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(54) **Title**: SPIROBIFLUORENE COMPOUNDS FOR LIGHT EMITTING DEVICES

(57) **Abstract**: Novel spirobifluorene compounds for light emitting devices where the spirobifluorene ring system comprises at least one acridine-type substituent.

Spirobifluorene compounds for light emitting devices

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

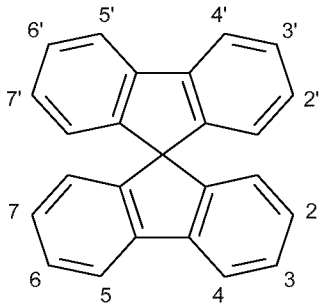
[0002] Various organic light emitting devices have been under active study and development, particularly those based on electroluminescence (EL) from small organic materials. For such organic devices, the ability to form morphologically stable amorphous films is a key requirement for the development of small materials for organic light emitting diodes (OLEDs). That is because when a small molecule compound is used in the organic light-emitting layer, crystallization usually occurs if the molecule of the compound is too small and its structure is too symmetrical. Therefore, when applied in an organic 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.

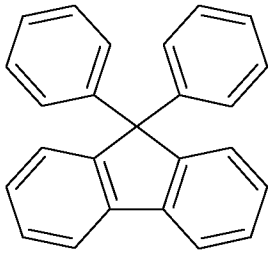
[0004] US2006/0141287 discloses light-emitting layers which include a solid organic material containing a mixture of at least two components. The first host component is an organic compound capable of transporting electrical charges and also forms an aggregate. The second component of the mixture is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

second component, various compounds such as substituted fluorene derivatives, and spirobifluorene derivatives, etc. are used.

[0005] Spirobifluorene , as used herein denotes a structural element of formula (1) and is referred to as SBF hereinafter, whereas Open SBF denotes a system of formula (2) below.



(1)



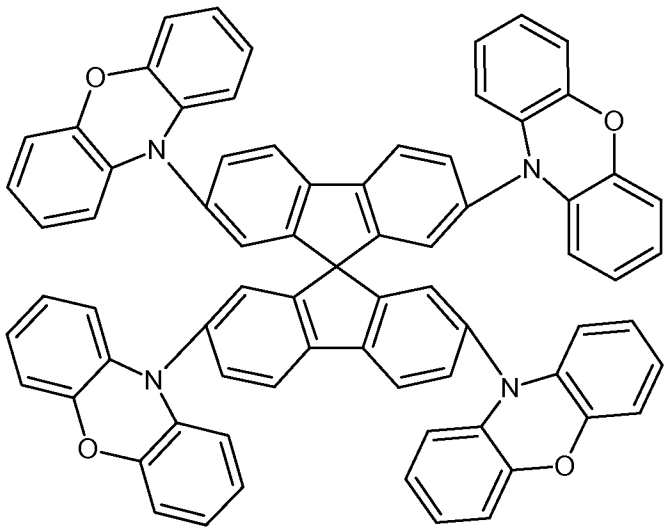
(2)

[0006]

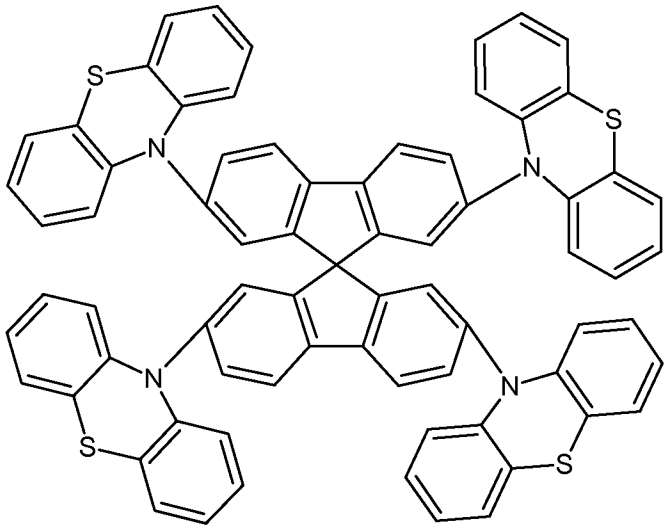
[0007] Substituted spirobifluorene compounds have been extensively described in the prior art, in particular with a substitution of the SBF ring system in “para-position (i.e. the 2, 7, 2’ or 7’ position of the SBF) by a heteroatom.

[0008] Substituted spirobifluorene of this type where the heteroatom bound to the spirobifluorene unit is part of a ring system have also been described.

[0009] Salbeck et al., Chem.Rev. 2007, 107, 1011-1065 provides a good overview of spiro compounds useful in organic optoelectronics. Thus, compounds (16) and (17) in Salbeck are the following



[0010]

[0011] 

[0012] These compounds are reported to have absorption maxima below 400 nm and emission maxima of 491 and 511 nm, respectively. No data on efficiency are given.

[0013] Salbeck further reports that replacement of diphenylamino substituents like in the compounds above by carbazole ligands results in a distinct hypsochromic shift of absorption and emission. As an example the compound where the substituents are replaced by N-carbazole shows an absorption maximum below 350 nm and an emission maximum at 372 nm.

[0014] Spirobifluorene compounds with diphenylamino substituents in para-postion of the SBF unit are again disclosed in Salbeck et al., see e.g. compounds 42 to 48 thereof.

[0015] WO 2011/06574 discloses 4 and 4,4'diphenylamino-substituted SBF compounds (which may be referred to as ortho-substituted compounds relative to the direct bond linking the phenyl rings of the SBF unit).

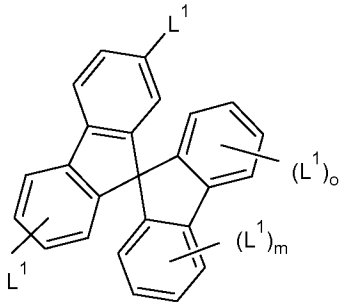
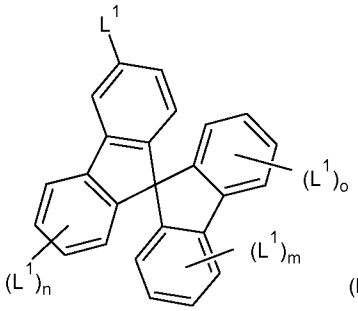
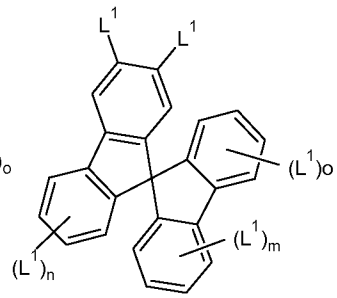
[0016] European Patent Application 2 312 667 discloses compositions for organic electroluminescence elements comprising at least two different materials fulfilling a certain mathematical equation related to the solubility of the materials. Among an extended list of suitable materials having as a common structural feature substituted diphenylamino groups, 3,6-Bis-N,N'-di(4-tert.butylphenyl)amino-spirobifluorene as well as the respective Open SBF derivative are mentioned.

