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(54) HIGH POLYMER, MIXTURE CONTAINING SAME, COMPOSITION, ORGANIC ELECTRONIC COMPONENT, AND MONOMER FOR POLYMERIZATION

(57) A high polymer, a mixture containing the same, a composition, an organic electronic component, and a monomer for polymerization. The high polymer comprises a repeat unit E1 and a repeat unit E2. An E1 group on a side chain of the repeat unit E1 and an E2 group on a side chain of the repeat unit E2 have features for forming Exciplexes, $\min((LUMO(E1)-HOMO(E2), LUMO(E2)-HOMO(E1)) \leq \min(E_T(E1), E_T(E2))+0.1eV$ being satisfied, and accordingly a high polymer suitable for printing technologies is provided, thereby reducing manufacturing costs of OLEDs.

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Description

RELATED APPLICATION

[0001] The present disclosure claims priority to Chinese Patent Application No. 201611047040.7 entitled "exciplex, organic electronic device comprising the same and application thereof", filed on November 23, 2016, the entire contents of which are incorporated herein by reference.

TECHNICAL FIELD

[0002] The present disclosure relates to the field of electroluminescent materials, and in particular to a polymer, a mixture, a formulation, and an organic electronic device comprising the same, and a monomer for polymerization.

BACKGROUND

[0003] Organic light emitting diodes (OLEDs) have great potential in implementation of novel optoelectronic devices, such as in applications of flat panel displays and lighting, because of the synthetic diversity of organic semiconductor materials, the possibility of achieving large-area flexible devices, low manufacturing costs, and excellent optical and electrical properties. In order to improve the luminous efficiency of organic light-emitting diodes, various light-emitting material systems based on fluorescence and phosphorescence have been developed. The organic light-emitting diodes using phosphorescent materials have achieved quite a high performance, for example, almost an internal luminescence quantum efficiency of 100%. However, so far, the phosphorescent host materials which have a practical value are a bipolar transport compound or a co-host compound, and its material combination is relatively complicated, which cause imbalance between hole ransport and electron transport when applied to the device, therefore, the lifetime of the phosphorescent device is short. Kim proposed the concept of exciplex as a phosphorescent host material, so that two different organic compounds can be used to form an intermediate state, i.e., an exciplex, to achieve a long lifetime of phosphorescent OLED devices. This can be achieved by the exciplex host material, see Kim et al., Adv. Mater., Vol 26, 5864, (2014).

[0004] In order to take full advantage of organic materials, it is desirable to prepare OLEDs at a low cost and in a large area by printing. Reported existing organic materials capable of forming an exciplex are small molecular materials, and have a relatively low molecular weight, which are not suitable for a printing process.

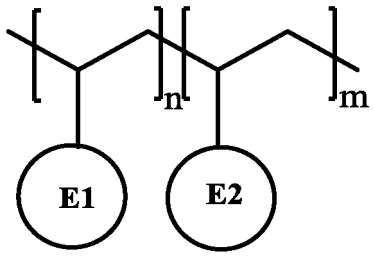
[0005] Therefore, novel material systems suitable for the printing has yet to be developed.

SUMMARY

[0006] In view of the aforementioned deficiencies of the prior art, it is an object of the present disclosure to provide a novel polymeric material to solve the problem that the conventional exciplex materials are not suitable for the printing process.

[0007] The technical solution of the present disclosure is as follows:

[0008] A polymer includes a repeating unit represented by general formula (1),where n and m are integers greater than or equal to 1; $\min((LUMO(E1)-HOMO(E2), LUMO(E2)-HOMO(E1)) \leq \min(E_T(E1), E_T(E2)) + 0.1$ eV, where LUMO(El), HOMO(El), and $E_T(E1)$ are energy levels of a highest occupied molecular orbital, a lowest unoccupied molecular orbital, and a triplet excited state of E1 group, respectively; LUMO(E2), HOMO(E2), and $E_T(E2)$ are energy levels of a highest occupied molecular orbital, a lowest unoccupied molecular orbital, and a triplet excited state of E2 group, respectively.

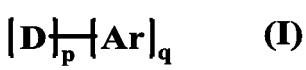


(1)

[0009] Preferably, a ratio of n: m in the polymer ranges from 3:7 to 7:3.

[0010] Preferably, the E1 group includes an electron-donating group D, and/or the E2 group includes an electron-

accepting group. Preferably, the E1 group and/or the E2 group has a (HOMO-(HOMO-1) greater than or equal to 0.3 eV. In some preferred embodiments, the E1 group and the E2 group have a structural unit represented by the following general formula (I) or (II), respectively:

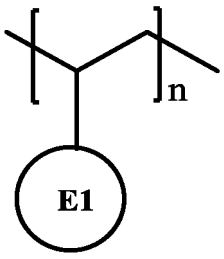


(I)

(II)

[0011] Ar is an aromatic or heteroaromatic structural unit. The electron-donating group D may be the same or different in multiple occurrences, and the electron-accepting group A may be the same or different in multiple occurrences, p and r are an integer between 1 and 6, and q and s are 0 or 1.

[0012] Another related but different polymer is represented by the following general formula (4), where n is an integer greater than or equal to 1:



(4)

[0013] Wherein (HOMO-(HOMO-1) of the E1 group is greater than or equal to 0.3 eV.

[0014] A polymerizable monomer including the above E1 group or the above E2 group, and combinations thereof are provided.

[0015] A formulation includes any of the aforementioned polymers and at least one organic solvent.

[0016] An application of any of the aforementioned polymers in an organic electronic device.

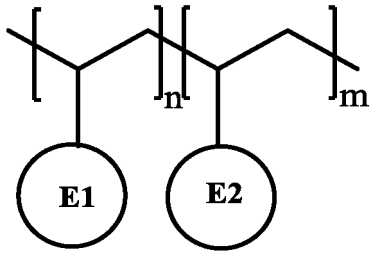
[0017] An organic electronic device includes at least any of the aforementioned polymers.

[0018] Advantageous effects: the polymers of the general formula (1) according to the present disclosure are prone to form an exciplex, which, when used for a phosphorescent host, can improve the efficiency of the device, while providing a better material solution for printing OLEDs due to better solubility in an organic solvent and good film forming performance. The polymers of the general formula (4) have high stability and are easy to be solution processed.

DETAILED DESCRIPTION OF EMBODIMENTS

[0019] In order to make the objects, technical solutions, and advantages of the present disclosure more clearly, the present disclosure will be further described in detail below with reference to the accompanying drawings and embodiments. It is understood that the specific examples described herein are merely illustrative of the disclosure and are not intended to limit the disclosure.

[0020] A polymer includes a repeating unit represented by general formula (1),where n and m are integers greater than or equal to 1; $\min((LUMO(E1)-HOMO(E2), LUMO(E2)-HOMO(E1)) \leq \min(E_T(E1), E_T(E2)) + 0.1$ eV, where LUMO(E1), HOMO(El), and $E_T(E1)$ are energy levels of a highest occupied molecular orbital, a lowest unoccupied molecular orbital, and a triplet excited state of E1 group, respectively; LUMO(E2), HOMO(E2), and $E_T(E2)$ are energy levels of a highest occupied molecular orbital, a lowest unoccupied molecular orbital, and a triplet excited state of E2 group, respectively.



(1)

[0021] In a preferred embodiment, min((LUMO(E1)-HOMO(E2), LUMO(E2)-HOMO(E1)) ≤ min(E_T (E1), E_T (E2));
In a more preferred embodiment, min((LUMO(E1)-HOMO(E2), LUMO(E2)-HOMO(E1)) ≤ min(E_T(E1), E_T (E2)) - 0.05eV;
In a still more preferred embodiment, min((LUMO(E1)-HOMO(E2), LUMO(E2)-HOMO(E1)) ≤ min(E_T(E1), E_T(E2)) - 0.1 eV;
In a very preferred embodiment, min((LUMO(E1)-HOMO(E2), LUMO(E2)-HOMO(E1)) ≤ min(E_T(E1), E_T(E2)) - 0.15eV;
In a most preferred embodiment, min((LUMO(E1)-HOMO(E2), LUMO(E2)-HOMO(E1)) ≤ min(E_T(E1), E_T(E2)) - 0.2eV;
In embodiments of the present disclosure, triplet excited state energy level E_T, HOMO, and LUMO play a key role in the energy level structure of the organic material. The determination of these energy levels is introduced as follows.

[0022] HOMO and LUMO energy levels can be measured by photoelectric effects, such as XPS (X-ray photoelectron spectroscopy) and UPS (UV photoelectron spectroscopy), or by cyclic voltammetry (hereinafter referred to as CV). Recently, quantum chemical methods, such as density functional theory (hereinafter referred to as DFT), have also become effective methods for calculating molecular orbital energy levels.

[0023] The triplet excited state energy level E_T of an organic material can be measured by a low-temperature time-resolved spectroscopy or by quantum simulation calculation (for example, by Time-dependent DFT), such as by commercial software Gaussian 03W (Gaussian Inc.). Detailed simulation methods can be found in WO2011141110 or as described below in the examples.

[0024] It should be noted that the absolute values of HOMO, LUMO, and E_T depend on the measurement method or calculation method used, and even for the same method but different evaluation method, for example, different HOMO/LUMO value can be provided at the starting point and peak point on a CV curve. Therefore, a reasonable and meaningful comparison should be carried out using the same measurement method and the same evaluation method. As described in the embodiments of the present disclosure, the values of HOMO, LUMO, and E_T are simulations based on Time-dependent DFT, without affecting the application of other measurement or calculation methods.

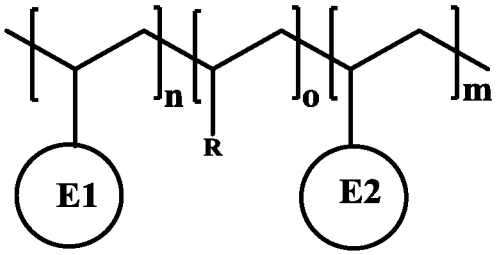
[0025] The polymer according to the present disclosure has an advantage that the E1 group and the E2 group are linked as a side chain structure through a non-conjugated polymer backbone to achieve a higher molecular weight while maintaining the energy structure of a single repeating unit, that is, HOMO, LUMO, and E_T of the single repeating unit remain substantially unchanged relative to the E1 group or the E2 group, while forming an exciplex in the polymer.

[0026] In the disclosure, (HOMO-1) is defined as an energy level of the second highest occupied molecular orbital, (HOMO-2) is an energy level of the third highest occupied molecular orbital, and so on. (LUMO+1) is defined as an energy level of the second lowest unoccupied molecular orbital, (LUMO+2) is an energy level of the third lowest occupied molecular orbital, and so on.

[0027] In the present disclosure, a repeating unit in which the E1 group is located is defined as a repeating unit E1, and a repeating unit in which the E2 group is located is defined as a repeating unit E2. Generally, a ratio n: m between the number of the repeating units E1 and the number of the repeating units E2 in the polymer ranges from 3:7 to 7:3.

[0028] In a preferred embodiment, the ratio n: m between the number of the repeating units E1 and the number of the repeating units E2 in the polymer ranges from 4:6 to 7:3, more preferably ranges from 4:6 to 6:4, still more preferably ranges from 5:5 to 6:4, and most preferably is 5:5.

[0029] In order to improve the solubility and processability of the polymer, an additional group R is generally attached to the backbone of the polymer to increase the solubility of the polymer while increasing the molecular weight of the polymer to provide better luminescence performance and device performance. In a preferred embodiment, the polymer according to the present disclosure includes a repeating unit represented by general formula (2).



(2)

[0030] R is selected from the group consisting of a linear alkane containing 1 to 15 carbon atoms, a branched alkane containing 1 to 15 carbon atoms, a cycloalkane containing 1 to 15 carbon atoms, an aromatic ring system containing 2 to 20 carbon atoms, a heteroaromatic ring system containing 2 to 20 carbon atoms, and a non-aromatic ring system containing 2 to 20 carbon atoms. o is an integer greater than or equal to 0.

[0031] In a preferred embodiment, R has a structural unit corresponding to an organic functional material, and the organic functional material may be selected from the group consisting of HTM, ETM, a fluorescent material, a phosphorescent material, and a host material.

[0032] In a more preferred embodiment, R has a structural unit corresponding to a fluorescent material or a phosphorescent material.

[0033] According to the polymer of the present disclosure, an exciplex can be formed between the repeating unit E1 and the repeating unit E2, and can be used as a host material or an emitter in the light-emitting layer. When it is used as the host material, in some embodiments, the exciplex formed by the repeating unit E1 and the repeating unit E2 has a proportion in the polymer ranging from 70% to 99.9%.

[0034] In a preferred embodiment, the repeating unit E1 or the repeating unit E2 may be present in an amount of from 30 mol% to 50 mol%, preferably from 35 mol% to 50 mol%, more preferably from 40 mol% to 50 mol%, even more preferably from 40 mol% to 48 mol%, and most preferably from 41mol% to 46 mol% in the polymer.

[0035] In a preferred embodiment, the R group in the general formula (2) further includes an emitter unit. In some embodiments, the repeating unit R may be present in an amount of from 0.1 mol% to 30 mol% in the polymer. In the present disclosure, a repeating unit where the R group is located is defined as the repeating unit R.

[0036] In a more preferred embodiment, the repeating unit R containing the emitter may be present in an amount of from 1 mol% to 52 mol%, preferably from 2 mol% to 20 mol%, more preferably from 3 mol% to 81 mol%, even more preferably from 4 mol% to 61 mol%, and most preferably from 5 mol% to 15 mol% in the polymer.

[0037] In the present disclosure, the host material, the matrix material, Host material, and Matrix material have the same meaning and are interchangeable. Singlet and singlet state have the same meaning and can be interchanged. Triplet and triplet excited state have the same meaning and can be interchangeable.

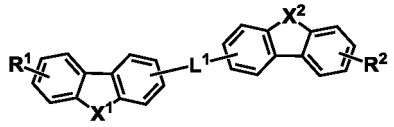
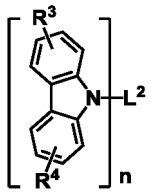
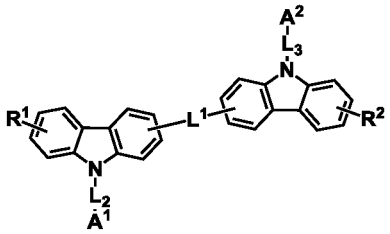
[0038] As used herein, the term "small molecule" refers to a molecule that is not a polymer, oligomer, dendrimer, or blend. In particular, there is no repeating structure in the small molecule. The small molecule has a molecular weight less than or equal to 3000 g/mol, preferably $\leq$ 2000 g/mol, and most preferably $\leq$ 1500 g/mol.

[0039] The polymer includes a homopolymer, a copolymer, and a block copolymer. In addition, in the present disclosure, the polymer also includes a dendrimer. Regarding the synthesis and application of the dendrimer, see [Dendrimers and Dendrons, Wiley-VCH Verlag GmbH & Co. KGaA, 2002, Ed. George R. Newkome, Charles N. Moorefield, Fritz Vogtle.].

[0040] The backbone of the conjugated polymer is mainly composed of sp^2 hybrid orbital of carbon (C) atoms. Famous examples are: polyacetylene and poly(phenylene vinylene). The C atom on the backbone thereof can also be substituted by other non-C atoms, and it is still considered to be a conjugated polymer when the sp^2 hybridization on the backbone is interrupted by some natural defects. In addition, in the present disclosure, the conjugated polymer further includes aryl amine, aryl phosphine and other heteroarmotics, organometallic complexes, and the like. The polymer according to the present disclosure may also be a non-conjugated polymer.

[0041] In some embodiments, according to the polymer of the present disclosure, at least one of the E1 group and the E2 group has a ((HOMO-(HOMO-1)) greater than or equal to 0.2 eV, preferably greater than or equal to 0.25 eV, more preferably greater than or equal to 0.3 eV, even more preferably greater than or equal to 0.35 eV, very preferably greater than or equal to 0.4 eV, and most preferably greater than or equal to 0.45eV. It's facilitated to the the stability of the hole transport when Δ((HOMO-(HOMO-1)) of the E1 group and/or the E2 group is larger.

[0042] In a preferred embodiment, the E1 group contains one or more of the structural units represented by the following formulas (2) to (9):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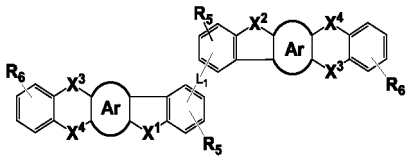
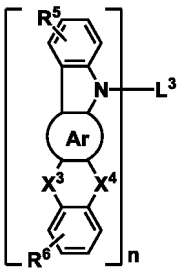
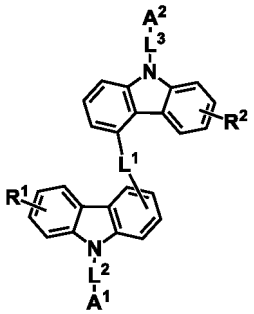
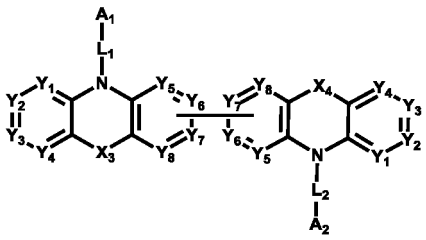
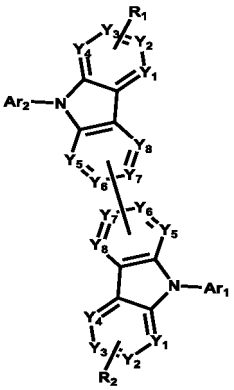
		
(5)	(6)	(7)
		
(8)	(9)	

[0043] Wherein, L^1 represents a single bond, an aromatic group containing 6 to 30 carbon atoms or a heteroaromatic group containing 3 to 30 carbon atoms, and L^1 may be linked to any carbon atom on the benzene ring;

Ar, Ar_1, and Ar_2 independently represent an aromatic group containing 6 to 30 carbon atoms or a heteroaromatic group containing 3 to 30 carbon atoms;

A^1 and A^2 independently represent an aromatic group containing 6 to 30 carbon atoms or a heteroaromatic group containing 3 to 30 carbon atoms;

L^2 and L^3 independently represent an aromatic group containing 6 to 30 carbon atoms or a heteroaromatic group containing 3 to 30 carbon atoms;

X^1 and X^2 independently represent N(R), $C(R)_2$, $Si(R)_2$, O, C=N(R), $C=C(R)_2$, P(R), P(=O)R, S, S=O, or SO_2;

X^3 and X^4 independently represent a single bond, N(R), $C(R)_2$, $Si(R)_2$, O, C=N(R), $C=C(R)_2$, P(R), P(=O)R, S, S=O, or SO_2, but cannot be single bonds at the same time;

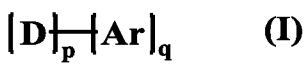
Y^1 to Y^8 independently represent N(R), $C(R)_2$, $Si(R)_2$, O, C=N(R), $C=C(R)_2$, P(R), P(=O)R, S, S=O, or SO_2;

R^1, R^2, R^3, R^4, R^5, R^6, and R independently represent H, D (deuterium atom), F, CN, alkenyl, alkynyl, nitrile, amino, nitro, acyl, alkoxy, carbonyl, sulfone, an alkyl containing 1 to 30 carbon atoms, a cycloalkyl containing 3 to 30 carbon atoms, an aryl containing 6 to 60 carbon atoms, or an aromatic heterocyclic group containing 3 to 60 carbon atoms. R^1, R^2, R^3, R^4, R^5, and R^6 may be linked to any carbon atom on the fused ring.

n represents an integer from 1 to 6.

[0044] In a preferred embodiment, according to the polymer of the present disclosure, the E1 group contains an electron-donating group D and/or the E2 group contains an electron-accepting group A.

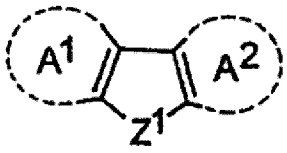
[0045] In a more preferred embodiment, according to the polymer of the present disclosure, the E1 group contains a structural unit represented by general formula I:



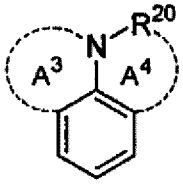
(I)

[0046] Ar is an aromatic or heteroaromatic structural unit, and D may be independently selected from the same or different electron-donating groups in multiple occurrences. p is an integer between 1 and 6, and q is 0 or 1.

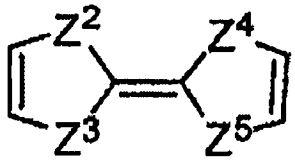
[0047] Suitable electron-donating groups D may be selected from groups having any basic structure of the following general formulas I-1, I-2, and I-3:



I-1



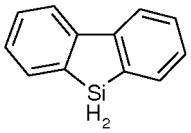
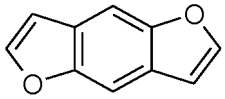
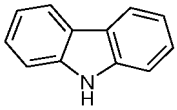
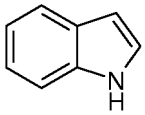
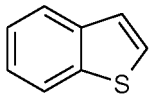
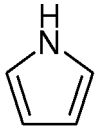
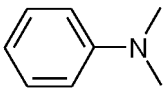
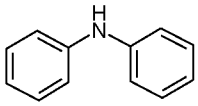
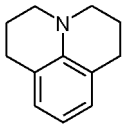
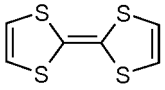
I-2



I-3

[0048] Z^1=H, O, S, or Si, and A^1 and A^2 may independently form an aromatic ring, a heteroaromatic ring, an aliphatic ring, or a non-aromatic heterocyclic ring, respectively. R^{20} represents H, aryl, or an atomic group necessary to form a ring represented by A^4. A^3 and A^4 may also independently form a heteroaromatic ring or a non-heteroaromatic ring, respectively. Z^2, Z^3, Z^4, and Z^5 independently represent O or S, respectively.

[0049] In a preferred embodiment, the aforementioned electron-donating group D is selected from groups having at least one of basic structures of the following structural formulas D1 to D15:

				
D1	D2	D3	D4	D5
				
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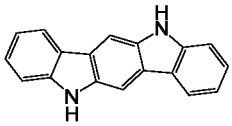
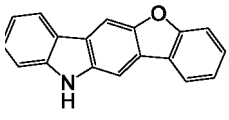
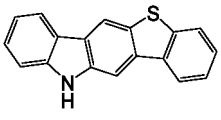
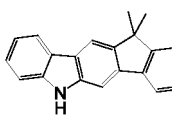
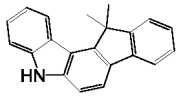
				
D11	D12	D13	D14	D15

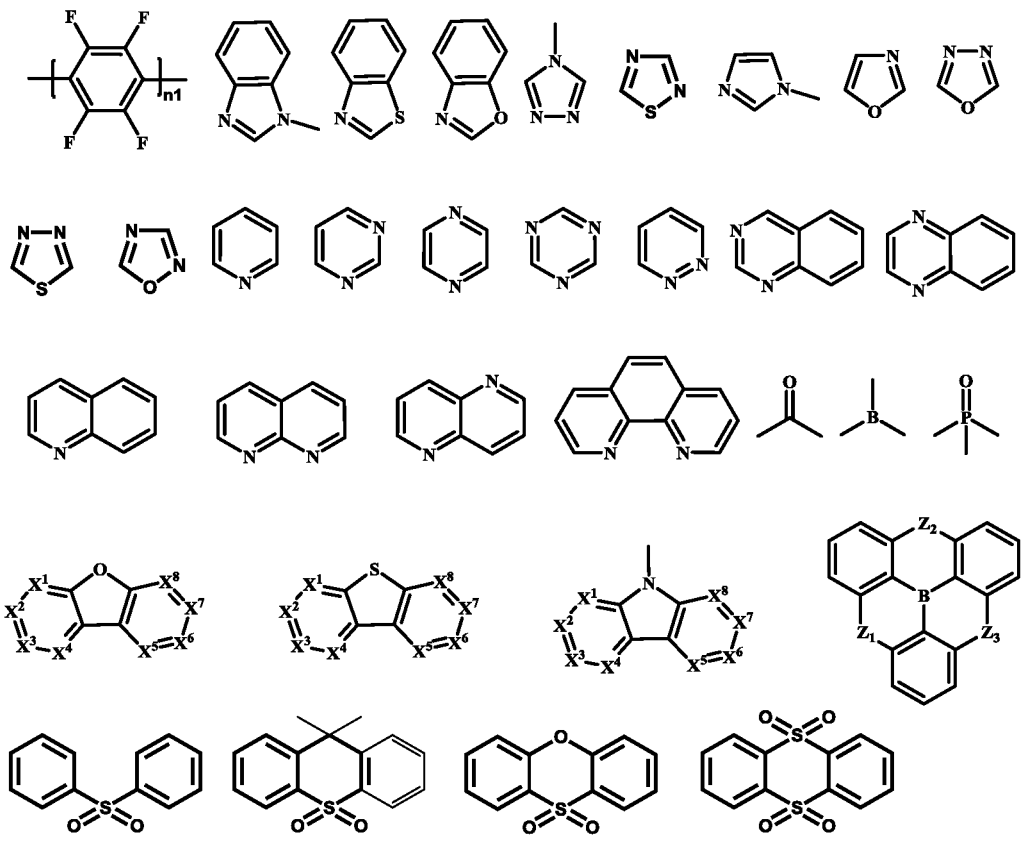
[0050] In another more preferred embodiment, according to the polymer of the present disclosure, the E2 group contains a structure represented by general formula II:

(II)

[0051] Ar is an aromatic or heteroaromatic structural unit, and the electron-accepting group A may be independently

selected from the same or different electron-accepting groups in multiple occurrences, r is an integer between 1 and 6, and s is 0 or 1.

