



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
20.04.2016 Bulletin 2016/16

(51) Int Cl.:
C09K 11/06 (2006.01) H01L 51/50 (2006.01)

(21) Application number: **15189883.0**

(22) Date of filing: **15.10.2015**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
MA

(30) Priority: **17.10.2014 KR 20140140969**
17.10.2014 KR 20140140970
15.09.2015 KR 20150130519
15.09.2015 KR 20150130518

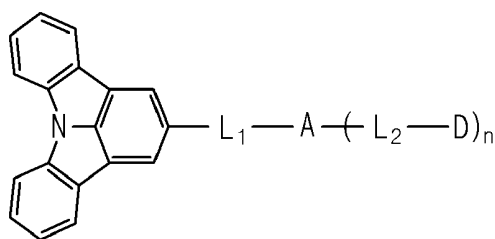
(71) Applicant: **LG Display Co., Ltd.**
Yeongdeungpo-gu
Seoul
150-721 (KR)

(72) Inventors:
• **YANG, Joong-Hwan**
14243 Gyeonggi-do (KR)
• **YOON, Kyung-Jin**
10242 Gyeonggi-do (KR)
• **NOH, Hyo-Jin**
10845 Gyeonggi-do (KR)
• **YOON, Dae-Wi**
10819 Gyeonggi-do (KR)
• **SHIN, In-Ae**
10885 Gyeonggi-do (KR)
• **KIM, Jun-Yun**
10401 Gyeonggi-do (KR)

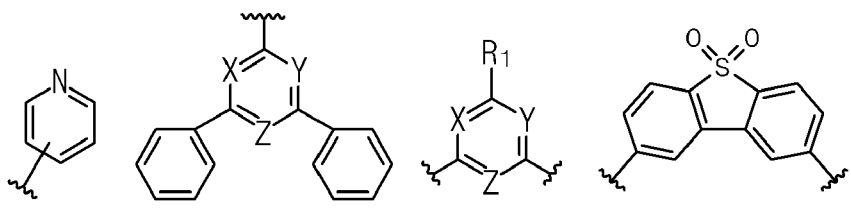
(74) Representative: **Ter Meer Steinmeister & Partner**
Patentanwälte mbB
Nymphenburger Straße 4
80335 München (DE)

(54) **DELAYED FLUORESCENCE COMPOUND, AND ORGANIC LIGHT EMITTING DIODE AND DISPLAY DEVICE USING THE SAME**

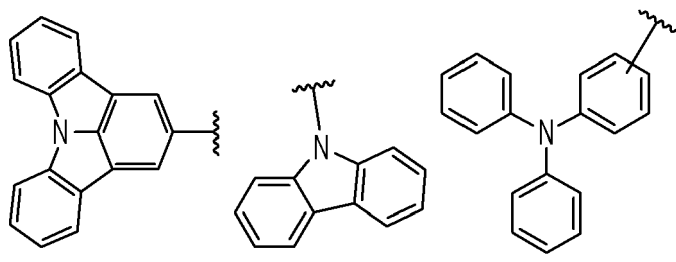
(57) Discussed is a delayed fluorescence compound of Formula 1:



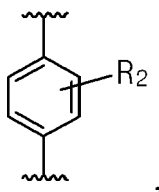
wherein n is 1 or 0, and A is selected from Formula 2:



wherein D is selected from Formula 3:



and each of "L1" and "L2" is independently selected from Formula 4:



wherein R₁ in the Formula 2 is selected from hydrogen or phenyl, and each of X, Y and Z is independently selected from carbon and nitrogen, and wherein at least two selected from X, Y and Z are nitrogen, and R₂ in the Formula 4 is selected from hydrogen or C₁~C₁₀ alkyl.

Description**CROSS-REFERENCE TO RELATED APPLICATIONS**

[0001] This application claims priority to and the benefit of Korean Patent Application Nos. 10-2014-0140969, 10-2014-0140970, 10-2015-0130519 and 10-2015-0130518, filed in Korea on October 17, 2014 and September 15, 2015, respectively, all of which are hereby incorporated by reference in their entirety.

BACKGROUND OF THE INVENTION**Field Of The Invention**

[0002] The embodiments of the invention relate to an organic light emitting diode (OLED) and more particularly to a delayed fluorescence compound having excellent emitting efficiency and an OLED and a display device using the delayed fluorescence compound.

Discussion Of The Related Art

[0003] The requirements of the large-size display device have led to developments in flat panel display devices as an image displaying device. Among the flat panel display devices, the OLED is rapidly developed.

[0004] In the OLED, when the electron and the hole from a cathode, which serves as an electron-injecting electrode, and an anode, which serves as a hole-injecting electrode, are injected into an emitting material layer, the electron and the hole are combined and become extinct such that the light is emitted from the OLED. A flexible substrate, for example, a plastic substrate, can be used as a base substrate for the OLED, and the OLED has excellent characteristics of driving voltage, power consumption and color purity.

[0005] The OLED includes a first electrode as an anode on a substrate, a second electrode as a cathode facing the first electrode and an organic emitting layer therebetween.

[0006] To improve the emitting efficiency, the organic emitting layer may include a hole injection layer (HIL), a hole transporting layer (HTL), an emitting material layer (EML), an electron transporting layer (ETL) and an electron injection layer (EIL) sequentially stacked on the first electrode.

[0007] The hole is transferred into the EML from the first electrode through the HIL and the HTL, and the electron is transferred into the EML from the second electrode through the EIL and the ETL.

[0008] The electron and the hole are combined in the EML to generate excitons, and the excitons are transitioned from an excited state to a ground state such that the light is emitted.

[0009] The External quantum efficiency (η_{ext}) of the emitting material for the EML can be expressed by:

$$\eta_{\text{ext}} = \eta_{\text{int}} \times \Gamma \times \Phi \times \eta_{\text{out-coupling}}$$

[0010] In the above equation, " η_{int} " is the internal quantum efficiency, " Γ " is the charge balance factor, " Φ " is the radiative quantum efficiency, and " $\eta_{\text{out-coupling}}$ " is the out-coupling efficiency.

[0011] The charge balance factor " Γ " means a balance between the hole and the electron generating the exciton. Generally, assuming 1:1 matching of the hole and the electron, the charge balance factor has a value of "1". The radiative quantum efficiency " Φ " is a value regarding an effective emitting efficiency of the emitting material. In the host-dopant system, the radiative quantum efficiency depends on a fluorescent quantum efficiency of the dopant.

[0012] The internal quantum efficiency " η_{int} " is a ratio of the excitons generating the light to the excitons generated by the combination of the hole and the electron. In the fluorescent compound, a maximum value of the internal quantum efficiency is 0.25. When the hole and the electron are combined to generate the exciton, a ratio of the singlet excitons to the triplet excitons is 1:3 according to the spin structure. However, in the fluorescent compound, only the singlet excitons excluding the triplet excitons are engaged in the emission.

[0013] The out-coupling efficiency " $\eta_{\text{out-coupling}}$ " is a ratio of the light emitted from the display device to the light emitted from the EML. When the isotropic compounds are deposited in a thermal evaporation method to form a thin film, the emitting materials are randomly oriented. In this instance, the out-coupling efficiency of the display device may be assumed as 0.2.

[0014] Accordingly, the maximum emitting efficiency of the OLED including the fluorescent compound as the emitting material is less than about 5%.

[0015] To overcome the disadvantage of the emitting efficiency of the fluorescent compound, the phosphorescent

compound, where both the singlet excitons and the triplet excitons are engaged in the emission, has been developed for the OLED.

[0016] The red and green phosphorescent compound having a relatively high efficiency are introduced and developed. However, there is no blue phosphorescent compound meeting the requirements in the emitting efficiency and the reliability.

SUMMARY OF THE INVENTION

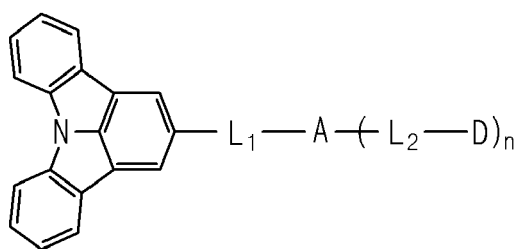
[0017] Accordingly, the embodiment of the invention is directed to a delayed fluorescence compound and an OLED and a display device using the same that substantially obviate one or more of the problems due to limitations and disadvantages of the related art.

[0018] An object of the embodiment of the invention is to provide a delayed fluorescence compound having high emitting efficiency.

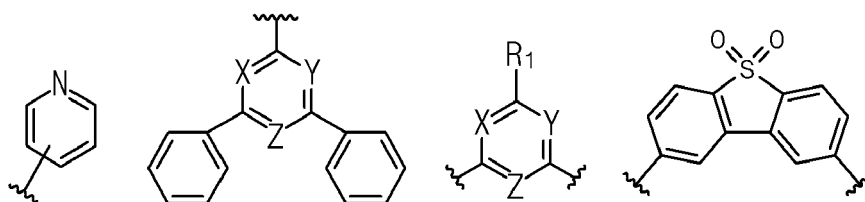
[0019] Another object of the embodiment of the invention is to provide an OLED and a display device having an improved emission efficiency.

[0020] Additional features and advantages of the invention will be set forth in the description which follows, and in part will be apparent from the description, or may be learned by practice of the invention. The objectives and other advantages of the invention will be realized and attained by the structure particularly pointed out in the written description and claims hereof as well as the appended drawings.

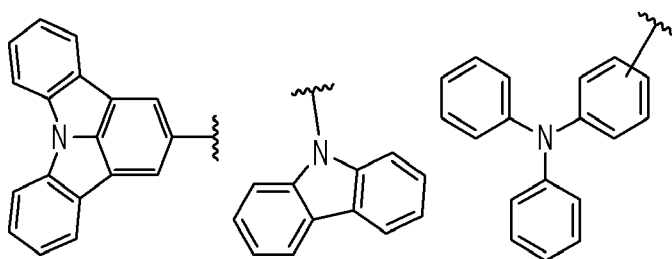
[0021] To achieve these and other advantages and in accordance with the purpose of the embodiments of the invention, as embodied and broadly described herein, an aspect of an embodiment of the invention provides a delayed fluorescence compound of Formula 1:



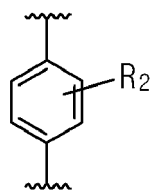
wherein n is 1 or 0, and A is selected from Formula 2:



, wherein D is selected from Formula 3:

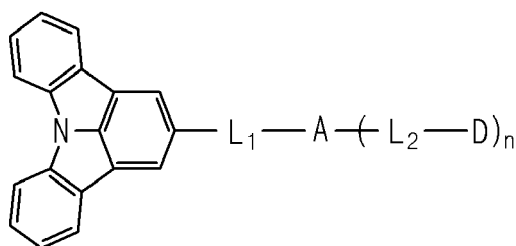


and each of L1 and L2 is independently selected from Formula 4:

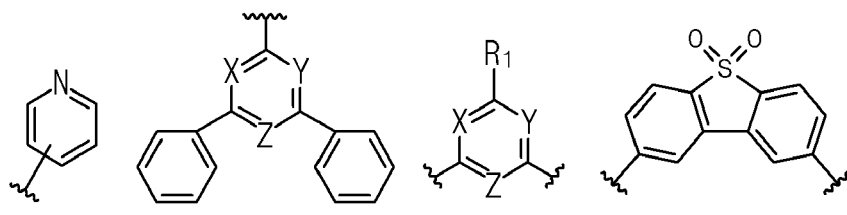


wherein R1 in the Formula 2 is selected from hydrogen or phenyl, and each of X, Y and Z is independently selected from carbon and nitrogen, and wherein at least two selected from X, Y and Z are nitrogen, and R2 in the Formula 4 is selected from hydrogen or C1~C10 alkyl.

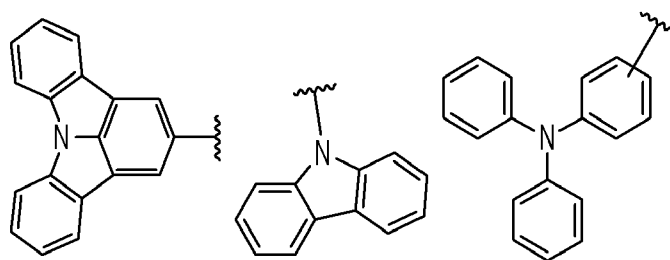
[0022] In another aspect of the embodiment of the invention provided is an organic light emitting diode including a first electrode; a second electrode facing the first electrode; and an organic emitting layer between the first and second electrodes and including a delayed fluorescence compound of Formula 1:



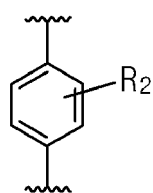
wherein n is 1 or 0, and A is selected from Formula 2:



wherein D is selected from Formula 3:



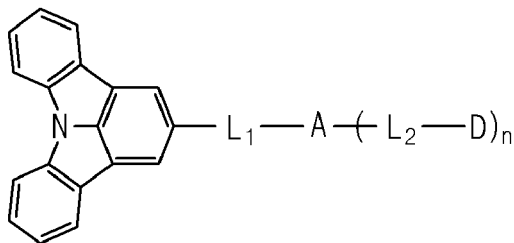
and each of L1 and L2 is independently selected from Formula 4:



wherein R1 in the Formula 2 is selected from hydrogen or phenyl, and each of X, Y and Z is independently selected

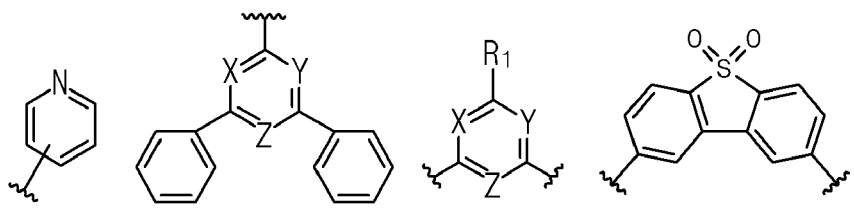
from carbon and nitrogen, and wherein at least two selected from X, Y and Z are nitrogen, and R2 in the Formula 4 is selected from hydrogen or C1~C10 alkyl.

[0023] In another aspect of the embodiment of the invention provided is a display device including a substrate; an organic light emitting diode on the substrate and including a first electrode, a second electrode facing the first electrode and an organic emitting layer between the first and second electrodes and including a delayed fluorescence compound of Formula 1:

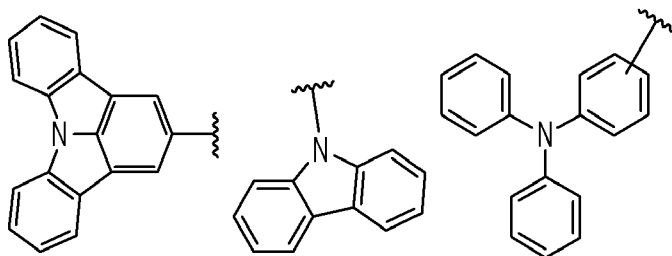


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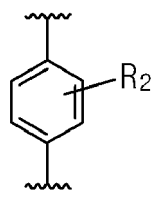
an encapsulation film on the organic light emitting diode; and a cover window on the encapsulation film, wherein n is 1 or 0, and A is selected from Formula 2:



wherein D is selected from Formula 3:



and each of L1 and L2 is independently selected from Formula 4:



wherein R1 in the Formula 2 is selected from hydrogen or phenyl, and each of X, Y and Z is independently selected from carbon and nitrogen, and wherein at least two selected from X, Y and Z are nitrogen, and R2 in the Formula 4 is selected from hydrogen or C1~C10 alkyl.

[0024] It is to be understood that both the foregoing general description and the following detailed description are by example and explanatory and are intended to provide further explanation of the invention as claimed.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025] The accompanying drawings, which are included to provide a further understanding of the invention and are incorporated in and constitute a part of this specification, illustrate embodiments of the invention and together with the description serve to explain the principles of the invention.

FIG. 1 is a view illustrating an emission mechanism of a delayed fluorescence compound according to the present invention.

FIGs. 2A to 2D respectively show distribution of HOMO and LUMO of compound 1 of the present invention.

FIG. 3 is a "Lippert-Mataga plot" graph of a delayed fluorescence compound according to the present invention.

FIG. 4 is a schematic cross-sectional view of an OLED according to the invention.

DETAILED DESCRIPTION OF THE EMBODIMENTS

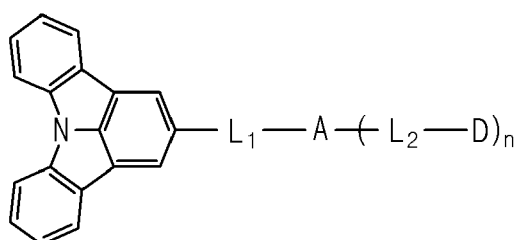
[0026] The meanings of terms described in the present specification should be understood as follows.