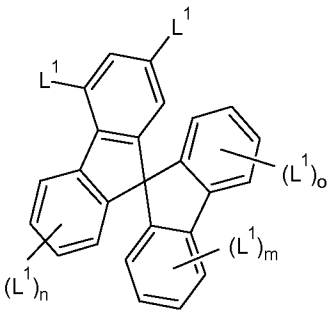
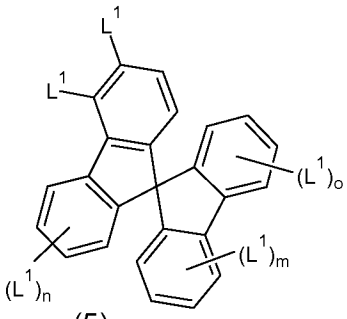
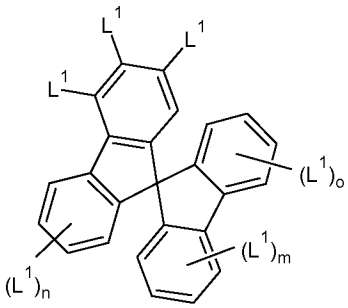
[0017] None of the above-disclosed materials meets all the requirements necessary for OLED application, particularly suitable energy level for high phosphorescent efficiency (high triplet energy), high morphological stability, while maintaining other electro-optic and processing properties under operational conditions of the device, such as emission color, dimensional stability, etc, in a fully satisfactory manner. Thus, there has been a need to develop new host materials, which are capable of satisfying all of the requirements indicated above.

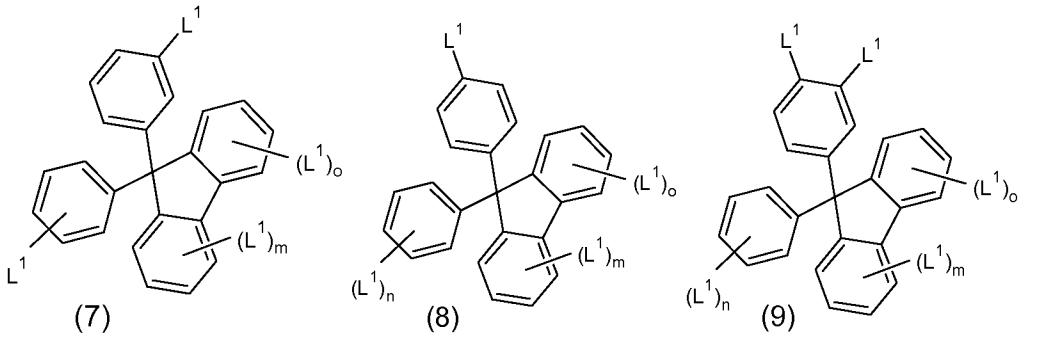
[0018] Surprisingly, it has been found that spirobifluorene compounds as defined in claim 1 possess a property spectrum which makes them particularly suitable for use in organic electroluminescent devices.

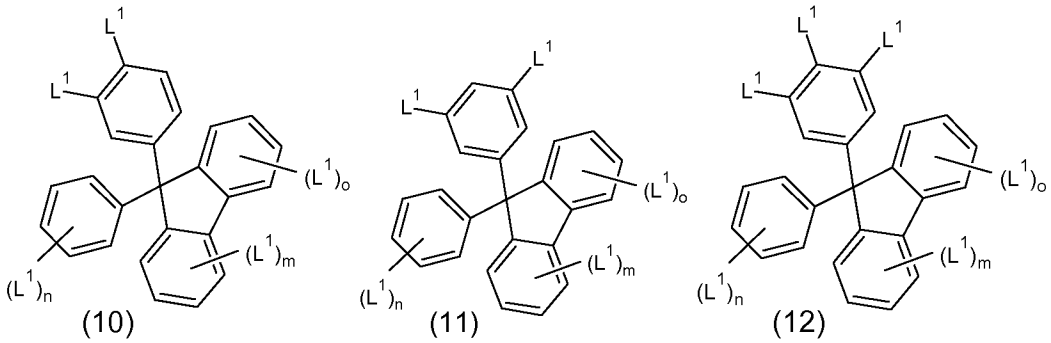
[0019] Preferred compounds in accordance with the instant invention are described in the dependent claims and the detailed specification hereinafter.

[0020] The compounds of the present invention are characterized by formulae 1 to 12 below

[0021]  (1)  (2)  (3)

[0022]  (4)  (5)  (6)

[0023] 
(7) (8) (9)

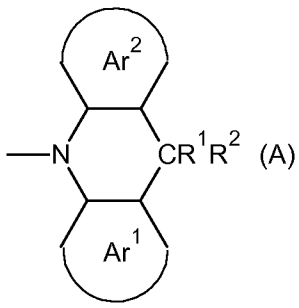

(10) (11) (12)

[0024]

[0025] wherein n, m and o may be the same or different and represent an integer of from 0 to 3 with the proviso that in compounds of formula 1 at least one of m or o is zero,
each of the phenyl rings may carry no ligands other than L^1 or may be substituted by ligands other than L^1,

[0026] L^1, which may be the same or different in each position, has the formula A

[0027]

[0028] 
(A)

[0029] wherein

[0030] R^1 and R^2 may be the same or different in each position and represent hydrogen or an aliphatic group, a carbocyclic group, an aromatic group or a heterocyclic group, all of which may comprise 1 to 20 carbon atoms, and all of which may be substituted or unsubstituted,
or a group OR^3, a group NR^4R^5 or a group SR^6, wherein R^3 to R^6 may be

the same or different and represent hydrogen, an alkyl group, a carbocyclic group, an aryl group, a heteroaryl group or a heterocyclic group having 1 to 20 carbon atoms, and

[0031] Ar^1 and Ar^2 represent optionally substituted aromatic or heteroaromatic ring systems comprising 4 to 20 ring atoms (the two ring atoms of the heterocyclic ring shown in formula I being part of the aromatic or heteroaromatic ring system for the purpose of counting ring atoms).

[0032] For the purpose of the present invention, the term "aliphatic" is intended to denote generally an acyclic hydrocarbon group which may be substituted or unsubstituted and in which the carbon atoms of the main sceleton can be partly replaced by heteroatoms, which heteroatoms are preferably selected from O, N and S. In a narrower sense, aliphatic group refers to molecules comprising carbon atoms linked in open chains.

[0033] The term heteroaryl, for the purpose of the present invention includes monocyclic or polycyclic aromatic ring systems comprising at least one heteroatom, which is preferably selected from nitrogen, oxygen or sulfur, in the ring or at least one of the rings.

[0034] In accordance with a first preferred embodiment R^1 and R^2, which may be the same or different, represent hydrogen, an alkyl group, a carbocyclic group, an aryl group or a heteroaryl group, which groups are substituted or unsubstituted.

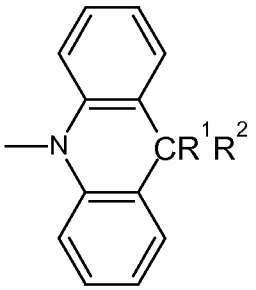
[0035] In accordance with a second preferred embodiment R^1 and R^2, which may be the same or different, represent OR^3, NR^4R^5 or SR^6 wherein R^3 to R^6 have the meaning as defined above.

[0036] The compounds in accordance with the present invention share the common feature that the SBF or Open SBF unit is substituted by a nitrogen atom, which is part of a ring system comprising two aromatic or heteroaromatic rings.

[0037] The substitution in the SBF system may be para, meta or ortho to the bond linking the phenyl rings in the SBF unit or in the analogous positions of the Open SBF unit.

[0038] It has been found that for certain purposes compounds having at least one substituent L^1 in meta position can be advantageous in terms of efficiency when used in organic electronic devices.