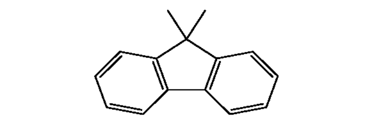
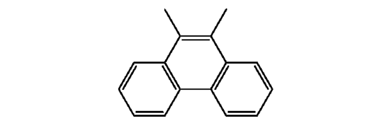
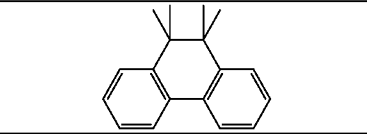
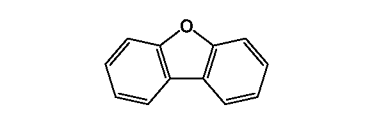
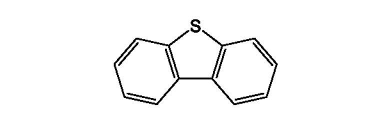
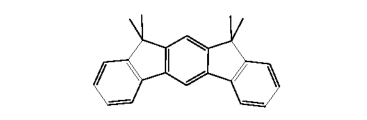
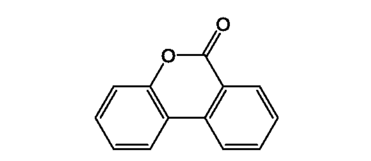
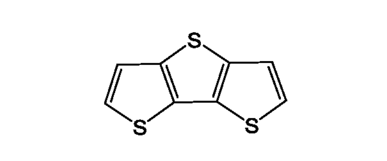
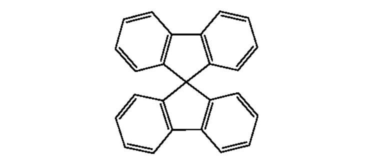
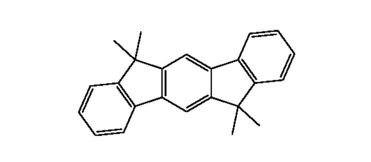
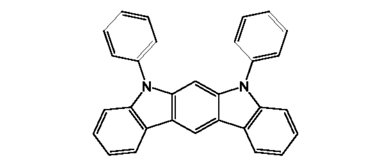
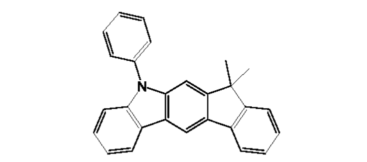
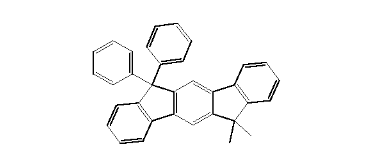
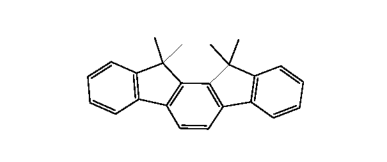
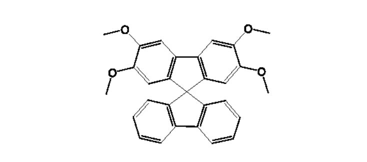
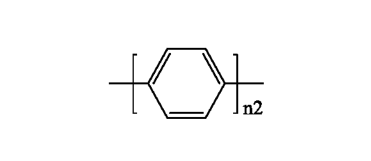
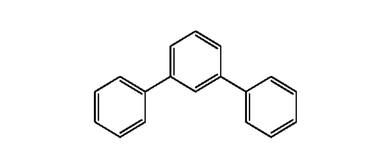
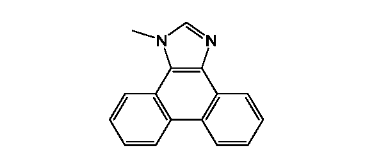
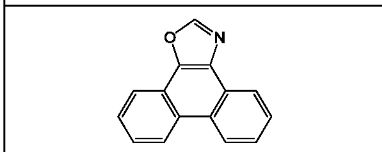
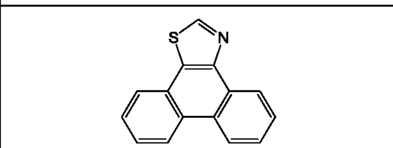
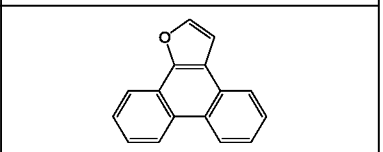
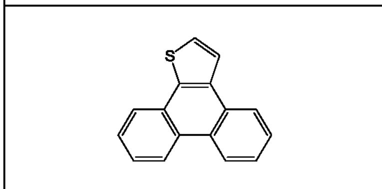
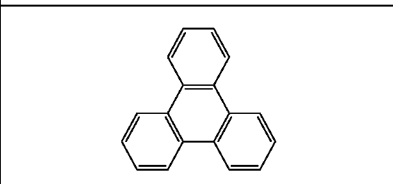
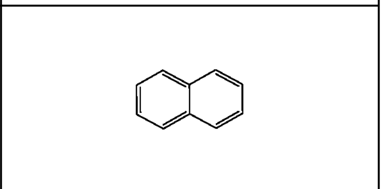
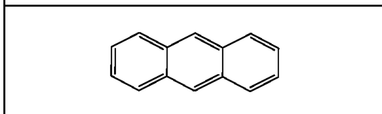
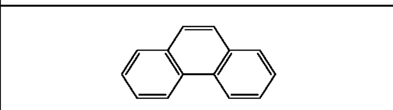
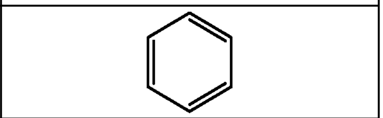
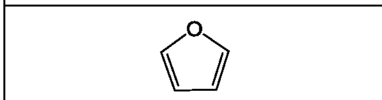
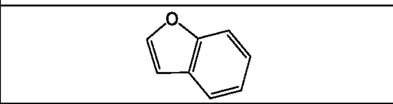
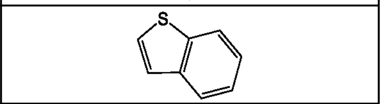
[0052] In a preferred embodiment, suitable electron-accepting groups A may be selected from F, a cyano group, or at least one of groups having any basic structure of the following general formulas:



[0053] n1 is an integer from 1 to 3. X^1 to X^8 are selected from CR^{12} or N, and at least one of X^1 to X^8 is N. R^{12} may be selected from the group consisting of hydrogen, alkyl, alkoxy, amino, alkenyl, alkynyl, aralkyl, heteroalkyl, aryl, and heteroaryl. Z_1 to Z_3 are a single bond, C $(R^{12})_2$, O, or S. When the electron-aceepting group A is F or a cyano group, s is 1.

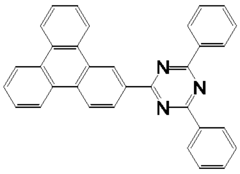
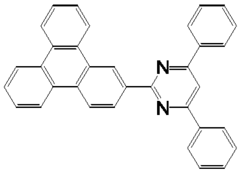
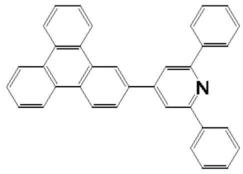
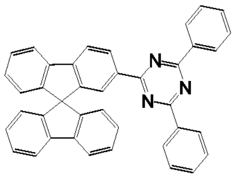
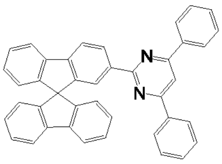
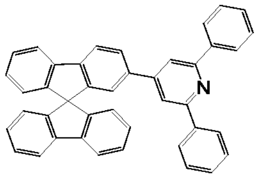
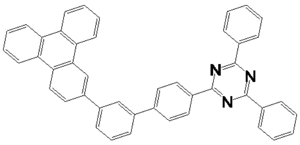
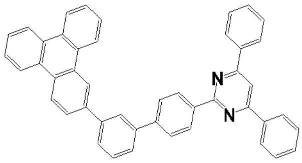
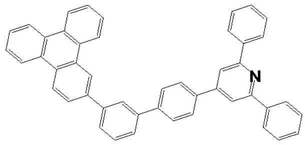
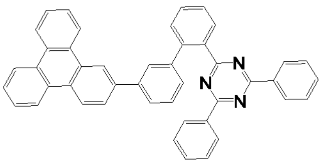
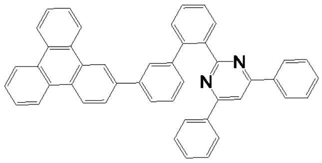
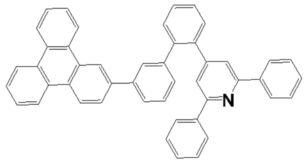
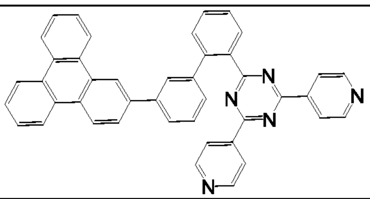
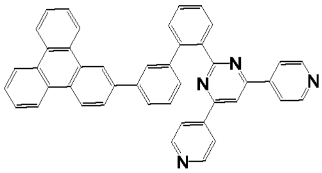
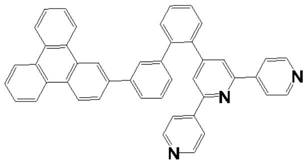
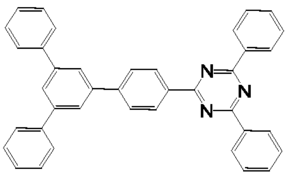
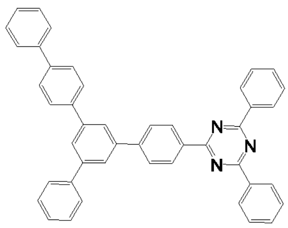
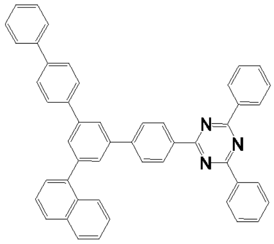
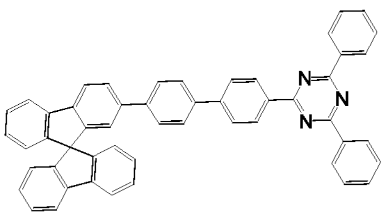
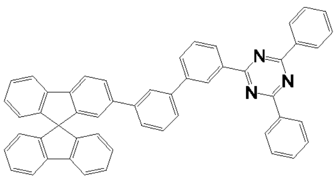
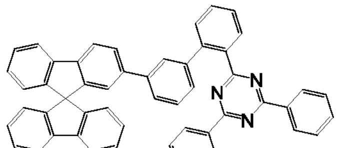
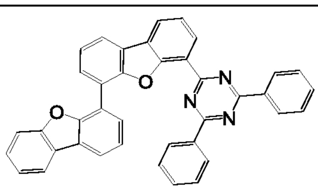
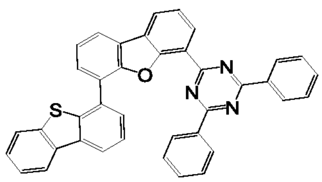
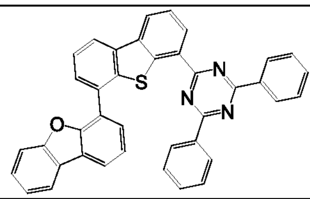
[0054] In a preferred embodiment, the suitable electron-aceepting group A is selected from a cyano group, and s is 1.

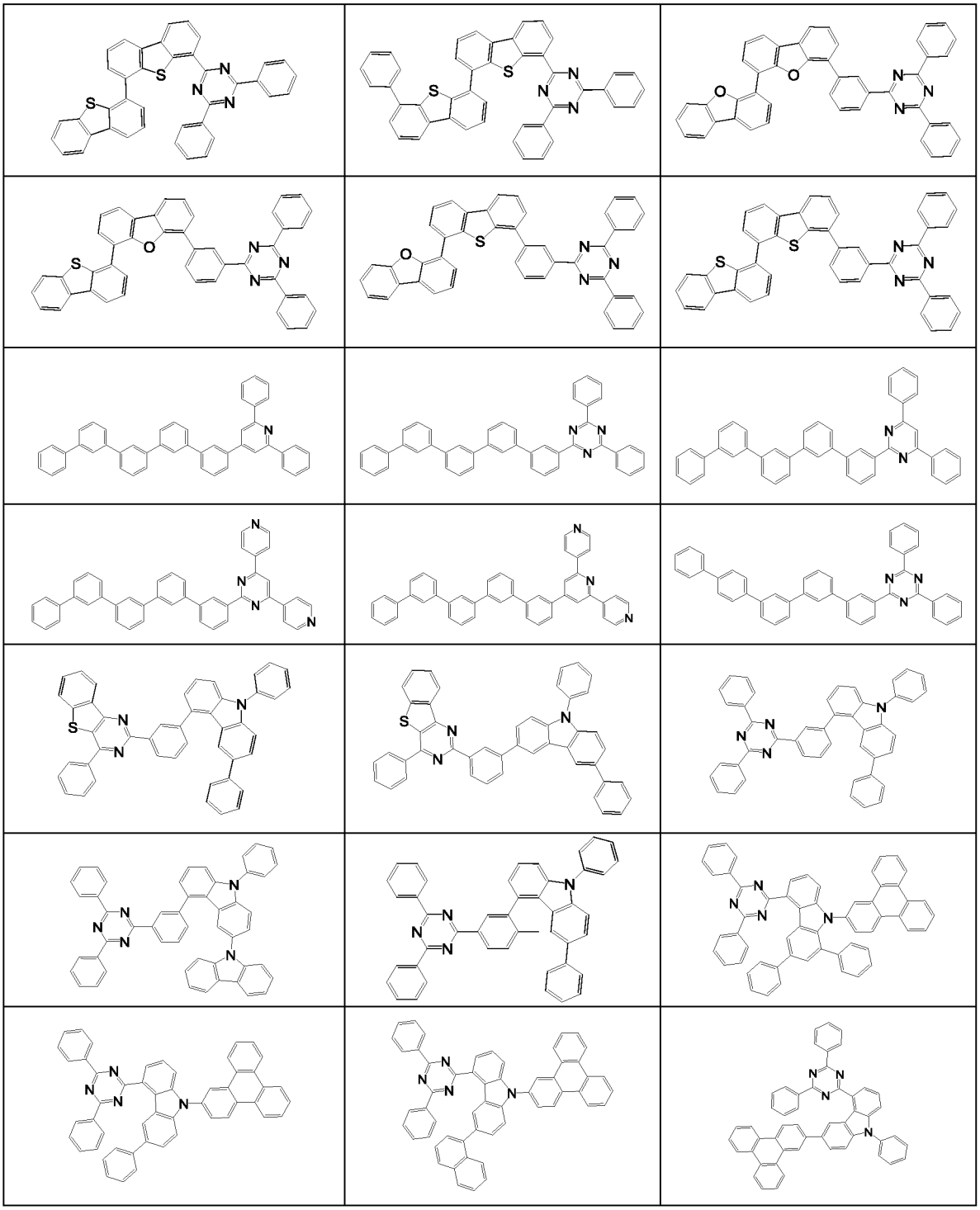
[0055] In a preferred embodiment, according to the polymer of the present disclosure, Ar in the general formula I and the general formula II is selected from groups as follows:

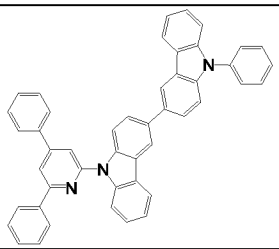
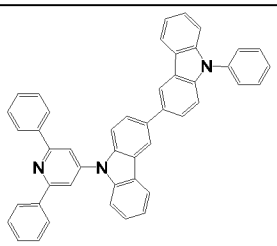
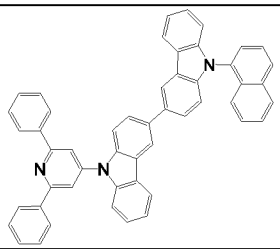
[0056] n2 is 1, 2, 3, or 4. Ar in the general formula I and the general formula II may be the same or different.

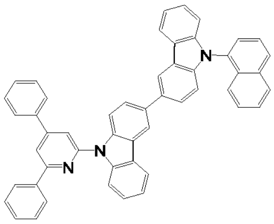
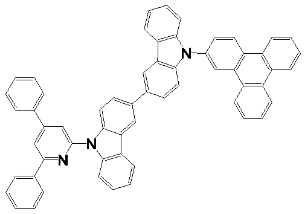
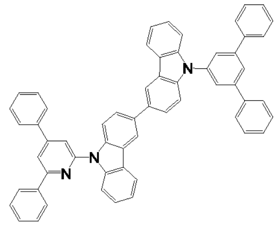
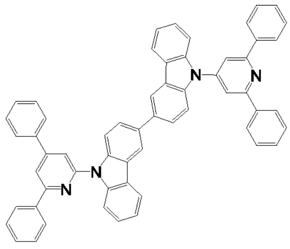
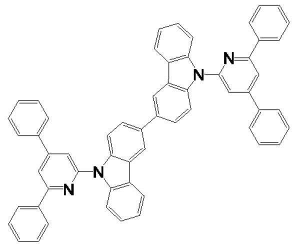
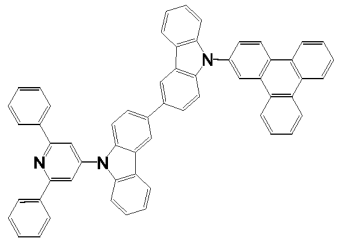
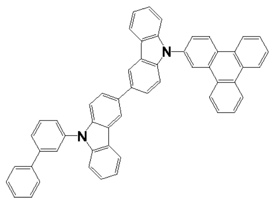
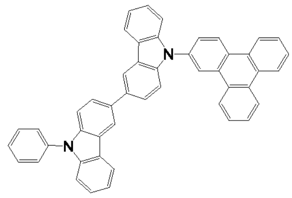
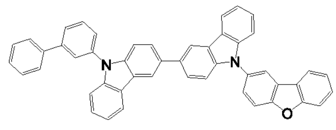
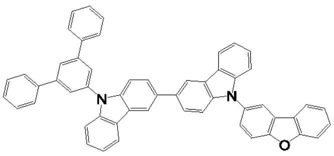
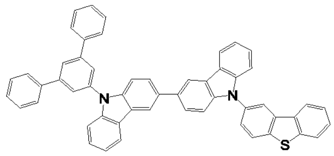
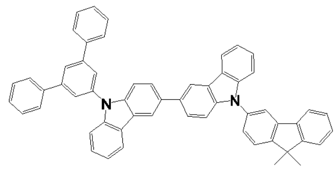
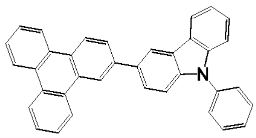
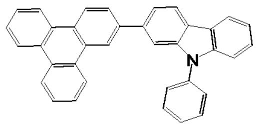
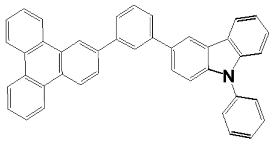
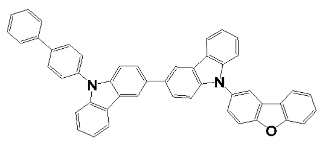
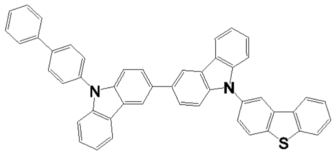
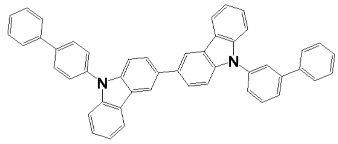
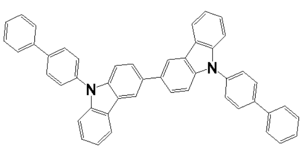
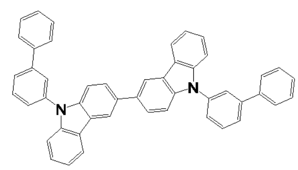
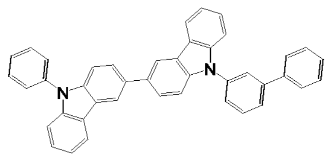
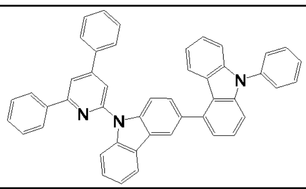
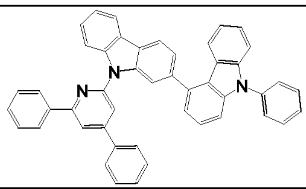
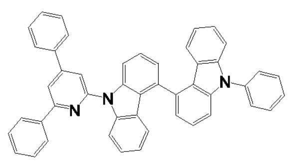
[0057] Examples of structural units that can be used for the E1 group in the polymer according to the present disclosure are:

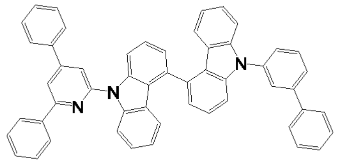
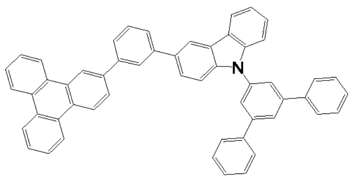
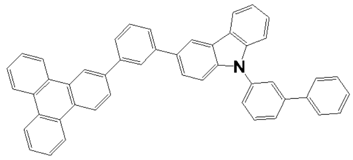
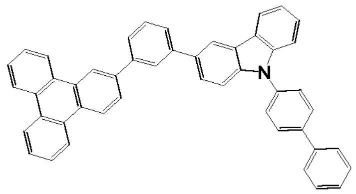
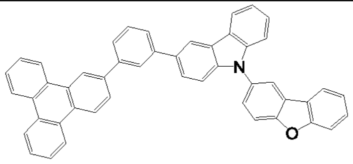
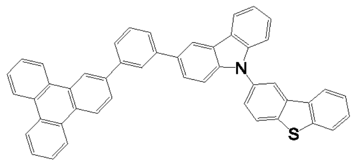
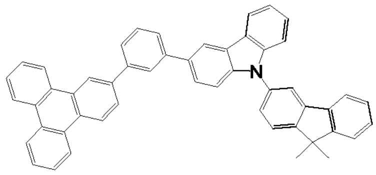
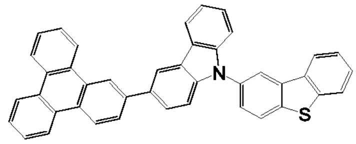
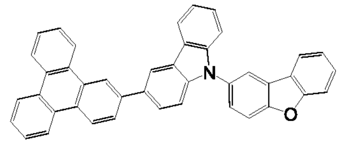
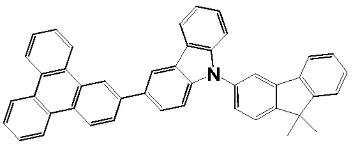
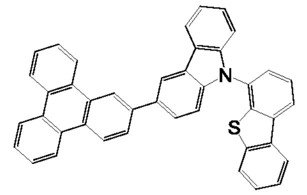
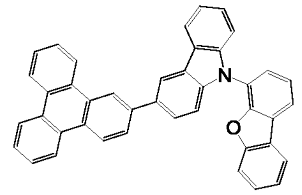
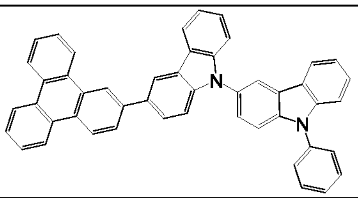
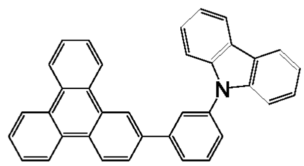
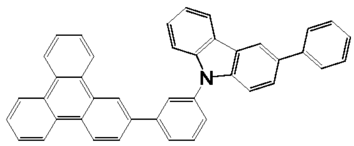
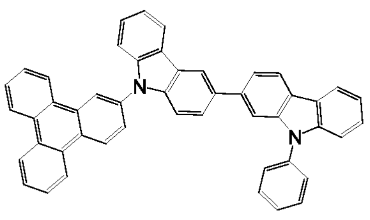
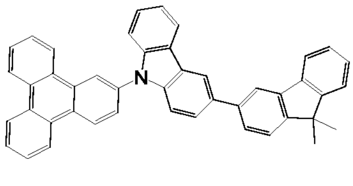
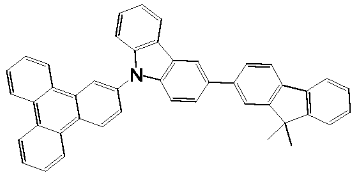
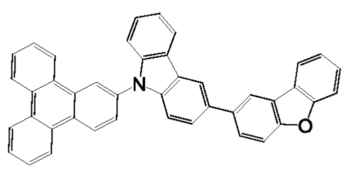
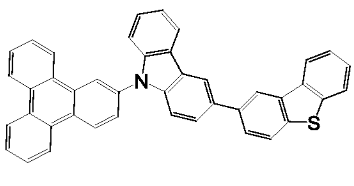
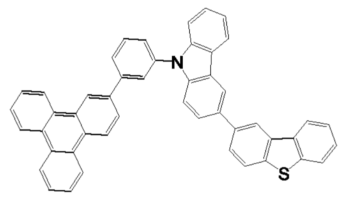
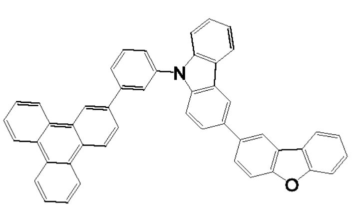
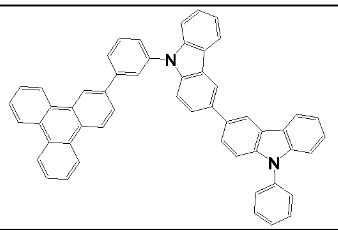
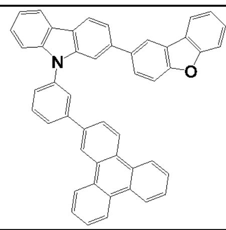
		
		
		
		
		
		
		
		



[0058] In a preferred embodiment, examples of structural units that can be used for the E2 group in the polymer according to the present disclosure are:

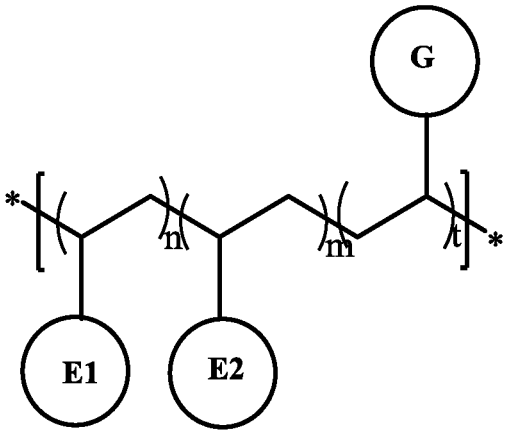
		
		
		
		
		
		
		
		

[0059] In the present disclosure, the plurality of E1 groups in the plurality of repeating units E1 may be the same or different, and the plurality of E2 groups in the plurality of repeating units E2 may be the same or different.

[0060] The polymer according to the present disclosure further contains another organic functional group.

[0061] In some embodiments, the polymer according to the present disclosure has a structure represented by the following general formula (3):



(3)

[0062] Wherein, G is another organic functional group, and n and m have the same meanings in the general formula (3) as in the general formula (1) and the general formula (2), and t is an integer greater than or equal to 0.

[0063] The other organic functional group G may be the same or different in multiple occurrences and independently selected from the group consisiting of a hole (also called an electron hole) injection or transport group, a hole blocking group, an electron injection or transport group, an electron blocking group, an organic host group, a singlet emitter group (fluorescent emitter group), a triplet emitter group (phosphorescent emitter group), and a thermally activated delayed fluorescent (TADF) emitter group in multiple occurrences. The small molecular organic functional materials corresponding to these organic functional groups are a hole (also called an electron hole) injection or transport material (HIM/HTM), a hole blocking material (HBM), an electron injection or transport material (EIM/ETM), an electron blocking material (EBM), an organic host material (Host), a singlet emitter (fluorescent emitter), a triplet emitter (phosphorescent emitter), and a TADF emitter. These organic functional materials are described in detail in, for example, WO2010135519A1, US20090134784A1, and WO2011110277A1. The three patent documents are specially incorporated herein by reference in their entirety.

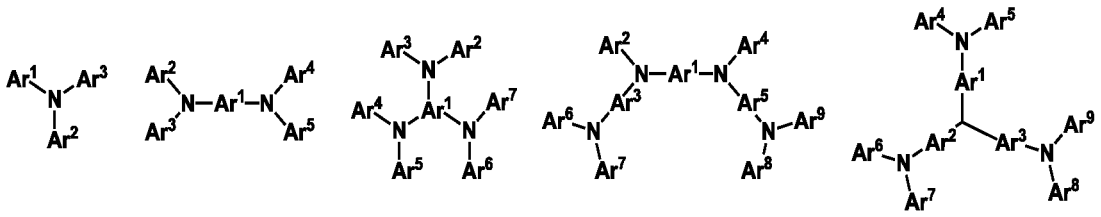
[0064] The following is a more detailed description of these functional materials (but not limited thereto).

1. HIM/HTM/EBM

[0065] Suitable organic HIM/HTM materials may be selected from the compounds containing the following structural units: phthalocyanines, porphyrins, amines, aryl amines, biphenyl triaryl amines, thiophenes, fused thiophenes such as dithiophenethiophene and thiophthene, pyrrole, aniline, carbazole, indeno-fluorene, and derivatives thereof. In addition, suitable HIMs also include: fluorocarbon-containing polymers; polymers containing conductive dopants; conductive polymers such as PEDOT/PSS; self-assembled monomers such as compounds containing phosphonic acid and silane derivatives; metal oxides such as MoOx; metal complexes and crosslinking compounds, and the like.

