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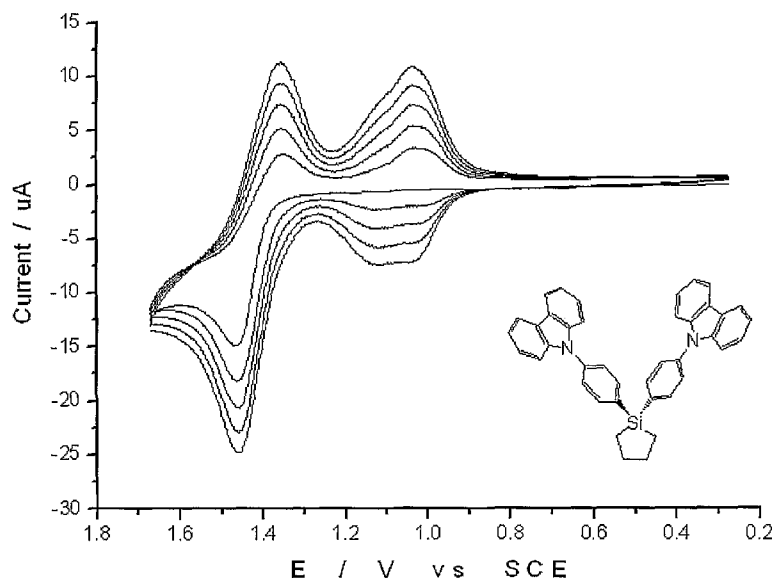
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(54) Title: SILICON TYPE COMPOUND HAVING BISPHENYLCARBAZOL IN MOLECULE AND METHOD FOR PREPAR-
ING ORGANIC THIN LAYER OF ORGANIC LIGHT EMITTING DEVICES USING THE SAME



(57) Abstract: The invention provides a silicon type compound having bis(phenylcarbazol) in molecule and a method for preparing an organic thin layer of organic light emitting devices using the same and in particular, the compound of the invention has excellent blue luminescent characteristics and hole transmission characteristics and at the same time, it not only can be used as a blue luminescent material or used as a host to a variety of phosphorescent or fluorescent dopants such as red, green, blue and white but also can be applied to organic light emitting devices through electrochemical deposition and further, it enables high efficient luminescence and can confer such performances as low voltage, high brightness and long longevity.



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Description

SILICON TYPE COMPOUND HAVING BISPHENYLCARBAZOL IN MOLECULE AND METHOD FOR PREPARING ORGANIC THIN LAYER OF ORGANIC LIGHT EMITTING DEVICES USING THE SAME

Technical Field

- [1] The present invention relates to a silicon type compound having bis(phenylcarbazol) group in molecule and a method for preparation of an organic thin layer of organic light emitting devices using the same and more particularly, to a compound having bis(phenylcarbazol) group in molecule having excellent blue luminescent characteristics and hole transmission characteristics and at the same time, capable of not only being used as a blue luminescent material or used as a host to a variety of phosphorescent or fluorescent dopants such as red, green, blue and white but also being applied to organic light emitting devices through electrochemical deposition, and further enabling high efficient luminescence and conferring such performances as low voltage, high brightness and long longevity and a method for preparation of an organic thin layer of organic light emitting devices using the same.

Background Art

- [2] Recently, in display fields, organic light emitting devices (OLED) have been spotlighted as display devices because they have wide viewing angle as a self light emitting device and excellent contrast as well as fast response time and when compared with inorganic EL devices, they are excellent in brightness, driving voltage and response rate and polychrome is also available.
- [3] General organic EL devices have a structure of an anode which is formed on the top of a substrate, a light emitting layer in organic thin layer form which is formed on the anode, and a cathode formed thereon in sequence. Further, they may have a hole injection layer or hole transport layer between the anode and the light emitting layer, or they may have an electron transport layer or electron injection layer between the light emitting layer and the cathode. The hole injection layer, hole transport layer, electron transport layer and electron injection layer are organic thin layers consisting of organic compounds.
- [4] The organic light emitting devices having the above structure have the following driving mechanism.
- [5] First, when voltage is applied between the anode and cathode, hole injected from the anode is transported to the light emitting layer via the hole transport layer. Meanwhile,

electron is injected into the light emitting layer from the cathode via the electron transport layer and carriers are re-coupled in the light emitting layer zone to produce exciton. This exciton is changed from its excited state to ground state and due to this change, fluorescent molecules in the light emitting layer emit light, thereby forming screen image. Fluorescence refers to luminescence occurring when the excited state is dropped to the ground state through singlet excited state and phosphorescence is luminescence occurring when it is dropped to the ground state through triplet excited state. In the case of the fluorescence, the possibility of having singlet excited state is 25 % (triplet state 75 %) and the efficiency of luminescence has limits, but because the use of the phosphorescence makes it possible to use triplet 75 % and singlet excited state 25 %, it can be said that internal quantum efficiency of 100 % is theoretically possible.

- [6] High efficiency organic green and red electroluminescence devices have been developed by effectively emitting light even in triplet state (phosphorescence) by use of as dopants, Ir(ppy)_3 and PtOEP which are phosphorescent pigments having heavy elements such as Ir and Pt with huge spin-orbital coupling in their center. In the devices, CBP(4,4'-N,N'-dicarbazole-biphenyl) was used as a host.
- [7] However, as the glass transition temperature of CBP is low, e.g., not higher than 100 °C and its crystallization readily occurs, the aforementioned organic electroluminescence devices have short life of not longer than 150 hours, which is insufficient in terms of commercial exploitation. Accordingly, studies about new compounds addressing these problems are in need.

Disclosure of Invention

Technical Problem

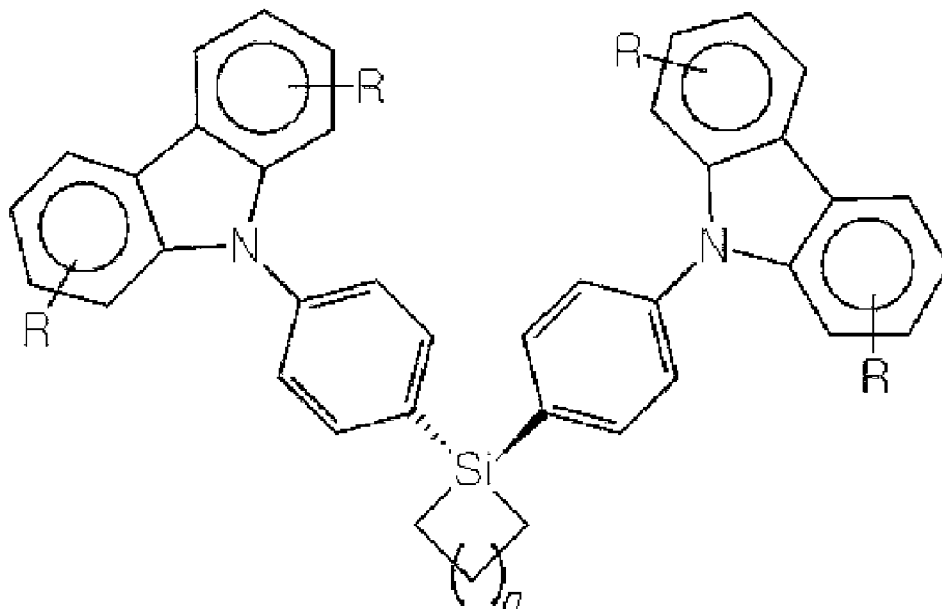
- [8] In order to solve the problems of the prior arts, it is an object of the invention to provide a silicon type compound having bis(phenylcarbazol) group in molecule having excellent blue luminescent characteristics and hole transmission characteristics and at the same time, capable of being used as a blue luminescent material or used as a host to a variety of phosphorescent or fluorescent dopants such as red, green, blue and white and a method for preparation of the same.
- [9] It is another object of the invention to provide an organic thin layer of organic light emitting devices enabling high efficient luminescence and conferring such performances as low voltage, high brightness and long longevity by being applied with the compound having bis(phenylcarbazol) group in molecule, and a display device comprising the same.

Technical Solution

- [10] To achieve the aforementioned objects, the present invention provides a silicon type

compound having bis(phenylcarbazol) group in molecule represented by formula 1 or 2:

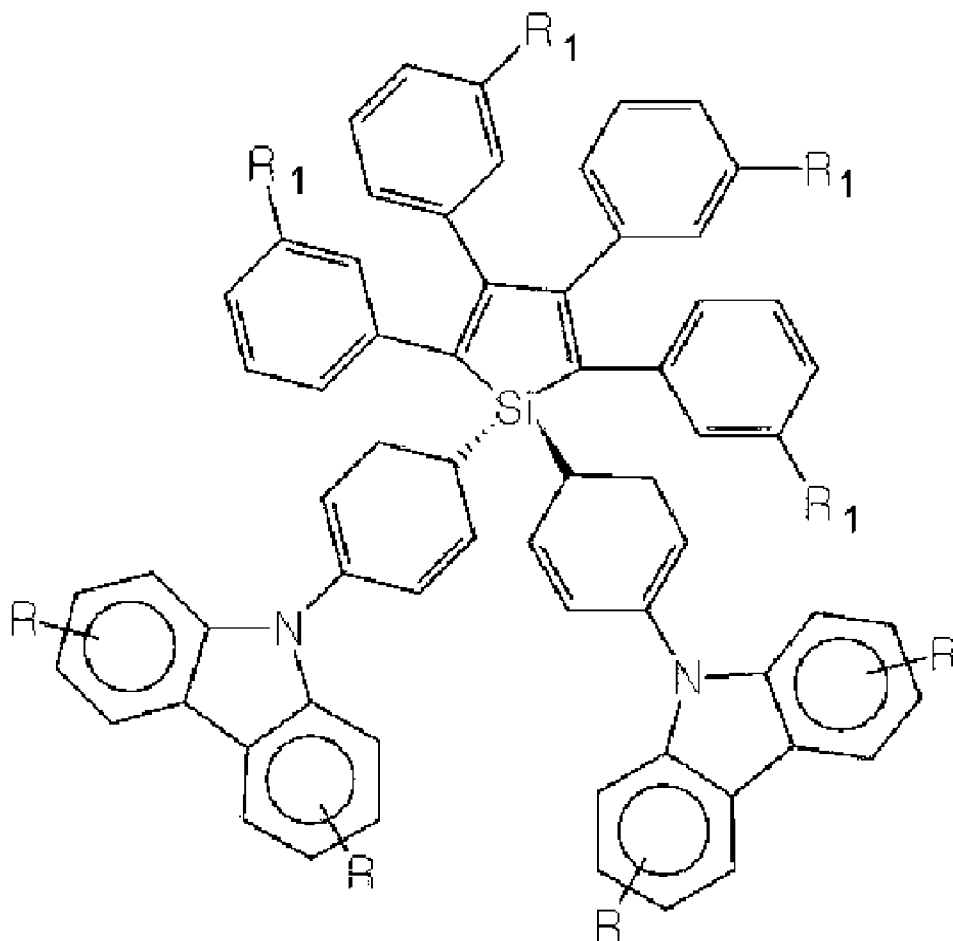
[11]



