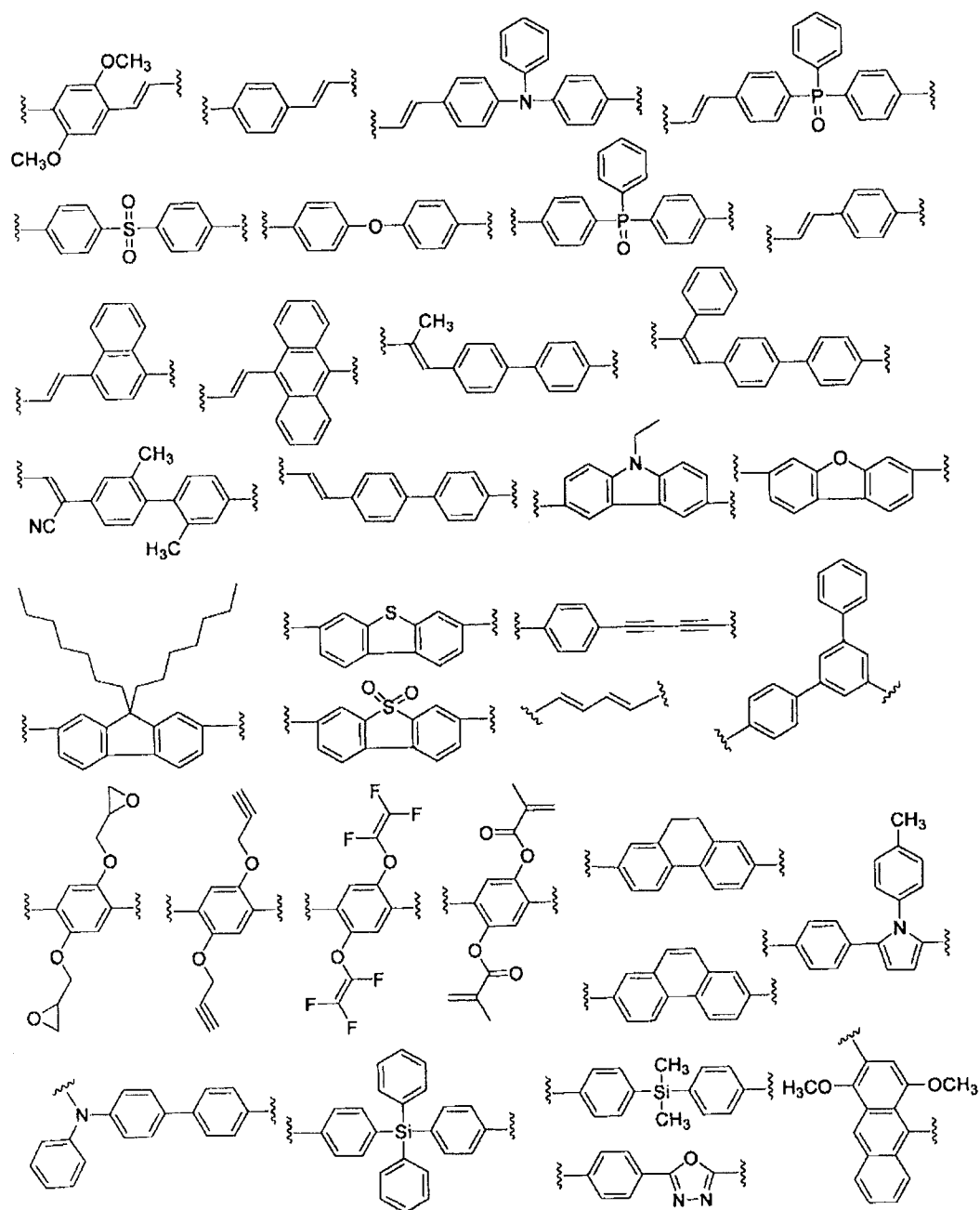
C₅) alkenylene to form a fused ring, and carbon of the fused ring may be substituted into heteroatoms selected from oxygen, sulfur, or nitrogen;

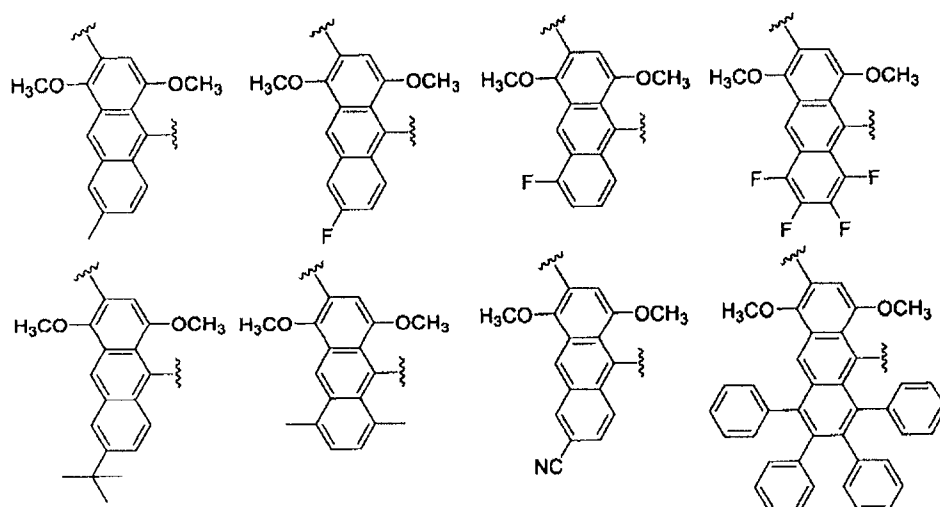
R₇₁ to R₇₄ are independent from each and are (C₁-C₂₂) alkyl, (C₃-C₂₂)cycloalkyl, (C₆-C₃₀) aryl, mono- or di(C₁-C₁₀)alkylamino, mono- or di(C₆-C₃₀)arylamino, or amino, and alkyl, cycloalkyl, or aryl of the R₇₁ to R₇₄ may further be substituted into at least one selected from halogen, (C₁-C₂₂) alkyl, (C₆-C₃₀) aryl, (C₁-C₂₂) alkoxy, 3-member to 7-member heterocycloalkyl including at least one of oxygen, nitrogen, or sulfur, or cyano;

R₈₁ to R₈₃ are independent from each other and are hydrogen, (C₁-C₂₂) alkyl, (C₆-C₃₀) aryl, halogen, (C₂-C₃₀) heteroaryl, cyano, carboxylic acid, (C₁-C₁₀) alkylsilyl, (C₆-C₃₀) arylsilyl, (C₆-C₃₀)ar(C₁-C₂₂)alkyl, (C₁-C₂₂)alkyl(C₆-C₃₀)aryl, or (C₁-C₂₂)alkoxy; and

m and n are independent from each other and are integers of 1 to 4.]

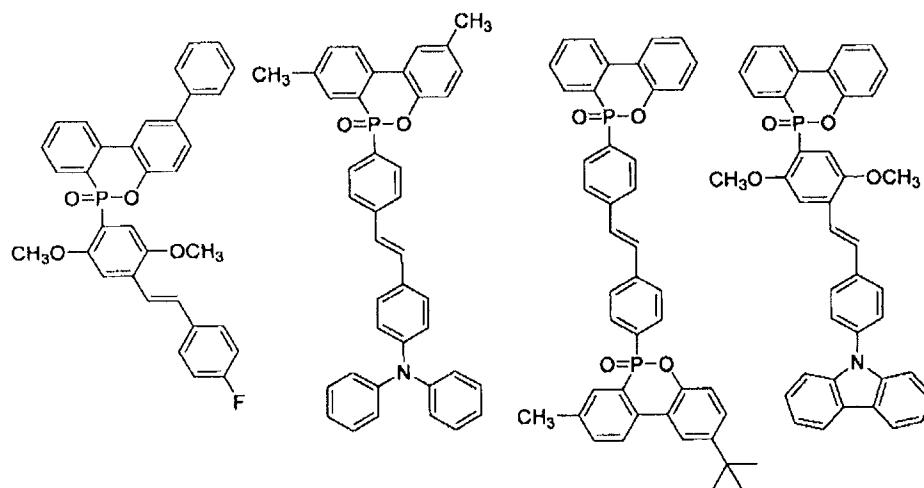
Specifically, the $\{L_1-L_2\}$ is selected from the following chemical structure.

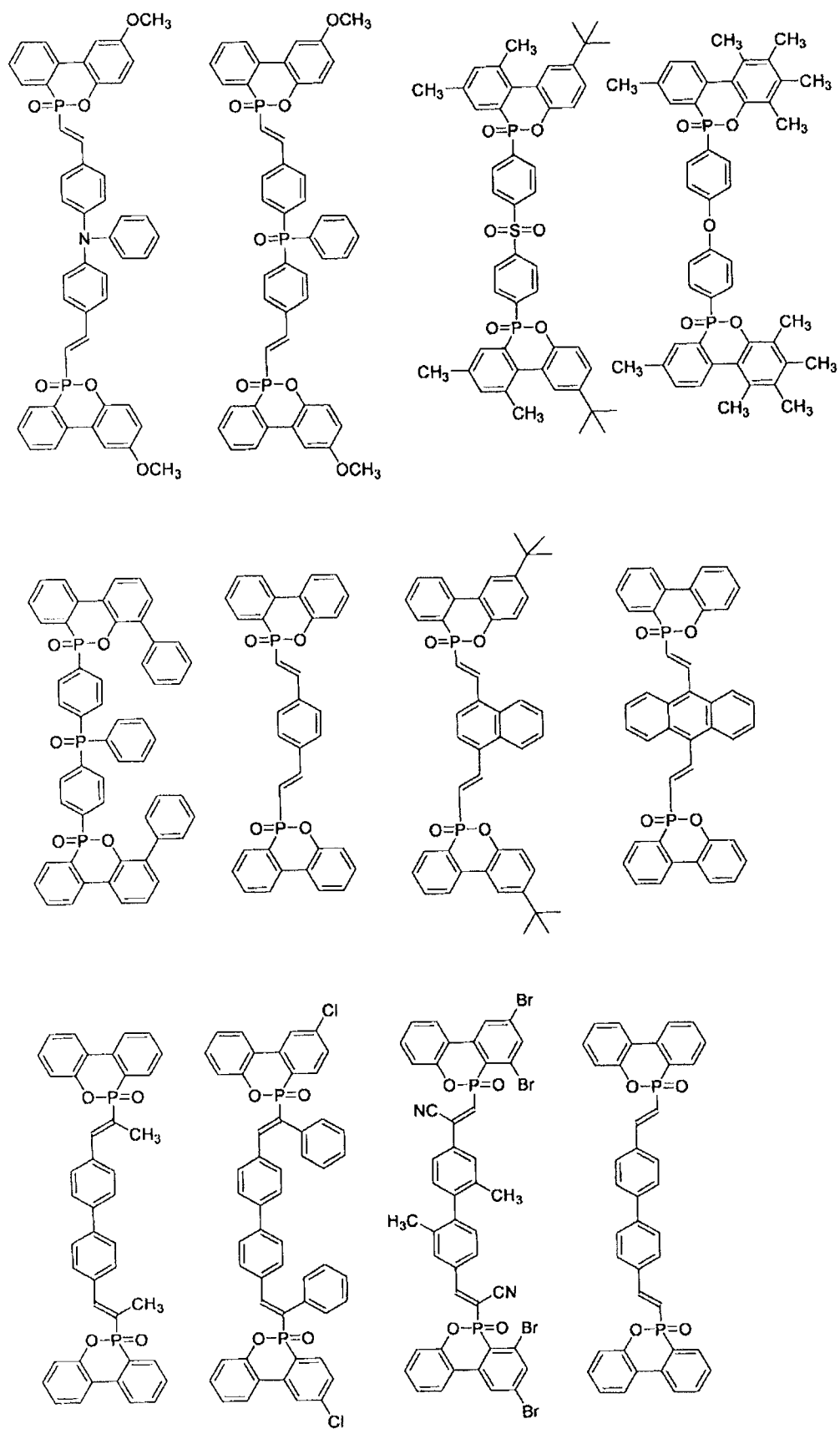


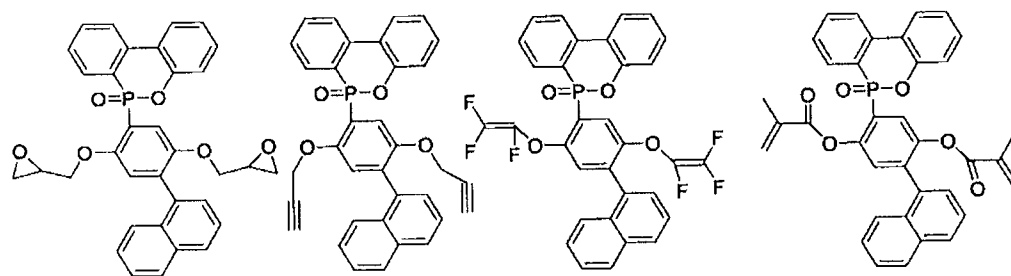
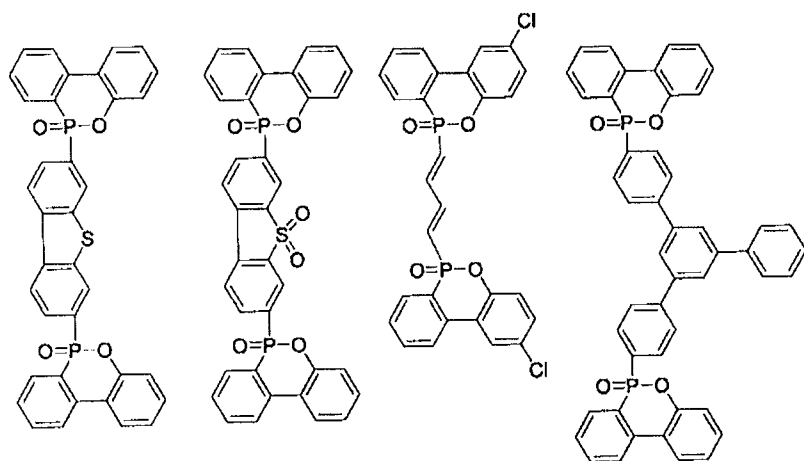
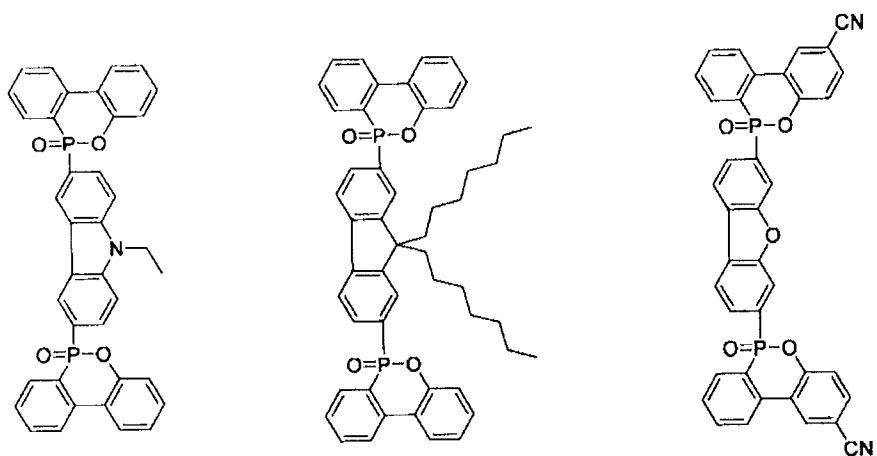


