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(54) HOLE TRANSPORT MATERIALS INCLUDING OLED APPLICATIONS

LOCHTRANSPORTMATERIALIEN MIT OLED-ANWENDUNGEN

MATÉRIAUX DE TRANSPORT DE TROU Y COMPRIS POUR LES APPLICATIONS À OLED

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Description

BACKGROUND

[0001] A need exists to provide better organic electronic devices such as organic light emitting devices (OLEDs) including better materials used in the devices. In particular, better OLED devices and materials, including hole transporting materials, are needed. An OLED operation is based on injection, transport and recombination of two types of charge carriers: holes and electrons. It is important in an OLED device to control the injection and transport of these two types of carriers so as to enable the recombination to occur in the emissive layer where the luminescent species are located. The location where these species meet and recombine can dictate the efficiency and lifetime of the device.

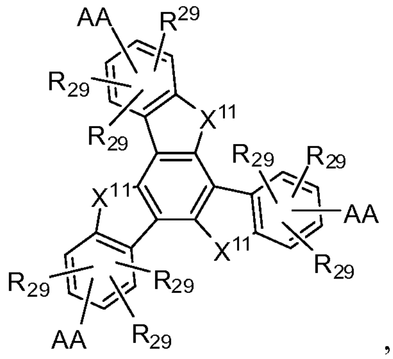
[0002] In particular, a need exists for novel hole transporting materials with great properties such as solubility, thermal stability, and electronic energy levels such as HOMO and LUMO, so that the materials can be adapted for different applications and to function with different materials such as light emitting layers, photoactive layers, and electrodes. In particular, good solubility and intractability properties are important. The ability to formulate the system for a particular application and provide the required balance of properties are also important.

[0003] Additional background material can be found in, for example, (a) Charge carrier transporting molecular materials and their applications in devices, Shirota, et al., Chem. Rev., 2007, 107, 953 - 1010, (b) Organic electroluminescent diodes, Tang, et al., Appl. Phys. Lett. 1987, 51, 913 - 915. Hole transport is important for a variety of electronics applications.

SUMMARY

[0004] Provided herein are compositions comprising one or more novel hole transporting compounds, said hole transporting compound comprising a hole transporting core covalently bonded to three arylamine (AA) groups, each AA group is optionally substituted with one or more intractability groups. In the structures shown below, additional AA groups can be included as appropriate.

[0005] In a first embodiment, the hole transporting compound is represented by



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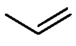
wherein each of X^{11} is S or CR_2, wherein each R is an optionally substituted alkyl, aryl, heteroalkyl, heteroaryl, or intractability group, and wherein each of R^{29} is H, F, or an optionally substituted alkyl, aryl, heteroalkyl, heteroaryl, or intractability group, and wherein the compound comprises at least one intractability group from the group consisting of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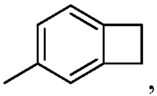
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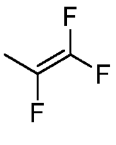

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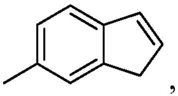
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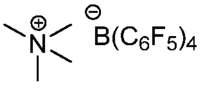

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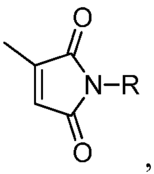

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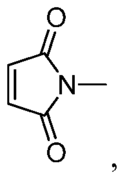

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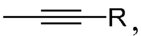

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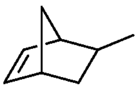
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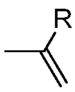

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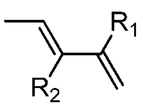

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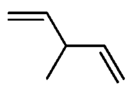
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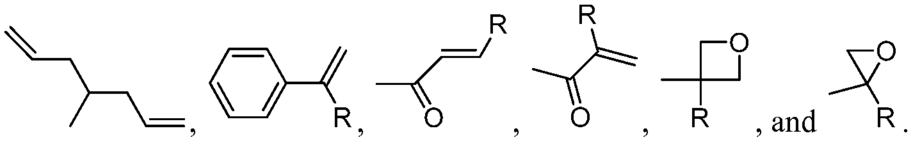


[0006] Also provided is a device comprising a hole transport layer, wherein the hole transport layer comprises any of the hole transporting compounds described above. In one embodiment, the device is OLED.

[0007] Moreover, also provided is a method comprising: (i) providing a substrate comprising a hole injection layer, (ii) coating the substrate with at least one ink composition comprising any of the hole transporting compounds described above to form a coated substrate, and (iii) heating the coated substrate.

[0008] Furthermore, also provided is a method for making a composition comprising any of the hole transporting compound described above, comprising reacting arylamine with a hole transporting core.

[0009] Also provided is a method comprising at least one catalytic amination reacting step of at least one aryl triflate compound with at least one arylamine compound in the presence of at least one metal and at least two phosphine compound ligands for the metal. The metal can be, for example, palladium. The aryl triflate compound can comprise at least two triflate groups. The arylamine compound can be, for example, at least one primary arylamine compound or at least one secondary arylamine compound. The at least two phosphine compound ligands can comprise, for example, (i) a trialkylphosphine such ast t-Bu_3P, and (ii) Xphos, ("2-Dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl").

[0010] At least one advantage for at least one embodiment described herein is that good mobility can be achieved which can, for example, lower the device operating voltage.

[0011] At least one advantage for at least one embodiment described herein is improved synthesis enabling production of new compounds with better purities under commercially realistic conditions.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012]

Figure 1 shows DSC data of an exemplary embodiment of the hole transporting compounds described herein.
Figure 2 shows TGA data of an exemplary embodiment of the hole transporting compounds described herein.
Figure 3 shows UV-Vis and PL absorption spectra of an exemplary embodiment of the hole transporting compounds described herein.

DETAILED DESCRIPTION

INTRODUCTION

[0013] Organic electronics devices, including OLEDs, as well as materials to make organic electronic devices including hole injection layers and hole transport layers, are described in, for example US2006/063037, the following patent publications assigned to Plextronics, Inc.: WO 2006/036,755; WO 2006/086,480; WO 2008/073,149; WO 2009/126,918; WO 2009/111675; WO 2009/111339; WO 2010/051,259; WO 2010/059,240; WO 2010/059,646; WO 2010/062,558 and PCT/US2011/042861. OLED devices can comprise a variety of sub-categories including, for example, PLEDs, SMOLEDs, PHOLEDs, WOLEDs, and the like. OLED devices, materials, and methods are also described in, for example, (1) Highly Efficient OLEDS with Phosphorescent Materials (Ed. H. Yerrin), 2008, Wiley-VCH, (2) Organic Light Emitting Devices: Synthesis, Properties, and Applications (Eds. Mullen, Scherf), 2006, (3) Organic Light Emitting Methods and Devices, (Li and Meng), 2007, CRC.

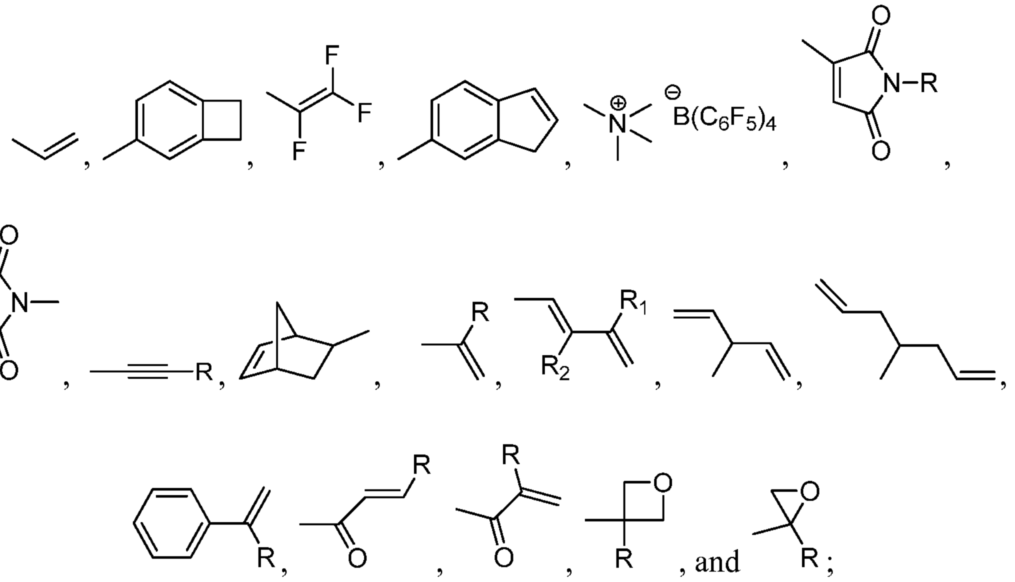
[0014] Electroluminescent devices are described in, for example, Friend et al., "Electroluminescence in Conjugated Polymers," Nature, 397, 121-128, January 14, 1999. Hole injection and transport are described in, for example, Shen et al., "How to Make Ohmic Contact to Organic Semiconductors," ChemPhysChem, 2004, 5, 16-25. OLED devices are described in, for example, Forrest, "The Path to Ubiquitous and Low-Cost Organic Electronic Appliances on Plastic," Nature, 428, April 29, 2004, 911-918.

[0015] Compounds and units within compounds which provide hole transport are known in the art. See, for example, US Patent Nos. 5,034,296; 5,055,366; 5,149,609; 5,589,320; 5,759,709; 5,895,692; and 7,125,633, as well as US Patent Publication Nos. 2005/0184287 and 2008/0286566. Hole transport materials, morphology, and devices (including arylamine compounds) are also described extensively in "Charge Carrier Transporting Molecular Materials and their Applications in Devices," Shirota et al., Chem. Rev., 2007, 107, 953-1010.

HOLE TRANSPORTING COMPOUNDS WITH A VARIETY OF CORE, ARYLAMINE, AND INTRACTABILITY GROUPS

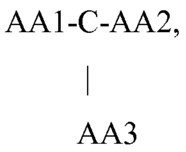
[0016] Hole transport materials and compounds are known in the art. They typically comprise pi-electron systems. A leading example of a hole transport material is the arylamine set of compounds.

[0017] One embodiment provides, for example, a composition comprising: at least one compound comprising a hole transporting core; wherein the core is covalently bonded to a first arylamine group and also covalently bonded to a second and third arylamine group; and wherein the compound comprises at least one intractability group selected from the group consisting of



wherein the at least one intractability group is covalently bonded to the hole transporting core, the first arylamine group, the second arylamine group, or a combination thereof; and wherein the compound has a molecular weight of about 5,000 g/mole or less.

[0018] The hole transporting core is a trivalent group which links to a first, a second and a third arylamine group. This compound arrangement can be also represented by



$$\begin{array}{c} AA1\text{-}C\text{-}AA2, \\ | \\ AA3 \end{array}$$

wherein AA1 represents the first arylamine group, AA2 represents the second arylamine group, AA3 represents the third arylamine group, and C represents the hole transporting core. The one or more intractability groups can be bonded to one or more of C, AA1, AA2 and AA3. In addition, the compound can comprise additional arylamine groups either in the hole transporting core or in the groups linked to the arylamine groups outside of the core.

[0019] Aryl or heteroaryl groups can be used in the hole transporting core. Examples of aryl and heteroaryl groups, which can be optionally substituted, are known in the art and include benzene, naphthalene, anthracene, phenanthrene, perylene, tetracene, pyrene, benzpyrene, chrysene, triphenylene, acenaphtene, fluorene, and those derived therefrom. Examples of heteroaryls include furan, benzofuran, thiophene, benzothiophene, pyrrole, pyrazole, triazole, imidazole, oxadiazole, oxazole, thiazole, tetrazole, indole, cabazole, pyrroloimidazole, pyrrolopyrazole, pyrrolopyrole, thienopyrrole, thienothiophene, furopyrrole, furofuran, thienofuran, benzoisoxazole, benzoisothiazole, benzoimidazole, pyridine, pyrazine, pyridazine, pyrimidine, triazine, quinoline, isoquinoline, cinnnoline, quinoxaline, phenanthridine, benzoimidazole, perimidine, quinazoline, quinazolinone, azulene, and those derived therefrom. The aryl or heteroaryl groups can comprise fused ring systems.

[0020] Aryl and heteroaryl groups can be optionally substituted with a variety of substituents and/or solubilizing groups. Examples can be (independently) H, F, alkyl, aryl, alkoxy, aryloxy, fluoroalkyl, fluoroaryl, fluoroalkoxy, fluoroaryloxy, polyether, as well as intractability groups described herein. The substituent may optionally comprise at least one perfluoroalkyl group. Substituents on neighboring rings can fuse together to form a ring.

[0021] In one embodiment, the hole transporting core comprises at least six aryl or heteroaryl rings.

[0022] The hole transporting core comprises heteroatoms such as S. In one embodiment, the hole transport core comprises at least one, at least two, or at least three, heteroatoms. In one embodiment, the hole transporting core comprises S heteroatoms.

[0023] In one embodiment, the hole transport core comprises at least one heteroarylmoiety comprising at least one S.

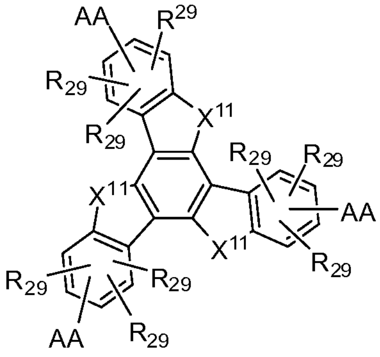
[0024] The hole transporting core can comprise fused rings. In one embodiment, the hole transport core comprises at least two, or at least three, or at least four, at least five, at least six or at least seven fused rings.

[0025] One or more substituent groups can be covalently bonded to the hole transporting core to increase solubility. A common example of such a solubilizing group is an optionally substituted alkyl or heteroalkyl moiety (an alkyl group, if used in a bivalent situation as spacer, can be also called alkylene; for example, propyl can be a propylene spacer). For example, C4 to C30, or C4 to C20, or C4 to C12 solublizing groups can be used. Heteroatoms include, for example, oxygen, nitrogen, and sulfur. One skilled in the art can examine the impact of the substituent group on solubility. In one embodiment, the hole transport core is functionalized with at least one solubilizing group. In one embodiment, the hole transport core is functionalized with at least two solubilizing groups. In one embodiment, the hole transport core is functionalized with at least one solubilizing group which has a least four carbon atoms. In one embodiment, the hole transport core is functionalized with at least one solublizing group which as an alkylene group comprising at least four carbon atoms. In one embodiment, the hole transport core is functionalized with at least one solubilizing group comprising at least one perfluoroalkyl group. Other solubilizing groups are shown in the structures herein.

[0026] The hole transporting compounds described herein include, but are not limited to, compounds represented by formula PLX-8.

PLX-8 HOLE TRANSPORTING COMPOUNDS

[0027] Hole transporting compounds, PLX-8, are represented by formula (XV):



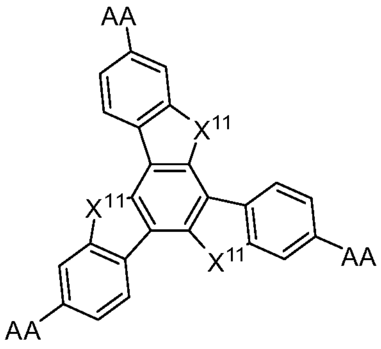
(XV)

[0028] Each of X^{11} can comprise, S or CR_2. Each R can be, for example, an optionally substituted alkyl, aryl, heteroalkyl, heteroaryl, or intractability group. In one embodiment, R comprises a moiety for improving solubility such as an optionally substituted linear or branched alkyl, alkoxy or polyether. In another embodiment, R comprises an intractability group which can be a crosslinking or non-crosslinking group. In a further embodiment, R comprises a crosslinking or polymerizable group, such as vinyl.

[0029] Each of R^{29} can be, for example, H, F, or an optionally substituted alkyl, aryl, heteroalkyl, heteroaryl, or intractability group. In one embodiment, each of R^{29} is hydrogen. In another embodiment, at least one of R^{29} comprises a moiety for improving solubility such as an optionally substituted linear or branched alkyl, alkoxy or polyether. In a further embodiment, at least one of R^{29} comprises an intractability group which can be a crosslinking or non-crosslinking group. In an additional embodiment, at least one of R^{29} comprises a crosslinking or polymerizable group, such as vinyl.

