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(54) Title: POLYMERIC CHARGE TRANSFER LAYER AND ORGANIC ELECTRONIC DEVICE CONTAINING THE SAME

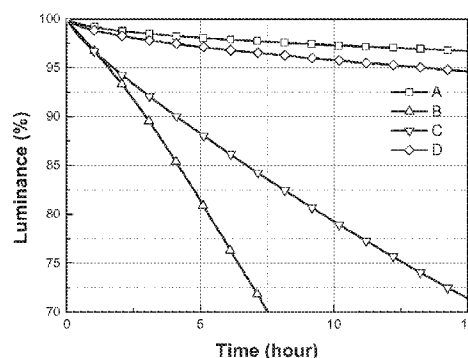


FIGURE 1

(57) Abstract: The present invention relates to a polymeric charge transfer layer comprising a polymer and a p-dopant. The polymer comprises as polymerized units, Monomer A, Monomer B, and Monomer C crosslinking agent. The present invention further relates to an organic electronic device, especially an organic light emitting device containing the polymeric charge transfer layer.

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POLYMERIC CHARGE TRANSFER LAYER AND ORGANIC ELECTRONIC DEVICE CONTAINING THE SAME

FIELD OF THE INVENTION

5 The present invention relates to a polymeric charge transfer layer comprising a polymer and a p-dopant. The polymer comprises as polymerized units, Monomer A, Monomer B, and Monomer C crosslinking agent. The present invention further relates to an organic electronic device, especially, a light emitting device containing the polymeric charge transfer layer.

INTRODUCTION

10 Organic electronic devices are devices that carry out electrical operations using at least one organic material. They are endowed with advantages such as flexibility, low power consumption, and relatively low cost over conventional inorganic electronic devices. Organic electronic devices usually include organic light emitting devices, organic solar cells, organic memory devices, organic sensors, organic thin film transistors, and power generation and storage devices such as organic batteries, fuel cells, and organic supercapacitors. Such organic electronic devices are prepared from hole injection or transportation materials, electron injection or transportation materials, or light emitting materials.

20 A typical organic light emitting device is an organic light emitting diode (OLED) having a multi-layer structure, and typically includes an anode, and a metal cathode. Sandwiched between the anode and the metal cathode are several organic layers such as a hole injection layer (HIL), a hole transfer layer (HTL), an emitting layer (EL), an electron transfer layer (ETL) and an electron injection layer (EIL). New material discovery for ETL and HTL in OLEDs have been targeted to improve device performance and lifetimes. In the case of HTL layer, as a typical polymeric charge transfer layer, the process by which the layer is deposited is critical for its end-use application. Methods for depositing HTL layer, in small display applications, involve evaporation of a small organic compound with a fine metal mask to direct the deposition. In the case of large displays, this approach is not practical from a material usage and high throughput perspective. With these findings in mind, new processes are needed to deposit HTLs that satisfy these challenges, and which can be directly applied to large display applications.

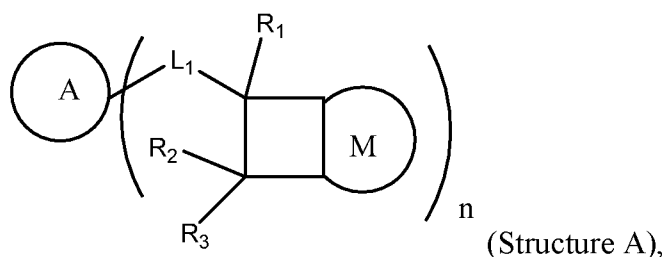
One approach that appears promising is a solution process which involves the deposition of a small molecule HTL material attached with crosslinking or polymerization moiety. Solution process based methods include spin-coating, inkjet printing, and screen printing which are well-known in the art. There have been extensive efforts in this area, along these lines; however, these approaches have their own shortcomings. In particular, the mobility of the charges in the HTL becomes reduced, as a result of crosslinking or polymerization chemistry. This reduced hole mobility leads to poor device lifetime.

Therefore, it is still desired to provide new polymeric charge transfer layer compositions for organic electronic devices, specifically for organic light emitting devices, organic solar cells, or organic memory devices with improved device lifetime.

SUMMARY OF THE INVENTION

The present invention provides a polymeric charge transfer layer, and an organic electronic device, especially a light emitting device comprising the polymeric charge transfer layer. The polymeric charge transfer layer is formed from a composition comprising, from 1wt% to 20wt% based on total weight of the composition, a p-dopant component; and a polymer comprising, as polymerized units, Monomer A, and Monomer C crosslinking agent.

Monomer A has Structure A:



wherein A and M are each substituted or unsubstituted aromatic moiety or a substituted or unsubstituted heteroaromatic moiety; and

wherein n is from 2 to 10; and

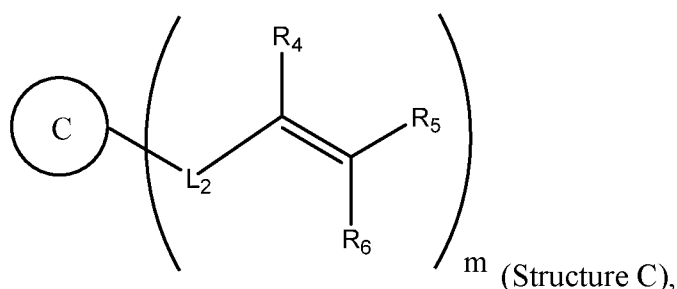
wherein R_1 through R_3 are each independently selected from the following: hydrogen; deuterium; a hydrocarbyl, further a C_1 - C_{100} hydrocarbyl, further a C_3 - C_{100} hydrocarbyl, further a C_{10} - C_{100} hydrocarbyl, further a C_{20} - C_{100} hydrocarbyl, further a C_{30} - C_{100} hydrocarbyl; a substituted hydrocarbyl, further a C_1 - C_{100} substituted hydrocarbyl, further a C_3 - C_{100} substituted hydrocarbyl, further a C_{10} - C_{100} substituted hydrocarbyl, further a C_{20} - C_{100} substituted hydrocarbyl, further a C_{30} - C_{100} substituted hydrocarbyl; a

heterohydrocarbyl, further a C₁-C₁₀₀ heterohydrocarbyl, further a C₃-C₁₀₀ heterohydrocarbyl, further a C₁₀-C₁₀₀ heterohydrocarbyl, further a C₂₀-C₁₀₀ heterohydrocarbyl, further a C₃₀-C₁₀₀ heterohydrocarbyl; a substituted heterohydrocarbyl, further a C₁-C₁₀₀ substituted heterohydrocarbyl, further a C₃-C₁₀₀ substituted heterohydrocarbyl, further a C₁₀-C₁₀₀ substituted heterohydrocarbyl, further a C₂₀-C₁₀₀ substituted heterohydrocarbyl, further a C₃₀-C₁₀₀ substituted heterohydrocarbyl; a halogen; a cyano; an aryl, further a C₅-C₁₀₀ aryl, further a C₆-C₁₀₀ aryl, further a C₁₀-C₁₀₀ aryl, further a C₂₀-C₁₀₀ aryl, further a C₃₀-C₁₀₀ aryl; a substituted aryl, further a C₅-C₁₀₀ substituted aryl, further a C₆-C₁₀₀ substituted aryl, further a C₁₀-C₁₀₀ substituted aryl, further a C₂₀-C₁₀₀ substituted aryl, further a C₃₀-C₁₀₀ substituted aryl; a heteroaryl, further a C₅-C₁₀₀ heteroaryl, further a C₆-C₁₀ heteroaryl, further a C₁₀-C₁₀₀ heteroaryl, further a C₂₀-C₁₀₀ heteroaryl, further a C₃₀-C₁₀₀ heteroaryl; a substituted heteroaryl, further a C₅-C₁₀₀ substituted heteroaryl, further a C₆-C₁₀₀ substituted heteroaryl, further a C₁₀-C₁₀₀ substituted heteroaryl, further a C₂₀-C₁₀₀ substituted heteroaryl, further a C₃₀-C₁₀₀ substituted heteroaryl; and

wherein L₁ is selected from a heteroatom, an aromatic moiety, a heteroaromatic moiety, a C₁-C₁₀₀ hydrocarbyl, a C₁-C₁₀₀ substituted hydrocarbyl, a C₁-C₁₀₀ heterohydrocarbyl, and a C₁-C₁₀₀ substituted heterohydrocarbyl; and

wherein two or more of R₁ through R₃ may optionally form one or more ring structures.

Monomer C crosslinking agent has Structure C:



wherein C is an aromatic moiety, a heteroaromatic moiety, a C₁-C₅₀ hydrocarbyl, a C₁-C₅₀ substituted hydrocarbyl, a C₁-C₅₀ heterohydrocarbyl, or a C₁-C₅₀ substituted heterohydrocarbyl; and

wherein R₄ through R₆ are each independently selected from the following: hydrogen, deuterium, a C₁-C₅₀ hydrocarbyl, a C₁-C₅₀ substituted hydrocarbyl, a C₁-C₅₀ heterohydrocarbyl, a C₁-C₅₀ substituted heterohydrocarbyl, halogen, cyano, a C₅-C₅₀ aryl, a C₅-C₅₀ substituted aryl, a C₅-C₅₀ heteroaryl, a C₅-C₅₀ substituted heteroaryl; and

wherein L_2 is selected from a heteroatom, an aromatic moiety, a heteroaromatic moiety, a C_1 - C_{100} hydrocarbyl, a C_1 - C_{100} substituted hydrocarbyl, a C_1 - C_{100} heterohydrocarbyl, or a C_1 - C_{100} substituted heterohydrocarbyl; and

wherein m is from 2 to 25; and

5 wherein each chemical group of L_2 is independently bonded to C ; and

wherein two or more of R_4 through R_6 may optionally form one or more ring structures.

The p-dopant is selected from tropylium salts, imidazolium salts, and trityl salts.

10 BRIEF DESCRIPTION OF THE DRAWING

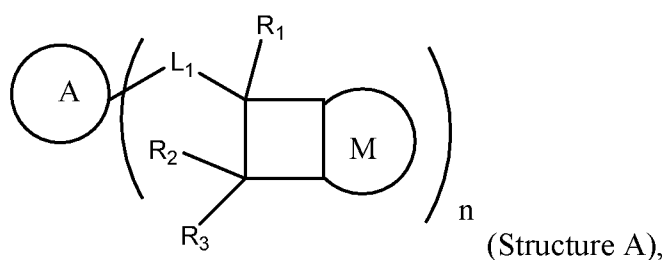
Figure 1 depicts the luminescence decay curves of OLED Devices A to D; OLED Devices A and D showed slower decay rates compared to those of OLED Devices B and C, and none of the OLED Devices A to D showed overshooting phenomena.

15 DETAILED DESCRIPTION OF THE INVENTION

The polymeric charge transfer layer composition of the present invention comprises from 1wt% to 20wt%, preferably from 3wt% to 15wt%, and more preferably from 5wt% to 12wt%, based on total weight of the composition, a p-dopant component, and a polymer comprising, as polymerized units, Monomer A, optional Monomer B, and
20 Monomer C crosslinking agents.

The Polymer

The polymer comprises Monomer A having a Structure A:



25 wherein A and M are each substituted or unsubstituted aromatic moiety or a substituted or unsubstituted heteroaromatic moiety; and

wherein n is from 2 to 10; and

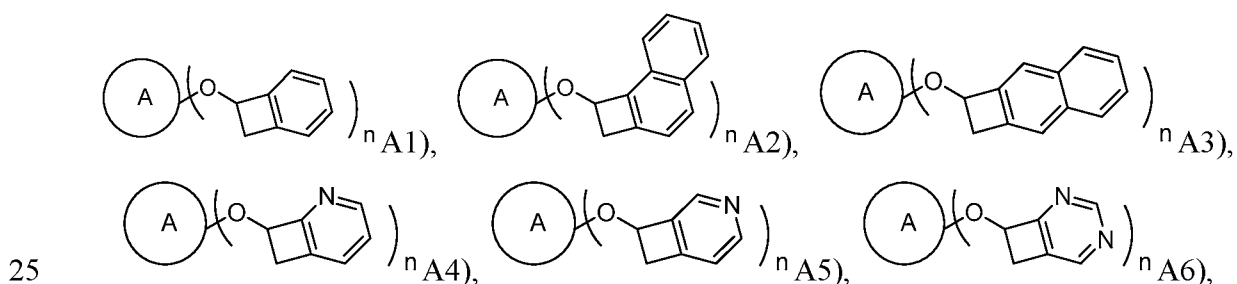
wherein R_1 through R_3 are each independently selected from the following:
hydrogen; deuterium; a hydrocarbyl, further a C_1 - C_{100} hydrocarbyl, further a C_3 - C_{100} hydrocarbyl, further a C_{10} - C_{100} hydrocarbyl, further a C_{20} - C_{100} hydrocarbyl, further a C_{30} -
30 C_{100} hydrocarbyl; a substituted hydrocarbyl, further a C_1 - C_{100} substituted hydrocarbyl,