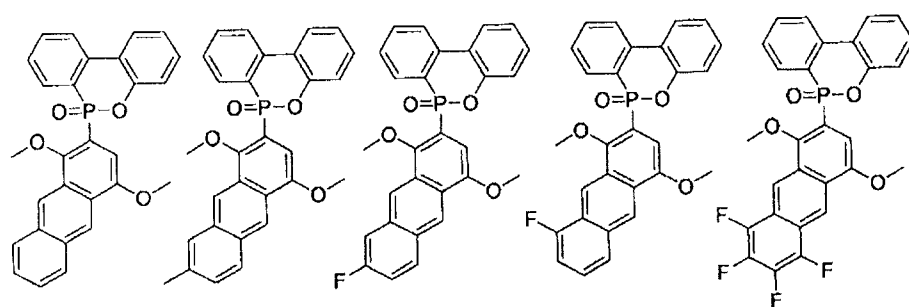
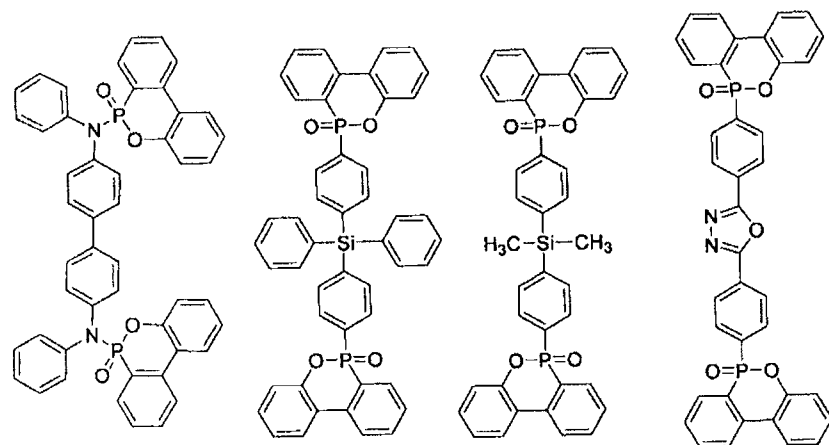
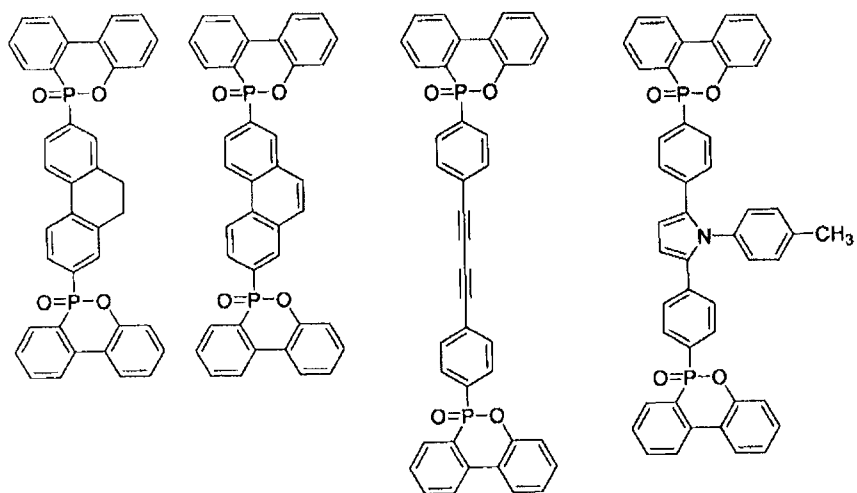
The phosphaphenanthrene compounds according to the present invention may be illustrated by the following compounds, but the present invention is not limited to the

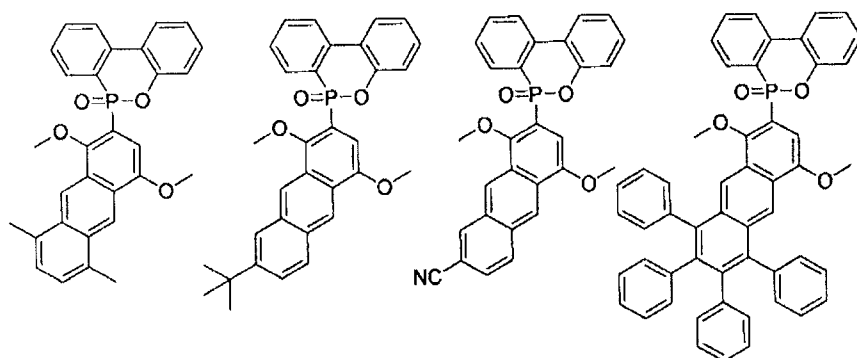
5 following compounds.











【Advantageous Effects】

Also, the present invention provides an organic EL diode wherein the electron transporting layer, the light emitting layer, and the light emitting/electron transporting layer include the phosphaphenanthrene compounds represented by the chemical formula 1. The phosphaphenanthrene compounds represented by the chemical formula 1 are useful as electron transporting materials or light emitting materials. In particular, the phosphaphenanthrene compounds according to the present invention are useful as electron transporting materials. Therefore, the OLED wherein the electron transporting layer or the light emitting layer includes the phosphaphenanthrene compounds according to the present invention can be driven at low power and can maintain the light emitting efficiency even when it is driven for a long time, making it possible to achieve the long lifetime of the OLED.

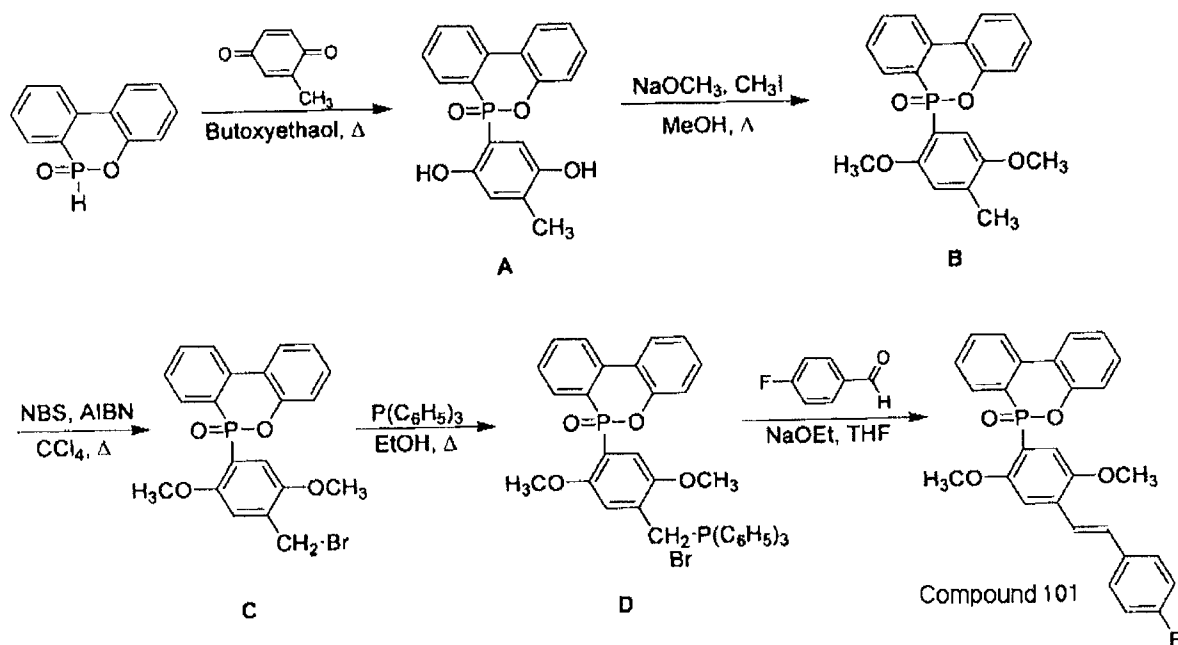
Meanwhile, in preparing the phosphaphenanthrene compounds

represented by the chemical formula 1 of the present invention, any known methods can be used when the structure of final materials is the same, including the method described herein. In other words, solvent, reaction temperature, concentration, or catalyst, or the like, for preparing the phosphaphenanthrene compounds represented by the chemical formula 1 of the present invention are not specially limited and have nothing to do with preparing yield. For example, a reaction formula 1 will be described in detail.

10 In the case of the reaction formula 1, derivatives in a phenol form are synthesized by an addition reaction of phosphaphenanthrene derivatives to quinone. In order to make the synthesized derivatives into halogenated methyl, hydroxy group is alkoxylated. The halogenated methyl reacts with the triphenyl phosphonium so that it is synthesized as precursor 15 capable of performing Wittig reaction. Monomers used in the Wittig reaction, which are generally phosphonium salt and phenyl aldehyde derivatives, react with strong base catalyst, such as sodium or alkyl lithium, using organic solvent, such as tetrahydrofuran.

20

[Reaction Formula 1]



5 【Description of Drawings】

The above and other objects, features and advantages of the present invention will become apparent from the following description of preferred embodiments given in conjunction with the accompanying drawings, in which:

10 Fig. 1 is a ^1H -NMR spectrum of compound 101 prepared according to a first embodiment;

 Fig. 2 is ultraviolet absorption (UV-vis) and photoluminescence (PL) spectrums of an OLED to which the compound 101 prepared according to the first embodiment is
15 applied;

Fig. 3 is ultraviolet absorption (UV-vis) and photoluminescence (PL) spectrums of an OLED to which compound 108 prepared according to a eighth embodiment is applied;

Fig. 4 is ultraviolet absorption (UV-vis) and photoluminescence (PL) spectrums of an OLED to which compound 109 prepared according to a ninth embodiment is applied;

Fig. 5 is an electroluminescence (EL) spectrum of the OLED to which the compound 101 prepared according to the first embodiment is applied;

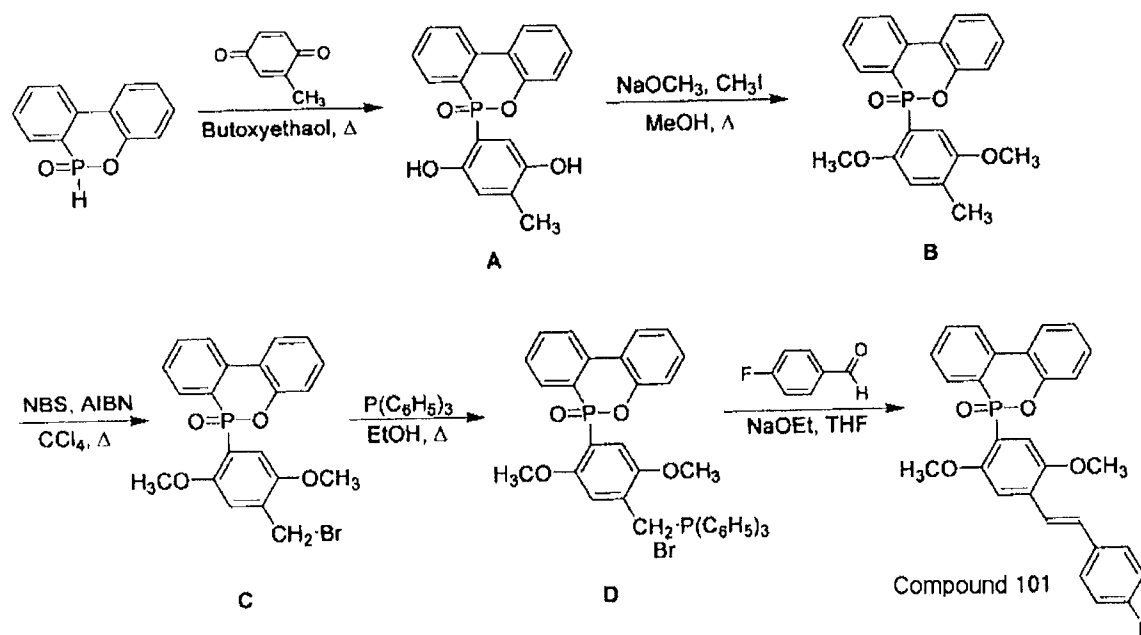
Fig. 6 is an electroluminescence (EL) spectrum of the OLED to which the compound 108 prepared according to the eighth embodiment is applied; and

Fig. 7 is an electroluminescence (EL) spectrum of the OLED to which the compound 109 prepared according to the ninth embodiment is applied

【Best Mode】

Hereinafter, a method of preparing new phosphaphenanthrene compounds according to the present invention will be described with reference to embodiments of the present invention. However, the following embodiments are provided to help understanding of the present invention and therefore, the scope of the present invention is not limited to the embodiments.

[First Embodiment] Synthesis of 10-{4'-[2-(4-fluorophenyl)-vinyl]-2',5'-dimethoxyphenyl}-9-oxa-10-phosphaphenanthrene-10-oxide (compound 101)



5 Synthesis of 10-(4'-methyl-2', 5'-dihydroxyphenyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (compound A)

9,10-dihydroxy-9-oxa-10-phosphaphenanthrene-10-oxide 200g (0.93mol), methyl-1,4-benzoquinone 107g (0.88mol), and 2-butoxyethanol 300ml are put in a 1000ml single round bottom flask under argon atmosphere and are then heated and recirculated for 12 hours. After the reaction is completed, they are slowly cooled at a normal temperature to produce precipitates. The precipitates are filtrated under reduced pressure using methanol to obtain targeted compound, that is, 10-(4'-methyl-2', 5'-dihydroxyphenyl)-9,10-dihydro-9-oxa-10-

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phosphaphenanthrene-10-oxide (compound A) as a white solid 254g (yield: 81%).

^1H NMR(CDCl_3), δ =2.15(s, 3H, CH_3), 6.24(d, 1H, aromatic), 6.75(d, 1H, aromatic), 7.08~7.96(m, 8H, aromatic)

5 Synthesis of 10-(4'-methyl-2', 5'-dimethoxyphenyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (compound B)

During 10-(4'-methyl-2', 5'-dihydroxyphenyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (compound A) 20g (0.06mol) and methanol 200ml are put and stirred in a 500ml
10 single round bottom flask under argon atmosphere, sodium methoxide 7g(0.13mol) and iodomethane 83g(0.59mol) are sequentially put in the flask. Thereafter, they are heated and recirculated for 4 hours. After the reaction is completed, methanol 100ml is further added thereto and ethyl acetate is
15 extracted by 200ml three times. The extracted filtrates are washed two times with distilled water, is dried using magnesium sulfate anhydride, and are then filtrated under reduced pressure to obtain targeted compound, that is, 10-(4'-methyl-2',
5'-dimethoxyphenyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (compound B) as a white solid
20 12.6g (yield: 58%).

^1H NMR(CDCl_3), δ =2.17(s, 3H, CH_3), 3.14(s, 3H, OCH_3), 3.81(s, 3H, OCH_3), 6.56(d, 1H, aromatic), 7.03~7.94(m, 9H, aromatic)

Synthesis of 10-(4'-bromomethyl-2', 5'-dimethoxyphenyl)-
9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (compound
C)

During 10-(4'-methyl-2',5'-dimethoxyphenyl)-9,10-dihydro-
5 9-oxa-10-phosphaphenanthrene-10-oxide (compound B) 1g
(27mmol) and tetrachloromethane 20ml are put and stirred in a
100ml single round bottom flask under argon atmosphere, AIBN
0.02g(1.08mmol) and N-bromosuccinimide 0.97g (54mmol) are
sequentially put in the flask. Thereafter, they are then
10 heated and recirculated for 12 hours. After the reaction is
completed, dichloromethane 80ml is further added thereto, is
washed two times with distilled water, is dried using
magnesium sulfate anhydride, and then filtrated under reduced
pressure to obtain a brown solid 1.23g. This is separated from
15 a by-product using developing solution (ethyl acetate/N-
hexane:1/2) by quick chromatography to obtain targeted
compound, that is, 10-(4'-bromomethyl-2',5'-dimethoxyphenyl)-
9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (compound C)
as a white solid 0.42g (yield:33%).

20 ^1H NMR(CDCl_3), δ =3.14(s, 3H, OCH_3), 3.86(s, 3H, OCH_3),
4.41(s, 3H, CH_2Br), 6.72(d, 1H, aromatic), 7.08~7.95(m, 9H,
aromatic)

Synthesis of 10-(4'-triphenyl phosphonium bromide-2', 5'-
dimethoxyphenyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-

oxide(compound D)

10-(4'-bromomethyl-2',5'-dimethoxyphenyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide(compound C) 14.85g (0.03mol) and ethanol 100mg are put and stirred in a 500ml single round bottom flask and triphenylphosphine 10.26g (0.04mol) are then put in the flask. Thereafter, they are heated and recirculated for 4 hours. After the reaction is completed, they are slowly cooled at a normal temperature. Precipitates produced after the cooling are filtered using diethyl ether to obtain targeted compound, that is, 10-(4'-triphenyl phosphonium bromide-2',5'-dimethoxyphenyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide(compound D) as a white solid 23.31g (yield:99%).