[0030] Each AA is an arylamine group optionally substituted with one or more intractability groups, such as vinyl.

[0031] In one embodiment of PLX-8, each of R^{29} is hydrogen, and the hole transporting compound is represented by:



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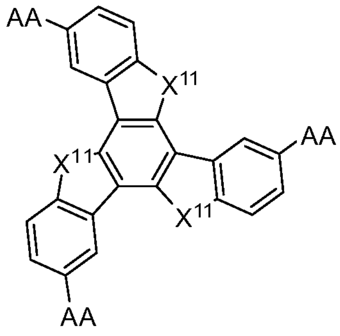

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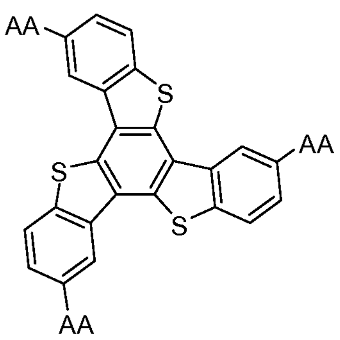
[0032] In another embodiment of PLX-8, each of R^{29} is hydrogen, X^{11} is S, and the hole transporting compound is represented by:



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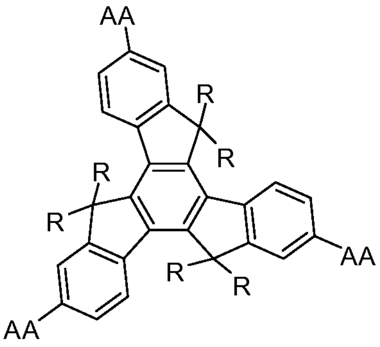
[0033] In a further embodiment of PLX-8, each of R^{29} is hydrogen, X^{11} is CR_2, and the hole transporting compound is represented by:



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ARYLAMINE GROUPS

[0034] Arylamine groups are generally known in the art. See, for example, US Pat. Pub. No. 2011/0017988 Yasukawa et. Al and other references cited herein. The arylamine group will have one valency on the nitrogen bonded to the hole transport core. The other two valencies on the nitrogen are bonded to aryl groups. This can be represented by N(R1)(R2)(R3), wherein R1-R3 are aryl groups which can be the same or different, independently of each other. The arylgroup can be a group free of heteroatoms or can be a heteroaryl group comprising at least one heteroatom.

[0035] In one embodiment, the first and second arylamine groups are the same arylamine group. In one embodiment, the first and second arylamine groups are different arylamine groups.

[0036] In one embodiment, each of the first and second arylamine groups are independently represented by -N(R1)(R2), wherein R1 and R2 are optionally substituted aryl or heteroaryl groups which may be the same or different.

[0037] In one embodiment, each of the first and second arylamine groups are independently represented by -N(R1)(R2), wherein at least one of R1 and R2 is an optionally substituted phenyl group (the remaining valency on the arylamine is linked to the hole transporting core).

[0038] In one embodiment, each of the first and second arylamine groups are independently represented by -N(R1)(R2), wherein at least one of R1 and R2 is an optionally substituted biphenyl group.

[0039] In one embodiment, each of the first and second arylamine groups are independently represented by -N(R1)(R2), wherein at least one of R1 and R2 is an optionally substituted carbazole group.

[0040] In one embodiment, each of the first and second arylamine groups are independently represented by -N(R1)(R2), wherein -N(R1)(R2) form an optionally substituted carbazole group.

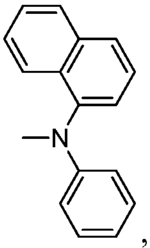
[0041] In one embodiment, each of the first and second arylamine groups are independently represented by -N(R1)(R2), wherein at least one of R1 and R2 is an optionally substituted naphthyl group.

[0042] In one embodiment, each of the first and second arylamine groups are independently represented by -N(R1)(R2), wherein at least one of R1 and R2 is an optionally substituted thienobenzene group.

[0043] In one embodiment, each of the first and second arylamine groups are independently represented by -N(R1)(R2), wherein at least one of R1 and R2 is an optionally substituted fluorene group.

[0044] In one embodiment, each of the first and second arylamine groups are independently represented by -N(R1)(R2), wherein at least one of R1 and R2 is an optionally substituted group comprising at least two fused aromatic rings.

[0045] Some specific examples of arylamine groups described here are provided below:



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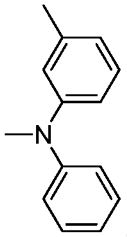

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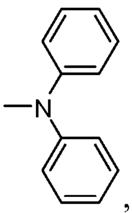

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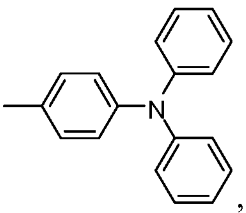

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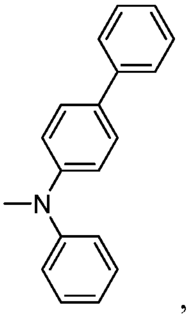

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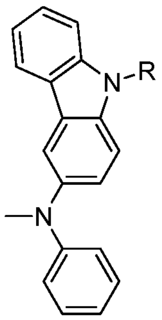

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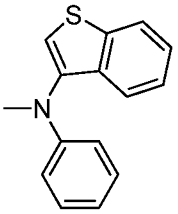

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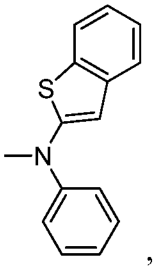

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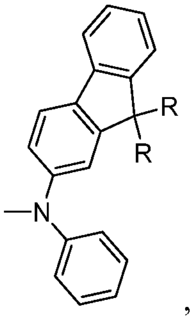

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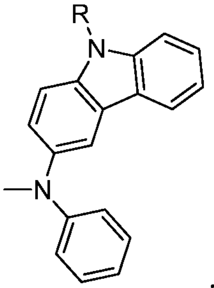

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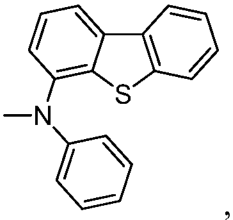

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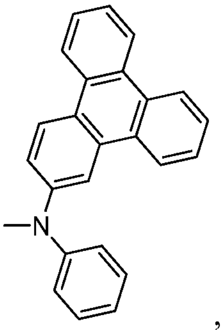

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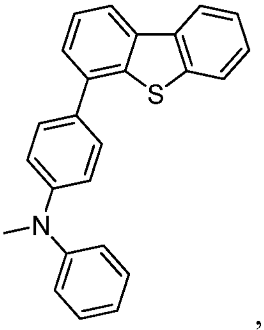

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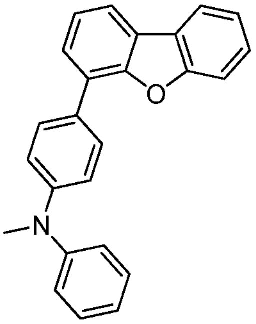

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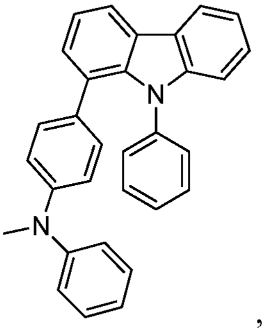

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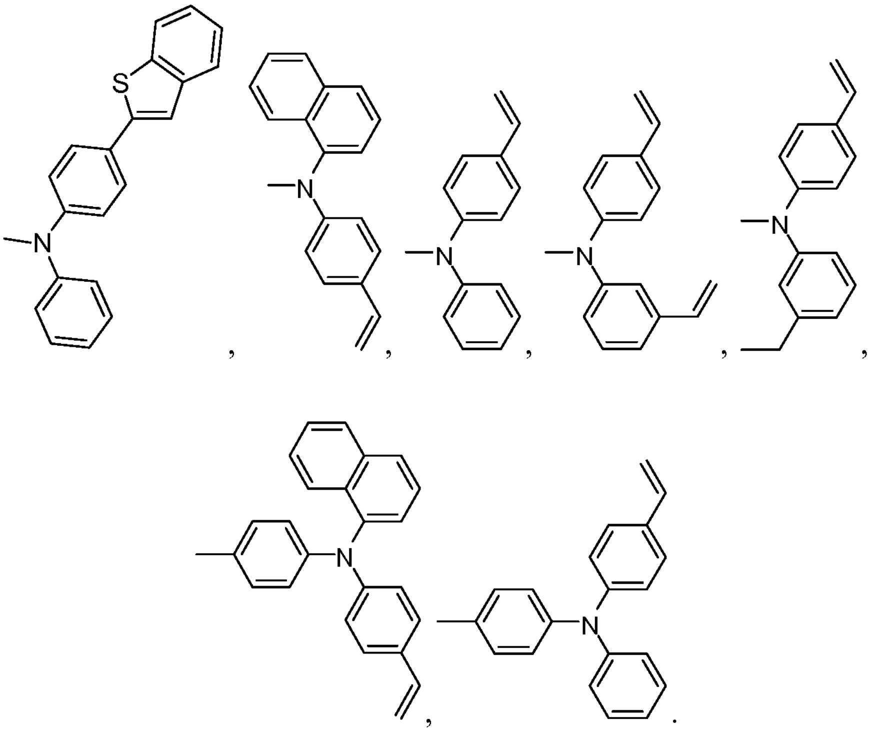
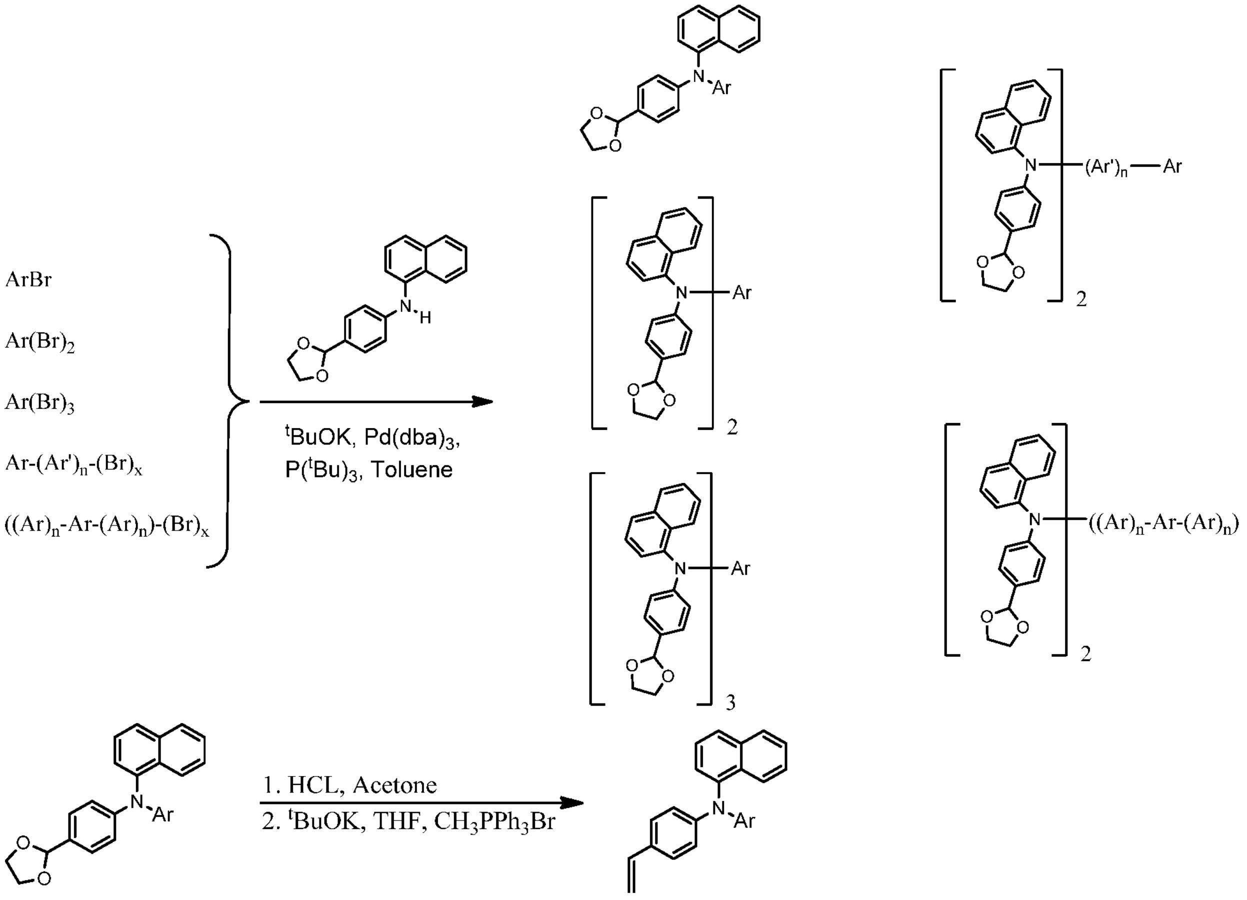


[0046] In one embodiment, arylamine groups optionally comprising one or more intractability groups can be covalently linked to the hole transporting core according to the following scheme:



INTRACTABILITY GROUPS

[0047] Intractability of hole transport materials is known in the art. See, for example, US Pat. Pub. Nos. 2009/0256117; 2010/0273007; and 2010/0292399. Intractability groups allow the materials to be sufficiently chemical and solvent resistant, allowing for solution processing.

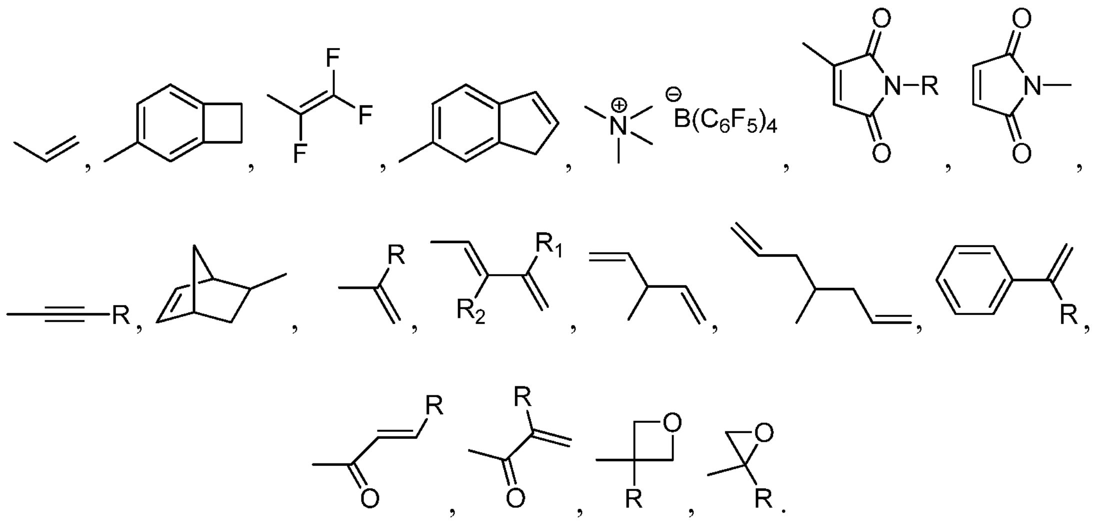
[0048] In one embodiment, the intractability group comprises a polymerizable or crosslinking group. The crosslinking group allows for a covalent linkage between molecules and buildup of molecular weight to provide intractable, chemically resistant, and solvent resistant materials. In one embodiment, the intractability group comprises a non-crosslinking group. A non-crosslinking group can be a salt group, comprising cation and anion. Organic anions can be used including borates. Ammonium cations can be used.

[0049] In one embodiment, the intractability group can be linked to the rest of the molecule via a spacer. Examples of spacers include solubilizing groups, described herein, including alkylene groups. In one embodiment, the intractability group is a vinyl group, but is either linked to a non-aromatic group or is only linked to a single aromatic group as in a styrene conformation. In one embodiment, the intractability group is separated from a larger delocalized structure such as fused aromatic ring systems. This may, in some cases, improve stability. In one embodiment, the styrene group can be linked to the hole transporting core via a non-conjugated spacer such as an alkylene moiety.