[12]

[1]

[13]



- [14] [2]
- [15] wherein R is each independently a substituted or unsubstituted alkyl group of 1 to 50 carbon atoms, a substituted or unsubstituted aryl group of 6 to 50 carbon atoms, a substituted or unsubstituted hetero ring group of 6 to 50 carbon atoms or a substituted or unsubstituted heterocyclic ring group of 6 to 50 carbon atoms,
- [16] R₁ is each independently a hydrogen atom or a substituted or unsubstituted alkyl group of 1 to 50 carbon atoms, and
- [17] n is an integer of 1 to 3.
- [18] Also, the invention provides a method for preparation of the silicon type compound having bis(phenylcarbazol) group in molecule represented by formula 1 as defined above comprising reacting bromobenzene and carbazol to prepare a (bromophenyl)carbazol compound, adding n-butyllithium to the (bromophenyl)carbazol compound to a (lithiumphenyl)carbazol compound, and reacting the (lithiumphenyl)carbazol compound and silanecyclodichloride.
- [19] Also, the invention provides a method for preparation of the silicon type compound having bis(phenylcarbazol) group in molecule represented by formula 2 as defined above comprising reacting bromobenzene and carbazol to prepare a (bromophenyl)carbazol compound and reacting the (bromophenyl)carbazol compound and dichlorotetraphenylsilane.
- [20] Also, the invention provides an organic thin layer of organic light emitting devices formed from the silicon type compound having bis(phenylcarbazol) group in molecule represented by formula 1 or 2 above.
- [21] Also, the invention provides an organic light emitting device comprising at least one organic thin layer between anode and cathode characterized in that the organic light emitting device comprises at least one layer or more of the above-mentioned organic thin layer.
- [22] Also, the invention provides a display device comprising the above organic light emitting device.

Advantageous Effects

- [23] The silicon type compounds having bis(phenylcarbazol) in molecule represented by formula 1 or 2 in accordance with the present invention have excellent blue luminescent characteristics and hole transmission characteristics and at the same time, they not only can be used as blue luminescent materials or used as a host to a variety of phosphorescent or fluorescent dopants such as red, green, blue and white but also enable high efficient luminescence when applied to organic light emitting devices and can confer such performances as low voltage, high brightness and long longevity.

Brief Description of the Drawings

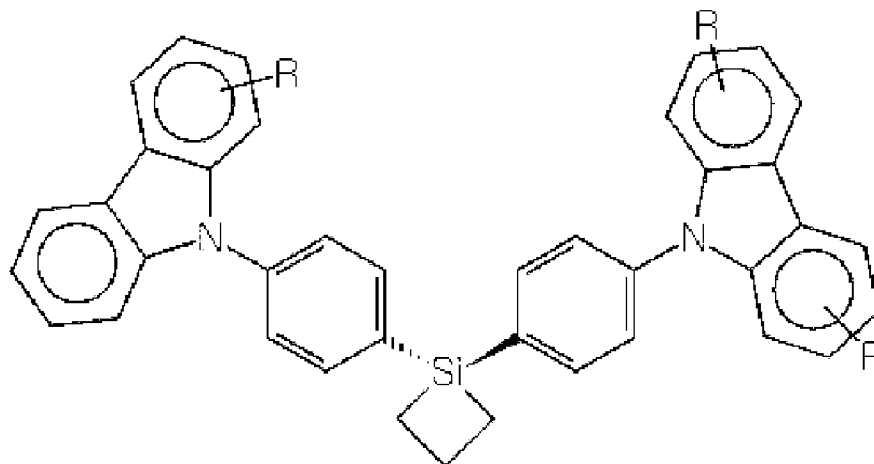
- [24] Fig. 1 is a cyclic voltammonogram showing electrochemical deposition by a silicon type compound having bis(phenylcarbazol) group in molecule represented by formula 1 according to an embodiment of the invention.
- [25] Fig. 2 is a cyclic voltammonogram showing electrochemical deposition by a silicon type compound having bis(phenylcarbazol) group in molecule represented by formula 1 according to another embodiment of the invention.
- [26] Fig. 3 is a cyclic voltammonogram showing electrochemical deposition by a silicon type compound having bis(phenylcarbazol) group in molecule represented by formula 1 according to another embodiment of the invention.
- [27] Fig. 4 is a cyclic voltammonogram showing electrochemical deposition by a silicon type compound having bis(phenylcarbazol) group in molecule represented by formula 2 according to another embodiment of the invention.
- [28] Fig. 5 is a UV spectrum of a compound of formula 2 according to another embodiment of the invention that has been diluted in chloroform.
- [29] Fig. 6 is a PL spectrum of a compound of formula 2 according to another embodiment of the invention that has been diluted in chloroform.

Mode for the Invention

- [30] This invention is further described in detail.
- [31] The silicon type compounds having bis(phenylcarbazol) group in molecule represented by above formula 1 or 2 of the invention have excellent blue luminescent characteristics and hole transmission characteristics or electron transmission characteristics and are suitable to be used as blue luminescent materials or phosphorescent or fluorescent host materials.
- [32] In the above formula 1, R can be a substituted or unsubstituted alkyl group of 1 to 50 carbon atoms, a substituted or unsubstituted aryl group of 6 to 50 carbon atoms, a substituted or unsubstituted hetero ring group of 6 to 50 carbon atoms or a substituted or unsubstituted heterocyclic ring group of 6 to 50 carbon atoms.
- [33] The specific examples of the alkyl group of 1 to 50 carbon atoms includes methyl, ethyl, propyl, isobutyl, sec-butyl, pentyl, iso-amyl, hexyl and so on, and one or more hydrogen atoms of the alkyl group may be substituted by a halogen atom, hydroxyl group, nitro group, cyano group, amino group, amidino group, hydrazine, hydrozone, carboxyl group or salt thereof, sulfonic acid group or salt thereof, phosphoric acid or salt thereof, indole, azindole, alkyl group of 1 to 50 carbon atoms, alkenyl group of 1 to 50 carbon atoms, alkynyl group of 1 to 50 carbon atoms, aryl group of 6 to 50 carbon atoms, arylalkyl group of 7 to 50 carbon atoms, heteroaryl group of 2 to 50 carbon atoms, or heteroarylalkyl group of 3 to 50 carbon atoms and of them, two or more may form a saturated or unsaturated ring by binding or fusing with each other.

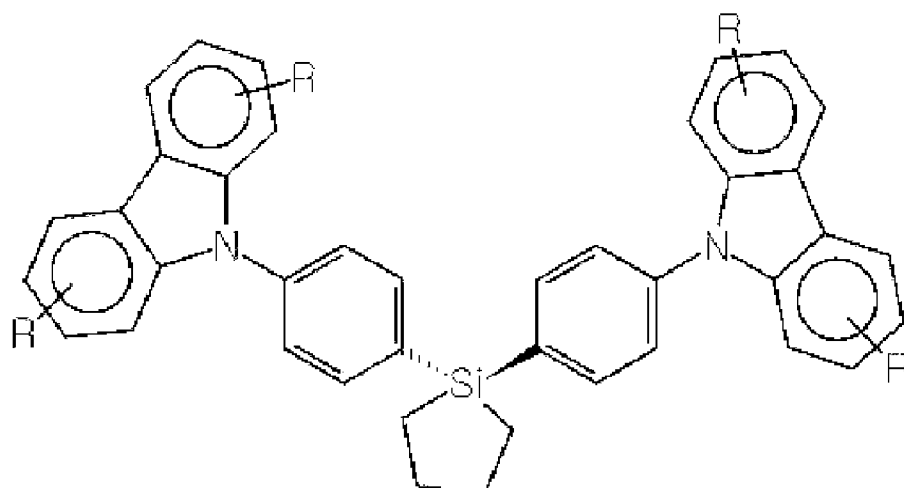
- [34] The unsubstituted aryl group in above refers to a carbocycle aromatic system of 6 to 50 carbon atoms containing one or more rings alone or in combination, and the rings can be attached or fused together in a pendant manner. The aryl includes aromatic radicals such as phenyl, naphthyl and tetrahydronaphthyl and one or more hydrogen atoms of the aryl group may be substituted by the same substituents as enumerated for the alkyl group.
- [35] The unsubstituted hetero ring group refers to a monovalent monocyclic or bicyclic aromatic organic compound of 6 to 50 ring atoms containing 1, 2 or 3 hetero atoms selected from N, O, P or S and having C as remaining ring atoms. One or more hydrogen atoms of the hetero aryl group may be substituted by the same substituents as enumerated for the alkyl group.
- [36] The unsubstituted heterocyclic ring group refers to a ring type moiety formed by the fusion of two or more rings constituting the aryl group or hetero ring as defined above and one or more hydrogen atoms of the heterocyclic ring group may be substituted by the same substituents as enumerated for the alkyl group.
- [37] The specific examples of the silicon type compounds having bis(phenylcarbazol) group in molecule represented by formula 1 above of the invention include compounds of the following formulae 1-1 to 1-4, and the compound represented by formula 2 is preferable when R or R₁ is hydrogen or methyl.

