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(54) **Title**: OXADIAZOLE AND TRIAZOLE META-LINKED N-PHENYL CARBAZOLE AMBIPOLAR HOST MATERIALS

(57) **Abstract**: Ambipolar compounds comprising, for example, carbazole moieties and oxadiazole moieties. Can be used for organic electronics including OLEDs including electron transfer layers and emitter hosts. The compounds can have an electron deficient core having a substituent comprising a first phenyl group which is substituted with a second phenyl group that is substituted with a relatively electron rich moiety.

OXADIAZOLE AND TRIAZOLE META-LINKED N-PHENYL CARBAZOLE AMBIPOLAR HOST MATERIALS

BACKGROUND

Considerable research has been directed toward the synthesis of organic light-emitting diodes (OLEDs), in view of their potential applications in full-color flat panel displays and solid-state lighting. Such OLEDs often contain a light emissive layer comprising a luminescent material as a guest, dispersed and/or dissolved in a mixture of host/carrier materials capable of transporting holes, electrons, and/or excitons into contact with the luminescent guest. The light emissive layer is typically disposed between an anode and a cathode.

Compounds comprising the carbazole group have been utilized as hole transporter and/or electron blocking materials in OLED applications, and in some cases as hole-transporting hosts for luminescent guests. In addition, small-molecule 2,5-diaryl oxadiazoles are known as suitable electron transport materials for use in making electron transport layers for OLED devices, and have also been used as electron transport hosts for luminescent guests.

Identifying host materials that can efficiently perform important functions can be difficult, especially for use with guest materials that emit at relatively high photon energy at the blue part of the visible spectrum. In order to maximize energy transfer from the host materials to the guest emitters, the energies of both the singlet and triplet states of the hole and/or electron transport materials in the host should be at least somewhat higher than the energies of the corresponding singlet and triplet states of the guest emitters. To achieve such high energy excited states, the conjugation of the organic host materials must be limited, in order to provide for singlet and triplet energy levels higher than those of the guest emitters. This can be challenging for OLEDs employing high photon energy guest emitters.

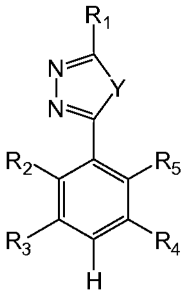
In some cases, mixtures of hole transport and electron transport materials have been used to form a host material for phosphorescent guests in the emissions layers of multi-layer OLEDs. However, devices based on such mixtures of hole transport and electron transport materials in their emission layers can undergo undesirable phase separations, partial crystallizations, and/or otherwise degrade upon extended OLED device operation, decreasing OLED device efficiency and/or lifetimes over time.

Progress on efficient hosts for higher photon energy phosphorescent emitters has been significantly slower, and the efficiencies and lifetimes of such PhOLEDs remain in need of significant improvement. Accordingly, there remains an unmet need in the art for improved host materials that can efficiently and stably transport holes and electrons into contact with phosphorescent emitters in OLED emission layers.

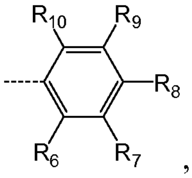
SUMMARY

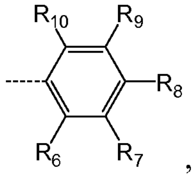
Embodiments described herein include compounds and compositions, and methods of making and using the same. Also described are articles and devices.

For example, one embodiment provides a compound represented by formula (I):

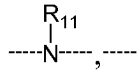
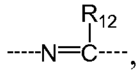


(I), wherein:

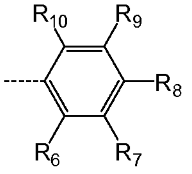
a) one or two of R_2, R_3, R_4 and R_5 are represented by , and the remaining of R_2, R_3, R_4 and R_5 are independently selected from hydrogen, halogen and a $C_{1\text{-}20}$ organic group;

b) for each , one or two of R_6, R_7, R_8, R_9 and R_{10} are optionally substituted carbazole groups; and the remaining of R_6, R_7, R_8, R_9 and R_{10} are independently selected from hydrogen, halogen and a $C_{1\text{-}20}$ organic group;

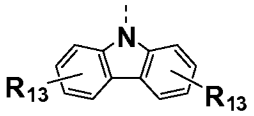
c) R1 is an optionally substituted aryl group, an optionally substituted heteroaryl group, an optionally substituted alkyl group or an optionally substituted heteroalkyl group; and

d) Y is selected from -----O-----,  $\text{-----}\underset{}{\overset{R_{11}}{\overset{|}{N}}}\text{-----}$, -----N=N---- and  $\text{-----}N{=}\overset{R_{12}}{\overset{|}{C}}\text{-----}$, wherein R_{11} is an optionally substituted aryl group, an optionally substituted heteroaryl group, an optionally substituted alkyl group or an optionally substituted heteroalkyl group, and wherein R_{12} is hydrogen, an optionally substituted aryl group, an optionally substituted heteroaryl group, an optionally substituted alkyl group or an optionally substituted heteroalkyl group.

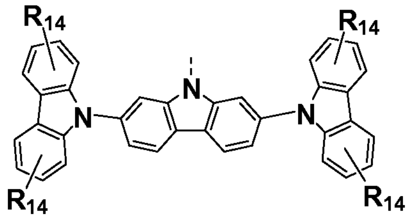
Another embodiment provides that: (i) the remaining of R_2, R_3, R_4 and R_5 are independently selected from hydrogen, fluoro, cyano, alkyl, fluoroalkyl, alkoxide and fluoroalkoxide group; (ii) the carbazole group is unsubstituted or is substituted with one or more groups selected from fluoro, cyano, alkyl, fluoroalkyl, alkoxide, fluoroalkoxide and an optionally substituted carbazole; (iii) the remaining of R_6, R_7, R_8, R_9 and R_{10} are independently selected from hydrogen, fluoro, cyano, alkyl, fluoroalkyl, alkoxide and fluoroalkoxide; (iv) R_1, R_{11} and R_{12} are unsubstituted or substituted with one or more groups selected from hydroxyl, fluoro, cyano, alkyl, fluoroalkyl, alkoxide, and fluoroalkoxide.

Another embodiment provides that  is present at R_3 and/or R_4 but not at R_2 or R_5, and wherein the optionally substituted carbazole group is present at R_7 and/or R_9 but not at R_6, R_8 or R_{10}.

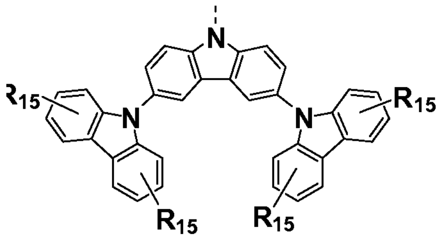
Another embodiment provides that the optionally substituted carbazole group is selected from formulae (II), (III), (IV), (V) and (VI):



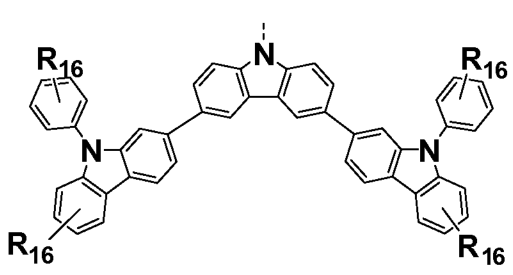
(II)



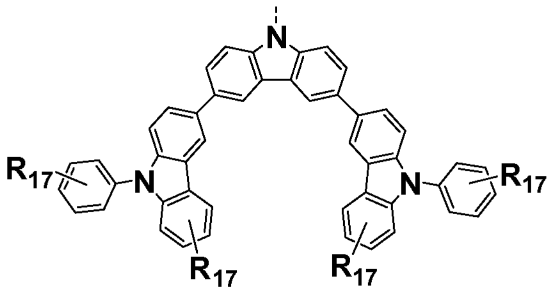
(III)



(IV)

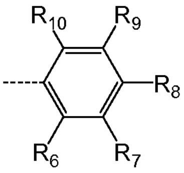


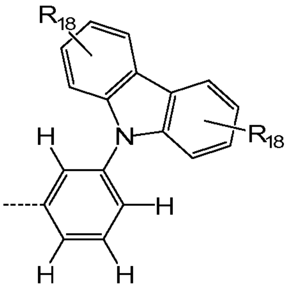
(V)

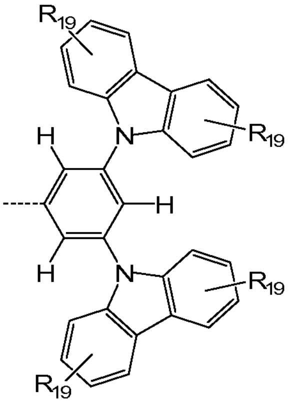


(VI)

wherein each R_{13}, R_{14}, R_{15}, R_{16} and R_{17} is independently hydrogen, fluoro, cyano, a C_{1-20} linear or branched alkyl, a C_{1-20} linear or branched fluoroalkyl, a C_{1-20} linear or branched alkoxide, or a C_{1-20} linear or branched fluoroalkoxide group.

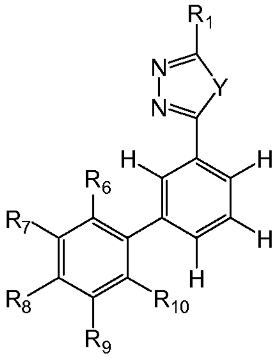
Another embodiment provides that  is selected from formulae (VII) and (VIII):

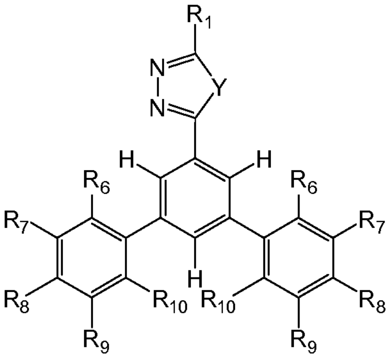

(VII)

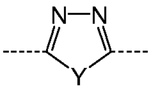
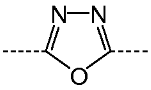

(VIII)

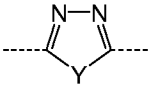
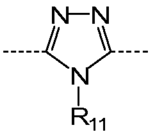
wherein each R_{18} and R_{19} is independently hydrogen, fluoro, cyano, a C_{1-20} linear or branched alkyl, a C_{1-20} linear or branched fluoroalkyl, a C_{1-20} linear or branched alkoxide, a C_{1-20} linear or branched fluoroalkoxide group, or an optionally substituted carbazole.

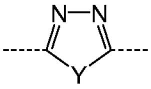
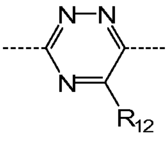
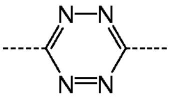
Another embodiment provides that the compound is selected from formulae (IX) and (X):


(IX)

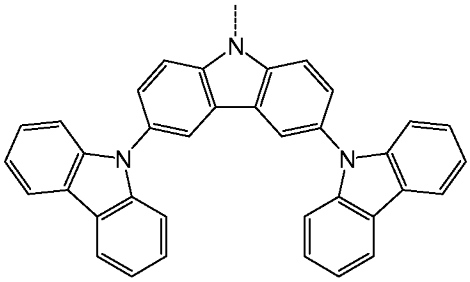

(X).

Another embodiment provides that  is  .

Another embodiment provides that  is  .

Another embodiment provides that  is  or  .

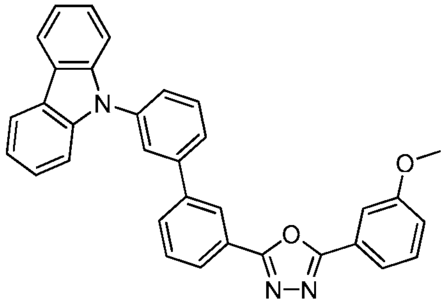
Another embodiment provides that the compound comprises at least one triscarbazole group represented by



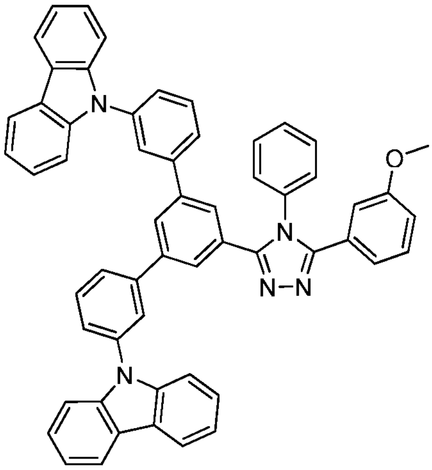
.

Another embodiment provides that R_1 comprises at least one crosslinkable group.

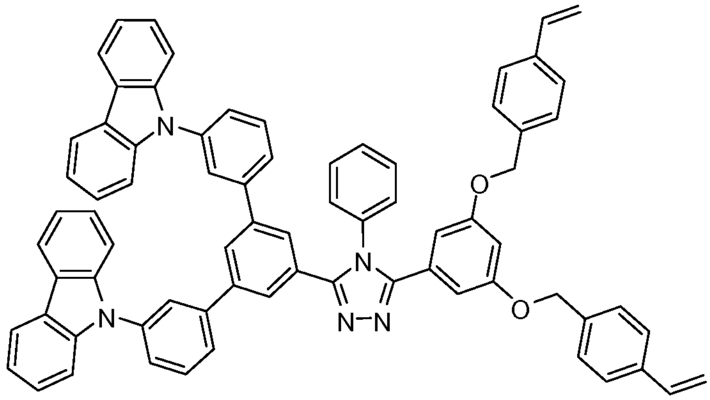
Another embodiment provides that the compound is selected from:



,

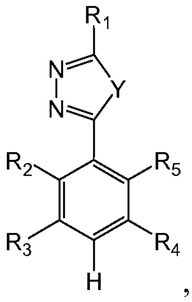


, and



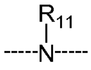
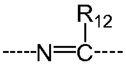
.

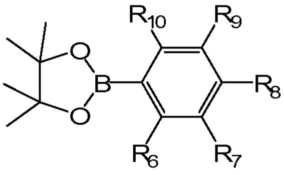
Another embodiment provides a method for making the compounds described herein, comprising reacting a first compound with a second compound, wherein:

(a) the first compound is represented by , wherein

(i) one or two of R_2, R_3, R_4 and R_5 are Br, and the remaining of R_2, R_3, R_4 and R_5 in the formula representing the first compound have the same definition as their R_2, R_3, R_4 and R_5 homologues as described herein;

(ii) R_1 in the formula representing the first compound has the same definition as its R_1 homologues contained in the formula of the compound described herein; and

(iii) Y is selected from ----O----,  $\overset{R_{11}}{\overset{|}{\text{-----N-----}}}$,----N=N---- and  $\overset{\quad R_{12}}{\text{----N=}\overset{|}{\text{C}}\text{----}}$, wherein R_{11} and R_{12} in the formula representing the first compound have the same definition as their R_{11} and R_{12} homologues contained in the formula of the compound described herein;

(b) the second compound is represented by , wherein R_6, R_7, R_8, R_9 and R_{10} in the formula representing the second compound have the same definition as their R_6, R_7, R_8, R_9 and R_{10} homologues contained in the formula of the compound described herein.