[0050] In one embodiment, the intractability group comprises at least one ethylene moiety. In one embodiment, the intractability group comprises a vinyl group. In one embodiment, the vinyl group is linked to an oxygen atom (vinyleneoxy group) or in another embodiment to a carbon atom which is part of an aliphatic or aromatic group (e.g., propenyl; other examples include acryloyl, or methacryloyl). In one embodiment, the intractability group comprises a benzocyclobutane group. In one embodiment, the intractability group comprises an indene group (or indenyl).

[0051] In one embodiment for a non-crosslinking group, the intractability group comprises a quaternary ammonium group. In one embodiment, the intractability group comprises a quaternary ammonium group comprising a tetraarylborate anion. In one embodiment, the intractability group comprises a quaternary ammonium group comprising a pentafluorophenylborate anion. A spacer group can be used to provide linkage between the quaternary ammonium group and the arylamine group.

[0052] Intractability groups of the present invention include :



[0053] In one embodiment, for example, the compound comprises at least three intractability groups, and at least one intractability group is covalently bonded to the hole transport core, and at least one intractability group is covalently bonded to the first arylamine group, and at least one intractability group is covalently bonded to the second arylamine group.

[0054] In another embodiment, for example, the intractability group is, or the intractability groups are, covalently bonded to the hole transport core but not the first arylamine group or the second or third arylamine group.

[0055] In a further embodiment, for example, the intractability group is, or the intractability groups are, covalently bonded to the first arylamine group, the second arylamine group, or both, but is not bonded to the hole transport core.

[0056] In one embodiment, the compound comprises one intractability group. In another embodiment, the compound comprises two or more intractability groups. In a further embodiments, the compound comprises three, four, five, or six or more intractability groups. No particular upper limit exists, but the number of intractability groups can be 12 or less, or 10 or less, or 8 or less, or 6 or less.

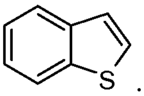
SYNTHESIS OF HOLE TRANSPORTING COMPOUNDS

[0057] One skilled in the art can use organic chemistry to link together the core moiety, the arylamine moieties, and the intractability group or groups. Synthesis is described in, for example, March's Advanced Organic Chemistry, 6th Ed., Wiley, 2007, as well as in references cited herein. Synthesis of hole transporting compounds is described herein.

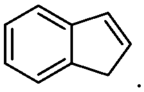
Synthesis of PLX-8

[0058] PLX-8 hole transporting compound can be synthesized according to, for example, the following steps: linking three fused-ring moieties together; ring-closing to fuse the three fused-ring moieties together and to form a hole transporting core comprising at least seven rings fused together in a star fashion; functioning the hole transporting core with arylamine groups; and optionally forming one or more intractability groups on either the hole transporting core or the arylamine groups via deprotection.

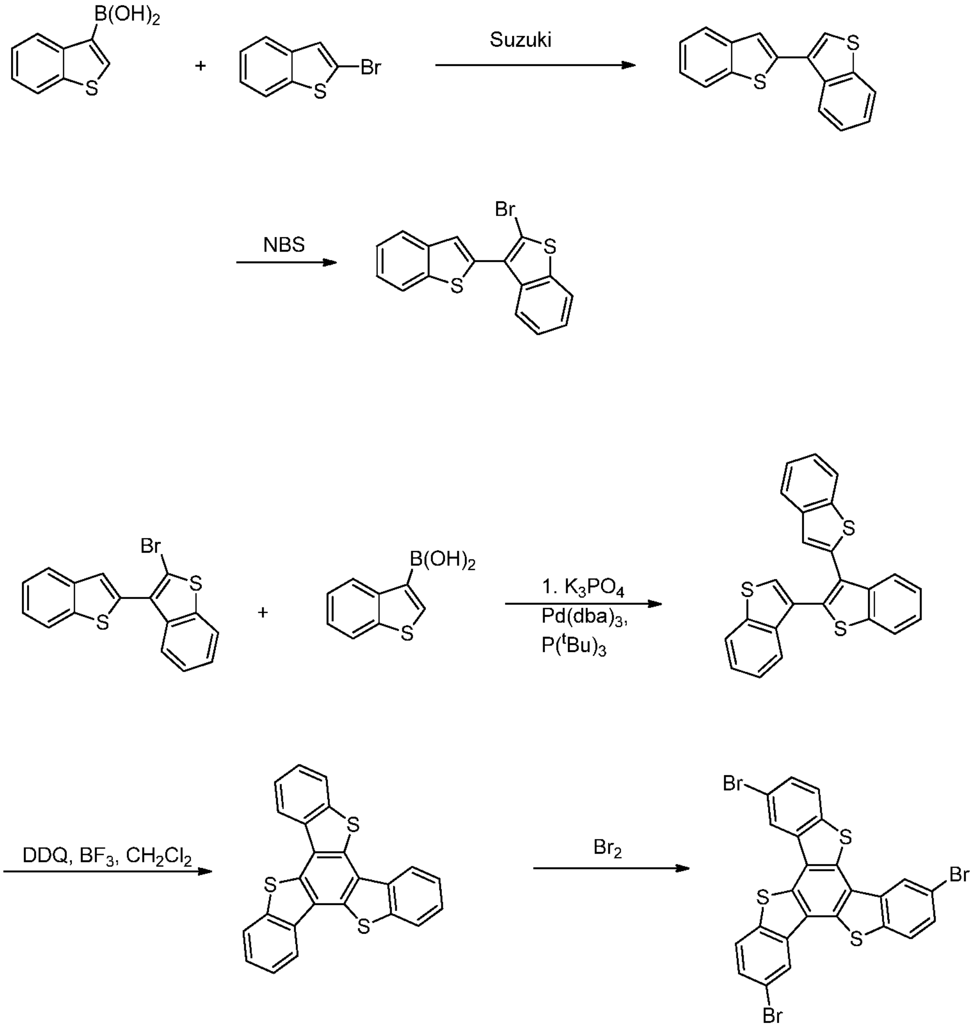
[0059] In one embodiment, the fused-ring moiety is

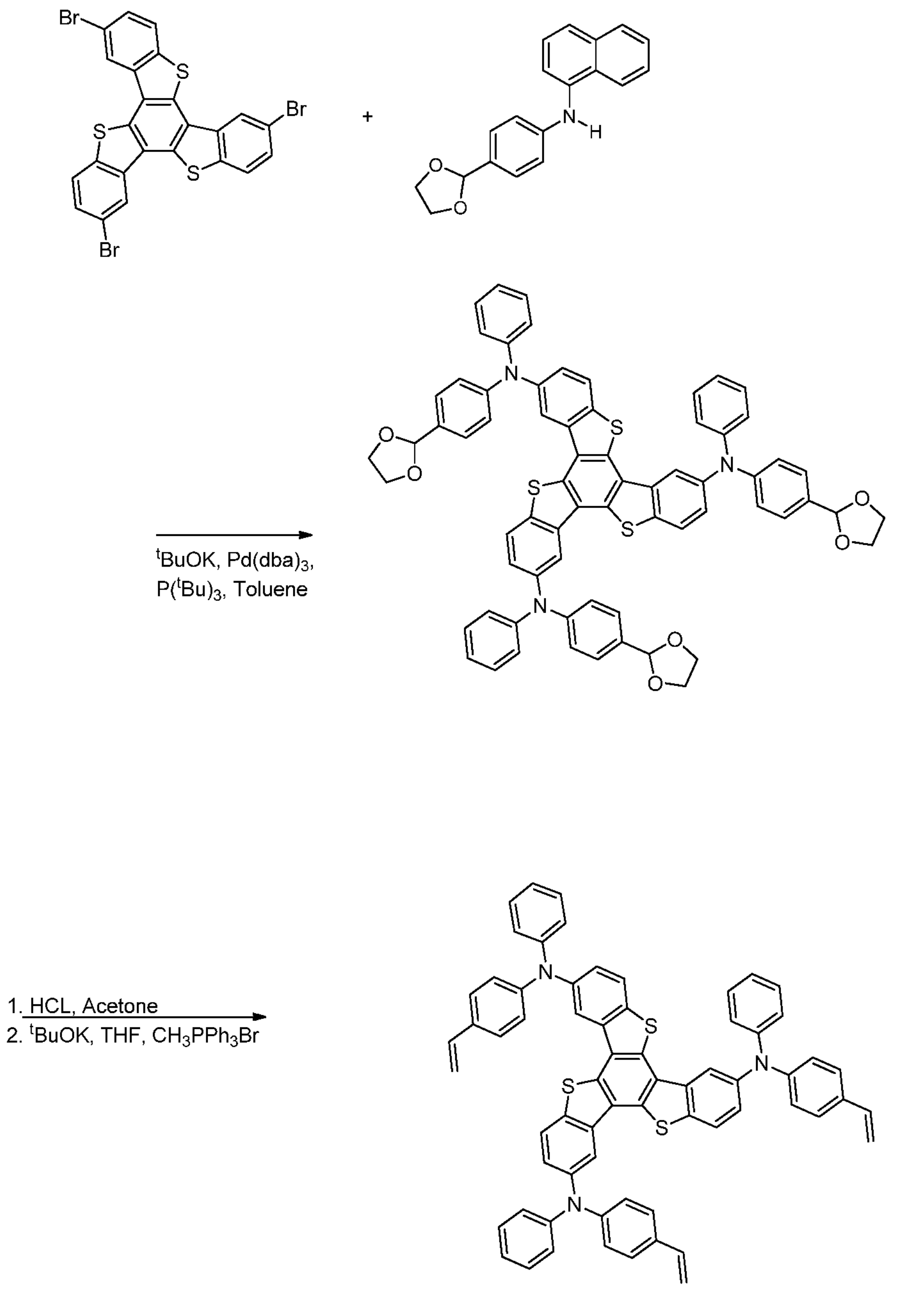


In another embodiment, the fused-ring moiety is

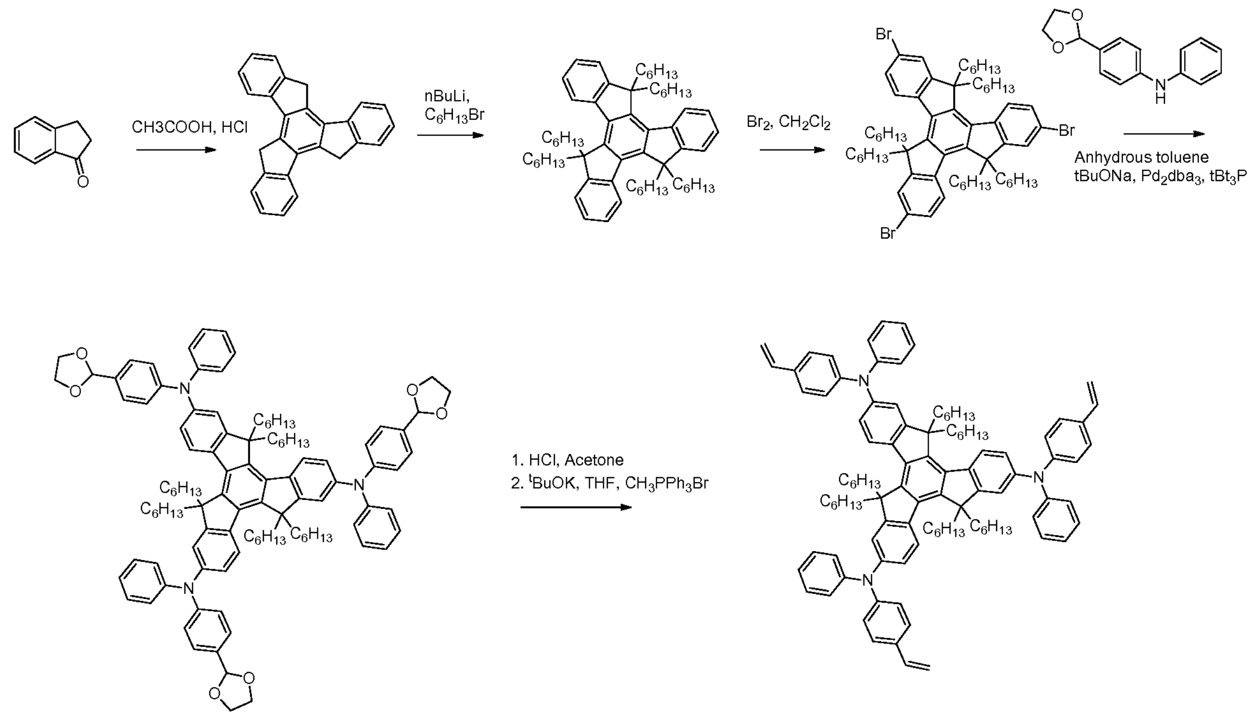


[0060] In one embodiment of PLX-8 according to formula (XV), wherein X^{11} is S and each of R^{29} is hydrogen, the hole transporting compound can be synthesized, for example, as follows.


B(OH)2
Br
Suzuki
NBS
1. K3PO4
Pd(dba)3,
P(tBu)3
DDQ, BF3, CH2Cl2
Br2



[0061] In another embodiment of PLX-8 according to formula (XV), wherein X^{11} is CR_2 and each of R^{29} is hydrogen, the hole transporting compound can be synthesized, for example, as follows.



MOLECULAR WEIGHT

[0062] In addition, the molecular weight (g/mol) for the hole transport compound can be adapted for an application. The molecular weight can be, for example, about 5,000 g/mol or less, or about 4,000 g/mol or less, or about 3,000 g/mol or less, or about 2,000 g/mol or less, or about 1,000 g/mol or less. In one embodiment, the compound's molecular weight is about 400 g/mol to about 5,000 g/mol, or about 400 g/mol to about 2,000 g/mol. In one embodiment, the compound's molecular weight is about 2,000 g/mol to about 5,000 g/mol. The molecular weight can be greater than, for example, about 250 g/mol, or greater than about 400 g/mol.

EXCLUSION OF POLYMER BEFORE CROSSLINKING

[0063] In one embodiment, the composition described here can be free or substantially free of polymeric materials before crosslinking. For example, the composition can be free or substantially free of materials having a molecular weight of more than 5,000 g/mole or more, or free of materials having a molecular weight of more than 10,000 g/mol. The composition, before crosslinking, can comprise only materials having lower molecular weights such as below 5,000 g/mol, or below 2,000 g/mole, or below 1,000 g/mol. The amount of polymer can be less than 1 wt.%, or less than 0.1 wt.%, or less than 0.01 wt.%, for example.

INKS AND SOLVENT SYSTEM

[0064] The compositions described herein can be used in solid or can be formulated into liquid form as inks. Hence, in one embodiment, the composition further comprises a solvent system to form an ink. Solvent systems are known. See, for example, WO 2010/093592 (Cheon et al.).

[0065] The solid content of the ink can be adapted for a particular application. In one embodiment, the composition further comprises a solvent system to form an ink, wherein the solid content of the ink is at least 0.1 w/w% of solvent, or at least 0.3 w/w% of the solvent, or at least 1 w/w% of solvent.

[0066] The solvent system can comprise one solvent, two solvents, or three or more solvents (e.g., solvent blends can be used). Organic solvents can be used. In one embodiment, the solvent system comprises toluene as solvent.

[0067] Solvents can include aromatic hydrocarbons in the neutral and oxidized forms. Solvents such as tetrahydrofuran, chloroform, or aromatic hydrocarbons in the neutral and oxidized forms can be used. Additional solvents include tetrahydrofuran, chloroform, alkylated benzenes, halogenated benzenes, NMP, DMF, DMAc, DMSO, methyl ethyl ketone, cyclohexanone, chloroform, dichloromethane, acetone, THF, dioxanes, ethyl acetate, ethyl benzoate, ethylene carbonate, propylene carbonate, or combinations thereof.

