

(51) International Patent Classification:
C09K 11/06 (2006.01)(21) International Application Number:
PCT/US2010/025718(22) International Filing Date:
1 March 2010 (01.03.2010)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
12/493,781 29 June 2009 (29.06.2009) US(71) Applicant (for all designated States except US): **GENERAL ELECTRIC COMPANY** [US/US]; 1 River Road, Schenectady, NY 12345 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **CELLA, James, Anthony** [US/US]; 30 Lace Lane, Clifton Park, NY 12065 (US). **SHIANG, Joseph, John** [US/US]; 2524 Hilltop Road, Niskayuna, NY 12309 (US).(74) Agents: **DIMAURO, Peter T.** et al.; GENERAL ELECTRIC COMPANY, Global Patent Operation, 2 Corporate Drive, Suite 648, Shelton, CT 06484 (US).

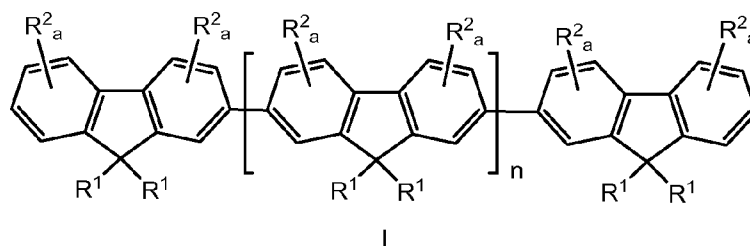
(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: FLUORENE DIMERS AND TRIMERS AND OPTOELECTRONIC DEVICES USING THE SAME

(57) Abstract: Optoelectronic devices include triplet blocking compounds of formula I wherein R^1 is, independently at each occurrence, C_{1-20} hydrocarbyl and at least one of R^1 is R^3 ; R^2 is independently at each occurrence C_{1-20} hydrocarbyl, C_{1-20} hydrocarbyloxy, C_{1-20} thioether, C_{1-20} hydrocarbylcarbonyloxy or cyano; R^3 is $-R^4XR^5$; R^4 is a direct bond, C_{1-20} aryl, C_{1-20} arylalkyl, C_{1-20} alkylaryl, C_{1-20} substituted aryl, C_{1-20} substituted arylalkyl, or C_{1-20} substituted alkylaryl; R^5 is C_{1-20} hydrocarbyl or C_{1-20} hydrocarbyl containing at least one S, N, O or P atom between carbon atoms; R^6 is C_{1-20} alkyl or C_{1-20} substituted alkyl; X is -O-, -S-, -COO-, -OOC-, -CSS-, -SSC-, NR^6 or PR^6 ; a is independently at each occurrence 0, 1 or 2; and n is 0 or 1.

FLUORENE DIMERS AND TRIMERS AND OPTOELECTRONIC DEVICES USING THE SAME

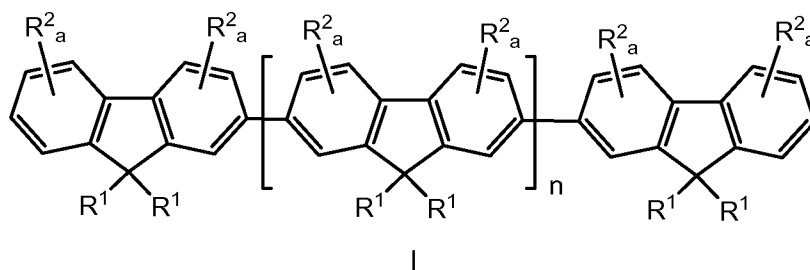
BACKGROUND

[0001] In an OLED device, electrons and holes injected from the cathode and anode respectively combine in an emissive layer producing singlet and triplet excitons that can decay radiatively producing light or non-radiatively producing heat. For most organic molecules, light emission from the triplet state is a spin-forbidden process that does not compete well with non-radiative modes of decay, so triplet excitons are not very emissive. Transition metal complexes, by virtue of spin-orbit coupling, can radiatively decay with an efficiency that competes with non-radiative pathways. When these complexes are incorporated into OLED devices it is possible to achieve nearly 100% internal quantum efficiency since both singlet and triplet excitons produced in the device can emit light.

[0002] For solution processable OLED devices the transition metal complexes are typically incorporated into polymeric hosts by blending or via covalent attachment to the polymer host. Suitable polymeric hosts for these types of devices have triplet energies higher than the emissive guest transition metal complexes to ensure favorable energy transfer. Triplet excitons generated in the host polymer migrate until they encounter an emissive guest, when energy transfer excites the guest and light emission occurs. Triplet excitons from the host can also migrate toward the anode or cathode where they may be quenched in a non-radiative fashion. It is therefore desirable to confine the triplet excitons to maximize the probability of encounter with an emissive guest and prevent migration toward the electrodes, particularly the cathode. One way to prevent exciton migration toward the cathode is to insert a blocking layer having a triplet energy that is greater than that of the host emissive layer between the cathode and the emissive layer. The blocking layer may also promote electron injection from the cathode and have good electron mobility.