[38]



[39] [1-1]

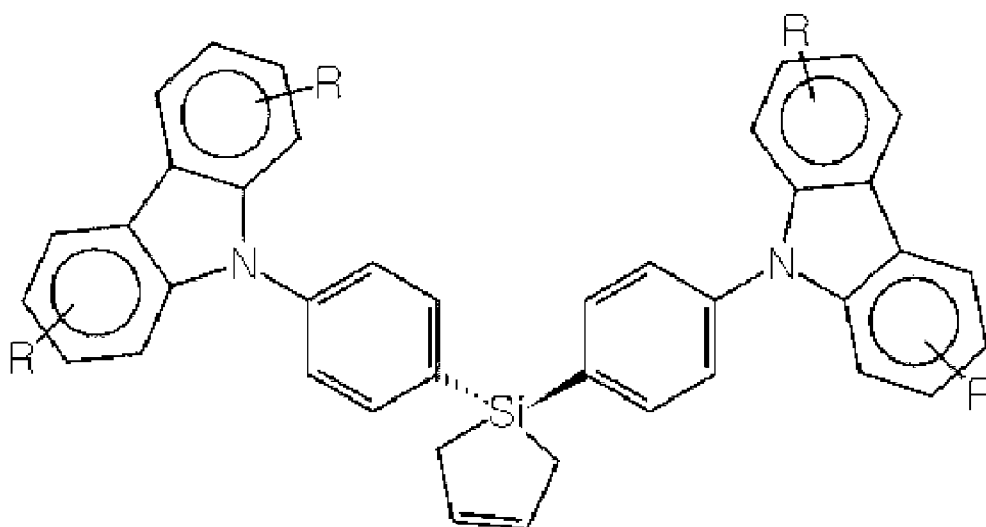
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[41]

[1-2]

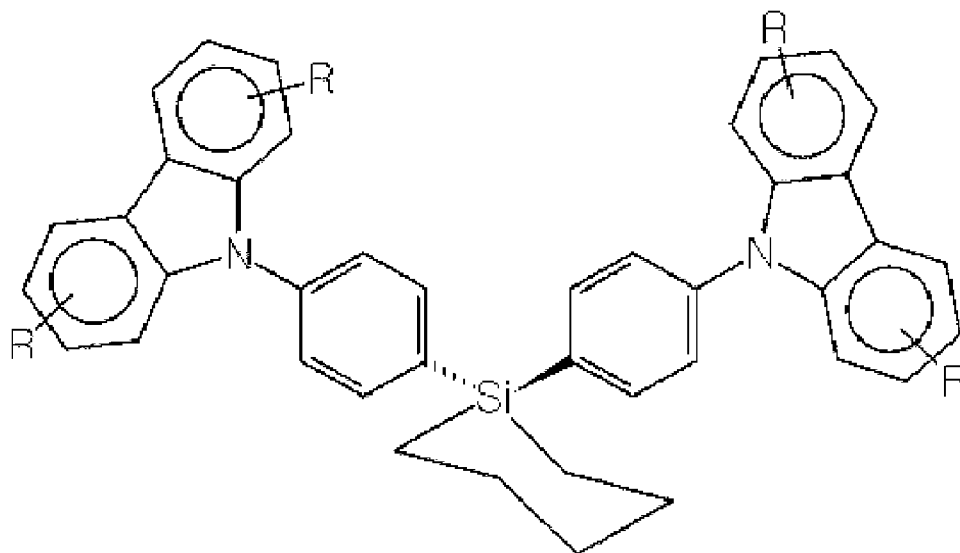
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[43]

[1-3]

[44]



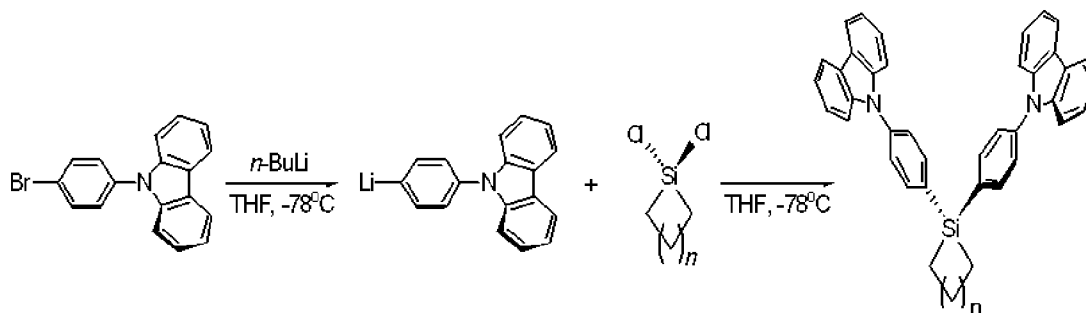
[45] [1-4]

[46] In the above formulae 1-1 to 1-4, R is the same as defined above and preferably, R is hydrogen.

[47] The silicon type compounds having bis(phenylcarbazol) group in molecule represented by formula 1 of the invention can be prepared by reacting bromobenzene and carbazol to prepare a (bromophenyl)carbazol compound, adding *n*-butyllithium to the (bromophenyl)carbazol compound to a (lithiumphenyl)carbazol compound, and reacting the (lithiumphenyl)carbazol compound and silanecyclodichloride.

[48] In particular, the compounds having bis(phenylcarbazol) group in molecule of the invention can be prepared in accordance with the following reaction formula 1, but this is merely one embodiment for preparing the compound having bis(phenylcarbazol) group in molecule of the invention and it does not limit the method for preparation of the compounds having bis(phenylcarbazol) group in molecule represented by formula 1 according to the invention in any way.

[49]



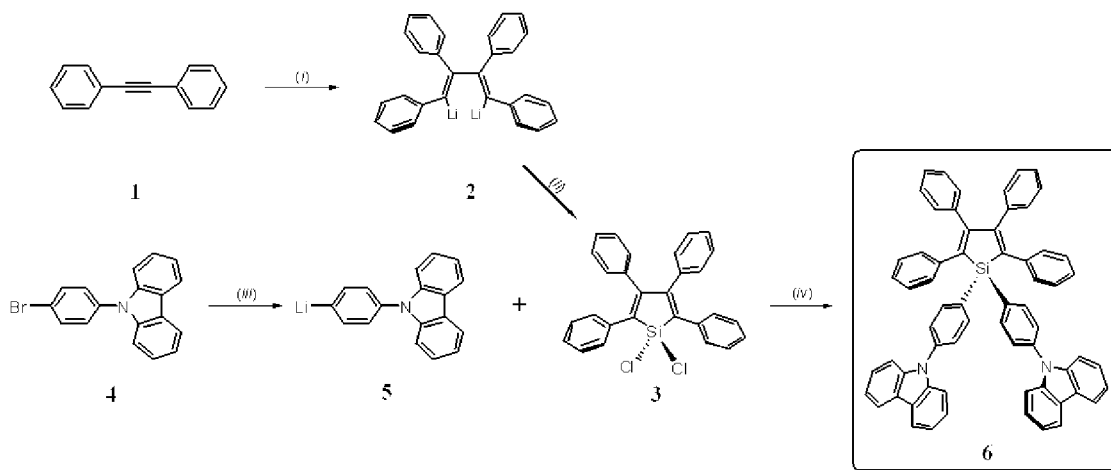
[50] [Reaction Formula 1]

[51] In the above reaction formula 1, *n* is an integer of 1 to 3.

[52] Further, the silicon type compounds having bis(phenylcarbazol) group in molecule

represented by formula 2 of the invention can be prepared by reacting bromobenzene and carbazole to prepare a (bromophenyl)carbazol compound and reacting the (bromophenyl)carbazol compound and dichlorotetraphenylsilane and in particular, they can be prepared in accordance with the following reaction formula 2, but this formula is merely one embodiment for preparing the silicon type compound having bis(phenylcarbazol) group in molecule of the invention and it does not limit the method for preparation of the compounds having bis(phenylcarbazol) group in molecule represented by formula 2 according to the invention in any way.

[53]



[54] [Reaction Formula 2]

[55] Also, the invention provides an organic thin layer of organic light emitting devices formed from the silicon type compounds having bis(phenylcarbazol) in molecule represented by the above formula 1 or 2 according to the invention and an organic light emitting device comprising at least one or more layers of the above organic thin layers. The organic light emitting devices are prepared by the following procedures.

[56] In general, the organic light emitting devices can comprise at least one or more organic thin layers between anode and cathode such as hole injection layer (HIL), hole transport layer (HTL), emitting layer (EML), hole blocking layer (HBL), electron transport layer (ETL) and electron injection layer (EIL), and the organic thin layer described in the invention is one of the organic layers formed between anode and cathode and can be a hole injection layer, hole transport layer, emitting layer, hole blocking layer, electron transport layer or electron injection layer and preferably, it is a hole injection layer, hole transport layer or emitting layer.

[57] First, anode is formed on the top of substrates by depositing materials for anode electrode having high work function. Any substrates used in common organic light emitting devices can be employed as the substrates and it is preferable to use organic substrates or clear plastic substrates with excellent mechanical strength, thermal stability, clearness, surface flatness, easy handling and waterproof. Also, as materials for anode electrode, indium tin oxide (ITO), indium zinc oxide (IZO), tin oxide (SnO_2),

zinc oxide (ZnO), etc. can be used. The materials for anode electrode can be deposited by conventional anode forming methods and in particular, they can be deposited by deposition method or sputtering method.

