



US 20170012206A1

(19) **United States**(12) **Patent Application Publication**  
**UEDA et al.**(10) **Pub. No.: US 2017/0012206 A1**(43) **Pub. Date: Jan. 12, 2017**(54) **ORGANIC-ELECTROLUMINESCENT-ELEMENT  
MATERIAL AND ORGANIC  
ELECTROLUMINESCENT ELEMENT USING  
SAME****Publication Classification**(51) **Int. Cl.****H01L 51/00** (2006.01)**C09K 11/02** (2006.01)**C07F 5/02** (2006.01)**C09K 11/06** (2006.01)(52) **U.S. Cl.**CPC ..... **H01L 51/008** (2013.01); **C09K 11/06**(2013.01); **C09K 11/025** (2013.01); **C07F****5/027** (2013.01); **H01L 51/0085** (2013.01);**H01L 51/5016** (2013.01)(71) Applicant: **NIPPON STEEL & SUMIKIN  
CHEMICAL CO., LTD.**, Tokyo (JP)(72) Inventors: **Tokiko UEDA**, Kitakyushu-shi (JP);  
**Junya OGAWA**, Kitakyushu-shi (JP);  
**Takahiro KAI**, Kitakyushu-shi (JP);  
**Masashi TADA**, Kitakyushu-shi (JP)(73) Assignee: **NIPPON STEEL & SUMIKIN  
CHEMICAL CO., LTD.**, Tokyo (JP)(21) Appl. No.: **15/117,788**(22) PCT Filed: **Feb. 23, 2015**(86) PCT No.: **PCT/JP2015/055074**

§ 371 (c)(1),

(2) Date: **Aug. 10, 2016**(30) **Foreign Application Priority Data**

Mar. 28, 2014 (JP) ..... 2014-069998

**ABSTRACT**

Disclosed is an organic electroluminescent device (organic EL device) that is improved in luminous efficiency, sufficiently secures driving stability, and has a simple construction. The device is an organic electroluminescent device having organic layers including a light-emitting layer between an anode and a cathode laminated on a substrate, in which a carborane compound is incorporated into at least one layer of the organic layers, or is incorporated as a host material into a light-emitting layer containing a phosphorescent light-emitting dopant and the host material. The carborane compound has a structure in which a N-containing fused aromatic ring is bonded to a carborane ring. The N-containing fused aromatic ring is a quinoline ring or has a structure obtained by substituting 1 to 3 ring-forming carbon atoms in a quinoline ring with N atoms.

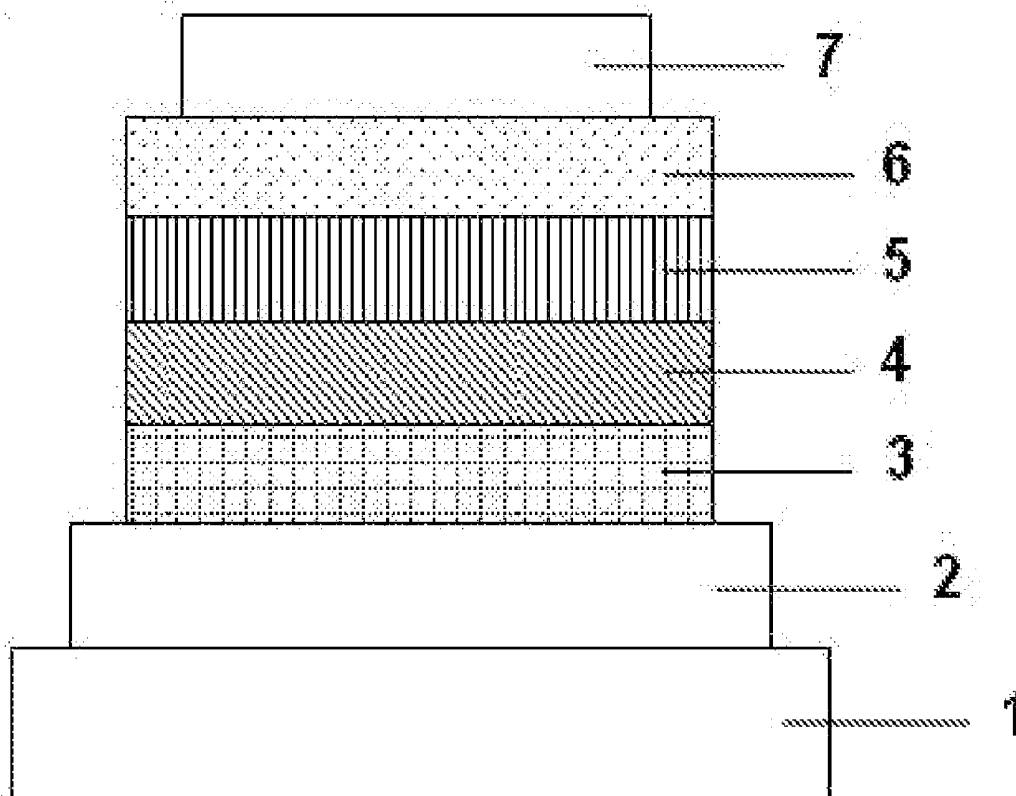
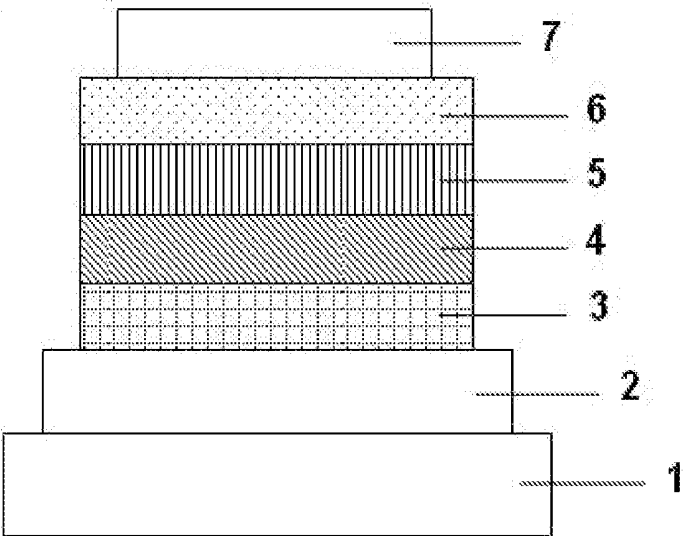


Fig. 1



**ORGANIC-ELECTROLUMINESCENT-ELEMENT  
MATERIAL AND ORGANIC  
ELECTROLUMINESCENT ELEMENT USING  
SAME**

**TECHNICAL FIELD**

**[0001]** The present invention relates to an organic electroluminescent device using a carborane compound as a material for an organic electroluminescent device, and more specifically, to a thin film-type device that emits light by applying an electric field to a light-emitting layer containing an organic compound.

**BACKGROUND ART**

**[0002]** In general, an organic electroluminescent device (hereinafter referred to as organic EL device) includes a light-emitting layer and a pair of counter electrodes interposing the light-emitting layer therebetween in its simplest structure. That is, the organic EL device uses the phenomenon that, when an electric field is applied between both the electrodes, electrons are injected from a cathode and holes are injected from an anode, and each electron and each hole recombine in the light-emitting layer to emit light.

**[0003]** In recent years, progress has been made in developing an organic EL device using an organic thin film. In order to enhance luminous efficiency particularly, the optimization of the kind of electrodes has been attempted for the purpose of improving the efficiency of injection of carriers from the electrodes. As a result, there has been developed a device in which a hole-transporting layer formed of an aromatic diamine and a light-emitting layer formed of an 8-hydroxyquinoline aluminum complex ( $\text{Alq}_3$ ) are formed between electrodes as thin films, resulting in a significant improvement in luminous efficiency, as compared to related-art devices in which a single crystal of anthracene or the like is used. Thus, the development of the above-mentioned organic EL device has been promoted in order to accomplish its practical application to a high-performance flat panel having features such as self-luminescence and rapid response.

**[0004]** Further, investigations have been made on using phosphorescent light rather than fluorescent light as an attempt to raise the luminous efficiency of a device. Many kinds of devices including the above-mentioned device in which a hole-transporting layer formed of an aromatic diamine and a light-emitting layer formed of  $\text{Alq}_3$  are formed emit light by using fluorescent light emission. However, by using phosphorescent light emission, that is, by using light emission from a triplet excited state, luminous efficiency is expected to be improved by from about three

times to about four times, as compared to the case of using related-art devices in which fluorescent light (singlet) is used. In order to accomplish this purpose, investigations have been made on adopting a coumarin derivative or a benzophenone derivative as a light-emitting layer, but extremely low luminance has only been provided. Further, investigations have been made on using a europium complex as an attempt to use a triplet state, but highly efficient light emission has not been accomplished. In recent years, many investigations have been made mainly on an organic metal complex, such as an iridium complex, for the purpose of attaining high luminous efficiency and a long lifetime.

**CITATION LIST**

**Patent Literature**

- [0005]** [PTL 1] WO 01/041512 A1
- [0006]** [PTL 2] JP 2001-313178 A
- [0007]** [PTL 3] JP 2005-162709 A
- [0008]** [PTL 4] JP 2005-166574 A
- [0009]** [PTL 5] US 2012/0319088 A1
- [0010]** [PTL 6] WO 2013/094834 A1

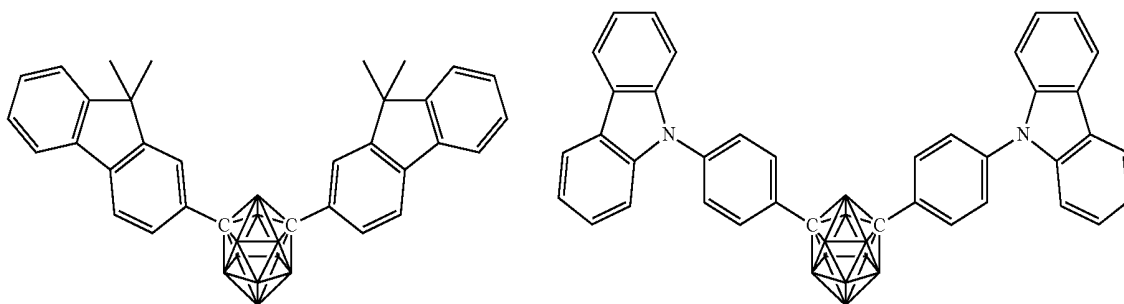
**Non Patent Literature**

- [0011]** [NPL 1] J. Am. Chem. Soc. 2012, 134, 17982-17990

**[0012]** In order to obtain high luminous efficiency, host materials that are used with the dopant materials described above play an important role. A typical example of the host materials proposed is 4,4'-bis(9-carbazolyl)biphenyl (CBP) as a carbazole compound disclosed in Patent Literatures 1 and 2. When CBP is used as a host material for a green phosphorescent light-emitting material typified by a tris(2-phenylpyridine) iridium complex ( $\text{Ir}(\text{ppy})_3$ ), the injection balance between charges is disturbed because CBP has the characteristic of facilitating the delivery of holes and not facilitating the delivery of electrons. Thus, excessively delivered holes flow out into an electron-transporting layer side, with the result that the luminous efficiency from  $\text{Ir}(\text{ppy})_3$  lowers.

**[0013]** In order to provide high luminous efficiency to an organic EL device as described above, it is necessary to use a host material that has high triplet excitation energy, and is striking a good balance in both charge (hole and electron)-injecting/transporting property. Further desired is a compound that is electrochemically stable and has high heat resistance and excellent amorphous stability, and hence further improvement has been demanded.

**[0014]** In Patent Literatures 3, 4, 5, and 6 and Non Patent Literature 1, there are disclosures of such carborane compounds as shown below.





aromatic heterocyclic group having 3 to 17 carbon atoms, or a linked aromatic group formed by linking 2 to 6 aromatic groups each selected from the aromatic hydrocarbon group and the aromatic heterocyclic group.

(3)  $L^1$  and  $L^2$  each independently represent a single bond, a substituted or unsubstituted aromatic heterocyclic group having 3 to 30 carbon atoms, or a linked aromatic group formed by linking 2 to 6 aromatic groups each selected from the aromatic heterocyclic group.

(4)  $m$  represents an integer of 0.

[0027] Part or all of hydrogen atoms in the carborane compound represented by the general formula (1) may each be substituted with a deuterium atom.

[0028] The present invention also relates to an organic electroluminescent device having a structure in which an anode, an organic layer, and a cathode are laminated on a substrate, in which the organic layer includes an organic layer containing the above-mentioned material for an organic electroluminescent device.

[0029] Further, it is preferred that the organic layer containing the material for an organic electroluminescent device include a phosphorescent light-emitting dopant.

[0030] The material for a phosphorescent device of the present invention adopts a structure in which a nitrogen-containing fused heterocyclic group formed by fusing two six-membered rings and a carborane skeleton are directly bonded to each other. The lowest unoccupied molecular orbital (LUMO) that affects an electron-injecting/transporting property is widely distributed over the entirety of a molecule of the carborane compound having such structural feature, and hence the electron-injecting/transporting property of the device can be controlled at a high level. Further, its electron-injecting/transporting property and hole-injecting/transporting property can be regulated by changing the kinds of  $L^1$  and  $L^2$ , or the substituent R. By virtue of the foregoing features, the use of the compound in an organic EL device has achieved a reduction in driving voltage of the device and high luminous efficiency.

[0031] In addition, the material for an organic electroluminescent device of the present invention shows a satisfactory amorphous characteristic and high heat stability, and at the same time, is extremely stable in an excited state. Accordingly, an organic EL device using the material has a long driving lifetime and durability at a practical level.

#### BRIEF DESCRIPTION OF DRAWINGS

[0032] FIG. 1 is a sectional view for illustrating an example of the structure of an organic EL device.

#### DESCRIPTION OF EMBODIMENTS

[0033] A material for an organic electroluminescent device of the present invention is a carborane compound represented by the general formula (1) and having a nitrogen-containing fused heterocyclic group that is formed by fusing two six-membered rings and contains at least one nitrogen atom. The carborane compound may exhibit such excellent effects as described above because the compound has a structure in which the nitrogen-containing fused heterocyclic group formed by fusing the two six-membered rings and a carborane skeleton are directly bonded to each other.

[0034] When the same symbol is present in plurality in the general formula (1), those represented by the same symbol

may be identical to or different from each other. For example, those represented not only by the ring A or X that is present in plurality in a molecule but also by, for example,  $L^2$  or R that may be present in plurality depending on a number represented by  $n$ ,  $s$ , or  $m$  may be identical to or different from each other.

[0035]  $L^1$  represents a single bond, an  $m+1$ -valent substituted or unsubstituted aromatic hydrocarbon group having 6 to 30 carbon atoms, an  $m+1$ -valent substituted or unsubstituted aromatic heterocyclic group having 3 to 30 carbon atoms, or an  $m+1$ -valent linked aromatic group formed by linking 2 to 6 of the substituted or unsubstituted aromatic rings. The linked aromatic group may be linear or branched, and the aromatic rings to be linked may be identical to or different from each other. When  $m=1$ ,  $s=1$  and  $L^1$  represents a group containing at least one aromatic heterocyclic group or a single bond.

[0036]  $L^2$  represents a single bond, a divalent substituted or unsubstituted aromatic hydrocarbon group having 6 to 30 carbon atoms, a divalent substituted or unsubstituted aromatic heterocyclic group having 3 to 30 carbon atoms, or a divalent linked aromatic group formed by linking 2 to 6 of the substituted or unsubstituted aromatic rings. The linked aromatic group may be linear or branched, and the aromatic rings to be linked may be identical to or different from each other. In addition,  $L^2$ -H at a terminal may represent an alkyl group having 1 to 12 carbon atoms or an alkoxy group having 1 to 12 carbon atoms.

[0037] R represents a hydrogen atom, an alkyl group having 1 to 12 carbon atoms, an alkoxy group having 1 to 12 carbon atoms, a substituted or unsubstituted aromatic hydrocarbon group having 6 to 30 carbon atoms, a substituted or unsubstituted aromatic heterocyclic group having 3 to 30 carbon atoms, or a linked aromatic group formed by linking 2 to 6 of the substituted or unsubstituted aromatic rings. The linked aromatic group may be linear or branched, and the aromatic rings to be linked may be identical to or different from each other.

[0038] In the description of  $L^1$ ,  $L^2$ , and R, descriptions concerning the aromatic hydrocarbon group, the aromatic heterocyclic group, and the linked aromatic group are common to  $L^1$ ,  $L^2$ , and R except that  $L^1$  represents an  $m+1$ -valent group,  $L^2$  represents a divalent group, and R represents a monovalent group.

