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(54) A SPIROBIFLUORENE COMPOUND FOR LIGHT EMITTING DEVICES

SPIROBIFLUORENVERBINDUNG FÜR LICHTEMITTIERENDE VORRICHTUNGEN

COMPOSÉ SPIROBIFLUORÈNE POUR DISPOSITIFS ÉLECTROLUMINESCENTS

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(56) References cited:
WO-A1-2010/015306 **WO-A1-2011/075359**
JP-A- 2010 027 681 **US-A1- 2008 220 286**

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Description

Technical Field

[0001] The present invention relates to compounds based on spirobifluorene and light emitting devices comprising said compounds.

Background Art

[0002] Various organic light emitting devices have been under active study and development, particularly those based on electroluminescence (EL) from small organic materials. For such organic devices, the ability to form morphologically stable amorphous films is a key requirement for the development of small materials for organic light emitting diodes (OLEDs). That is because when a small molecule compound is used as the organic light-emitting material, crystallization usually occurs if the molecule of the compound is too small and its structure is too symmetrical. Therefore, when applied in an organic light-emission layer, the small molecule compound is vulnerable to morphological change such as crystallization, and once the crystal is formed, it yields negative impacts upon the light-emitting nature and service life of the OLED.

[0003] Thermal stress during device operation can lead to such phase transitions from the amorphous state to the thermodynamically stable polycrystalline state leading to dramatic degradation of the device. As a result it is crucial to design materials featuring high glass transition temperature (Tg >150°C) in order to stabilize the amorphous state. For improving the stability of devices in order to increase operational lifetime, several host materials have been reported. Especially, designing materials having a spiro linkage has been a very successful strategy to obtain OLEDs materials with enhanced morphological stability while keeping their electro-optical functionality.

[0004] US2006/0141287 discloses light-emitting layers which include a solid organic material containing a mixture of at least two components. The first host component is an organic compound capable of transporting electrical charges and also forms an aggregate. The second component of the mixture is an organic compound capable of transporting electrical charges and, upon mixing with the first host component, is capable of forming a continuous and substantially pinhole-free layer. In the reference, as the second component, various compounds such as substituted fluorene derivatives, and spirobifluorene derivatives, etc. are used.

[0005] US2010/0072887 also discloses light-emitting devices which are made of layers containing organoselenium compounds such as dibenzoselenophene, benzo[b]selenophene, or benzo[c]selenophene derivatives. These organoselenium compounds may serve as hosts for phosphorescent organometallic dopants.

[0006] In addition to the above patent references, there are several literature references disclosing spirobifluorene compounds. In Advanced Materials (Weinheim, Germany) (2004), 16(18), 1624-1629, hosts based on oligomers of the carbazole and 9,9'-spirobifluorene (spiro) building blocks, especially para and meta interconnected oligomers, suitable for efficient color-tunable triplet emission, are investigated in terms of the triplet excited-state properties. In this literature reference, the improvement of hole and electron injection in hosts for blue-, green- and red-light emission is also expected for the oligomer. Further, Chemical Physics Letters (2008), 461(1-3), 9-15 also includes simulation results on a series of spiro-linked oligofluorenes and derivatives.

[0007] JP 2010/027681 discloses 3,6-Bis-N-carbazolyl-9,9'spirobifluorene.

[0008] WO 2010/015306 relates to organic electroluminescent devices, comprising fluorene derivatives and spirobifluorene compounds as a material mix for phosphorescent emitters. Spirobifluorene compounds are disclosed comprising a group Ar either as s substituent of the phenyl rings of the spirobifluorene group or as a linker of two spirobifluorene compounds.

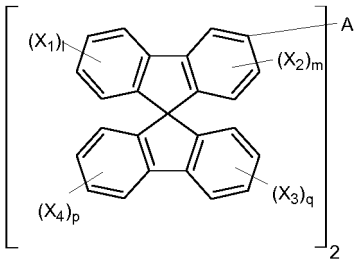
[0009] Non-prepublished patent application WO 2011/075359 provides an OLED device comprising an anode, a cathode and a light emitting layer located therebetween, said light emitting layer comprising an anthracene host and a styrylamine blue light emitting compound; and, located between the said light emitting layer and the cathode, a first electron-transporting layer greater than 0.5 nm and less than 5 nm thick and a second electron-transporting layer consisting essentially of an anthracene located between the first electron-transporting layer and the cathode; and wherein the first electron transporting-layer includes a compound with a less negative LUMO value than the anthracene in the second electron-transporting layer. Compound B4, a bis-spirobifluorenylcompound is disclosed as compound for the first electron-transporting layer.

[0010] However, none of the above-disclosed materials meets all the requirements necessary for OLED application, particularly suitable energy level for high phosphorescent efficiency (high triplet energy), high morphological stability, while maintaining other electro-optic and processing properties under operational conditions of the device, such as emission color, dimensional stability, etc. Thus, there has been a need to develop new host materials, which are capable of satisfying all of the requirements indicated above.

Summary of invention

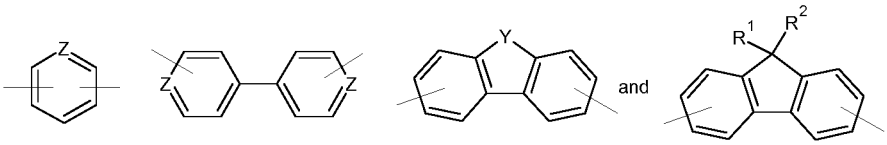
[0011] Surprisingly, it has been found that a spirobifluorene-based compound substituted by an appropriate substituent as defined in the appended claims exhibits both a good life-time and a good efficiency when it is used in light emitting devices.

[0012] In one aspect of the present invention, compounds represented by Formula (I) or (II) are provided as below.



Formula (I)

wherein A is a single bond or a divalent residue of biphenyl, triphenyl,

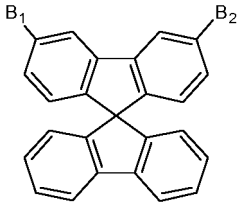


in each of which one or more hydrogen atoms attached in the carbon atoms may be replaced by a substituent other than hydrogen, wherein Z is any one selected from N, O, S, and SiR, Y is N-R, O, S or $Si(R)_2$ where R is C_{1-20} alkyl or aryl, R^1 and R^2 are independently selected from hydrogen and C_{1-20} alkyl;

X_1 to X_4 are independently selected from substituents other than spirobifluorenyl;

1, p and q are independently selected from integers of from 0 to 4;

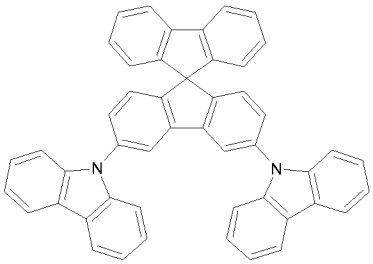
m is an integer of from 0 to 3,



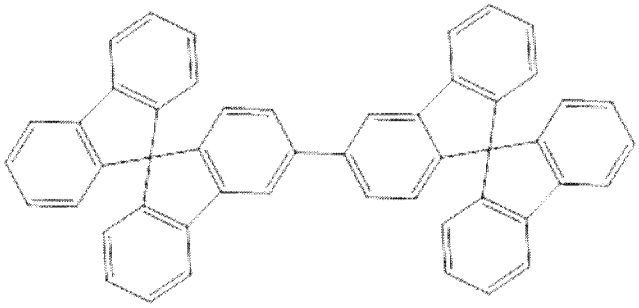
Formula (II)

wherein B_1 and B_2 are independently selected from hydrogen, and a heterocyclic group selected from carbazole, dibenzothiophene, dibenzofurane, acridine, dibenzosilole, and bipyridine each of which is optionally substituted by one or more substituents other than hydrogen;

with the proviso that B_1 and B_2 are not hydrogen simultaneously with the exception of 3,6-Bis-N-carbazolyl-9,9'-spirobifluorene of the formula



and further with the exception of



[0013] The compounds of the present invention can be used in various applications, including in OLED, photovoltaic cells or organic semiconductor devices. For example, those compounds can act as an efficient host material for phosphorescent emitters in OLED. The present invention also provides a device, preferably a light emitting device, comprising said compound.

Brief description of drawings

[0014]

FIG. 1 shows an organic light emitting device having separate electron transport, hole transport, and emissive layers, as well as other layers.

FIG. 2 shows external quantum efficiency versus luminance for the device of Example 2.

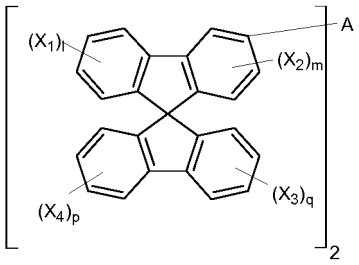
FIG. 3 shows the electroluminescence(EL) spectrum for Example 2.

FIG. 4 shows lifetest data (luminescence versus time at L_0 = 2000 Cd/m^2) for the device of Example 2.

Description of embodiments

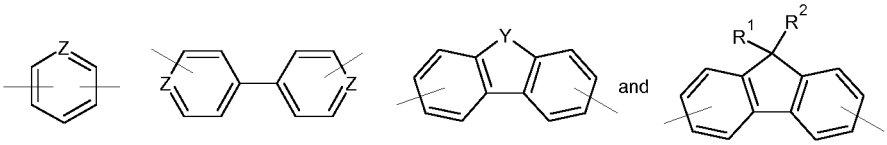
[0015] Designing materials having a spiro linkage has been a very successful strategy to obtain OLEDs materials with enhanced morphological stability while keeping their electro-optical functionality. This concept is based on the idea of connecting two molecular π-systems with equal or different functions (emission, charge transport) via a common sp3-hybridized atom. In addition to the spiro linkage, in a compound of the present invention, a substituent is introduced in specific positions to control the triplet energy of the present compound.

[0016] The present invention provides a host material, which can be represented by Formula (I) or (II).



Formula (I)

wherein A is a single bond or a divalent residue of biphenyl, triphenyl,

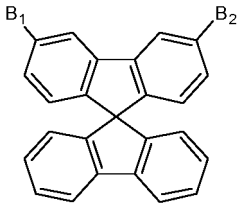


in each of which one or more hydrogen atoms attached in the carbon atoms may be replaced by a substituent other than hydrogen, wherein Z is any one selected from N, O, S, and SiR, Y is N-R, O, S or $Si(R)_2$ where R is C_{1-20} alkyl or aryl, R^1 and R^2 are independently selected from hydrogen and C_{1-20} alkyl;

X_1 to X_4 are independently selected from substituents other than spirobifluorenyl,

1, p and q are integers of from 0 to 4;

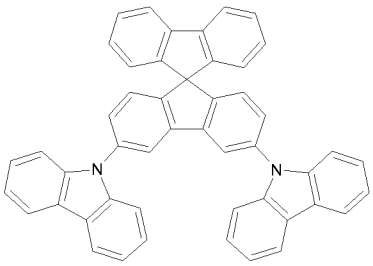
m is an integer of from 0 to 3,



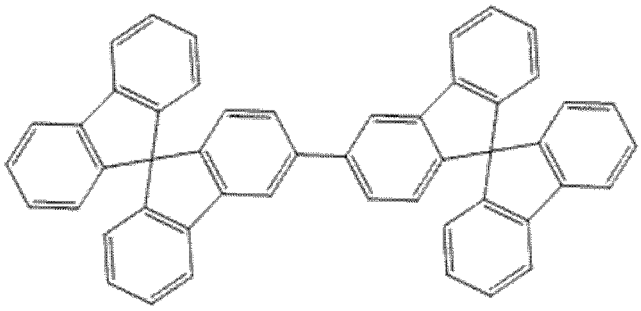
Formula (II)

wherein B_1 and B_2 are independently selected from hydrogen and a heterocyclic group selected from carbazole, dibenzothiophene, dibenzofurane, acridine, dibenzosilole, and bipyridine each of which is optionally substituted by one or more substituents other than hydrogen;

with the proviso that B_1 and B_2 are not hydrogen simultaneously, with the exception of 3,6-Bis-N-carbazolyl-9,9'-spirobifluorene of the following formula



and further with the exception of



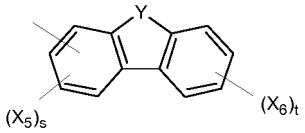
[0017] In some embodiments, the compound is represented by Formula (I) and 1, m, p and q are 0..