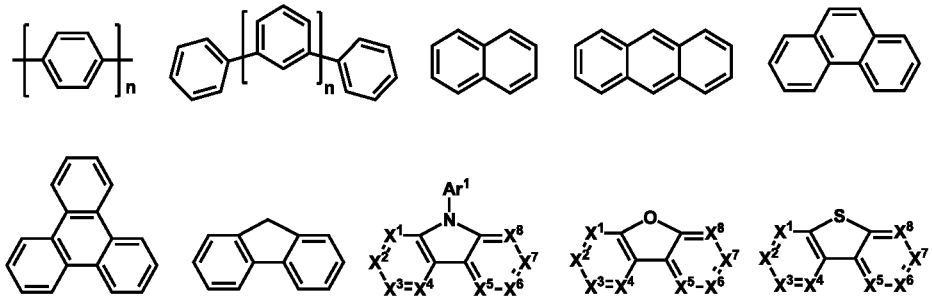
[0066] The electron blocking layer (EBL) is used to block electrons from adjacent functional layers, particularly the light-emitting layers. In contrast to a light-emitting device without a blocking layer, the presence of EBL typically results in an increase in luminous efficiency. The electron blocking material (EBM) of the electron blocking layer (EBL) requires a higher LUMO than an adjacent functional layer such as the light-emitting layer. In a preferred embodiment, the HBM has a greater energy level of excited state than the adjacent light-emitting layer, such as a singlet or triplet, depending on the emitter, while the EBM has a hole transport function. Typically, HIM/HTM materials with high LUMO energy levels can be used as EBMs.

[0067] Examples of cyclic aromatic amine-derived compounds that can be used as HIM, HTM, or EBM include, but are not limited to, the general structures as follows:



[0068] Each of Ar^1 to Ar^9 may be independently selected from the group consisting of cyclic aromatic hydrocarbon compounds, such as benzene, biphenyl, triphenyl, benzo, naphthalene, anthracene, phenalene, phenanthrene, fluorene, pyrene, chrysene, perylene, azulene; and aromatic heterocyclic compounds such as dibenzothiophene, dibenzofuran, furan, thiophene, benzofuran, benzothiophene, carbazole, pyrazole, imidazole, triazole, isoxazole, thiazole, oxadiazole, oxatriazole, dioxazole, thiadiazole, pyridine, pyridazine, pyrimidine, pyrazine, triazine, oxazine, oxathiazin, oxadiazine, indole, benzimidazole, indoxazine, bisbenzoxazole, isoxazole, benzothiazole, quinoline, isoquinoline, cinnoline, quinazoline, quinoxaline, naphthalene, phthalein, pteridine, xanthene, acridine, phenazine, phenothiazine, phenoxazine, dibenzoselenophene, benzoselenophene, benzofuropyridine, indolocarbazole, pyridylindole, pyrrolodipyridine, furodipyridine, benzothienopyridine, thienodipyridine, benzoselenophenopyridine and selenophenodipyridine; and groups containing 2 to 10 ring structures, which may be the same or different types of cyclic aryl or aromatic heterocyclic groups, and are linked to each other directly or through at least one of the following groups, such as an oxygen atom, a nitrogen atom, a sulfur atom, a silicon atom, a phosphorus atom, a boron atom, a chain structural unit, and an aliphatic ring group. Each Ar may be further substituted, and the substituents may be selected from the group consisting of hydrogen, alkyl, alkoxy, amino, alkene, alkyne, aralkyl, heteroalkyl, aryl, and heteroaryl.

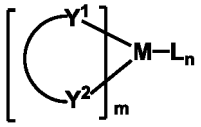
[0069] In one aspect, Ar^1 to Ar^9 may be independently selected from the group consisting of:



[0070] n is an integer from 1 to 20; X^1 to X^8 are CH or N; Ar^1 is defined as above.

[0071] Additional examples of cyclic aromatic amine-derived compounds can be found in US3567450, US4720432, US5061569, US3615404, and US5061569.

[0072] Examples of metal complexes that may be used as HTM or HIM include, but are not limited to, the general structure as follows:



M is a metal having an atomic weight greater than 40;

$(Y^1\text{-}Y^2)$ is a bidentate ligand, Y^1 and Y^2 are independently selected from the group consisting of C, N, O, P, and S; L is an auxiliary ligand; m is an integer with the value from 1 to the maximum coordination number of the metal; m+n is the maximum coordination number of the metal.

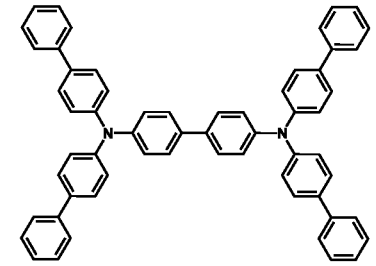
[0073] In one embodiment, $(Y^1\text{-}Y^2)$ is a 2-phenylpyridine derivative.

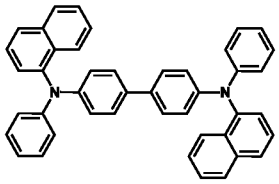
[0074] In another embodiment, $(Y^1\text{-}Y^2)$ is a carbene ligand.

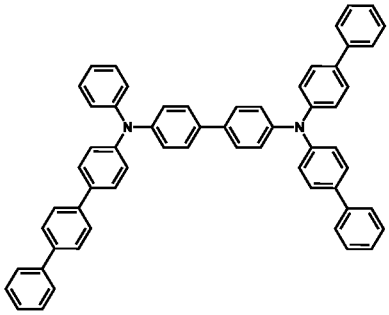
[0075] In another embodimen, M is selected from the group consisting of Ir, Pt, Os, and Zn.

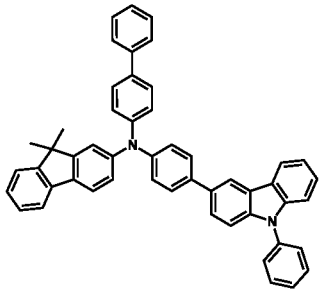
[0076] In another aspect, the HOMO of the metal complex is greater than -5.5 eV (relative to the vacuum level).

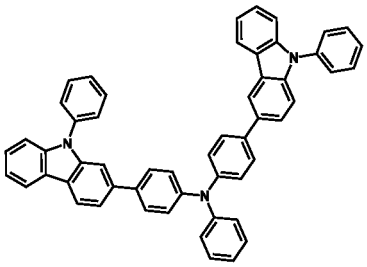
[0077] Examples of suitable HIM/HTM compounds are listed in the following table:

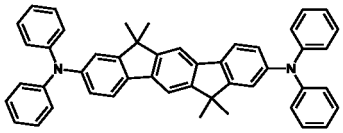


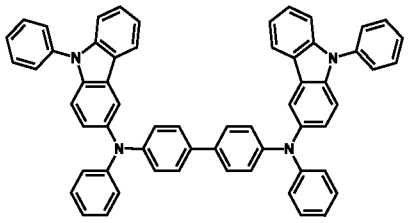


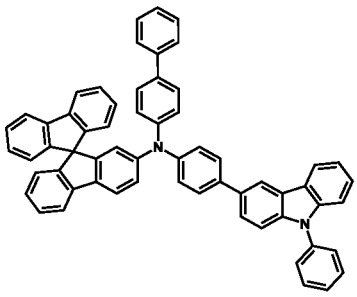


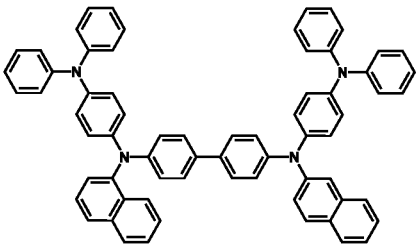


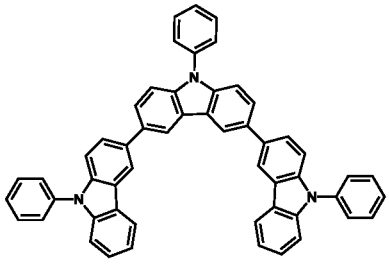


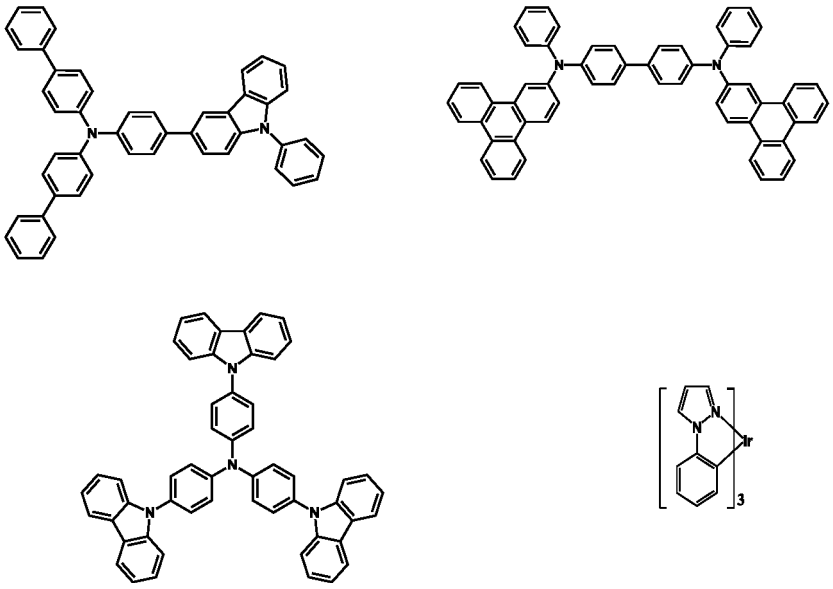










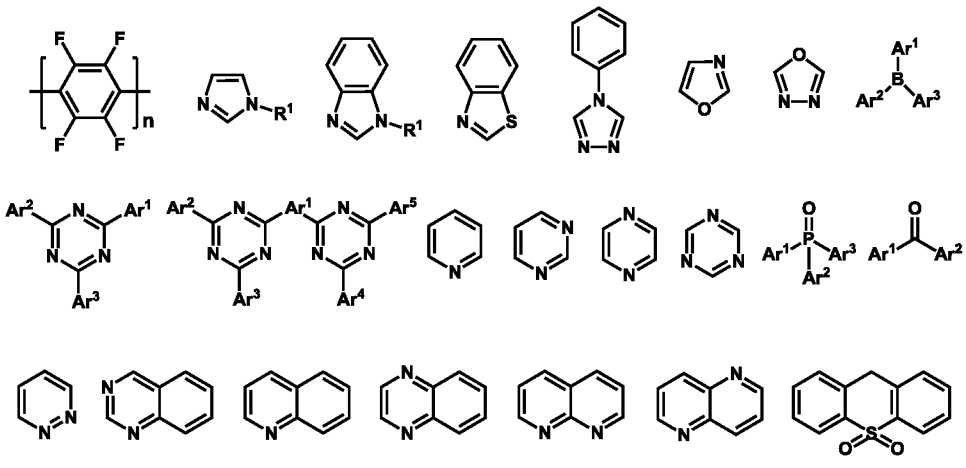


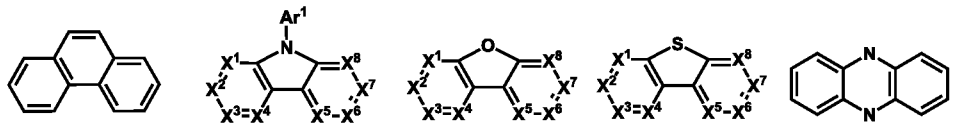
2. EIM/ETM/HBM

[0078] Examples of EIM/ETM material are not particularly limited, and any metal complex or organic compound may be used as EIM/ETM as long as they can transport electrons. Preferred organic EIM/ETM materials may be selected from the group consisting of tris (8-hydroxyquinoline)aluminum (A1Q3), phenazine, phenanthroline, anthracene, phenanthrene, fluorene, bifluorene, spirobifluorene, p-phenylacetylene, pyridazine, pyrazine, triazine, triazole, imidazole, quinolone, isoquinoline, quinoxaline, oxazole, isoxazole, oxadiazole, thiadiazole, pyridine, pyrazole, pyrrole, pyrimidine, acridine, pyrene, perylene, trans-indenofluorene, cis-indenonfluorene, dibenzol-indenofluorene, indenonaphthalene, benzanthracene, azaphosphole, azaborole, aromatic ketone, lactam, and derivatives thereof.

[0079] The hole blocking layer (HBL) is typically used to block holes from adjacent functional layers, particularly the light-emitting layers. In contrast to a light-emitting device without a blocking laye, the presence of HBL typically results in an increase in luminous efficiency. The hole blocking material (HBM) of the hole blocking layer (HBL) requires a lower HUMO than an adjacent functional layer, such as the light-emitting layer. In a preferred embodiment, the HBM has a larger energy level of excited state than the adjacent light-emitting layer, such as a singlet or triplet, depending on the emitter. In another preferred embodiment, the HBM has an electron transport function. Typically, EIM/ETM materials with deep HUMO energy levels can be used as HBMs.

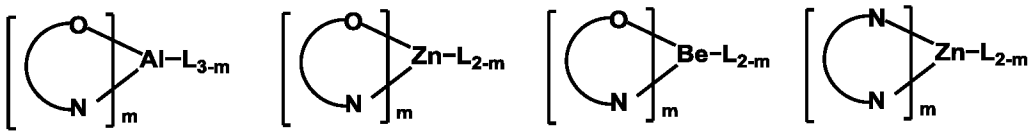
[0080] In another aspect, compounds that may be used as EIM/ETM/HBM may be molecules containing at least one of the following groups:





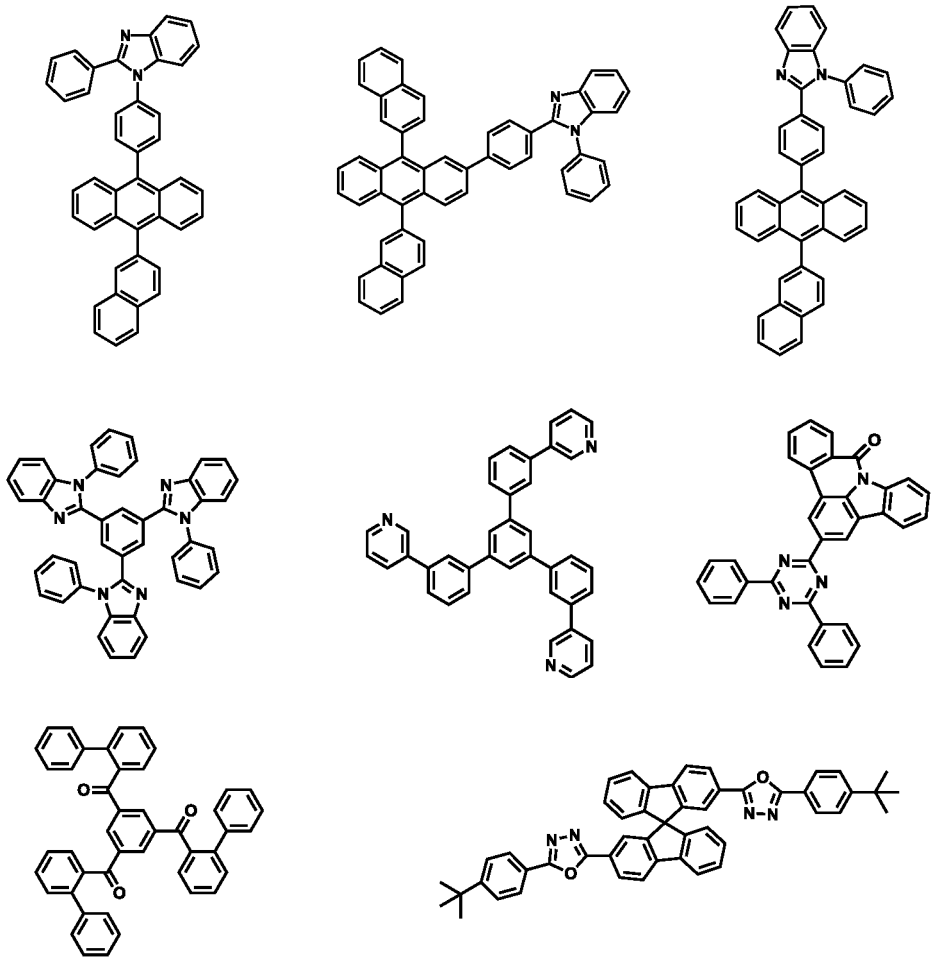
[0081] R^1 may be selected from the group consisting of hydrogen, alkyl, alkoxy, amino, alkenyl, alkynyl, aralkyl, heteroalkyl, aryl, and heteroaryl, which have the same meaning as Ar^1 and Ar^2 in HTM as described above when they are aryl or heteroaryl. Ar^1 to Ar^5 have the same meaning as Ar^1 in HTM as described above. n is an integer from 0 to 20. X^1 to X^8 are selected from CR^1 or N.

[0082] On the other hand, examples of metal complexes that may be used as EIM/ETM include, but are not limited to, the following general structures:



[0083] (O-N) or (N-N) is bidentate ligand, and the metal coordinates with O, N, or N, N. L is an auxiliary ligand. m is an integer whose value ranges from 1 to the maximum coordination number of the metal.

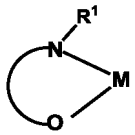
[0084] Examples of suitable ETM compounds are listed in the following table:



[0085] In another preferred embodiment, an organic alkali metal compound can be used as the EIM. In the present disclosure, the organic alkali metal compound may be understood as a compound having at least one alkali metal, i.e., lithium, sodium, potassium, rubidium, and cesium, and further including at least one organic ligand.

[0086] Suitable organic alkali metal compounds include the compounds described in US7767317B2, EP1941562B1, and EP1144543B1.

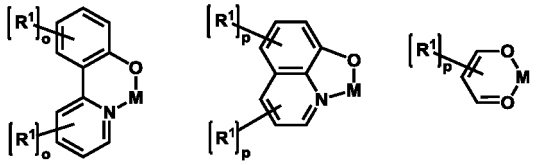
[0087] Preferred organic alkali metal compounds are compounds of the following formula:



[0088] R^1 has the same meaning as described above, and the arc represents bond linking two or three atoms and the bond to form a 5- or 6-membered ring with metal M when necessary, while the atoms may also be substituted with one or more R^1. M is an alkali metal selected from the group consisting of lithium, sodium, potassium, rubidium, and cesium.

[0089] The organic alkali metal compound may be in the form of a monomer, as described above, or in the form of an aggregate, for example, two alkali metal ions with two ligands, 4 alkali metal ions with 4 ligands, 6 alkali metal ions with 6 ligands or in other forms.

[0090] Preferred organic alkali metal compounds are compounds of the following formula:



the symbols used are as defined above, and in addition:

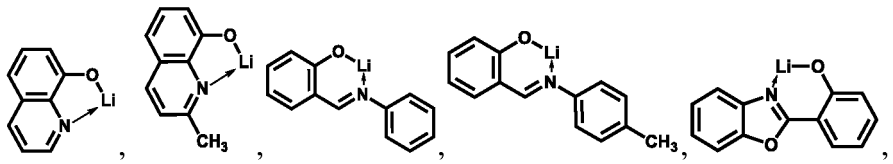
o may be the same or different at each occurrence, and selected from 0, 1, 2, 3, or 4; and
p may be the same or different at each occurrence, and selected from 0, 1, 2, or 3.

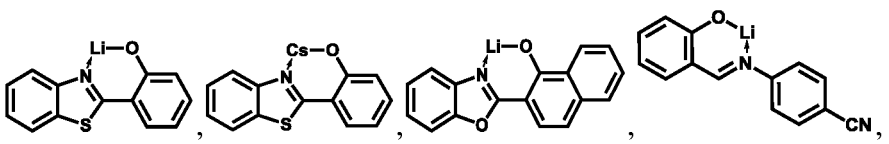
[0091] In a preferred embodiment, the alkali metal M is selected from the group consisting of lithium, sodium, and potassium, more preferably lithium or sodium, and most preferably lithium.

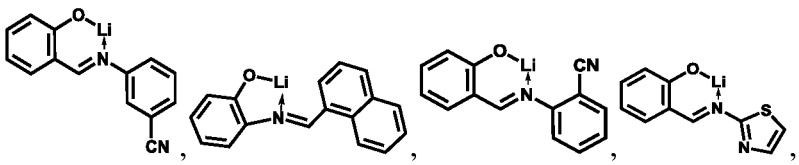
[0092] In a preferred embodiment, the organic alkali metal compound is used in the electron injection layer. More preferably, the electron injection layer consists of the organic alkali metal compound.

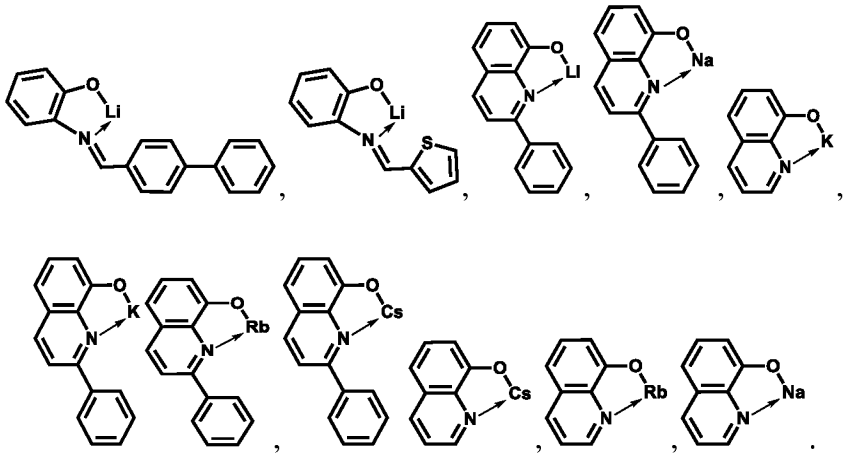
[0093] In another preferred embodiment, the organic alkali metal compound is doped into other ETMs to form an electron transport layer or is doped into an electron injection layer. More preferably, it is doped into the electron transport layer.

[0094] Examples of suitable organic alkali metal compounds are listed in the following table:



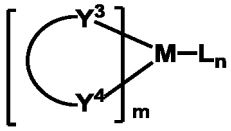






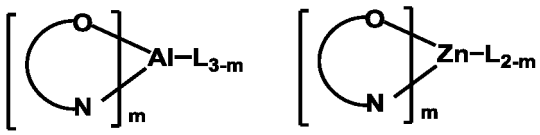
3. Triplet matrix material (Triplet Host):

[0095] Examples of the triplet host materials are not particularly limited, and any metal complex or organic compound may be used as the host material as long as its triplet energy is greater than that of the emitter, particularly a triplet emitter or a phosphorescent emitter. Examples of metal complexes that can be used as the triplet hosts include, but are not limited to, the general structure as follows:



[0096] M is a metal; (Y^3-Y^4) is a bidentate ligand, Y^3 and Y^4 are independently selected from the group consisting of C, N, O, P, and S. L is an auxiliary ligand; m is an integer whose value ranges from 1 to the maximum coordination number of the metal. m+n is the maximum coordination number of the metal.

[0097] In a preferred embodiment, the metal complex which can be used as the triplet host has the following form:

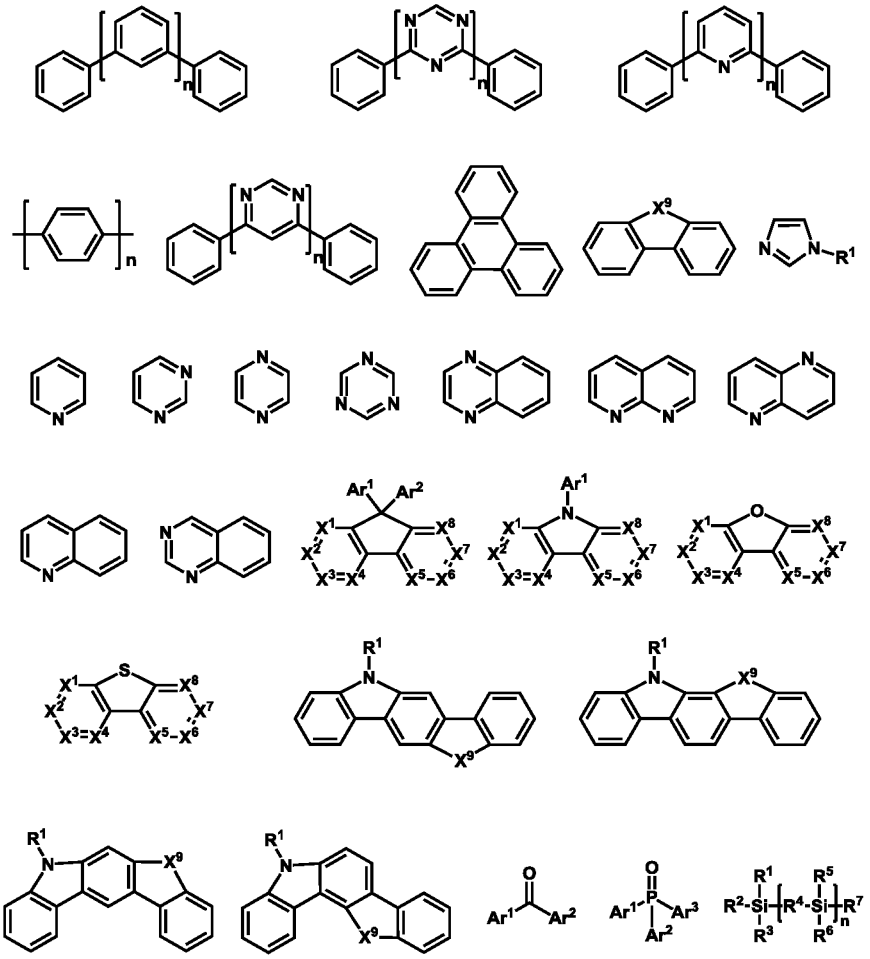


[0098] (O-N) is a bidentate ligand in which the metal coordinates with O and N atoms.

[0099] In one embodiment, M may be selected form Ir and Pt.