Other embodiments provide for a composition comprising the compounds described herein or made by the methods described herein.

Another embodiment is an electroluminescence device, comprising an anode, a cathode, and an emissive layer, wherein the emissive layer comprises the compound as described herein or made by the methods as described herein, or the composition as described herein.

Another embodiment provides that the emissive layer comprises at least one phosphorescent emitter, and wherein the external quantum efficiency of the electroluminescence device at a luminance of 1,000 cd/m^2 is at least 5%.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows performance of OLED devices with spin-coated Compound H hole transport layer and evaporation-deposited Compound A: Ir(ppy)3 emitting layer.

FIG. 2 shows performance of OLED devices with spin-coated Compound H hole transport layer and evaporation-deposited Compound A: FIrpic emitting layer.

DETAILED DESCRIPTION

INTRODUCTION

All references described herein are hereby incorporated by reference in their entireties. Various terms are further described herein below:

“A”, “an”, and “the” refers to “at least one” or “one or more” unless specified otherwise.

“Optionally substituted” groups can refer to, for example, functional groups that may be substituted or unsubstituted by additional functional groups. For example, when a group is unsubstituted, it can be referred to as the group name, for example alkyl or aryl. When a group is substituted with additional functional groups, it may more generically be referred to as substituted alkyl or substituted aryl.

“Alkyl” can refer to, for example, linear, branched, or cyclic alkyl groups. This term is exemplified by groups such as methyl, ethyl, n-propyl, isopropyl, n-butyl, t-butyl, n-pentyl, ethylhexyl, dodecyl, isopentyl, etc.

“Aryl” can refer to, for example, aromatic carbocyclic groups having one or more single rings (e.g., phenyl or biphenyl) or multiple condensed rings (e.g., naphthyl or anthryl).

“Heteroalkyl” can refer to, for example, an alkyl group wherein one or more carbon atoms are substituted with heteroatoms.

“Heteroaryl” can refer to, for example, an aryl group wherein one or more carbon atoms are substituted with heteroatoms.

“Alkoxide” can refer to, for example, the group “alkyl-O-”. This term is exemplified by groups such as methoxy, ethoxy, n-propyloxy, isopropyloxy, n-butyloxy, t-butyloxy, etc.

“Fluoroalkyl” can refer to, for example, an alkyl group wherein one or more hydrogen atoms are substituted with fluorine. Fluoroalkyl described herein include partially fluorinated alkyl groups as well as perfluoroalkyl groups.

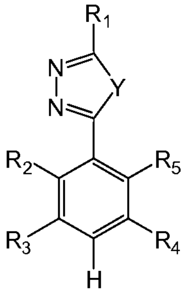
“Fluoroalkoxide” can refer to, for example, an alkoxide group wherein one or more hydrogen atoms are substituted with fluorine. Fluoroalkoxide described herein include partially fluorinated alkoxide groups as well as perfluoroalkoxide groups.

"Triscarbazole" can refer to, for example, three or more carbazole groups connected to each other through aryl carbon-nitrogen bond and/or aryl carbon-carbon bond.

AMBIPOLAR HOST COMPOUND

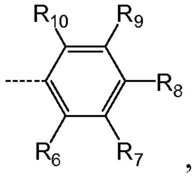
Ambipolar host compounds are described in, for example, WO 2010149618, WO 2010149620, WO 2010149622, and PCT/US2011/066597, all of which are incorporated herein by reference in their entireties.

Many embodiments described herein relate to a compound represented by formula (I):

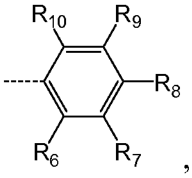


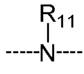
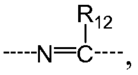
(I), wherein:

(a) R_1 is an optionally substituted aryl group, an optionally substituted heteroaryl group, an optionally substituted alkyl group or an optionally substituted heteroalkyl group;

(b) one or two of R_2, R_3, R_4 and R_5 are represented by 

, and the remaining of R_2, R_3, R_4 and R_5 are independently selected from hydrogen, halogen and a $C_{1\text{-}20}$ organic group;

(c) for each 

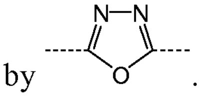
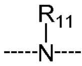
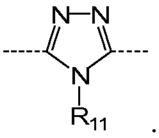
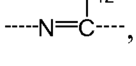
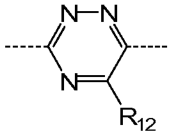
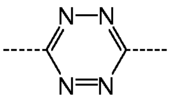
, one or two of R_6, R_7, R_8, R_9 and R_{10} are optionally substituted carbazole groups; and the remaining of R_6, R_7, R_8, R_9 and R_{10} are independently selected from hydrogen, halogen and a $C_{1\text{-}20}$ organic group; and (d) Y is selected from from -----O-----, 
$\text{-----}\overset{R_{11}}{\text{N}}\text{-----}$
, ----N=N---- and 
$\text{----N}{=}\overset{R_{12}}{\text{C}}\text{----}$
, wherein R_{11} is an optionally substituted aryl group, an optionally substituted heteroaryl group, an optionally substituted alkyl group or an optionally substituted heteroalkyl group, and wherein R_{12} is hydrogen, an optionally substituted aryl group, an optionally substituted heteroaryl group, an optionally substituted alkyl group or an optionally substituted heteroalkyl group.

R_1 can be, for example, an optionally substituted $C_{5\text{-}30}$ aryl or heteroaryl group, or an optionally substituted $C_{5\text{-}20}$ aryl or heteroaryl group, or an optionally substituted $C_{5\text{-}14}$ aryl or heteroaryl group, including the optional substituent. R_1 can be, for example, an optionally substituted $C_{1\text{-}30}$ linear or branched alkyl or heteroalkyl group, or an optionally substituted $C_{1\text{-}20}$ linear or branched alkyl or heteroalkyl group, or an optionally substituted $C_{1\text{-}12}$ linear or branched alkyl or heteroalkyl group, or an optionally substituted $C_{1\text{-}6}$ linear or branched alkyl or heteroalkyl group, including the optional substituent. R_1 can be, for example, an optionally substituted $C_{1\text{-}30}$ monocyclic, bicyclic or tricyclic alkyl or heteroalkyl group, or an optionally substituted $C_{1\text{-}20}$ monocyclic, bicyclic or tricyclic alkyl or heteroalkyl group, or an optionally substituted $C_{1\text{-}12}$ monocyclic, bicyclic or tricyclic alkyl or heteroalkyl group, or an optionally substituted $C_{1\text{-}6}$ monocyclic, bicyclic or tricyclic alkyl or heteroalkyl group, including the optional substituent.

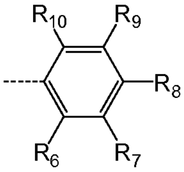
R_1 can be, for example, unsubstituted. R_1 can be, for example, substituted with one or more substituents selected from fluoro, cyano, hydroxyl, alkyl, fluoroalkyl, alkoxide, and fluoroalkoxide.

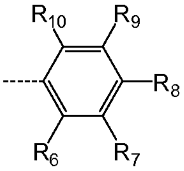
In one embodiment, R_1 comprises at least one crosslinkable or polymerizable group. In one embodiment, R_1 comprises at least two crosslinkable or polymerizable groups.

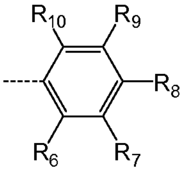
In one embodiment, R_1 is an optionally substituted phenyl group. In one embodiment, R_1 is a phenyl group substituted with at least one or at least two crosslinkable or polymerizable groups.

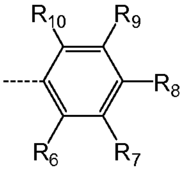
In one embodiment, Y is -----O-----, and the ambipolar host material comprises an oxadiazole moiety represented by . In another embodiment, Y is  $-N(R_{11})-$, and the ambipolar host material comprises a triazole moiety represented by . In a further embodiment, Y is  $-N{=}C(R_{12})-$, and the ambipolar host material comprises a triazine moiety represented by . In an additional embodiment, Y is -----N=N-----, and the ambipolar host material comprises a tetrazine moiety represented by .

R_{11} and R_{12} can be, for example, an optionally substituted C_{1-30} alkyl or heteroalkyl group, or an optionally substituted C_{1-20} alkyl or heteroalkyl group, or an optionally substituted C_{1-6} alkyl or heteroalkyl group, including the optional substituent. R_{11} and R_{12} can also be, for example, an optionally substituted C_{5-30} aryl or heteroaryl group, or an optionally substituted C_{5-20} aryl or heteroaryl group, or an optionally substituted C_{5-14} aryl or heteroaryl group, including the optional substituent. R_{11} and R_{12} can be, for example, unsubstituted. R_{11} and R_{12} can also be, for example, substituted with one or more substituents selected from fluoro, cyano, hydroxyl, alkyl, fluoroalkyl, alkoxide, and fluoroalkoxide.

In one embodiment, the 

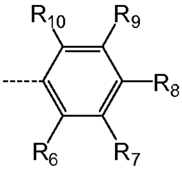
moiety is present at R_3 or R_4. In another embodiment, the 

moiety is present at R_2 or R_5. In a further embodiment, the 

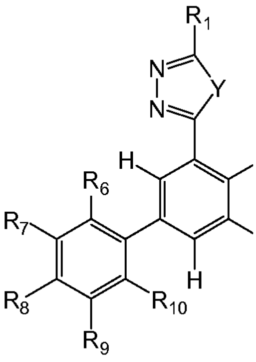
moiety is present at both R_3 and R_4. In an additional embodiment, the 

moiety is not present at R_2 or R_5.

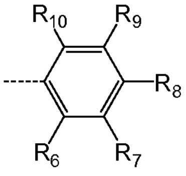
The remaining of R_2, R_3, R_4 and R_5 can be, for example, independently selected from hydrogen, fluoro, cyano, alkyl, fluoroalkyl, alkoxide and fluoroalkoxide.

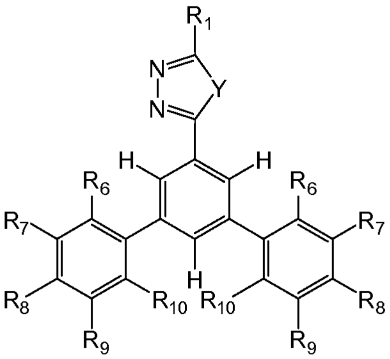
In one embodiment, wherein the 

moiety is present at R_3, and wherein R_2, R_4 and R_5 are each hydrogen, the ambipolar host compound is represented by formula (IX):



(IX).

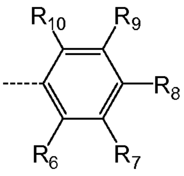
In another embodiment, wherein the  moiety is present at both R_3 and R_4, and wherein R_2 and R_5 are each hydrogen, the ambipolar host compound is represented by formula (X):



(X).

In one embodiment, R_7 or R_9 is an optionally substituted carbazole group. In another embodiment, R_8 is an optionally substituted carbazole group. In a further embodiment, R_6 or R_{10} is an optionally substituted carbazole group. In an additional embodiment, both R_7 and R_9 are optionally substituted carbazole groups.

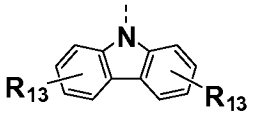
Other than the optionally substituted carbazole groups, the remaining of R_6, R_7, R_8, R_9 and R_{10} can be, for example, hydrogen, fluoro, cyano, alkyl, fluoroalkyl, alkoxide and fluoroalkoxide. In a particular embodiment, the remaining of R_6, R_7, R_8, R_9 and R_{10} are each hydrogen.

In some embodiments, the  moiety is present at R_3 and/or R_4 but not at R_2 or R_5, and wherein the optionally substituted carbazole group is present at R_7 and/or R_9 but not at R_6, R_8 or R_{10}.

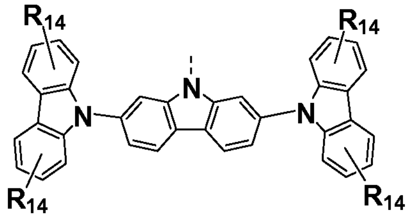
CARBAZOLE GROUP

The optionally substituted carbazole groups can comprise, for example, a monocarbazole group or triscarbazole group. The synthesis of triscarbazole group is described in, for example, Jiang *et al.*, *J. Mater. Chem.* 21:4918-4926 (2011) and Brunner *et al.*, *J. Am. Chem. Soc.* 126:6035-6042 (2004), both of which are incorporated herein by reference in their entireties. The monocarbazole group or triscarbazole group can be unsubstituted. The monocarbazole group or triscarbazole group can also be substituted with one or more groups selected from fluoro, cyano, alkyl, fluoroalkyl, alkoxide, fluoroalkoxide, and carbazole.

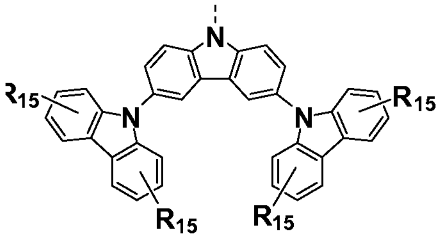
The optionally substituted carbazole groups described herein can be represented by, for example, formulae (II), (III), (IV), (V) and (VI).