[0018] In accordance with the present invention, A, B_1 and B_2 are substituted in meta position of the spirobifluorene ring since the substitution in the meta position should break the conjugation between the spirobifluorene moieties and the rest of the molecule, ensuring a high triplet energy, and the oligomers of meta-substituted spirobifluorene have higher triplet energy compared to para-substituted ones so that the former are more suitable as hosts for blue emitters. Moreover, the presence of the spiro moieties leads to a high glass transition temperature and promotes the formation of morphologically stable amorphous films, which are essential features for hosts in the OLED emissive layer to produce blue or white light.

[0019] In a specific aspect of the invention, A is a single bond.

[0020] In another aspect, B_1 is hydrogen and B_2 is a heterocyclic group selected from carbazole, dibenzothiophene, dibenzofurane, acridine, dibenzosilole, and bipyridine each of which is optionally substituted by one or more substituents other than hydrogen.

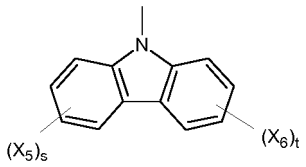
[0021] In one specific embodiment, the heterocyclic group is represented by Formula (III).



Formula (III)

wherein Y is N-R, O, S or $Si(R)_2$ where R is C_{1-20} alkyl or C_{1-20} aryl; X_5 and X_6 are independently selected from substituents other than hydrogen; and s is an integer of from 0 to 3 and t is an integer of from 0 to 4.

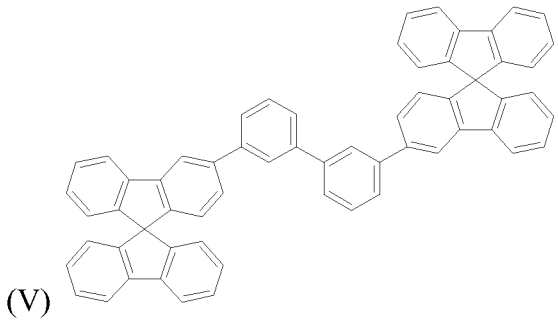
[0022] In another embodiment, the heterocyclic group is represented by Formula (IV).



(IV)

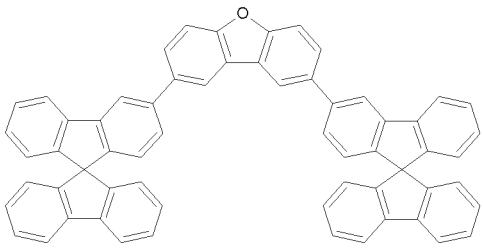
wherein X_5 and X_6 are independently selected from substituents other than hydrogen; and s and t are independently selected from integers of from 0 to 4.

[0023] In more specific embodiments, the compounds of the present invention are represented by any one of Formulae (V) to (VIII).

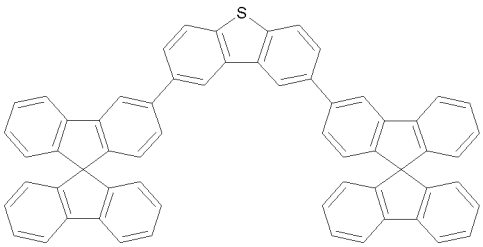


(V)

(VI)

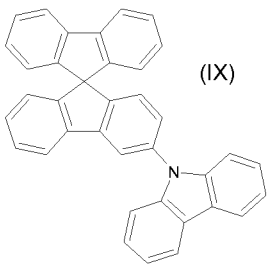


(VII)

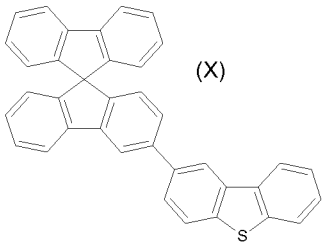


(VIII)

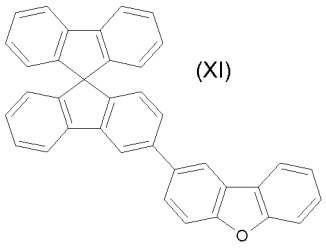
[0024] In another specific aspect of the present invention, the compounds are represented by any one of the following formulae IX to XVI



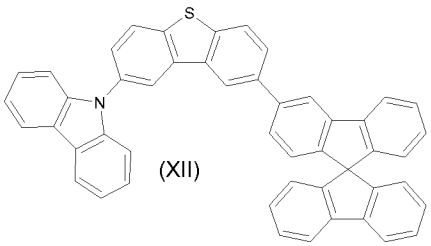
(IX)



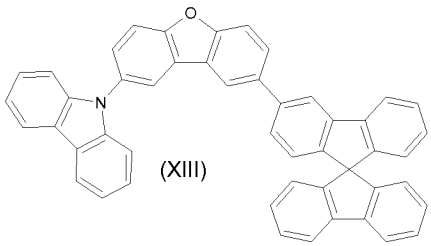
(X)



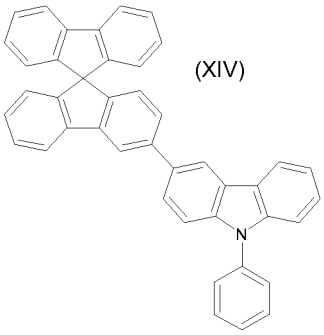
(XI)



(XII)



(XIII)



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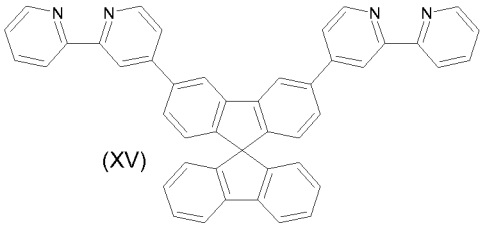
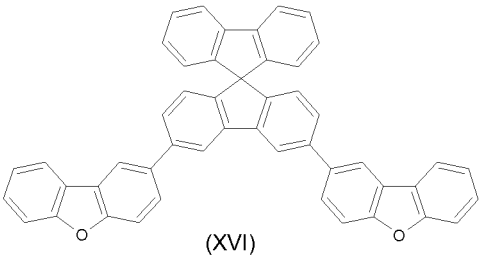


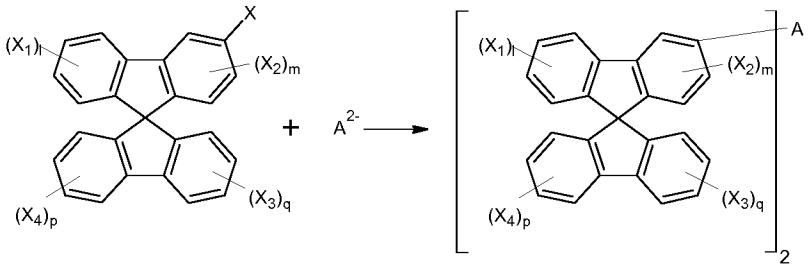
(XV)



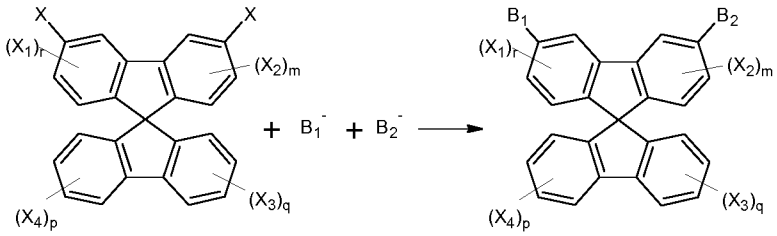
(XVI)

[0025] The synthesis of the compounds of the present invention can be accomplished by any known method. Generally, according to the embodiments of the present invention, the compounds of Formulae (I) and (II) can be prepared by the following reaction schemes:

Scheme 1.



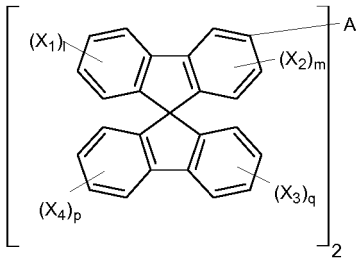
Scheme 2.



wherein X is a leaving group such as halogen, preferably a bromine atom.

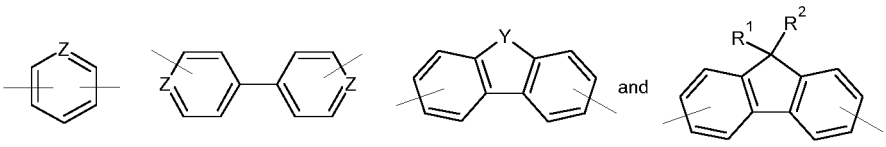
[0026] The present invention is also directed to a light emitting device comprising the spirobifluorene compounds of Formula (I) or (II) as above and a light emitting compound.

[0027] Accordingly, another object of the present invention is a light emitting device comprising a compound C of formula I



Formula (I)

wherein A is a divalent residue of biphenyl, triphenyl,

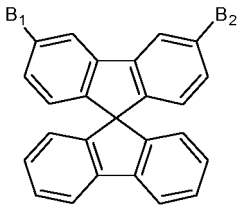


each of which one or more hydrogen atoms attached in the carbon atoms may be replaced by a substituent other than hydrogen, wherein Z is any one selected from N, O, S, and SiR, Y is N-R, O, S or $Si(R)_2$ where R is C_{1-20} alkyl or aryl, R^1 and R^2 are independently selected from hydrogen and C_{1-20} alkyl;

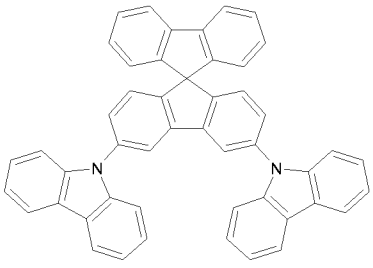
X_1 to X_4 are independently selected from substituents other than spirobifluorenyl;

1, p and q are integers of from 0 to 4;

m is an integer of from 0 to 3,
or of formula II

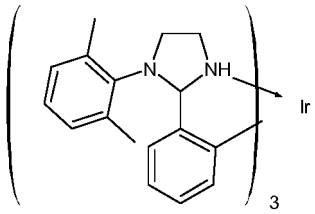


wherein B_1 and B_2 are independently selected from hydrogen, and a heterocyclic group selected from carbazole, dibenzothiophene, dibenzofurane, acridine, dibenzosilole, and bipyridine each of which is optionally substituted by one or more substituents other than hydrogen and with the proviso that B_1 and B_2 are not hydrogen simultaneously, with the exception of 3,6-Bis-N-carbazolyl-9,9'-spirobifluorene of the formula



and a light emitting compound.