[0027] The singular forms should be understood as including the plural forms as well unless the context clearly indicates otherwise. The terms "first", "second", and the like are used to discriminate any one element from other elements and the scope of the present invention is not intended to be limited by these terms. The terms "comprises" "includes" and the like should be understood as not precluding the presence or addition of one or more other features, integers, steps, operations, elements, components, or combinations thereof. The term "at least one" should be understood as including all combinations that may be suggested from one or more associated items. For example, the meanings of "at least one selected from a first item, a second item, and a third item" includes not only each of the first item, the second item, and the third item, but also all combinations of these items that may be suggested from two or more ones of the first item, the second item, and the third item. In addition, when any one element is referred to as being "on" another element, it can be directly on the upper surface of the other element or a third intervening element may also be present.

[0028] Reference will now be made in detail to example embodiments, examples of which are illustrated in the accompanying drawings.

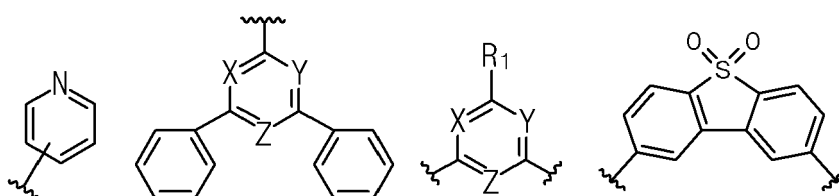
[0029] A delayed fluorescence compound of the present invention has a first structure in that an electron donor moiety of indolo-[3,2,1-j,k]carbazole is combined or linked to an electron acceptor moiety with a linker therebetween or a second structure in that a first electron donor moiety of indolo-[3,2,1-j,k]carbazole and a second electron donor moiety are respectively combined or linked to an electron acceptor moiety with first and second linkers therebetween. The delayed fluorescent compound of the present invention has Formula 1 of following.

[Formula 1]



[0030] In the Formula 1, the electron acceptor moiety "A" is selected from materials in Formula 2-1 of following.

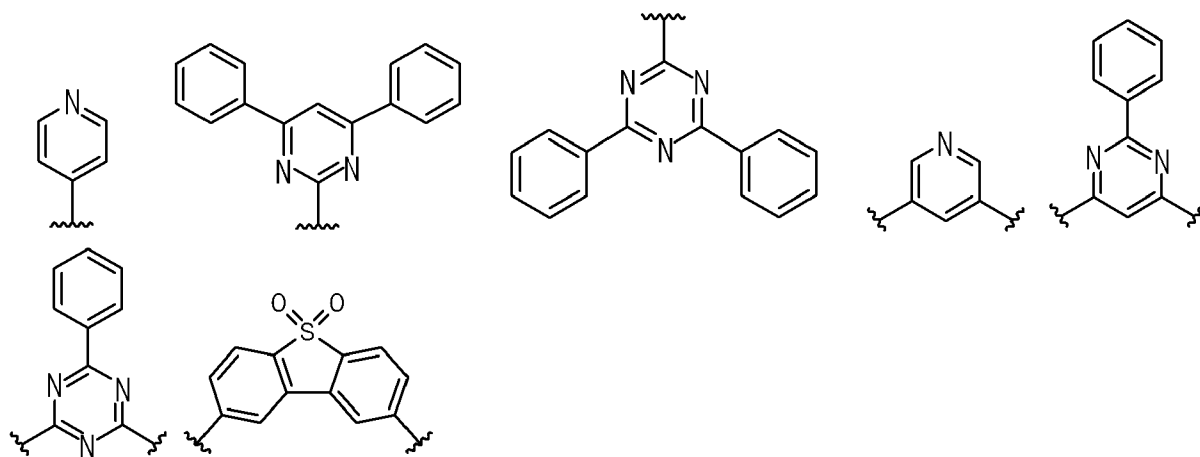
[Formula 2-1]



[0031] In the Formula 2-1, "R1" is selected from hydrogen or phenyl, and each of X, Y and Z is independently selected

from carbon and nitrogen. At least two selected from X, Y and Z are nitrogen, and X, Y and Z are same or different. For example, X and Y may be nitrogen, and Z may be carbon. Alternatively, all of X, Y and Z may be nitrogen. For example, the electron acceptor moiety A may be selected from materials in Formula 2-2 of following.

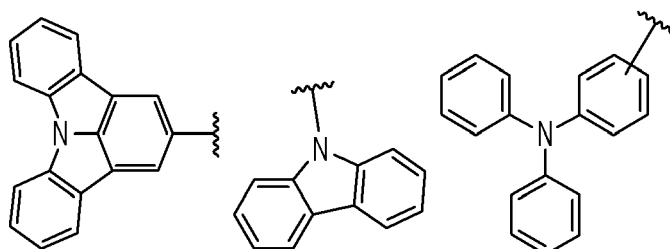
[Formula 2-2]



[0032] Namely, the electron acceptor moiety "A" may be selected from pyridine, diphenyl pyrimidine, diphenyl triazine, phenyl pyrimidine, phenyl triazine or dibenzothiophene sulfone.

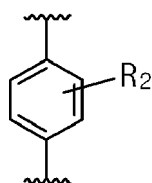
[0033] In the Formula 1, the second electron donor moiety "D" is selected from indolo-[3,2,1-j,k]carbazole, carbazole or triphenylamine. For example, the second electron donor moiety "D" may be selected from materials in Formula 3 of following.

[Formula 3]



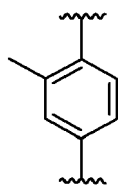
[0034] In the Formula 1, each of "L1" and "L2" is independently selected from substituted or non-substituted benzene in Formula 4-1 of following.

[Formula 4-1]



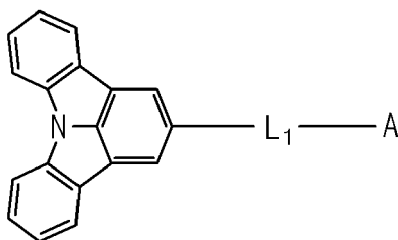
[0035] In the Formula 4-1, "R2" is selected from hydrogen or C1~C10 alkyl. For example, "R2" may be selected from materials in Formula 4-1 of following.

[Formula 4-2]

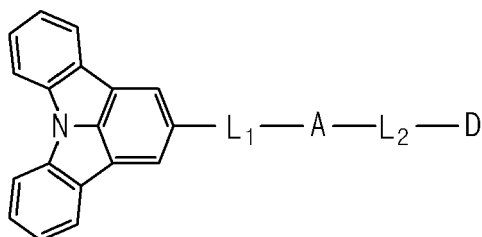


[0036] In Formula 1, "n" is 1 or 0 (zero). Namely, the delayed fluorescent compound in the Formula 1 may have Formula 5-1 or Formula 5-2 followings:

[Formula 5-1]



[Formula 5-2]



[0037] In other words, as shown in the Formula 5-1, the delayed fluorescence compound of the present invention may have a structure in that an electron donor moiety of indolo-[3,2,1-j,k]carbazole and an electron acceptor moiety are combined (or linked) to a linker without another electron donor moiety and another linker.

[0038] Alternatively, as shown in the Formula 5-2, the delayed fluorescence compound of the present invention may have a structure in that a first electron donor moiety of indolo-[3,2,1-j,k]carbazole and a second electron donor moiety are respectively combined (or linked) to an electron acceptor moiety with a first linker between the first electron donor moiety and the electron acceptor and a second linker between the second electron donor moiety and the electron acceptor.

[0039] Since the delayed fluorescence compound includes the electron donor moiety and the electron acceptor moiety with or without another electron donor moiety, the charge transfer is easily generated in the molecule and the emitting efficiency is improved. In addition, the dipole from the first and second electron donor moieties to the electron acceptor moiety is generated such that the dipole moment in the molecule is increased. As a result, the emitting efficiency is further improved.

[0040] Moreover, in the delayed fluorescent compound of the present invention, the excitons in the triplet state are engaged in the emission such that the emitting efficiency of the delayed fluorescent compound is increased.

[0041] Further, since indolo-[3,2,1-j,k]carbazole, which has high triplet energy and excellent hole property, is used for the first electron donor moiety and optionally for the second electron donor moiety, the increase of the emitting efficiency is further increased. (HOMO : - 5.56eV, LUMO : - 1.25eV, E_T = 3.04 eV)

[0042] Since the delayed fluorescence compound of the present invention has a rigid structure due to indolo-[3,2,1-j,k]carbazole such that the vibration in the molecule is decreased. As a result, the color shift problem is decreased, and the color purity is improved. In addition, since the delayed fluorescence compound of the present invention has large molecular weight, the thermal stability is increased.

[0043] In the delayed fluorescence compound of the present invention, the electron donor moiety or the first and second electron donor moieties and the electron acceptor moiety are combined or linked in the molecule such that an overlap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is reduced. As a result, a field activated complex is generated, and the emitting efficiency of the delayed fluorescence compound is improved.

[0044] Due to the steric hindrance of the linker or the first and second linkers, the red shift problem in the light emitted from the emitting layer including the delayed fluorescence compound is further decreased. Namely, the emitting layer with the delayed fluorescence compound of the present invention provides the deep blue emission.

[0045] On the other hand, the overlap between the HOMO and the LUMO may be increased by the linker. However, the compound has a specially bent shape by the linker such that the increase of the overlap between the HOMO and the LUMO can be minimized. As a result, the delayed fluorescence compound of the present invention may provide a field activated property.

[0046] Referring to FIG. 1, which is a view illustrating an emission mechanism of a delayed fluorescence compound according to the present invention, in the delayed fluorescence compound of the present invention, the triplet excitons as well as the singlet excitons are engaged in the emission such that the emitting efficiency is improved.

[0047] Namely, the triplet exciton is activated by a field, and the triplet exciton and the singlet exciton are transferred into an intermediated state " I_1 " and transited into a ground state " S_0 " to emit the light. In other words, the singlet state " S_1 " and the triplet state " T_1 " are transited into the intermediated state " I_1 " ($S_1 \rightarrow I_1 \leftarrow T_1$), and the singlet exciton and the triplet exciton in the intermediated state " I_1 " are engaged in the emission such that the emitting efficiency is improved. The compound having the above emission mechanism may be referred to as a field activated delayed fluorescence (FADF) compound.

[0048] In the related art fluorescence compound, since the HOMO and the LUMO are dispersed throughout an entirety of the molecule, the interconversion of the HOMO and the LUMO is impossible. (Selection Rule)

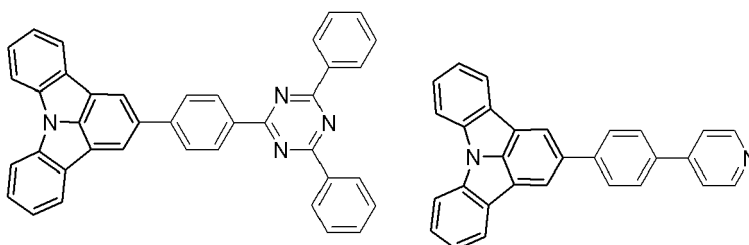
[0049] However, in the FADF compound, since the overlap between the HOMO and the LUMO in the molecule is relatively small, the interaction between the HOMO and the LUMO is small. Accordingly, changes of the spin state of one electron do not affect other electrons, and new charge transfer band, which does not comply the Selection Rule, is generated.

[0050] Moreover, since the electron donor moiety and the electron acceptor moiety is spatially spaced apart from each other in the molecule, the dipole moment is generated in a polarized state. In the polarized state dipole moment, the interaction between the HOMO and the LUMO is further reduced such that the emission mechanism does not comply the Selection Rule. Accordingly, in the FADF compound, the transition from the triplet state " T_1 " and the singlet state " S_1 " into the intermediated state " I_1 " can be generated such that the triplet exciton can be engaged in the emission.

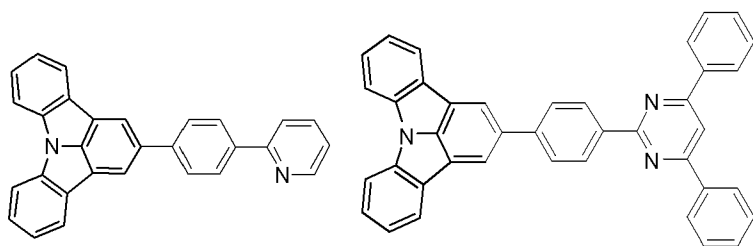
[0051] When the OLED is driven, the intersystem transition (intersystem crossing) from 25% singlet state " S_1 " excitons and 75% triplet state " T_1 " excitons to the intermediated state " I_1 " is generated, and the singlet and triplet excitons in the intermediated state " I_1 " are transited into the ground state to emit the light. As a result, the FADF compound has the theoretic quantum efficiency of 100%.

[0052] For example, the delayed fluorescence compound in the Formula 1 may be one of compounds in Formula 6. (Compounds 1 to 15 in an order)

[Formula 6]

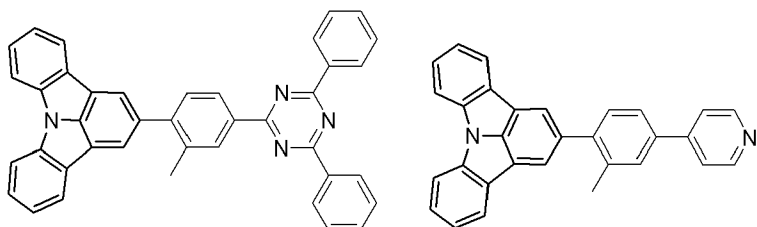


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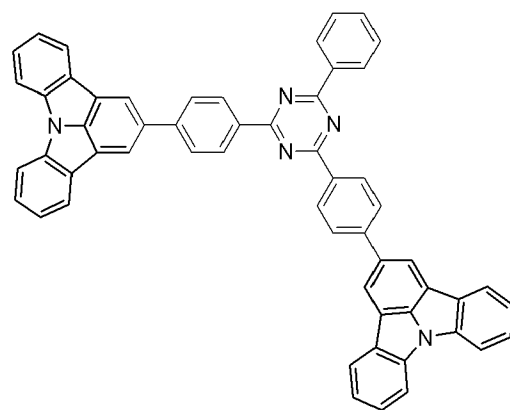
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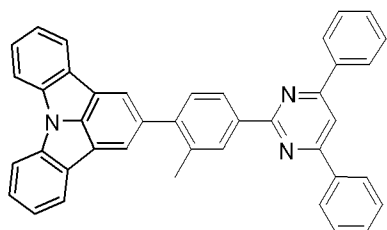


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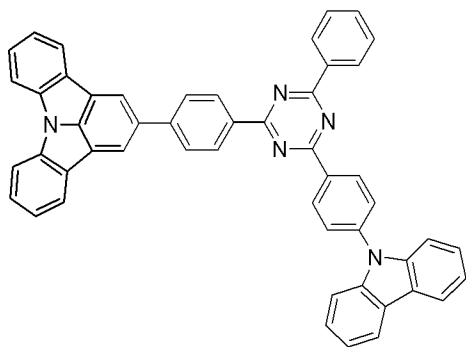
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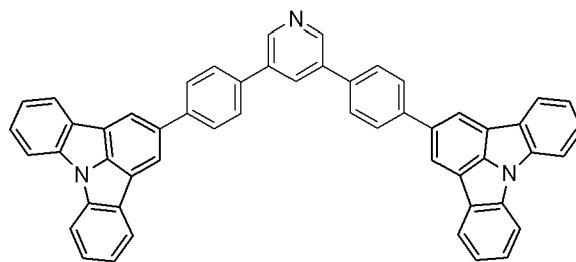
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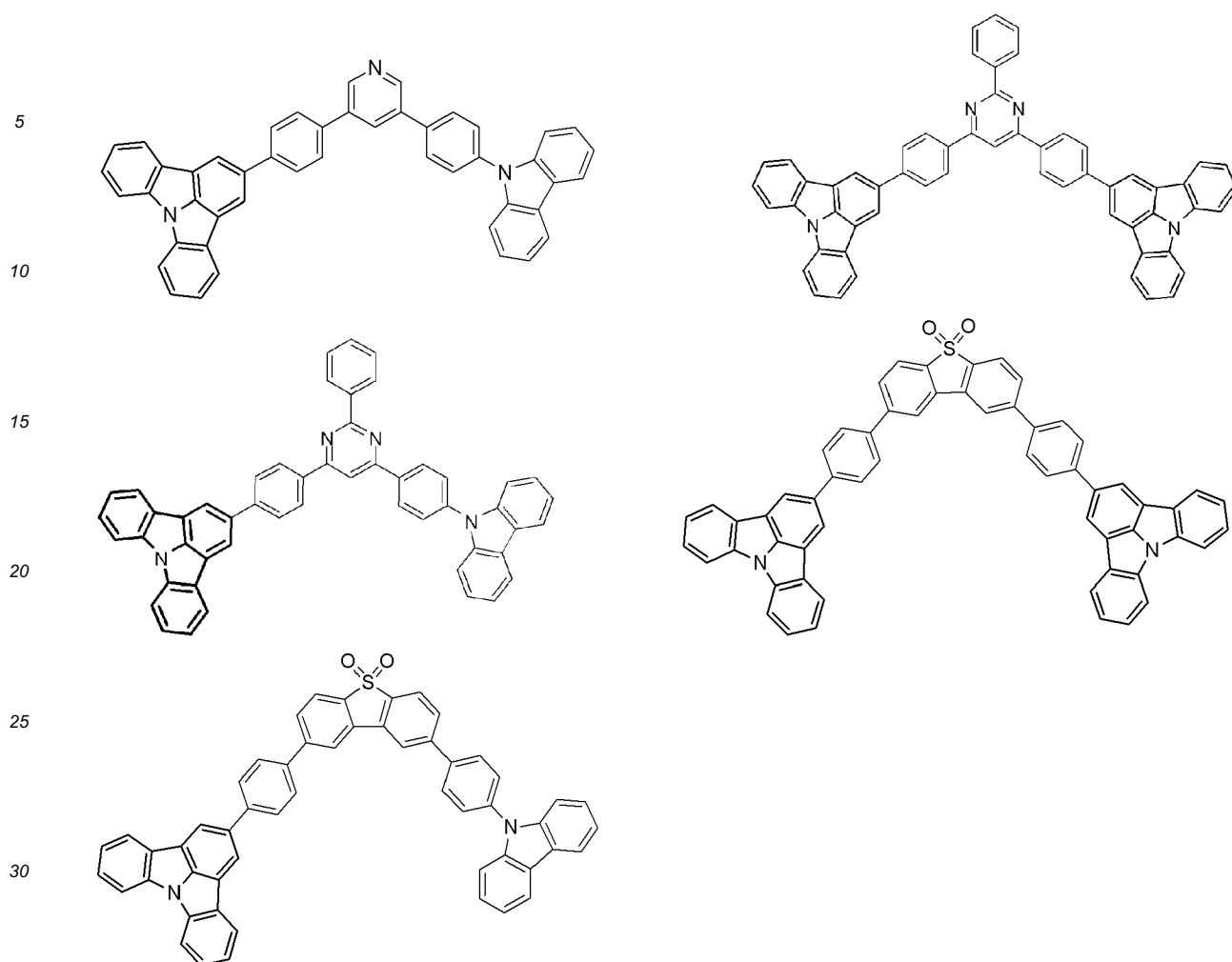
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[0053] The HOMO, the LUMO and the energy band gap of the compounds 1 to 15 are listed in Table 1.