[0068] For environmental compliance, one or more nonhalogenated solvents may be selected. Halogenated solvents can be substantially or totally excluded (e.g., used in less than 10%, or less than 5%, or less than 1%, or less than 0.1% by volume of total solvent carrier). In weighing such additional factors, it may be helpful to consult references such as, for example, Cheremisnoff, N.P., Industrial Solvents Handbook, 2nd Ed. (Marcel Dekker, New York, 2003); Ash, M, Handbook of Solvents, 2nd Ed. (Syapse Information Resources, 2003); Wypych, G., Handbook of Solvents (Chemical) (Noyes Publications, 2000); Hansen, C.M., Durkee, J. and Kontogeorgis, G, Hanson Solubility Parameters: A User's Handbook (Taylor and Francis, 2007).

[0069] Solvents to be considered may include ethers (optionally substituted with C1-C10 alkyl chains) such as anisole, ethoxybenzene, dimethoxy benzenes and glycol ethers, such as: ethylene glycol diethers such as 1,2-dimethoxy ethane, 1,2-diethoxy ethane, 1,2-dibutoxy ethane; diethylene glycol diethers such as diethylene glycol dimethyl ether, diethylene glycol diethyl ether; propylene glycol diethers such as propylene glycol dimethyl ether, propylene glycol diethyl ether, propylene glycol dibutyl ether; dipropylene glycol diethers such as dipropylene glycol dimethyl ether, dipropylene glycol diethyl ether, dipropylene glycol dibutyl ether; also, higher analogs (tri- and tetra-) of the ethylene glycol and propylene glycol ethers mentioned above.

[0070] Still other solvents can be considered, such as ethylene glycol monoether acetates and propylene glycol monoether acetates, wherein the ether can be selected, for example, from: methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, tert-butyl, cyclohexyl. Also, higher glycol ether analogs of above list such as di-, tri- and tetra-. Examples include, but are not limited to, propylene glycol methyl ether acetate, 2-ethoxyethyl acetate, 2-butoxyethyl acetate.

[0071] Yet other possible solvents include aliphatic and aromatic ketones such as acetonyl acetone, methyl isobutyl ketone, methyl isobutenyl ketone, 2-hexanone, 2-pentanone, acetophenone, ethyl phenyl ketone, cyclohexanone, cyclopentanone.

[0072] Additional possible solvents include N,N-dimethyl formamide, N,N-dimethyl acetamide, N-methyl pyrrolidone, dimethyl sulfoxide, tetramethylene sulfoxide, acetonitrile, benzonitrile, ethylene carbonate, propylene carbonate, and the like.

[0073] Other examples include cyclic ethers such as, for example, tetrahydropyran (THP). Solvent can be used such that polymerization of the solvent can be avoided. Another example is methoxyproprionitrile.

[0074] The one or more solvents can be used in varying proportions to improve the ink characteristics such as substrate wettability, ease of solvent removal, viscosity, surface tension, and j ettability.

[0075] Alternatively, it may be useful to select more than one solvent, for example, a first solvent and a second solvent. In one example, the solutes can have a higher solubility in the first solvent than in the second solvent. The hole transporting compound can also have a higher solubility in the second solvent than in the first solvent. The solvent can be selected such that the first solvent can be removed at a faster rate than the second solvent in a drying step.

[0076] In one embodiment, the ink composition further comprises an additive. The additive can be, for example, a shrinkage reducer, stabilizer, or activator. The additive can also be, for example, a radical scavenger, initiator, deforming agent, wetting agent, or surfactant.

REACTED AND DRIED FORM OF COMPOSITIONS

[0077] Also described herein are compositions, wherein the reactive compositions are not reacted, partially reacted or fully reacted. For example, in one embodiment, the intractable groups are polymerizable groups, and the polymerizable groups are reacted. In one embodiment, a composition is prepared by reaction of the intractability groups of the first and second compound of the compositions described herein.

[0078] The compositions can be converted into films by methods known in the art. Hence, in one embodiment, the intractable groups are polymerizable groups, and the polymerizable groups are reacted, and the composition is in the form of a thin film.

METHODS OF FORMING FILMS

[0079] Coated substrates can be formed. One or more layers of film can be added to a preexisting film or substrate. For example, another embodiment provides a method comprising: providing a substrate comprising a hole injection layer, coating the substrate with at least one ink comprising at least one hole transport material comprising intractability groups to form a coated substrate, heating the coated substrate. The hole transport material can comprise one or more of the compositions described herein.

[0080] In one embodiment, the ink is subjected to pre-crosslinking before coating the ink on the substrate. In one embodiment, the ink is subjected to thermal pre-crosslinking before coating the ink on the substrate. In one embodiment, the ink is subjected to thermal pre-crosslinking to form a gel before coating the ink on the substrate. In one embodiment, the ink is subjected to thermal pre-crosslinking at at least 150°C to form a gel before coating the ink on the substrate. In one embodiment, the ink is subjected to UV light pre-crosslinking before coating the ink on the substrate.

[0081] In one embodiment, the ink is not subjected to pre-crosslinking before coating the ink on the substrate.

[0082] In one embodiment, the coated substrate is subjected to UV light to induce pre-crosslinking before heating the coated substrate.

[0083] In one embodiment, the coated substrate is heated to at least 200°C. In one embodiment, the coated substrate is heated to at least 250°C.

[0084] The quality of the film can be examined by optical microscopy, looking for film defects, formation of aggregates and beads, dewetting of the film, and pinholes.

[0085] In one embodiment, which is comparative, after heating, the coated substrate shows films with beads formed on the top layer interspersed with the area of the lower film where the top hole transport layer film has dewetted (in the optical microscope).

[0086] In one embodiment, after heating, the coated substrate shows defect free, smooth and continuous films conforming and wetting well on the lower lying hole injection layer (in the optical microscope).

[0087] Films can be evaluated at both low and high magnifications to isolate the presence of both large and small scale defects and ensure an overall smooth continuous coating.

[0088] The film formation can be carried out by methods known in the art including drop coating, spin coating, ink jet printing, slot die coating, nozzle printing, screen printing, and the like.

CHARACTERIZING FILMS

[0089] In one embodiment, after heating the coated substrate is stable to toluene solvent wash so that retains at least 90% of the initial thickness before the wash. In one embodiment, after heating the coated substrate is stable to toluene solvent wash so that retains at least 95% of the initial thickness before the wash.

[0090] In one embodiment, after heating the coated substrate is stable to immersion in toluene for 5-10 minutes so that it retains at least 90% of the initial thickness before wash and does not show an increase in the thickness beyond 110% of the initial thickness.

[0091] In one embodiment, after heating the coated substrate is stable to immersion in toluene for 5-10 minutes so that it retains at least 95% of the initial thickness before wash and does not show an increase in the thickness beyond 105% of the initial thickness.

[0092] The film quality (smoothness) can be evaluated by atomic force microscopy, and films can show an rms roughness of 5 nm or below. The AFM micrographs can help to ensure good film quality at the nanoscale and also helps in understanding film morphology and its effect on device performance.

[0093] On the films deposited on the substrates, other measurements can be performed such as AC2 can be used to measure the HOMO energy of films . Absorption measurements (UV-VIS) can be done to calculate the bandgap of the hole transport material. The LUMO can be estimated by subtracting the band gap from the HOMO. Also photoluminescence measurements can be done on the hole transport films to study their emission characteristics.

[0094] In one embodiment, the coating of the coated substrate shows a Tg of less than 200°C, or less than 150°C.

SUBSTRATE AND HOLE INJECTION LAYER

[0095] Solution processing for OLED fabrication is known in the art. Orthogonal solubility principles can be used. In particular, the hole transport compounds and formulations can be applied on top of a hole injection layer (HIL) material or film. The hole injection layers can be materials soluble in water or organic solvents. Solution process can provide depositing materials from a liquid medium, including solutions, dispersions, emulsions, or other forms.

[0096] In one embodiment, the hole injection layer is an aqueous hole injection layer. For example, the HIL layer material can be soluble in water.

[0097] In one embodiment, the hole injection layer is a non-aqueous hole injection layer. For example, the HIL layer material can be soluble in organic solvent.

[0098] In one embodiment, the hole injection layer comprises a polymer. In one embodiment, the hole injection layer comprises a conjugated polymer. In one embodiment, the hole injection layer comprises a polythiophene. In one embodiment, the hole injection layer comprises a polythiophene comprising at least one alkoxy substituent. In one embodiment, the hole injection layer comprises a sulfonated polythiophene. In one embodiment, the hole injection layer comprises a polymeric arylamine. In one embodiment, the hole injection layer comprises a regioregular polythiophene. In one embodiment, the hole injection layer comprises a conjugated polymer which is soluble in water. In one embodiment, the hole injection layer comprises a conjugated polymer which is soluble in organic solvent.

[0099] For example, hole injection layers are described in the following US Patent Publications (assignee: Plextronics): 2006/0078761; 2008/0248313; 2009/0256117; 2009/0230361; 2010/0108954; 20100292399; 2010/0072462; 2010/0109000; 2011/0147725.

[0100] Examples of aqueous hole injection layers are described in 2008/0248313 (Seshadri et al.)

[0101] Examples of non-aqueous hole injection layers are described in 2006/0078761 and 2009/0256117 (Seshadri et al.). For example, the HIL can be based on a 3,4-disubstituted polythiophene including a poly(3,4-dialkoxythiophene).

[0102] OLED devices are also fabricated with emitting layers and other layers known in the art of OLED devices. In one embodiment, the method further comprises the step of coating an emitting layer on the coated substrate.

[0103] In one embodiment, the ink comprises at least two hole transport materials comprising intractability groups. In one embodiment, the ink comprises at least two hole transport materials each comprising a different intractability group. The two different intractability groups can be adapted to function together during film formation. For example, one might react at a lower temperature, and one might react at a higher temperature. In general, one tries to have all or as many as possible of the intractability groups to react.

DEVICE FABRICATION AND CHARACTERIZATION

[0104] Devices can be fabricated by methods known in the art and can be characterized by methods known in the art.

[0105] An organic light emitting diode (OLED) can comprise a series of layers including, for example,

- ITO: Transparent anode, typically
- HIL: Hole injection layer to facilitate charge injection
- HTL: Hole transport layer which carries charges
- EML: Emissive layer where light is emitted
- HBL: Hole blocking layer to prevent charge leakage
- ETL: Electron transport layer to facilitate charge injection
- Cathode

[0106] Layers can be supported by substrates including flexible, or rigid, or organic, or inorganic substrates.

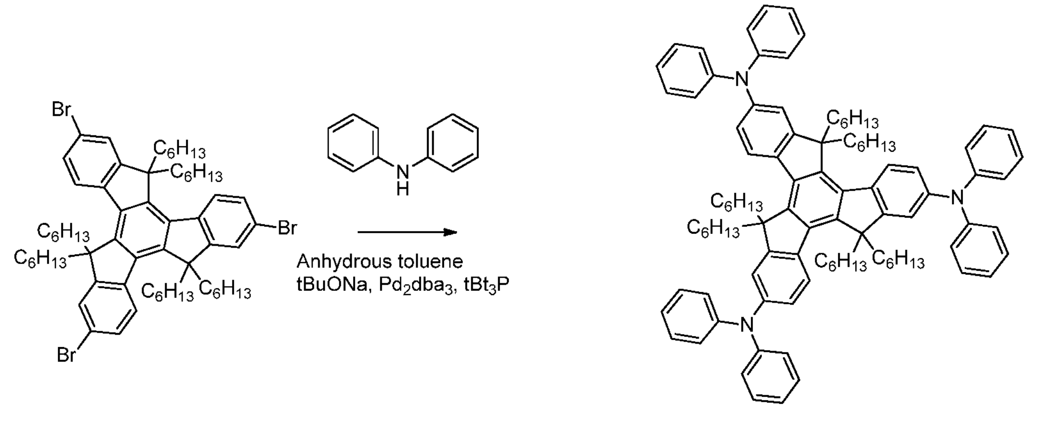
[0107] Additional examples of layers and devices, and related methods of making, testing, and using, can be found in, for example, US Patent Publication Nos. 2005/0184287; 2006/0032528; 2008/0286566; 2009/0159877; 2010/0187500; 2010/0187510; 2010/0207109; 2010/0213446; 2010/0244665; WO 07076146; WO 07079103; WO 07120143; WO 07145979; WO 08024378; WO 08024379; WO 08024380; WO 08106210; WO 08150872; WO 08150943; WO 09018009; WO 09052085; WO 09055532; WO 09067419; WO 09097377; WO 09140570.

APPLICATIONS

[0108] Hole transport materials can be used in a variety of electronic devices including organic electronic devices such as ,for example, OLED, OPV, and OFET OLEDs can be used in, for example, display or lighting applications. They can be used in layers for hole injection and/or hole transport. Other applications are described in, for example, (1) Highly Efficient OLEDS with Phosphorescent Materials (Ed. H. Yerrin), 2008, Wiley-VCH, (2) Organic Light Emitting Devices: Synthesis, Properties, and Applications (Eds. Mullen, Scherf), 2006, (3) Organic Light Emitting Methods and Devices, (Li and Meng), 2007, CRC. See also Shirota et al., Chem. Rev., 2007, 107, 953-1010 for OLEDs, OPVs, OFETs, and other applications.

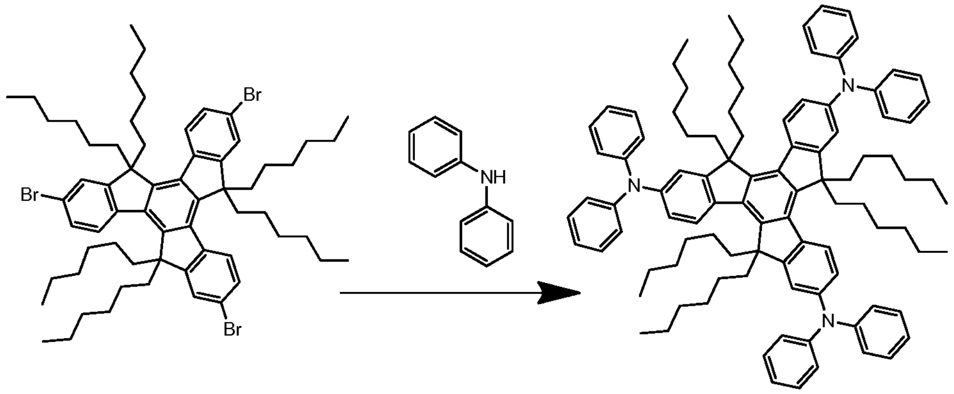
WORKING EXAMPLES

[0109] An exemplary hole transporting compound was synthesized according to the below scheme. The DSC and TGA data and UV-Vis and PL absorption spectra of the hole transporting compound are shown in Figures 1-3. The arylamine groups of this compound may be substituted with one or more intractability groups.



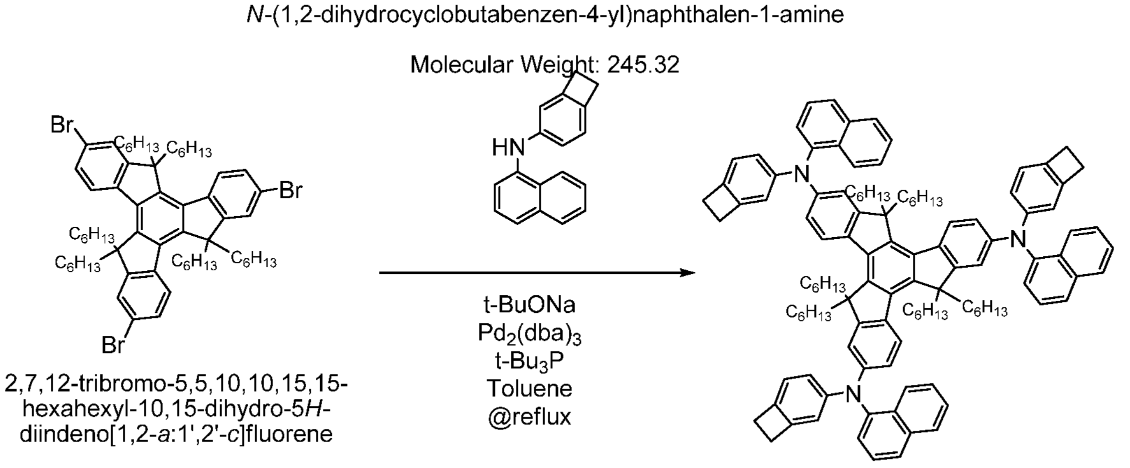
[0110] The compounds can be functionalized with intractability groups or polymerizable groups, and can also be functionalized with one or more arylamine groups. In at least some cases, compounds are designed as known in the art to have a high triplet energy. Triplet energy can be measured or calculated by methods known in the art.