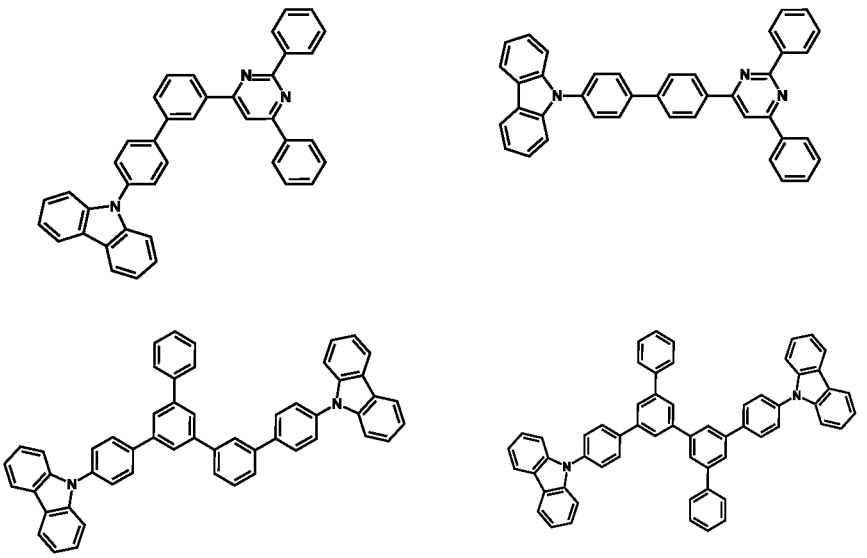
[0100] Examples of organic compounds which can be used as the triplet hosts are selected from the group consisting of: compounds containing cyclic aryl groups, such as benzene, biphenyl, triphenyl, benzo, and fluorene; and compounds containing aromatic heterocyclic groups, such as dibenzothiophene, dibenzofuran, dibenzoselenophen, furan, thiophene, benzofuran, benzothiophene, benzoselenophene, carbazole, indolocarbazole, indolopyridine, pyrrolodipyridine, pyrazole, imidazole, triazole, oxazole, thiazole, oxadiazole, oxatriazole, dioxazole, thiadiazole, pyridine, pyridazine, pyrimidine, pyrazine, triazine, oxazine, oxathiazin, oxadiazine, indole, benzimidazole, indazole, oxazole, bisbenzoxazole, benzoisoxazole, benzothiazole, quinoline, isoquinoline, cinnoline, quinazoline, quinoxaline, naphthalene, phthalein, pteridine, xanthene, acridine, phenazine, phenothiazine, phenoxazine, benzofuropyridine, furanpyridine, benzothienopyridine, thienopyridine, benzoselenophenopyridine, and selenophenodipyridine; and groups containing 2 to 10 ring structures, which may be the same or different types of cyclic aryl or aromatic heterocyclic groups, and are linked to each other directly or through at least one of the following groups, such as an oxygen atom, a nitrogen atom, a sulfur atom, a silicon atom, a phosphorus atom, a boron atom, a chain structure unit, and an aliphatic ring group. Each Ar may be further substituted and the substituents may be selected from the group consisting of hydrogen, alkyl, alkoxy, amino, alkenyl, alkynyl, aralkyl, heteroalkyl, aryl, and heteroaryl.

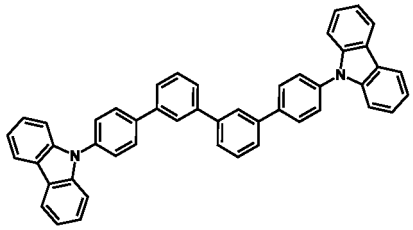
[0101] In a preferred embodiment, the triplet host materials can be selected from compounds containing at least one of the following groups:



[0102] R^1 to R^7 may be independently selected from the group consisting of hydrogen, alkyl, alkoxy, amino, alkenyl, alkynyl, aralkyl, heteroalkyl, aryl, and heteroaryl, which have the same meaning as Ar^1 and Ar^2 described above when they are aryl or heteroaryl. n is an integer from 0 to 20. X^1 to X^8 are selected from CH or N; and X^9 is selected from CR^1R^2 or NR^1.

[0103] Examples of suitable triplet host materials are listed in the following table:



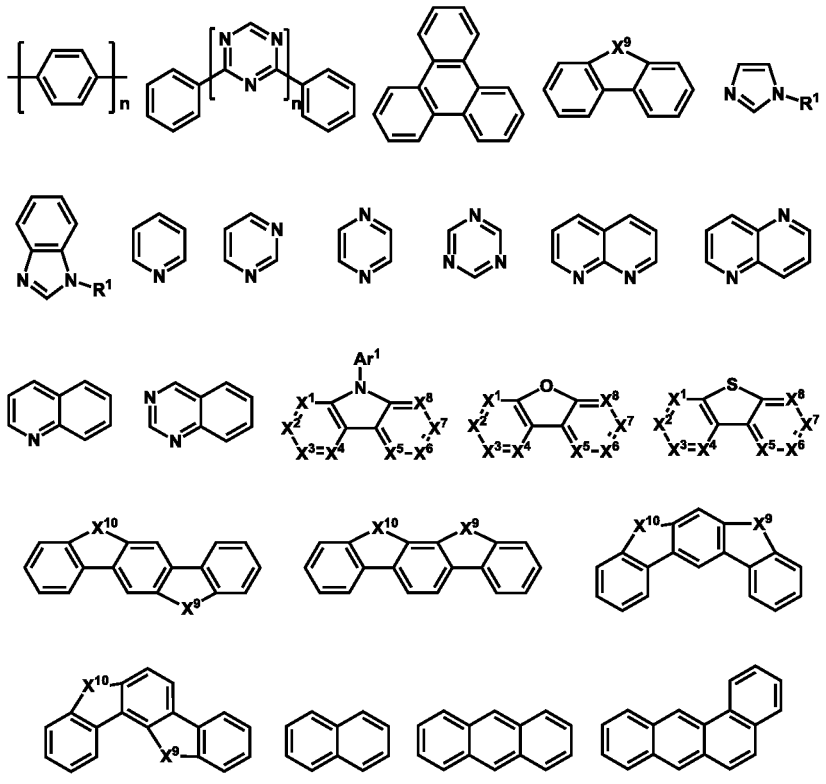


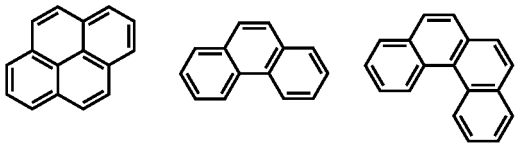
4. Singlet matrix material (Singlet Host):

[0104] Examples of the singlet host materials are not particularly limited, and any organic compound may be used as the host as long as its singlet energy is greater than that of the emitter, particularly a singlet emitter or a fluorescent emitter.

[0105] Examples of organic compounds used as the singlet host materials may be selected from the group consisting of: compounds containing cyclic aryl groups, such as benzene, biphenyl, triphenyl, benzo, naphthalene, anthracene, phenalene, phenanthrene, fluorene, pyrene, chrysene, perylene, azulene; and aromatic heterocyclic compounds such as dibenzothiophene, dibenzofuran, dibenzoselenophen, furan, thiophene, benzofuran, benzothiophene, benzoselenophene, carbazole, indolocarbazole, indolopyridine, pyrrolodipyridine, pyrazole, imidazole, triazole, isoxazole, thiazole, oxadiazole, oxatriazole, dioxazole, thiadiazole, pyridine, pyridazine, pyrimidine, pyrazine, triazine, oxazine, oxathiazin, oxadiazine, indole, benzimidazole, indazole, indolizine, benzoxazole, benzoisoxazole, benzothiazole, quinoline, isoquinoline, cinnoline, quinazoline, quinoxaline, naphthalene, phthalein, pteridine, xanthene, acridine, phenazine, phenothiazine, phenoxazine, benzofuropyridine, furodipyridine, benzothienopyridine, thienodipyridine, benzoselenophenopyridine, and selenophenodipyridine; and groups containing 2 to 10 ring structures, which may be the same or different types of cyclic aryl or aromatic heterocyclic groups, and are linked to each other directly or through at least one of the following groups, such as an oxygen atom, a nitrogen atom, a sulfur atom, a silicon atom, a phosphorus atom, a boron atom, a chain structure unit, and an aliphatic ring group.

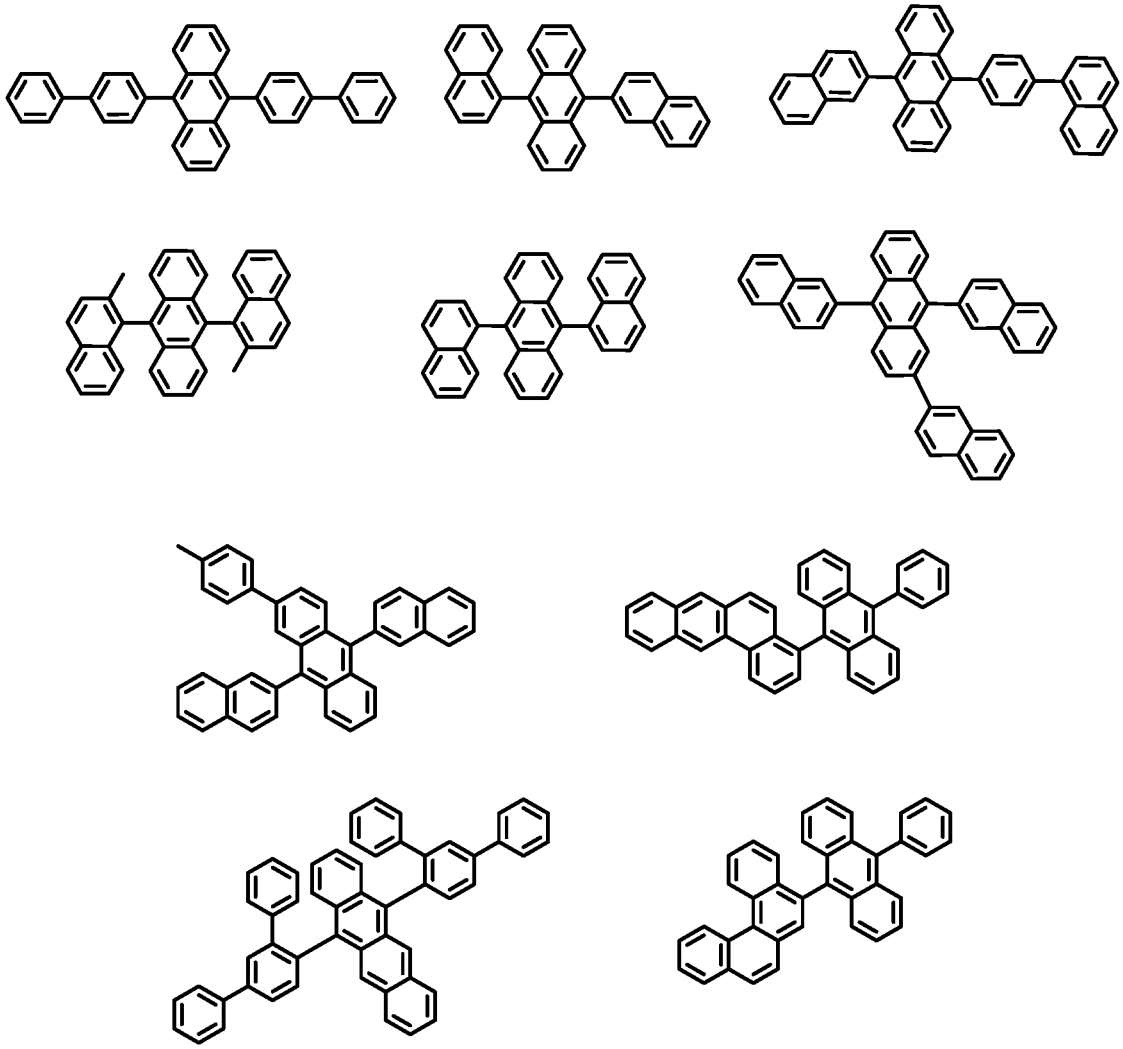
[0106] In a preferred embodiment, the singlet host material may be selected from compounds containing at least one of the following groups:





[0107] R^1 may be independently selected from the group consisting of hydrogen, alkyl, alkoxy, amino, alkenyl, alkynyl, aralkyl, heteroalkyl, aryl, and heteroaryl. Ar^1 is aryl or heteroaryl and has the same meaning as Ar^1 defined in the HTM above. n is an integer from 0 to 20; X^1 to X^8 are selected from CH or N; and X^9 and X^{10} are selected from CR^1R^2 or NR^1.

[0108] Some examples of anthryl singlet host materials are listed in the following table:



5. Singlet emitter

[0109] The singlet emitters tend to have longer conjugated π-electron systems. To date, there have been many examples, such as styrylamine and its derivatives disclosed in JP2913116B and WO2001021729A1, and indenofluorene and its derivatives disclosed in WO2008/006449 and WO2007/140847.

[0110] In a preferred embodiment, the singlet emitter can be selected from the group consisting of monostyrylamines, distyrylamines, tristyrylamines, tetrastyrylamines, styrylphosphines, styryl ethers, and arylamines.

[0111] The monostyrylamine refers to a compound which includes one unsubstituted or substituted styryl group and at least one amine, most preferably an aromatic amine. The distyrylamine refers to a compound which includes two unsubstituted or substituted styryl groups and at least one amine, most preferably an aromatic amine. The tristyrylamine refers to a compound which includes three unsubstituted or substituted styryl groups and at least one amine, most preferably an aromatic amine. The tetrastyrylamine refers to a compound which includes four unsubstituted or substituted

styryl groups and at least one amine, most preferably an aromatic amine. Preferred styrene is stilbene, which may be further substituted. The corresponding phosphines and ethers are defined similarly to amines. Aryl amine or aromatic amine refers to a compound containing three unsubstituted or substituted aromatic ring or heterocyclic systems directly attached to nitrogen. At least one of these aromatic ring or heterocyclic systems is preferably selected from fused ring systems and most preferably has at least 14 aryl ring atoms. Preferred examples are aromatic anthramine, aromatic anthradiamine, aromatic pyreneamine, aromatic pyrenediamine, aromatic chryseneamine, and aromatic chrysenediamine. An aromatic anthramine refers to a compound in which one diarylamino group is directly attached to anthracene, most preferably at position 9. An aromatic anthradiamine refers to a compound in which two diarylamino groups are directly attached to anthracene, most preferably at positions 9, 10. Aromatic pyreneamine, aromatic pyrenediamine, aromatic chryseneamine, and aromatic chrysenediamine are similarly defined, and the diarylamino group is most preferably attached to position 1 or 1 and 6 of pyrene.

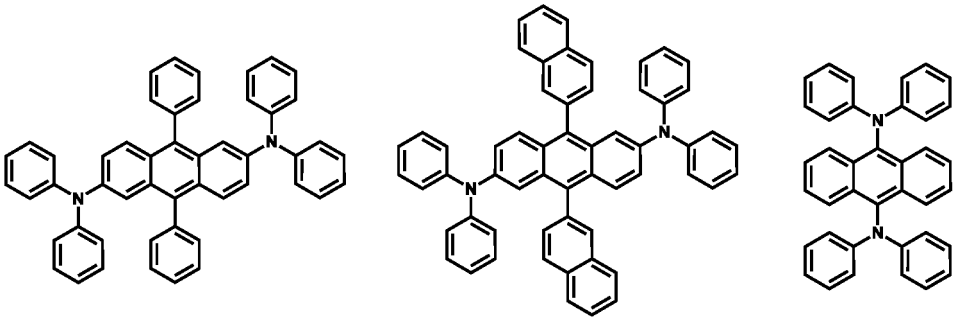
[0112] Examples of singlet emitters based on vinylamine and arylamine are also preferred examples which can be found in the following patent documents: WO2006/000388, WO2006/058737, WO2006/000389, WO2007/065549, WO2007/115610, US7250532B2, DE102005058557A1, CN1583691A, JP08053397A, US6251531B1, US2006/210830A, EP1957606A1, and US2008/0113101A1. The patent documents listed above are specially incorporated herein by reference in their entirety.

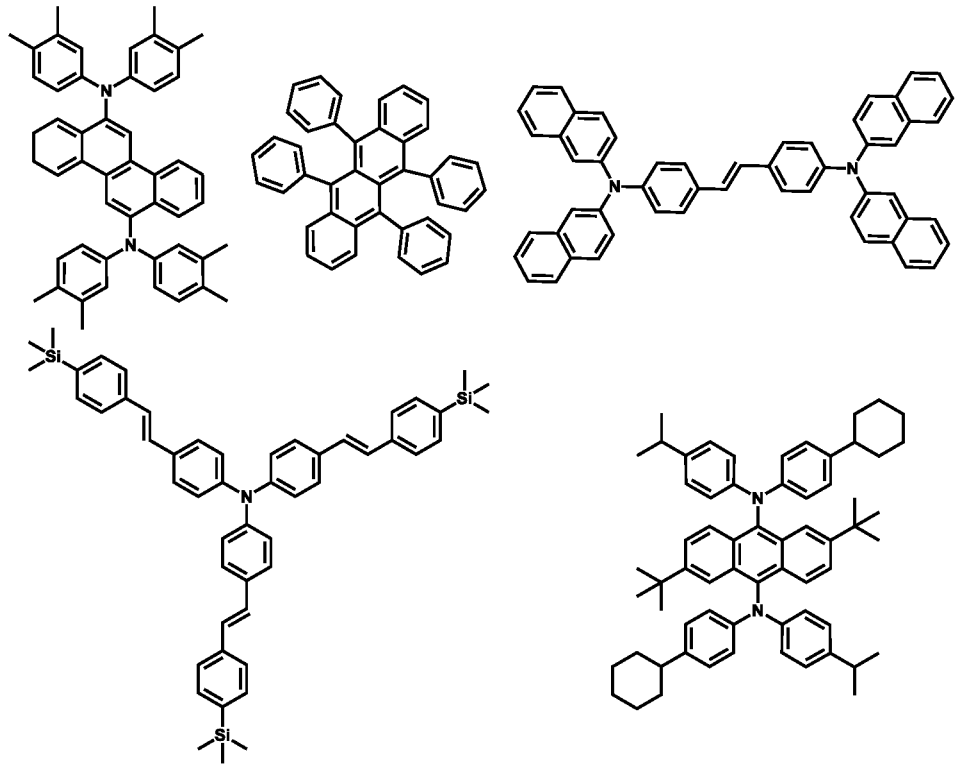
[0113] Examples of singlet emitters based on distyrylbenzene and its derivatives may be found in, for example, US5121029.

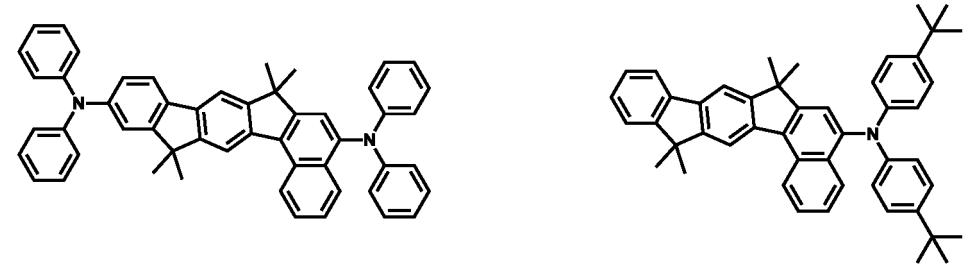
[0114] More preferred singlet emitters may be selected from indenofluorene-amine and indenofluorene-diamine disclosed in WO 2006/122630; benzoindenofluorene-amine and benzoindenofluorene-diamine disclosed in WO 2008/006449, and dibenzoindenofluorene-amine and dibenzoindenofluorene-diamine disclosed in WO 2007/140847.

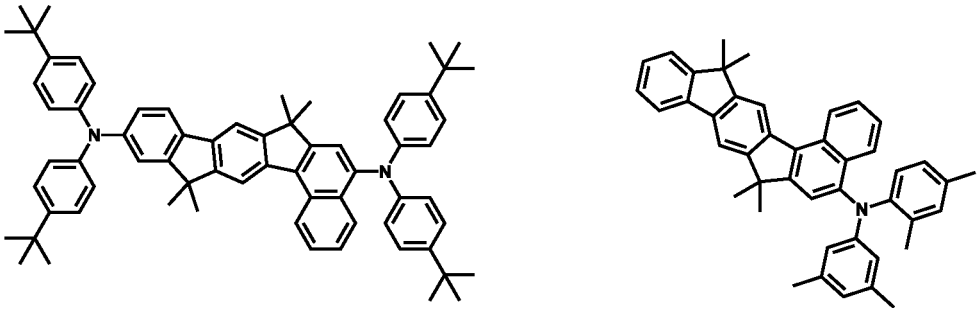
[0115] Other materials useful as singlet emitters include polycyclic aryl compounds, especially one selected from the derivatives of the following compounds: anthracenes such as 9, 10-dinaphthylanthracene, naphthalene, tetraphenyl, phenanthrene, perylene such as 2, 5, 8, 11-tetra-t-butylatedylene, indenoperylene, phenylenes such as 4, 4'-(bis(9-ethyl-3-carbazovinylene)-1, 1'-biphenyl, periflanthene, decacyclene, coronene, fluorene, spirobifluorene, arylpyren (e.g., US20060222886), arylenevinylene (e.g., US5121029, US5130603), cyclopentadiene such as tetraphenylcyclopentadiene, rubrene, coumarine, rhodamine, quinacridone, pyrane such as 4 (dicyanoethylene)-6-(4-dimethylaminostyryl-2-methyl)-4H-pyrane (DCM), thiapyran, bis (azinyl) imine-boron compounds (US2007/0092753A1), bis (azinyl) methene compounds, carbostyryl compounds, oxazone, benzoxazole, benzothiazole, benzimidazole, and diketopyrrolopyrrole. Some singlet emitter materials may be found in the following patent documents: US20070252517A1, US4769292, US6020078, US2007/0252517A1, and US2007/0252517A1. The patent documents listed above are specially incorporated herein by reference in their entirety.

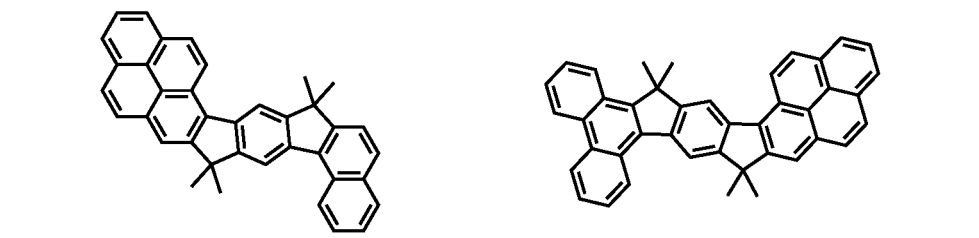
[0116] Examples of suitable singlet emitters are listed in the following table:











6. Thermally Activated Delayed Fluorescent Material (TADF):

[0117] Conventional organic fluorescent materials can only emit light by using 25% singlet excitons formed by electrical excitation, and the internal quantum efficiency of the device is low (up to 25%). The phosphorescent material enhances the intersystem crossing due to the strong spin-orbit coupling of the center of the heavy atom, the singlet excitons and triplet excitons formed by electrical excitation can be effectively utilized to emit light, so that the internal quantum efficiency of the device can reach 100%. However, the problems of expensive phosphorescent materials, poor material stability, and severe roll-off of device efficiency limit their application in OLEDs. The thermally activated delayed fluorescent material is a third-generation organic luminescent material developed after the organic fluorescent materials and the organic phosphorescent materials. Such materials generally have a small singlet-triplet excited state energy level difference (ΔEst), the triplet excitons can be converted into the singlet excitons by reverse intersystem crossing to emit light. This can make full use of the singlet excitons and triplet excitons formed under electrical excitation, and the internal quantum efficiency of the device can reach 100%. In addition, the material has a controllable structure, stable property, and cheap price, no precious metal is required, and the applications in the OLED field is promising.

[0118] The TADF material needs to have a small singlet-triplet excited state energy level difference (ΔEst), preferably ΔEst < 0.3 eV, more preferably ΔEst < 0.2 eV, and most preferably ΔEst < 0.1 eV. In a preferred embodiment, the TADF material has a relatively small ΔEst, and in another preferred embodiment, TADF has a better fluorescence quantum efficiency. Some TADF luminescent materials can be found in the following patent documents: CN 103483332(A), TW 201309696(A), TW 201309778(A), TW 201343874(A), TW 201350558(A), US 20120217869(A1), WO 2013133359(A1), WO 2013154064(A1), Adachi, et.al. Adv. Mater., 21, 2009, 4802, Adachi, et.al. Appl. Phys. Lett., 98, 2011, 083302, Adachi, et.al. Appl. Phys. Lett., 101, 2012, 093306, Adachi, et.al Chem. Commun., 48, 2012, 11392, Adachi, et.al. Nature Photonics, 6, 2012, 253, Adachi, et.al. Nature, 492, 2012, 234, Adachi, et.al. J. Am Chem. Soc, 134, 2012, 14706, Adachi, et.al. Angew. Chem. Int. Ed, 51, 2012,11311, Adachi, et.al. Chem. Commun., 48, 2012, 9580, Adachi, Et.al. Chem. Commun., 48, 2013, 10385, Adachi, et.al. Adv. Mater., 25, 2013, 3319, Adachi, et.al. Adv. Mater., 25, 2013, 3707, Adachi, et.al. Chem. Mater., 25, 2013, 3038, Adachi, et.al. Chem. Mater., 25, 2013, 3766, Adachi, et.al. J. Mater. Chem. C., 1, 2013, 4599, Adachi, et.al. J. Phys. Chem. A., 117, 2013, 5607. The entire contents of the above-listed patents and literature documents are hereby incorporated by reference.

7. Triplet Emitter

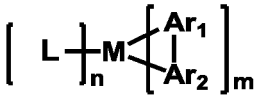
[0119] The triplet emitter is also called a phosphorescent emitter. In an preferred embodiment, the triplet emitter is a metal complex of the general formula M(L)n, in which M may be a metal atom; L may be the same or different ligand at each occurrence, and may be bonded or coordinated to the metal atom M at one or more positions; n may be an integer greater than 1, preferably 1, 2, 3, 4, 5, or 6. Alternatively, these metal complexes may be attached to a polymer by one or more positions, most preferably through an organic ligand.

[0120] In a preferred embodiment, the metal atom M may be selected from the group consisting of transition metal elements, lanthanide elements, and actinide elements, preferably Ir, Pt, Pd, Au, Rh, Ru, Os, Sm, Eu, Gd, Tb, Dy, Re, Cu, or Ag, and particularly preferably Os, Ir, Ru, Rh, Re, Pd, or Pt.

[0121] Preferably, the triplet emitter includes a chelating ligand, i.e., a ligand, and is coordinated to the metal by at least two bonding sites. Particularly preferably, the triplet emitter includes two or three identical or different bidentate or multidentate ligands. The chelating ligand is beneficial for improving the stability of metal complexes.

[0122] Examples of organic ligands may be selected from the group consisting of phenylpyridine derivative, 7, 8-benzoquinoline derivative, 2(2-thienyl) pyridine derivative, 2(1-naphthyl) pyridine derivative, and 2-phenylquinoline derivative. All of these organic ligands may be substituted, for example, by fluoromethyl or trifluoromethyl. The auxiliary ligand may be selected from acetylacetonate or picric acid.

[0123] In a preferred embodiment, the metal complex which may be used as the triplet emitter has the following form:



[0124] Where M is a metal selected from the group consisting of transition metal elements, lanthanide elements, and actinide elements.

[0125] Ar_1 may be the same or different cyclic group at each occurrence, which includes at least one donor atom, that is, an atom having a lone pair of electrons, such as nitrogen or phosphorus, through which the cyclic group is coordinated to a metal. Ar_2 may be the same or different cyclic group at each occurrence, which includes at least one C atom through which the cyclic group is bonded to the metal. Ar_1 and Ar_2 are covalently bonded together, and each of Ar_1 and Ar_2 can

have one or more substituents, which may also be linked together by the substituents. L may be the same or different at each occurrence and is an auxiliary ligand, preferably a bidentate chelate ligand, most preferably is a monoanionic bidentate chelate ligand. m is selected from 1, 2 or 3, preferably 2 or 3, and particularly preferably 3. n is selected from 0, 1, or 2, preferably 0 or 1, and particularly preferably 0.