[0039] A first preferred group of compounds are those where L^1 has the formula A 1



(A-1)

[0040]

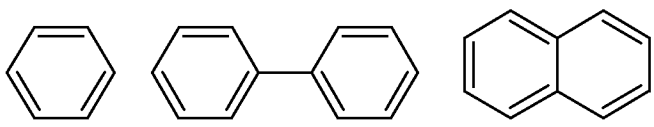
[0041] where R^1 and R^2 are as defined above.

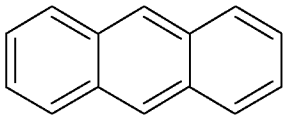
[0042] If R^1 or R^2 represents an alkyl group, same has preferably 1 to 20, especially 1 to 8 carbon atoms and may be straight chain or branched. Particularly preferred alkyl groups are C_1 to C_4 alkyl like methyl, ethyl, i- or n-propyl and i-, n- and t-butyl. The alkyl groups may themselves be substituted or unsubstituted.

[0043] Preferred carbocyclic groups for R^1 and R^2 are 5 to 7 membered carbocyclic ring systems, which may be saturated or unsaturated like e.g. cyclopentane, cyclohexane or cyclohexene, to give only three examples. As for the alkyl groups, the carbocyclic groups may be substituted or unsubstituted.

[0044] Preferred aryl groups for R^1 and R^2 are are phenyl, napththyl, anthracenyl, biphenyl or terphenyl, which may be unsubstituted or substituted by substituents selected from the group consisting of halogen, alkyl, alkoxy, amino, cyano, alkenyl, alkynyl, arylalkyl, aryl and heteroaryl groups or the aryl group may be part of an annealed ring system.

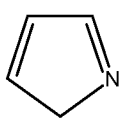
[0045] Especially preferred aryl substituents are derived from the following substituted or unsubstituted aryl systems

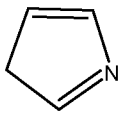
[0046] 

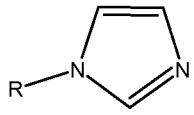
[0047] 

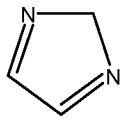
[0048] of which phenyl and biphenyl are especially preferred.

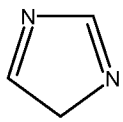
[0049] A particularly preferred group of heteroaryl groups for R^1 and R^2 are the following:

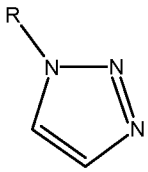

2*H*-pyrrole

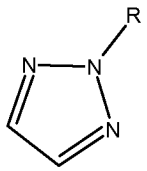

3*H*-pyrrole

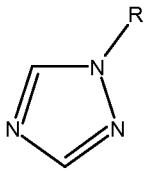

1-substituted 1*H*-imidazole

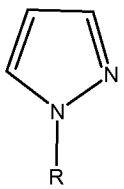

2H-imidazole

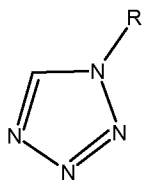

4*H*-imidazole

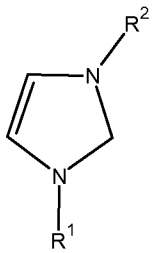

1-substituted-1*H*-1,2,3-triazole


2-substituted-2H-1,2,3-triazole

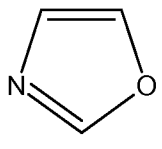

1-substituted-1*H*-1,2,4-triazole


1-substituted-1*H*-pyrazole

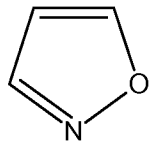

1-substituted 1H-1,2,3,4-tetrazole


1,3-disubstituted imidazol-2-ylidene

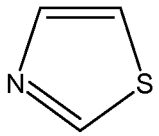
[0050] In all these ring systems one or more of the nitrogen atoms may be replaced by another heteroatom like O or S, to name only two examples as shown below:



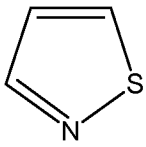
oxazole



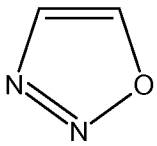
isoxazole



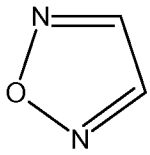
thiazole



isothiazole



1,2,3-oxadiazole



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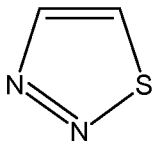
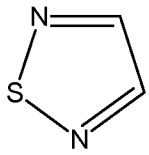
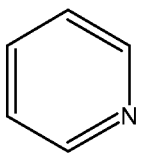


1,2,3-thiadiazole

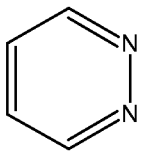


1,2,5-thiadiazole

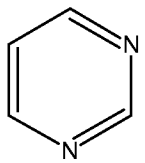
[0051] Still another preferred group of heteroaryl substituents comprises the 6-membered ring systems shown below:



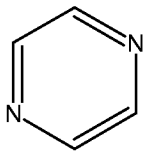
pyridine



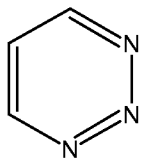
pyridazine



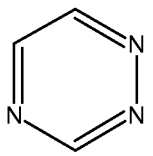
pyrimidine



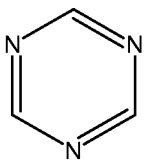
pyrazine



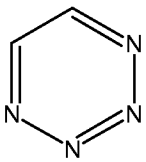
1,2,3-triazine



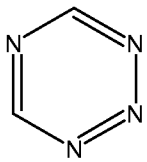
1,2,4-triazine



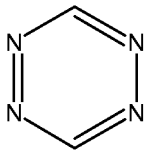
1,3,5-triazine



1,2,3,4-tetrazine



1,2,3,5-tetrazine



1,2,4,5-tetrazine

[0052] The heteroaryl groups may form or be part of an annealed ring system where several rings are condensed or annealed.

[0053] The optional substituents of the aforementioned aliphatic, carbocyclic, aromatic or heterocyclic groups, are preferably selected from aliphatic groups, carbocyclic groups, aromatic groups or heterocyclic groups, oxo, OR^7, NR^8R^9 and SR^{10} groups, wherein R^7 to R^{10} are the same or different

and represent hydrogen, an aliphatic group, a carbocyclic group, an aromatic group or a heterocyclic group having 1 to 20 carbon atoms.

[0054] In accordance with still another preferred embodiment, the substituents of the aliphatic, carbocyclic, aromatic or heteroaromatic groups are selected from the group consisting of halogen, alkyl, alkoxy, aryloxy, oxo, amino, substituted amino, cyano, alkenyl, alkynyl, arylalkyl, aryl and heteroaryl groups, even more preferably from halogen, alkyl, alkoxy, amino, cyano, alkenyl, alkynyl, arylalkyl, aryl and heteroaryl groups.

