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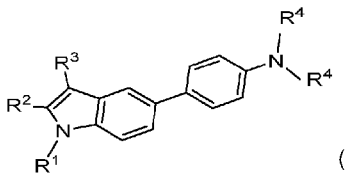
(54) Title: ORGANIC INDOLYL TRIARYLAMINE COMPOUNDS AND ELECTRONIC DEVICES COMPRISING AN ORGANIC LAYER CONTAINING SUCH COMPOUNDS



(1)

(57) Abstract: Organic compounds of formula (I) comprising 2,3 dialkyl- or indeno- substituted, preferably, 2,3 dimethyl- or 5,6-dihydroindeno- substituted N-phenyl indole containing triaryl amines suitable for organic layers of electronic devices, such as hole transfer layers (HTL) and hole induction layers (HIL) in organic light emitting diodes (OLEDs) that show increased luminous efficiency. Such as hole throughput or hole injection layers.

ORGANIC INDOLYL TRIARYLAMINE COMPOUNDS AND ELECTRONIC DEVICES COMPRISING AN ORGANIC LAYER CONTAINING SUCH COMPOUNDS

The present invention relates to 2,3 dialkyl- or indeno- substituted indole containing triaryl amine organic compounds, preferably, a 2,3 dialkyl- or indeno-substituted N-phenyl indole containing triaryl amine, for use as hole transport layers or hole initiation layers in organic light-emitting diode (OLED) displays, and to organic light-emitting diode (OLED) displays comprising an organic hole transport layer or hole initiation layer made from the organic compounds.

Organic light emitting diodes (OLEDs) are display devices that employ stacks of organic layers including electron transport layers (ETLs) and hole transport layers (HTLs). OLEDs have drawn much attention in recent years for use in next-generation displays because of their many performance advantages including light weight, energy savings and high contrast. However, in today's increasingly mobile world, many devices in which the displays are used, such as phones, tablets, display glasses and other mobile devices have a limited battery life, with the attendant need to limit power consumption. To improve the performance of organic light emitting diodes (OLEDs), recent improvements have targeted new electron transport layers (ETLs) and hole transport layers (HTLs). In the case of HTLs, the state of the art technology uses triarylamine-group containing materials to satisfy many of the current needs for luminescent and phosphorescent OLED designs. However, further gains in efficiency, lifetime, lower driving voltage and brightness remain issues for the mass production of blue light OLEDs; and there remains a need for new OLED compounds to address these issues.

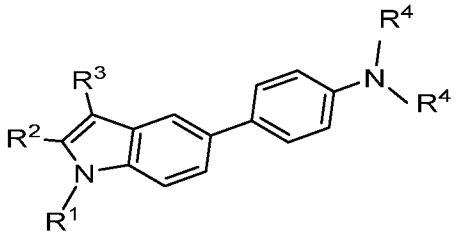
U.S. patent publication no. 2012/0305906 A1 to Kim et al. discloses indole containing compounds for use in organic electrode elements. Some of the indole containing compounds in Kim have triarylamine groups within them. However, compositions such as those disclosed in Kim may not enable the necessary level of minimized power consumption needed for today's mobile devices.

The present inventors have endeavored to provide OLEDs with improved device performance including minimized power consumption, especially for battery-powered mobile applications.

SUMMARY OF THE INVENTION

In accordance with the present invention, organic compounds comprise at least one 2,3 dialkyl- or indeno- substituted indole containing triaryl amine, such as a 2,3 dialkyl- or indeno- substituted N-phenyl indole containing triaryl amine.

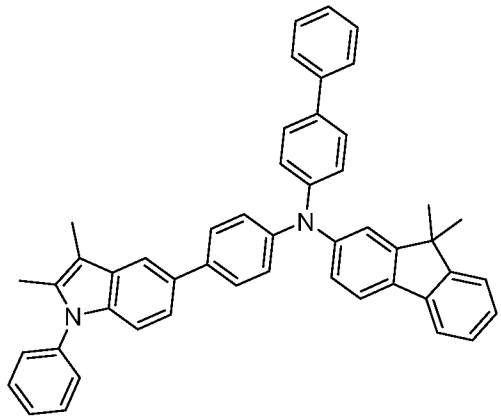
In accordance with the organic compounds of the present invention, the 2,3 dialkyl- or indeno- substituted indole containing triaryl amines compounds have a structure represented by formula (1):



(1)

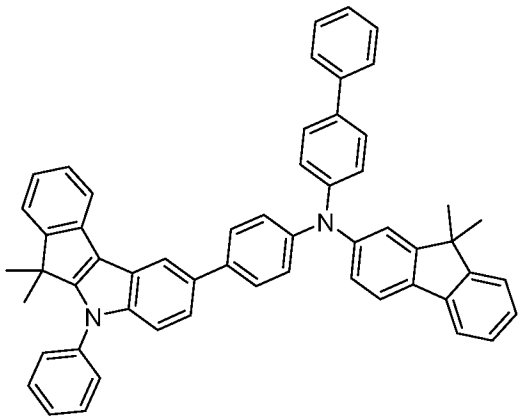
wherein R^1 is a C_1 to C_{20} alkyl group or alkenyl group, a C_6 to C_{30} aryl group or arylene group, such as a flourenyl group, a heteroatom substituted C_1 to C_{20} alkyl group or alkenyl group, a heteroatom substituted C_6 to C_{30} aryl group or arylene group, such as a benzyloxy group, or, preferably, a C_6 to C_{12} aryl group, or, more preferably, a phenyl group; further wherein, each of R^2 and R^3, independently, is a C_1 to C_{20} alkyl group, preferably, a C_1 to C_4 alkyl group, more preferably, a methyl group, or, even more preferably, each of R^2 and R^3 is a methyl group; or, further wherein R^2 and R^3 together form a C_7 to C_{12} bicyclic alkylaryl group or alkyl substituted bicyclic alkylaryl group, preferably a dihydroindeno group, or, more preferably, a 5,6-dihydroindeno group; and, still further wherein, each R^4 is, independently, a biphenyl, indenyl, fluorenyl group, such as 1-fluorenyl, 2-fluorenyl, 3-fluorenyl, 4-fluorenyl and 9-fluorenyl, or any of an alkenyl group containing biphenyl or flourenyl group, or, preferably, wherein one R^4 is a biphenyl group and one R^4 is a fluorenyl group.

In accordance with the organic compounds of the present invention as represented by formula (1), above, the organic compounds comprise 2,3 dimethyl substituted indole containing triaryl amines having a structure represented by formula (2):



(2).

In accordance with the organic compounds of the present invention represented by formula (1), above, the organic compounds comprise 5,6 dihydro indeno substituted indole containing triaryl amines having a structure represented by formula (3):



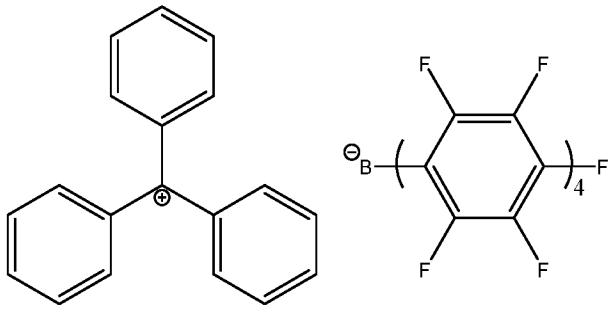
(3).

In accordance with another aspect of the present invention, a film comprises an organic layer containing from 10 to 100 wt.% or, preferably, from 80 to 100 wt.% of at least one 2,3 dialkyl- or indeno- substituted indole containing triaryl amine, such as a 2,3 dialkyl- or indeno- substituted N-phenyl indole containing triaryl amine, or, preferably, at least one organic compound having the structure represented by formula (1) or, more preferably, at least one organic compound represented by formula (2), above, or formula (3), above.

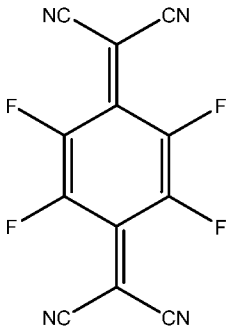
In accordance with the film of present invention, the film further comprises one or more film forming organic polymer, such as those chosen from vinyl or acrylic polymers, polyesters or polyamides or, preferably, acrylic or vinyl polymers, for example, poly (methyl methacrylate) or polystyrene.

In accordance with the film or organic layer of the present invention, wherein the film further comprises a dopant, such as the dopants shown in the formulas, below.

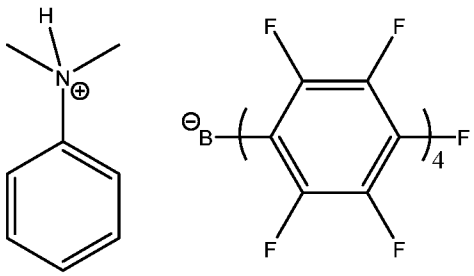
Suitable dopants may include, for example, trityl penta-fluoro-phenyl-borate, dimethyl anilinium penta-fluoro-phenyl-borate; anilinium penta-fluoro-phenyl-borate; 2,3,5,6-tetrafluoro-tetracyanoquinodimethane (F_4TCNQ), hexaazatriphenylenehexacarbonitrile (HATCN), diphenyliodonium penta-fluoro-phenyl-borate; tropilium penta-fluoro-phenyl-borate; [1,2,3,4,5-pentaphenyl-1H-imidazol-3-ium] [tetrakis (pentafluorophenyl) borate]; [1,1'-biphenyl]-4,4'-diylbis(diphenylmethylium) [tetrakis(pentafluorophenyl)borate]$_2$; tetrakis(4-cyanophenyl)phosphonium [tetrakis(pentafluorophenyl) borate]; tetrakis(4-(trifluoromethyl)phenyl)phosphonium [tetrakis(pentafluorophenyl) borate]; tetrakis(4-cyanophenyl)ammonium [tetrakis(pentafluorophenyl)borate]; tetrakis(4-(trifluoromethyl)phenyl)ammonium [tetrakis(pentafluorophenyl)borate]; tris(4-cyanophenyl)methylium [tetrakis(pentafluorophenyl)borate]; tris(4-trifluoromethylphenyl)methylium [tetrakis(pentafluorophenyl)borate].