- [58] Next, hole injection layer (HIL) materials can be formed on the top of the anode electrode by methods such as vacuum deposition, spin coating, casting, LB (Langmuir-Blodgett) method and electrochemical deposition and particularly, the electrochemical deposition is preferably used.
- [59] In the case of forming the hole injection layer by the electrochemical deposition, substrates to be deposited are put in a reaction vessel where the silicon type compounds having bis(phenyl)carbazol group in molecule represented by above formula 1 or 2 to be intended for the formation of the hole injection layer and electrolytes are dissolved in solvents and the compounds intended to deposit are then deposited onto the substrates to be deposited when power is applied, thereby forming the hole injection layer.
- [60] Any solvents capable of dissolving the electrolytes and the compounds intended to deposit can be used in the above reaction vessel and as specific examples, there are dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), acetonitrile (CH_3CN), benzonitrile ($\text{C}_6\text{H}_5\text{CN}$), propylene carbonate, and toluene ($\text{C}_6\text{H}_5\text{CH}_3$). In the case of forming the organic thin layers having two or more layers, however, it would be advisable to avoid the use of solvents capable of dissolving the compounds of the previously formed organic thin layers. The amount of the solvents to be used is preferably 0.01 to 10 mM on the basis of the concentration of the compounds. If the concentration is too thin, there is a possibility that the electrochemical deposition is not performed properly and if it is too thick, problems may happen in connection with the control of the electrochemical deposition film thickness and voltage drop.
- [61] The electrolytes that can be used in the reaction vessel are dissolved in the above solvents and they are not limited to special ones as long as they are able to ionize the compounds intended to deposit when power is applied, and as specific examples, there are Me NBF_4 , Et NBF_4 , Pr NBF_4 , Bu NBF_4 , Me NClO_4 , Et NClO_4 , Pr NClO_4 , Bu NClO_4 , Me NPF_6 , Et NPF_6 , Pr NPF_6 , Bu NPF_6 , LiClO_4 , LiBF_4 , LiPF_6 , and LiBOB . The concentration of the supporting electrolytes is preferably 50 to 500 mM. If the concentration of the electrolytes is too thin, such problems as voltage drop may happen.
- [62] In addition to the silicon type compounds of the present invention, any hole injection layer materials can be used and for example, phthalocyanine compounds such as copper phthalocyanine disclosed in US Patent No. 4,356,429, starburst type amine derivatives, TCTA, m-MTDATA, m-MTDAPB (Advanced Material, 6, p677 (1994)), etc. can be used as hole injection layer materials.
- [63] Next, hole transport layer materials can be formed on the top of the hole injection

layer by methods such as vacuum deposition, spin coating, casting, LB method, and electrochemical deposition. Particularly, the formation by the electrochemical deposition is preferable. In the case of forming the hole transport layer by the electrochemical deposition, the conditions can be varied depending on the compounds to be used, but in general, they are preferably chosen within almost the same conditions as used for the formation of the hole injection layer.

- [64] The hole transport layer materials are not limited to specific ones and for example, the silicon type compounds having bis(phenylcarbazol) group in molecule represented by formula 1 or 2 according to the invention can be used or any conventional materials known to be used in the hole transport layers can be selected and used. Particularly, in addition to the silicon type compounds having bis(phenylcarbazol) group in molecule represented by formula 1 or 2 according to the invention, there can be used N-carbazol derivatives such as phenylcarbazol and polyvinylcarbazol, and conventional amine derivatives having an aromatic condensed ring such as N,N'-bis(3-methylphenyl)-N,N'-diphenyl-[1,1-biphenyl]-4,4'-diamine (TPD) and N,N'-di(naphthalene-1-yl)-N,N'-diphenyl benzidine (α -NPD) as the hole transport layer materials.
- [65] Then, emitting layer (EML) materials can be formed on the top of the hole transport layer by methods such as vacuum deposition, spin coating, casting, LB method, and electrochemical deposition. Particularly, the formation by the electrochemical deposition is preferable. In the case of forming the emitting layer by the electrochemical deposition, the conditions can be varied depending on the compounds to be used, but in general, they are preferably chosen within almost the same conditions as used for the formation of the hole injection layer.
- [66] The emitting layer materials are not limited to specific ones and for example, the silicon type compounds represented by formula 1 or 2 of the invention can be used alone or they can be used as a host.
- [67] In the case of the silicon type compounds represented by formula 1 or 2 as luminescence host, phosphorescent or fluorescent dopants can be used together to form the emitting layer. As the fluorescent dopants, IDE102 or IDE105 commercially available from Idemitsu Co., Ltd. can be used and as the phosphorescent dopants, the green phosphorescent dopant Ir(ppy)₃(fac tris(2-phenylpyridine) iridium), the blue phosphorescent dopant F2Irp(III)bis[4,6-di-fluorophenyl]-pyridinato-N,C2' picolinate) and the red phosphorescent dopant RD 61 from UDC Co., Ltd. can be jointly vacuum deposited (doping).
- [68] The doping concentration of the dopants is not especially limited but it is preferred that the concentration of the dopants is 0.01 to 15 parts by weight of 100 parts by weight of host. If the content of the dopants is less than 0.01 parts by weight, the

doping amount is not sufficiently enough for color development, and if it exceeds 15 parts by weight, efficiency may be rapidly reduced due to concentration quenching. When the phosphorescent dopant is co-used in the emitting layer, it is preferred that hole blocking layer (HBL) materials are further laminated by vacuum deposition or spin coating method to prevent triplet excited state or hole from diffusing into the electron transport layer (ETL). The hole blocking materials are not limited to specific ones and any known materials that have been used as hole blocking materials can be used. For example, there are oxadiazole derivatives or triazole derivatives, phenanthroline derivatives, or hole blocking materials described in Japan Patent Laid-Open No. 11-329734 (A1), and typically, Balq, phenanthroline type compounds (e.g.: BCP of UDC Co., Ltd.), etc. can be used.

- [69] On the top of the thus formed emitting layer are formed electron transport layer materials, and the electron transport layer can be formed by methods such as vacuum deposition, spin coating, casting, and electrochemical deposition and preferably, it is formed by the electrochemical deposition.
- [70] The electron transport layer materials function to stably transport electrons injected from electron injection electrode (cathode) and are not limited to specific ones and for example, quinoline derivatives, especially tris(8-quinolinolate)aluminum (Alq₃) can be employed. Also, on the top of the electron transport layer can be laminated electron injection layer (EIL) which has materials capable of making the injection of electrons from cathode easy and as the electron injection layer materials, such materials as LiF, NaCl, CsF, Li₂O, and BaO can be used.
- [71] After that, on the top of the electron transport layer can be formed electron injection layer (EIL) materials, and the electron injection layer can be formed with ordinary electron injection layer materials by methods such as vacuum deposition, spin coating, casting, and electrochemical deposition and preferably, it is formed by the electrochemical deposition.
- [72] Finally, metal for the formation of cathode is formed on the top of the electron injection layer by methods such as vacuum deposition or sputtering method and this is used as cathode. For the metal for the formation of cathode, there can be used metals, alloys, electrically conductive compounds, and mixture thereof having low work function. In particular, there are lithium (Li), magnesium (Mg), aluminum (Al), aluminum-lithium (Al-Li), calcium (Ca), magnesium-indium (Mg-In), magnesium-silver (Mg-Ag) and the like. Furthermore, to obtain front light emitting devices, transmissive cathode using ITO or IZO can be used.
- [73] The organic light emitting devices of the invention not only have the structure of anode, hole injection layer (HIL), hole transport layer (HTL), emitting layer (EML), electron transport layer (ETL), electron injection layer (EIL) and cathode but also can

be embodied in various structures, and if necessary, it is possible to form another intermediate layers of one or two layers. Also, it is noted that although the hole injection layer (HIL), electron injection layer (EIL), hole blocking layer (HBL), etc. are not necessarily necessary, light emitting efficiency can be improved with the formation of these layers.

[74] Further, in the invention, another intermediate layer of one or more layers can be formed between the layers selected from anode, hole injection layer (HIL), hole transport layer (HTL), emitting layer (EML), hole blocking layer (HBL), electron transport layer (ETL), electron injection layer (EIL) and cathode.

[75] The thickness of the organic thin layers formed in accordance with the present invention can be adjusted, depending on the required level and it is preferably 10 to 1,000 Å and more preferably, 20 to 150 Å.

[76] Furthermore, after the formation of the organic thin layers, washing step or dry step can be further carried out, if necessary. Through the washing step can be eliminated foreign substances that might be present in the organic thin layers and in connection with the dry process, any conventional dry methods that are carried out after the formation of organic thin layers for known organic light emitting devices can be applied.

[77] The organic thin layers formed by depositing the silicon type compounds having bis(phenylcarbazol) in molecule represented by formula 1 or 2 above of the invention have excellent adhesion strength to substrates and they have uniform surface and excellent morphological stability because the thickness of the organic thin layers can be controlled at a molecule level.

[78] For better understanding of the present invention, preferred embodiments follow. The following examples are intended to merely illustrate the invention without limiting the scope of the invention.

[79]

[80] [EXAMPLES]

[81] All the works in the examples of the invention were done under nitrogen or argon atmosphere using standard Schlenk technology. Tetrahydrofuran (THF) was distilled using potassium benzophenone immediately before in use. ¹H and ¹³C NMRs were determined using Varian mercury 300 of 300.1 and 75.4 MHz. All the chemical shifts of hydrogen and carbon were determined using residual benzene of quenching solvent (99.5% CDCl₃) on the basis of tetramethylsilane (Me₄Si). The element analysis was carried out using CHNS-O EA 1108 analyzer of Carlo Erba Co., Ltd. Fluorescent quantum yield was obtained through dilution methods on the basis of 9,10-diphenylanthracene. For the CV experiment, BAS 100 electrochemical analyzer was used. Three-electrode system - glassy carbon as a working electrode, platinum

electric wire as a counter electrode and silver electric wire as a reference electrode - was used. Normal-butyllithium diluted in 1,4-dibromobenzene 2.5 M hexane was purchased from Aldrich Co., Ltd. and used without further purification.

[82]

[83] Example 1. Synthesis of 9,9'-bis(phenylcarbazol) derivatives containing silicon ring (compounds of formulae a-d below)

[84] 9,9'-bis(phenylcarbazol) containing a silicon ring (compounds of formula a-d below) was synthesized in accordance with reaction formula 1 below. 1,4-dibromobenzene and carbazol were reacted using Ullmann's reaction to prepare (bromophenyl)carbazol compounds, to which normal-butyllithium and silanecyclochloride were added and then reacted to synthesize 9,9'-bis(phenylcarbazol) derivative compounds a-d. However, in the case of 4-CBP compound a, ring coupling angle was unstable so quadrangular ring shortly became loose. All the 9,9'-bis(phenylcarbazol) derivatives containing silicon ring except for the quadrangle could be separated through columns with yields of 40-50%.