Table 1

	HOMO (eV)	LUMO (eV)	Band gap
compound 1	-5.53	-1.86	3.67
compound 2	-5.56	-1.42	4.14
compound 3	-5.42	-1.31	4.11
compound 4	-5.42	-1.63	3.79
compound 5	-5.62	-1.75	3.87
compound 6	-5.61	-1.41	4.20
compound 7	-5.47	-1.62	3.80
Compound 8	-5.52	-1.80	3.72
Compound 9	-5.39	-1.92	3.47
Compound 10	-5.47	-1.37	4.10
Compound 11	-5.37	-1.41	3.96
Compound 12	-5.51	-1.68	3.83
Compound 13	-5.40	-1.81	3.59

(continued)

	HOMO (eV)	LUMO (eV)	Band gap
Compound 14	-5.58	-1.85	3.73
Compound 15	-5.48	-1.96	3.52

[0054] As shown in Table 1, the delayed fluorescence compound of the present invention has large energy band gap such that the emitting efficiency of an OLED or a display device including the compound may be increased.

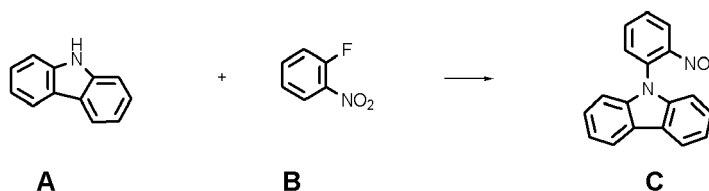
Synthesis

1. synthesis of compound 1

(1) compound C

[0055]

[Reaction Formula 1-1]

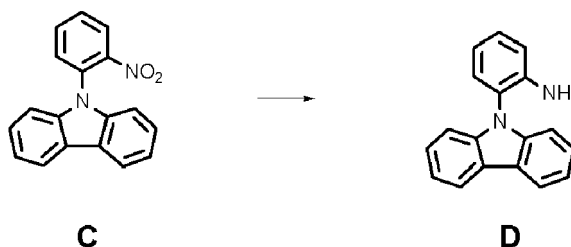


[0056] In the N₂ gas purging system, compound A, compound B (1.1 equivalent) and cesium carbonate (1.5 equivalent) were put into dimethylsulfoxide, and the mixture was stirred. After stirring for about 2 hour under the room temperature, the mixture was additionally stirred in the oil bath of a temperature of 60 °C. 8 hours after, the mixture was put into iced-DI water such that yellow solids were obtained. The yellow solids were filtered and extracted by using dichloromethane and DI water. Moisture was removed by MgSO₄. After removing the organic solvent, the resultant was re-crystallized by using dichloromethane and methanol such that compound C was obtained.

(2) compound D

[0057]

[Reaction Formula 1-2]

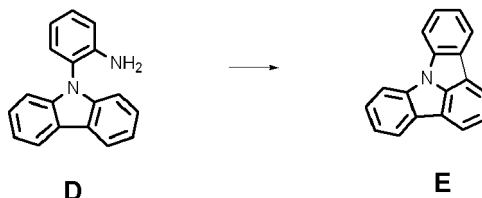


[0058] In the N₂ gas purging system, compound C and SnCl₂·2H₂O (3 equivalent) were put into ethanol, and the mixture was stirred for 8 hours under a temperature of 70 °C. After completion of the reaction, the mixture was cooled into the room temperature. The mixture was added into 1N sodium hydroxide aqueous solution to obtain solids. The solids were filtered and dissolved in dichloromethane. 1N sodium hydroxide aqueous solution was added to be extracted. The aqueous layer was removed to obtain an organic layer. The organic layer was extracted by DI water, and moisture was removed by MgSO₄. The organic solvent was removed such that compound D was obtained.

(3) compound E

[0059]

[Reaction Formula 1-3]

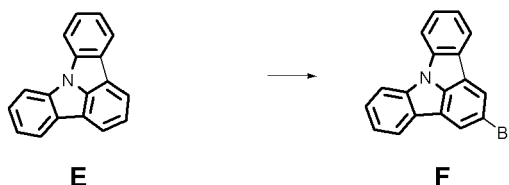


[0060] In the ice bath, compound D was put into acetic acid, and sulfuric acid was added and stirred. Sodium nitride (1.1 equivalent) was dissolved in DI water, and the solution was slowly added into the flask including the compound D for 15 minutes and was additionally stirred for 10 minutes. The flask was transferred into the oil bath, and the mixture was reacted for 20 minutes under a temperature of 130 °C. After completion of the reaction, the mixture was cooled into the room temperature, and DI water was put into the resultant to obtain the precipitates. The precipitates were filtered and washed by methanol. The filtered precipitated was columned and re-crystallized by using dichloromethane and methanol such that compound E was obtained.

(4) compound F

[0061]

[Reaction Formula 1-4]

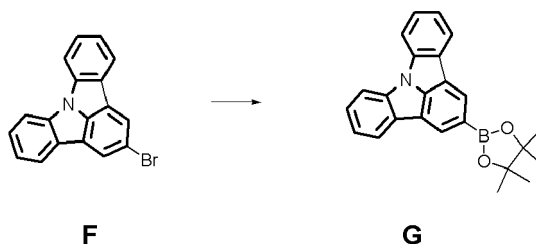


[0062] In the N₂ gas purging system, compound E and N-bromosuccinimide (1.1 equivalent) was put into dichloromethane in the flask, where the light was blocked out, and the mixture was stirred for 12 hours. After completion of the reaction, the mixture was extracted by using dichloromethane and DI water, and moisture was removed by MgSO₄. The resultant was refined such that compound F was obtained.

(5) compound G

[0063]

[Reaction Formula 1-5]

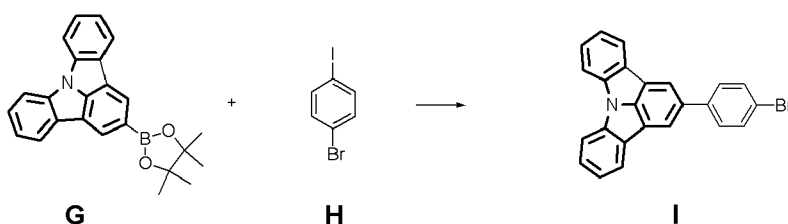


[0064] In the N₂ gas purging system, compound F, bis(pinacolate)diboron (1.2 equivalent), [1,1-bis(diphenylphosphino)ferrocene]palladium(II), dichloride dichloromethane, 1,1-bis(diphenylphosphino)ferrocene and potassium acetate were put into the mixed solvent of 1,4-dioxane and toluene (1:1) in the flask, where the light was blocked out, and stirred. After the bubbles were disappeared, the mixture was stirred for 17 hours under a temperature of 120°C in the oil bath. After completion of the reaction, the mixture was cooled into the room temperature, and the solvent was removed. The resultant was washed by dichloromethane and refined such that compound G was obtained.

(6) compound I

[0065]

[Reaction Formula 1-6]

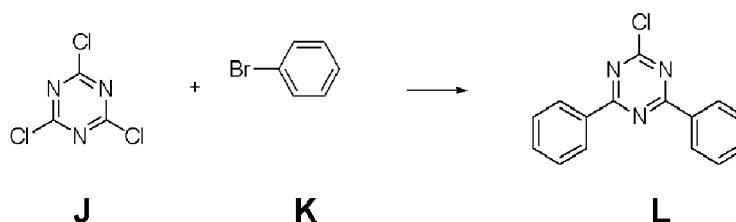


[0066] In the N₂ gas purging system, compound G was dissolved in tetrahydrofuran and toluene solution (5:1), and compound H (0.9 equivalent) was added in the solution. Potassium carbonate (4.4 equivalent) was dissolved in DI water, and Pd (0.05 equivalent) was added. The mixture was refluxed under a temperature of 80°C and stirred for 24 hours. After completion of the reaction, the mixture was extracted by the organic solvent, and the organic solvent was removed. The resultant was columned such that compound I was obtained.

(7) compound L

[0067]

[Reaction Formula 1-7]



[0068] In the N₂ gas purging system, compound K (2 equivalent) was dissolved in tetrahydrofuran in the flask, where the light is blocked out, under a temperature of -78 °C, and n-butyl lithium was slowly dropped. In the N₂ gas system, compound J was dissolved in tetrahydrofuran in another flask. Compound J was dropped into the another flask including compound K with the N₂ gas system using the cannula, and the mixture was stirred for 8 hours. After completion of the reaction, the resultant was refined such that compound L was obtained.

(8) compound 1

[0069]

[Reaction Formula 1-8]



15

20

[0071]

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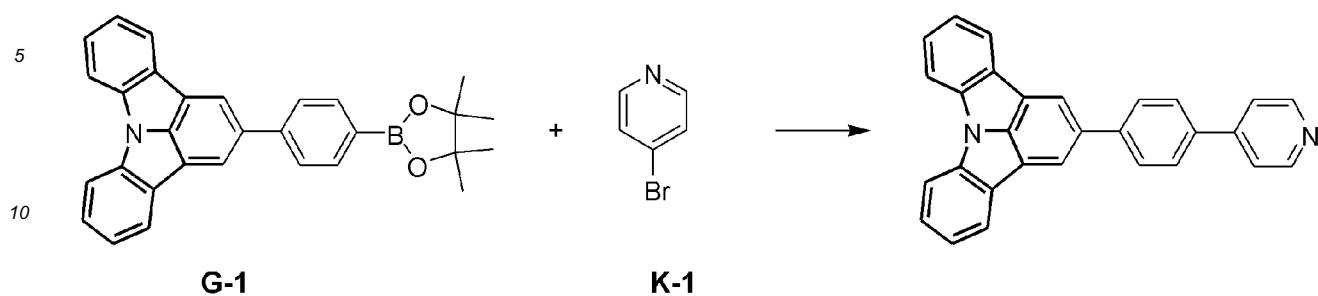


40

45

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[Reaction Formula 2-2]

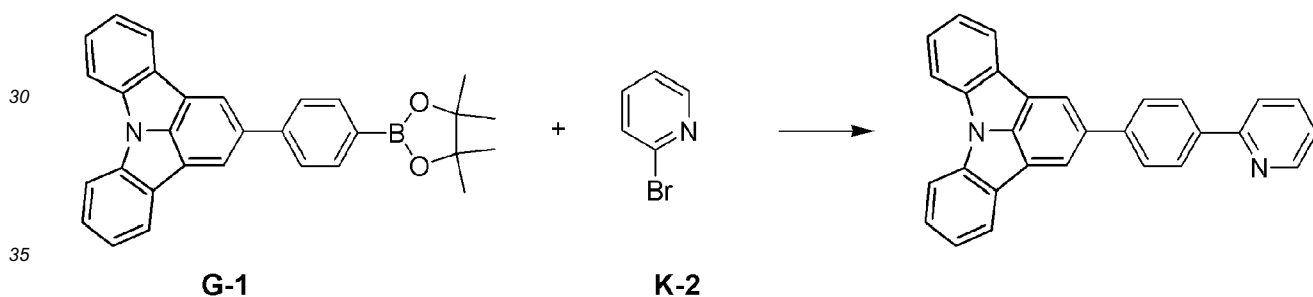


15 **[0074]** In the N₂ gas purging system, compound K-1 was dissolved in toluene, and compound G-1 (1.2 equivalent) was added. K₂CO₃ (4.4 equivalent), which was dissolved in DI water, was added into the mixture. After adding tetrahydrofuran, and Pd (0.05 equivalent) was added. The mixture was refluxed and stirred under a temperature of 80 °C. The mixture was extracted and was re-crystallized for separation of compound G-1, compound K-1 and the by-products. The resultant was columned by dichloromethane and hexane such that compound 2 was obtained.

20 3. synthesis of compound 3

[0075]

[Reaction Formula 3]

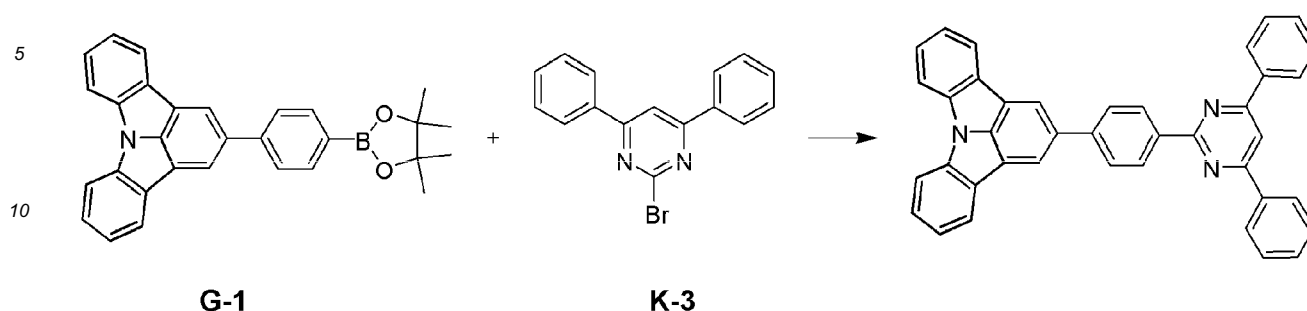


40 **[0076]** In the N₂ gas purging system, compound K-2 was dissolved in toluene, and compound G-1 (1.2 equivalent) was added. K₂CO₃ (4.4 equivalent), which was dissolved in DI water, was added into the mixture. After adding tetrahydrofuran, and Pd (0.05 equivalent) was added. The mixture was refluxed and stirred under a temperature of 80 °C. The mixture was extracted and was re-crystallized for separation of compound G-1, compound K-2 and the by-products. The resultant was columned by dichloromethane and hexane such that compound 3 was obtained.

45 4. synthesis of compound 4

[0077]

[Reaction Formula 4]



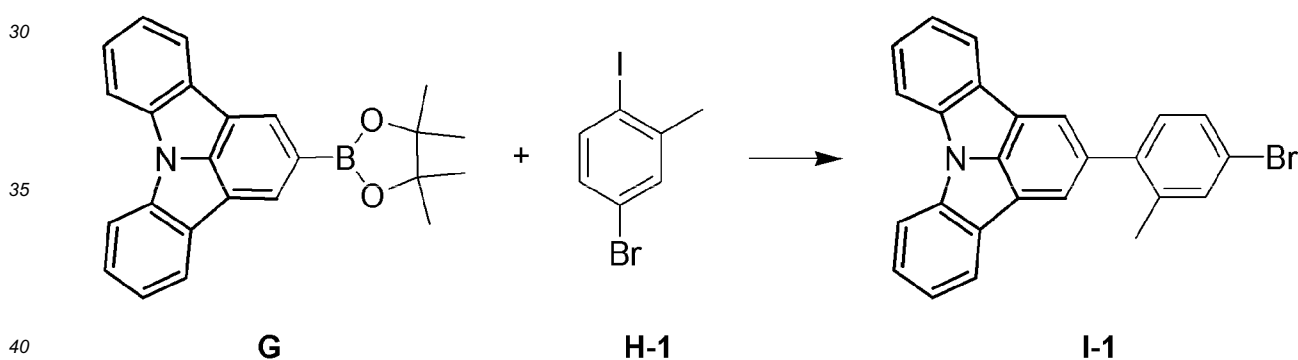
15 **[0078]** In the N₂ gas purging system, compound K-3 was dissolved in toluene, and compound G-1 (1.2 equivalent) was added. K₂CO₃ (4.4 equivalent), which was dissolved in DI water, was added into the mixture. After adding tetrahydrofuran, and Pd (0.05 equivalent) was added. The mixture was refluxed and stirred under a temperature of 80 °C. The mixture was extracted and was re-crystallized for separation of compound G-1, compound K-3 and the by-products. The resultant was columned by dichloromethane and hexane such that compound 4 was obtained.