BRIEF DESCRIPTION

[0003] Briefly, in one aspect, the present invention relates to optoelectronic devices, particularly OLEDs, that include triplet blocking compounds of formula I



wherein

R^1 is, independently at each occurrence, C_{1-20} hydrocarbyl and at least one of R^1 is R^3 ;

R^2 is independently at each occurrence C_{1-20} hydrocarbyl, C_{1-20} hydrocarbyloxy, C_{1-20} thioether, C_{1-20} hydrocarbylcarbonyloxy or cyano;

R^3 is $-R^4XR^5$;

R^4 is a direct bond, C_{1-20} aryl, C_{1-20} arylalkyl, C_{1-20} alkylaryl, C_{1-20} substituted aryl, C_{1-20} substituted arylalkyl, or C_{1-20} substituted alkylaryl;

R^5 is C_{1-20} hydrocarbyl or C_{1-20} hydrocarbyl containing at least one S, N, O or P atom between carbon atoms;

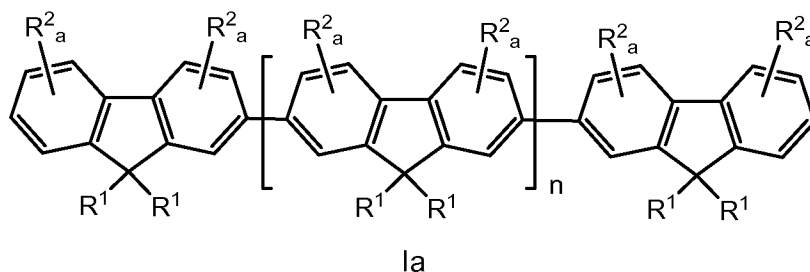
R^6 is C_{1-20} alkyl or C_{1-20} substituted alkyl;

X is $-O-$, $-S-$, $-COO-$, $-OOC-$, $-CSS-$, $-SSC-$, NR^6 or PR^6 ;

a is independently at each occurrence 0, 1 or 2; and

n is 0 or 1.

[0004] In another aspect, the present invention relates to compounds of formula Ia



R^1 is, independently at each occurrence, C_{1-20} hydrocarbyl and at least one of R^1 is R^{3a} ;

R^2 is independently at each occurrence C_{1-20} hydrocarbyl, C_{1-20} hydrocarbyloxy, C_{1-20} thioether, C_{1-20} hydrocarbylcarbonyloxy or cyano;

R^{3a} is C_{1-20} hydrocarbyl containing at least one S, N, O or P atom between carbon atoms;

a is independently at each occurrence 0, 1 or 2; and

n is 0 or 1.

DETAILED DESCRIPTION

[0005] The present invention relates to optoelectronic devices that include a series of layers: an anode, typically indium tin oxide (ITO), a hole injection layer to facilitate the injection of positive charge carriers from the ITO into the organic layers; one or more emissive layers in which electrons and holes recombine to emit light, an electron transporting and triplet blocking layer that includes compounds of formula I or Ia, and an electron injecting cathode.

[0006] Table 1 shows the ordering of energy levels as the total number of fluorene units in the oligomer is changed. Polymers comprised of oligomeric units also have comparable LUMO levels (thus promoting the injection of electrons into the emissive layer) and somewhat deeper HOMO levels, thus inhibiting holes from migrating from the emissive layer. Finally, these materials have solubility properties that enable the solution processed fabrication of a multilayer device.

Table 1 Spectroscopic data of reference 7 showing the measured evolution of triplet energies with oligomer length.

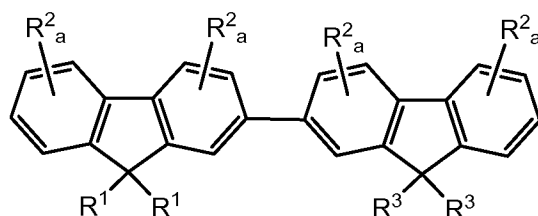
Number of fluorene units	Triplet Energy (eV)
1	2.85
3	2.25
5	2.18
7	2.16
polymer	2.11

Thus, the compounds of formula I are well suited for use as triplet blocking layers in devices in which triplet level of the emissive layer is equal to or lower than that of polyfluorene ($T_1 = 2.11$ eV).