¹H NMR(CDCl₃), δ=3.14(s, 3H, OCH₃), 3.26(s, 3H, OCH₃), 5.15(t, 1H, CH₂P), 5.67(t, 1H, CH₂P), 7.16~8.00(m, 15H, aromatic)

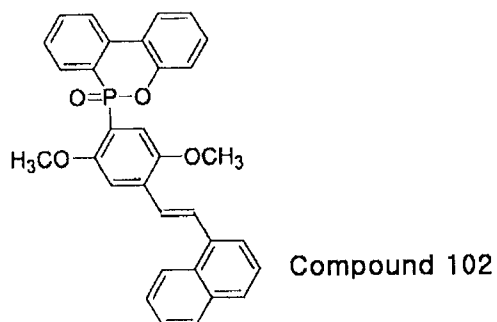
Synthesis of 10-{4'-[2-(4-fluorophenyl)-vinyl]-2',5'-dimethoxyphenyl}-9-oxa-10-phosphaphenanthrene-10-oxide (compound 101)

After 10-(4'-triphenyl phosphonium bromide-2',5'-dimethoxyphenyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide(compound D) 5g (69.6mmol), 4-fluoro benzaldehyde 0.95g(76.6mmol), and tetrahydrofuran anhydride 50ml are put

and stirred in a 100ml single round bottom flask under argon atmosphere, 21%-sodium ethoxide 3.3ml (21% ethanol solution, 83.5mmol) is slowly dropped thereinto. They are stirred at a normal temperature for 2 hours. After the reaction is completed, they are evaporated under reduced pressure. This mixture is obtained as targeted compound, that is, a white solid 2.92g (yield:89%) of 10-{4'-[2-(4-fluorophenyl)-vinyl]-2',5'-dimethoxyphenyl}-9-oxa-10-phosphaphenanthrene-10-oxide (compound 101) using developing solution (ethyl acetate /N-hexane:1/1).

^1H NMR (CDCl_3), δ =2.83 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 6.51~7.96 (m, 16H, vinyl and aromatic)

[Second embodiment] Synthesis of 10-{4'-[2-(naphthalene)-vinyl]-2',5'-dimethoxyphenyl}-9-oxa-10-phosphaphenanthrene-10-oxide (compound 102)

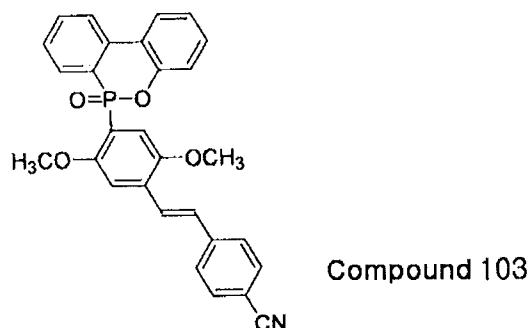


After 10-(4'-triphenyl phosphonium bromide-2',5'-dimethoxyphenyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (compound D) 1g (69.6mmol), 1-naphthylaldehyde

0.21g(13.9mmol), and tetrahydrofuran anhydride 50ml are put and stirred in a 100ml single round bottom flask under argon atmosphere, 21%-sodium ethoxide 3.3ml(21% ethanol solution, 83.5mmol) is slowly dropped thereinto. They are stirred at a normal temperature for 2 hours. After the reaction is completed, they are evaporated under reduced pressure. This mixture is obtained as targeted compound, that is, a white solid 0.39g (yield:56%) of 10-{4'-[2-(naphthalene)-vinyl]-2',5'-dimethoxyphenyl}-9-oxa-10-phosphaphenanthrene-10-oxide (compound 102) using developing solution (ethyl acetate /N-hexane:1/1).

^1H NMR(CDCl_3), δ =2.83(s, 3H, OCH_3), 3.80(s, 3H, OCH_3), 6.51~7.96(m, 19H, vinyl and aromatic)

[Third embodiment] Synthesis of 10-{4'-[2-(cyanophenyl)-vinyl]-2',5'-dimethoxyphenyl}-9-oxa-10-phosphaphenanthrene-10-oxide (compound 103)

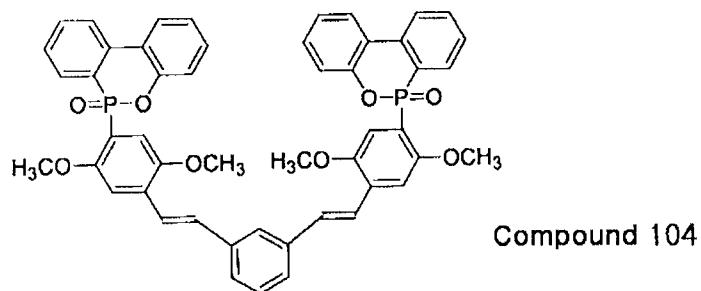


After 10-(4'-triphenyl phosphonium bromide-2',5'-dimethoxyphenyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-

oxide (compound D) 1g (14mmol), 4-cyano benzaldehyde 0.2g (15.4mmol), and tetrahydrofuran anhydride 30ml are put and stirred in a 50ml single round bottom flask under argon atmosphere, 21%-sodium ethoxide 0.66ml (21% ethanol solution, 5 16.8mmol) is slowly dropped thereinto. They are stirred at a normal temperature for 2 hours. After the reaction is completed, they are evaporated under reduced pressure. This mixture is obtained as targeted compound, that is, a white solid 0.42g (yield: 65%) of 10-{4'-[2-(4-cyanophenyl)-vinyl]-
10 2',5'-dimethoxyphenyl}-9-oxa-10-phosphaphenanthrene-10-oxide (compound 103) using developing solution (ethyl acetate /N-hexane: 1/1).

^1H NMR (CDCl_3), δ =3.30 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3),
15 6.92~7.93 (m, 16H, vinyl and aromatic)

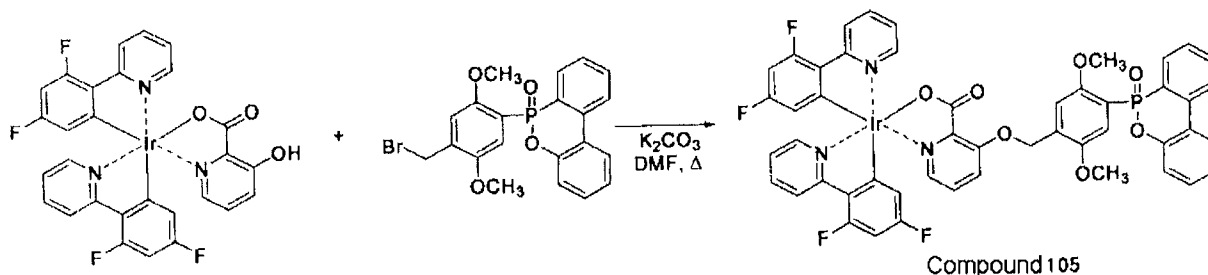
[Fourth embodiment] Synthesis of 10-{4'-[2-(3-phenylvinyl)-2',5'-dimethoxyphenyl]-9-oxa-10-phosphaphenanthrene-10-oxide)-vinyl]-2',5'-
dimethoxyphenyl }-9-oxa-10-phosphaphenanthrene-10-oxide
20 (compound 104)



After 10-(4'-triphenyl phosphonium bromide-2',5'-dimethoxyphenyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (compound D) 1g (14mmol), benzene 1,3-carbaldehyde 0.1g (15.4mmol), and tetrahydrofuran anhydride 50ml are put and stirred in a 50ml single round bottom flask under argon atmosphere, 21%-sodium ethoxide 0.66ml (21% ethanol solution, 16.8mmol) is slowly dropped thereinto. They are stirred at a normal temperature for 2 hours. After the reaction is completed, they are evaporated under reduced pressure. This mixture is obtained as targeted compound, that is, a white solid 0.23g (yield:20%) of 10-{4'-[2-(3-phenylvinyl)-2',5'-dimethoxyphenyl]-9-oxa-10-phosphaphenanthrene-10-oxide)-vinyl]-2',5'-dimethoxyphenyl}-9-oxa-10-phosphaphenanthrene-10-oxide (compound 104) using developing solution (ethyl acetate /N-hexane:1/1).

^1H NMR (CDCl_3), $\delta=3.22(\text{s}, 3\text{H}, \text{OCH}_3)$, $3.70(\text{s}, 3\text{H}, \text{OCH}_3)$, $6.40\sim 7.96(\text{m}, 28\text{H}, \text{vinyl and aromatic})$

[Fifth embodiment] Synthesis of 10-{4'-[2-(FIrpic)]-2',5'-dimethoxyphenyl}-9-oxa-10-phosphaphenanthrene-10-oxide (compound 105)



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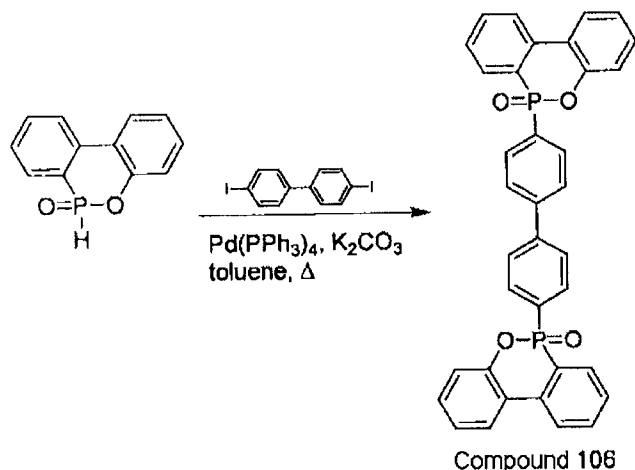
FIrpic alcohol 0.72g (0.11mmol) and 10-(4'-bromomethyl-2',5'-dimethoxyphenyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide 0.5g (0.11mmol) are mixed with dimethylformamide 15ml in a 100ml flask and potassium carbonate 0.46g(0.33mmol) is put in the flask. After the addition, they are reacted by heat and recirculation at 100°C for 48 hours. After the reaction, dichloro methane 100ml is added thereto and is then washed with water to produce filtrates. Water in the filtrates is removed by magnesium sulfate. The dichloro methane is removed and concentrated under reduced pressure to obtain targeted compound, that is, 10-{4'-[2-(FIrpic)]-2',5'-dimethoxyphenyl}-9-oxa-10-phosphaphenanthrene-10-oxide (compound 105) as a yellow solid 0.98g (yield: 81%).

¹H NMR(CDCl₃), δ=3.24(s, 3H, OCH₃), 3.71(s, 3H, OCH₃),

20

4.52(s, 2H, CH₂), 6.40~7.96(m, 27H, vinyl and aromatic)

[Sixth embodiment] Synthesis of 10-biphenyl-(4-(9-oxa-10-phosphaphenanthrene)-9-oxa-10-phosphaphenanthrene) 10-oxide (compound 106)



5

9,10-dihydroxy-9-oxa-10-phosphaphenanthrene-10-oxide 10g(0.05mol), potassium carbonate 6.4g(0.05mol), 4-4'-iodobiphenyl 9.38g(0.023mol), palladium catalyst 1.6g(23mol), and dioxane 60ml are put in a 100ml single round bottom flask under argon atmosphere. They are heated and recirculated for 24 hours. After the reaction is completed, they are slowly cooled at a normal temperature, are distilled under reduced pressure, are dissolved in dichloro methane solution, and are washed with distilled water several times. They are dried and filtered by magnesium sulfate to remove and concentrate solvent under reduced pressure and is purified by silica gel column chromatography method (ethyl acetate:hexane=1:1) to obtain targeted compound, that is, 10-biphenyl-(4-(9-oxa-10-

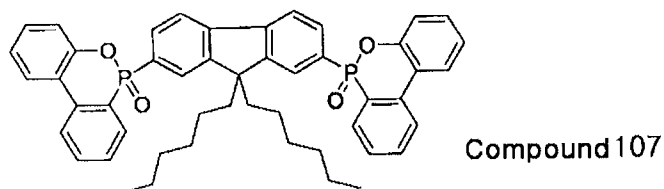
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phosphaphenanthrene)-9-oxa-10-phosphaphenanthrene 10-oxide (compound 106) as a white solid 18.32g (yield:68%)

^1H NMR(CDCl_3), δ =6.56(d, 1H, aromatic), 7.01~7.99(m, 23H, aromatic)

5 [Seventh Embodiment] Synthesis of 9,9-dihexyl -(2,7-(9-oxa-10-phosphaphenanthrene)-9-oxa-10-phosphaphenanthrene 10-oxide) fluorene (compound 107)



9,10-dihydroxy-9-oxa-10-phosphaphenanthrene-10-oxide

10 10g(0.05mol), potassium carbonate 6.4g(0.05mol), 4,4'-iodine 9,9-dihexyl fluorene 13.5g(0.023ml), palladium catalyst 1.6g (23mmol), and dioxane 100ml are put in a 100ml single round bottom flask under argon atmosphere. They are heated and recirculated for 48 hours. After the reaction is completed,

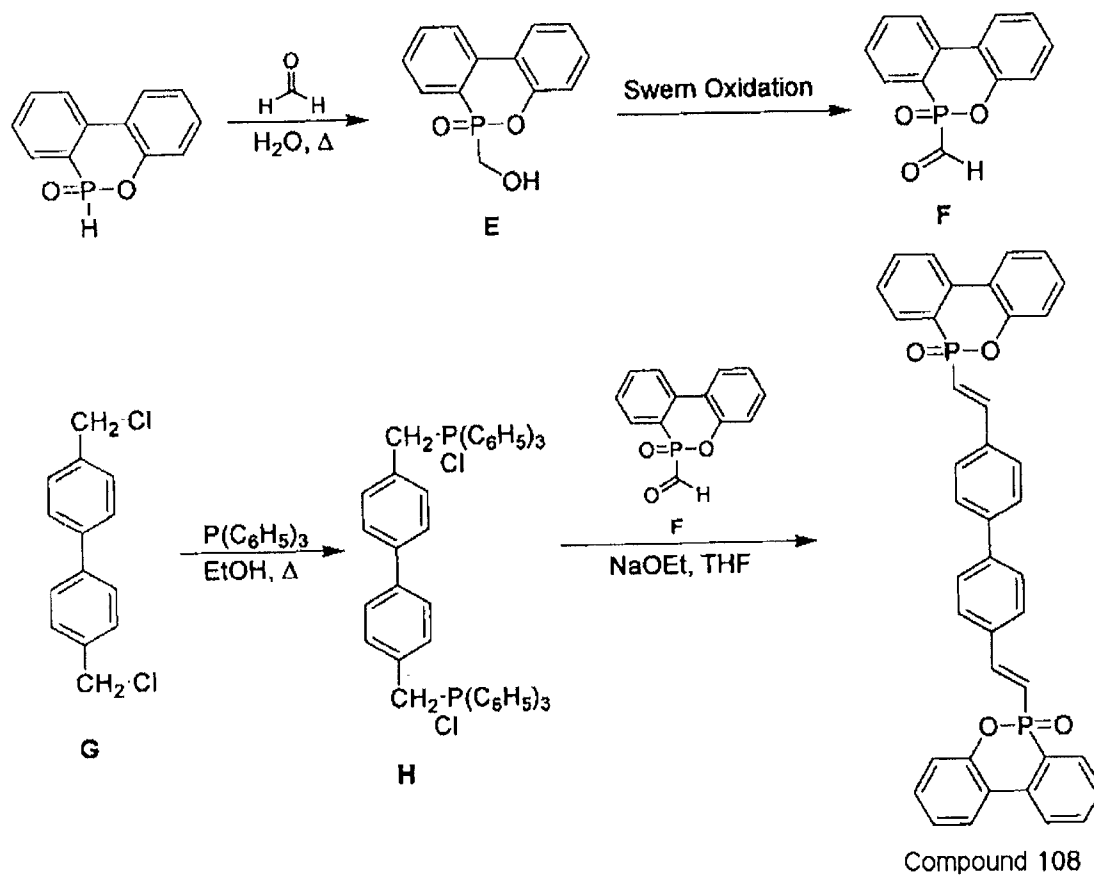
15 they are slowly cooled at a normal temperature, are distilled under reduced pressure, are dissolved in dichloro methane solution, and are then washed with distilled water several times. This is dried and filtered by magnesium sulfate to remove and concentrate solvent under reduced pressure and is

20 then purified by silica gel column chromatography method (ethyl acetate:hexane=1:1) to obtain targeted compound, that is, 9,9-dihexyl -(2,7-(9-oxa-10-phosphaphenanthrene)-9-oxa-10-

phosphaphenanthrene 10-oxide) fluorene (compound 107) as a white solid 14.4g (yield:40%)

^1H NMR(CDCl_3), $\delta=0.35\sim 2.1(\text{m}, 26\text{H}, \text{dihexyl group}), 7.05\sim 8.29(\text{m}, 22\text{H}, \text{aromatic})$

5 [Eighth Embodiment] Synthesis of 10-(2-p-9-oxa-10-phosphaphenanthrene-vinyl)-9-oxa-10-phosphaphenanthrene 10-oxide (compound 108)



Synthesis of (10-oxo-10H-9-oxa-10-phosphaphenanthrene -

10 10-yl)-methanol (compound E)

9-oxa-10-phosphaphenanthrene 10-oxide 20g (0.09mol) and paraformaldehyde 3.0g (0.10mol) are dissolved in distilled

water 100ml and are then heated and recirculated for 6 hours. After the reaction is completed, they are cooled at normal temperature and at the same time, is slowly added with diethyl ether to produce precipitates. The produced precipitates are
5 filtered and dried in a reduced pressure oven to obtain targeted compound, that is, (10-oxo-10H-9-oxa-10-phosphaphenanthrene -10-yl)-methanol (compound E) as a white solid 20.3g (yield: 89%).