20 5. synthesis of compound 5

(1) compound I-1

25 **[0079]**

[Reaction Formula 5-1]



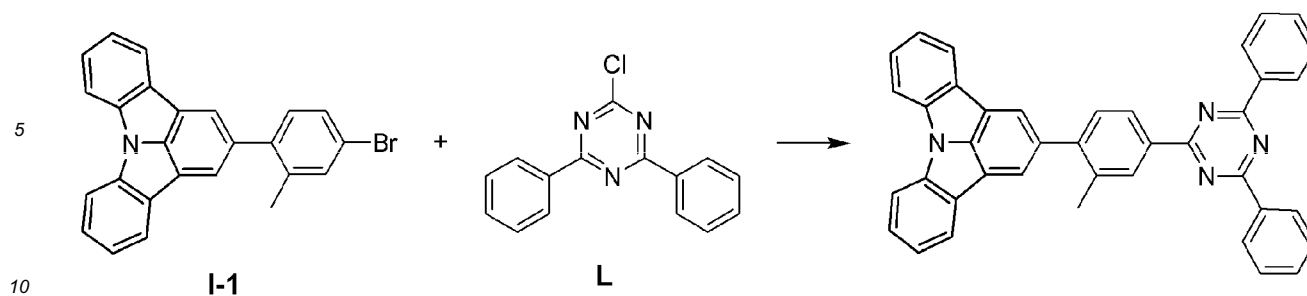
45 **[0080]** In the N₂ gas purging system, compound G was dissolved in tetrahydrofuran and toluene solution (5:1), and compound H-1 (0.9 equivalent) was added in the solution. Potassium carbonate (4.4 equivalent) was dissolved in DI water, and Pd (0.05 equivalent) was added. The mixture was refluxed under a temperature of 80 °C and stirred for 24 hours. After completion of the reaction, the mixture was extracted by the organic solvent, and the organic solvent was removed. The resultant was columned such that compound I-1 was obtained.

(2) compound 5

50 **[0081]**

[Reaction Formula 5-2]

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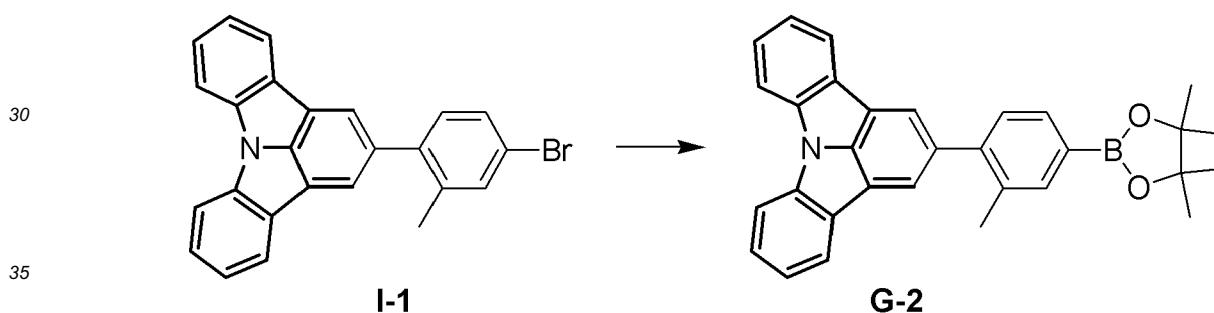
[0082] In the N₂ gas purging system, compound I-1 (1.2 equivalent) was dissolved in tetrahydrofuran in the flask, where the light is blocked out, under a temperature of -78 °C, and n-butyl lithium was slowly dropped. In the N₂ gas system, compound L was dissolved in tetrahydrofuran in another flask. Compound I-1 was dropped into the another flask including compound L with the N₂ gas system using the cannula, and the mixture was stirred for 8 hours. After completion of the reaction, the resultant was refined such that compound 5 was obtained.

6. synthesis of compound 6

(1) compound G-2

[0083]

[Reaction Formula 6-1]

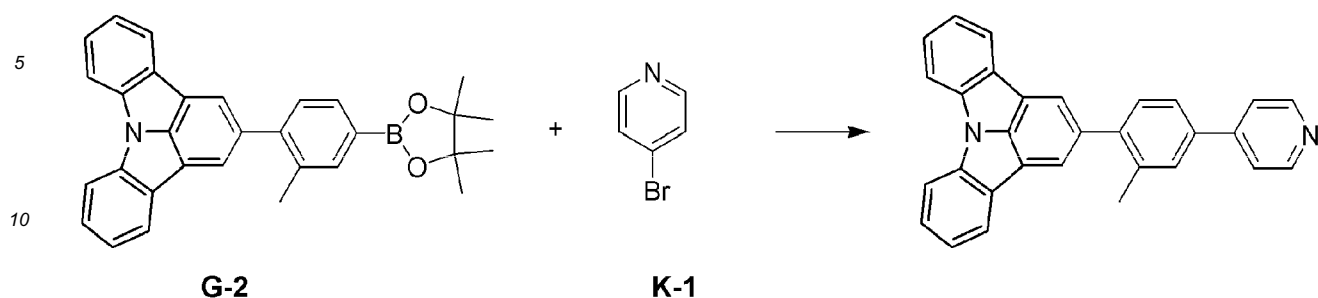


[0084] In the N₂ gas purging system, compound I-1, bis(pinacolate)diboron (1.2 equivalent), [1,1-bis(diphenylphosphineo)ferrocene]palladium(II), dichloride dichloromethane, 1,1-bis(diphenylphosphino)ferrocene and potassium acetate were put into the mixed solvent of 1,4-dioxane and toluene (1:1) in the flask, where the light was blocked out, and stirred. After the bubbles were disappeared, the mixture was stirred for 17 hours under a temperature of 120°C in the oil bath. After completion of the reaction, the mixture was cooled into the room temperature, and the solvent was removed. The resultant was washed by toluene and refined such that compound G-2 was obtained.

(2) compound 6

[0085]

[Reaction Formula 6-2]

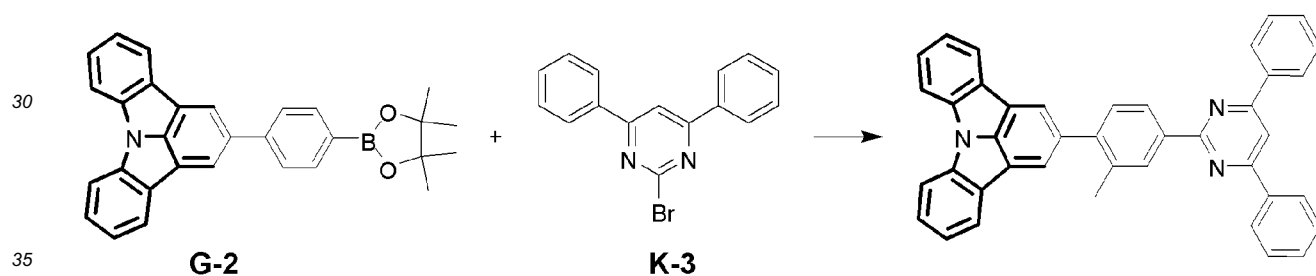


15 **[0086]** In the N₂ gas purging system, compound K-1 was dissolved in toluene, and compound G-2 (1.2 equivalent) was added. K₂CO₃ (4.4 equivalent), which was dissolved in DI water, was added into the mixture. After adding tetrahydrofuran, and Pd (0.05 equivalent) was added. The mixture was refluxed and stirred under a temperature of 80 °C. The mixture was extracted and was re-crystallized for separation of compound G-2, compound K-1 and the by-products. The resultant was columned by dichloromethane and hexane such that compound 6 was obtained.

20 7. synthesis of compound 7

25 **[0087]**

[Reaction Formula 7]

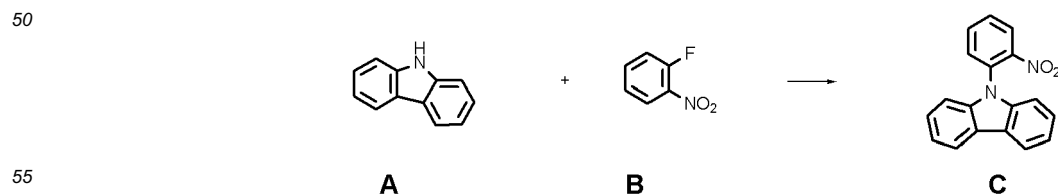


40 **[0088]** In the N₂ gas purging system, compound K-3 was dissolved in toluene, and compound G-2 (1.2 equivalent) was added. K₂CO₃ (4.4 equivalent), which was dissolved in DI water, was added into the mixture. After adding tetrahydrofuran, and Pd (0.05 equivalent) was added. The mixture was refluxed and stirred under a temperature of 80 °C. The mixture was extracted and was re-crystallized for separation of compound G-2, compound K-3 and the by-products. The resultant was columned by dichloromethane and hexane such that compound 7 was obtained.

8. synthesis of compound 8

45 **[0089]**

[Reaction Formula 8-1]



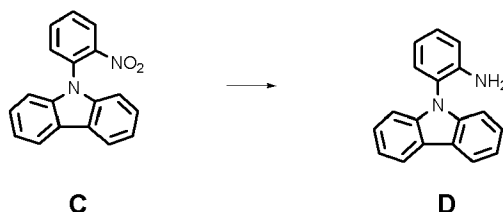
[0090] In the N₂ gas purging system, compound A, compound B (1.1 equivalent) and cesium carbonate (1.5 equivalent)

were put into dimethylsulfoxide, and the mixture was stirred. After stirring for about 2 hour under the room temperature, the mixture was additionally stirred in the oil bath of a temperature of 60 °C. 8 hours after, the mixture was put into iced-DI water such that yellow solids were obtained. The yellow solids were filtered and extracted by using dichloromethane and DI water. Moisture was removed by MgSO_4 . After removing the organic solvent, the resultant was re-crystallized by using dichloromethane and methanol such that compound C was obtained.

(2) compound D

[0091]

[Reaction Formula 8-2]

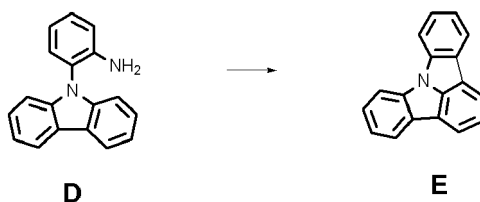


[0092] In the N_2 gas purging system, compound C and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (3 equivalent) were put into ethanol, and the mixture was stirred for 8 hours under a temperature of 70 °C. After completion of the reaction, the mixture was cooled into the room temperature. The mixture was added into 1N sodium hydroxide aqueous solution to obtain solids. The solids were filtered and dissolved in dichloromethane. 1N sodium hydroxide aqueous solution was added to be extracted. The aqueous layer was removed to obtain an organic layer. The organic layer was extracted by DI water, and moisture was removed by MgSO_4 . The organic solvent was removed such that compound D was obtained.

(3) compound E

[0093]

[Reaction Formula 8-3]

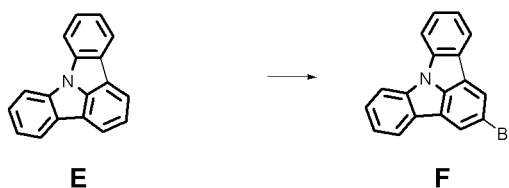


[0094] In the ice bath, compound D was put into acetic acid, and sulfuric acid was added and stirred. Sodium nitride (1.1 equivalent) was dissolved in DI water, and the solution was slowly added into the flask including the compound D for 15 minutes and was additionally stirred for 10 minutes. The flask was transferred into the oil bath, and the mixture was reacted for 20 minutes under a temperature of 130 °C. After completion of the reaction, the mixture was cooled into the room temperature, and DI water was put into the resultant to obtain the precipitates. The precipitates was filtered and washed by methanol. The filtered precipitated was columned and re-crystallized by using dichloromethane and methanol such that compound E was obtained.

(4) compound F

[0095]

[Reaction Formula 8-4]

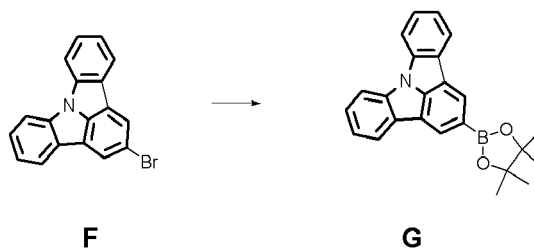


[0096] In the N₂ gas purging system, compound E and N-bromosuccinimide (1.1 equivalent) was put into dichloromethane in the flask, where the light was blocked out, and the mixture was stirred for 12 hours. After completion of the reaction, the mixture was extracted by using dichloromethane and DI water, and moisture was removed by MgSO₄. The resultant was refined such that compound F was obtained.

(5) compound G

[0097]

[Reaction Formula 8-5]

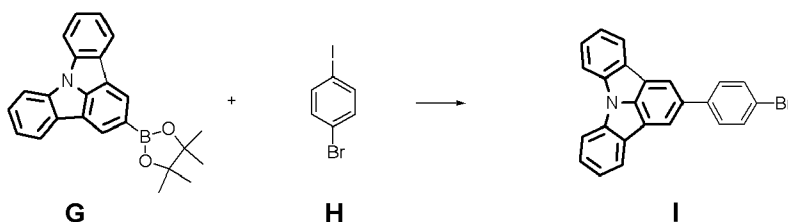


[0098] In the N₂ gas purging system, compound F, bis(pinacolate)diboron (1.2 equivalent), [1,1-bis(diphenylphosphino)ferrocene]palladium(II), dichloride dichloromethane, 1,1-bis(diphenylphosphino)ferrocene and potassium acetate were put into the mixed solvent of 1,4-dioxane and toluene (1:1) in the flask, where the light was blocked out, and stirred. After the bubbles were disappeared, the mixture was stirred for 17 hours under a temperature of 120°C in the oil bath. After completion of the reaction, the mixture was cooled into the room temperature, and the solvent was removed. The resultant was washed by dichloromethane and refined such that compound G was obtained.

(6) compound I

[0099]

[Reaction Formula 8-6]



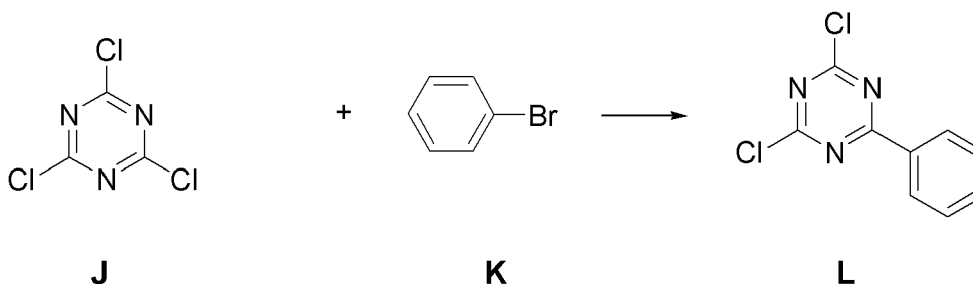
[0100] In the N₂ gas purging system, compound G was dissolved in tetrahydrofuran and toluene solution (5:1), and compound H (0.9 equivalent) was added in the solution. Potassium carbonate (4.4 equivalent) was dissolved in DI water, and Pd (0.05 equivalent) was added. The mixture was refluxed under a temperature of 80°C and stirred for 24 hours. After completion of the reaction, the mixture was extracted by the organic solvent, and the organic solvent was removed.

The resultant was columned such that compound I was obtained.

