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Korai et al.

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(54) **COPOLYMER, ORGANIC LIGHT-EMITTING DEVICE MATERIAL INCLUDING THE SAME, AND ORGANIC LIGHT-EMITTING DEVICE INCLUDING THE ORGANIC LIGHT-EMITTING DEVICE MATERIAL**

(71) Applicant: **SAMSUNG ELECTRONICS CO., LTD.**, Suwon-si, Gyeonggi-do (KR)

(72) Inventors: **Keisuke Korai**, Yokohama (JP);
Mitsunori Ito, Yokohama (JP)

(73) Assignee: **SAMSUNG ELECTRONICS CO., LTD.**, Gyeonggi-Do (KR)

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C08F 226/12 (2006.01)
H01L 51/00 (2006.01)

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CPC **C08F 226/12** (2013.01); **H01L 51/0039** (2013.01); **H01L 51/0043** (2013.01); **H01L 51/5016** (2013.01); **H01L 51/5056** (2013.01)

(58) **Field of Classification Search**
None
See application file for complete search history.

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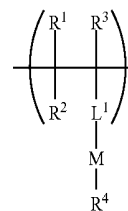
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Primary Examiner — Gregory D Clark

(74) *Attorney, Agent, or Firm* — Cantor Colburn LLP

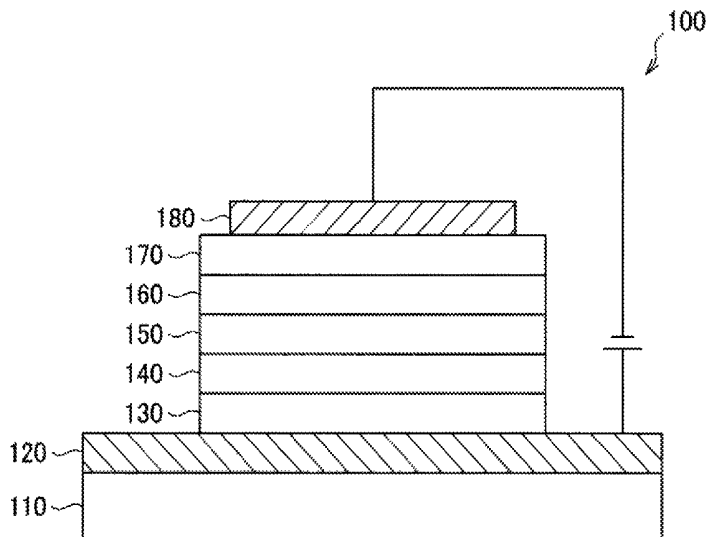
(57) **ABSTRACT**

A copolymer including a unit represented by Formula 1 and a unit represented by Formula 2:

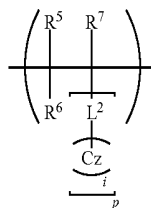


Formula 1

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Formula 2

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wherein, in Formulae 1 and 2, groups and variables are the same as described in the specification.

20 Claims, 1 Drawing Sheet

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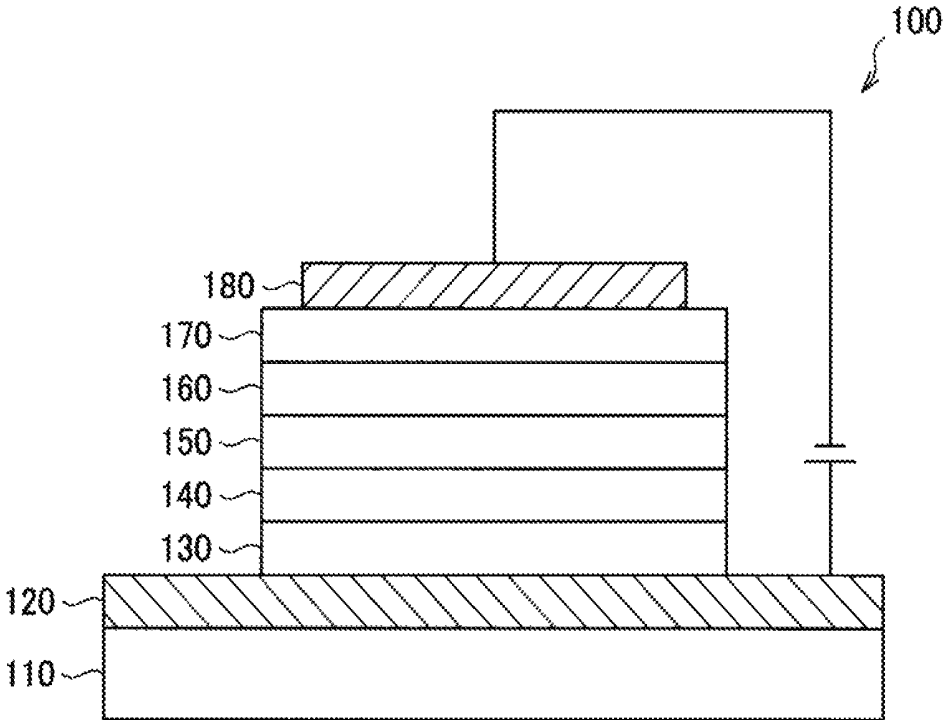
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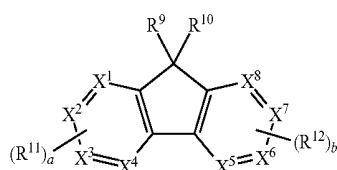
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group; a substituted or unsubstituted C6-C30 oxyarylene group; a substituted or unsubstituted C7-C40 aralkyl arylene group; a substituted or unsubstituted C6-C30 amino arylene group; a silylene group substituted with a C1-C20 alkyl group; a silylene group substituted with a C6-C30 aryl group, and a combination thereof,

R⁹ may be selected from a hydrogen, a substituted or unsubstituted C1-C20 alkyl group; a substituted or unsubstituted C3-C16 cycloalkyl group; a substituted or unsubstituted C6-C30 aryl group; a substituted or unsubstituted C1-C20 alkoxy group; a substituted or unsubstituted C3-C16 cyclo alkoxy group; a substituted or unsubstituted C6-C30 aryloxy group; a substituted or unsubstituted C7-C40 aralkyl group; a substituted or unsubstituted C1-C30 heteroaryl group; a substituted or unsubstituted C2-C40 heteroaralkyl group; a substituted or unsubstituted C1-C20 alkylamino group; and a substituted or unsubstituted C6-C30 arylamino group, wherein R⁸ may optionally form a ring by binding with L³ or L⁴, and

* may be a binding site with an adjacent atom. The copolymer may improve the emission lifespan of an organic light-emitting device.

In some embodiments, A in M of Formula 1 may be a group represented by Formula 4, in which any two of R⁹ to R¹² may be bound to adjacent atoms:



Formula 4

wherein, in Formula 4,

R⁹ to R¹² may each independently be selected from a hydrogen, a halogen atom, a hydroxyl group, an amino group, a nitro group, a cyano group; a substituted or unsubstituted silyl group; a substituted or unsubstituted C1-C20 alkyl group; a substituted or unsubstituted C3-C16 cycloalkyl group; a substituted or unsubstituted C6-C30 aryl group; a substituted or unsubstituted C6-C30 aryloxy group; a substituted or unsubstituted C7-C40 aralkyl group; a substituted or unsubstituted C1-C30 heteroaryl group; a substituted or unsubstituted C2-C40 heteroaralkyl group; a substituted or unsubstituted C1-C20 alkylamino group; a substituted or unsubstituted C6-C30 arylamino group, and a substituted or unsubstituted C6-C30 arylsulfonyl group, wherein any two adjacent groups selected from R⁹ to R¹² may optionally form a ring,

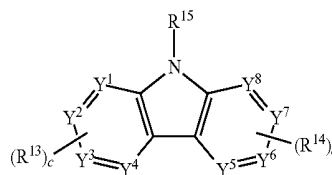
a and b may each independently be an integer from 1 to 4, and

X¹ to X⁸ may each independently be CH or N. The copolymer may improve the emission lifespan of an organic light-emitting device.

In some embodiments, X¹ to X⁹ may each independently be CH or N. The copolymer may improve the lifespan of an organic light-emitting device.

In some embodiments, Cz may be represented by Formula 5. Any two of R¹³ to R¹⁵ in Formula 5 may be bound to an adjacent atom:

4



Formula 5

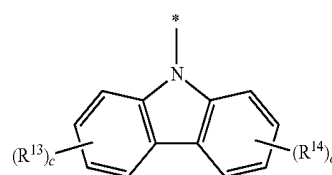
wherein, in Formula 5,

Y¹ to Y⁸ may each independently be CH or N,

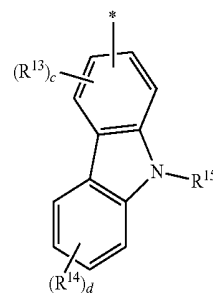
R¹³ to R¹⁵ may each independently be a hydrogen, a halogen atom, a hydroxyl group, an amino group, a nitro group, a cyano group; a substituted or unsubstituted silyl group; a substituted or unsubstituted C1-C20 alkyl group; a substituted or unsubstituted C1-C20 amino alkyl group; a substituted or unsubstituted C3-C16 cycloalkyl group; a substituted or unsubstituted C6-C30 aryl group; a substituted or unsubstituted C6-C30 amino aryl group; a substituted or unsubstituted C1-C30 heteroaryl group; a substituted or unsubstituted C1-C20 alkoxy group; a substituted or unsubstituted C3-C16 cyclo alkoxy group; a substituted or unsubstituted C6-C30 aryloxy group; a substituted or unsubstituted C7-C40 aralkyl group; a substituted or unsubstituted C2-C40 heteroaralkyl group; a substituted or unsubstituted C1-C20 alkylamino group, or a substituted or unsubstituted C6-C30 arylamino group, wherein any two adjacent groups selected from R¹³ to R¹⁵ may optionally form a ring, and

c and d may each independently be an integer from 0 to 4.

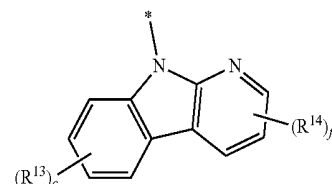
In some embodiments, Cz may be represented by Formula 6 or Formula 7, and any one of R¹³ and R¹⁴ may be bound to an adjacent atom:



Formula 6



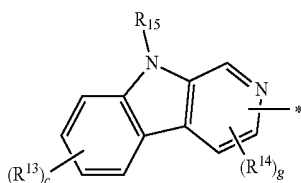
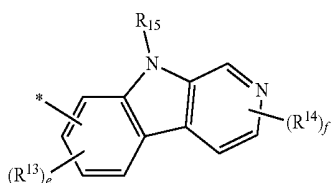
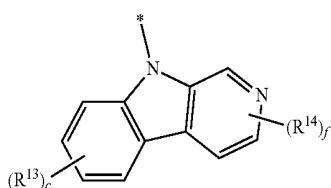
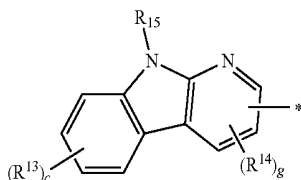
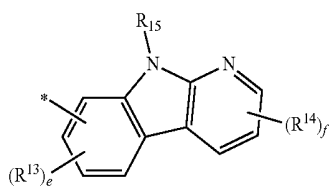
Formula 7



Formula 8

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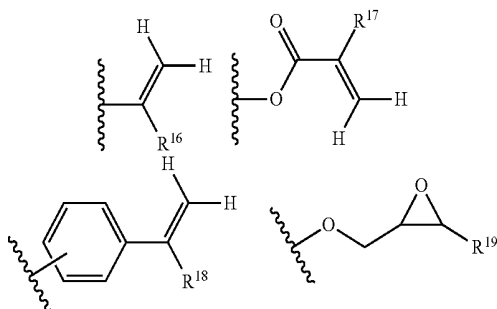
wherein, in Formula 6 to Formula 13,

R^{13} to R^{15} , c, and d may be the same as in Formula 5, e and f may each independently be an integer from 0 to 3, g may be an integer from 0 to 2, and

* may be a binding site with an adjacent atom.

In some embodiments, the copolymer may further include a polymerizable comonomer. The polymerizable comonomer may include at least one of cross-linking groups represented by the following formulae:

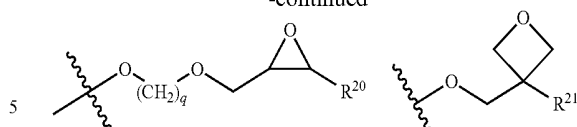
Cross-Linking Groups



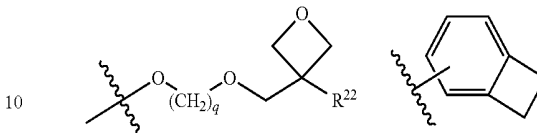
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Formula 9



Formula 10

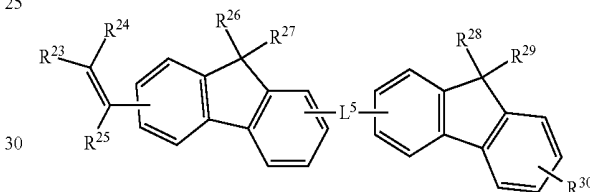


Formula 11

wherein, in the above formulae of the cross-linking groups, R^{16} to R^{22} may each independently be a hydrogen; or a substituted or unsubstituted C1-C10 alkyl group, and q may be an integer from 1 to 10. The copolymer may improve the emission lifespan of an organic light-emitting device.

The polymerizable comonomer may be a compound represented by Formula 14:

Formula 12



Formula 13

wherein, in Formula 14, R^{23} to R^{25} may each independently be selected from a hydrogen; a substituted or unsubstituted C1-C10 alkyl group; and a substituted or unsubstituted C6-C30 aryl group, R^{26} to R^{30} may each independently be selected from a hydrogen, a halogen atom, a hydroxyl group, an amino group, a nitro group, a cyano group; a substituted or unsubstituted silyl group; a substituted or unsubstituted C1-C10 alkyl group; a substituted or unsubstituted C3-C16 cycloalkyl group; a substituted or unsubstituted C6-C30 aryl group; a substituted or unsubstituted C1-C20 alkoxy group; a substituted or unsubstituted C6-C30 aryloxy group; a substituted or unsubstituted C7-C40 aralkyl group; a substituted or unsubstituted C1-C30 heteroaryl group; a substituted or unsubstituted C1-C20 alkylamino group, and a substituted or unsubstituted C6-C30 arylamino group, wherein any two adjacent groups selected from R^{26} to R^{30} may optionally form a ring,

L^5 may be selected from a single bond, a substituted or unsubstituted C1-C20 alkylene group; a substituted or unsubstituted C3-C16 cycloalkylene group; a substituted or unsubstituted C6-C30 arylene group; a substituted or unsubstituted C1-C20 oxyalkylene group; a substituted or unsubstituted C3-C16 oxycycloalkylene group; a substituted or unsubstituted C6-C30 oxyarylene group; a substituted or unsubstituted C7-C40 aralkylene group; a substituted or unsubstituted C1-C30 heteroarylene group; a substituted or unsubstituted C6-C30 amino arylene group; a silylene group substituted with a C1-C20 alkyl group, a silylene group substituted with a C6-C30 aryl group, and a combination thereof, and

at least one of R^{26} to R^{30} may be selected from the cross-linking groups. The copolymer may further improve the emission lifespan of an organic light-emitting device.

example, low-molecular weight materials and high-molecular weight materials are currently being considered. Among these materials, high-molecular weight materials have a high coating uniformity and may easily form stacked layers, and thus are under vigorous development. In particular, such high-molecular weight materials are applicable to displays or lighting fixtures, development of polymer-based hole transport materials is expected.

For example, organic light-emitting device materials obtained by polymerization of low-molecular weight materials through partial substitution of the low-molecular weight material with a vinyl group are disclosed in the following documents:

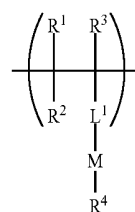
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 JP2001-098023
 JP2002-110359
 JP2003-313240
 JP2004-059743
 JP2006-237592
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However, organic light-emitting devices manufactured using the organic light-emitting devices materials disclosed in the above-identified documents by the solution coating method may have insufficient emission lifespan.

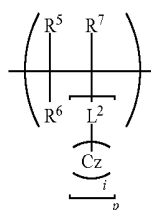
Therefore, to address this drawback, the present disclosure provides a copolymer having a novel structure that may improve the emission lifespan of an organic light-emitting device, an organic light-emitting device material including the copolymer, and an organic light-emitting device including the organic light-emitting device material.

Copolymer

According to an aspect of the present disclosure, a copolymer includes a unit represented by Formula 1 (hereinafter, also referred to as "aminofluorene unit") and a unit represented by Formula 2 (hereinafter, also referred to as "carbazole unit").



Formula 1



Formula 2

wherein, in Formulae 1 and 2,

R^1 to R^7 may each independently be selected from a hydrogen, a deuterium, a halogen atom, a hydroxyl group, an amino group, a nitro group, a cyano group; a substituted or unsubstituted silyl group; a substituted or unsubstituted C1-C20 alkyl group; a substituted or unsubstituted C3-C16 cycloalkyl group; a substituted or unsubstituted C6-C30 aryl group; a substituted or unsubstituted C1-C20 alkoxy

group; a substituted or unsubstituted C3-C16 cycloalkoxy group; a substituted or unsubstituted C6-C30 aryloxy group; a substituted or unsubstituted C7-C40 aralkyl group; a substituted or unsubstituted C1-C30 heteroaryl group; a substituted or unsubstituted C2-C40 heteroaralkyl group; a substituted or unsubstituted C1-C20 alkylamino group; and a substituted or unsubstituted C6-C30 arylamino group,

L^1 may be selected from a single bond, a substituted or unsubstituted C1-C20 alkylene group; a substituted or unsubstituted C3-C30 cycloalkylene group; a substituted or unsubstituted C10-C30 arylene group; a substituted or unsubstituted C1-C30 heteroarylene group; a substituted or unsubstituted divalent alkylamino group; a substituted or unsubstituted divalent arylamino group, and a combination thereof,

L^2 may be selected from a single bond, a substituted or unsubstituted C1-C20 alkylene group; a substituted or unsubstituted C3-C30 cycloalkylene group; a substituted or unsubstituted C6-C30 arylene group; a substituted or unsubstituted C1-C30 heteroarylene group; a substituted or unsubstituted divalent alkylamino group; a substituted or unsubstituted divalent arylamino group, and a combination thereof, when L^1 is an arylene group, the arylene group may be a C10-C30 arylene group,

Cz may be a group including a carbazole ring system or an aza carbazole ring system,

i may be an integer from 1 to 20,

M may be a group represented by $-(A-B)_n-A_m-$ or $-(B-A)_n-B_m-$,

n may be an integer from 1 to 20,

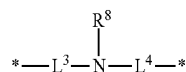
m may be an integer from 0 to 10,

p may be an integer from 1 to 10,

A may be a group including a fluorene ring system or an aza fluorene ring system, and

B may be a group represented by Formula 3,

Formula 3



40

wherein, in Formula 3,

L^3 and L^4 may each independently be selected from a single bond, a substituted or unsubstituted C1-C20 alkylene group; a substituted or unsubstituted C3-C16 cycloalkylene group; a substituted or unsubstituted C6-C30 arylene group; a substituted or unsubstituted C1-C20 oxyalkylene group; a substituted or unsubstituted C3-C16 oxycycloalkylene group; a substituted or unsubstituted C6-C30 oxyarylene group; a substituted or unsubstituted C7-C40 aralkyl arylene group; a substituted or unsubstituted C6-C30 amino arylene group; a silylene group substituted with a C1-C20 alkyl group; a silylene group substituted with a C6-C30 aryl group, and a combination thereof,

R^8 may be selected from a hydrogen, a substituted or unsubstituted C1-C20 alkyl group; a substituted or unsubstituted C3-C16 cycloalkyl group; a substituted or unsubstituted C6-C30 aryl group; a substituted or unsubstituted C1-C20 alkoxy group; a substituted or unsubstituted C3-C16 cycloalkoxy group; a substituted or unsubstituted C6-C30 aryloxy group; a substituted or unsubstituted C7-C40 aralkyl group; a substituted or unsubstituted C1-C30 heteroaryl group; a substituted or unsubstituted C2-C40 heteroaralkyl group; a substituted or unsubstituted C1-C20 alkylamino group; and a substituted or unsubsti-

tuted C6-C30 arylamino group, wherein R⁸ may optionally form a ring by binding with L³ or L⁴, and

* may be a binding site with an adjacent atom.