[0028] Suitable emitting compounds can be selected from those known in the art and hereafter developed including, without limitation, a metal complex represented by Formula (XX) as disclosed in US 2008/238305:



Formula (XX)

[0029] The above mentioned metal complexes, in particular iridium complexes, can exhibit a phosphorescent emission in the visible region of the spectrum. In specific embodiments, the emissive compound exhibits a phosphorescent emission in the blue region of the spectrum.

[0030] Another aspect of the present invention relates to an OLED comprising the compound of Formula (I) or (II) and a light emitting compound, specifically a metal complex.

[0031] Another aspect of the present invention relates to use of the compound of Formula (I) or (II) and a light emitting compound such as metal complexes as defined above in an OLED.

[0032] The OLED device generally comprises:

a glass substrate;
a generally transparent anode such as an indium-tin oxide (ITO) anode;
a hole transporting layer (HTL);
an emissive layer (EML);
an electron transporting layer (ETL); and
a generally metallic cathode such as an Al layer. The emissive layer comprises the host material, and also comprises an emissive material (dopant). The emissive material is adapted to emit light when voltage is applied across the device. The emissive material can be a phosphorescent emitter, more specifically an iridium complex such as those represented by Formula (IX) as above. Those layers are well known in the art, as recited in US 2010/0190984, the disclosures of which are incorporated herein for entirety.

[0033] If the emissive material is used as a dopant in a host layer comprising the spirobifluorene compound, then it is generally used in an amount of at least 1 wt%, specifically at least 3 wt%, and more specifically at least 5 wt%, with respect to the total weight of the host and the dopant. Further, it is generally used in an amount of at most 30 wt%, specifically at most 25 wt%.

[0034] The present invention also relates to a use of the compounds according to the present invention in OLED, photovoltaic cells or organic semiconductor devices.

Examples

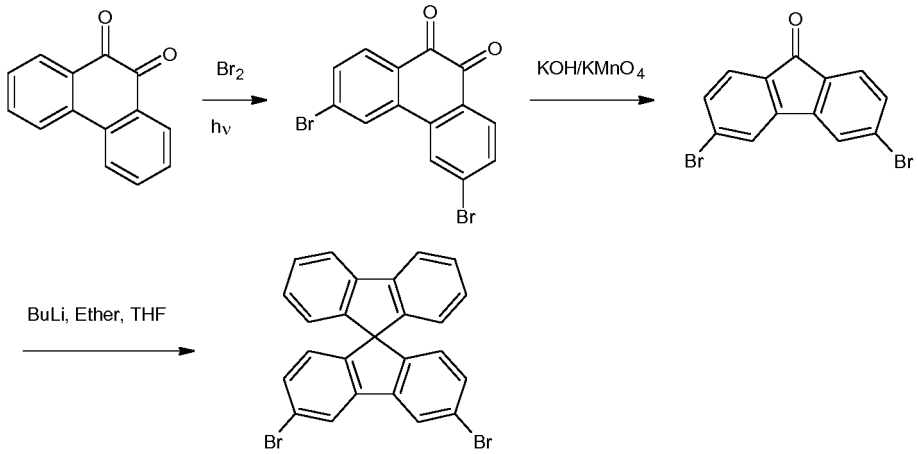
[0035] Hereinafter, the present invention will be explained in detail with reference to examples and comparative examples. These examples, however, should not in any sense be interpreted as limiting the scope of the present invention. Further, units are expressed by weight unless otherwise described.

Synthetic Methods

[0036] All reactions were realized under inert atmosphere. The boronic esters used were purchased or synthesized following the usual methods. The solvents and reagents were used as received. All products tested in device were sublimed twice.

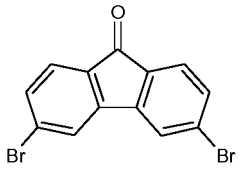
Synthetic Example 1

[0037]



3,6-dibromo-fluorenone

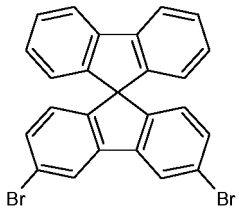
[0038]



[0039] This compound was synthesized following the method of Yong Cao et al. (Advanced Materials. (2008), 20, 2359-2364).

3,6-dibromo-spirobifluorene (3,6-Di-Br-SBF)

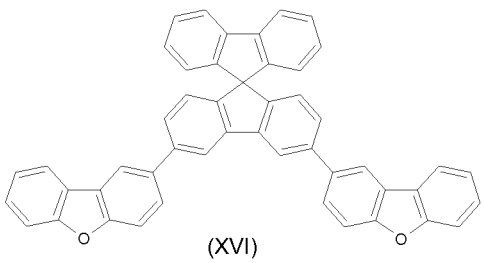
[0040]



[0041] Following the method used hereinafter for the formation of 3-bromospirobifluorene, the dibromo compound was isolated with 48 % yield.

Compound XVI

[0042]

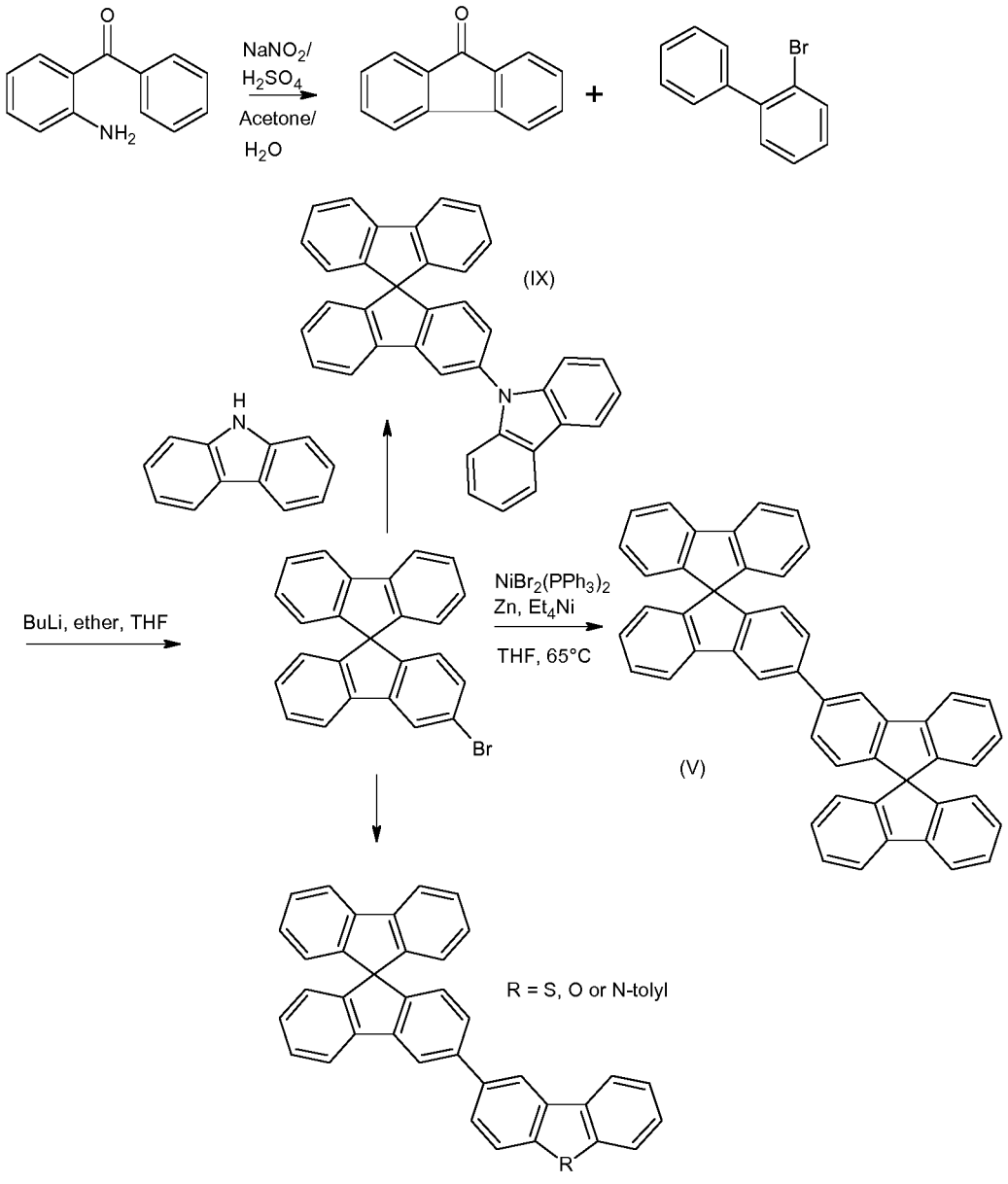


(XVI)

[0043] 3 equivalents of the boronic ester of dibenzofurane (17.1 mmol) and 3,6-Di-Br-SBF (5.7 mmol) were solubilized in toluene. The catalyst $Pd(PPh_3)_4$, the Na_2CO_3 and EtOH were then added and the medium was warmed to reflux for 24 h. After evaporation and usual work-up, a white solid was recovered and a flash chromatography afforded the desired product (yield 60 %).

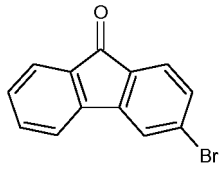
Synthetic Examples 2-6

[0044]



3-Bromo-fluorenone

[0045]

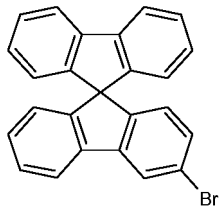


[0046] In a three ways flask 60 ml of water were added to 8.9 ml of HCl (37 % w/w, 2.1 equivalents) and the medium was cooled to 0°C. $NaNO_2$ (1.5 equivalents), dissolved in 50 ml of water, was added dropwise at 0°C. At the end of the addition, 4-amino-2-bromobenzophenone (one equivalent, 15.0 g, 51.6 mmol) solubilized in a mixture of acetone/water (400/230 ml), was added carefully. After 30 minutes at room temperature, the mixture was warmed at 60 °C for 3 hours.

[0047] After extraction with methylene chloride and evaporation of the organic phase, a brown solid was recovered (17.4 g) and a flash chromatography was realized. The pure compound was recovered after crystallization with hexane (4.2 g, 32 % yield).

3-bromo-spirobifluorene (3-SBF)

[0048]

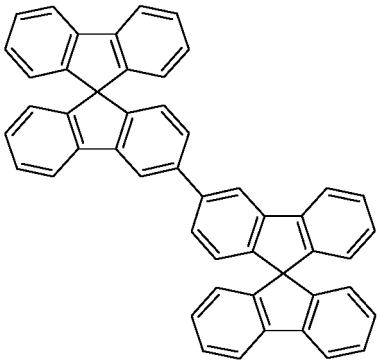


[0049] This compound was made in two steps from 3-bromofluorenone. First, 2-bromobiphenyl (1.05 equivalents, 4.0 g, 16.5 mmol) was solubilized in 102 ml of anhydrous diethyl ether (Et_2O). This solution was cooled to -60°C and BuLi (1.16 eq.) was added dropwise. After 10 min at this temperature, a white precipitate appeared which was redissolved when the medium was warmed to room temperature. 3-bromofluorenone was then added and the reaction mixture was let at 45 °C for one night.