[0126] Examples of triplet emitter materials and applications thereof may be found in the following patent documents and references: WO200070655, WO200141512, WO200202714, WO200215645, EP1191613, EP1191612, EP1191614, WO2005033244, WO2005019373, US2005 /0258742, WO2009146770, WO2010015307, WO2010031485, WO2010054731, WO2010054728, WO2010086089, WO2010099852, WO2010102709, US20070087219A1, US20090061681A1, US20010053462A1, Baldo, Thompson et al. Nature 403, (2000), 750-753, US 20090061681 A1, US 20090061681 A1, Adachi et al. Appl. Phys. Lett. 78 (2001), 1622-1624, J. Kido et al. Appl. Phys. Lett. 65 (1994), 2124, Kido et al. Chem. Lett. 657, 1990, US 2007/0252517 A1, Johnson et al., JACS 105, 1983, 1795, Wrighton, JACS 96, 1974, 998, Ma et al., Synth. Metals 94, 1998, 245, US 6824895, US 7029766, US 6835469, US 6830828, US 20010053462 A1, WO2007095118 A1, US2012004407A1, WO 2012007088A1, WO2012007087A1, WO2012007086A1, US2008027220A1, WO2011157339A1, CN102282150A, WO2009118087A1. The entire contents of the above-listed patent documents and literatures are hereby incorporated by reference.

[0127] In a preferred embodiment, the organic functional group G is selected from the triplet matrix groups.

[0128] In a preferred embodiment, the organic functional group G is selected from the TADF emitter groups.

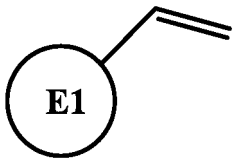
[0129] In another preferred embodiment, the organic functional group G is selected from the triplet emitter groups.

[0130] In another preferred embodiment, the organic functional group G is selected from the singlet emitter groups.

[0131] In another preferred embodiment, the organic functional group G includes organic functional groups G1 and G2, and the organic functional group G1 is selected from the triplet matrix groups and the organic functional group G2 is selected from the triplet emitter groups.

[0132] In another preferred embodiment, the organic functional group G includes organic functional groups G1 and G2, and the organic functional group G1 is selected from the hole transport groups and the organic functional group G2 is selected from the electron transport groups.

[0133] The present disclosure further provides a first monomer having the following general formula (5),

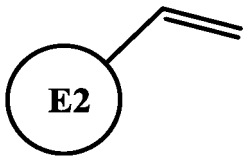


(5)

[0134] The E1 group has a (HOMO-(HOMO-1) greater than or equal to 0.3 eV.

[0135] In a preferred embodiment, (HOMO-(HOMO-1) of the E1 group is greater than or equal to 0.3 eV, preferably greater than or equal to 0.35 eV, more preferably greater than or equal to 0.4 eV, even more preferably greater than or equal to 0.45 eV, and most preferably greater than or equal to 0.5 eV.

[0136] The present disclosure further provides a mixed monomer including the first monomer and a second monomer. The second monomer has the following general formula (6):



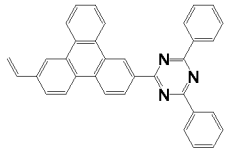
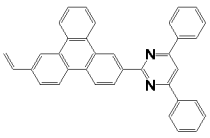
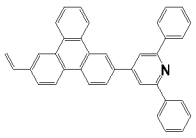
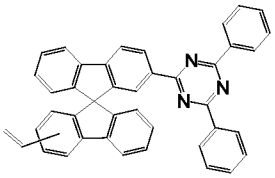
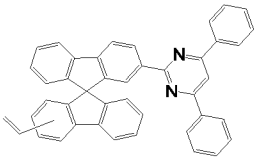
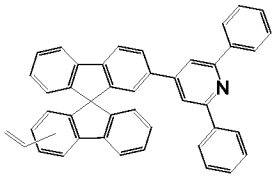
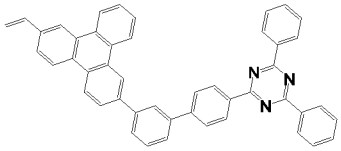
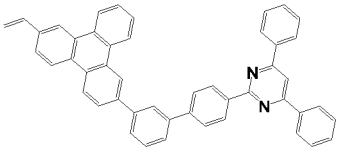
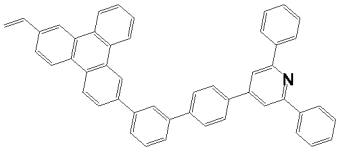
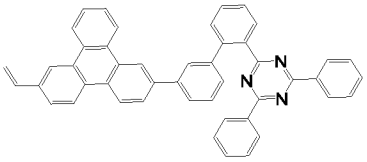
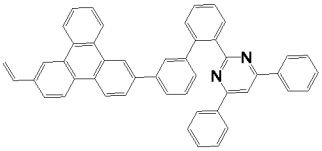
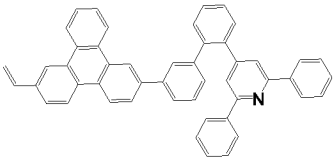
(6)

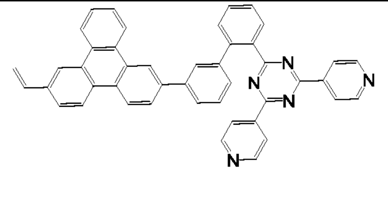
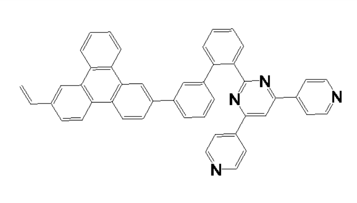
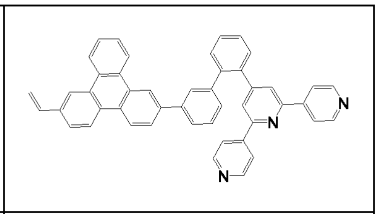
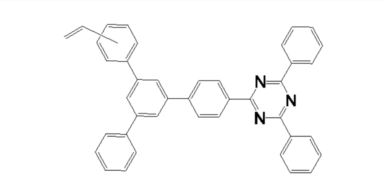
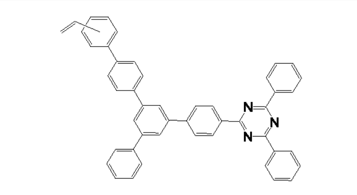
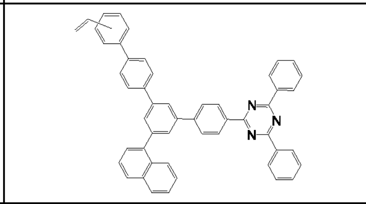
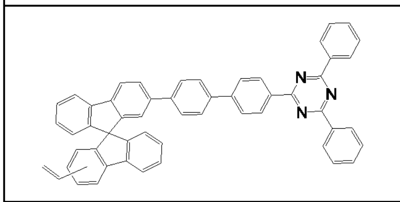
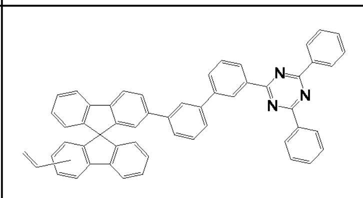
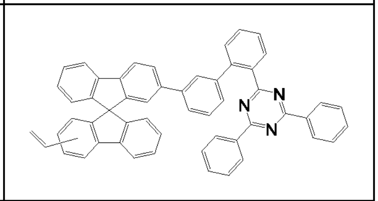
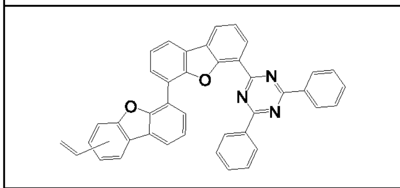
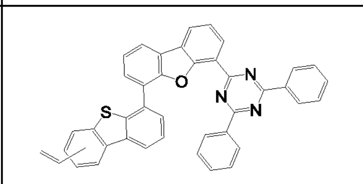
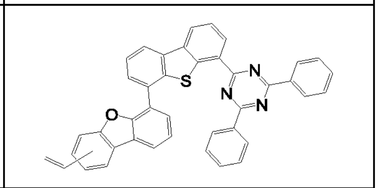
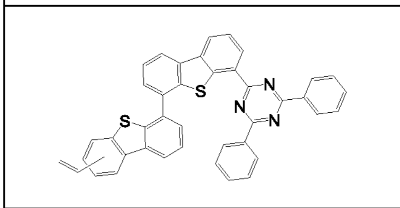
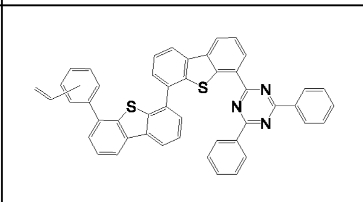
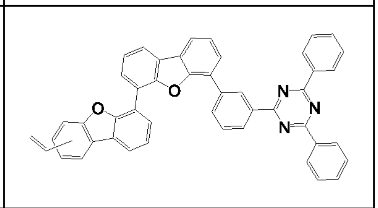
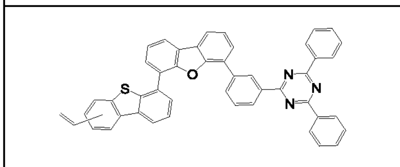
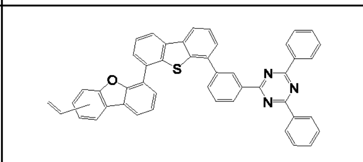
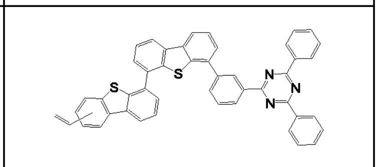
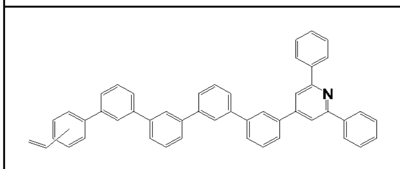
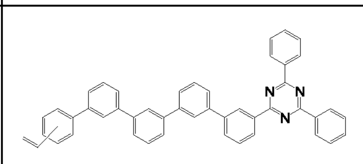
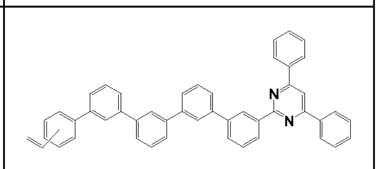
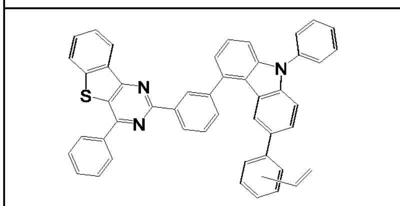
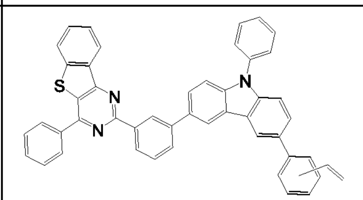
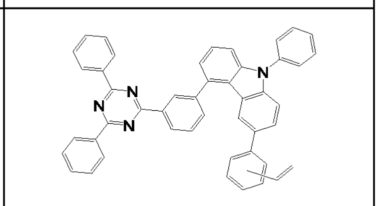
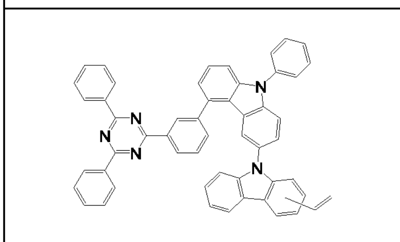
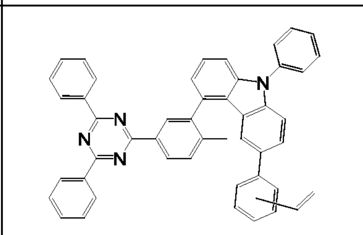
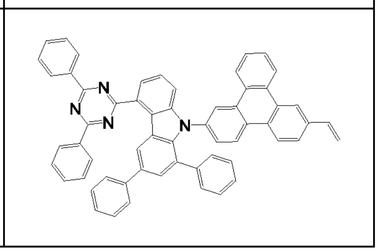
[0137] $\min((LUMO(E1)-HOMO(E2), LUMO(E2)-HOMO(E1)) \leq \min(E_T(E1), E_T(E2)) + 0.1eV$.

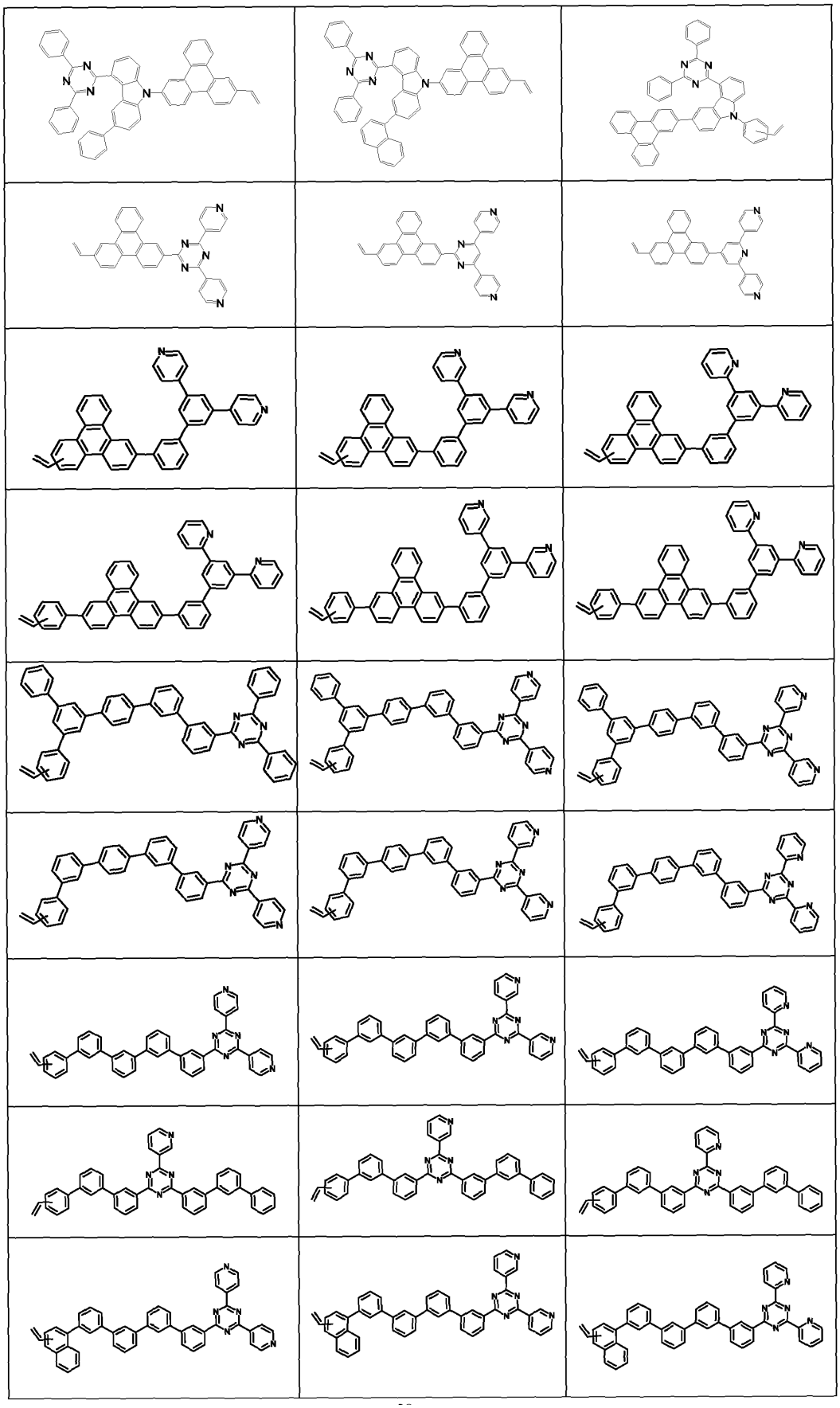
[0138] In a preferred embodiment, $\min((LUMO(E1)-HOMO(E2), LUMO(E2)-HOMO(E1))-\min(E_T(E1), E_T(E2)) \leq 0$ eV, preferably ≤ 0.05 eV, more preferably ≤ 0.10 eV, even more preferably ≤ 0.15 eV, and most preferably ≤ 0.20 eV.

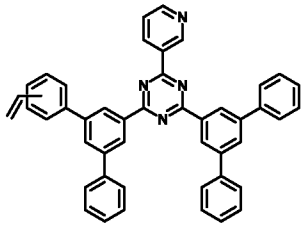
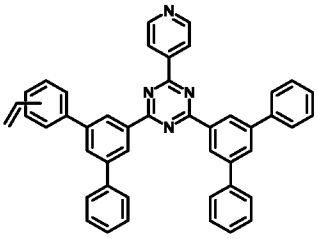
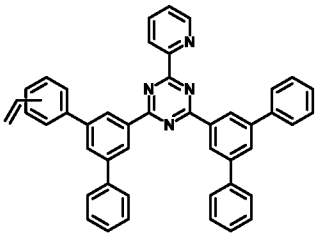
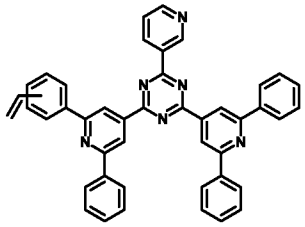
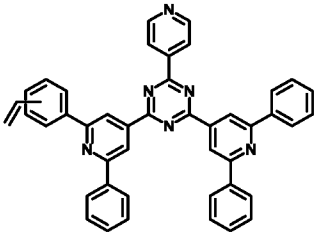
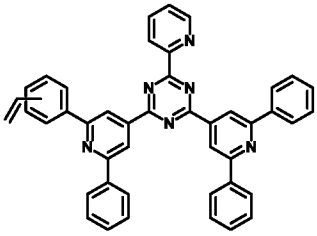
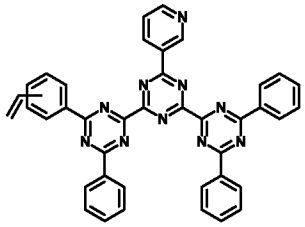
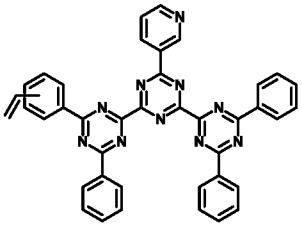
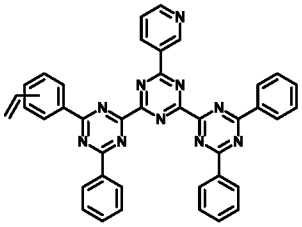
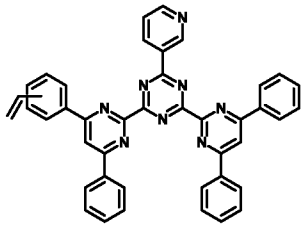
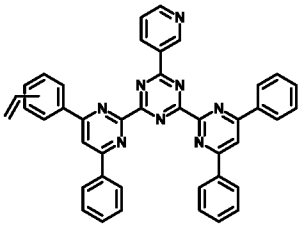
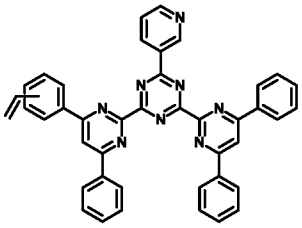
[0139] The E1 group in the first monomer and the E2 group in the second monomer are the same meaning as the E1 group and the E2 group in the polymer, respectively, and are not described herein again.

[0140] Examples of suitable first monomers are listed below:

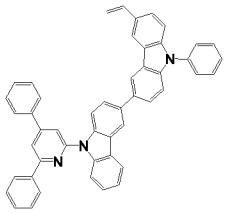
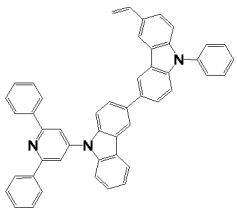
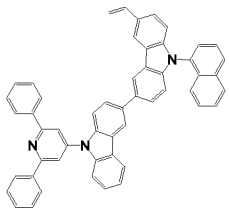
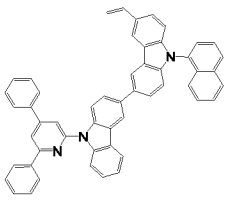
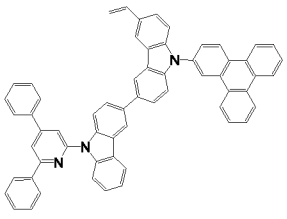
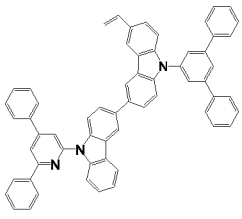
		
		
		
		

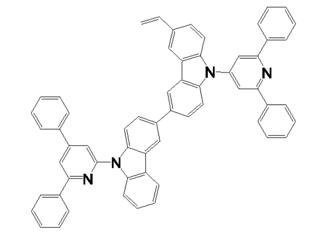
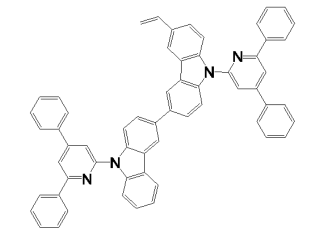
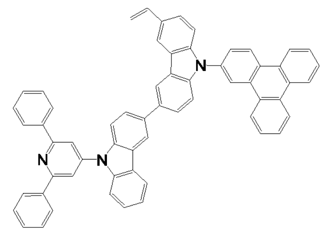
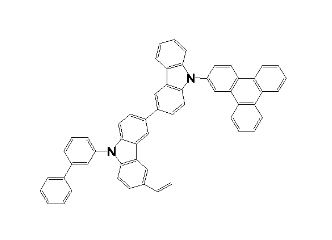
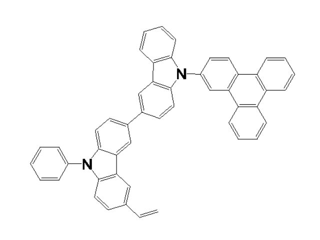
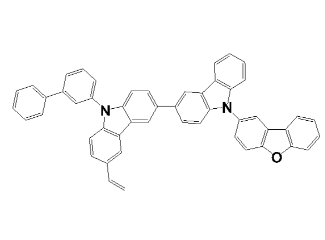
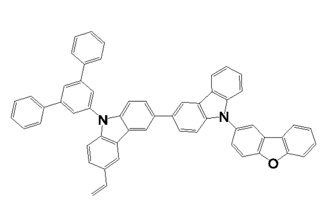
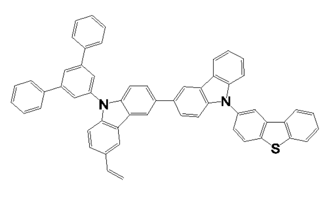
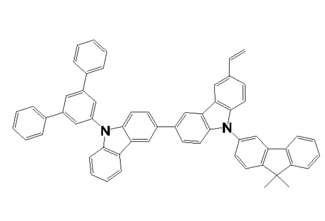
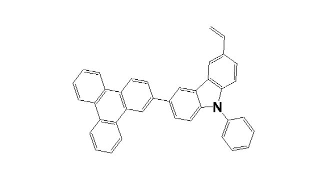
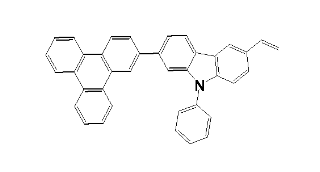
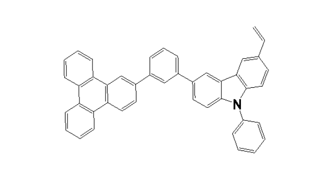
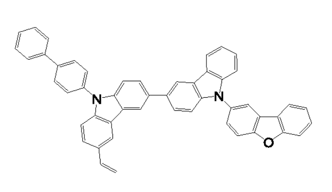
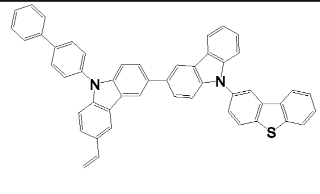
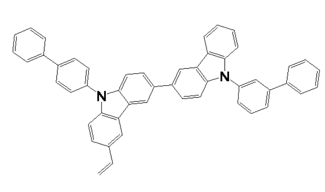
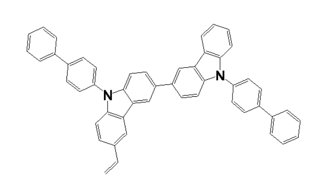
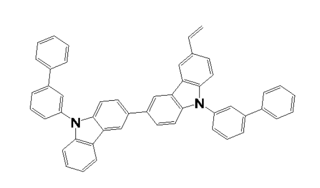
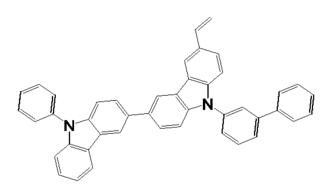
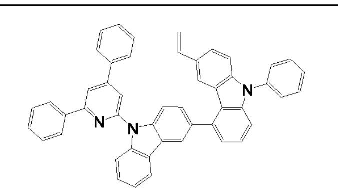
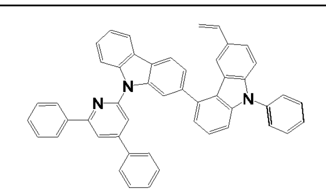
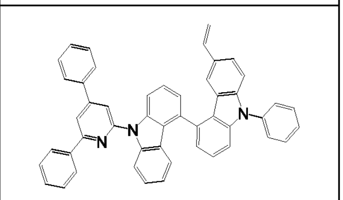
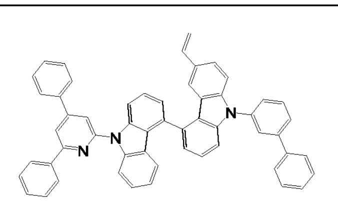
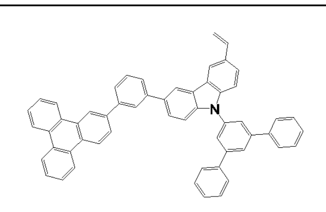
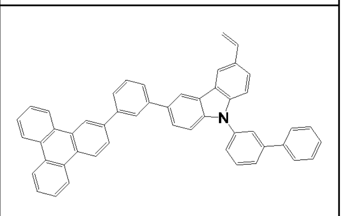
		
		
		
		
		
		
		
		
		