Synthesis of (10-oxo-10H-9-oxa-10 phosphaphenanthrene-10-
10 carbaldehyde (compound F)

Purified dichloro methane anhydride 100ml is cooled using dry ice and acetone. When the cooling is completed, oxalyl chloride 42.5ml(0.05mol) and dimethyl sulfur oxide 5.76ml (0.08mol) are added. Thereafter, they are stirred for 10
15 minutes. Then, (10-oxo-10H-9-oxa-10-phosphaphenanthrene-10-yl)-methanol (compound F) 10g (0.04mol) is added thereto. Thereafter, they are stirred for 1 hour. Then, triethylamine 22ml is slowly added thereto. Thereafter, they are stirred at a normal temperature for 12 hours. When the reaction is
20 completed, distilled water 100ml is added thereto. Thereafter, solution is extracted using dichloro methane. The extracted solution is processed using 1N-hydrochloric acid water, saturated sodium bicarbonate solution, saturated brine water, or the like, and is dried using magnesium sulfate anhydride.

The dried solution is filtered under reduced pressure and evaporated under reduced pressure to obtain brown solution. The obtained product is used for reaction in immediately subsequent step.

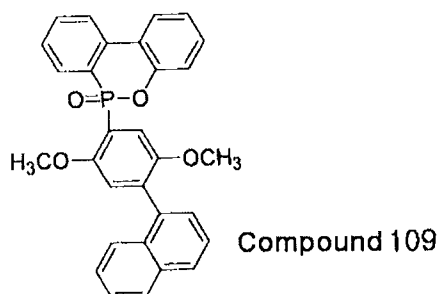
5 Synthesis of 10-(2-p-9-oxa-10-phosphaphenanthrene-vinyl)-
9-oxa-10-phosphaphenanthrene 10-oxide (compound 108)

The product 7.73g (0.03 mol), phosphonium salt 12.7g(0.02mol), and tetrahydrofuran anhydride 100ml are added to make suspension. Thereafter, they are stirred and at the
10 same time, 21%-sodium ethoxide solution is dropped therein. They are stirred for 24 hours after the dropping is completed. Thereafter, ethyl acetate 100ml is added. Then, they are washed with distilled water several times. solution is dried using magnesium sulfate anhydride and filtered under reduced
15 pressure and evaporated under reduced pressure to obtain a dark yellow solid. The produced solid is purified using ethyl acetate:hexane (1:1) developing solution to remove by-product, that is, triphenyloxide, thereby obtaining targeted compound, that is, 10-(2-p-9-oxa-10-phosphaphenanthrene-vinyl)-9-oxa-10-
20 phosphaphenanthrene 10-oxide (compound 108) as a white solid 6.42g (yield:32%).

^1H NMR(CDCl_3), δ =5.40(d, 4H, vinyl), 6.88~8.89(m, 24H, aromatic)

[Ninth Embodiment] Synthesis of 10-{4'-[2-naphthyl]}-

2',5'-dimethoxyphenyl}-9-oxa-10-phosphaphenanthrene-10-oxide
(compound 109)



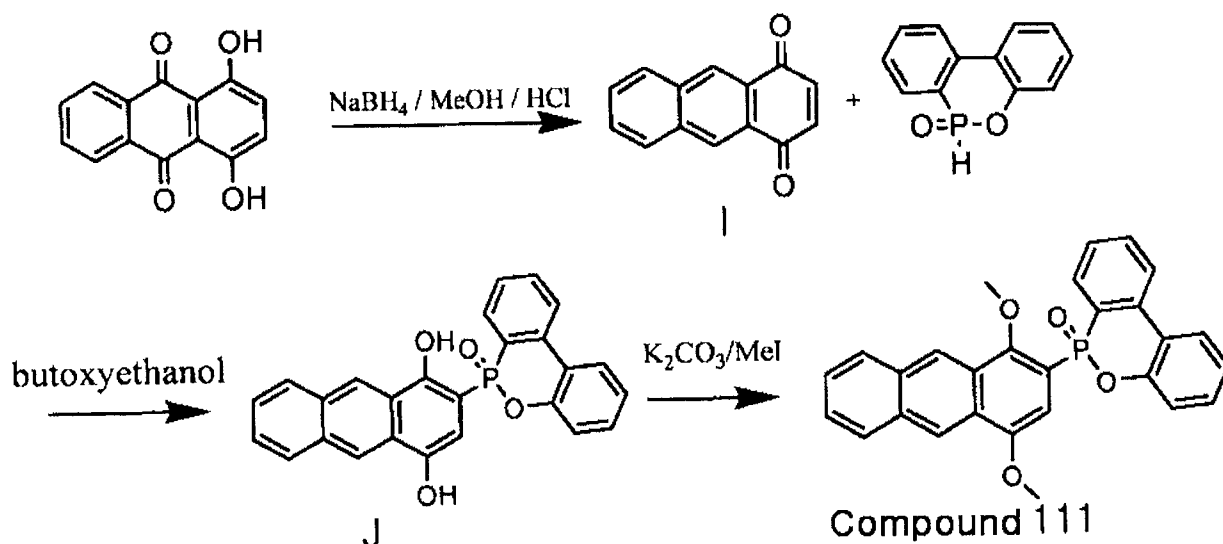
9,10-dihydroxy-9-oxa-10-phosphaphenanthrene-10-oxide

5 3.97g (0.02mol), 2-naphthyl-1,4-benzoquinone 4.05g (0.02mol),
and 2-ethoxyethanol 10ml are put in a 100ml single round
bottom flask under argon atmosphere. They are heated and
recirculated for 12 hours. After the reaction is completed,
they are slowly cooled at a normal temperature to produce
10 precipitates. This precipitates are filtered under reduced
pressure using methanol to obtain a powder 3.61g of light
color. This powder to which Iodomethane 4.5g (0.03mol),
potassium carbonate 4.43g (0.03mol), acetone 50ml are
sequentially added is heated and circulated for 4 hours. After
15 the reaction is completed, this is extracted using dichloro
methane and distilled water. This is dried using magnesium
sulfate anhydride and then filtered under reduced pressure to
remove solvent, thereby obtaining targeted compound, that is,
10-{4'-[2-naphthyl]-2',5'-dimethoxyphenyl}-9-oxa-10-
20 phosphaphenanthrene-10-oxide (compound 109) as a white solid

3.6g (yield:44%).

^1H NMR(CDCl_3): δ =2.15(s, 3H, OCH_3), 6.24(d, 1H, aromatic), 6.75(d, 1H, aromatic), 7.08~7.96(m, 8H, aromatic)

5 [Tenth Embodiment] Synthesis of 10-(1,4-dimethoxyanthracene-2-yl)-9-oxa-10-phosphaphenanthrene-10-oxide (compound 111)



10

Synthesis of 1,4-anthraquinone (compound I)

1,4-dihydroxy-anthraquinone 25g and methanol anhydride 250ml are put in a 500ml round bottom flask under argon atmosphere and NaBH_4 15.7g is slowly added at 0°C . After one hour is elapsed, 6N HCL is slowly added to this mixture at 0°C to produce orange precipitates. The precipitates are filtered and then washed with water and methanol. The precipitates are

15

reprecipitated into methylene chloride and ether to obtain targeted compound, that is, 1,4-anthraquinone(compound I) as an orange solid 15.3g (yield:70%).

¹H NMR(CDCl₃): δ=7.06(d, 2H), 7.70(q, 2H), 8.06(q, 2H),
5 8.60(s, 2H)

Synthesis of 2-(10-oxo-10H-9-oxa-10-phosphaphenanthrene-10-yl)anthracene-1,4-diol (compound J)

1.4-anthraquinone(compound I) 17g, 9-oxa-10-phosphaphenanthrene 10-oxide 21g, and 2-butoxyethanol 110ml
10 are put in a 500ml round bottom flask under argon atmosphere. Thereafter, they are heated and recirculated for 4 hours. The 2-butoxyethanol is removed under high-temperature vacuum and is then purified with column chromatography (EA:n-Hex =1:1) to obtain targeted compound, that is, 2-(10-oxo-10H-9-oxa-10-phosphaphenanthrene-10-yl)anthracene-1,4-diol (compound J) as
15 a solid 14.6g (yield:42%).

¹H NMR(acetone-d₆): δ=8.46(s, 1H), 8.25(d, 1H), 8.20(t, 1H), 8.04(d, 1H), 7.89(t, 1H), 7.84(s, 1H), 7.78(t, 1H), 7.64(d, 1H), 7.55(m, 1H), 7.49(m, 5H), 7.29(d, 2H), 6.73(d,
20 1H)

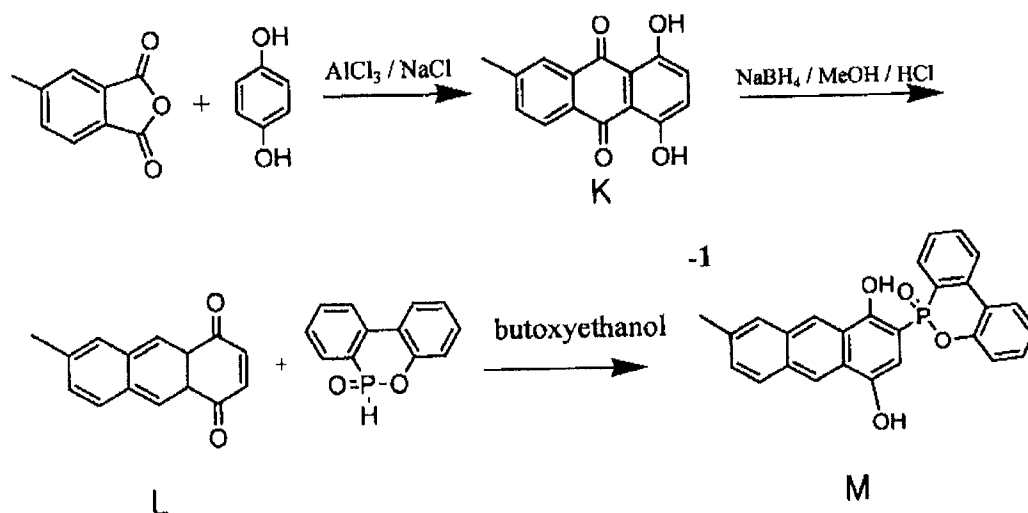
Synthesis of 10-(1,4-dimethoxyanthracene-2-yl)-9-oxa-10-phosphaphenanthrene-10-oxide (compound 111)

2-(10-oxo-10H-9-oxa-10-phospha-phenanthrene-10-yl)-anthracene-1,4-diol 5g, K₂CO₃ 6.5g, CH₃I 5ml, and acetone 100ml

are put in a 250ml round flask. Thereafter, they are heated and recirculated for 4 hours. After the reaction is completed, the acetone is removed. Thereafter, this is extracted using water and ethyl acetate and then reprecipitated into THF and
 5 hexane to obtain 10-(1,4-dimethoxyanthracene-2-yl)-9-oxa-10-phosphaphenanthrene-10-oxide (compound 111) as a solid 1.5g (yield:30%).

^1H NMR(acetone- d_6): δ =8.73(s, 1H), 8.27(q, 1H), 8.22(t, 1H), 8.07(q, 1H), 8.01(t, 1H), 7.84(s, 1H), 7.80(t, 1H),
 10 7.67(d, 1H), 7.57(m, 1H), 7.50(m, 3H), 7.40(d, 1H), 7.30(d, 1H), 6.77(d, 1H), 4.05(s, 6H)

[Eleventh Embodiment] Synthesis of 10-(1,4-dimethoxy-7-methyl-anthracene-2-yl)-9-oxa-10-phospha-phenanthrene
 10-oxide (compound 112)



1,4-dihydroxy-6-methyl-anthraquinone (compound K)

4-methylphthal anhydride 50g, hydroquinone 34g, aluminum

chloride 120g, and NaCl 24g are put in a 500ml Erlenmeyer flask. They are is stirred at 250°C for 10 minutes. A red solid is produced during the progress of reaction. Heat is reduced and water and HCl are then added thereto to produce an orange
5 solid. This is filtered and is then reprecipitated into THF and hexane to obtain targeted compound, that is, 1,4-dihydroxy-6-methyl-anthraquinone(compound K) as an orange solid 16.7g (yield:35%).

¹H NMR(CDCl₃): δ=12.92(s, 1H), 12.88(s, 1H), 8.21(d, 1H),
10 8.11(s, 1H), 7.61(d, 1H), 7.28(s, 1H), 2.54(s, 3H)

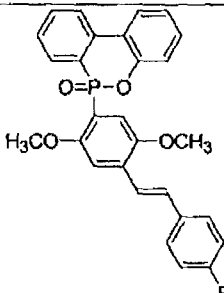
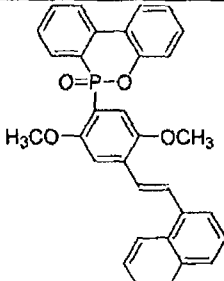
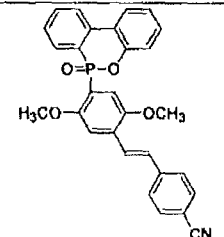
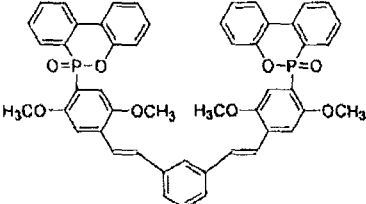
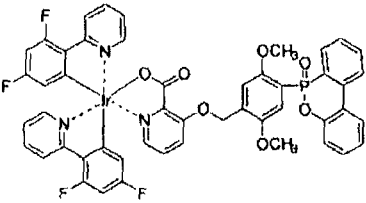
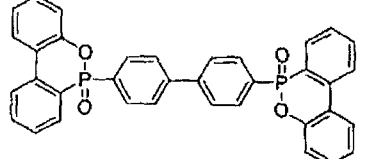
6-methyl-1,4-anthraquinone (compound L), 7-methyl-2-(10-oxo-10H-9-oxa-10-phospha-phenanthrene-10-yl)-anthracene-1,4-diol (compound M), and 10-(1,4-dimethoxy-7-methyl-anthracene-2-yl)-9-oxa-10-phospha-phenanthrene 10-oxide (compound 112)
15 are prepared by the same method as the tenth embodiment.

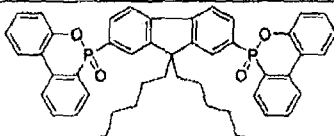
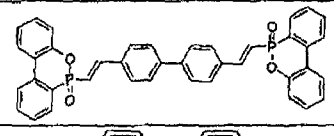
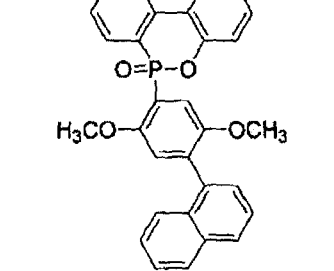
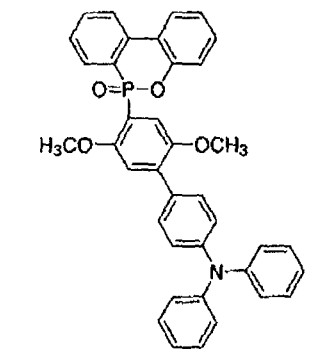
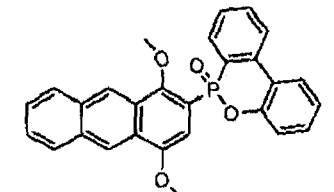
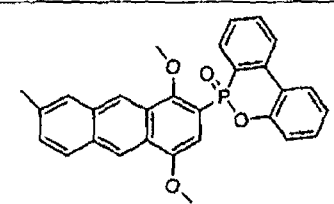
[Test example] Ultraviolet and photoluminescence property test

Measured values of UV-vis and photoluminescence (hereinafter, referred to as PL) for the compounds synthesized
20 according to the present invention are listed in a table 1. Shimatzu UV/Vis spectro photometer is used for the measurement of UV-vis and LS55 luminescence spectrometer available from Perkin Elmer Co. is used for the measurement of PL. A measurement sample is prepared using dichloromethane solution.

The UV-vis spectrum of the prepared sample is obtained and the PL property is obtained in a wavelength where the UV-vis peak represents a most extreme value.