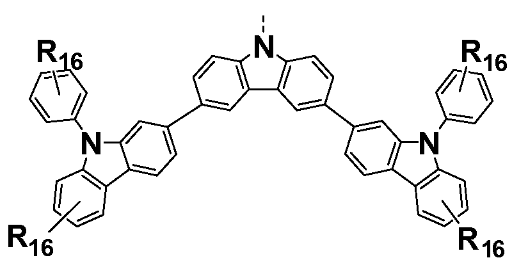
(II)



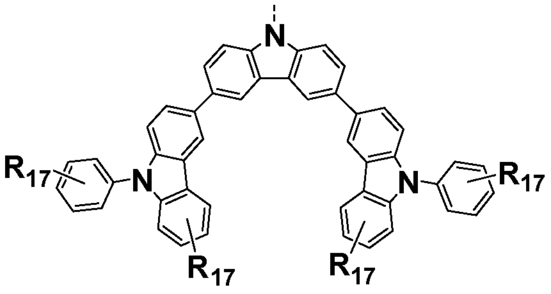
(III)



(IV)

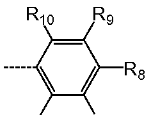


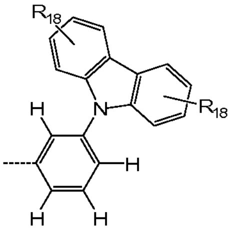
(V)



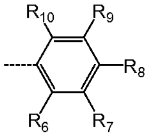
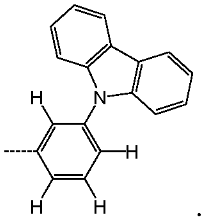
(VI)

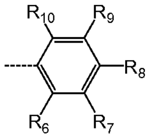
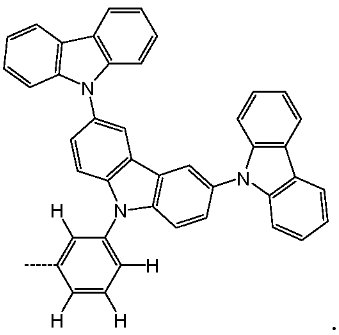
wherein each of R_{13}, R_{14}, R_{15}, R_{16} and R_{17} is independently hydrogen, fluoro, cyano, a C_{1-20} or C_{1-6} linear or branched alkyl, a C_{1-20} or C_{1-6} linear or branched fluoroalkyl, a C_{1-20} or C_{1-6} linear or branched alkoxide, or a C_{1-20} or C_{1-6} linear or branched fluoroalkoxide group. In one embodiment, each of R_{13}, R_{14}, R_{15}, R_{16} and R_{17} is hydrogen.

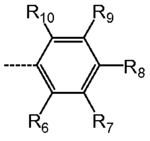
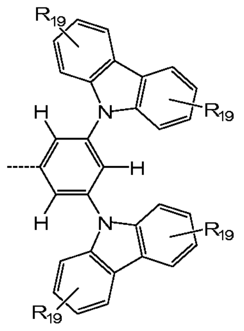
In some embodiments, wherein R_9 is an optionally substituted carbazole group, and R_6, R_7, R_8 and R_{10} are each hydrogen, the  moiety is represented by formula (VII):

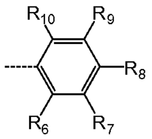
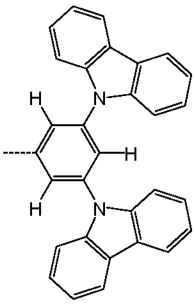


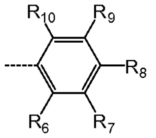
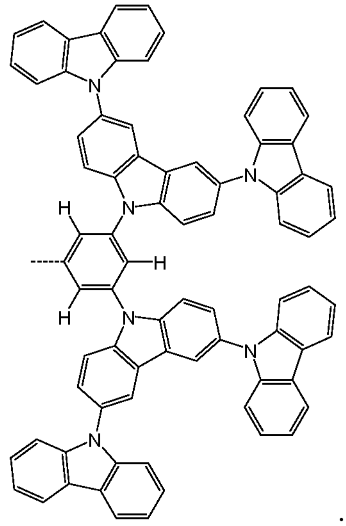
(VII), wherein R_{18} is independently hydrogen, fluoro, cyano, a $C_{1\text{-}20}$ or $C_{1\text{-}6}$ linear or branched alkyl, a $C_{1\text{-}20}$ or $C_{1\text{-}6}$ linear or branched perfluoroalkyl, a $C_{1\text{-}20}$ or $C_{1\text{-}6}$ linear or branched alkoxide, a $C_{1\text{-}20}$ or $C_{1\text{-}6}$ linear or branched fluoroalkoxide group, or an optionally substituted carbazole.

In one embodiment, the carbazole group at the R_9 position is an unsubstituted monocarbazole, and the  moiety is  .

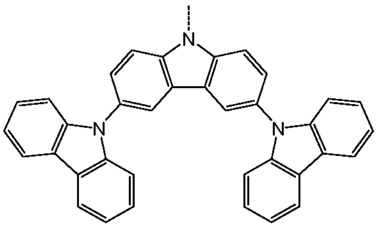
In another embodiment, the carbazole group at the R_9 position is an unsubstituted triscarbazole, and the  moiety is  .

In some embodiments, wherein R_7 and R_9 are each an optionally substituted carbazole group, and R_6, R_8 and R_{10} are each hydrogen, the  moiety is represented by formula (VIII):  (VIII), wherein R_{13} is independently hydrogen, carbazole, fluoro, cyano, a $C_{1\text{-}20}$ or $C_{1\text{-}6}$ linear or branched alkyl, a $C_{1\text{-}20}$ or $C_{1\text{-}6}$ linear or branched perfluoroalkyl, a $C_{1\text{-}20}$ or $C_{1\text{-}6}$ linear or branched alkoxide, a $C_{1\text{-}20}$ or $C_{1\text{-}6}$ linear or branched fluoroalkoxide group, or an optionally substituted carbazole.

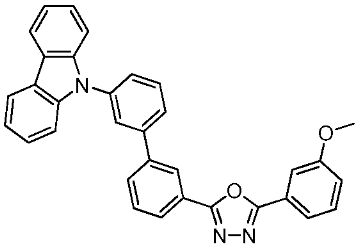
In one embodiment, the carbazole group at the R_7 and R_9 position are each an unsubstituted monocarbazole, and the  moiety is  .

In another embodiment, the carbazole group at the R_7 and R_9 position are each an unsubstituted triscarbazole, and the  moiety is  .

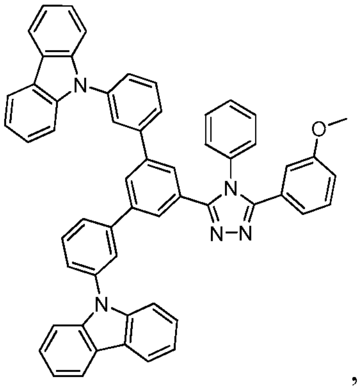
In one embodiment, the ambipolar host material described herein comprises at least one optionally substituted triscarbazole group. In a further embodiment, the ambipolar host material described herein comprises at least one unsubstituted triscarbazole group represented by:

 .

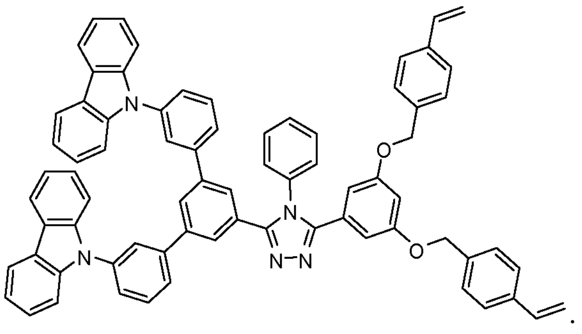
Specific examples of the ambipolar host compounds described herein include the followings:



,



, and



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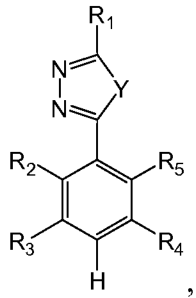
MATERIAL PROPERTIES OF THE AMBIPOLAR HOST COMPOUND

Many of the ambipolar host compounds described herein are either sublimable under high vacuum or readily soluble in common organic solvent, and therefore can be readily processed to form compositions useful in organic electronic devices, especially when mixed and/or co-deposited with phosphorescent guest emitters to form the emissive layers of OLED devices.

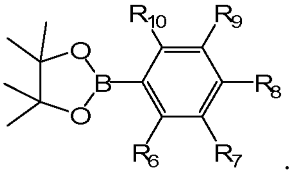
Further, many of the ambipolar host compounds described herein have high glass transition temperature which is advantageous for OLED applications. For example, the glass transition temperature can be at least 120°C, or at least 130°C, or at least 140°C, or at least 150°C, or at least 160°C, or at least 170°C, or at least 180°C, or at least 190°C, or at least 200°C.

METHODS FOR MAKING AMBIPOLAR HOST COMPOUND

Methods for making the ambipolar host compound described herein are disclosed in detail in the Working Examples. For example, a first compound can be reacted with a second



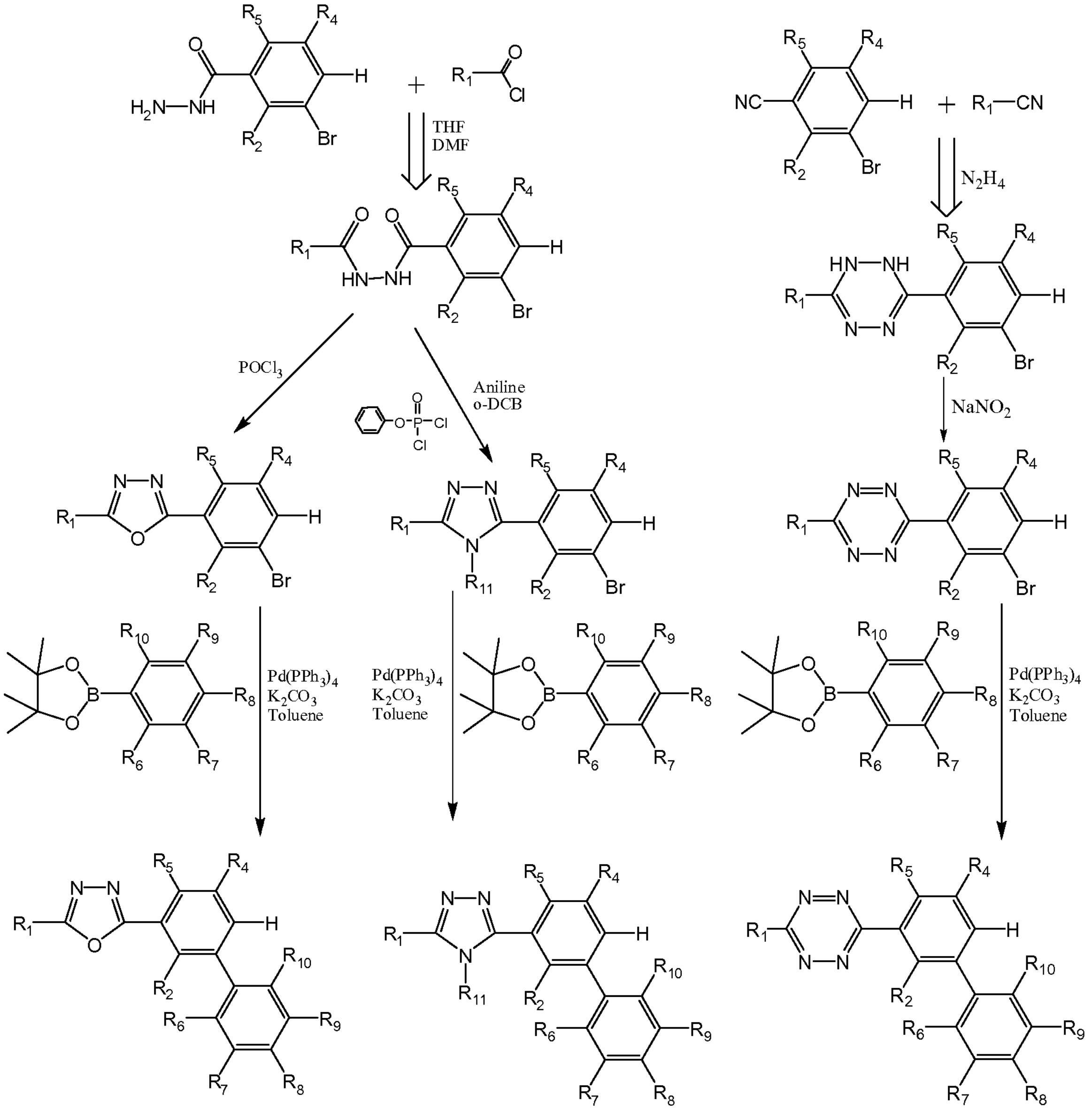
compound, wherein the first compound is represented by , one or two of R_2, R_3, R_4 and R_5 are halogen such as Br or I, and second compound is represented by

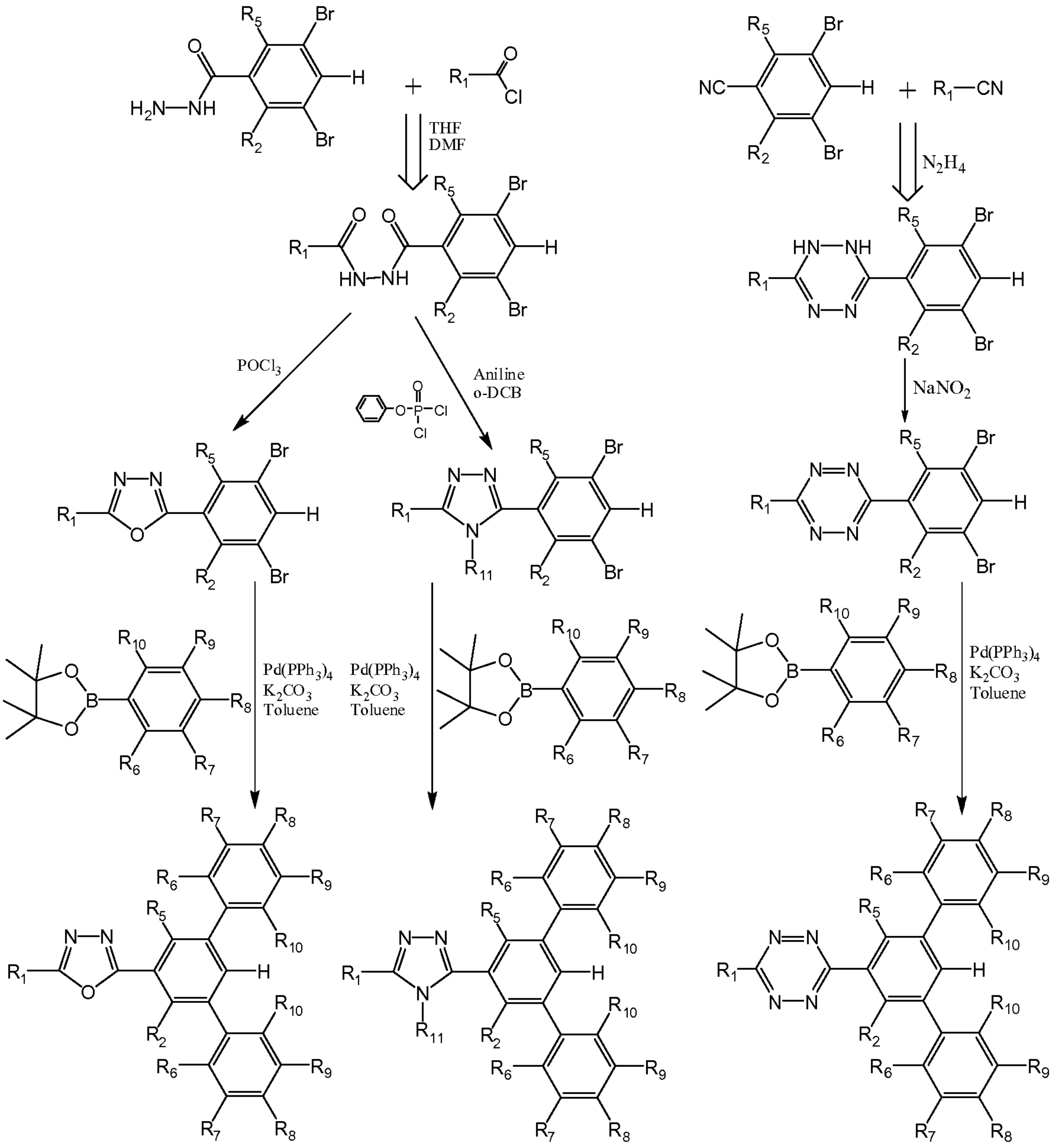


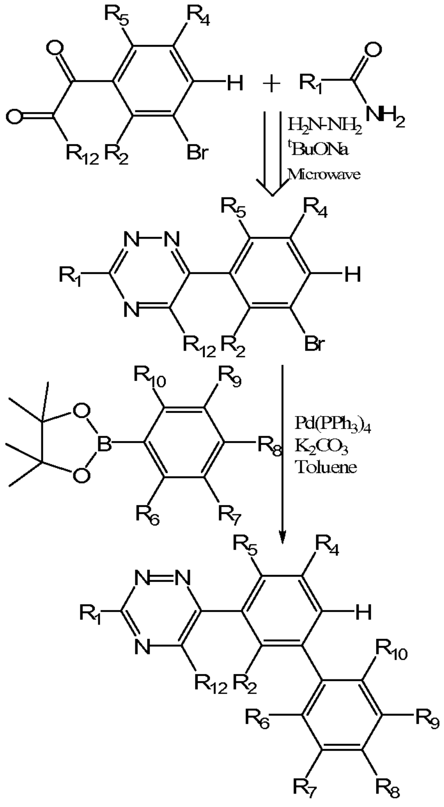
. R_1, R_6, R_7, R_8, R_9, R_{10}, as well as the remaining of R_2, R_3 and R_4 and R_5, have been defined in the foregoing sections.