[0039] Specific examples of the unsubstituted aromatic hydrocarbon group include groups each produced by removing a hydrogen atom from an aromatic hydrocarbon compound, such as benzene, naphthalene, fluorene, anthracene, phenanthrene, triphenylene, tetraphenylene, fluoranthene, pyrene, or chrysene, or an aromatic hydrocarbon compound in which a plurality of those compounds are linked to each other. Of those, a group produced by removing a hydrogen atom from benzene, naphthalene, fluorene, phenanthrene, or triphenylene is preferred.

[0040] Specific examples of the unsubstituted aromatic heterocyclic group include groups each produced by removing a hydrogen atom from an aromatic heterocyclic compound, such as pyridine, pyrimidine, triazine, quinoline, isoquinoline, quinoxaline, naphthyridine, carbazole, acridine, azepine, tribenzazepine, phenazine, diazafluorene, phenoxazine, phenothiazine, dibenzophosphole, or dibenzoborole, or an aromatic heterocyclic compound in which a plurality of those compounds are linked to each other. Of those, a group produced by removing a hydrogen atom from

pyridine, pyrimidine, triazine, or carbazole is preferred, and a group produced by removing a hydrogen atom from dibenzothiophene or dibenzofuran is not preferred.

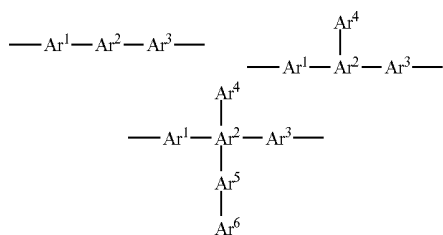
**[0041]** The group produced by removing a hydrogen atom from an aromatic compound in which a plurality of aromatic hydrocarbon compounds or aromatic heterocyclic compounds are linked to each other is referred to as "linked aromatic group." The linked aromatic group is a group formed by linking 2 to 6 aromatic rings. The aromatic rings to be linked may be identical to or different from each other, and both an aromatic hydrocarbon group and an aromatic heterocyclic group may be included. The number of the aromatic rings to be linked is preferably from 2 to 4, more preferably 2 or 3.

**[0042]** Specific examples of the linked aromatic group include groups each produced by removing a hydrogen atom from biphenyl, terphenyl, phenylnaphthalene, diphenylnaphthalene, phenylanthracene, diphenylanthracene, diphenylfluorene, bipyridine, bipyrimidine, bitriazine, biscarbazole, phenylpyridine, phenylpyrimidine, phenyltriazine, phenylcarbazole, diphenylpyridine, diphenyltriazine, bis(carbazolyl)benzene, or the like.

**[0043]** In  $L^1$ ,  $L^2$ , and R, the aromatic hydrocarbon group, the aromatic heterocyclic group, or the linked aromatic group may have a substituent. When any aromatic group has a substituent, the substituent is an alkyl group having 1 to 12 carbon atoms, an alkoxy group having 1 to 12 carbon atoms, or an acetyl group, and the alkyl group and the alkoxy group may be linear, branched, or cyclic. The substituent is preferably an alkyl group having 1 to 4 carbon atoms, an alkoxy group having 1 or 2 carbon atoms, or an acetyl group.

**[0044]** Herein, the "alkyl group" means a non-aromatic hydrocarbon group, and includes a chain hydrocarbon group, and as well, a cyclic hydrocarbon group generated from a cyclohydrocarbon group, a terpene, or the like. Specific examples of the alkyl group include: chain or branched alkyl groups, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, a pentyl group, a hexyl group, and an octyl group; and cyclic alkyl groups, e.g., cycloalkyl groups, such as a cyclopentyl group and a cyclohexyl group. Specific examples of the alkoxy group include alkoxy groups, such as a methoxy group and an ethoxy group, which are derived from the alkyl groups, such as a methyl group and an ethyl group.

**[0045]** When the linked aromatic group is a divalent group, the group is represented by, for example, any one of the following formulae, and its aromatic rings may be linked in a linear manner or a branched manner.



**[0046]** ( $Ar^1$  to  $Ar^6$  each represent an unsubstituted aromatic hydrocarbon ring or aromatic heterocycle.)

**[0047]** In addition, when  $L^2$ -H at a terminal represents an alkyl group having 1 to 12 carbon atoms or an alkoxy group having 1 to 12 carbon atoms, the alkyl group and the alkoxy group are the same as the alkyl group and the alkoxy group described as the substituent, respectively.

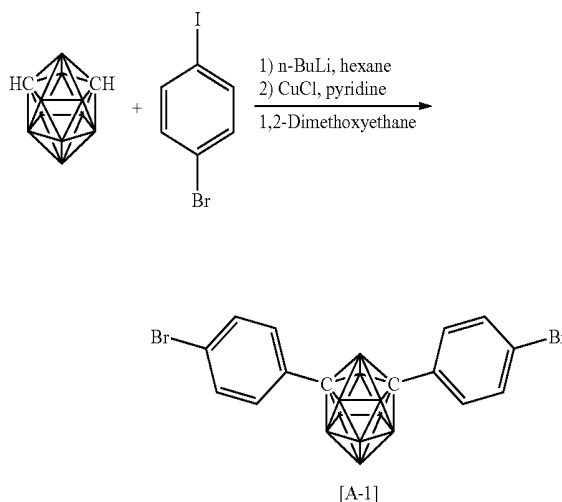
**[0048]** In the general formula (1), s represents a number of repetitions and represents an integer of from 1 to 4. m and n each represent a number of substitutions, and m represents an integer of from 0 to 4 and n represents an integer of from 0 to 6, provided that when  $m=1$ ,  $s=1$ . m preferably represents 0 or 1, and more preferably represents 0. n preferably represents 0, 1, or 2.

**[0049]** In the general formula (1), X's each represent N, CH, or C, and 1 to 4 of X's each represent N. The compound preferably contains one N or two N's. When X represents C, C has a bonding hand to be bonded to R or the ring A.

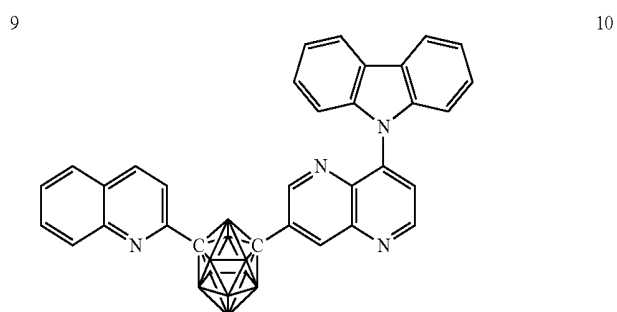
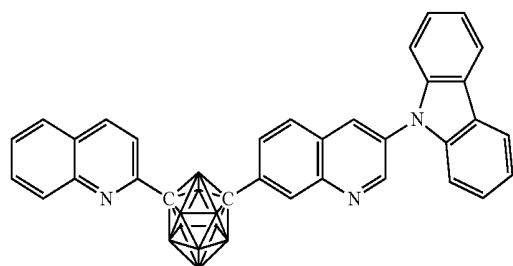
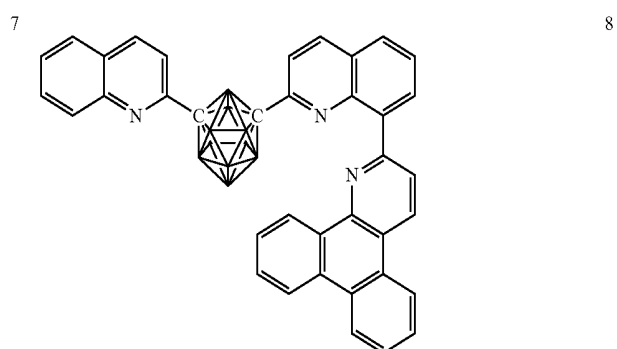
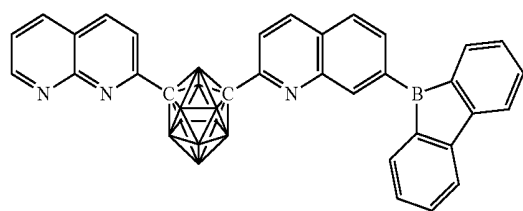
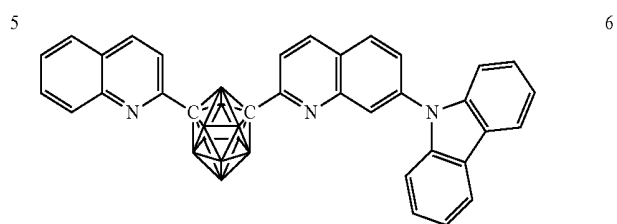
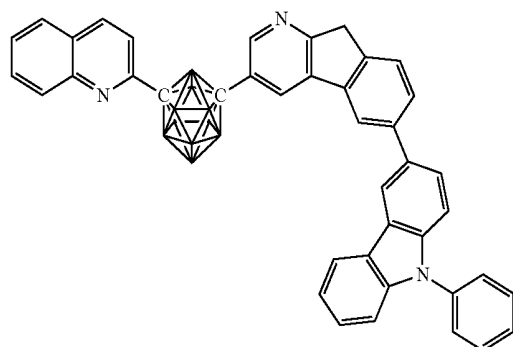
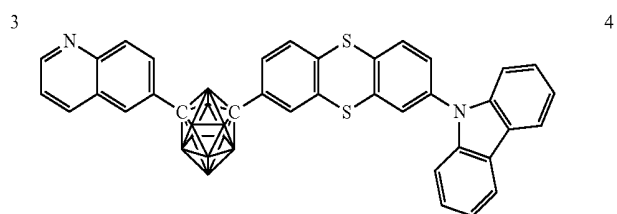
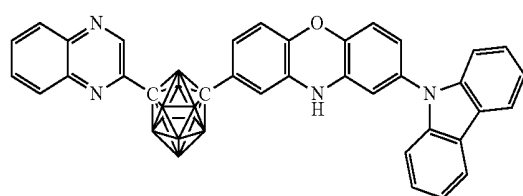
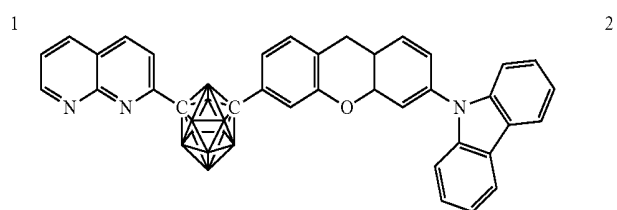
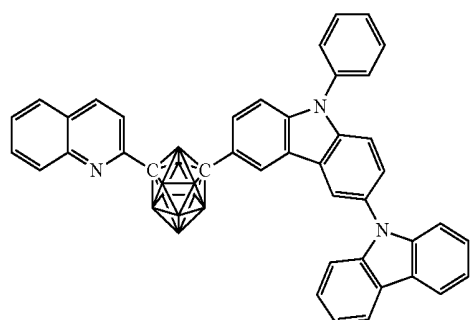
**[0050]** In the general formula (1), the ring A represents a divalent carborane group  $C_2B_{10}H_{10}$  represented by the formula (1a) or (1b). The ring A is preferably a carborane group represented by the formula (1a). The two bonding hands of the formula (1a) or (1b) may each be produced from C or may each be produced from B, but a bonding hand to be bonded to  $L^1$  or  $L^2$  is preferably produced from C.

**[0051]** The carborane compound represented by the general formula (1) can be synthesized from raw materials selected in accordance with the structure of the target compound by using a known approach.

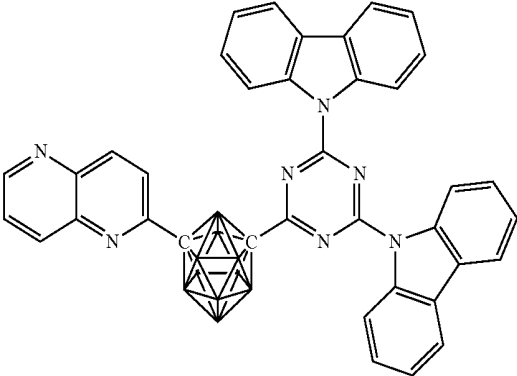
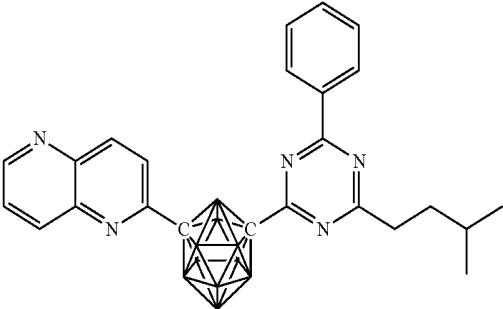
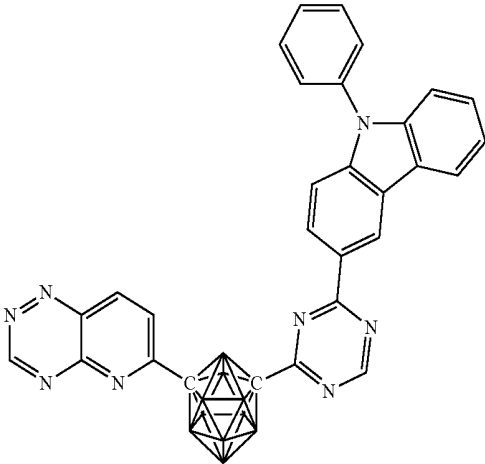
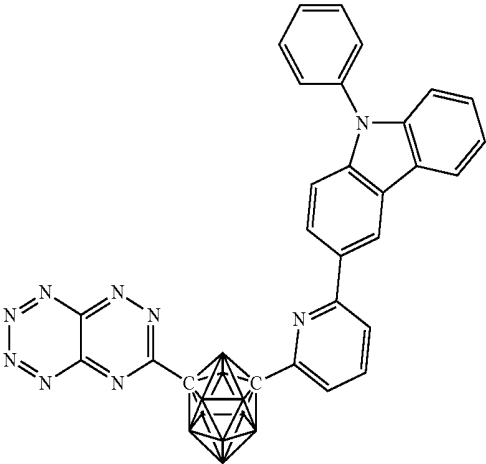
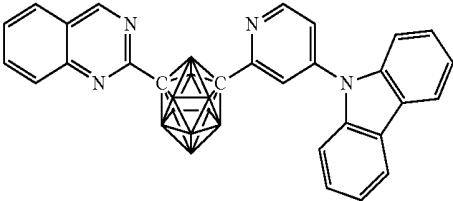
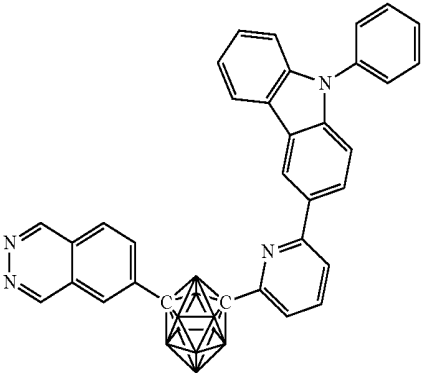
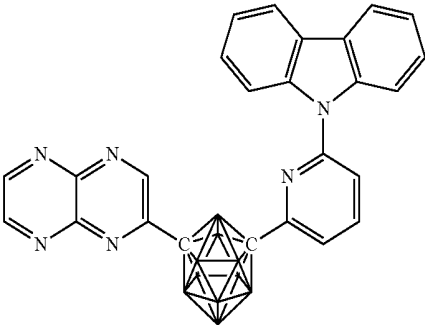
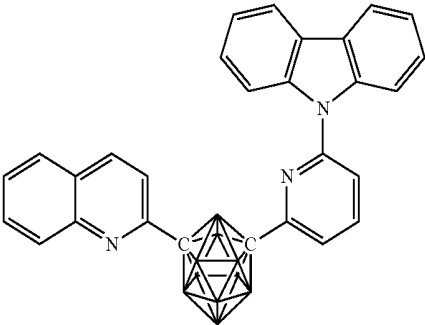
**[0052]** (A-1) can be synthesized through the following reaction formula with reference to a synthesis example described in Journal of Organometallic Chemistry, 1993, 462, p19-29.