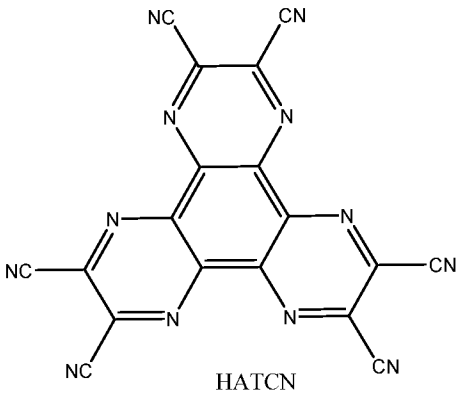
Trityl penta-fluoro-phenyl-Borate ;



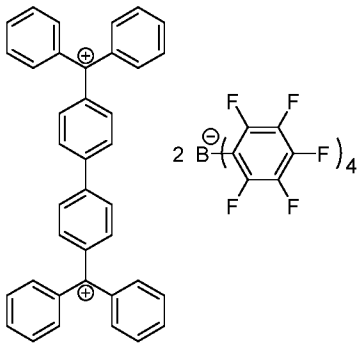
F_4TCNQ ;



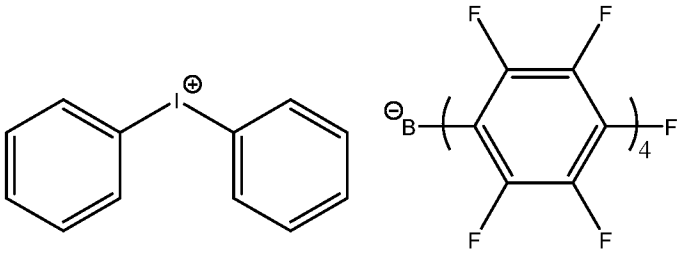
Anilinium penta-fluoro-phenyl-Borate ;



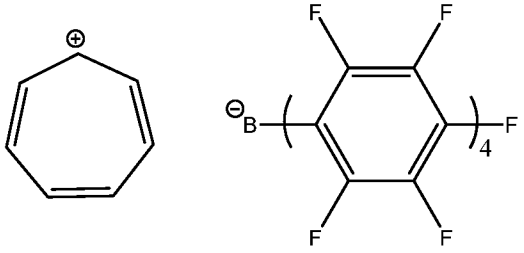
HATCN ;



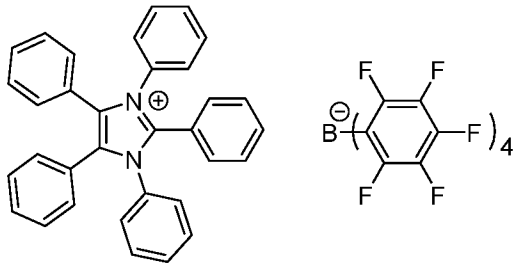
{[1,1'-biphenyl]-4,4'-diylbis(diphenylmethylium)} {tetrakis(pentafluorophenyl)borate}$_2$;



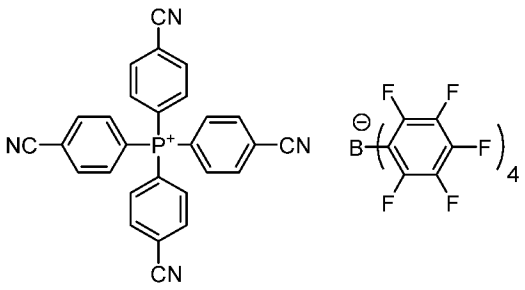
Diphenyliodonium penta-fluoro-phenyl-Borate ;



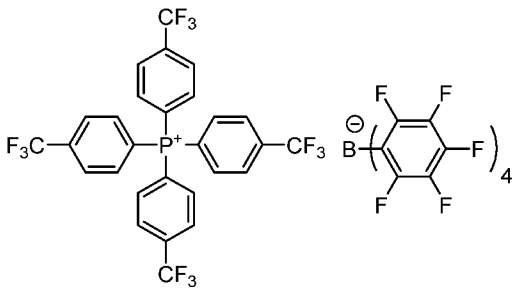
Tropilium penta-fluoro-phenyl-Borate ;



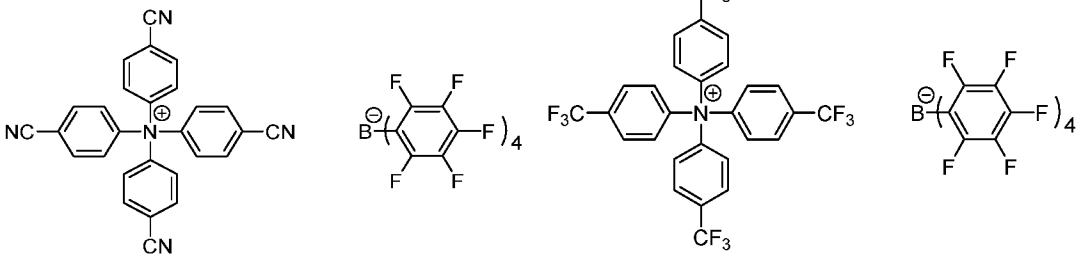
[1,2,3,4,5-pentaphenyl-1 *H*-imidazol-3-ium] [tetrakis(pentafluorophenyl)borate] ;



[tetrakis(4-cyanophenyl)phosphonium] [tetrakis(pentafluorophenyl)borate]



[tetrakis(4-(trifluoromethyl)phenyl)phosphonium] [tetrakis(pentafluorophenyl)borate]

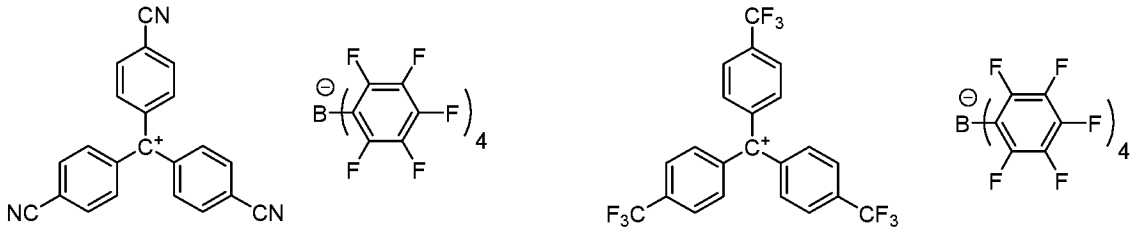


[tetrakis(4-cyanophenyl)ammonium] [tetrakis(pentafluorophenyl)borate]

;

[tetrakis(4-(trifluoromethyl)phenyl)ammonium] [tetrakis(pentafluorophenyl)borate]

;

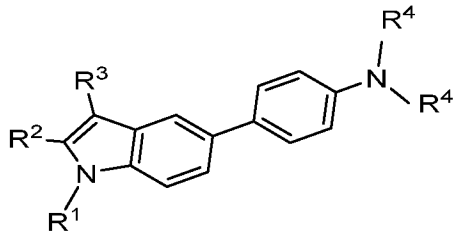


tris(4-cyanophenyl)methylium [tetrakis(pentafluorophenyl)borate]

tris(4-trifluoromethylphenyl)methylium [tetrakis(pentafluorophenyl)borate]

Dopants may be used in the amount of from 0 to 25 wt.%, or, preferably, up to 10 wt.%, based on the total solids weight of the film.

In accordance with the film of the present invention, wherein the organic compound has a structure represented by formula (1):

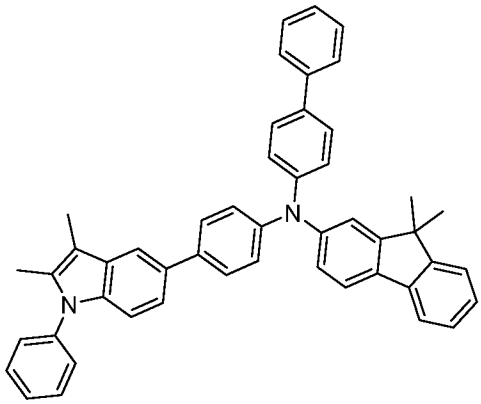


(1)

wherein R^1 is a C_1 to C_{20} alkyl group or alkenyl group, a C_6 to C_{30} aryl group or arylene group, such as a flourenyl group, a heteroatom substituted C_1 to C_{20} alkyl group or alkenyl group, a heteroatom substituted C_6 to C_{30} aryl group or arylene group, such as a benzyloxy group, or, preferably, a C_6 to C_{12} aryl group, or, more preferably, a phenyl group; further wherein, each of R^2 and R^3, independently, is a C_1 to C_{20} alkyl group, preferably, a C_1 to C_4 alkyl group, more preferably, a methyl group, or, even more preferably, each of R^2 and R^3 is a methyl group; or, further wherein R^2 and R^3 together form a C_7 to C_{12} bicyclic alkylaryl group or alkyl

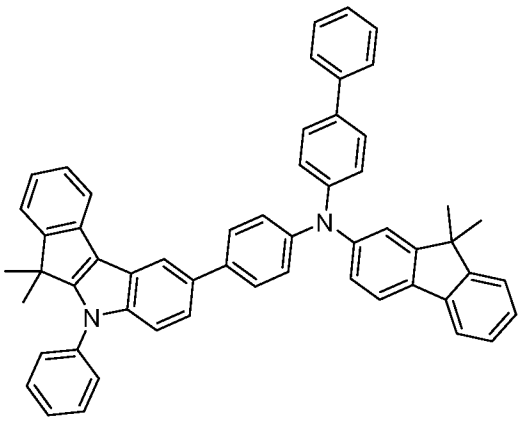
substituted bicyclic alkylaryl group, preferably a dihydroindeno group, or, more preferably, a 5,6-dihydroindeno group; and, still further wherein, each R^4 is, independently, a biphenyl, indenyl, fluorenyl group, such as 1-fluorenyl, 2-fluorenyl, 3-fluorenyl, 4-fluorenyl and 9-fluorenyl, or any of an alkenyl group containing biphenyl or flourenyl group, or, preferably, wherein one R^4 is a biphenyl group and one R^4 is a fluorenyl group.