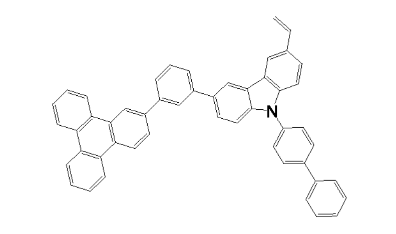
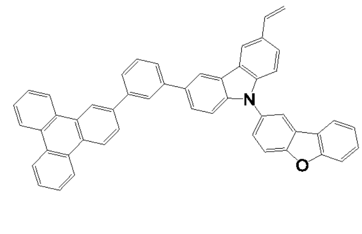
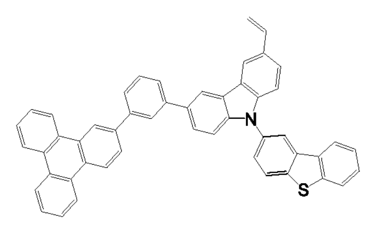
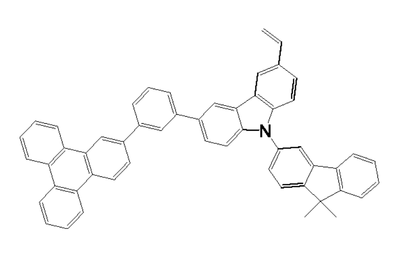
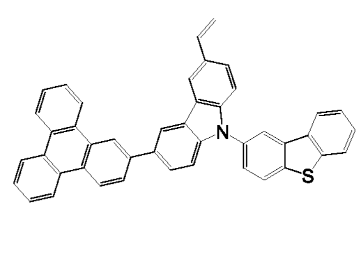
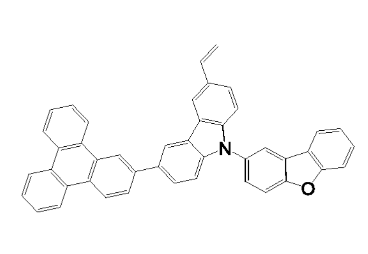
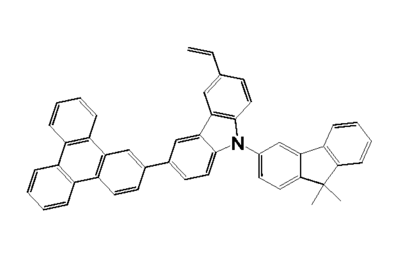
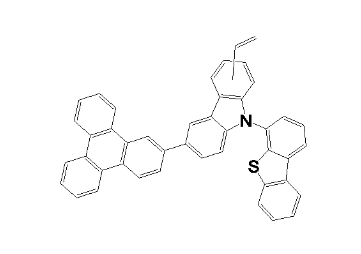
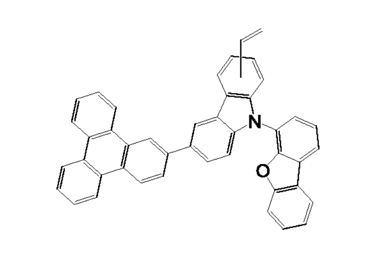
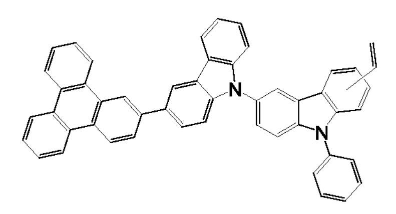
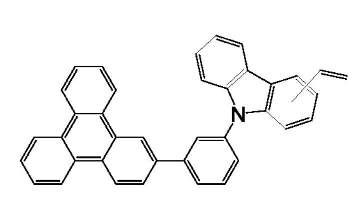
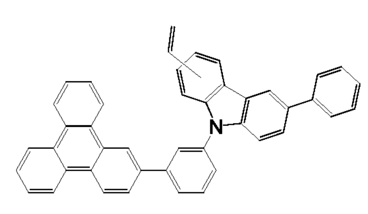
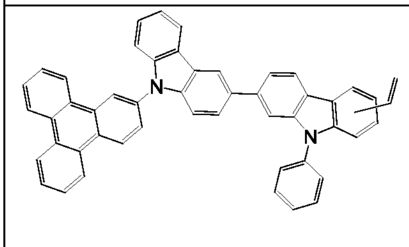
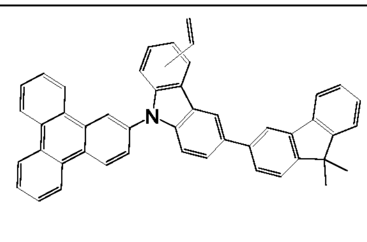
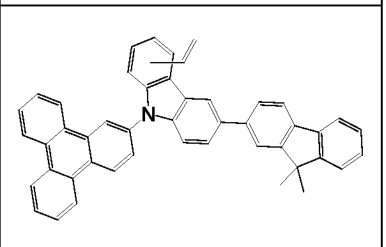
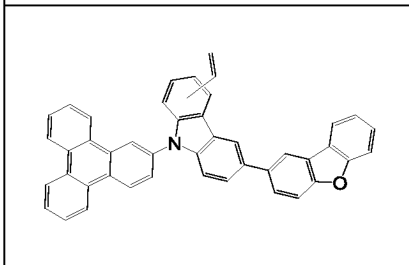
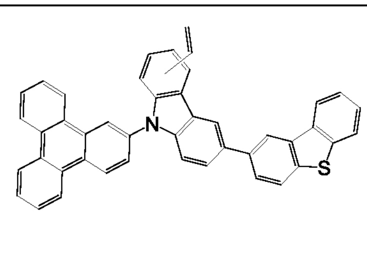
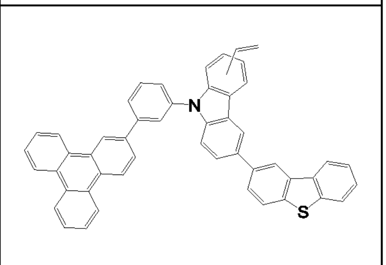
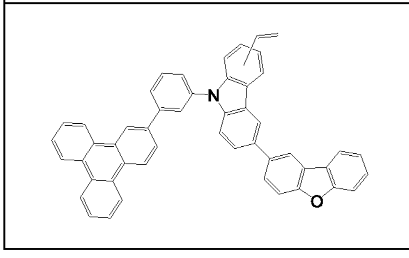
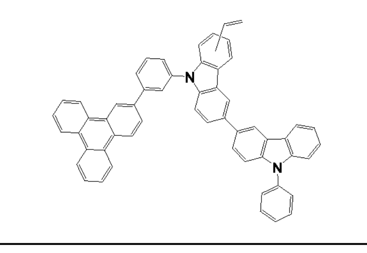
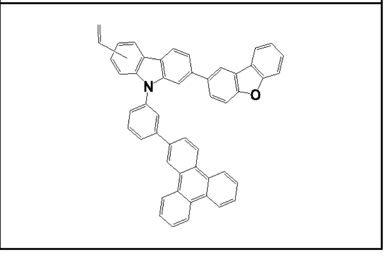


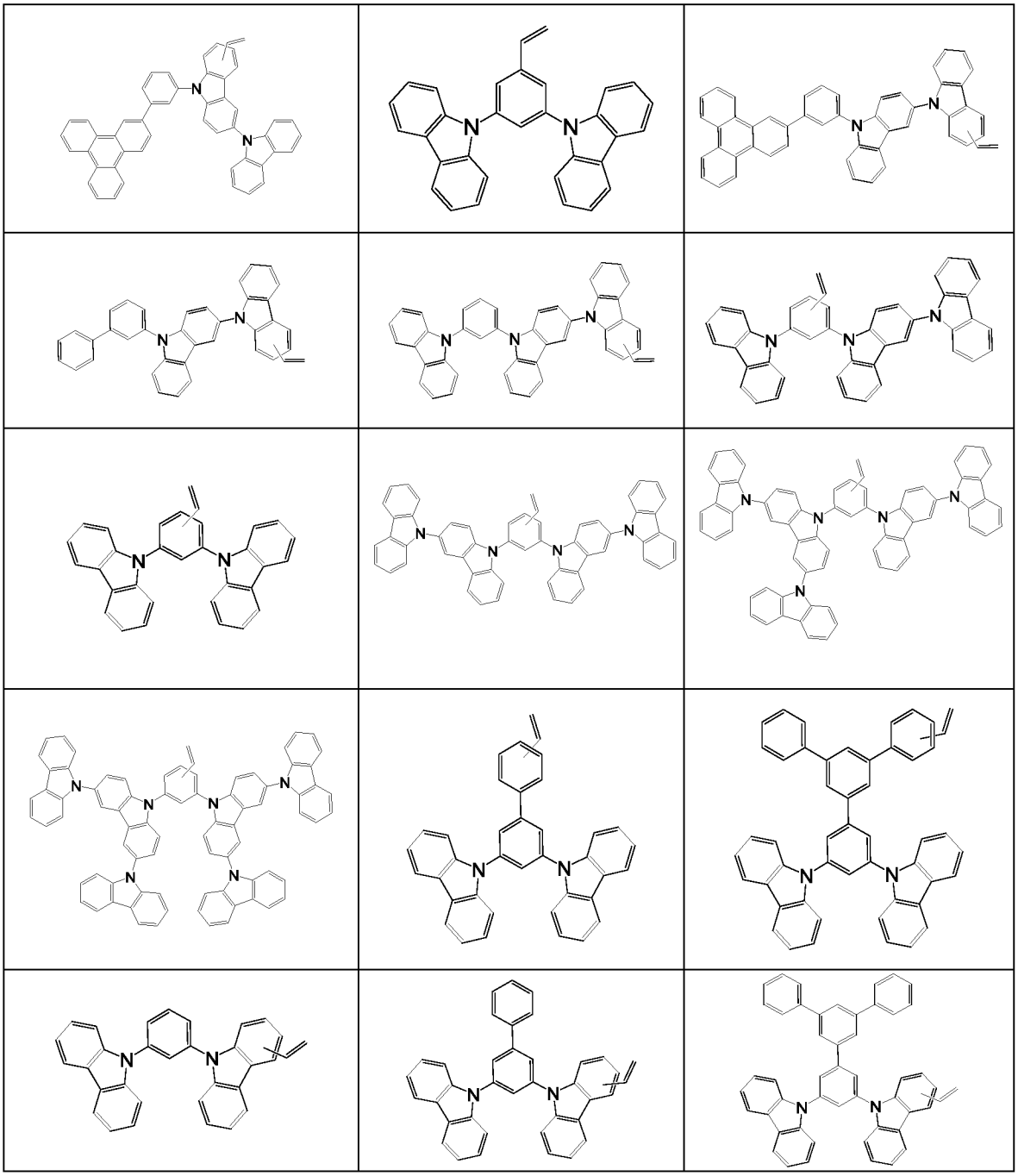
		
		
		
		

[0141] Examples of suitable second monomers are listed below:

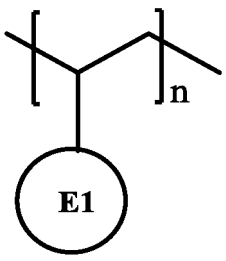
		
		



[0142] The present disclosure further relates to a polymer represented by the following general formula (4), and n is an integer greater than or equal to 1:



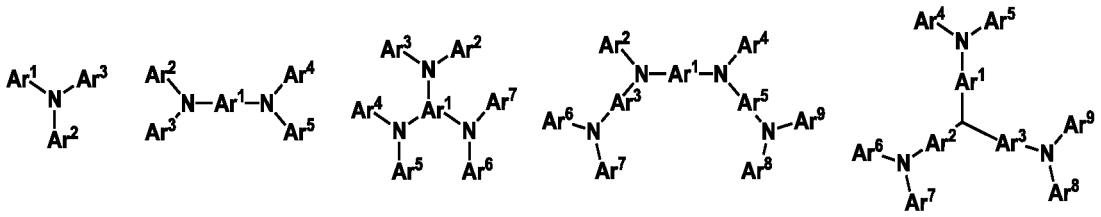
(4)

[0143] (HOMO-(HOMO-1)) of the E1 group is greater than or equal to 0.3 eV; and when n is greater than 1, E1 may be selected from different groups as long as (HOMO-(HOMO-1)) of each E1 is greater than or equal to 0.3 eV.

[0144] In some embodiments, ((HOMO-(HOMO-1)) of the E1 group in the general formula (4) is greater than or equal to 0.35 eV, preferably greater than or equal to 0.4 eV, more preferably greater than or equal to 0.45eV, and most preferably greater than or equal to 0.5 eV.

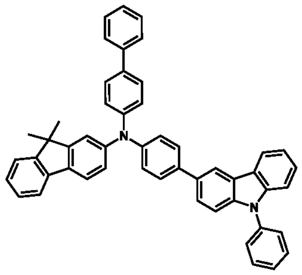
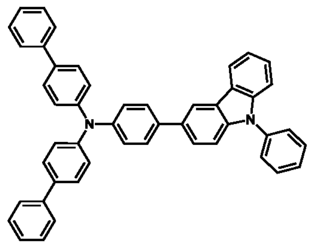
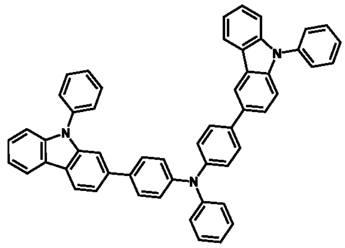
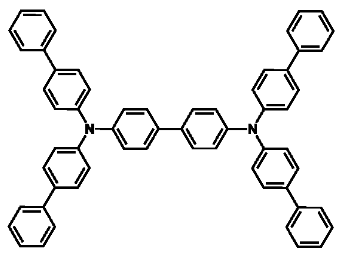
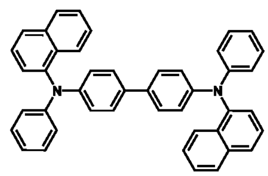
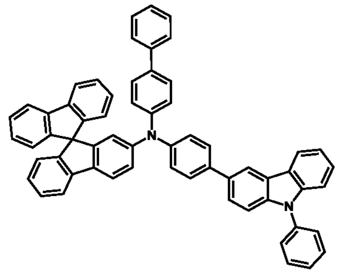
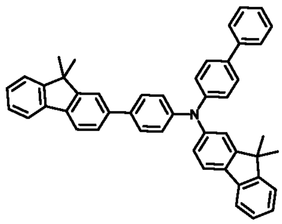
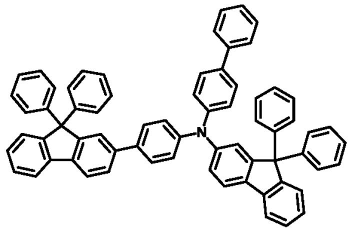
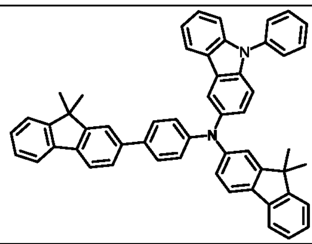
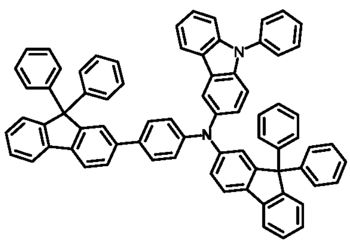
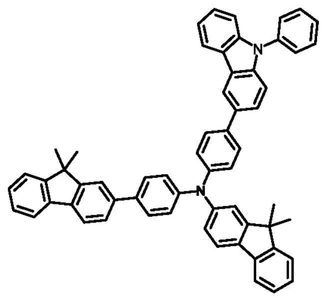
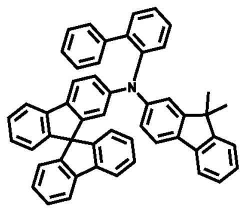
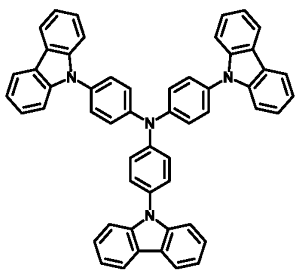
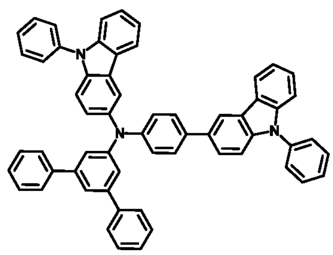
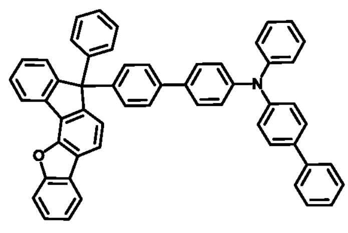
[0145] In a preferred embodiment, the E1 group in the general formula (4) contains a structural unit represented by one of the general formulas (2) to (5) as described above.

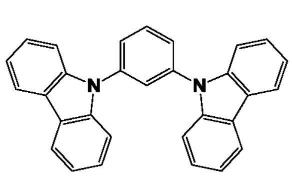
[0146] In another preferred embodiment, the E1 group in the general formula (4) contains the following structural units:



[0147] Each of Ar^1 to Ar^9 may be independently selected from the group consisting of cyclic aromatic hydrocarbon compounds, such as benzene, biphenyl, triphenyl, benzo, naphthalene, anthracene, phenalene, phenanthrene, fluorene, pyrene, chrysene, perylene, azulene; and aromatic heterocyclic compounds such as dibenzothiophene, dibenzofuran, furan, thiophene, benzofuran, benzothiophene, carbazole, pyrazole, imidazole, triazole, isoxazole, thiazole, oxadiazole, oxatriazole, dioxazole, thiadiazole, pyridine, pyridazine, pyrimidine, pyrazine, triazine, oxazine, oxathiazin, oxadiazine, indole, benzimidazole, indoxazine, bisbenzoxazole, isoxazole, benzothiazole, quinoline, isoquinoline, cinnoline, quinazoline, quinoxaline, naphthalene, phthalein, pteridine, xanthene, acridine, phenazine, phenothiazine, phenoxazine, dibenzoselenophene, benzoselenophene, benzofuropyridine, indolocarbazole, pyridylindole, pyrrolodipyridine, furodipyridine, benzothienopyridine, thienodipyridine, benzoselenophenopyridine and selenophenodipyridine; and groups containing 2 to 10 ring structures, which may be the same or different types of cyclic aryl or aromatic heterocyclic groups, and are linked to each other directly or through at least one of the following groups, such as an oxygen atom, a nitrogen atom, a sulfur atom, a silicon atom, a phosphorus atom, a boron atom, a chain structural unit, and an aliphatic ring group. Each Ar may be further substituted, and the substituents may be selected from the group consisting of hydrogen, alkyl, alkoxy, amino, alkene, alkyne, aralkyl, heteroalkyl, aryl, and heteroaryl.

[0148] Preferably, according to the polymer of the general formula (4), the E1 group may contain one or more of the following structural units:

[0149] The present disclosure further provides a mixture including one of the polymers represented by the general formulas (1) to (4) and another organic functional material. The organic functional material may be selected from the group consisting of a hole (also called an electron hole) injection or transport material (HIM/HTM), a hole blocking material (HBM), an electron injection or transport material (EIM/ETM), an electron blocking material (EBM), an organic host material (Host), a singlet emitter (fluorescent emitter), a triplet emitter (phosphorescent emitter), and a TADF material. These functional materials have been previously described. In a preferred embodiment, the organic functional material is a fluorescent emitter. In another preferred embodiment, the organic functional material is a phosphorescent emitter. In another preferred embodiment, the organic functional material is a TADF material.

[0150] The present disclosure further relates to a formulation including one of the polymers represented by the general formulas (1) to (4) and an organic solvent. Examples of the organic solvents include, but are not limited to, methanol, ethanol, 2-methoxyethanol, dichloromethane, trichloromethane, chlorobenzene, o-dichlorobenzene, tetrahydrofuran, anisole, morpholine, toluene, o-xylene, m-xylene, p-xylene, 1,4-dioxahexane, acetone, methyl ethyl ketone, 1, 2-dichloroethane, 3-phenoxytoluene, 1, 1, 1-trichloroethane, 1, 1, 2, 2-tetrachloroethane, ethyl acetate, butyl acetate, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, tetrahydronaphthalene, decalin, indene and/or their combination.

[0151] In a preferred embodiment, the formulation according to the present disclosure is a solution.

[0152] In another preferred embodiment, the formulation according to the present disclosure is a suspension.

[0153] In the embodiments of the present disclosure, the polymer in the formulation has a weight percent range from 0.01 wt% to 20 wt%, preferably from 0.1 wt% to 15 wt %, more preferably from 0.2 wt% to 10 wt%, and most preferably from 0.25 wt% to 5 wt %.

[0154] The present disclosure also relates to the use of the formulation as a coating or printing ink in the preparation of organic electronic devices, particularly preferably by printing or coating.

[0155] Suitable printing or coating techniques include, but are not limited to, inkjet printing, typography printing, screen printing, dip coating, spin coating, blade coating, roller printing, torsion printing, lithography, flexographic printing, rotary printing, spraying, brushing or pad printing, or slit-type extrusion coating and so on. Preferred are gravure printing, screen printing, and inkjet printing. The solution or suspension may additionally include one or more components such as surfactants, lubricants, wetting agents, dispersing agents, hydrophobic agents, binders and so on, for adjusting the viscosity and film forming properties, and improving adhesion. Detailed information relevant to printing technology and related requirements for related solutions, such as solvent, concentration, viscosity, and the like, may be referred to Handbook of Print Media: Technologies and Production Methods, Helmut Kipphan, ISBN 3-540-67326-1.

[0156] Based on the above polymer, the present disclosure further provides an application of the polymer as described above, that is, the application of the polymer to an organic electronic device. The organic electronic device may be selected from, but not limited to, an organic light-emitting-diode (OLED), an organic photovoltaic cell (OPV), an organic light-emitting electrochemical cell (OLEEC), an organic field effect transistor (OFET), an organic light-emitting field effect transistor, an organic laser, an organic spin electronic device, an organic sensor, and an organic plasmon emitting diode, especially an OLED. In embodiments of the present disclosure, the organic compound is preferably used in the light-emitting layer of the OLED device.

[0157] In a preferred embodiment, the polymer represented by the general formula (1) is used in the light-emitting layer of the OLED device.

[0158] In another preferred embodiment, the polymer represented by the general formula (4) is used in the hole transport layer of the OLED device.

[0159] The present disclosure further provides an organic electronic device including at least one of the polymers as described above. Generally, such an organic electronic device includes at least a cathode, an anode, and a functional layer between the cathode and the anode, and the functional layer includes at least one of the polymers as described above. The organic electronic device may be selected from, but not limited to, an organic light-emitting-diode (OLED), an organic photovoltaic cell (OPV), an organic light-emitting electrochemical cell (OLEEC), an organic field effect transistor (OFET), an organic light-emitting field effect transistor, an organic laser, an organic spin electronic device, an organic sensor, and an organic plasmon emitting diode.

[0160] In a particularly preferred embodiment, the organic electronic device is an OLED including a substrate, an anode, at least one light-emitting layer, and a cathode.

[0161] The substrate may be opaque or transparent. A transparent substrate can be used to manufacture a transparent light-emitting component. See, for example, Bulovic et al., Nature 1996, 380, p29, and Gu et al., Appl. Phys. Lett. 1996, 68, p2606. The substrate may be rigid or flexible. The substrate can be plastic, metal, semiconductor wafer, or glass. Most preferably, the substrate has a smooth surface. The substrates without surface defects are particularly desirable. In a preferred embodiment, the substrate is flexible and may be selected from polymer films or plastic having a glass transition temperature Tg greater than 150 °C, preferably greater than 200 °C, more preferably greater than 250 °C, and most preferably greater than 300 °C. Examples of suitable flexible substrates are poly(ethylene terephthalate) (PET) and polyethylene glycol (2, 6-naphthalene) (PEN).

[0162] The anode can include a conductive metal or a metal oxide, or a conductive polymer. The anode can easily

inject holes into the hole injection layer (HIL) or the hole transport layer (HTL) or the light-emitting layer. In one embodiment, the absolute value of the difference between the work function of the anode and the HOMO energy level or the valence band energy level of the emitter in the light-emitting layer or of the p-type semiconductor material as the HIL or HTL or electron blocking layer (EBL) is less than 0.5 eV, preferably less than 0.3 eV, and most preferably less than 0.2 eV. Examples of the anode materials include, but are not limited to, Al, Cu, Au, Ag, Mg, Fe, Co, Ni, Mn, Pd, Pt, ITO, aluminum-doped zinc oxide (AZO), and the like. Other suitable anode materials are already known, and may be readily selected for use by one of ordinary skill in the art. The anode material can be deposited using any suitable technique, such as suitable physical vapor deposition process, including radio frequency magnetron sputtering, vacuum thermal evaporation, electron beam (e-beam), and the like. In some embodiments, the anode is patterned. A patterned ITO conductive substrate is commercially available and can be used to fabricate the device according to the present dsclosure.

[0163] The cathode can include a conductive metal or a metal oxide. The cathode can easily inject electrons into the EIL or ETL or directly into the light-emitting layer. In one embodiment, the absolute value of the difference between the work function of the cathode and the LUMO energy level or the conduction band energy level of the emitter in the light-emitting layer or of the n-type semiconductor material as the electron injection layer (EIL) or the electron transport layer (ETL) or the hole blocking layer (HBL) is less than 0.5 eV, preferably less than 0.3 eV, and most preferably less than 0.2 eV. In principle, all the materials that can be used as the cathode of the OLED can serve as the cathode material for the device of the present disclosure. Examples of the cathode material include, but are not limited to, Al, Au, Ag, Ca, Ba, Mg, LiF/Al, MgAg alloy, BaF_2/Al, Cu, Fe, Co, Ni, Mn, Pd, Pt, ITO, and the like. The cathode material can be deposited using any suitable technique, such as suitable physical vapor deposition process, including radio frequency magnetron sputtering, vacuum thermal evaporation, and electron beam (e-beam), and the like.

[0164] OLEDs may further include other functional layers such as a hole injection layer (HIL), a hole transport layer (HTL), an electron blocking layer (EBL), an electron injection layer (EIL), an electronic transport layer (ETL), and a hole blocking layer (HBL). Suitable materials for these functional layers are described in WO2010135519A1, US20090134784A1, and WO2011110277A1 in detail above. The three patent documents are specially incorporated herein by reference in their entirety.

[0165] In a preferred embodiment, in the light-emitting device according to the present disclosure, the light-emitting layer thereof contains the polymer represented by the general formula (1) of the present disclosure.

[0166] In another preferred embodiment, in the light-emitting device according to the present disclosure, the hole transport layer thereof contains the polymer represented by the general formula (4) of the present disclosure.

[0167] The light-emitting device according to the present disclosure has a light emission wavelength between 300 nm and 1000 nm, preferably between 350 nm and 900 nm, and more preferably between 400 nm and 800 nm.

[0168] The present disclosure also relates to the application of the organic electronic device according to the present disclosure in various electronic devices including, but not limited to, display equipments, lighting equipments, light sources, sensors, and the like.

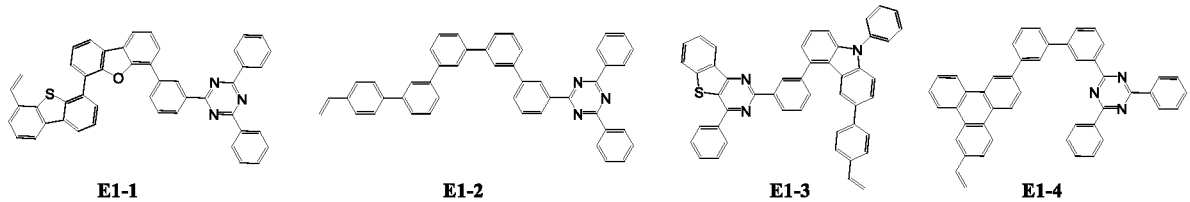
[0169] The present disclosure also relates to an electronic equipment including the organic electronic device according to the present disclosure. The electronic equipment includes, but not limited to, display equipments, lighting equipments, light sources, sensors, and the like.

[0170] The disclosure will now be described with reference to the preferred embodiments, but the disclosure is not to be construed as being limited to the following examples. It is to be understood that the appended claims are intended to cover the scope of the disclosure. Those skilled in the art will understand that modifications can be made to various embodiments of the disclosure with the teaching of the present disclosure, which will be covered by the spirit and scope of the claims of the disclosure.