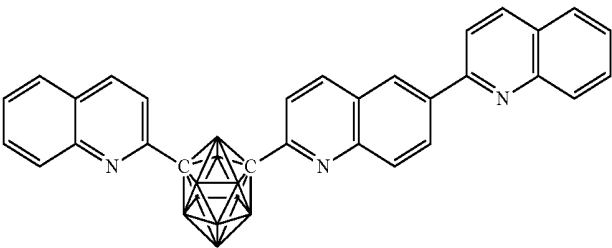
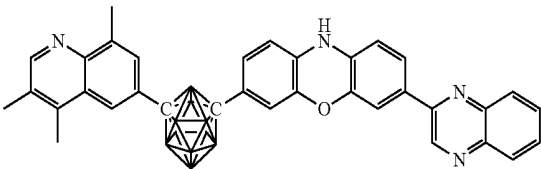
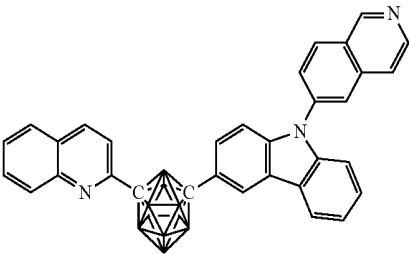
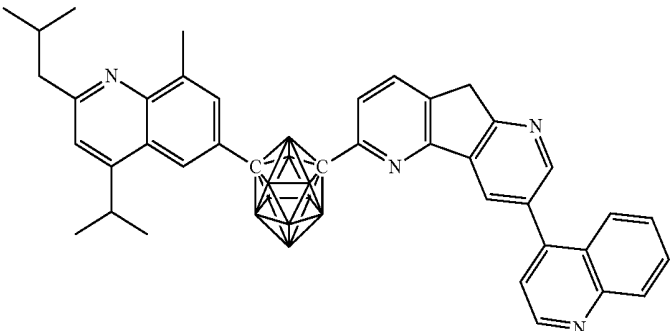
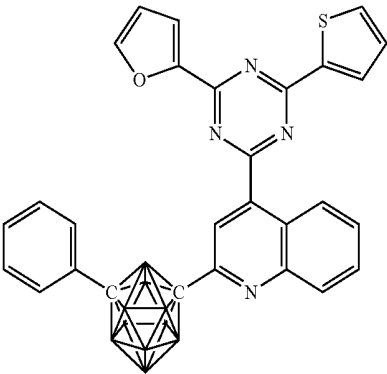
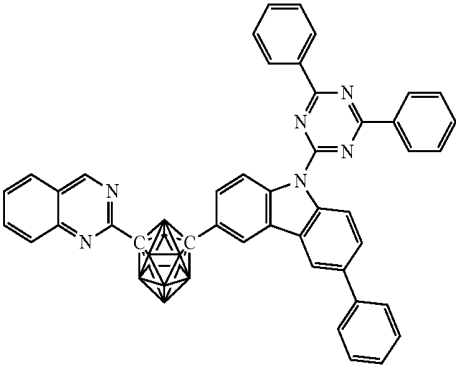
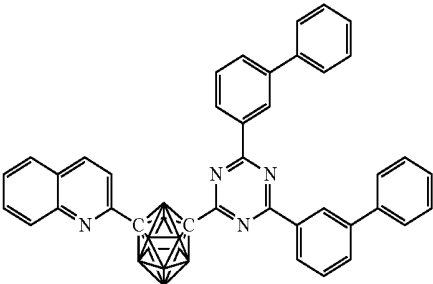
**[0053]** Specific examples of the carborane compound represented by the general formula (1) are shown below. However, the material for an organic electroluminescent device of the present invention is not limited thereto.



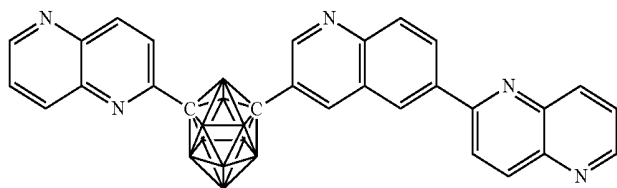
-continued



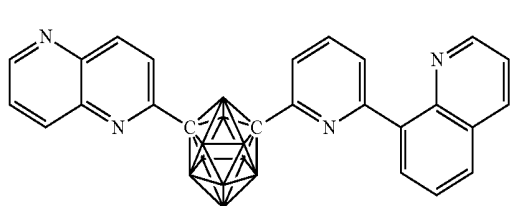
-continued  
19



-continued

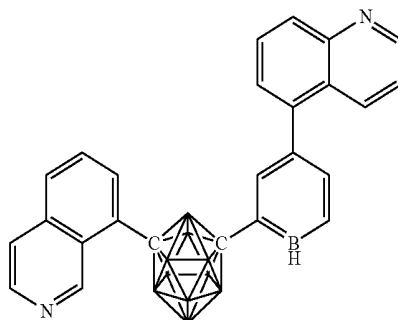


26



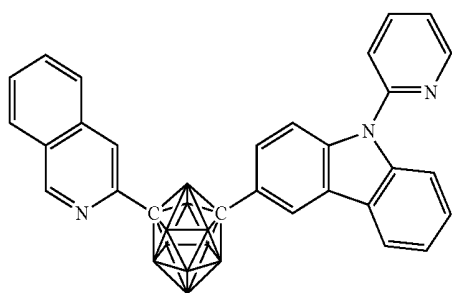
27

28



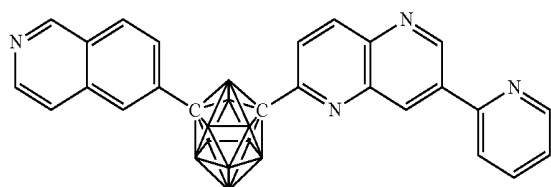
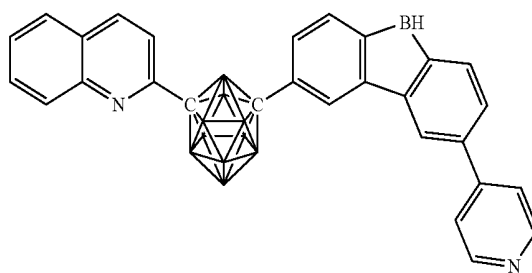
29

30



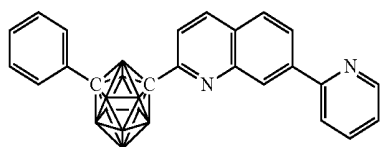
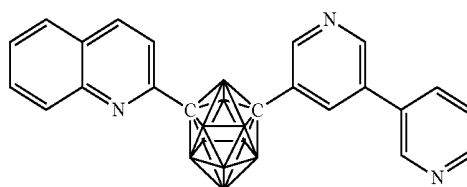
31

32



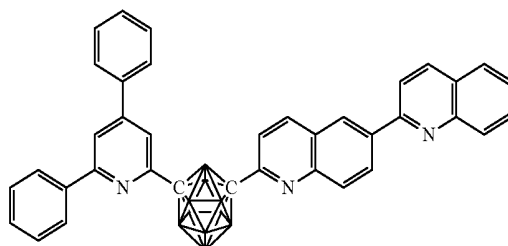
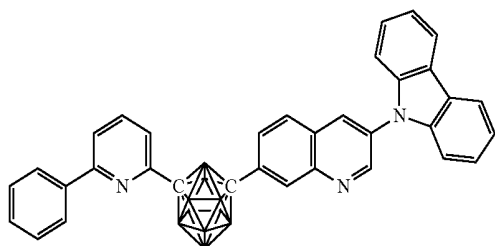
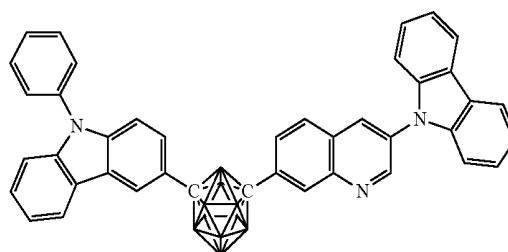
33