In some embodiments, when used in an organic light-emitting device, the copolymer may improve the emission lifespan. For example, the carbazole unit of the copolymer may contribute to increasing a glass transition temperature of the copolymer. Accordingly, the copolymer may have a high glass transition temperature, and thus, improved thermal stability. Therefore, an organic light-emitting device including the copolymer may be stable against heat generated during the operation. Thus, deterioration and deformation of the organic light-emitting device caused by the operating heat may be suppressed, so that the organic light-emitting device including the copolymer may have improved emission lifespan, as compared with conventional organic light-emitting devices.

Since the copolymer has a high glass transition temperature, denaturation or deformation of the copolymer by heat may not occur during solution coating. Furthermore, a layer formed from the copolymer may be insoluble in a solvent that is used to form another layer, so that the copolymer may be suitable to form stacked layers by a solution coating method.

An organic layer formed from the copolymer by a solution coating method may have no stains and may have a uniform thickness. Furthermore, the organic layer may have a planar surface, so that staining of the organic layer may be suppressed during application of a driving voltage or light emission.

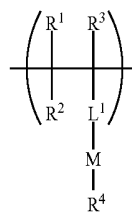
In detail, a carbon-carbon bond dissociation energy of a vinyl polymer in the cation radical state may be about 3 times higher than that of a vinyl polymer having a fluorenyl group at a polymerization site. Therefore, the copolymer according to an embodiment including a fluorenyl group at a polymerization site may be chemically stable, so that an organic light-emitting device including the copolymer may have improved emission lifespan.

The copolymer may have improved hole transport ability and improved hole injection ability. Therefore, the copolymer may be suitable for use as a hole transport material, a hole injection material, or a host material of an emission layer.

Hereinafter, the units of the copolymer according to an embodiment will now be described.

Aminofluorene Unit

The aminofluorene unit represented by Formula 1 is described below.



Formula 1

In Formula 1 of the aminofluorene unit, R¹ to R⁴ may each independently be selected from a hydrogen, a deuterium, a halogen atom, a hydroxyl group, an amino group, a nitro group, a cyano group; a substituted or unsubstituted silyl group; a substituted or unsubstituted C1-C20 alkyl group; a substituted or unsubstituted C3-C16 cyclo alkyl group; a substituted or unsubstituted C6-C30 aryl group; a substi-

tuted or unsubstituted C1-C20 alkoxy group; a substituted or unsubstituted C3-C16 cyclo alkoxy group; a substituted or unsubstituted C7-C40 aryloxy group; a substituted or unsubstituted C1-C30 heteroaryl group; a substituted or unsubstituted C1-C20 alkylamino group, and a substituted or unsubstituted C6-C30 arylamino group.

As used herein, the term “aza carbazole” is construed to include any and all compounds, in which at least one carbon of the carbazole ring system is replaced with nitrogen.

As used herein, the term “aza fluorene” is construed to include any and all compounds, in which at least one carbon in the fluorene ring system is replaced with nitrogen.

As used herein, the “hydrogen” is construed to also include deuterium, unless this term is recited together with “deuterium”. In addition, hydrogens in each substituent may also be interchangeable with deuterium, unless explicitly described to exclude deuterium.

As used herein, the “alkyl group” may be a linear or branched alkyl group. The linear or branched alkyl group is not specifically limited, and may be, for example, a linear alkyl group such as a methyl group, an ethyl group, a propyl group, a butyl group, an octyl group, a decyl group, and a pentadecyl group, or a branched alkyl group such as an iso-propyl group or a tert-butyl group (t-butyl group). For example, the number of carbon atoms of the linear or branched alkyl group may be 1 to 15, and in some embodiments, 1 to 10, and in some other embodiments, 2 to 9.

As used herein, the “cycloalkyl group” may be a monocyclic hydrocarbon group such as cyclobutyl group, a cyclopentyl group, a cyclohexyl group, and a cycloheptyl group, or may be a bridged hydrocarbon group such as a bicycloalkyl group and tricycloalkyl group. The number of carbon atoms of the cycloalkyl group is not specifically limited, and may be, for example, 3 to 12, and in some embodiments, 3 to 10, and in some other embodiments, 4 to 7.

As used herein, the “aryl group” may be, for example, a monocyclic aromatic group such as a phenyl group, or a condensed polycyclic aromatic group such as a biphenyl group, a terphenyl group, a quaterphenyl group, a quinquephenyl group, a fluorenyl group, a fluoranthenyl group, a triperylene group, a naphthyl group, an anthracenyl group, an indenyl group, a pyrenyl group, and an acenaphthenyl group. For example, the number of carbon atoms of the aryl group may be 6 to 18, and in some embodiments, 6 to 12.

As used herein, the “heteroaryl group” may be a polycyclic heteroaryl group, for example, a pyrrolyl group, an imidazolyl group, a pyrazolyl group, an oxazolyl group, an isoxazolyl group, an oxadiazolyl group, a thiazolyl group, a furanyl group, a pyranyl group, a thienyl group, a pyridyl group, a pyrazyl group, a pyrimidinyl group, a pyridazinyl group, a triazinyl group, a quinolinyl group, an isoquinolinyl group, a benzofuranyl group, a benzothienyl group, an indolyl group, a carbazolyl group, a carbolinyl group, a phenanthridinyl group, an acridinyl group, a phenanthrolinyl group, a benzoxazolyl group, a benzothiazolyl group, a quinoxalinyl group, a benzimidazolyl group, a pyrazolyl group, a dibenzofuranyl group, and a dibenzothiophenyl group. For example, the number of carbon atoms of the heteroaryl group may be 3 to 24, and in some embodiments, 5 to 12.

As used herein, the “halogen atom” may be, for example, a fluorine atom, a chlorine atom, a bromine atom, or an iodine atom.

As used herein, the “alkoxy group”, “cyclo alkoxy group”, and “aryl alkoxy group” may refer to an alkyl group,

a cyclo alkyl group, and an aryl alkyl group, respectively, each of which has an oxygen atom at a binding site with another group.

As used herein, the “alkylamino group” and the term “arylamino group” may be, for example, an amino group substituted with one, two, or three of the above-described alkyl groups and aryl groups, respectively.

As used herein, the “aralkyl group” refers to an alkyl group substituted with at least one of the above-described aryl groups.

As used herein, the “heteroaralkyl group” refers to an alkyl group substituted with at least one of the above-described heteroaryl groups.

Substituents of each of the above-described groups are not specifically limited. For example, the substituents may include a cyano group, a silyl group, a C1-C10 mono-, di-, or tri-alkylsilyl group, a C1-C10 linear or branched alkyl group, a C1-C10 linear or branched alkoxy group, a C6-C15 aryl group, a C6-C15 aryloxy group, a C6-C14 aryl carbonyl group, a C1-C32 heterocycloalkyl group, and a C6-C15 mono- or di-arylamino group. When the expression “substituted” is simply used, it may be construed as being substituted with these substituents unless stated otherwise.

For example, R¹ to R³ may each independently be a hydrogen or a substituted or unsubstituted C1-C20 alkyl group, and in some embodiments, a hydrogen or a unsubstituted C1-C5 alkyl group, and in some other embodiments, a hydrogen.

In some embodiments, R⁴ may be a hydrogen, a substituted or unsubstituted C1-C20 alkyl group; a substituted or unsubstituted C3-C16 cycloalkyl group; or a substituted or unsubstituted C6-C30 aryl group.

In some embodiments, R⁴ may be a hydrogen or unsubstituted C1-C20 alkyl group, and in some other embodiments, a hydrogen or unsubstituted C1-C5 alkyl group.

In some embodiments, L¹ may be the same as described above.

The “alkylene group” may be, for example, a C1-C20 linear or branched alkylene group, and in some embodiments, a C1-C10 linear or branched alkylene group, and in some other embodiments, a C1-C3 linear or branched alkylene group. Examples of the alkylene group are a methylene group, an ethylene group, an n-propylene group, and an n-butylene group.

The “arylene group” may be, for example, a phenylene group, a biphenylene group, a terphenylene group, or a naphthylene group. The number of carbon atoms of the arylene group may be, for example, 6 to 30, 6 to 24, or 6 to 12.

The “cycloalkylene group” may be, for example, a polycyclic group such as a cyclopropylene group, a cyclobutylene group, a cyclopentylene group, a cyclohexylene group, a decahydronaphthalene group, or a bicyclo undecanylene group; or a bridged hydrocarbon group such as a bicycloalkylene group or a tricycloalkylene group. For example, the “cycloalkylene group” may be a norbornylene group. The number of carbon atoms of the cycloalkylene group may be, for example, 3 to 30, 3 to 24, or 3 to 12.

The “heteroarylene group” may be, for example, a bicyclic aromatic heteroarylene group, such as a pyrrolylene group, a thiophenylene group, a furanylene group, a pyrazolylene group, an imidazolylene group, an oxazolylene group, an isoxazolylene group, an oxadiazolylene group, a triazolylene group, a thiazolylene group, an isothiazolylene group, a pyridinylene group, a pyridazinylene group, a pyrimidinylene group, a pyrazinylene group, an indolylene group, an isoindolylene group, a benzothiophenylene group,

an isobenzothiophenylene group, an indazolinylene group, an imidazopyridinylene group, a benzothiazolylene group, or a quinolinylene group. The number of carbon atoms of the heteroarylene group may be, for example, 1 to 30, 1 to 24, or 1 to 12.

When a group containing a specified number of carbon atoms is substituted with any of the groups listed in the preceding paragraphs, the number of carbon atoms in the resulting “substituted” group is defined as the sum of the carbon atoms contained in the original (unsubstituted) group and the carbon atoms (if any) contained in the substituent. For example, when the term “substituted C1-C30 alkyl” refers to a C1-C30 alkyl group substituted with C6-C30 aryl group, the total number of carbon atoms in the resulting aryl substituted alkyl group is C7-C60.

In some embodiments, in Formula 1, X¹ to X⁹ may be —CH—.

In some embodiments, R⁹ and R¹⁰ may each independently be a hydrogen or a substituted or unsubstituted C1-C20 alkyl group.

In some embodiments, X¹ to X⁹ may be —CH—, and R⁹ and R¹⁰ may each independently be a hydrogen or a substituted or unsubstituted C1-C20 alkyl group.

In some embodiments, L¹ may be selected from a single bond, a substituted or unsubstituted C5-C30 cycloalkylene group; a substituted or unsubstituted C10-C30 arylene group; and a substituted or unsubstituted C1-C30 heteroarylene group.

In some other embodiments, L¹ may be selected from a single bond, a substituted or unsubstituted C5-C30 cycloalkylene group; and a substituted or unsubstituted C1-C30 heteroarylene group.

In some other embodiments, L¹ may be a single bond or unsubstituted cycloalkylene group.

In some other embodiments, L¹ may be a single bond, a substituted or unsubstituted naphthylene group, or a substituted or unsubstituted norbornylene group.

In some other embodiments, L¹ may be a single bond, or a naphthylene group or norbornylene group.

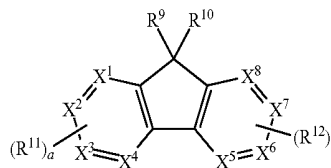
For example, L¹ may be a single bond.

In some embodiments, M in Formula 1 may be a group represented by the formula -(A-B)_n-A_m- or a group represented by the formula -(B-A)_n-B_m-, as described above.

In some embodiments, A in the formula of M may be a group including a fluorene ring system or an aza fluorene ring system.

In some embodiments, A in the formula of M may be represented by Formula 4. In Formula 4, any two of groups R⁹ to R¹² may be bound to adjacent atoms.

Formula 4



In some embodiments, R⁹ and R¹⁰ are not specifically limited to the above-described groups, and may each independently be a hydrogen, a substituted or unsubstituted C1-C20 alkyl group or a substituted or unsubstituted C6-C30 aryl group. In some embodiments, R⁹ and R¹⁰ may each independently be a hydrogen or unsubstituted C1-C12 alkyl group. The description of the alkyl group and aryl

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group provided above in connection with R^1 to R^4 may apply to the alkyl group and aryl group of R^9 and R^{10} .

In some embodiments, R^{11} and R^{12} are not specifically limited to the above-described groups, and may each independently be a hydrogen, a substituted or unsubstituted C1-C20 alkyl group; a substituted or unsubstituted C6-C30 aryl group; or a substituted or unsubstituted C1-C30 heteroaryl group. In some other embodiments, R^{11} and R^{12} may each independently be a hydrogen or a C1-C20 linear alkyl group. The description of the alkyl group and aryl group provided above in connection with R^1 to R^4 may apply to the alkyl group and aryl group of R^{11} and R^{12} .

In some embodiments, when R^{11} and R^{12} each independently are an aryl group or a heteroaryl group, R^{11} and R^{12} may form a condensed ring by condensation with a fluorene ring system or an aza fluorene ring system in Formula 4.

In some embodiments, one of X^1 to X^4 may be N or none of X^1 to X^4 may be N. For example, all of X^1 to X^4 may be CH.

In some embodiments, one of X^5 to X^8 may be N, or none of X^5 to X^8 may be N. For example, all of X^5 to X^8 may be CH.

In some embodiments, a in Formula 4 may be an integer smaller than the number of CH groups of X^1 to X^4 .

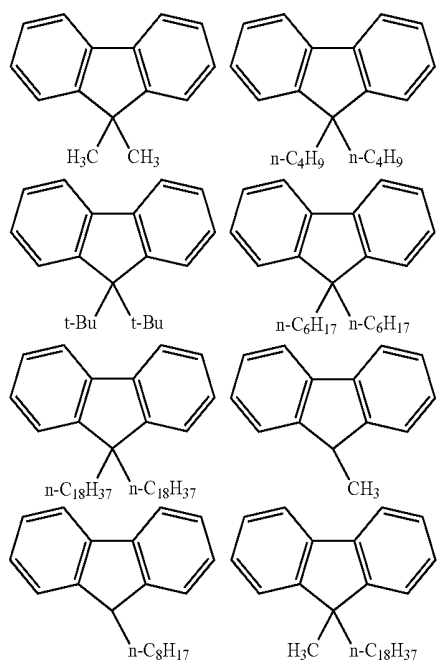
In some embodiments, b in Formula 4 may be an integer smaller than the number of CH groups of X^5 to X^8 .

In some embodiments, X^1 to X^8 may be CH.

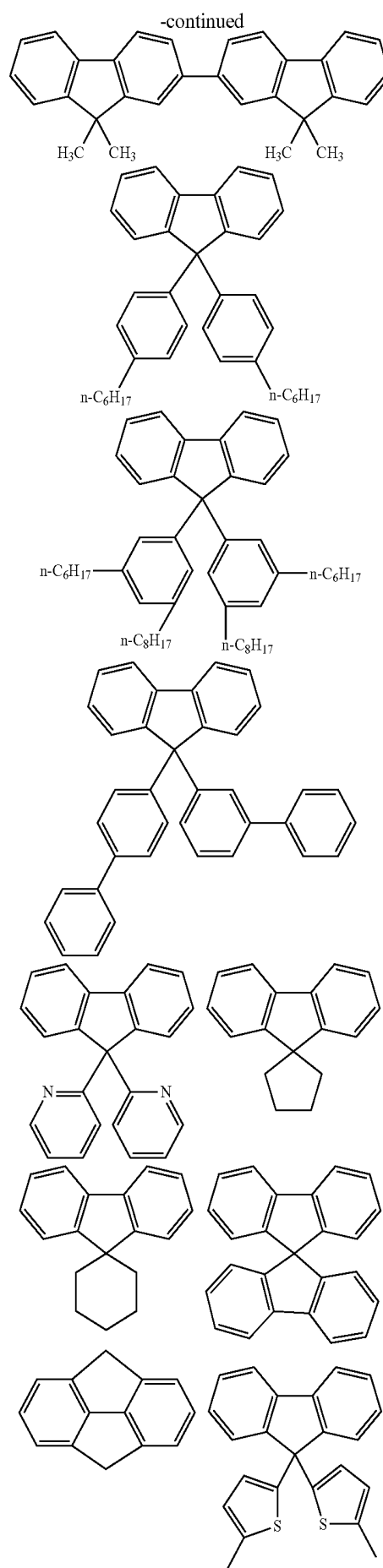
In some embodiments, R^9 and R^{19} may each independently be a hydrogen or a substituted or unsubstituted C1-C20 alkyl group.

In some embodiments, X^1 to X^8 may be CH, and R^9 and R^{19} may each independently be a hydrogen or a substituted or unsubstituted C1-C20 alkyl group.

In some embodiments, the group represented by Formula 4 may be one selected from the structures represented by the following formulae, wherein a hydrogen in each of the structures may be substituted with substituents.