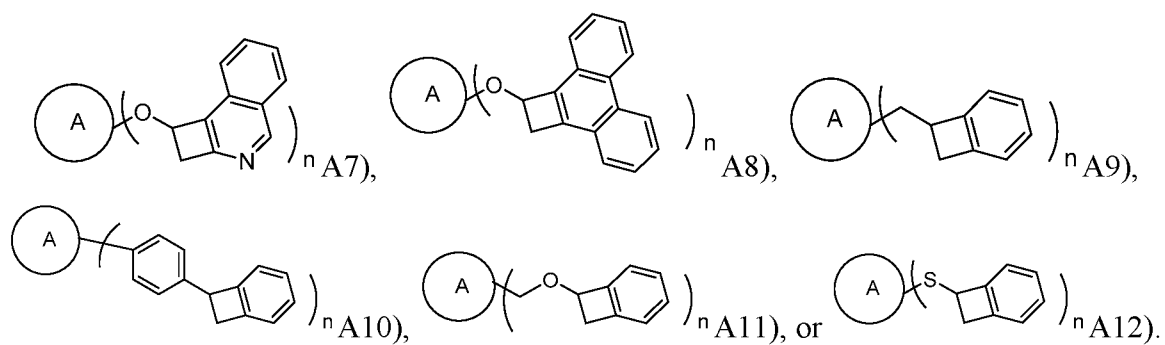
further a C₃-C₁₀₀ substituted hydrocarbyl, further a C₁₀-C₁₀₀ substituted hydrocarbyl, further a C₂₀-C₁₀₀ substituted hydrocarbyl, further a C₃₀-C₁₀₀ substituted hydrocarbyl; a heterohydrocarbyl, further a C₁-C₁₀₀ heterohydrocarbyl, further a C₃-C₁₀₀ heterohydrocarbyl, further a C₁₀-C₁₀₀ heterohydrocarbyl, further a C₂₀-C₁₀₀ heterohydrocarbyl, further a C₃₀-C₁₀₀ heterohydrocarbyl; a substituted heterohydrocarbyl, further a C₁-C₁₀₀ substituted heterohydrocarbyl, further a C₃-C₁₀₀ substituted heterohydrocarbyl, further a C₁₀-C₁₀₀ substituted heterohydrocarbyl, further a C₂₀-C₁₀₀ substituted heterohydrocarbyl, further a C₃₀-C₁₀₀ substituted heterohydrocarbyl; a halogen; a cyano; an aryl, further a C₅-C₁₀₀ aryl, further a C₆-C₁₀₀ aryl, further a C₁₀-C₁₀₀ aryl, further a C₂₀-C₁₀₀ aryl, further a C₃₀-C₁₀₀ aryl; a substituted aryl, further a C₅-C₁₀₀ substituted aryl, further a C₆-C₁₀₀ substituted aryl, further a C₁₀-C₁₀₀ substituted aryl, further a C₂₀-C₁₀₀ substituted aryl, further a C₃₀-C₁₀₀ substituted aryl; a heteroaryl, further a C₅-C₁₀₀ heteroaryl, further a C₆-C₁₀ heteroaryl, further a C₁₀-C₁₀₀ heteroaryl, further a C₂₀-C₁₀₀ heteroaryl, further a C₃₀-C₁₀₀ heteroaryl; a substituted heteroaryl, further a C₅-C₁₀₀ substituted heteroaryl, further a C₆-C₁₀₀ substituted heteroaryl, further a C₁₀-C₁₀₀ substituted heteroaryl, further a C₂₀-C₁₀₀ substituted heteroaryl, further a C₃₀-C₁₀₀ substituted heteroaryl; and

wherein L₁ is selected from a heteroatom, an aromatic moiety, a heteroaromatic moiety, a C₁-C₁₀₀ hydrocarbyl, a C₁-C₁₀₀ substituted hydrocarbyl, a C₁-C₁₀₀ heterohydrocarbyl, and a C₁-C₁₀₀ substituted heterohydrocarbyl; and

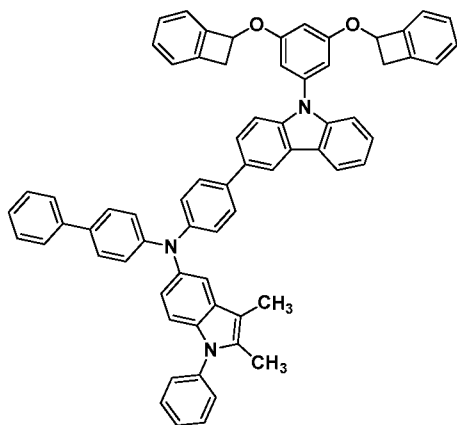
wherein two or more of R₁ through R₃ may optionally form one or more ring structures.

In one embodiment, Monomer A is selected from the following A1 through A12:

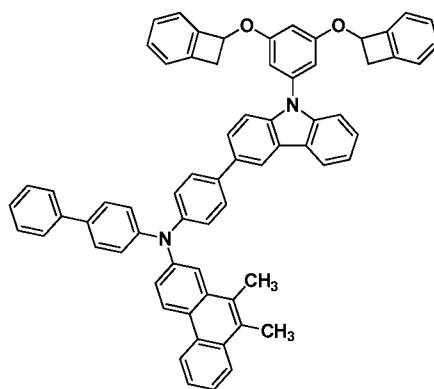




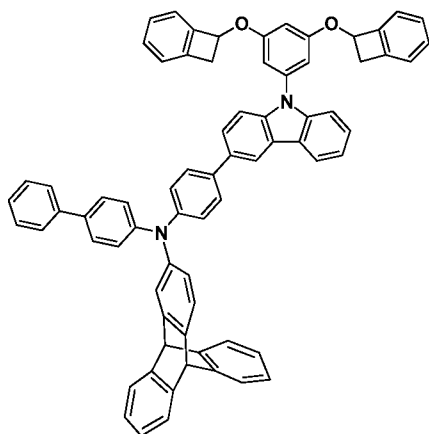
In one embodiment, Structure A is selected from the following A13 through A28:



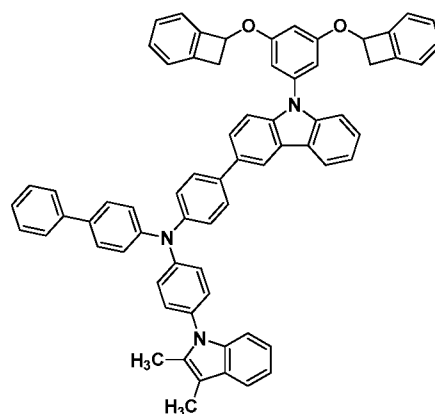
A13),



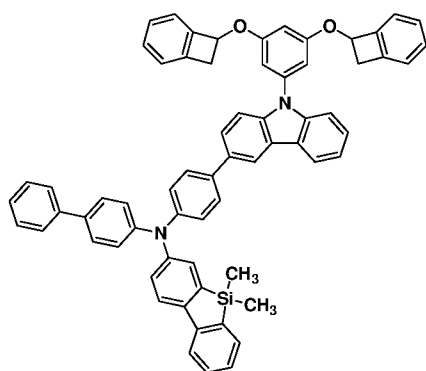
A14),

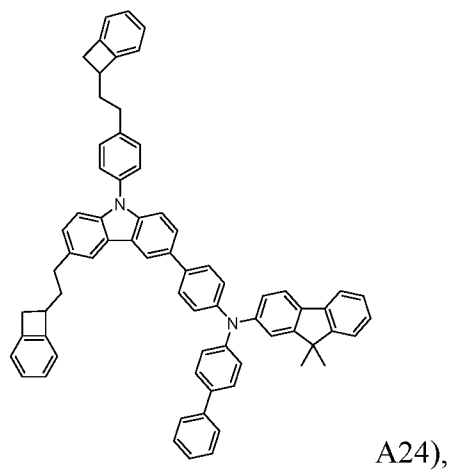
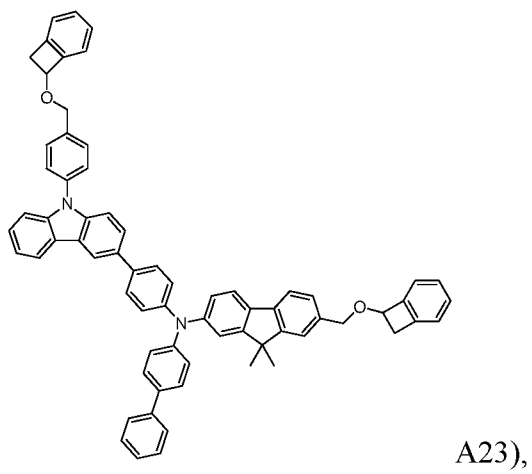
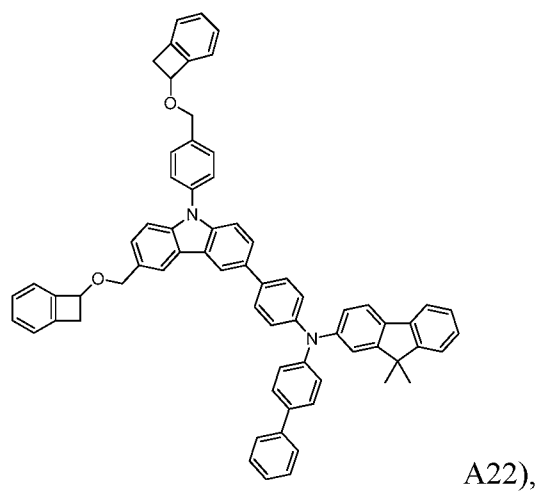
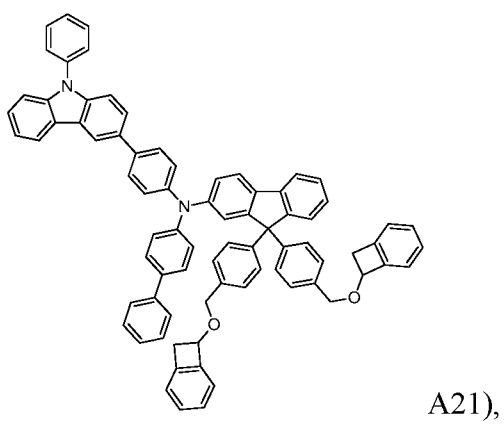
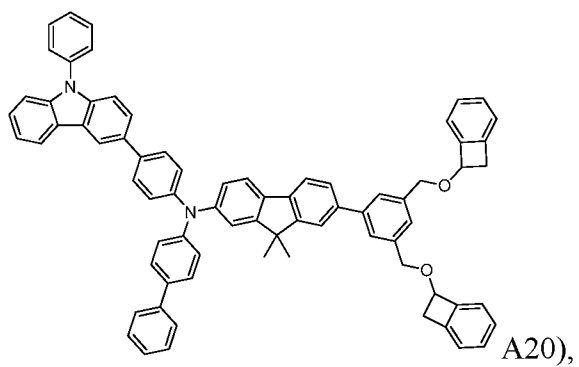
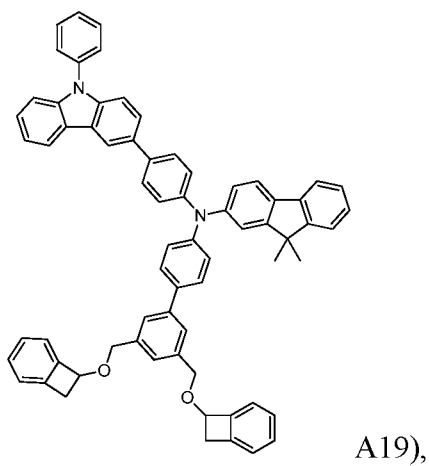


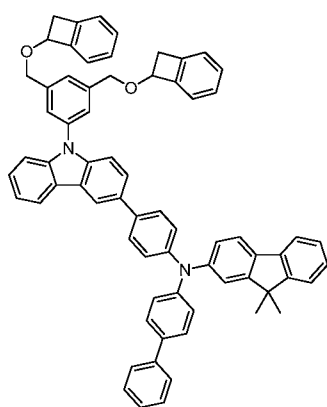
A15),



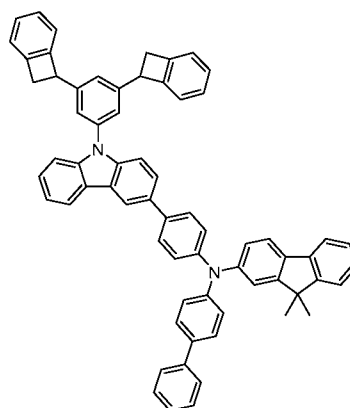
A16),



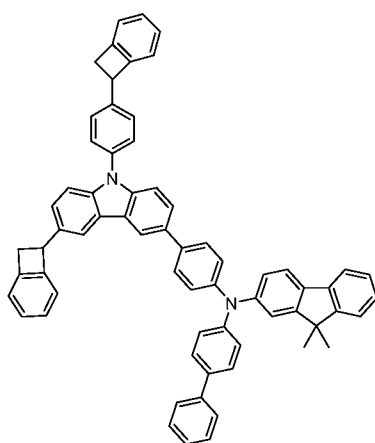




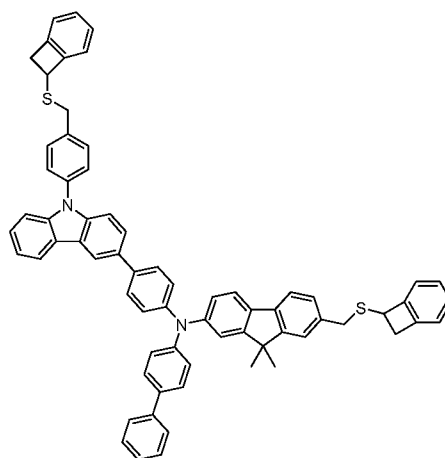
A25),



A26),

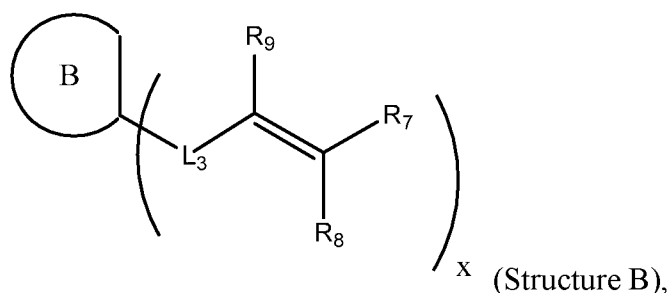


A27), or



A28).