34

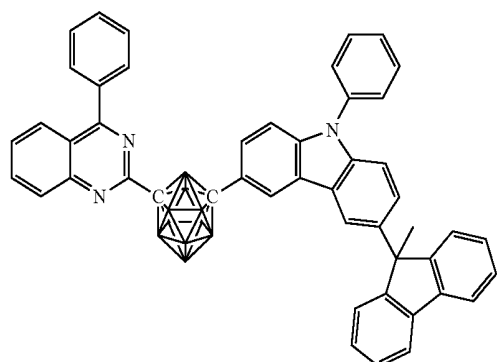


35

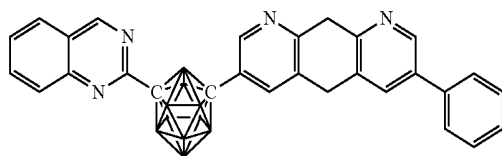
36



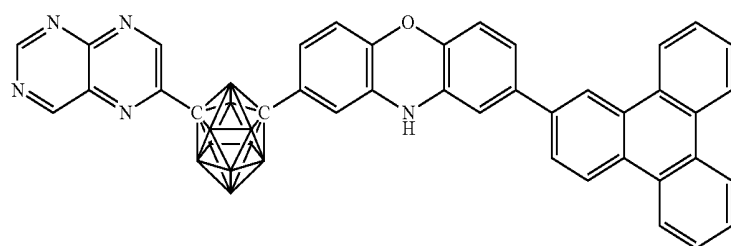
-continued



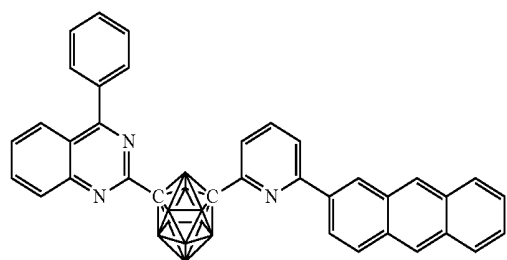
37



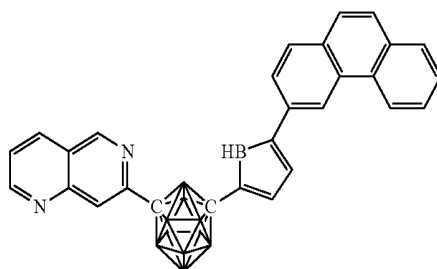
38



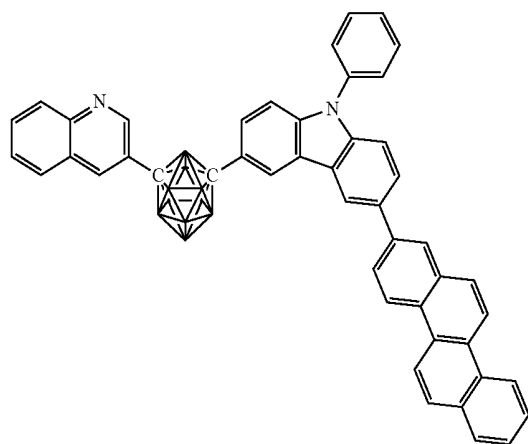
39



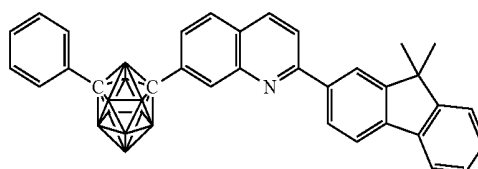
40



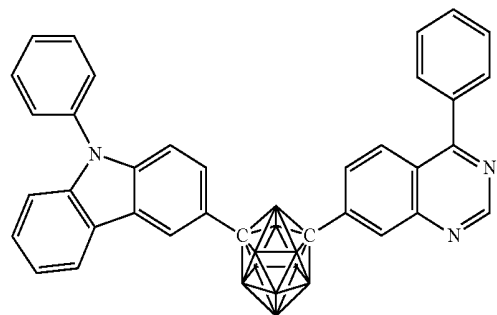
41



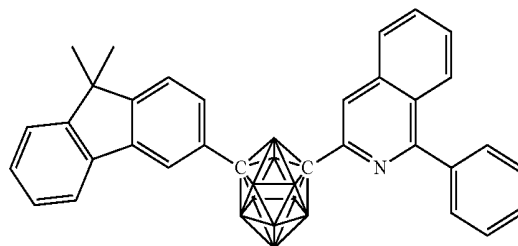
42



43

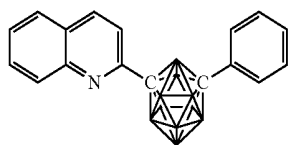


44

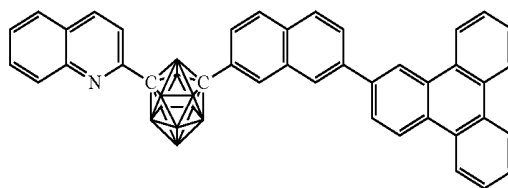


45

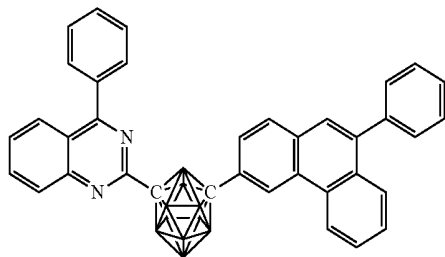
-continued



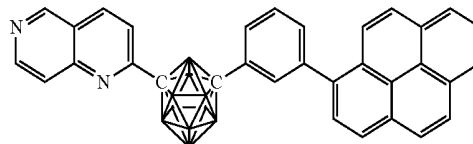
46



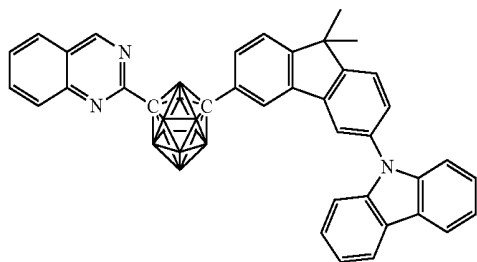
47



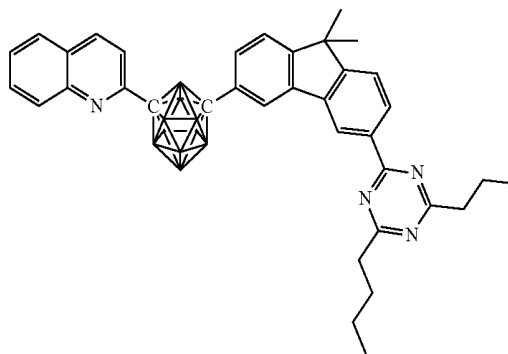
48



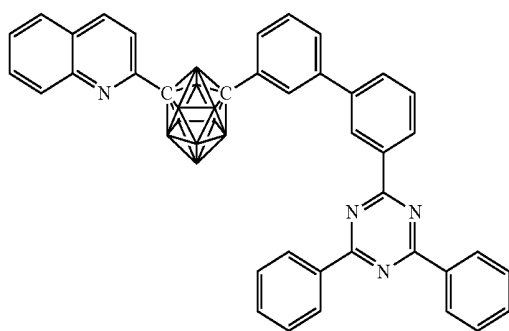
49



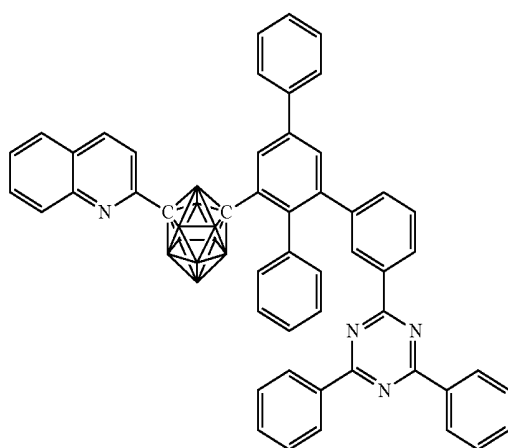
50



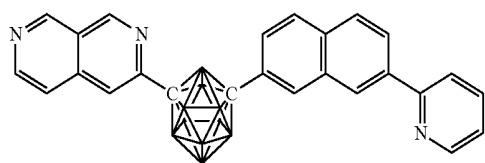
51



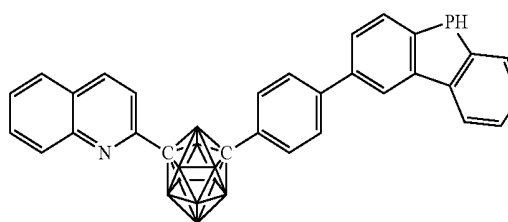
52



53



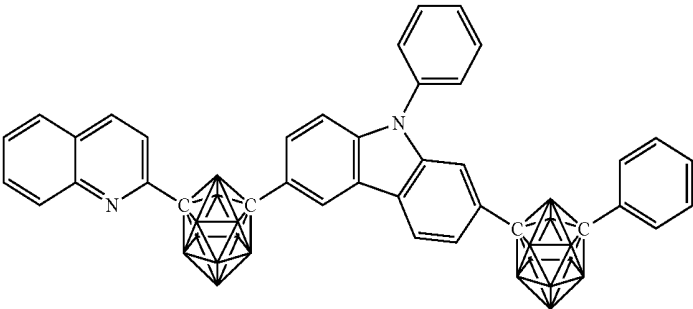
54



55

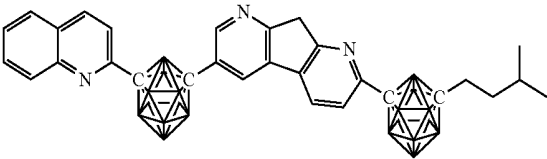
-continued

56



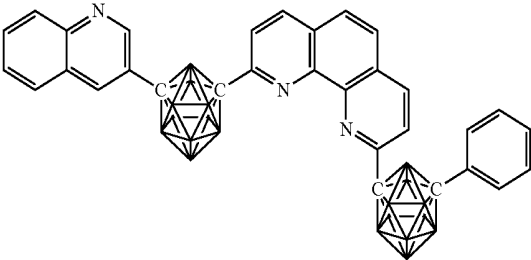
57

58



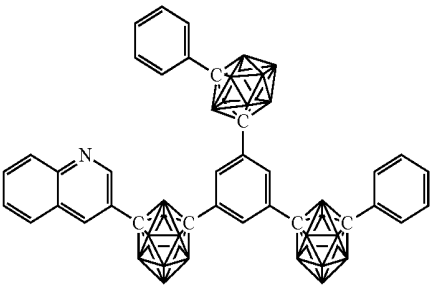
59

60



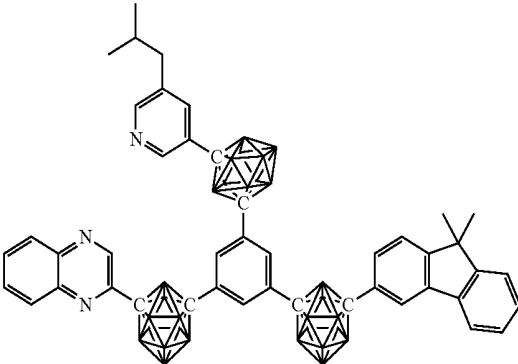
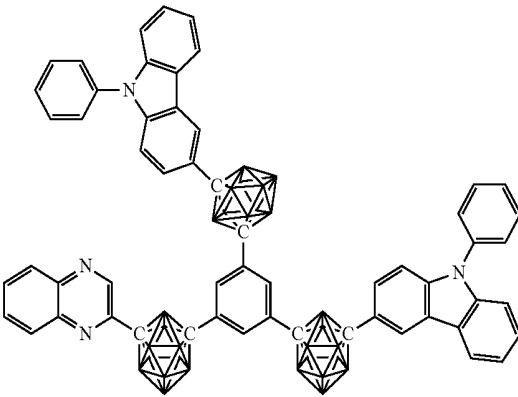
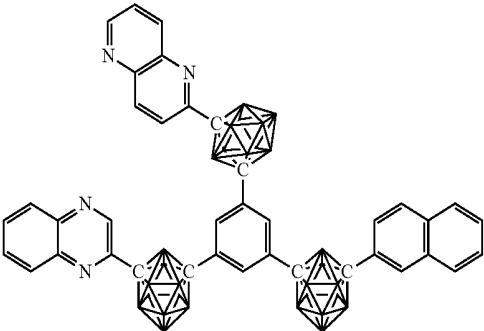
61