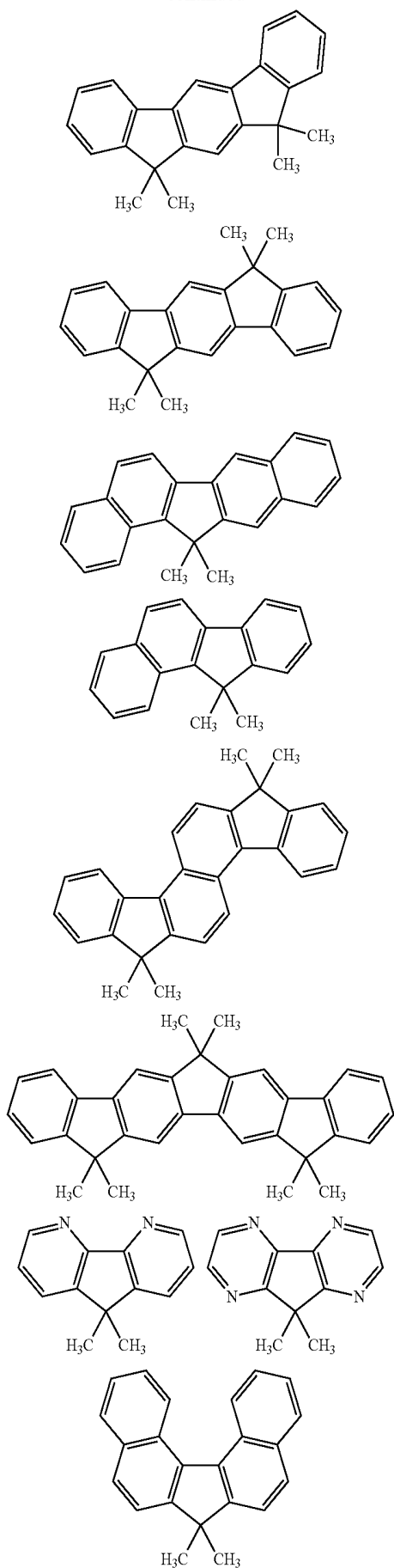


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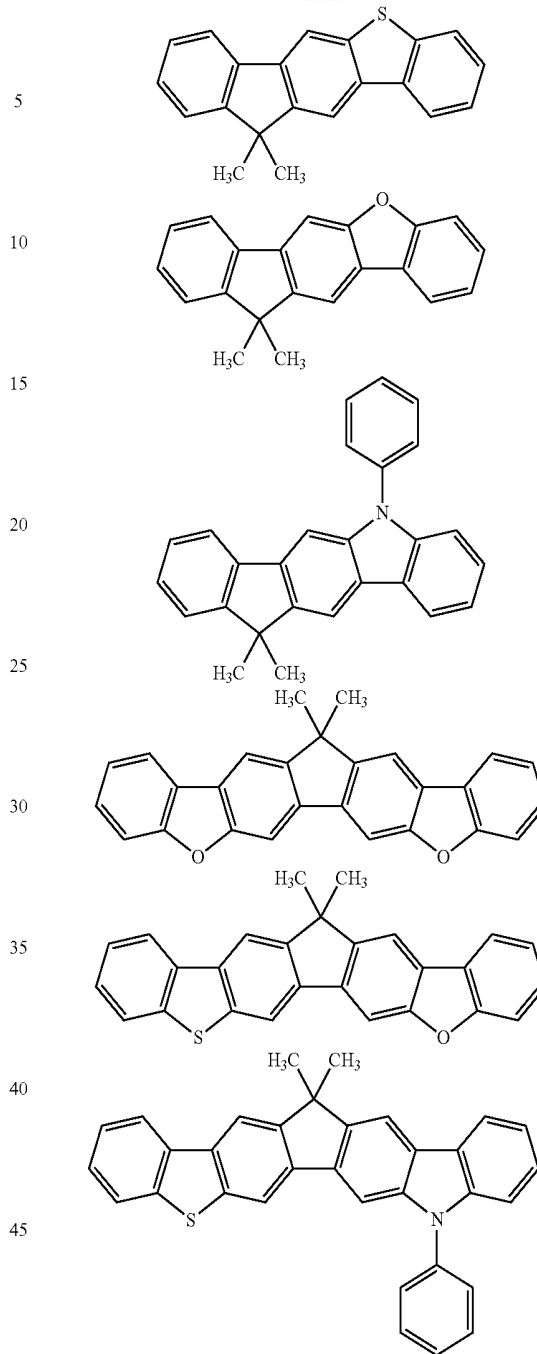
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In some embodiments, B in the formula of M may be a group represented by Formula 3.



Formula 3

In some embodiments, L^3 and L^4 are not specifically limited to the above-described groups, and may each independently be a single bond, or a substituted or unsubstituted C6-C30 arylene group. In some embodiments, L^3 and L^4 may each independently be a single bond, a phenylene group, a biphenylene group, or a naphthylene group. In some embodiments, L^3 and L^4 may each independently be a single bond.

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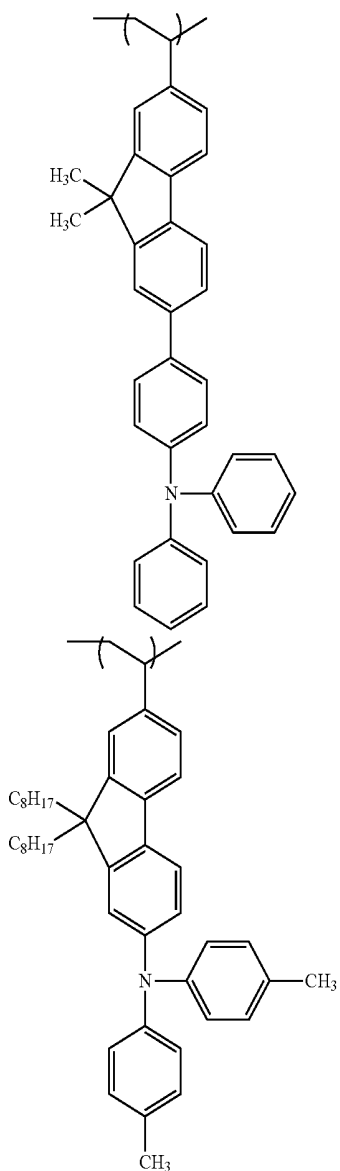
In some embodiments, one of L^3 and L^4 may be a single bond, and the remaining one of L^3 and L^4 may be a substituted or unsubstituted C6-C30 arylene group.

In some embodiments, R^8 is not specifically limited to the above-described groups, and may be, for example, a hydrogen, a substituted or unsubstituted C1-C2 alkyl group, or a substituted or unsubstituted C6-C30 aryl group. In some embodiments, R^8 may be a C6-C12 aryl group substituted with an alkyl group. The description of the alkyl group and aryl group provided above in connection with R^1 to R^4 may apply to the alkyl group and aryl group of R^8 .

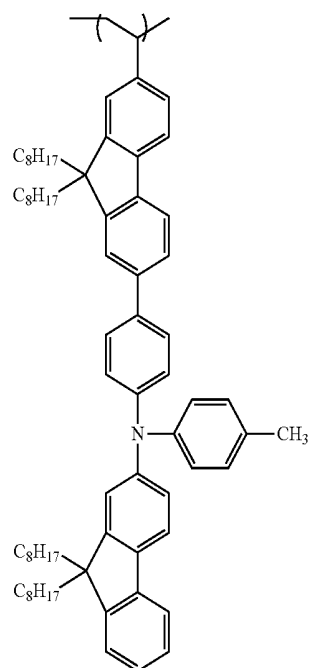
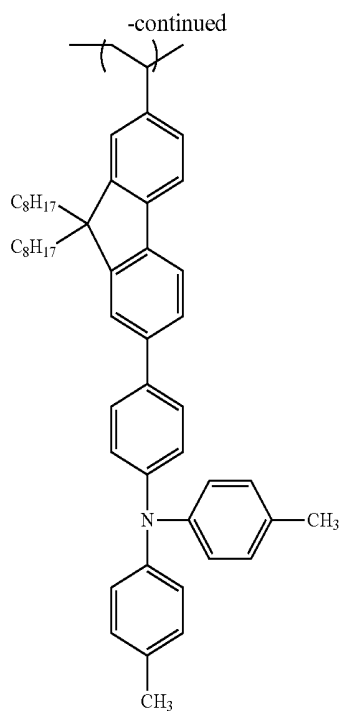
In some embodiments, the C6 to 30 aryl group substituted with an alkyl group may be a methylphenyl group or an ethylphenyl group.

In some embodiments, in Formula 4, n may be an integer from 1 to 20, for example, an integer from 1 to 10, or an integer from 1 to 5. In some embodiments, in Formula 4, n may be 1 or 2.

In some embodiments, the unit represented by Formula 1 may be selected from the structures represented by the following formulae, but is not limited thereto.

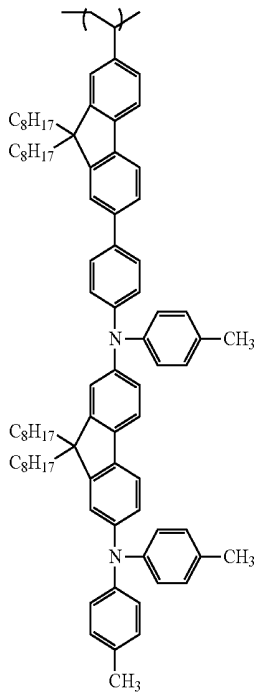


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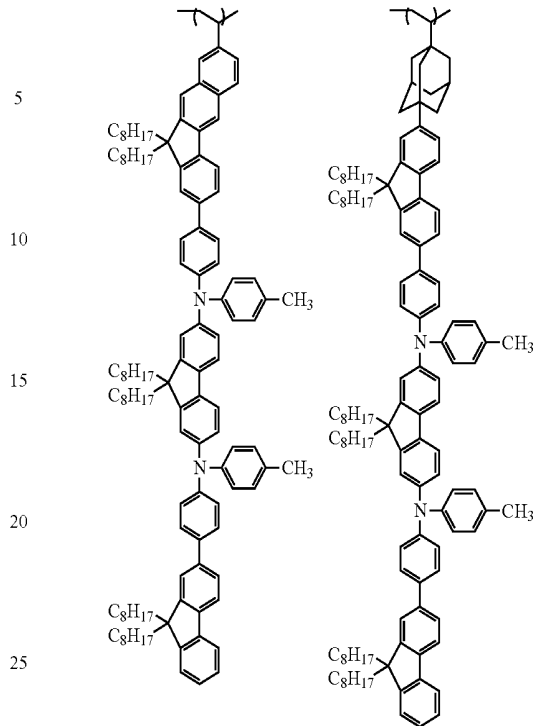
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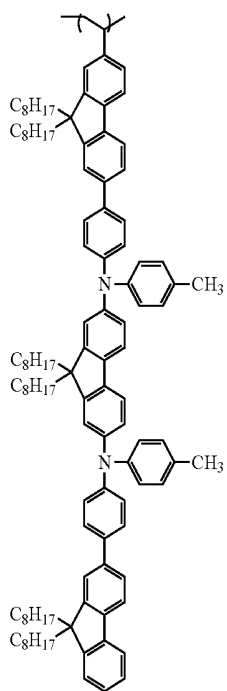
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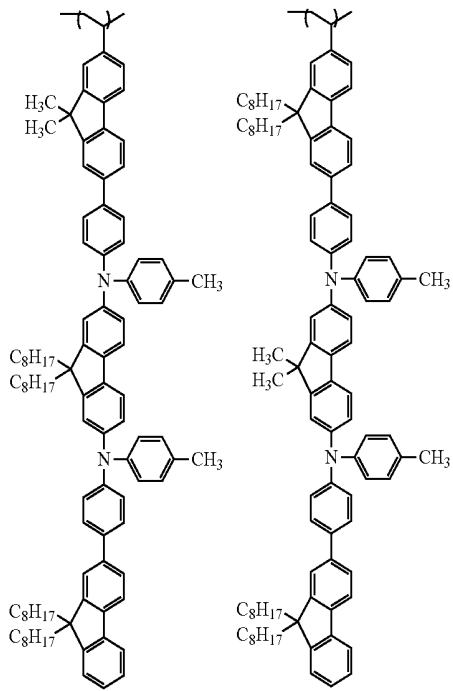
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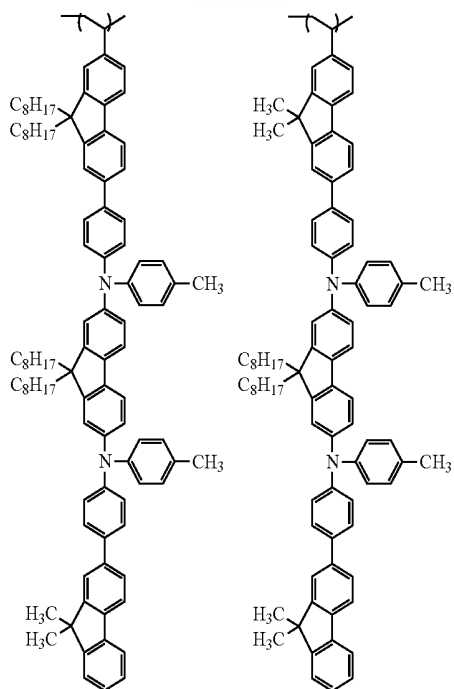
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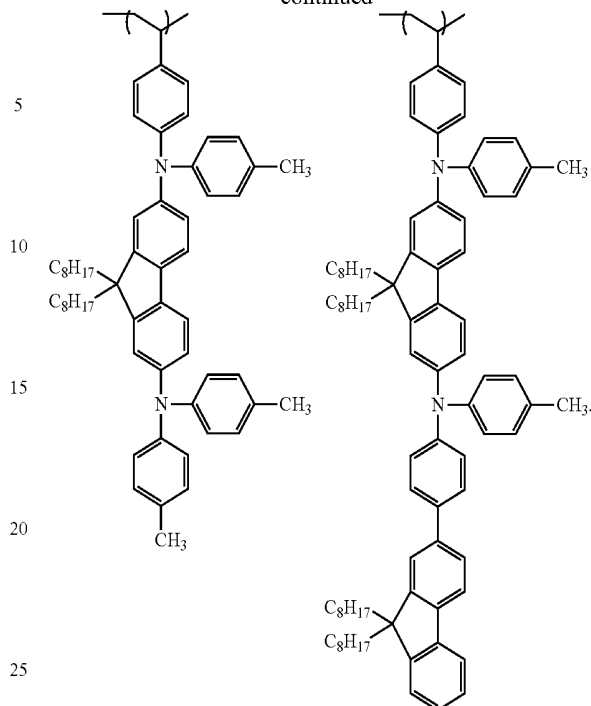
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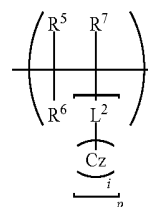
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Carbazole Unit

Hereinafter, the carbazole unit represented by Formula 2 will now be described in detail.

Formula 2



In some embodiments, R^5 to R^7 may be the same as R^1 to R^4 described above.

In some embodiments, the carbazole unit represented by Formula 2 may be a chain group in which L^2 and Cz are alternately polymerized, wherein the number of each of the groups L^2 and Cz may be p.

In some embodiments, L^2 may be a single bond, a substituted or unsubstituted C5-C30 cycloalkylene group, a substituted or unsubstituted C6-C30 arylene group, or a substituted or unsubstituted C1-C30 heteroarylene group.

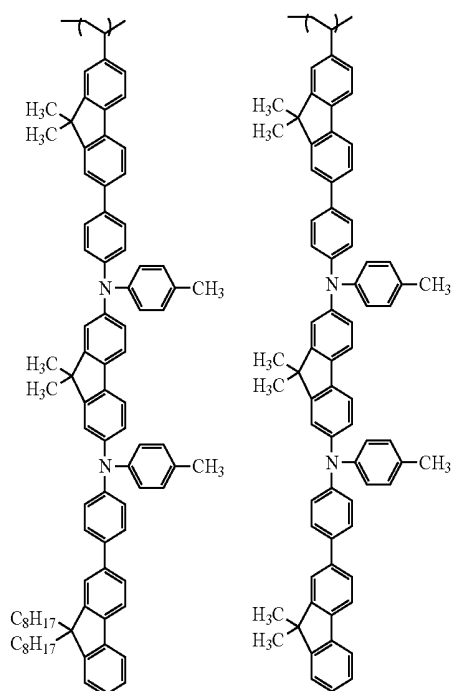
In some embodiments, L^2 may be selected from a single bond, a substituted or unsubstituted C5-C30 cycloalkylene group, and a substituted or unsubstituted C1-C30 heteroarylene group.

In some other embodiments, L^2 may be a single bond, a substituted or unsubstituted phenylene group, or a substituted or unsubstituted fluorenylene group.

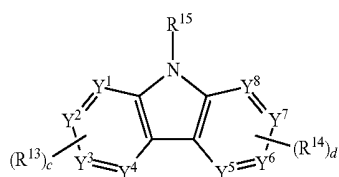
In some other embodiments, L^2 may be a single bond, a phenylene group, or a fluorenylene group substituted with an alkyl group.

In some embodiments, L^2 may be a single bond.

In some embodiments, Cz may be a carbazole ring system or an aza carbazole ring system. For example, Cz may be represented by Formula 5. In Formula 5, two of R^{13} to R^{15} may be bound to adjacent atoms.



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Formula 5

In Formula 5,

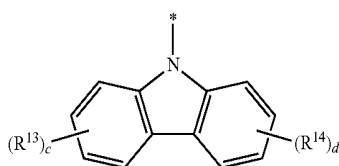
Y^1 to Y^8 may each independently be CH or N,

R^{13} to R^{15} may each independently be a hydrogen, a halogen atom, a hydroxyl group, an amino group, a nitro group, a cyano group, a substituted or unsubstituted silyl group, a substituted or unsubstituted C1-C20 alkyl group, a substituted or unsubstituted C1-C20 amino alkyl group, a substituted or unsubstituted C3-C16 cycloalkyl group, a substituted or unsubstituted C6-C30 aryl group, a substituted or unsubstituted C6-C30 amino aryl group, a substituted or unsubstituted C1-C30 heteroaryl group, a substituted or unsubstituted C1-C20 alkoxy group, a substituted or unsubstituted C3-C16 cycloalkoxy group, a substituted or unsubstituted C6-C30 aryloxy group, a substituted or unsubstituted C7-C40 aralkyl group, a substituted or unsubstituted C2-C40 heteroaralkyl group; a substituted or unsubstituted C1-C20 alkylamino group, or a substituted or unsubstituted C6-C60 arylamino group; wherein any two adjacent groups selected from R^{13} to R^{15} may optionally form a ring, and

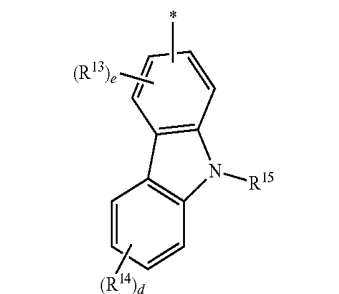
c and d may each independently be an integer from 0 to 4. In some embodiments, one of Y^1 to Y^4 may be N, or none of Y^1 to Y^4 may be N. For example, all of Y^1 to Y^4 may be CH.

