



US 20160380199A1

(19) **United States**(12) **Patent Application Publication**  
**OGAWA et al.**(10) **Pub. No.: US 2016/0380199 A1**(43) **Pub. Date: Dec. 29, 2016**(54) **ORGANIC-ELECTROLUMINESCENT-ELEMENT  
MATERIAL AND ORGANIC  
ELECTROLUMINESCENT ELEMENTS  
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)

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§ 371 (c)(1),

(2) Date: **Aug. 4, 2016**(30) **Foreign Application Priority Data**

Mar. 24, 2014 (JP) ..... 2014-059925

**ABSTRACT**

Disclosed are an organic electroluminescent device that is improved in luminous efficiency, sufficiently secures driving stability, and has a simple construction, and a material for an organic electroluminescent device to be used in the device. The material is a material for an organic electroluminescent device formed of a carborane compound having an indolo-carbazole skeleton and one or two or more carborane groups each bonded thereto directly or through a divalent group. In addition, 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 at least one layer of the organic layers contains the material for an organic electroluminescent device. In addition, the device is an organic electroluminescent device containing, as a host material for a light-emitting layer containing a phosphorescent light-emitting dopant and the host material, the material for an organic electroluminescent device.

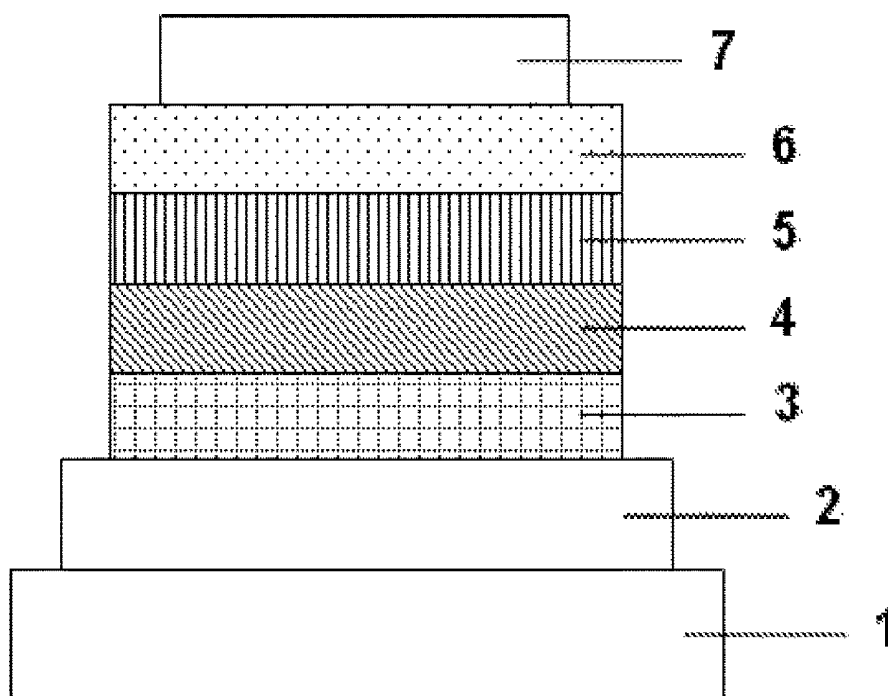


FIG. 1

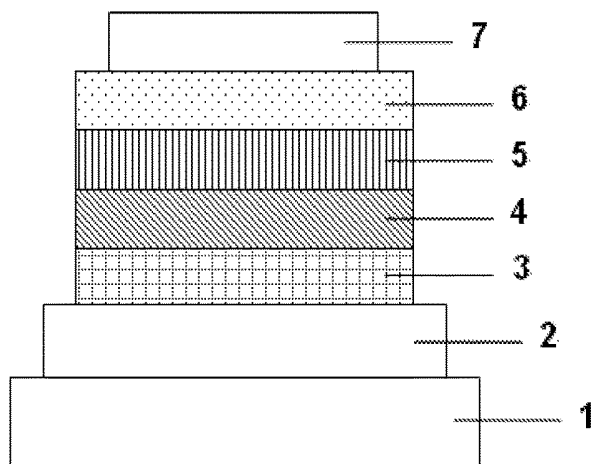
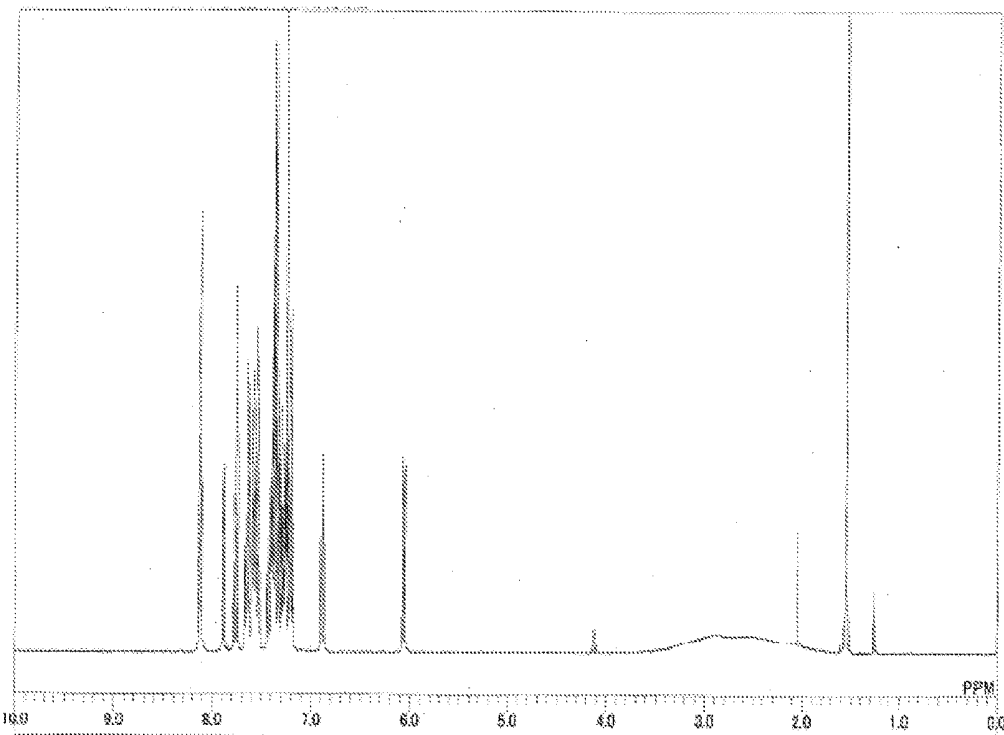


FIG. 2



**ORGANIC-ELECTROLUMINESCENT-ELEMENT  
MATERIAL AND ORGANIC  
ELECTROLUMINESCENT ELEMENTS  
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] WO 2013/094834 A1
- [0010] [PTL 6] US 2009/0167162 A1

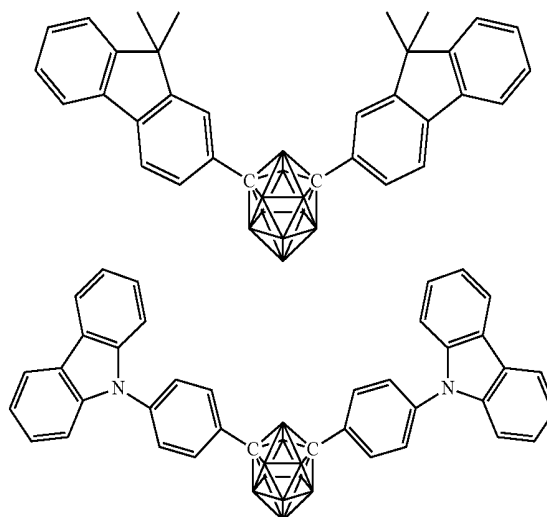
**Non Patent Literature**

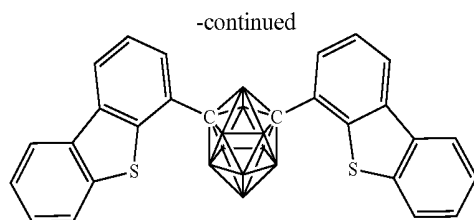
[0011] [NPL 1] J. Am. Chem. Soc. 2012, 134, 17982-17990

[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.



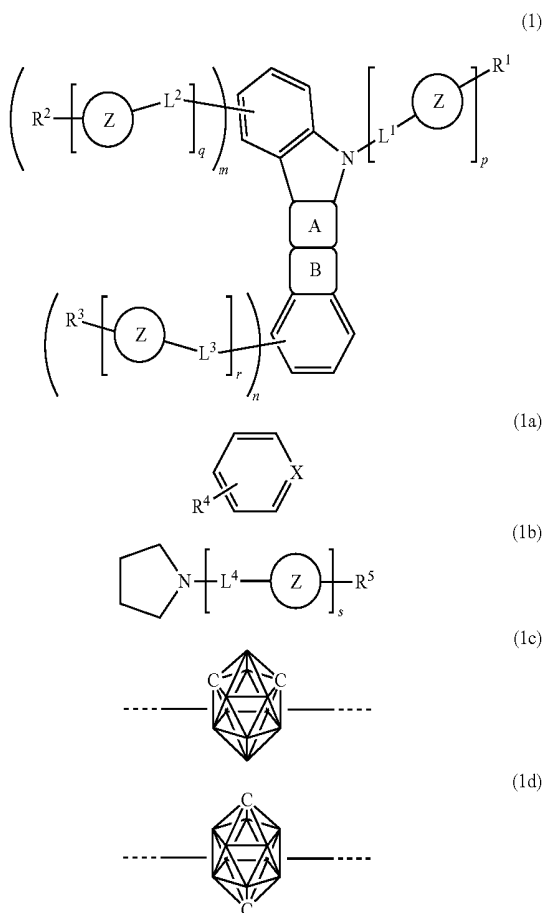


## SUMMARY OF INVENTION

**[0015]** In order to apply an organic EL device to a display device in a flat panel display or the like, it is necessary to improve the luminous efficiency of the device and also to ensure sufficiently the stability in driving the device. The present invention has an object to provide, in view of the above-mentioned circumstances, an organic EL device that has high efficiency and high driving stability and is practically useful and a compound suitable for the organic EL device.

**[0016]** The inventors of the present invention have made extensive investigations, and as a result, have found that when a compound having at least one carborane group bonded onto an indolocarbazole group is used in an organic EL device, the device shows excellent characteristics. Thus, the inventors have completed the present invention.

**[0017]** The present invention relates to a material for an organic electroluminescent device including a carborane compound represented by the general formula (1).



**[0018]** In the formulae, a ring A represents an aromatic ring represented by the formula (1a), the ring being fused with an adjacent ring at an arbitrary position, a ring B represents a heterocycle represented by the formula (1b) whose nitrogen-containing five-membered ring having a substituent is fused with an adjacent ring at an arbitrary position, X represents a methine group or a nitrogen atom, a ring Z represents a divalent carborane group  $C_2B_{10}H_{10}$  represented by the formula (1c) or the formula (1d), and when the plurality of rings Z's are present in a molecule, the rings may be identical to or different from each other. p, q, r, and s each represent a number of repetitions, and m and n each represent a number of substitutions. p, q, r, and s, and m and n each represent an integer of from 0 to 5, provided that any one of  $q \times m$ ,  $r \times n$ , p, and s represents an integer of 1 or more.

**[0019]**  $L^1$  and  $L^4$  each independently represent a single bond, a substituted or unsubstituted aromatic hydrocarbon group having 6 to 22 carbon atoms, a substituted or unsubstituted aromatic heterocyclic group having 3 to 16 carbon atoms, or a linked aromatic group formed by linking 2 to 6 arbitrary aromatic groups each selected from the substituted or unsubstituted aromatic hydrocarbon group and the substituted or unsubstituted aromatic heterocyclic group, and the linked aromatic group may be linear or branched.

**[0020]**  $L^2$  and  $L^3$  each independently represent a single bond, a substituted or unsubstituted aromatic hydrocarbon group having 6 to 22 carbon atoms, a substituted or unsubstituted aromatic heterocyclic group having 3 to 18 carbon atoms, or a linked aromatic group formed by linking 2 to 6 arbitrary aromatic groups each selected from the substituted or unsubstituted aromatic hydrocarbon group and the substituted or unsubstituted aromatic heterocyclic group, and the linked aromatic group may be linear or branched.

**[0021]**  $R^1$  and  $R^5$  each independently represent a hydrogen atom, a substituted or unsubstituted aromatic hydrocarbon group having 6 to 22 carbon atoms, a substituted or unsubstituted aromatic heterocyclic group having 3 to 16 carbon atoms, or a linked aromatic group formed by linking 2 to 6 arbitrary aromatic groups each selected from the substituted or unsubstituted aromatic hydrocarbon group and the substituted or unsubstituted aromatic heterocyclic group, and the linked aromatic group may be linear or branched.

**[0022]**  $R^2$ ,  $R^3$ , and  $R^4$  each independently represent a hydrogen atom, a substituted or unsubstituted aromatic hydrocarbon group having 6 to 22 carbon atoms, a substituted or unsubstituted aromatic heterocyclic group having 3 to 18 carbon atoms, or a linked aromatic group formed by linking 2 to 6 arbitrary aromatic groups each selected from the substituted or unsubstituted aromatic hydrocarbon group and the substituted or unsubstituted aromatic heterocyclic group, and the linked aromatic group may be linear or branched.

**[0023]** A preferred aspect of the present invention is as follows: in the general formula (1), X represents a methine group, the ring Z represents a divalent carborane group  $C_2B_{10}H_{10}$  represented by the formula (1c), or q and r each represent an integer of 0.

**[0024]** It is preferred that  $L^1$  and  $L^4$  each independently represent a substituted or unsubstituted aromatic hydrocarbon group having 6 to 18 carbon atoms, a substituted or unsubstituted aromatic heterocyclic group having 3 to 16 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, and  $L^2$  and  $L^3$  each independently represent a substituted or unsubstituted aromatic hydrocarbon group having 6 to 18 carbon atoms, a substituted or unsubstituted aromatic heterocyclic group having 3 to 18 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.

[0025] It is more preferred that  $L^1$  and  $L^4$  each independently represent a substituted or unsubstituted aromatic heterocyclic group having 3 to 16 carbon atoms, or a linked aromatic group formed by linking 2 to 6 aromatic groups each selected from the aromatic heterocyclic group, and  $L^2$  and  $L^3$  each independently represent a substituted or unsubstituted aromatic heterocyclic group having 3 to 18 carbon atoms, or a linked aromatic group formed by linking 2 to 6 aromatic groups each selected from the aromatic heterocyclic group.

[0026] It is preferred that  $R^1$  and  $R^5$  each independently represent a substituted or unsubstituted aromatic hydrocarbon group having 6 to 18 carbon atoms, a substituted or unsubstituted aromatic heterocyclic group having 3 to 16 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, and  $R^2$ ,  $R^3$ , and  $R^4$  each independently represent a substituted or unsubstituted aromatic hydrocarbon group having 6 to 18 carbon atoms, a substituted or unsubstituted aromatic heterocyclic group having 3 to 18 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.

[0027] 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.

[0028] Further, it is preferred that the organic layer containing the material for an organic electroluminescent device include a phosphorescent light-emitting dopant. In addition, it is desired that the emission wavelength of the phosphorescent light-emitting dopant have an emission maximum wavelength at 600 nm or less.