In accordance with the film of the present invention containing the organic compound represented by Formula (1), wherein the organic compound is a 2,3 dimethyl substituted indole containing triaryl amine having a structure represented by formula (2):



(2).

In accordance with the film of the present invention containing the organic compound represented by Formula (1), wherein the organic compounds are 5,6 dihydro indeno substituted indole containing triaryl amines having a structure represented by formula (3):



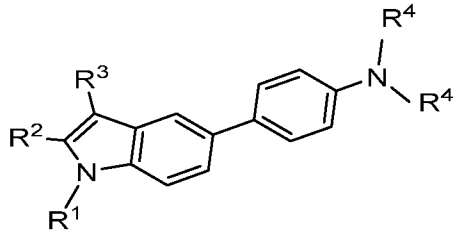
(3).

The films of the present invention can comprise one or more dopants and one or more film forming organic polymer.

In accordance with yet another aspect of the present, an organic light emitting

diode (OLED) comprises an organic layer or film containing at least one organic compound chosen from 2,3 dialkyl- or indeno- substituted indole containing triaryl amines, preferably, a 2,3 dialkyl- or indeno- substituted N-phenyl indole containing triaryl amine.

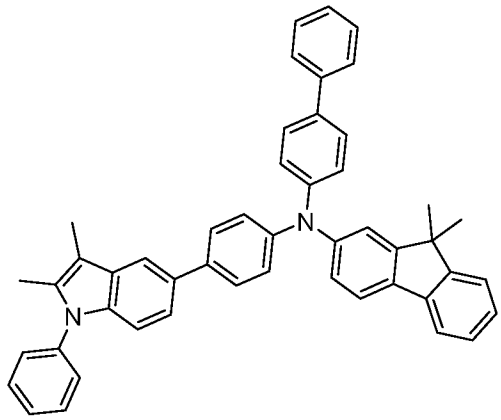
In accordance with the organic light emitting diode (OLED) of the present invention, wherein OLED comprise an organic layer or film containing an organic compound that has a structure represented by Formula (1):



(1)

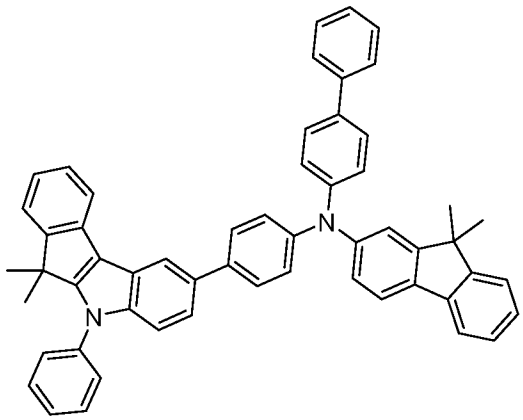
wherein R^1 is a C_1 to C_{20} alkyl group or alkenyl group, a C_6 to C_{30} aryl group or arylene group, such as a flourenyl group, a heteroatom substituted C_1 to C_{20} alkyl group or alkenyl group, a heteroatom substituted C_6 to C_{30} aryl group or arylene group, such as a benzyloxy group, or, preferably, a C_6 to C_{12} aryl group, or, more preferably, a phenyl group; further wherein, each of R^2 and R^3, independently, is a C_1 to C_{20} alkyl group, preferably, a C_1 to C_4 alkyl group, more preferably, a methyl group, or, even more preferably, each of R^2 and R^3 is a methyl group; or, further wherein R^2 and R^3 together form a C_7 to C_{12} bicyclic alkylaryl group or alkyl substituted bicyclic alkylaryl group, preferably a dihydroindeno group, or, more preferably, a 5,6-dihydroindeno group; and, still further wherein, each R^4 is, independently, a biphenyl, indenyl, fluorenyl group, such as 1-fluorenyl, 2-fluorenyl, 3-fluorenyl, 4-fluorenyl and 9-fluorenyl, or any of an alkenyl group containing biphenyl or flourenyl group, or, preferably, wherein one R^4 is a biphenyl group and one R^4 is a fluorenyl group.

In accordance with the organic light emitting diode (OLED) of the present invention, wherein the organic layer or film containing an organic compound represented by Formula (1) contains at least one 2,3 dimethyl substituted indole containing triaryl amine having a structure represented by formula (2):



(2).

In accordance with the organic light emitting diode (OLED) of the present invention, wherein the organic layer or film containing an organic compound represented by Formula (1) contains at least one 5,6 dihydro indeno substituted indole containing triaryl amine having a structure represented by formula (3):



(3).

In accordance with the organic light emitting diode (OLED) of the present invention, the OLED comprises an organic light emitting diode having an anode layer, such as an indium tin oxide (ITO) coated glass substrate, a cathode layer, such as aluminum, one or more of an organic electron transport layer, an organic electron injection layer, or both, interposed between the anode and the cathode, and one or more of an organic hole transport layer, an organic hole injection layer, or both, wherein at least one of the organic hole transport layer or the organic hole injection layer contains at least one 2,3 dialkyl- or indeno- substituted indole containing triaryl amine, preferably, a 2,3 dialkyl-or indeno- substituted N-phenyl indole containing triaryl amine or at least one organic compound represented by formula (1), above, or, more preferably, at least one organic compound represented by formula (2), above, or formula (3) above.

In accordance with the organic light emitting diode (OLED) of the present

invention, the OLED comprises in order, from bottom to top, the anode, the electron injection layer (EIL), the electron transport layer (ETL), the emitting material layer (EML), one or more, such as, two or more hole transport layers (HTL), one or more, such as, two or more hole injection layers (HIL), and the cathode, wherein at least one of the organic hole transport layer or the organic hole injection layer contains at least one 2,3 dialkyl- or indeno- substituted indole containing triaryl amine, preferably, a 2,3 dialkyl-or indeno- substituted N-phenyl indole containing triaryl amine, or at least one organic compound represented by formula (1), above, or, more preferably, at least one organic compound represented by formula (2), above, or formula (3) above.

In accordance with the organic light emitting diode (OLED) of the present invention, wherein the at least one organic hole transport layer, at least one organic hole injection layer, or both, comprises from 10 to 100 wt.% or, preferably, from 80 to 100 wt.% of the at least one 2,3 dialkyl- or indeno- substituted indole containing triaryl amine or, preferably, at least one 2,3 dialkyl-or indeno- substituted N-phenyl indole containing triaryl amine or an organic compound having the structure represented by formula (1) or, more preferably, at least one organic compound represented by formula (2), above, or formula (3), above.

In accordance with the organic light emitting diode (OLED) of the present invention, wherein the at least one organic hole transport layer or the at least one organic hole injection layer, or both, further comprises one or more film forming organic polymer, such as those chosen from vinyl or acrylic polymers, polyesters or polyamides or, preferably, acrylic or vinyl polymers, for example, polystyrene.

In accordance with the organic light emitting diode (OLED) of the present invention, wherein the at least one organic hole transport layer or the at least one organic hole injection layer, or both, further comprises a dopant.

As used herein, the term “alkyl,” refers to both linear and branched species. Examples of alkyls comprise methyl, ethyl, propyl, iso-propyl, butyl, iso-butyl, tert-butyl, pentyl, and hexyl.

As used herein, the term “aryl” refers to an organic radical derived from aromatic hydrocarbon by the removal of 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 6, preferably, from 5 to 6 atoms. Structures wherein two or more aryl groups are combined through single bond(s) are also comprised. Examples of aryls comprise

phenyl, naphthyl, biphenyl, anthryl, indenyl, fluorenyl, benzofluorenyl, phenanthryl, triphenylenyl, pyrenyl, perylenyl, chrysenyl, naphtacenyl, fluoranthenyl and the like. Naphthyl groups may be 1-naphthyl or 2-naphthyl. Anthryl groups may be 1-anthryl, 2-anthryl or 9-anthryl. Fluorenyl groups may be any one of 1-fluorenyl, 2-fluorenyl, 3-fluorenyl, 4-fluorenyl and 9-fluorenyl.

As used herein, the term "bicyclic" means a group or substituent having two rings.

As used herein, the term "heteroatom" means the atoms O, N, P and S. Thus, for example, a "heteroatom substituted aryl" group refers to an aryl in which at least one hydrogen atom is substituted with a heteroatom or a chemical group, such as an alkyl group containing at least one heteroatom. Examples of chemical groups containing at least one heteroatom herein comprise OR, NR_2, PR_2, $P(=O)R_2$, and SiR_3; wherein each R is hydrogen or a C_1-C_{30} hydrocarbyl which can be a C_1 to C_{20} alkyl or a C_1 to C_{30} aryl.

Specific examples of heteroatom substituted aryl groups are 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.