PLX-8-A



[0111] Prepared clean oven dried 500mL 3 neck round bottom flask, stir bar, and matching coil condenser by cooling and purging with $N_{2(g)}$. Charged reaction vessel with 1.3g (0.0012 mol) 2,7,12-tribromo-5,5,10,10,15,15-hexahexyl-10,15-dihydro-5H-diindeno[1,2-a:l',2'-c]fluorene and .731g (0.0043 mol) diphenylamine. Dissolved reagents with ~250 mL dry Toluene via cannula. Purged mixture with $N_{2(g)}$ for 20 minutes. Weighed 0.519g (0.0054 mol) sodium *tert*-butoxide and 0.1g (~0.0001 mol) Pd_2dba_3 together in disposable vial then added quickly to reaction mixture with glass funnel. Dissolved 0.07g (~0.0003 mol) tri-*tert*-butyl phosphine in 6 mL dry Toluene and added to reaction mixture via Luer lock syringe. Heated reaction to reflux with heating mantle (~30% on variac) while stirring at 500 R.P.M. Allowed reaction to reflux for 4 hours then monitored progress of reaction with thin layer chromatography. TLC confirmed reaction completion. Heating mantle was removed and mixture was allowed to cool to room temperature. Prepared a large fritted glass filter funnel with celite, coarse silica gel (60-200 μm), and filter paper. Filtered reaction mixture through plug and washed with EtOAc until TLC showed minimal spotting. Solvents were removed via rotary evaporation. The crude was washed in methanol to remove excess diphenylamine. Ran manual column chromatography and collected similarly pure fractions. Solvents were via rotary evaporation. Pure material was redissolved in dichloromethane and precipitated in ice-cold HPLC grade methanol. Final mass of pure product was 1.38g. NMR confirmed the presence of desired product: 5,5,10,10,15,15-hexahexyl-N^2,N^2,N^7,N^7,N^{12},N^{12}-hexaphenyl-10,15-dihydro-5H-diindeno[1,2-a:1',2'-c]fluorene-2,7,12-triamine.

PLX-8-B



2,7,12-tribromo-5,5,10,10,15,15-hexahexyl-10,15-dihydro-5*H*-diindeno[1,2-*a*:1',2'-*c*]fluorene

Molecular Weight: 1084.08

N^2,*N*^{7},*N*^{12}-tris(1,2-dihydrocyclobutabenzen-4-yl)-5,5,10,10,15,15-hexahexyl-*N*^{2},*N*^{7},*N*^{12}-tri(naphthalen-1-yl)-10,15-dihydro-5*H*-diindeno[1,2-*a*:1',2'-*c*]fluorene-2,7,12-triamine

Molecular Weight: 1577.30

Procedure:

[0112] Degassed ~250mL anhydrous Toluene with $N_{2(g)}$. Prepared clean oven dried 250mL 2 neck round bottom flask, stir bar, and matching spiral condenser by cooling and purging with $N_{2(g)}$. Charged reaction vessel with 2.005g (0.00185 mol) 2,7,12-tribromo-5,5,10,10,15,15-hexahexyl-10,15-dihydro-5H-diindeno[1,2-a:1',2'-c]fluorene and 1.584g (0.00646 mol) N-(1,2-dihydrocyclobutabenzen-4-yl)naphthalen-1-amine while under inert atmosphere. Dissolved reagents with ~150 mL dry Toluene via cannula. Purged mixture with $N_{2(g)}$ for 15 minutes. Weighed 0.7995g (0.00832 mol) tBuONa, 0.1045g (0.000114 mol) $Pd_2(dba)_3$, and 0.0696 (0.000344 mol) tBu_3P in septa vial and dissolved in ~10 mL dry Toluene and added to reaction mixture via Luer lock syringe. Heated reaction to reflux with heating mantle (~30% on variac) while stirring at 360 R.P.M. Monitored progress of reaction with thin layer chromatography every hour. When TLC confirmed the reaction was complete, heating mantle was removed, and mixture was allowed to cool.

[0113] Prepared large fritted glass filter with celite, coarse silica gel (60-200 μm), and filter paper on top. Filtered reaction mixture through plug and washed with ~1.0 L EtOAc. Continued flushing with solvent until TLC of filtrate shows all of N2,N7,N12-tris(1,2-dihydrocyclobutabenzen-4-yl)-5,5,10,10,15,15-hexahexyl-N2,N7,N12-tri(naphthalen-1-yl)-10,15-dihydro-5H-diindeno[1,2-a:1',2'-c]fluorene-2,7,12-triamine is through. Removed solvents with rotary evaporator to a volume of ~20mL. Precipitated the 20mL of solution in 800 mL of stirring cold MeOH. Vacuum filtered solid with 5.0 μm Millipore filter and rinsed with ~500 mL MeOH. Ran TLC of solid vs. filtrate. Very little product is present in filtrate. TLC of solid shows some impurity not in line with starting materials. Prepared 2 inch diameter by 18 inch long 500 mL column with ~200g coarse silica gel slurry. Added crude product in a wet load with 100% hexanes and started flash chromatography column with 100% Hexanes. Eluted product with 10L of 100% Hexanes. Separation from starting material was not successful however the separation of an unknown impurity from crude was. Solvent was removed via rotary evaporation in a 2L round bottom flask to a volume small enough to transfer to a smaller tare weighed round bottom flask. Placed N2,N7,N12-tris(1,2-dihydrocyclobutabenzen-4-yl)-5,5,10,10,15,15-hexahexyl-N2,N7,N12-tri(naphthalen-1-yl)-10,15-dihydro-5H-diindeno[1,2-a:1',2'-c]fluorene-2,7,12-triamine under vacuum.
Yield of pure product =2.44g

Dehalogenations I&II

Procedure:

[0114] Prepared clean oven dried 250mL 2 neck round bottom flask, stir bar, and matching spiral condenser by cooling and purging with $N_{2(g)}$. Cannulated ~50mL THF into round bottom flask containing N2,N7,N12-tris(1,2-dihydrocyclobutabenzen-4-yl)-5,5,10,10,15,15-hexahexyl-N2,N7,N12-tri(naphthalen-1-yl)-1 0,15-dihydro-5H-diindeno[1,2-a:1 ',2'-c]fluorene-2,7,12-triamine. Solution is clear, yellow. Cannulated the solution into 250mL round bottom flask while under inert atmosphere. Repeated cannulations 2 more times to ensure all product is in solution. Added 4.0 mL Et_3N (2.902g, 0.0287mol) to reaction vessel with Luer Lock syringe. Next 1.0mL HCOOH (1.22g, 0.0265 mol) was also added to the reaction vessel with a Luer Lock syringe. Purged mixture with $N_{2(g)}$ for 15 minutes. Weighed 0.0.0790g (3.519×10^{-4} mol) $Pd(OAc)_2$ in disposable vial then added quickly to reaction mixture with glass funnel. Mixture is slightly orange in color. Dissolved 0.0964g (4.765×10^{-4} mol) tri-*tert*-butyl phosphine in 4 mL dry Toluene and added to reaction mixture via Luer lock syringe. Heated reaction to reflux with heating mantle (~20% on variac) while stirring at 400 R.P.M. After 2 hours reaction mixture had turned black. Heating mantle was removed and mixture was allowed to cool to room temperature.

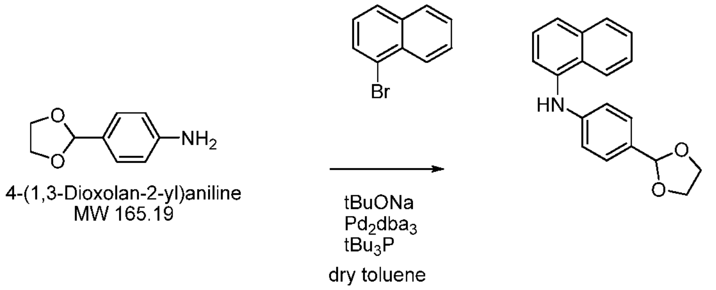
[0115] Prepared large fritted glass filter with celite, coarse silica gel (60-200 μm), and filter paper on top. Filtered reaction mixture through plug and washed with 2.0 L THF until TLC of filtrate shows all product is through. Removed solvents in round bottom flask via rotary evaporation until dry and placed under vacuum.

Purification

[0116] Added ~100mL of room temperature MeOH to the round bottom flask containing N2,N7,N12-tris(1,2-dihydrocyclobutabenzen-4-yl)-5,5,10,10,15,15-hexahexyl-N2,N7,N12-tri(naphthalen-1-yl)-10,15-dihydro-5H-diindeno[1,2-a:1',2'-c]fluorene-2,7,12-triamine and three small egg stir bars. Used a metal spatula to break large pieces of solid then began stirring. Fitted flask with rubber septum and placed contents under $N_{2(g)}$. Occasionally rinsed the sides with MeOH to remove any solid that had clung to the walls of the flask. Turned stirring to 800 r.p.m.'s and allowed to stir overnight. Vacuum filtered the cloudy grey mixture with a 5.0 μm Millipore filter. Rinsed with ~200mL MeOH. Collected solid, dissolved with THF and Hexanes, and prepared a dry load. Used enough coarse silica gel to produce a free flowing powder when dry. Prepared column with ~200 g coarse silica gel in a slurry with Hexanes. Started column with 5% EtOAc in Hexanes. Colored bands began to move quickly through the column so the polarity was reduced to 100% Hexanes. Collected and combined fractions that share similar spots on TLC. Removed solvents via rotary evaporator and placed N2,N7,N12-tris(1,2-dihydrocyclobutabenzen-4-yl)-5,5,10,10,15,15-hexahexyl-N2,N7,N12-tri(naphthalen-1-yl)-10,15-dihydro-5H-diindeno[1,2-a:1',2'-c]fluorene-2,7,12-triamine under vacuum. Performed two more precipitations in MeOH. The first used dry HPLC grade THF as the solvent to dissolve product and 400mL cold HPLC grade MeOH. The second used HPLC grade Acetone as the solvent and room temperature HPLC grade MeOH to precipitate. Both times after the precipitation the solid was vacuum filtered and washed with ~500 mL room temperature MeOH. The final product was collected and placed under vacuum.

[0117] Final mass of product after purification = 1.79g

PLX-8-C



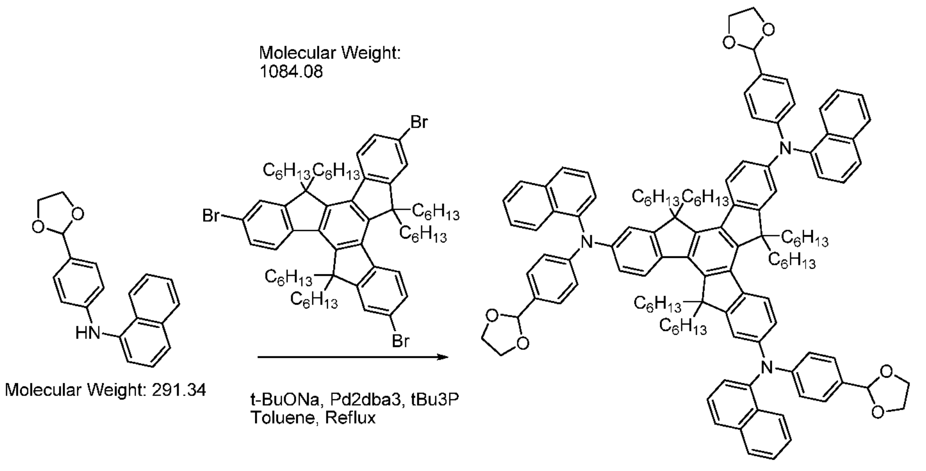
Procedure:

[0118] Prepared clean oven dried 1000mL 2 neck round bottom flask, stir bar, and matching spiral condenser by cooling and purging with $N_{2(g)}$. Charged reaction vessel with 10.141g (0.0490 mol, 6.852 mL) 1-bromonaphthalene and 9.573g (0.0588 mol) 4-(1.3-Dioxolan-2-yl)aniline while under inert atmosphere. Dissolved reagents with ~500 mL dry Toluene via cannula. Purged mixture with $N_{2(g)}$ for 15 minutes. Weighed 6.942g (0.0735 mol) sodium *tert*-butoxide and 0.897g (0.0010 mol) $Pd_2(dba)_3$ together in disposable vial then added quickly to reaction mixture with glass funnel. Mixture is dark purple. Dissolved 0.596g (0.0029 mol) tri-*tert*-butyl phosphine in 4 mL dry Toluene and added to reaction mixture via Luer lock syringe. Heated reaction to reflux with heating mantle (~30% on variac) while stirring at 500 R.P.M. Allowed reaction to reflux overnight then monitored progress of reaction with thin layer chromatography the next morning. TLC confirmed reaction is complete. Heating mantle was removed and mixture was allowed to cool to room temperature.

[0119] Prepared large fritted glass filter with celite, coarse silica gel (60-200 μm), and filter paper on top. Treated plug with 1% triethylamine (Et_3N) in 99% ethyl acetate (EtOAc). Filtered reaction mixture through plug and washed with (~3.0 L) 1% Et_3N/99% EtOAc until TLC of filtrate shows all product is through. Removed most solvents with rotary evaporator and added enough silica gel treated with ~5 mL Et_3N to prepare a dry load for column chromatography.

[0120] Prepared 500 mL 18 inch column with ~200g coarse silica gel slurry treated with Et_3N. Added crude product in a dry load and started flash chromatography column with 99% Hexanes/1%Et_3N. Increased polarity by 2.5% with EtOAc until a polarity of 10% was reached. After 12 fractions (250 mL each) product began to elute. Several impure product fractions were collected and set aside. Ten pure product fractions total were collected and solvent was removed via rotary evaporation in a round bottom flask. Fitted flask with rubber septum and placed N-(4-(1,3-dioxolan-2-yl)phenyl)naphthalen-1-amine under vacuum. Final mass of pure product =7.380g.

Amination Reaction



Procedure:

[0121] Prepared clean oven dried 1000mL 2 neck round bottom flask, stir bar, and matching spiral condenser by cooling and purging with $N_{2(g)}$. Charged reaction vessel with 7.596g (0.0070 mol) 2,7,12-tribromo-5,5,10,10,15,15-hexahexyl-10,15-dihydro-5H-diindeno[1,2-a:1',2'-c]fluorene and 7.349g (0.0252 mol) N-(4-(1,3-dioxolan-2-yl)phenyl)naphthalen-1-amine. Dissolved reagents with ~500 mL dry Toluene via cannula. Purged mixture with $N_{2(g)}$ for 15 minutes. Weighed 3.030 (0.0315 mol) sodium *tert*-butoxide and 0.385g (0.0004 mol) Pd_2dba_3 together in disposable vial then added quickly to reaction mixture with glass funnel. Mixture is dark purple. Dissolved 0.255g (0.0013 mol) tri-*tert*-butyl phosphine in 6 mL dry Toluene and added to reaction mixture via Luer lock syringe. Heated reaction to reflux with heating mantle (~30% on variac) while stirring at 500 R.P.M. Allowed reaction to reflux for 4 hours then monitored progress of reaction with thin layer chromatography. TLC confirmed reaction is complete. Heating mantle was removed and mixture was allowed to cool to room temperature.