[0029] The material for an organic electroluminescent device of the present invention adopts a structure in which at least one carborane group or a group including the carborane group is bonded to an indolocarbazole ring. In the carborane compound having such structural feature, the lowest unoccupied molecular orbital (LUMO) that affects an electron-injecting/transporting property is distributed on a carborane group, and the highest occupied molecular orbital (HOMO) that affects a hole-injecting/transporting property is distributed on the indolocarbazole group. Accordingly, the charge-injecting/transporting properties can be controlled at high levels by changing the number of carborane groups, or the kinds or number of substituents for substituting a carborane group or an indolocarbazole ring. Further, the compound enables efficient light emission from a dopant because the compound has the lowest triplet excitation energy (T1 energy) high enough to confine the T1 energy of the dopant. By virtue of the foregoing features, the use of the compound in an organic EL device can achieve a reduction in driving voltage of the device and high luminous efficiency.

[0030] 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

[0031] FIG. 1 is a sectional view for illustrating an example of the structure of an organic EL device.

[0032] FIG. 2 is an NMR chart of a carborane compound of the present invention.

#### 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). The carborane compound has an indolocarbazole ring and at least one carborane group, and hence may exhibit the excellent effect as described above.

[0034] In the formulae,  $L^1$  and  $L^4$  each independently represent a single bond, a substituted or unsubstituted aromatic hydrocarbon group having 6 to 22 carbon atoms, a substituted or unsubstituted aromatic heterocyclic group having 3 to 16 carbon atoms, or a linked aromatic group.

[0035] The term "linked aromatic group" as used herein refers to an aromatic group formed by linking 2 to 6 aromatic rings of an aromatic group selected from the aromatic hydrocarbon group and the aromatic heterocyclic group in a chain manner. 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. The description of the linked aromatic group is identical to the description of a linked aromatic group in each of  $L^2$ ,  $L^3$ , and  $R^1$  to  $R^5$ .

[0036]  $L^2$  and  $L^3$  each independently represent a single bond, a substituted or unsubstituted aromatic hydrocarbon group having 6 to 22 carbon atoms, a substituted or unsubstituted aromatic heterocyclic group having 3 to 18 carbon atoms, or a linked aromatic group formed by linking 2 to 6 aromatic rings of an aromatic group selected from the aromatic hydrocarbon group and the aromatic heterocyclic group. When a plurality of  $L^1$ 's,  $L^2$ 's,  $L^3$ 's, or  $L^4$ 's are present in a molecule, the groups may be identical to or different from each other.

[0037] In the formulae,  $R^1$  and  $R^5$  each independently represent a hydrogen atom, a substituted or unsubstituted aromatic hydrocarbon group having 6 to 22 carbon atoms, a substituted or unsubstituted aromatic heterocyclic group having 3 to 16 carbon atoms, or a linked aromatic group formed by linking 2 to 6 aromatic rings of an aromatic group selected from the aromatic hydrocarbon group and the aromatic heterocyclic group.

[0038]  $R^2$ ,  $R^3$ , and  $R^4$  each independently represent a hydrogen atom, a substituted or unsubstituted aromatic hydrocarbon group having 6 to 22 carbon atoms, a substituted or unsubstituted aromatic heterocyclic group having 3 to 18 carbon atoms, or a linked aromatic group formed by linking 2 to 6 aromatic rings of an aromatic group selected from the aromatic hydrocarbon group and the aromatic heterocyclic group. When a plurality of  $R^2$ 's or  $R^3$ 's are present in a molecule, the groups may be identical to or different from each other.

**[0039]** In the description of  $L^1$  to  $L^4$  and  $R^1$  to  $R^5$ , 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.

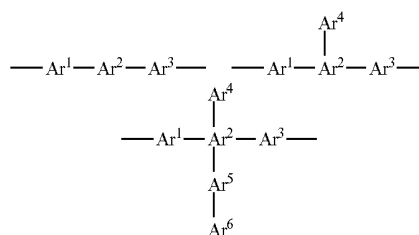
**[0040]** Specific examples of the unsubstituted aromatic heterocyclic group include linking groups each produced by removing a hydrogen atom from an aromatic heterocyclic compound, such as pyridine, pyrimidine, triazine, quinoline, isoquinoline, quinoxaline, quinazoline, naphthyridine, carbazole, acridine, azepine, tribenzazepine, phenazine, 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. When  $L^2$ ,  $L^3$ ,  $R^2$ ,  $R^3$ , or  $R^4$  represents an aromatic heterocyclic group or a linked aromatic group containing the group, the number of the carbon atoms of the aromatic heterocyclic group is from 3 to 18, and hence the group can be a group produced by removing a hydrogen atom from an aromatic heterocyclic compound having 17 or 18 carbon atoms, such as an indolocarbazole, in addition to the foregoing.

**[0041]** The linked aromatic 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 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 maybe 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]** The aromatic hydrocarbon group, the aromatic heterocyclic group, or the linked aromatic group may have a substituent. When any such group has a substituent, the substituent is preferably an alkyl group having 1 to 12 carbon atoms, an alkoxy group having 1 to 12 carbon atoms, or an acetyl group. The substituent is more preferably an alkyl group having 1 to 4 carbon atoms, an alkoxy group having 1 or 2 carbon atoms, or an acetyl group.

**[0044]** Here, 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.



**[0045]** ( $\text{Ar}^1$  to  $\text{Ar}^6$  each represent an unsubstituted aromatic hydrocarbon ring or aromatic heterocycle.)

**[0046]** In the formulae, p, q, r, and s each represent a number of repetitions, and each represent an integer of from 0 to 5. In addition, m and n each represent a number of substitutions, and each represent an integer of from 0 to 5, provided that any one of  $q \times m$ ,  $r > n$ , p, and s represents an integer of 1 or more.

**[0047]** It is preferred that (m+n) represent an integer of from 0 to 3, and it is more preferred that (m+n) be equal to from 0 to 1. One, or each of both, of p and s preferably represents an integer of 1 or more. The number of the rings Z's is preferably 1 or 2.

**[0048]** In the general formula (1), the ring A represents an aromatic ring represented by the formula (1a), the ring being fused with an adjacent ring at an arbitrary position, and the ring B represents a heterocycle represented by the formula (1b), the ring being fused with an adjacent ring at an arbitrary position, and a five-membered ring containing nitrogen is fused with the adjacent ring.

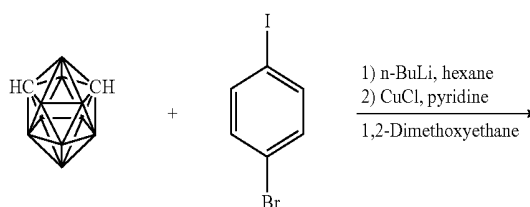
**[0049]** In the formula (1a), X represents a methine group or a nitrogen atom, preferably a methine group.

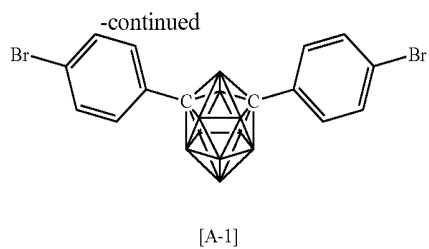
**[0050]** In the formulae, the ring Z represents a divalent carborane group ( $\text{C}_2\text{B}_{10}\text{H}_{10}$ ) represented by the formula (1c) or (1d). The two bonding hands of the formula (1c) or (1d), which may each occur from C or B forming a carborane skeleton, each preferably occur from C.

**[0051]** Of the carborane groups each represented by the formula (1c) or (1d), a carborane group represented by the formula (1c) is preferred.

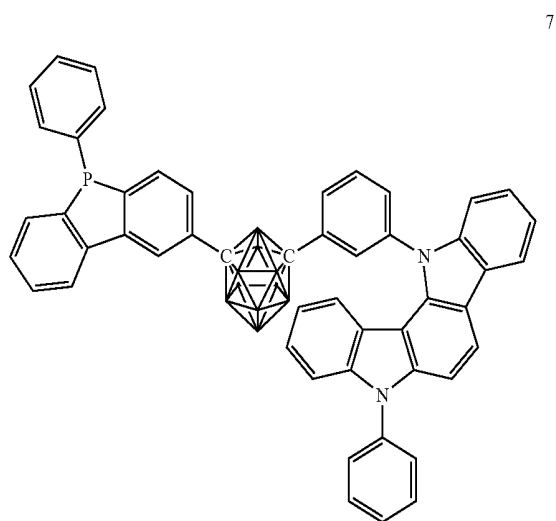
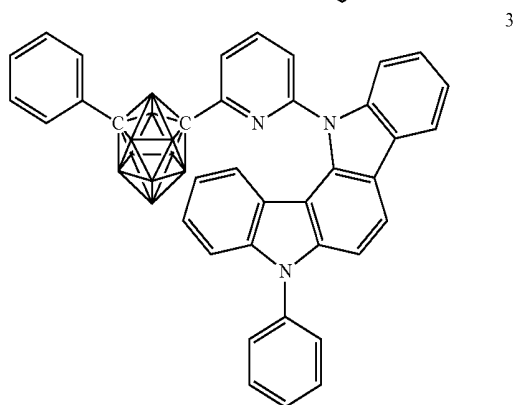
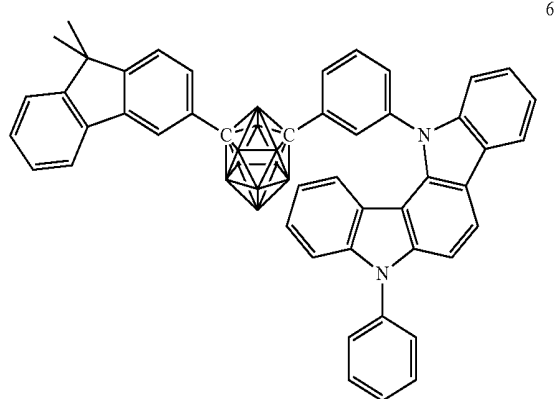
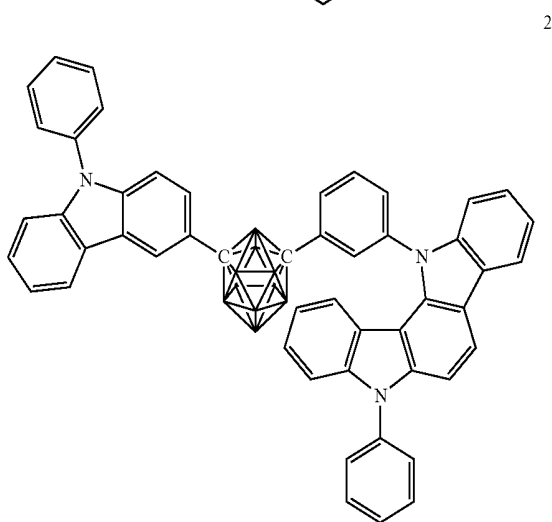
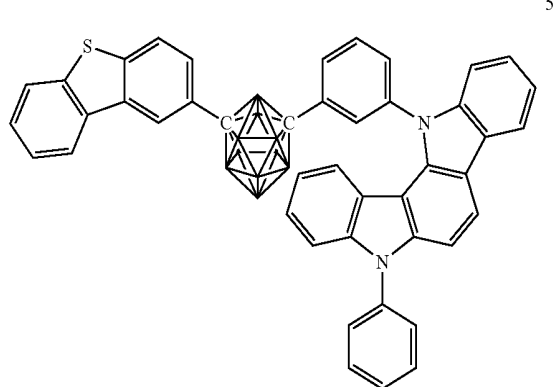
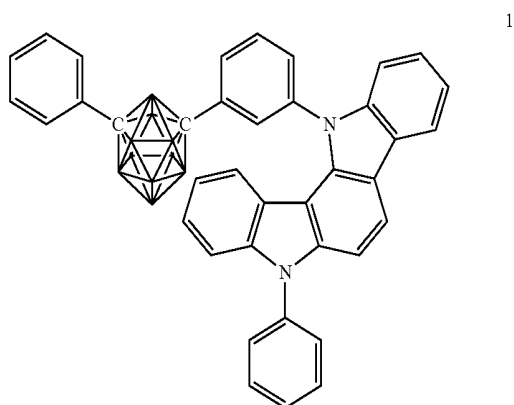
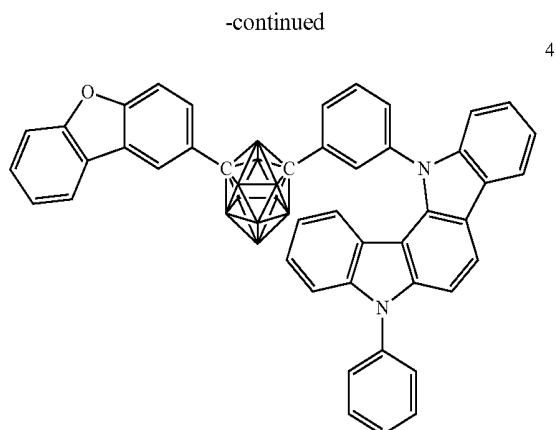
**[0052]** The carborane compound represented by the general formula (1) can be synthesized from raw materials selected in accordance with the structure of the target compound by using a known approach.

**[0053]** (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.

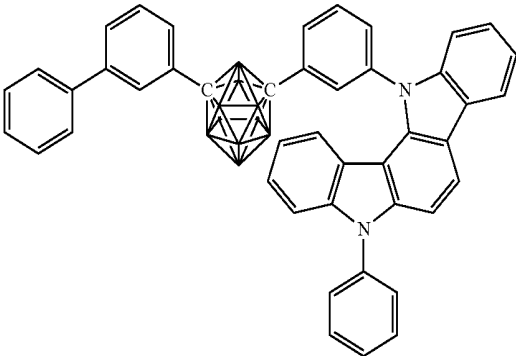




**[0054]** Specific examples of the carborane compound represented by the general formula (1) are shown below. However, the material for an organic electroluminescent device of the present invention is not limited thereto.