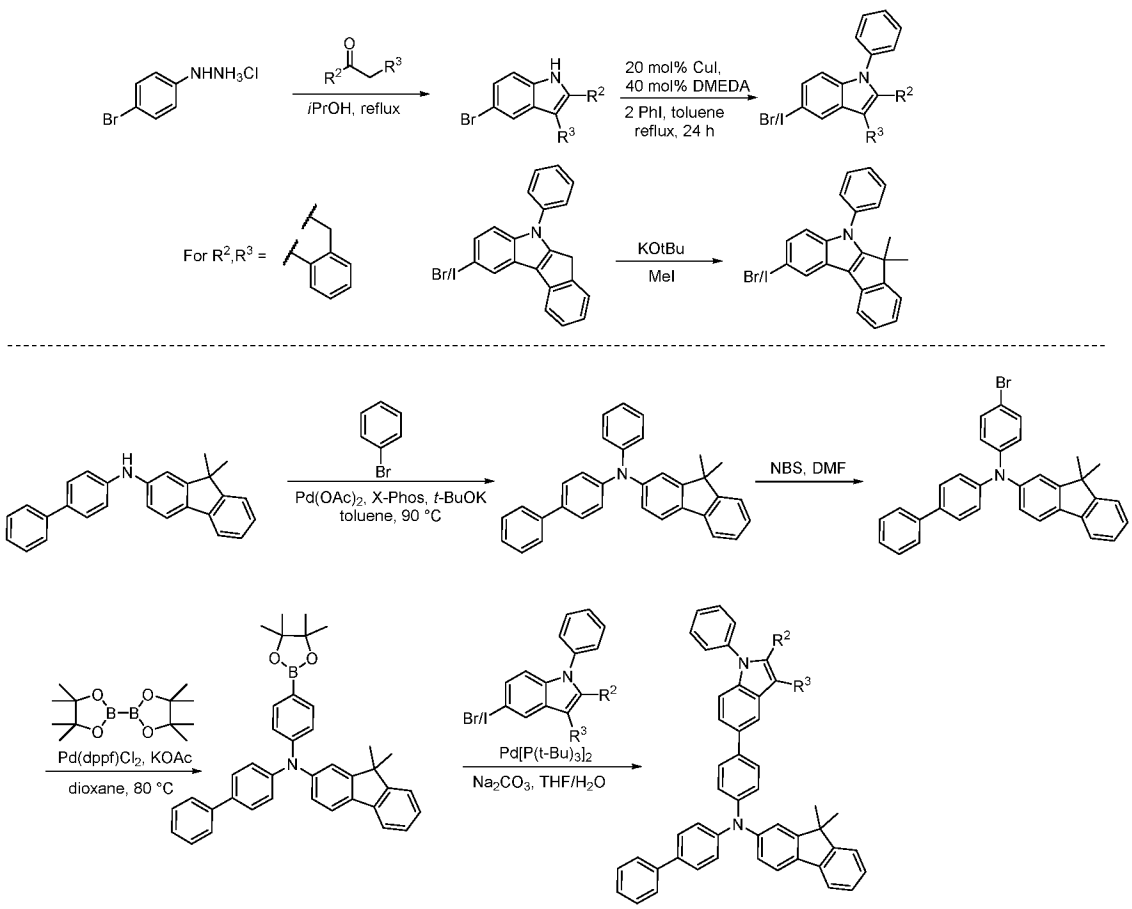
As used herein, the term "hydrocarbyl," as described herein, refers to a chemical group containing only hydrogen and carbon atoms.

As used herein, the term "cycloalkyl" refers to a monocyclic hydrocarbon or a polycyclic hydrocarbon such as an alkyl, aryl or heteroatom substituted C_7-C_{24} bicycloalkyl or adamantyl group.

The present inventors have found that organic compounds of the present invention comprising 2,3 dialkyl- or indeno- substituted indole containing triaryl amines enable the provision of organic light emitting diodes (OLED) that require less energy to power on or "turn on voltage" and provide more emissive output relative to the amount of energy input into the OLED. This can, in turn, increase the battery life of mobile devices, such as smart phones.

The compounds of this invention may be prepared by methods known in the art, e.g., by those methods illustrated in the examples and variations thereof that will be known to those skilled in the art.

The organic compounds of the present invention may be prepared by the following the reactions indicated below. In the reaction above the dotted line, below, condensation of a bromophenyl hydrazine and a ketone make an alkyl, aryl, indeno-, or halo or substituted indole, is followed by a Ullman type phenylation to make an halogenated N-phenyl indole. In the reaction below the dotted line, below, the secondary amine *N*-([1,1'-biphenyl]-4-yl)-9,9-dimethyl-9*H*-fluoren-2-amine was coupled with bromobenzene via a Pd-catalyzed Buchwald-Hartwig reaction. The resulting *N*-([1,1'-biphenyl]-4-yl)-9,9-dimethyl-*N*-phenyl-9H-fluoren-2-amine was selectively brominated using *N*-bromosuccinimide in *N*,*N*-dimethylformamide to provide *N*-([1,1'-biphenyl]-4-yl)-*N*-(4-bromophenyl)-9,9-dimethyl-9H-fluoren-2-amine. Using a Pd-catalyzed Miyaura reaction, the bromide was converted to the borolane pinacol ester, *N*-([1,1'-biphenyl]-4-yl)-9,9-dimethyl-l-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-fluoren-2-amine which serves as a common intermediate in the syntheses of the organic compounds of the present invention. The intermediate is then reacted with the halogenated N-phenyl indole from the reaction above the dotted line, below, in a Pd catalyzed addition to form the organic compounds of the present invention.



Preferably, the compounds of this invention have a molecular weight from 550 to 1000, preferably from 600 to 800.

The organic compounds of the present invention may be used in electronic devices including organic light emitting diode (OLED) devices. Light emitting devices are electronic devices that emitting light when electrical currents are applied across two electrodes in the devices. Suitable OLED devices can be the front light emitting OLEDs, rear-radiating OLEDs or double-side light emitting OLEDs.

The organic compounds of the present invention can be used, for example, in layers in red, green, blue (RGB) OLED devices and WOLED (White Organic Light Emitting Device) devices comprising, from top to bottom, red, green and blue light emitting layers as in with color filters in conventional liquid crystal devices (LCD), and wherein the blue (B) organic light-emitting layer emits whit light by phosphorescence.

The organic compounds of the present invention may be used in organic layers including hole transport layers (HTL) and hole injection layers (HIL) in electronic devices.

In addition to the organic compounds of the present invention, the at least one organic layer, for example the at least on HTL or HIL, or both may comprise one or more “dopants”. A dopant has the effect of shifting the Fermi level of the original material (i.e., the “host”), which results in a material with predominantly negative (n-type) or positive (p-type) charge carriers depending on the dopant variety.

Layers or films of the organic compounds of the present invention may comprise one or more film forming polymers and the organic compound or, an organic solvent and the organic compound. The layers or film of such organic compounds can further comprise one or more dopants.

The organic compounds of the present invention can be attached to a polymer which forms a film which can be present in an HIL an HTL or both.

Preferably, the film has a layer thickness of at least 5 nm, preferably at least 10 nm, preferably at least 20 nm, preferably no more than 90 nm, preferably no more than 80 nm, preferably no more than 70 nm, preferably no more than 60 nm, preferably no more than 50 nm.

Preferably, the organic compound(s) of the present invention are in the at least one HTL or at least one HIL layer of the OLED device and are present in a total amount of from 10 to 100 wt.%, preferably, from 80 to 100 wt.%, based on the total weight of the HTL or HIL layer. Additional hosts or dopants can be present in the device.

The layers or films of the present invention may be formed from a solution of the organic compound in an organic solvent, such as butyl acetate, o-xylene, toluene and anisole. The layers or films can also be formed from an evaporative process.

The layers or films of the present invention, include any of the organic layers of the OLED of the present invention may further comprise an organic film forming polymer, such as a vinyl or acrylic polymer, a polyester or a polyamide. Where the layers or films comprise at least one of a 2,3 dialkyl-or indeno- substituted N-phenyl indole containing triaryl amine, including, preferably, any of a 2,3 dialkyl-or indeno-substituted N-phenyl indole containing triaryl amine compound of the present invention the organic compounds of formula (1), formula (2) or formula (3), such layer or film can be synthesized by a mixture of the organic polymer and at least one organic compound of the present invention.

The layers or films of the present invention can comprise the at least one 2,3 dialkyl- or indeno- substituted indole containing triaryl amine compound, including,

preferably, any of a 2,3 dialkyl-or indeno- substituted N-phenyl indole containing triaryl amine, or the organic compounds of formula (1), formula (2) or formula (3) in oligomerized or polymerized form. Such layers or films can be formed by polymerizing a vinyl or acrylic monomer, preferably an aromatic group containing, vinyl or acrylic monomer in the presence of a thermal initiator, such as benzoyl peroxide, and in the presence of the organic compound.

The layers or films of the present invention comprising the OLED compounds can be deposited using conventional evaporative vacuum deposition or solution methods, such as spin coating, slot die coating or ink-jet printing.

EXAMPLES

The following examples illustrate embodiments of the present invention. Unless otherwise indicated, all units of temperature and pressure are room temperature and standard pressure; and, unless otherwise indicated, all parts and percentages are by weight.

Materials and NMR information

Commercially available materials purchased from third party sources were used as received. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on Bruker AVANCE III (400 MHz) spectrometer (Bruker, Freeport, Tx). Chemical shifts were recorded in parts per million (ppm) relative to tetramethylsilane (0.00). ^{1}H NMR splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), multiplet (m), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br).

Modeling of Electronic properties All computations used the Gaussian 09 or G09 suite of programs as described in Gaussian 09, Revision A.02, Frisch, M.J. *et al.*, Gaussian, Inc., Wallingford CT, 2009. The calculations were performed with the hybrid Density Functional Theory (DFT) method, Becke, 3-parameter, Lee-Yang-Parr (B3LYP), as described in Becke, A.D. *J. Chem. Phys.* 1993, *98*, 5648; Lee, C. *et al., Phys. Rev B* 1988, *37*, 785; and Miehlich, B. *et al. Chem. Phys. Lett.* 1989, *157*, 200; and the 6-31G* basis set as described in Ditchfield, R. *et al.*, *J. Chem. Phys.* 1971, *54*, 724; Hehre, W.J. *et al.*, *J. Chem. Phys.* 1972, *56*, 2257; and Gordon, M.S. *Chem. Phys. Lett.* 1980, *76*, 163. The singlet state calculations use the closed shell approximation, and the triplet state calculations use the open shell approximation. All disclosed values are quoted in electron volts (eV). The Highest Occupied

Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) values are determined from the orbital energies of the optimized geometry of the singlet ground state. The triplet energies are determined as the difference between the total energy of the optimized triplet state and the optimized ground singlet state.