Optionally, the polymer further comprises Monomer B comprising at least two dienophile moieties and has a Structure B:



5

wherein B is a substituted or unsubstituted aromatic moiety or a substituted or unsubstituted heteroaromatic moiety; and

wherein L₃ is selected from a heteroatom, an aromatic moiety, a heteroaromatic moiety, a C₁-C₁₀₀ hydrocarbyl, a C₁-C₁₀₀ substituted hydrocarbyl, a C₁-C₁₀₀ heterohydrocarbyl, and a C₁-C₁₀₀ substituted heterohydrocarbyl; and

10

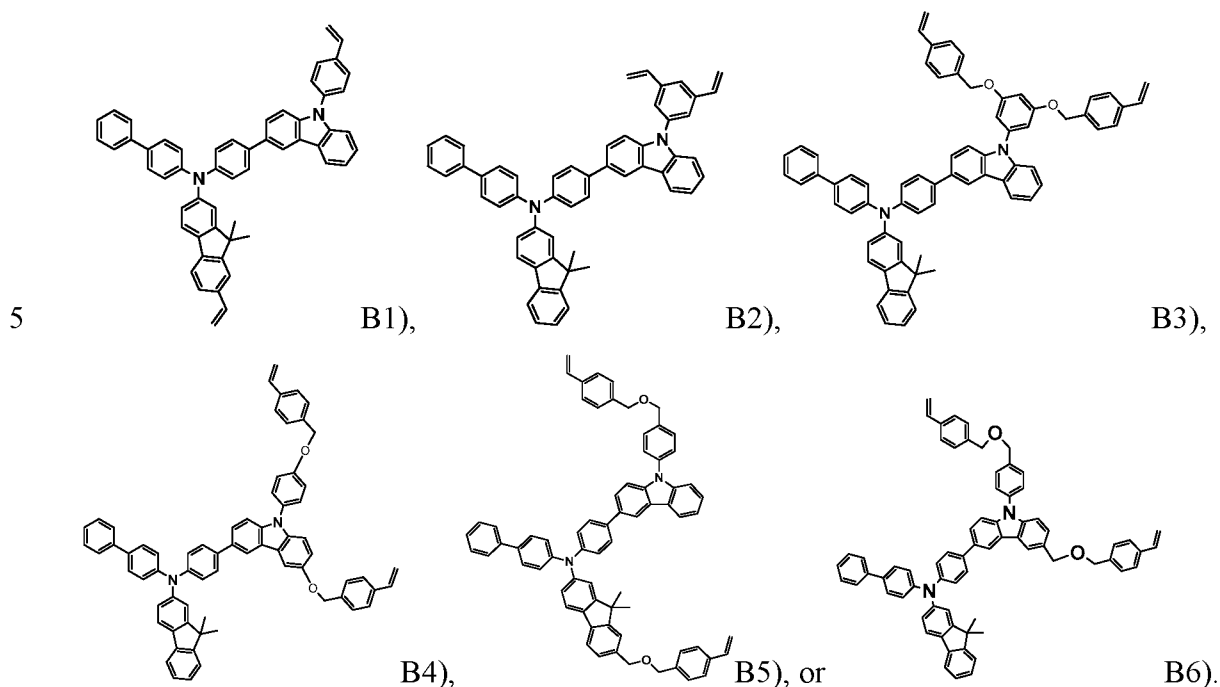
wherein x is from 2 to 10; and

wherein R₇ through R₉ are each independently selected from the following: hydrogen, deuterium, a C₁-C₅₀ hydrocarbyl, a C₁-C₅₀ substituted hydrocarbyl, a C₁-C₅₀ heterohydrocarbyl, a C₁-C₅₀ substituted heterohydrocarbyl, halogen, cyano, a C₅-C₅₀ aryl, a

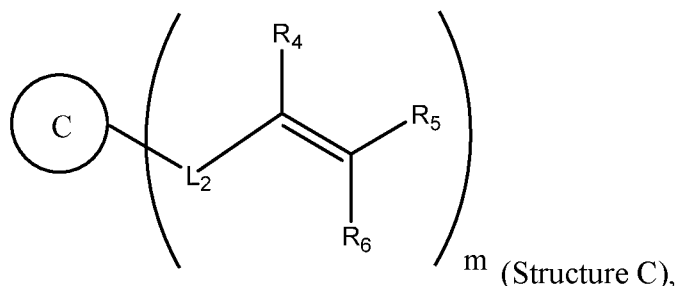
C₅-C₅₀ substituted aryl, a C₅-C₅₀ heteroaryl, and a C₅-C₅₀ substituted heteroaryl; and

wherein two or more of R₇ through R₉ may optionally form one or more ring structures.

In one embodiment, Monomer B is selected from the following B1 through B6:



The polymer further comprises Monomer C crosslinking agent having Structure C:



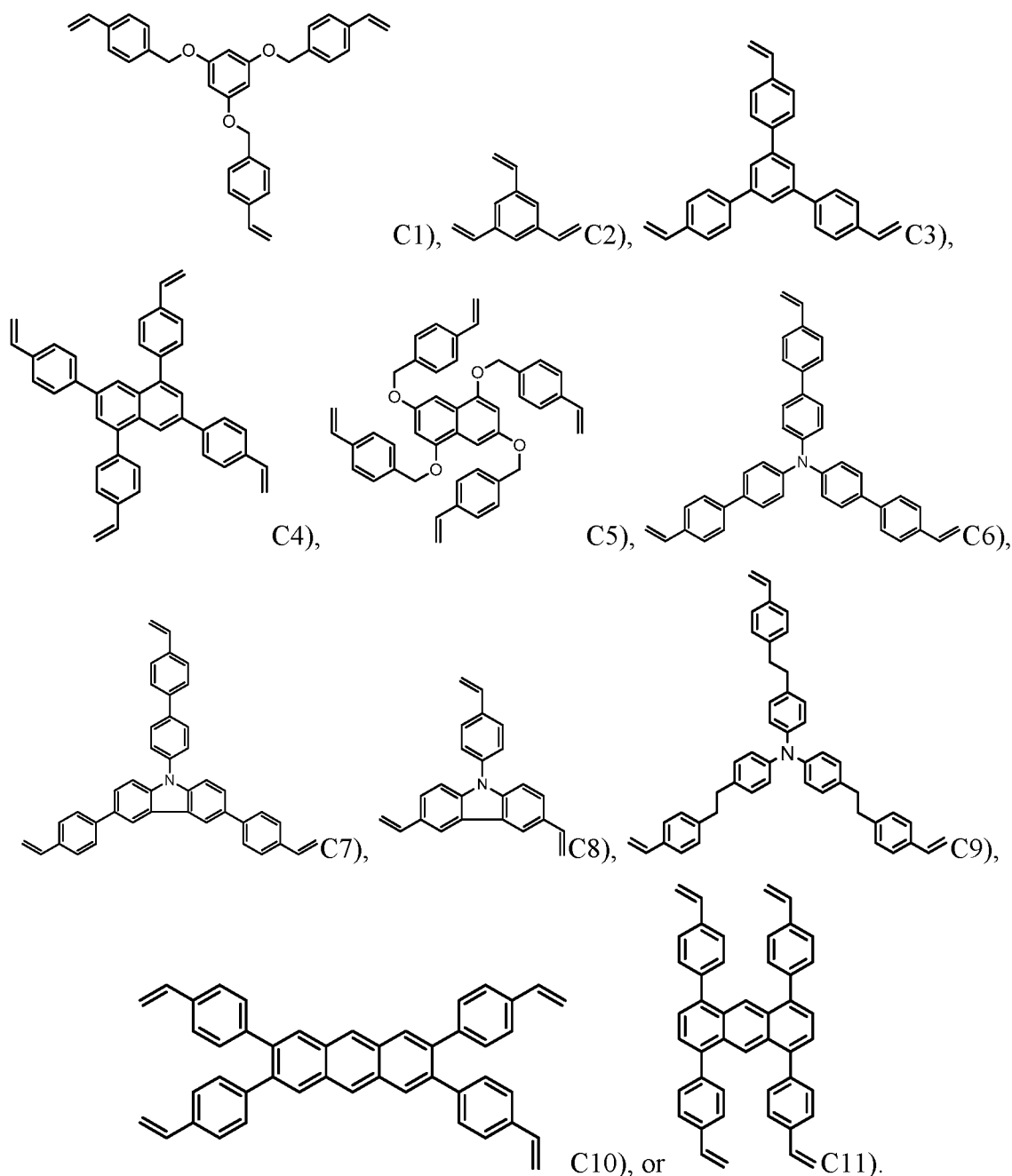
wherein C is an aromatic moiety, a heteroaromatic moiety, a C₁-C₅₀ hydrocarbyl, a C₁-C₅₀ substituted hydrocarbyl, a C₁-C₅₀ heterohydrocarbyl, or a C₁-C₅₀ substituted heterohydrocarbyl; and

wherein R₄ through R₆ are each independently selected from the following: hydrogen, deuterium, a C₁-C₅₀ hydrocarbyl, a C₁-C₅₀ substituted hydrocarbyl, a C₁-C₅₀ heterohydrocarbyl, a C₁-C₅₀ substituted heterohydrocarbyl, halogen, cyano, a C₅-C₅₀ aryl, a C₅-C₅₀ substituted aryl, a C₅-C₅₀ heteroaryl, a C₅-C₅₀ substituted heteroaryl; and

wherein L₂ is selected from a heteroatom, an aromatic moiety, a heteroaromatic moiety, a C₁-C₁₀₀ hydrocarbyl, a C₁-C₁₀₀ substituted hydrocarbyl, a C₁-C₁₀₀ heterohydrocarbyl, or a C₁-C₁₀₀ substituted heterohydrocarbyl; and

wherein m is from 2 to 25; and
 wherein each chemical group of L_2 is independently bonded to C; and
 wherein two or more of R_4 through R_6 may optionally form one or more ring structures.

5 In one embodiment, the crosslinking agent is selected from the following C1-C11:



10 In one embodiment, Monomer C crosslinking agent is present in an amount from 0.1 to 50mole%, preferably from 0.5 to 15mole%, and more preferably from 5 to 12mole% based on the sum moles of Monomer A (Structure A).

In one embodiment, the molar ratio of Monomer A to Monomer B is from 0.8 to

1.2, and preferably from 0.9 to 1.1.

In one embodiment, the molecule weight of either of Monomer A, Monomer B, and Monomer C is from 500g/mole to 28000g/mole, preferably from 700g/mole to 14000g/mole, and more preferably from 1000g/mole to 4000g/mole.

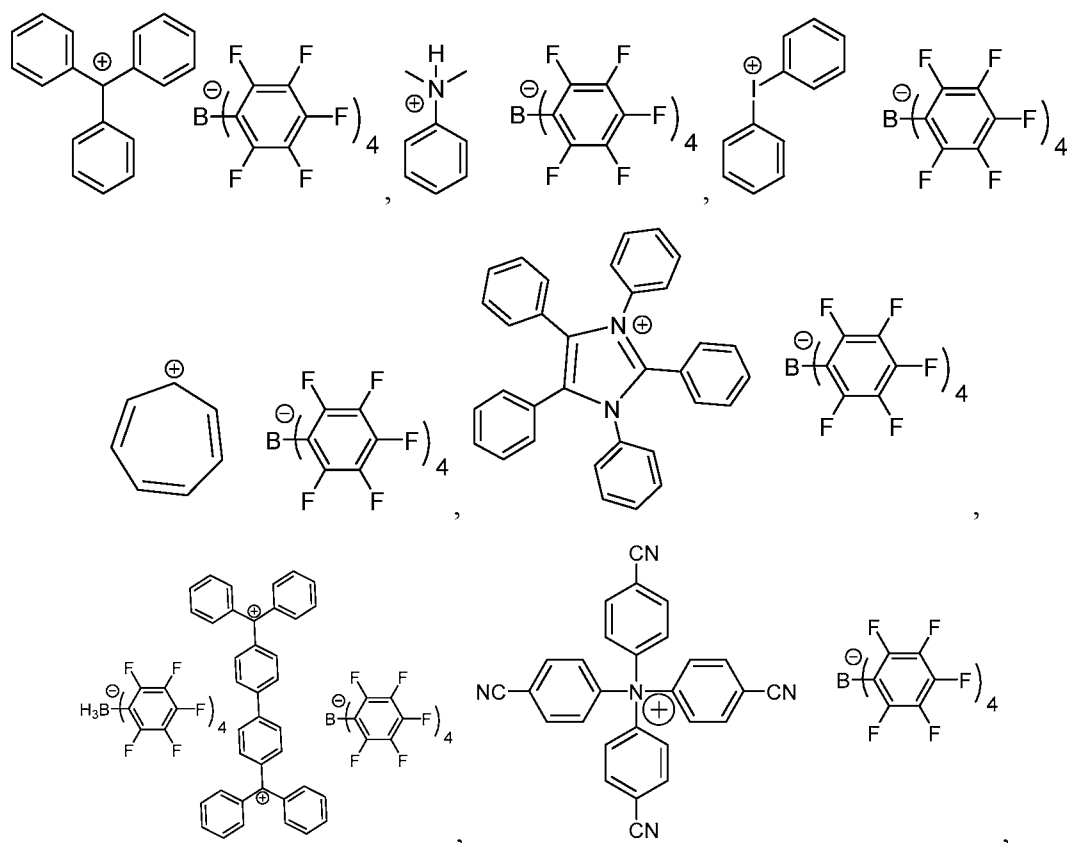
In one embodiment, the purity of either of Monomer A, Monomer B and Monomer C is equal to or above 99%, preferably is equal to or above 99.4%, and more preferably is equal to or above 99.5%. The said purify is achieved through well-known methods in the art to remove the impurities, and includes fractionation, sublimation, chromatography, crystallization and precipitation methods.