[0050] After addition of NH_4Cl (5% aq., 260 ml) and extraction with Et_2O, 7.0 g of the alcohol was obtained. This solid was solubilized in 141 ml of AcOH and hydrolized by the addition of 78 ml of HCl/dioxane (20 eq.). After evaporation of the solvents, the solid was chromatographied to afford 5.86 g of the target compound (94 % yield).

Dispirobifluorene (Compound V) - for comparison

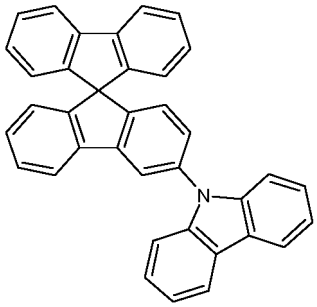
[0051]



[0052] 3-BrSBF (5.3 g, 14.5 mmol) was solubilized in 125 ml of anhydrous THF at RT. Zn (1.54 eq.) and Et_4Ni (1 eq) were added to the reaction and the whole mixture was warmed during 2 h to 65°C. $NiBr_2(PPh_3)_2$ was then added and the medium was warmed to reflux during 72 h. During the reaction, 0.05 equivalents of nickel catalyst could be added. After 48 h the reaction was stopped and the reaction medium was filtered through silica pad. After flash chromatography, the dimer was recovered with 30 % yield (m = 1.41 g).

3-N-Carbazole-spirobifluorene (Compound IX)

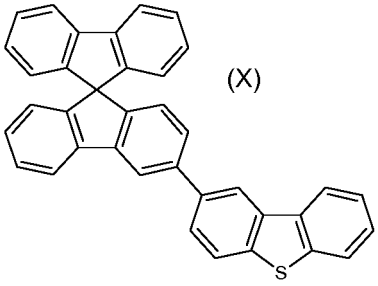
[0053]



[0054] Pd-bis-dibenzylidenacetone $Pd(dba)_2$ (catalyst, 4 % mol) and tris-t.-butyl phosphine ($P(tBu)_3$, 0.2 eq) were introduced at room temperature in toluene in a two ways flask. After 15 min under nitrogen, the other reagents (3 Br-SBF (1.9 g, 4.8 mmol), Carbazole (0.84 g, 5.0 mmol) and tBuO Na (1.44 g, 15 mmol)) were introduced and the reaction medium was warmed at 90 °C for 3 hours. After filtration and solvent evaporation, the solid was flash chromatographied to afford 1.7 g of Compound IX (yield 74 %, 3.5 mmol).

3-Dibenzothiophene-spirobifluorene (Compound X)

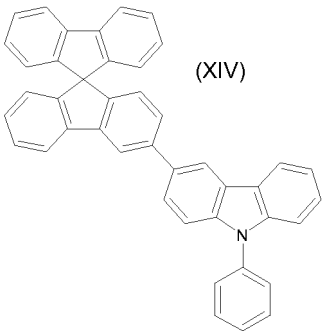
[0055]



[0056] Compound X was prepared in the identical manner as compound XI below except the boronic ester of dibenzothiophene was used instead of that of dibenzofurane (yield 65 %).

3-(N-tolyl-carbazole)-spirobifluorene (Compound XIV)

[0057]

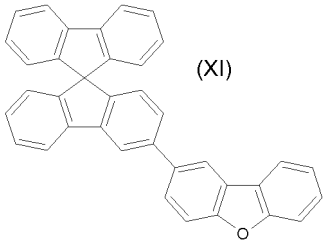


[0058] To a flask containing N-tolyl-3-boronic ester carbazole (5.3 mmol, 2.1 eq), 3-Br-SBF (1 eq, 2.5 mmol, 1.0 g) and $Pd(PPh_3)_4$ (2 % mol, 58 mg), toluene (50 ml), EtOH (10 ml) and 5 equivalents of Na_2CO_3 aq. 2 M (5 equivalents) was added. After stiring at reflux for 2 days, the reaction was cooled and the product extracted with ether. The organic

phases were washed with water and brine. After having been dried over anhydrous $MgSO_4$ and vacuum evaporation of the solvent, the product was recovered by flash chromatography (m = 1.4 g, yield 95 %).

3-dibenzofurane-spirobifluorene (Compound XI)

[0059]



(XI)

[0060] As for the compound XVI, the boronic ester of dibenzofurane (9.1 mmol) and the 3-Br-SBF (5.7 mmol) were solubilized in toluene. The catalyst $Pd(PPh_3)_4$, the Na_2CO_3 and EtOH were then added and the medium was warmed to reflux for 20 h. After evaporation and usual work-up, 4.5 g of solid was recovered and a chromatography afforded 1.56 g of the pure product (yield 54 %).

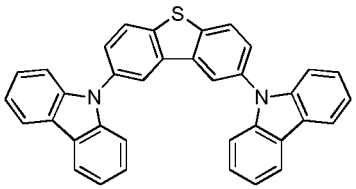
Characterization of spirobifluorene compounds of the present invention

[0061] All device examples were fabricated by high vacuum thermal evaporation, except for the hole injecting layer, which was deposited by spin-coating technique. The anode electrode was 120 nm of indium tin oxide (ITO). The cathode consisted of 1 nm of LiF followed by 100 nm of Al. All devices were encapsulated with a glass lid sealed with an epoxy resin in a nitrogen glovebox (<1 ppm of H_2O and O_2) immediately after fabrication, and a moisture getter was incorporated inside the package. The devices were characterized optically and electrically with a C9920-12 External Quantum Efficiency Measurement System from HAMAMATSU. EQE refers to external quantum efficiency expressed in %, PE refers to power efficiency expressed in lm/W, while CIE refers to the 1931 Commission Internationale de l'Eclairage (CIE) coordinates. Lifetime tests were done by driving the devices at continuous current at room temperature. LT50 is a measure of lifetime and corresponds to the time for light output to decrease by 50% of the initial value, when the device is driven at a constant current.

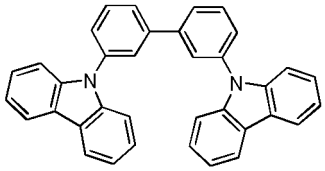
[0062] The organic stack of Examples 1 and 2 consisted of sequentially, from the ITO surface, 60nm of Plexcore OC AQ-1100 (supplied from Plextronics Inc.) deposited by spin coating and dried on a hot plate at 200 °C for 10 min, 30 nm of N,N'-Bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine (□-NPD) as the hole transporting layer (HTL), 30nm of compound V or compound IX doped with 9, 12.5 or 15% of mc3 (Ir- complex of formula 20) as the emissive layer (EML), 5nm of 3,3'-di(9H-carbazol-9-yl)biphenyl (mCBP) as the blocking layer (BL), and 40 nm of Bis(2-methyl-8-quinolinolate)-4-(phenylphenolato)aluminium (BAlq) as the electron transporting layer (ETL).

[0063] Comparative Examples 1 and 2 were fabricated similarly to Examples 1 and 2, except that DCzT was used as host material and blocking layer in Comparative Example 1, together with Tris(8-hydroxy-quinolinato)aluminium (Alq3) as ETL; while mCBP was used as host material in Comparative Example 2.

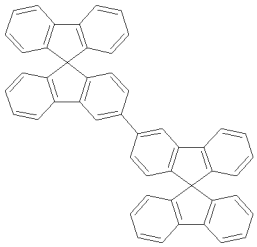
[0064] The device structures are summarized in Table 1 while Table 2 shows the corresponding measured results for those devices. Percentages are in wt%. As used herein, DCzT, mCBP, compound V and compound IX have the following structures:



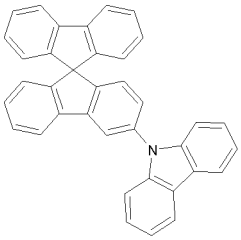
DCzT



mCBP



Compound V



Compound IX

Table 1.

Device	HIL	HTL	Host	Dopant	BL	ETL
Comparative example 1	Plexcore 60nm	NPD 30nm	DCzT	mc3 12.5%	DCzT 5nm	Alq3 40nm
Comparative example 2	Plexcore 60nm	NPD 30nm	mCBP	mc3 9%	mCBP 5nm	BAlq 40nm
Example 1	Plexcore 60nm	NPD 30nm	Cpd. V	mc3 15%	mCBP 5nm	BAlq 40nm
Example 2	Plexcore 60nm	NPD 30nm	Cpd. IX	mc3 15%	mCBP 5nm	BAlq 40nm

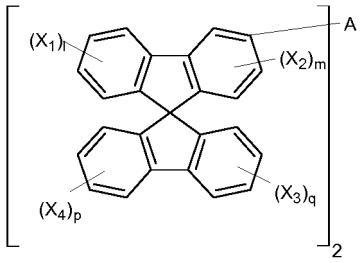
[0065] As shown in Table 2, the host materials of the invention demonstrated efficiency and lifetime that were better than the comparative examples. In particular, at an initial luminance of 1000 Cd/m^2, the results for the lifetimes of the devices show that devices with incorporated the host materials of the present invention had at least a 20% improvement compared to the Comparative Examples.

Table 2.

	1000 cd/m^2			
Device Example	EQE	PE	CIE (x,y)	LT50 (hrs)
Comparative Example 1	13.4	16.2	0.24/0.47	1260
Comparative Example 2	12.7	10.4	0.21/0.44	1400
Example 1	9.3	7.5	0.22/0.46	150
Example 2	11.4	10.7	0.22/0.45	1700

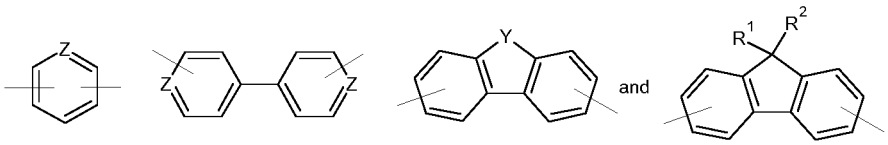
Claims

1. Compounds represented by Formula (I) or (II).

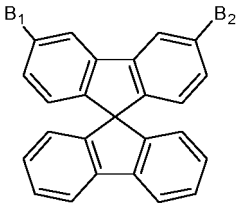


Formula (I)

wherein A is a single bond or a divalent residue of biphenyl, triphenyl,

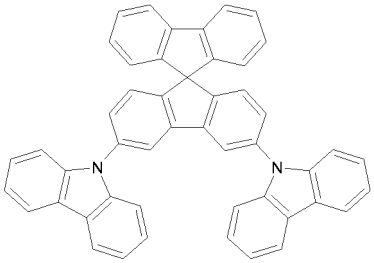


each of which one or more hydrogen atoms attached in the carbon atoms may be replaced by a substituent other than hydrogen, wherein Z is any one selected from N, O, S, and SiR, Y is N-R, O, S or $Si(R)_2$ where R is $C_{1\text{-}20}$ alkyl or aryl, R^1 and R^2 are independently selected from hydrogen and $C_{1\text{-}20}$ alkyl;
X_1 to X_4 are independently selected from substituents other than spirobifluorenyl;
1, p and q are integers of from 0 to 4;
m is an integer of from 0 to 3,

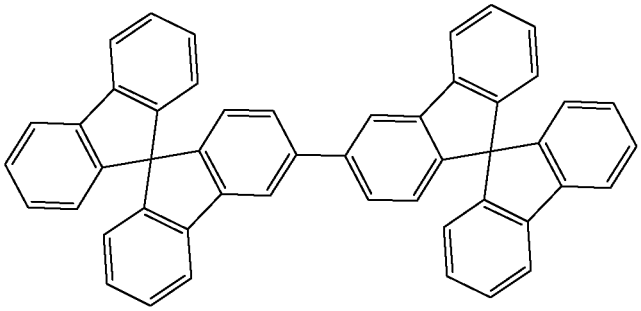


Formula (II)

wherein B_1 and B_2 are independently selected from hydrogen, and a heterocyclic group selected from carbazole, dibenzothiophene, dibenzofurane, acridine, dibenzosilole, and bipyridine each of which is optionally substituted by one or more substituents other than hydrogen;
and
with the proviso that B_1 and B_2 are not hydrogen simultaneously, with the exception of 3,6-Bis-N-carbazolyl-9,9'-spirobifluorene of the formula



and further with the exception of



2. Compounds in accordance with claim 1 represented by formula (I) as defined in claim 1.

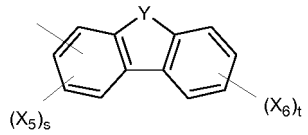
3. Compounds in accordance with claim 1 represented by formula (II) as defined in claim 1.