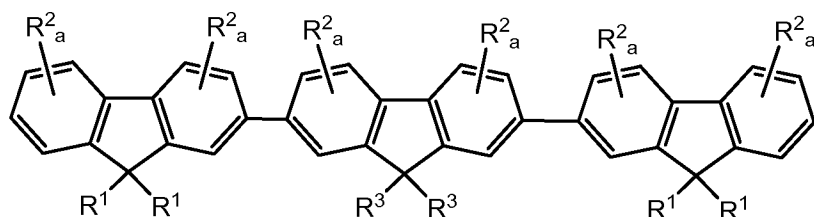
[0007] In order to satisfy the requirement that these materials promote electron injection and mobility, the optoelectronic devices of the present invention include compounds that bear polar substituents in the 9-position of the fluorene segments. Accordingly, in one aspect, the present invention relates to compounds of formula 1 that may be used as triplet blocking materials in an optoelectronic device. The polar

substituents include at least one S, N, O or P atom between carbon atoms, and may include up to about 10 S, N, O or P heteroatoms. The term “between carbon atoms” means that the heteroatom is not part of a terminal group such as hydroxyl, carbonyl, carboxyl, aldehydic (-CHO); groups that are between carbon atoms include, but are not limited to ether, thioether, ester, thioester, and amino groups. The heteroatoms may be all of one type, for example, all O atoms, or may be a mixture of some or all of S, N, O and P. In particular, the heteroatoms may be present as part of one or more ether, thioether, ester, thioester, or amino groups.

[0008] In particular embodiments, the compounds of formula I are of formula

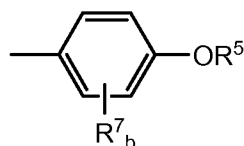


In other embodiments, the compounds of formula I are of formula



R¹ may be, independently at each occurrence, alkyl or R³.

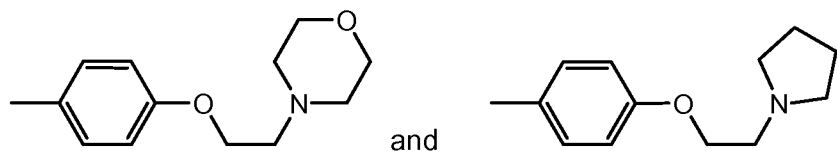
[0009] More specifically, in the compounds of formula 1, R³ may be



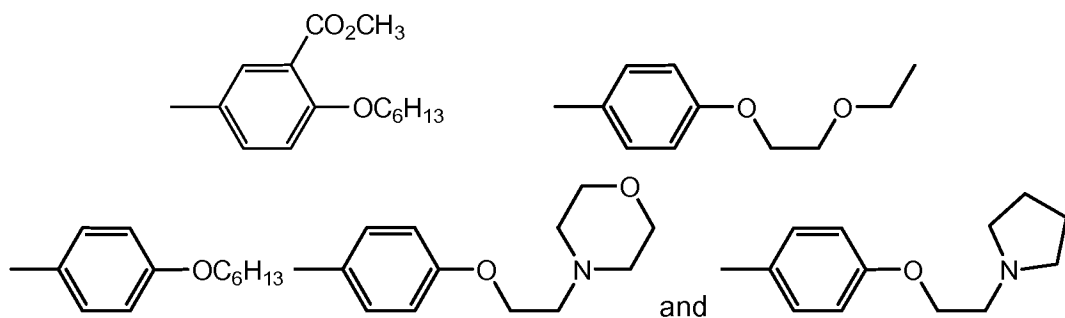
wherein

R⁷ is C₁₋₂₀ hydrocarbyl, C₁₋₂₀ hydrocarbyloxy, C₁₋₂₀ thioether, C₁₋₂₀ hydrocarbylcarbonyloxy or cyano; and
b is 0, 1 or 2.

R^5 may be morpholinyl or pyrrolidinyl, and particularly, R^5 may be selected from

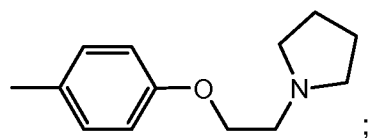
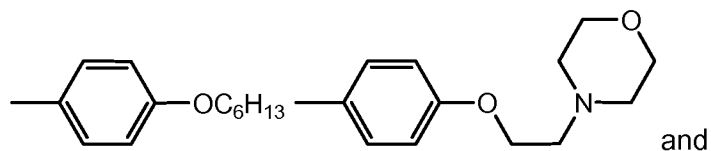
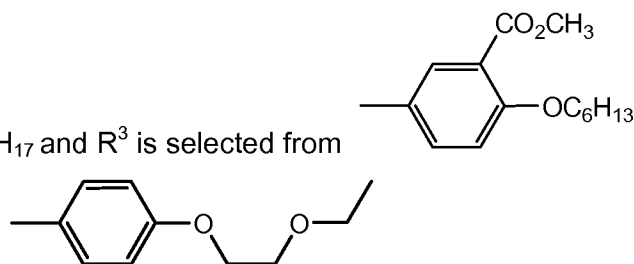