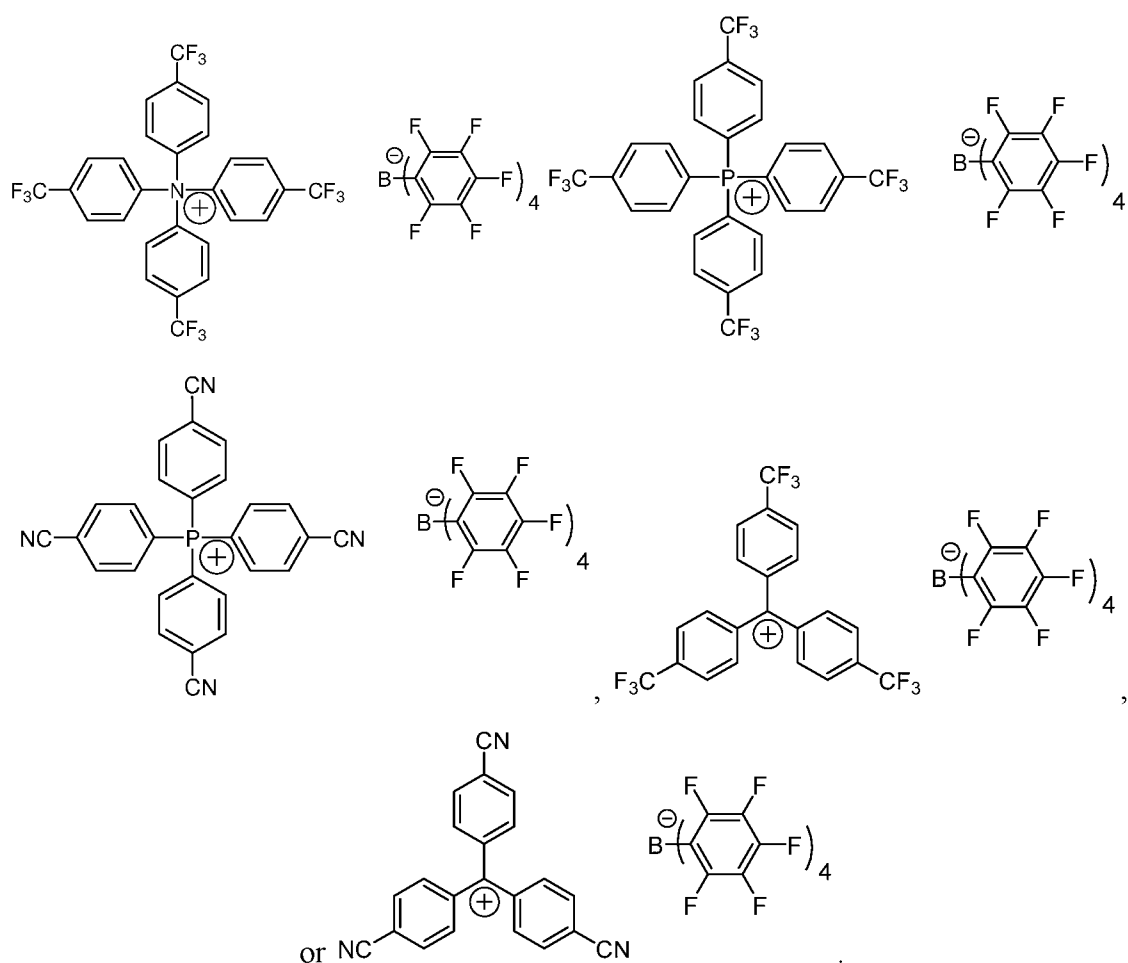
In one embodiment, either of Monomer A, Monomer B and Monomer C is further purified through ion exchange beads to remove cationic impurities and anionic impurities, such as metal ion, sulfate ion, formate ion, oxalate ion and acetate ion.

The P-DOPANT

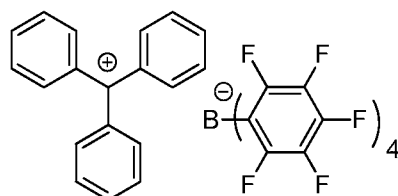
In one embodiment, the p-dopant is selected from tropylium salts, imidazolium salts, and trityl salts.

In yet another embodiment, the p-dopant has a structure selected from one of the following:





Preferably, the p-dopant has the structure:



5

ORGANIC ELECTRONIC DEVICE

The present invention provides a method of making an organic electronic device. The method comprises providing a polymeric charge transfer layer solution, and dissolving or dispersing the polymeric charge transfer layer solution in any of the organic solvents known or proposed to be used in the fabrication of an organic electronic device by solution process. Such organic solvents include including tetrahydrofuran (THF), cyclohexanone, chloroform, 1,4-dioxane, acetonitrile, ethyl acetate, tetralin, chlorobenzene, toluene, xylene, anisole, mesitylene, tetralone, and any combination thereof. The polymeric charge transfer layer solution was filtered through a membrane or a filter to remove particles larger than 50nm.

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The polymeric charge transfer layer solution is then deposited over a first electrode, which may be an anode or cathode. The deposition may be performed by any of various types of solution processing techniques known or proposed to be used for fabricating light emitting devices. For example, the polymeric charge transfer layer solution can be deposited using a printing process, such as inkjet printing, nozzle printing, offset printing, transfer printing, or screen printing; or for example, using a coating process, such as spray coating, spin coating, or dip coating. After deposition of the solution, the solvent is removed, which may be performed by using conventional method such as vacuum drying or heating.

The polymeric charge transfer layer solution is further cross-linked to form the layer. Cross-linking may be performed by exposing the layer solution to heat and/or actinic radiation, including UV light, gamma rays, or x-rays. Cross-linking may be carried out in the presence of an initiator that decomposed under heat or irradiation to produce free radicals or ions that initiate the cross-linking reaction. The cross-linking may be performed in-situ during the fabrication of a device. After cross-linking, the polymeric charge transfer layer made thereof is preferably free of residual moieties which are reactive or decomposable with exposure to light, positive charges, negative charges or excitons.

The process of solution deposition and cross-linking can be repeated to create multiple layers.

The organic light emitting device of the present invention comprises a first conductive layer, an electron transport layer (ETL) and a hole transport layer (HTL) and a second conductive layer. The hole transport layer, as the typical polymeric charge transfer layer, is prepared according to the above process. The first conductive layer is used as an anode and in general is a transparent conducting oxide, for example, fluorine-doped tin oxide, antimony-doped tin oxide, zinc oxide, aluminum-doped zinc oxide, indium tin oxide, metal nitride, metal selenide and metal sulfide. The second conductive layer is a cathode and comprises a conductive material. It is preferred that the material has a good thin film-forming property to ensure sufficient contact between the second conductive layer and hole transport layer to promote the electron injection under low voltage and provide better stability. For example, the material of the cathode can be a metal such as aluminum and calcium, a metal alloy such as magnesium/silver and aluminum/lithium, and any combination thereof. Moreover, an extremely thin film of lithium fluoride may be optionally placed between the cathode and the emitting layer. Lithium fluoride can

effectively reduce the energy barrier of injecting electrons from the cathode to the emitting layer. In addition, the emitting layer plays a very important role in the whole structure of the light emitting device. In addition to determining the color of the device, the emitting layer also has an important impact on the luminance efficiency in a whole.

- 5 Common luminescent materials can be classified as fluorescence and phosphorescence depending on the light emitting mechanism.

DEFINITIONS

The term “dienophile,” refers to a molecule that possesses 2 π -electrons, and which can participate in Diels-Alder cycloaddition reactions. Examples of this include
10 alkenes, alkynes, nitriles, enol ethers, and enamines.

The term “organic electronic device,” refers to a device that carries out an electrical operation with the presence of organic materials. Specific example includes organic light emitting devices, organic solar cells, organic memory devices, organic sensors, organic thin film transistors, and power generation and storage devices such as
15 organic batteries, fuel cells, and organic supercapacitors.

The term “organic light emitting device,” refers to a device that emits light when an electrical current is applied across two electrodes. Specific example includes light emitting diodes.

The term “polymeric charge transfer layer,” refers to a polymeric material that can
20 transport charge carrying moieties, either holes or electrons. Specific example includes hole transport layer.

The term “aromatic moiety,” refers to an organic moiety derived from aromatic hydrocarbon by deleting at least one hydrogen atom therefrom. An aromatic moiety may be a monocyclic and/or fused ring system, each ring of which suitably contains from 4 to
25 7, preferably from 5 or 6 atoms. Structures wherein two or more aromatic moieties are combined through single bond(s) are also included. Specific examples include phenyl, naphthyl, biphenyl, anthryl, indenyl, fluorenyl, benzofluorenyl, phenanthryl, triphenylenyl, pyrenyl, perylenyl, chrysenyl, naphhtaceny, and fluorantheny. The naphthyl may be 1-naphthyl or 2-naphthyl, the anthryl may be 1-anthryl, 2-anthryl or 9-anthryl, and the fluorenyl may be any one of 1-fluorenyl, 2-fluorenyl, 3-fluorenyl, 4-fluorenyl and 9-fluorenyl.
30

The term “heteroaromatic moiety,” refers to an aromatic moiety, in which at least one carbon atom or CH group or CH₂ group is substituted with a heteroatom or a chemical group containing at least one heteroatom. The heteroaromatic moiety may be a

5- or 6-membered monocyclic heteroaryl, or a polycyclic heteroaryl which is fused with one or more benzene ring(s), and may be partially saturated. The structures having one or more heteroaromatic moieties bonded through a single bond are also included. Specific examples include monocyclic heteroaryl groups, such as furyl, thiophenyl, pyrrolyl, imidazolyl, pyrazolyl, thiazolyl, thiadiazolyl, isothiazolyl, isoxazolyl, oxazolyl, oxadiazolyl, triazinyl, tetrazinyl, triazolyl, tetrazolyl, furazanyl, pyridyl, pyrazinyl, pyrimidinyl, pyridazinyl; polycyclic heteroaryl groups, such as benzofuranyl, fluoreno[4, 3-b]benzofuranyl, benzothiophenyl, fluoreno[4, 3-b]benzothiophenyl, isobenzofuranyl, benzimidazolyl, benzothiazolyl, benzisothiazolyl, benzisoxazolyl, benzoxazolyl, isoindolyl, indolyl, indazolyl, benzothia- diazolyl, quinolyl, isoquinolyl, cinnolinyl, quinazolinyl, quinoxalinyl, carbazolyl, phenanthridinyl and benzodioxolyl.

The term “hydrocarbyl,” refers to a chemical group containing only hydrogen and carbon atoms.

The term “substituted hydrocarbyl,” refers to a hydrocarbyl in which at least one hydrogen atom is substituted with a heteroatom or a chemical group containing at least one heteroatom.

The term “heterohydrocarbyl,” refers to a chemical group containing hydrogen and carbon atoms, and wherein at least one carbon atom or CH group or CH₂ group is substituted with a heteroatom or a chemical group containing at least one heteroatom.

The term “substituted heterohydrocarbyl,” refers to a heterohydrocarbyl in which at least one hydrogen atom is substituted with a heteroatom or a chemical group containing at least one heteroatom.

The term “aryl,” refers to an organic radical derived from aromatic hydrocarbon by deleting one hydrogen atom therefrom. An aryl group may be a monocyclic and/or fused ring system, each ring of which suitably contains from 4 to 7, preferably from 5 or 6 atoms. Structures wherein two or more aryl groups are combined through single bond(s) are also included. Specific examples include phenyl, naphthyl, biphenyl, anthryl, indenyl, fluorenyl, benzofluorenyl, phenanthryl, triphenylenyl, pyrenyl, perylenyl, chrysenyl, naphacenyl, and fluoranthenyl. The naphthyl may be 1-naphthyl or 2-naphthyl, the anthryl may be 1-anthryl, 2-anthryl or 9-anthryl, and the fluorenyl may be any one of 1-fluorenyl, 2-fluorenyl, 3-fluorenyl, 4-fluorenyl and 9-fluorenyl.

The term “substituted aryl,” refers to an aryl in which at least one hydrogen atom is substituted with a heteroatom or a chemical group containing at least one heteroatom.

The term “heteroaryl,” refers to an aryl group, in which at least one carbon atom or CH group or CH₂ group is substituted with a heteroatom or a chemical group containing at least one heteroatom. The heteroaryl may be a 5- or 6-membered monocyclic heteroaryl or a polycyclic heteroaryl which is fused with one or more benzene ring(s), and may be partially saturated. The structures having one or more heteroaryl group(s) bonded through a single bond are also included. The heteroaryl groups may include divalent aryl groups of which the heteroatoms are oxidized or quaternized to form *N*-oxides, quaternary salts, or the like. Specific examples include, but are not limited to, monocyclic heteroaryl groups, such as furyl, thiophenyl, pyrrolyl, imidazolyl, pyrazolyl, thiazolyl, thiadiazolyl, isothiazolyl, isoxazolyl, oxazolyl, oxadiazolyl, triazinyl, tetrazinyl, triazolyl, tetrazolyl, furazanyl, pyridyl, pyrazinyl, pyrimidinyl, pyridazinyl; polycyclic heteroaryl groups, such as benzofuranyl, fluoreno[4, 3-*b*]benzofuranyl, benzothiophenyl, fluoreno[4, 3-*b*]benzothiophenyl, isobenzofuranyl, benzimidazolyl, benzothiazolyl, benzisothiazolyl, benzisoxazolyl, benzoxazolyl, isoindolyl, indolyl, indazolyl, benzothiadiazolyl, quinolyl, isoquinolyl, cinnolinyl, quinazolinyl, quinoxalinyl, carbazolyl, phenanthridinyl and benzodioxolyl; and corresponding *N*-oxides (for example, pyridyl *N*-oxide, quinolyl *N*-oxide) and quaternary salts thereof.

The term “substituted heteroaryl,” refers to a heteroaryl in which at least one hydrogen atom is substituted with a heteroatom or a chemical group containing at least one heteroatom.

Heteroatoms include O, N, P, P(=O), Si, B and S.

The term “polymer,” refers to a polymeric compound prepared by polymerizing monomers, whether of the same or a different type. The generic term polymer thus embraces the term homopolymer (employed to refer to polymers prepared from only one type of monomer, with the understanding that trace amounts of impurities can be incorporated into and/or within the polymer structure), and the term interpolymer as defined hereinafter.

The term “interpolymer,” refers to polymers prepared by the polymerization of at least two different types of monomers. The generic term interpolymer thus includes copolymers (employed to refer to polymers prepared from two different types of monomers), and polymers prepared from more than two different types of monomers.

EXAMPLES

I. Reagents and Test Methods

All solvents and reagents were obtained from commercial vendors, for example, Sigma-Aldrich, TCI, and Alfa Aesar, and were used in the highest available purities, and/or when necessary, recrystallized before use. Dry solvents were obtained from in-house purification/dispensing system (hexane, toluene, and tetrahydrofuran), or purchased from Sigma-Aldrich. All experiments involving “water sensitive compounds” were conducted in “oven dried” glassware, under nitrogen atmosphere, or in a glovebox.