4. Compounds in accordance with Claim 1, wherein the compounds are represented by Formula (I) and 1, m, p and q are 0.

5. Compounds in accordance with claim 1 or 4, wherein A is a single bond.

6. Compounds in accordance with Claim 1, wherein B_1 is hydrogen and B_2 is a heterocyclic group as defined in Claim 1.

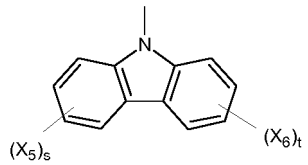
7. Compounds in accordance with Claim 1 or 6, wherein the heterocyclic group is represented by Formula (III).



(III)

wherein Y is N-R, O, S or $Si(R)_2$ where R is C_{1-20} alkyl or aryl; X_5 and X_6 are independently selected from substituents other than hydrogen; s is an integer of from 0 to 3 and t is an integer of from 0 to 4.

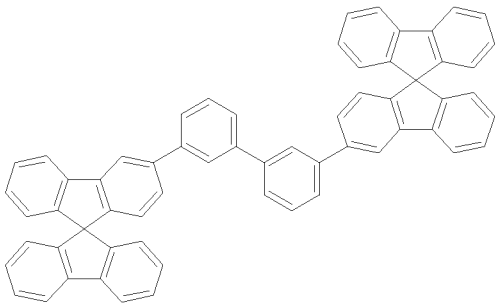
8. Compounds in accordance with Claim 1 or 6, wherein the heterocylic group is represented by Formula (IV).



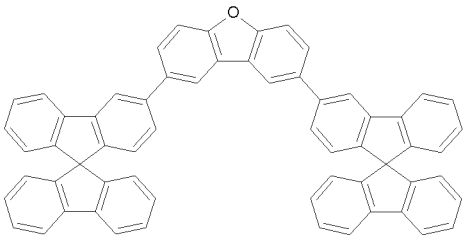
(IV)

wherein X_5 and X_6 are independently selected from substituents other than hydrogen; and s and t are independently selected from integers of from 0 to 4.

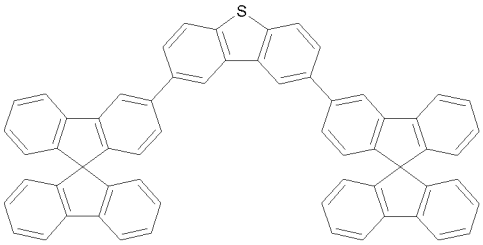
9. Compounds in accordance with claim 1 represented by any one of Formulae (VI) to (VIII).



(VI)

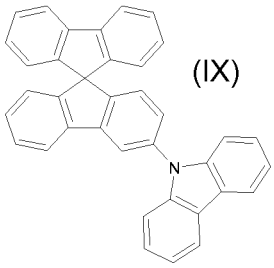


(VII)

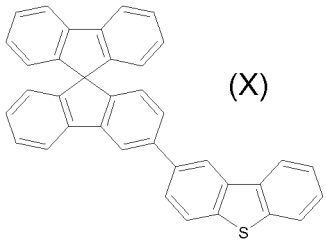


(VIII)

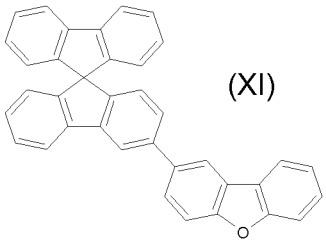
10. Compounds in accordance with claim 1, represented by any one of the following formulae.



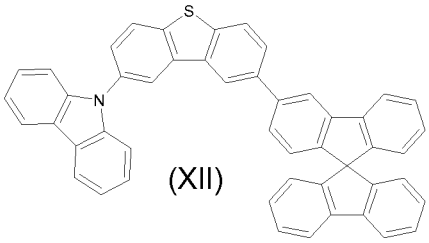
(IX)



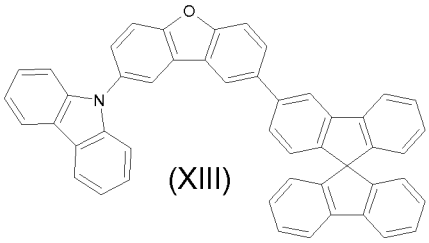
(X)



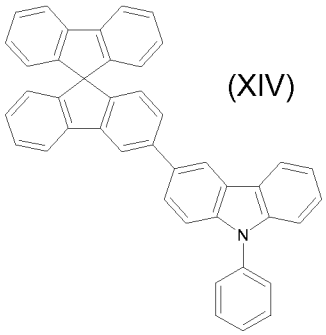
(XI)



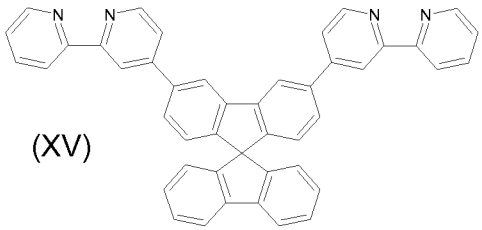
(XII)



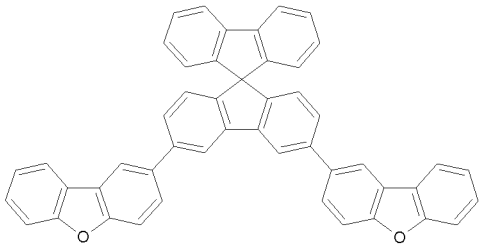
(XIII)



(XIV)

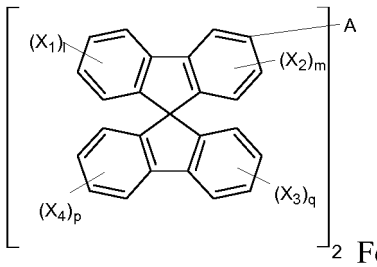


(XV)



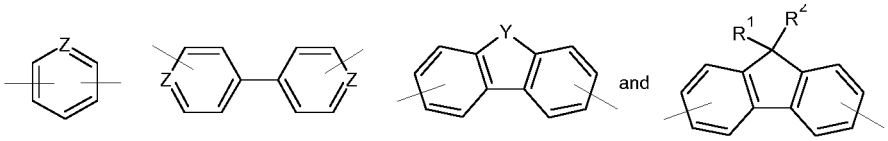
(XVI)

11. A light emitting device comprising a compound C of formula I



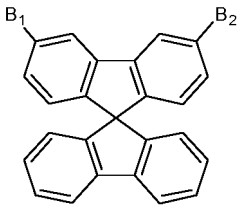
Formula (I)

wherein A is a divalent residue of biphenyl, triphenyl,



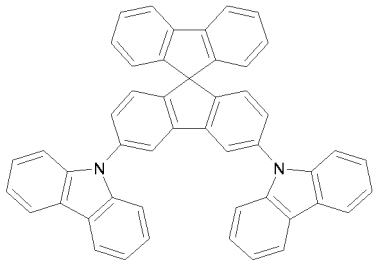
each of which one or more hydrogen atoms attached in the carbon atoms may be replaced by a substituent other than hydrogen, wherein Z is any one selected from N, O, S, and SiR, Y is N-R, O, S or $Si(R)_2$ where R is C_{1-20} alkyl or aryl, R^1 and R^2 are independently selected from hydrogen and C_{1-20} alkyl, and
wherein X_1 to X_4 are independently selected from substituents other than spirobifluorenyl,
1, p and q are integers of from 0 to 4,
m is an integer of from 0 to 3,

or of formula II



Formula (II)

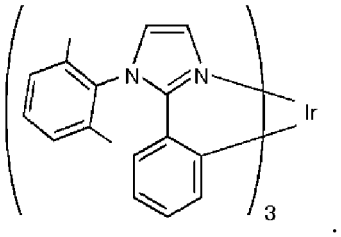
wherein B_1 and B_2 are independently selected from hydrogen, and a heterocyclic group selected from carbazole, dibenzothiophene, dibenzofurane, acridine, dibenzosilole, and bipyridine each of which is optionally substituted by one or more substituents other than hydrogen;
and with the proviso that B_1 and B_2 are not hydrogen simultaneously, with the exception of 3,6-Bis-N-carbazolyl-9,9'-spirobifluorene of the formula



and a light emitting compound.

12. The device of claim 11 wherein the compound C) is as defined in any of claims 2 to 4 and 6 to 10.

13. The light emitting device of claim 11 or 12, wherein the light emitting compound comprises the following compound:

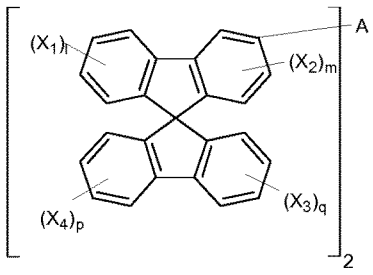


14. Use of the compounds as defined in any of claims 1 to 10 in an organic light emitting device.

15. The use of Claim 14, wherein the device is an organic light emitting diode.

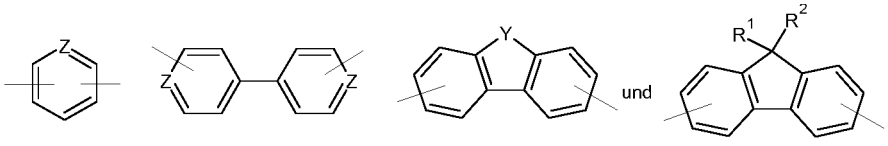
Patentansprüche

1. Verbindungen, die durch Formel (I) oder (II) wiedergegeben werden:



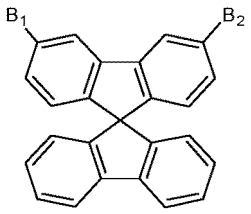
Formel (I)

wobei A für eine Einfachbindung oder einen zweiwertigen Rest von Biphenyl, Triphenyl,