(7) compound L

[0101]

[Reaction Formula 8-7]

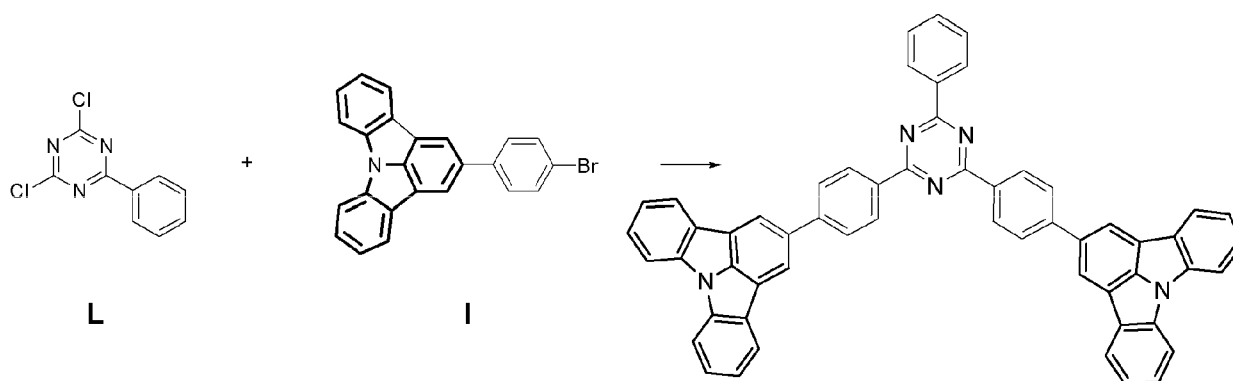


[0102] In the N₂ gas purging system, compound K (1 equivalent) was dissolved in tetrahydrofuran in the flask, where the light is blocked out, under a temperature of -78 °C, and n-butyl lithium was slowly dropped. In the N₂ gas system, compound J was dissolved in tetrahydrofuran in another flask. Compound J was dropped into the another flask including compound K with the N₂ gas system using the cannula, and the mixture was stirred for 8 hours. After completion of the reaction, the resultant was refined such that compound L was obtained.

(8) compound 1

[0103]

[Reaction Formula 8-8]



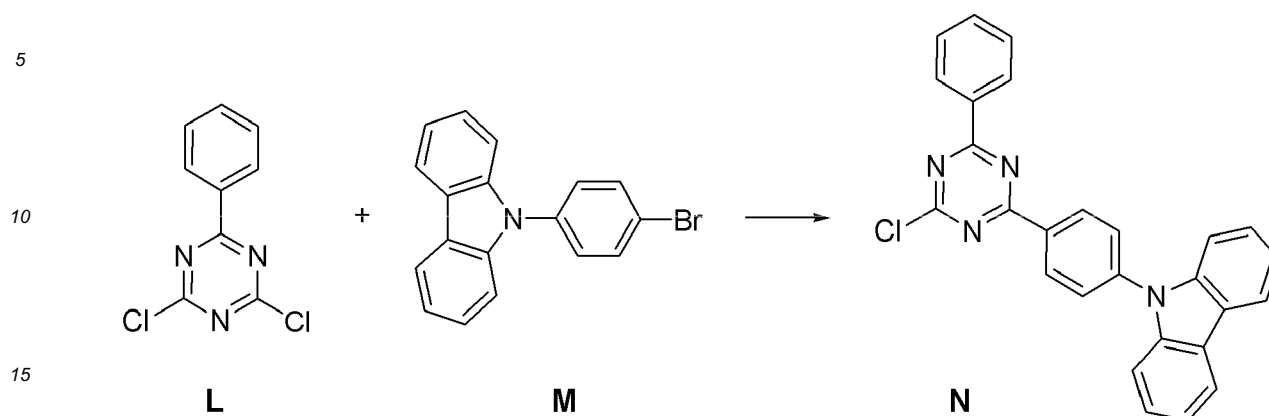
[0104] In the N₂ gas purging system, compound I (2.2 equivalent) was dissolved in tetrahydrofuran in the flask, where the light is blocked out, under a temperature of -78 °C, and n-butyl lithium was slowly dropped. In the N₂ gas system, compound L was dissolved in tetrahydrofuran in another flask. Compound I was dropped into the another flask including compound L with the N₂ gas system using the cannula, and the mixture was stirred for 8 hours. The mixture was cooled into the room temperature and was extracted by using ethyl acetate to remove the organic solvent. The resultant was columned by using dichloromethane and hexane such that compound 8 was obtained.

9. synthesis of compound 9

(1) compound N

[0105]

[Reaction Formula 9-1]

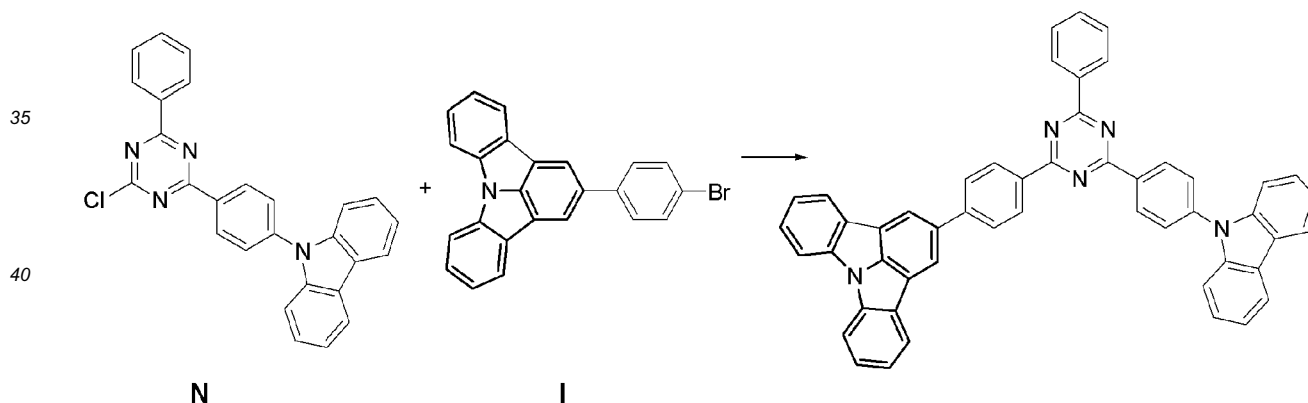


[0106] In the N₂ gas purging system, compound M (1.2 equivalent) was dissolved in tetrahydrofuran in the flask, where the light is blocked out, under a temperature of -78 °C, and n-butyl lithium was slowly dropped. In the N₂ gas system, compound L was dissolved in tetrahydrofuran in another flask. Compound M was dropped into the another flask including compound L with the N₂ gas system using the cannula, and the mixture was stirred for 8 hours. The mixture was cooled into the room temperature and was extracted by using ethyl acetate to remove the organic solvent. The resultant was columned by using dichloromethane and hexane such that compound N was obtained.

(2) compound 2

[0107]

[Reaction Formula 9-2]



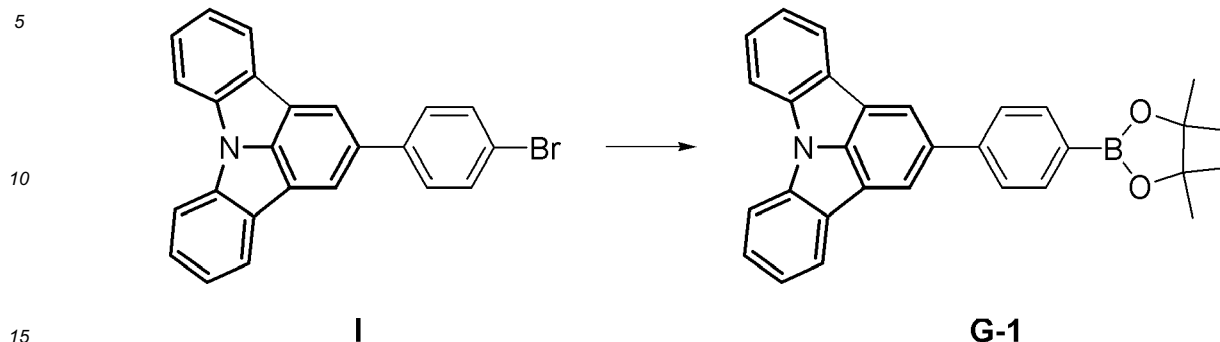
[0108] In the N₂ gas purging system, compound I (1.2 equivalent) was dissolved in tetrahydrofuran in the flask, where the light is blocked out, under a temperature of -78 °C, and n-butyl lithium was slowly dropped. In the N₂ gas system, compound N was dissolved in tetrahydrofuran in another flask. Compound I was dropped into the another flask including compound N with the N₂ gas system using the cannula, and the mixture was stirred for 8 hours. The mixture was cooled into the room temperature and was extracted by using ethyl acetate to remove the organic solvent. The resultant was columned by using dichloromethane and hexane such that compound 2 was obtained.

10. synthesis of compound 10

(1) compound G-1

[0109]

[Reaction Formula 10-1]

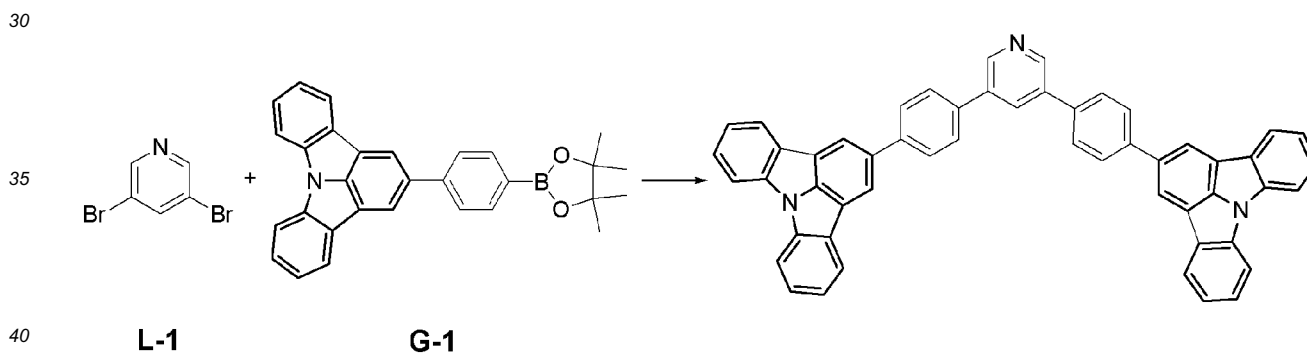


[0110] In the N₂ gas purging system, compound I, bis(pinacolate)diboron (1.2 equivalent), [1,1-bis(diphenylphosphino)ferrocene]palladium(II), dichloride dichloromethane, 1,1-bis(diphenylphosphino)ferrocene and potassium acetate were put into the mixed solvent of 1,4-dioxane and toluene (1:1) in the flask, where the light was blocked out, and stirred. After the bubbles were disappeared, the mixture was stirred for 20 hours under a temperature of 120°C in the oil bath. After completion of the reaction, the mixture was cooled into the room temperature, and the solvent was removed. The resultant was washed by toluene and refined such that compound G-1 was obtained.

(2) compound 10

[0111]

[Reaction Formula 10-2]



[0112] In the N₂ gas purging system, compound L-1 was dissolved in toluene, and compound G-1 (2.4 equivalent) was added. K₂CO₃ (8.8 equivalent), which was dissolved in DI water, was added into the mixture. After adding tetrahydrofuran, and Pd (0.1 equivalent) was added. The mixture was refluxed and stirred under a temperature of 80 °C. The mixture was extracted and was re-crystallized for separation of compound G-1, compound L-1 and the by-products. The resultant was columned by dichloromethane and hexane such that compound 10 was obtained.

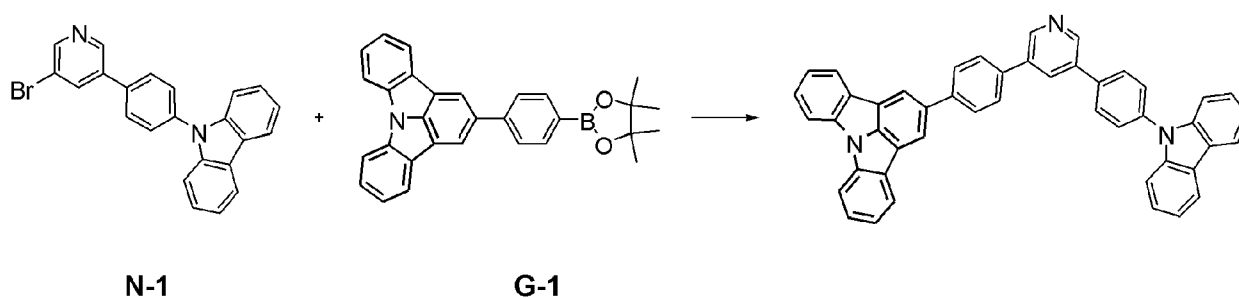
11. synthesis of compound 11

(1) compound N-1

[0113]

(2) compound 11

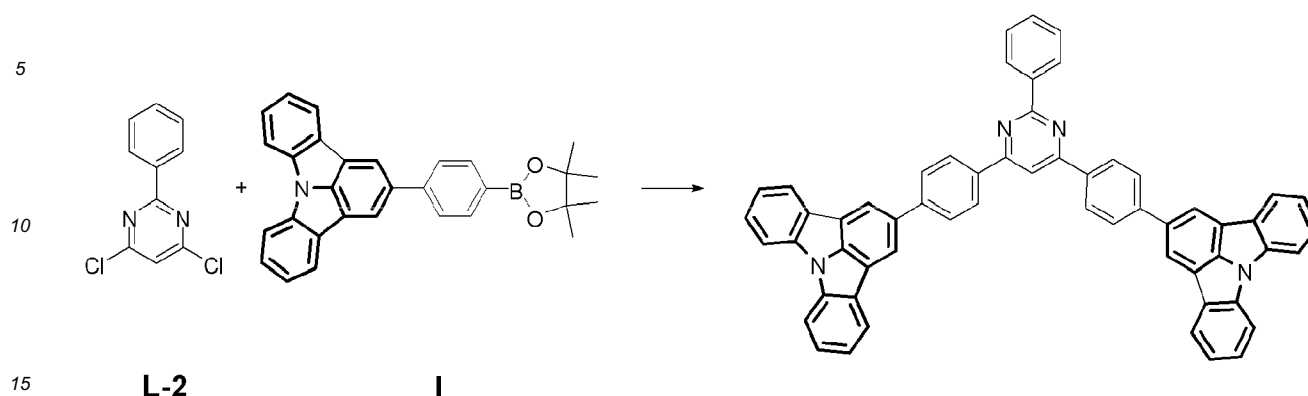
[Reaction Formula 11-2]



12. synthesis of compound 12

[0117]

[Reaction Formula 12]



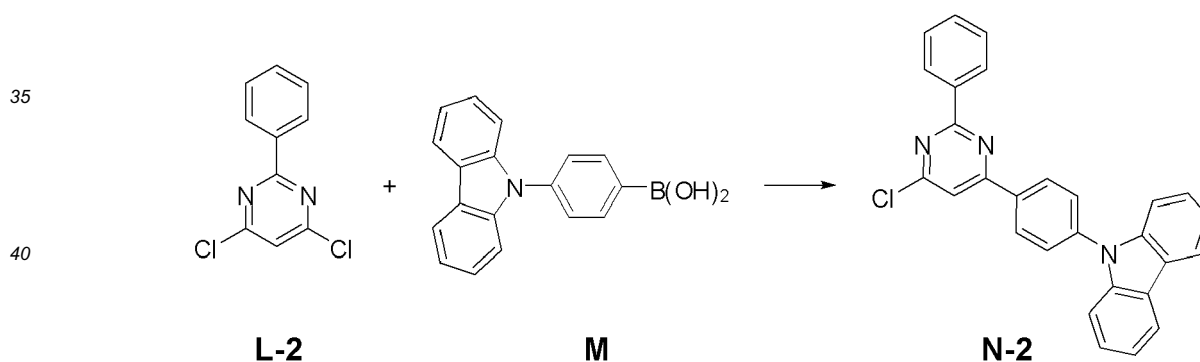
[0118] In the N₂ gas purging system, compound L-2 was dissolved in toluene, and compound I (1.2 equivalent) was added. K₂CO₃ (4.4 equivalent), which was dissolved in DI water, was added into the mixture. After adding tetrahydrofuran, and Pd (0.05 equivalent) was added. The mixture was refluxed and stirred under a temperature of 80 °C. The mixture was extracted by using ethyl acetate and DI water, and the organic solvent was removed. The mixture was re-crystallized for separation of compound I, compound L-2 and the by-products. The resultant was columned by dichloromethane and hexane such that compound 12 was obtained.

13. Compound 13

(1) compound N-2

[0119]

[Reaction Formula 13-1]

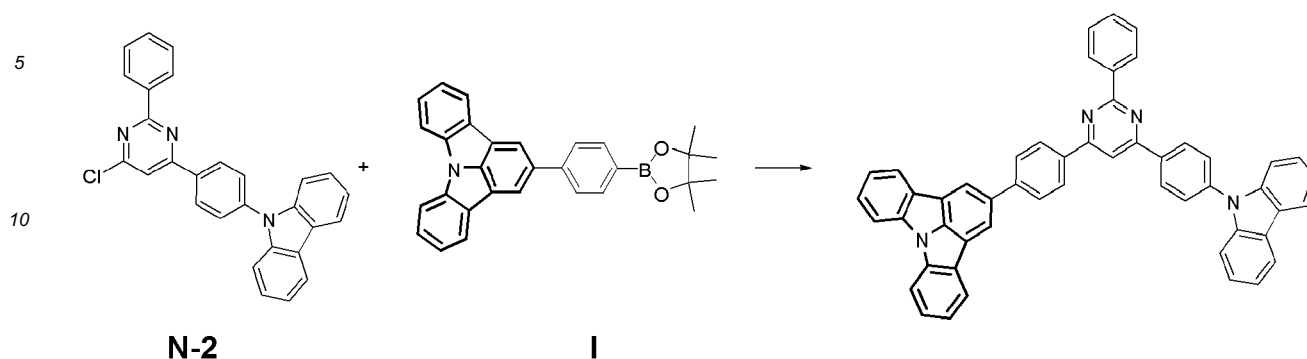


[0120] In the N₂ gas purging system, compound L-2 was dissolved in toluene, and compound M (1.2 equivalent) was added. K₂CO₃ (4.4 equivalent), which was dissolved in DI water, was added into the mixture. After adding tetrahydrofuran, and Pd (0.05 equivalent) was added. The mixture was refluxed and stirred under a temperature of 80 °C. The mixture was extracted by using ethyl acetate, and the organic solvent was removed. The mixture was re-crystallized for separation of compound M, compound L-2 and the by-products. The resultant was columned by dichloromethane and hexane such that compound N-2 was obtained.