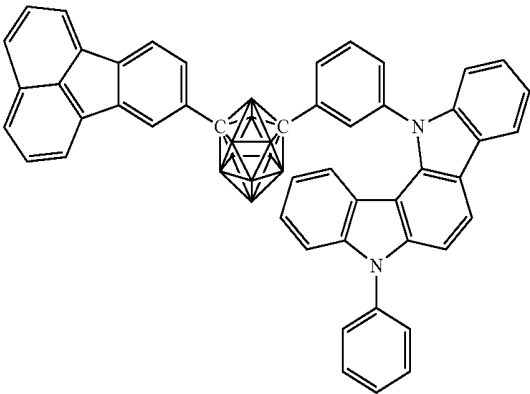


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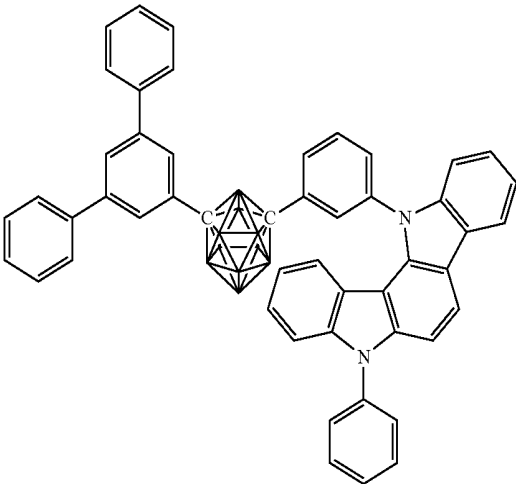


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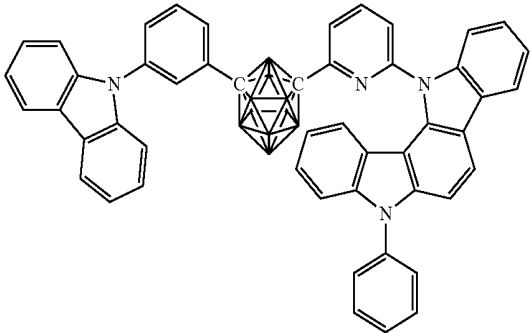
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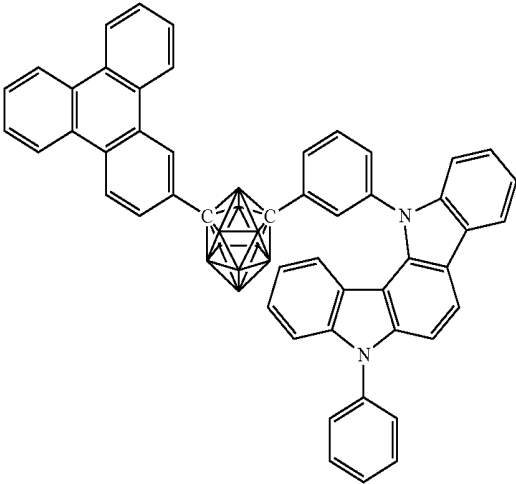
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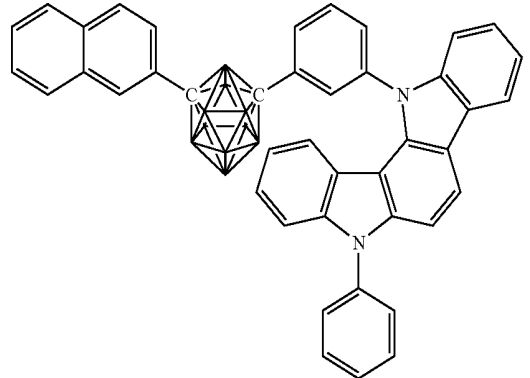
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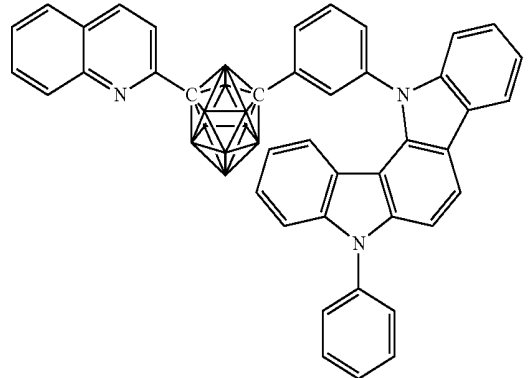
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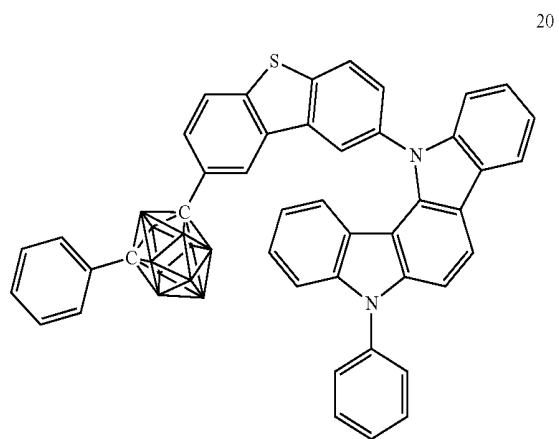
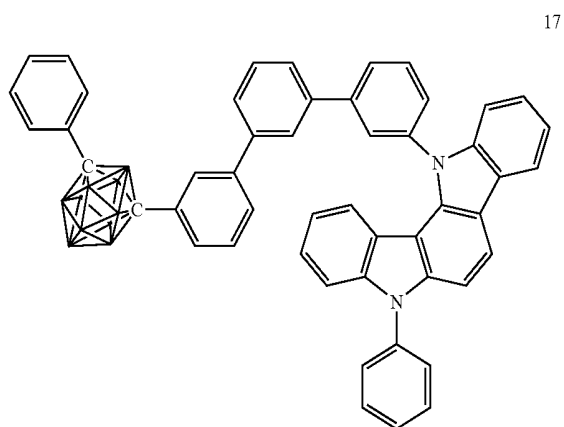
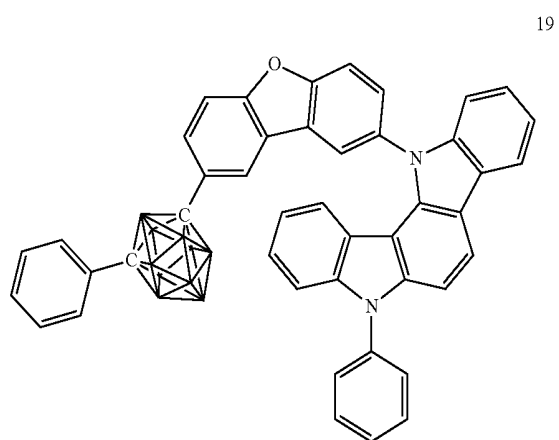
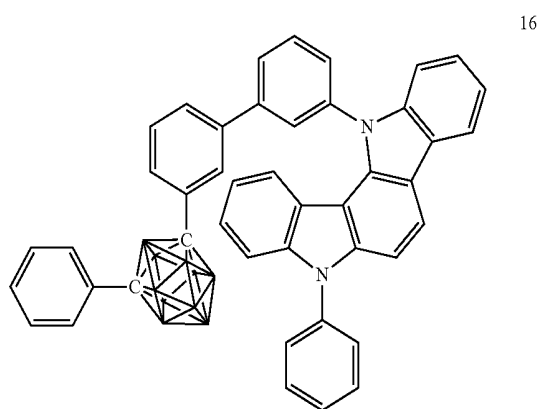
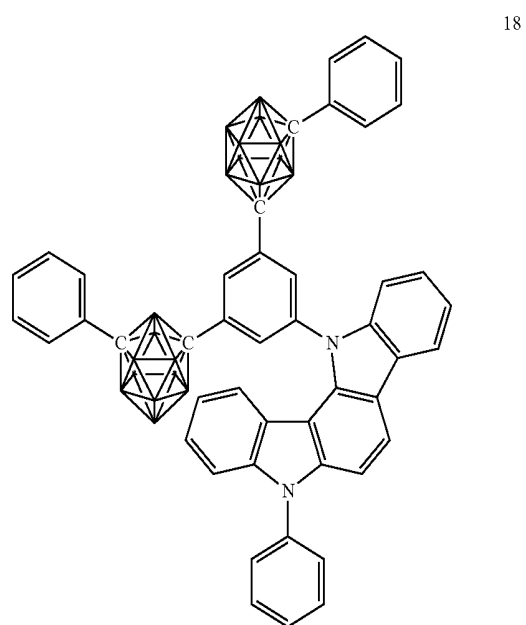
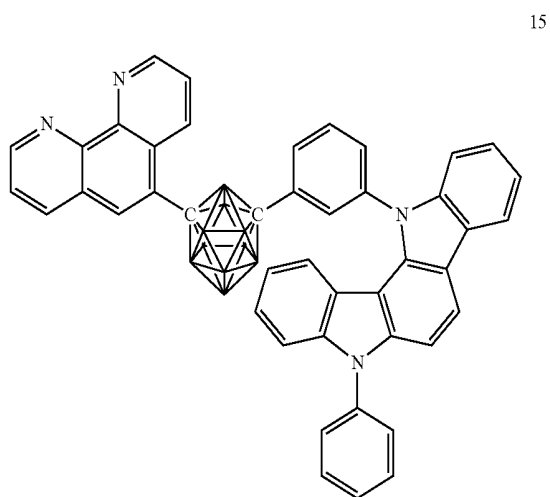
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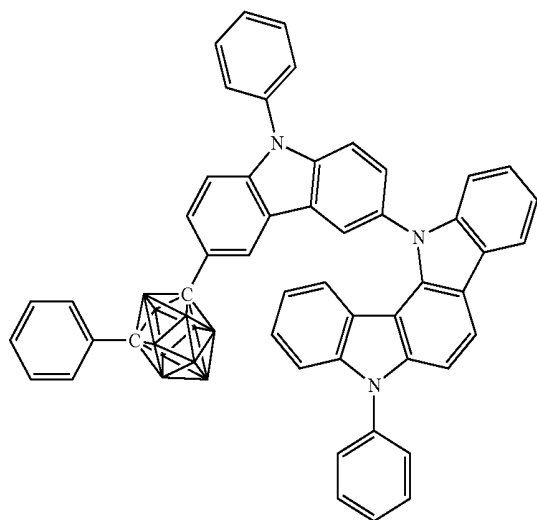
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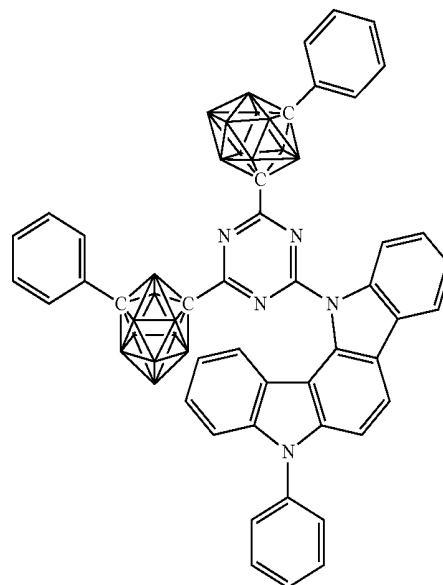
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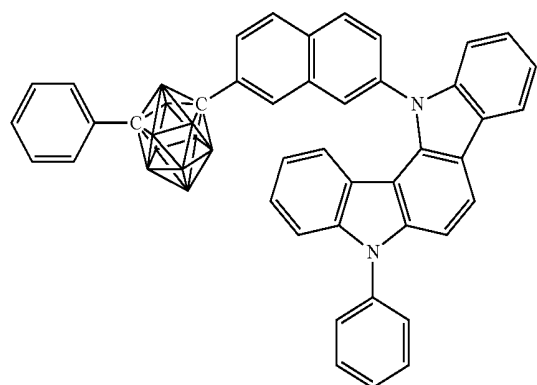


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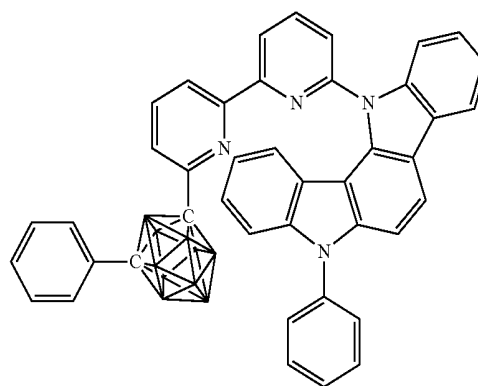
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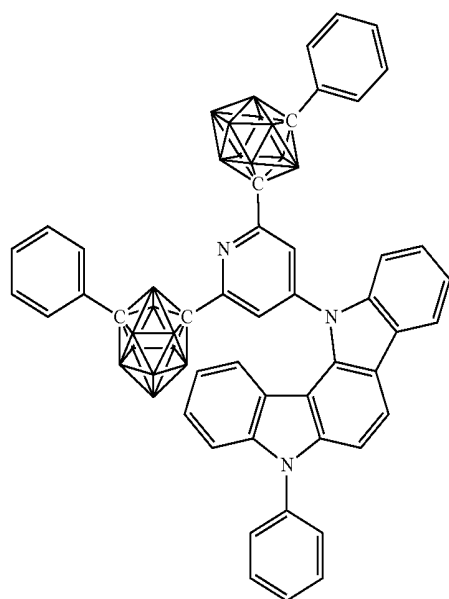
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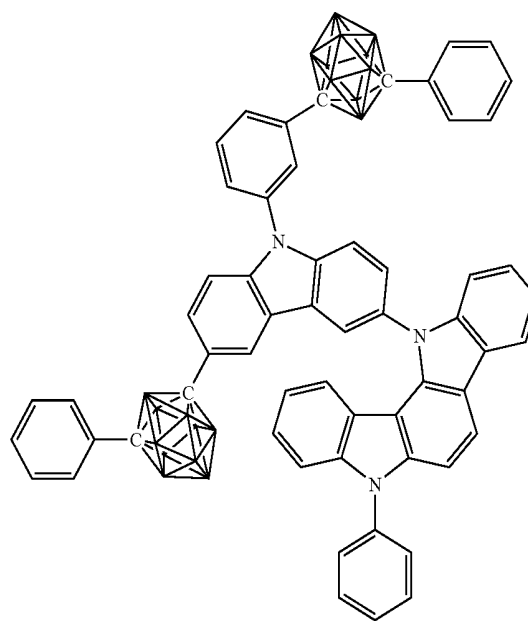
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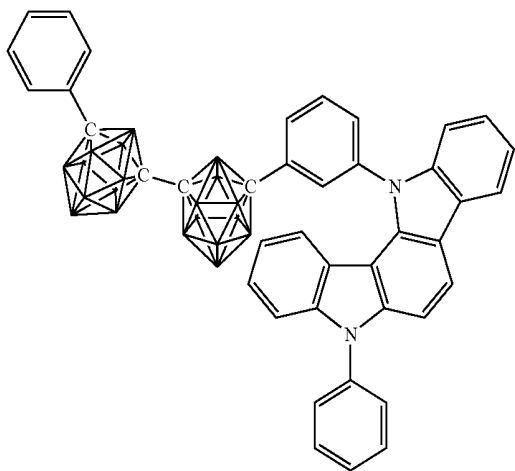
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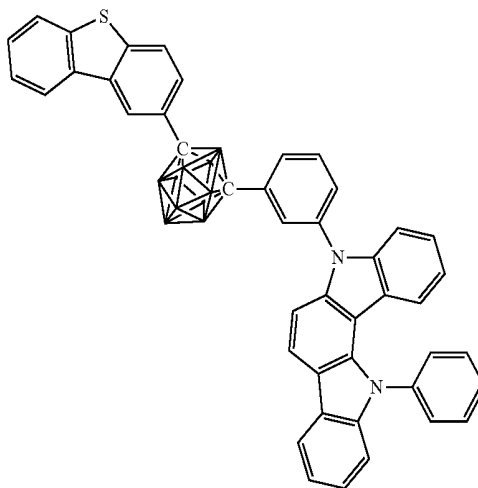
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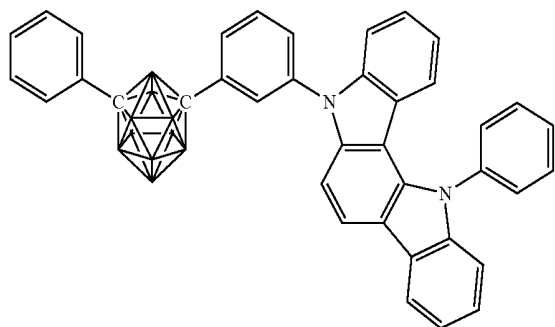
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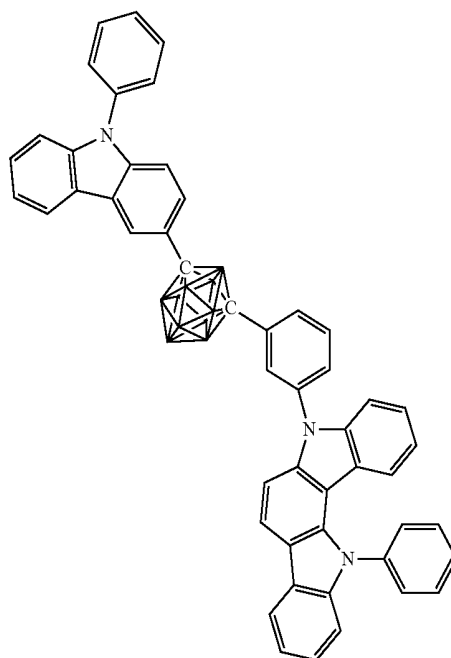
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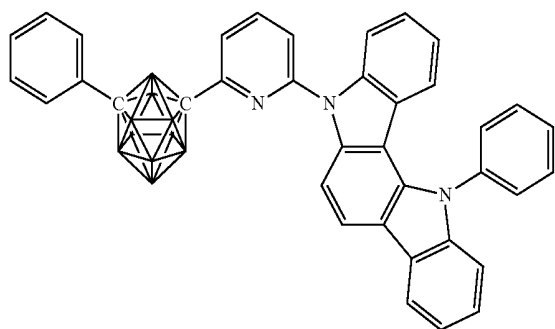
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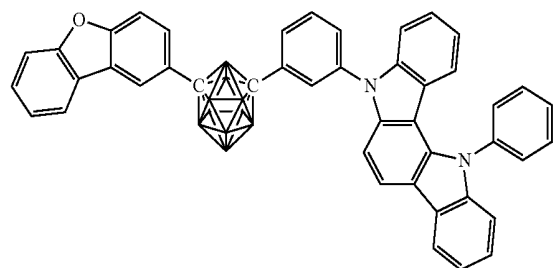
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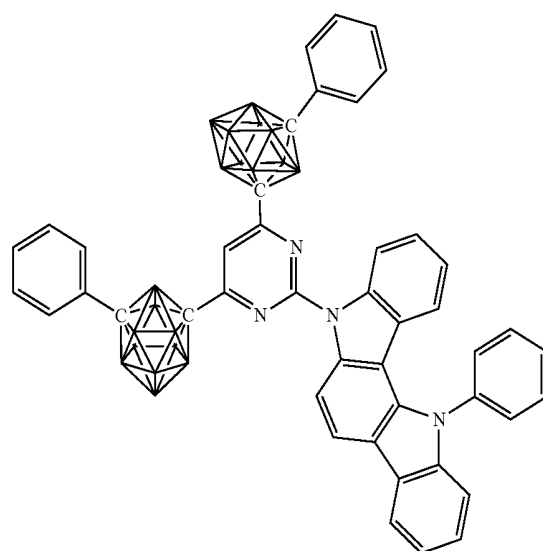
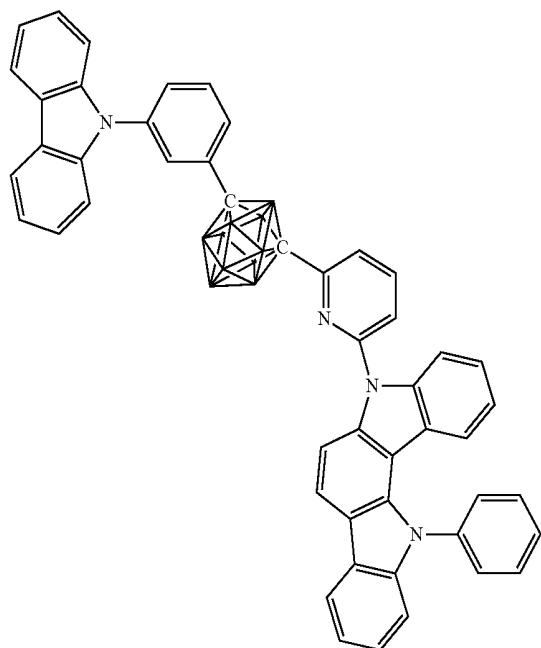