62



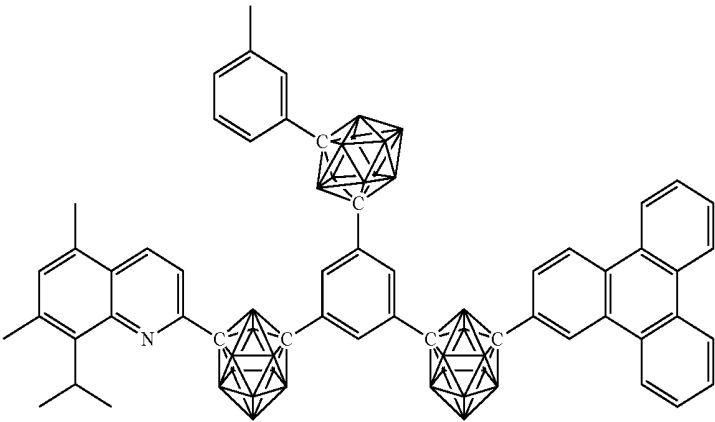
63

64

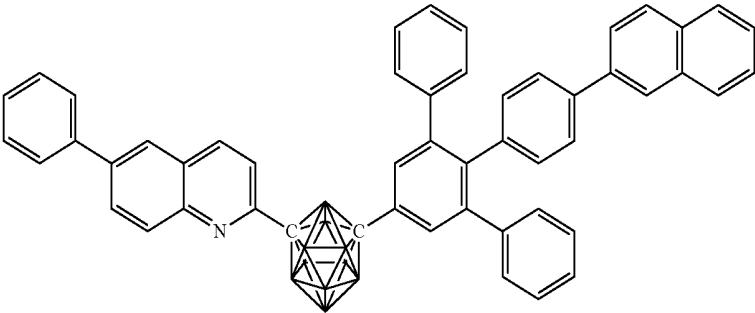


-continued

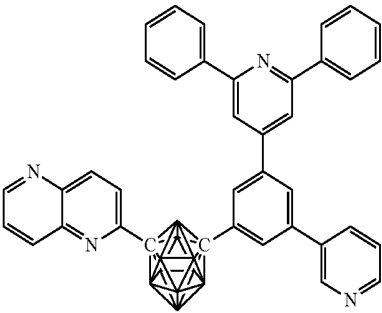
65



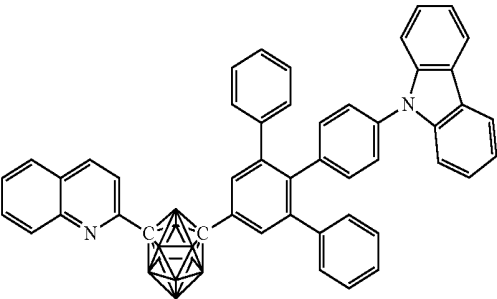
66



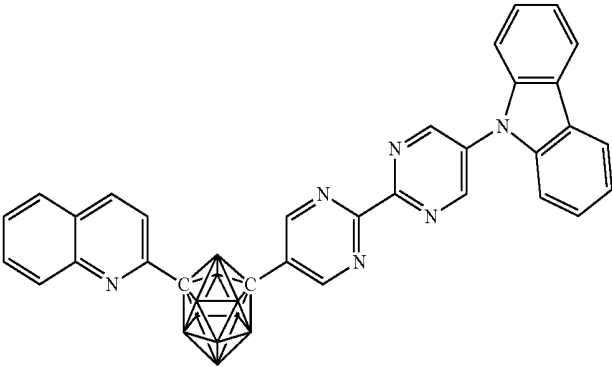
67



68

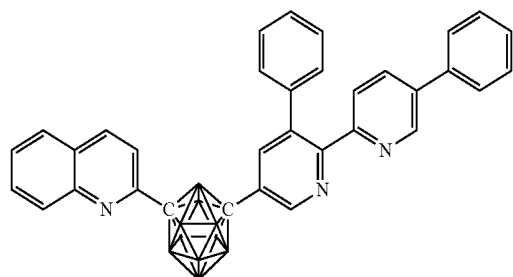


69

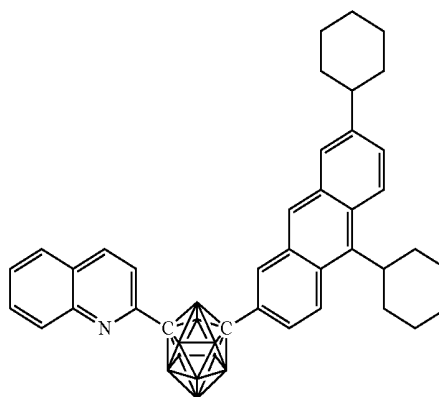


-continued

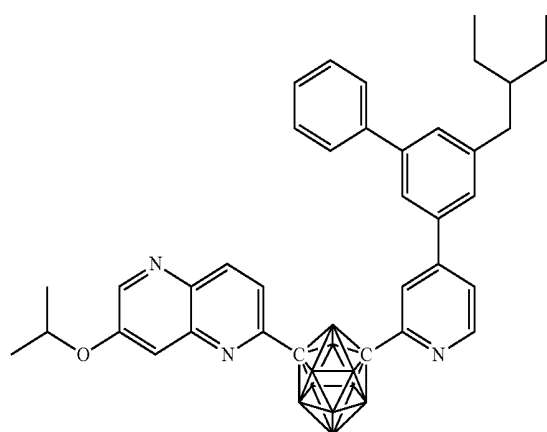
71



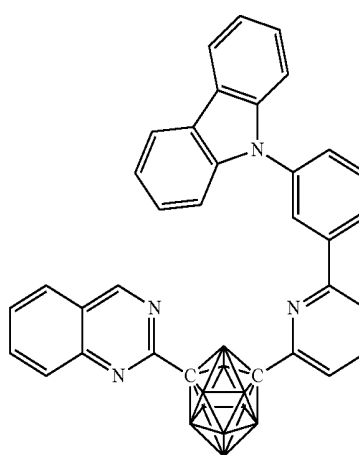
72



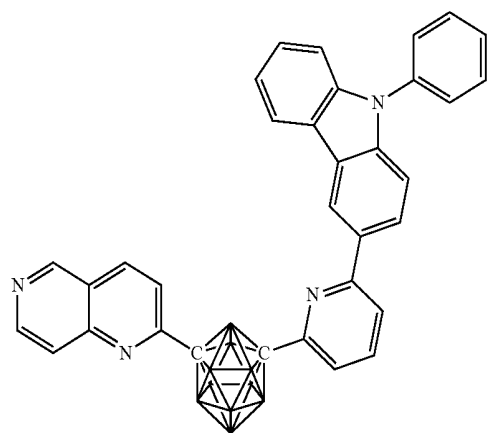
72-2



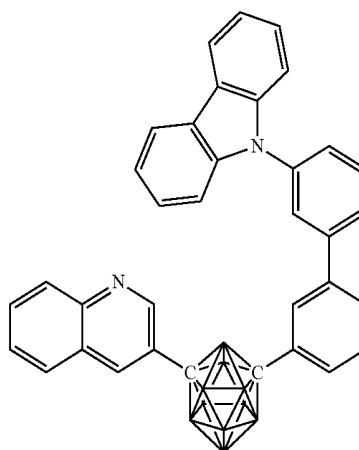
73



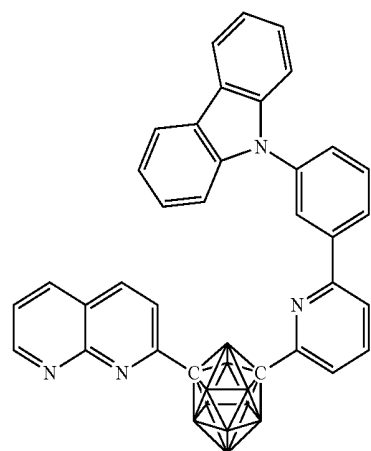
74



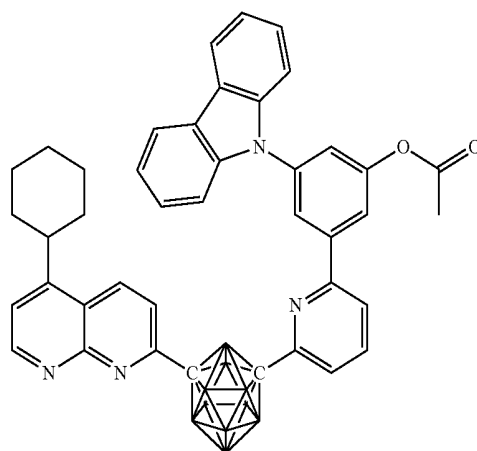
75



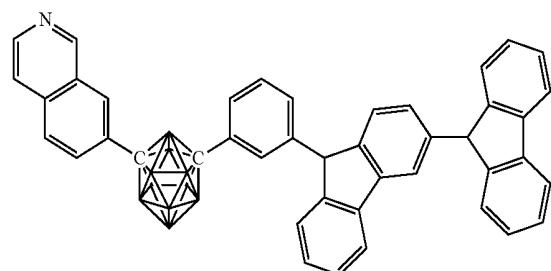
-continued



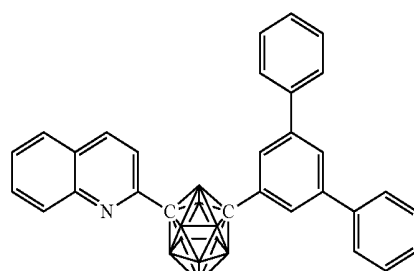
76



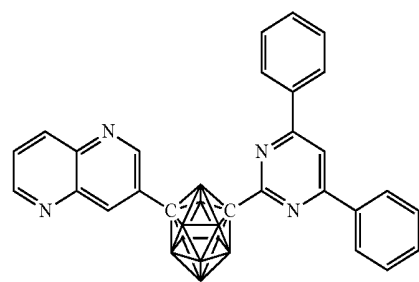
77



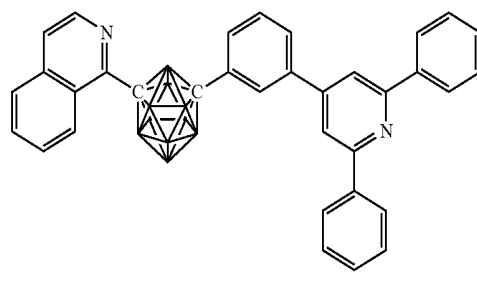
78



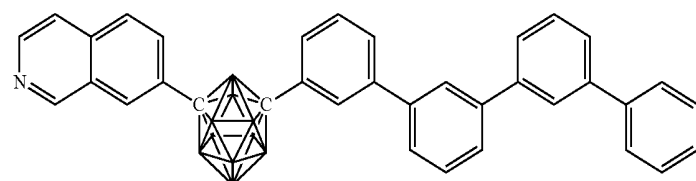
79



80



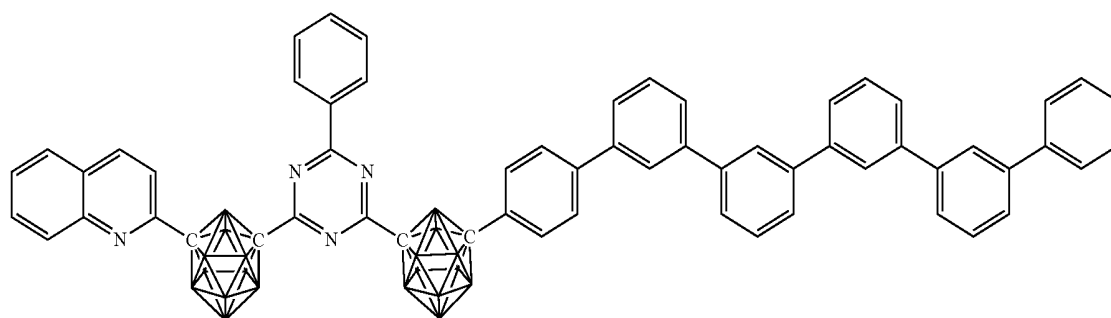
81



82

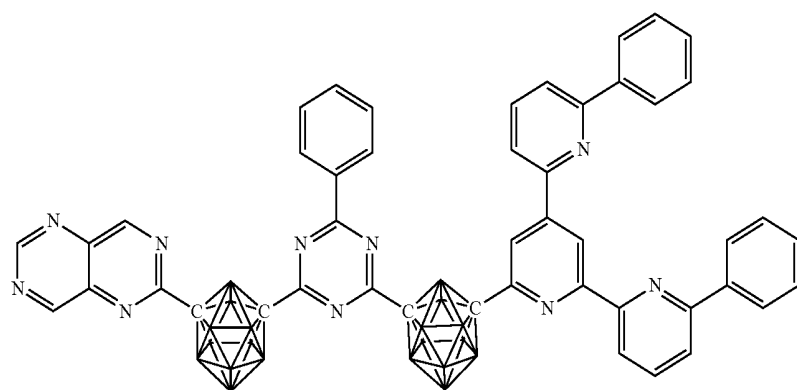
-continued

83

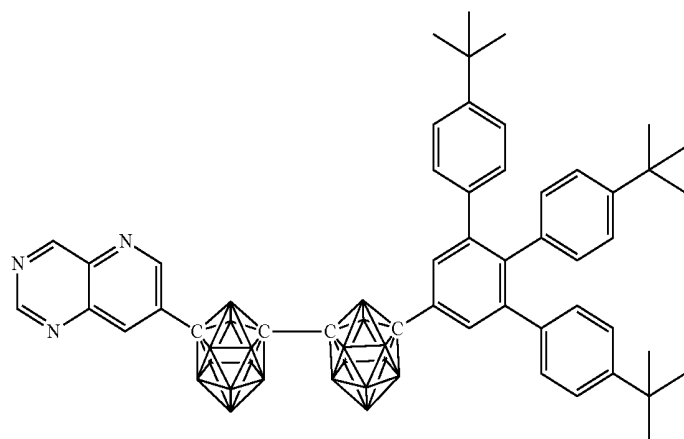


83

84

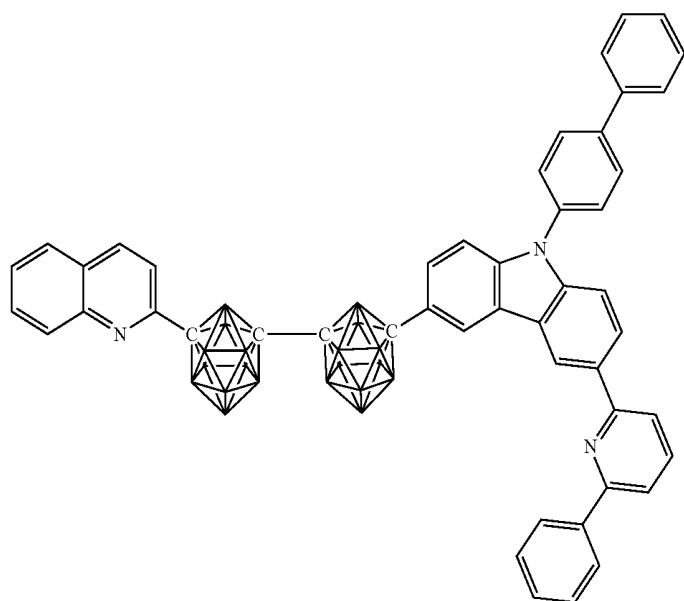


85



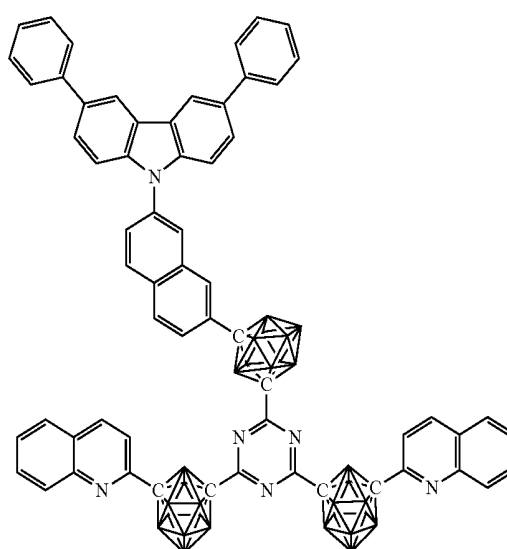
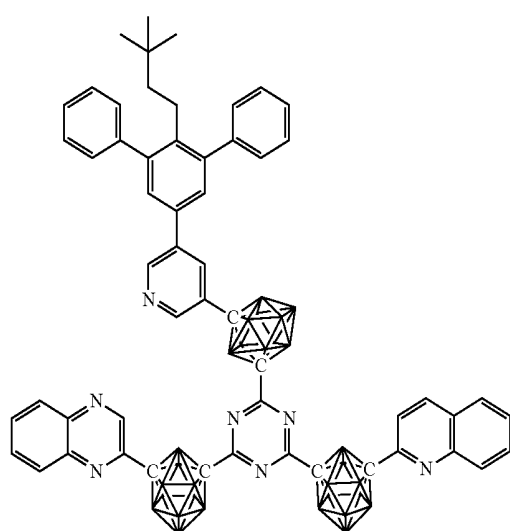
-continued

86



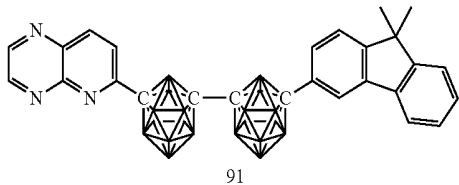
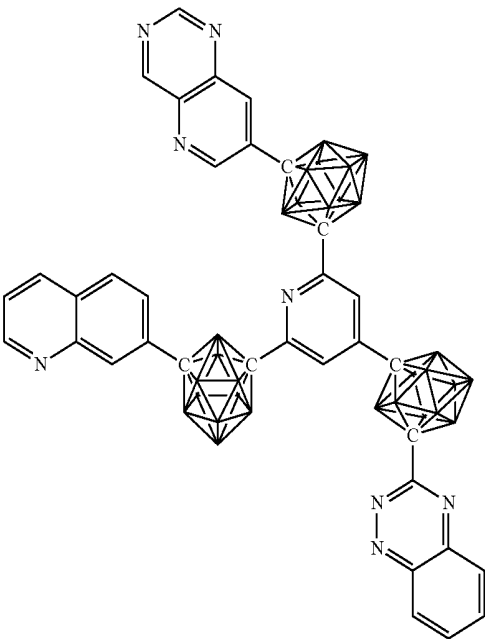
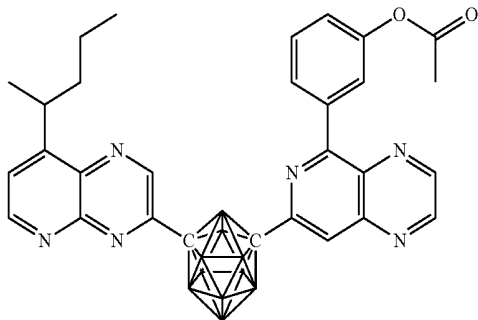
87

88



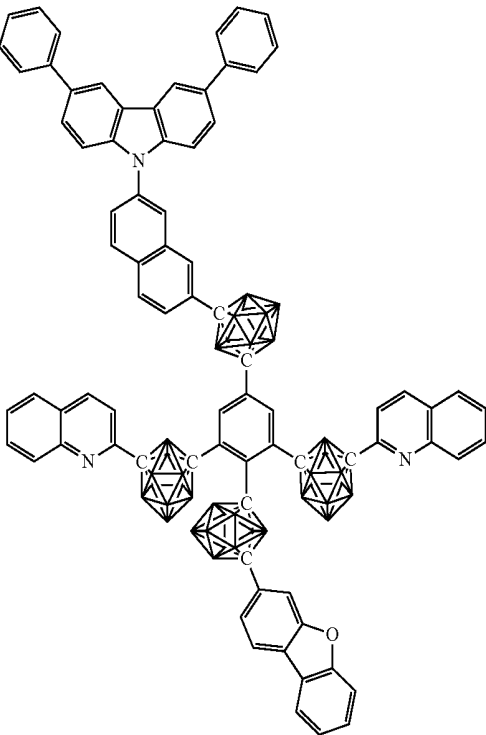
-continued  
89

90



91

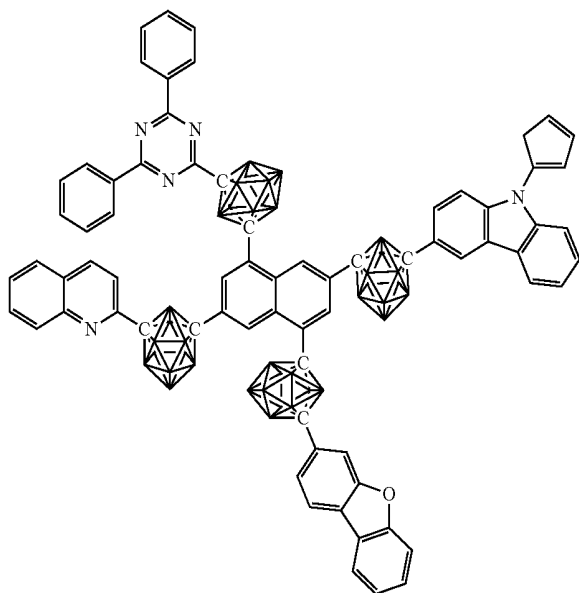
92



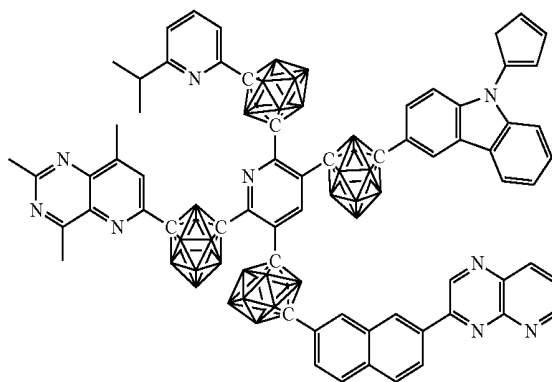
92

-continued

93



94



[0054] When the material for an organic electroluminescent device of the present invention is contained in at least one of a plurality of organic layers of an organic EL device having a structure in which an anode, the plurality of organic layers, and a cathode are laminated on a substrate, an excellent organic electroluminescent device is provided. A light-emitting layer, an electron-transporting layer, or a hole-blocking layer is suitable as the organic layer in which the material is contained. Here, when the compound of the present invention is used in the light-emitting layer, the compound can be used as a host material for the light-emitting layer containing a fluorescent light-emitting, delayed fluorescent light-emitting, or phosphorescent light-emitting dopant. In addition, the compound of the present invention can be used as an organic light-emitting material that radiates fluorescence and delayed fluorescence. When the compound of the present invention is used as an organic light-emitting material that radiates fluorescence and delayed fluorescence, any other organic compound having a value for at least one of excited singlet energy or excited triplet energy higher than that of the compound is preferably used as the host material. The compound of the present invention is particularly preferably incorporated as a host material for the light-emitting layer containing the phosphorescent light-emitting dopant.

[0055] Next, an organic EL device using the material for an organic electroluminescent device of the present invention is described.

[0056] The organic EL device of the present invention includes organic layers including at least one light-emitting layer between an anode and a cathode laminated on a substrate. In addition, at least one of the organic layers contains the material for an organic electroluminescent device of the present invention. The material for an organic electroluminescent device of the present invention is advantageously contained in the light-emitting layer together with a phosphorescent light-emitting dopant.

[0057] Next, the structure of the organic EL device of the present invention is described with reference to the drawings. However, the structure of the organic EL device of the present invention is by no means limited to one illustrated in the drawings.

[0058] FIG. 1 is a sectional view for illustrating an example of the structure of a general organic EL device used in the present invention. Reference numeral 1 represents a substrate, reference numeral 2 represents an anode, reference numeral 3 represents a hole-injecting layer, reference numeral 4 represents a hole-transporting layer, reference numeral 5 represents a light-emitting layer, reference numeral 6 represents an electron-transporting layer, and reference numeral 7 represents a cathode. The organic EL device of the present invention may include an exciton-blocking layer adjacent to the light-emitting layer, or may include an electron-blocking layer between the light-emitting layer and the hole-injecting layer. The exciton-blocking layer may be inserted on any of the anode side and the cathode side of the light-emitting layer, and may also be inserted simultaneously on both sides. The organic EL device of the present invention includes the substrate, the anode, the light-emitting layer, and the cathode as its essential layers. The organic EL device of the present invention preferably includes a hole-injecting/transporting layer and an electron-injecting/transporting layer in addition to the essential layers, and more preferably includes a hole-blocking layer between the light-emitting layer and the electron-injecting/transporting layer. The hole-injecting/transporting layer means any one or both of the hole-injecting layer and the hole-transporting layer, and the electron-injecting/transporting layer means any one or both of an electron-injecting layer and the electron-transporting layer.

[0059] It is possible to adopt a reverse structure as compared to FIG. 1, that is, the reverse structure being formed by laminating the layers on the substrate 1 in the order of the cathode 7, the electron-transporting layer 6, the light-emitting layer 5, the hole-transporting layer 4, the hole-injecting

layer 3, and the anode 2. In this case as well, some layers may be added or eliminated as required.

**[0060]** —Substrate—

**[0061]** The organic EL device of the present invention is preferably supported by a substrate. The substrate is not particularly limited, and any substrate that has long been conventionally used for an organic EL device may be used. For example, a substrate made of glass, a transparent plastic, quartz, or the like may be used.

**[0062]** —Anode—

**[0063]** Preferably used as the anode in the organic EL device is an anode formed by using, as an electrode substance, any of a metal, an alloy, an electrically conductive compound, and a mixture thereof, all of which have a large work function (4 eV or more). Specific examples of such electrode substance include metals such as Au and conductive transparent materials, such as CuI, indium tin oxide (ITO),  $\text{SnO}_2$ , and  $\text{ZnO}$ . In addition, a material such as IDIXO ( $\text{In}_2\text{O}_3\text{—ZnO}$ ), which can produce an amorphous, transparent conductive film, may be used. In order to produce the anode, it may be possible to form any of those electrode substances into a thin film by using a method such as vapor deposition or sputtering and form a pattern having a desired shape thereon by photolithography. Alternatively, in the case of not requiring high pattern accuracy (about 100  $\mu\text{m}$  or more), a pattern may be formed via a mask having a desired shape when any of the above-mentioned electrode substances is subjected to vapor deposition or sputtering. Alternatively, when a coatable substance, such as an organic conductive compound, is used, a wet film-forming method, such as a printing method or a coating method, may be used. When luminescence is taken out from the anode, the transmittance of the anode is desirably controlled to more than 10%. In addition, the sheet resistance of the anode is preferably several hundred ohms per square ( $\Omega/\square$ ) or less. Further, the thickness of the film is, depending on its material, selected from the range of generally from 10 nm to 1,000 nm, preferably from 10 nm to 200 nm.

**[0064]** —Cathode—

**[0065]** Meanwhile, used as the cathode is a cathode formed by using, as an electrode substance, any of a metal (electron-injecting metal), an alloy, an electrically conductive compound, and a mixture thereof, all of which have a small work function (4 eV or less). Specific examples of such electrode substance include sodium, a sodium-potassium alloy, magnesium, lithium, a magnesium/copper mixture, a magnesium/silver mixture, a magnesium/aluminum mixture, a magnesium/indium mixture, an aluminum/aluminum oxide ( $\text{Al}_2\text{O}_3$ ) mixture, indium, a lithium/aluminum mixture, and a rare earth metal. Of those, for example, a mixture of an electron-injecting metal and a second metal, which is a stable metal having a larger work function value than the former metal, such as a magnesium/silver mixture, a magnesium/aluminum mixture, a magnesium/indium mixture, an aluminum/aluminum oxide ( $\text{Al}_2\text{O}_3$ ) mixture, or a lithium/aluminum mixture, or aluminum, is suitable from the viewpoints of an electron-injecting property and durability against oxidation or the like. The cathode can be produced by forming any of those electrode substances into a thin film by using a method such as vapor deposition or sputtering. In addition, the sheet resistance of the cathode is preferably several hundred  $\Omega/\square$  or less, and the thickness of the film is selected from the range of generally from 10 nm to 5  $\mu\text{m}$ , preferably from 50 nm to 200 nm. In order for

luminescence produced to pass through, any one of the anode and cathode of the organic EL device is preferably transparent or semi-transparent, because the light emission luminance improves.

**[0066]** In addition, after the above-mentioned metal has been formed into a film having a thickness of from 1 nm to 20 nm as a cathode, the conductive transparent material mentioned in the description of the anode is formed into a film on the cathode, thereby being able to produce a transparent or semi-transparent cathode. Through the application of this, a device in which both the anode and cathode have transparency can be produced.

**[0067]** —Light-Emitting Layer—

**[0068]** The light-emitting layer is a layer that emits light after the production of an exciton by the recombination of a hole injected from the anode and an electron injected from the cathode, and the light-emitting layer contains an organic light-emitting material and a host material.

**[0069]** When the light-emitting layer is a fluorescent light-emitting layer, at least one kind of fluorescent light-emitting material may be used alone as the fluorescent light-emitting material. However, it is preferred that the fluorescent light-emitting material be used as a fluorescent light-emitting dopant and the host material be contained.

**[0070]** The carborane compound represented by the general formula (1) can be used as the fluorescent light-emitting material in the light-emitting layer. However, the fluorescent light-emitting material is known through, for example, many patent literatures, and hence can be selected therefrom. Examples thereof include a benzoxazole derivative, a benzothiazole derivative, a benzimidazole derivative, a styrylbenzene derivative, a polyphenyl derivative, a diphenylbutadiene derivative, a tetraphenylbutadiene derivative, a naphthalimide derivative, a coumarin derivative, a fused aromatic compound, a perinone derivative, an oxadiazole derivative, an oxazine derivative, an aldazine derivative, a pyrrolidine derivative, a cyclopentadiene derivative, a bisstyrylanthracene derivative, a quinacridone derivative, a pyrrolopyridine derivative, a thiadiazolopyridine derivative, a styrylamine derivative, a diketopyrrolopyrrole derivative, an aromatic dimethylened compound, various metal complexes typified by a metal complex of an 8-quinolinol derivative, and a metal complex, rare earth complex, or transition metal complex of a pyromethene derivative, polymer compounds, such as polythiophene, polyphenylene, and polyphenylene vinylene, and an organic silane derivative. Of those, for example, the following compound is preferred: a fused aromatic compound, a styryl compound, a diketopyrrolopyrrole compound, an oxazine compound, or a pyromethene metal complex, transition metal complex, or lanthanoid complex. For example, the following compound is more preferred: naphthacene, pyrene, chrysene, triphenylene, benzo[c]phenanthrene, benzo[a]anthracene, pentalene, perylene, fluoranthene, acenaphthofluoranthene, dibenzo[a,h]anthracene, dibenzo[a,h]anthracene, dibenzo[a,h]anthracene, benzo[a]naphthacene, hexacene, anthanthrene, naphtho[2,1-f]isoquinoline,  $\alpha$ -naphthaphenanthridine, phenanthroxazole, quinolino[6,5-f]quinoline, or benzothiophanthrene. Those compounds may each have an alkyl group, aryl group, aromatic heterocyclic group, or diarylamino group as a substituent.