(2) compound 13

[0121]

[Reaction Formula 13-2]



15

[0122] In the N₂ gas purging system, compound N-2 was dissolved in toluene, and compound I (1.2 equivalent) was added. K₂CO₃ (4.4 equivalent), which was dissolved in DI water, was added into the mixture. After adding tetrahydrofuran, and Pd (0.05 equivalent) was added. The mixture was refluxed and stirred under a temperature of 80 °C. The mixture was extracted by using ethyl acetate, and the organic solvent was removed. The mixture was re-crystallized for separation of compound I, compound N-2 and the by-products. The resultant was columned by dichloromethane and hexane such that compound 13 was obtained.

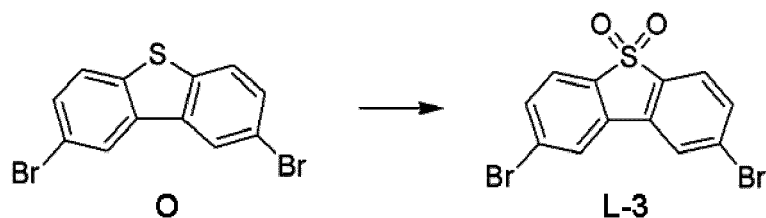
20

14. synthesis of compound 14

(1) compound L-3

[0123]

[Reaction Formula 14-1]



40

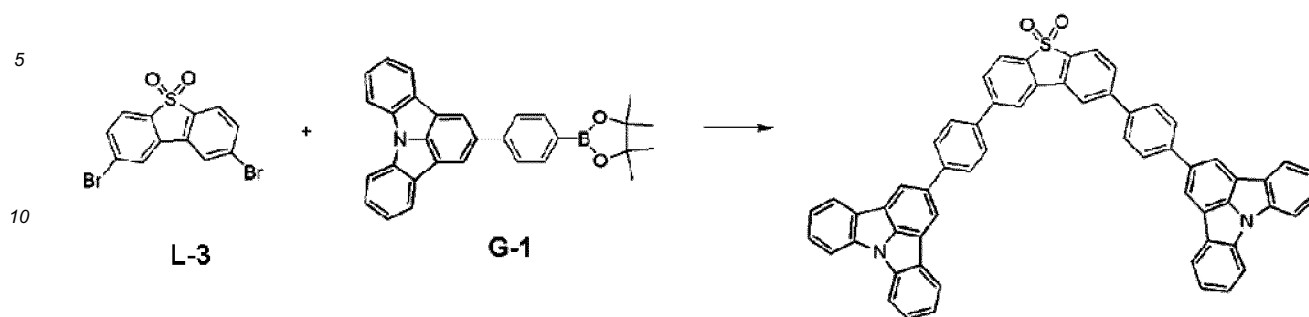
[0124] In the N₂ gas purging system, compound O are stirred with the solvent of acetic acid, and 30% hydrogen peroxide was excessively added. The mixture was refluxed for 8 hours under a temperature of 110 °C, and the reaction was completed. The mixture was cooled into the room temperature and slowly added into water to be precipitate. The mixture was stirred for about 30 minutes, and the precipitate was filtered. The resultant was washed by water such that compound L-3 was obtained.

45

(2) compound 14

[0125]

[Reaction Formula 14-2]



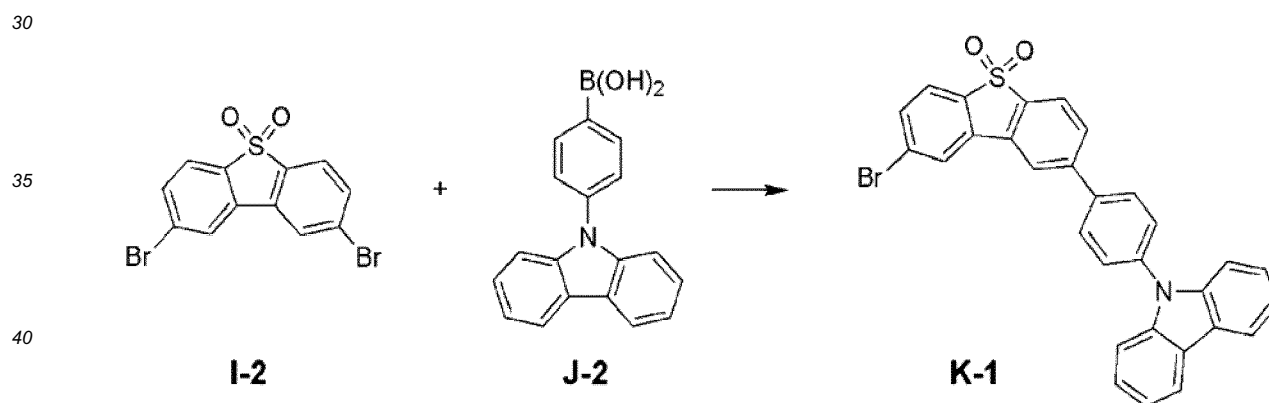
15 **[0126]** In the N₂ gas purging system, compound L-3 was dissolved in toluene, and compound G-1 (2.4 equivalent) was added. K₂CO₃ (8.8 equivalent), which was dissolved in DI water, was added into the mixture. After adding tetrahydrofuran, and Pd (0.1 equivalent) was added. The mixture was refluxed and stirred under a temperature of 80 °C. The mixture was extracted and was re-crystallized for separation of compound L-3, compound G-1 and the by-products. The resultant was columned by dichloromethane and hexane such that compound 14 was obtained.

20 15. Compound 15

(1) compound K-1

25 **[0127]**

[Reaction Formula 15-1]

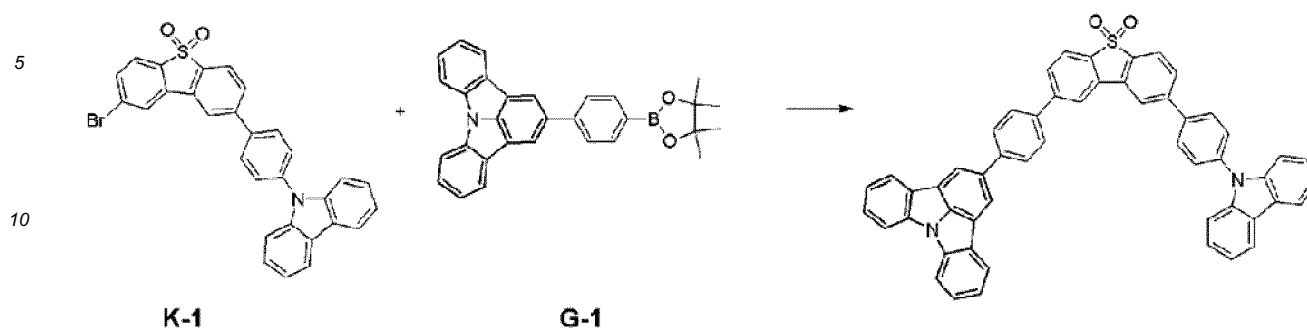


45 **[0128]** In the N₂ gas purging system, compound I-2 was dissolved in toluene, and compound J-2 (0.9 equivalent) was added. K₂CO₃ (4.4 equivalent), which was dissolved in DI water, was added into the mixture. After adding tetrahydrofuran, and Pd (0.05 equivalent) was added. The mixture was refluxed and stirred under a temperature of 80 °C. The mixture was extracted and was re-crystallized for separation of compound I-2, compound J-2 and the by-products. The resultant was columned by dichloromethane and hexane such that compound K-1 was obtained.

50 (2) compound 15

[0129]

[Reaction Formula 15-2]



[0130] In the N₂ gas purging system, compound K-1 was dissolved in toluene, and compound G-1 (1.2 equivalent) was added. K₂CO₃ (4.4 equivalent), which was dissolved in DI water, was added into the mixture. After adding tetrahydrofuran, and Pd (0.05 equivalent) was added. The mixture was refluxed and stirred under a temperature of 80 °C. The mixture was extracted and was re-crystallized for separation of compound K-1, compound G-1 and the by-products. The resultant was columned by dichloromethane and hexane such that compound 15 was obtained.

[0131] The mass spectrum data of the above compounds 1 to 15 are listed in Table 2.

Table 2

		Calculation	Found (M(H ⁺))
Com1	C ₃₉ H ₂₄ N ₄	548.20	548.57
Com2	C ₂₉ H ₁₈ N ₂	394.15	395.35
Com3	C ₂₉ H ₁₈ N ₂	394.15	395.24
Com4	C ₄₀ H ₂₅ N ₃	547.20	547.95
Com5	C ₄₀ H ₂₆ N ₄	562.22	563.17
Com6	C ₃₀ H ₂₀ N ₂	408.16	408.96
Com7	C ₄₁ H ₂₇ N ₃	561.22	562.18
Com8	C ₅₇ H ₃₃ N ₅	787.27	787.94
Com9	C ₅₁ H ₃₁ N ₅	713.26	714.03
Com10	C ₅₃ H ₃₁ N ₃	709.25	710.32
Com11	C ₄₇ H ₂₉ N ₃	635.24	636.04
Com12	C ₅₈ H ₃₄ N ₄	786.28	787.16
Com13	C ₅₂ H ₃₂ N ₄	712.26	713.04
Com14	C ₆₀ H ₃₄ N ₂ O ₂ S	846.23	846.94
Com15	C ₅₄ H ₃₂ N ₂ O ₂ S	772.22	773.16

[0132] The emission properties of the above compounds 1, 2, 8 and 9 (Com1, Com2, Com8 and Com9) are measured and the results are listed in Table 3 and shown in FIGs. 2A to 12D. (Quantarus tau apparatus of Hamamatsu Co., Ltd. O₂ free condition)

Table 3

	Prompt (ns)	Delayed (ns)
Com1	9.87	6510.17
Com2	11.58	363.95
Com8	1062	4427.47
Com9	13.75	3829.81

[0133] As shown in Table 3 and FIGs. 2A to 2D, the delayed fluorescence compounds (Com1, Com2, Com8 and Com9) of the present invention show the delayed fluorescent emission of hundreds to hundreds of thousands nano-seconds (ns).

[0134] The maximum absorption peak (MAP), the maximum emission peak (MEP) and Stocks-shift value of the above compound 1 are listed in Table 4.

Table 4

	Δf	최대 흡수파장 cm ⁻¹ (nm)	발광 파장 cm ⁻¹ (nm)	Stock shift cm ⁻¹
CHCl ₃	0.1492	29586 (338)	21366 (468)	8220
Toluene	0.0159	29586 (338)	23041 (434)	6545
Mx1 ^{a)}	0.0730	29586 (338)	22173 (451)	7413
MX2 ^{b)}	0.1798	29586(338)	20833(480)	8753
MX3 ^{c)}	0.1131	29586 (338)	21505 (465)	8081
MX4 ^{d)}	0.1035	29586 (338)	21724 (460)	7862
a)Mx1 (mixed solvent of CHCl ₃ /Cyclohexane = 1/1), b)Mx2 (Mixed solvent of CHCl ₃ /THF = 1/1), c)MX3 (Mixed solvent of Toluene/THF = 1/1), d)Mx4 (Mixed solvent of Cyclohexane/THF = 1/1)				

[0135] As listed in Table 4, the delayed fluorescence compounds of the present invention has the maximum absorption peak of 338nm regardless the kinds of the solvents, while the emission spectrums are various according to the kinds of the solvents. Namely, the delayed fluorescence compound of the present invention has a relatively low maximum emission peak, i.e., 434nm, in the solvent of toluene having a relatively low polarity and a relatively high maximum emission peak, i.e., 480nm, in the solvent of CHCl₃ and THF having a relatively low polarity. As a result, as the polarity of the solvent is increased, the maximum emission peak of the delayed fluorescence compound is red-shifted.

[0136] As mentioned above, the delayed fluorescence compound of the present invention is activated by the field such that the excitons in the singlet state "S₁" and the triplet state "T₁" are transited into the intermediated state "I₁". As a result, both the exciton in the singlet state "S₁" and the exciton in the triplet state "T₁" are engaged in the emission.

[0137] The FADF compound is a single molecule compound having the electron donor moiety and the electron acceptor moiety in the single molecule with or without another electron donor moiety such that the charge transfer is easily generated. In the FADF compound with particular conditions, the charge can be separated from the electron donor moiety to the electron acceptor moiety.

[0138] The FADF compound is activated by outer factors. It can be verified by comparing the absorption peak and the emission peak of the solution of the compounds.

$$\Delta\nu = \nu_{abs} - \nu_{fl} = \frac{2\Delta\mu^2}{hca^3}\Delta f + constant \quad (\text{Lippert - Mataga equation})$$

[0139] In the above equation, " $\Delta\nu$ " is the Stock-shift value, and " ν_{abs} " and " ν_{fl} " are the wave-number of the maximum absorption peak and the maximum emission peak, respectively. " h " is Planck's constant, " c " is the velocity of light, " a " is the onsager cavity radius, and " $\Delta\mu$ " is a difference between the dipole moment of the excited state and the dipole moment of the ground state. ($\Delta\mu = \mu_e - \mu_g$)

[0140] " Δf " is a value indicating the orientational polarizability of the solvent and may be a function of the dielectric constant of the solvent (ϵ) and the refractive index of the solvent (n).

$$\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$

[0141] Since the intensity of dipole moment in the excited state is determined by the peripheral polarity (e.g., the polarity of the solvent), the FADF can be verified by comparing the absorption peak and the emission peak of the solution of the compounds.

[0142] The orientational polarizability (Δf) of the mixed solvent can be calculated by using the orientational polarizability of each pure solvent and their mole fraction. When " Δf " and " $\Delta\nu$ " are linearly plotted by using above "Lippert-Mataga equation", the compound may provide the FADF emission.

[0143] Namely, when the FADF complex is stabilized according to the orientational polarizability of the solvent, the emission peak is shifted in a long wavelength according to the degree of the stabilization. Accordingly, when the compound

provides the FADF emission, " Δf " and " Δv " are plotted in a linear line. When " Δf " and " Δv " are plotted in a linear line, the compound provides the FADF emission.

[0144] Referring to FIG. 3, which are "Lippert-Mataga plot" graphs of the compound 1 (Com1), " Δf " and " Δv " in the compound 1 provide the linear relation ($R^2 > 0.94$). Namely, the delayed fluorescence compound of the present invention

provides the FADF emission where both the singlet exciton and the triplet exciton are engaged in the emission.
[0145] In the delayed fluorescence compound of the present invention, the 25% excitons in the singlet state and the 75% excitons in the triplet state are transited into the intermediate state by an outer force, i.e., a field generated when the OLED is driven. (Intersystem crossing) The excitons in the intermediate state are transited into the ground state such that the emitting efficiency is improved. Namely, in the fluorescent compound, since the singlet exciton and the triplet exciton are engaged in the emission, the emitting efficiency is improved.

OLED

[0146] An ITO layer is deposited on a substrate and washed to form an anode (3mm*3mm). The substrate is loaded in a vacuum chamber, and a hole injecting layer (40Å, NPB(N,N'-di(naphthalen-1-yl)-N,N'-diphenyl-benzidine)), a hole transporting layer (10Å, mCP(N,N'-Dicarbazolyl-3,5-benzene)), an emitting material layer (200Å, host (bis{2-[di(phenyl)phosphino]phenyl}ether oxide) and dopant (15%)), an electron transporting layer (300Å, 1,3,5-tri(phenyl-2-benzimidazole)-benzene), an electron injecting layer (10Å, LiF), and a cathode (Al) are sequentially formed on the anode under a base pressure of about 10^{-6} to 10^{-7} Torr.

(1) Comparative Example (Ref)

[0147] The reference compound in Formula 6 is used as the dopant to form the OLED.

(2) Example 1 (Ex1)

[0148] The compound 1 is used as the dopant to form the OLED.

(3) Example 2 (Ex2)

[0149] The compound 2 is used as the dopant to form the OLED.

(4) Example 3 (Ex3)

[0150] The compound 4 is used as the dopant to form the OLED.

(5) Example 4 (Ex4)

[0151] The compound 8 is used as the dopant to form the OLED.

(6) Example 5 (Ex5)

[0152] The compound 9 is used as the dopant to form the OLED.

(7) Example 6 (Ex6)

[0153] The compound 11 is used as the dopant to form the OLED.

(8) Example 7 (Ex7)

[0154] The compound 12 is used as the dopant to form the OLED.