In some embodiments, one of Y^5 to Y^8 may be N, or none of Y^5 to Y^8 may be N. For example, all of Y^5 to Y^8 may be CH.

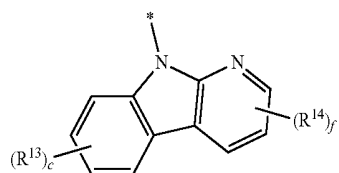
In some embodiments, Cz may be a structure represented by one of Formula 6 to Formula 13. In Formula 6 to Formula 13, any one of R^{13} and R^{14} may be bound to an adjacent atom.



Formula 6



Formula 7

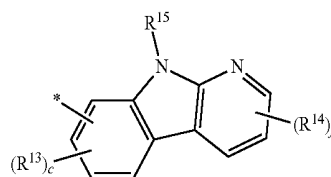


Formula 8

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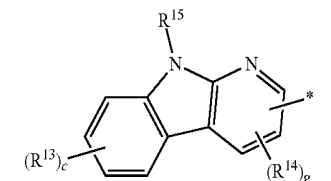
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Formula 9



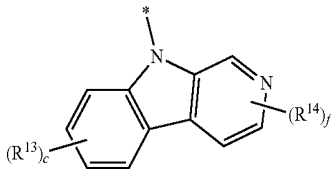
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Formula 10



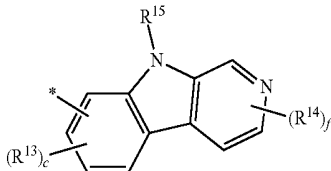
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Formula 11



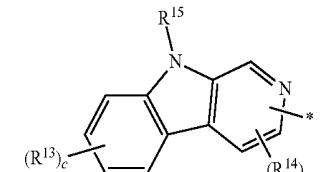
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Formula 12



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Formula 13



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In Formula 6 to Formula 13, R^{13} to R^{15} , c , and d may be the same as those defined in Formula 5,

e and f may each independently be an integer from 0 to 3, g may be an integer from 0 to 2, and

$*$ may be a binding site with an adjacent atom.

In some embodiments, R^{13} to R^{15} may each independently

be a hydrogen, a substituted or unsubstituted C1-C20 alkyl group, a substituted or unsubstituted C1-C20 alkoxy group, a substituted or unsubstituted C6-C30 aryl group, or a substituted or unsubstituted C6-C30 amino aryl group. In some embodiments, R^{13} to R^{15} may each independently be a hydrogen, a substituted or unsubstituted C1-C20 alkyl group or a substituted or unsubstituted C6-C30 aryl group. In some other embodiments, R^{13} to R^{15} may each independently be a hydrogen, a C1-C15 linear alkyl group, a substituted or unsubstituted phenyl group, or a substituted or unsubstituted fluorenyl group.

In some embodiment, when at least two of R^{13} to R^{14} are adjacent to one another, the at least two of R^{13} to R^{14} may have a carbazole ring system or aza carbazole ring system represented by Formula 5, or may form a condensed ring by condensation with each other. The condensed ring may be, for example, an indolecarbazole ring.

In some embodiments, R^{13} to R^{15} may each independently be a C1-C15 linear alkyl group, for example, a C1-C12 linear alkyl group.

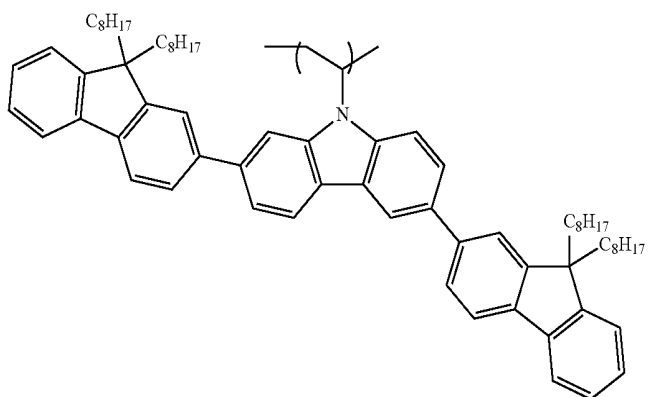
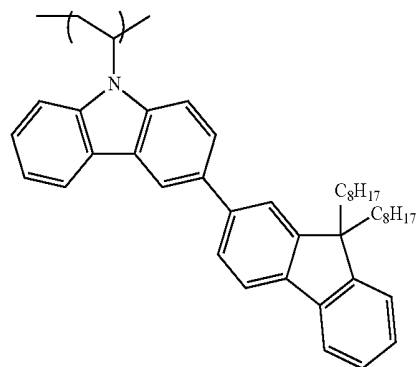
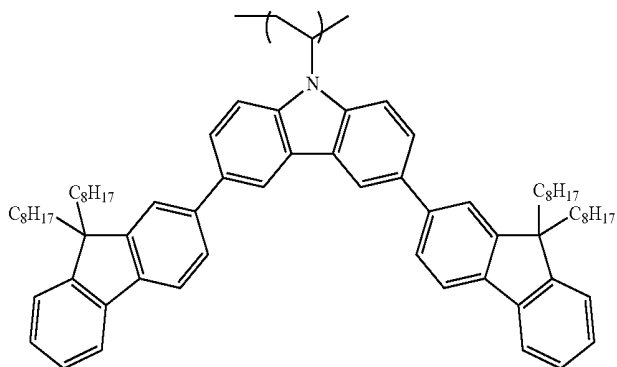
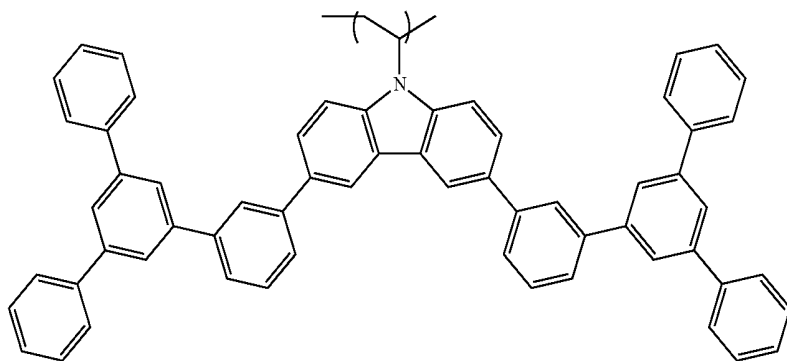
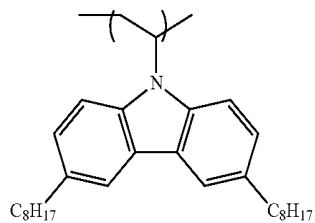
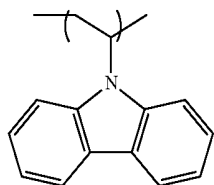
In some embodiments, in Formula 2, p may be an integer from 1 to 10, and in some other embodiments, an integer from 1 to 5. For example, p may be an integer of 1 or 2.

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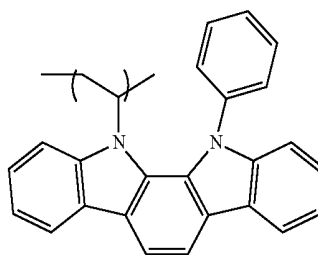
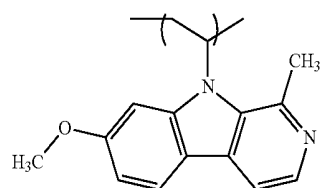
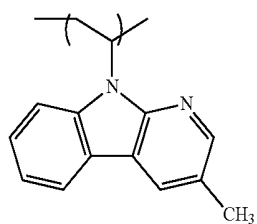
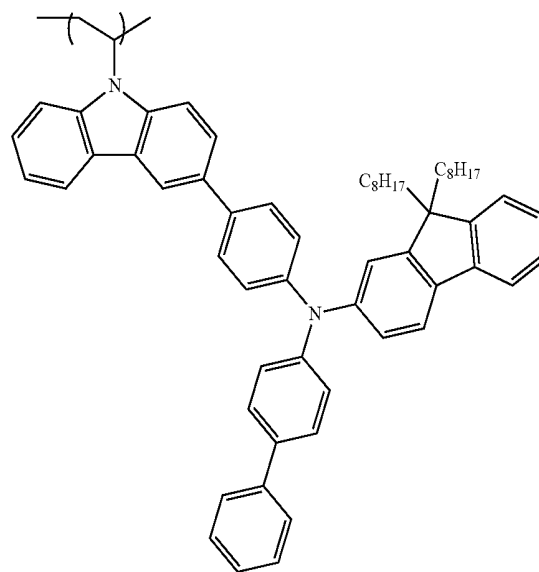
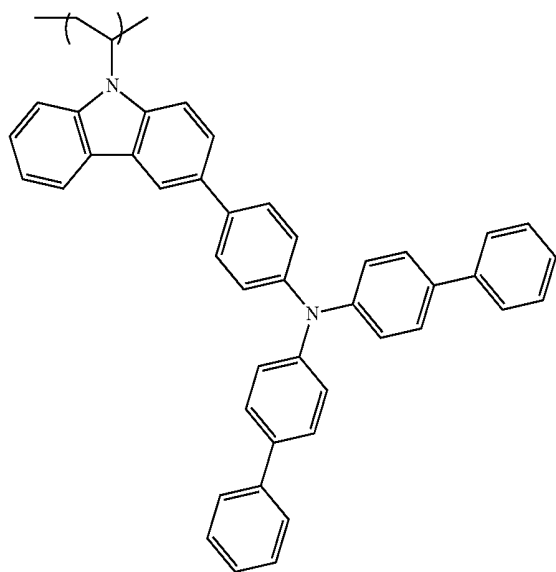
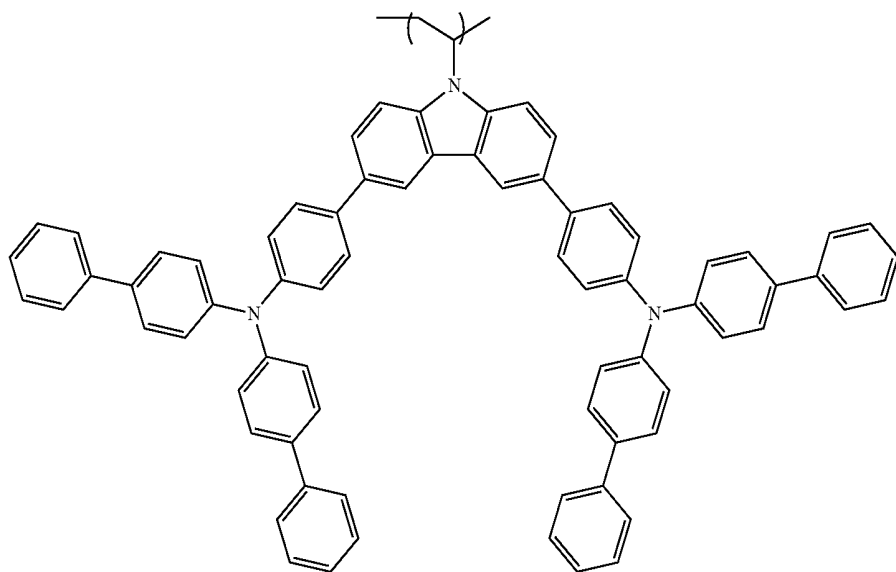
In some embodiments, the unit represented by Formula 2 may be selected from the structures represented by the

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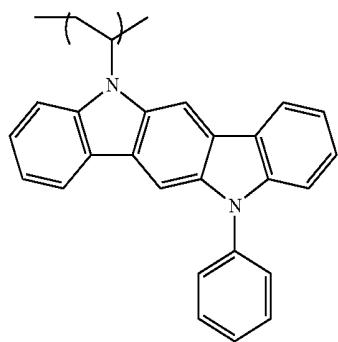
following formulae. However, embodiments are not limited thereto.



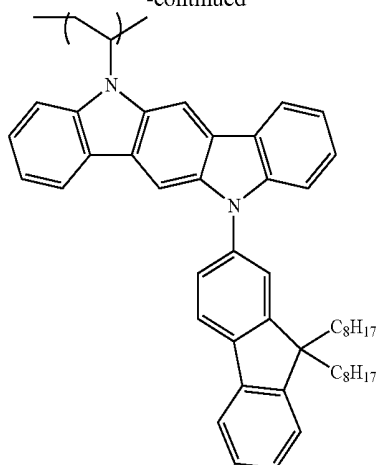
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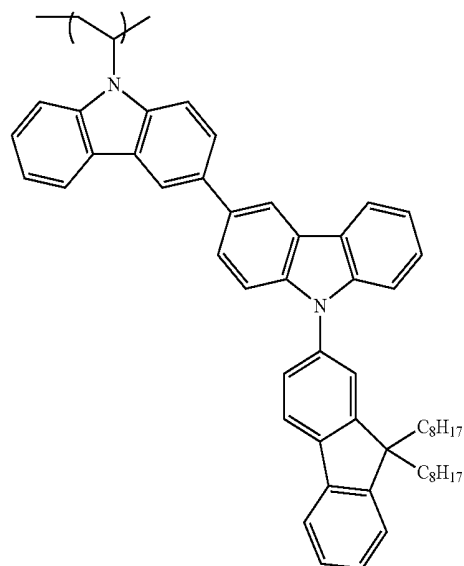
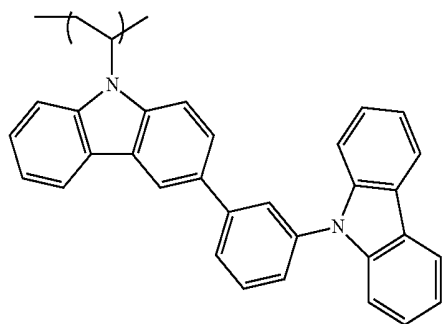
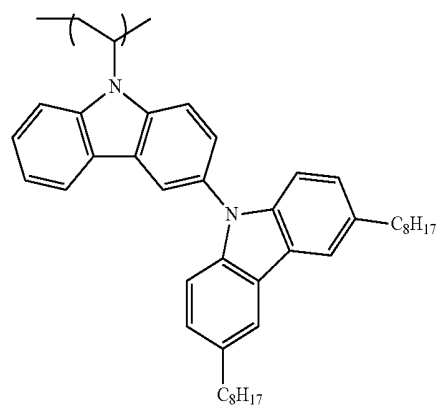
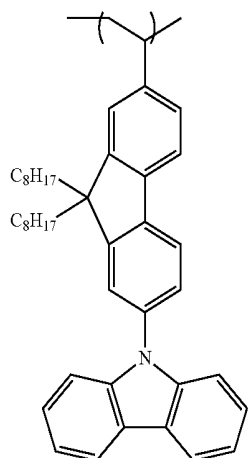
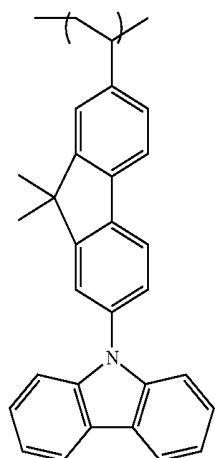
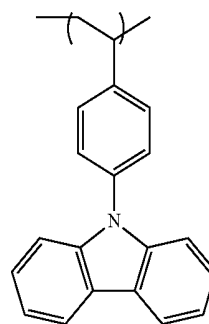
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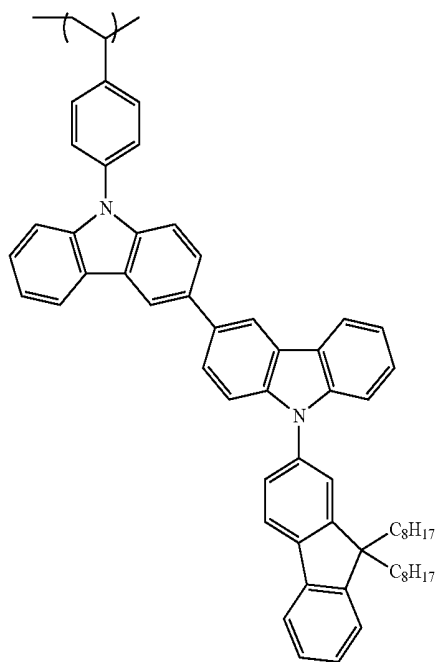
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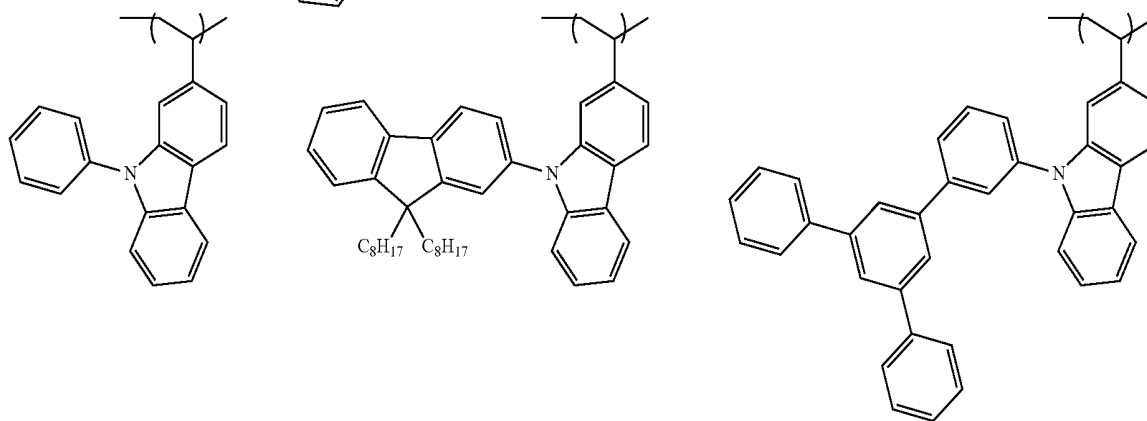
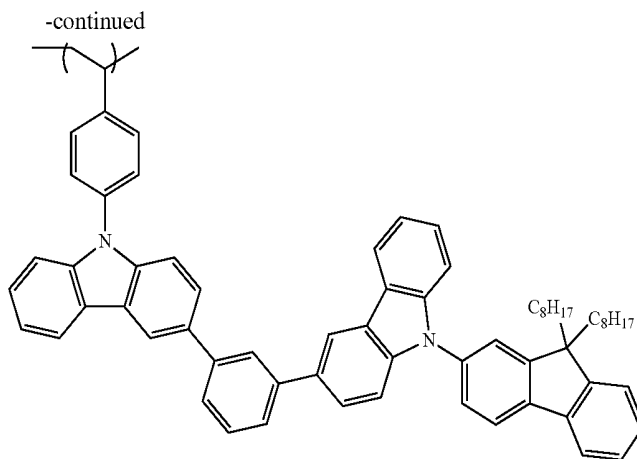
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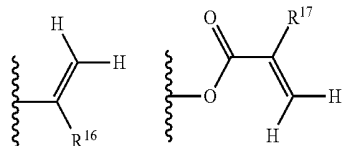
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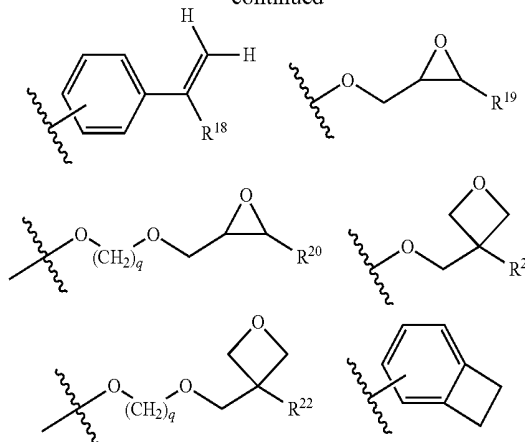
Other Units

In some embodiments, the copolymer may further include a unit, in addition to the above-described units. For example, the copolymer may further include a polymerizable unit, for example, a polymerizable comonomer including at least one group selected from the cross-linking groups represented by the following formulae. That is, the copolymer may further include a polymerizable comonomer, and the polymerizable comonomer may include at least one cross-linking group selected from the cross-linking groups represented by the following formulae.