**[0071]** The carborane compound represented by the general formula (1) can be used as a fluorescent host material in the light-emitting layer. However, the fluorescent host mate-

rial is known through, for example, many patent literatures, and hence can be selected therefrom. For example, the following material can be used: a compound having a fused aryl ring, such as naphthalene, anthracene, phenanthrene, pyrene, chrysene, naphthacene, triphenylene, perylene, fluo-ranthen, fluorene, or indene, or a derivative thereof; an aromatic amine derivative, such as N,N'-dinaphthyl-N,N'-diphenyl-4,4'-diphenyl-1,1'-diamine; a metal chelated oxinoid compound typified by tris(8-quinolinato)aluminum (III); a bisstyryl derivative, such as a distyrylbenzene derivative; a tetraphenylbutadiene derivative; an indene derivative; a coumarin derivative; an oxadiazole derivative; a pyrrolopyridine derivative; a perinone derivative; a cyclopentadiene derivative; a pyrrolopyrrole derivative; a thiadiazolopyridine derivative; a dibenzofuran derivative; a carbazole derivative; an indolocarbazole derivative; a triazine derivative; or a polymer-based derivative, such as a poly-phenylene vinylene derivative, a poly-p-phenylene derivative, a polyfluorene derivative, a polyvinyl carbazole derivative, or a polythiophene derivative. However, the fluorescent host material is not particularly limited thereto.

**[0072]** When the fluorescent light-emitting material is used as a fluorescent light-emitting dopant and the host material is contained, the content of the fluorescent light-emitting dopant in the light-emitting layer desirably falls within the range of from 0.01 wt % to 20 wt %, preferably from 0.1 wt % to 10 wt %.

**[0073]** An organic EL device typically injects charges from both of its electrodes, i.e., its anode and cathode into a light-emitting substance to produce a light-emitting substance in an excited state, and causes the substance to emit light. In the case of a charge injection-type organic EL device, it is said that 25% of the produced excitons are excited to a singlet excited state and the remaining 75% of the excitons are excited to a triplet excited state. As described in *Advanced Materials* 2009, 21, 4802-4806, it has been known that after a specific fluorescent light-emitting substance has undergone an energy transition to a triplet excited state as a result of intersystem crossing or the like, the substance is subjected to inverse intersystem crossing to a singlet excited state by triplet-triplet annihilation or the absorption of thermal energy to radiate fluorescence, thereby expressing thermally activated delayed fluorescence. The organic EL device of the present invention can also express delayed fluorescence. In this case, the light emission can include both fluorescent light emission and delayed fluorescent light emission. Light emission from the host material may be present in part of the light emission.

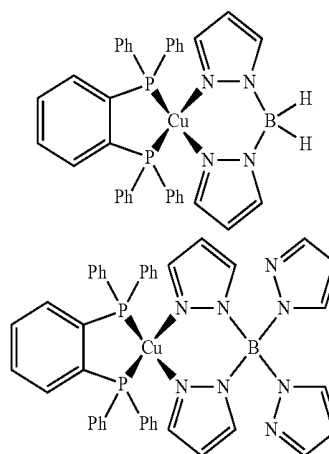
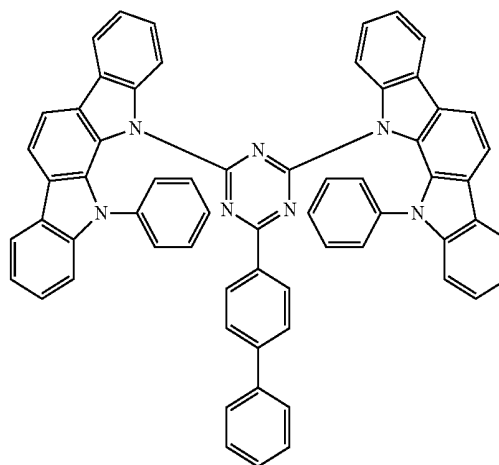
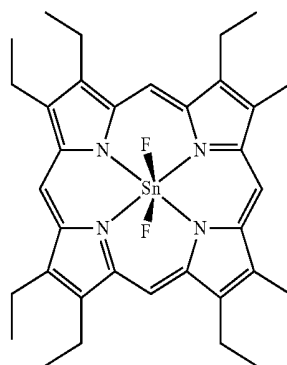
**[0074]** When the light-emitting layer is a delayed fluorescent light-emitting layer, at least one kind of delayed fluorescent light-emitting material may be used alone as a delayed fluorescent light-emitting material. However, it is preferred that the delayed fluorescent light-emitting material be used as a delayed fluorescent light-emitting dopant and the host material be contained.

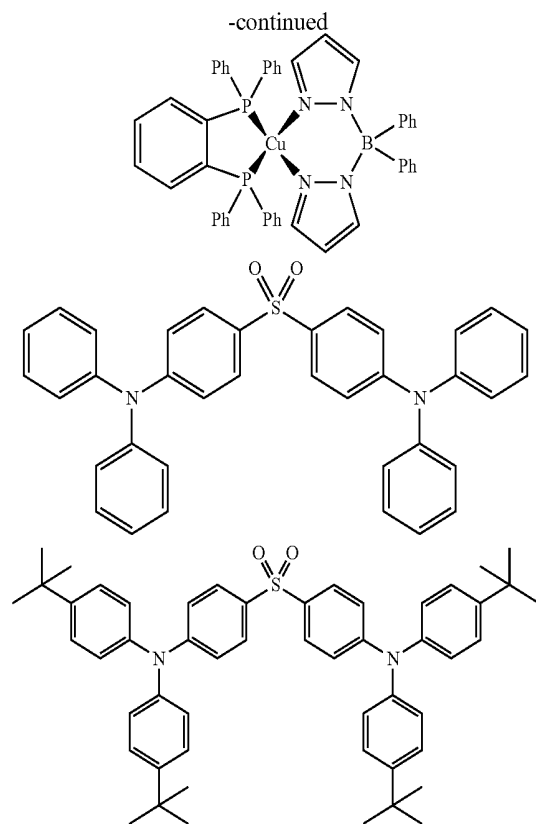
**[0075]** Although the carborane compound represented by the general formula (1) can be used as the delayed fluorescent light-emitting material in the light-emitting layer, a material selected from known delayed fluorescent light-emitting materials can also be used. Examples thereof include a tin complex, an indolocarbazole derivative, a copper complex, and a carbazole derivative. Specific

examples thereof include, but not limited to, compounds described in the following non patent literatures and patent literature.

**[0076]** (1) *Adv. Mater.* 2009, 21, 4802-4806, (2) *Appl. Phys. Lett.* 98, 083302 (2011), (3) JP 2011-213643 A, and (4) *J. Am. Chem. Soc.* 2012, 134, 14706-14709.

**[0077]** Specific examples of the delayed fluorescent light-emitting material are shown below, but the delayed fluorescent light-emitting material is not limited to the following compounds.





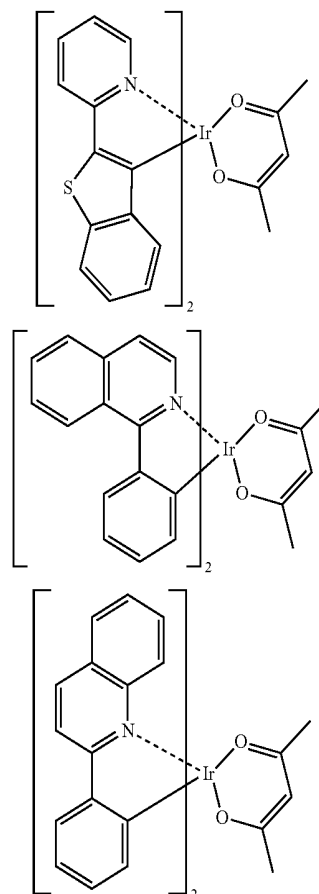
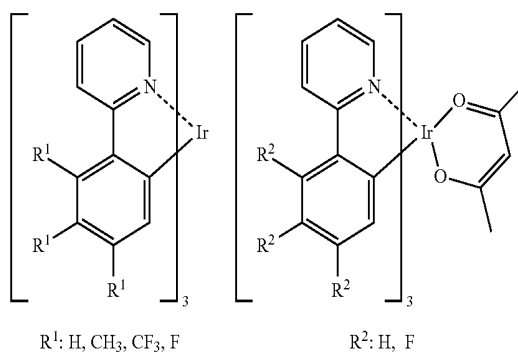
**[0078]** When the delayed fluorescent light-emitting material is used as a delayed fluorescent light-emitting dopant and the host material is contained, the content of the delayed fluorescent light-emitting dopant in the light-emitting layer desirably falls within the range of from 0.01 wt % to 50 wt %, preferably from 0.1 wt % to 20 wt %, more preferably from 0.01 wt % to 10 wt %.

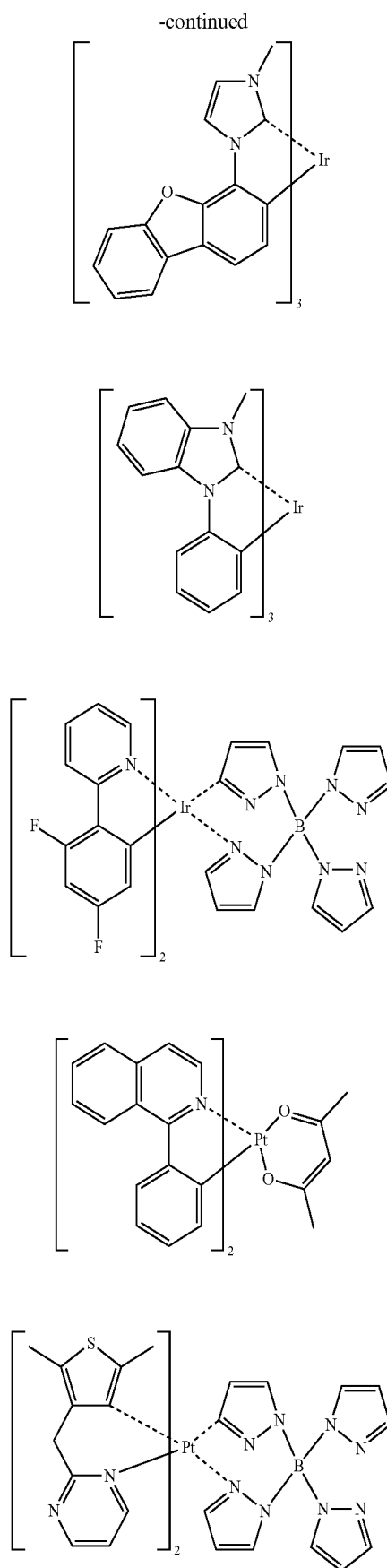
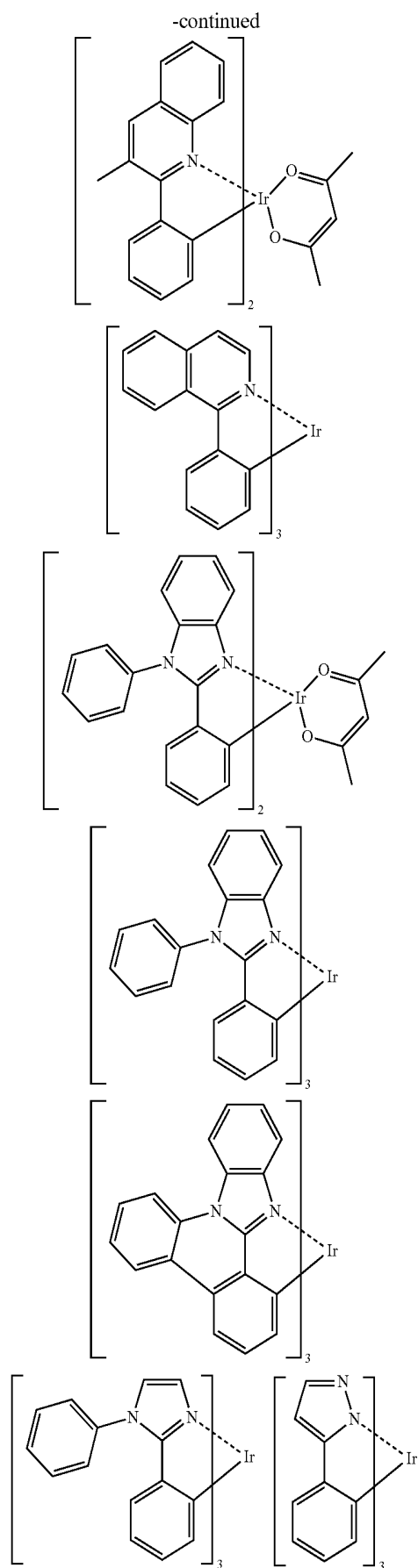
**[0079]** The carborane compound represented by the general formula (1) can be used as the delayed fluorescent host material in the light-emitting layer. However, the delayed fluorescent host material can also be selected from compounds except the carborane. For example, the following compound can be used: a compound having a fused aryl ring, such as naphthalene, anthracene, phenanthrene, pyrene, chrysene, naphthacene, triphenylene, perylene, fluorene, or indene, or a derivative thereof; an aromatic amine derivative, such as

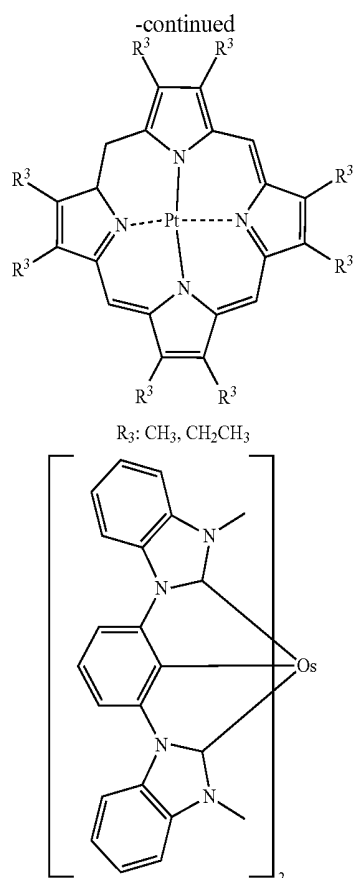
**[0080]** N,N'-dinaphthyl-1,1'-diamine; a metal chelated oxinoid compound typified by tris(8-quinolinato)aluminum(III); a bisstyryl derivative, such as a distyrylbenzene derivative; a tetraphenylbutadiene derivative; an indene derivative; a coumarin derivative; an oxadiazole derivative; a pyrrolopyridine derivative; a perinone derivative; a cyclopentadiene derivative; a pyrrolopyrrole derivative; a thiadiazolopyridine derivative; a dibenzofuran derivative; a carbazole derivative; an indolocarbazole derivative; a triazine derivative; or a polymer-based derivative, such as a polyphenylene vinylene derivative, a poly-p-phenylene derivative, a polyfluorene derivative, a polyvinyl carbazole derivative, a polythiophene derivative, or an arylsilane derivative. However, the delayed fluorescent host material is not particularly limited thereto.

**[0081]** When the light-emitting layer is a phosphorescent light-emitting layer, the light-emitting layer contains a phosphorescent light-emitting dopant and a host material. It is recommended to use, as a material for the phosphorescent light-emitting dopant, a material containing an organic metal complex including at least one metal selected from ruthenium, rhodium, palladium, silver, rhenium, osmium, iridium, platinum, and gold.

**[0082]** Preferred examples of the phosphorescent light-emitting dopant include complexes such as Ir(ppy)<sub>3</sub>, complexes such as Ir(bt)<sub>2</sub>.acac<sub>3</sub>, and complexes such as PtOEt<sub>3</sub>, the complexes each having a noble metal element, such as Ir, as a central metal. Specific examples of those complexes are shown below, but the complexes are not limited to the following compounds.







**[0083]** It is desired that the content of the phosphorescent light-emitting dopant in the light-emitting layer fall within the range of from 2 wt % to 40 wt %, preferably from 5 wt % to 30 wt %.

**[0084]** When the light-emitting layer is a phosphorescent light-emitting layer, it is preferred to use, as a host material in the light-emitting layer, the carborane compound represented by the general formula (1) according to the present invention. However, when the carborane compound is used in any other organic layer except the light-emitting layer, the material to be used in the light-emitting layer may be another host material except the carborane compound, or the carborane compound and any other host material may be used in combination. Further, a plurality of kinds of known host materials may be used in combination.

**[0085]** It is preferred to use, as a usable known host compound, a compound that has a hole-transporting ability or an electron-transporting ability, is capable of preventing luminescence from having a longer wavelength, and has a high glass transition temperature.