[85] (Synthesis of 9-(4-bromophenyl)carbazol (Compound a))

[86] Teflon magnetic stir bar, 1,4-dibromobenzene (25.184 g, 200 mmol), carbazol (8.36 g, 50 mmol), K_2CO_3 (13.82 g, 100 mmol), and $CuSO_4$ (7.98 g, 50 mmol) were put in a 100-mL one-neck flask and stirred at 210 °C for 16 hours without solvents. After the completion of the reaction, the mixture was diluted with methylenechloride and filtered and then, the filtered solution was washed with distilled water and brine. The thus obtained organic layer was dried using $MgSO_4$.

[87] 1H NMR ($CDCl_3$): δ 8.21 (d, 2H), 7.40 (d, 2H), 7.25 (t, 2H), 7.13 (t, 2H), 7.35 (d, 2H), 7.16 (d, 2H) ^{13}C NMR ($CDCl_3$): δ 111.1, 122.5, 125.7, 128.1, 130.2, 133.3

[88] (Synthesis of 9,9'-bis(phenylcarbazole) containing pentagonal silicon ring (Compound b))

[89] After 9-(4-bromophenyl)carbazole (1) (2.25 g, 12.5 mmol) was diluted in distilled tetrahydrofuran (THF) (10 mL), 2.5 M normal-butyllithium was dropwise added thereto at -78 °C. Stirring was carried out at the same temperature for 30 min and then dichlorocyclopentylsilane (2 mmol) was slowly dropwise added thereto. After the completion of dropwise addition, the reaction temperature was raised to room temperature and the mixture was stirred again for 3 hours. After the elimination of the solvents, the residuals were separated through silica gel column using ethylacetate/hexane (volume ratio 1:10) as a developer and the yield was 43%.

[90] 1H NMR ($CDCl_3$): δ 8.055, 7.753, 7.320, 7.215 (m, 16H, Cz), 7.536, 7.408 (m, 8H, Ph), 1.839 (m, 4H, CH_2), 1.198 (t, 4H, CH_2). ^{13}C NMR ($CDCl_3$): 12.741, 28.158 (CH_2), 110.098, 120.265, 120.538, 123.695, 126.145, 126.555, 135.963, 136.464, 139.05, 140.811 (CH).

[91] (Synthesis of 9,9'-bis(phenylcarbazole) containing silicon ring having pentagonal double bond (Compound c))

[92] This compound was synthesized in accordance with the same method as used for Compound b above, using dichloropentenylsilane instead of dichlorocyclopentylsilane in synthesis of Compound b and separated with a yield of 47%.

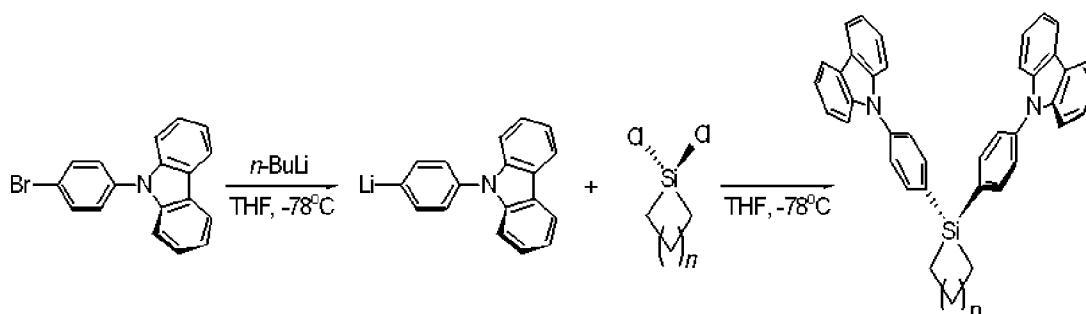
[93] ^1H NMR (CDCl_3): 8.152, 7.877, 7.414, 7.297 (m, 16H, Cz), 7.654, 7.501 (m, 8H, Ph), 6.145 (m, H, CH_2), 2.027 (d, 4H, CH). ^{13}C NMR (CDCl_3): 0.359, 17.361 (CH_2), 110.038, 120.265, 120.516, 123.672, 126.130, 126.600, 131.229, 134.787, 136.464, 140.743 (CH).

[94] (Synthesis of 9,9'-bis(phenylcarbazole) containing silicon ring having hexagon (Compound d))

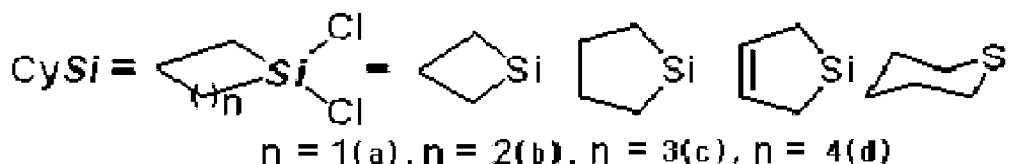
[95] This compound was synthesized in accordance with the same method as used for Compound b above, using dichlorohexylsilane instead of dichlorocyclopentylsilane in synthesis of Compound b and separated with a yield of 50%.

[96] ^1H NMR (CDCl_3): 8.125, 7.805, 7.380, 7.266 (m, 16H, Cz), 7.588, 7.474 (m, 8H, Ph), 1.890 (m, 4H, CH_2), 1.614 (m, 2H, CH_2), 1.334 (t, 4H, CH_2). ^{13}C NMR (CDCl_3): 12.073, 24.789, 30.305 (CH_2), 110.159, 120.273, 120.561, 123.710, 126.168, 126.585, 135.902, 136.236, 138.930, 140.81 (CH).

[97]



[98]



[99] [Reaction formula 1]

[100]

[101] Example 2. Synthesis of 1,1'-bis(9-phenylcarbazole)-2,3,4,5-tetraphenylsilole

[102] (Bromophenyl)carbazole was dissolved in distilled THF (10 ml), to which normal-butyllithium diluted in 2.5 M hexane was then dropwise added at -78°C . The mixture was stirred at the same temperature for 30 min and then dropwise added toward dichlorotetraphenylsilane compound diluted in THF (20 ml) using a cannula. After dropwise addition, the reaction temperature was raised to room temperature and

stirring was further carried out for 4 hours. After water was added to the mixture, it was extracted using ethyl acetate and washed with water and brine. The organic layer was dried using MgSO_4 . The solvent was removed under reduced pressure and the residue was separated by silica gel column using ethyl acetate and hexane developer (volume ratio 1:10), affording 1,1-bis(9-phenylcarbazol)-2,3,4,5-tetraphenylsilole.

[103] ^1H NMR (CDCl_3): 8.15 (d, 4H), 7.97 (d, 4H), 7.66 (d, 4H), 7.53 (d, 4H), 7.43 (t, 8H), 7.30 (m, 8H), 7.28 (m, 8H) ^{13}C NMR (CDCl_3): 111.1, 122.5, 125.7, 128.1, 130.2, 133.3

[104]

[105] **Example 3. Electrochemical deposition**

[106] The electrochemical properties and the HOMO and LUMO levels of the compounds synthesized in Examples 1 and 2 above, CV experiments were performed using Pt working electrode, Pt counter electrode, and $\text{Ag}/\text{Ag}^+(0.1\text{M})$ electrode as reference electrode. CV was carried out with the variation of several measuring speeds by dissolving 0.1 M tetrabutylammoniumtetrafluoroborate (Bu_4NBF_4) as an electrolyte in methylenechloride solvent and blowing nitrogen gas at room temperature. The measured values were examined on the basis of ferrocene. The electrochemical deposition using CV was carried out at a rate of 100 mV/s. First, the electrochemical properties of 9,9-bis(phenylcarbazol) derivatives containing silicon ring were investigated. In the course of analyzing the electrochemical properties, it was found that a certain amount of films were formed on the working electrode. The CV pictures of the compounds synthesized in Example 1 are shown in Fig. 1 to Fig. 3 and the CV picture of the compound synthesized in Example 2 is shown in Fig. 4.

[107] As seen in Fig. 1 to Fig. 4, they were all deposited electrochemically.

[108] Also, the compound synthesized in Example 2 was diluted in chloroform and then UV spectrum and PL spectrum were determined. The pictures are shown in Figures 5 to 6.

[109] The emission of silole compound was increased as the viscosity of the silole solution increased. Such results show that AIE (Aggregation-Induced Emission) effects were resulted from the rotation of an aromatic ring substituted at its end relative to single bond axis having silole in its center. Thus, when the compound was dissolved in acetone solution, it did not emit light whereas when some water incapable of dissolving the compound was added to the acetone solution, strong PL spectrum occurred. From this experiment, it was identified that the compound of Example 2 caused AIE phenomena.