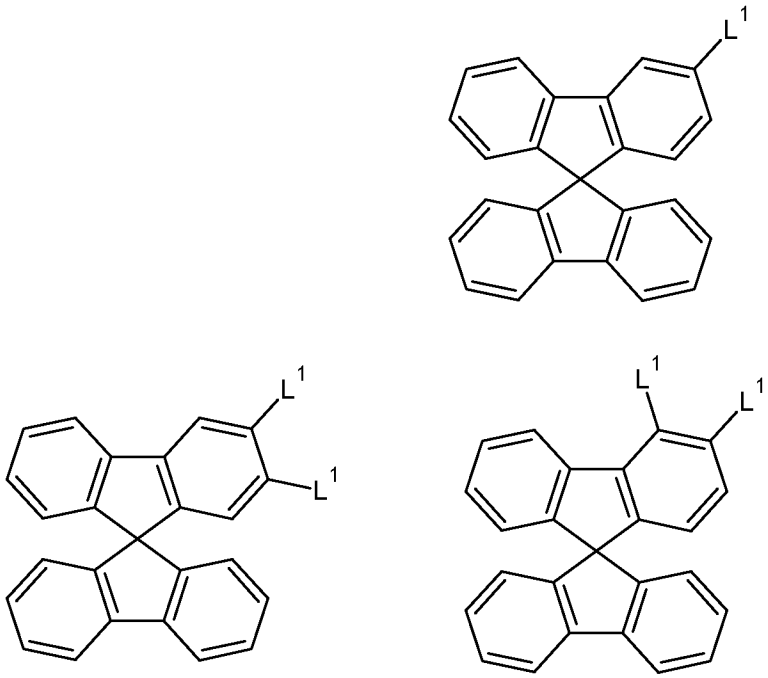
[0055] It is apparent to the skilled person that steric reasons may exclude or render difficult a certain combination of R^1 and R^2 in the compounds of the present invention, no further explanations n this regard being necessary here.

[0056] Ar^1 and Ar^2, which may be the same or different can be selected from the aromatic or heteroaromatic ring systems described above for substitutents R^1 to R^5 and thus reference thereto is made at this point. Preferably, Ar^1 and or Ar^2, which may be the same or different, are aryl ring systems as defined above, preferably phenyl or naphthyl, which may be substituted or unsubstituted.

[0057] A further group of preferred compounds in accordance with the present invention are those wherein at least one of n, m or o represents an integer of from 1 to 3.

[0058] Also preferred are compounds wherein m and o are both zero.

[0059] Further preferred amongst such compounds (where m and o are zero) are compounds of general formula

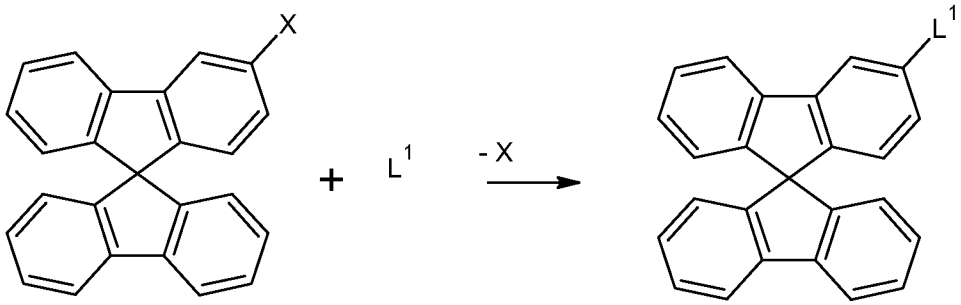
[0060] 

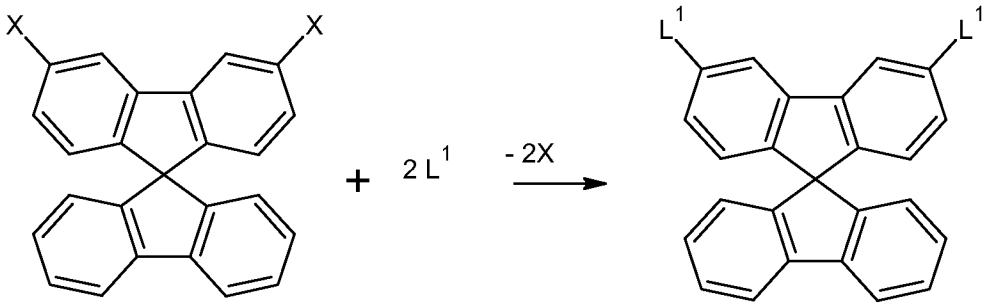
[0061] where L^1 can have any of the meanings defined above.

[0062] The SBF or open SBF ring system may or may not comprise further substituents in addition to substituents L^1. If present, such additional substituents, which may be the same or different in each position they occur, are generally selected from of halogen, alkyl, alkoxy, amino, cyano, alkenyl, alkynyl, arylalkyl, aryl and heteroaryl groups.

[0063] The compounds in accordance with the present invention may be synthesized by any known and suitable method. The skilled person is aware of suitable manufacturing processes.

[0064] Generally, the compounds of the present invention with meta-substituents may be prepared by the following general reaction schemes, which show an exemplary way for compounds carrying one or two ligands L^1



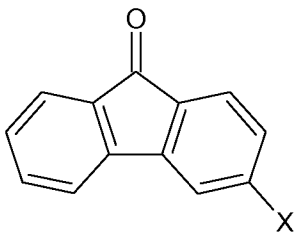


[0065] wherein X is a leaving group selected from known leaving groups for such reactions such as halogen, OH, OR, SR , OCN, SCN or CN, especially preferably halogen, in particular chlorine or bromine.

[0066] The skilled person will select the suitable reactants and reaction conditions based on the individual needs of a specific synthesis.

[0067] The starting materials for such synthesis with at least one leaving group in a meta-position of the SBF or Open SBF ring system may be synthesized in accordance with various process routes which the skilled person will select in accordance with the specific needs. Generally, such compounds are not easily accessible through introduction of the substituents directly into a SBF or Open SBF core as these routes generally yield the para-substituted products preferably due to their higher reactivity. Accordingly, the substituents X have to be introduced through suitable precursor substances e.g. fluorene derivatives, benzophenone derivatives or biphenyl derivatives, to mention only three examples, which are thereafter reacted to yield the SBF or Open SBF structure.

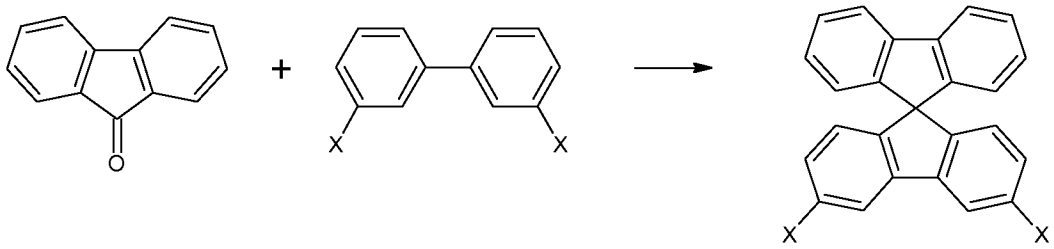
[0068] Thus respective compounds may for example be obtained from substituted fluorenone derivatives of formula



[0069]

[0070] with suitable biphenyl compounds.

[0071] Another possibility is the reaction of fluorenones with suitable substituted biphenyl compounds in accordance with the general reaction scheme



[0072]

[0073] which is described in more detail in JP 2006/089585 for X= OH and which may be adopted for other substituents X.

[0074] Another embodiment of the present invention is directed to the use of the compounds of the present invention in an organic light emitting device, especially an organic light emitting diode (OLED).

[0075] The compounds in accordance with the present invention may advantageously be used, together with an emitting material, in the emissive layer of an organic light emitting device.

[0076] The compounds of the present invention are also suitable as materials for other layers of organic electronic devices.