[Table 1] Compound structure and UV/PL data

No.	Structure	Molecular formula (molecular weight)	UV(CH ₂ Cl ₂) λ _{max} (nm)	PL(CH ₂ Cl ₂) λ _{max} (nm)
Compound 101		C ₂₈ H ₂₂ FO ₄ P (472.12)	355	415
Compound 102		C ₃₂ H ₂₅ O ₄ P (504.15)	356	440
Compound 103		C ₂₉ H ₂₂ NO ₄ P (479.13)	368	463
Compound 104		C ₅₀ H ₄₀ O ₈ P ₂ (830.22)	353	420
Compound 105		C ₄₉ H ₃₃ F ₄ IrN ₃ O ₇ P (1075.16)	265	511
Compound 106		C ₃₆ H ₂₄ O ₄ P ₂ (582.11)	270	407

Compound 107		$C_{49}H_{48}O_4P_2$ (762.30)	318	345
Compound 108		$C_{40}H_{28}O_4P_2$ (634.15)	270	243
Compound 109		$C_{30}H_{23}O_4P$ (478.13)	327	418
Compound 110		$C_{38}H_{30}NO_4P$ (595.19)	386	557
Compound 111		$C_{28}H_{21}O_4P$ (452.44)	257	441
Compound 112		$C_{29}H_{23}O_4P$ (466.46)	257	437

Electroluminescence property evaluation I

An organic light emitting diode in the most generally used form, which is configured of a cathode, a hole injecting layer, a hole transporting layer, a light emitting layer, an electron transporting layer, an electron injecting layer, and an anode, is prepared as follows in order to perform the electroluminescence (hereinafter, referred to as EL) property test.

The hole injecting layer is formed by depositing a 4,4',4''-tris(N-(2-naphthyl)-N-phenyl-amino)-triphenylamine film(hereinafter, referred to as '2-TNATA film') with a film thickness of 60nm on a patterned ITO transparent electrode and a 4,4-bis[N-(1-naphthyl)-N-phenyl-amino] biphenyl film (hereinafter, referred to as 'NPD film') with a film thickness of 15nm is formed on the 2-TNATA film. The NPD film functions as the hole transporting layer.

Next, the light emitting layer is formed by depositing the compound 101, the compound 103, or the compound 104 on the NPD film at a film thickness of 30nm and a 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline film (hereinafter, referred to as 'BCP film') with a film thickness of 5nm is deposited on the film to form a hole stopping layer. Thereafter, a tris(8-quinolinol) aluminum film (hereinafter, referred to as 'Alq film') with a film thickness of 30nm is deposited on the film

to form the electron injecting layer.

Finally, an Li/F film is formed on the film at a thickness of 1nm and a metal Al(film thickness of 200nm) is deposited thereon to form a metal cathode, thereby preparing
5 the organic light emitting diode.

Electroluminescence property evaluation II

An organic light emitting diode in the most generally used form, which is configured of a cathode, a hole injecting layer, a hole transporting layer, a light emitting layer, an
10 electron transporting layer, an electron injecting layer, and an anode, is prepared as follows in order to perform the electroluminescence (hereinafter, referred to as EL) property test.

The hole injecting layer is formed by depositing a
15 4,4',4''-tris(N-(2-naphthyl)-N-phenyl-amino)-triphenylamine film(hereinafter, referred to as '2-TNATA film') with a film thickness of 40nm on a patterned ITO transparent electrode and a 4,4-bis[N-(1-naphthyl)-N-phenyl-amino] biphenyl film (hereinafter, referred to as 'NPD film') with a film thickness
20 of 10nm is formed on the 2-TNATA film. The NPD film functions as the hole transporting layer.

Next, the light emitting layer is formed by depositing the compound 112 on the NPD film at a film thickness of 40nm and a 4,7-diphenyl-1,10-phenanthroline film (hereinafter,

referred to as 'BPhen film') with a film thickness of 10nm is deposited on the film to form a hole stopping layer.

Finally, an Li/F film is formed on the film at a thickness of 1nm and a metal Al(film thickness of 200nm) is deposited thereon to form a metal cathode, thereby preparing the organic light emitting diode.

The following table 2 represents the electroluminescence properties of the compound 112.

[Table 2]

	Turn-on (V)	E.Q.E	Efficiency (cd/A)	Efficiency (lm/A)	Color coordinate(CIE)	ELmax (nm)
Compound 112	3.4	1.56	2.06	1.13	0.16, 0.16	450

10

【Industrial Applicability】

The new phosphaphenanthrene compounds according to the present invention can be used as core materials of the OLED as well as can be used as materials for an optical switch, a sensor, a module, a wave guide, or an optical storage or amplification, non-linear optical materials, photoconductor, optical absorber, or the like.

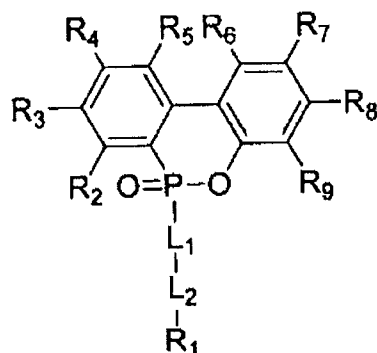
15

【CLAIMS】

【Claim 1】

phosphaphenanthrene compounds represented by the following chemical formula 1.

5 [Chemical Formula 1]



[In the chemical formula 1, L₁ is chemical bond or (C₂-C₁₀) alkenylene, (C₆-C₃₀) arylene or NR₁₁ and alkenylene or arylene of the L₁ may further be substituted into at least one
10 selected from (C₁-C₂₂) alkyl, (C₆-C₃₀) aryl, (C₂-C₃₀) heteroaryl, (C₆-C₃₀) ar (C₁- C₂₂)alkyl, (C₁- C₂₂)alkyl(C₆-C₃₀)aryl, halogen, (C₁-C₁₀) alkylsilyl, (C₆-C₃₀)arylsilyl, carboxylic acid, cyano, or OR₃₁;

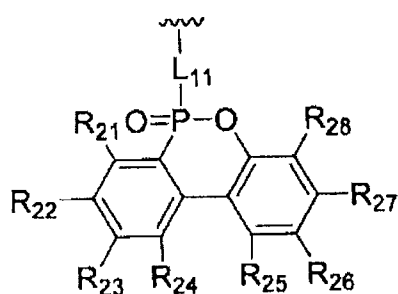
L₂ is (C₂-C₁₀) alkenylene, (C₂-C₁₀) alkynylene, (C₆-C₃₀)
15 arylene, (C₂-C₃₀) heteroarylene or -Ar₁-A- Ar₂- and alkenylene, arylene, or heteroarylene of the L₂ may further be substituted into at least one selected from (C₁-C₂₂) alkyl, halogen, cyano, carboxylic acid, (C₁- C₁₀) alkylsilyl, (C₆-C₃₀) arylsilyl, (C₆-C₃₀) aryl, (C₂- C₃₀) heteroaryl, (C₆- C₃₀)ar (C₁- C₂₂)alkyl, (C₁-

C_{22})alkyl (C_6 - C_{30})aryl or OR_{31} ;

Ar_1 and Ar_2 are independent from each other and are (C_6 -
 C_{30}) arylene or (C_2 - C_{30}) heteroarylene. Arylene or
heteroarylene of the Ar_1 and Ar_2 may further be substituted
5 into at least one selected from (C_1 - C_{22})alkyl, (C_6 - C_{30}) aryl,
(C_6 - C_{30}) aryloxy, (C_2 - C_{30})heteroaryl, halogen, (C_1 - C_{10})
alkylsilyl, (C_6 - C_{30}) arylsilyl, (C_1 - C_{22})alkoxy, carboxylic acid
or cyano;

A is NR_{12} , $(O=)PR_{13}$, $SiR_{14}R_{15}$, SO_2 or 0;

10 R_1 is hydrogen, (C_1 - C_{22})alkyl, (C_6 - C_{30}) aryl, (C_2 - C_{30})
heteroaryl, halogen, cyano, (C_1 - C_{22})alkoxy, (C_6 - C_{30}) aryloxy,
(C_6 - C_{30}) arylsulfonyl, mono-or di (C_1 - C_{10})alkylamino, mono-or
di(C_6 - C_{30})arylamino, (C_2 - C_7)alkenyloxy, (C_2 - C_7) alkynyloxy, (C_2 -
 C_7) alkenylcarbonyloxy, (C_2 - C_7) alkynylcarbonyloxy, (C_1 - C_{10})
15 alkylsilyl, (C_6 - C_{30}) arylsilyl or



and alkyl, aryl, heteroaryl, alkoxy,
aryloxy, arylsulfonyl,

alkylamino, arylamino, alkenyloxy, alkynyloxy, alkylsilyl
20 or arylsilyl of the R_1 may further be substituted into at least

one selected from (C₁-C₁₀)alkyl, halogen, cyano, nitro, carboxylic acid, (C₆-C₃₀) aryl, mono-or di(C₁-C₁₀)alkylamino, mono-or di(C₆-C₃₀)arylamino, (C₁-C₁₀) alkylsilyl, or (C₆-C₃₀) arylsilyl;

5 L₁₁ is chemical bond or (C₂-C₁₀) alkenylene, (C₆-C₃₀) arylene or NR₁₆ and alkenylene or arylene of the L₁₁ may further be substituted into at least one selected from (C₁-C₂₂) alkyl, (C₁-C₂₂) alkoxy, (C₃-C₂₂)cycloalkyl, (C₆-C₃₀) aryl, cyano, halogen, amino, mono-or di(C₁-C₁₀)alkylamino, mono-or di(C₆-
10 C₃₀)arylamino, nitro, or hydroxy;

 R₂ to R₉ are independent from each other and are hydrogen, (C₁-C₂₂) alkyl, (C₁-C₂₂) alkyl including oxygen, nitrogen, or sulfur, (C₁-C₂₂)alkoxy, (C₃-C₂₂)cycloalkyl, (C₃-C₂₂)cycloalkyl (C₁-C₂₂) alkyl, (C₆-C₃₀) aryl, halogen, cyano, amino, mono-or
15 di(C₁-C₁₀)alkylamino, mono-or di(C₆-C₃₀)arylamino, hydroxy, nitro, mono-or di-benzylamino, or (C₃-C₁₀)cycloalkylamino and the R₂ to R₉ are combined with carbon of neighboring substituent by (C₃-C₅) alkylene or (C₃-C₅) alkenylene to form a fused ring, carbon of the fused ring may be substituted into
20 heteroatoms selected from oxygen, sulfur, or nitrogen, alkyl, alkoxy, cycloalkyl, cycloalkylalkyl, aryl, or amino of the R₂ to R₉ may further be substituted into at least one selected from (C₁-C₁₀) alkyl, halogen, (C₆-C₃₀) aryl, (C₁-C₁₀) alkylsilyl, or (C₆-C₃₀) arylsilyl;

R₁₁ to R₁₆ are independent from each other and are (C₁-C₂₂) alkyl, (C₃-C₂₂)cycloalkyl, (C₆-C₃₀) aryl, mono-or di(C₁-C₁₀)alkylamino, mono-or di(C₆-C₃₀)arylamino, or amino and alkyl, cycloalkyl, or aryl of the R₁₁ to R₁₆ may further be substituted
5 into at least one selected from halogen, (C₁-C₂₂) alkyl, (C₆-C₃₀) aryl, (C₁-C₂₂) alkoxy, 3-member to 7-member heterocycloalkyl including at least one of oxygen, nitrogen, or sulfur, or cyano;

R₂₁ to R₂₈ are independent from each other and are hydrogen,
10 (C₁-C₂₂) alkyl, (C₁-C₂₂) alkyl including oxygen, nitrogen, or sulfur, (C₁-C₂₂)alkoxy, (C₃-C₂₂)cycloalkyl, (C₃-C₂₂)cycloalkyl (C₁-C₂₂) alkyl, (C₆-C₃₀) aryl, halogen, cyano, amino, mono-or di(C₁-C₁₀)alkylamino, mono-or di(C₆-C₃₀)arylamino, hydroxy, nitro, mono-or di-benzylamino, or (C₃-C₁₀)cycloalkylamino and
15 the R₂₁ to R₂₈ are combined with carbon of neighboring substituent by (C₃-C₅) alkylene or (C₃-C₅) alkenylene to form a fused ring, carbon of the fused ring may be substituted into heteroatoms selected from oxygen, sulfur, or nitrogen, alkyl, alkoxy, cycloalkyl, cycloalkylalkyl, aryl, or amino of the R₂₁
20 to R₂₈ may further be substituted into at least one selected from (C₁-C₁₀) alkyl, halogen, (C₆-C₃₀) aryl, (C₁-C₁₀) alkylsilyl, or (C₆-C₃₀) arylsilyl; and

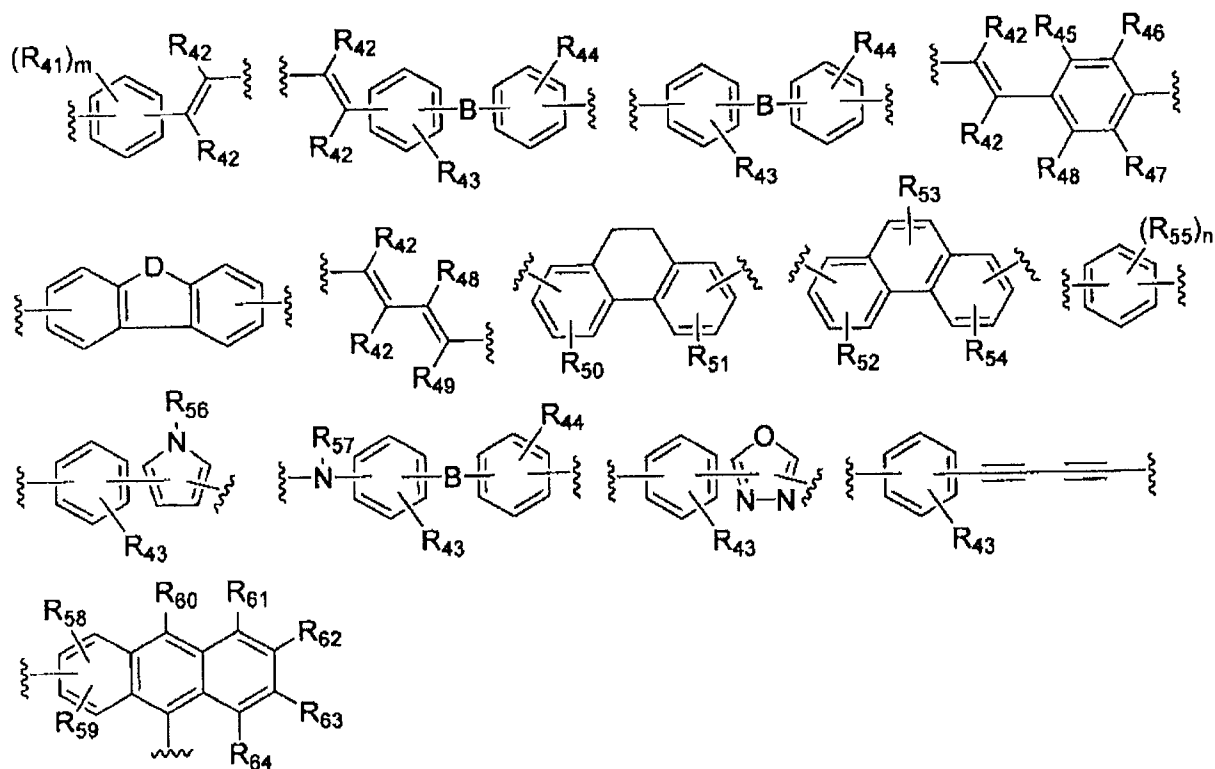
R₃₁ is (C₁-C₂₂) alkyl, (C₆-C₃₀) aryl, (C₂-C₁₀) alkenyl, or (C₁-C₂₂) alkylcarbonyl and alkyl, aryl, or alkylcarbonyl of the

R₃₁ may further be substituted into at least one selected from 3-member to 5-member heterocycloalkyl including at least one from N, O, and S, (C₃-C₂₂)cycloalkyl, (C₂-C₁₀) alkynyl, (C₂-C₁₀) alkenyl, cyano, or halogen.]

5

【Claim 2】

The phosphaphenanthrene compounds according to claim 1, wherein $\{L_1-L_2\}$ is selected from the following structure.