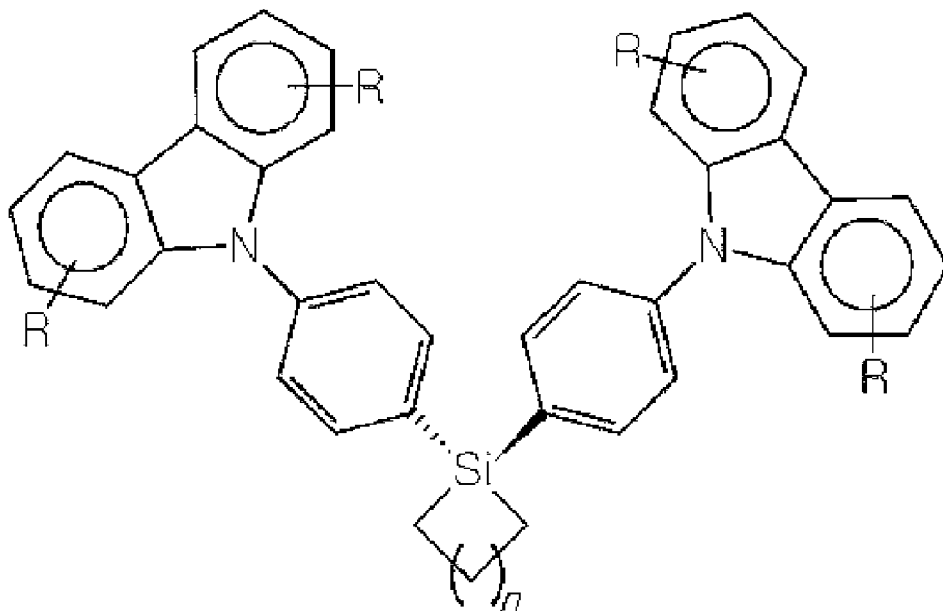
Industrial Applicability

[110] The silicon type compounds having bis(phenylcarbazol) in molecule represented by

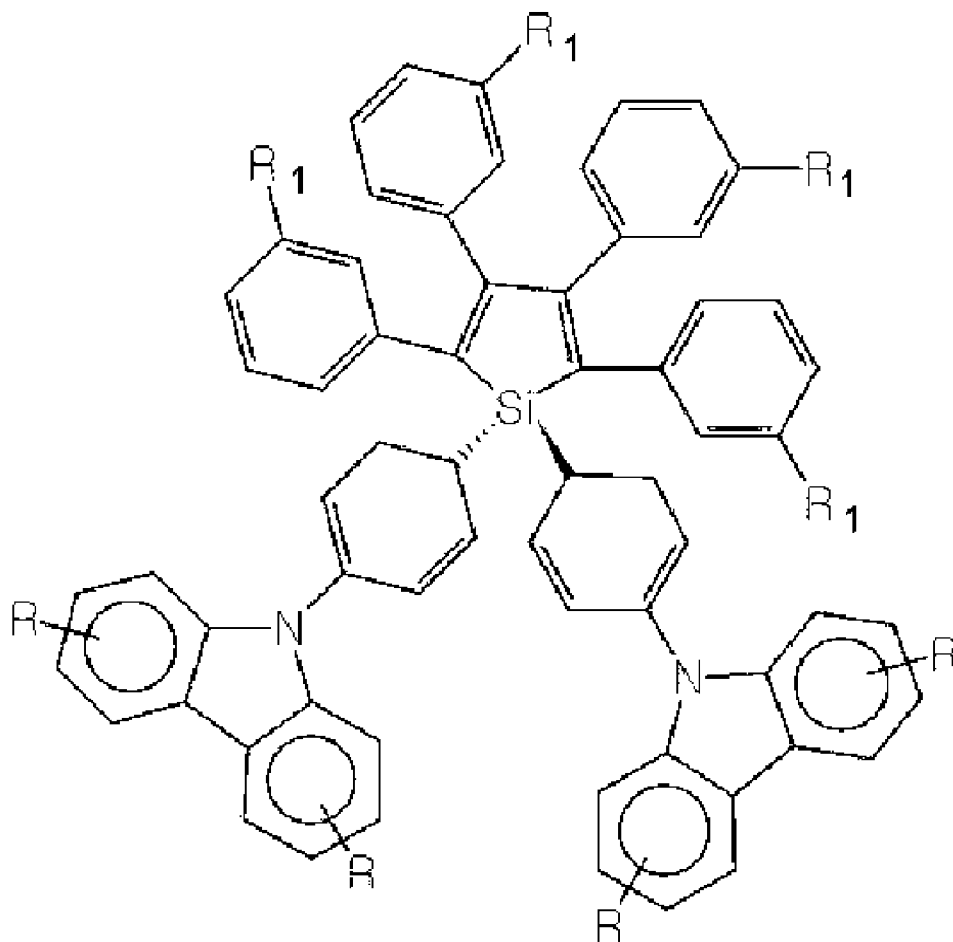
formula 1 or 2 in accordance with the present invention have excellent blue luminescent characteristics and hole transmission characteristics and at the same time, they not only can be used as blue luminescent materials or used as a host to a variety of phosphorescent or fluorescent dopants such as red, green, blue and white but also enable high efficient luminescence when applied to organic light emitting devices and can confer such performances as low voltage, high brightness and long longevity.

Claims

- [1] A silicon type compound having bis(phenylcarbazol) group in molecule represented by formula 1 or 2:



[1]



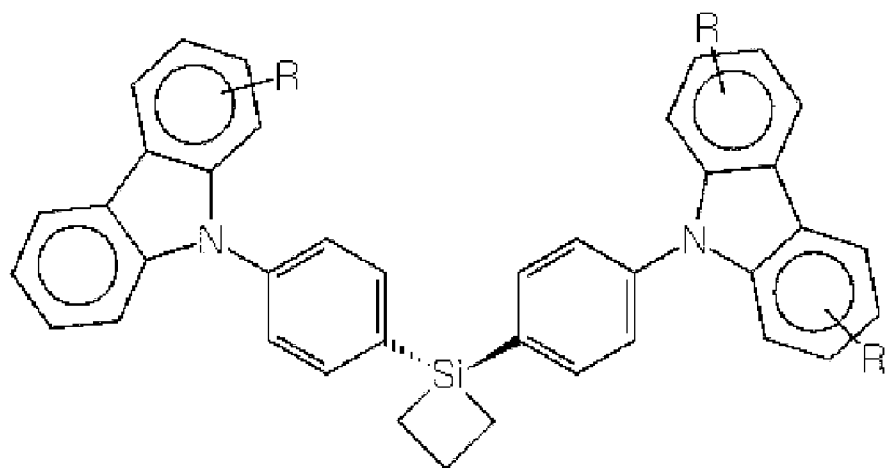
[2]

wherein R is each independently a substituted or unsubstituted alkyl group of 1 to 50 carbon atoms, a substituted or unsubstituted aryl group of 6 to 50 carbon atoms, a substituted or unsubstituted hetero ring group of 6 to 50 carbon atoms or a substituted or unsubstituted heterocyclic ring group of 6 to 50 carbon atoms, R_1 is each independently a hydrogen atom or a substituted or unsubstituted alkyl group of 1 to 50 carbon atoms, and

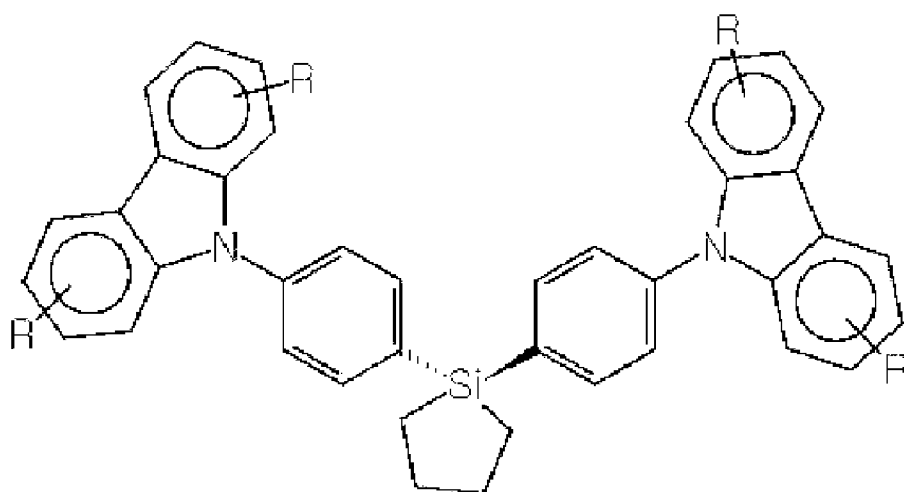
n is an integer of 1 to 3.

[2]

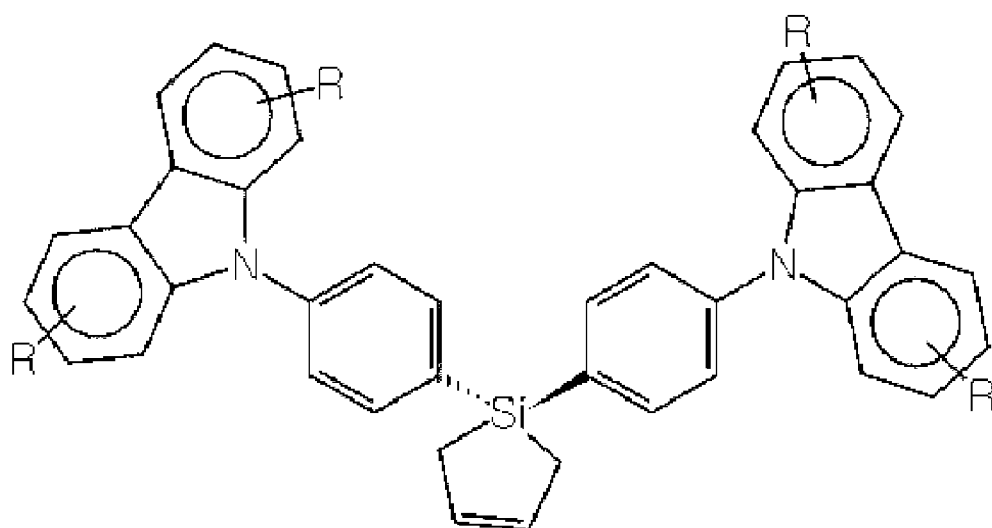
The silicon type compound having bis(phenylcarbazol) group in molecule according to claim 1, wherein the compound is represented by any one of formulae 1-1 to 1-4:



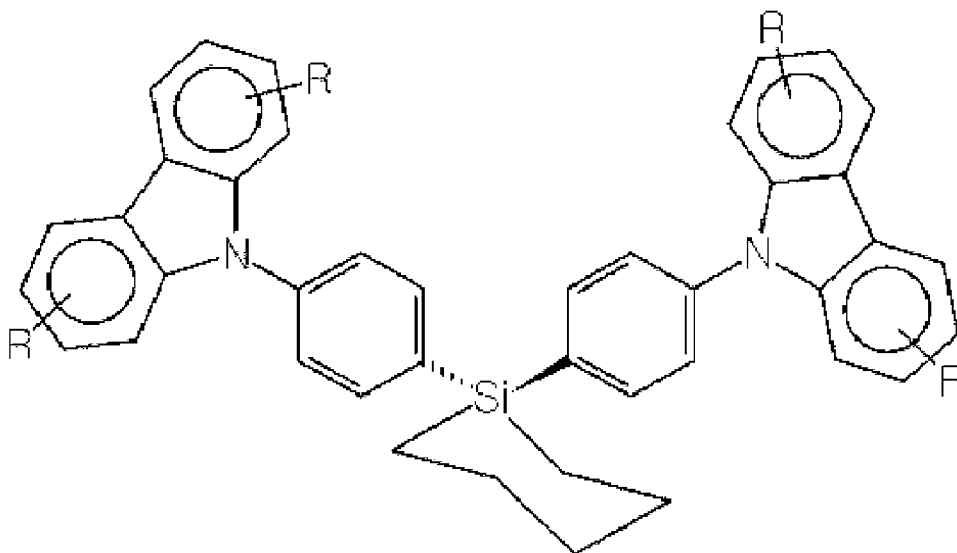
[1-1]



[1-2]



[1-3]



[1-4]

wherein R is each independently a substituted or unsubstituted alkyl group of 1 to 50 carbon atoms, a substituted or unsubstituted aryl group of 6 to 50 carbon atoms, a substituted or unsubstituted hetero ring group of 6 to 50 carbon atoms or a substituted or unsubstituted heterocyclic ring group of 6 to 50 carbon atoms.