**[0086]** Any such other host material is known through, for example, many patent literatures, and hence can be selected therefrom. Specific examples of the host material include, but are not particularly limited to, an indole derivative, a carbazole derivative, an indolocarbazole derivative, a triazole derivative, an oxazole derivative, an oxadiazole derivative, an imidazole derivative, a polyarylethane derivative, a pyrazoline derivative, a pyrazolone derivative, a phenylenediamine derivative, an arylamine derivative, an amino-substituted chalcone derivative, a styrylanthracene derivative, a fluorenone derivative, a hydrazone derivative, a

stilbene derivative, a silazane derivative, an aromatic tertiary amine compound, a styrylamine compound, an aromatic dimethylidene-based compound, a porphyrin-based compound, an anthraquinodimethane derivative, an anthrone derivative, a diphenylquinone derivative, a thiopyran dioxide derivative, a heterocyclic tetracarboxylic acid anhydride, such as naphthalene perylene, a phthalocyanine derivative, various metal complexes typified by a metal complex of an 8-quinolinol derivative, a metal phthalocyanine, and metal complexes of benzoxazole and benzothiazole derivatives, and polymer compounds, such as a polysilane-based compound, a poly(N-vinylcarbazole) derivative, an aniline-based copolymer, a thiophene oligomer, a polythiophene derivative, a polyphenylene derivative, a polyphenylenevinylene derivative, and a polyfluorene derivative.

**[0087]** The light-emitting layer, which may be any one of a fluorescent light-emitting layer, a delayed fluorescent light-emitting layer, and a phosphorescent light-emitting layer, is preferably the phosphorescent light-emitting layer.

**[0088]** —Injecting Layer—

**[0089]** The injecting layer refers to a layer formed between an electrode and an organic layer for the purposes of lowering a driving voltage and improving light emission luminance, and includes a hole-injecting layer and an electron-injecting layer. The injecting layer may be interposed between the anode and the light-emitting layer or the hole-transporting layer, or may be interposed between the cathode and the light-emitting layer or the electron-transporting layer. The injecting layer may be formed as required.

**[0090]** —Hole-Blocking Layer—

**[0091]** The hole-blocking layer has, in a broad sense, the function of an electron-transporting layer, and is formed of a hole-blocking material that has a remarkably small ability to transport holes while having a function of transporting electrons, and hence the hole-blocking layer is capable of improving the probability of recombining an electron and a hole by blocking holes while transporting electrons.

**[0092]** It is preferred to use the carborane compound represented by the general formula (1) according to the present invention for the hole-blocking layer. However, when the carborane compound is used in any other organic layer, a known material for a hole-blocking layer may be used. In addition, a material for the electron-transporting layer to be described later can be used as a material for the hole-blocking layer as required.

**[0093]** —Electron-Blocking Layer—

**[0094]** The electron-blocking layer is formed of a material that has a remarkably small ability to transport electrons while having a function of transporting holes, and hence the electron-blocking layer is capable of improving the probability of recombining an electron and a hole by blocking electrons while transporting holes.

**[0095]** A material for the hole-transporting layer to be described later can be used as a material for the electron-blocking layer as required. The thickness of the electron-blocking layer is preferably from 3 nm to 100 nm, more preferably from 5 nm to 30 nm.

**[0096]** —Exciton-Blocking Layer—

**[0097]** The exciton-blocking layer refers to a layer for blocking excitons produced by the recombination of a hole and an electron in the light-emitting layer from diffusing into charge-transporting layers. The insertion of this layer enables efficient confinement of the excitons in the light-emitting layer, thereby being able to improve the luminous

efficiency of the device. The exciton-blocking layer may be inserted on any of the anode side and the cathode side of the adjacent light-emitting layer, and may also be inserted simultaneously on both sides.

**[0098]** Although the carborane compound represented by the general formula (1) can be used as a material for the exciton-blocking layer, as other materials therefor, there are given, for example, 1,3-dicarbazoylbenzene (mCP) and bis(2-methyl-8-quinolinolato)-4-phenylphenolatoaluminum (III) (BALq).

**[0099]** —Hole-Transporting Layer—

**[0100]** The hole-transporting layer is formed of a hole-transporting material having a function of transporting holes, and a single hole-transporting layer or a plurality of hole-transporting layers can be formed.

**[0101]** The hole-transporting material has a hole-injecting property or a hole-transporting property or has an electron-blocking property, and any of an organic material and an inorganic material can be used as the hole-transporting material. Although it is preferred to use the carborane compound represented by the general formula (1) as a known hole-transporting material that can be used, any compound selected from conventionally known compounds can be used. Examples of the known hole-transporting material that can be used include a triazole derivative, an oxadiazole derivative, an imidazole derivative, a polyaryl-alkane derivative, a pyrazoline derivative and a pyrazolone derivative, a phenylenediamine derivative, an arylamine derivative, an amino-substituted chalcone derivative, an oxazole derivative, a styrylanthracene derivative, a fluorenone derivative, a hydrazone derivative, a stilbene derivative, a silazane derivative, an aniline-based copolymer, and a conductive high-molecular weight oligomer, in particular, a thiophene oligomer. However, an aromatic tertiary amine compound, such as a phenylenediamine derivative or an arylamine derivative, is preferably used.

**[0102]** —Electron-Transporting Layer—

**[0103]** The electron-transporting layer is formed of a material having a function of transporting electrons, and a single electron-transporting layer or a plurality of electron-transporting layers can be formed.

**[0104]** An electron-transporting material (which also serves as a hole-blocking material in some cases) only needs to have a function of transferring electrons injected from the cathode into the light-emitting layer. Although it is preferred to use the carborane compound represented by the general formula (1) according to the present invention for the electron-transporting layer, any compound selected from conventionally known compounds can be used. Examples thereof include a nitro-substituted fluorene derivative, a diphenylquinone derivative, a thiopyran dioxide derivative, a carbodiimide, a fluorenylidene methane derivative, anthraquinodimethane and anthrone derivatives, and an oxadiazole derivative. Further, a thiaziazole derivative prepared by substituting an oxygen atom on an oxadiazole ring with a sulfur atom in the oxadiazole derivative or a quinoxaline derivative that has a quinoxaline ring known as an electron withdrawing group can be used as the electron-transporting material. Further, a polymer material in which any such material is introduced in a polymer chain or is used as a polymer main chain can be used.

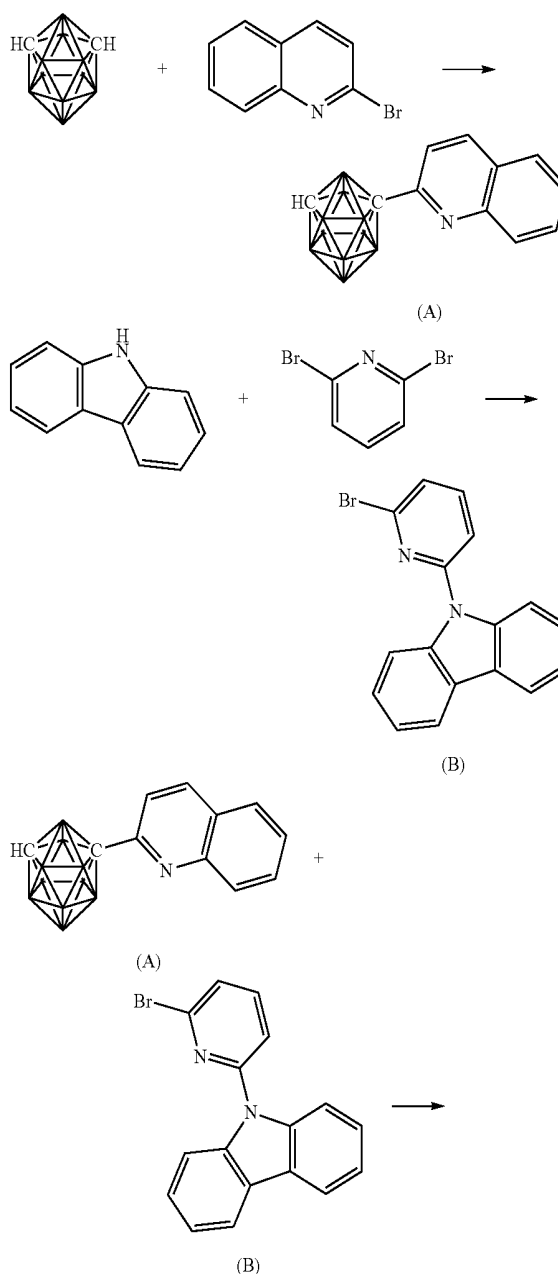
## EXAMPLES

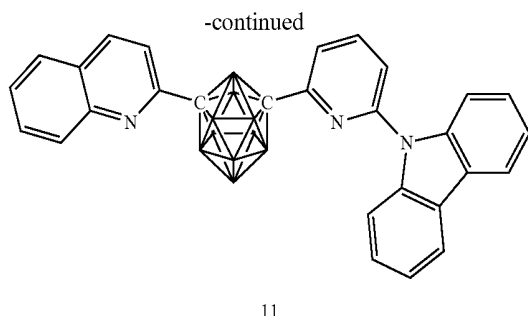
**[0105]** Now, the present invention is described in more detail by way of Examples. It should be appreciated that the present invention is not limited to Examples below and can be carried out in various forms as long as the various forms do not deviate from the gist of the present invention.

**[0106]** The route described below was used to synthesize a carborane compound to be used as a material for an organic electroluminescent device. The number of each compound corresponds to the number given to the chemical formula.

### Example 1

**[0107]** A compound 11 is synthesized in accordance with the following reaction formulae.





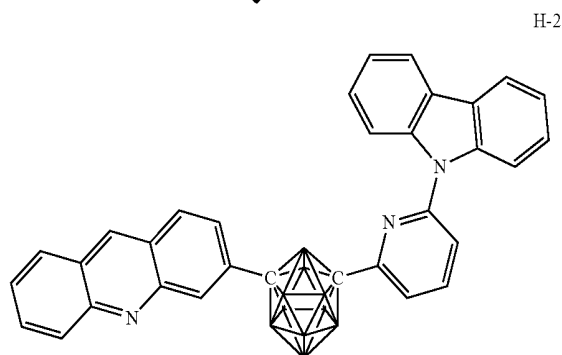
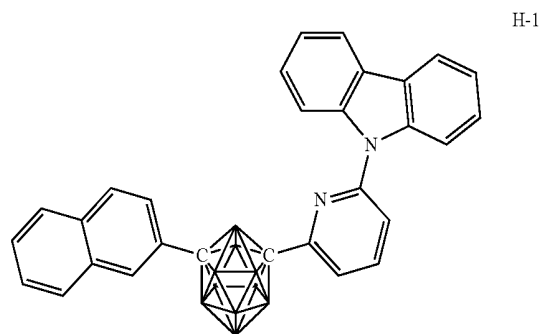
**[0108]** Under a nitrogen atmosphere, 35.0 g (0.243 mol) of m-carborane and 200 mL of 1,2-dimethoxyethane (DME) were added, and the resultant DME solution was cooled to 0° C. 96.8 mL of a 2.69 M solution of n-butyllithium in hexane was dropped to the solution, and the mixture was stirred under ice cooling for 30 min. 70 mL of pyridine was added to the resultant and the mixture was stirred at room temperature for 10 min. After that, 75.6 g (0.763 mol) of copper(I) chloride was added to the resultant and the mixture was stirred at 65° C. for 30 min. After that, 58.3 g (0.280 mol) of 2-bromoquinoline was added to the resultant and the mixture was stirred at 95° C. overnight. The reaction solution was cooled to room temperature, and then the precipitated crystal was taken by filtration and the solvent was distilled off under reduced pressure. The resultant residue was purified by silica gel column chromatography to provide 7.98 g (29.2 mmol, yield: 12.0%) of an intermediate A.

**[0109]** Under a nitrogen atmosphere, 34.9 g (0.146 mol) of 2,6-dibromopyridine, 24.4 g (0.146 mol) of carbazole, 2.78 g (14.6 mmol) of copper iodide, 92.9 g (0.438 mol) of tripotassiumphosphate, 5.3 mL (43.8 mmol) of trans-1,2-cyclohexanediamine, and 1 L of 1,4-dioxane were added, and the mixture was stirred at 115° C. overnight. The reaction solution was cooled to room temperature, and then the precipitated crystal was taken by filtration and the solvent was distilled off under reduced pressure. The resultant residue was purified by silica gel column chromatography to provide 14.2 g (43.8 mmol, yield: 30%) of an intermediate B as a white solid.

**[0110]** Under a nitrogen atmosphere, 6.7 g (0.0245 mol) of the intermediate A and 138 mL of 1,2-dimethoxyethane (DME) were added, and the resultant DME solution was cooled to 0° C. 9.89 mL of a 2.69 M solution of n-butyllithium in hexane was dropped to the solution, and the mixture was stirred under ice cooling for 30 min. 6.7 mL of pyridine was added to the resultant and the mixture was stirred at room temperature for 10 min. After that, 7.5 g (76.0 mmol) of copper (I) chloride was added to the resultant and the mixture was stirred at 65° C. for 30 min. After that, 8.47 g (0.0262 mol) of the intermediate B was added to the resultant and the mixture was stirred at 95° C. for 2 d. The reaction solution was cooled to room temperature, and then the precipitated crystal was taken by filtration and the solvent was distilled off under reduced pressure. The resultant residue was purified by silica gel column chromatography to provide 2.90 g (5.63 mmol, yield: 23%) of a compound 11.

**[0111]** Compounds 6, 25, 32, 48, and 58, and H-1 and H-2 were synthesized in conformity with the synthesis example of the compound 11 and the synthesis method described herein.

**[0112]** In addition, organic EL devices were produced by using the compounds 6, 11, 25, 32, 48, and 58, and the following compounds H-1 and H-2.



#### Example 1

**[0113]** Each thin film was laminated by a vacuum deposition method at a degree of vacuum of  $2.0 \times 10^{-5}$  Pa on a glass substrate on which an anode formed of indium tin oxide (ITO) having a thickness of 110 nm had been formed. First, copper phthalocyanine (CuPC) was formed into a layer having a thickness of 25 nm on the ITO. Next, 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB) was formed into a layer having a thickness of 55 nm to serve as a hole-transporting layer. Next, the compound 11 obtained in Synthesis Example 1 serving as a host material and bis(2-(2'-benzo[4,5-a]thienyl)pyridinato-N, C3) iridium (acetylacetonate) [(Btp) 2 Iracac] serving as a phosphorescent light-emitting dopant were co-deposited from different deposition sources onto the hole-transporting layer to form a light-emitting layer having a thickness of 47.5 nm. The concentration of (Btp)2Iracac in the light-emitting layer was 5.0 wt %. Next, tris(8-hydroxyquinolino)aluminum (III) (Alq3) was formed into a layer having a thickness of 30 nm to serve as an electron-transporting layer. Further, lithium fluoride (LiF) was formed into a layer having a thickness of 1.0 nm to serve as an electron-injecting layer on the electron-transporting layer. Finally, aluminum (Al) was formed into a layer having a thickness of 170 nm to serve as an electrode on the electron-injecting layer. Thus, an organic EL device was produced.

**[0114]** An external power source was connected to the resultant organic EL device to apply a DC voltage to the device. As a result, it was confirmed that the device had such light-emitting characteristics as shown in Table 1. The columns "luminance", "voltage", and "luminous efficiency" in Table 1 show values at 10 mA/cm<sup>2</sup> (initial characteristics).

The maximum wavelength of the emission spectrum of the device was 620 nm, and hence the acquisition of light emission from (Btp)2Iracac was found.

#### Examples 2 to 9

**[0115]** Organic EL devices were each produced in the same manner as in Example 1 except that the compound 6, 25, 32, 48, or 58 was used instead of the compound 11 as the host material for the light-emitting layer.

#### Comparative Example 1

**[0116]** An organic EL device was produced in the same manner as in Example 1 except that phenylphenolatoaluminum(III) (BALq) was used as the host material for the light-emitting layer.

#### Comparative Examples 2 and 3

**[0117]** Organic EL devices were each produced in the same manner as in Example 1 except that the compound H-1 or H-2 was used as the host material for the light-emitting layer.

**[0118]** The organic EL devices obtained in Examples 2 to 6 and Comparative Examples 1 to 3 were evaluated in the same manner as in Example 1. As a result, it was confirmed that the devices had such light-emitting characteristics as shown in Table 1. The maximum wavelength of each of the emission spectra of the organic EL devices obtained in Examples 2 to 6 and Comparative Examples 1 to 3 was 620 nm, and hence the acquisition of light emission from (Btp)2Iracac was identified.