10 [B is chemical bond or NR₇₁, (O=)PR₇₁, SiR₇₃R₇₄, SO₂, or O;

D is CR₈₁R₈₂, NR₈₃, O, S, or SO₂;

R₃₁ is (C₁-C₂₂) alkyl, (C₆-C₃₀) aryl, (C₂-C₁₀) alkenyl, or (C₁-C₂₂) alkylcarbonyl and alkyl, alkenyl, or alkylcarbonyl of the R₃₁ may further be substituted into at least one selected

from 3-member to 5-member heterocycloalkyl including at least one from N, O, and S, (C₃-C₂₂)cycloalkyl, (C₂-C₁₀) alkynyl, (C₂-C₁₀) alkenyl, cyano, or halogen;

R₄₁ to R₆₄ are independent from each other and are hydrogen,
5 (C₁-C₂₂) alkyl, (C₆-C₃₀) aryl, halogen, (C₂-C₃₀) heteroaryl, cyano, carboxylic acid, (C₁-C₁₀) alkylsilyl, (C₆-C₃₀) arylsilyl, (C₆-C₃₀) ar(C₁-C₂₂) alkyl, (C₁-C₂₂)alkyl(C₆-C₃₀)aryl or OR₃₁, or R₄₅ and R₄₆ or R₄₇ and R₄₈ are coupled with (C₃-C₅) alkylene or (C₃-C₅) alkenylene to form a fused ring, and carbon of the fused
10 ring may be substituted into heteroatoms selected from oxygen, sulfur, or nitrogen;

R₇₁ to R₇₄ are independent from each and are (C₁-C₂₂) alkyl, (C₃-C₂₂)cycloalkyl, (C₆-C₃₀) aryl, mono-or di(C₁-C₁₀)alkylamino, mono-or di(C₆-C₃₀)arylamino, or amino and alkyl, cycloalkyl, or
15 aryl of the R₇₁ to R₇₄ may further be substituted into at least one selected from halogen, (C₁-C₂₂) alkyl, (C₆-C₃₀) aryl, (C₁-C₂₂) alkoxy, 3-member to 7-member heterocycloalkyl including at least one of oxygen, nitrogen, or sulfur, or cyano;

R₈₁ to R₈₃ are independent from each other and are hydrogen,
20 (C₁-C₂₂) alkyl, (C₆-C₃₀) aryl, halogen, (C₂-C₃₀) heteroaryl, cyano, carboxylic acid, (C₁-C₁₀) alkylsilyl, (C₆-C₃₀) arylsilyl, (C₆-C₃₀)ar(C₁-C₂₂)alkyl, (C₁-C₂₂)alkyl(C₆-C₃₀)aryl, or (C₁-C₂₂)alkoxy; and

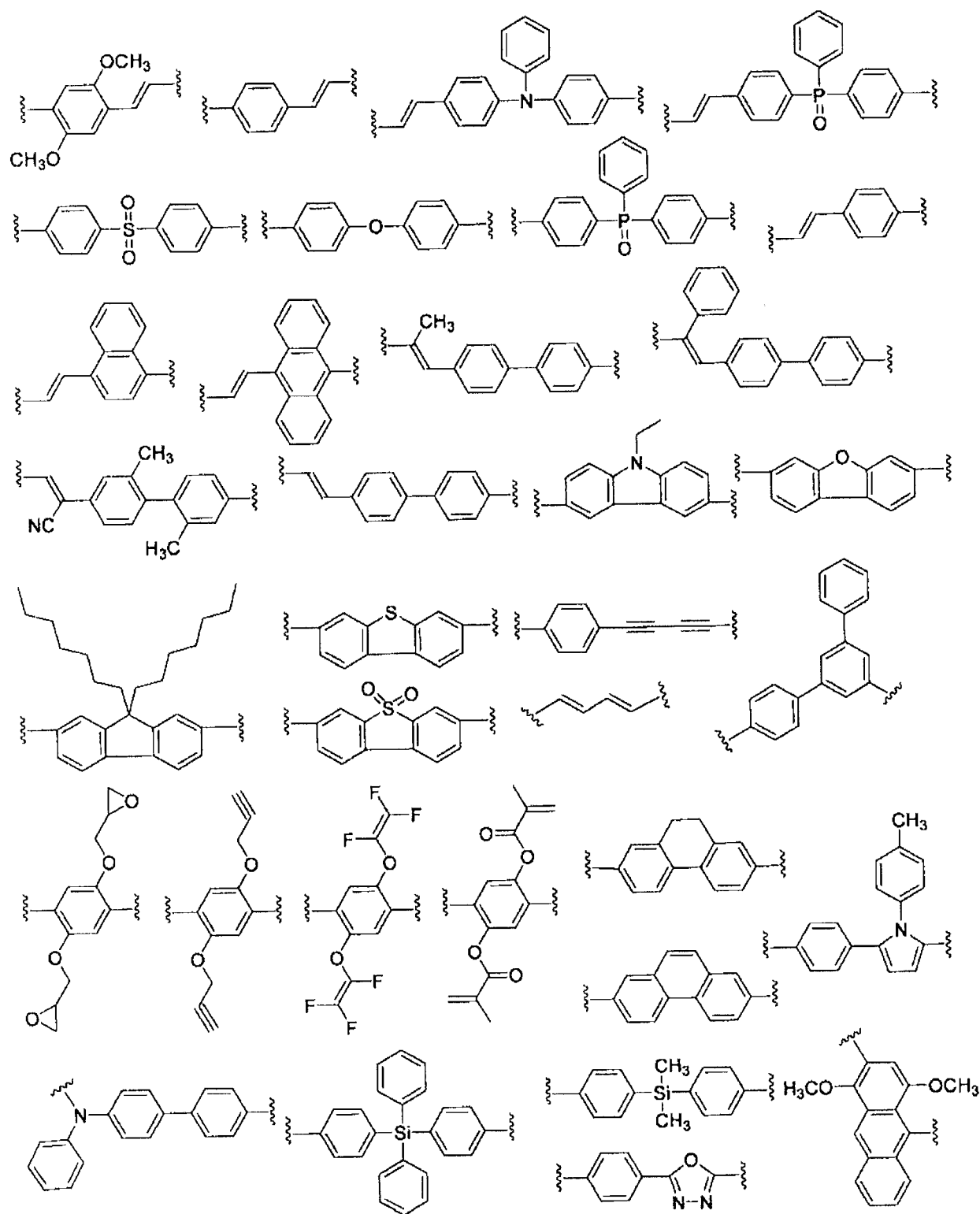
m and n are independent from each other and are integers

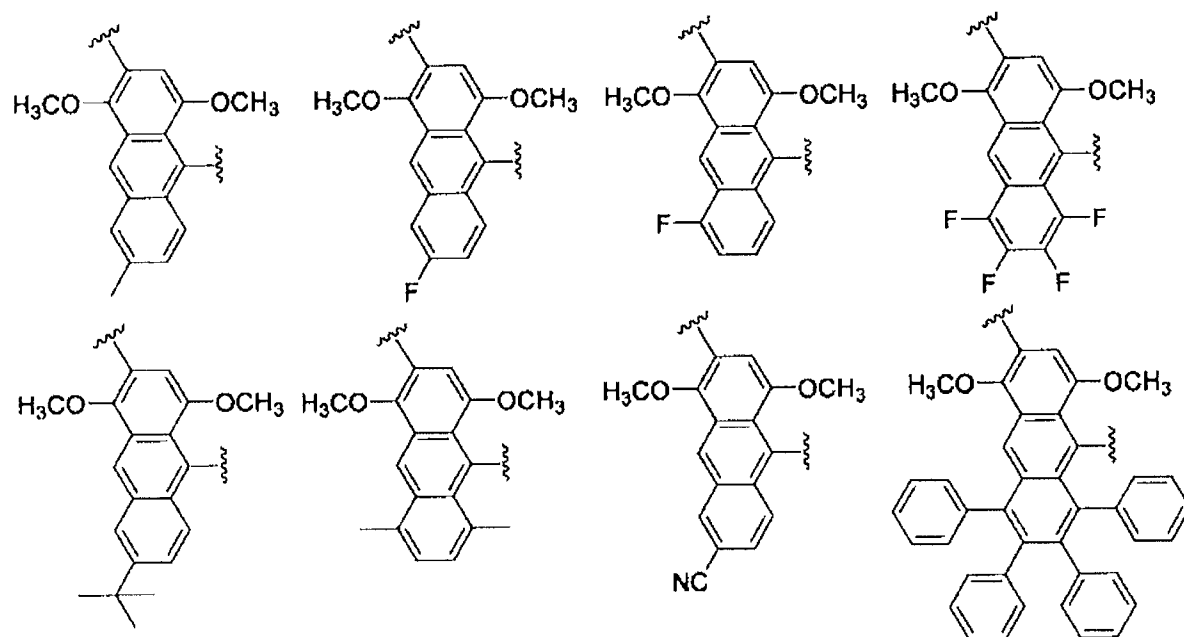
of 1 to 4.]

【Claim 3】

The phosphaphenanthrene compounds according to claim 1,

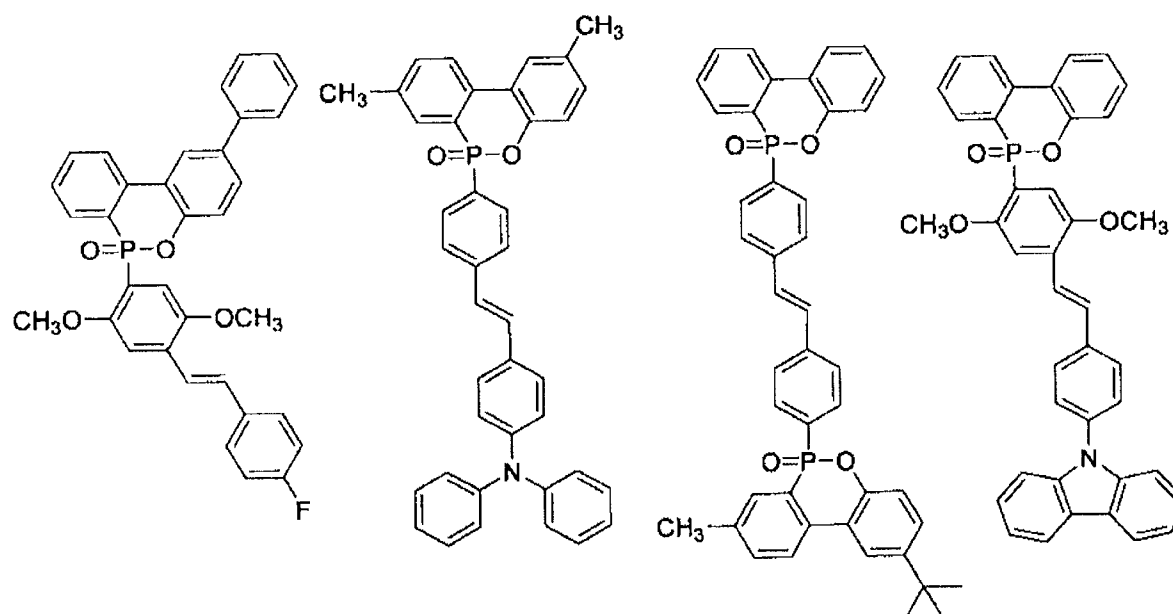
5 wherein $\begin{array}{c} \text{\textasciitilde} \\ \text{\textasciitilde} \\ \text{\textasciitilde} \end{array} \text{---} \text{L}_1 \text{---} \text{L}_2 \text{---} \begin{array}{c} \text{\textasciitilde} \\ \text{\textasciitilde} \\ \text{\textasciitilde} \end{array}$ is selected from the following structure.