Cross-Linking Groups



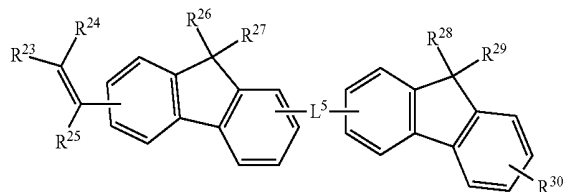
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In the above formulae of the cross-linking groups, R¹⁶ to R²² may each independently be a hydrogen, or a substituted or unsubstituted C1-C10 alkyl group, and q may be an integer from 1 to 10.

In some embodiments, the polymerizable copolymer may originate from a compound represented by Formula 14.

Formula 14



In Formula 14,

R^{23} to R^{25} may each independently be a hydrogen, a substituted or unsubstituted C1-C10 alkyl group, or a substituted or unsubstituted C6-C30 aryl group,

R^{26} to R^{30} may each independently be a hydrogen, a halogen atom, a hydroxyl group, an amino group, a nitro group, a cyano group, a substituted or unsubstituted silyl group, a substituted or unsubstituted C1-C10 alkyl group, a substituted or unsubstituted C3-C16 cycloalkyl group, a substituted or unsubstituted C6-C30 aryl group, a substituted or unsubstituted C1-C20 alkoxy group, a substituted or unsubstituted C6-C30 aryloxy group, a substituted or unsubstituted C7-C40 aralkyl group, a substituted or unsubstituted C1-C30 heteroaryl group, a substituted or unsubstituted

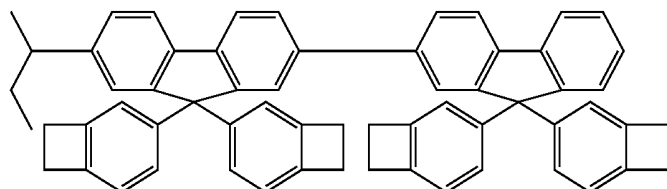
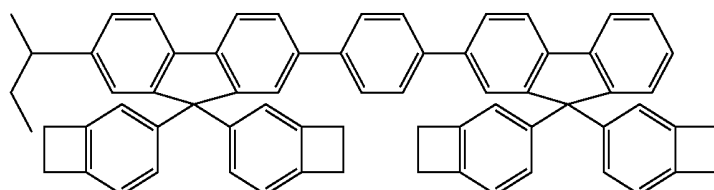
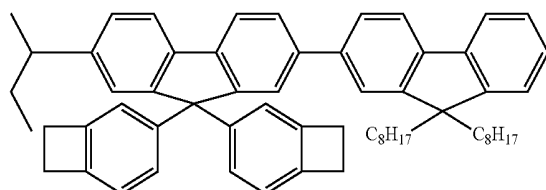
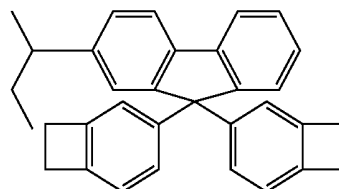
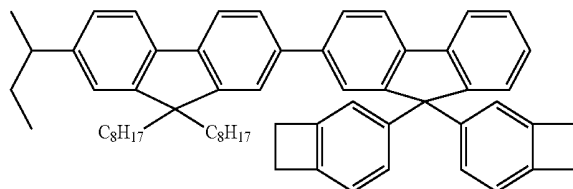
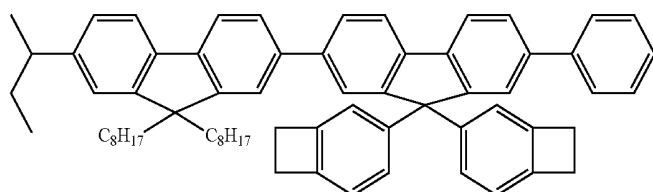
C1-C20 alkylamino group, or a substituted or unsubstituted C6-C60 arylamino group; wherein any two adjacent groups selected from R^{26} to R^{30} may optionally form a ring,

L^5 may be a single bond, a substituted or unsubstituted C1-C20 alkylene group, a substituted or unsubstituted C3-C16 cycloalkylene group, a substituted or unsubstituted C6-C30 arylene group, a substituted or unsubstituted C1-C20 oxyalkylene group, a substituted or unsubstituted C3-C16 oxycycloalkylene group, a substituted or unsubstituted C6-C30 oxyarylene group, a substituted or unsubstituted C7-C40 aralkylene group, a substituted or unsubstituted C1-C30 heteroarylene group, a substituted or unsubstituted C6-C30 amino arylene group, a silylene group substituted with an alkyl group or an aryl group, or a combination thereof, and

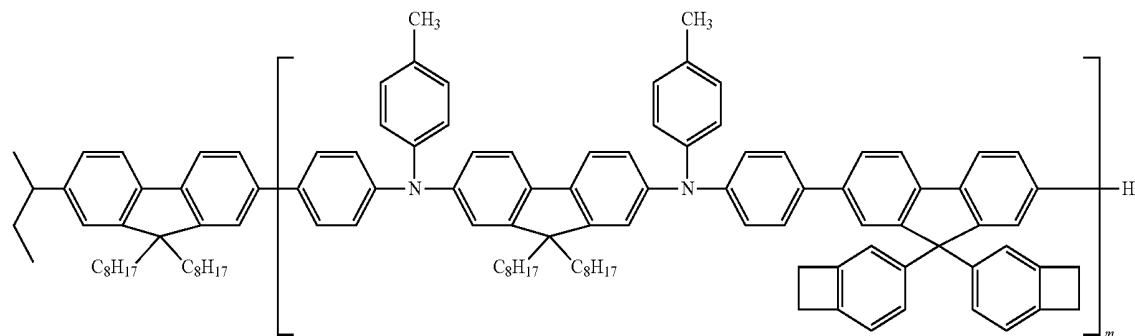
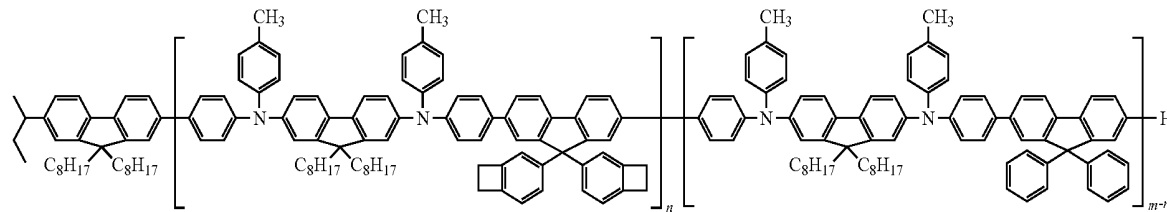
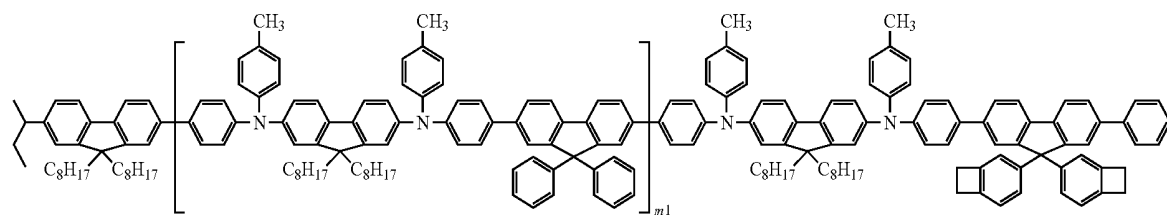
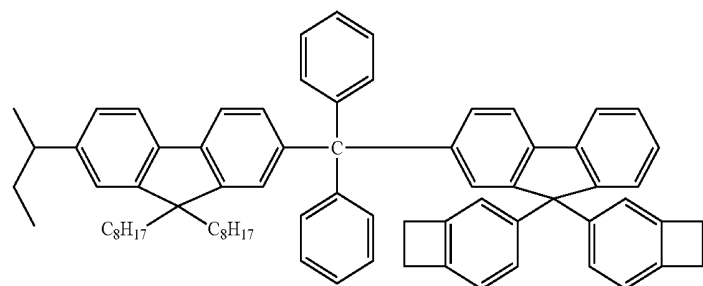
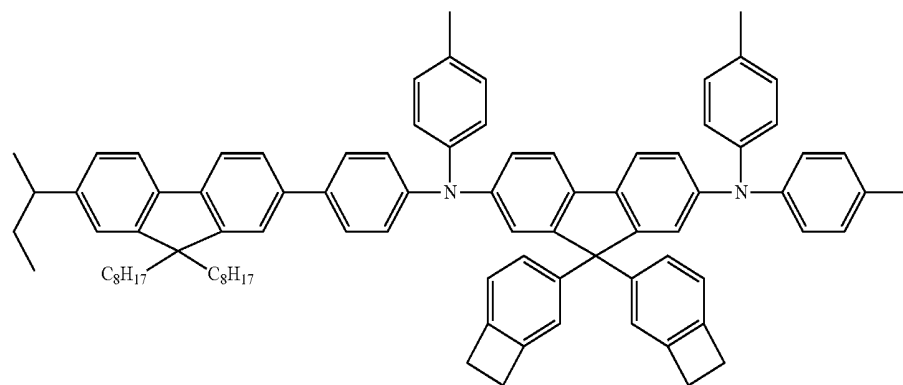
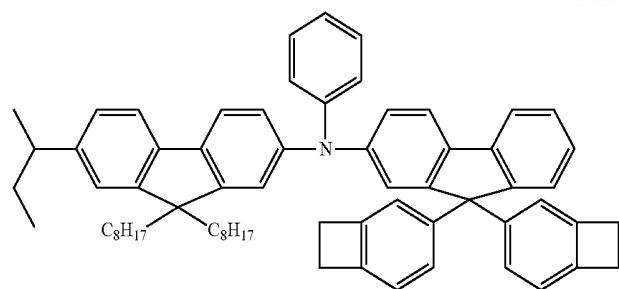
at least one of R^{26} to R^{30} may be selected from the cross-linking groups represented above.

In some embodiments, R^{16} to R^{29} may be the same as R^1 to R^4 described above.

In some embodiments, a unit (repeating unit) corresponding to the polymerizable comonomer including at least one of the cross-linking groups may be selected from the structures represented by the following formulae. However, embodiments are not limited thereto.



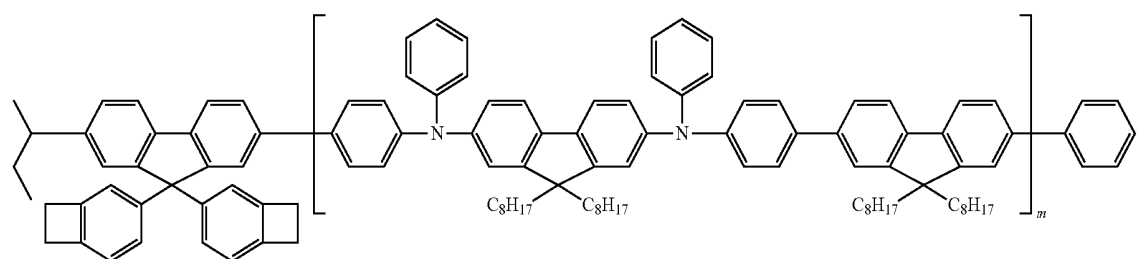
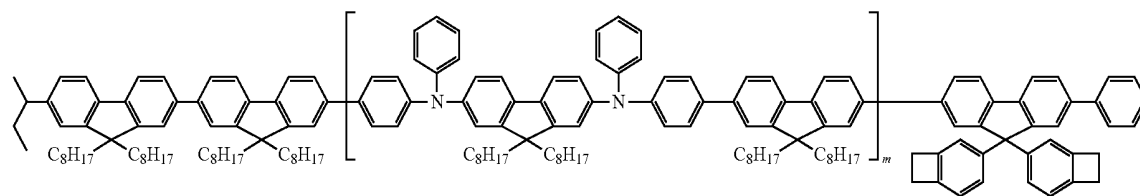
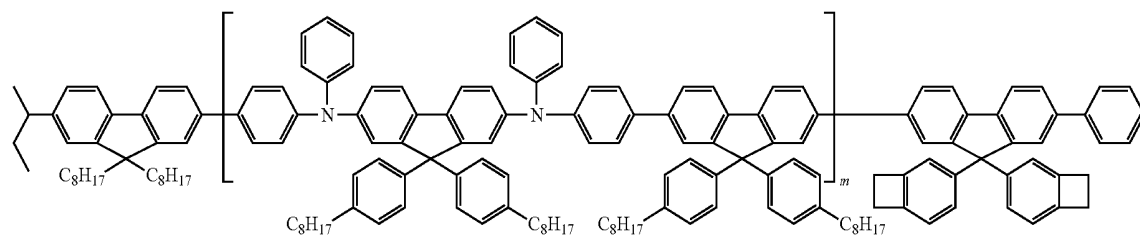
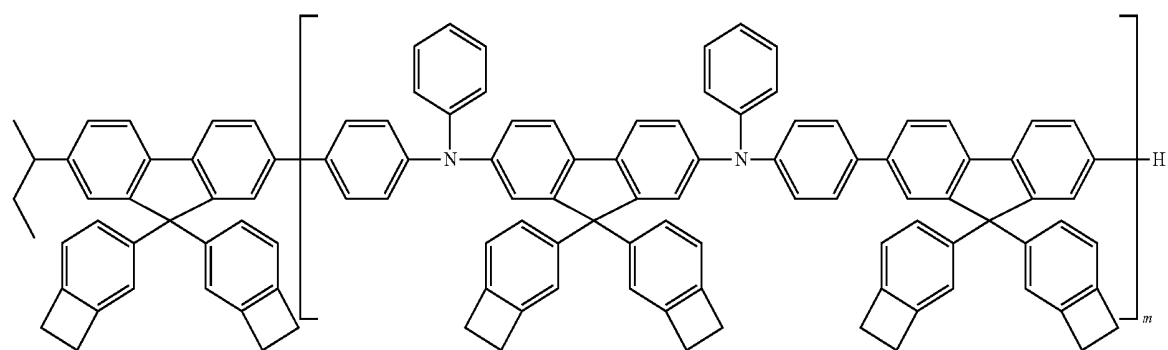
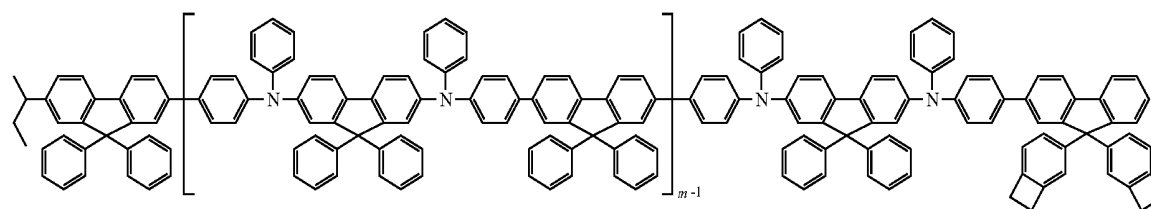
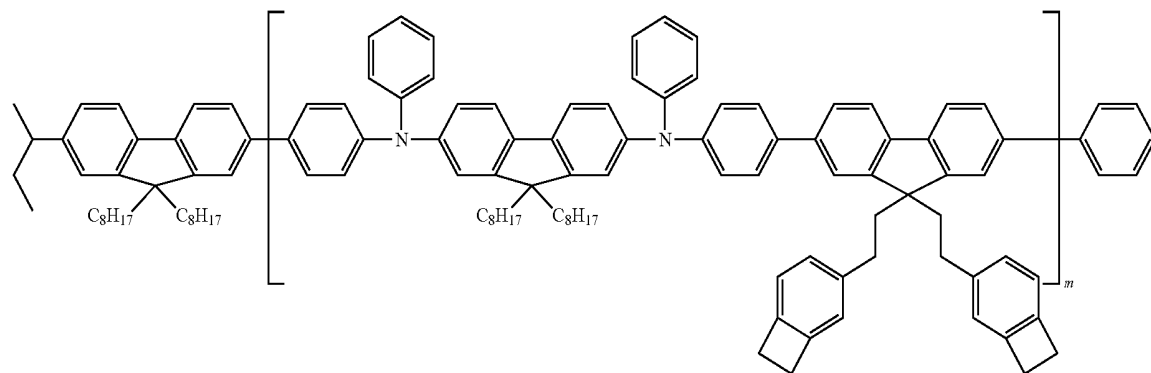
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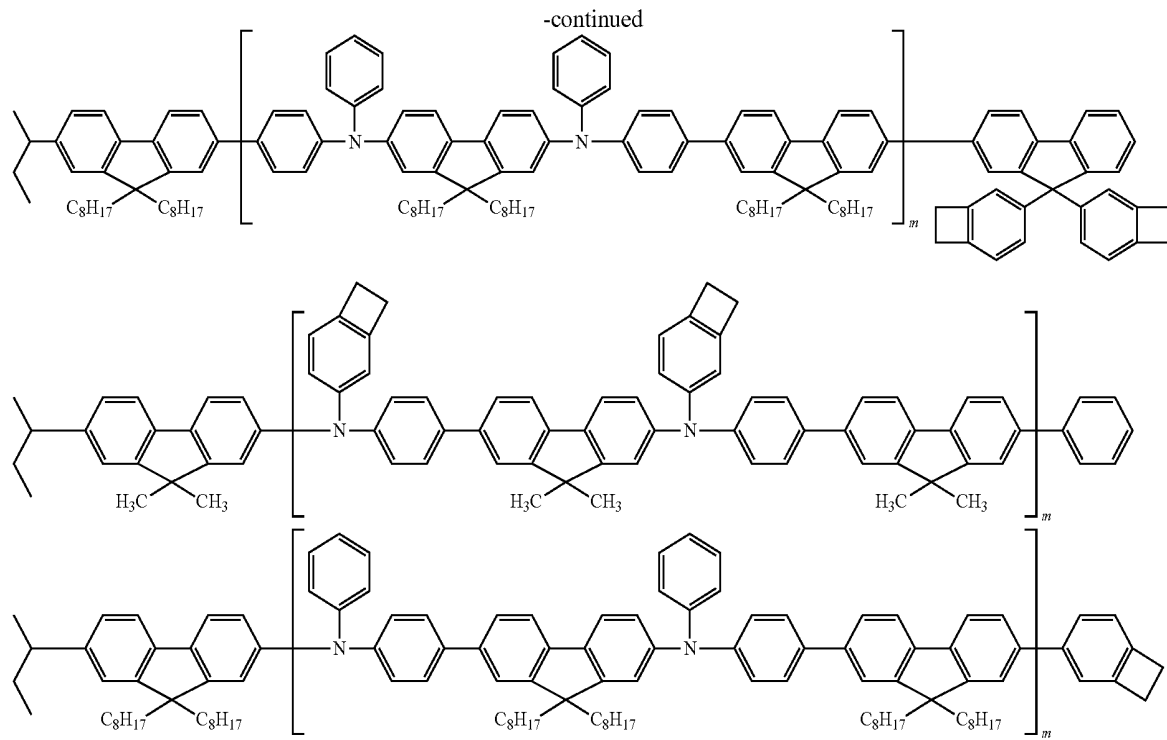
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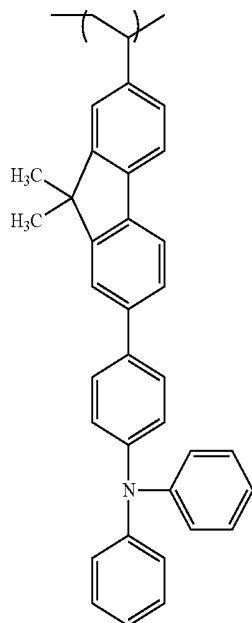
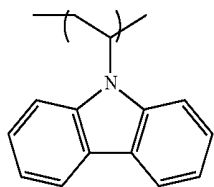
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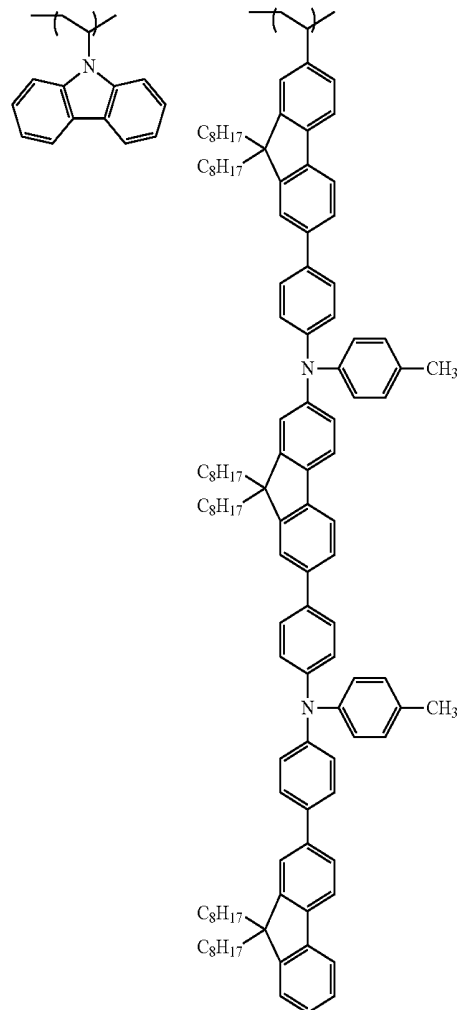
In the above formulae, m and n may each independently be, for example, an integer from 1 to 10.