TABLE 1

|                       | Host material compound | Luminance (cd/m <sup>2</sup> ) | Voltage (V) | Visual luminous efficiency (lm/W) |
|-----------------------|------------------------|--------------------------------|-------------|-----------------------------------|
| Example 1             | 11                     | 1,200                          | 8.6         | 4.1                               |
| Example 2             | 6                      | 1,100                          | 8.4         | 4.3                               |
| Example 3             | 25                     | 1,000                          | 8.2         | 3.9                               |
| Example 4             | 32                     | 1,200                          | 8.5         | 4.3                               |
| Example 5             | 48                     | 1,200                          | 7.8         | 4.4                               |
| Example 6             | 58                     | 1,100                          | 7.7         | 4.6                               |
| Comparative Example 1 | BALq                   | 1,000                          | 8.4         | 3.8                               |
| Comparative Example 2 | H-1                    | 1,000                          | 9.8         | 3.3                               |
| Comparative Example 3 | H-2                    | 700                            | 7.6         | 3.0                               |

**[0119]** As shown in Table 1, when the carborane compound of the present invention is used in the light-emitting layer in each of Examples 1 to 6, a characteristic more satisfactory than those of Comparative Examples 1 to 3 is exhibited in terms of luminous efficiency.

#### Example 7

**[0120]** Each thin film was laminated by a vacuum deposition method at a degree of vacuum of  $2.0 \times 10^{-5}$  Pa on a glass substrate on which an anode formed of indium tin oxide (ITO) having a thickness of 70 nm had been formed. First, copper phthalocyanine (CuPC) was formed into a layer having a thickness of 30 nm to serve as a hole-injecting layer on the ITO. Next, diphenyl naphthyl diamine (NPD) was formed into a layer having a thickness of 15 nm to serve

as a hole-transporting layer. Next, the compound 11 serving as a host material for a light-emitting layer and Ir(ppy)<sub>3</sub> serving as a dopant were co-deposited from different deposition sources onto the hole-transporting layer to form a light-emitting layer having a thickness of 30 nm. The concentration of Ir(ppy)<sub>3</sub> was 10%. Next, Alq<sub>3</sub> was formed into a layer having a thickness of 25 nm to serve as an electron-transporting layer. Further, lithium fluoride (LiF) was formed into a layer having a thickness of 1 nm to serve as an electron-injecting layer on the electron-transporting layer. Finally, aluminum (Al) was formed into a layer having a thickness of 70 nm to serve as an electrode on the electron-injecting layer. Thus, an organic EL device was produced.

**[0121]** An external power source was connected to the resultant organic EL device to apply a DC voltage to the device. As a result, it was confirmed that the device had such light-emitting characteristics as shown in Table 2. The columns "luminance", "voltage", and "luminous efficiency" in Table 2 show values at the time of driving at 20 mA/cm<sup>2</sup> (initial characteristics). The maximum wavelength of the emission spectrum of the device was 530 nm, and hence the acquisition of light emission from Ir(ppy)<sub>3</sub> was found.

#### Examples 8 to 11

**[0122]** Organic EL devices were each produced in the same manner as in Example 7 except that the compound 6, 32, 48, or 58 was used instead of the compound 11 as the host material for the light-emitting layer.

#### Comparative Examples 4 to 6

**[0123]** Organic EL devices were each produced in the same manner as in Example 7 except that CBP, H-1, or H-2 was used as the host material for the light-emitting layer.

**[0124]** The organic EL devices obtained in Examples 8 to 11 and Comparative Examples 4 to 6 were evaluated in the same manner as in Example 7. As a result, it was confirmed that the devices had such light-emitting characteristics as shown in Table 2. The maximum wavelength of each of the emission spectra of the organic EL devices obtained in Examples 8 to 11 and Comparative Examples 4 to 6 was 530 nm, and hence the acquisition of light emission from Ir(ppy)<sub>3</sub> was identified.

TABLE 2

|                       | Host material compound | Luminance (cd/m <sup>2</sup> ) | Voltage (V) | Visual luminous efficiency (lm/W) |
|-----------------------|------------------------|--------------------------------|-------------|-----------------------------------|
| Example 7             | 11                     | 1,200                          | 7.0         | 2.7                               |
| Example 8             | 6                      | 1,200                          | 6.8         | 2.6                               |
| Example 9             | 32                     | 1,200                          | 6.9         | 2.8                               |
| Example 10            | 48                     | 1,100                          | 6.3         | 2.9                               |
| Example 11            | 58                     | 1,200                          | 6.3         | 3.0                               |
| Comparative Example 4 | CBP                    | 1,100                          | 8.7         | 2.0                               |
| Comparative Example 5 | H-1                    | 1,000                          | 8.2         | 1.9                               |
| Comparative Example 6 | H-2                    | 700                            | 6.4         | 1.8                               |

**[0125]** As shown in Table 2, in the case where the carborane compound of the present invention is used in the light-emitting layer (each of Examples 7 to 11), luminous

efficiency more satisfactory than that of any other case (each of Comparative Examples 4 to 6) is exhibited.

### Example 12

**[0126]** Each thin film was laminated by a vacuum deposition method at a degree of vacuum of  $2.0 \times 10^{-5}$  Pa on a glass substrate on which an anode formed of indium tin oxide (ITO) having a thickness of 70 nm had been formed. First, copper phthalocyanine (CuPC) was formed into a layer having a thickness of 30 nm to serve as a hole-injecting layer on the ITO. Next, diphenyl naphthyl diamine (NPD) was formed into a layer having a thickness of 15 nm to serve as a hole-transporting layer. Next, CBP serving as a host material for a light-emitting layer and Ir(ppy)<sub>3</sub> serving as a dopant were co-deposited from different deposition sources onto the hole-transporting layer to form a light-emitting layer having a thickness of 30 nm. The concentration of Ir(ppy)<sub>3</sub> was 10 wt %. Next, the compound 11 was formed into a layer having a thickness of 5 nm to serve as a hole-blocking layer on the light-emitting layer. Next, Alq<sub>3</sub> was formed into a layer having a thickness of 20 nm to serve as an electron-transporting layer. Further, lithium fluoride (LiF) was formed into a layer having a thickness of 1.0 nm to serve as an electron-injecting layer on the electron-transporting layer. Finally, aluminum (Al) was formed into a layer having a thickness of 70 nm to serve as an electrode on the electron-injecting layer. The resultant organic EL device has such a layer construction that the electron-injecting layer is added between the cathode and the electron-transporting layer and the hole-blocking layer is added between the light-emitting layer and the electron-transporting layer in the organic EL device illustrated in FIG. 1.

[0127] An external power source was connected to the resultant organic EL device to apply a DC voltage to the device. As a result, it was confirmed that the device had such light-emitting characteristics as shown in Table 3. The columns "luminance", "voltage", and "luminous efficiency" in Table 3 show values at the time of driving at 20 mA/cm<sup>2</sup> (initial characteristics). The maximum wavelength of the emission spectrum of the device was 530 nm, and hence the acquisition of light emission from Ir(ppy)<sub>3</sub> was found.

## Examples 13 to 17

**[0128]** Organic EL devices were each produced in the same manner as in Example 12 except that the compound 6, 25, 32, 48, or 58 was used instead of the compound 11 as the hole-blocking material.

### Comparative Example 7

**[0129]** An organic EL device was produced in the same manner as in Example 12 except that the thickness of AlG<sub>3</sub> serving as the electron-transporting layer was changed to 25 nm and the hole-blocking layer was not formed.

### Comparative Examples 8 and 9

**[0130]** Organic EL devices were each produced in the same manner as in Example 12 except that the compound H-1 or H-2 was used as the hole-blocking material.

**[0131]** The organic EL devices obtained in Examples 13 to 17 and Comparative Examples 7 to 9 were evaluated in the same manner as in Example 12. As a result, it was confirmed that the devices had such light-emitting characteristics as shown in Table 3. The maximum wavelength of each of the

emission spectra of the organic EL devices obtained in Examples 13 to 17 and Comparative Examples 7 to 9 was 530 nm, and hence the acquisition of light emission from Ir(ppy)<sub>3</sub> was identified. Each of the host materials for the light-emitting layers used in Examples 13 to 17 and Comparative Examples 7 to 9 is mCP.

TABLE 3

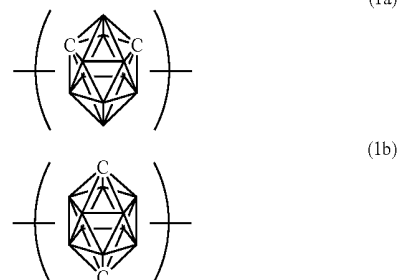
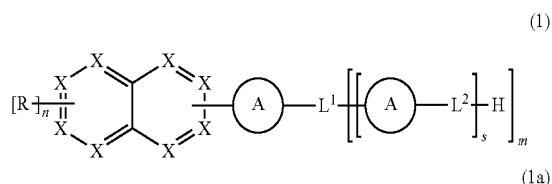
|                          | Hole-blocking<br>material<br>compound | Luminance<br>(cd/m <sup>2</sup> ) | Voltage<br>(V) | Visual<br>luminous<br>efficiency<br>(lm/W) |
|--------------------------|---------------------------------------|-----------------------------------|----------------|--------------------------------------------|
| Example 12               | 11                                    | 1,300                             | 8.3            | 2.4                                        |
| Example 13               | 6                                     | 1,200                             | 8.1            | 2.3                                        |
| Example 14               | 25                                    | 1,200                             | 7.9            | 2.4                                        |
| Example 15               | 32                                    | 1,500                             | 8.2            | 2.8                                        |
| Example 16               | 48                                    | 1,200                             | 7.5            | 2.5                                        |
| Example 17               | 58                                    | 1,400                             | 7.4            | 3.0                                        |
| Comparative<br>Example 7 | —                                     | 1,100                             | 8.7            | 2.0                                        |
| Comparative<br>Example 8 | H-1                                   | 1,200                             | 9.9            | 1.9                                        |
| Comparative<br>Example 9 | H-2                                   | 900                               | 9.9            | 1.4                                        |

**[0132]** As shown in Table 3, all systems showed improvements in initial characteristics as compared to Comparative Example 7 not using the hole-blocking material. Of those systems, the systems each using the carborane compound of the present invention in its hole-blocking layer show better characteristics.

## INDUSTRIAL APPLICABILITY

**[10133]** When the material for an organic electroluminescent device of the present invention is contained in at least one of a plurality of organic layers of an organic EL device having a structure in which an anode, the plurality of organic layers, and a cathode are laminated on a substrate, an excellent organic electroluminescent device is provided. A light-emitting layer, an electron-transporting layer, or a hole-blocking layer is suitable as the organic layer in which the material is contained.

1. A material for an organic electroluminescent device, comprising a carborane compound represented by the general formula (1):



where:

rings A's each independently represent a divalent carborane group  $C_2B_{10}H_{10}$  represented by the formula (1a) or the formula (1b), and when the plurality of rings A's are present in a molecule, the rings may be identical to or different from each other, s's each independently represent a number of repetitions and an integer of from 1 to 4, m and n each represent a number of substitutions, and m represents an integer of from 0 to 4 and n represents an integer of from 0 to 6, provided that when  $m=1$ ,  $s=1$ ;

X's each independently represent N, CH, or C, and 1 to 4 of X's each represent N;

R represents an alkyl group having 1 to 12 carbon atoms, an alkoxy group having 1 to 12 carbon atoms, a substituted or unsubstituted aromatic hydrocarbon group having 6 to 30 carbon atoms, a substituted or unsubstituted aromatic heterocyclic group having 3 to 30 carbon atoms, or a linked aromatic group formed by linking 2 to 6 of the substituted or unsubstituted aromatic rings, the linked aromatic group may be linear or branched, and the aromatic rings to be linked may be identical to or different from each other;

$L^1$  represents a single bond, an  $m+1$ -valent substituted or unsubstituted aromatic hydrocarbon group having 6 to 30 carbon atoms, an  $m+1$ -valent substituted or unsubstituted aromatic heterocyclic group having 3 to 30 carbon atoms, or an  $m+1$ -valent linked aromatic group formed by linking 2 to 6 of the substituted or unsubstituted aromatic rings, the linked aromatic group may be linear or branched, and the aromatic rings to be linked may be identical to or different from each other, and when  $m=1$ ,  $L^1$  represents a group containing at least one aromatic heterocyclic group or a single bond; and

$L^2$ 's each independently represent a single bond, a divalent substituted or unsubstituted aromatic hydrocarbon group having 6 to 30 carbon atoms, a divalent substituted or unsubstituted aromatic heterocyclic group having 3 to 30 carbon atoms, or a divalent linked aromatic group formed by linking 2 to 6 of the substituted or unsubstituted aromatic rings, the linked aromatic group may be linear or branched, and the aromatic rings to be linked may be identical to or different from each other,

and  $L^2$ -H at a terminal may represent an alkyl group having 1 to 12 carbon atoms or an alkoxy group having 1 to 12 carbon atoms.

2. A material for an organic electroluminescent device according to claim 1, wherein m in the general formula (1) represents 0 or 1.

3. A material for an organic electroluminescent device according to claim 1, wherein the ring A represents a divalent carborane group  $C_2B_{10}H_{10}$  represented by the formula (1a).

4. A material for an organic electroluminescent device according to claim 1, wherein  $L^1$  and  $L^2$  in the general formula (1) each independently represent a single bond, a substituted or unsubstituted aromatic hydrocarbon group having 6 to 18 carbon atoms, a substituted or unsubstituted aromatic heterocyclic group having 3 to 17 carbon atoms, or a linked aromatic group formed by linking 2 to 6 aromatic groups each selected from the aromatic hydrocarbon group and the aromatic heterocyclic group.

5. A material for an organic electroluminescent device according to claim 1, wherein  $L^1$  and  $L^2$  in the general formula (1) each independently represent a single bond, a substituted or unsubstituted aromatic heterocyclic group having 3 to 30 carbon atoms, or a linked aromatic group formed by linking 2 to 6 aromatic groups each selected from the aromatic heterocyclic group.

6. A material for an organic electroluminescent device according to claim 1, wherein m in the general formula (1) represents an integer of 0.

7. An organic electroluminescent device having a structure in which an anode, organic layers, and a cathode are laminated on a substrate, comprising an organic layer containing the material for an organic electroluminescent device of any one of claims 1 to 6.

8. An organic electroluminescent device according to claim 7, wherein the organic layer containing the material for an organic electroluminescent device comprises at least one layer selected from the group consisting of a light-emitting layer, an electron-transporting layer, and a hole-blocking layer.

9. An organic electroluminescent device according to claim 8, wherein the organic layer containing the material for an organic electroluminescent device comprises a light-emitting layer containing a phosphorescent light-emitting dopant.

\* \* \* \* \*

|                |                                                                                                                                      |         |            |
|----------------|--------------------------------------------------------------------------------------------------------------------------------------|---------|------------|
| 专利名称(译)        | 有机电致发光元件材料和使用它的有机电致发光元件                                                                                                              |         |            |
| 公开(公告)号        | <a href="#">US20170012206A1</a>                                                                                                      | 公开(公告)日 | 2017-01-12 |
| 申请号            | US15/117788                                                                                                                          | 申请日     | 2015-02-23 |
| [标]申请(专利权)人(译) | 新日铁化学株式会社                                                                                                                            |         |            |
| 申请(专利权)人(译)    | NIPPON STEEL住金化工有限公司.                                                                                                                |         |            |
| 当前申请(专利权)人(译)  | NIPPON STEEL住金化工有限公司.                                                                                                                |         |            |
| [标]发明人         | UEDA TOKIKO<br>OGAWA JUNYA<br>KAI TAKAHIRO<br>TADA MASASHI                                                                           |         |            |
| 发明人            | UEDA, TOKIKO<br>OGAWA, JUNYA<br>KAI, TAKAHIRO<br>TADA, MASASHI                                                                       |         |            |
| IPC分类号         | H01L51/00 C09K11/02 C07F5/02 C09K11/06                                                                                               |         |            |
| CPC分类号         | H01L51/008 C09K11/06 C09K11/025 C07F5/027 H01L51/0085 H01L51/5096 C09K2211/185 C09K2211/1029 C09K2211/1092 C09K2211/1007 H01L51/5016 |         |            |
| 优先权            | 2014069998 2014-03-28 JP                                                                                                             |         |            |
| 其他公开文献         | US10446767                                                                                                                           |         |            |
| 外部链接           | <a href="#">Espacenet</a> <a href="#">USPTO</a>                                                                                      |         |            |

#### 摘要(译)

本发明公开了一种有机电致发光器件（有机EL器件），其发光效率得到改善，充分确保了驱动稳定性，并且结构简单。该器件是具有有机层的有机电致发光器件，所述有机层包括层叠在基板上的阳极和阴极之间的发光层，其中碳硼烷化合物结合到至少一层有机层中，或者作为主体结合。将材料制成含有磷光发光掺杂剂和主体材料的发光层。碳硼烷化合物具有其中含N稠合芳环与碳硼烷环键合的结构。含N稠合芳环是喹啉环或具有通过用N原子取代喹啉环中的1至3个成环碳原子而获得的结构。