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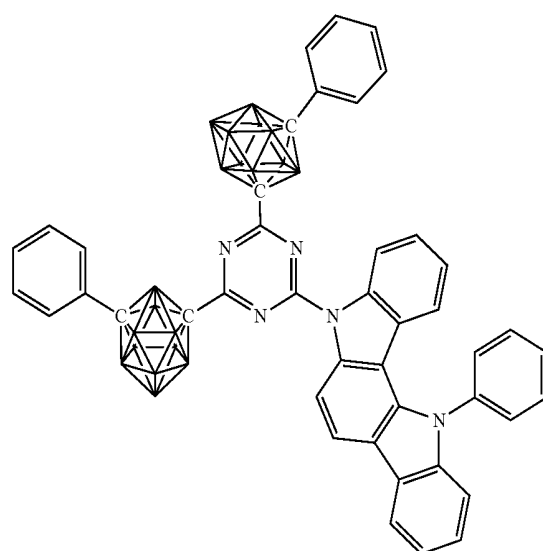
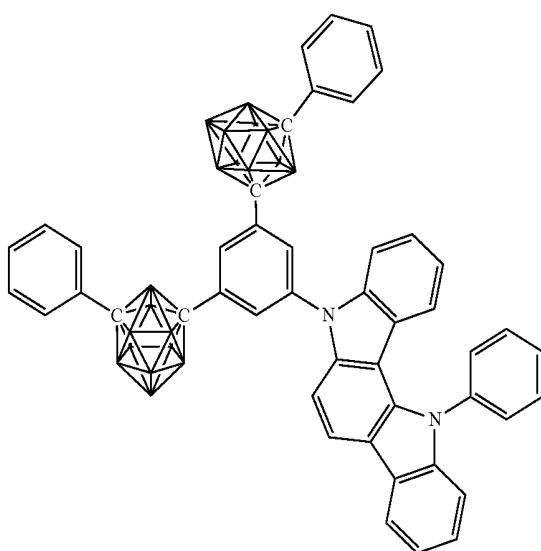
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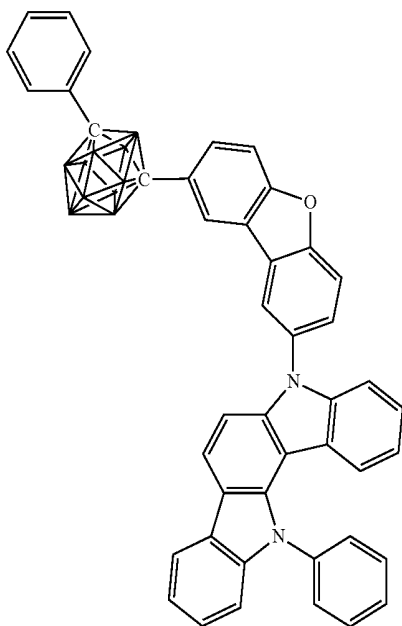
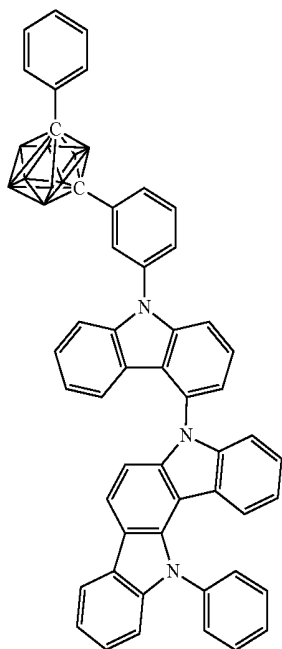


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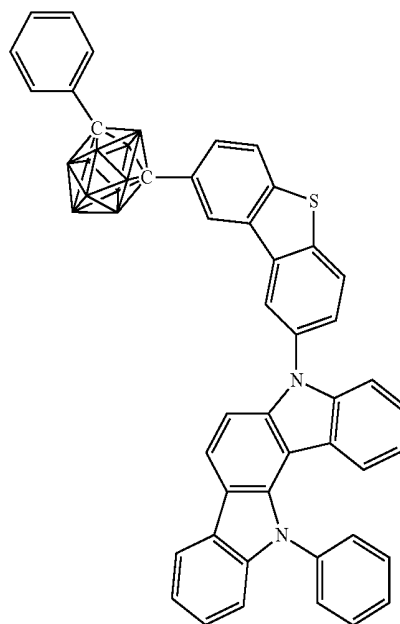


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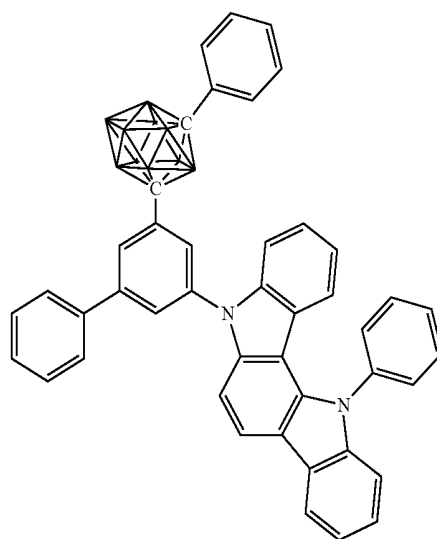


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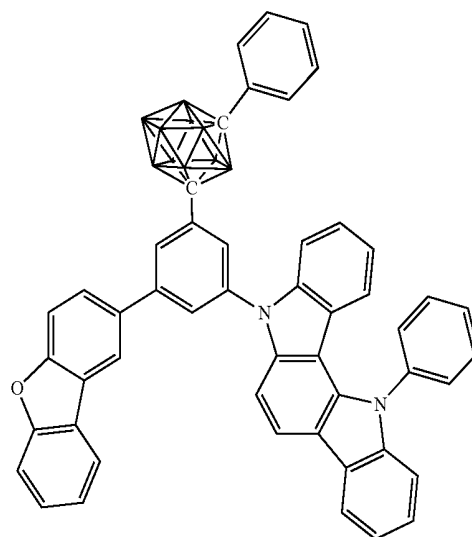
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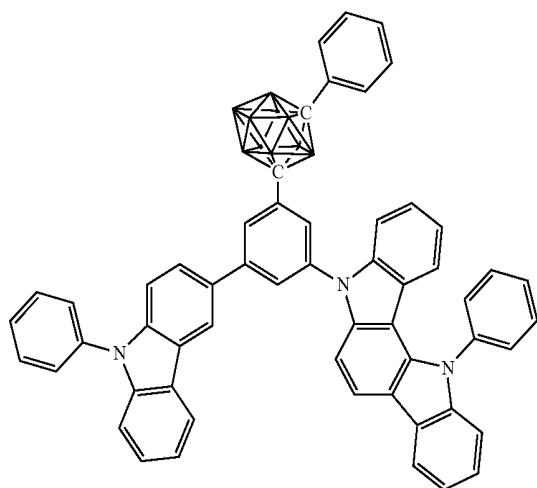
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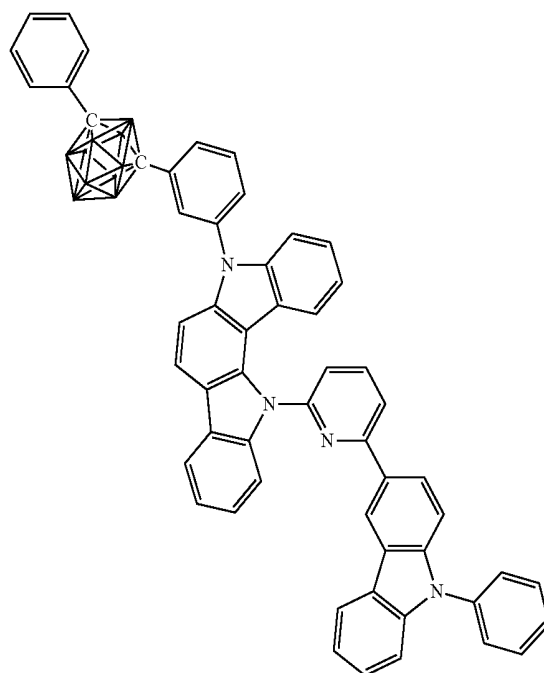
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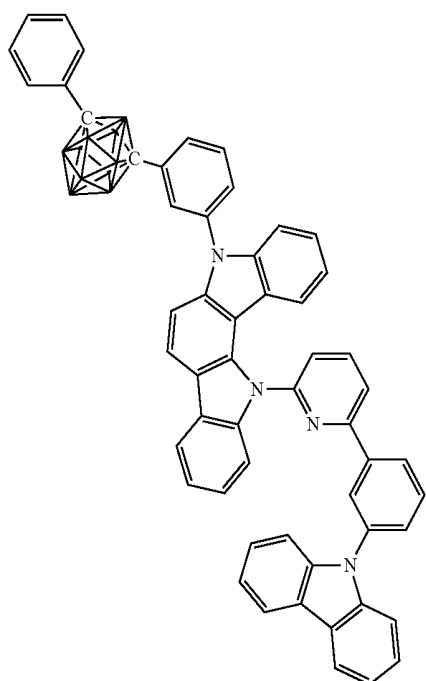
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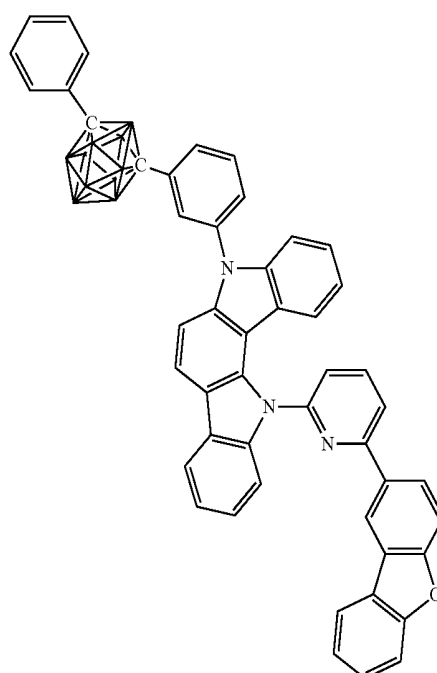
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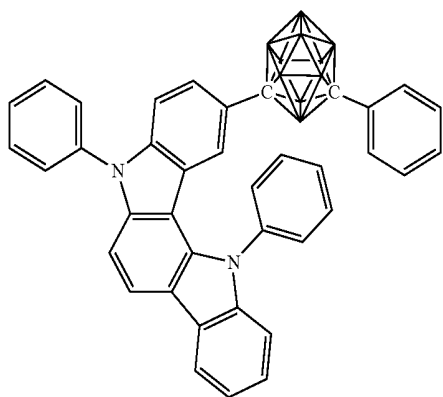
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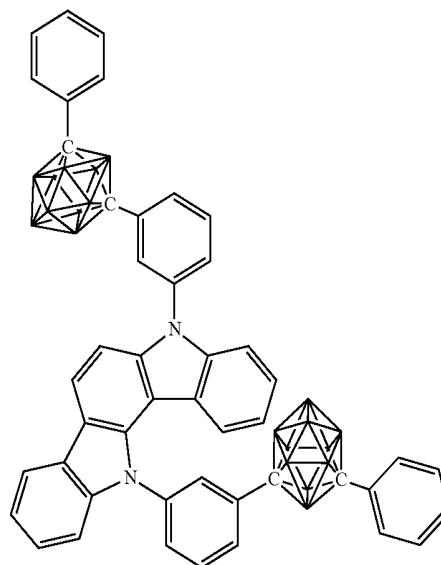