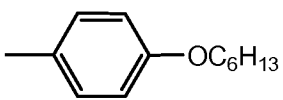
In specific embodiments, R^3 may be $-O(CH_2CH_2O)_mCH_2CH_2NR^6$; and m is 0 or an integer from 0 to about 20, or R^3 may be selected from

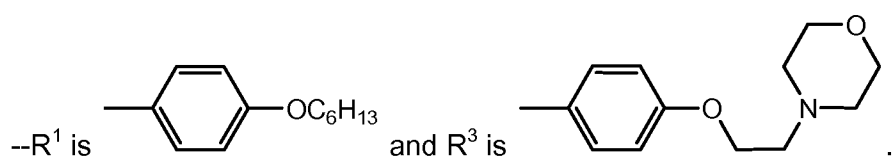
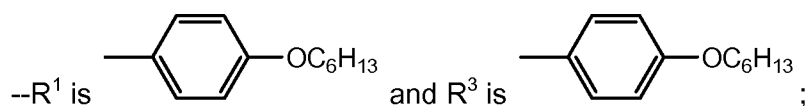
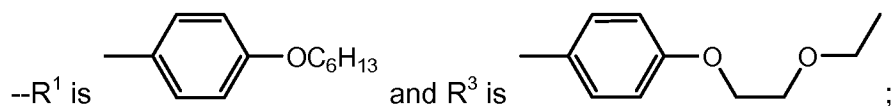
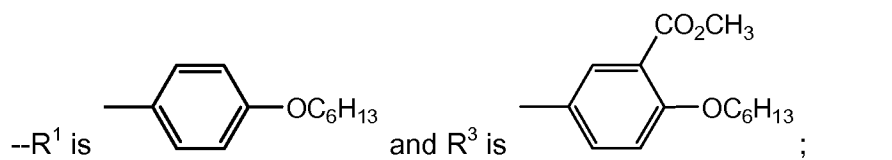
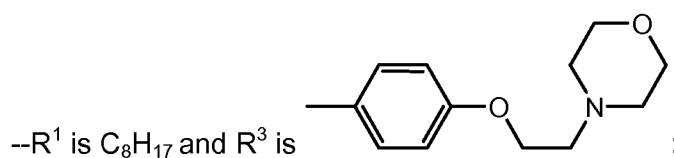
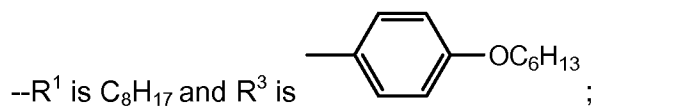
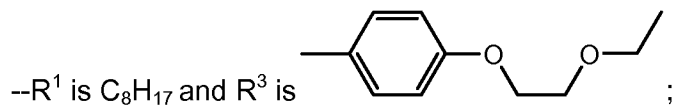
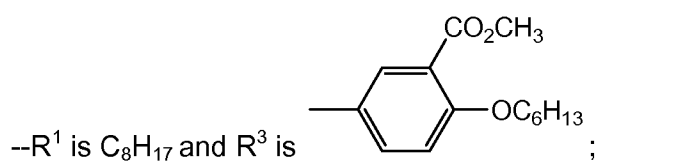
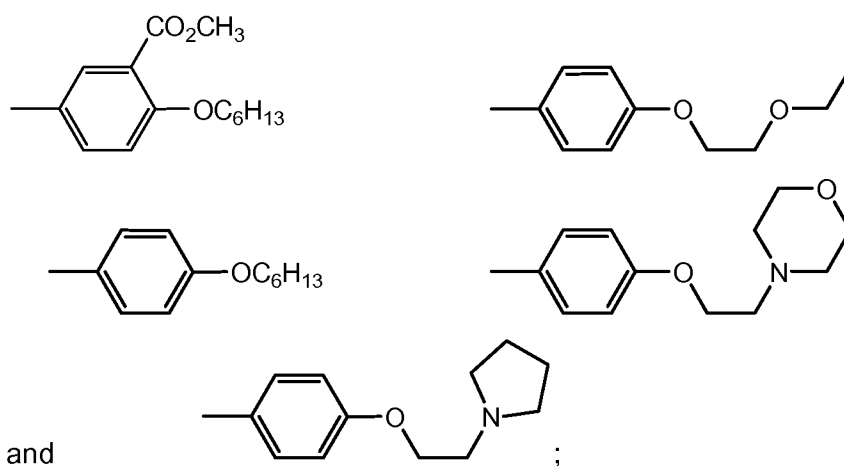


[0010] In exemplary compounds of the present invention,

-- R^1 is C_8H_{17} and R^3 is selected from



-- R^1 is  and
 R^3 is selected from

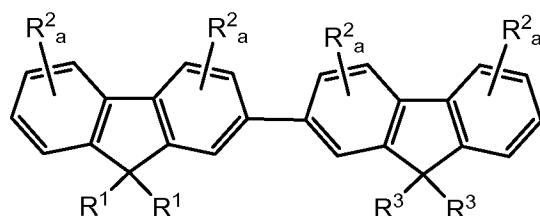


[0011] In another aspect, the present invention relates to optoelectronic devices comprising