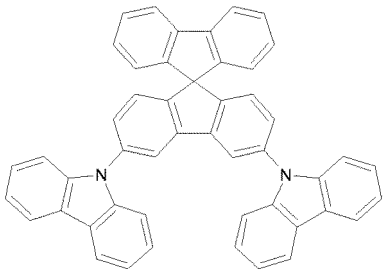
steht, wobei ein oder mehrere Wasserstoffatome, die an die Kohlenstoffatome gebunden sind, jeweils durch einen von Wasserstoff verschiedenen Substituenten ersetzt sein können, wobei Z aus N, O, S und SiR ausgewählt ist, Y für N-R, O, S oder $Si(R)_2$ steht,
wobei R für C_{1-20}-Alkyl oder Aryl steht, R^1 und R^2 unabhängig aus Wasserstoff und C_{1-20}-Alkyl ausgewählt sind;

X_1 bis X_4 unabhängig aus Substituenten, die von Spirobifluorenyl verschieden sind, ausgewählt sind; l, p und q für ganze Zahlen von 0 bis 4 stehen;
m für eine ganze Zahl von 0 bis 3 steht,

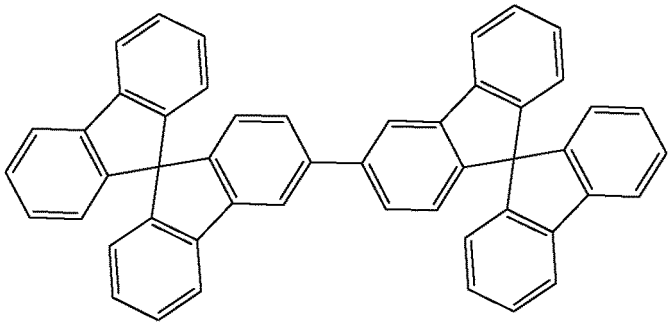


Formel (II)

wobei B_1 und B_2 unabhängig aus Wasserstoff und einer heterocyclischen Gruppe, die aus Carbazol, Dibenzothiophen, Dibenzofuran, Acridin, Dibenzosilol und Bipyridin ausgewählt ist, wobei jede dieser Gruppen gegebenenfalls durch einen oder mehrere von Wasserstoff verschiedene Substituenten substituiert ist, ausgewählt sind;
und
mit der Maßgabe, dass B_1 und B_2 nicht gleichzeitig für Wasserstoff stehen, mit Ausnahme von 3,6-Bis-N-carbazolyl-9,9'-spirobifluoren der Formel



und ferner mit Ausnahme von



2. Verbindungen nach Anspruch 1, wiedergegeben durch die Formel (I) gemäß Anspruch 1.

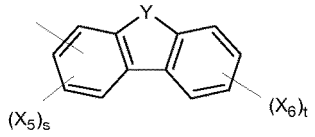
3. Verbindungen nach Anspruch 1, wiedergegeben durch die Formel (II) gemäß Anspruch 1.

4. Verbindungen nach Anspruch 1, wobei die Verbindungen durch Formel (I) wiedergegeben werden und l, m, p und q für 0 stehen.

5. Verbindungen nach Anspruch 1 oder 4, wobei A für eine Einfachbindung steht.

6. Verbindungen nach Anspruch 1, wobei B_1 für Wasserstoff steht und B_2 für eine heterocyclische Gruppe gemäß Anspruch 1 steht.

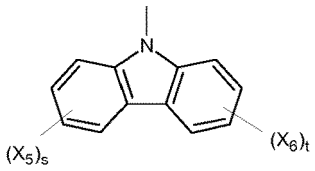
7. Verbindungen nach Anspruch 1 oder 6, wobei die heterocyclische Gruppe durch Formel (III) wiedergegeben wird:



(III)

wobei Y für N-R, O, S oder $Si(R)_2$ steht, wobei R für C_{1-20}-Alkyl oder Aryl steht; X_5 und X_6 unabhängig aus von Wasserstoff verschiedenen Substituenten ausgewählt sind; s für eine ganze Zahl von 0 bis 3 steht und t für eine ganze Zahl von 0 bis 4 steht.

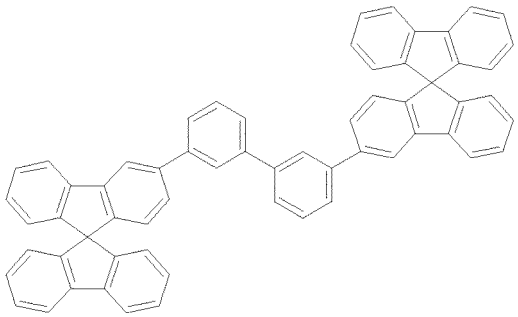
8. Verbindungen nach Anspruch 1 oder 6, wobei die heterocyclische Gruppe durch Formel (IV) wiedergegeben wird:



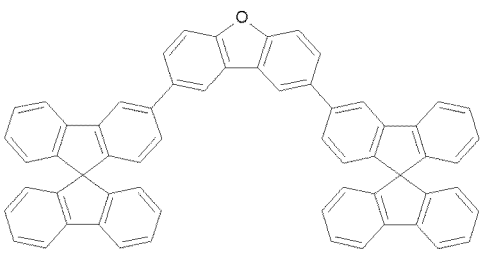
(IV)

wobei X_5 und X_6 unabhängig aus von Wasserstoff verschiedenen Substituenten ausgewählt sind; s und t unabhängig aus ganzen Zahlen von 0 bis 4 ausgewählt sind.

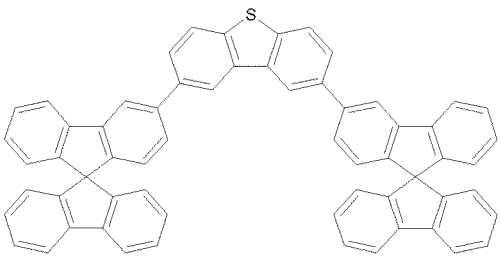
9. Verbindungen nach Anspruch 1, die durch eine der Formeln (VI) bis (VIII) wiedergegeben werden:



(VI)

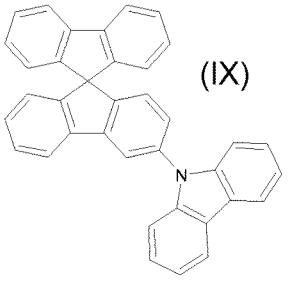


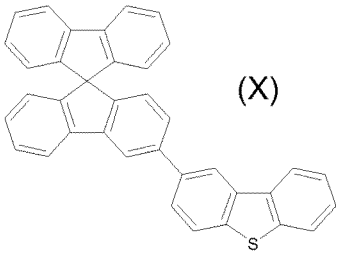
(VII)

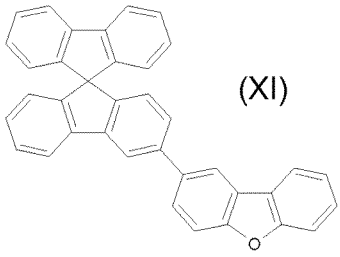


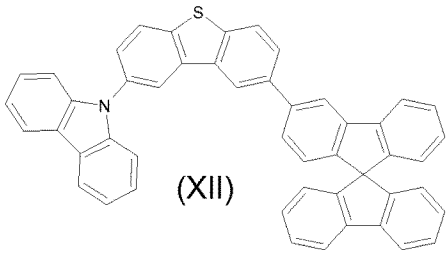
(VIII)

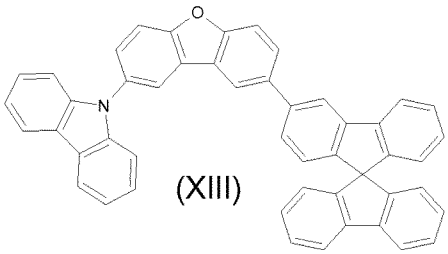
10. Verbindungen nach Anspruch 1, die durch eine der folgenden Formeln wiedergegeben werden:

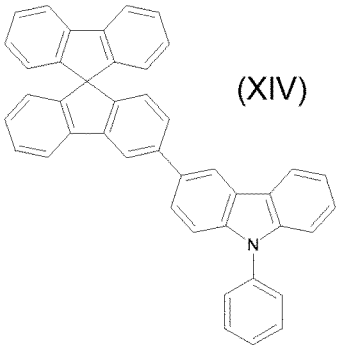

(IX)

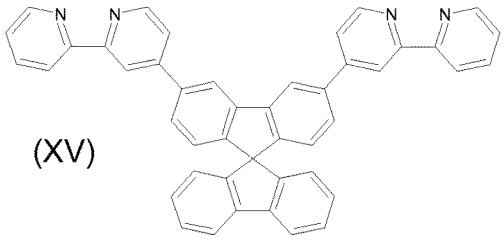

(X)

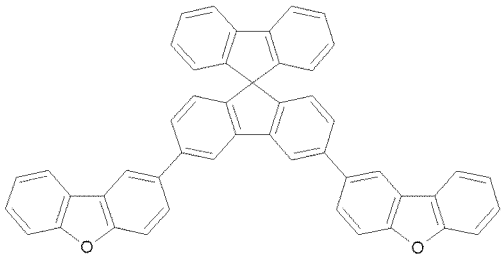

(XI)


(XII)

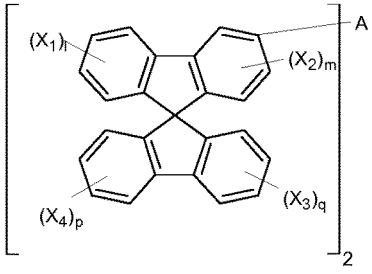

(XIII)


(XIV)

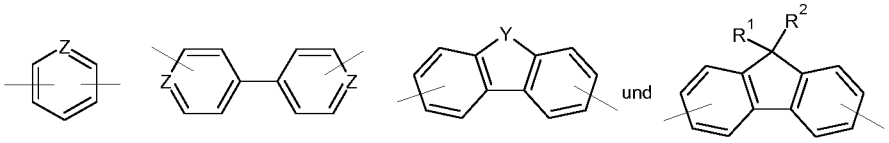

(XV)


(XVI)

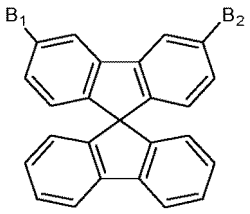
11. Lichtemittierende Vorrichtung, umfassend eine Verbindung C der Formel I


Formel (I)

wobei A für einen zweiwertigen Rest von Biphenyl, Triphenyl,

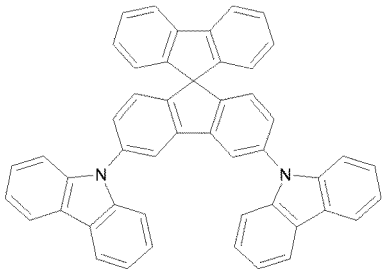


steht, wobei ein oder mehrere Wasserstoffatome, die an die Kohlenstoffatome gebunden sind, jeweils durch einen von Wasserstoff verschiedenen Substituenten ersetzt sein können, wobei Z aus N, O, S und SiR ausgewählt ist, Y für N-R, O, S oder $Si(R)_2$ steht, wobei R für C_{1-20}-Alkyl oder Aryl steht, R^1 und R^2 unabhängig aus Wasserstoff und C_{1-20}-Alkyl ausgewählt sind,
X_1 bis X_4 unabhängig aus Substituenten, die von Spirobifluorenyl verschieden sind, ausgewählt sind, l, p und q für ganze Zahlen von 0 bis 4 steht,
m für eine ganze Zahl von 0 bis 3 steht,
oder der Formel II



Formel (II)

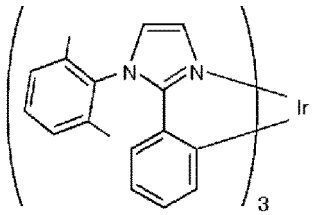
wobei B_1 und B_2 unabhängig aus Wasserstoff und einer heterocyclischen Gruppe, die aus Carbazol, Dibenzothiophen, Dibenzofuran, Acridin, Dibenzosilol und Bipyridin ausgewählt ist, wobei jede dieser Gruppen gegebenenfalls durch einen oder mehrere von Wasserstoff verschiedene Substituenten substituiert ist, ausgewählt sind;
und mit der Maßgabe, dass B_1 und B_2 nicht gleichzeitig für Wasserstoff stehen, mit Ausnahme von 3,6-Bis-N-carbazolyl-9,9'-spirobifluoren der Formel



und eine lichtemittierende Verbindung.