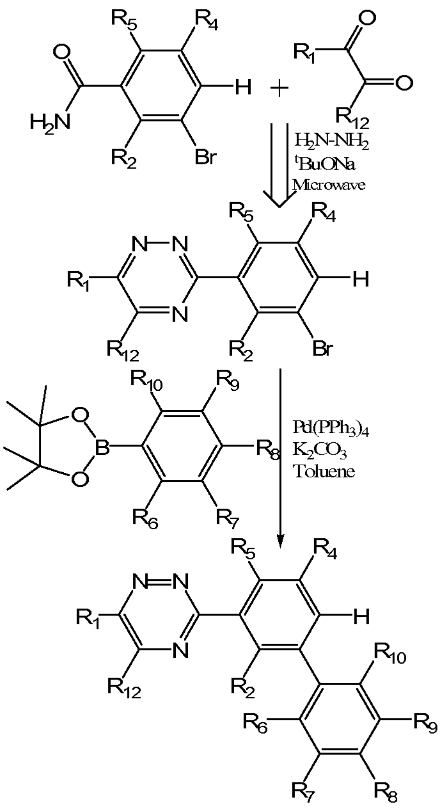
Methods for synthesizing triazine and tetrazine-based compounds are disclosed in Yang *et al.*, *Angew. Chem. Int. Ed.* 51:5222-5225 (2012) and Phucho *et al.*, ARKIVOC 2008 (xv):79-87, both of which are hereby incorporated by reference in their entireties.

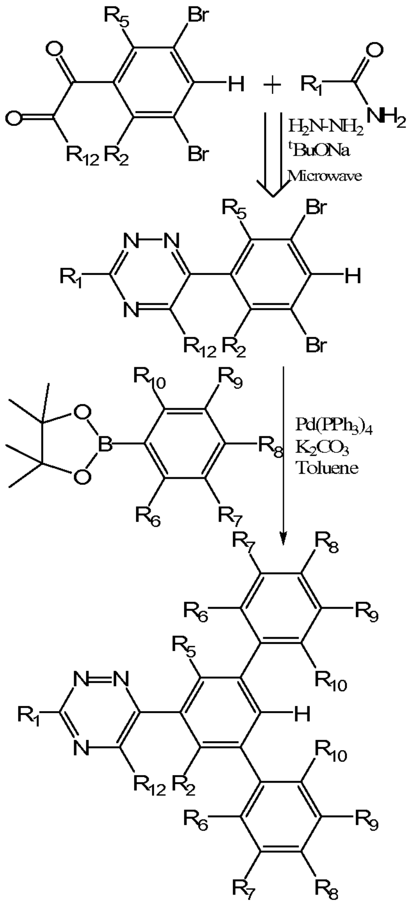
In some embodiments, the ambipolar host compound described herein are synthesized according to the following general schemes.

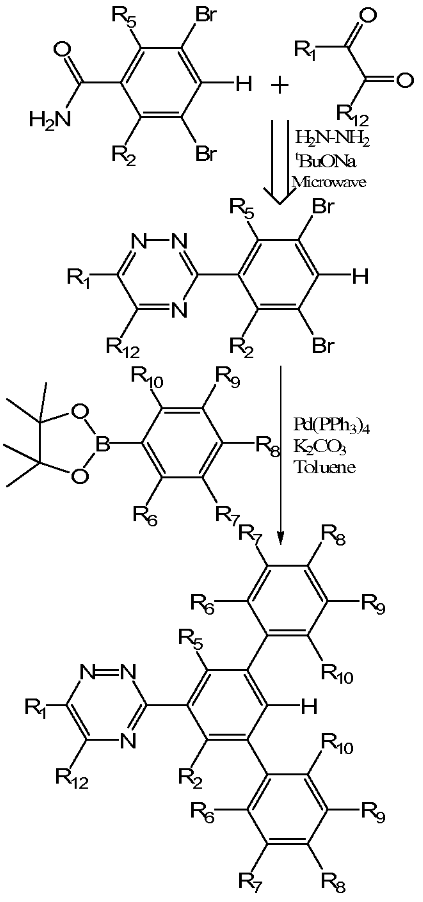

THF
DMF
POCl3
Aniline
o-DCB
N2H4
NaNO2
Pd(PPh3)4
K2CO3
Toluene
R1
R2
R4
R5
R6
R7
R8
R9
R10
R11
H
Br
NC
CN
Cl
H2N—NH
HN—NH
O-P-Cl
Cl


THF
DMF
N₂H₄
POCl₃
Aniline
o-DCB
NaNO₂
Pd(PPh₃)₄
K₂CO₃
Toluene


H2N-NH2
tBuONa
Microwave
Pd(PPh3)4
K2CO3
Toluene


H2N-NH2
tBuONa
Microwave
Pd(PPh3)4
K2CO3
Toluene

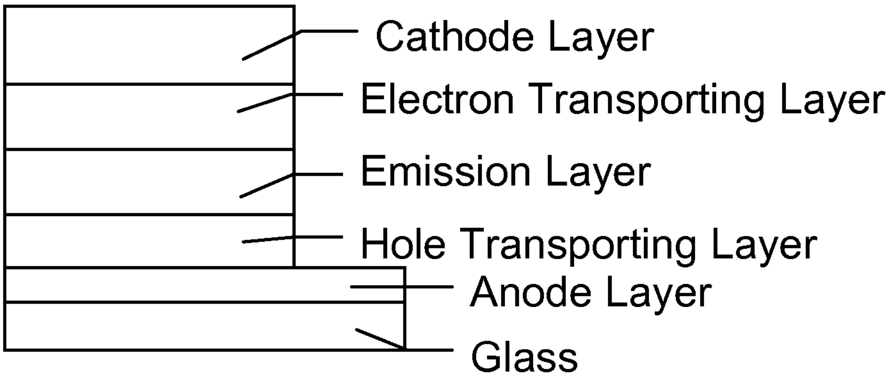

H2N-NH2
tBuONa
Microwave
Pd(PPh3)4
K2CO3
Toluene


H2N-NH2
tBuONa
Microwave
Pd(PPh3)4
K2CO3
Toluene

ELECTROLUMINESCENCE DEVICES COMPRISING AMBIPOLAR HOST COMPOUND

The solution-processed ambipolar transport layer described herein can be used in various electronic devices, including electroluminescence devices such as OLED devices.

Although other alternatives are known in the art, in many embodiments, the OLED devices comprise at least an anode layer, a hole transport layer, an emission layer, an electron transport layer, and a cathode layer. Such devices are illustrated in the diagram below.



The thickness of the anode layer, the cathode layer, the emissive layer, the hole transport layer, and the electron transport layer can be, for example, about 0.001-100 μm, about 0.005-10 μm, or about 0.01-1 μm, or about 0.02-0.1 μm.

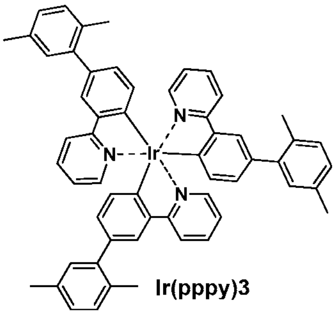
Many suitable materials for anode in electroluminescence devices are known in the art and include, for example, ITO, which can be applied, for example, as a vacuum-deposited layer over an inert and transparent substrate such as glass. Other examples include metal oxide with high work function, such as zinc oxide and indium zinc oxide.

Many suitable materials for cathode in electroluminescence devices are known in the art and include, for example, a combination of LiF as electron injecting material coated with a vacuum deposited layer of Al, and optionally an additional layer of Ag.

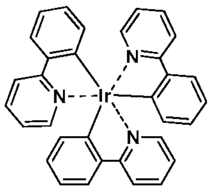
Many suitable materials for the hole transporting or hole injection layer of electroluminescence devices are known in the art. Suitable hole transporting materials include, for example, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), hole transporting materials described in WO 2009/080799, US 61/579394, US 61/579402 and US 61/579418, all of which are incorporated herein by reference in their entireties, as well as other hole transporting materials known in the art. In one embodiment, the hole transport layer is fabricated by solution processing (e.g., spin coating) from a solution comprising the hole transporting material.

Many suitable materials for the electron transport layer of electroluminescence devices are known in the art and include, for example, 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), as well as those described in WO 2012/024132, WO 2009/080796 and WO 2009/080797, all of which are incorporated herein by reference in their entireties. In one embodiment, the electron transport layer is fabricated by solution processing (e.g., spin coating) from a solution comprising the electron transporting material (see WO 2012/024132).

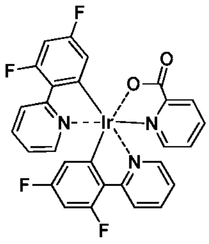
Many suitable guest emitters for the emissive layer of electroluminescence devices are known in the art and include, for example, Iridium complexes such as Tris(5-phenyl-10,10-dimethyl-4-aza- tricycloundeca-2,4,6-triene)Iridium(III) (Ir(pppy)$_3$), Tris(2-phenylpyridine)iridium(III) (Ir(ppy)$_3$) and Bis(3,5-difluoro-2-(2-pyridyl)phenyl-(2-carboxypyridyl)iridium (III) (FIr(pic)), guest materials described in US 2006/0127696, WO 2009/026235, WO 2011000873 and PCT/US2011/066597, all of which are incorporated herein by reference in their entirety, as well as other guest materials known in the art. The emissive layer can comprise at least one blue emitter, at least one green emitter, at least one red emitter, or a combination thereof.



Ir(pppy)3



Ir(ppy)3



FIr(pic)

In one embodiment, the OLED devices described herein comprise a solution-processed hole transport layer and a solution-processed emissive layer. In another embodiment, the OLED devices described herein comprise a solution-processed hole transport layer and a vacuum-deposited emissive layer. In a further embodiment, the OLED devices described herein comprise a solution-processed hole transport layer, a solution-processed emissive layer, and a solution-processed electron transport layer.

In some embodiments, the OLED device described herein comprises an emitter having wavelengths between, for example, 400-700 nm including red, green, and blue phosphorescent emitters. The external quantum efficiency of said OLED device at 1,000 cd/m^2 can be, for example, at least 5%, or at least 8%, or at least 10%, or at least 12%, or at least 15%, or at least 18%, or at least 20%.

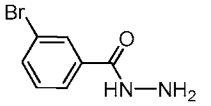
In some embodiments, the OLED device described herein comprises a green phosphorescent emitter. The external quantum efficiency of said OLED device at 1,000 cd/m^2 can be, for example, at least 5%, or at least 8%, or at least 10%, or at least 12%, or at least 15%, or at least 18%, or at least 20%.

In some embodiments, the OLED device described herein comprises a blue phosphorescent emitter. The external quantum efficiency of said OLED device at 1,000 cd/m^2 can be, for example, at least 5%, or at least 8%, or at least 10%, or at least 12%, or at least 15%, or at least 18%, or at least 20%.

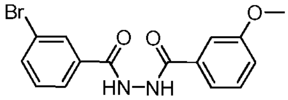
Additional embodiments are provided by the following non-limiting working examples.

WORKING EXAMPLES

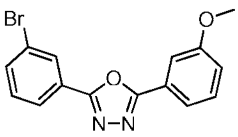
EXAMPLE 1- Synthesis of Compound A



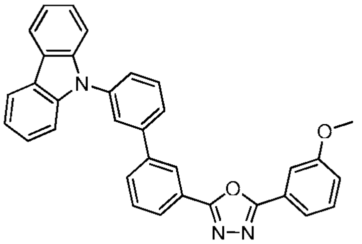
S4.13: Synthesized according to the literature. ^{1}H NMR was consistent with the literature.