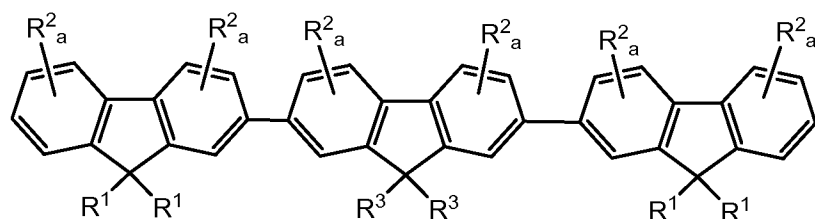
- a cathode;
- an anode;
- an electroluminescent layer disposed between the cathode and the anode;
- and
- a layer disposed between the electroluminescent layer and the cathode, and comprising a compound of formula Ia.

The genus encompassed by the compounds of formula Ia includes the compounds of formula I

[0012] In some embodiments, the compound of formula Ia is



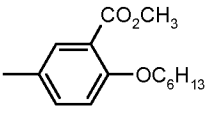
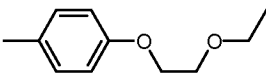
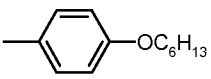
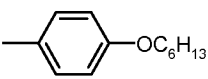
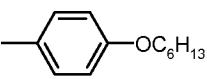
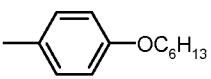
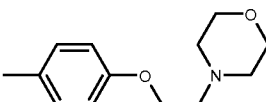
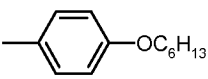
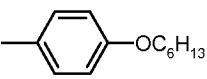
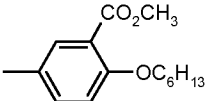
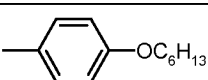
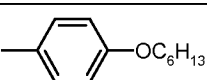
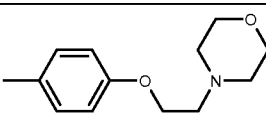
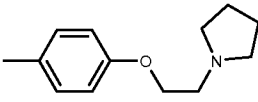
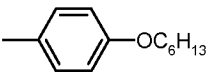
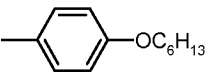
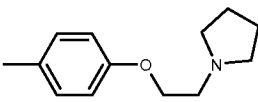
and in others, the compound of formula Ia is



In yet other embodiments, the optoelectronic device includes compounds of formula 1a, wherein R^{3a} is C_{1-20} hydrocarbyl containing at least one ether, thioether, ester, thioester, or alkylamino group.

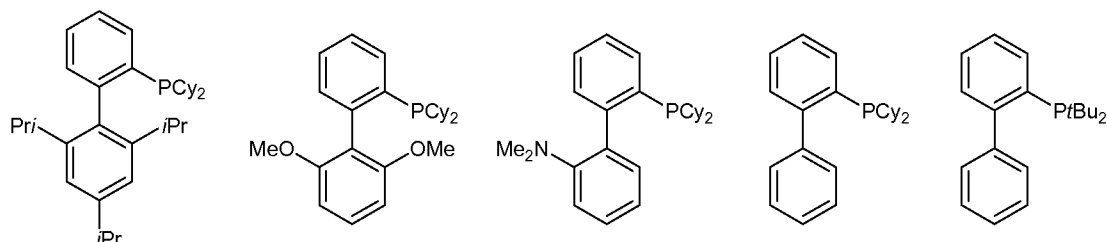
[0013] Some examples of suitable oligomer blocking layers are presented in Table 2.

Table 2. Oligofluorene Triplet Blocking Materials

#	R	R'	R''	Mw
392-38	C ₈ H ₁₇	C ₈ H ₁₇		1408
392-57	C ₈ H ₁₇	C ₈ H ₁₇		1270
392-59	C ₈ H ₁₇	C ₈ H ₁₇		1294
392-65				1550
392-74	C ₈ H ₁₇	C ₈ H ₁₇		1352
392-83				1664
392-84				1608
392-85	C ₈ H ₁₇	C ₈ H ₁₇		1320
392-89				1576

[0014] The compounds of formula I are typically amorphous materials that can be cast into thin films by evaporative casting from a suitable organic solvent. As long as the fluorene oligomer length does not exceed about 3 fluorene segments, the triplet energies of these oligomers is higher than most emissive hosts materials and triplet blocking may occur.