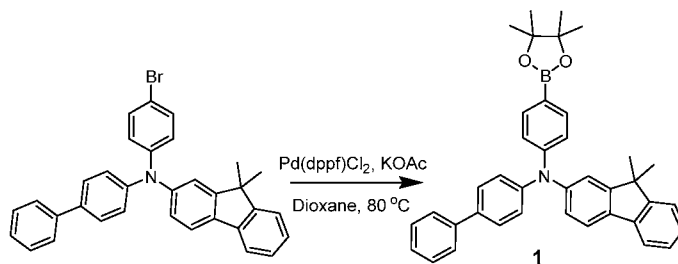
¹H-NMR-spectra (500MHz or 400MHz) was obtained on a Varian VNMRS-500 or VNMRS-400 spectrometer, at 30°C, unless otherwise noted. The chemical shifts were referenced to tetramethylsilane (TMS, $\delta=0.00$) in CDCl₃.

Routine liquid chromatography/mass spectrometry (LC/MS) studies were carried out as follows. One microliter aliquots of the sample, as “1mg/ml solution in tetrahydrofuran (THF),” were injected on an Agilent 1200SL binary liquid chromatography (LC), coupled to an Agilent 6520 quadruple time-of-flight (Q-TOF) MS system, via a dual electrospray interface (ESI), operating in the PI mode. The following analysis conditions were used: Column: Agilent Eclipse XDB-C18, 4.6*50mm, 1.7 μ m; Column oven temperature: 30°C; Solvent A: THF; Solvent B: 0.1% formic acid in water/Acetonitrile (v/v, 95/5); Gradient: 40-80% Solvent A in 0-6min, and held for 9min; Flow: 0.3mL/min; UV detector: diode array, 254nm; MS condition: Capillary Voltage: 3900kV (Neg), 3500kV (Pos); Mode: Neg and Pos; Scan: 100-2000amu; Rate: 1s/scan; Desolvation temperature: 300°C.

Gel permeation chromatography (GPC) studies were carried out as follows. 2mg of B-staged HTL polymer was dissolved in 1mL THF. The solution was filtrated through a 0.20 μ m polytetrafluoroethylene (PTFE) syringe filter and 50 μ l of the filtrate was injected to the GPC system. The following analysis conditions were used: Pump: Waters™ e2695 Separations Modules at a nominal flow rate of 1.0mL/min; Eluent: Fisher Scientific HPLC grade THF (unstabilized); Injector: Waters e2695 Separations Modules; Columns: two 5 μ m mixed-C columns from Polymer Laboratories Inc., held at 40°C; Detector: Shodex RI-201 Differential Refractive Index (DRI) Detector; Calibration: 17 polystyrene standard materials from Polymer Laboratories Inc., fit to a 3rd order polynomial curve over the range of 3,742kg/mol to 0.58 kg/mol.

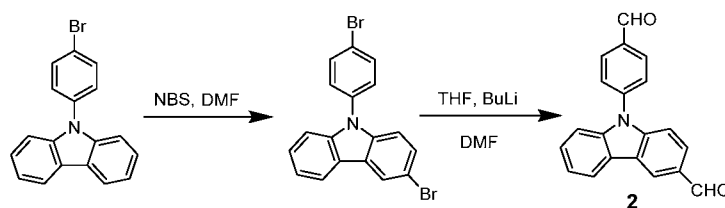
II. Examples

1. Synthesis of N-([1,1'-biphenyl]-4-yl)-9,9-dimethyl-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-fluoren-2-amine (Formula 1)



A mixture of N-([1,1'-biphenyl]-4-yl)-N-(4-bromophenyl)-9,9-dimethyl-9H-fluoren-2-amine (15.48g, 30mmol), 4,4,4',4',5,5,5',5'-octamethyl -2,2'-bi(1,3,2-dioxaborolane) (9.14g, 36mmol), Pd(dppf)₂Cl₂ (571mg, 0.75mmol), CH₃COOK (4.41g, 45mmol), and 60mL of dry dioxane were heated at 85°C under nitrogen atmosphere for 12h. After cooling to room temperature, solvent was removed under vacuum and then water was added. The mixture was extracted with CH₂Cl₂. The organic phase was collected and dried over anhydrous sodium sulphate. After filtration, the filtrate was evaporated to remove solvent and the residue was purified through column chromatography on silica gel to give white solid (84% yield). The product had the following characteristic: MS (ESI): 564.30 [M+H]⁺. ¹H-NMR (CDCl₃, 400MHz, TMS, ppm): δ 7.65 (d, 2H), 7.59 (d, 2H), 7.50 (d, 2H), 7.40 (m, 8H), 7.17 (m, 3H), 7.05 (m, 3H), 1.42 (s, 6H), 1.38 (s, 12H).

2. Synthesis of 9-(4-formylphenyl)-9H-carbazole-3-carbaldehyde (Formula 2)

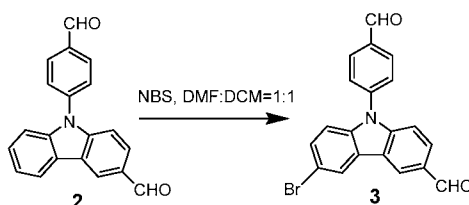


To a solution of 9-(4-bromophenyl)-9H-carbazole (32.2g, 100mmol) in 150mL dimethyl formamide (DMF), N-bromosuccinimide (NBS) (17.8g, 100mmol) in 100mL DMF was added dropwise in 30min. After addition, the mixture was stirred at room temperature for 12h and then poured into water to precipitate. The solid was filtrated and recrystallized from dichloromethane and ethanol to give white solid (92% yield) and used for the next step. The product had the following characteristic: MS (ESI): 402.09 [M+H]⁺.

To a solution of 3-bromo-9-(4-bromophenyl)-9Hcarbazole (8.02g, 20mmol) in THF (500mL), *n*-BuLi (24mL of a 2.5M solution in hexanes, 60mmol) was added at a rate to keep the internal temperature below -78°C. The mixture was stirred at -78°C for

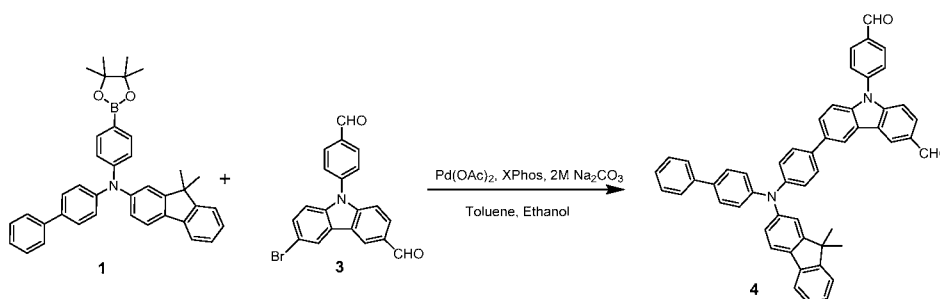
1h and 10mL DMF with 10mL THF were added dropwise. After the addition, the reaction mixture was stirred at -45°C for 30min and at 0°C for an additional 30min. Saturated aqueous NH_4Cl (400mL) was added and the organic solvent was evaporated. The residue was extracted with CH_2Cl_2 (2 x 100mL) and the combined organic phase was dried over anhydrous MgSO_4 . After removing solvent, the crude product was purified through column chromatography to give crude product (65% yield). The product had the following characteristics: MS (ESI): 300.09 $[\text{M}+\text{H}]^+$. $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, TMS, ppm): δ 10.15 (s, 1H), 10.13 (s, 1H), 8.67 (s, 1H), 8.23 (d, 1H), 8.17 (d, 2H), 7.99 (d, 1H), 7.80 (d, 2H), 7.54 (m, 3H), 7.40 (m, 1H).

3. Synthesis of 6-bromo-9-(4-formylphenyl)-9H-carbazole-3-carbaldehyde (Formula 3)



To a solution of Formula 2 chemical (0.898g, 3mmol) in CH_2Cl_2 (20mL) and DMF (20mL), NBS (0.587mg, 3.3mmol) was added in portion. After stirred for 4h, the precipitates formed was filtered and washed with DMF and CH_2Cl_2 for several times to afford the crude product (84% yield). The product had the following characteristic: MS (ESI): 378.01 $[\text{M}+\text{H}]^+$. (Fail to get $^1\text{H-NMR}$ data due to low solubility).

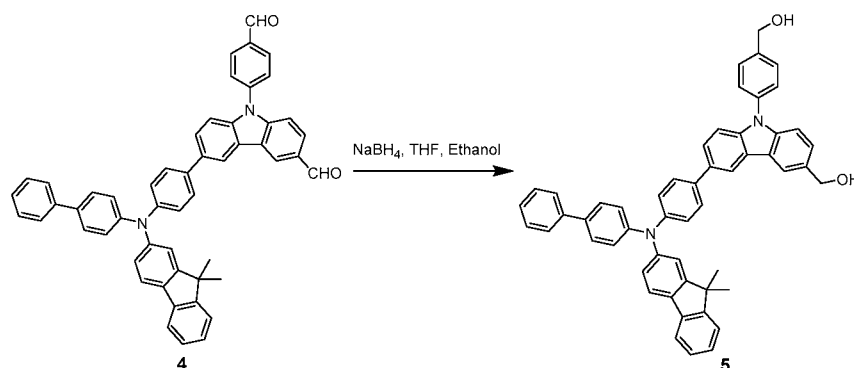
4. Synthesis of 6-(4-([1,1'-biphenyl]-4-yl(9,9-dimethyl-9H-fluoren-2-yl)amino)phenyl)-9-(4-formylphenyl)-9H-carbazole-3-carbaldehyde (Formula 4)



To a mixture of Formula 3 chemical (0.756g, 2mmol), Formula 1 chemical (1.24g, 2.2mmol), $\text{Pd}(\text{OAc})_2$ (12.8mg, 0.06mmol) and X-Phos (28.6mg, 0.06mmol), 20mL mixed solvents with proportion of 1:1:2 mixture of 2.0M Na_2CO_3 :Ethanol:toluene were added under flow of nitrogen. The reaction mixture was stirred overnight under nitrogen atmosphere at 90°C . After evaporation of toluene and ethanol, water was added and the mixture was extracted with CH_2Cl_2 (2 x 30mL) and the combined organic phase was

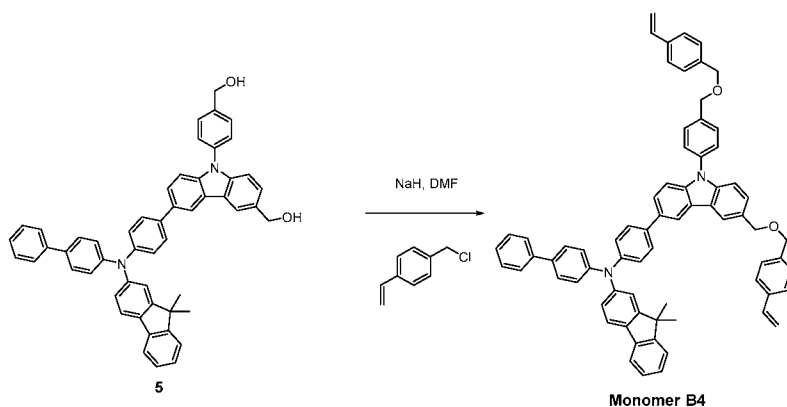
dried over MgSO_4 . The solvent was removed under reduced pressure and the residue was purified through column chromatography on silica gel to give yellow solid (64% yield). The product had the following characteristics: MS (ESI): 735.29 $[\text{M}+\text{H}]^+$. ^1H -NMR (CDCl_3 , 400 MHz, TMS, ppm): δ 10.12 (s, 1H), 10.09 (s, 1H), 8.36 (s, 1H), 8.20 (d, 1H), 7.64 (m, 12H), 7.53 (m, 2H), 7.42 (m, 6H), 7.32 (m, 7H), 7.15 (d, 1H), 4.88 (s, 2H), 4.85 (s, 2H), 1.45 (s, 6H).

5. Synthesis of (4-(3-(4-([1,1'-biphenyl]-4-yl)(9,9-dimethyl-9H-fluoren-2-yl)amino)phenyl)-6-(hydroxymethyl)-9H-carbazol-9-yl)phenyl)methanol (Formula 5)



To a solution of Formula 4 chemical (734mg, 1mmol) in 10mL THF and 10mL ethanol at 40°C , NaBH_4 (302mg, 8mmol) was added under nitrogen atmosphere. The solution was allowed to stir at room temperature for 2h. Then, aqueous hydrochloric acid solution was added until pH 5 and the mixture was kept stirring for 30min. The solvent was removed under vacuum and the residue was extracted with dichloromethane. The product was then dried under vacuum and used for the next step without further purification (95% yield). The product had the following characteristics: MS (ESI): 739.32 $[\text{M}+\text{H}]^+$. ^1H -NMR (CDCl_3 , 400 MHz, TMS, ppm): δ 8.36 (s, 1H), 8.20 (d, 1H), 7.64 (m, 12H), 7.53 (m, 2H), 7.42 (m, 6H), 7.32 (m, 7H), 7.15 (d, 1H), 4.88 (s, 2H), 4.85 (s, 2H), 3.74 (m, 2H), 1.45 (s, 6H).

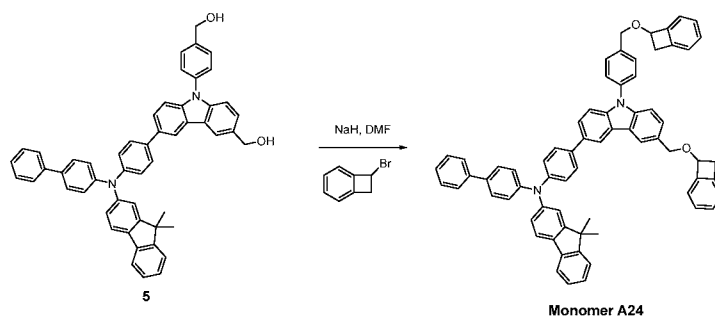
6. Synthesis of Monomer B chemical, N-([1,1'-biphenyl]-4-yl)-9,9-dimethyl-N-(4-(6-(((4-vinylbenzyl)oxy)methyl)-9-(4-(((4-vinylbenzyl)oxy)methyl)phenyl)-9H-carbazol-3-yl)phenyl)-9H-fluoren-2-amine (99.6% purity)



To a solution of Formula **5** chemical (3.69g, 5mmol) in 50mL dry DMF was added NaH (432mg, 18mmol), the mixture was stirred at room temperature for 1h. And 1-(chloromethyl)-4-vinylbenzene (2.75g, 15mmol) was added to above solution via syringe.