12. Vorrichtung nach Anspruch 11, wobei die Verbindung C) wie in einem der Ansprüche 2 bis 4 und 6 bis 10 definiert ist.

13. Lichtemittierende Vorrichtung nach Anspruch 11 oder 12, wobei die lichtemittierende Verbindung die folgende Verbindung umfasst:



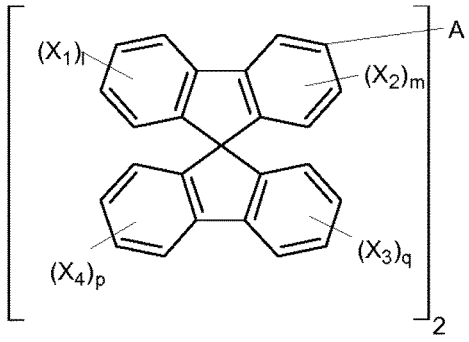
.

14. Verwendung der Verbindungen gemäß einem der Ansprüche 1 bis 10 in einer organischen lichtemittierenden Vorrichtung.

15. Verwendung nach Anspruch 14, wobei es sich bei der Vorrichtung um eine organische lichtemittierende Diode handelt.

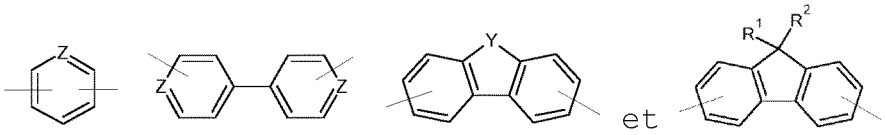
Revendications

1. Composés représentés par la formule (I) ou (II).

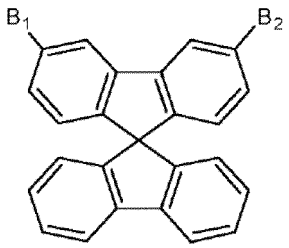


Formule (I)

dans laquelle A est une simple liaison ou un résidu divalent de biphényle, triphényle,

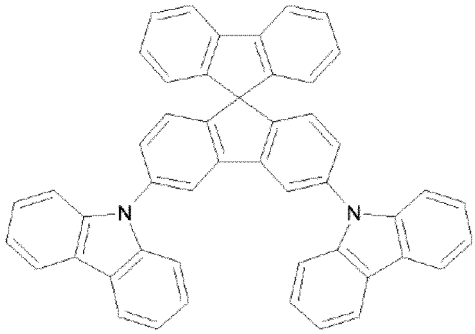


dans chacun desquels un ou plusieurs atomes d'hydrogène liés aux atomes de carbone peuvent être remplacés par un substituant autre qu'hydrogène, où Z est l'un quelconque choisi parmi N, O, S et SiR, Y est N-R, O, S ou $Si(R)_2$ où R est alkyle en C_{1-20} ou aryle, R^1 et R^2 sont indépendamment choisis parmi hydrogène et alkyle en C_{1-20} ;
X_1 à X_4 sont indépendamment choisis parmi des substituants autres que spirobifluorényle ;
l, p et q sont des entiers de 0 à 4;
m est un entier de 0 à 3,

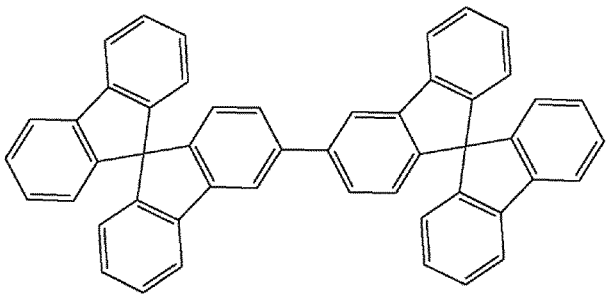


Formule (II)

dans laquelle B_1 et B_2 sont indépendamment choisis parmi hydrogène, et un groupe hétérocyclique choisi parmi carbazole, dibenzothiophène, dibenzofurane, acridine, dibenzosilole et bipyridine, dont chacun est facultativement substitué par un ou plusieurs substituants autres qu'hydrogène ;
et
à condition que B_1 et B_2 ne soient pas simultanément hydrogène, à l'exception du 3,6-bis-N-carbazolyl-9,9'-spirobifluorène de formule



et en outre à l'exception de



2. Composés selon la revendication 1, représentés par la formule (I) telle que définie dans la revendication 1.

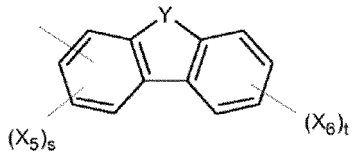
3. Composés selon la revendication 1, représentés par la formule (II) telle que définie dans la revendication 1.

4. Composés selon la revendication 1, les composés étant représenté par la formule (I) et l, m, p et q étant 0.

5. Composés selon la revendication 1 ou 4, dans lesquels A est une simple liaison.

6. Composés selon la revendication 1, dans lesquels B_1 est hydrogène et B_2 est un groupe hétérocyclique tel que défini dans la revendication 1.

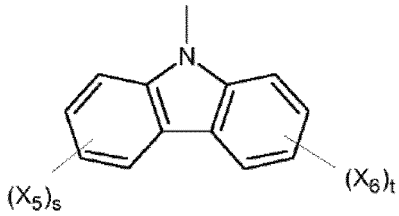
7. Composés selon la revendication 1 ou 6, dans lesquels le groupe hétérocyclique est représenté par la formule (III).



(III)

dans laquelle Y est N-R, O, S ou $Si(R)_2$ où R est alkyle en C_{1-20} ou aryle ; X_5 et X_6 sont indépendamment choisis parmi des substituants autres qu'hydrogène ; s est un entier de 0 à 3 et t est un entier de 0 à 4.

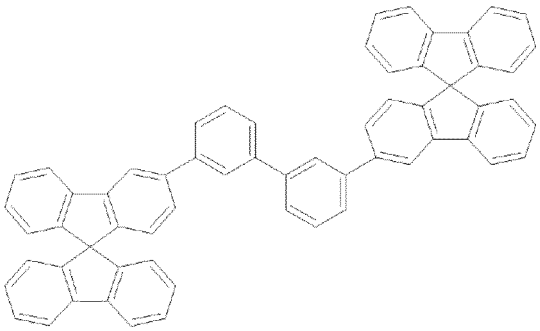
8. Composés selon la revendication 1 ou 6, dans lesquels le groupe hétérocyclique est représenté par la formule (IV).



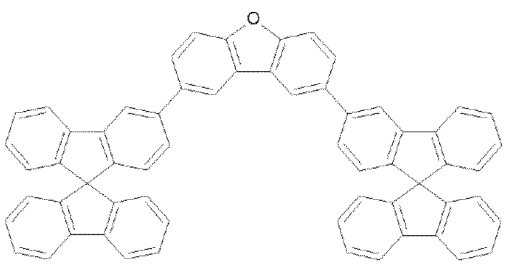
(IV)

dans laquelle X_5 et X_6 sont indépendamment choisis parmi des substituants autres qu'hydrogène ; et s et t sont indépendamment choisis parmi des entiers de 0 à 4.

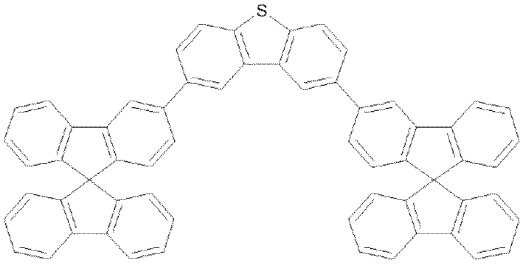
9. Composés selon la revendication 1, représentés par l'une quelconque des formules (VI) à (VIII).



(VI)

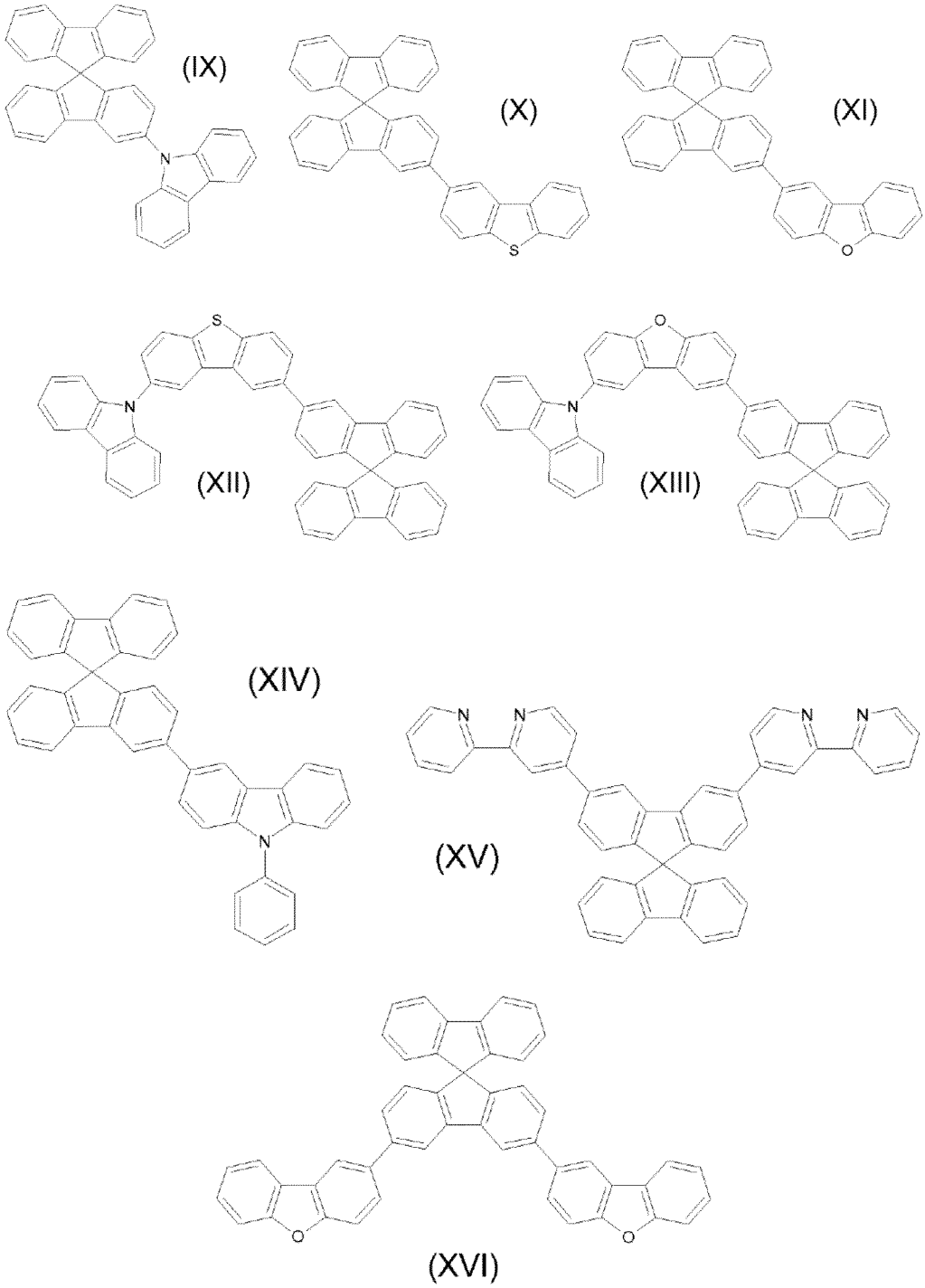


(VII)