S4.14: **S4.13** (3.990 g, 18.6 mmol) was dissolved in a mixture of THF and *N,N*-dimethylformamide (20 mL: 20 mL) under inert atmosphere. 3-methoxybenzoyl chloride was added dropwise and reaction was stirred overnight. A precipitate that formed overnight was collected by filtration and addition of water to the filtrate produced more solids. Solids were combined and dried to afford a white powder (3.53 g, 54.4%). ^{1}H (300 MHz, DMSO-d_6): δ 10.64 (s, 1H), 10.55 (s, 1H), 8.07 (t, *J* = 1.7 Hz, 1H), 7.95-7.88 (m, 1H), 7.84-7.77 (m, 1H), 7.53-7.39 (m, 4H), 7.18-7.12 (m, 1H), 3.81 (s, 3H). ^{13}C {^{1}H} (75 MHz, DMSO-d_6): δ 165.9, 164.9, 159.7, 135.1, 134.2, 131.4, 130.6, 130.2, 127.0, 122.3, 120.1, 118.3, 112.9, 55.8. MS (EI) m/z = 348.0 [M+]. Anal. calcd. for $C_{15}H_{13}BrN_2O_3$: C, 51.60; H, 3.75; N, 8.02. Found: C, 51.74; H, 3.67; N, 8.08

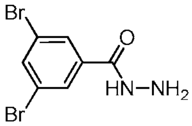


S4.15: **S4.14** (1.501 g, 4.30 mmol) was combined with $POCl_3$ (15 mL) under inert atmosphere and heated to 100 °C overnight. DCM (200 mL) was added to the cooled mixture and phases were separated and solvents removed *in vacuo*. The crude was purified by column chromatography (silica gel ; hexanes:ethyl acetate = 70:30) to afford a white powder (1.039 g, 73.2%). ^1H (300 MHz, DMSO-d_6): δ 8.27 (t, J = 1.6 Hz, 1H), 8.14-8.09 (dm, 1H), 7.85-7.80 (dm, 1H), 7.73-7.68 (dm, 1H), 7.64-7.61 (m, 1H), 7.59-7.48 (m, 2H), 7.19 (dd, J = 8.4, 2.6, 0.9 Hz, 1H), 3.85 (s, 3H). $^{13}C\{^1H\}$ (75 MHz, DMSO-d_6): δ 164.7, 163.3, 160.1, 135.2, 132.0, 131.1, 129.5, 126.2, 125.9, 124.7, 122.9, 119.6, 118.6, 112.1, 56.0. MS (EI) m/z = 330.0 [M+]. Anal. calcd. for $C_{15}H_{11}BrN_2O_2$: C, 54.40; H, 3.35; N, 8.46. Found: C, 54.55; H, 3.22; N, 8.45.

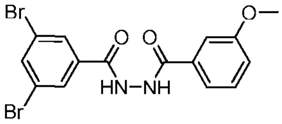


4.35 (Compound A): **S4.15** (0.900 g, 2.72 mmol), 9-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole (1.206 g, 3.27 mmol), and $Pd(PPh_3)_4$ (0.127 g, 0.110 mmol) were dissolved in a solution of anhydrous toluene (80 mL) and absolute ethanol (40 mL). In a separate flask, K_2CO_3 (11.06 g, 80.0 mmol) was dissolved in deionized water (40 mL) and the resulting solution was added to the reaction mixture, which was then refluxed for 27 hours. Upon cooling, the reaction mixture was diluted with deionized water (150 mL) and brine (50 mL) were added and the organic layer was extracted once chloroform (200 mL) then twice more with 50 mL portions of chloroform. The organic layers were combined, washed with brine (100 mL), dried over magnesium sulfate, and concentrated *in vacuo* to afford a dark oily solid. The crude material was purified by column chromatography (silica ; dichloromethane:ethyl acetate = 90:10) as a white solid and was then washed with pentane to give the final product (0.945 g, 70%). ^1H (300 MHz, $CDCl_3$): δ 8.40 (t, J = 1.5 Hz, 1H), 8.19-8.15 (m, 3H), 7.89-7.61 (m, 8H), 7.61-7.41 (m, 5H), 7.34-7.29 (m, 2H), 7.12-7.08 (m, 1H), 3.90 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 164.83, 164.53, 160.10, 141.97, 141.33, 140.94, 138.58, 130.69, 130.59, 130.37, 129.94, 126.69, 126.38, 126.19, 125.90, 125.68, 125.03, 124.77, 123.59, 120.53, 120.23, 119.52, 118.35, 111.81, 109.86, 55.70. MS (EI) m/z = 492.9 [M+]. Anal. calcd. for $C_{33}H_{23}N_3O_2$: C, 83.31; H, 4.70; N, 8.51. Found: C, 83.01; H, 4.64; N, 8.47.

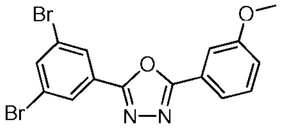
EXAMPLE 2 - Synthesis of Compound B



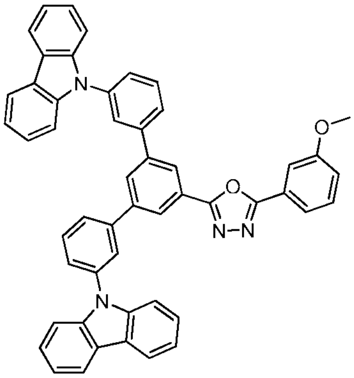
S4.8: Synthesized according to the literature. ^{1}H NMR was consistent with the literature.



S4.9: **S4.8** (5.002 g, 17.0 mmol) was dissolved in anhydrous THF (40 mL) under inert atmosphere. Due to poor solubility, anhydrous *N,N*-dimethylformamide (40 mL) was added and the mixture cooled to 0 °C in an ice-water bath. After cooling, 3-methoxybenzoyl chloride (3.304 g, 19.4 mmol) was added dropwise. After 24 h, the mixture was added to deionized water and a precipitate formed, was collected, and dried to afford a white powder (2.291 g, 31.5%). ^{1}H (300 MHz, DMSO-d_6): δ 10.75 (s, 1H), 10.61 (s, 1H), 8.14-8.10 (m, 1H), 8.09-8.07 (m, 2H), 7.51-7.39 (m, 3H), 7.18-7.12 (m, 1H), 3.81 (s, 3H). ^{13}C{^{1}H} NMR (75MHz, DMSO-d_6): δ 165.89, 163.53, 159.68, 137.18, 136.38, 134.05, 130.21, 129.88, 123.31, 120.16, 118.37, 112.95, 55.77. MS (EI) m/z = 425.9 [M+]. Anal. calcd. for $C_{15}H_{12}Br_2N_2O_3$: C, 42.09; H, 2.83; N, 6.54. Found: C, 42.28; H, 2.63; N, 6.48.

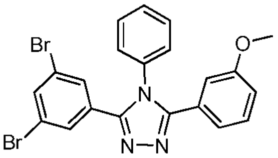


S4.10: **S4.9** (2.365 g, 5.526 mmol) in neat $POCl_3$ (15.0 mL) was stirred under nitrogen atmosphere at 100 °C for 2 hours. Upon cooling, the reaction mixture was poured slowly into *ca.* 400 mL of an ice-water mixture, resulting in the formation of a white precipitate, which was collected by filtration and washed with deionized water. Chromatography of the crude material (silica ; dichloromethane:ethyl acetate = 95:5) yielded the final product as a white solid (1.471 g, 65%).^{1}H (300 MHz, $CDCl_3$): δ 8.18 (d, J = 1.7 Hz, 2H), 7.81 (t, J = 1.7 Hz, 1H), 7.70-7.65 (m, 1H), 7.64-7.60 (m, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.08 (ddd, J_1 = 8.3, J_2 = 2.6, J_3 = 0.8 Hz, 1H), 3.88 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 165.14, 162.14, 160.04, 137.05, 130.34, 128.43, 128.40, 126.95, 124.45, 123.71, 119.47, 118.62, 11.71, 55.60. MS (EI) m/z = 409.9 [M+]. Anal. calcd. for $C_{15}H_{10}Br_2N_2O_2$: C, 43.94; H, 2.46; N, 6.83. Found: C, 43.64; H, 2.32; N, 6.75.

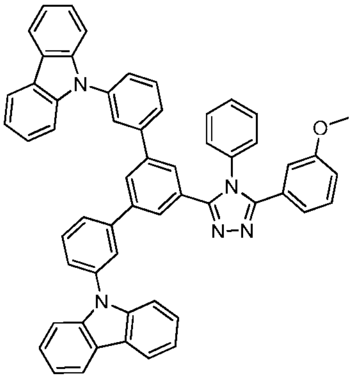


4.33 (Compound B): **S4.10** (1.302 g, 3.175 mmol), 9-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole (2.815 g, 7.623 mmol), and $Pd(PPh_3)_4$ (0.148 g, 0.128 mmol) were dissolved in a solution of anhydrous toluene (100 mL) and absolute ethanol (50 mL) under nitrogen atmosphere. In a separate flask, K_2CO_3 (13.84 g, 100.1 mmol) was dissolved in deionized water (50 mL) and the resulting solution was added to the reaction mixture, which was then refluxed with stirring for 24 hours. Upon cooling, the reaction mixture was diluted with 150mL of deionized water, 50 mL of brine were added, and the organic layer was extracted once with 400mL of chloroform, then twice more with 100 mL portions of chloroform. The organic layers were combined, washed with brine (1 x 250 mL) then dried over magnesium sulfate, and concentrated *in vacuo* to yield a dark yellow, oily solid. The oil was purified by column chromatography (silica gel; dichloromethane:ethyl acetate = 95:5) and then precipitated in methanol to afford a white solid (1.648 g, 72%).^{1}H (300 MHz, $CDCl_3$): δ 8.42 (s, 1H), 8.41 (s, 1H), 8.18-8.15 (m, 4H), 8.06 (t, J = 1.7 Hz, 1H), 7.93 (t, J = 1.7 Hz, 2H), 7.94-7.63 (m, 8H), 7.50-7.39 (m, 9H), 7.33-7.28 (m, 4H), 7.12-7.08 (m, 1H), 3.89 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 164.90, 164.29, 160.05, 142.08, 141.68, 140.84, 138.56, 130.67, 130.26, 129.32, 126.87, 126.42, 126.09, 126.03, 125.95, 125.36, 124.85, 124.81, 123.47, 120.44, 120.13, 119.47, 118.27, 111.82, 109.74, 55.68. MS (EI) m/z = 734.2 [M+]. Anal. calcd. for $C_{51}H_{34}N_4O_2$: C, 83.36; H, 4.66; N, 7.62. Found: C, 83.22; H, 4.55; N, 7.68.

EXAMPLE 3- Synthesis of Compound C

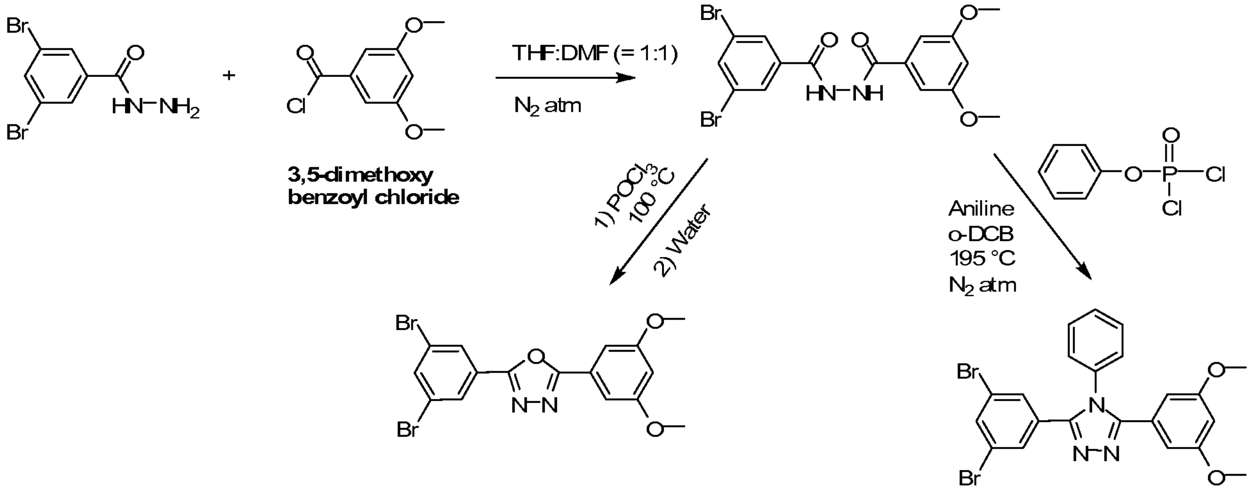


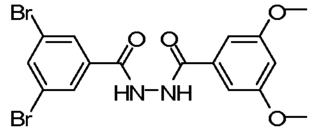
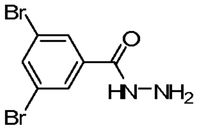
S4.19: Aniline (4.499 g, 11.7 mmol) and anhydrous o-dichlorobenzene (50 mL) were combined and cooled in ice-water bath under inert atmosphere. After the mixture was cooled to 0 °C, phenyl phosphorodichloridate (2.508 g, 11.9 mmol) was added dropwise and the ice-water bath removed. **S4.10** (3.759 g, 5.79 mmol) was added portion-wise and then the mixture was heated to 195 °C. Additional o-dichlorobenzene was added (25 mL) to achieve complete dissolution of solids. After 24 h, heating was stopped and 2N HCl (100 mL) was added to the cooled mixture followed by dichloromethane (200 mL). The phases were separated and the aqueous layer was extracted with dichloromethane (2 x 200 mL). The combined organic phases were washed with deionized water (200 mL), dried over magnesium sulfate, filtered, and solvents were removed *in vacuo* to afford an oil that was purified by column chromatography (silica gel ; gradient from 100% dichloromethane to 100% ethyl acetate). The product was precipitated with deionized water, filtered, and dried to obtain a white powder (2.972 g, 52.4%).^{1}H (300 MHz, DMSO-d_6): δ 7.94 (t, J = 1.8 Hz, 1H), 7.62-7.52 (m, 7H), 7.31 (t, J = 7.9 Hz, 1H), 7.05-6.98 (m, 2H), 6.94-6.92 (m, 1H), 3.65 (s, 3H). ^{13}C{^{1}H} (75 MHz, DMSO-d_6): δ 159.3, 154.8, 152.2, 135.0, 131.0, 130.7, 130.5, 130.2, 128.8, 128.2, 122.9, 121.1, 116.1, 114.2, 55.5. MS (EI) m/z = 486.0 [M+]. Anal. calcd. for $C_{21}H_{15}Br_2N_3O$: C, 51.99; H, 3.12; N, 8.66. Found: C, 51.80; H, 3.04; N, 8.72.