[0077] The present invention is also directed to an organic light emitting device (OLED) comprising an emissive layer (EML), said emissive layer comprising the compounds of the present invention as host material, said host material being notably suitable in an emissive layer (EML) in an OLED.

[0078] An OLED generally comprises :

a substrate, for example (but not limited to) glass, plastic, metal;

an anode, generally transparent anode, such as an indium-tin oxide (ITO) anode;

a hole injection layer (HIL) for example (but not limited to) PEDOT/PSS;

a hole transporting layer (HTL);

an emissive layer (EML);

an electron transporting layer (ETL);

an electron injection layer (EIL) such as LiF, Cs_2CO_3

a cathode, generally a metallic cathode, such as an Al layer.

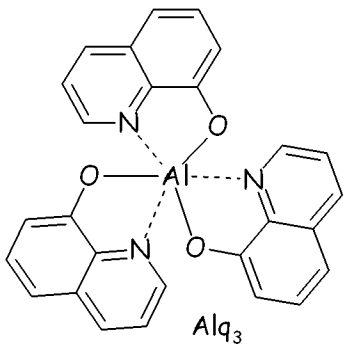
[0079] For a hole conducting emissive layer, one may have a hole blocking layer (HBL) that can also act as an exciton blocking layer between the emissive layer and the electron transporting layer. For an electron conducting

emissive layer, one may have an electron blocking layer (EBL) that can also act as an exciton blocking layer between the emissive layer and the hole transporting layer. The emissive layer may be equal to the hole transporting layer (in which case the exciton blocking layer is near or at the anode) or to the electron transporting layer (in which case the exciton blocking layer is near or at the cathode).

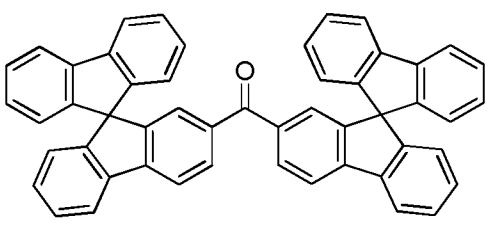
[0080] The compounds of the present invention may be used preferably used as hosts in an emissive layer.

[0081] Optionally, the emissive layer may also contain a polarization molecule, present as a dopant in said host material and having a dipole moment that generally affects the wavelength of light emitted.

[0082] A layer formed of an electron transporting material is advantageously used to transport electrons into the emissive layer comprising the light emitting material and the (optional) host material. The electron transporting material may be an electron-transporting matrix selected from the group of metal quinoxolates (e.g. Alq_3, Liq), oxadiazoles, triazoles and ketones (e.g. Spirobifluorene ketones SBFK). Examples of electron transporting materials are tris-(8-hydroxyquinoline)aluminum of formula ["Alq_3"] and spirobifluoreneketone SBFK:

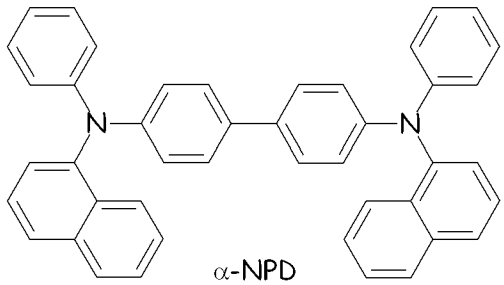


Alq_3



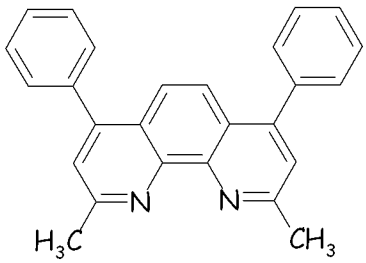
SBFK

[0083] A layer formed of a hole transporting material is advantageously used to transport holes into the emissive layer comprising the light emitting material as above described and the (optional) host material. An example of a hole transporting material is 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl ["α-NPD"].



α-NPD

[0084] The use of an exciton blocking layer ("barrier layer") to confine excitons within the luminescent layer ("luminescent zone") is greatly preferred. For a hole-transporting host, the blocking layer may be placed between the emissive layer and the electron transport layer. An example of a material for such a barrier layer is 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (also called bathocuproine or “BCP”), which has the formula



BCP

[0085] The OLED has preferably a multilayer structure, as depicted in Figure 1, wherein **1** is a glass substrate, **2** is an ITO layer, **3** is a HIL layer comprising PEDOT/PSS, **4** is a HTL layer comprising α-NPD, **5** is an EML comprising mCBP as host material and the light emitting material or mixture of these materials as above defined as dopant in an amount of about 15 % wt with respect to the total weight of host plus dopant; **6** is a

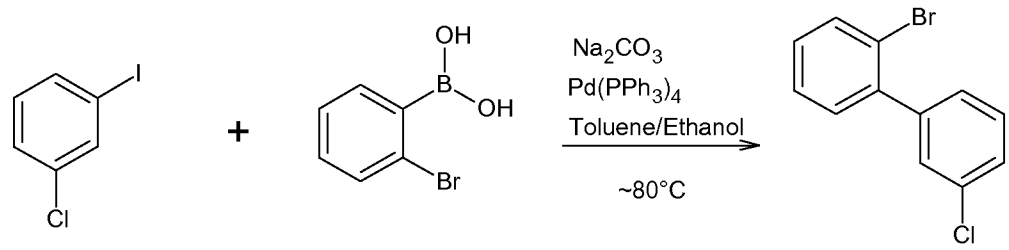
HBL comprising BCP; **7** is an ETL comprising Alq_3; **8** is an EIL comprising LiF and **9** is an Al layer cathode.

[0086] Examples of the present invention are reported hereinafter, whose purpose is merely illustrative but not limitative of the scope of the invention itself.

[0087] Example 1

[0088] Synthesis of 3-Chloro-SBF

[0089] Step 1: Synthesis of 1-Bromo-7-chloro-biphenyl

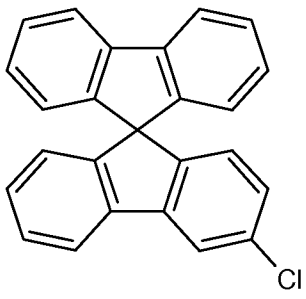


[0090]

[0091] A 50-ml round-bottom flask under nitrogen atmosphere was charged sequentially with $Pd(OAc)_2$ (1.07 g, 0.0047 mol), PPh_3 (5,0 g, 0.0032 mol) and dioxane (35 ml). This mixture was added to a 500 ml round bottom flask already filled with 1-Chloro-3-iodobenzene (13.6g, 0.056 mol) in dioxane (150 ml), 2N aqueous sodium carbonate (180 ml) and 2-Bromophenylboronic acid (12.3 g, 0.059 mol). This mixture was heated at reflux under N_2 for 1.5 h and cooled to room temperature. The reaction medium was partitioned between water and ethyl acetate. The combined organic layers were washed with brine, dried over MgS04, and concentrated. The residue was purified by column chromatography (CH_2Cl_2/hexane) to afford the desired product with 76.6 % yield.