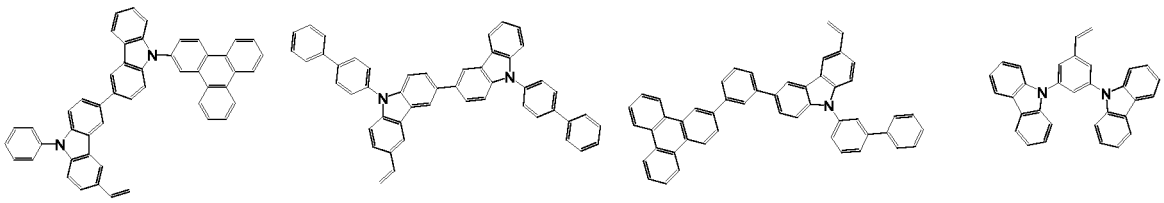
Specific Examples

1. Synthesis of monomers

[0171]



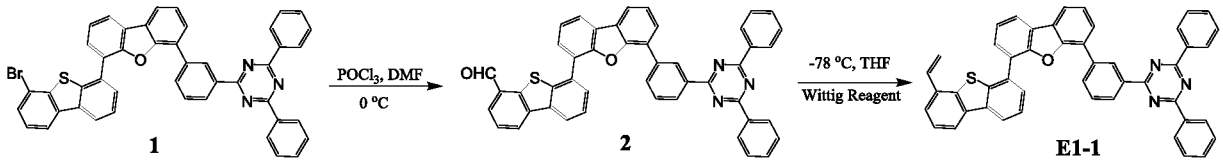
E1-1 E1-2 E1-3 E1-4



E2-1 E2-2 E2-3 E2-4

(1) Synthesis of monomer E1-1

[0172] An experimental synthetic route is shown as below:



Synthesis steps are as follows:

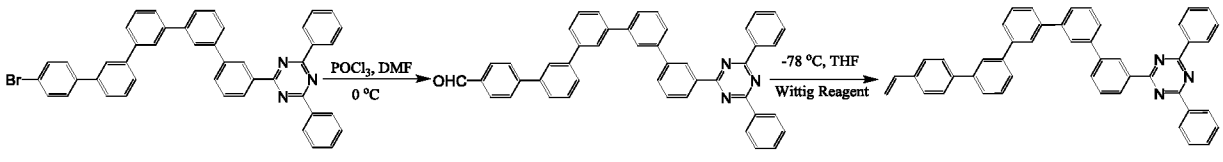
[0173]

a. 10 mmol of compound 1 was dissolved in 250 ml of dry DMF solution under a nitrogen atmosphere, the resulting reaction solution was placed in an ice bath and stirred, and 11.0 mmol of phosphorus oxychloride ($POCl_3$) solution was added dropwise. After the dropwise addition is completed, the reaction was continued for 30 minutes, allowed to gradually warm up to room temperature and reacted for 2 hours. The reaction was quenched with water, the reaction solution was extracted with dichloromethane, and washed with water. The organic phase was combined, dried with anhydrous sodium sulfate, and filtered. The organic solvent was distilled off to give a crude product of compound 2. The crude product was recrystallized with dichloromethane and n-hexane to obtain 8 mmol of a product, which was dried under vacuum for use. MS (ASAP) = 685.2.

b. 5.0 mmol of the compound 2 obtained above was dissolved in 200 ml of dry tetrahydrofuran (THF) solution. The reaction solution was placed at a temperature of -78 °C and stirred under a nitrogen atmosphere, and 8.0 mmol of methylene triphenyl phosphorate (Wittig reagent) was added dropwise. After the addition is completed, the reaction solution was allowed to gradually warm up to room temperature and continued to stir overnight at room temperature. The reaction was quenched with water. All the reaction solution was extracted with dichloromethane. The organic phase was washed with water, and finally the organic phase was combined, dried with anhydrous sodium sulfate, and filtered. The organic solvent was distilled off. The resulting product was purified by silica gel column with mobile phase being dichloromethane: petroleum ether = 1: 2, finally obtaining 4.1 mmol of monomer E1-1, which was dried under vacuum for use. MS (ASAP) = 683.2.

(2) Synthesis of monomer E1-2

[0174] An experimental synthetic route is shown as below:



Synthesis steps are as follows:

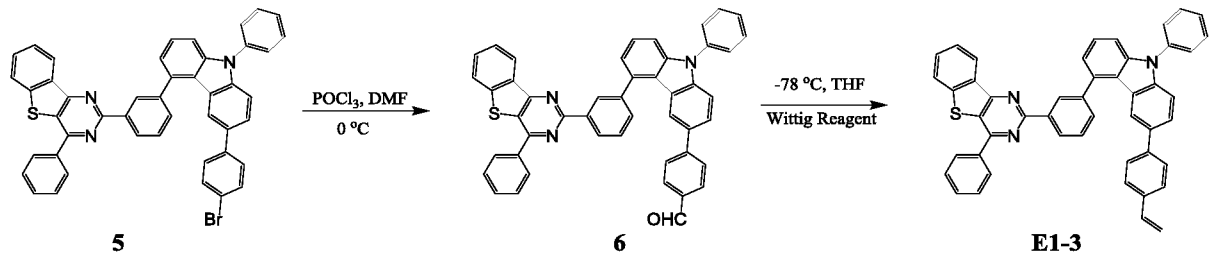
[0175]

a. 10 mmol of compound 3 was dissolved in 250 ml of dry DMF solution under a nitrogen atmosphere, the resulting reaction solution was placed in an ice bath and stirred, and 11.0 mmol of phosphorus oxychloride ($POCl_3$) solution was added dropwise. After the dropwise addition is completed, the reaction was continued for 30 minutes, allowed to gradually warm up to room temperature and reacted for 2 hours. The reaction was quenched with water, the reaction solution was extracted with dichloromethane, and washed with water. The organic phase was combined, dried with anhydrous sodium sulfate, and filtered. The organic solvent was distilled off to give a crude product of compound 4. The crude product was recrystallized with dichloromethane and n-hexane to obtain 8.4 mmol of a product, which was dried under vacuum for use. MS (ASAP) = 641.3.

b. 5.0 mmol of the compound 4 obtained above was dissolved in 200 ml of dry tetrahydrofuran (THF) solution. The reaction solution was placed at a temperature of -78 °C and stirred under a nitrogen atmosphere, and 8.0 mmol of methylene triphenyl phosphorate (Wittig reagent) was added dropwise. After the addition is completed, the reaction solution was allowed to gradually warm up to room temperature and continued to stir overnight at room temperature. The reaction was quenched with water. All the reaction solution was extracted with dichloromethane. The organic phase was washed with water, and finally the organic phase was combined, dried with anhydrous sodium sulfate, and filtered. The organic solvent was distilled off. The resulting product was purified by silica gel column with mobile phase being dichloromethane: petroleum ether = 4: 1, finally obtaining 4.5 mmol of monomer E1-2, which was dried under vacuum for use. MS (ASAP) = 639.4.

(3) Synthesis of monomer E1-3

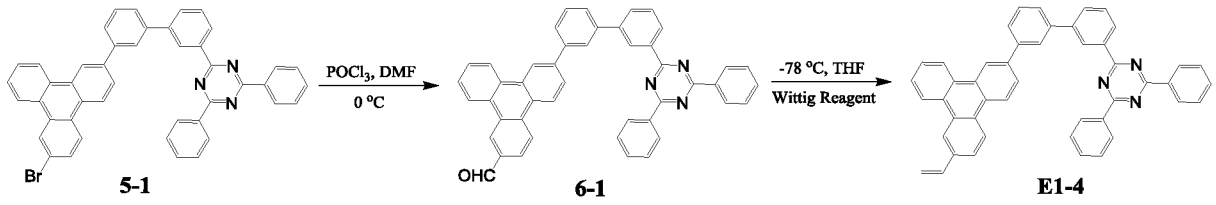
[0176] An experimental synthetic route is shown as below:



[0177] The synthesis steps of monomer E1-3 are similar to the synthesis steps of monomer EI-2, except that compound 5 was used in the first step, and the subsequently resulting aldehyde-containing intermediate was compound 6. Finally, an intermediate E1-3 was obtained as a white solid powder. MS (ASAP) = 681.2.

(4) Synthesis of monomer E1-4

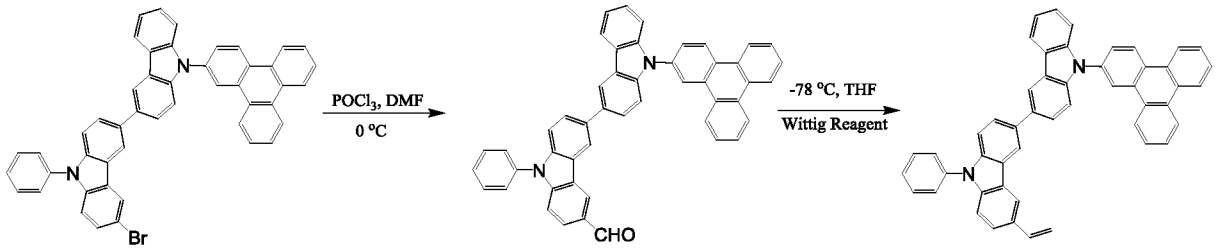
[0178] An experimental synthetic route is shown as below:



[0179] The synthesis steps of monomer E1-4 are similar to the synthesis steps of monomer EI-2, except that compound 5-1 was used in the first step, and the subsequently resulting aldehyde-containing intermediate was compound 6-1. Finally, an intermediate E1-4 was obtained as a white solid powder. MS (ASAP) = 637.2.

(5) Synthesis of monomer E2-1

[0180] An experimental synthetic route is shown as below:

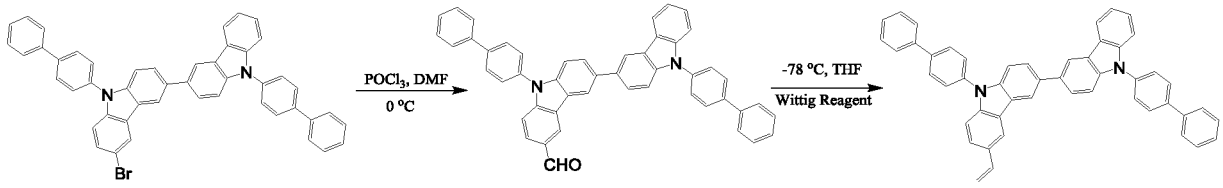


7 8 E2-1

[0181] The synthesis steps of monomer E2-1 are similar to the synthesis steps of monomer E1-1, except that compound 7 was used in the first step, and the subsequently resulting aldehyde-containing intermediate was compound 8. Finally, an intermediate E2-1 was obtained as a creamy white solid powder. MS (ASAP) = 660.3.

(6) Synthesis of monomer E2-2

[0182] An experimental synthetic route is shown as below:

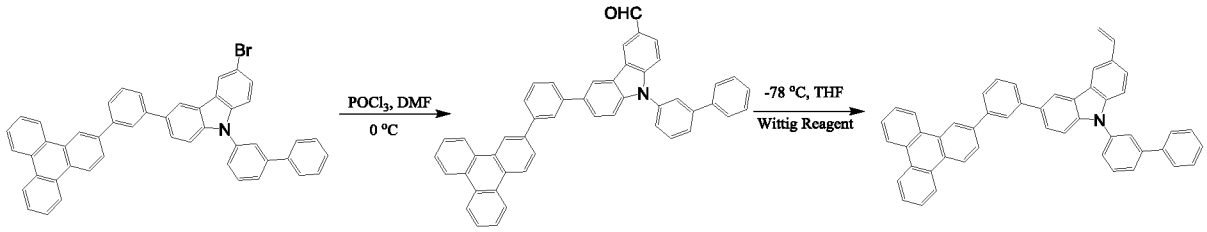


9 10 E2-2

[0183] The synthesis steps of monomer E2-2 are similar to the synthesis steps of monomer E1-1, except that compound 9 was used in the first step, and the subsequently resulting aldehyde-containing intermediate was compound 10. Finally, an intermediate E2-2 was obtained as a creamy white solid powder. MS (ASAP) = 662.3.

(7) Synthesis of monomer E2-3

[0184] An experimental synthetic route is shown as below:

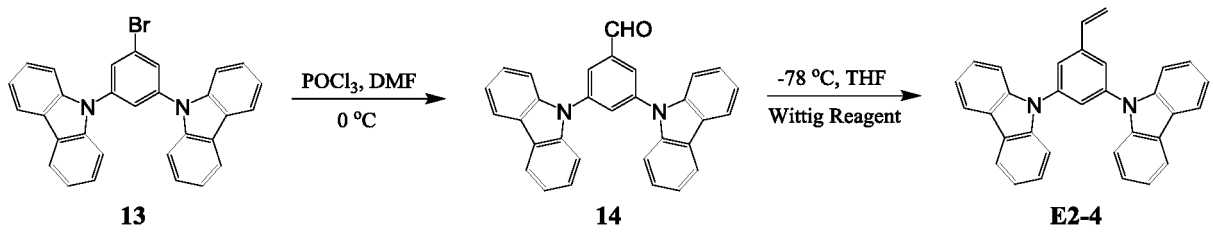


11 12 E2-1

[0185] The synthesis steps of monomer E2-3 are similar to the synthesis steps of monomer E1-1, except that compound 11 was used in the first step, and the subsequently resulting aldehyde-containing intermediate was compound 12. Finally, an intermediate E2-3 was obtained as a creamy white solid powder. MS (ASAP) = 647.3.

(8) Synthesis of monomer E2-4

[0186]



[0187] The synthesis steps of monomer E2-4 are similar to the synthesis steps of monomer E1-1, except that compound 13 was used in the first step, and the subsequently resulting aldehyde-containing intermediate was compound 14. Finally, an intermediate E2-4 was obtained as a creamy white solid powder. MS (ASAP) = 434.4.

2. Energy structure of monomers

[0188] The energy level of the organic repeating structural unit can be calculated by quantum, for example, by using TD-DFT (time-dependent density functional theory) by Gaussian03W (Gaussian Inc.), and specific simulation methods can be found in WO2011141110. Firstly, the molecular geometry is optimized by semi-empirical method "Ground State/Semi-empirical/Default Spin/AMI" (Charge 0/Spin Singlet). Then, the energy structure of organic molecules is determined by TD-DFT (time-density functional theory) Calculate "TD-SCF/DFT/Default Spin/B3PW91" and the base group "6-31G (d)" (Charge 0/Spin Singlet). The HOMO and LUMO energy levels are calculated using the following calibration formula: S1 and T1 are used directly.

HOMO(eV) = ((HOMO(G)×27.212)-0.9899)/1.1206
LUMO(eV) = ((LUMO(G)×27.212)-2.0041)/1.385

[0189] Wherein HOMO (G) and LUMO (G) are the direct results of Gaussian 03W, in units of Hartree. The results are shown in Table 1, in which ΔHOMO=HOMO-(HOMO-1):

Table 1

Structural Unit	HOMO [eV]	LUMO [eV]	S1 [eV]	T1 [eV]	ΔHOMO [eV]
E1-1	-5.99	-2.79	3.25	2.80	0.32
E1-2	-6.25	-2.76	3.27	2.87	0.09
E1-3	-5.58	-2.76	3.10	2.86	0.48
E1-4	-6.06	-2.80	3.31	2.71	0.18
E2-1	-5.44	-2.36	3.17	2.69	0.42
E2-2	-5.43	-2.24	3.11	2.90	0.41
E2-3	-5.70	-2.33	3.22	2.71	0.34
E2-4	-5.82	-2.12	3.39	3.11	0.38

3. Synthesis of polymer

[0190] The main synthesis steps for the synthesis of polymers are as follows: taking the synthesis of P1 polymer for example, monomers of 0.5 mmol of E1-1 and 0.50 mmol of E2-1 were dissolved in toluene solvent under the protection of nitrogen while 0.01 mmol of 2, 2-azobisisobutyronitrile (AIBN initiator) was added by a syringe; the reaction solution was sealed and reacted at 60 °C for 4 hours. After the reaction, the reaction solution was cooled to room temperature and the polymer was precipitated out with methanol. The precipitate was dissolved in tetrahydrofuran (THF) and precipitated with methanol again. This was repeated for 3 to 5 times and the product was dried under vacuum to obtain a solid of polymer P1.

[0191] The synthesis steps for P2 to P17 are similar to those of P1, except for containing different proportions of vinyl monomer. The monomers and proportions contained in P2 to P17 are shown in the following table:

Polymer	E1-1	E1-2	E1-3	E1-4	E2-1	E2-2	E2-3	E2-4
P1	50				50			
P2		40					60	
P3			70			30		
P4	50					50		
P5		50			50			
P6	15		30				55	
P7		60				40		
P8			50		50			
P9				50				50
P10	100							
P11			100					
P12					100			
P13						100		
P14							100	
P15								100
P16					50	50		
P17					50		50	

[0192] Where P1 to P9 are polymers represented by the general formula (1) in the present disclosure, and P10 to P17 are polymers represented by the general formula (4) in the present disclosure.

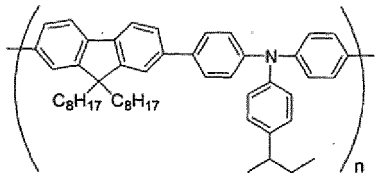
4. Preparation and Measurement of OLED Devices

[0193] The preparation process of the OLED devices above will be described in detail with reference to specific examples below. The structure of the OLED devices is as follows: ITO/HIL/HTL/EML/ETL/cathode. The preparation steps are as follows:

a. cleaning of ITO (indium tin oxide) conductive glass substrate: washing with the use of various solvents (such as one or more of chloroform, acetone, or isopropyl alcohol) and then treating with UV and ozone;

b. HIL (hole injection layer, 60 nm): 60 nm PEDOT (polyethylenedioxythiophene, Clevios™ AI4083) was obtained by spin-coating as an HIL in an ultra clean chamber, and treated on a hot plate at 180 °C for 10 minutes;

c. HTL (hole transport layer, 20 nm): 20 nm TFB or PVK (Sigma Aldrich, having an average Mn of 25,000 to 50,000) was obtained by spin-coating in a nitrogen glove box, and the solution used was TFB or PVK (Sigma Aldrich) added into a toluene solvent, with a solubility of solution of 5 mg/ml, followed by a treatment on a hot plate at 180 °C for 60 minutes; TFB (H.W. SandsCorp.) is a hole transport material for HTL, and its structure is as follows:



"TFB" ;

d. EML (organic light-emitting layer): EML was formed by spin-coating in a nitrogen glove box and the solution used was the polymer (P1 to P10) added into a toluene solvent and a certain amount of $Ir(PPy)_3$, with a solubility of solution of 10 mg/ml, followed by a treatment on a hot plate at 180 °C for 10 minutes. The component and thickness of EML of the devices are listed in Table 2.

Table 2

OLED device	HTL	Component and thichness of EML
OLED1	PVK	P1: (15%)Ir(ppy)$_3$(80nm)
OLED2	PVK	P2: (15%)Ir(ppy)$_3$(65nm)
OLED3	TFB	P3: (15%)Ir(ppy)$_3$(80nm)
OLED4	TFB	P4: (15%)Ir(ppy)$_3$(80nm)
OLED5	TFB	P5: (15%)Ir(ppy)$_3$(80nm)
OLED6	PVK	P6: (15%)Ir(ppy)$_3$(65nm)
OLED7	PVK	P7: (15%)Ir(ppy)$_3$(65nm)
OLED8	TFB	P8: (15%)Ir(ppy)$_3$(65nm)
OLED9	TFB	P9: (15%)Ir(ppy)$_3$(65nm)

e. cathode: Ba/Al(2 nm/100 nm) was deposited in high vacuum (1×10^{-6} mbar) by the thermal evaporation;
f. encapsulation: the device was encapsulated in the nitrogen glove box with UV curing resin.

[0194] The current-voltage and luminescence (IVL) characteristics of each OLED device are characterized by characterization equipment, while recording important parameters such as efficiency, lifetime, and driving voltage. The performance of OLED devices is summarized in Table 3.

Table 3

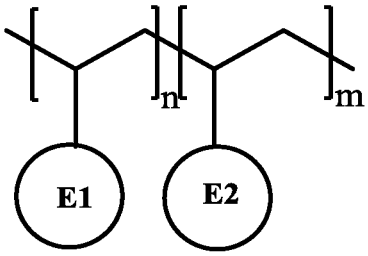
OLED device	Colour	V @ 1knits [V]	Current efficiency @ 1knits [cd/A]
OLED1	green	8.5	43
OLED2	green	8.3	44
OLED3	green	7.5	44
OLED4	green	7.8	39
OLED5	green	6.4	42
OLED6	green	7.6	45
OLED7	green	7.7	46
OLED8	green	6.7	48
OLED9	green	6.5	50

[0195] Similarly, P10 to P17 can be used as a HTL for OLEDs instead of TFB or PVK.

[0196] The polymers represented by the general formulas (1) to (3) of the present disclosure tend to easily form an exciplex, which, when used for a phosphorescent host, can improve the efficiency of the device, while providing a better material solution for printing OLEDs due to better solubility in an organic solvent and good film forming performance. The polymers represented by the general formula (4) of the present disclosure have high stability and are easy to be solution processed.

Claims

1. A polymer comprising a repeating unit represented by general formula (1):



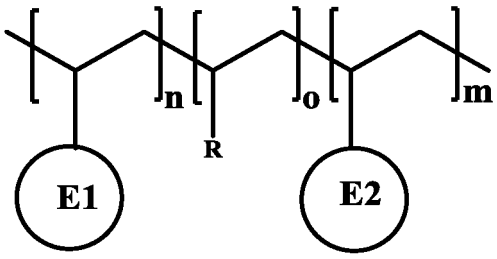
general formula (1),

wherein n and m are integers greater than or equal to 1;
$\min((LUMO(E1)-HOMO(E2), LUMO(E2)-HOMO(E1)) \leq \min(E_T(E1), E_T(E2)) + 0.1$ eV, wherein LUMO(El), HOMO(E1), and $E_T(E1)$ are energy levels of a highest occupied molecular orbital, a lowest unoccupied molecular orbital, and a triplet excited state of E1 group, respectively; LUMO(E2), HOMO(E2), and $E_T(E2)$ are energy levels of a highest occupied molecular orbital, a lowest unoccupied molecular orbital, and a triplet excited state of E2 group, respectively.

2. The polymer of claim 1, wherein HOMO(E1)-(HOMO-1)(E1) ≥ 0.3 eV and/or HOMO(E2)-(HOMO-1)(E2) ≥ 0.3 eV, wherein (HOMO-1)(E1) is an energy level of a second highest occupied molecular orbital of the E1 group, (HOMO-1)(E2) is an energy level of a second highest occupied molecular orbital of the E2 group.

3. The polymer of any one of claims 1 to 2, wherein a ratio of n: m ranges from 3:7 to 7:3.

4. The polymer of any one of claims 1 to 3, comprising a repeating unit represented by general formula (2):

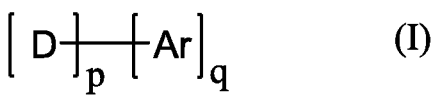


general formula (2)

wherein R is at least one selected from the group consisting of a linear alkane containing 1 to 15 carbon atoms, a branched alkane containing 1 to 15 carbon atoms, an aromatic ring system containing 2 to 20 carbon atoms, a heteroaromatic ring system containing 2 to 20 carbon atoms, and a non-aromatic ring system containing 2 to 20 carbon atoms; o is an integer greater than or equal to 0.

5. The polymer of any one of claims 1 to 4, wherein the E1 group comprises an electron-donating group D, and/or the E2 group comprises an electron-accepting group A.

6. The polymer of any one of claims 1 to 5, wherein the E1 group comprises a structural unit represented by general formula (I):

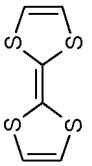
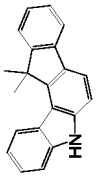
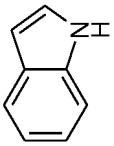
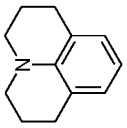
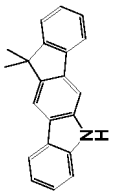
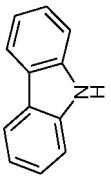
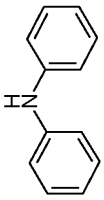
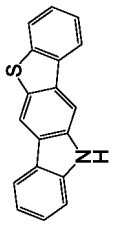
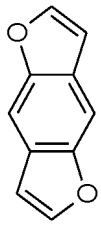
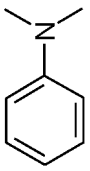
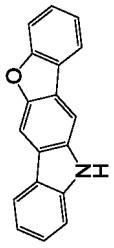
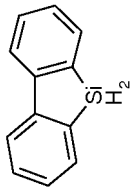
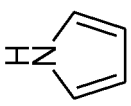
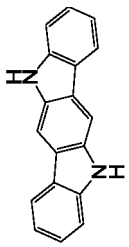


(I)

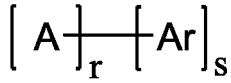
,

wherein Ar is an aromatic or heteroaromatic structural unit, the electron-donating group D is the same or different in multiple occurrences, p is an integer between 1 and 6, and q is 0 or 1.

7. The polymer of claim 6, wherein the electron-donating group D comprises at least one of substituted or unsubstituted structural units represented by structural formulas D1 to D15:

	D5		D10		D15
	D4		D9		D14
	D3		D8		D13
	D2		D7		D12
	D1		D6		D11

8. The polymer of any one of claims 1 to 7, wherein the E2 group comprises a structural unit represented by general formula (II):

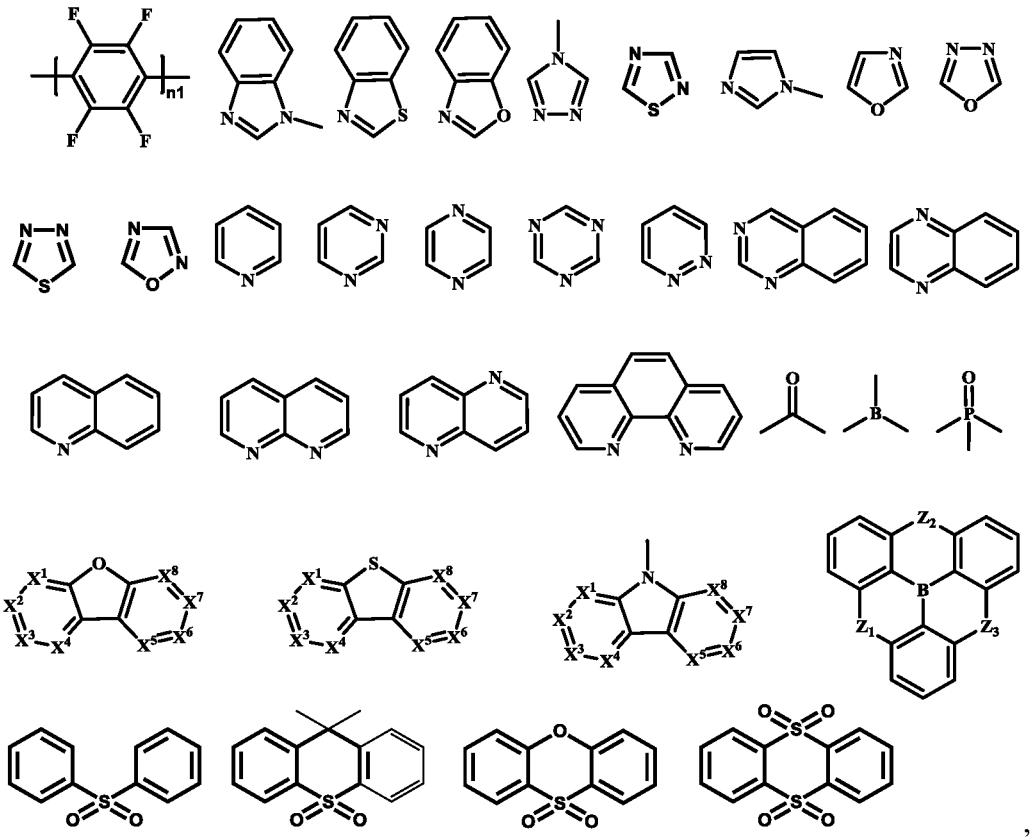


(II)

,

wherein Ar is an aromatic or heteroaromatic structural unit, the electron-accepting group A is the same or different in multiple occurrences, r is an integer between 1 and 6, and s is 0 or 1.