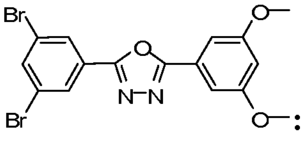
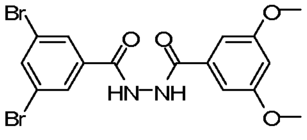


4.38 (Compound C): 9-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole (2.677 g, 7.21 mmol), **S4.19** (1.412 g, 2.89 mmol), 2.0 M aq. potassium carbonate solution (50 mL), and toluene (100 mL) were combined under inert atmosphere and nitrogen was bubbled through the solution for ~ 30 min. Pd $(PPh_3)_4$ (0.169 g, 0.14 mmol) was added and the mixture was set to reflux overnight. The reaction mixture was cooled, deionized water (200 mL) was added, and then the mixture was extracted with chloroform (3 x 200 mL). The organic phase was washed with brine (1 x 200 mL), dried over magnesium sulfate, filtered, and solvents removed *in vacuo*. The crude was purified by column chromatography (silica gel ; gradient from 100% dichloromethane to dichloromethane:ethyl acetate = 75:25) and recrystallized from acetone to afford a white powder (0.827 g, 35.3%). ^{1}H (300 MHz, DMSO-d_6): δ 8.25 (d, J = 7.4 Hz, 4H), 8.17 (s, 1H), 7.82 (d, J = 7.5 Hz, 2H), 7.76-7.69 (m, 6H), 7.61 (d, J = 7.5 Hz, 2H), 7.48-7.35 (m, 10H), 7.33-7.20 (m, 5H), 7.08 (t, J = 7.5 Hz, 2H), 7.02-6.87 (m, 3H), 6.82 (t, J = 7.5 Hz, 1H), 3.58 (s, 3H). $^{13}C\{^1H\}$ (75 MHz, DMSO-d_6): δ 159.29, 154.57, 154.39, 141.61, 140.64, 138.04, 135.56, 131.3, 130.18, 130.15, 130.0, 129.91, 128.96, 128.72, 128.44, 126.95, 126.77, 125.65, 123.22, 121.0, 120.56, 115.98, 114.07, 110.20, 55.42. MS (EI) m/z = 809.4 [M+]. Anal. calcd. for $C_{57}H_{39}N_5O$: C, 84.52; H, 4.85; N, 8.65. Found: C, 84.26; H, 4.85; N, 8.58.

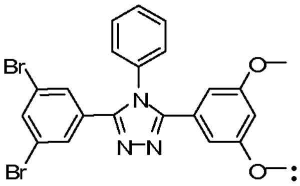
EXAMPLE 4 - Synthesis of Compound D

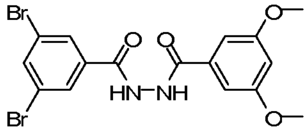


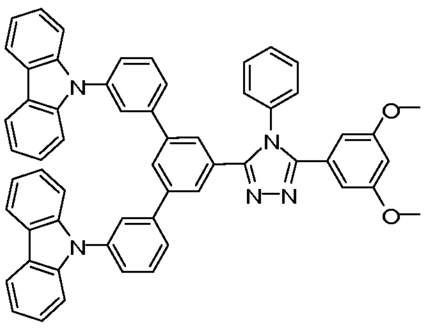
 :  (4.994 g, 17.0 mmol) (*Macromolecules* **2005**, *38*(16), 6755-6758) was dissolved in a mixture of THF and DMF (20 mL: 20 mL) under inert atmosphere. 3,5-dimethoxybenzoyl chloride was added portion-wise and the reaction was stirred overnight. A precipitate that formed overnight was collected by filtration and addition of water to the filtrate produced more solids. Solids were combined and dried to afford a pale yellow powder (5.764 g, crude). ^1H (300MHz, *DMSO-d_6*): δ 10.74 (s, 1H), 10.59 (s, 1H), 8.12-8.06 (m, 3H), 7.09-7.02 (m, 3H), 6.73-6.69 (m, 2H), 3.78 (s, 6H), 3.76 (s, 3H).

 :  (2.009 g, 4.37 mmol) was combined with $POCl_3$ (15 mL) under inert atmosphere and heated to 100 °C overnight. DCM (200 mL) was added to the cooled mixture followed by deionized water (200 mL) and phases were separated and solvents removed in vacuo from the organic phase. The crude was purified by column chromatography (silica gel ; (8:2) = Hexanes:EtOAc) and recrystallization from

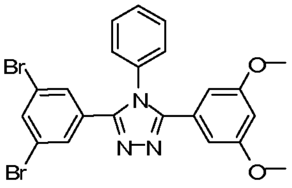
ethanol to afford a white powder (0.695 g, 36.1%). ^{1}H (300MHz, *DMSO-d$_6$*): δ 8.29 (s, 2H), 8.01 (s, 1H), 7.27 (s, 2H), 6.75 (s, 1H), 3.85 (s, 6H). ^{13}C{^{1}H} (75MHz, *DMSO-d$_6$*): δ165.0, 161.5, 128.7, 127.3, 125.0, 123.9, 105.2, 104.6, 56.2. EI-MS (*m/z*): M^{+} calcd for $C_{16}H_{12}Br_2N_2O_3$, 437.9; found 437.9. Elemental anal. calcd. for $C_{16}H_{12}Br_2N_2O_3$: C, 43.67; H, 2.75; N, 6.37. Found: C, 43.65; H, 2.65; N, 6.32.

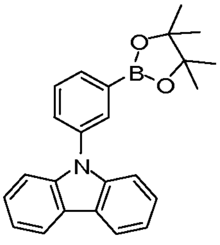

: Aniline (2.520 g, 27.1 mmol) and anhydrous o-dichlorobenzene (40 mL) were combined with phenyl phosphorodichloridate (1.513 g, 7.17 mmol) under inert atmosphere and the mixture was heated at 100 °C for 1 h.


(2.9983 g, 6.55 mmol) was added portion-wise and then the mixture was heated to 195°C. After 24h, heating was stopped and 2N HCl (100 mL) and then DCM (200 mL) was added to the cooled mixture. Phases were separated and aqueous layer was extracted with dichloromethane (2 x 200 mL) then solvents were removed in vacuo. The crude oil was purified (silica gel ; (8:2) = DCM:EtoAC to (1:1) = DCM:EtOAc) to afford a white powder (1.677, 49.8%). 1H (300MHz, DMSO-d6): δ 7.88 (t, J = 1.8 Hz, 1H), 7.58-7.47 (m, 7H), 6.51 (s, 3H), 3.60 (s, 6H).



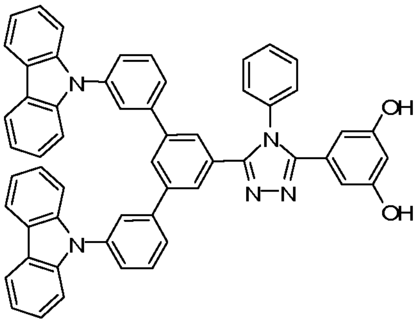
(Compound D):


(1.499 g, 2.91 mmol),

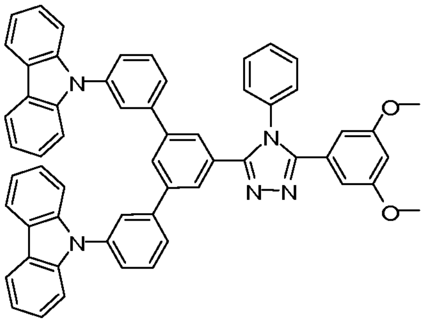

(2.704 g, 7.32 mmol) (also available from Aquila Pharmatech), and toluene (100 mL) were combined under inert atmosphere. Pd(PPh3)4 and 2M K2CO3 (50 mL) were added and the mixture was heated to

reflux for 24 h. After cooling, the solution was added to deionized water (200 mL) and stirred. The phases were separated and the aqueous phase was extracted with chloroform (2 x 200 mL). The combined organic phases were washed with brine (200 mL), dried over magnesium sulfate, and filtered. Solvents were removed in vacuo and the crude was purified by column chromatography (silica gel; (8:2) = DCM:EtOAc) to afford a white powder (2.128 g, 86.9%). 1H (300MHz, DMSO-d6): δ 8.26 (d, J = 7.5 Hz, 4H), 8.18 (s, 1H), 7.82 (d, J = 7.5 Hz, 2H), 7.78-7.68 (m, 6H), 7.62 (d, J = 7.5 Hz, 2H), 7.51-7.36 (m, 10H), 7.32-7.24 (m, 4H), 7.07 (t, J = 7.8 Hz, 2H), 6.80 (t, J = 7.3 Hz, 1H), 6.52-6.47 (m, 3H), 3.56 (s, 6H). 13C{1H} (75MHz, DMSO-d6): δ 160.6, 154.1, 141.6, 140.6, 138.0, 135.6, 131.3, 130.1, 129.0, 128.8, 128.7, 127.0, 126.8, 125.6, 123.2, 121.0, 120.6, 110.2, 106.8, 55.6. EI-MS (m/z): M+ calcd for C58H41N5O2, 839.3; found 839.4. Elemental anal. calcd. for C58H41N5O2: C, 82.93; H, 4.92; N, 8.34. Found: C, 82.83; H, 4.75; N, 8.26.

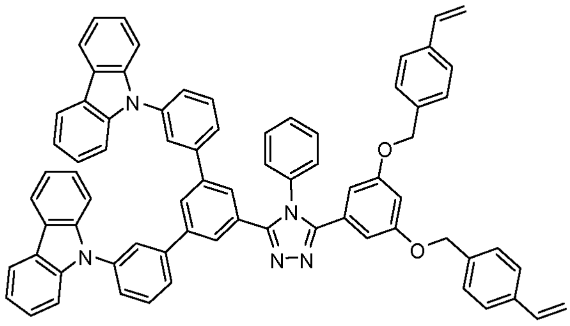
EXAMPLE 5 - Synthesis of Compound E



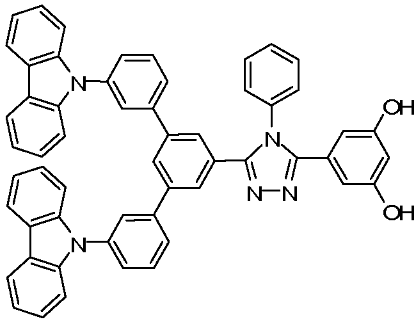
:



(1.007 g, 1.19 mmol) dissolved in anhydrous dichloromethane (15 mL) and set to cool to -78 °C in a dry ice/aceton bath. After cooling, 1M boron tribromide in dichloromethane (10 mL) was added dropwise. After stirring overnight, the solution was dropped into ice-water (100 mL) and a white precipitate was obtained that was collected and dried to afford a crude powder that was subjected to column chromatography (silica gel; gradient (1:1) = DCM:EtOAC to 100% EtOAc) to afford a powder (0.311 g, crude). [The final product is labeled "crude" as impurities were still present]. 1H (300MHz, CDCl3): δ 9.43 (s, 2H), 8.26 (d, J = 7.6 Hz, 4H), 8.16 (s, 1H), 7.82 (d, J = 7.7 Hz, 2H), 7.77-7.69 (m, 6H), 7.63 (d, J = 7.7 Hz, 2H), 7.48-7.35 (m, 10H), 7.33-7.25 (m, 4H), 7.12-7.03 (m, 2H), 6.80 (t, J = 7.5 Hz, 1H), 6.25 (d, J = 2.0 Hz, 2H), 6.20 (t, J = 2.0 Hz, 1H).

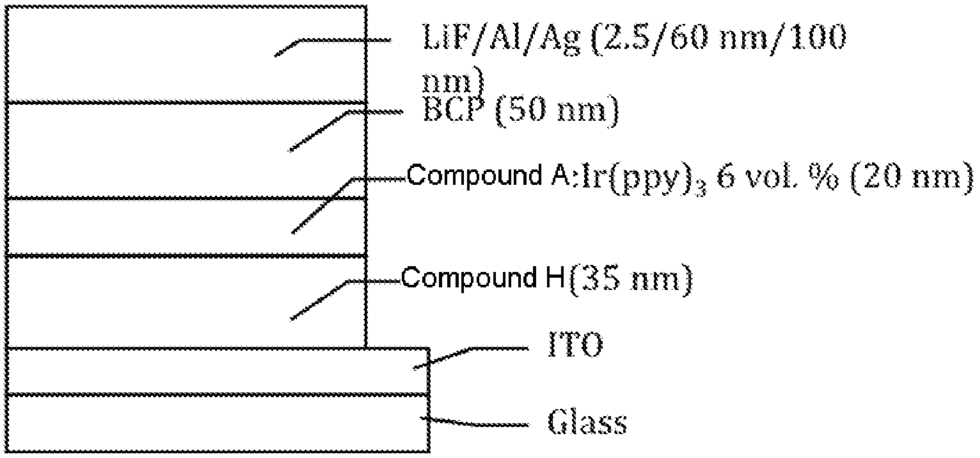


(Compound E):

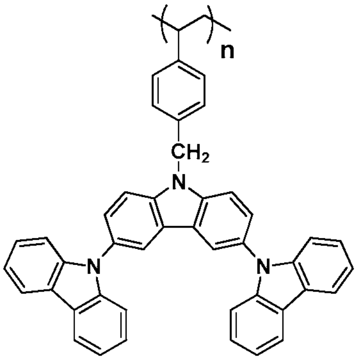


(0.294 g, 0.36 mmol), potassium carbonate (0.624 g, 4.5 mmol), and DMF (10 mL) were combined. 4-vinylbenzyl chloride (0.155 g, 1.0 mmol) was added dropwise and reaction was covered with foil. After 24 h, deionized water (100 mL) was added and the solution was extracted with dichloromethane (2 x 200 mL). The organic phase was concentrated in vacuo and purified by column chromatography (silica gel; gradient 100% DCM to (8:2) = DCM:EtOAc) to afford a nearly white powder.

EXAMPLE 6

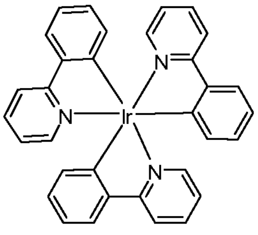


Indium tin oxide (ITO)-coated glass slides (Colorado Concept Coatings LLC) with a sheet resistivity of ~15 Ω/sq were used as substrates for the OLEDs fabrication. The ITO substrates were masked partially with kapton tape and the exposed ITO was etched in acid vapor (1:3 by volume, HNO_3: HCl) for 5 min at 60 °C. The substrates were cleaned in an ultrasonic bath in the following solutions: detergent water, distilled water, acetone, and isopropanol for 20 min in each step. At the end the substrates were blown dry with nitrogen. Subsequently, ITO substrates were O_2 plasma treated for 2 min.

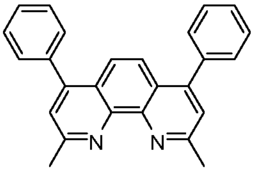


Polymer H

Polymer H was synthesized according to US provisional serial no. 61/579394 filed December 22, 2011, incorporated by reference in its entirety. Polymer H was processed in the glove box under nitrogen. 10 mg of Compound H was dissolved in 1ml of anhydrous chlorobenzene (Aldrich). 35 nm thick films of the hole-transport material were spin-coated at 1500 rpm, acceleration 1,000 rpm/sec for 60 sec. The films were then heated on a hot plate at 120 °C for 20 minutes.