(9) Example 8 (Ex8)

[0155] The compound 15 is used as the dopant to form the OLED.

[Formula 6]

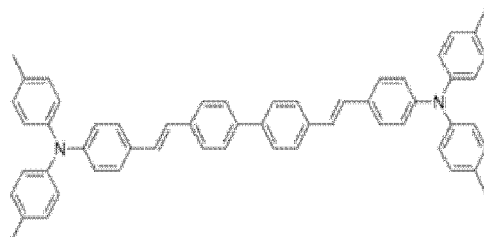


Table 5

	Voltage (V)	Cd/A	lm/W	EQE (%)	CIE (X)	CIE (Y)
Ref	7.94	4.84	1.91	2.99	0.182	0.169
Ex1	5.89	15.26	8.14	7.20	0.173	0.108
Ex2	5.51	10.61	6.05	6.29	0.175	0.111
Ex3	5.15	11.55	7.05	6.87	0.170	0.103
Ex4	5.21	12.14	7.32	6.78	0.174	0.094
Ex5	5.73	12.12	6.65	6.93	0.171	0.107
Ex6	5.09	11.54	7.12	6.87	0.170	0.121
Ex7	6.05	10.74	5.57	6.36	0.172	0.116
Ex8	4.67	8.48	5.71	5.45	0.163	0.128

[0156] As shown in Table 5, in the OLEDs using the compounds of the present invention (Ex1 to Ex8), the properties in the driving voltage, the color purity and the emitting efficiency are improved.

[0157] FIG. 4 is a schematic cross-sectional view of an OLED according to the invention.

[0158] As shown in FIG. 4, the OLED "E" is formed on a substrate (not shown). The OLED "E" includes a first electrode 110 as an anode, a second electrode 130 as a cathode and an organic emitting layer 120 therebetween.

[0159] Although not shown, an encapsulation film, which includes at least one inorganic layer and at least one organic layer and covers the OLED "E", and a cover window on the encapsulation film may be further formed to form a display device including the OLED "E". The substrate, the encapsulation film and the cover window may have a flexible property such that a flexible display device may be provided.

[0160] The first electrode 110 is formed of a material having a relatively high work function, and the second electrode 130 is formed of a material having a relatively low work function. For example, the first electrode 110 may be formed of indium-tin-oxide (ITO), and the second electrode 130 may be formed of aluminum (Al) or Al alloy (AlNd). The organic emitting layer 120 may include red, green and blue emitting patterns.

[0161] The organic emitting layer 120 may have a single-layered structure. Alternatively, to improve the emitting efficiency, the organic emitting layer 120 includes a hole injection layer (HIL) 121, a hole transporting layer (HTL) 122, an emitting material layer (EML) 123, an electron transporting layer (ETL) 124 and an electron injection layer (EIL) 125 sequentially stacked on the first electrode 110.

[0162] At least one selected from the HIL 121, the HTL 122, the EML 123, the ETL 124 and the EIL 125 includes the delayed fluorescence compound in the Formula 1.

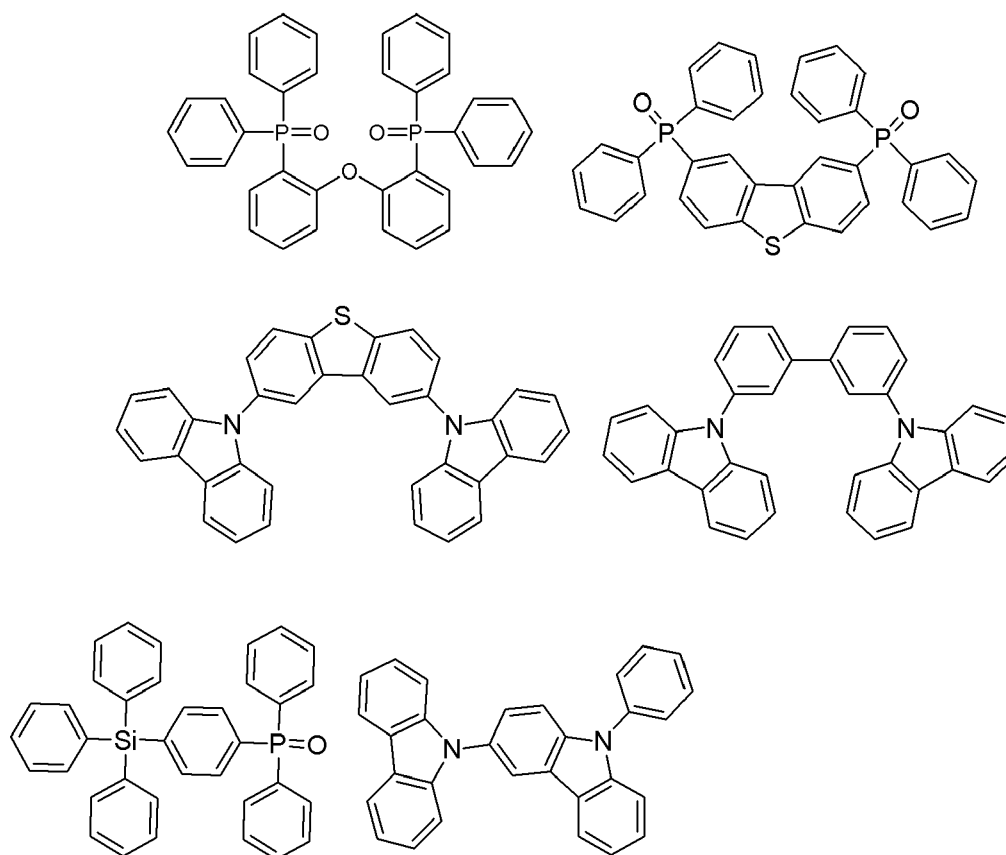
[0163] For example, the EML 123 may include the delayed fluorescence compound in the Formula 1. The delayed fluorescence compound acts as the dopant, and the EML 123 may further include a host to emit the blue light. In this instance, the dopant has about 1 to 30 weight % with respect to the host.

[0164] A difference between the HOMO of the host "HOMO_{Host}" and the HOMO of the dopant "HOMO_{Dopant}" or a difference between the LUMO of the host "LUMO_{Host}" and the LUMO of the dopant "LUMO_{Dopant}" is less than 0.5 eV. ($|HOMO_{Host} - HOMO_{Dopant}| \leq 0.5\text{eV}$ or $|LUMO_{Host} - LUMO_{Dopant}| \leq 0.5\text{eV}$) In this instance, the charge transfer efficiency from the host to the dopant may be improved.

[0165] For example, the host, which meets the above condition, may be selected from materials in Formula 7. (Bis[2-(diphenylphosphino)phenyl]ether oxide (DPEPO), 2,8-bis(diphenylphosphoryl)dibenzothiophene (PPT), 2,8-

di(9H-carbazol-9-yl)dibenzothiophene (DCzDBT), m-bis(carbazol-9-yl)biphenyl (m-CBP), Diphenyl-4-triphenylsilylphenyl-phosphine oxide (TPSO1), 9-(9-phenyl-9H-carbazol-6-yl)-9H-carbazole (CCP) in an order)

[Formula 7]



[0166] The triplet energy of the dopant is smaller than the triplet energy of the host, and a difference between the singlet energy of the dopant and the triplet energy of the dopant is less than 0.3eV. ($\Delta E_{ST} \leq 0.3\text{eV}$) As the difference " ΔE_{ST} " is smaller, the emitting efficiency is higher. In the delayed fluorescence compound of the present invention, even if the difference " ΔE_{ST} " between the singlet energy of the dopant and the triplet energy of the dopant is about 0.3eV, which is relatively large, the excitons in the singlet state "S1" and the excitons in the triplet state "T1" can be transited into the intermediate state "II".

[0167] On the other hand, the delayed fluorescence compound of the present invention may act as a host in the EML 123, and the EML 123 may further include a dopant to emit the blue light. In this instance, the dopant has about 1 to 30 weight % with respect to the host. Since the development of the blue host having excellent properties is insufficient, the delayed fluorescence compound of the present invention may be used as the host to increase the degree of freedom for the host. In this instance, the triplet energy of the dopant may be smaller than the triplet energy of the host of the delayed fluorescence compound of the present invention.

[0168] The EML 123 may include a first dopant of the delayed fluorescence compound of the present invention, a host and a second dopant. The weight % summation of the first and second dopants may be about 1 to 30 to emit the blue light. In this instance, the emitting efficiency and the color purity may be further improved.

[0169] In this instance, the triplet energy of the first dopant, i.e., the delayed fluorescence compound of the present invention, may be smaller than the triplet energy of the host and larger than the triplet energy of the second dopant. In addition, a difference between the singlet energy of the first dopant and the triplet energy of the first dopant is less than 0.3eV. ($\Delta E_{ST} \leq 0.3\text{eV}$) As the difference " ΔE_{ST} " is smaller, the emitting efficiency is higher. In the delayed fluorescence compound of the present invention, even if the difference " ΔE_{ST} " between the singlet energy of the dopant and the triplet energy of the dopant is about 0.3eV, which is relatively large, the excitons in the singlet state "S₁" and the excitons in the triplet state "T₁" can be transited into the intermediate state "I₁".

[0170] As mentioned above, since the delayed fluorescence compound of the present invention includes the electron donor moiety and the electron acceptor with or without another electron donor moiety, the charge transfer in the molecule

is easily generated such that the emitting efficiency of the compound is improved. In addition, the dipole from the first and second electron donor moieties to the electron acceptor moiety is generated such that the dipole moment in the molecule is increased. As a result, the emitting efficiency is further improved. Moreover, in the delayed fluorescent compound of the present invention, the excitons in the triplet state are engaged in the emission such that the emitting efficiency of the delayed fluorescent compound is increased.

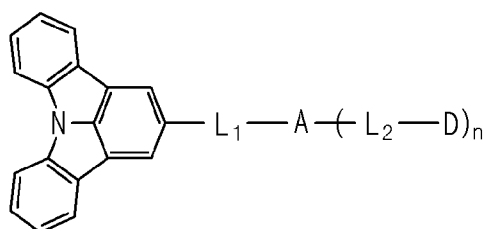
[0171] Accordingly, the OLED and the display device using or including the delayed fluorescence compound of the present invention has an advantage in the emitting efficiency.

[0172] It will be apparent to those skilled in the art that various modifications and variations can be made in the embodiment of the invention without departing from the spirit or scope of the invention. Thus, it is intended that the embodiment of the invention cover the modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.

Claims

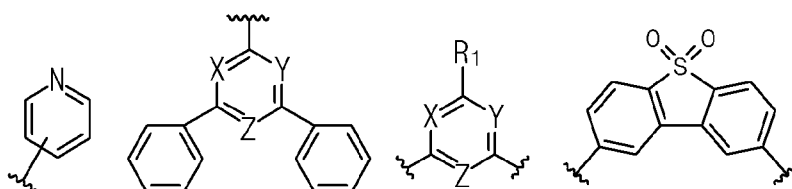
1. A delayed fluorescence compound of Formula 1:

[Formula 1]

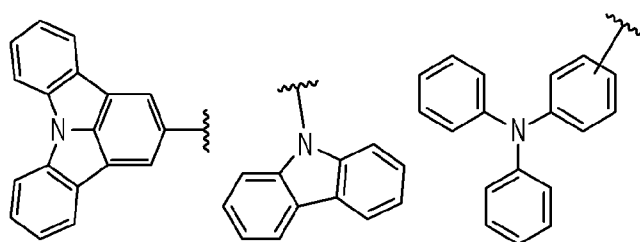


wherein n is 1 or 0, and A is selected from Formula 2, wherein D is selected from Formula 3, and each of L1 and L2 is independently selected from Formula 4:

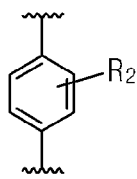
[Formula 2]



[Formula 3]



[Formula 4]



wherein R1 in the Formula 2 is selected from hydrogen or phenyl, and each of X, Y and Z is independently selected from carbon and nitrogen, and wherein at least two selected from X, Y and Z are nitrogen, and R2 in the Formula 4 is selected from hydrogen or C1~C10 alkyl.

2. The delayed fluorescence compound according to claim 1, wherein a difference between a singlet energy of the delayed fluorescence compound and a triplet energy of the delayed fluorescence compound is less than 0.3eV.

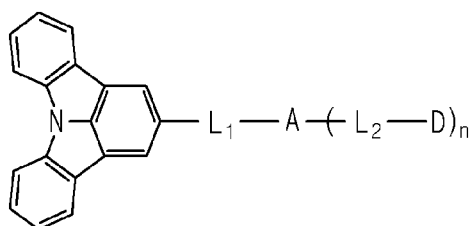
3. An organic light emitting diode, comprising:

a first electrode;

a second electrode facing the first electrode; and

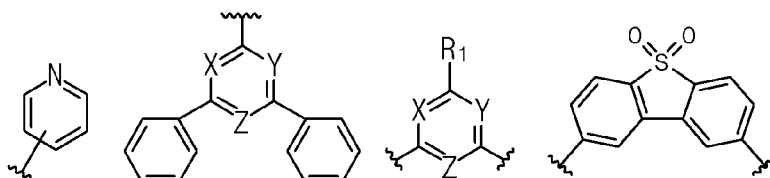
an organic emitting layer between the first and second electrodes and including a delayed fluorescence compound of Formula 1:

[Formula 1]

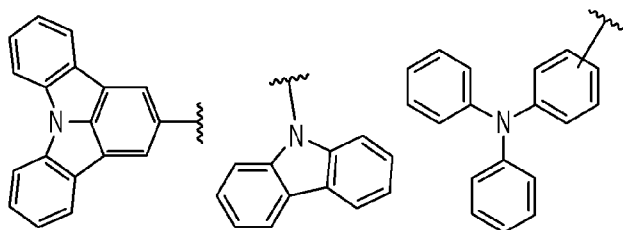


wherein n is 1 or 0, and A is selected from Formula 2, wherein D is selected from Formula 3, and each of L1 and L2 is independently selected from Formula 4:

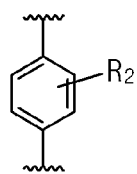
[Formula 2]



[Formula 3]



[Formula 4]



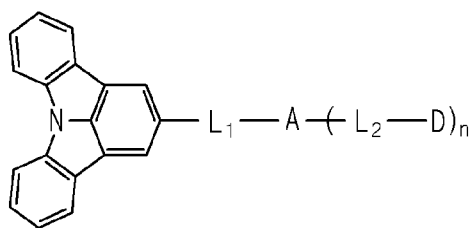
wherein R1 in the Formula 2 is selected from hydrogen or phenyl, and each of X, Y and Z is independently selected from carbon and nitrogen, and wherein at least two selected from X, Y and Z are nitrogen, and R2 in the Formula 4 is selected from hydrogen or C1~C10 alkyl.

4. The organic light emitting diode according to claim 3, wherein the organic emitting layer includes a hole injection layer (HIL), a hole transporting layer (HTL), an emitting material layer (EML), an electron transporting layer (ETL) and an electron injection layer (EIL), and wherein at least one from selected the HIL, the HTL, the EML, the ETL and the EIL includes the delayed fluorescence compound.
5. The organic light emitting diode according to claim 3 and/or claim 4, wherein a difference between a singlet energy of the delayed fluorescence compound and a triplet energy of the delayed fluorescence compound is less than 0.3eV.
6. The organic light emitting diode according to any one of claims 3 to 5, wherein the organic emitting layer further includes a host, and the delayed fluorescence compound is used as a dopant.
7. The organic light emitting diode according to claim 6, wherein a difference between a HOMO of the host and a HOMO of the dopant or a difference between the LUMO of the host and the LUMO of the dopant is less than 0.5 eV.
8. The organic light emitting diode according to any one of claims 3 to 5, wherein the organic emitting layer further includes a dopant, and the delayed fluorescence compound is used as a host.
9. The organic light emitting diode according to any one of claims 3 to 5, wherein the organic emitting layer further includes a host and a first dopant, and the delayed fluorescence compound is used as a second dopant, and wherein a triplet energy of the second host is smaller than the triplet energy of the host and larger than the triplet energy of the first dopant.
10. A display device, comprising:
 - a substrate;
 - an organic light emitting diode on the substrate and including a first electrode, a second electrode facing the first electrode and an organic emitting layer between the first and second electrodes and including a delayed fluorescence compound of Formula 1;
 - an encapsulation film on the organic light emitting diode; and
 - a cover window on the encapsulation film,

[Formula 1]

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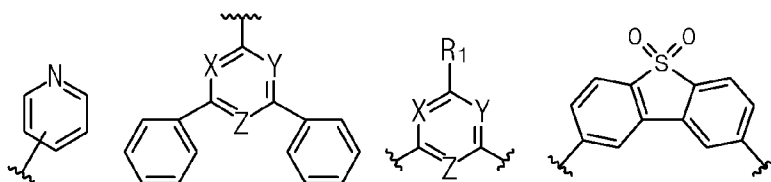
wherein n is 1 or 0, and A is selected from Formula 2, wherein D is selected from Formula 3, and each of L1 and L2 is independently selected from Formula 4:

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[Formula 2]

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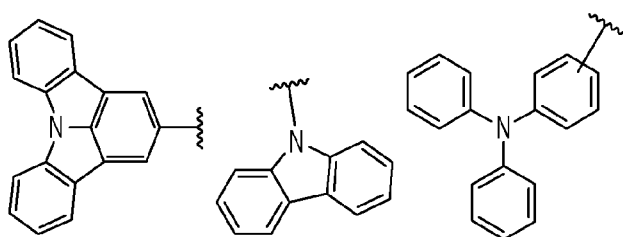


[Formula 3]

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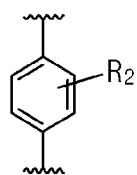
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[Formula 4]

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wherein R1 in the Formula 2 is selected from hydrogen or phenyl, and each of X, Y and Z is independently selected from carbon and nitrogen, and wherein at least two selected from X, Y and Z are nitrogen, and R2 in the Formula 4 is selected from hydrogen or C1~C10 alkyl.