[0122] Prepared large fritted glass filter funnel with celite, coarse silica gel (60-200 μm), and filter paper. Treated plug with 1% triethylamine (Et_3N) in ethyl acetate (EtOAc). Filtered reaction mixture through plug and washed with (~3.0 L) 1% Et_3N/99% EtOAc until TLC shows all product is through. Removed solvents via rotary evaporation.The crude product was dissolved in 50 mL EtOAc and added slowly drop wise to a stirring flask of ~500 mL room temperature MeOH. Vacuum filtered the mixture using a 5.0 μm Millipore filter paper. Prepared 4 inch diameter by 12 inch long 2000 mL column with ~400g coarse silica gel slurry treated with 2%Et_3N/98% Hexanes. Started flash chromatography column with 99% Hexanes/1%Et_3N and increased polarity by 2.5% with EtOAc until a polarity of 10% was reached. Ran TLC on each fraction and combined fractions with similar spots. Removed solvents in round bottom flask via rotary evaporation and placed under vacuum.
Final mass of pure product = 9.078g

Dehalogenation I& II

Procedure:

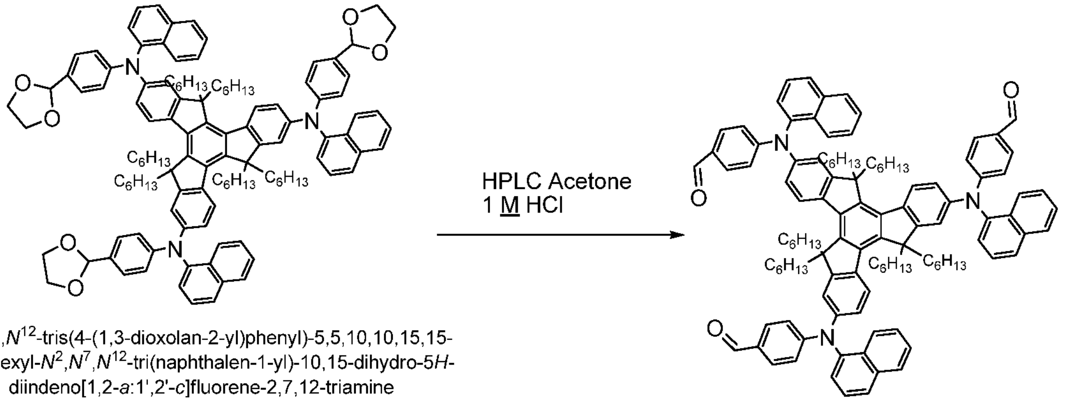
[0123] Prepared clean oven dried 1000mL 2 neck round bottom flask, stir bar, and matching spiral condenser by cooling and purging with $N_{2(g)}$. Cannulated ~100mL THF into round bottom flask containing N2,N7,N12-tris(4-(1,3-dioxolan-2-yl)phenyl)-5,5,10,10,15,15-hexahexyl-N2,N7,N12-tri(naphthalen-1-yl)-10,15-dihydro-5H-diindeno[1,2-a:1',2'-c]fluorene-2, 7,12-triamine. Solution is clear, yellow. Cannulated THF solution into 1000mL round bottom flask while under inert atmosphere. Repeated cannulations 2 more times to ensure all solution was transferred. Added 10.183g

Et_3N (13.3mL, 0.0953mol) to reaction vessel with 24.0 mL Luer Lock syringe. Next 3.66g HCOOH (3.0mL, 0.0794 mol) was added to the reaction vessel with a 5.0 mL Luer Lock syringe. Purged mixture with $N_{2(g)}$ for 15 minutes. Weighed 0.1859g ($7.938x10^{-4}$ mol) $Pd(OAc)_2$ in disposable vial then added quickly to reaction mixture with glass funnel. Mixture is slightly orange in color. Dissolved 0.2418g ($1.191x10^{-3}$ mol) tri-*tert*-butyl phosphine in 4 mL dry Toluene and added to reaction mixture via Luer lock syringe. Heated reaction to reflux with heating mantle (~20% on variac) while stirring at 500 R.P.M. After 2 hours reaction mixture had turned dark purple. Heating mantle was removed and mixture was allowed to cool to room temperature.Prepared large fritted glass filter with celite, coarse silica gel (60-200 μm), and filter paper on top. Treated plug with 1% triethylamine (Et_3N) in 99% ethyl acetate (EtOAc). Filtered reaction mixture through plug and washed with (~3.0 L) 1% Et_3N/99% EtOAc until TLC of filtrate shows all product is through. Removed solvents in round bottom flask via rotary evaporation until dry and placed under vacuum.

*Repeated twice

Final mass of product after 2nd dehalogenation = 9.50g

Deprotection



N^2,N^7,N^{12}-tris(4-(1,3-dioxolan-2-yl)phenyl)-5,5,10,10,15,15-hexahexyl-N^2,N^7,N^{12}-tri(naphthalen-1-yl)-10,15-dihydro-5*H*-diindeno[1,2-*a*:1',2'-*c*]fluorene-2,7,12-triamine

4,4',4''-(5,5,10,10,15,15-hexahexyl-10,15-dihydro-5*H*-diindeno[1,2-*a*:1',2'-*c*]fluorene-2,7,12-triyl)tris(naphthalen-1-ylazanediyl)tribenzaldehyde

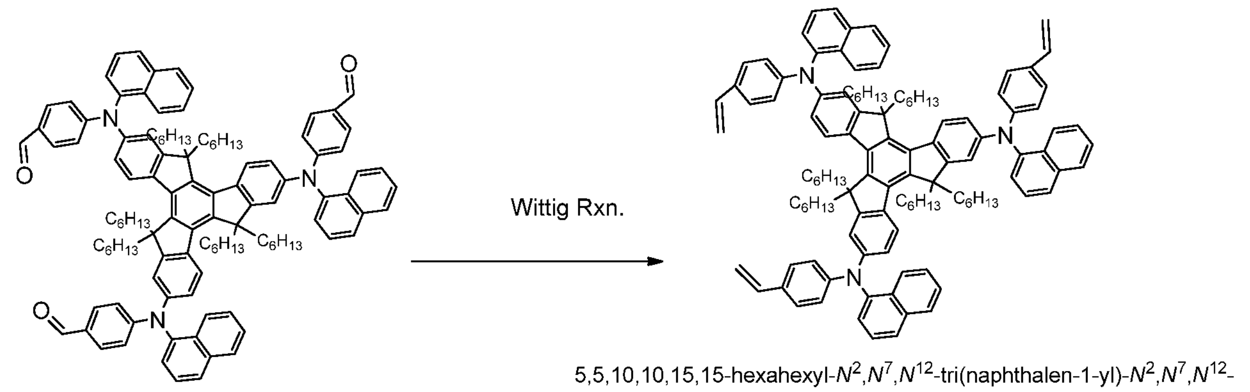
Procedure:

[0124] Prepared clean oven dried 1000 mL 2 neck (24/40) round bottom flask and magnetic stir bar by cooling and purging with $N_{2(g)}$. Dissolved N2,N7,N12-tris(4-(1,3-dioxolan-2-yl)phenyl)-5,5,10,10,15,15-hexahexyl-N2,N7,N12-tri(naphthalen-1-yl)-10,15-dihydro-5H-diindeno[1,2-a:1',2'-c]fluorene-2,7,12-triamine in 500 mL HPLC grad Acetone. Solution is clear reddish purple. Slowly added 4 mL 1 M_HCl with Luer Lock syring over the course of 5 minutes. Let solution stir. After 30 minutes TLC was run to check if the reaction had gone to completion. Reaction complete after 40 minutes. Removed solvents completely with rotary evaporator. Prepared clean dry separatory funnel. Dissolved 4,4',4''-(5,5,10,10,15,15-hexahexyl-10,15-dihydro-5H-diindeno[1,2-a:1',2'-c]fluorene-2,7,12-triyl)tris(naphthalen-1-ylazanediyl)tribenzaldehyde in EtOAc. Solution is clear purple. Added the solution to a separatory funnel. Added 300 mL D.I. water, capped, inverted 3 times, burped and let mixture settle. An emulsion formed but was easily treated with 20 mL saturated NaCl solution. Separated aqueous layer and pH=3. Repeated washes 2 more times until pH= ~6. Placed organic layer in clean 1000 mL Erlenmeyer with magnetic stir bar and added $MgSO_4$ (anhydrous) until clumps of the hydrated salt no longer formed. Stirred for 5 minutes. Gravity filtered the mixture into a clean 2000 mL round bottom flask using a ground glass funnel (24/40) and fluted filter paper. Rinsed with 500 mL EtOAc. Evaporated solvents to a volume of ~200 mL via rotary evaporator then completed removal of solvents in a clean dry 500 mL round bottom flask.

[0125] Prepared 2 inch diameter by 12 inch long 500 mL chromatography column with ~80 g coarse silica gel and wrapped in aluminum foil. Prepared dry load with product dissolved in $CHCl_3$ and enough silica gel to create a free flowing powder when dry. Started column at 10% $CHCl_3$ and increased concentration by 2.5% until a concentration of 20% was reached. Once 20% was reached the concentration of $CHCl_3$ was increased by 5% until a final concentration of 40%. Monitored fractions with TLC combined like spots discarding those not containing product. The product fractions were combined in a 2 L round bottom flask for rotary evaporation and covered with aluminum foil during evaporation. Removed enough solvent to transfer into a smaller round bottom flask then finished removing solvent. Placed 4,4',4''-(5,5,10,10,15,15-hexahexyl-10,15-dihydro-5H-diindeno[1,2-a:1',2'-c]fluorene-2,7,12-triyl)tris(naphthalen-1-ylazanediyl)tribenzaldehyde under vacuum and covered in aluminum foil.

Final mass of purified product = 7.730g

Wittig Reaction



4,4',4''-(5,5,10,10,15,15-hexahexyl-10,15-dihydro-5*H*-diindeno[1,2-*a*:1',2'-*c*]fluorene-2,7,12-triyl)tris(naphthalen-1-ylazanediyl)tribenzaldehyde

5,5,10,10,15,15-hexahexyl-N^2,N^7,N^{12}-tri(naphthalen-1-yl)-N^2,N^7,N^{12}-tris(4-vinylphenyl)-10,15-dihydro-5*H*-diindeno[1,2-*a*:1',2'-*c*]fluorene-2,7,12-triamine

Synthesis of 5,5,10,10,15,15-hexahexyl-N2,N7,N12-tri(naphthalen-1-yl)-N2,N7,N12-tris(4-vinylphenyl)-10,15-dihydro-5H-diindeno[1,2-a:l',2'-c]fluorene-2,7,12-triamine

[0126] Prepared clean oven dried 1000 mL 3 neck(24/40) round bottom flask with stir bar and 100 mL addition funnel by cooling/purging with $N_{2(g)}$. Purged an open 1.0 L bottle of dry THF with $N_{2(g)}$ for 15 minutes. Added 7.7727g (0.0220 mol) triphenylmethylbromide and 2.6029g (0.0227mol) to the round bottom flask while under an inert atmosphere. Cannulated ~400 mL THF into the round bottom flask and began stirring. Wrapped the 1000 mL flask with aluminum foil. Cannulated ~100 mL THF into a flask containing 4,4',4''-(5,5,10,10,15,15-hexahexyl-10,15-dihydro-5H-diindeno[1,2-a:1',2'-c]fluorene-2,7,12-triyl)tris(naphthalen-1-ylazanediyl)tribenzaldehyde. Once solid was completely in solution it was cannulated into the addition funnel. Began the addition of the solution at a rate of ~3drops/sec. After 2.5 hours the addition is complete the mixture is cloudy and orange. Ran TLC to ensure the reaction went to completion.

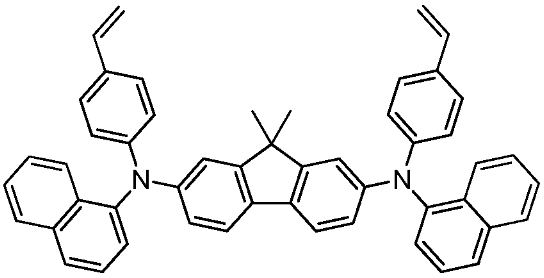
[0127] Prepared fritted glass filter funnel with celite, coarse silica gel, and a filter paper on top. Filtered the reaction mixture through the plug and flushed with ~2 L EtOAc. Filtrate is clear, orange. Rotovapped to dryness and placed under vacuum. Prepared a dry load for column chromatography by dissolving 5,5,10,10,15,15-hexahexyl-N2,N7,N12-tri(naphthalen-1-yl)-N2,N7,N12-tris(4-vinylphenyl)-10,15-dihydro-5H-diindeno[1,2-a:1',2'-c]fluorene-2,7,12-triamine in EtOAc and adding enough silica gel treated with Et_3N so when dry it forms a free flowing powder.

[0128] Prepared a 2 inch x 18 inch long 500 mL column with ~125 g coarse silica gel. One previous attempt at purification resulted in a precipitate forming in the solvent head above the dry load making it impossible to run a flash column. Cold hexane was found to help stop this from happening. ~250 mL cold hexane was flushed through the column prior to adding the dry load. Another 250 mL was poured into the column and the dry load was immediately added. Started with 100% hexane and TLC shows product immediately began to elute from the column. TLC pure product completely removed with 100% hexane with no need to increase polarity. Rotovapped pure product fractions to dryness and placed under vacuum. Dissolved product in the minimum amount of HPLC grade EtOAc. Allowed ~800 mL HPLC grade MeOH in an Erlenmeyer flask to cool in an ice bath while stirring at ~500 r.p.m. Slowly added the EtOAc/product solution to the cold MeOH with a Luer lock syringe fitted with a 22 gauge needle. An off white precipitate immediately formed. Once all the solution was precipitated, the mixture was vacuum filtered using a 5.0 μm Millipore filter. A TLC of solid vs. filtrate was run to verify the solid was indeed the desired product. The solid was collected and allowed to dry under vacuum. Final mass of pure product = 4.40g

[0129] Mobility values were measured relative to a control as shown in below Table 2. The control composition and other compositions included use of compounds represented below as compound K and compound O.

[0130] The hole-only device comprises the following device stack: from the ITO surface, ca. 50 nm layer of hole-injection layer Plexcore OC polythiophene polymer was deposited by spin-casting, 150 nm of HTL layer (having composition shown in Table 2) deposited by spin-casting, a 5nm layer of MoOx and a 100 nm layer of aluminum deposited by thermal evaporation as cathode.