[0015] The compounds of formula I may be readily prepared by typical aryl coupling reactions such as the Suzuki or Yamamoto coupling. In particular, the compounds may be prepared by Suzuki cross-coupling reactions. The general procedure for Suzuki cross-coupling reactions includes mixing an aryl halide and aryl borate (or boronic acid) in a suitable solvent, in the presence of a base and Pd catalyst, and heating under an inert atmosphere. Suitable solvents include, but are not limited, to dioxane, THF, ethanol, toluene and mixtures thereof. Exemplary bases include Na_2CO_3 , K_2CO_3 , Cs_2CO_3 , potassium phosphate and hydrates thereof. The bases may be added to the reaction as a solid powder or as an aqueous solution. Suitable catalysts include $\text{Pd}(\text{PPh}_3)_4$, $\text{Pd}(\text{OAc})_2$, and $\text{Pd}(\text{dba})_2$ with the addition of a secondary ligand. Exemplary ligands include dialkylphosphinobiphenyl ligands shown below, in which Cy is cyclohexyl.



[0016] An optoelectronic device includes, in the simplest case, an anode layer and a corresponding cathode layer with an electroluminescent layer disposed between the anode and the cathode. When a voltage bias is applied across the electrodes, electrons are injected by the cathode into the electroluminescent layer while electrons are removed from (or “holes” are “injected” into) the electroluminescent layer from the anode. For an organic light emitting device (OLED), light emission occurs as holes combine with electrons within the electroluminescent layer to form singlet or triplet excitons, light emission occurring as singlet and/or triplet excitons decay to their ground states via radiative decay. For a photovoltaic (PV) device, light absorption results in an electric current flow.

[0017] Other components which may be present in an optoelectronic device in addition to the anode, cathode and light emitting material include a hole injection layer, an electron injection layer, and an electron transport layer. The electron transport layer need not be in direct contact with the cathode, and frequently the electron transport layer also serves as a hole blocking layer to prevent holes migrating toward the cathode. Additional components which may be present in an

organic light-emitting device include hole transporting layers, hole transporting emission (emitting) layers and electron transporting emission (emitting) layers.

[0018] The organic electroluminescent layer, i.e., the emissive layer, is a layer within an organic light emitting device which when in operation contains a significant concentration of both electrons and holes and provides sites for exciton formation and light emission. A hole injection layer is a layer in contact with the anode which promotes the injection of holes from the anode into the interior layers of the OLED; and an electron injection layer is a layer in contact with the cathode that promotes the injection of electrons from the cathode into the OLED; an electron transport layer is a layer which facilitates conduction of electrons from the cathode and/or the electron injection layer to a charge recombination site. During operation of an organic light emitting device comprising an electron transport layer, the majority of charge carriers (i.e. holes and electrons) present in the electron transport layer are electrons and light emission can occur through recombination of holes and electrons present in the emissive layer. A hole transporting layer is a layer which when the OLED is in operation facilitates conduction of holes from the anode and/or the hole injection layer to charge recombination sites and which need not be in direct contact with the anode. A hole transporting emission layer is a layer in which when the OLED is in operation facilitates the conduction of holes to charge recombination sites, and in which the majority of charge carriers are holes, and in which emission occurs not only through recombination with residual electrons, but also through the transfer of energy from a charge recombination zone elsewhere in the device. An electron transporting emission layer is a layer in which when the OLED is in operation facilitates the conduction of electrons to charge recombination sites, and in which the majority of charge carriers are electrons, and in which emission occurs not only through recombination with residual holes, but also through the transfer of energy from a charge recombination zone elsewhere in the device.

[0019] Materials suitable for use as the anode includes materials having a bulk resistivity of preferred about 1000 ohms per square, as measured by a four-point probe technique. Indium tin oxide (ITO) is frequently used as the anode because it is substantially transparent to light transmission and thus facilitates the escape of light emitted from electro-active organic layer. Other materials, which may be utilized as

the anode layer, include tin oxide, indium oxide, zinc oxide, indium zinc oxide, zinc indium tin oxide, antimony oxide, and mixtures thereof.

[0020] Materials suitable for use as the cathode include general electrical conductors including, but not limited to metals which can inject negative charge carriers (electrons) into the inner layer(s) of the OLED. Metal oxides such as ITO may also be used. Metals suitable for use as the cathode include K, Li, Na, Cs, Mg, Ca, Sr, Ba, Al, Ag, Au, In, Sn, Zn, Zr, Sc, Y, elements of the lanthanide series, alloys thereof, and mixtures thereof. Suitable alloy materials for use as the cathode layer include Ag-Mg, Al-Li, In-Mg, Al-Ca, and Al-Au alloys. Layered non-alloy structures may also be employed in the cathode, such as a thin layer of a metal such as calcium, or a metal fluoride, such as LiF, covered by a thicker layer of a metal, such as aluminum or silver. In particular, the cathode may be composed of a single metal, and especially of aluminum metal.