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FIG. 1

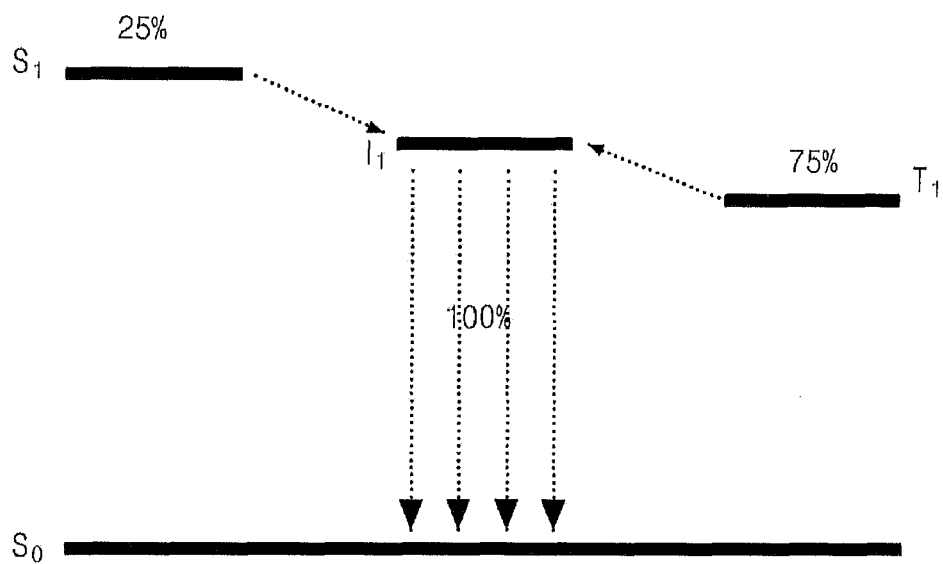


FIG. 2A

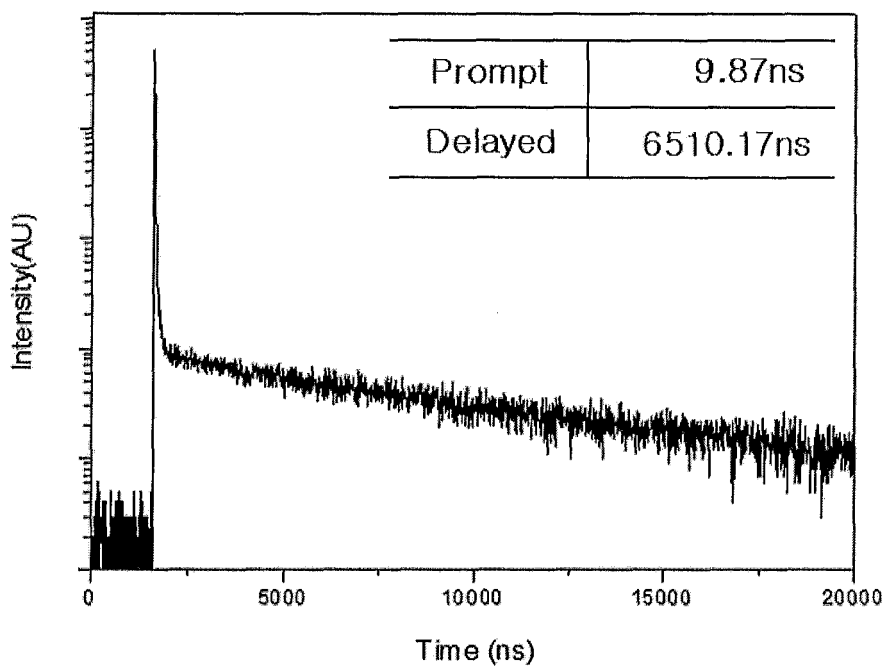


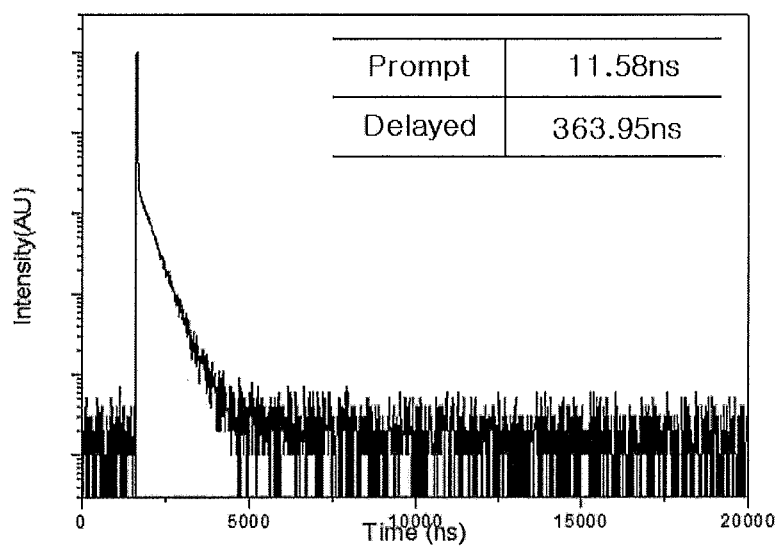
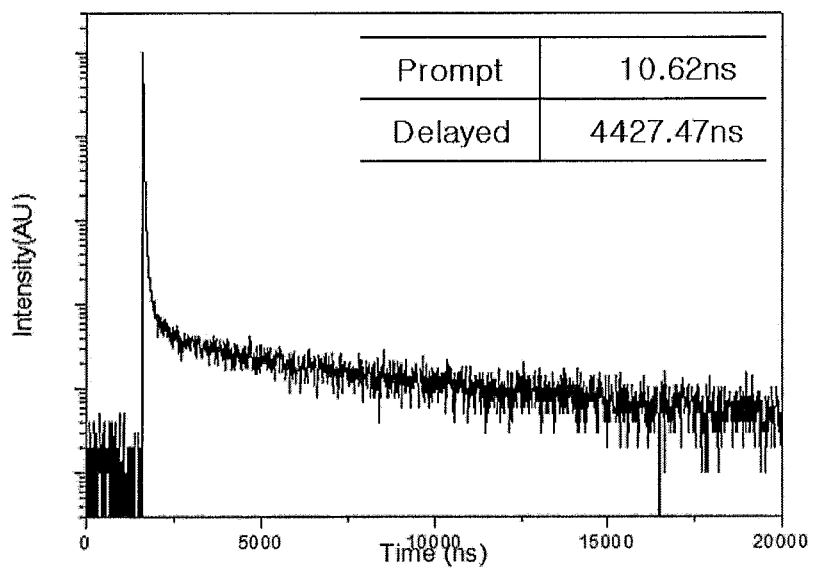
FIG. 2B**FIG. 2C**

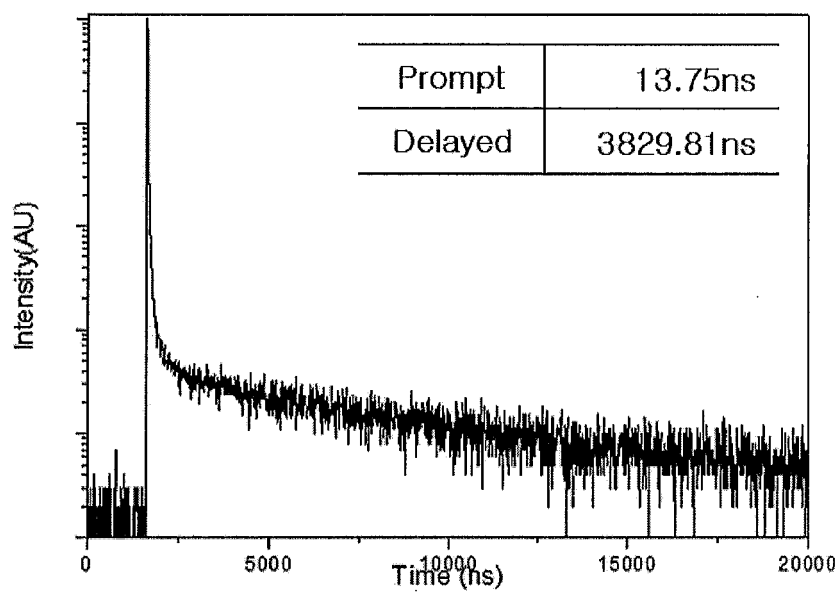
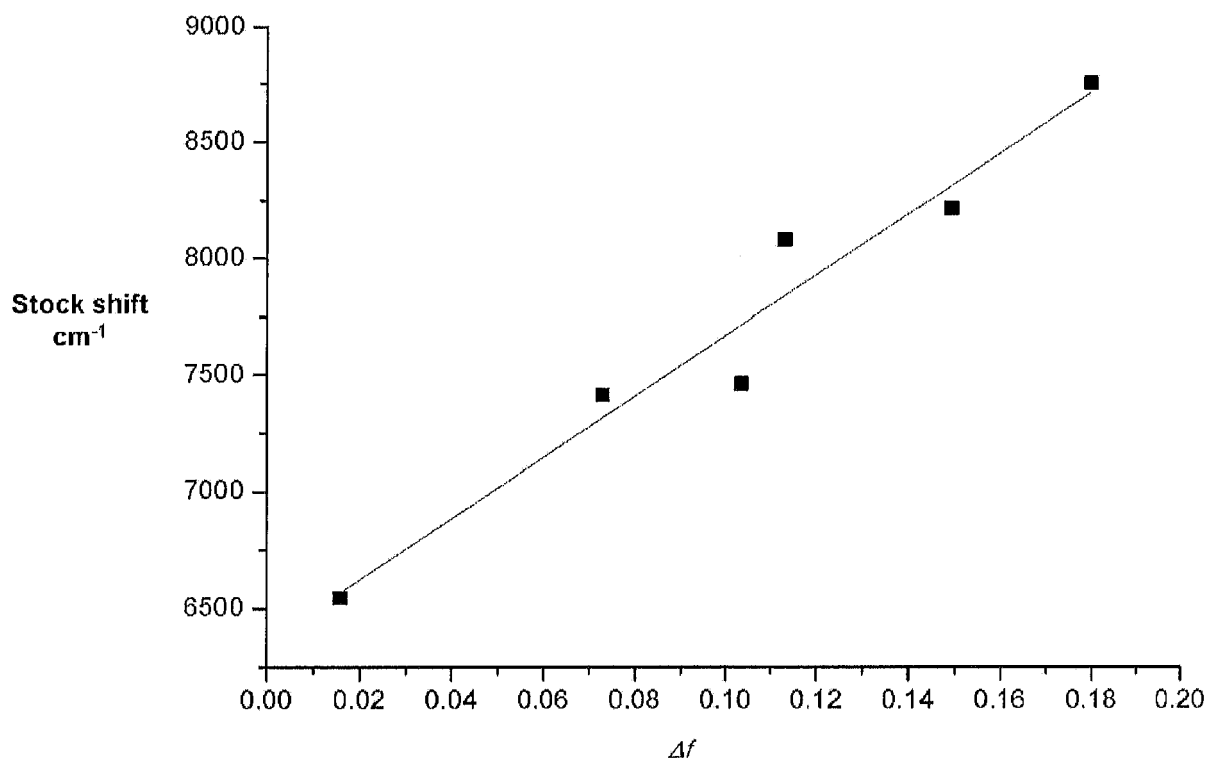
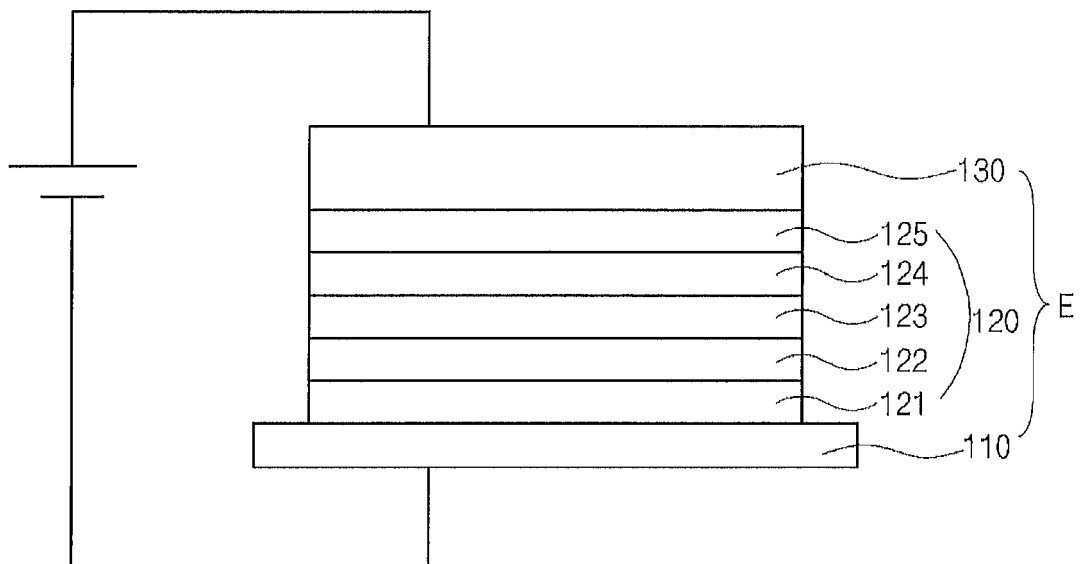
FIG. 2D**FIG. 3**

FIG. 4





EUROPEAN SEARCH REPORT

Application Number
EP 15 18 9883

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A	US 2014/034914 A1 (TAKADA SAKI [JP] ET AL) 6 February 2014 (2014-02-06) * paragraph [0111] * * claim 1 * -----	1-10	TECHNICAL FIELDS SEARCHED (IPC)
A	JP 2012 191031 A (KONICA MINOLTA HOLDINGS INC) 4 October 2012 (2012-10-04) * compounds 1-103 * -----	1-10	C09K H01L
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 12 February 2016	Examiner Poole, Robert
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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EP 15 18 9883

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12-02-2016

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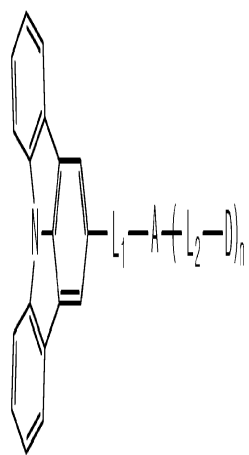
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专利名称(译)	延迟荧光化合物，以及使用其的有机发光二极管和显示装置		
公开(公告)号	EP3009494A1	公开(公告)日	2016-04-20
申请号	EP2015189883	申请日	2015-10-15
[标]申请(专利权)人(译)	乐金显示有限公司		
申请(专利权)人(译)	LG DISPLAY CO. , LTD.		
当前申请(专利权)人(译)	LG DISPLAY CO. , LTD.		
[标]发明人	YANG JOONG HWAN YOON KYUNG JIN NOH HYO JIN YOON DAE WI SHIN IN AE KIM JUN YUN		
发明人	YANG, JOONG-HWAN YOON, KYUNG-JIN NOH, HYO-JIN YOON, DAE-WI SHIN, IN-AE KIM, JUN-YUN		
IPC分类号	C09K11/06 H01L51/50 C07D487/06 C09K11/02 H01L27/32 H01L51/00		
CPC分类号	H01L51/0072 C07D487/06 C09K11/02 C09K11/06 C09K2211/1007 C09K2211/1011 C09K2211/1029 C09K2211/1044 C09K2211/1059 C09K2211/1092 H01L27/3258 H01L51/005 H01L51/0067 H01L51/0074 H01L51/5004 H01L51/5012 H01L51/5016 H01L2251/552		
审查员(译)	普尔ROBERT		
优先权	1020140140970 2014-10-17 KR 1020140140969 2014-10-17 KR 1020150130518 2015-09-15 KR 1020150130519 2015-09-15 KR		
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摘要(译)

讨论的是式1的延迟荧光化合物：其中n是1或0，并且A选自式2：其中D选自式3：并且“L1”和“L2”中的每一个独立地选自式4：其中式2中的R 1选自氢或苯基，X，Y和Z各自独立地选自碳和氮，并且其中选自X，Y和Z中的至少两个是氮，并且式4中的R 2选自氢或C1~C10烷基。



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