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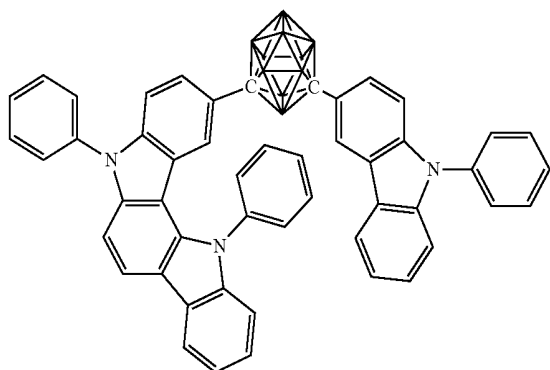


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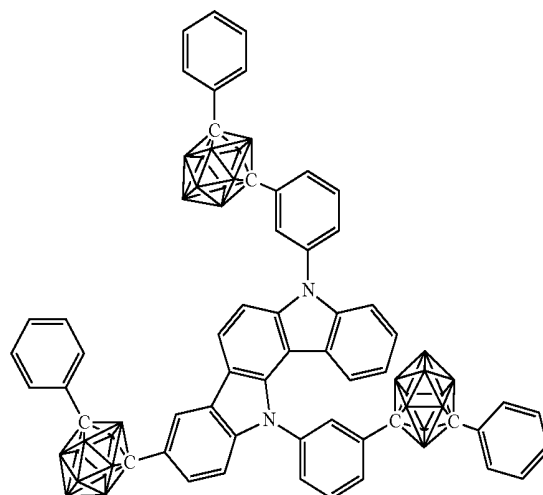
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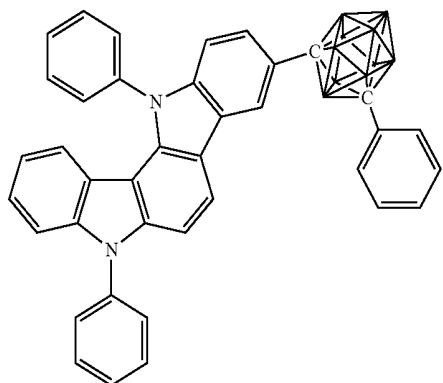
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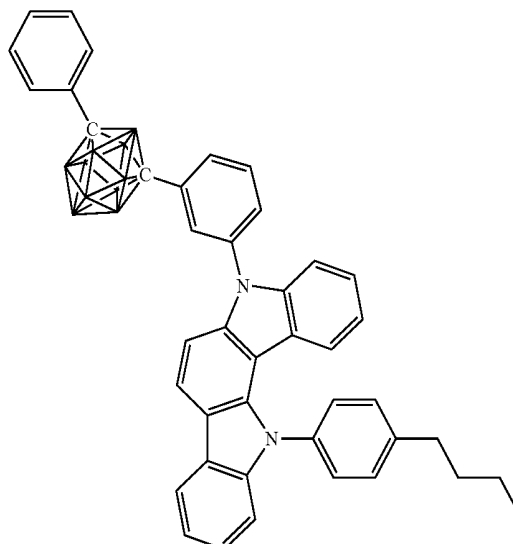
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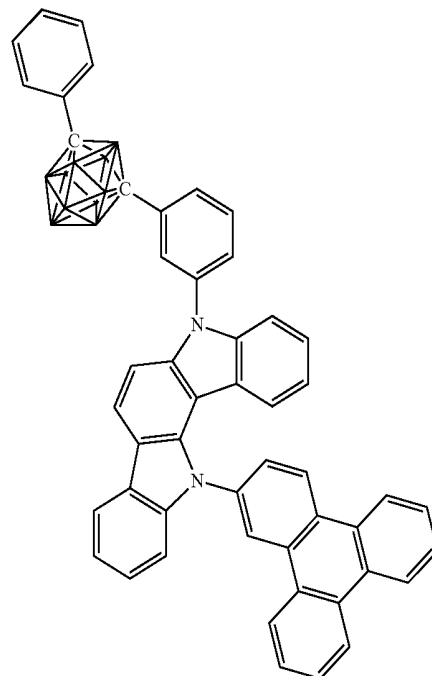
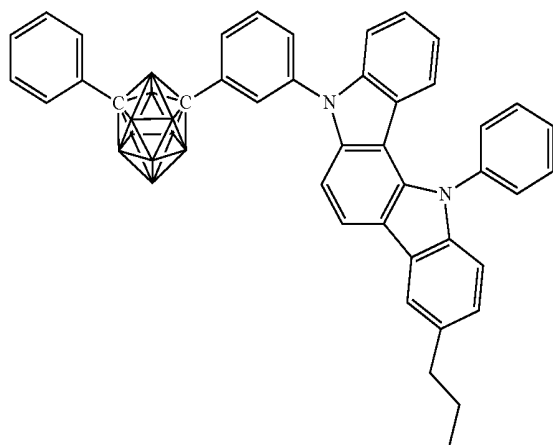
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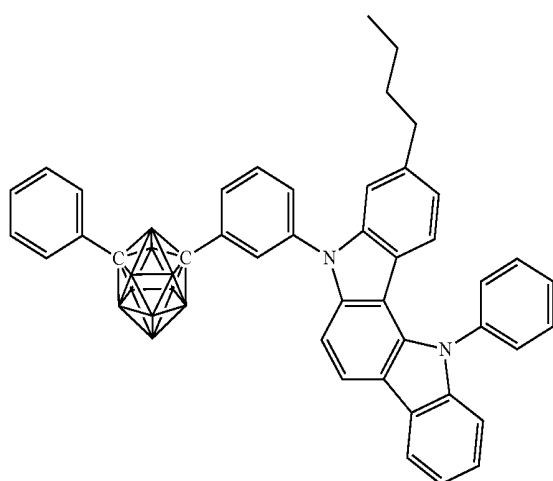
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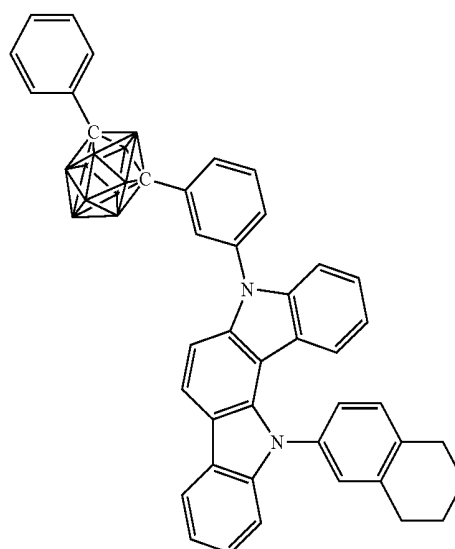
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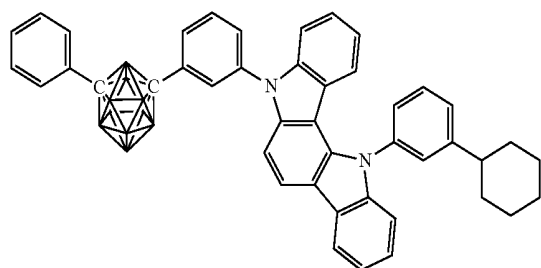
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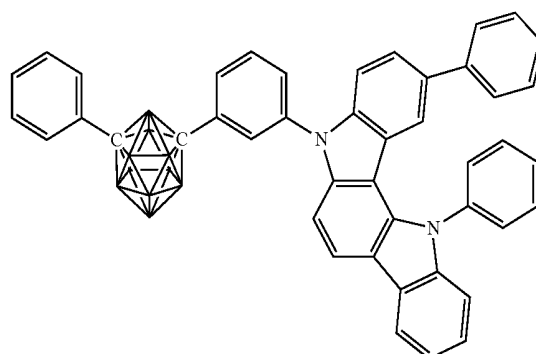
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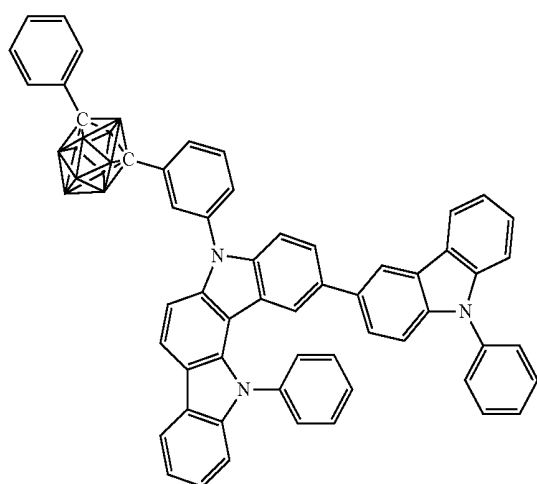
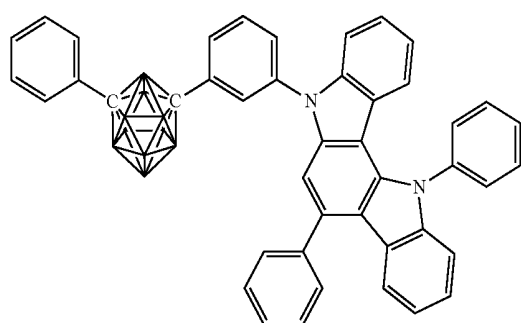
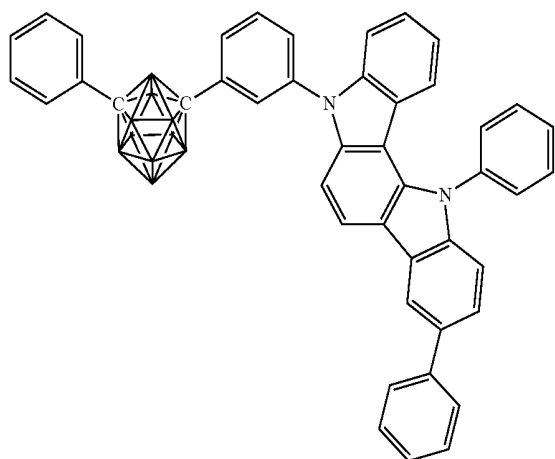
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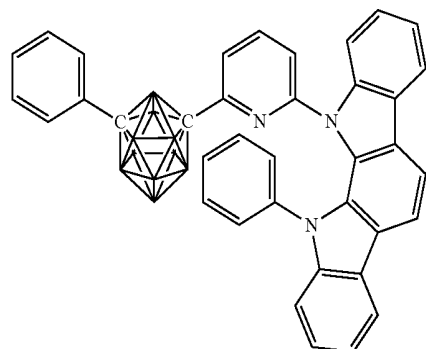
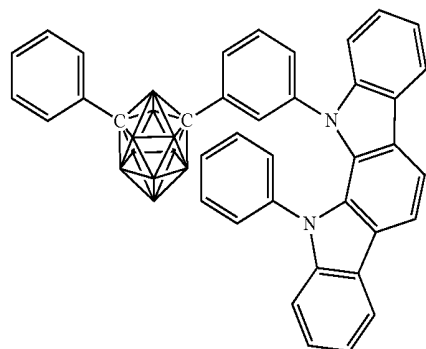
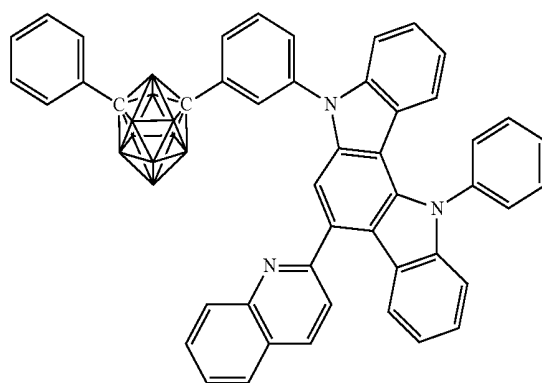
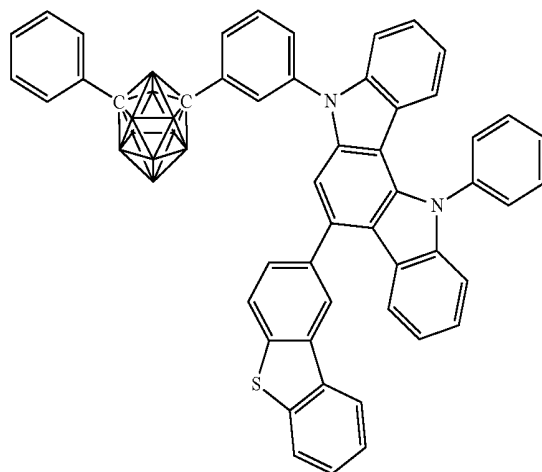
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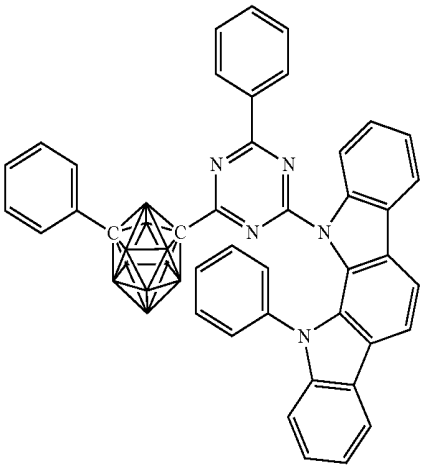
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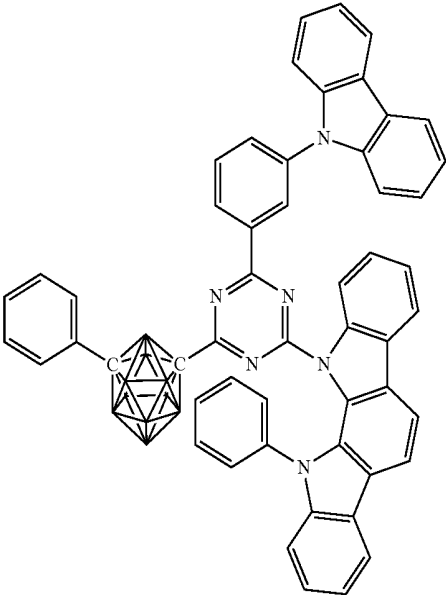


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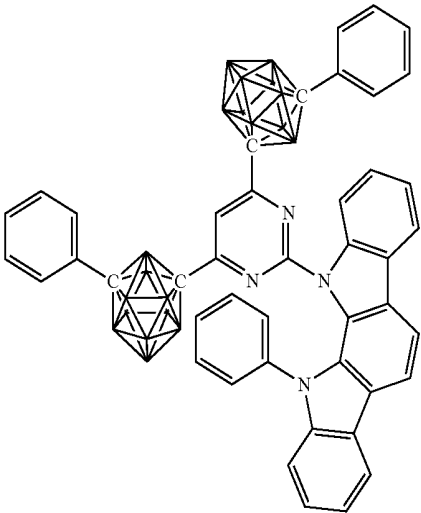