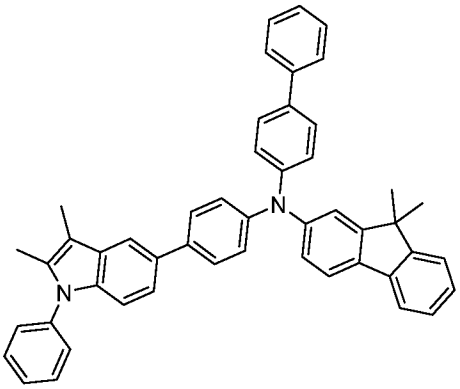
Compounds in accordance with the present invention, along with their HOMO, LUMO and triplet values are presented, below.

HOMO Range: -4.4 eV to -5.0 eV

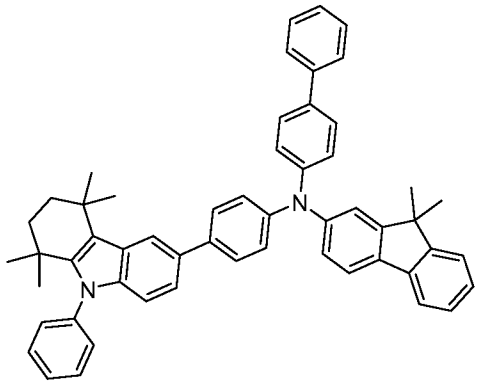
LUMO Range: Shallower than -1.25 eV

Preferred HOMO range: -4.5 eV to -4.8 eV

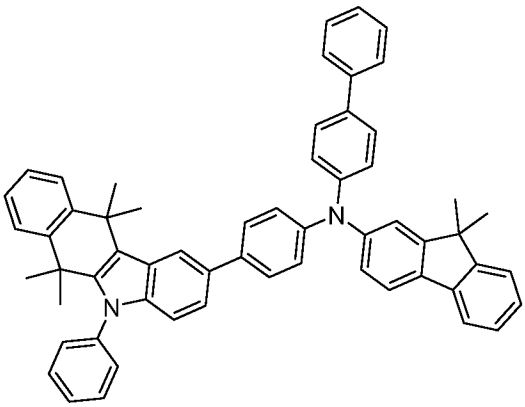
Preferred LUMO Range: Shallower than -1.0 eV



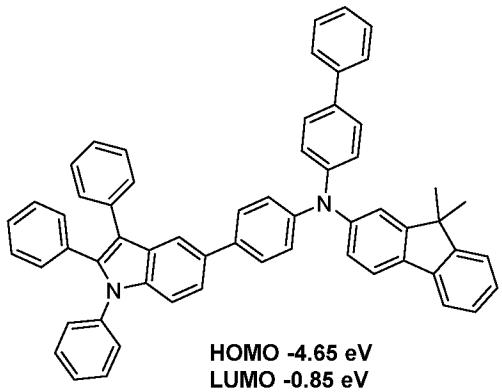
HOMO -4.63 eV
LUMO -0.85 eV
Triplet 2.61 eV



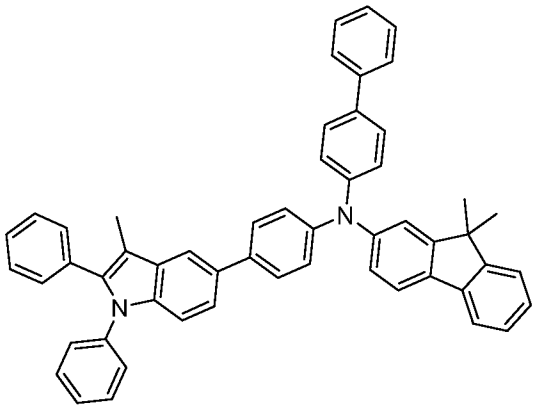
HOMO -4.62 eV
LUMO -0.84 eV
Triplet 2.61 eV



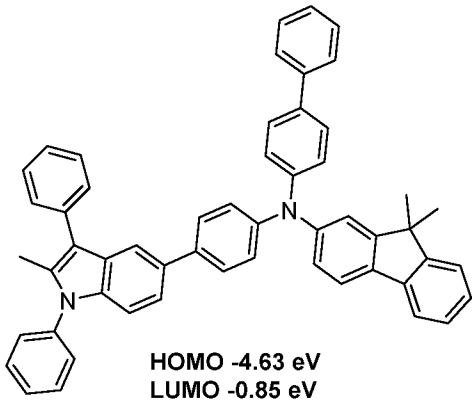
HOMO -4.65 eV
LUMO -0.85 eV
Triplet 2.61 eV



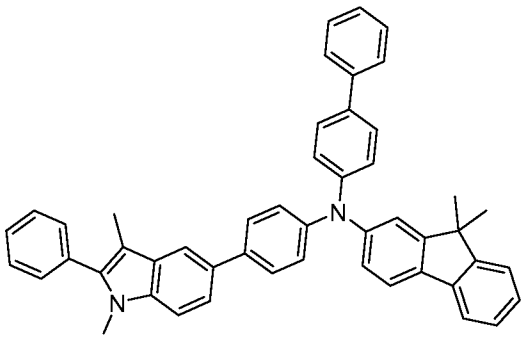
HOMO -4.65 eV
LUMO -0.85 eV
Triplet 2.61 eV



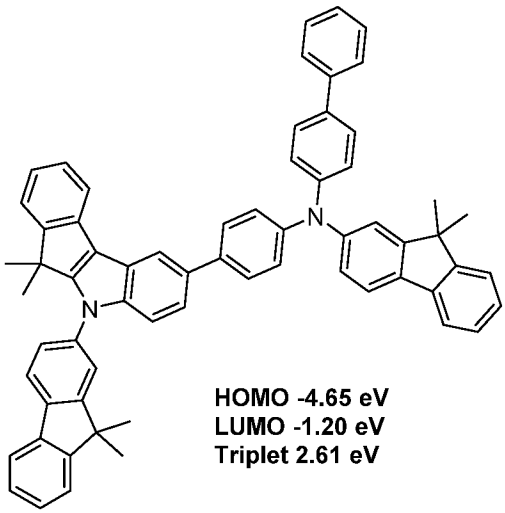
HOMO -4.66 eV
LUMO -0.86 eV
Triplet 2.61 eV



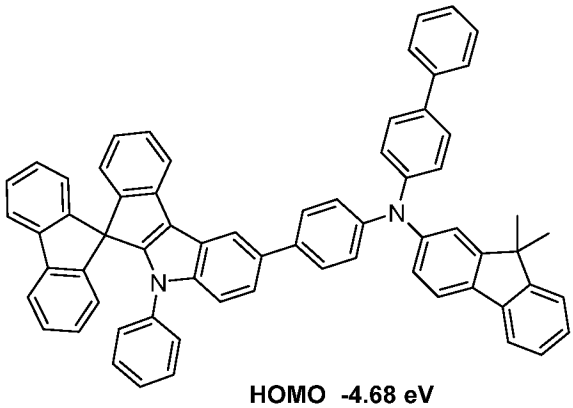
HOMO -4.63 eV
LUMO -0.85 eV
Triplet 2.63 eV



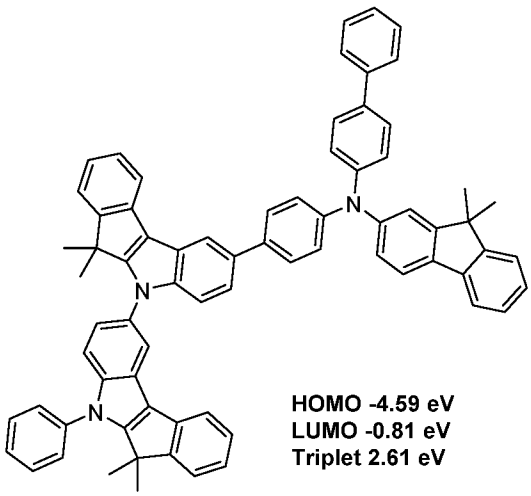
HOMO -4.64 eV
LUMO -0.86 eV
Triplet 2.59 eV



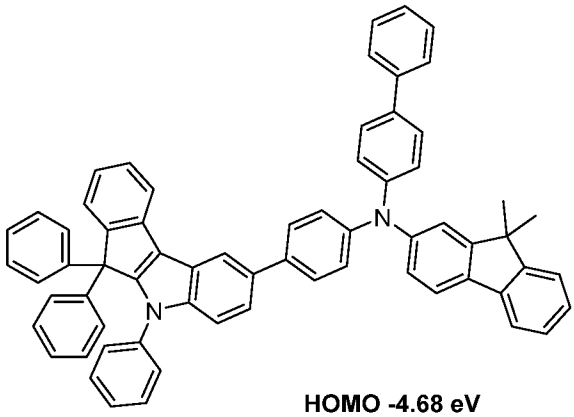
HOMO -4.65 eV
LUMO -1.20 eV
Triplet 2.61 eV



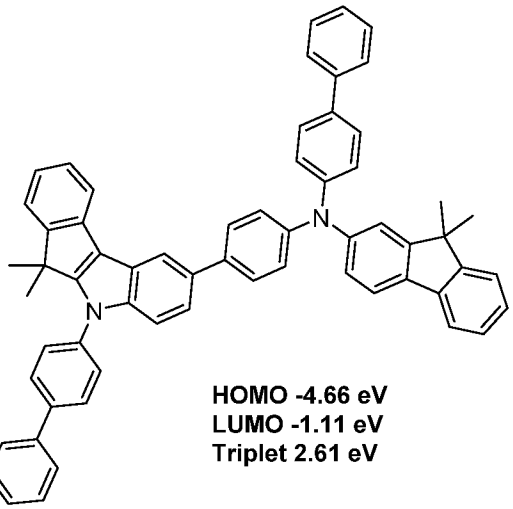
HOMO -4.68 eV
LUMO -0.91 eV
Triplet 2.61 eV