5 The mixture was heated to 60°C overnight. After quenched with water, the mixture was poured into water to remove DMF. The residue was filtrated and the resulting solid was dissolved with dichloromethane, which was then washed with water. The solvent was removed under vacuum and the residue was extracted with dichloromethane. The product was then obtained by column chromatography on silica gel (55% yield). The product had the following characteristics: MS (ESI): 943.42 [M+H]⁺. ¹H-NMR (CDCl₃, 400 MHz, TMS, ppm): δ 8.35 (s, 1H), 8.17 (d, 1H), 7.62 (m, 12H), 7.42 (m, 14H), 7.29 (m, 10H), 6.72 (dd, 2H), 5.77 (d, 2H), 5.24 (d, 2H), 4.74 (s, 2H), 4.67 (s, 4H), 4.60 (s, 2H), 1.45 (s, 6H).

15 7. Synthesis of Monomer A chemical, N-([1,1'-biphenyl]-4-yl)-N-(4-(6-((bicyclo[4.2.0]octa-1(6),2,4-trien-7-yloxy)methyl)-9-(4-((bicyclo[4.2.0]octa-1(6),2,4-trien-7-yloxy)methyl)phenyl)-9H-carbazol-3-yl)phenyl)-9,9-dimethyl-9H-fluoren-2-amine (99.6% purity)



20 To a solution of Formula **5** chemical (3.69g, 5mmol) in 50mL dry DMF was added NaH (432mg, 18mmol), the mixture was stirred at room temperature for 1h. And 7-bromobicyclo[4.2.0]octa-1,3,5-triene (Br-BCB) (2.75g, 15mmol) was added to above solution via syringe. The mixture was heated to 60°C and stirred overnight. After

quenched with water, the mixture was poured into water to remove DMF. The residue was filtrated and the resulting solid was dissolved with dichloromethane, which was then washed with water. The solvent was removed under vacuum and the residue was extracted with dichloromethane. The product was then obtained by column chromatography on silica gel (65% yield). The product had the following characteristics: MS (ESI): 943.42 $[M+H]^+$. 1H -NMR ($CDCl_3$, 400 MHz, TMS, ppm): δ 8.35 (s, 1H), 8.22 (d, 1H), 7.65 (m, 12H), 7.47 (d, 2H), 7.43 (m, 6H), 7.29 (m, 10H), 7.15 (m, 6H), 5.27 (d, 2H), 4.89 (s, 2H), 4.82 (s, 2H), 3.55 (d, 2H), 3.22 (d, 2H), 1.45 (s, 6H).

8. B-Staged HTL Polymer Preparation

A mixture of Monomer A chemical (Monomer A24, 657.1mg, 0.697mmol), Monomer B chemical (Monomer B4, 479.7mg, 0.494mmol), and tris(4'-vinyl-[1,1'-biphenyl]-4-yl)amine (Monomer C6) (72.7mg, 0.132mmol, 99.6% purity) was dissolved in 1.2mL electronic anisole to make a 10wt% solution. The B-staging of the above solution was carried out at 105°C for 5hr under nitrogen atmosphere. After cooling to room temperature, the B-staged HTL solution was diluted to 4wt% with electronic solvent. Equal volume of electronic methanol was then added into the diluted B-staged HTL solution for precipitating HTL polymer out of the solution. The B-staged HTL polymer was then collected via filtration and dried in vacuum oven at 40°C overnight. The resulting B-staged HTL polymer was re-dissolved in electronic anisole to make a 4wt% solution and the above precipitation was repeated once more to completely remove residual HTL monomer. Finally, 0.71g (59% yield) B-staged HTL polymer product was collected in the form of yellow crystalline-like solid. Table 1 showed the B-staged HTL polymer molecular weights and distributions before and after precipitation. It is worthwhile to note that the molecular weight distributions of the B-staged HTL polymer were very broad ranging from 2×10^3 g/mol (dimer) to 1×10^6 g/mol.

TABLE 1. Molecular weights of B-staged HTL polymer

Description (g/mol)	M_n	M_w	M_z	M_{z+1}	M_w/M_n
Initial B-staged polymer	2,315	6,973	18,812	31,263	3.012
1 st precipitation	3,513	9,774	39,049	154,783	2.782
2 nd precipitation	4,243	16,001	155,113	437,472	3.771

9. Light Emitting Device Fabrication

Indium tin oxide (ITO) glass substrates (2*2cm) were cleaned with solvents ethanol, acetone, and isopropanol by sequence, and then were treated with a UV Ozone

cleaner for 15min. The hole injection layer (HIL) material Plexcore™ OC AQ-1200 from Plextronics Company was spin-coated from water solution onto the ITO substrates in glovebox and annealed at 150°C for 20min. After that, for comparative evaporative HTL, N-([1,1'-biphenyl]-4-yl)-9,9-dimethyl-N-(4-(9-phenyl-9H-carbazol-3-yl)phenyl)-9H-

5 fluoren-2-amine, the substrate was transferred into a thermal evaporator for the deposition of the HTL, emitting materials layer (EML), electron transfer layer (ETL) and cathode; for inventive HTL for solution process, HTL materials (B-staged HTL polymers) were deposited from anisole solution and annealed at 150°C for 10 min to remove organic solvent. After that, the crosslinking of B-staged material was carried out on a hotplate in
10 glovebox at 205°C for 5min. Then subsequent phosphorescent green (Ph-Green) EML, ETL and cathode were deposited in sequence. Finally these devices were hermetically sealed prior to testing.

To evaluate electroluminescent (EL) performances of the B-staged polymer as hole-transporting layer material, OLED devices with the following structures were
15 fabricated:

Device A: ITO/AQ-1200/Comparative HTL (evaporated, 800Å)/EML/ETL/Al;

Device B: ITO/AQ-1200/B-staged HTL (not crosslinked, 400Å)/EML/ETL/Al;

Device C: ITO/AQ-1200/B-staged HTL (crosslinked, 390Å)/EML/ETL/Al;

Device D: ITO/AQ-1200/B-staged HTL with 10% p-dopant (crosslinked,
20 290Å)/EML/ETL/Al.

The thicknesses of HIL (AQ-1200), EML, ETL and cathode Al are 470, 400, 350 and 800Å, respectively.

III. Results

25 The current-voltage-luminance (J-V-L) characterizations for the OLED devices, that is, driving voltage (V), luminance efficiency (Cd/A), and international commission on illumination (CIE) data at 1000nit and 50mA/cm² luminance, and lifetime at 15000nit for 10hr were performed with a Keithly™ 238 High Current Source-Measurement Unit and a CS-100A Color and Luminance Meter from Konica Minolta Company and were
30 listed in Table 2. Electroluminescence (EL) spectra of the OLED devices were collected by a calibrated CCD spectrograph and were fixed at 516nm for all the four OLED device examples.

Device A was fabricated with evaporative Comparative HTL, while Device D was deposited with the inventive B-staged HTL polymer comprising a p-dopant component

(trityl tetrakis(pentafluorophenyl)borate from Acros Company) through a solution process. Device B or C was deposited with non-crosslinked B-staged HTL polymer or crosslinked B-staged HTL polymer respectively, without comprising the p-dopant component. Device D, compared to Devices B and C, had a higher lifetime (from 60.2% and 79.2% to 95.8%), which demonstrated the critical role played by the p-dopant component in the HTL polymer. Device C, compared to Device B, had also a higher lifetime (from 79.2% to 95.8%), and demonstrated the critical role played by the Monomer C crosslinking agent.

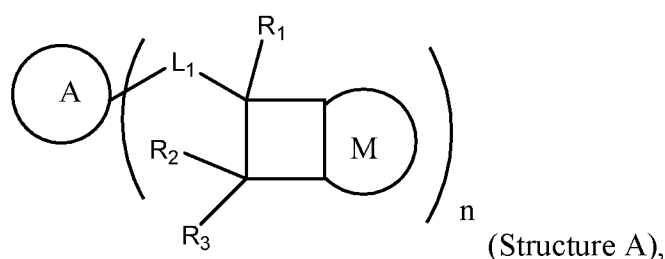
It should be noted that the by adding the p-dopant component and the crosslinking agent of the present invention, the solution process deposited OLED device performance, in detail, the device lifetime was significantly improved, and was very close to that of evaporative device (Device A).

TABLE 2

Devices	OLED J-V-L characterizations				
	V		Cd/A	CIE	Lifetime
	1000nit	50mA/cm ²			
A	3.0/ 5.0		46.9	293, 657	97.2%
B	3.6/ 6.4		50.8	292, 656	60.2%
C	3.8/ 6.6		50.6	292, 656	79.2%
D	3.6/ 6.4		49.5	295 653	95.8%

What is claimed is:

1. A polymeric charge transfer layer formed from a composition comprising, from 1wt% to 20wt% based on total weight of the composition, a p-dopant component; and a polymer comprising, as polymerized units, Monomer A, and Monomer C crosslinking agent; wherein Monomer A has Structure A:



wherein A and M are each substituted or unsubstituted aromatic moiety or a substituted or unsubstituted heteroaromatic moiety; and

wherein n is from 2 to 10; and

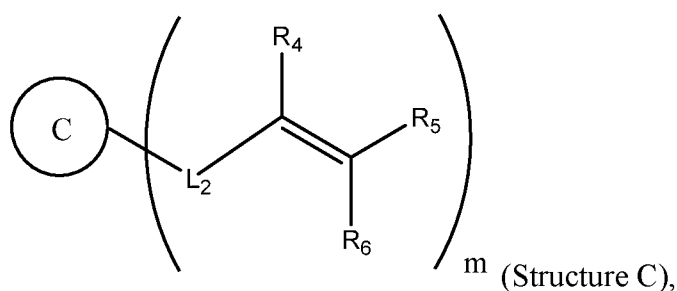
wherein R₁ through R₃ are each independently selected from the following:
hydrogen; deuterium; a hydrocarbyl, further a C₁-C₁₀₀ hydrocarbyl, further a C₃-C₁₀₀
hydrocarbyl, further a C₁₀-C₁₀₀ hydrocarbyl, further a C₂₀-C₁₀₀ hydrocarbyl, further a C₃₀-
C₁₀₀ hydrocarbyl; a substituted hydrocarbyl, further a C₁-C₁₀₀ substituted hydrocarbyl,
further a C₃-C₁₀₀ substituted hydrocarbyl, further a C₁₀-C₁₀₀ substituted hydrocarbyl,
further a C₂₀-C₁₀₀ substituted hydrocarbyl, further a C₃₀-C₁₀₀ substituted hydrocarbyl; a
heterohydrocarbyl, further a C₁-C₁₀₀ heterohydrocarbyl, further a C₃-C₁₀₀
heterohydrocarbyl, further a C₁₀-C₁₀₀ heterohydrocarbyl, further a C₂₀-C₁₀₀
heterohydrocarbyl, further a C₃₀-C₁₀₀ heterohydrocarbyl; a substituted heterohydrocarbyl,
further a C₁-C₁₀₀ substituted heterohydrocarbyl, further a C₃-C₁₀₀ substituted
heterohydrocarbyl, further a C₁₀-C₁₀₀ substituted heterohydrocarbyl, further a C₂₀-C₁₀₀
substituted heterohydrocarbyl, further a C₃₀-C₁₀₀ substituted heterohydrocarbyl; a halogen;
a cyano; an aryl, further a C₅-C₁₀₀ aryl, further a C₆-C₁₀₀ aryl, further a C₁₀-C₁₀₀ aryl,
further a C₂₀-C₁₀₀ aryl, further a C₃₀-C₁₀₀ aryl; a substituted aryl, further a C₅-C₁₀₀
substituted aryl, further a C₆-C₁₀₀ substituted aryl, further a C₁₀-C₁₀₀ substituted aryl,
further a C₂₀-C₁₀₀ substituted aryl, further a C₃₀-C₁₀₀ substituted aryl; a heteroaryl, further
a C₅-C₁₀₀ heteroaryl, further a C₆-C₁₀ heteroaryl, further a C₁₀-C₁₀₀ heteroaryl, further a
C₂₀-C₁₀₀ heteroaryl, further a C₃₀-C₁₀₀ heteroaryl; a substituted heteroaryl, further a C₅-
C₁₀₀ substituted heteroaryl, further a C₆-C₁₀₀ substituted heteroaryl, further a C₁₀-C₁₀₀

substituted heteroaryl, further a C₂₀-C₁₀₀ substituted heteroaryl, further a C₃₀-C₁₀₀ substituted heteroaryl; and

wherein L₁ is selected from a heteroatom, an aromatic moiety, a heteroaromatic moiety, a C₁-C₁₀₀ hydrocarbyl, a C₁-C₁₀₀ substituted hydrocarbyl, a C₁-C₁₀₀ heterohydrocarbyl, and a C₁-C₁₀₀ substituted heterohydrocarbyl; and

wherein two or more of R₁ through R₃ may optionally form one or more ring structures;

Monomer C crosslinking agent has Structure C:



wherein C is an aromatic moiety, a heteroaromatic moiety, a C₁-C₅₀ hydrocarbyl, a C₁-C₅₀ substituted hydrocarbyl, a C₁-C₅₀ heterohydrocarbyl, or a C₁-C₅₀ substituted heterohydrocarbyl; and

wherein R₄ through R₆ are each independently selected from the following: hydrogen, deuterium, a C₁-C₅₀ hydrocarbyl, a C₁-C₅₀ substituted hydrocarbyl, a C₁-C₅₀ heterohydrocarbyl, a C₁-C₅₀ substituted heterohydrocarbyl, halogen, cyano, a C₅-C₅₀ aryl, a C₅-C₅₀ substituted aryl, a C₅-C₅₀ heteroaryl, a C₅-C₅₀ substituted heteroaryl; and

wherein L₂ is selected from a heteroatom, an aromatic moiety, a heteroaromatic moiety, a C₁-C₁₀₀ hydrocarbyl, a C₁-C₁₀₀ substituted hydrocarbyl, a C₁-C₁₀₀ heterohydrocarbyl, or a C₁-C₁₀₀ substituted heterohydrocarbyl; and

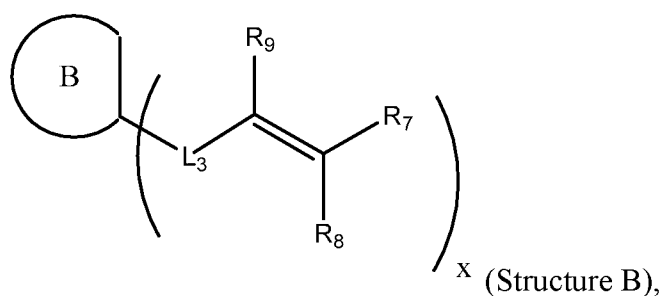
wherein m is from 2 to 25; and

wherein each chemical group of L₂ is independently bonded to C; and

wherein two or more of R₄ through R₆ may optionally form one or more ring structures; and

the p-dopant is selected from tropylium salts, imidazolium salts, and trityl salts.