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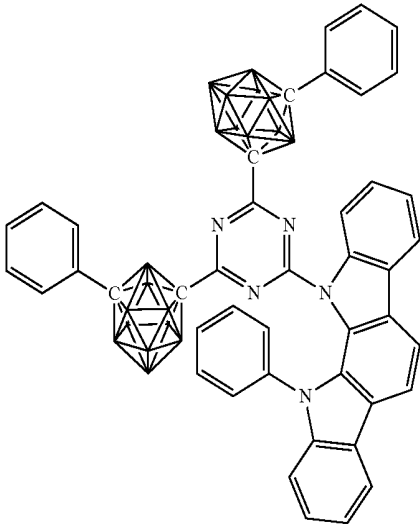
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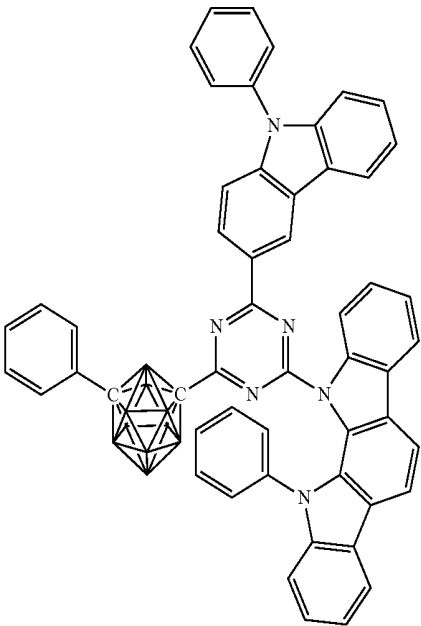
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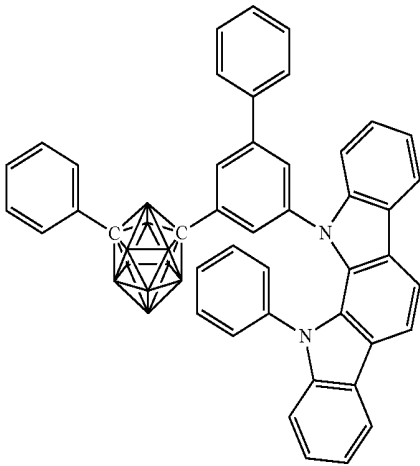
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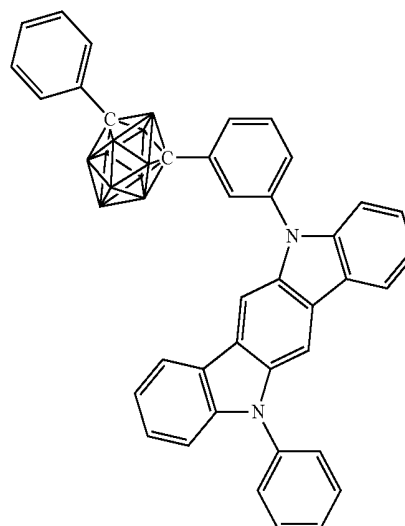
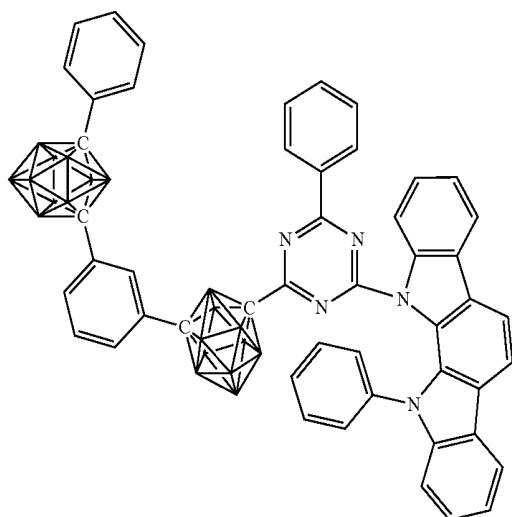


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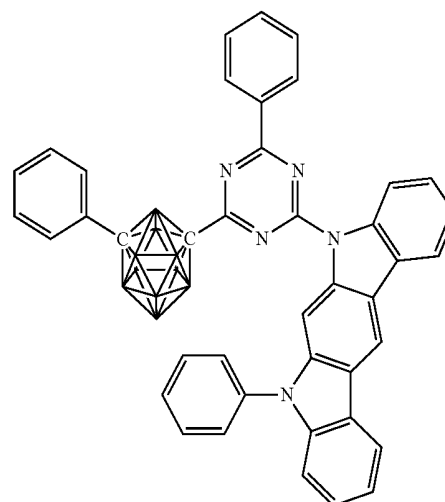
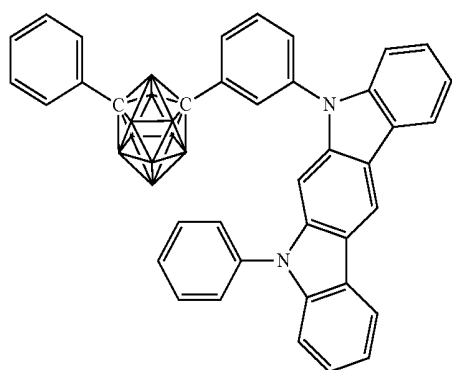
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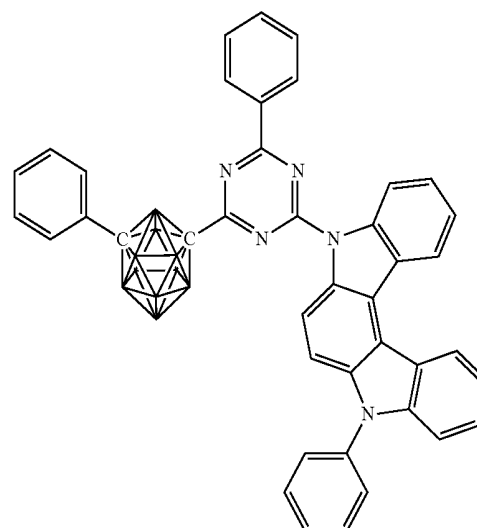
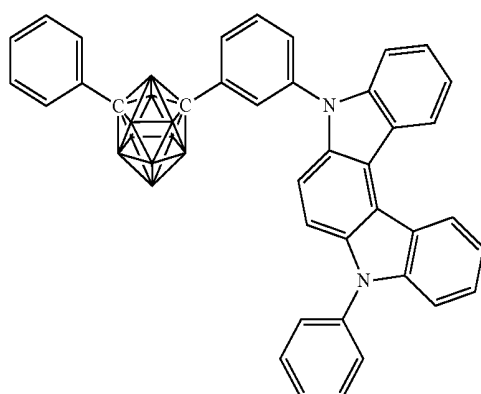
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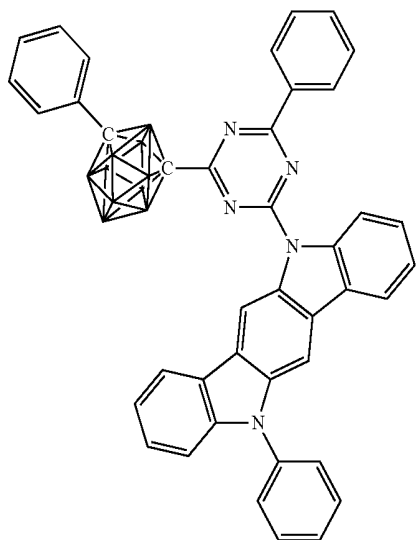
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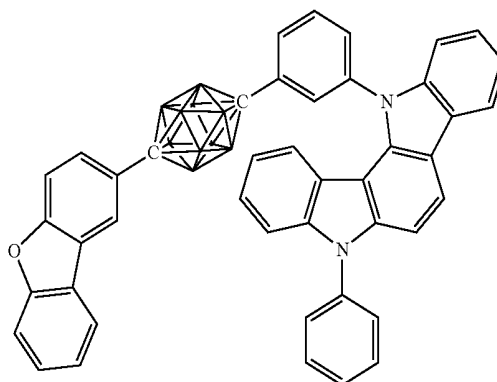


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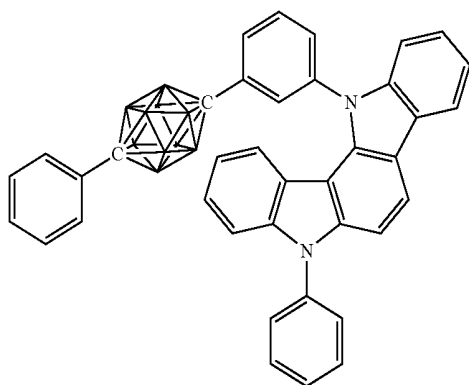


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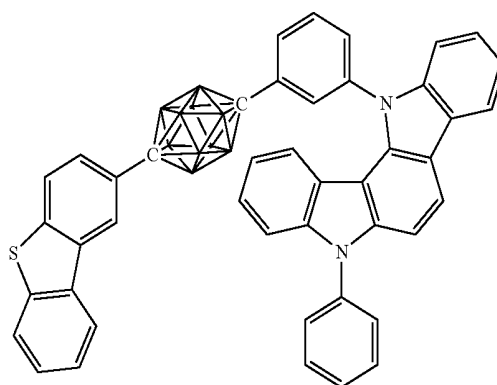
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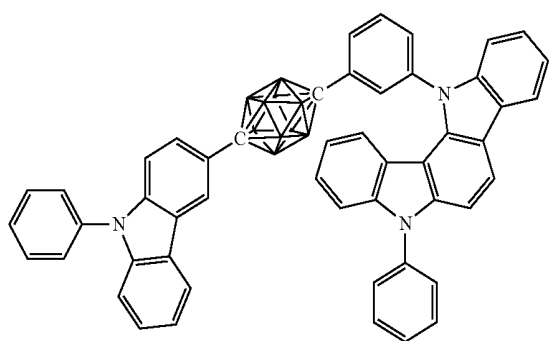
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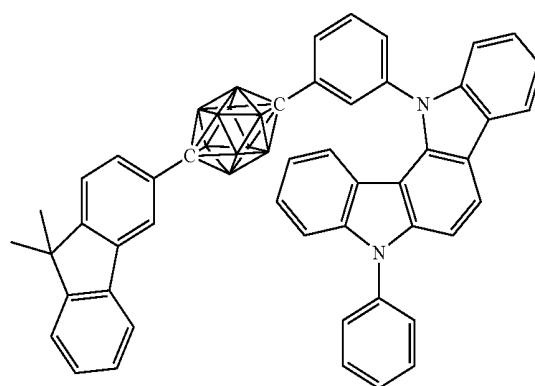
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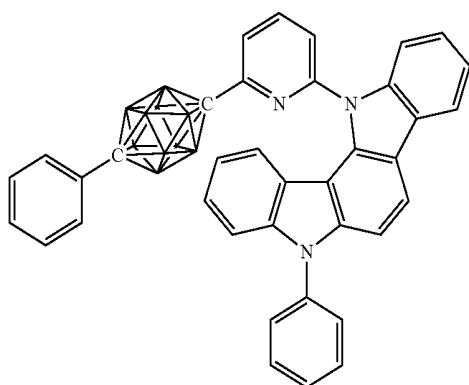
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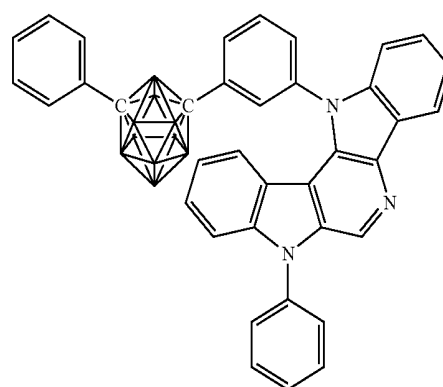
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[0055] The material for an organic electroluminescent device of the present invention is formed of the carborane compound (also referred to as carborane compound of the

present invention or material of the present invention) represented by the general formula (1). When the carborane compound 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 carborane compound of the present invention is contained. Here, when the carborane 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 carborane compound of the present invention can be used as an organic light-emitting material that radiates fluorescence and delayed fluorescence. When the carborane 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 carborane compound of the present invention is particularly preferably incorporated as a host material for the light-emitting layer containing the phosphorescent light-emitting dopant.

**[0056]** Next, an organic EL device using the material for an organic electroluminescent device of the present invention is described.

**[0057]** 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.

**[0058]** 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.

**[0059]** 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.

**[0060]** 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, and the anode 2. In this case as well, some layers may be added or eliminated as required.

**[0061]** —Substrate—

**[0062]** 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.

**[0063]** —Anode—

**[0064]** 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), SnO<sub>2</sub>, and ZnO. In addition, a material such as IDIXO (In<sub>2</sub>O<sub>3</sub>—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 μm 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 (Ω/□) 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.

**[0065]** —Cathode—

**[0066]** Meanwhile, used as the cathode is a cathode formed by using, as an electrode substance, any of a metal (referred to as 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 (Al<sub>2</sub>O<sub>3</sub>) 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.

**[0067]** 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.

**[0068]** —Light-emitting Layer—

**[0069]** 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.

**[0070]** 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.

**[0071]** The carborane compound of the present invention 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 dimethylidene 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 pyrromethene 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 pyrromethene 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, pentacene, perylene, fluoranthene, acenaphthofluoranthene, dibenzo[a,j]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.

**[0072]** The carborane compound of the present invention can be used as a fluorescent host material in the light-emitting layer. However, the fluorescent host material 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, fluoranthene, 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 polyphenylene 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.