Ir(ppy)$_3$

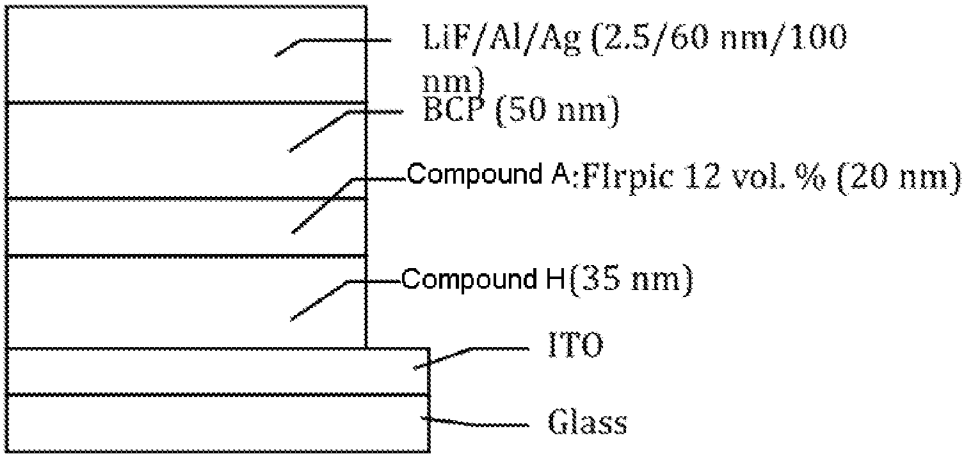


BCP

The emissive layer, consisting of a host, Compound A, and an emitter, Ir(ppy)$_3$ (Lumtec), was deposited by co-evaporation of the two components at 0.94 Å/s and 0.06 Å/s respectively. The electron transport layer, BCP (Aldrich), the electron-injection layer, LiF (Aldrich) and aluminum were thermally evaporated at 1 Å/s, 0.2 Å/s and 2 Å/s respectively. The pressure in the vacuum chamber was 1×10^{-7} Torr. The active area of the tested devices was about 0.1 cm^2. The devices were tested in a glove box under nitrogen. The performance of the device is shown in Figure 1.

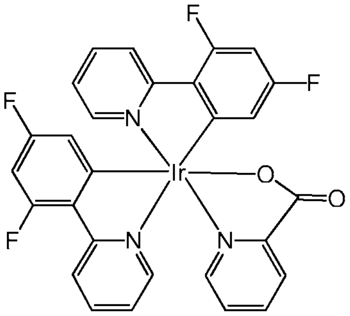
With an external quantum efficiency (EQE) of 25.1 % at a luminance of 100 cd/m^2 , an EQE of 23.3% at a luminance of 1,000 cd/m^2, and an EQE of 18.2% at a luminance of 10,000 cd/m^2, the performance of these devices is among the best ever reported in the field for devices comprised of just an HTL, an emissive layer doped with Ir(ppy)$_3$, and an ETL. The high efficiency was achieved without any light extraction mechanism.

EXAMPLE 7



Indium tin oxide (ITO)-coated glass slides (Colorado Concept Coatings LLC) with a sheet resistivity of ~15 Ω/sq were used as substrates for the OLEDs fabrication. The ITO substrates were masked partially with kapton tape and the exposed ITO was etched in acid vapor (1:3 by volume, HNO_3: HCl) for 5 min at 60 °C. The substrates were cleaned in an ultrasonic bath in the following solutions: detergent water, distilled water, acetone, and isopropanol for 20 min in each step. At the end the substrates were blown dry with nitrogen. Subsequently, ITO substrates were O_2 plasma treated for 2 min.

Compound H was processed in the glove box under nitrogen. 10 mg of Compound H was dissolved in 1ml of anhydrous chlorobenzene (Aldrich). 35 nm thick films of the hole-transport material were spin-coated at 1500 rpm, acceleration 1,000 rpm/sec for 60 sec. The films were then heated on a hot plate at 120 °C for 20 minutes.



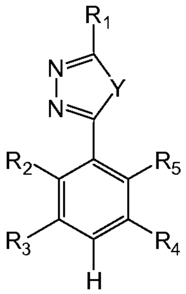
FIrpic

The emissive layer, consisting of a host, Compound A, and an emitter, FIrpic (Lumtec), was deposited by co-evaporation of the two components at 0.88 Å/s and 0.12 Å/s respectively. The electron transport layer, BCP (Aldrich), the electron-injection layer, LiF (Aldrich) and aluminum were thermally evaporated at 1 Å/s, 0.2 Å/s and 2 Å/s respectively. The pressure in the vacuum chamber was 1×10^{-7} Torr. The active area of the tested devices was about 0.1 cm^2. The devices were tested in a glove box under nitrogen. The performance of the device is shown in Figure 2.

The performance of the device is shown in Figure 2. The plot on the left shows current density voltage characteristic of the diode. The plot on the right shows luminance values (solid symbols) and external quantum efficiency (EQE) (empty symbols) as a function of applied voltage. The value of EQE between 10 and 1000 cd/m^2 is above 10% and maximum luminance shown is around 10,000 cd/m^2. This high level of performance in terms of efficiency and luminance proves the suitability of these compositions for blue-emitting organic light-emitting diode applications.

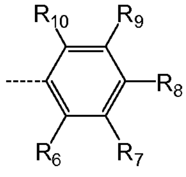
WHAT IS CLAIMED IS:

1. A compound represented by formula (I):

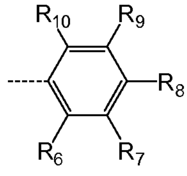


(I),

wherein:

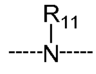


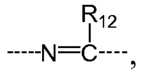
a) one or two of R_2, R_3, R_4 and R_5 are represented by , and the remaining of R_2, R_3, R_4 and R_5 are independently selected from hydrogen, halogen and a $C_{1\text{-}20}$ organic group;



b) for each , one or two of R_6, R_7, R_8, R_9 and R_{10} are optionally substituted carbazole groups; and the remaining of R_6, R_7, R_8, R_9 and R_{10} are independently selected from hydrogen, halogen and a $C_{1\text{-}20}$ organic group;

c) R1 is an optionally substituted aryl group, an optionally substituted heteroaryl group, an optionally substituted alkyl group or an optionally substituted heteroalkyl group; and

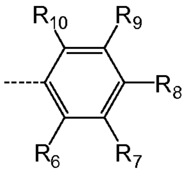




d) Y is selected from ---O---, $\text{---}\overset{R_{11}}{\overset{|}{N}}\text{---}$, $\text{---N{=}N---}$ and $\text{---N}{=}\overset{R_{12}}{\overset{|}{C}}\text{---}$, wherein R_{11} is an optionally substituted aryl group, an optionally substituted heteroaryl group, an optionally substituted alkyl group or an optionally substituted heteroalkyl group, and wherein R_{12} is hydrogen, an optionally substituted aryl group, an optionally substituted heteroaryl group, an optionally substituted alkyl group or an optionally substituted heteroalkyl group.

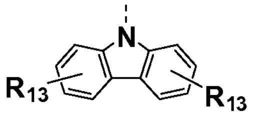
2. The compound of claim 1, wherein: (i) the remaining of R_2, R_3, R_4 and R_5 are independently selected from hydrogen, fluoro, cyano, alkyl, fluoroalkyl, alkoxide and fluoroalkoxide group; (ii) the carbazole group is unsubstituted or is substituted with one or more groups selected from fluoro, cyano, alkyl, fluoroalkyl, alkoxide, fluoroalkoxide and

optionally substituted carbazole; (iii) the remaining of R_6, R_7, R_8, R_9 and R_{10} are independently selected from hydrogen, fluoro, cyano, alkyl, fluoroalkyl, alkoxide and fluoroalkoxide; (iv) R_1, R_{11} and R_{12} are unsubstituted or substituted with one or more groups selected from hydroxyl, fluoro, cyano, alkyl, fluoroalkyl, alkoxide, and fluoroalkoxide.

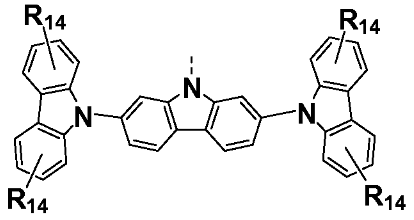
3. The compound of claim 1 or 2, wherein 

is present at R_3 and/or R_4 but not at R_2 or R_5, and wherein the optionally substituted carbazole group is present at R_7 and/or R_9 but not at R_6, R_8 or R_{10}.

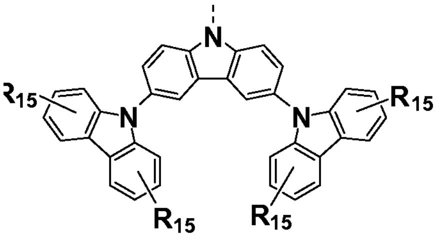
4. The compound of any of claims 1-3, wherein the optionally substituted carbazole group is selected from formulae (II), (III), (IV), (V) and (VI):



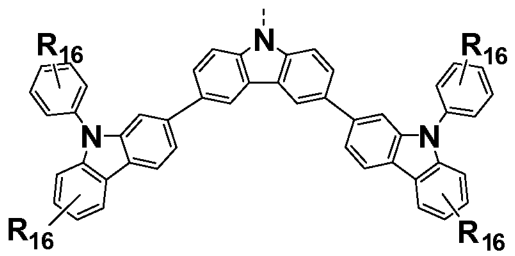
(II)



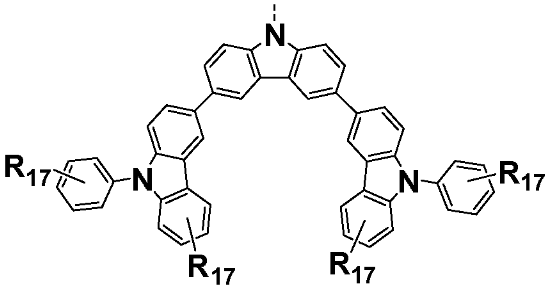
(III)



(IV)

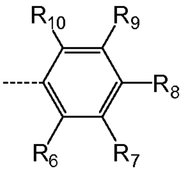


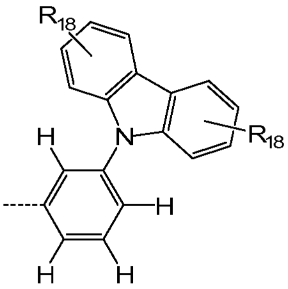
(V)



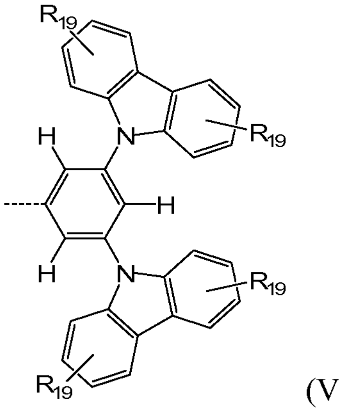
(VI)

wherein each R_{13}, R_{14}, R_{15}, R_{16} and R_{17} is independently hydrogen, fluoro, cyano, a C_{1-20} linear or branched alkyl, a C_{1-20} linear or branched fluoroalkyl, a C_{1-20} linear or branched alkoxide, or a C_{1-20} linear or branched fluoroalkoxide group.

5. The compound of any of claims 1-3, wherein  is selected from formulae (VII) and (VIII):



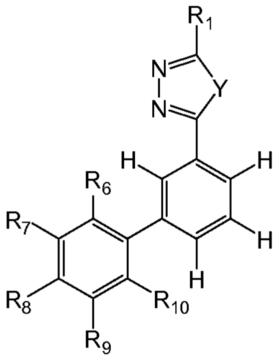
(VII)



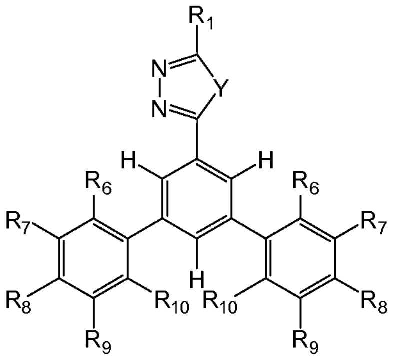
(VIII)

wherein each R_{18} and R_{19} is independently hydrogen, fluoro, cyano, a C_{1-20} linear or branched alkyl, a C_{1-20} linear or branched fluoroalkyl, a C_{1-20} linear or branched alkoxide, a C_{1-20} linear or branched fluoroalkoxide group, or an optionally substituted carbazole.

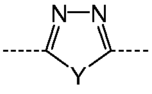
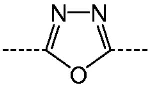
6. The compound of any of claims 1-5, wherein the compound is selected from formulae (IX) and (X):

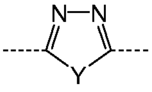
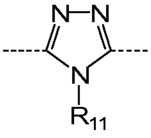


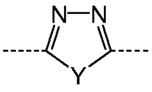
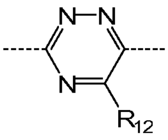
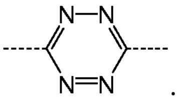
(IX)



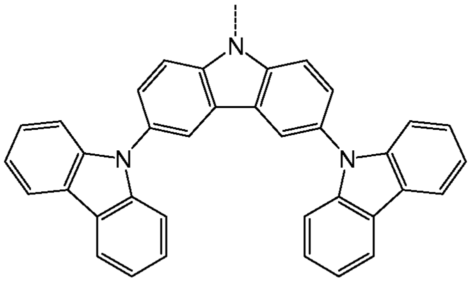
(X).

7. The compound of any of claims 1-6, wherein  is  .

8. The compound of any of claims 1-6, wherein  is  .

9. The compound of any of claims 1-6, wherein  is  or  .

10. The compound of claim 1, wherein the compound comprises at least one triscarbazole group represented by



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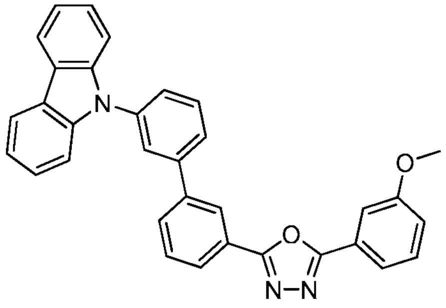
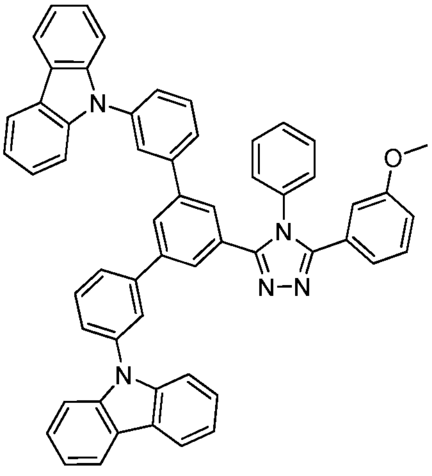
11. The compound of any of claims 1-10, wherein R_1 comprises at least one crosslinkable group.