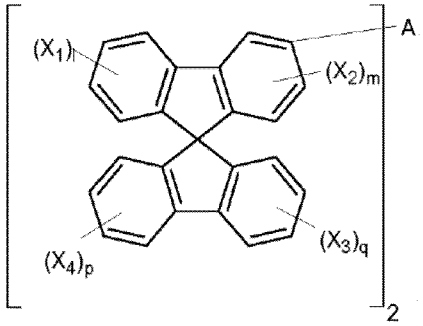


(VIII)

10. Composés selon la revendication 1, représentés par l'une quelconque des formules suivantes.

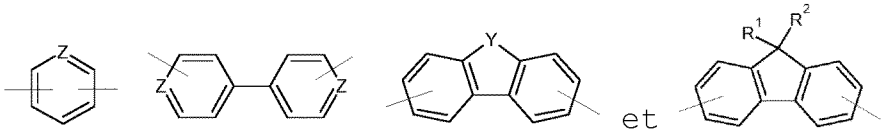


11. Dispositif électroluminescent comprenant un composé C de formule I



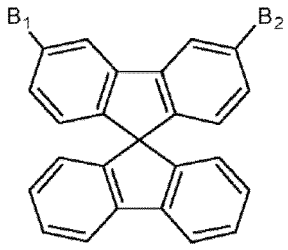
Formule (I)

dans laquelle A est un résidu divalent de biphényle, triphényle,



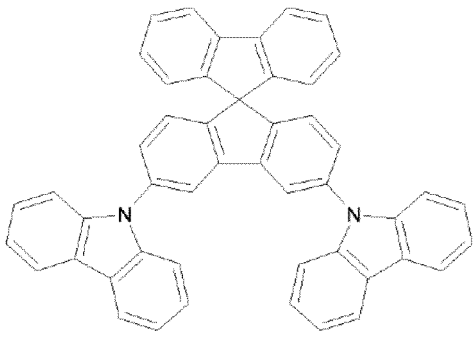
dans chacun desquels un ou plusieurs atomes d'hydrogène liés aux atomes de carbone peuvent être remplacés par un substituant autre qu'hydrogène, où Z est l'un quelconque choisi parmi N, O, S et SiR, Y est N-R, O, S ou $Si(R)_2$ où R est alkyle en C_{1-20} ou aryle, R^1 et R^2 sont indépendamment choisis parmi hydrogène et alkyle en C_{1-20}, et
dans laquelle X_1 à X_4 sont indépendamment choisis parmi des substituants autres que spirobifluorényle ;
l, p et q sont des entiers de 0 à 4 ;
m est un entier de 0 à 3,

ou de formule II



Formule (II)

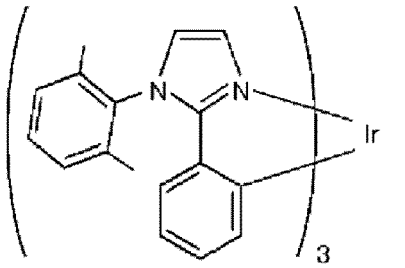
dans laquelle B_1 et B_2 sont indépendamment choisis parmi hydrogène, et un groupe hétérocyclique choisi parmi carbazole, dibenzothiophène, dibenzofurane, acridine, dibenzosilole et bipyridine, chacun desquels étant facultativement substitué par un ou plusieurs substituants autres qu'hydrogène ;
à condition que B_1 et B_2 ne soient pas simultanément hydrogène, à l'exception du 3,6-bis-N-carbazolyl-9,9'-spirobifluorène de formule



et un composé électroluminescent.

12. Dispositif selon la revendication 11, dans lequel le composé C) est tel que défini dans l'une quelconque des revendications 2 à 4 et 6 à 10.

13. Dispositif électroluminescent selon la revendication 11 ou 12, dans lequel le composé électroluminescent comprend le composé suivant:



14. Utilisation des composés tels que définis dans l'une quelconque des revendications 1 à 10 dans un dispositif électroluminescent organique.

15. Utilisation selon la revendication 14, dans laquelle le dispositif est une diode électroluminescente organique.

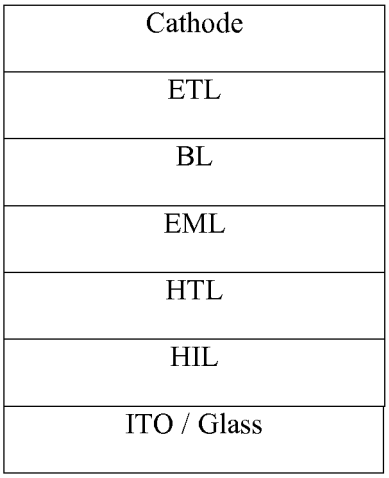

Cathode
ETL
BL
EML
HTL
HIL
ITO / Glass

Fig. 1

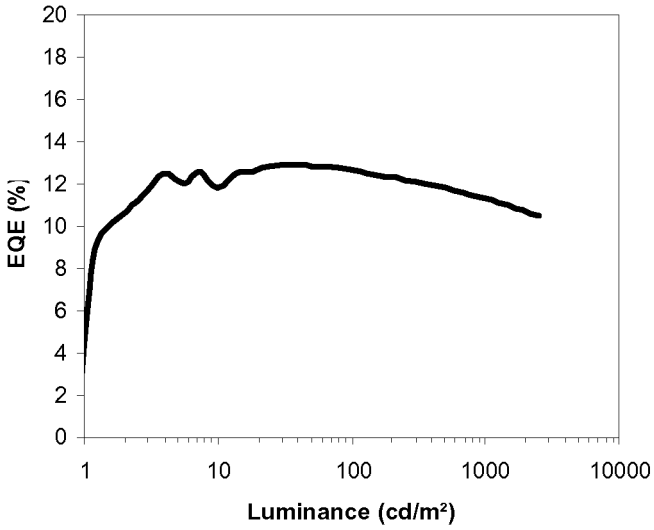

EQE (%)
0
2
4
6
8
10
12
14
16
18
20
1
10
100
1000
10000
Luminance (cd/m²)

Fig. 2

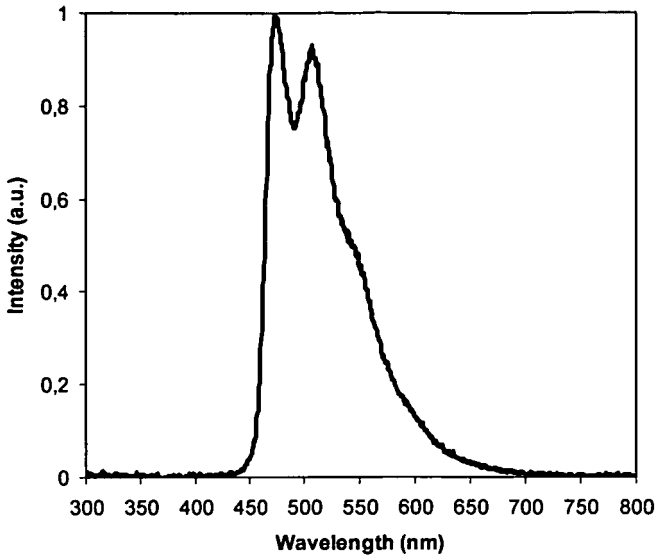

1
0,8
0,6
0,4
0,2
0
Intensity (a.u.)
300 350 400 450 500 550 600 650 700 750 800
Wavelength (nm)

Fig. 3

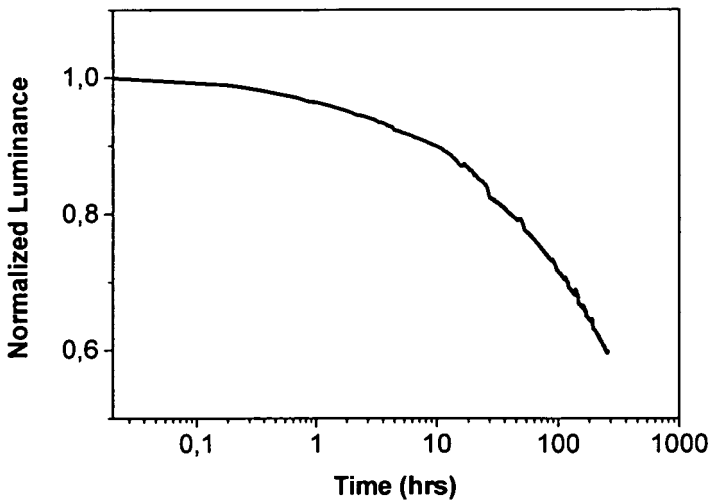

1,0
0,8
0,6
Normalized Luminance
0,1 1 10 100 1000
Time (hrs)

Fig. 4

REFERENCES CITED IN THE DESCRIPTION

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专利名称(译)	螺二芴化合物用于发光器件		
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申请号	EP2011778793	申请日	2011-10-07
[标]申请(专利权)人(译)	索尔维公司		
申请(专利权)人(译)	SOLVAY SA		
当前申请(专利权)人(译)	住友化学有限公司.		
[标]发明人	MAUNOURY JONATHAN ORSELLI ENRICO BASCOUR DOMINIQUE		
发明人	MAUNOURY, JONATHAN ORSELLI, ENRICO BASCOUR, DOMINIQUE		
IPC分类号	H05B33/20 C07C25/22 H01L51/50 C07D405/04 C07D333/76 C07D409/04 C07D307/91 C07D209/86 C07C13/72		
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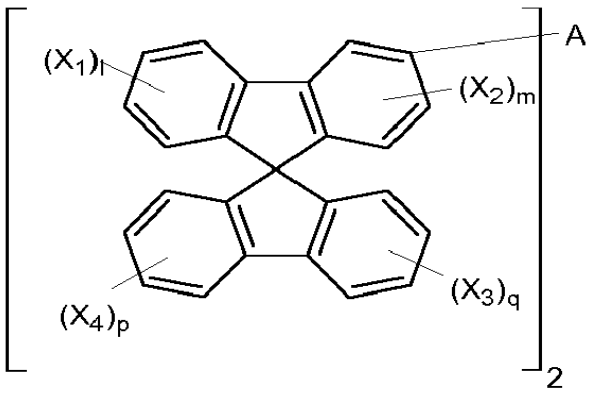
优先权	2010187159 2010-10-11 EP		
其他公开文献	EP2628362A1		
外部链接	Espacenet		

摘要(译)

还要求保护此类化合物在OLED中的用途。



Formula (I)