[0021] The compounds of formula I may be used in electron transport layers in place of, or in addition to traditional materials such as poly(9,9-dioctyl fluorene), tris(8-hydroxyquinolato) aluminum (Alq₃), 2,9-dimethyl-4,7-diphenyl-1,1-phenanthroline, 4,7-diphenyl-1,10-phenanthroline, 2-(4-biphenyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole, 3-(4-biphenyl)-4-phenyl-5-(4-t-butylphenyl)-1,2,4-triazole, 1,3,4-oxadiazole-containing polymers, 1,3,4-triazole-containing polymers, quinoxaline-containing polymers, and cyano-PPV.

[0022] Materials suitable for use in hole transporting layers include 1,1-bis((di-4-tolylamino) phenyl)cyclohexane, N,N'-bis(4-methylphenyl)-N,N'-bis(4-ethylphenyl)-(1,1'-(3,3'-dimethyl)biphenyl)-4,4'-diamine, tetrakis-(3-methylphenyl)-N,N,N',N'-2,5-phenylenediamine, phenyl-4-N,N-diphenylaminostyrene, p-(diethylamino) benzaldehyde diphenylhydrazone, triphenylamine, 1-phenyl-3-(p-(diethylamino)styryl)-5-(p-(diethylamino)phenyl)pyrazoline, 1,2-trans-bis(9H-carbazol-9-yl)cyclobutane, N,N,N',N'-tetrakis(4-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine, copper phthalocyanine, polyvinylcarbazole, (phenylmethyl)polysilane; poly(3,4-ethylenedioxythiophene) (PEDOT), polyaniline, polyvinylcarbazole, triaryldiamine, tetraphenyldiamine, aromatic tertiary amines, hydrazone derivatives, carbazole derivatives, triazole derivatives, imidazole derivatives, oxadiazole derivatives having an amino group, and polythiophenes as disclosed in U.S. Pat. No. 6,023,371.

[0023] Materials suitable for use in the light emitting layer include electroluminescent polymers such as polyfluorenes, preferably poly(9,9-dioctyl fluorene) and copolymers thereof, such as poly(9,9'-dioctylfluorene-co-bis-*N,N'*-(4-butylphenyl)diphenylamine) (F8-TFB); poly(vinylcarbazole) and polyphenylenevinylene and their derivatives. In addition, the light emitting layer may include a blue, yellow, orange, green or red phosphorescent dye or metal complex, or a combination thereof. Materials suitable for use as the phosphorescent dye include, but are not limited to, tris(1-phenylisoquinoline) iridium (III) (red dye), tris(2-phenylpyridine) iridium (green dye) and Iridium (III) bis(2-(4,6-difluorephenyl)pyridinato-N,C2) (blue dye). Commercially available electrofluorescent and electrophosphorescent metal complexes from ADS (American Dyes Source, Inc.) may also be used. ADS green dyes include ADS060GE, ADS061GE, ADS063GE, and ADS066GE, ADS078GE, and ADS090GE. ADS blue dyes include ADS064BE, ADS065BE, and ADS070BE. ADS red dyes include ADS067RE, ADS068RE, ADS069RE, ADS075RE, ADS076RE, ADS067RE, and ADS077RE.

DEFINITIONS

[0024] the term hydrocarbonyl as used herein means any organic moiety containing only hydrogen and carbon unless specified otherwise, and may include aromatic, aliphatic, cycloaliphatic and moieties containing two or more of aliphatic, cycloaliphatic and aromatic moieties

[0025] As used herein, alkyl is intended to include linear, branched, or cyclic hydrocarbon structures and combinations thereof, including lower alkyl and higher alkyl. Preferred alkyl groups are those of C₂₀ or below. Lower alkyl refers to alkyl groups of from 1 to 6 carbon atoms, preferably from 1 to 4 carbon atoms, and includes methyl, ethyl, *n*-propyl, isopropyl, and *n*-, *s*- and *t*- butyl. Higher alkyl refers to alkyl groups having seven or more carbon atoms, preferably 7-20 carbon atoms, and includes *n*-, *s*- and *t*-heptyl, octyl, and dodecyl. Cycloalkyl is a subset of alkyl and includes cyclic hydrocarbon groups of from 3 to 8 carbon atoms. Examples of cycloalkyl groups include cyclopropyl, cyclobutyl, cyclopentyl, and norbornyl. Alkenyl and alkynyl refer to alkyl groups wherein two or more hydrogen atoms are replaced by a double or triple bond, respectively.