[0092]

[0093] Step 2: 3-chloro-SBF

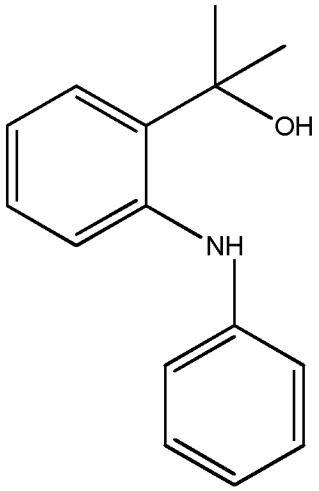
[0094] 

[0095] To a solution of 1-Bromo-7-Chloro-biphenyl (10 g, 0.037mol) in anhydrous THF (100 ml) cooled to -78°C a solution of 1.6 M n-BuLi in hexane (0.037 mol, 23.2 ml) was added dropwise. The reaction mixture was stirred at -78°C for 1h and a solution of fluorenone (0.031 mol, 5.58g) in anhydrous THF (25 ml) was added dropwise. After addition, the mixture was allowed to warm to room temperature and stirred for 2h. The mixture was quenched with saturated NH_4Cl (200 ml) and extracted with ethyl acetate (3*125 ml). The combined organic layers were washed with brine, dried over Na_2SO4 (or $MgSO_4$) and concentrated in vacuo. The residue was purified by flash chromatography to afford the target compound with ~20% yield.

[0096] Step 3 - Preparation of 9,9-dimethyl-9,10-dihydroacridine

[0097] 2-(phenylamino)benzoic acid (50 g, 0.23 mol) was dissolved in methanol (1 L), put in an ice bath and stirred for ten minutes. After slowly adding $SOCl_2$ (60 mL, 0.58 mol) thereto at 0°C, the mixture was stirred under reflux for 12 hours at 90°C.Upon completion of the reaction, the reaction mixture was washed with distilled water and extracted with ethyl acetate. After drying the organic layer with magnesium sulfate and removing the solvent by a rotary type evaporator, 2-(phenylamino) methyl benzoate (47 g, 92%) was obtained through purification by column chromatography using ethyl acetate as developing solvent.

[0098] 90 g 2-(phenylamino)methyl benzoate (90g, 0.3 mole) was added to THF (1.5 L) and methyl magnesium bromide (462 mL, 1.38 mole) was slowly added to the mixture, which was thereafter stirred at room temperature for 12 hours. Upon completion of the reaction, the reaction mixture was neutralized with distilled water and extracted with ethyl acetate. After drying the organic layer with magnesium sulfate and removing the solvent by a rotary type evaporator, 80 g (90%) of

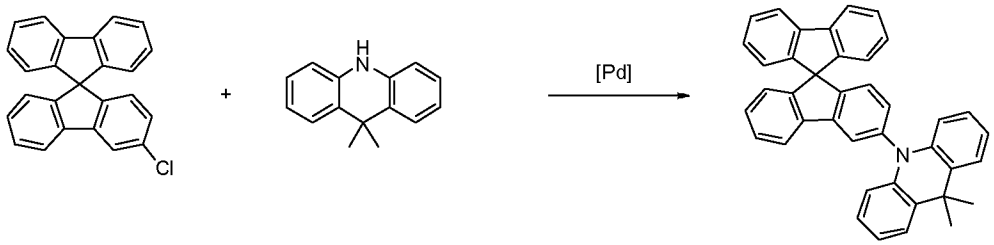


[0099]

[00100] was obtained through purification by column chromatography using ethyl acetate as developing solvent

[00101] 80 g (0.35 mole) of the compound obtained in the previous step was added to 1.7L of phosphoric acid and the mixture was stirred for 12 hours at room temperature. Upon completion of the reaction, the reaction mixture was neutralized with distilled water and the produced solid was filtered while being washed with water. The solid was dissolved in dichloromethane, extracted and neutralized with sodium hydroxide. After drying the organic layer with magnesium sulfate and removing the solvent by a rotary type evaporator, 64 g 9,9-dimethyl-9,10-dihydroacridine (87%) was obtained via recrystallization in hexane.

[00102] : 3-(9,9-dimethyl-9,10-dihydroacridine) –SBF



[00103] Catalyst $Pd(dba)_2$ (5 % mol, 490 mg) and the phosphine $P(tBu)_3$ (4% mol, 0.675 mL of 1M $P(tBu)_3$ in toluene) were introduced at room temperature in toluene (10 mL, anhydrous and well degassed) in a two way flask. After 15 min under nitrogen, the other reagents 3 Cl-SBF (1eq, 5.98 g, 16.9 mmol), 9,9-dimethyl-9,10-dihydroacridine (1eq, 3.53 g, 16.9 mmol) and tBuONa (3 eq, 5.0 g, 60.6 mmol) were introduced and the reaction medium was warmed at 90 °C for 3 hours. At the end of the reaction, the medium was filtrated on diatomaceous earth (celite) and solvent was

evaporated under vacuum. The solid was absorbed on silica gel and a dry flash chromatography was realized (methylene chloride / hexane). After solvent evaporation, the solid was recrystallized in hexane (m = 7.66 g, yield = 87%).

[00104] The HOMO level was determined to -5.29 eV, the LUMO level to -1.49 eV and the triplet energy to 2.88 eV.

[00105] The HOMO level ($E_{HOMO)}$ has been calculated from the half wave potential obtained from the first oxidation ($E_{1ox}^{1/2}$) using the following equation: $E_{HOMO} - (-4.8) = -[E_{1ox}^{1/2} - E_{ox}^{1/2}(Fc/Fc^{+})]$ where E_{HOMO} (ferrocene) has been taken equal to 4.8 eV below the vacuum level.

[00106] The E LUMO (CV) have been calculated from the 1st reduction potential.

[00107] The triplet energy has been calculated from the highest energy phosphorescence peak in 2-MetTHF (2-methyl tetrahydrofurane) at 77 K.

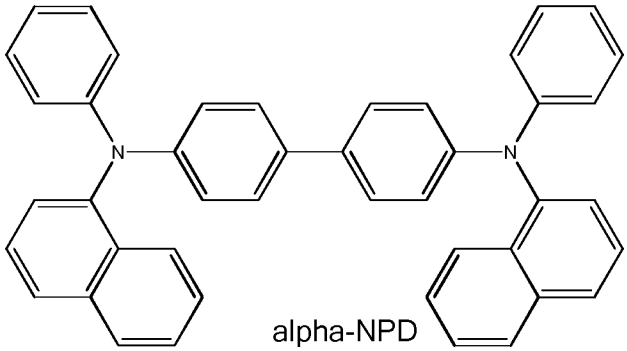
[00108] Device Examples

[00109] 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 is 120 nm of indium tin oxide (ITO). 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 %, while operational stability tests were done by driving the devices at continuous current at room temperature. LT_{50} 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.

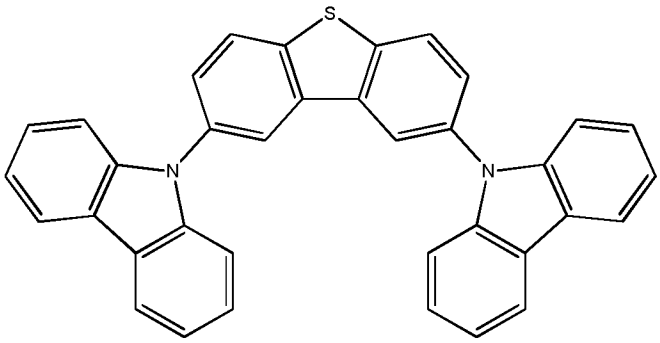
[00110] The OLED stack consisted of sequentially, from the ITO surface, 30nm of Plexcore OC (a self-doping polymer poly(thiophene-3-[2[(2-methoxyethoxy)ethoxy]-2,5-diyl), supplied from Plextronics Inc.) deposited by spin-coating and dried on a hot plate at 200 °C for 20 min. On top of the HIL, 15 nm of NPB were deposited by vacuum-thermal evaporation as hole transporting layer (HTL).