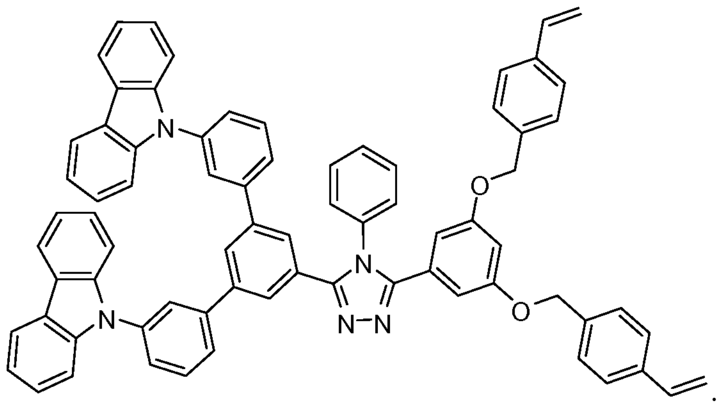
12. The compound of claim 1, wherein the compound is selected from:



,



, and



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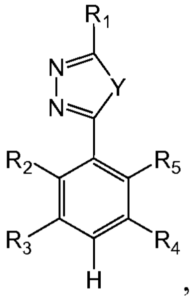
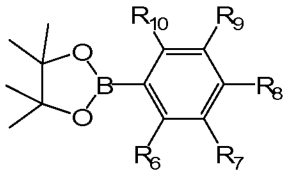
13. A method for making the compounds of any of claims 1-12, comprising reacting a first compound with a second compound, wherein:

(a) the first compound is represented by  , wherein

(i) one or two of R_2, R_3, R_4 and R_5 are Br, and the remaining of R_2, R_3, R_4 and R_5 in the formula representing the first compound have the same definition as their R_2, R_3, R_4 and R_5 homologues contained in the formula of the compound claimed in any of claims 1-12;

(ii) R_1 in the formula representing the first compound has the same definition as its R_1 homologues contained in the formula of the compound claimed in any of claims 1-12; and

(iii) Y is selected from -----O-----, $\text{-----}\overset{R_{11}}{\overset{|}{N}}\text{-----}$, $\text{-----N{=}N----}$ and $\text{-----N{=}}\overset{R_{12}}{\overset{|}{C}}\text{----}$, wherein R_{11} and R_{12} in the formula representing the first compound have the same definition as their R_{11} and R_{12} homologues contained in the formula of the compound claimed in any of claims 1-12;

(b) the second compound is represented by 

, wherein R_6, R_7, R_8, R_9 and R_{10} in the formula representing the second compound have the same definition as their R_6, R_7, R_8, R_9 and R_{10} homologues contained in the formula of the compound claimed in any of claims 1-12.

14. A composition comprising the compound of any of claims 1-12 or made by the method of claim 13.

15. An electroluminescence device, comprising an anode, a cathode, and an emissive layer, wherein the emissive layer comprises the compound of any of the claims 1-12 or made by the method of claim 13, or the composition of claim 14.

16. The electroluminescence device of claim 15, wherein the emissive layer comprises at least one phosphorescent emitter, and wherein the external quantum efficiency of the electroluminescence device at 1,000 cd/m^2 is at least 5%.

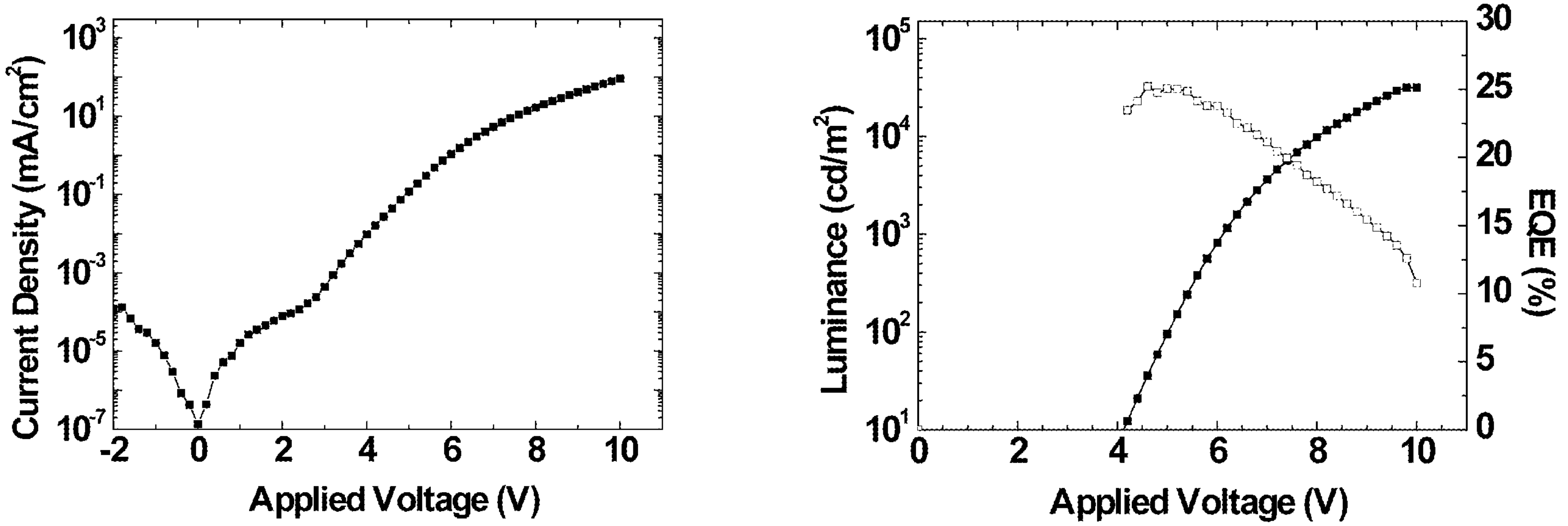

Current Density (mA/cm^2)
10^3
10^1
10^{-1}
10^{-3}
10^{-5}
10^{-7}
-2
0
2
4
6
8
10
Applied Voltage (V)
Luminance (cd/m^2)
10^5
10^4
10^3
10^2
10^1
0
2
4
6
8
10
Applied Voltage (V)
EQE (%)
30
25
20
15
10
5
0

FIGURE 1

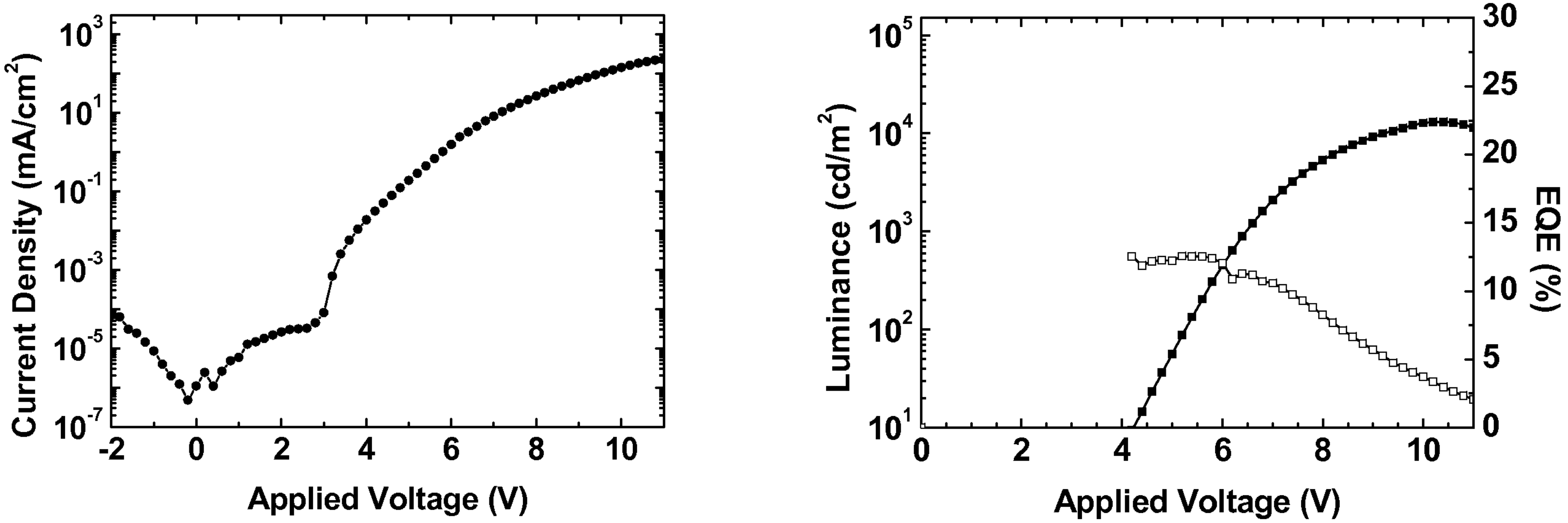

Current Density (mA/cm^2)
10^3
10^1
10^{-1}
10^{-3}
10^{-5}
10^{-7}
-2
0
2
4
6
8
10
Applied Voltage (V)
Luminance (cd/m^2)
10^5
10^4
10^3
10^2
10^1
0
2
4
6
8
10
Applied Voltage (V)
EQE (%)
30
25
20
15
10
5
0

FIGURE 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/049329

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D413/14 C07D403/14 C07D413/10 H05B33/14
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 H05B

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, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JINYONG ZHUANG ET AL: "Configuration effect of novel bipolar triazole/carbazole-based host materials on the performance of phosphorescent OLED devices", ORGANIC ELECTRONICS, vol. 13, no. 10, 2 July 2012 (2012-07-02), pages 2210-2219, XP055073894, ISSN: 1566-1199, DOI: 10.1016/j.orgel.2012.06.025	1-6,8,11,14
Y	page 2210 page 2211; compounds 3, 4	7,9,10,12,13,15,16

-/--

☒ 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

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search 9 August 2013	Date of mailing of the international search report 21/08/2013
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Jeanjean, Fabien

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/049329

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KATHARINE E. LINTON ET AL: "Colour tuning of blue electroluminescence using bipolar carbazole-oxadiazole molecules in single-active-layer organic light emitting devices (OLEDs)", JOURNAL OF MATERIALS CHEMISTRY, vol. 22, no. 23, 1 January 2012 (2012-01-01), page 11816, XP055073896, ISSN: 0959-9428, DOI: 10.1039/c2jm31825c page 11816 page 11817; compounds 1, 4-5, 7 -----	1-16
Y	WO 2010/061989 A1 (CHEIL IND INC [KR]; KIM HYUNG-SUN [KR]; LEE HO-JAE [KR]; YU EUN-SUN [K) 3 June 2010 (2010-06-03) page 24 page 41; claim 9 -----	1-16
Y	WO 2010/027004 A1 (SEMICONDUCTOR ENERGY LAB [JP]; SEO SATOSHI [JP]; KAWAKAMI SACHIKO; NOM) 11 March 2010 (2010-03-11) page 176; compound (421) page 1, paragraph 1 -----	1-16
Y	US 2009/160324 A1 (NOMURA HIROKO [JP] ET AL) 25 June 2009 (2009-06-25) page 62; claim 5; compound (G3) page 63; claim 20 -----	1-16
A	US 2010/244669 A1 (NOMURA HIROKO [JP] ET AL) 30 September 2010 (2010-09-30) page 26; claim 1; compound (G1) -----	1-16
A	US 2004/214036 A1 (BENTSEN JAMES G [US] ET AL) 28 October 2004 (2004-10-28) page 80; compound CCXIII -----	1-16
A	MIN GUAN ET AL: "High-performance blue electroluminescent devices based on 2-(4-biphenylyl)-5-(4-carbazol-9-yl)phenyl-1,3,4-oxadiazole", CHEMICAL COMMUNICATIONS; [6015D], ROYAL SOCIETY OF CHEMISTRY, UK, no. 21, 1 January 2003 (2003-01-01), pages 2708-2709, XP002486376, ISSN: 1359-7345 [retrieved on 2003-09-30] page 2708 -----	1-16
A	EP 1 939 208 A1 (SEMICONDUCTOR ENERGY LAB [JP]) 2 July 2008 (2008-07-02) page 47, paragraph 229; compound YGAO11 ----- -/--	1-16

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2008/286607 A1 (NOMURA HIROKO [JP] ET AL) 20 November 2008 (2008-11-20) page 59; claim 2; compound (G3) -----	1-16
A	WO 2012/088316 A1 (GEORGIA TECH RES INST [US]; ZHANG YADONG [US]; ZUNIGA CARLOS [US]; CAI) 28 June 2012 (2012-06-28) page 56; claim 1 -----	1-16
X,P	WO 2013/096921 A1 (GEORGIA TECH RES INST [US]; SOLVAY [BE]) 27 June 2013 (2013-06-27) page 7; compound C -----	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2013/049329

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2010061989 A1	03-06-2010	US 2011291083 A1	01-12-2011
		WO 2010061989 A1	03-06-2010
WO 2010027004 A1	11-03-2010	CN 102144313 A	03-08-2011
		EP 2321862 A1	18-05-2011
		JP 2010083876 A	15-04-2010
		KR 20110063749 A	14-06-2011
		US 2010060155 A1	11-03-2010
		US 2013112961 A1	09-05-2013
		WO 2010027004 A1	11-03-2010
US 2009160324 A1	25-06-2009	EP 2229382 A1	22-09-2010
		JP 2009167173 A	30-07-2009
		KR 20100101668 A	17-09-2010
		US 2009160324 A1	25-06-2009
		WO 2009081718 A1	02-07-2009
US 2010244669 A1	30-09-2010	CN 101845042 A	29-09-2010
		JP 2010248181 A	04-11-2010
		KR 20100108284 A	06-10-2010
		US 2010244669 A1	30-09-2010
US 2004214036 A1	28-10-2004	AU 2003287043 A1	23-11-2004
		CN 1764708 A	26-04-2006
		EP 1618169 A1	25-01-2006
		JP 2006523611 A	19-10-2006
		KR 20060006812 A	19-01-2006
		MX PA05010928 A	25-11-2005
		US 2004214036 A1	28-10-2004
		US 2008026135 A1	31-01-2008
		WO 2004096948 A1	11-11-2004
EP 1939208 A1	02-07-2008	CN 101274945 A	01-10-2008
		EP 1939208 A1	02-07-2008
		JP 2008179607 A	07-08-2008
		KR 20080061300 A	02-07-2008
		TW 200844099 A	16-11-2008
		US 2008160345 A1	03-07-2008
US 2008286607 A1	20-11-2008	CN 101679383 A	24-03-2010
		JP 2008308490 A	25-12-2008
		US 2008286607 A1	20-11-2008
		US 2012199818 A1	09-08-2012
		WO 2008143019 A1	27-11-2008
WO 2012088316 A1	28-06-2012	NONE	
WO 2013096921 A1	27-06-2013	NONE	