In some embodiments, the copolymer may be selected from the structures represented by the following formulae.

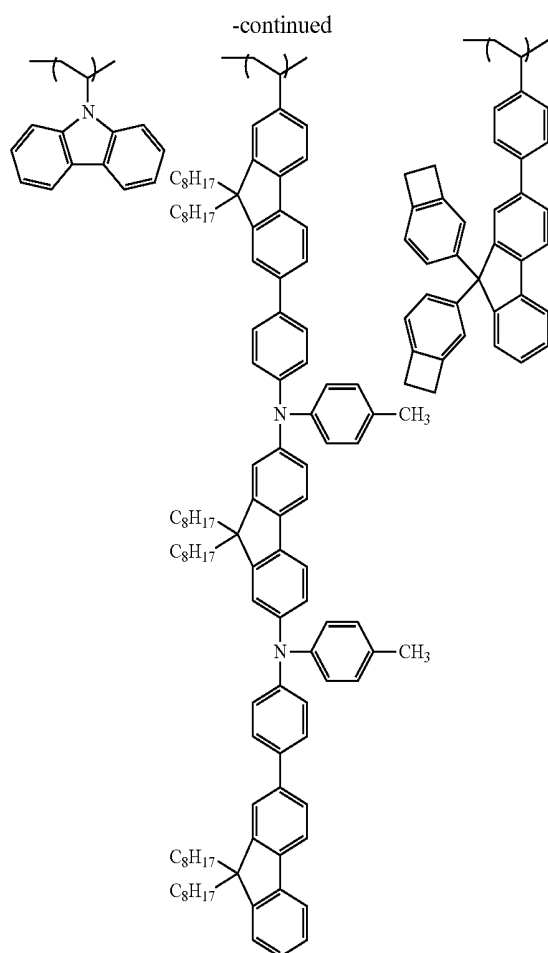


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43



In some embodiments, the copolymer may be, for example, a random copolymer, an alternating copolymer, or a block copolymer. However, embodiments are not limited thereto.

In some embodiments, the copolymer may have a number average molecular weight of about 10,000 to 100,000 Daltons, for example, about 30,000 to 100,000 Daltons, or about 50,000 to 100,000 Daltons. However, embodiments are not limited thereto.

An organic light-emitting device including a copolymer according to any of the above-described embodiments may have improved lifespan. As the copolymer according to any of the above-described embodiments includes a polymerizable comonomer including such a cross-linking group as represented above, a coating layer including the copolymer may have improved stability, and the organic light-emitting device including the coating layer may have improved emission characteristics and stability.

A copolymer according to any of the above-described embodiments may be synthesized by a known synthesis method, for example, by a radical polymerization method. Detailed methods of preparing a copolymer according to any of the above-described embodiments will be understood based on the following examples.

Organic Light-Emitting Device Material

According to an aspect of the present disclosure, there is provided an organic light-emitting device material including

44

a copolymer according to any of the above-described embodiments. The copolymer may have application as an organic light-emitting device material. The copolymer may have hole transport and hole injection abilities. Thus, the organic light-emitting device material according to an embodiment may be used as, for example, a material of a hole transport layer, a hole injection layer, or an emission layer.

In some embodiments, the organic light-emitting device material may be a material of the emission layer, and the copolymer according to any of the above-described embodiment may be used as a host material. In this case, the organic light-emitting device material may further include a compound with hole transport ability.

The compound with hole transport ability is not specifically limited, and may be, for example, a hole injection material, a hole transport material, or a host material which are known in the art, which will be described below.

In some embodiments, the organic light-emitting device material may be a material of the emission layer, and may further include a light-emitting material, which may be selected from light-emitting materials which will be described below.

An organic light-emitting device material according to an embodiment may include a copolymer according to any of the above-described embodiments, and a solvent. In some embodiments, the organic light-emitting device material may be used, for example, to form a layer of an organic light-emitting device by using a solution coating method.

The solvent is not specifically limited, and may be, for example, a solvent capable of dissolving the organic light-emitting device material.

In some embodiments, the solvent may be, for example, an aromatic solvent, such as toluene, xylene, ethylbenzene, diethylbenzene, mesitylene, propylbenzene, cyclohexylbenzene, dimethoxybenzene, anisole, ethoxy toluene, phenoxy toluene, isopropylbiphenyl, dimethylanisole, phenyl acetate, phenyl propionate, methyl benzoate, and ethyl benzoate. However, embodiments are not limited thereto.

Organic Light-Emitting Device

An organic light-emitting device according to an embodiment will be described in detail with reference to FIG. 1.

Referring to FIG. 1, an organic light-emitting device 100 according to an embodiment may include a substrate 110, a first electrode 120 on the substrate 110, a hole injection layer 130 on the first electrode 120, a hole transport layer 140 on the hole injection layer 130, an emission layer 150 on the hole transport layer 140, an electron transport layer 160 on the emission layer 150, an electron injection layer 170 on the electron transport layer 160, and a second electrode 180 on the electron injection layer 170, i.e., which are sequentially in the stated order. However, the organic light-emitting device 100 may have a structure not limited thereto.

The substrate 110 may be any substrate used in general organic light-emitting devices. For example, the substrate 110 may be a glass substrate, a silicon substrate, or a transparent plastic substrate.

The first electrode **120** may be formed on the substrate **110**. The first electrode **12** may be, for example, an anode. The first electrode **12** may be formed of a metal, an alloy, or a conductive compound that have high work function. For example, first electrode **120** may be formed of a material having good transparency and good conductivity, for example, indium tin oxide (ITO), indium zinc oxide (IZO), tin oxide (SnO₂), or zinc oxide (ZnO). The first electrode **120** may be formed as a reflective electrode from, for example, magnesium (Mg) or aluminum (Al).

The hole injection layer **130** may be formed on the first electrode **120**. The hole injection layer **130** may facilitate injection of holes from the first electrode **120**. The hole injection layer **130** may have a thickness of about 10 nanometers (nm) to about 1,000 nm, in some embodiments, about 10 nm to about 500 nm, and in some other embodiments, about 10 nm to about 100 nm.

The hole injection layer **130** may be formed of a known hole injection material, for example, triphenylamine-containing poly(ether ketone) (TPAPEK), 4-isopropyl-4'-methyl-diphenyl iodonium tetrakis (pentafluorophenyl) borate (PPBI), N,N'-diphenyl-N,N'-diphenyl-N,N'-bis-[4-(phenyl-m-tolyl-amino)-phenyl]-biphenyl-4,4'-diamine (DNTPD), copper phthalocyanine, 4,4',4''-tris(N-3-methylphenyl-N-phenyl amino)triphenylamine (m-MTDATA), N,N'-di(1-naphthyl)-N,N'-diphenylamine (NPB), 4,4',4''-tris(N,N'-2-naphthylphenylamino) triphenylamine (2-TNATA), polyaniline/dodecylbenzene sulfonic acid, poly(3,4-ethylenedioxythiophene)/poly(4-styrene sulfonate), or polyaniline/10-camphor sulfonic acid.

The hole transport layer **140** may be formed on the hole injection layer **130**. The hole transport layer **140** may include a hole transporting material with the ability to form holes. The hole transport layer **140** may have a thickness of about 10 nm to about 150 nm, for example, about 10 nm to about 100 nm. The hole transport layer **140** may be formed using a copolymer according to any of the above-described embodiments by a solution coating method. This method using the copolymer may improve the emission lifespan of the organic light-emitting device **100** and may facilitate formation of a large-area film.

The emission layer **150** may be formed on the hole transport layer **140**. The emission layer **150** may be a fluorescent or phosphorescent emission layer. The emission layer **150** may be formed by a vacuum deposition method, a spin coating method, or an ink jet method. The emission layer **150** may have a thickness of, for example, about 10 nm to about 60 nm, or for example, about 10 nm to about 40 nm.

The emission layer **150** may include a known light-emitting material. For example, the emission layer **150** may include a light-emission material that may emit light (phosphorescence) from triplet excitons. This may further improve the emission lifespan of the organic light-emitting device **100**.

The emission layer **150** may include a host material, for example, tris(8-quinolinolato) aluminum (Alq₃), 4,4'-N,

N'-dicabazole-biphenyl (CBP), poly(n-vinylcabazole) (PVK), 9,10-di(naphthalen-2-yl)anthracene (ADN), 4,4',4''-tris(N-carbazole)triphenylene (TCTA), 1,3,5-tris(N-phenyl-benzimidazole-2-yl)benzene (TPBI), 3-tert-butyl-9,10-di(naphth-2-yl)anthracene (TBADN), distyrylarylene (DSA), or 4,4'-bis(9-carbazol)-2,2'-dimethylbiphenyl (dm-CBP).

The emission layer **150** may include a dopant material. Examples of the dopant material may include perylene and a derivative thereof, rubrene and a derivative thereof, coumarin and a derivative thereof, 4-(dicyanomethylene)-2-methyl-6[4-(dimethylamino)styryl]-4H-pyran (DCM) and a derivative thereof, an iridium (Ir) complex such as bis[2-(4,6-difluorophenyl) pyridinate]picolinate iridium (III) (FI-ripic), bis(1-phenylisoquinoline)(acetylacetonato)iridium (III) [Ir(piq)₂(acac)], and tris(2-phenylpyridine) iridium(III) [Ir(ppy)₃], an osmium (Os) complex, and a platinum (Pt) complex.

The electron transport layer **160** may be formed on the emission layer **150**. The electron transport layer **160** may be a layer capable of transporting electrons. The electron transport layer **160** may be formed by, for example, a vacuum deposition method, a spin coating method, or an inkjet method. For example, the electron transport layer **160** may have a thickness of about 15 nm to about 50 nm, for example, about 20 nm to about 35 nm.

The electron transport layer **160** may be formed of a known electron transport material. Examples of the known electron transport material are tris(8-quinolinolato) aluminum (Alq₃) and a compound having a nitrogen-containing aromatic ring. Examples of the nitrogen-containing aromatic ring are a pyridine ring-containing compound such as (1,3,5-tri[(3-pyridyl)-phenyl-3-yl]benzene), a triazine ring-containing compound such as 2,4,6-tris(3'-(pyridine-3-yl)biphenyl-3-yl)-1,3,5-triazine, and an imidazole ring-containing compound such as 2-(4-(N-phenylbenzoimidazolyl-1-yl-phenyl)-9,10-dinaphthylanthracene). In some embodiments, the electron transport layer **160** may use a commercially available electron transport material, for example, KLET-01, KLET-02, KLET-03, KLET-10, or KLET-M1 (available from Chemipro Kasei).

The electron injection layer **170** may be formed on the electron transport layer **160**. The electron injection layer **170** may facilitate injection of electrons from the second electrode **180**. The electron injection layer **170** may be formed on the electron transport layer **160** by, for example, a vacuum deposition method. For example, the electron injection layer **170** may have a thickness of about 0.3 nm to about 9 nm, for example, about 1 nm to about 5 nm.

The electron injection layer **170** may be formed of a known electron injection material, for example, (8-quinolinato)lithium (Liq), lithium fluoride (LiF), sodium chloride (NaCl), cesium fluoride (CsF), lithium oxide (Li₂O), barium oxide (BaO), or the like.

The second electrode **180** may be formed on the electron injection layer **170**. The second electrode **180** may be, for

47

example, a cathode. The second electrode **180** may be formed of a metal, an alloy, or a conductive compound that have a low work function. For example, the second electrode **180** may be formed of lithium (Li), magnesium (Mg), aluminum (Al), calcium (Ca), an aluminum-lithium (Al—Li) alloy, a magnesium-indium (Mg—In) alloy, a magnesium-silver (Mg—Ag) alloy, or the like. In some embodiments, the second electrode **180** may be formed as a transmissive electrode, for example, from indium tin oxide (ITO), indium zinc oxide (IZO), or the like.

Example embodiments of the structure of the organic light-emitting device **100** have been described above. The organic light-emitting device **100** according to an embodiment may have improved emission lifespan due to the inclusion of a copolymer according to any of the above-described embodiments.

Example embodiments of the structure of the organic light-emitting device **100** are described above. However, embodiments are not limited to the above-described structures of the organic light-emitting device **100**. The organic light-emitting device **100** as an embodiment of the present disclosure may have any of known various structures. For example, the organic light-emitting device **100** may have a structure without at least one of the hole injection layer **130**,

48

the hole transport layer **140**, the electron transport layer **160**, and the electron injection layer **170**. Each of these layers of the organic light-emitting device **100** may be formed as a single layer or multiple layers.