[00111] Then a 30nm layer of Compound B doped with different amounts of dopant Compound C was deposited by vacuum-thermal evaporation as the emissive layer (EML). Then a 5nm layer of Compound A was deposited by vacuum-thermal evaporation as the hole blocking layer (HBL). Then, a 40 nm layer of Alq3 was deposited by vacuum-thermal evaporation as the electron transporting layer (ETL). The cathode consisted of 1 nm of LiF followed by 100 nm of Aluminum.

[00112] As used herein, α-NPD, Compound A, Compound B, Compound C and Alq3 have the following structures

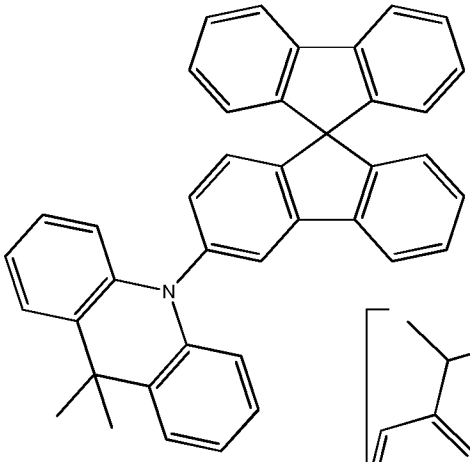


alpha-NPD

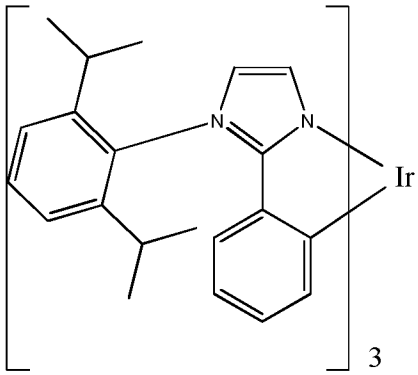


Compound A

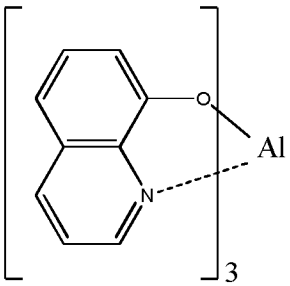
[00113]



Compound B



Compound C



Alq3

[00114]

[00115] The device structure is summarized in Figure 2 while Table 1 shows the results measured for the fabricated devices. Compound B was used as host and compound C was used as dopant. The values reported in Table 1 have been measured at a luminance of 1000 Cd/m^2.

[00116] Table 1

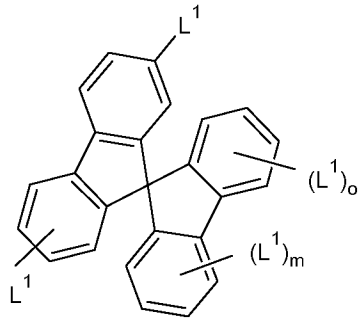
Ex.	Dopant %	V	EQE	Lm/W	Cd/A	X	Y	V_{on}	LT50@ 1000Cd/m2 hrs
1	10	7.6	8.8	9.1	22.0	0.19	0.43	3.8	64
2	15	6.3	11.7	14.5	29.0	0.19	0.43	3.3	296
3	20	5.6	12.0	16.8	29.9	0.19	0.43	2.9	317
4	25	5.4	12.1	17.6	30.1	0.20	0.43	3.0	66
5	30	4.9	11.7	18.5	28.8	0.19	0.43	2.9	23

[00117] As can be seen from the Examples, power efficiency increases with increasing dopant concentration. The lifetime of the devices shows a maximum in the concentration range of from 15 to 20 wt% dopant, relative to the amount of host. Colour coordinates remain nearly constant whereas EQE is lower for 10 Wt% dopant compared to higher concentrations.

[00118] The foregoing examples show that the compounds in accordance with the present invention are suitable as host materials in organic light emitting diodes.

Claims

1. Compounds of general formulae 1 to 12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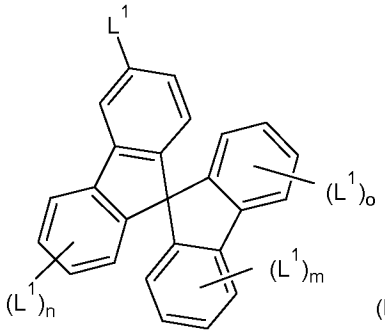
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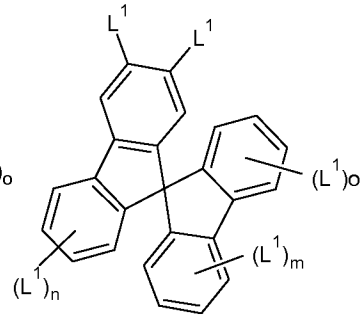
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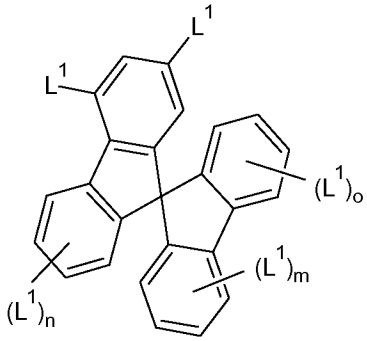
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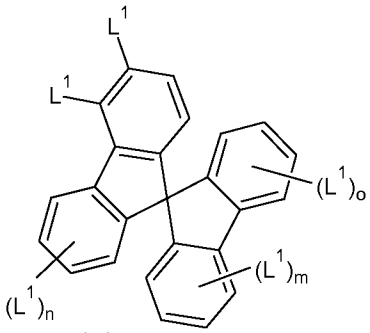
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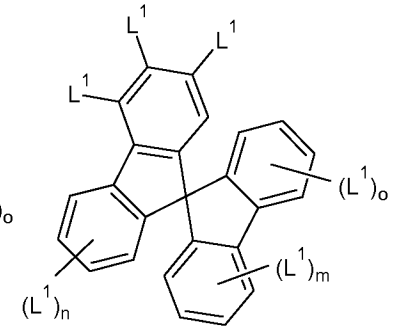
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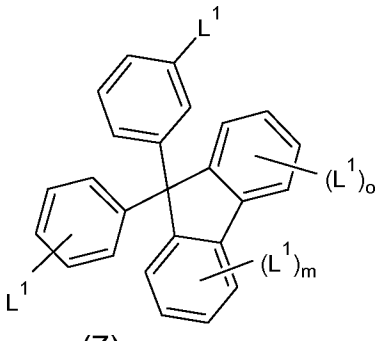
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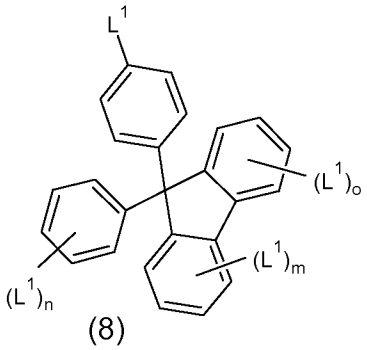
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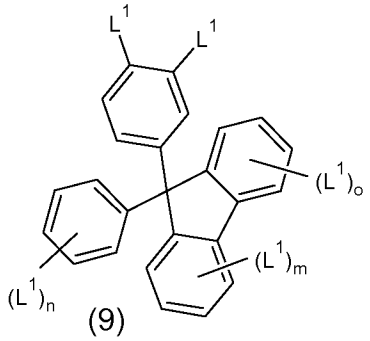
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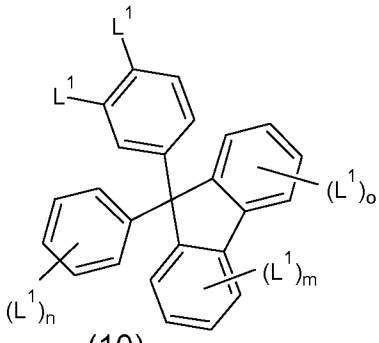
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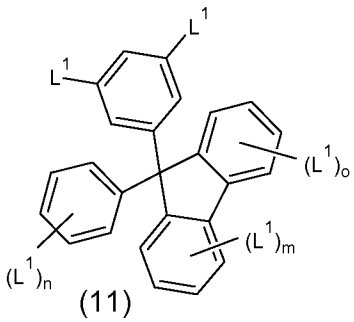
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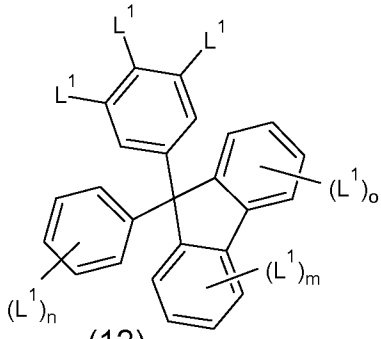
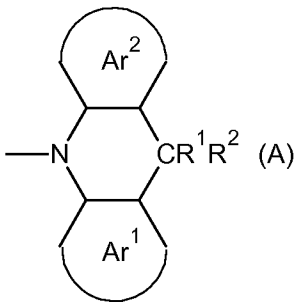