Compound K:



Compound O:

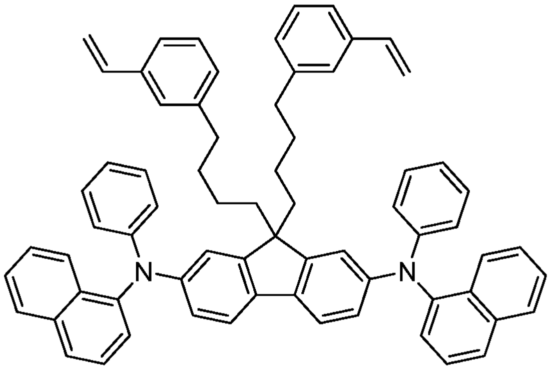
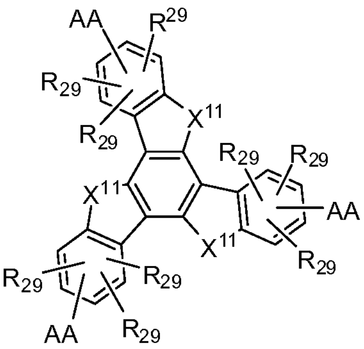


Table 2

Note that reverse bias measurement may provide a better indicator of mobility due to reduced injection barrier from the Mox side of the device compared to the HIL side of the device.							
						HOD reverse bias @ 3E7 V/m ratio of mobility versus control	***Forward bias voltage @ 10mA/cm 2 Ratio of mobility vs control***
						Ratio to Control	**Ratio to Control**
Component 1	***1 (wt.%)***	***Component 2***	***2 (wt.%)***	***Component 3***	***Composition 3***		
(control)O	***(control) 50***	***(control) K***	***(control) 50***			**1.00**	**1.00**
PLX-8-A	**100**					**46.26**	**0.30**
PLX-8-C	**50**	**O**	**50**			**5.52**	**1.23**
PLX-8-C	**100**					**0.86**	**1.11**
PLX-8-B	**100**					**1.84**	**0.74**
PLX-8-B	**50**	**Selkie**	**50**			**0.25**	**2.33**

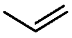
Claims

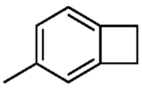
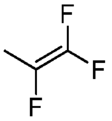
1. A composition comprising at least one hole transporting compound, said hole transporting compound comprising a hole transporting core covalently bonded to three arylamine (AA) groups, each AA group is optionally substituted with one or more intractability groups, wherein the hole transporting compound is represented by:

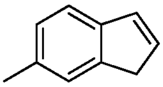
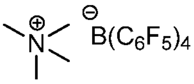


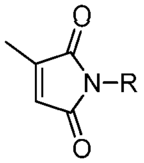
(viii-A) ,

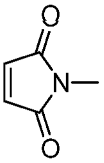
wherein each of X^{11} is S or CR_2, wherein each R is an optionally substituted alkyl, aryl, heteroalkyl, heteroaryl, or intractability group, and wherein each of R^{29} is H, F, or an optionally substituted alkyl, aryl, heteroalkyl, heteroaryl, or intractability group, and wherein the compound comprises at least one intractability group selected from the group consisting of

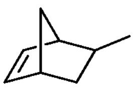
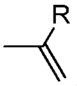
 ,





 ,


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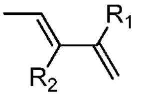

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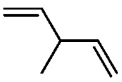
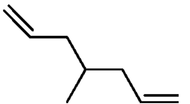
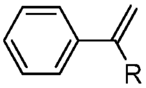
 ,
 ,


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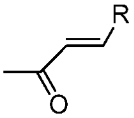

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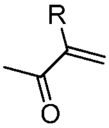

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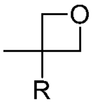

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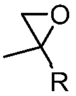

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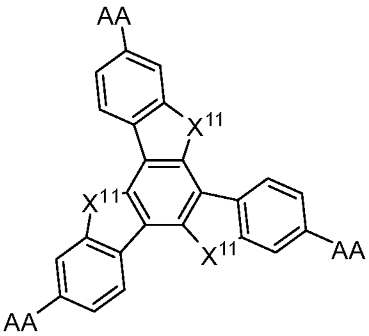
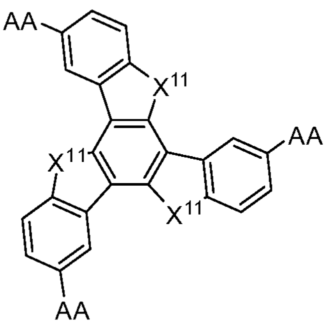
2. The composition of claim 1, wherein the hole transporting compound is represented by



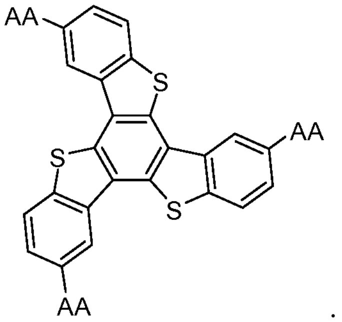
or



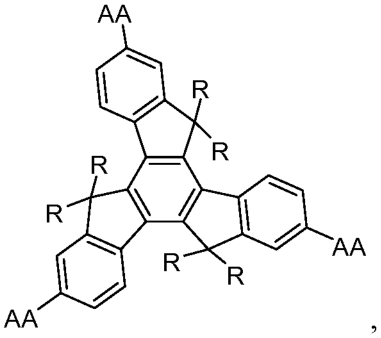
,

wherein each of X^{11} is S or CR_2, and wherein each R is an optionally substituted alkyl, aryl, heteroalkyl, heteroaryl, or intractability group.

3. The composition of any of claims 1-2, wherein the hole transporting compound is represented by



4. The composition of any of claims 1-2, wherein the hole transporting compound is represented by

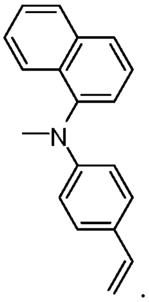


wherein each R is an optionally substituted alkyl, aryl, heteroalkyl, heteroaryl, or intractability group.

5. The composition of any of claims 1-4, wherein the arylamine (AA) group is a diarylamine or triarylamine group optionally substituted with one or more intractability groups.

6. The composition of any of claims 1-5, wherein the arylamine group is a diarylamine or triarylamine group substituted with one or more vinyl groups.

7. The composition of any of claims 1-6, wherein the arylamine group is



8. The composition of any of claims 1-7, wherein the hole transporting compound comprises at least two intractability groups.

9. The composition of any of claims 1-8, wherein the hole transporting compound comprises at least two intractability groups, wherein the intractability groups are crosslinking groups or polymerizable groups.

10. The composition of any of claims 1-8, wherein the hole transporting compound comprises at least two intractability groups, wherein the intractability groups are non-crosslinking groups.

11. A composition comprising a partially or fully reacted form of the composition of any of claims 1-10.

12. A device comprising a hole transport layer, wherein the hole transport layer comprises the composition of any of claims 1 to 11.

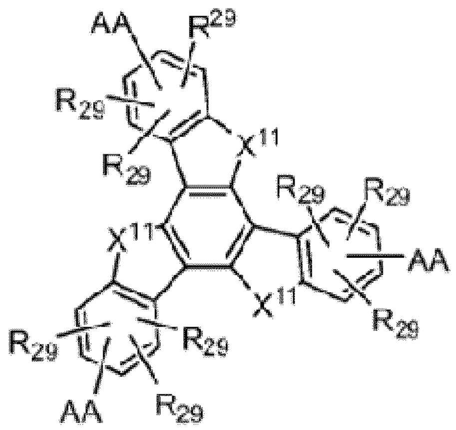
13. The device of claim 12, wherein the device is an OLED device.

14. A method comprising: providing a substrate comprising a hole injection layer, coating the substrate with at least one ink comprising the composition of claims 1-10 to form a coated substrate, and heating the coated substrate.

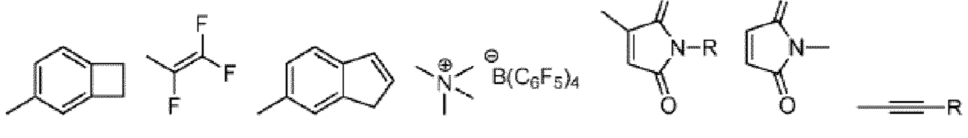
Patentansprüche

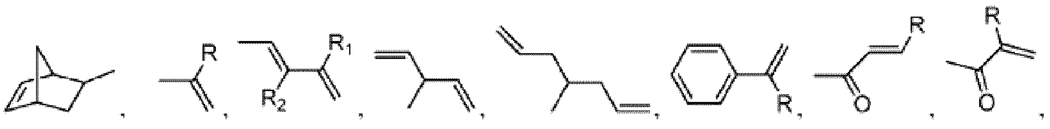
1. Zusammensetzung, umfassend mindestens eine lochtransportierende Verbindung, wobei die lochtransportierende Verbindung einen lochtransportierenden Kern umfasst, der kovalent an drei Arylamin(AA)-Gruppen gebunden ist, jede AA-Gruppe gegebenenfalls durch eine oder mehrere Intraktabilitätsgruppen substituiert ist, wobei die lochtransportierende Verbindung durch:

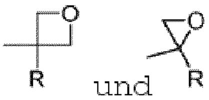
(viii-A)



wiedergegeben wird, wobei X^{11} jeweils für S oder CR_2 steht, wobei R jeweils für eine gegebenenfalls substituierte Alkyl-, Aryl-, Heteroalkyl-, Heteroaryl- oder Intraktabilitätsgruppe steht und wobei R^{29} jeweils für H, F oder eine gegebenenfalls substituierte Alkyl-, Aryl-, Heteroalkyl-, Heteroaryl- oder Intraktabilitätsgruppe steht und wobei die Verbindung mindestens eine Intraktabilitätsgruppe, die aus der Gruppe bestehend aus

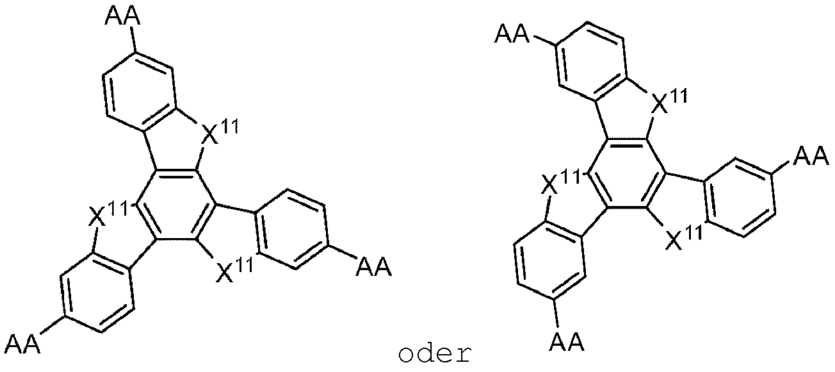






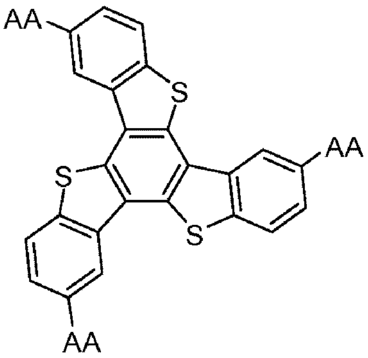
ausgewählt ist, umfasst.

2. Zusammensetzung nach Anspruch 1, wobei die lochtransportierende Verbindung durch



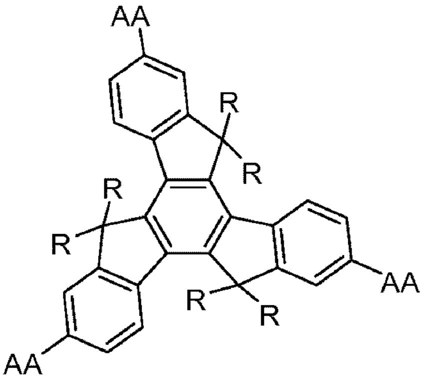
wiedergegeben wird, wobei X^{11} jeweils für S oder CR_2 steht und wobei R jeweils für eine gegebenenfalls substituierte Alkyl-, Aryl-, Heteroalkyl-, Heteroaryl- oder Intraktabilitätsgruppe steht.

3. Zusammensetzung nach einem der Ansprüche 1-2, wobei die lochtransportierende Verbindung durch



wiedergegeben wird.

4. Zusammensetzung nach einem der Ansprüche 1-2, wobei die lochtransportierende Verbindung durch

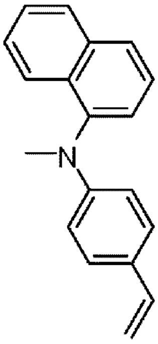


wiedergegeben wird, wobei R jeweils für eine gegebenenfalls substituierte Alkyl-, Aryl-, Heteroalkyl-, Heteroaryl- oder Intraktabilitätsgruppe steht.

5. Zusammensetzung nach einem der Ansprüche 1-4, wobei es sich bei der Arylamin(AA)-Gruppe um eine Diarylamin- oder Triarylamin-Gruppe, die gegebenenfalls durch eine oder mehrere Intraktabilitätsgruppen substituiert ist, handelt.

6. Zusammensetzung nach einem der Ansprüche 1-5, wobei es sich bei der Arylamin-Gruppe um eine Diarylamin- oder Triarylamin-Gruppe, die durch eine oder mehrere Vinylgruppen substituiert ist, handelt.

7. Zusammensetzung nach einem der Ansprüche 1-6, wobei es sich bei der Arylamingruppe um



handelt.

8. Zusammensetzung nach einem der Ansprüche 1-7, wobei die lochtransportierende Verbindung mindestens zwei Intraktabilitätsgruppen umfasst.

9. Zusammensetzung nach einem der Ansprüche 1-8, wobei die lochtransportierende Verbindung mindestens zwei Intraktabilitätsgruppen umfasst, wobei es sich bei den Intraktabilitätsgruppen um vernetzende Gruppen oder polymerisierbare Gruppen handelt.

10. Zusammensetzung nach einem der Ansprüche 1-8, wobei die lochtransportierende Verbindung mindestens zwei Intraktabilitätsgruppen umfasst, wobei es sich bei den Intraktabilitätsgruppen um nichtvernetzende Gruppen handelt.

11. Zusammensetzung, umfassend eine teilweise oder vollständig abreagierte Form der Zusammensetzung nach einem der Ansprüche 1-10.

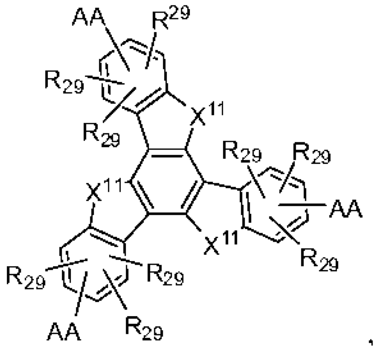
12. Vorrichtung mit einer Lochtransportschicht, wobei die Lochtransportschicht die Zusammensetzung nach einem der Ansprüche 1 bis 11 umfasst.

13. Vorrichtung nach Anspruch 12, wobei es sich bei der Vorrichtung um eine OLED-Vorrichtung handelt.

14. Verfahren, bei dem man ein Substrat mit einer Lochinjektionsschicht bereitstellt, das Substrat mit mindestens einer Tinte, die die Zusammensetzung nach den Ansprüchen 1-10 umfasst, beschichtet, wobei man ein beschichtetes Substrat erhält, und das beschichtete Substrat erhitzt.

Revendications

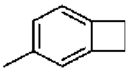
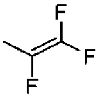
1. Composition comprenant au moins un composé transporteur de trou, ledit composé transporteur de trou comprenant un noyau transporteur de trou lié de façon covalente à trois groupes arylamine (AA), chaque groupe AA étant facultativement substitué par un ou plusieurs groupes d'intraitabilité, le composé transporteur de trou étant représenté par :

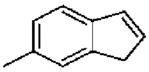
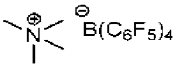


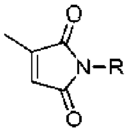
(viii-A) ,

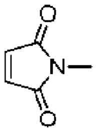
dans lequel chacun de X^{11} est S ou CR_2, où chaque R est un groupe alkyle, aryle, hétéroalkyle, hétéroaryle ou d'intraitabilité facultativement substitué, et dans lequel chaque R^{29} est H, F, ou un groupe alkyle, aryle, hétéroalkyle, hétéroaryle ou d'intraitabilité facultativement substitué, et le composé comprenant au moins un groupe d'intraitabilité choisi dans le groupe constitué de

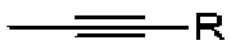
 ,







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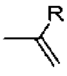
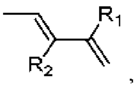
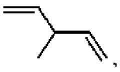
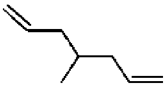
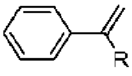
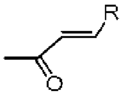
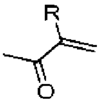
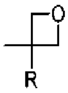
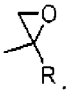
 ,

 ,

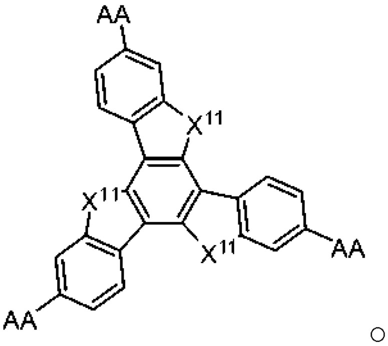
 ,
 ,
 ,

 ,

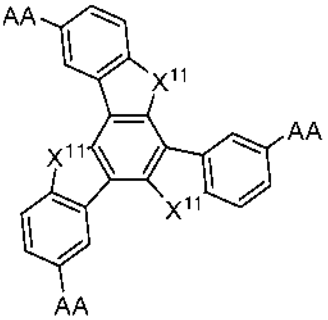
 ,

 et  .