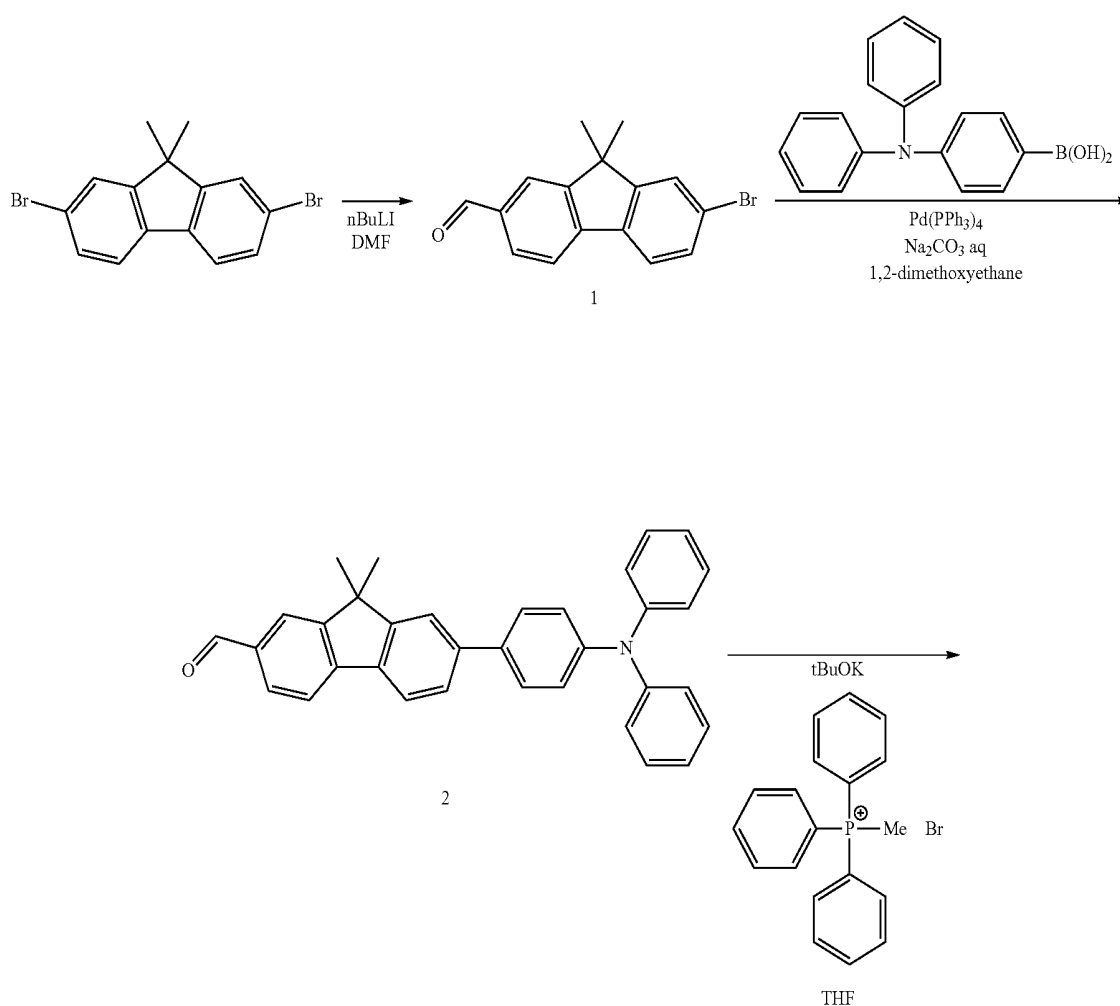
For example, the organic light-emitting device **100** may further include a hole blocking layer between the hole transport layer **140** and the emission layer **150** to prevent diffusion of triplet excitons or holes into the electron transport layer **160**. For example, the hole blocking layer may be formed of an oxadiazole derivative, a triazole derivative, a phenanthroline derivative, or the like.

One or more embodiments of copolymers, organic light-emitting device materials, organic light-emitting device preparation compositions, and organic light-emitting devices according to the present disclosure will now be described in detail with reference to the following examples. However, these examples are only for illustrative purposes and are not intended to limit the scope of the one or more embodiments of the present disclosure.

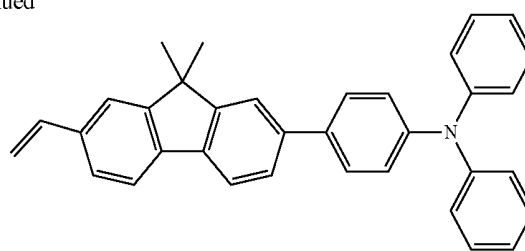
EXAMPLES

Synthesis of Monomer

A monomer A was synthesized according to the following processes.



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Monomer A

4.83 grams (g) (13.9 millimoles, mmol) of 2,7-dibromo-9,9-dimethyl-9H-fluorene was added to a 300-mL three-neck flask, followed by purging the flask with argon. 50 mL of anhydrous tetrahydrofuran (THF) was added to the flask, which was then cooled down with dry ice/acetone. After 5.6 mL of a 2.6 molar (M) n-butyllithium in hexane solvent was dropwise added thereto, the resulting mixture was maintained for about 1 hour and cooled down with a refrigerant, followed by dropwise addition of 1.7 mL of an anhydrous N,N-dimethylformamide (DMF) and stirring for about 1 hour. After the temperature increased to room temperature, impurities were separated from the resulting mixture with a Celite. Next, distilled water was added to the resulting solution, followed by extraction with toluene to collect an organic phase. This organic phase was concentrated to obtain a concentrate solution, and the concentrate solution was purified by column chromatography to obtain a compound 1.

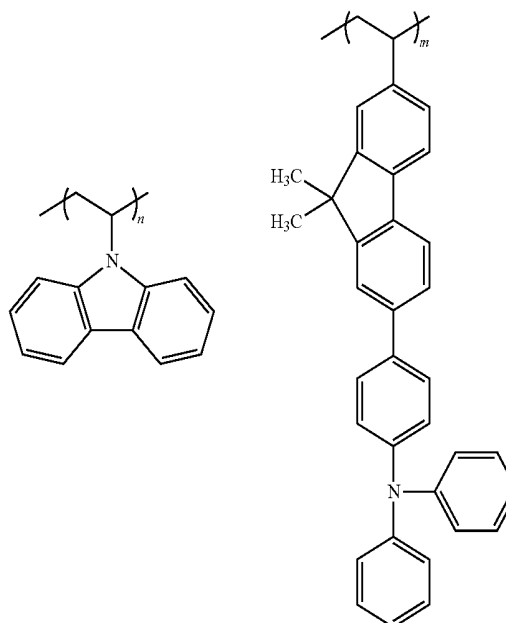
4.16 g (13.8 mmol) of the compound 1, 4.63 g (15.2 mmol) of diphenylaminophenylboronic acid, 0.48 g (0.41 mmol) of tetrakis(triphenylphosphine)palladium, 30 mL of 1,2-dimethoxyethane, and 16.5 mL of a 2 M aqueous sodium carbonate solution were added to a reactor under argon atmosphere, and the resulting mixture was stirred at about 80° C. for about 7 hours. After cooling down to room temperature, the resulting product was extracted three times with toluene/water to collect an organic phase. This organic phase was concentrated and then purified by column chromatography to obtain a compound 2.

4.07 g (11.4 mmol) of triphenylmethyl phosphonium bromide and 30 mL of anhydrous THF were added to a reactor under argon atmosphere, and then, cooled down with ice. Next, a solution of 1.29 g (11.5 mmol) of potassium t-butoxide (tBuOK) dissolved in 30 mL of anhydrous THF was dropwise added to the reactor, and then, a solution of 5.28 g (11.0 mmol) of the compound 2 dissolved in 30 mL of anhydrous THF was dropwise added thereto. After the temperature returned to room temperature, the resulting mixture was stirred at room temperature for about 3 hours. After the reaction was quenched, the resulting product was extracted three times with toluene/water, followed by purification by column chromatography, to obtain monomer A. A structure of the monomer A was identified by (high-performance) liquid chromatography-mass spectrometry (LC-MS).

Synthesis of Copolymer

Next, a polymer A was synthesized from the monomer A and vinylcabazole by the following method.

Polymer A



0.50 g (1.04 mmol) of the monomer A, 0.50 g (2.59 mmol) of vinylcabazole, 0.005 g (0.0305 mmol) of azobisisobutyronitrile (AIBN), and 10 mL of anhydrous toluene were added to a reactor under argon atmosphere and then stirred at about 80° C. for about 8 hours. After cooling the resulting mixture to room temperature, methanol was added thereto to obtain a precipitate. The resulting precipitate (solid) was dissolved in THF and purified by reprecipitation with acetone, to thereby obtain 0.24 g of the polymer A including units represented in the above formula. The polymer A had a number average molecular weight (Mn) of about 29,100 Daltons and a weight average molecular weight (Mw) of about 79,100 Daltons, as measured by gel permeation chromatography (GPC). The ratio of n to m in the polymer A was about 7:3.

Glass Transition Temperature Measurement

The glass transition temperature (Tg) of the polymer A was measured using a SII DSC 6220 (available from Seiko Instruments Inc.), according to the JIS K 7121.

Layer Stability Evaluation

The stability of a layer formed using the polymer A was evaluated according to the following processes. A solution of 1 percent by mass (mass %) of the polymer A in xylene was spin-coated on an indium tin oxide (ITO) layer having a thickness of about 150 nm formed on a glass substrate, to form a coating layer having a thickness of about 30 nm.

51

A surface of the formed coating layer was observed using an optical microscope to evaluate a surface state of the coating layer according to the following criteria.

○: The surface of the layer was uniform and no defect was observed.

△: A few dark spots were detected on the layer, but the layer was applicable to a device

×: Continuity of the layer not ensured, and the layer was not applicable to a device.

Example 1

Manufacture of Organic Light-Emitting Device

An organic light-emitting device including the above-described copolymer was manufactured according to the following processes.

First, a hole injection layer was formed by spin-coating PEDOT/PSS (available from Sigma-Aldrich) on a glass substrate having an indium tin oxide (ITO) first electrode (anode) in a stripe pattern to have a thickness of about 30 nm after drying.

Next, 1 mass % of the synthesized polymer A was dissolved in xylene to prepare a hole transport layer coating solution. The hole transport layer coating solution was coated on the hole injection layer to have a thickness of about 30 nm after being dried, and then heated at about 230° C. for about 1 hour to form a hole transport layer.

Next, triphenylenyl 3,6-bis-N-carbazolybenzene (TPSmCP) and 4,4'-bis(carbazole-9-yl)biphenyl (CBP) as host materials, and tris(2-(3-xylyl)phenyl)pyridine iridium (III) (TEG) as a dopant material were co-deposited on the hole transport layer using a vacuum deposition apparatus to form an emission layer having a thickness of about 30 nm. The ratio of TPSmCP to CBP was about 7:3 by mass, and a doped amount of tris(2-(3-xylyl)phenyl)pyridine iridium (III) was about 10 mass %.

Next, (8-quinolinolato) lithium (Liq) and KLET-03 (available from Chemipro Kasei) were co-deposited on the emission layer using the vacuum deposition apparatus to form an electron transport layer having a thickness of about 50 nm. Lithium fluoride (LiF) was then deposited on the electron transport layer using the vacuum deposition apparatus to form an electron injection layer having a thickness of about 1 nm. Aluminum was then deposited on the electron injection layer using the vacuum deposition apparatus to form a second electrode (cathode) having a thickness of about 100 nm, thereby finally manufacturing the organic light-emitting device.

Evaluation of Organic Light-Emitting Device

The current efficiency and emission lifespan of each organic light-emitting device were evaluated according to the following methods.

A predetermined voltage was applied to each organic light-emitting device using a direct current constant-voltage power source (Source meter, available from KEYENCE) to operate the organic light-emitting device. While the emis-

52

sion of the organic light-emitting device was measured using a luminance measurement apparatus (SR-3, available from Topcom), the current was gradually increased to measure a current density at a luminance of about 3000 candelas per square meter (cd/m^2), and then maintained constant. A current efficiency was calculated from the current density.

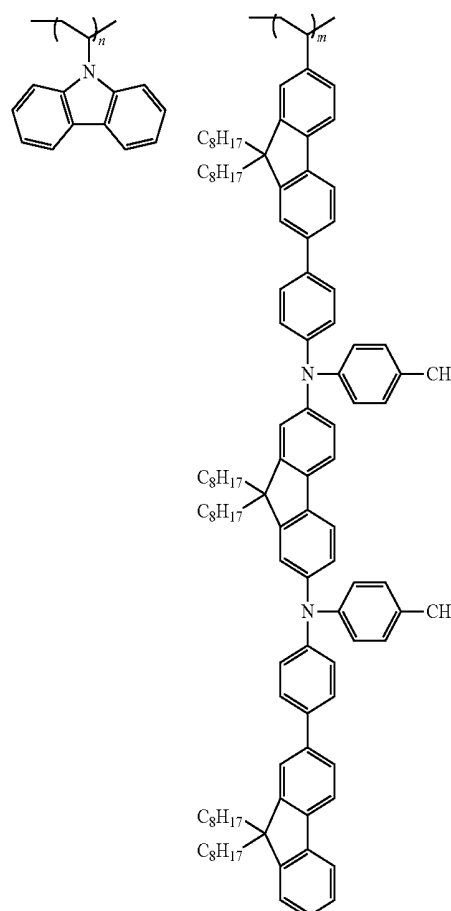
The emission lifespan of each organic light-emitting device was defined as the time took until an initial luminance measured using the luminance measurement apparatus was reduced by about 80%.

The evaluation results are shown in Table 1. In Table 1, the current efficiencies, and the emission lifespans as relative values to the emission lifespan of Comparative Example 1 assumed as 100 are represented.

Examples 2 and 3 and Comparative Examples 1 and 2

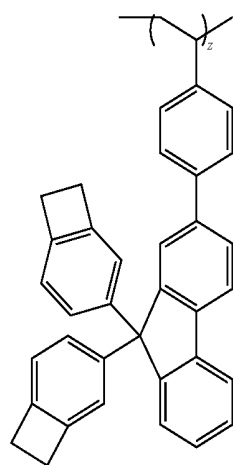
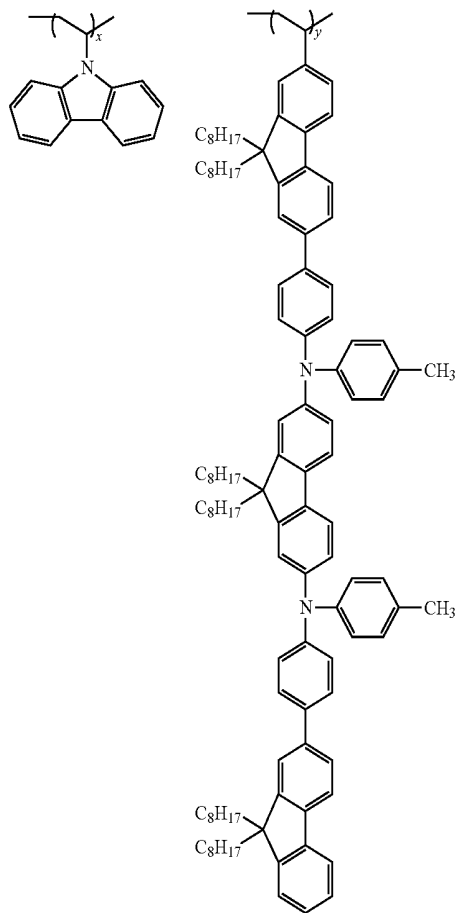
Organic light-emitting devices were manufactured in the same manner as in Example 1, except that hole transport layers were formed using different polymers, respectively, instead of the polymer used in Example 1. The results of evaluation of the organic light-emitting devices are shown in Table 1.

polymer B



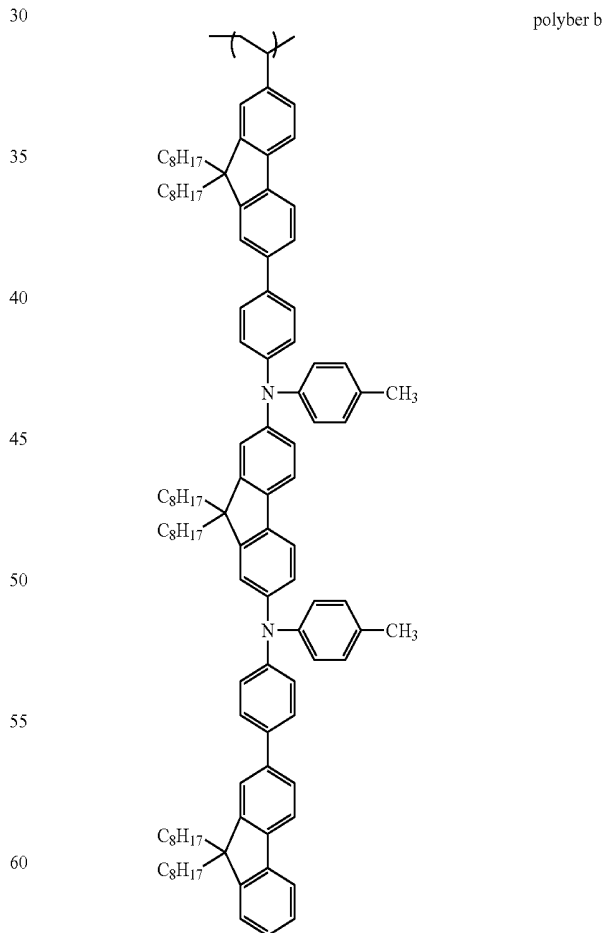
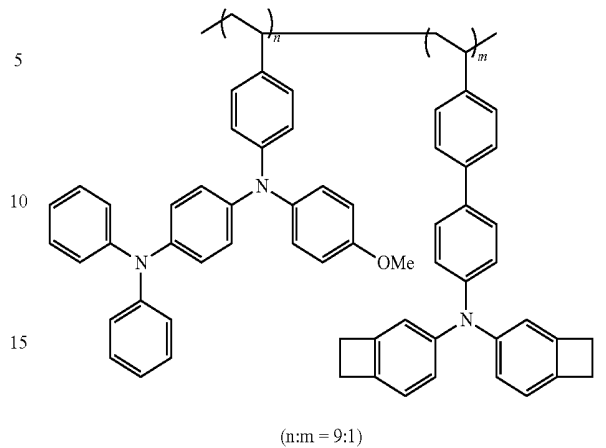
(n:m = 7:3)

53
-continued



(x:y:z = 65:25:10)

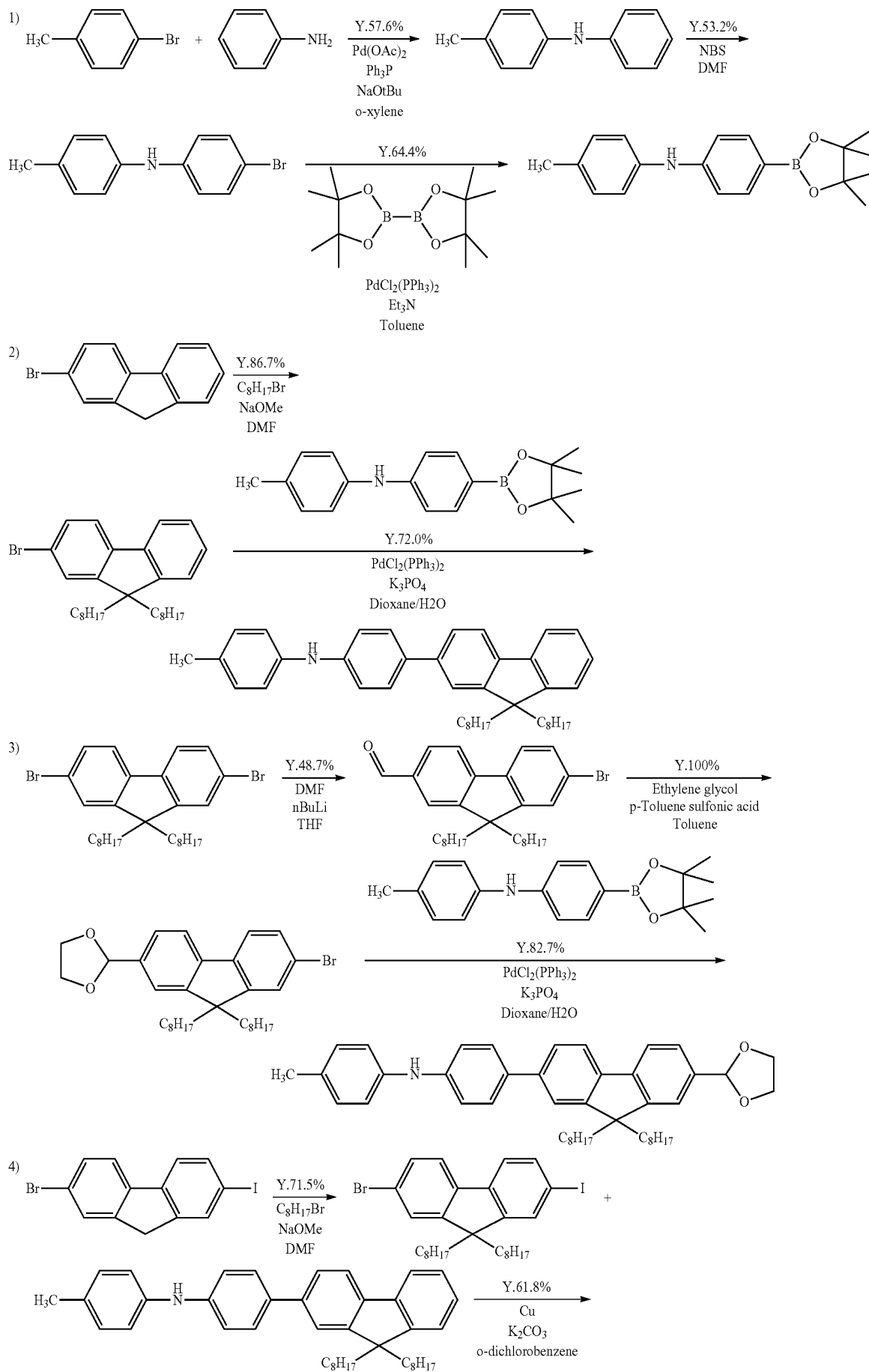
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65 Monomers used in the synthesis of polymers B, C and b were synthesized according to the following reaction schemes.