[3] A method for preparation of the compound having bis(phenylcarbazol) group in molecule represented by formula 1 as defined in claim 1 comprising reacting bromobenzene and carbazol to prepare a (bromophenyl)carbazol compound, adding n-butyllithium to the (bromophenyl)carbazol compound to a (lithiumphenyl)carbazol compound, and reacting the (lithiumphenyl)carbazol compound and silanecyclodichloride.

[4] A method for preparation of the silicon type compound having bis(phenylcarbazol) group in molecule represented by formula 2 as defined in claim 1 comprising reacting bromobenzene and carbazol to prepare a (bromophenyl)carbazol compound and reacting the (bromophenyl)carbazol compound and dichlorotetraphenylsilane.

[5] An organic thin layer of organic light emitting devices formed from the compound having bis(phenylcarbazol) group in molecule represented by formula 1 or 2 as defined in claim 1.

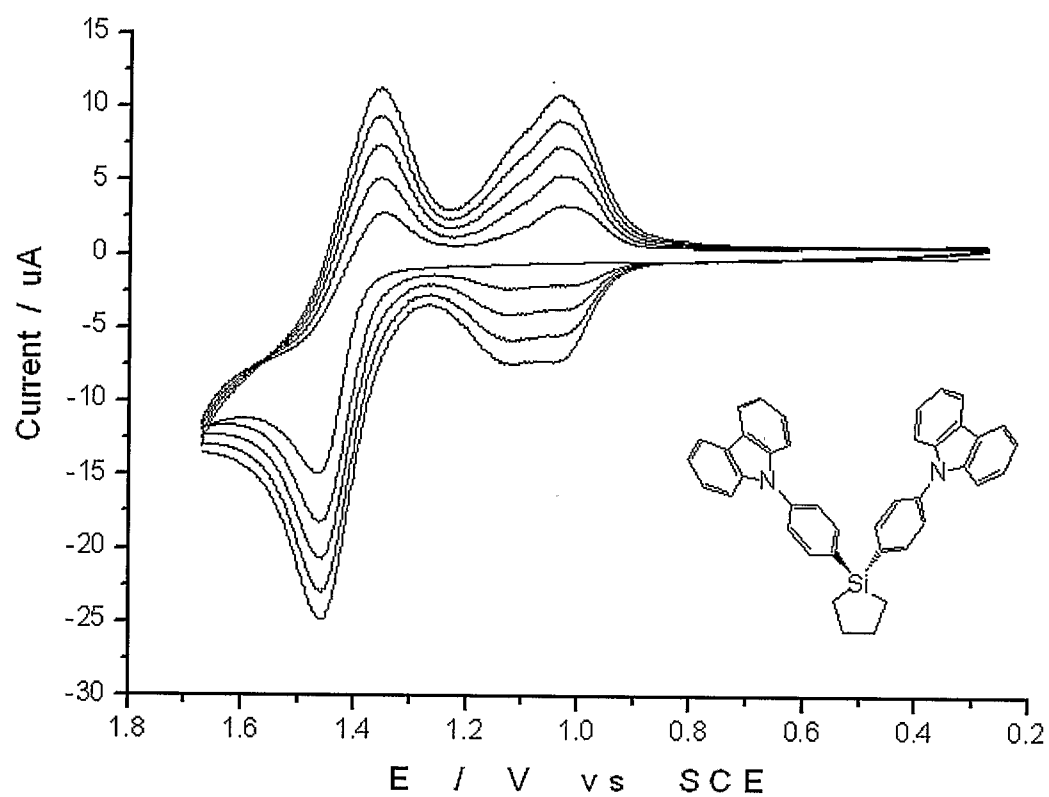
[6] The organic thin layer of organic light emitting devices according to claim 5 wherein the organic thin layer is hole injection layer (HIL), hole transport layer (HTL), emitting layer (EML), hole blocking layer (HBL), electron transport layer (ETL), or electron injection layer (EIL).

[7] The organic thin layer of organic light emitting devices according to claim 5 wherein the organic thin layer is formed by electrochemical deposition of the

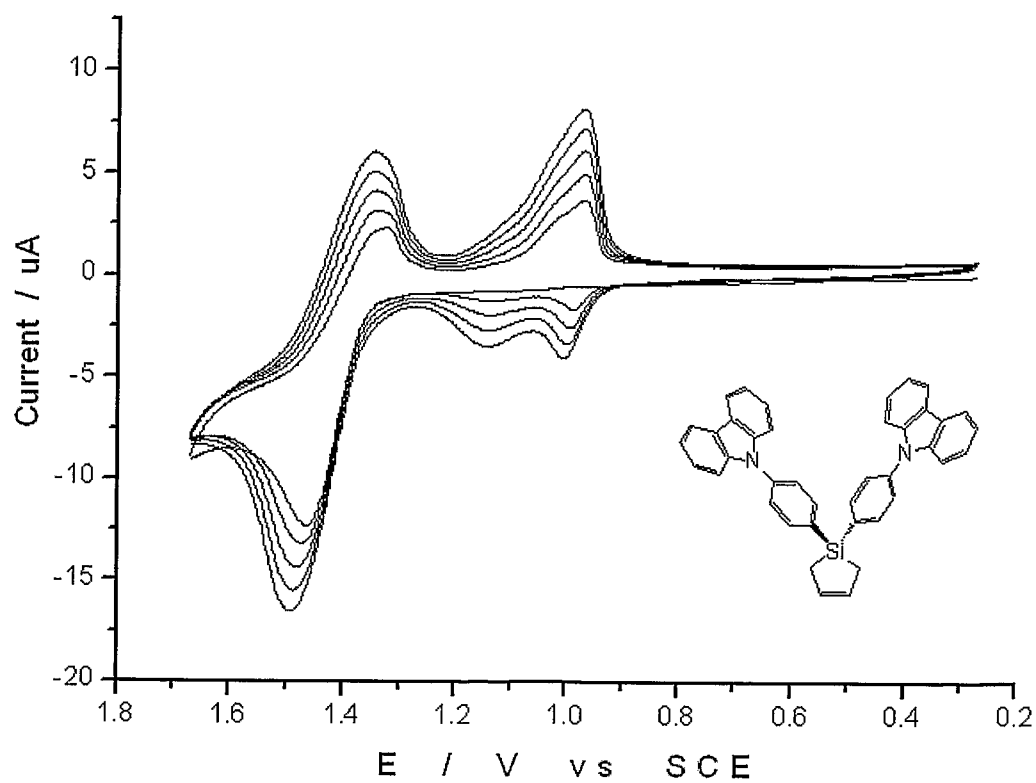
compound having bis(phenylcarbazol) group in molecule represented by formula 1 or 2.

- [8] An organic light emitting device comprising at least one organic thin layer between anode and cathode characterized in that it comprises at least one organic thin layer as described in claim 5.
- [9] The organic light emitting device according to claim 8 wherein the organic light emitting device comprises consecutive two or more organic thin layers as described in claim 5.
- [10] A display device comprising the organic light emitting device as described in claim 7.

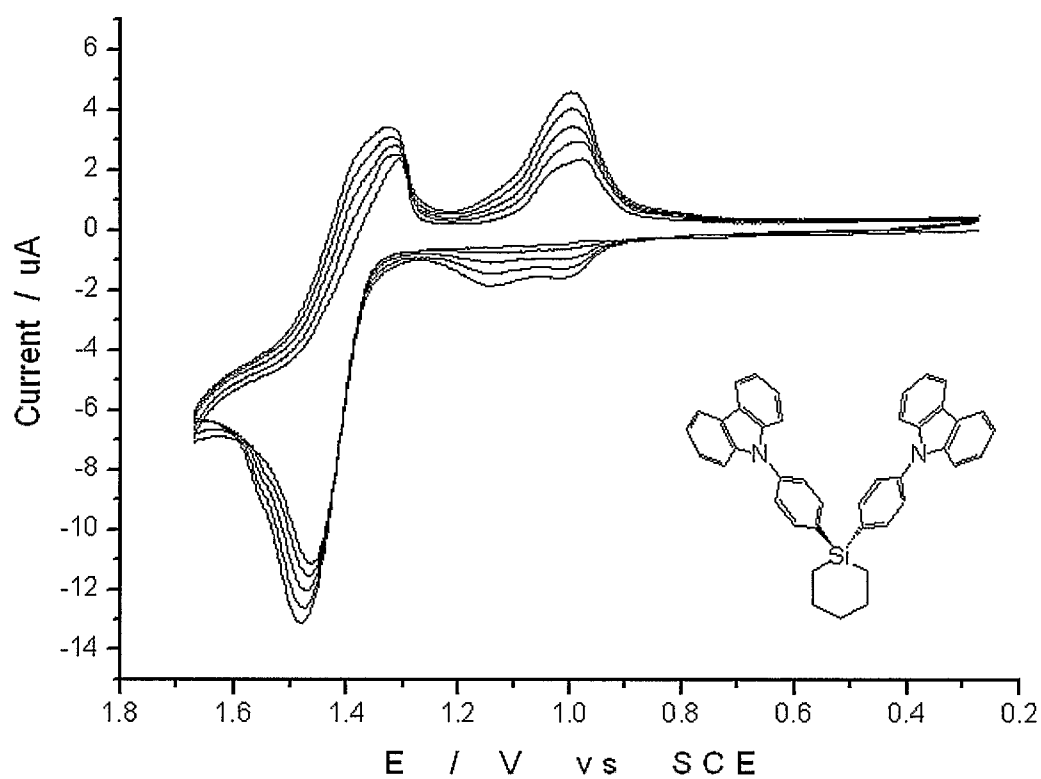
[Fig. 1]