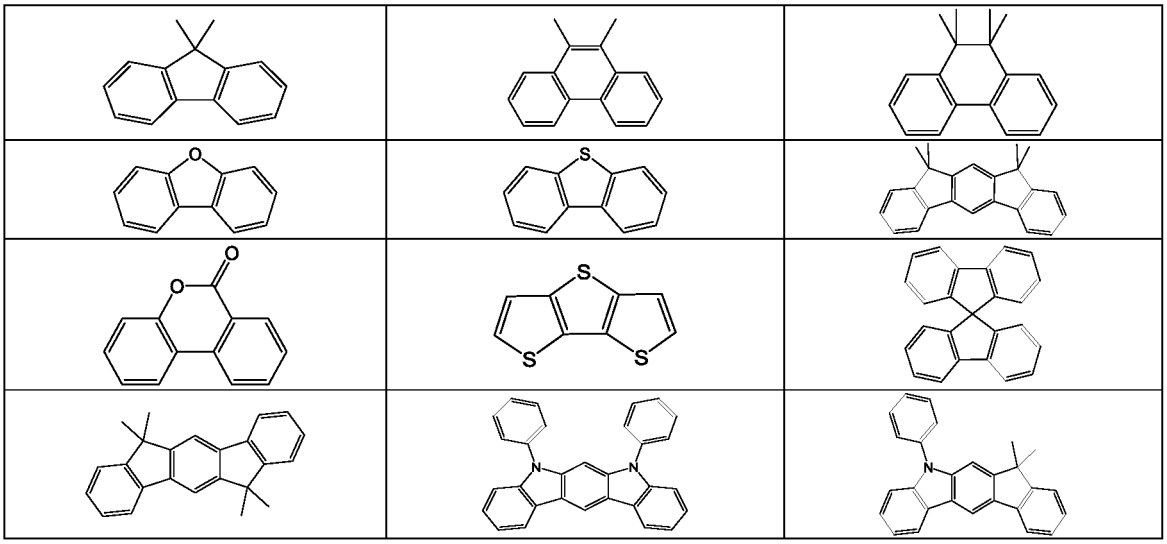
9. The polymer of claim 8, wherein the electron-accepting group A is selected from F or a cyano group, in which s is equal to 1; or the electron-accepting group A comprises at least one of substituted or unsubstituted structure units as follows:

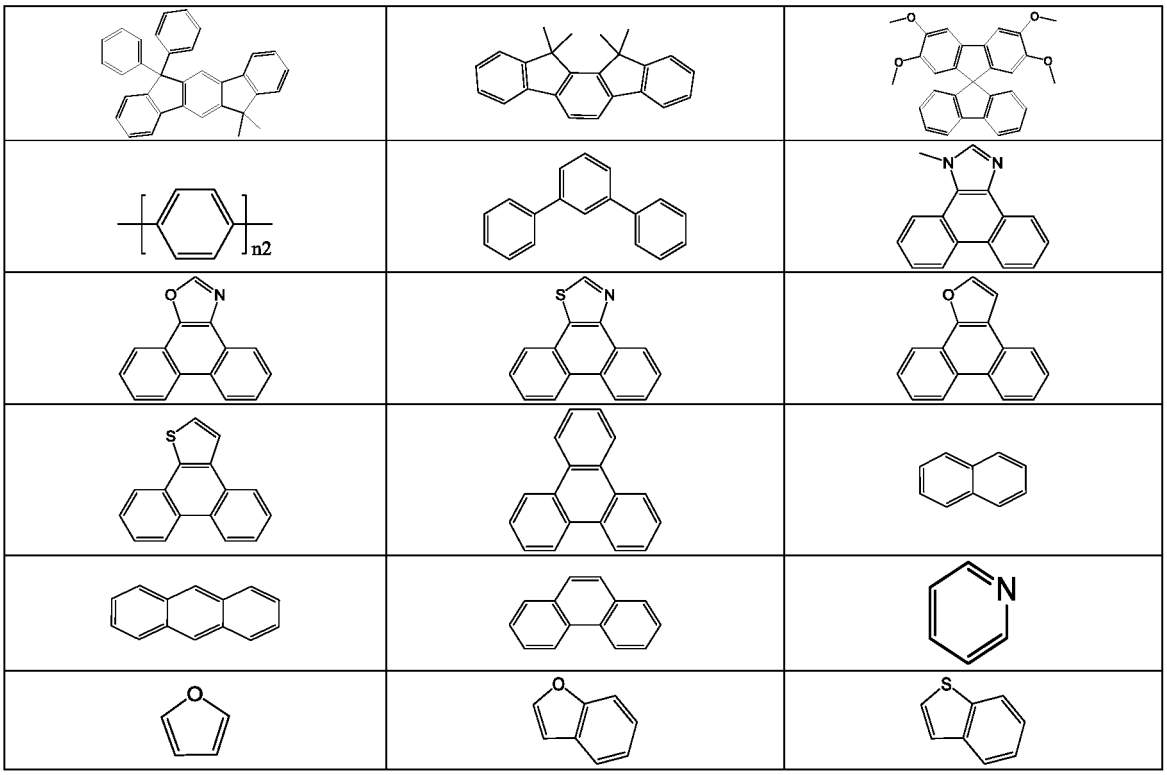


,

wherein n1 is an integer from 1 to 3; X^1 to X^8 are selected from CR^{12} or N, and at least one of X^1 to X^8 is N, wherein R^{12} is hydrogen, alkyl, alkoxy, amino, alkenyl, alkynyl, aralkyl, heteroalkyl, aryl, or heteroaryl; Zi to Z_3 are a single bond, $C(R^{12})_2$, O, or S.

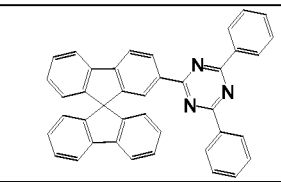
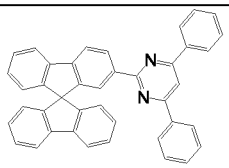
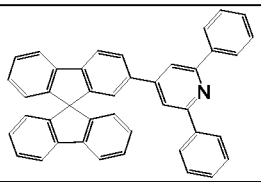
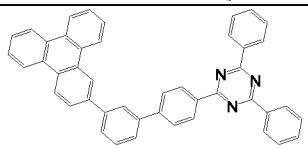
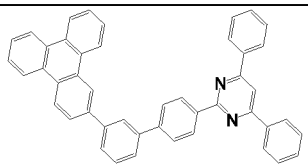
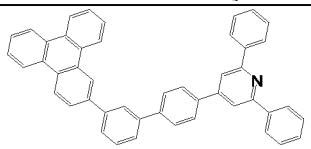
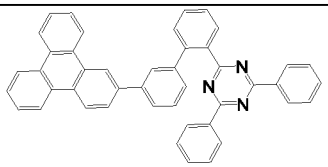
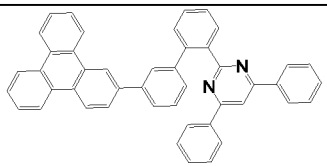
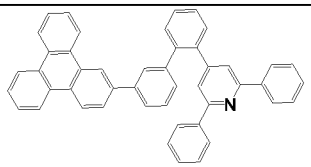
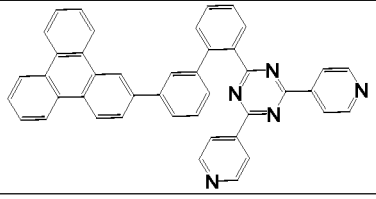
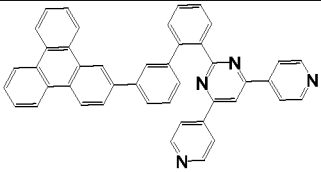
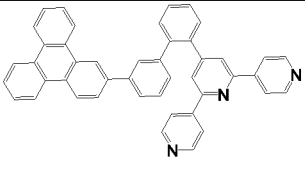
10. The polymer of any one of claims 6 and 8, wherein Ar comprises at least one of structural units as follows:

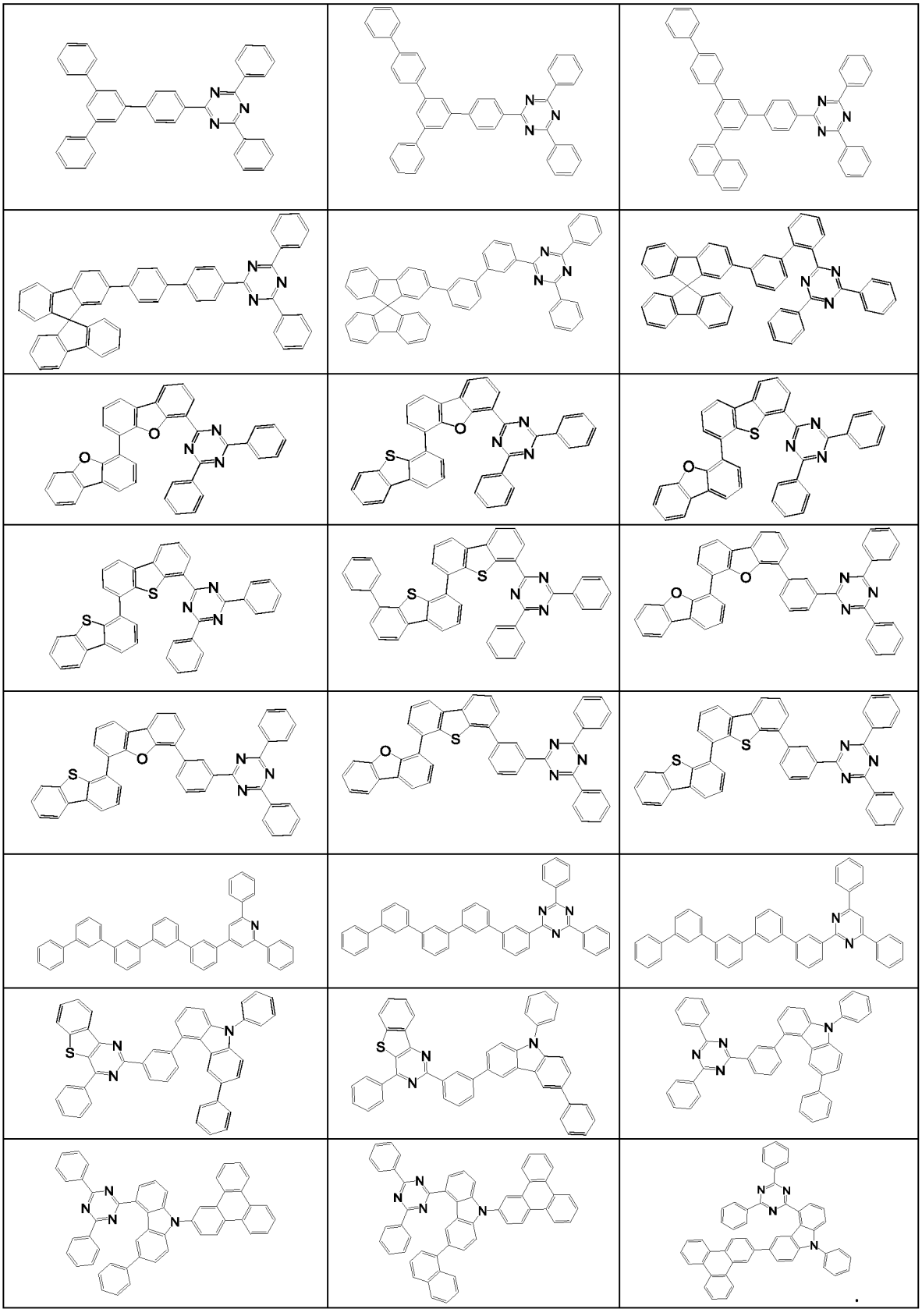




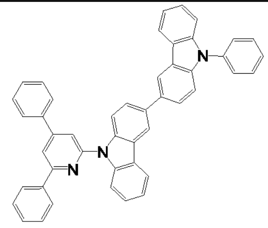
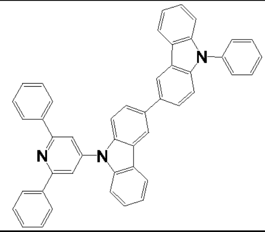
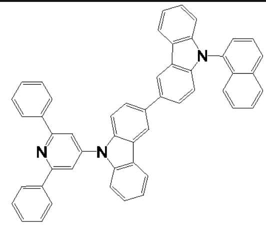
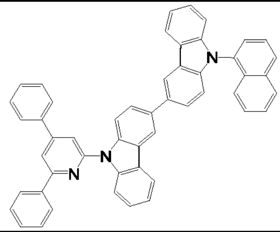
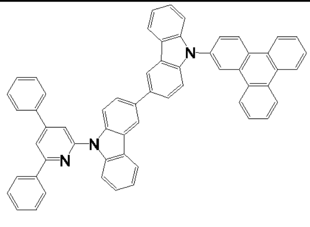
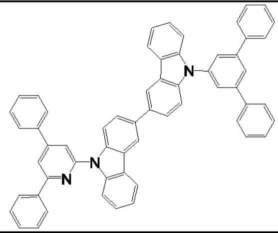
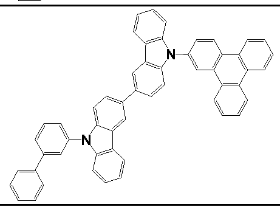
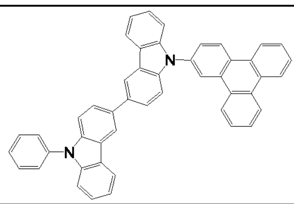
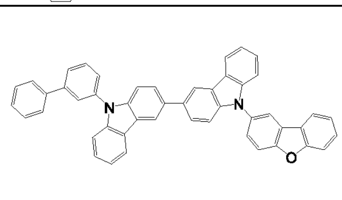
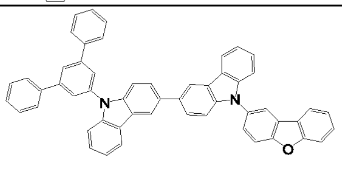
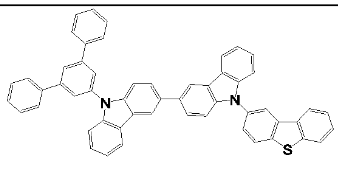
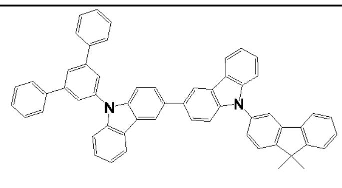
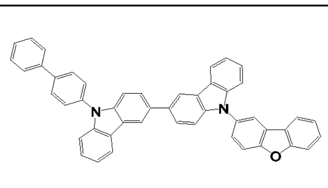
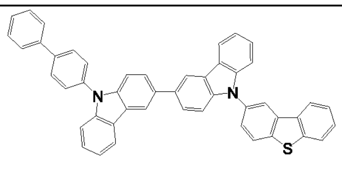
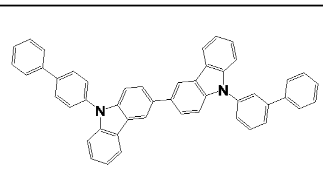
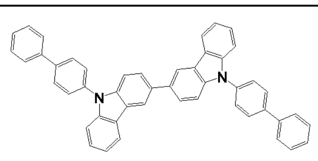
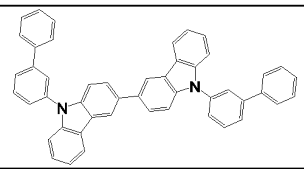
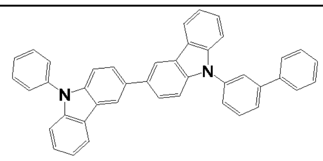
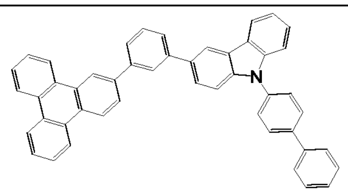
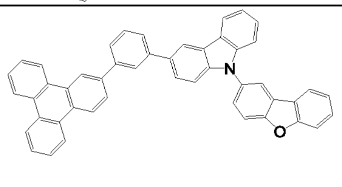
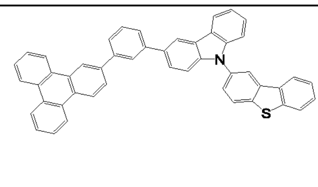
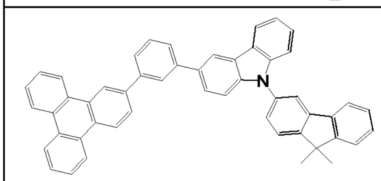
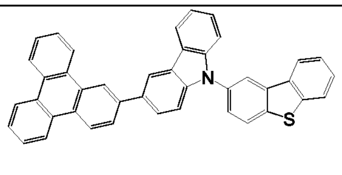
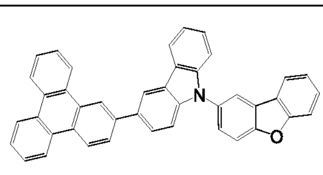
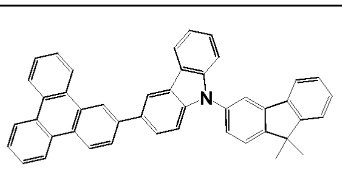
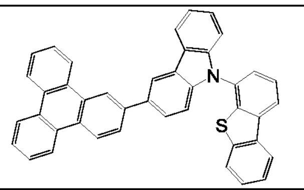
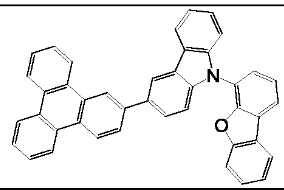
wherein n2 is 1, 2, 3, or 4.

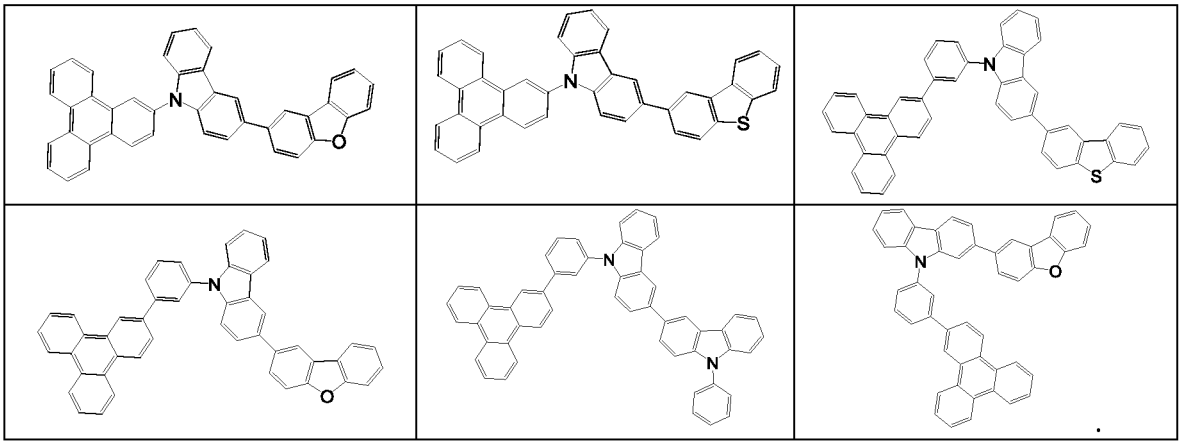
11. The polymer of any one of claims 1 to 10, wherein the E1 group comprises at least one of structural units containing the following structural formulas:



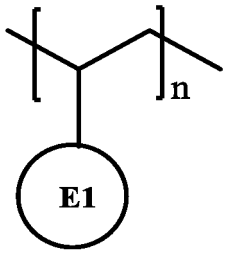
12. The polymer of any one of claims 1 to 11, wherein the E2 group comprises at least one of structural units containing the following structural formulas:



13. The polymer of any one of claims 1 to 12, further comprising at least one of a hole injection or transport group, a hole blocking group, an electron injection or transport group, an electron blocking group, an organic host group, a singlet emitter group (fluorescent emitter group), a triplet emitter group (phosphorescent emitter group), and a thermally activated delayed fluorescent (TADF) emitter group on a side chain thereof.

14. A polymer comprising a repeating unit represented by general formula (4):



general formula (4),

wherein, n is a natural number greater than or equal to 1, wherein E1 group is an electron-donating group, HOMO(E1)-(HOMO-1)(E1) ≥ 0.3 eV, wherein HOMO(El) is an energy level of a highest occupied molecular orbital of the E1 group, and (HOMO-1)(E1) is an energy level of a second highest occupied molecular orbital thereof.

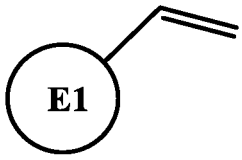
15. A mixture comprising a polymer of any one of claims 1 to 14, and further comprising at least one of a hole (also an electron hole) injection or transport material (HIM/HTM), a hole blocking material (HBM), an electron injection or transport material (EIM/ETM), an electron blocking material (EBM), an organic host material (Host), a singlet emitter (fluorescent emitter), a triplet emitter (phosphorescent emitter), and a TADF emitter.

16. A formulation comprising a polymer of any one of claims 1 to 14 and an organic solvent.

17. An organic electronic device comprising a polymer of any one of claims 1 to 14.

18. The organic electronic device of claim 17, wherein the organic electronic device is an organic light-emitting diode (OLED), an organic photovoltaic cell (OPV), an organic light-emitting cell (OLEEC), an organic field effect transistor (OFET), an organic light-emitting field effect transistor, an organic laser, an organic spin electron device, an organic sensor, or an organic plasmon emitting diode.

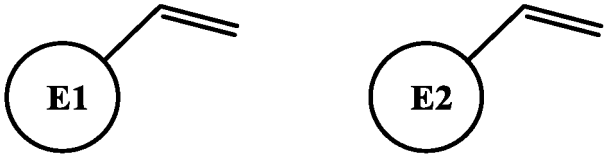
19. A monomer for polymerization comprising general formula (5):



general formula (5),

wherein (HOMO-(HOMO-1) of E1 group is greater than or equal to 0.3 eV, wherein HOMO is an energy level of a highest occupied molecular orbital of the E1 group, and HOMO-1 is an energy level of a second highest occupied molecular orbital of the E1 group.

20. A mixed monomer comprising a first monomer and a second monomer, the first monomer and the second monomer have general formula (5) and general formula (6), respectively:



wherein $\min((LUMO(E1)-HOMO(E2), LUMO(E2)-HOMO(El)) \leq \min(E_T(E1), E_T(E2))+0.1$ eV, wherein LUMO(E1), HOMO(E1), and $E_T(E1)$ are energy levels of a highest occupied molecular orbital, a lowest unoccupied molecular orbital, and a triplet excited state of E1 group, respectively; LUMO(E2), HOMO(E2), and $E_T(E2)$ are energy levels of a highest occupied molecular orbital, a lowest unoccupied molecular orbital, and a triplet excited state of E2 group, respectively.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2017/112716

A. CLASSIFICATION OF SUBJECT MATTER

H01L 51/50 (2006.01) i

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)

H01L 51/-

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)

CNPAT, WPI, EPODOC, STN: OLED, HOMO, LUMO, carbazole, exciplex, 有机发光二极管, 三线态, 咔唑, 能级, 激基络合物, 953414-49-8, 1187873-12-6

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	OTSUKI, Eiji et al. Vapor Deposition Polymerization of Vinyl Compounds and Fabrication of OLED Having Double Emmissive Layers. Thin Solid Films. 16 July 2009 (16.07.2009), 518(2), ISSN: 0040-6090, pages 703 to 706	14-19
X	US 2010171101 A1 (KONICA MINOLTA HOLDINGS INC.) 08 July 2010 (08.07.2010), description, paragraph [0063], and structural formulas 1-8	14-19
X	US 2010045171 A1 (KONICA MINOLTA HOLDINGS INC.) 25 February 2010 (25.02.2010), description, paragraph [0088], and structural formulas 1-5	14-19
X	US 2011084601 A1 (KONICA MINOLTA HOLDINGS INC.) 14 April 2011 (14.04.2011), description, paragraph [0171], and structural formulas 1-8	14-19

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&"document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
09 February 2018	22 February 2018
Name and mailing address of the ISA State Intellectual Property Office of the P. R. China No. 6, Xitucheng Road, Jimenqiao Haidian District, Beijing 100088, China Facsimile No. (86-10) 62019451	Authorized officer ZHENG, Kai Telephone No. (86-10) 53962195

Form PCT/ISA /210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2017/112716

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2009116414 X (KONICA MINOLTA HOLDINGS INC.) 21 July 2011 (21.07.2011), description, paragraph [0055], compound 9, and structural formulas 2-8	14-19
X	WO 2007119420 X (KONICA CORP. et al.) 27 August 2009 (27.08.2009), description, paragraph [0076], compound 12, and structural formulas H-1	14-19
A	CN 105679949 A (GUANGZHOU CHINARAY OPTOELECTRONIC MATERIALS LTD.) 15 June 2016 (15.06.2016), the description	1-20
A	CN 102270751 A (KUNSHAN VISIONOX DISPLAY TECHNOLOGY CO., LTD. et al.) 07 December 2011 (07.12.2011), the description	1-20

Form PCT/ISA /210 (continuation of second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2017/112716

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		JP WO2007119473 A1	27 August 2009
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US 2011084601 A1	14 April 2011	JP WO2010001830 A1	22 December 2011
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		WO 2007119420 A1	25 October 2007
		JP 5051125 B2	17 October 2012
CN 105679949 A	15 June 2016	None	
CN 102270751 A	07 December 2011	None	

Form PCT/ISA /210 (patent family annex) (July 2009)

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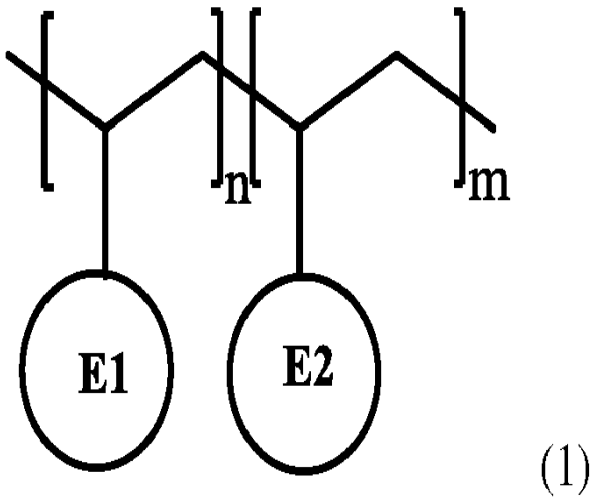
专利名称(译)	高聚物，含有该高聚物的混合物，组成，有机电子成分和聚合用单体		
公开(公告)号	EP3547384A1	公开(公告)日	2019-10-02
申请号	EP2017874343	申请日	2017-11-23
[标]申请(专利权)人(译)	广州华睿光电材料有限公司		
申请(专利权)人(译)	广州CHINARAY光电子材料有限公司.		
当前申请(专利权)人(译)	广州CHINARAY光电子材料有限公司.		
[标]发明人	PAN JUNYOU HUANG HONG		
发明人	PAN, JUNYOU HUANG, HONG		
IPC分类号	H01L51/50		
CPC分类号	H01L51/004 H01L51/0043 H01L51/0054 H01L51/0067 H01L51/0072 H01L51/0073 H01L51/0074 H01L51/0085 H01L51/5016 H01L2251/552 H01L51/50 C08G61/04 C08G2261/149 C08G2261/95 H01L51/0055		
优先权	201611047040.7 2016-11-23 CN		
其他公开文献	EP3547384A4		
外部链接	Espacenet		

摘要(译)

高分子聚合物，含有该高分子聚合物的混合物，组成，有机电子成分和聚合用单体。高聚物包括重复单元E1和重复单元E2。重复单元E1的侧链上的E1基团和重复单元E2的侧链上的E2基团具有形成复合物的特征，min（（（LUMO（E1）-HOMO（E2），LUMO（E2）-HOMO（E1））≤min（ET（E1），ET（E2））+ 0.1eV，因此提供了适用于印刷技术的高聚合物，从而降低了OLED的制造成本。



(1)