**[0073]** 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 %.

**[0074]** 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.

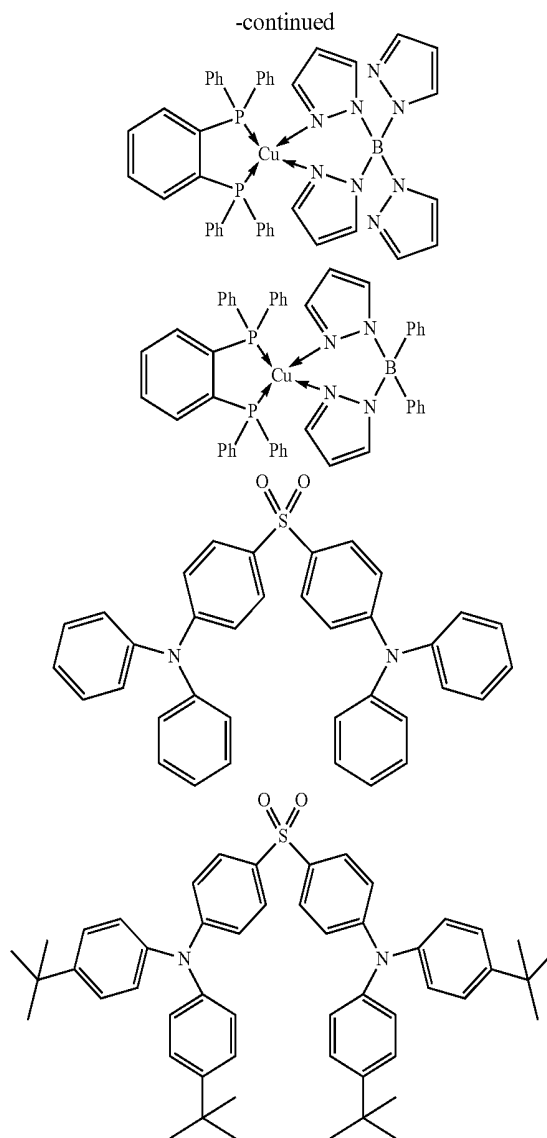
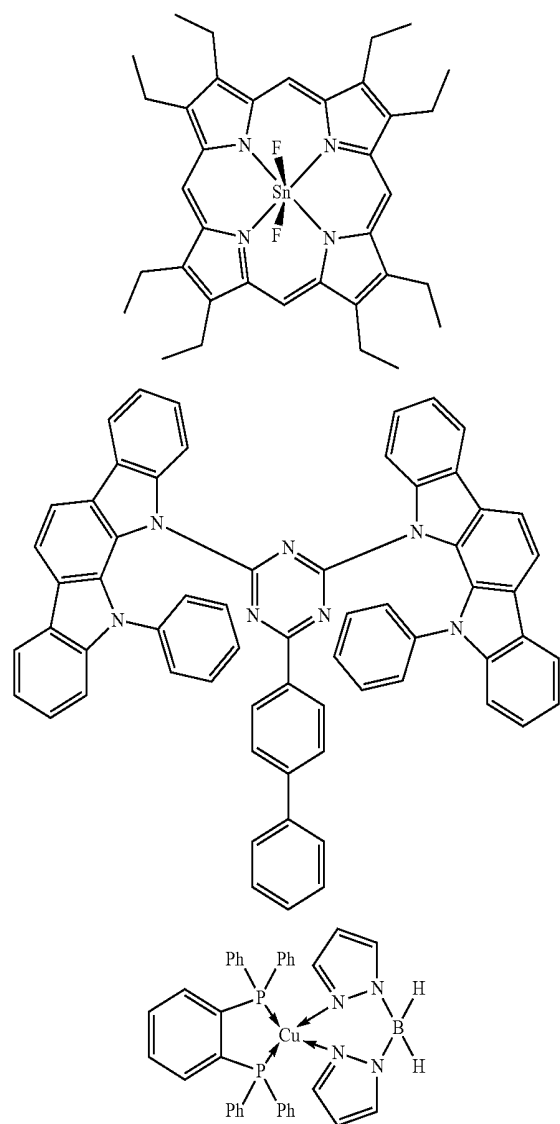
**[0075]** When the light-emitting layer is a delayed fluorescent light-emitting layer, at least one kind of delayed fluorescent light-emitting material may be used alone as a delayed fluorescent light-emitting material. However, it is

preferred that the delayed fluorescent light-emitting material be used as a delayed fluorescent light-emitting dopant and the host material be contained.

**[0076]** Although the carborane compound of the present invention 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.

**[0077]** (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.

**[0078]** 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.



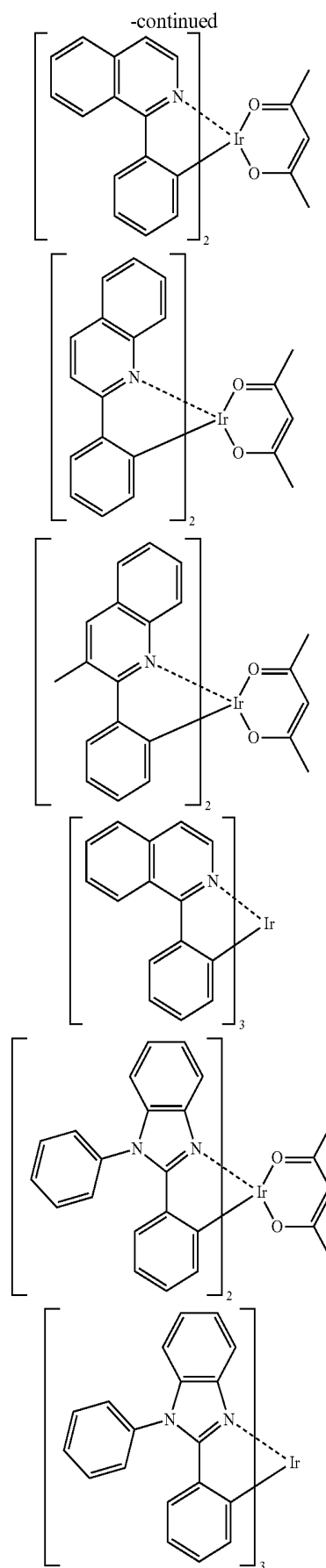
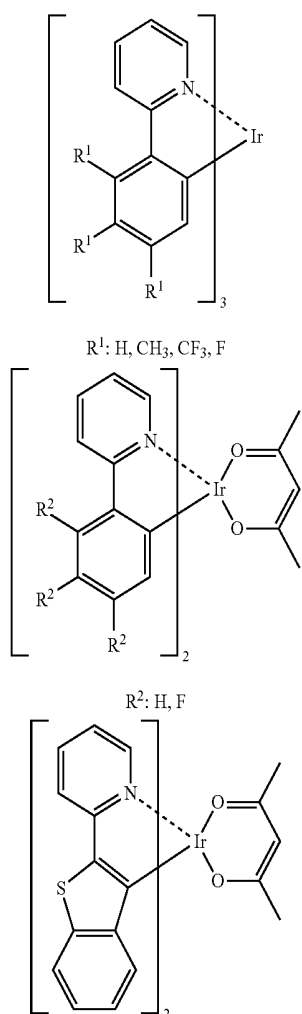
**[0079]** When the delayed fluorescent light-emitting material is used as a delayed fluorescent light-emitting dopant and the host material is contained, the content of the delayed fluorescent light-emitting dopant in the light-emitting layer desirably falls within the range of from 0.01 wt % to 50 wt %, preferably from 0.1 wt % to 20 wt %, more preferably from 0.01% to 10%.

**[0080]** The carborane compound of the present invention 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, naphthalene, triphenylene, perylene, fluoranthene, 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-quinolino)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 peri-

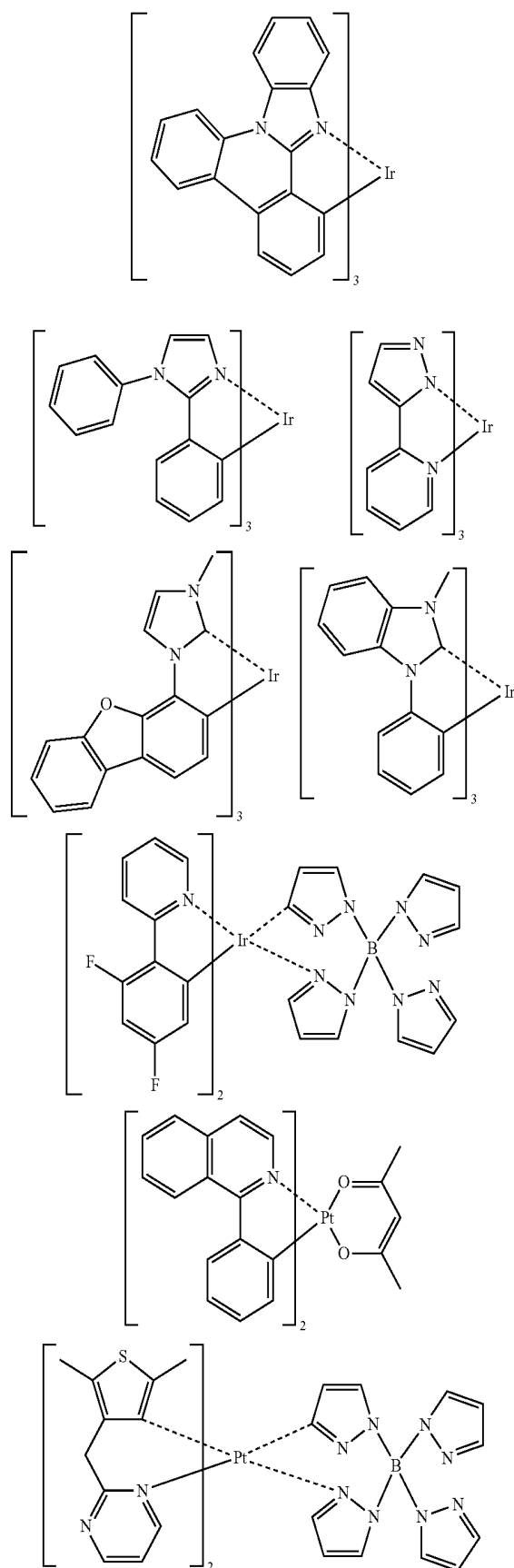
none derivative; a cyclopentadiene derivative; a pyrrolopyrrole derivative; a thiadiazolopyridine derivative; a dibenzofuran derivative; a carbazole derivative; an indolocarbazole derivative; a triazine derivative; or a polymer-based derivative, such as a polyphenylene vinylene derivative, a poly-p-phenylene 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.

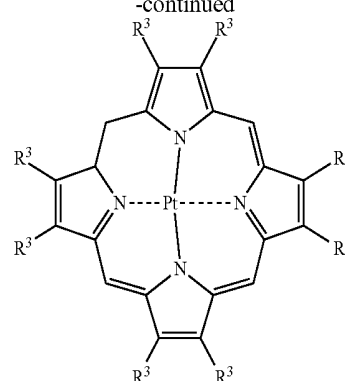
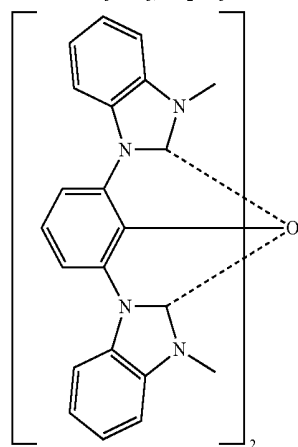
**[0082]** Preferred examples of the phosphorescent light-emitting dopant include complexes such as Ir(ppy)<sub>3</sub>, complexes such as Ir(bt)<sub>2</sub>•acac<sub>3</sub>, and complexes such as Pt(OEt)<sub>3</sub>, the complexes each having a noble metal element, such as Ir, as a central metal. Specific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



-continued



-continued


$$R_3: CH_3, CH_2CH_3$$


**[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 of the present invention. However, when the carborane compound of the present invention 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 of the present invention 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 polyaryllkane derivative, a pyrazoline derivative, a pyrazolone derivative, a phenylene-diamine derivative, an arylamine derivative, an amino-substituted chalcone derivative, a styrylanthracene deriva-

tive, a fluorenone derivative, a hydrazone derivative, a stilbene derivative, a silazane derivative, an aromatic tertiary amine compound, a styrylamine compound, an aromatic dimethyldene-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 of 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 of the present invention can be used as a material for the exciton-blocking layer, as other materials therefor, there are given, for example, 1,3-dicarbazolylbenzene (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 of the present invention 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 polyarylethane 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 of 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 thiadiazole 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

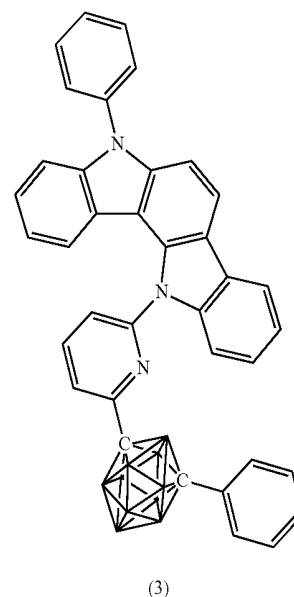
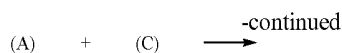
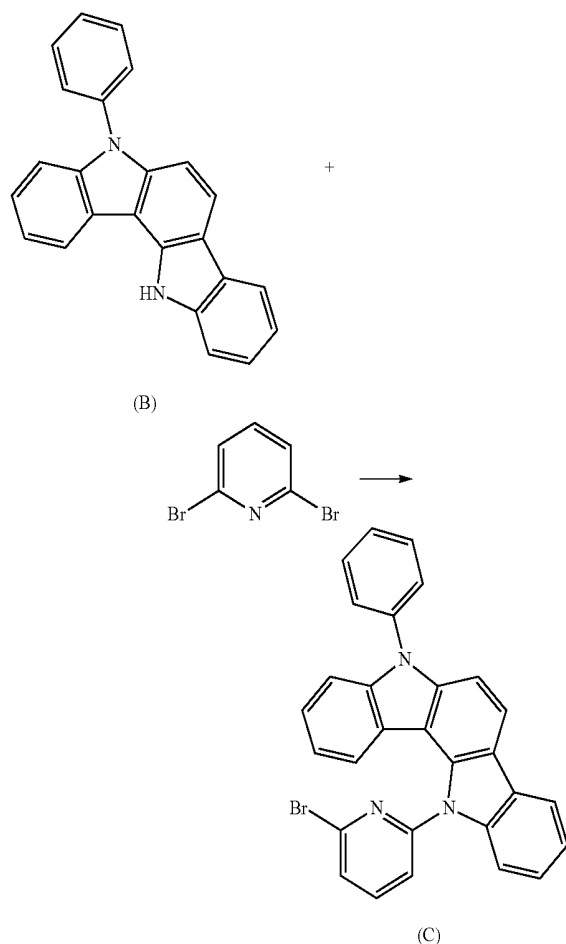
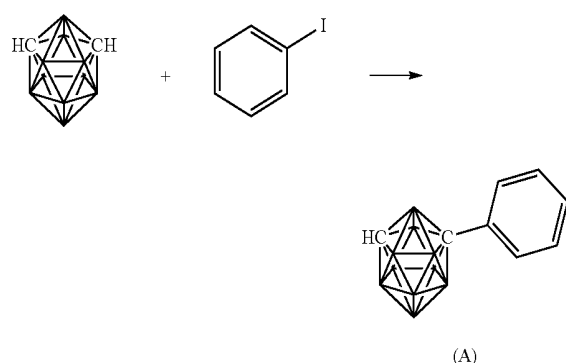
[0105] Now, the present invention is described in more detail by way of Examples. It should be appreciated that the present invention is not limited to Examples below and can

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 3 is synthesized in accordance with the following reaction formulae.



[0108] Under a nitrogen atmosphere, 35.0 g (0.243 mol) of m-carborane and 340 mL of 1,2-dimethoxyethane (DME) were added, and the resultant DME solution was cooled to 0° C. 96.6 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, 74.6 g (0.753 mol) of copper(I) chloride was added to the resultant and the mixture was stirred at 65° C. for 30 min. After that, 53.0 g (0.260 mol) of iodobenzene 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 38.7 g (0.191 mol, yield: 78.8%) of an intermediate A.

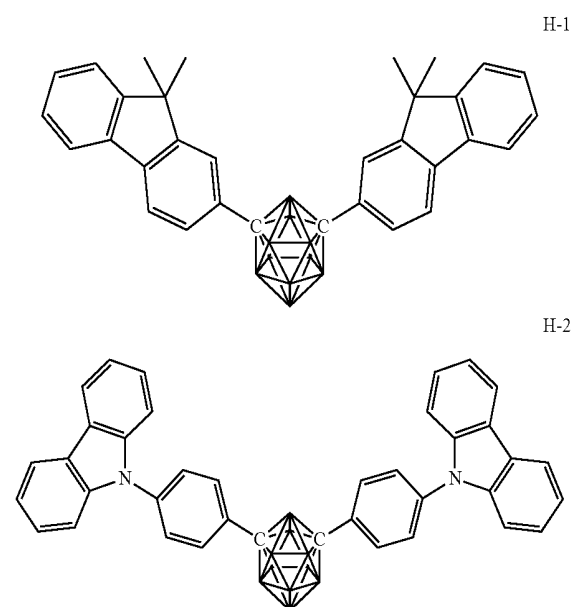
[0109] Under a nitrogen atmosphere, 50.0 g (0.15 mol) of an intermediate B, 142.6 g (0.60 mol) of 2,6-dibromopyridine, 5.60 g (0.028 mmol) of copper iodide, 160 g (0.760 mol) of tripotassium phosphate, 34.0 g (0.30 mol) of trans-1,2-cyclohexanediamine, and 1.5 L of 1,4-dioxane were added, and the mixture was stirred at 120° 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 41.6 g (85.2 mmol, yield: 56.8%) of an intermediate C as a white solid.