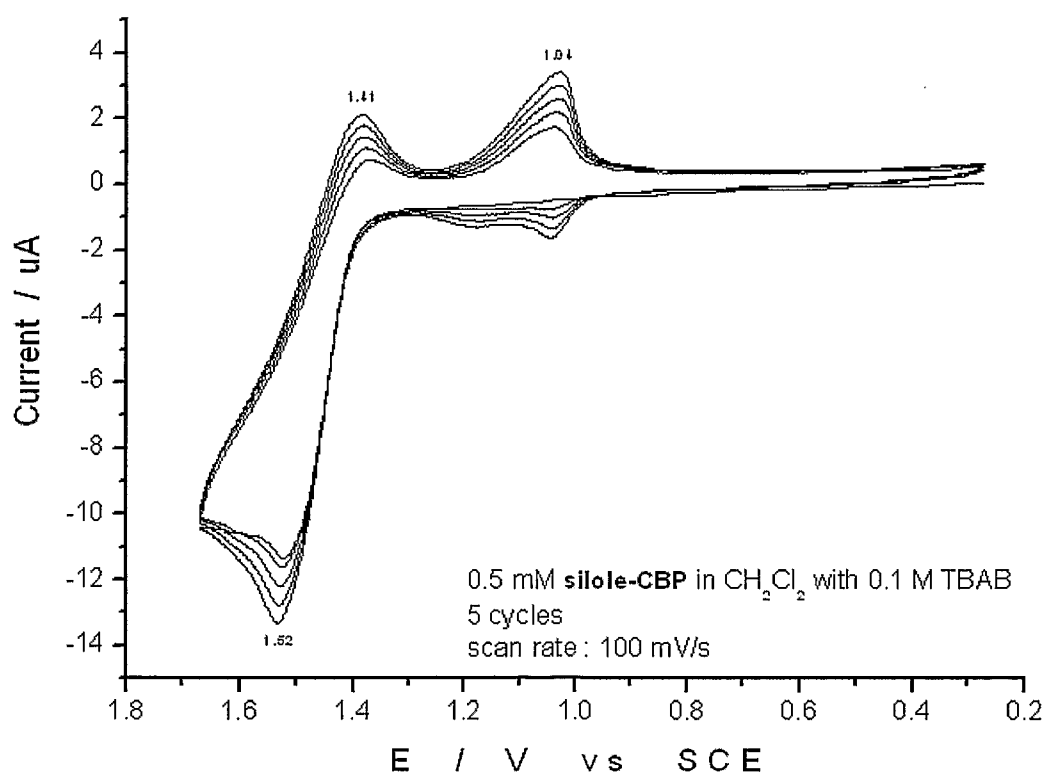
[Fig. 2]



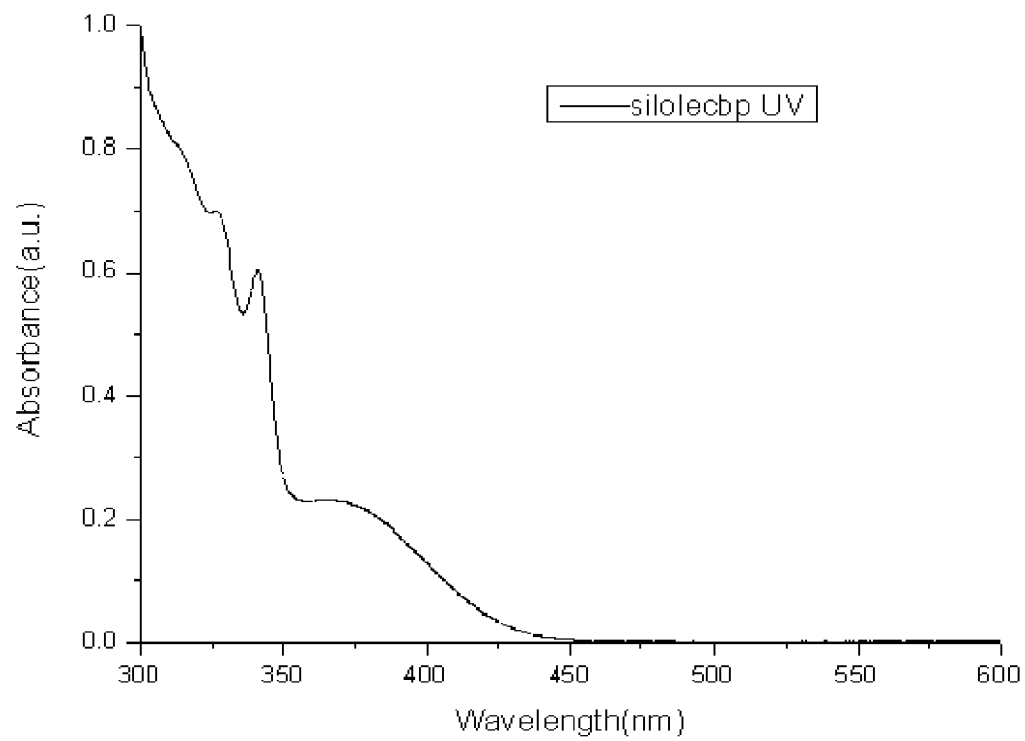
[Fig. 3]



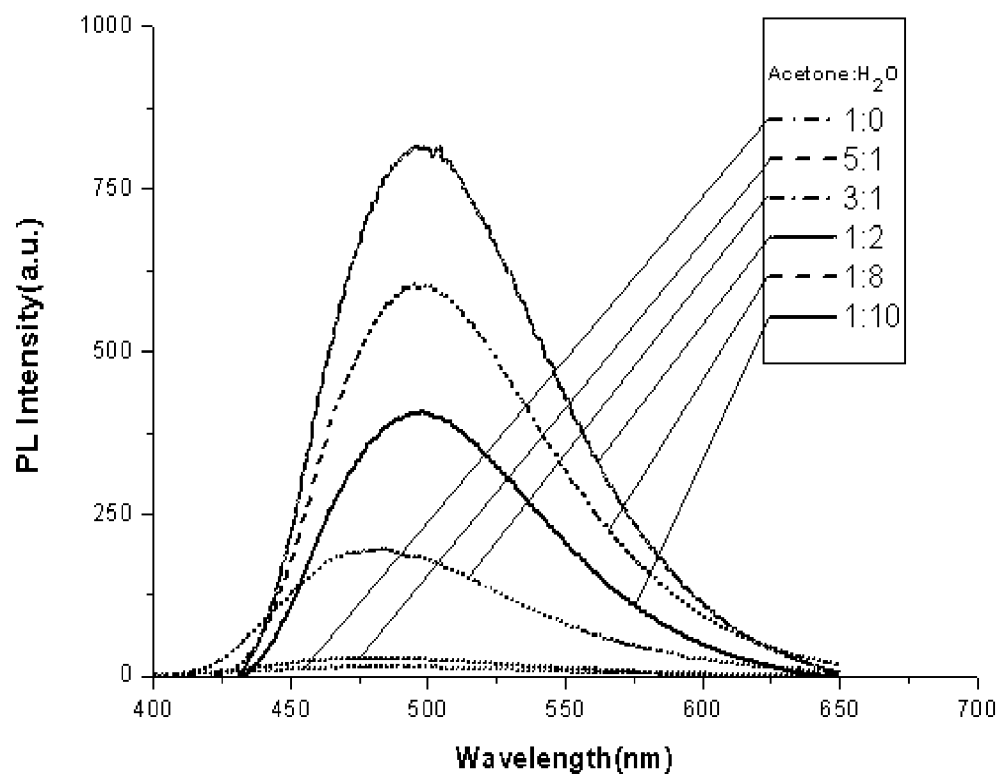
[Fig. 4]



[Fig. 5]



[Fig. 6]



VIII-5-1	Declaration: Non-prejudicial disclosure or exceptions to lack of novelty Declaration as to non-prejudicial disclosures or exceptions to lack of novelty (Rules 4.17(v) and 51bis.1(a)(v)): Name (LAST, First)	in relation to this international application HAN, Won-sik declares that the subject matter claimed in this international application was disclosed as follows:
VIII-5-1(i)	Kind of disclosure:	publication
VIII-5-1(i)	Date of disclosure:	01 December 2005 (01.12.2005)
VIII-5-1(i)	Title of disclosure:	CBP (N,N'-dicarbazoly-4,4'-biphenyl) Moieties as a host material in organic light-emitting diodes and their electrochemical properties
VIII-5-1(i)	Place of disclosure:	Paper for Degree of master in department of material chemistry, Graduate school, Korea University

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2007/002066**A. CLASSIFICATION OF SUBJECT MATTER***C07F 7/10(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)

IPC8 C07F

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

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

STN(CAPLUS), PAJ, e-KIPASS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2005-220088 A (CHEMIPROKASEI KAISHA LTD) 18 August 2005 See the whole document.	1-10
A	US 6,310,231 B (Fuji Photo Film Co., Ltd.) 30 October 2001 See the whole document.	1-10
A	US 2005/0064238 A (Seok Jong Lee et al.) 24 March 2005 See the whole document.	1-10
A	US 2005/0287393 A (Jun-Yeob Lee et al.) 29 December 2005 See the whole document.	1-10
A	US 2005/0214572 A (Fuji Photo Film Co., Ltd.) 29 September 2005 See the whole document.	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search

03 SEPTEMBER 2007 (03.09.2007)

Date of mailing of the international search report

03 SEPTEMBER 2007 (03.09.2007)

Name and mailing address of the ISA/KR

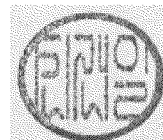
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SHIN, Gun Il

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2007/002066

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