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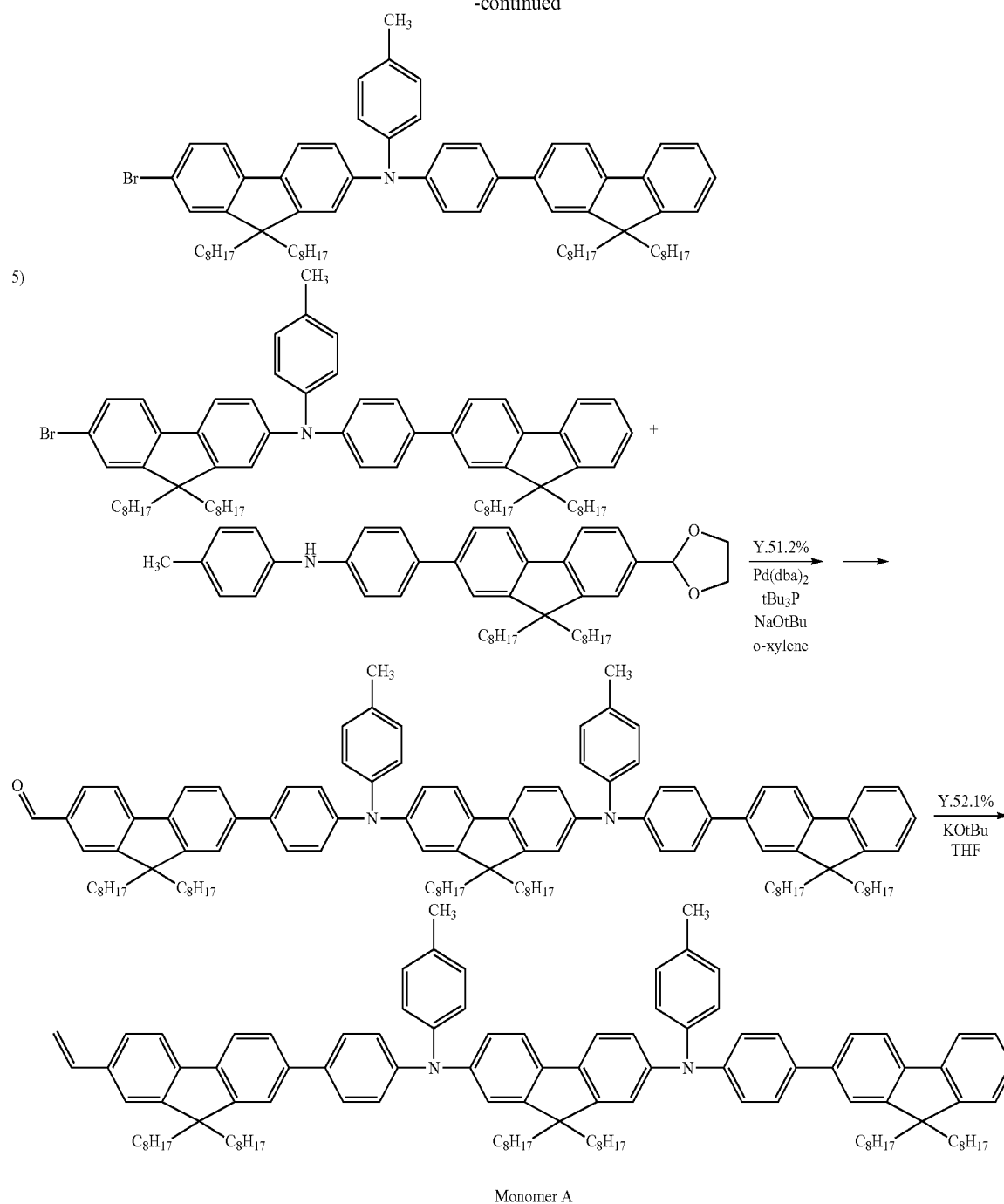
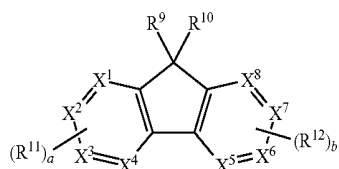


TABLE 1

	Hole transport layer	Mn	Mw	Tg(° C.)	Layer stability	Current efficiency	Emission lifespan
Example 1	polymer A	29,100	79,100	206	○	118	1,260
Example 2	polymer B	125,500	425,700	89	○	123	1,540
Example 3	polymer C	27,000	69,000	108	○	121	1,980
Comparative Example 1	polymer a	24,700	64,100	151	○	110	100
Comparative Example 2	polymer b	77,100	178,000	63	X	—	—

61

2. The copolymer of claim 1, wherein A is a group represented by Formula 4, in which any two of R⁹ to R¹² are bound to adjacent atoms:



Formula 4

wherein, in Formula 4,

R⁹ to R¹² each independently are selected from a hydrogen, a halogen atom, a hydroxyl group, an amino group, a nitro group, a cyano group; a substituted or unsubstituted silyl group; a substituted or unsubstituted C1-C20 alkyl group; a substituted or unsubstituted C3-C16 cycloalkyl group; a substituted or unsubstituted C6-C30 aryl group; a substituted or unsubstituted C6-C30 aryloxy group; a substituted or unsubstituted C7-C40 aralkyl group; a substituted or unsubstituted C1-C30 heteroaryl group; a substituted or unsubstituted C2-C40 heteroaralkyl group; a substituted or unsubstituted C1-C20 alkylamino group; a substituted or unsubstituted C6-C30 arylamino group, and a substituted or unsubstituted C6-C30 arylsulfonyl group, wherein any two adjacent groups selected from R⁹ to R¹² optionally form a ring,

a and b each independently are an integer from 1 to 4, and X¹ to X⁸ each independently are CH or N.

3. The copolymer of claim 2, wherein X¹ to X⁸ are CH.

4. The copolymer of claim 2, wherein R⁹ and R¹⁰ each independently are a hydrogen, a substituted or unsubstituted C1-C20 alkyl group, and a substituted or unsubstituted C6-C30 aryl group.

5. The copolymer of claim 1, wherein L¹ is selected from a single bond, a substituted or unsubstituted C5-C30 cycloalkylene group; a substituted or unsubstituted C10-C30 arylene group, and a substituted or unsubstituted C1-C30 heteroarylene group.

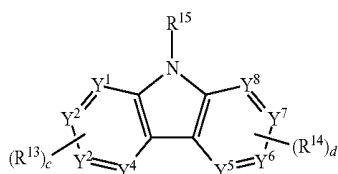
6. The copolymer of claim 1, wherein L¹ is a single bond, a substituted or unsubstituted naphthylene group, or a substituted or unsubstituted norbornylene group.

7. The copolymer of claim 1, wherein L² is selected from a single bond, a substituted or unsubstituted C5-C30 cycloalkylene group; a substituted or unsubstituted C6-C30 arylene group; and a substituted or unsubstituted C1-C30 heteroarylene group.

8. The copolymer of claim 1, wherein L² is a single bond, or a substituted or unsubstituted fluorenylene group.

9. The copolymer of claim 1, wherein Cz is represented by Formula 5, in which any two of R¹³ to R¹⁵ are bound to an adjacent atom:

Formula 5



wherein, in Formula 5,

Y¹ to Y⁸ each independently are CH or N, R¹³ to R¹⁵ each independently are a hydrogen, a halogen atom, a hydroxyl group, an amino group, a nitro group,

62

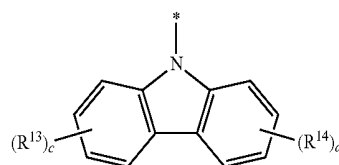
a cyano group; a substituted or unsubstituted silyl group;

a substituted or unsubstituted C1-C20 alkyl group; a substituted or unsubstituted C1-C20 amino alkyl group; a substituted or unsubstituted C3-C16 cycloalkyl group; a substituted or unsubstituted C6-C30 aryl group; a substituted or unsubstituted C6-C30 amino aryl group; a substituted or unsubstituted C1-C30 heteroaryl group; a substituted or unsubstituted C1-C20 alkoxy group; a substituted or unsubstituted C3-C16 cyclo alkoxy group; a substituted or unsubstituted C6-C30 aryloxy group; a substituted or unsubstituted C7-C40 aralkyl group; a substituted or unsubstituted C2-C40 heteroaralkyl group; a substituted or unsubstituted C1-C20 alkylamino group, or a substituted or unsubstituted C6-C30 arylamino group, wherein any two adjacent groups selected from R¹³ to R¹⁵ optionally form a ring, and

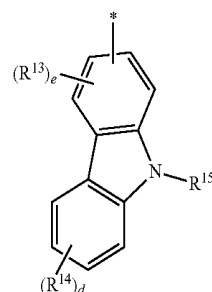
c and d each independently are an integer from 0 to 4.

10. The copolymer of claim 9, wherein Cz is represented by Formula 6 or Formula 7, in which any one of R¹³ and R¹⁴ is bound to an adjacent atom:

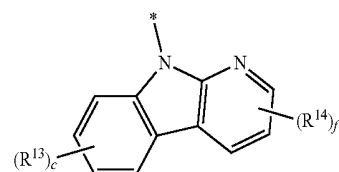
Formula 6



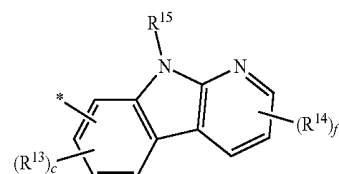
Formula 7



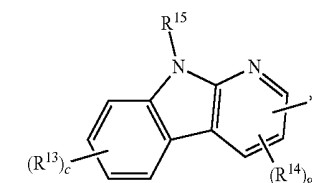
Formula 8



Formula 9

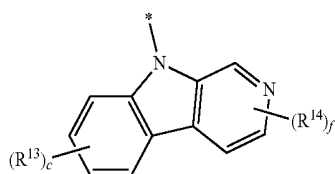


Formula 10

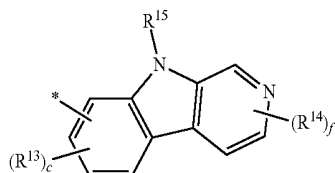


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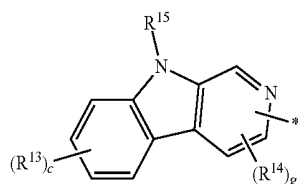
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Formula 11



Formula 12

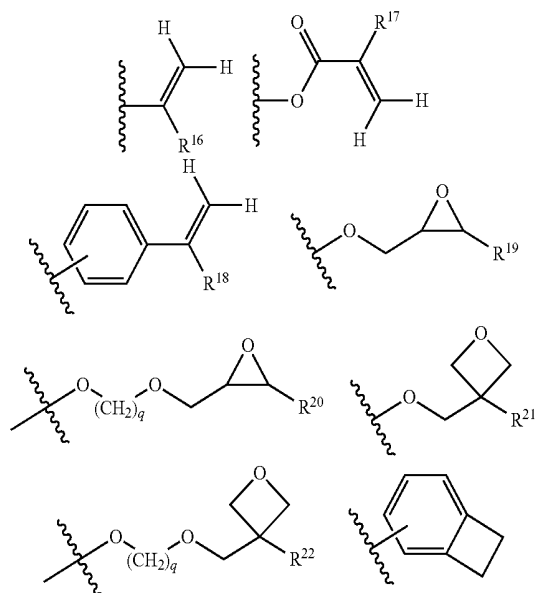


Formula 13

wherein, in Formula 6 to Formula 13, R^{13} to R^{15} , c, and d are the same as in Formula 5, e and f each independently are an integer from 0 to 3, g is an integer from 0 to 2, and * is a binding site with an adjacent atom.

11. The copolymer of claim 1, further comprising a polymerizable comonomer, and the polymerizable comonomer comprises at least one of cross-linking groups represented by the following formulae:

Cross-linking groups

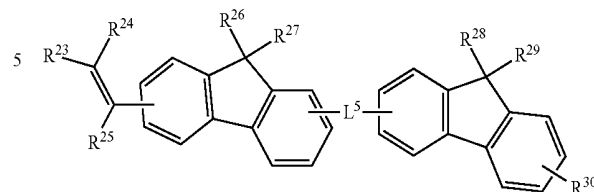


wherein, in the above formulae of the cross-linking groups,

R^{16} to R^{22} each independently are hydrogen; or a substituted or unsubstituted C1-C10 alkyl group, and q is an integer from 1 to 10.

12. The copolymer of claim 11, wherein the polymerizable comonomer is a compound represented by Formula 14:

64



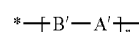
Formula 12

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wherein, in Formula 14, R^{23} to R^{25} each independently are selected from a hydrogen; a substituted or unsubstituted C1-C10 alkyl group; and a substituted or unsubstituted C6-C30 aryl group, R^{26} to R^{30} each independently are selected from a hydrogen, a halogen atom, a hydroxyl group, an amino group, a nitro group, a cyano group; a substituted or unsubstituted silyl group; a substituted or unsubstituted C1-C10 alkyl group; a substituted or unsubstituted C3-C16 cycloalkyl group; a substituted or unsubstituted C6-C30 aryl group; a substituted or unsubstituted C1-C20 alkoxy group; a substituted or unsubstituted C6-C30 aryloxy group; a substituted or unsubstituted C7-C40 aralkyl group; a substituted or unsubstituted C1-C30 heteroaryl group; a substituted or unsubstituted C2-C40 heteroaralkyl group; a substituted or unsubstituted C1-C20 alkylamino group, and a substituted or unsubstituted C6-C30 arylamino group, wherein any two adjacent groups selected from R^{26} to R^{30} optionally form a ring,

L^5 is selected from a single bond, a substituted or unsubstituted C1-C20 alkylene group; a substituted or unsubstituted C3-C16 cycloalkylene group; a substituted or unsubstituted C6-C30 arylene group; a substituted or unsubstituted C1-C20 oxyalkylene group; a substituted or unsubstituted C3-C16 oxycycloalkylene group; a substituted or unsubstituted C6-C30 oxyarylene group; a substituted or unsubstituted C7-C40 aralkylene group; a substituted or unsubstituted C1-C30 heteroarylene group; a substituted or unsubstituted C6-C30 amino arylene group; a silylene group substituted with a C1-C20 alkyl group, a silylene group substituted with a C6-C30 aryl group, and a combination thereof, and at least one of R^{26} to R^{30} is selected from the cross-linking groups.

13. The copolymer of claim 12, wherein L^5 is represented by Formula 15:



Formula 15

55

wherein, in Formula 15,

A' is represented by Formula 3, and

B' comprises a fluorene ring system or an aza fluorene ring system,

r is an integer from 1 to 20, and

* is a binding site with an adjacent atom.

14. The copolymer of claim 12, wherein L^5 is represented by Formula 3.

15. The copolymer of claim 1, wherein the copolymer has a number average molecular weight of about 10,000 to about 100,000 Daltons.

16. An organic light-emitting device comprising:

a first electrode;

a second electrode; and

an organic layer disposed between the first electrode and the second electrode, wherein the organic layer comprises the copolymer of claim 1. 5

17. The organic light-emitting device of claim 16,

wherein the organic layer comprises at least one layer, and

wherein the at least one layer is a hole transport layer comprising the copolymer. 10

18. The organic light-emitting device of claim 17, wherein the organic layer further comprises at least one layer that is an emission layer comprising a light-emitting material which ensures emission from triplet excitons.

19. An organic light-emitting device material comprising the copolymer of claim 1. 15

20. The organic light-emitting device material of claim 19, further comprising a solvent.

* * * * *

专利名称(译)	共聚物，包括其的有机发光器件材料，以及包括有机发光器件材料的有机发光器件		
公开(公告)号	US10040887	公开(公告)日	2018-08-07
申请号	US15/388925	申请日	2016-12-22
[标]申请(专利权)人(译)	三星电子株式会社		
申请(专利权)人(译)	SAMSUNG ELECTRONICS CO. , LTD.		
当前申请(专利权)人(译)	SAMSUNG ELECTRONICS CO. , LTD.		
[标]发明人	KORAI KEISUKE ITO MITSUNORI		
发明人	KORAI, KEISUKE ITO, MITSUNORI		
IPC分类号	H01L51/50 C08F226/12 H01L51/00		
CPC分类号	C08F226/12 H01L51/0039 H01L51/5016 H01L51/0043 H01L51/5056		
代理机构(译)	康托科尔伯恩LLP		
审查员(译)	CLARK , GREGORYð		
优先权	2015257422 2015-12-28 JP 1020160146911 2016-11-04 KR		
其他公开文献	US20170183439A1		
外部链接	Espacenet		

摘要(译)

包含由式1表示的单元和由式2表示的单元的共聚物：其中，在式1和式2中，基团和变量与说明书中描述的相同。