[0110] Under a nitrogen atmosphere, 7.7 g (0.0383 mol) of the intermediate A and 85 mL of DME were added, and the resultant DME solution was cooled to 0° C. 15.0 mL of a 2.65 M solution of n-butyllithium in hexane was dropped to the solution, and the mixture was stirred under ice cooling for 30 min. 10.5 mL of pyridine was added to the resultant, and the mixture was stirred at room temperature for 10 min. After that, 11.8 g (0.118 mol) of copper (I) chloride was added to the resultant and the mixture was stirred at 65° C. for 30 min. After that, 20 g (0.041 mol) of the intermediate C 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 4.3 g (6.85 mmol, yield: 17.9%) of the compound 3. APCI-TOF MS,  $m/z$  629  $[M+H]^+$ . The result of  $^1H$ -NMR measurement (measurement solvent:  $CDCl_3$ ) is shown in FIG. 2.

[0111] Compounds 1, 2, 4, 40, 66, and 71, and H-1 and H-2 were synthesized in conformity with the synthesis example of the compound 3 and a synthesis method described herein.

[0112] In addition, organic EL devices were produced by using the compounds 1, 2, 3, 4, 40, 66, and 71, and the following compounds H-1 and H-2.



Example 2

[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 70 nm had been formed. First, copperphthalocyanine (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 1 serving as a host material for a light-emitting layer and an iridium complex [iridium(III) bis(4,6-di-fluorophenyl)-pyridinato- $N,C2'$ ]picolinate] (Flrpic) serving as a blue phosphorescent material 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 Flrpic was 20%. Next,  $Alq_3$  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 1.0 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 in the organic EL device illustrated in FIG. 1.

[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  $2.5 \text{ mA/cm}^2$  (initial characteristics). The maximum wavelength of the emission spectrum of the device was 475 nm, and hence the acquisition of light emission from Flrpic was found.

#### Examples 3 to 6

[0115] Organic EL devices were each produced in the same manner as in Example 2 except that the compound 2, 3, 4, or 40 was used instead of the compound 1 as the host material for the light-emitting layer in Example 2.

#### Comparative Example 1

[0116] An organic EL device was produced in the same manner as in Example 2 except that mCP was used instead of the compound 1 as the host material for the light-emitting layer in Example 2.

#### Comparative Examples 2 and 3

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

[0118] The organic EL devices obtained in Examples 3 to 6 and Comparative Examples 1 to 3 were evaluated in the same manner as in Example 2. 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 3 to 6 and Comparative Examples 1 to 3 was 475 nm, and hence the acquisition of light emission from Flrpic was identified.

TABLE 1

|                       | Host material | Luminance (cd/m <sup>2</sup> ) | Voltage (V) | Visual luminous efficiency (lm/W) |
|-----------------------|---------------|--------------------------------|-------------|-----------------------------------|
| Example 2             | Compound 1    | 220                            | 9.2         | 3.0                               |
| Example 3             | Compound 2    | 220                            | 7.8         | 3.5                               |
| Example 4             | Compound 3    | 200                            | 6.9         | 3.6                               |
| Example 5             | Compound 4    | 200                            | 7.3         | 3.5                               |
| Example 6             | Compound 40   | 190                            | 6.7         | 3.6                               |
| Comparative Example 1 | mCP           | 140                            | 8.7         | 2.0                               |
| Comparative Example 2 | H-1           | 100                            | 7.7         | 1.6                               |
| Comparative Example 3 | H-2           | 140                            | 7.5         | 2.3                               |

#### Example 7

[0119] 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 1 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.

[0120] 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 13

[0121] Organic EL devices were each produced in the same manner as in Example 7 except that the compound 2, 3, 4, 40, 66, or 71 was used instead of the compound 1 as the host material for the light-emitting layer.

#### Comparative Examples 4 to 6

[0122] Organic EL devices were each produced in the same manner as in Example 7 except that CBP, H-1, or H-2 was used instead of the compound 1 as the host material for the light-emitting layer.

[0123] The organic EL devices obtained in Examples 7 to 13 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 7 to 13 and Comparative Examples 4 to 6 was 530 nm, and hence the acquisition of light emission from Ir (ppy)<sub>3</sub> was identified.

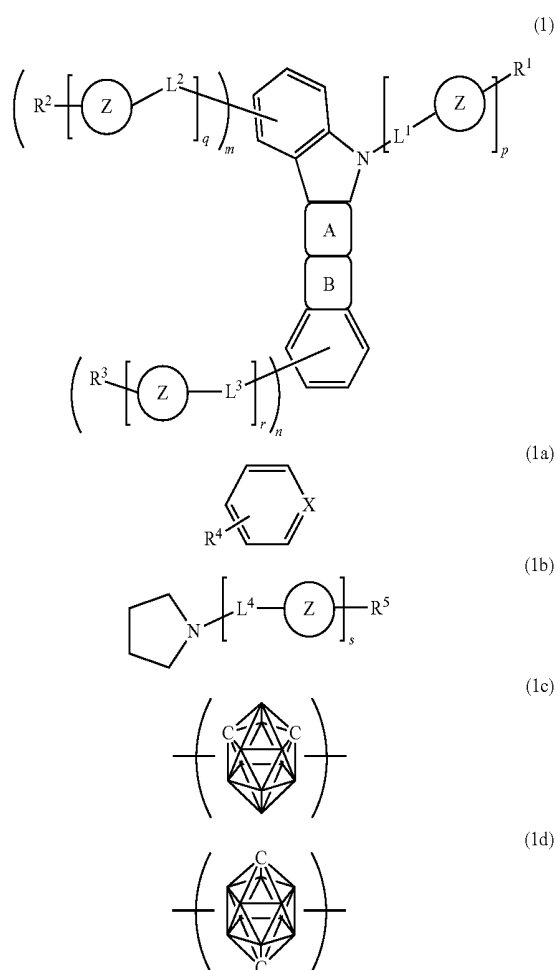
TABLE 2

|                       | Host material | Luminance (cd/m <sup>2</sup> ) | Voltage (V) | Visual luminous efficiency (lm/W) |
|-----------------------|---------------|--------------------------------|-------------|-----------------------------------|
| Example 7             | Compound 1    | 2,100                          | 11.1        | 3.0                               |
| Example 8             | Compound 2    | 2,100                          | 9.5         | 3.5                               |
| Example 9             | Compound 3    | 2,000                          | 8.3         | 3.8                               |
| Example 10            | Compound 4    | 1,900                          | 8.8         | 3.4                               |
| Example 11            | Compound 40   | 1,900                          | 8.1         | 3.7                               |
| Example 12            | Compound 66   | 1,800                          | 9.2         | 3.1                               |
| Example 13            | Compound 71   | 1,800                          | 9.2         | 3.1                               |
| Comparative Example 4 | CBP           | 1,120                          | 8.7         | 2.0                               |
| Comparative Example 5 | H-1           | 1,200                          | 8.5         | 2.2                               |
| Comparative Example 6 | H-2           | 1,000                          | 8.3         | 1.9                               |

#### INDUSTRIAL APPLICABILITY

[0124] The incorporation of the carborane compound of the present invention into at least one organic layer of an organic EL device obtained by laminating an anode, a plurality of organic layers, and a cathode on a substrate provides an excellent organic electroluminescent device. A light-emitting layer, an electron-transporting layer, or a hole-blocking layer is suitable as the organic layer into which the compound is incorporated.

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



where:

a ring A represents an aromatic ring represented by the formula (1a), the ring being fused with an adjacent ring at an arbitrary position, a ring B represents a heterocycle represented by the formula (1b) whose nitrogen-containing five-membered ring is fused with an adjacent ring at an arbitrary position, and X represents a methine group or a nitrogen atom;

a ring Z represents a divalent carborane group C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> represented by the formula (1c) or the formula (1d), and when the plurality of rings Z's are present in a molecule, the rings may be identical to or different from each other;

p, q, r, and s each represent a number of repetitions, and m and n each represent a number of substitutions, and p, q, r, and s, and m and n each represent an integer of from 0 to 5, provided that any one of  $q \times m$ ,  $r \times n$ , p, and s represents an integer of 1 or more;

$L^1$  and  $L^4$  each independently represent a single bond, a substituted or unsubstituted aromatic hydrocarbon group having 6 to 22 carbon atoms, a substituted or unsubstituted aromatic heterocyclic group having 3 to 16 carbon atoms, or a linked aromatic group formed by linking 2 to 6 arbitrary aromatic groups each selected from the substituted or unsubstituted aromatic hydrocarbon group and the substituted or unsubstituted aromatic heterocyclic group, and the linked aromatic group may be linear or branched;

$L^2$  and  $L^3$  each independently represent a single bond, a substituted or unsubstituted aromatic hydrocarbon group having 6 to 22 carbon atoms, a substituted or unsubstituted aromatic heterocyclic group having 3 to 18 carbon atoms, or a linked aromatic group formed by linking 2 to 6 arbitrary aromatic groups each selected from the substituted or unsubstituted aromatic hydrocarbon group and the substituted or unsubstituted aromatic heterocyclic group, and the linked aromatic group may be linear or branched;

$R^1$  and  $R^5$  each independently represent a hydrogen atom, a substituted or unsubstituted aromatic hydrocarbon group having 6 to 22 carbon atoms, a substituted or unsubstituted aromatic heterocyclic group having 3 to 16 carbon atoms, or a linked aromatic group formed by linking 2 to 6 arbitrary aromatic groups each selected from the substituted or unsubstituted aromatic hydrocarbon group and the substituted or unsubstituted aromatic heterocyclic group, and the linked aromatic group may be linear or branched; and

$R^2$ ,  $R^3$ , and  $R^4$  each independently represent a hydrogen atom, a substituted or unsubstituted aromatic hydrocarbon group having 6 to 22 carbon atoms, a substituted or unsubstituted aromatic heterocyclic group having 3 to 18 carbon atoms, or a linked aromatic group formed by linking 2 to 6 arbitrary aromatic groups each selected from the substituted or unsubstituted aromatic hydrocarbon group and the substituted or unsubstituted aromatic heterocyclic group, and the linked aromatic group may be linear or branched.

2. A material for an organic electroluminescent device according to claim 1, wherein X represents a methine group.

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

4. A material for an organic electroluminescent device according to claim 1, wherein q and r in the general formula (1) each represent an integer of 0.

5. A material for an organic electroluminescent device according to claim 1, wherein  $L^1$  and  $L^4$  each independently represent a substituted or unsubstituted aromatic hydrocarbon group having 6 to 18 carbon atoms, a substituted or unsubstituted aromatic heterocyclic group having 3 to 16 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, and  $L^2$  and  $L^3$  each independently represent a substituted or unsubstituted aromatic hydrocarbon group having 6 to 18

carbon atoms, a substituted or unsubstituted aromatic heterocyclic group having 3 to 18 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.

6. A material for an organic electroluminescent device according to claim 5, wherein  $L^1$  and  $L^4$  each independently represent a substituted or unsubstituted aromatic heterocyclic group having 3 to 16 carbon atoms, or a linked aromatic group formed by linking 2 to 6 aromatic groups each selected from the aromatic heterocyclic group, and  $L^2$  and  $L^3$  each independently represent a substituted or unsubstituted aromatic heterocyclic group having 3 to 18 carbon atoms, or a linked aromatic group formed by linking 2 to 6 aromatic groups each selected from the aromatic heterocyclic group.

7. A material for an organic electroluminescent device according to claim 1, wherein  $R^1$  and  $R^5$  each independently represent a substituted or unsubstituted aromatic hydrocarbon group having 6 to 18 carbon atoms, a substituted or unsubstituted aromatic heterocyclic group having 3 to 16 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, and  $R^2$ ,  $R^3$ , and  $R^4$  each independently represent a substituted or unsubstituted aromatic hydrocarbon group having 6 to 18 carbon atoms, a substituted or unsubstituted aromatic heterocyclic group having 3 to 18 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.

8. An organic electroluminescent device having a structure in which an anode, organic layers, and a cathode are laminated on a substrate, wherein at least one layer of the organic layers comprises an organic layer containing the material for an organic electroluminescent device of claim 1.

9. An organic electroluminescent device according to claim 8, 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.

10. 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.

11. An organic electroluminescent device according to claim 10, wherein an emission wavelength of the phosphorescent light-emitting dopant has an emission maximum wavelength at 600 nm or less.

12. An organic electroluminescent device having a structure in which an anode, organic layers, and a cathode are laminated on a substrate, wherein at least one layer of the organic layers comprises an organic layer containing the material for an organic electroluminescent device of claim 2.

13. An organic electroluminescent device having a structure in which an anode, organic layers, and a cathode are laminated on a substrate, wherein at least one layer of the organic layers comprises an organic layer containing the material for an organic electroluminescent device of claim 3.

14. An organic electroluminescent device having a structure in which an anode, organic layers, and a cathode are laminated on a substrate, wherein at least one layer of the

organic layers comprises an organic layer containing the material for an organic electroluminescent device of claim 4.

15. An organic electroluminescent device having a structure in which an anode, organic layers, and a cathode are laminated on a substrate, wherein at least one layer of the organic layers comprises an organic layer containing the material for an organic electroluminescent device of claim 5.

16. An organic electroluminescent device having a structure in which an anode, organic layers, and a cathode are laminated on a substrate, wherein at least one layer of the organic layers comprises an organic layer containing the material for an organic electroluminescent device of claim 6.

17. An organic electroluminescent device having a structure in which an anode, organic layers, and a cathode are laminated on a substrate, wherein at least one layer of the organic layers comprises an organic layer containing the material for an organic electroluminescent device of claim 7.

\* \* \* \* \*

|                |                                                                                                            |         |            |
|----------------|------------------------------------------------------------------------------------------------------------|---------|------------|
| 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="#">US20160380199A1</a>                                                                            | 公开(公告)日 | 2016-12-29 |
| 申请号            | US15/116540                                                                                                | 申请日     | 2015-02-23 |
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| IPC分类号         | H01L51/00 C09K11/02 C07F5/02 C09K11/06                                                                     |         |            |
| CPC分类号         | H01L51/008 C09K11/06 C09K11/025 C07F5/027 C09K2211/185 H01L51/5016 C09K2211/1007 C09K2211/1029 H01L51/0085 |         |            |
| 优先权            | 2014059925 2014-03-24 JP                                                                                   |         |            |
| 其他公开文献         | US10305048                                                                                                 |         |            |
| 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，其发光效率得到改善，足以确保驱动稳定性，并且具有简单的结构，以及用于该器件的有机电致发光器件的材料。该材料是由具有吡啶并咪唑骨架和一个或两个或多个碳硼烷基团的碳硼烷化合物形成的有机电致发光器件的材料，所述碳硼烷基团各自直接键合或通过二价基团键合。另外，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，其中至少一层有机层包含用于有机电致发光器件的材料。另外，该器件是有机电致发光器件，其包含作为用于包含磷光发光掺杂剂和主体材料的发光层的主体材料，用于有机电致发光器件的材料。