(12)

wherein n, m and o may be the same or different and represent an integer of from 0 to 3, with the proviso that for compounds of formula (1) and (7) at least one of m or o is zero,

each of the phenyl rings may carry no ligands other than L^1 or may be substituted by ligands other than L^1,

L1, which may be the same or different at each position, has the formula A



(A)

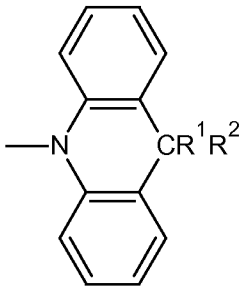
wherein

R^1 and R^2 may be the same or different and represent hydrogen or an aliphatic group, a carbocyclic group, an aromatic group or a heterocyclic group, all of which may comprise 1 to 20 carbon atoms and all of which may be substituted or unsubstituted, or

an OR^3 group, a NR^4R^5 group or a SR^6 group, wherein R^3 to R^6 represent hydrogen, an aliphatic group, a carbocyclic group, an aryl group, a heteroaryl group or a heterocyclic group having 1 to 20 carbon atoms, and

Ar^1 and Ar^2, which may be the same or different, represent optionally substituted aromatic or heteroaromatic ring systems comprising 4 to 20 ring atoms.

2. Compounds in accordance with claim 1, wherein L^1 has the formula A-1



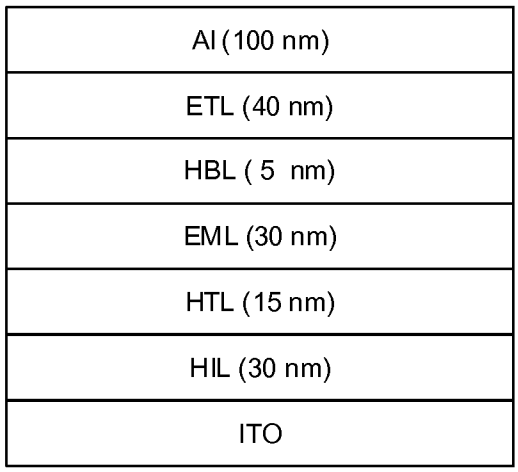
(A-1)

wherein R^1 and R^2 have the meaning as defined in claim 1.

3. Compounds in accordance with claim 1 or 2 wherein R^1 and R^2, which may be the same or different, represent hydrogen, an alkyl group, a carbocyclic group, an aryl group or a heteroaryl group, which groups are substituted or unsubstituted.
4. Compounds in accordance with any of claims 1 or 2 wherein R^1 and R^2, which may be the same or different, represent OR^3, NR^4R^5 or SR^6 wherein R^3 to R^6 have the meaning as defined in claim 1.
5. Compounds in accordance with any of claims 1 to 4 wherein R^1 and R^2 are the same or different and are unsubstituted or substituted by substituents selected from the group consisting of halogen, alkyl, alkoxy, aryloxy, oxo, amino, substituted amino, cyano, alkenyl, alkynyl, arylalkyl, aryl and heteroaryl.
6. Compounds in accordance with claim 5 wherein the substituents are selected from the group consisting of halogen, alkyl, alkoxy, amino, cyano, alkenyl, alkynyl, arylalkyl, aryl and heteroaryl.
7. Compounds in accordance with at least one of claims 1 to 6 wherein at least one of n, m or o represents an integer of from 1 to 4.
8. Compounds in accordance with at least one of claims 1 to 6 wherein n, m and o are zero.
9. Compounds in accordance with at least one of claims 1 to 8 wherein R^1 and/or R^2 represents an alkyl group having of from 1 to 20 carbon atoms.
10. Use of the compounds in accordance with at least one of claims 1 to 9 in an organic light emitting device.
11. The use of claim 10 wherein the light emitting device is an organic light emitting diode.
12. Use of the compounds according to at least one of claims 1 to 9 as host in an emissive layer.
13. An organic light emitting device (OLED) comprising an emissive layer (EML), said emissive layer comprising a compound according to at least one of claims 1 to 9, with an emitting material.

Figure 1

Figure 2



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/068809

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D265/38 C09K11/00 H01L51/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07D C09K H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6 893 743 B2 (SATO HIDEKI [JP] ET AL) 17 May 2005 (2005-05-17) formula III in columns 37-40, formula (III-1) in column 41, compounds H-149 to H-152 in Table 1 in column 45; columns 5,6; claims 20-22	1-13
Y	WO 2010/050781 A1 (GRACEL DISPLAY INC [KR]; CHO YOUNG JUN [KR]; KIM CHI SIK [KR]; EUM SUN) 6 May 2010 (2010-05-06) page 1; claim 1; compounds 80,106-110,112,167-171,173,202,228-234,262,263, compounds 287-289,291,324,350-354,356,690,783,873,905	1-13

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
13 November 2012	20/11/2012

Name and mailing address of the ISA/	Authorized officer
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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/068809

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2003/111107 A1 (SALBECK JOSEF [DE] ET AL) 19 June 2003 (2003-06-19) claims 1,2	1-5,7-12

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2012/068809

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6893743 B2	17-05-2005	NONE	
WO 2010050781 A1	06-05-2010	CN 102203076 A	28-09-2011
		EP 2182038 A1	05-05-2010
		JP 2012507508 A	29-03-2012
		KR 20100048203 A	11-05-2010
		WO 2010050781 A1	06-05-2010
US 2003111107 A1	19-06-2003	NONE	