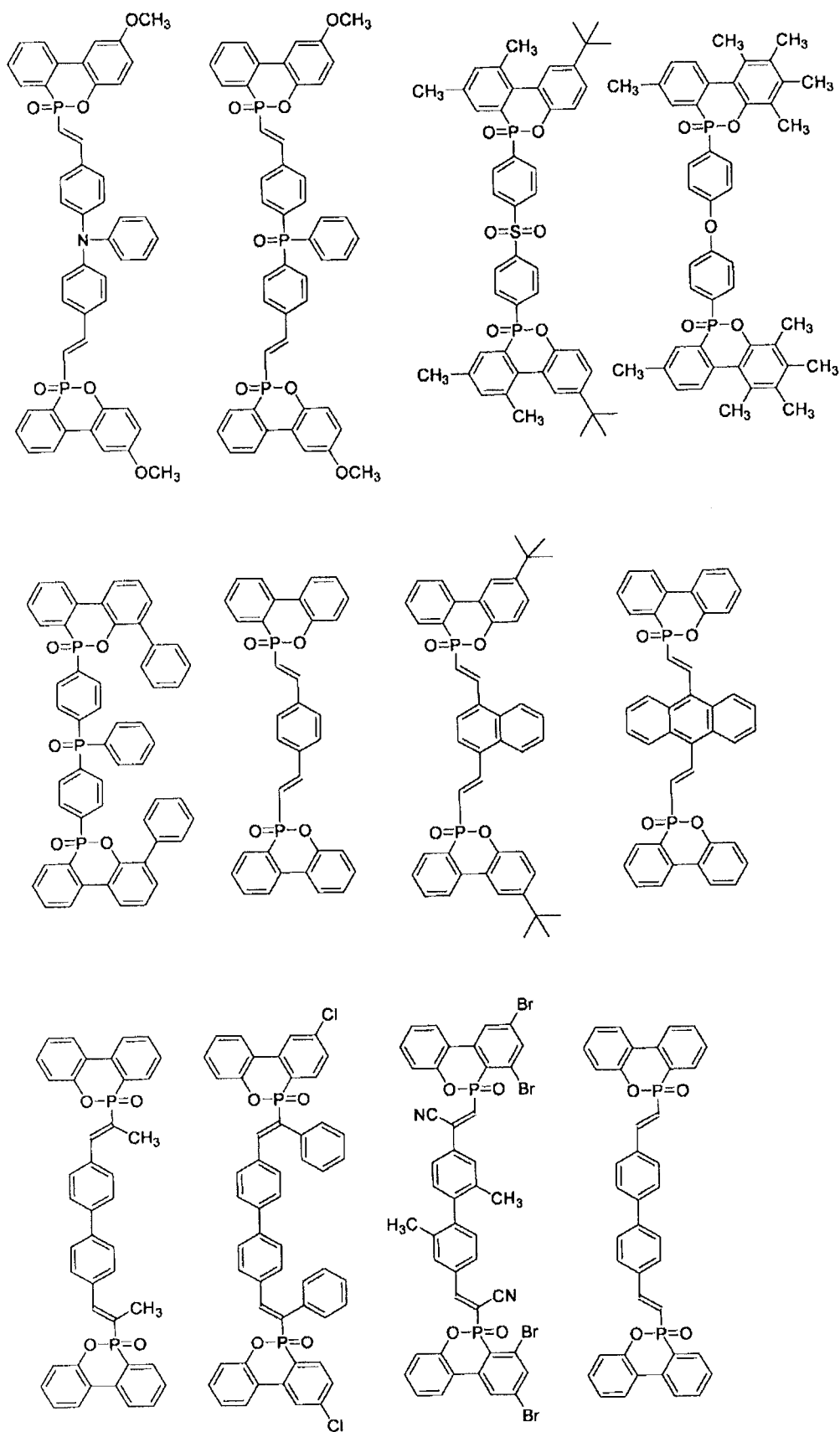


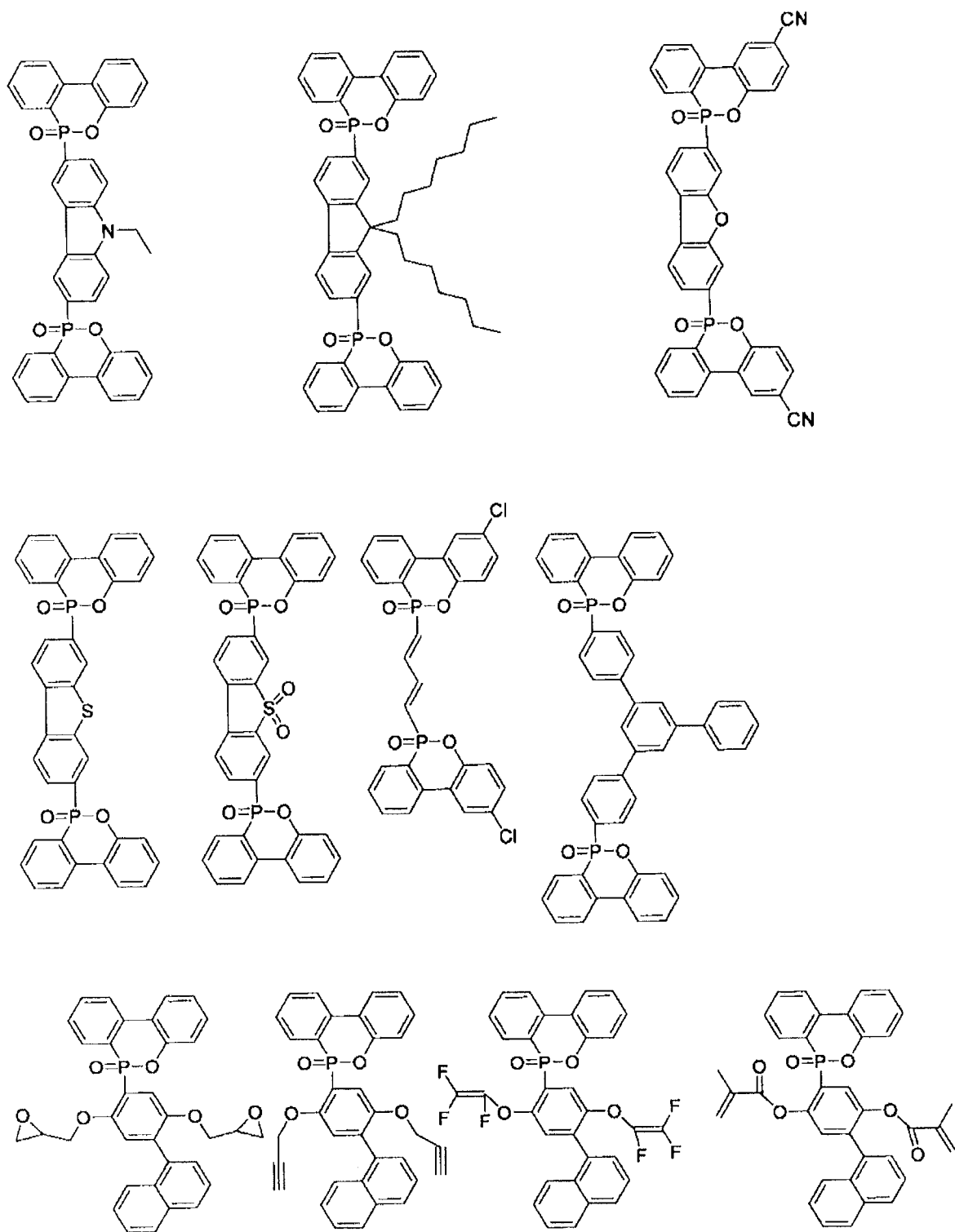


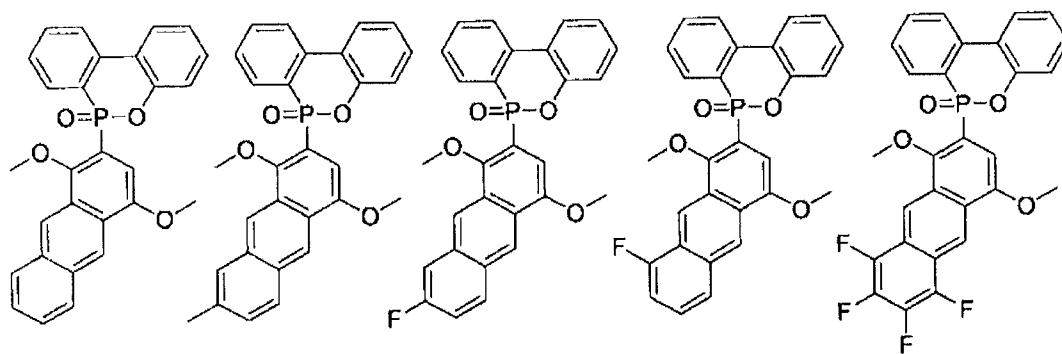
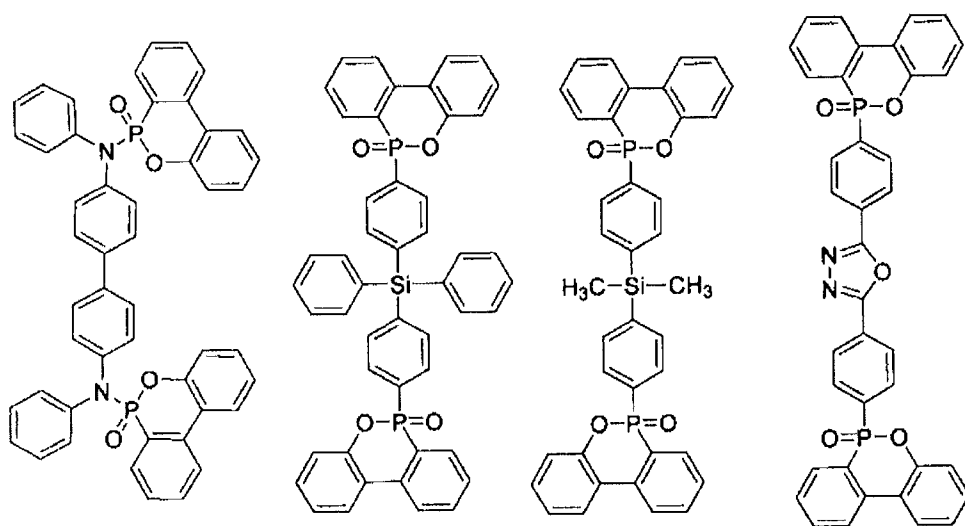
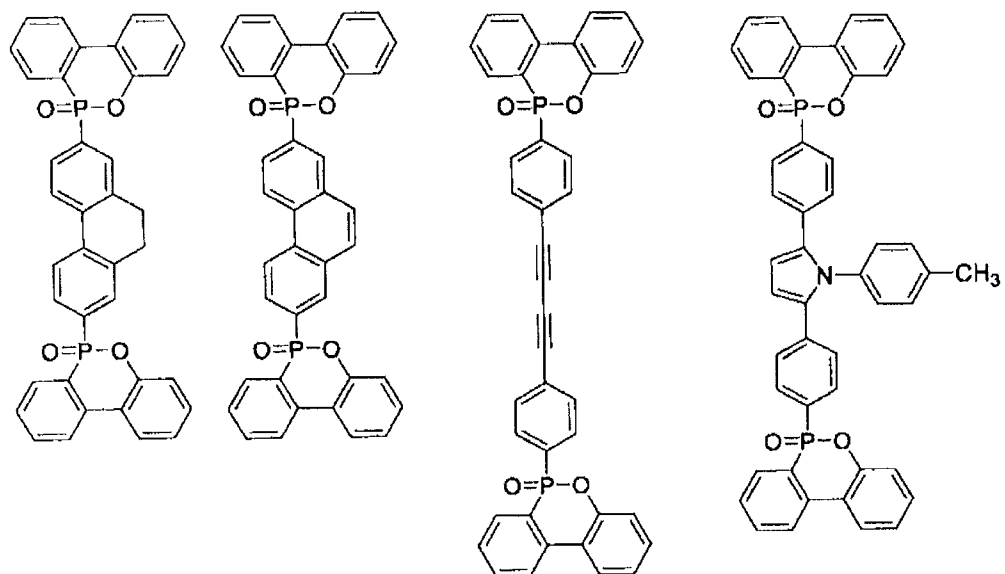
【Claim 4】

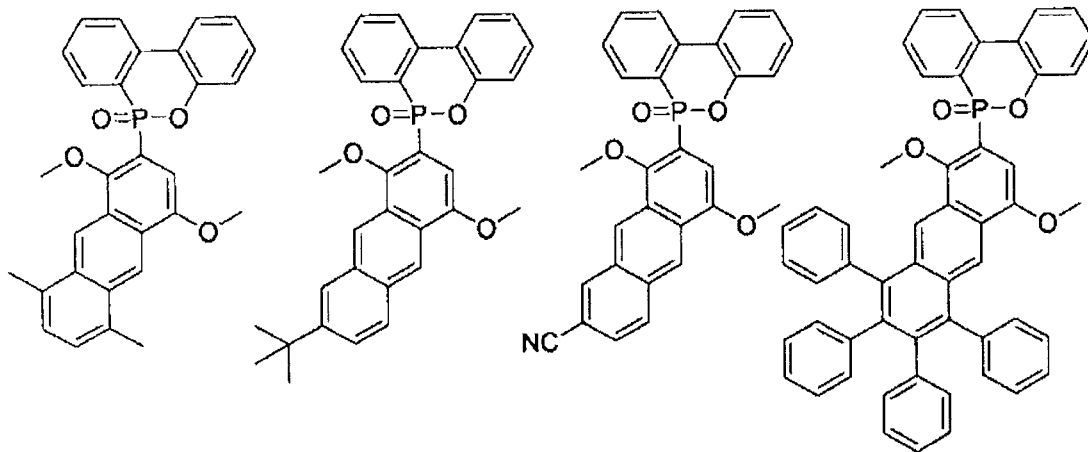
The phosphaphenanthrene compounds according to claim 3, wherein it is selected from the following compounds.











【Claim 5】

An organic light emitting diode including the phosphaphenanthrene compounds according to any one of claims 1 to 4.

【Claim 6】

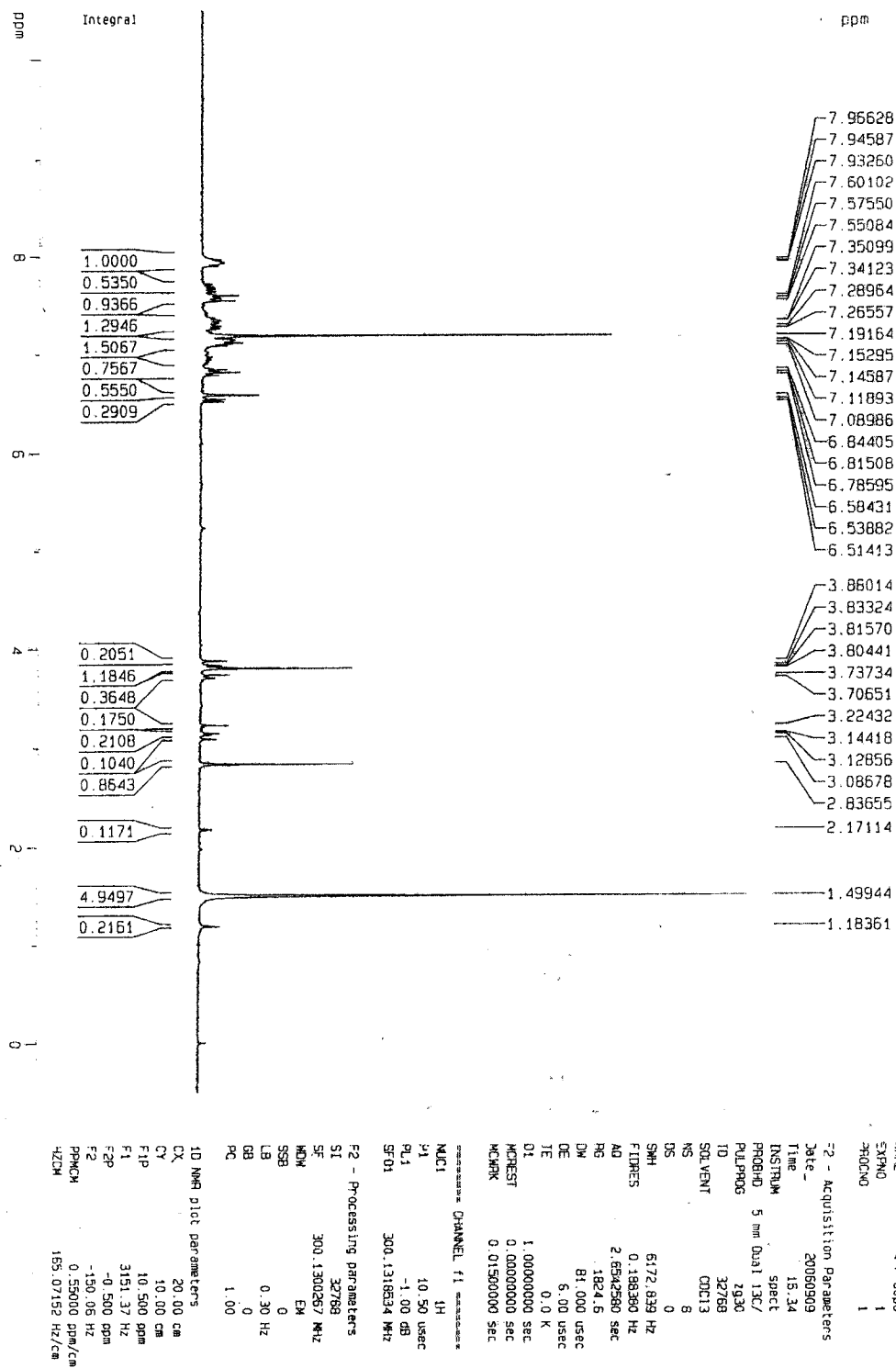
The organic light emitting diode according to claim 5, wherein the phosphaphenanthrene compounds are included in a layer selected from an electron transporting layer, a light emitting layer, or a mixing function layer thereof.

【Claim 7】

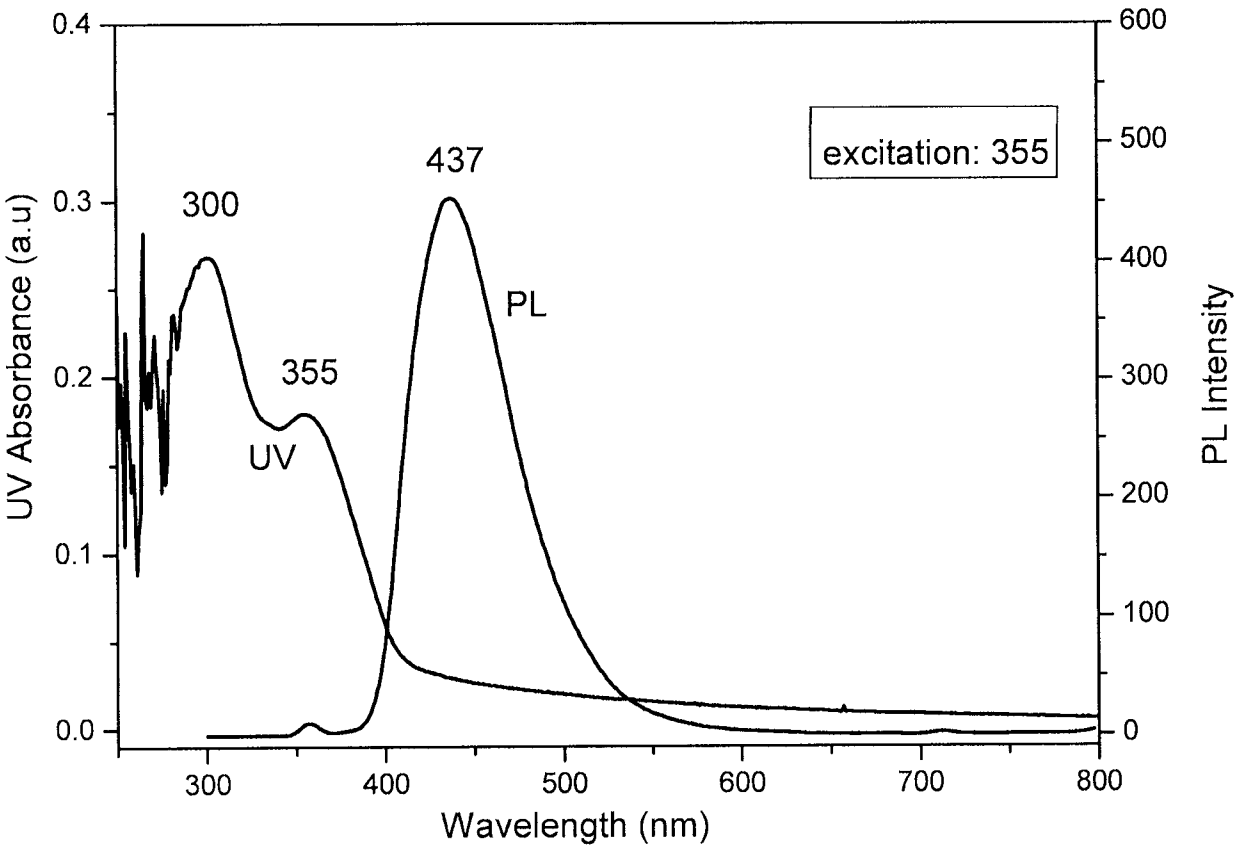
An organic semiconductor device including the phosphaphenanthrene compounds according to any one of claims 1 to 4.