2. Composition selon la revendication 1, dans laquelle le composé transporteur de trou est représenté par



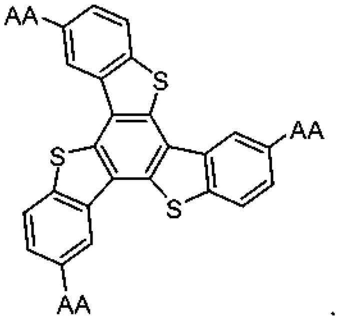
ou



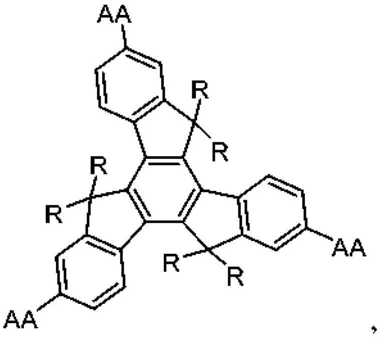
,

dans lequel chaque X^{11} est S ou CR_2, et dans lequel chaque R est un groupe alkyle, aryle, hétéroalkyle, hétéroaryle ou d'intraitabilité facultativement substitué.

3. Composition selon l'une quelconque des revendications 1 à 2, dans laquelle le composé transporteur de trou est représenté par



4. Composition selon l'une quelconque des revendications 1 à 2, dans laquelle le composé transporteur de trou est représenté par

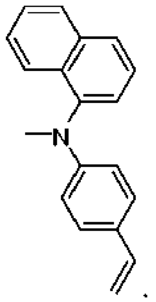


dans lequel chaque R est un groupe alkyle, aryle, hétéroalkyle, hétéroaryle ou d'intraitabilité facultativement substitué.

5. Composition selon l'une quelconque des revendications 1 à 4, dans laquelle le groupe arylamine (AA) est un groupe diarylamine ou triarylamine facultativement substitué par un ou plusieurs groupes d'intraitabilité.

6. Composition selon l'une quelconque des revendications 1 à 5, dans laquelle le groupe arylamine est un groupe diarylamine ou triarylamine substitué par un ou plusieurs groupes vinyle.

7. Composition selon l'une quelconque des revendications 1 à 6, dans laquelle le groupe arylamine est



8. Composition selon l'une quelconque des revendications 1 à 7, dans laquelle le composé transporteur de trou comprend au moins deux groupes d'intraitabilité.

9. Composition selon l'une quelconque des revendications 1 à 8, dans laquelle le composé transporteur de trou comprend au moins deux groupes d'intraitabilité, dans laquelle les groupes d'intraitabilité sont des groupes réticulables ou des groupes polymérisables.

10. Composition selon l'une quelconque des revendications 1 à 8, dans laquelle le composé transporteur de trou comprend au moins deux groupes d'intraitabilité, dans laquelle les groupes d'intraitabilité sont des groupes non

réticulables.

11. Composition comprenant une forme ayant partiellement ou complètement réagi de la composition selon l'une quelconque des revendications 1 à 10.

12. Dispositif comprenant une couche de transport de trou, dans lequel la couche de transport de trou comprend la composition selon l'une quelconque des revendications 1 à 11.

13. Dispositif selon la revendication 12, le dispositif étant un dispositif OLED.

14. Procédé comprenant : la fourniture d'un substrat comprenant une couche d'injection de trou, le revêtement du substrat avec au moins une encre comprenant la composition des revendications 1 à 10 pour former un substrat revêtu, et le chauffage du substrat revêtu.

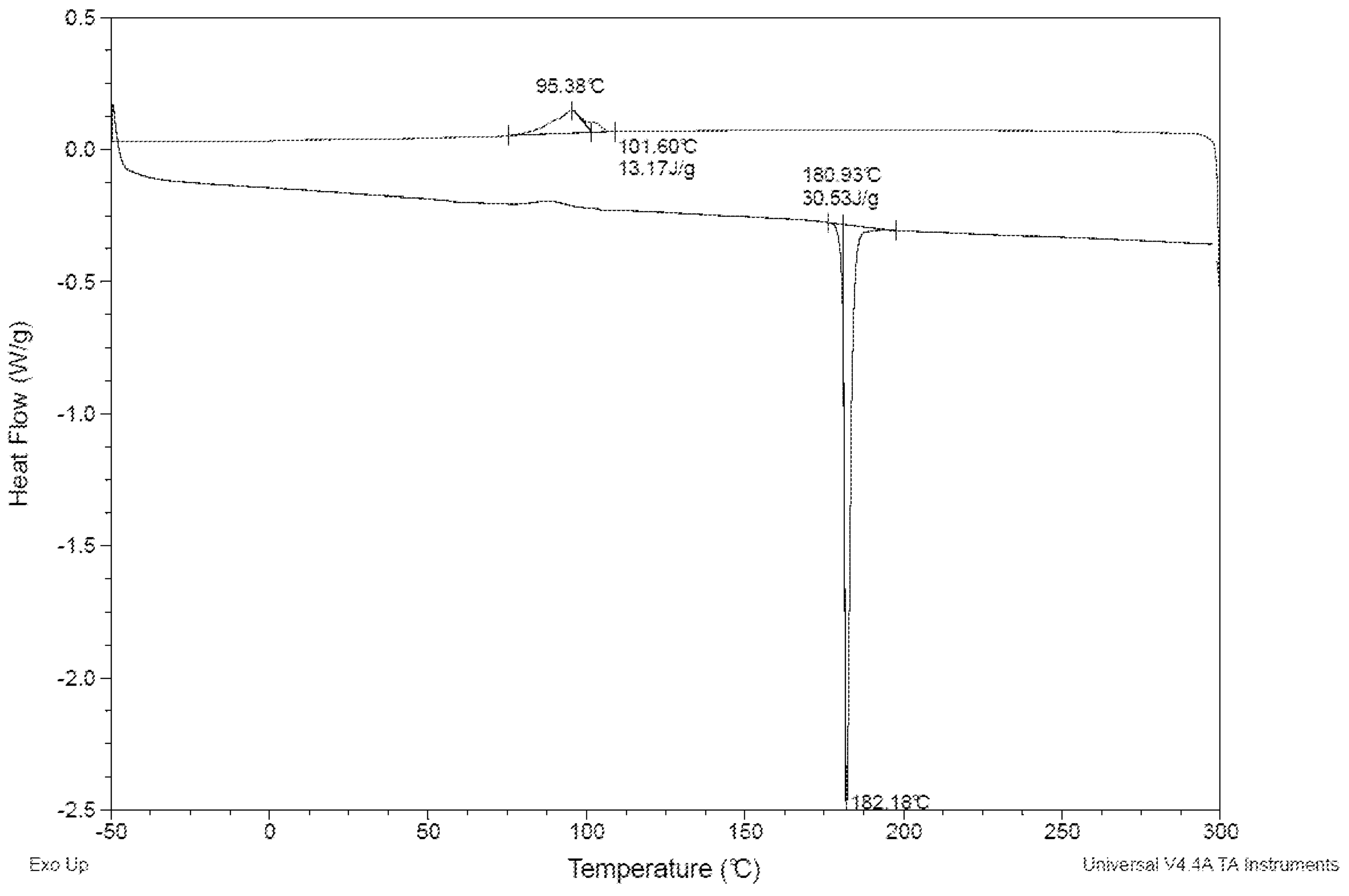

Heat Flow (W/g)
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
95.38°C
101.60°C
13.17J/g
180.93°C
30.53J/g
182.18°C
-50
0
50
100
150
200
250
300
Exo Up
Temperature (°C)
Universal V4.4A TA Instruments

FIGURE 1

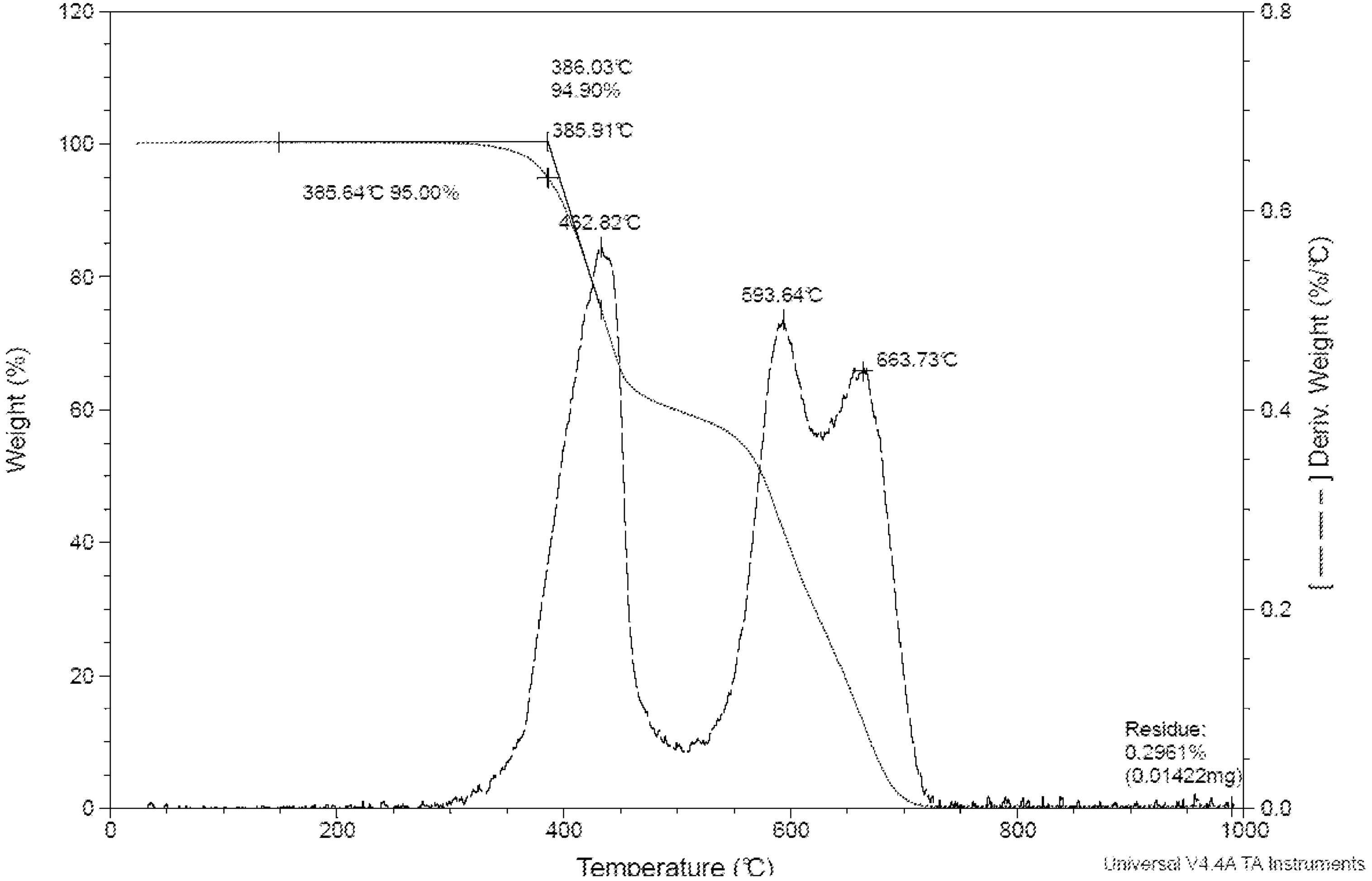
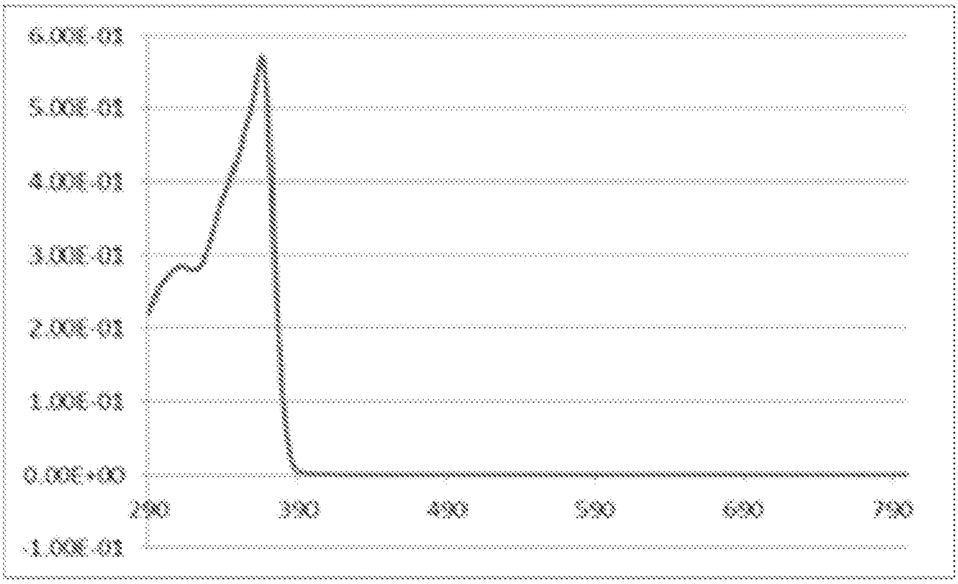
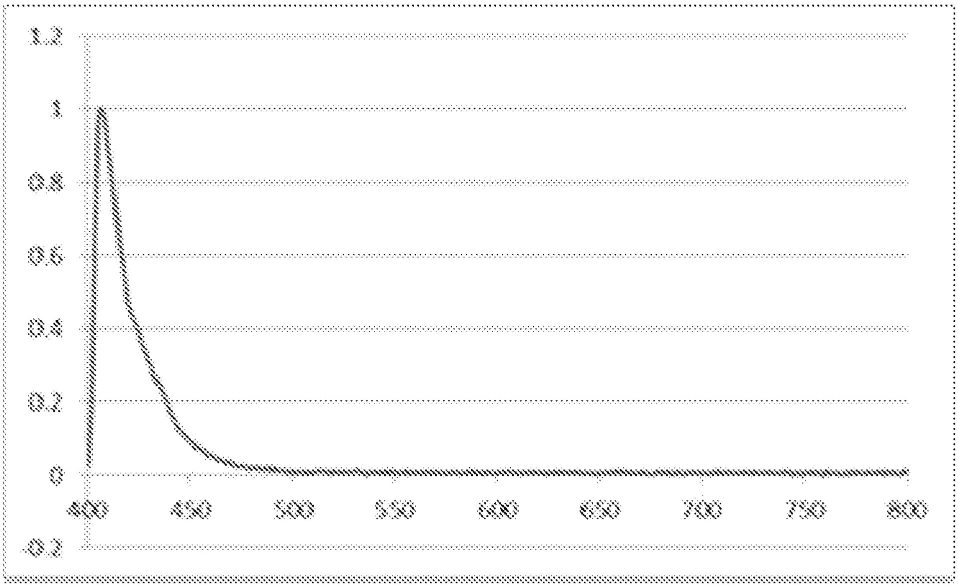

Weight (%)
120
100
80
60
40
20
0
0
200
400
600
800
1000
Temperature (℃)
[———] Deriv. Weight (%/℃)
0.8
0.6
0.4
0.2
0.0
386.03℃
94.90%
385.91℃
385.64℃ 95.00%
432.82℃
593.64℃
663.73℃
Residue:
0.2961%
(0.01422mg)
Universal V4.4A TA Instruments

FIGURE 2



UV-vis Ink – Peak 366nm



PL Ink – Peak 406nm

FIGURE 3

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- US 2006063037 A **[0013]**
- WO 2006036755 A **[0013]**
- WO 2006086480 A **[0013]**
- WO 2008073149 A **[0013]**
- WO 2009126918 A **[0013]**
- WO 2009111675 A **[0013]**
- WO 2009111339 A **[0013]**
- WO 2010051259 A **[0013]**
- WO 2010059240 A **[0013]**
- WO 2010059646 A **[0013]**
- WO 2010062558 A **[0013]**
- US 2011042861 W **[0013]**
- US 5034296 A **[0015]**
- US 5055366 A **[0015]**
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摘要(译)

本文所述的组合物包含至少一种空穴传输化合物，其中所述空穴传输化合物包含与至少两个芳基胺基团共价键合的核，其中所述芳基胺基基团任选地包含一个或多个难加工性基团。当涂覆到空穴注入层上时，该组合物可以提供良好的成膜性和稳定性。 OLED的空穴传输层的固溶处理可以通过本文所述的组合物实现。可以实现良好的移动性。