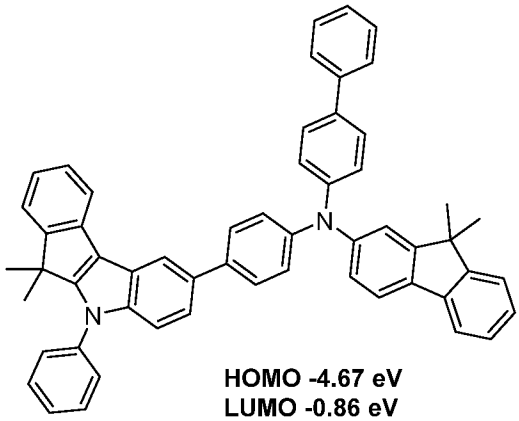
HOMO -4.59 eV
LUMO -0.81 eV
Triplet 2.61 eV



HOMO -4.68 eV
LUMO -0.88 eV
Triplet 2.61 eV



HOMO -4.66 eV
LUMO -1.11 eV
Triplet 2.61 eV



HOMO -4.67 eV
LUMO -0.86 eV
Triplet 2.61 eV

Example 1: Synthesis of the inventive compounds

In the synthesis examples that follow, Synthesis items 1-1 to 1-3 represent common intermediate steps used in making all of the compounds of the present invention; Synthesis items 1-A-1 and 1-A-2 represent steps used in making the dimethyl indole group containing triarylamine of the present invention; and Synthesis items 1-B-1, 1-B-2 and 1-B-3 represent steps used in making the indenoindole group containing triarylamines of the present invention.

1-1: Synthesis of N-([1,1'-biphenyl]-4-yl)-9,9-dimethyl-N-phenyl-9H-fluoren-2-amine 1

In a nitrogen atmosphere glovebox, N-([1,1'-biphenyl]-4-yl)-9,9-dimethyl-9H-fluoren-2-amine (10.0 g, 27.7 mmol), bromobenzene (3.9 mL, 37 mmol), palladium diacetate ($Pd(OAc)_2$) (155 mg, 0.69 mmol), 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (0.40 g, 0.83 mmol), potassium *tert*-butoxide (6.2 g, 55.3 mmol) were added into a 500 mL round-bottom flask equipped with a reflux

condenser. After addition of 150 mL dry toluene the solution turned bright yellow. The suspension was heated to 90 °C and the yellow suspension thickened considerable over the first hour. After an additional hour the solution had become less viscous and had turned brown. The reaction was allowed to continue at 90 °C and was stirred overnight. After cooling to room temperature, water was added and the organic layer was separated then dried over magnesium sulfate and filtered. The solvent was evaporated under vacuum, transferred to a large jar and then placed in the vacuum oven at 75 °C for 4 h. The brown residue (11.7 g, 97 %) was used for the next step without further purification.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dt, J = 7.5, 0.9 Hz, 1H), 7.62 – 7.56 (m, 3H), 7.52 – 7.47 (m, 2H), 7.46 – 7.36 (m, 3H), 7.35 – 7.26 (m, 4H), 7.22 – 7.15 (m, 4H), 7.10 – 7.00 (m, 2H), 1.42 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.10, 153.56, 147.83, 147.32, 147.10, 140.63, 138.94, 135.01, 134.34, 129.27, 128.73, 127.74, 126.96, 126.79, 126.63, 126.49, 124.32, 123.79, 123.54, 122.84, 122.46, 120.62, 119.43, 118.84, 46.84, 27.09.

1-2: Synthesis of N-([1,1'-biphenyl]-4-yl)-N-(4-bromophenyl)-9,9-dimethyl-9H-fluoren-2-amine 2

To a solution of N-([1,1'-biphenyl]-4-yl)-9,9-dimethyl-N-phenyl-9H-fluoren-2-amine (11.7 g, 26.7 mmol) in 50 mL N,N-dimethylformamide, N-bromosuccinimide (5.35 g, 30.0 mmol) in 30 mL N,N-dimethylformamide was added drop-wise in 30 min. After addition, the mixture was stirred at room temperature for 6 h and then poured into water to precipitate. The solid was filtrated and recrystallized from dichloromethane and ethanol to give a white solid. The white solid was sonicated in diethyl ether, filtered, and dried in a vacuum oven at 75 °C for 4 hours. First crop of solid yielded 6.4 g (46 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.62 (m, 1H), 7.62 – 7.55 (m, 3H), 7.53 – 7.47 (m, 2H), 7.46 – 7.38 (m, 3H), 7.38 – 7.34 (m, 2H), 7.32 (td, J = 7.2, 1.5 Hz, 2H), 7.28 (dd, J = 7.3, 1.4 Hz, 1H), 7.21 (d, J = 2.0 Hz, 1H), 7.19 – 7.15 (m, 2H), 7.08 – 7.02 (m, 3H), 1.43 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.26, 153.56, 147.01, 146.80, 146.58, 140.47, 138.76, 135.62, 134.84, 132.22, 128.77, 127.89, 127.01, 126.93, 126.66, 125.33, 124.07, 123.70, 122.49, 120.76, 119.52, 119.01, 114.95, 46.88, 27.08.

1-3: 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 3

A mixture of the N-([1,1'-biphenyl]-4-yl)-N-(4-bromophenyl)-9,9-dimethyl-9H-fluoren-2-amine (6.00 g, 11.6 mmol), 4,4,4',4',5,5,5',5'-octamethyl -2,2'-bi(1,3,2-

dioxaborolane) (3.54 g, 13.9 mmol), (1,1'-bis(diphenylphosphino)ferrocene)dichloropalladium (237 mg, 0.29 mmol), potassium acetate (1.71 g, 17.4 mmol), and 40 mL of dry 1,4-dioxane was heated at 85 °C under nitrogen atmosphere for 12 h. After cooling to room temperature, the solvent was removed under vacuum and then water was added. The mixture was extracted with dichloromethane. The organic layer was collected and dried over anhydrous sodium sulfate. After filtration, the filtrate was evaporated to remove solvent and the residue was purified through column chromatography on silica gel (eluent dichloromethane/hexane) to yield a fluffy white solid (2.6 g, 40 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 2H), 7.67 – 7.62 (m, 1H), 7.62 – 7.56 (m, 3H), 7.53 – 7.47 (m, 2H), 7.45 – 7.36 (m, 3H), 7.31 (ddd, *J* = 7.4, 6.4, 1.3 Hz, 2H), 7.27 (dd, *J* = 7.2, 1.6 Hz, 2H), 7.23 – 7.18 (m, 2H), 7.17 – 7.11 (m, 2H), 7.08 (dd, *J* = 8.2, 2.1 Hz, 1H), 1.42 (s, 6H), 1.34 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.14, 153.59, 150.53, 146.78, 146.61, 140.51, 138.82, 135.90, 135.76, 134.88, 128.74, 127.81, 126.97, 126.90, 126.67, 126.63, 124.71, 124.14, 122.47, 122.03, 120.69, 119.52, 119.48, 83.58, 46.85, 27.05, 24.87.

1-A-1: Synthesis of 5-bromo-2,3-dimethyl-1H-indole

A 500 mL three neck round bottomed flask equipped with a stir bar, thermocouple, heat mantle, and water condenser with nitrogen inlet was charged with 3-bromophenylhydrazine hydrochloride (19.84 g, 88.77 mmol) and isopropanol (240 mL). 2-Butanone (8.0 mL, 89.32 mmol) was added and the reaction was heated to 80 °C. After 4 days the reaction was allowed to cool to room temperature. The solvent was removed by rotary evaporation and the red residue dissolved in ethyl acetate (200 mL). The organic layer was washed with 1N hydrochloric acid (100 mL) and saturated aqueous sodium bicarbonate (100 mL). The organic layer was dried over magnesium sulfate, filtered, and concentrated by rotary evaporation to give 5-bromo-2,3-dimethyl-1H-indole as a red solid (15.94 g, 71.1 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.59 – 7.55 (m, 1H), 7.17 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.11 (dd, *J* = 8.4, 0.6 Hz, 1H), 2.35 (d, *J* = 0.8 Hz, 3H), 2.17 (q, *J* = 0.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.77, 132.10, 131.27, 123.54, 120.61, 112.26, 111.35, 107.02, 11.58, 8.35.

1-A-2: Synthesis of 5-iodo-2,3-dimethyl-1-phenyl-1H-indole

In a nitrogen glove box a 0.5 L round bottomed flask was filled with toluene (300 mL). It was then charged with 5-bromo-2,3-dimethyl-1H-indole (15.?**?**? g, 67.0

mmol), CuI (12.76 g, 67 mmol), K_3PO_4 (28.452 (134 mmol), and N,N'-dimethylethylene-1,2-diamine (10.82 mL, 100 mmol). The mixture was stirred and iodobenzene 20 (15 mL, 134 mmol) was added. The flask was fitted with a Stevens condenser and was refluxed for 3 days. The reaction was monitored by GC-MS and it was shown that 5-bromo-2,3-dimethyl-1H-indole was completely consumed. The reaction was allowed to cool to room temperature and was taken out of the box and poured into a 1L round bottomed flask that contained diethyl ether (500 mL). A precipitate formed and the mixture was filtered. Upon sitting for an additional 30 minutes more precipitate formed which was also filtered away. The crude product was isolated upon removing the organic solvent to afford 21 as a dark oil. The oil was deposited on silica using dichloromethane as the solvent. Purification by column chromatograph (0-15% dichloromethane in hexane) using a Biotage ® SNAP Ultra 340 g column, afforded 12 g (51.5% yield) of 5-iodo-2,3-dimethyl-1-phenyl-1H-indole that contained ca.10% of 5-bromo-2,3-dimethyl-1-phenyl-1H-indole. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 1.7 Hz, 1H), 7.50 (m, 2H), 7.42 (m, 1H), 7.36 – 7.23 (m, 3H), 6.84 (d, *J* = 8.5 Hz, 1H), 2.25 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.90, 136.58, 134.01, 131.49, 129.61, 129.41, 128.01, 127.88, 126.91, 111.86, 107.45, 82.96, 11.05, 8.90.