2. The polymeric charge transfer layer according to Claim 1 wherein the polymer further comprises Monomer B having Structure B:



wherein B is a substituted or unsubstituted aromatic moiety or a substituted or unsubstituted heteroaromatic moiety; and

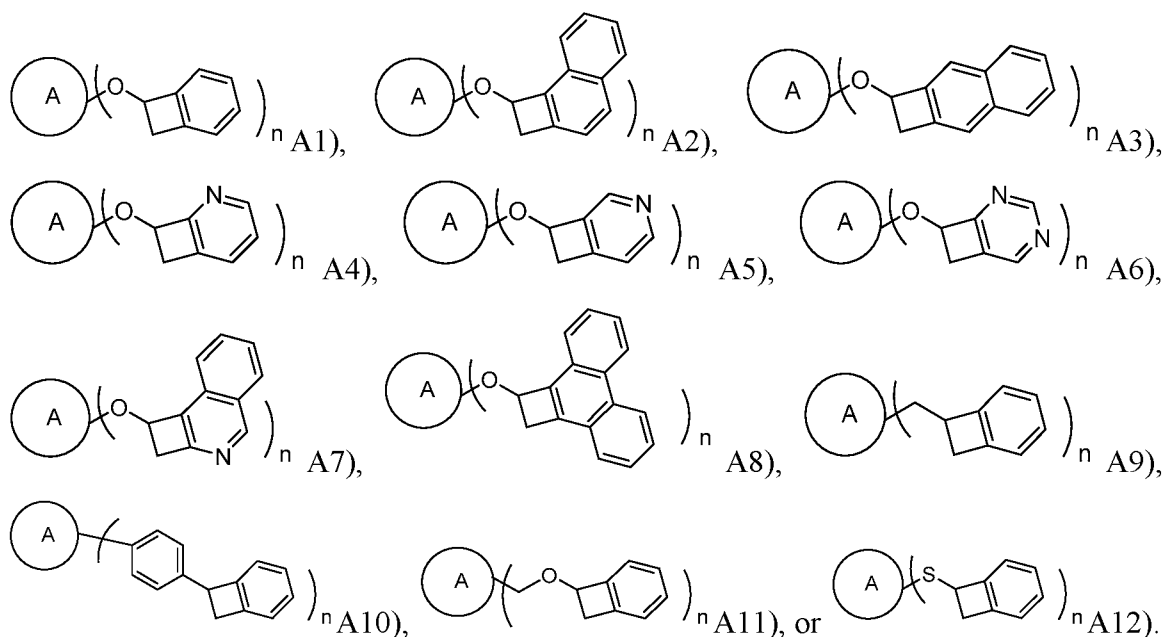
wherein x is from 2 to 10; and

5 wherein L_3 is selected from a heteroatom, an aromatic moiety, a heteroaromatic moiety, a C_1 - C_{100} hydrocarbyl, a C_1 - C_{100} substituted hydrocarbyl, a C_1 - C_{100} heterohydrocarbyl, and a C_1 - C_{100} substituted heterohydrocarbyl; and

wherein R_7 through R_9 are each independently selected from the following:
hydrogen, deuterium, a C_1 - C_{50} hydrocarbyl, a C_1 - C_{50} substituted hydrocarbyl, a C_1 - C_{50}
10 heterohydrocarbyl, a C_1 - C_{50} substituted heterohydrocarbyl, halogen, cyano, a C_5 - C_{50} aryl, a C_5 - C_{50} substituted aryl, a C_5 - C_{50} heteroaryl, and a C_5 - C_{50} substituted heteroaryl; and

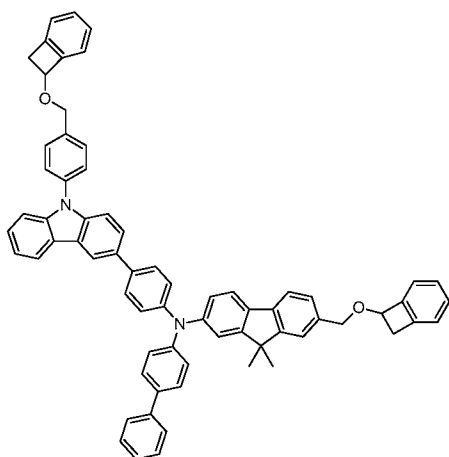
wherein two or more of R_7 through R_9 may optionally form one or more ring structures.

15 3. The polymeric charge transfer layer according to Claim 1 wherein Monomer A is selected from the following A1 through A12:

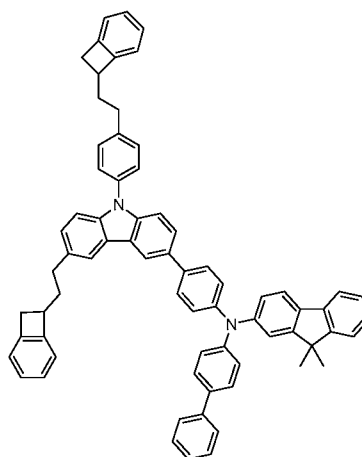


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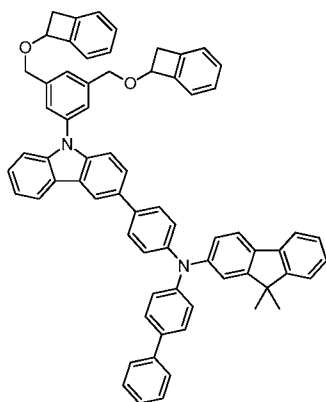




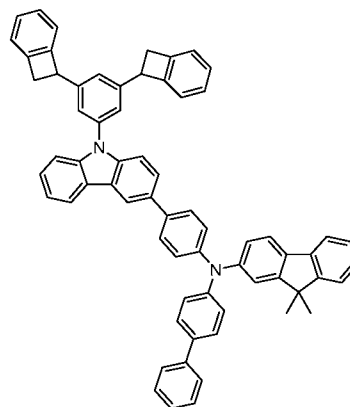
A23),



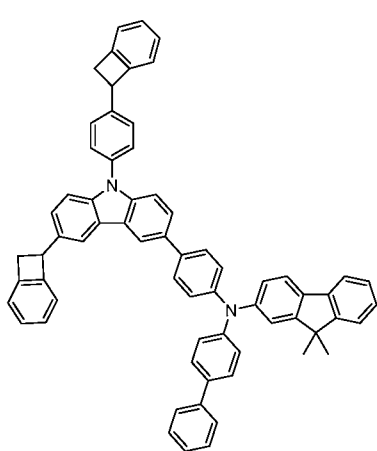
A24),



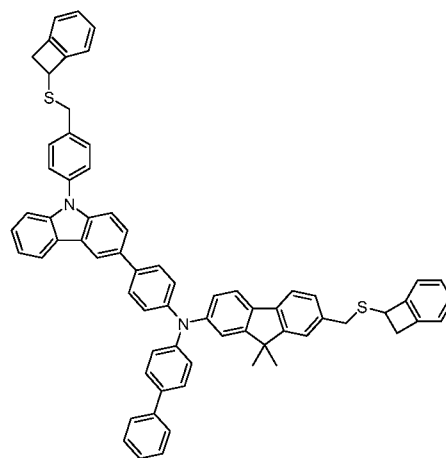
A25),



A26),

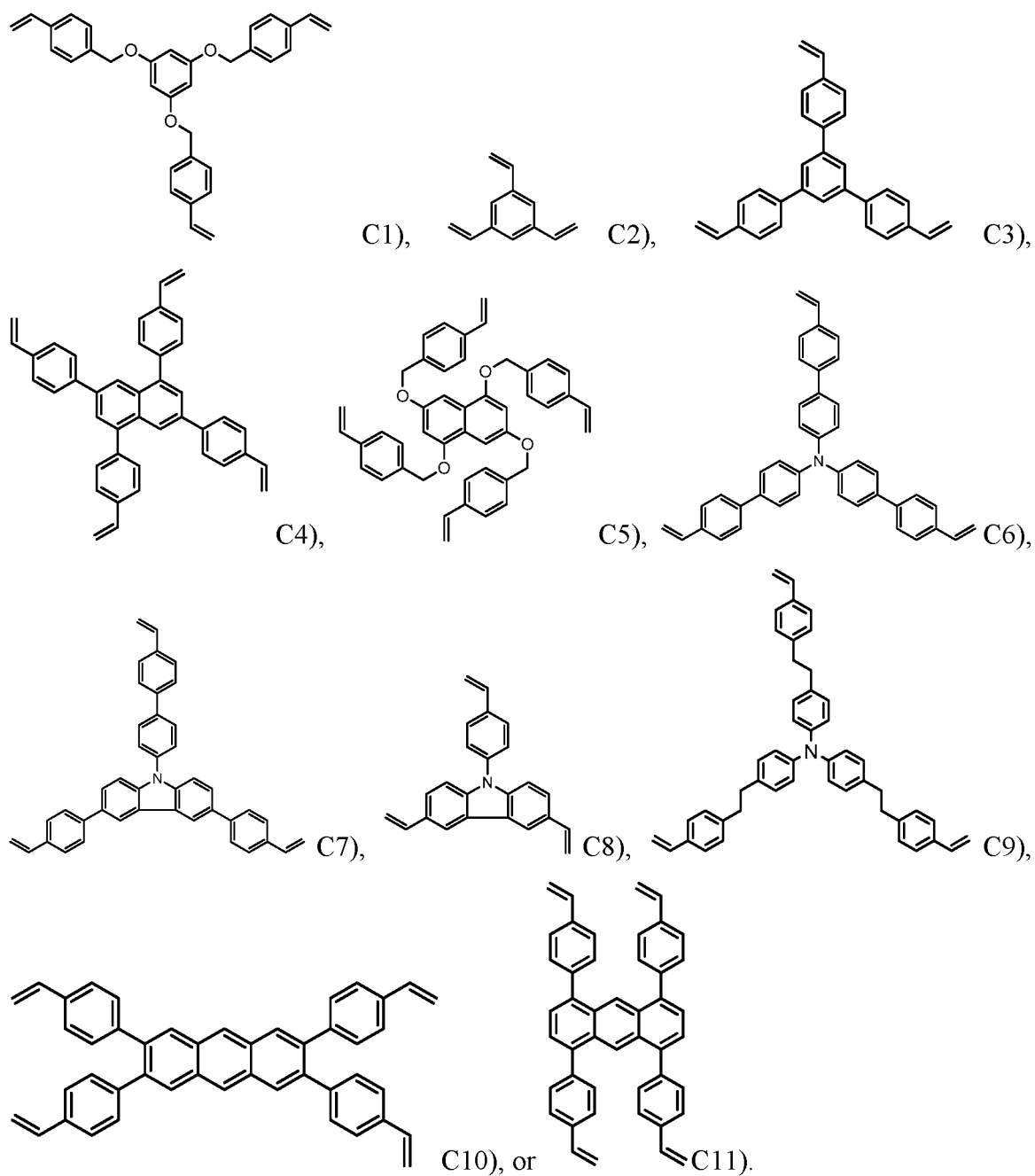


A27), or



A28).

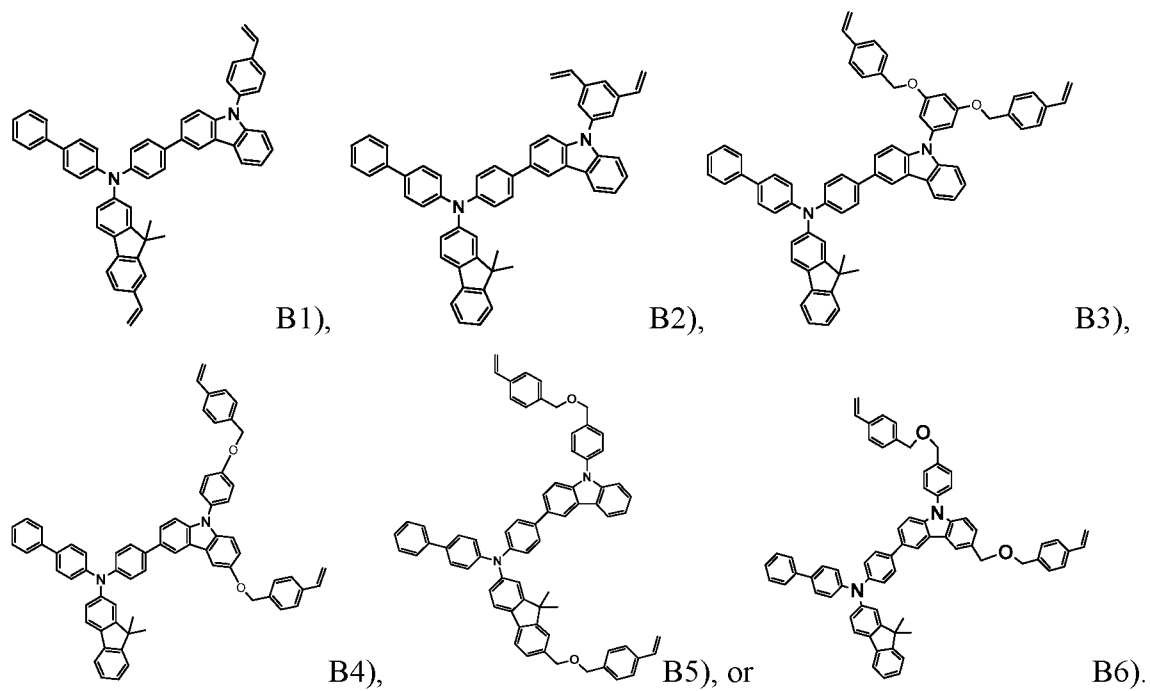
5. The polymeric charge transfer layer according to Claim 1, wherein Monomer C crosslinking agent is selected from the following C1-C11:



5

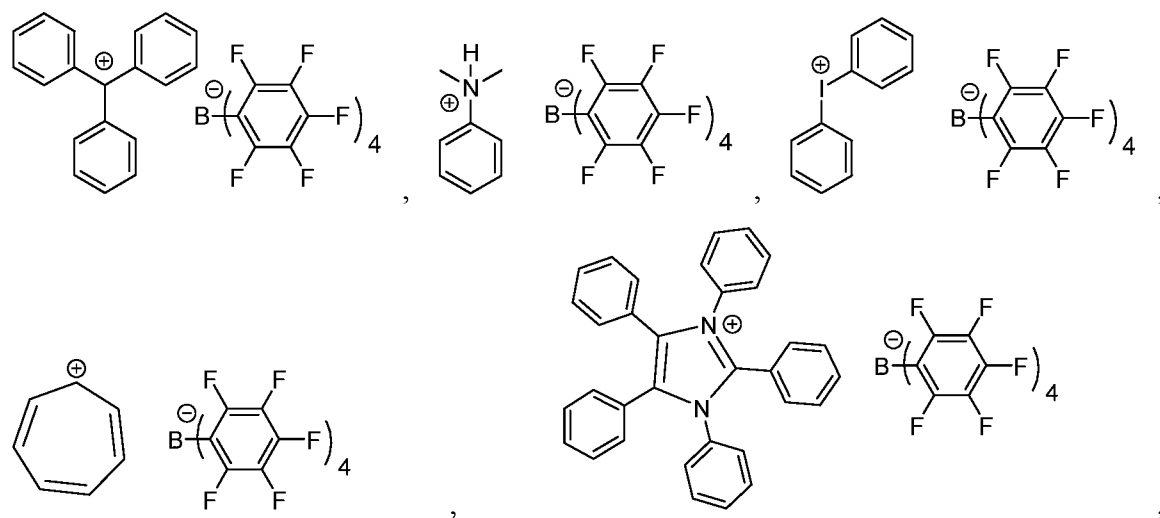
6. The polymeric charge transfer layer according to Claim 1 wherein Monomer C crosslinking agent is from 0.1 to 50mole% based on the sum moles of Monomer A.

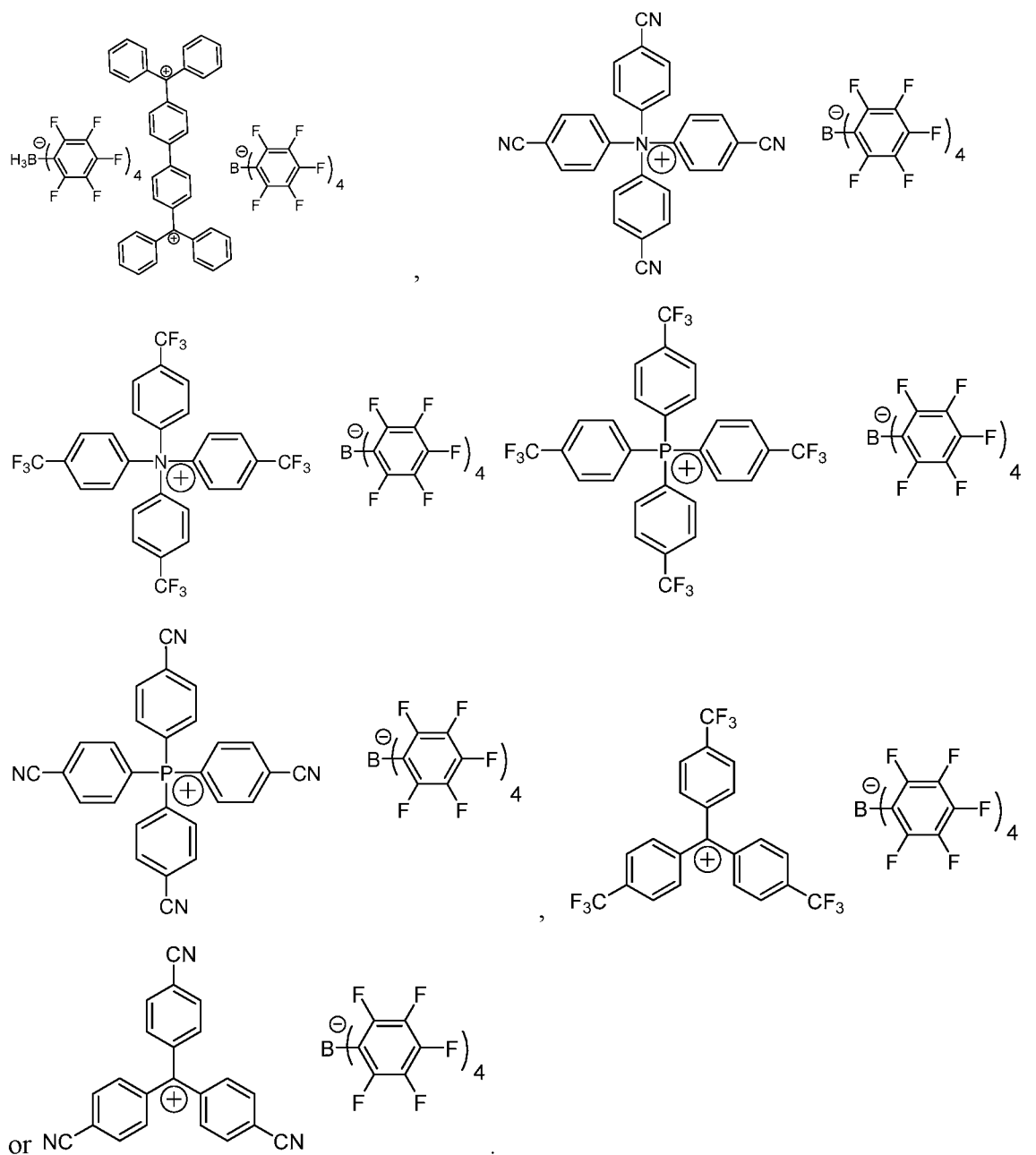
7. The polymeric charge transfer layer according to Claim 2 wherein Monomer B
10 is selected from the following B1 through B6:



8. The polymeric charge transfer layer according to Claim 2 wherein the molar ratio of Monomer A to Monomer B is from 0.8 to 1.2.

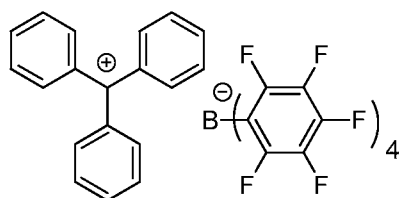
9. The polymeric charge transfer layer according to Claim 1 wherein the p-dopant has a structure selected from one of the following:





5

10. The polymeric charge transfer layer according to Claim 9 wherein the p-dopant has the structure:



11. The polymeric charge transfer layer according to Claim 2 wherein either of Monomer A, Monomer B, and Monomer C has a molecular weight of from 500g/mole to 28000g/mole.

5 12. The polymeric charge transfer layer according to Claim 1 wherein either of Monomer A, and Monomer C has a purity equal to or above 99%.

13. The polymeric charge transfer layer according to Claim 2 wherein either of Monomer A, Monomer B, and Monomer C has a purity equal to or above 99%.

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14. An organic light emitting device comprising the polymeric charge transfer layer of Claim 1.

15 15. An organic electronic device comprising the polymeric charge transfer layer of Claim 1.

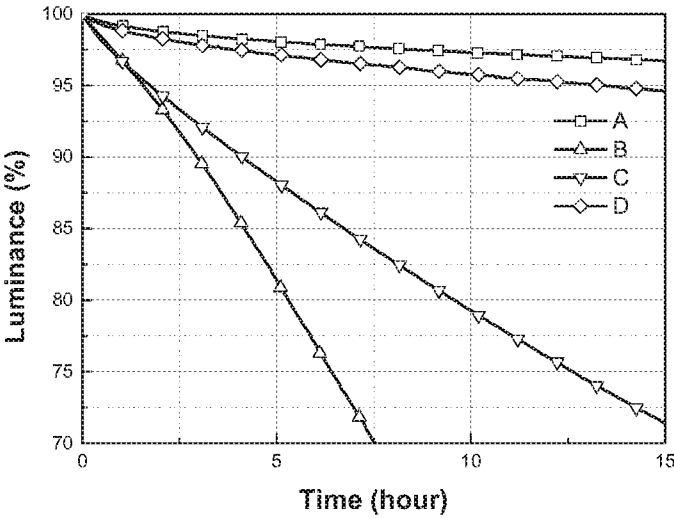


FIGURE 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2015/070355

A. CLASSIFICATION OF SUBJECT MATTER

H01L 51/54(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)

H01L51, C08G, C08L

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)

CNKI, CNPAT, WPI, EPODOC: organic, electron+, OLED, ETL, HTL, charge, transfer, electron, transfer, hole, transfer, polymer+, triphenylamine, triphenyl, cyclobutane, cyclobutanes, tetramethylene, diethylene, bicyclo, trine, Br, BCB, fluorene, fluoren, carbazol, dibenzopyrrole, biphenyl, diphenyl, crosslinking agent, p, dopant, dope+.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2009315453 A1 (KOBAYASHI SHIGEYA, ET AL.) 24 December 2009 (2009-12-24) the whole document	1-15
A	CN 102796260 A (DOW GLOBAL TECHNOLOGIES INC) 28 November 2012 (2012-11-28) the whole document	1-15
A	US 4639496 A (BBC BROWN BOVERI & CIE) 27 January 1987 (1987-01-27) the whole document	1-15
A	CN 103044661 A (CHINESE ACAD SCI CHEM INST) 17 April 2013 (2013-04-17) the whole document	1-15
A	JP 2012177029 A (MITSUBISHI CHEM CORP) 13 September 2012 (2012-09-13) the whole document	1-15
A	EP 1279689 A2 (MERCK PATENT GMBH) 29 January 2003 (2003-01-29) the whole document	1-15



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

15 May 2015

Date of mailing of the international search report

01 June 2015

Name and mailing address of the ISA/CN

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Telephone No. (86-10)62084549

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2015/070355**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 103288712 A (UNIV EAST CHINA NORMAL) 11 September 2013 (2013-09-11) the whole document	1-15
A	CN 1500093 A (COVION ORGANIC SEMICONDUCTORS GMBH) 26 May 2004 (2004-05-26) the whole document	1-15

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2015/070355

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
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				US	8815414	B2	26 August 2014
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				CN	101516960	B	12 March 2014
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				GB	2424897	A	11 October 2006
				US	2013085258	A1	04 April 2013
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				EP	0112522	A2	04 July 1984
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CN	103044661	A	17 April 2013	WO	2013053204	A1	18 April 2013
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EP	1279689	A2	29 January 2003	EP	1279689	B1	01 October 2008
				EP	1279689	A3	04 June 2003
				US	2003062509	A1	03 April 2003
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				US	2006065890	A1	30 March 2006
				EP	1379534	A1	14 January 2004
				DE	10116962	A1	10 October 2002

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2015/070355

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
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		DE 50201787 D1	20 January 2005
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		EP 1379534 B1	15 December 2004
		US 2004133004 A1	08 July 2004
		US 7534853 B2	19 May 2009

专利名称(译)	聚合物电荷转移层和含有它的有机电子器件		
公开(公告)号	EP3183761A1	公开(公告)日	2017-06-28
申请号	EP2015833181	申请日	2015-01-08
[标]申请(专利权)人(译)	陶氏环球技术有限责任公司 罗门哈斯电子材料有限公司		
申请(专利权)人(译)	DOW全球科技有限责任公司 罗门哈斯电子材料KOREA LTD. 罗门哈斯电子材料有限责任公司		
当前申请(专利权)人(译)	DOW全球科技有限责任公司 罗门哈斯电子材料KOREA LTD. 罗门哈斯电子材料有限责任公司		
[标]发明人	SPENCER LIAM NA HONG YEOP DOH YOO JIN LIU CHUN ZHU MINRONG FENG JICHANG TANG ZHENGMIN FENG SHAOGUANG KEARNS KENNETH DE VRIES TIMOTHY MUKHOPADHYAY SUKRIT KRAMER JOHN TREFONAS PETER III DEVORE DAVID D WOODWARD WILLIAM		
发明人	SPENCER, LIAM NA, HONG YEOP DOH, YOO JIN LIU, CHUN ZHU, MINRONG FENG, JICHANG TANG, ZHENGMIN FENG, SHAOGUANG KEARNS, KENNETH DE VRIES, TIMOTHY MUKHOPADHYAY, SUKRIT KRAMER, JOHN TREFONAS, PETER III DEVORE, DAVID D. WOODWARD, WILLIAM		
IPC分类号	H01L51/54		
CPC分类号	C07D209/86 H01L51/0003 H01L51/0034 H01L51/0043 H01L51/5056 H01L51/5072 H01L51/0059 H01L51/0072 C08G61/124 C08G2261/124 C08G2261/1424 C08G2261/1434 C08G2261/148 C08G2261/18 C08G2261/228 C08G2261/312 C08G2261/3142 C08G2261/3162 C08G2261/3241 C08G2261/512 C08G2261/95 H01L51/004 H01L51/005 H01L51/506		

代理机构(译)	霍顿MARK PHILLIP
优先权	PCT/CN2014/084915 2014-08-21 WO PCT/CN2014/084918 2014-08-21 WO
其他公开文献	EP3183761A4
外部链接	Espacenet

摘要(译)

本发明涉及包含聚合物和p-掺杂剂的聚合物电荷转移层。该聚合物包含作为聚合单元的单体A，单体B和单体C交联剂。本发明进一步涉及有机电子器件，尤其是包含聚合物电荷转移层的有机发光器件。