【Figures】

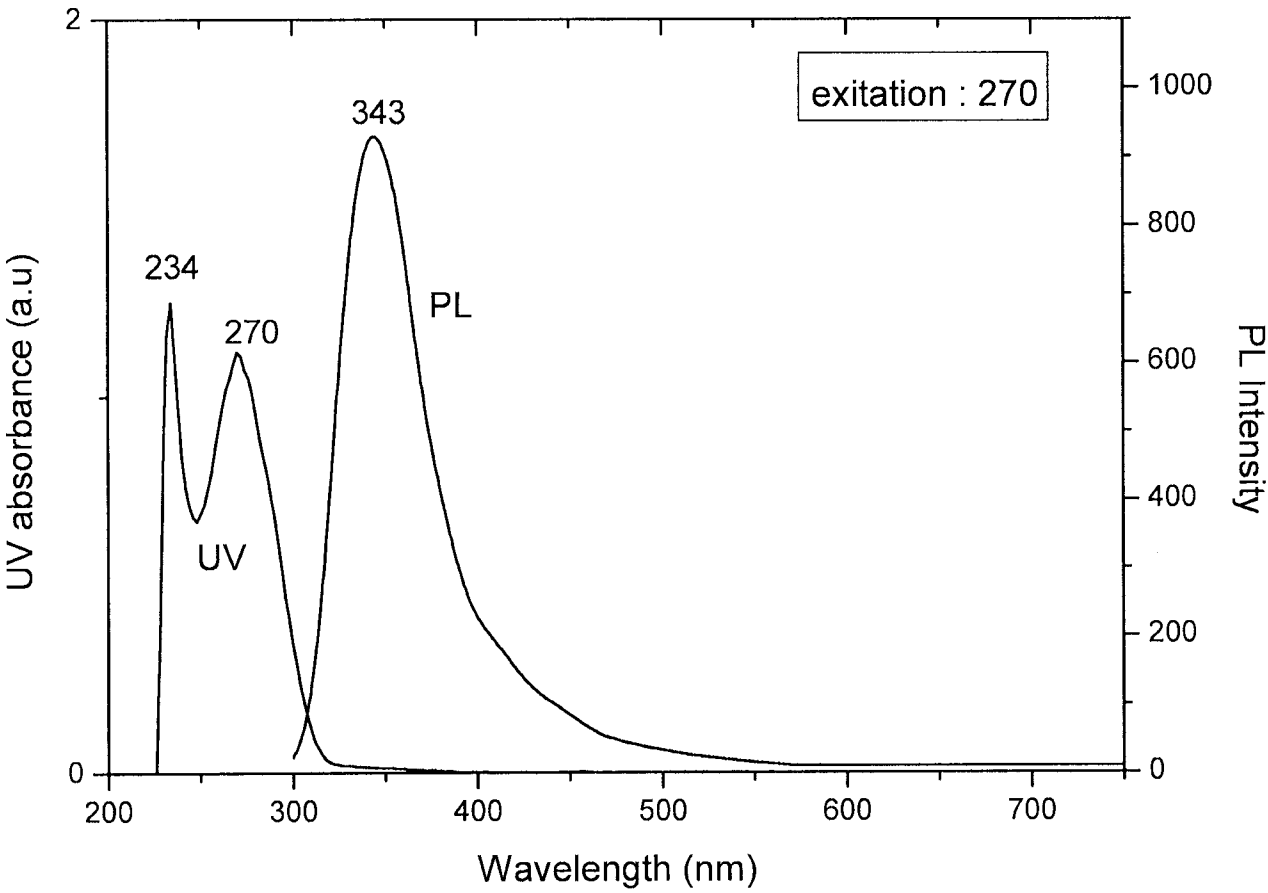
【Figure 1】



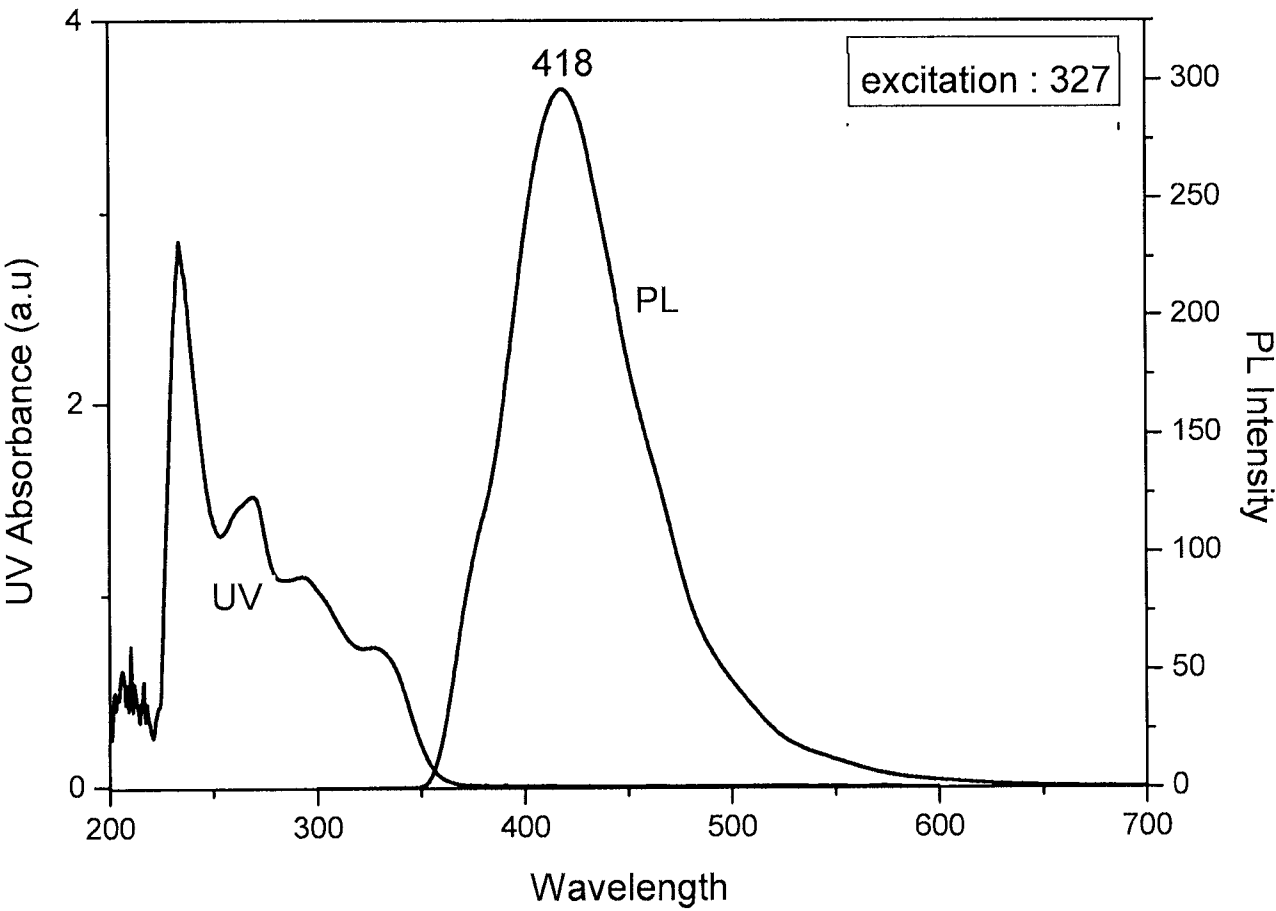
【Figure 2】



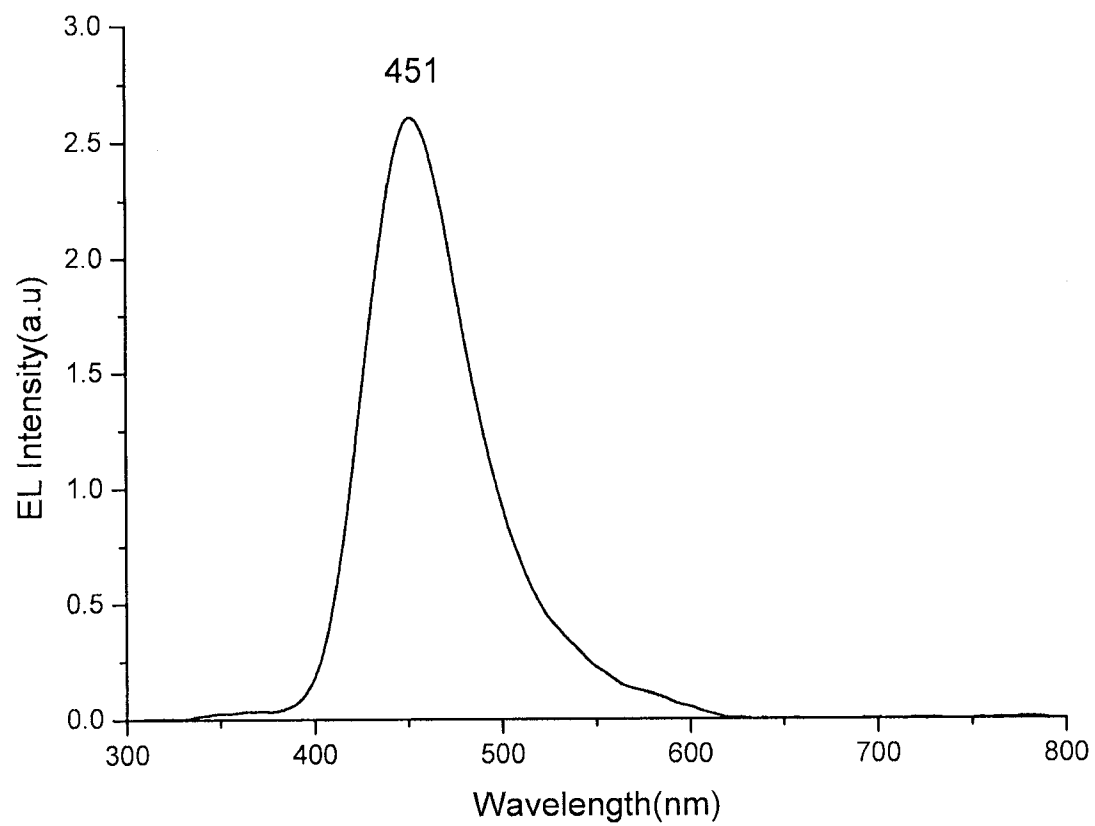
【Figure 3】



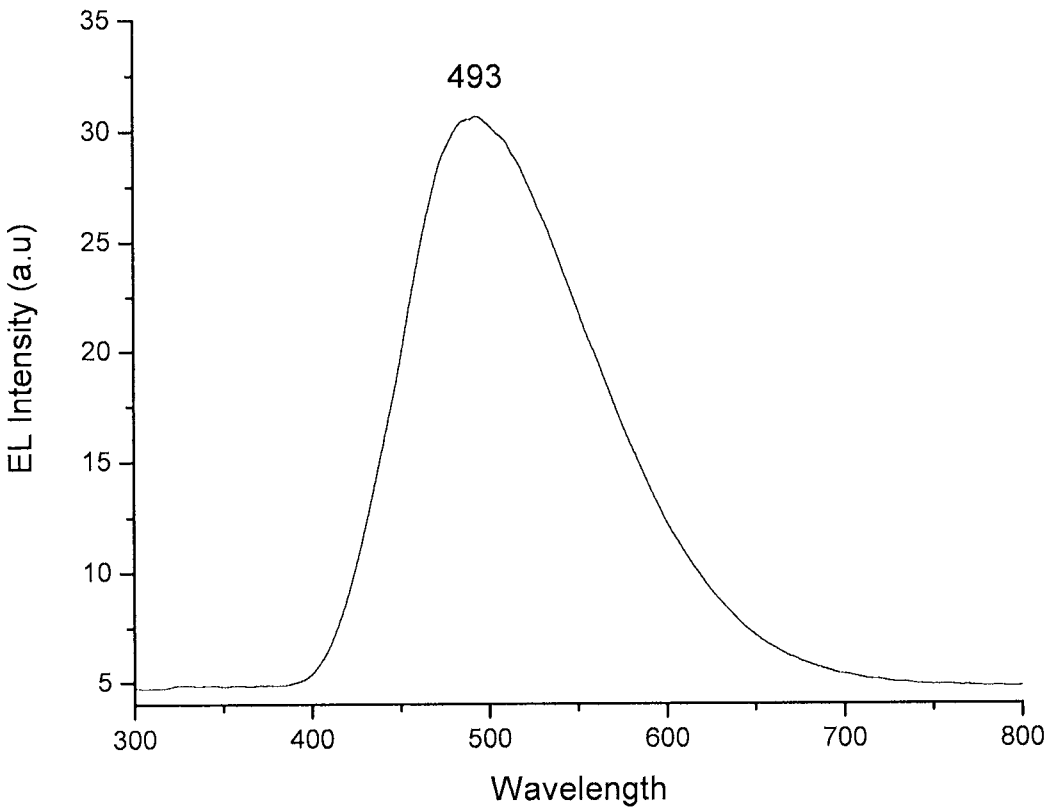
【Figure 4】



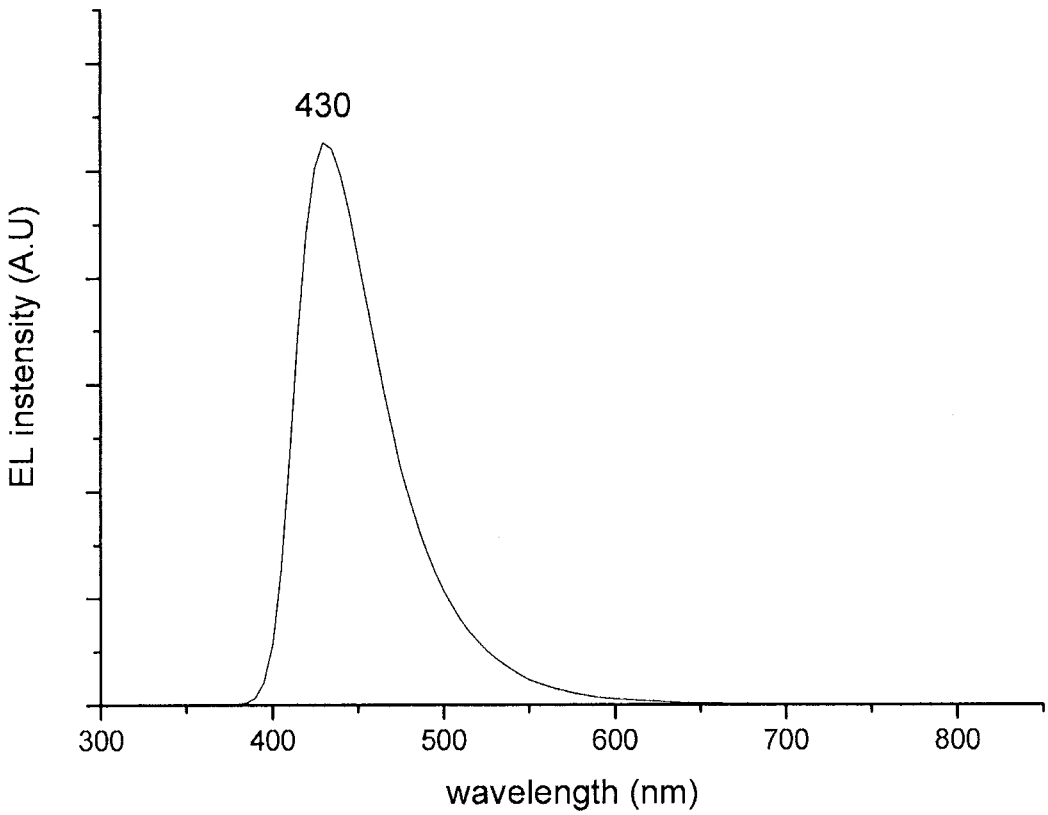
【Figure 5】



【Figure 6】



【Figure 7】



A. CLASSIFICATION OF SUBJECT MATTER*C09K 11/06(2006.01)i*

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 8 C09K 11

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

Korean Utility models and applications for Utility models since 1975

Japanese Utility models and applications for Utility models since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKIPASS (KIPO internal)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2002-193985 A, (DAINIPPON INK & CHEM INC), 10 July 2002 (10.07.2002) see the abstract, paragraphs [6] ~ [8], claims 1-4.	1 - 7
A	JP 2001-002769 A, (TAKEDA CHEM IND LTD), 09 January 2001 (09.01.2001) see the abstract, paragraph [4], claims 1 and 6.	1 - 7
A	JP 2002-020715 A, (TOSHIBA CHEM CORP), 23 January 2002 (23.01.2002) see the abstract, paragraph [12], claims 1-2.	1 - 7



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/KR2008/001943Patent document
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datePatent family
member(s)Publication
date

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NONE

专利名称(译)	磷杂菲化合物和使用它的有机发光二极管相同		
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摘要(译)

本发明涉及具有优异发光性能的新型磷杂菲化合物和使用该化合物的有机发光二极管 (OLED) 。