Example 1A: Final synthesis of dimethyl indole group containing triarylamine of the present invention

A two neck round bottom flask was charged with 5-iodo-2,3-dimethyl-1-phenyl-1H-indole (2.5 g, 7.2 mmol), 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 (4.9 g, 8.6 mmol, 1.2 equiv), toluene (60 mL), ethanol (16 mL), and potassium carbonate (1.2M aq: 20 mL). The flask was purged with nitrogen for 15 min after which time, palladium acetate (0.05 g, 0.2 mmol), and 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (0.21 g, 0.43 mmol) were added. The reaction was heated to 90 °C overnight. The following day, the reaction was cooled to room temperature, and the organic layer was isolated. The aqueous layer was extracted with toluene (40 mL). The combined organic fractions were washed with water (100 mL) and brine (100 mL). The organic fraction was then added to a flask containing silica for a dry pack on a Biotage™ 340 g SNAP Ultra column (Biotage, Charlotte, NC). The solvent was removed by rotary evaporation. The silica was transferred to the dry pack samplet which was connected to the column and purified on the Biotage™ automated purification

system (Biotage). Vials 8-10 were combined to form fraction A and were concentrated on the rotary evaporator (2.922 g, 62 %). Fraction A was analyzed by LC/MS yielding a purity of 98.8 %.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 1.7 Hz, 1H), 7.67 – 7.63 (m, 1H), 7.61 (d, J = 2.9 Hz, 1H), 7.60 (q, J = 2.0 Hz, 2H), 7.59 (d, J = 4.4 Hz, 2H), 7.56 – 7.47 (m, 5H), 7.46 – 7.38 (m, 5H), 7.38 – 7.34 (m, 2H), 7.34 – 7.27 (m, 4H), 7.27 – 7.20 (m, 6H), 7.15 (d, J = 8.2 Hz, 1H), 7.14 – 7.10 (m, 1H), 2.36 (s, 3H), 2.25 (s, 3H), 1.44 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.10, 153.58, 147.37, 147.14, 146.05, 140.68, 139.01, 138.28, 137.45, 136.68, 134.89, 134.21, 133.52, 132.55, 129.38, 129.30, 128.73, 128.04, 127.95, 127.79, 127.73, 127.42, 127.33, 126.95, 126.83, 126.75, 126.63, 126.53, 126.43, 124.60, 124.30, 123.97, 123.76, 123.63, 123.46, 122.46, 120.67, 120.63, 120.61, 119.46, 119.41, 118.93, 118.72, 116.05, 109.94, 108.36, 46.87, 27.12, 11.02, 8.93.

1-B-1: Synthesis of 2-bromo-5,6-dihydroindeno[2,1-b] indole 4

2-indanone (24.8 g, 188 mmol) and 4-bromophenylhydrazine hydrochloride (42.0 g, 188 mmol) were dissolved in isopropanol (300 mL) and stirred for 2 days at 80 °C. The solvent was removed and the resulting brown solid was recrystallized from methanol yielding the product as a tan solid (15 g, 28 %).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.97 (dt, J = 1.7, 0.8 Hz, 1H), 7.61 (dt, J = 7.4, 0.9 Hz, 1H), 7.47 – 7.39 (m, 1H), 7.35 (td, J = 7.5, 1.1 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.12 (td, J = 7.5, 1.2 Hz, 1H), 3.75 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.09, 142.25, 139.24, 139.14, 127.15, 124.78, 124.25, 123.64, 123.00, 121.88, 118.57, 113.62, 113.08, 31.27

1-B-2: Synthesis of 2-iodo-5-phenyl-5,6-dihydroindeno[2,1-b]indole 5

In a nitrogen atmosphere glovebox, a 0.5 L two-necked round bottom flask containing dry toluene (100 mL) was charged with the indenoindole (13.5 g, 47.4 mmol), phenyl iodide (14.5 g, 71.1 mmol), copper iodide (1.81 g, 9.48 mmol), finely ground potassium phosphate (20.1 g, 94.8 mmol) and N,N'-dimethylethylenediamine (1.67 g, 19.0 mmol). The flask was fitted with a Steven's condenser and the reaction mixture was refluxed overnight. The reaction was cooled and the volatiles were removed on a rotary evaporator. The solid residue was extracted with diethyl ether and filtered. Silica gel (SiO_2) was added to the ether filtrate and the material was concentrated onto the silica gel. The material was then purified by column chromatography (SiO_2) eluting with hexane/ethyl acetate (6.0 g, 31 %). The material produced by this step is predominately composed of the desired iodo species;

however, the brominated congener, 2-bromo-5-phenyl-5,6-dihydroindeno[2,1-b]indole, (~10-25 mol %) is also present. The two compounds could not be separated and the mixture was used without further purification for subsequent reactions. Chemical shifts are reported for the 2-iodo-5-phenyl-5,6-dihydroindeno[2,1-b]indole. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 1.7 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.60 – 7.48 (m, 4H), 7.48 – 7.39 (m, 3H), 7.36 (td, *J* = 7.0, 6.4, 1.6 Hz, 1H), 7.31 – 7.22 (m, 1H), 7.13 (td, *J* = 7.5, 1.1 Hz, 1H), 3.77 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.71, 141.98, 140.23, 139.19, 138.17, 130.19, 130.05, 128.44, 127.51, 127.36, 124.93, 124.80, 123.36, 122.18, 121.70, 118.91, 113.34, 84.63, 31.68.

1-B-3: Synthesis of 2-iodo-6,6-dimethyl-5-phenyl-5,6-dihydroindeno[2,1-b]indole 6

To an ice-cooled solution of 2-iodo-5-phenyl-5,6-dihydroindeno[2,1-b]indole (6.0 g, 15 mmol) in dry tetrahydrofuran (50 mL) under an argon atmosphere was added potassium *tert*-butoxide (3.3 g, 30 mmol, 2 equiv), and the solution was stirred at room temperature for 1.5 h. methyl iodide (1.8 mL, 30 mmol, 2 equiv) was added. The reaction mixture was stirred for a further 2 h. A white solid produced during the reaction was removed by filtration, and after evaporation of the filtrate the product was afforded as a yellow solid. The yellow solid was purified by column chromatography (silica gel) eluting with a gradient of hexane/dichloromethane. The desired fractions were combined and concentrated to yield the product as a slightly yellow solid (3.7 g, 57 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 1.6 Hz, 1H), 8.00 (d, J = 1.8 Hz, 0H), 7.61 (dt, J = 7.4, 0.9 Hz, 1H), 7.55 (qd, J = 4.1, 2.2 Hz, 4H), 7.43 (ddd, J = 7.2, 3.0, 1.3 Hz, 3H), 7.39 (dd, J = 8.6, 1.7 Hz, 1H), 7.32 (td, J = 7.5, 1.2 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.22 (dd, J = 8.7, 1.9 Hz, 0H), 7.13 (td, J = 7.5, 1.2 Hz, 2H), 6.92 (d, J = 8.7 Hz, 0H), 6.83 (d, J = 8.6 Hz, 1H), 1.37 (d, J = 2.0 Hz, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.03, 156.64, 153.85, 153.82, 142.23, 141.75, 137.30, 137.25, 136.60, 129.73, 129.51, 129.41, 128.87, 128.61, 128.51, 128.10, 127.16, 124.18, 124.02, 123.49, 123.20, 121.82, 121.61, 118.78, 118.74, 117.94, 117.67, 114.01, 113.04, 112.48, 84.31, 44.28, 25.26.

Example 1B: Synthesis of indenoindole group containing triarylamine of the present invention

To two-neck flask charged with 2-iodo-6,6-dimethyl-5-phenyl-5,6-dihydroindeno[2,1-b]indole (2.0 g, 4.6 mmol), 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__(3.1 g,

5.5 mmol, 1.2 equiv) , palladium diacetate (0.31 g, 0.14 mmol, 0.03 equiv) and 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (0.13 g, 0.28 mmol, 0.06 equiv) under nitrogen was added toluene (60 mL) to the mixture was added ethanol (16 mL) and potassium carbonate(1.2M aq: 20 mL). The reaction was heated to reflux overnight. The reaction was allowed to cool to room temperature, the solvent was removed on the rotary evaporator and extracted with dichloromethane. The organic layer washed with water, dried over sodium sulfate, filtered, concentrated, and purified using silica gel chromatography using a gradient of dichloromethane in hexanes to yield 2.22 g of HTL-104 in 99.6 % purity (65 % yield). An additional 1.05 g of material was also isolated in 85 % purity which was saved in case additional material was needed (total yield 95 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 1.7 Hz, 1H), 7.73 – 7.68 (m, 1H), 7.68 – 7.64 (m, 1H), 7.62 (ddd, J = 8.2, 3.7, 2.2 Hz, 4H), 7.58 – 7.47 (m, 7H), 7.47 – 7.37 (m, 4H), 7.37 – 7.21 (m, 11H), 7.18 – 7.07 (m, 3H), 1.46 (s, 6H), 1.41 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.68, 155.17, 154.06, 153.62, 147.35, 147.11, 146.41, 142.45, 140.69, 139.01, 137.80, 137.25, 137.00, 135.06, 134.36, 134.02, 129.36, 128.76, 128.63, 128.23, 127.79, 127.11, 126.98, 126.81, 126.67, 126.50, 124.49, 123.90, 123.61, 123.19, 122.49, 122.30, 121.59, 121.01, 120.69, 119.46, 118.87, 118.79, 118.75, 117.51, 111.28, 46.91, 44.34, 31.61, 27.15, 25.40, 22.67, 14.14.

Example 2: OLED Blue Device Fabrication

An OLED device containing the indicated organic compound as the hole transport layer was fabricated by thermally depositing the organic layers onto an indium tin oxide (ITO) coated glass substrate that serves as an anode, in order, from bottom to top, a hole injection layer (HIL), a hole transport layer (HTL), an emitting material layer (EML), an electron transport layer (ETL), and an electron injection layer (EIL), , and topping the resulting article with an aluminum cathode. Thermal deposition was conducted by chemical vapor deposition in a vacuum chamber with a base pressure of $<10^{-7}$ torr. The deposition rates of organic layers were maintained at 0.1-0.05 nm/s. The aluminum cathode was deposited at 0.5 nm/s. The active area of the OLED device was “3 mm x 3 mm.” Organic materials used in organic layers were all purified by sublimation before deposition, and were placed inside the vacuum chamber until it reached 10^{-6} torr. To evaporate each material, a controlled current was applied between the anode and the cathode to raise the temperature to keep the constant evaporation rate of 1A/s for each organic material.

The material used and thickness of each indicated organic layer are shown in Table 1, below.

A comparative OLED device containing the indicated comparative material as the hole transport layer (HTL) was prepared using the procedure described above and was tested as described below.

Table 1: Blue OLED Devices

Layer (thickness)		**Name** (CAS number)
HIL (60 nm)		N4,N4'-diphenyl-N4,N4'-bis(9-phenyl-9H-carbazol-3-yl)-[1,1'-biphenyl]-4,4'-diamine (CAS No. 887402-92-8)
HTL (25 nm)		N-([1,1'-biphenyl]-4-yl)-9,9-dimethyl-N-(4-(9-phenyl-9H-carbazol-3-yl)phenyl)-9H-fluoren-2-amine (HTL-C, CAS No. 1242056-42-3) (Example C: Comparative device)
		Example 1A or 1B (Inventive device)
EML (20 nm)	Host	9-phenyl-10-(4-phenylnaphthalen-1-yl)anthracene (CAS No. 1207336-74-0)
	Dopant (2 wt% of host)	N1,N6-bis(5'-fluoro-[1,1':3',1"-terphenyl]-4'-yl)-N1,N6-diphenylpyrene-1,6-diamine (CAS No. 1228525-73-2)
ETL (30 nm)		2,4-bis(9,9-dimethyl-9H-fluoren-2-yl)-6-(naphthalen-2-yl)-1,3,5-triazine (CAS No. 1459162-51-6) and lithium quinolate (CAS No. 25387-93-3) co-evaporated at a 1:1 weight ratio
EIL (2 nm)		lithium quinolate (CAS No. 25387-93-3)

The OLED devices were tested for Driving Voltage or turn on voltage and efficiency, as follows:

The current density-voltage-luminance (J-V-L) characterizations for the OLED devices were performed with a KEITHLEY 2635A-SYS Single-channel System Source Meter (Keithley Instruments, Cleveland, OH) and, to measure luminance, a MINOLTA CS-100A Chroma Meter (Konica Minolta, Osaka, JP). From these measurements, power efficiency in lm/W to achieve a desired light intensity output was by calculating according to formula:

Power Efficiency (lm/W)=

(π x luminance (Cd/m^2))/(V x Current density (mA/cm^2)) x 10^{-1}.

Cd/A: Luminous efficiency is calculated according to the following formula:

Cd/A= (Luminance (Cd/m^2)/Current density (mA/cm^2)) x 10^{-1}.

nit: Is a measure of light intensity output, a higher value is more intense; 1000 nit is high, akin to accelerated aging. 1 nit = 1 candela (Cd/m^2).

As shown in Table 2, below, at 500 nit, the inventive OLED devices using the compounds of the present invention had a significantly lower turn on voltage (Driving Voltage) and substantially higher Efficiency in terms of lumens per Watt compared to

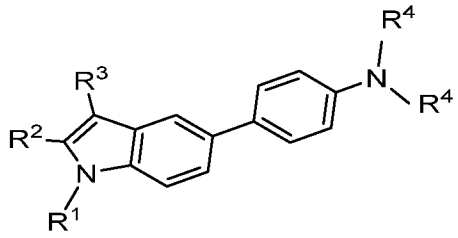
that of Comparative Device.

Table 2: Performance of Blue OLED Devices

Device (500nit)	**OLED in HTL**	**Driving Voltage** (V)	**Power Efficiency** (lm/W)
Comparative Device	Example C	4.5	3.8
Inventive Device 1	Example 1A	4.2	4.4
Inventive Device 2	Example 1B	4.3	4.4

We claim:

1. An organic compound for use in an electronic device having a structure represented by Formula (1):



(1)

wherein R^1 is a C_1 to C_{20} alkyl group or alkenyl group, a C_6 to C_{30} aryl group, a heteroatom substituted C_1 to C_{20} alkyl group or alkenyl group, a heteroatom substituted C_6 to C_{30} aryl group or arylene group; further wherein, each of R^2 and R^3, independently, is a C_1 to C_{20} alkyl group; or, further wherein R^2 and R^3 together form a C_7 to C_{12} bicyclic alkylaryl group or alkyl substituted bicyclic alkylaryl group; and, still further wherein, each R^4 is, independently, a biphenyl, indenyl, or fluorenyl, group.

2. The organic compound as claimed in claim 1, which is a 2,3 dialkyl- or indeno-substituted N-phenyl indole containing triaryl amine.

3. The organic compound as claimed in claim 1 which is a 2,3 dimethyl-substituted N-phenyl indole containing triaryl amine.

4. The organic compound as claimed in claim 1, wherein R^1 is, a C_6 to C_{12} aryl group or arylene group.

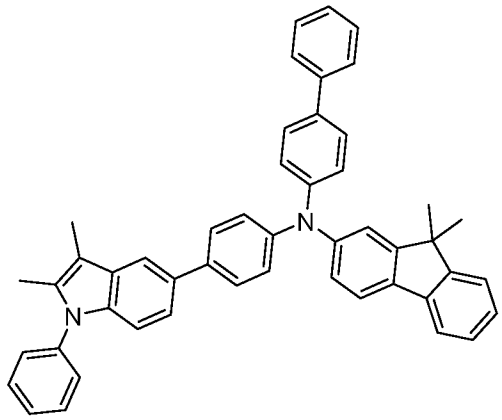
5. The organic compound as claimed in claim 1, wherein each of R^2 and R^3, independently, is C_1 to C_4 alkyl group,

6. The organic compound as claimed in claim 5, wherein each of R^2 and R^3 is a methyl group.

7. The organic compound as claimed in claim 1, wherein R^2 and R^3 together form a dihydroindeno group.

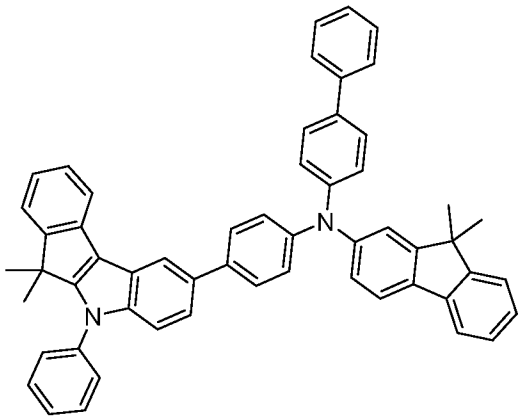
8. The organic compound as claimed in claim 1, wherein one R^4 is a biphenyl group and one is a fluorenyl group.

9. The organic compound as claimed in claim 1 comprising a 2,3 dimethyl substituted indole containing triaryl amine having a structure represented by Formula (2):



(2).

10. The organic compound as claimed in claim 1, which is a 5,6 dihydro indeno substituted indole containing triaryl amine having a structure represented by formula (3):



(3).

11. A film comprising an organic layer containing from 10 to 100 wt.% of at least one 2,3 dialkyl- or indeno- substituted indole as claimed in claim 1.

12. The film as claimed in claim 11, further comprising one or more film forming organic polymer, and/or one or more dopants.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/057496

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D209/08 H01L51/50
ADD.

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

B. FIELDS SEARCHED

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

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 298 737 A1 (SAMSUNG MOBILE DISPLAY CO LTD [KR]) 23 March 2011 (2011-03-23) compound 30 (page 15); claims; figures; tables 1, 2	1-6,8,9, 11,12
X A	WO 2015/174792 A1 (DONGJIN SEMICHEM CO LTD [KR]) 19 November 2015 (2015-11-19) paragraphs [0097], [0102]; claims; figure 1; table 1	1,2,4,8, 11,12 3,5,6,9

☐ 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
11 December 2017	19/03/2018

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Gavriliu, Daniela

1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2017/057496

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

3, 5, 6, 9(completely); 1, 2, 4, 8, 11, 12(partially)

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2017/057496

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 2298737 A1	23-03-2011	CN 102001987 A	06-04-2011
		EP 2298737 A1	23-03-2011
		JP 5343044 B2	13-11-2013
		JP 2011046689 A	10-03-2011
		KR 20110023088 A	08-03-2011
		US 2011049484 A1	03-03-2011
WO 2015174792 A1	19-11-2015	NONE	

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 3, 5, 6, 9(completely); 1, 2, 4, 8, 11, 12(partially)

   Indole derivatives of formula (I), wherein R2 and R3 are a C1-C20 group, useful as hole transporter layers in OLED

   ---

2. claims: 7, 10(completely); 1, 2, 4, 8, 11, 12(partially)

   Indole derivatives of formula (I), wherein R2 and R3 form together a bicycle useful as hole transporter layers in OLED.