[0026] Aryl and heteroaryl mean a 5- or 6-membered aromatic or heteroaromatic ring containing 0-3 heteroatoms selected from nitrogen, oxygen or sulfur; a bicyclic 9- or 10-membered aromatic or heteroaromatic ring system containing 0-3 heteroatoms selected from nitrogen, oxygen or sulfur; or a tricyclic 13- or 14-membered aromatic or heteroaromatic ring system containing 0-3 heteroatoms selected from nitrogen, oxygen or sulfur. The aromatic 6- to 14-membered carbocyclic rings include, for example, benzene, naphthalene, indane, tetralin, and fluorene; and the 5- to 10-membered aromatic heterocyclic rings include, e.g., imidazole, pyridine, indole, thiophene, benzopyranone, thiazole, furan, benzimidazole, quinoline, isoquinoline, quinoxaline, pyrimidine, pyrazine, tetrazole and pyrazole.

[0027] Arylalkyl means an alkyl residue attached to an aryl ring. Examples are benzyl and phenethyl. Heteroarylalkyl means an alkyl residue attached to a heteroaryl ring. Examples include pyridinylmethyl and pyrimidinylethyl. Alkylaryl means an aryl residue having one or more alkyl groups attached thereto. Examples are tolyl and mesityl.

[0028] Alkoxy or alkoxyl refers to groups of from 1 to 8 carbon atoms of a straight, branched, cyclic configuration and combinations thereof attached to the parent structure through an oxygen. Examples include methoxy, ethoxy, propoxy, isopropoxy, cyclopropyloxy, and cyclohexyloxy. Lower alkoxy refers to groups containing one to four carbons.

[0029] Acyl refers to groups of from 1 to 8 carbon atoms of a straight, branched, cyclic configuration, saturated, unsaturated and aromatic and combinations thereof, attached to the parent structure through a carbonyl functionality. One or more carbons in the acyl residue may be replaced by nitrogen, oxygen or sulfur as long as the point of attachment to the parent remains at the carbonyl. Examples include acetyl, benzoyl, propionyl, isobutyryl, *t*-butoxycarbonyl, and benzyloxycarbonyl. Lower-acyl refers to groups containing one to four carbons.

[0030] Heterocycle means a cycloalkyl or aryl residue in which one to two of the carbons is replaced by a heteroatom such as oxygen, nitrogen or sulfur. Examples of heterocycles that fall within the scope of the invention include pyrrolidine, pyrazole, pyrrole, indole, quinoline, isoquinoline, tetrahydroisoquinoline, benzofuran, benzodioxan, benzodioxole (commonly referred to as methylenedioxyphenyl, when

occurring as a substituent), tetrazole, morpholine, thiazole, pyridine, pyridazine, pyrimidine, thiophene, furan, oxazole, oxazoline, isoxazole, dioxane, and tetrahydrofuran.

[0031] Substituted refers to residues, including, but not limited to, alkyl, alkylaryl, aryl, arylalkyl, and heteroaryl, wherein up to three H atoms of the residue are replaced with lower alkyl, substituted alkyl, alkenyl, substituted alkenyl, aryl, substituted aryl, haloalkyl, alkoxy, carbonyl, carboxy, carboxalkoxy, carboxamido, acyloxy, amidino, nitro, halo, hydroxy, $\text{OCH}(\text{COOH})_2$, cyano, primary amino, secondary amino, acylamino, alkylthio, sulfoxide, sulfone, phenyl, benzyl, phenoxy, benzyloxy, heteroaryl, or heteroaryloxy.

[0032] Haloalkyl refers to an alkyl residue, wherein one or more H atoms are replaced by halogen atoms; the term haloalkyl includes perhaloalkyl. Examples of haloalkyl groups that fall within the scope of the invention include CH_2F , CHF_2 , and CF_3 .

[0033] Many of the compounds described herein may contain one or more asymmetric centers and may thus give rise to enantiomers, diastereomers, and other stereoisomeric forms that may be defined, in terms of absolute stereochemistry, as (R)- or (S)-. The present invention is meant to include all such possible isomers, as well as, their racemic and optically pure forms. Optically active (R)- and (S)- isomers may be prepared using chiral synthons or chiral reagents, or resolved using conventional techniques. When the compounds described herein contain olefinic double bonds or other centers of geometric asymmetry, and unless specified otherwise, it is intended that the compounds include both E and Z geometric isomers. Likewise, all tautomeric forms are also intended to be included.

[0034] Oxaalkyl refers to an alkyl residue in which one or more carbons have been replaced by oxygen. It is attached to the parent structure through an alkyl residue. Examples include methoxypropoxy, 3,6,9-trioxadecyl and the like. The term oxaalkyl is intended as it is understood in the art [see Naming and Indexing of Chemical Substances for Chemical Abstracts, published by the American Chemical Society, ¶196, but without the restriction of ¶127(a)], i.e. it refers to compounds in which the oxygen is bonded via a single bond to its adjacent atoms (forming ether bonds); it does not refer to doubly bonded oxygen, as would be found in carbonyl groups.

Similarly, thiaalkyl and azaalkyl refer to alkyl residues in which one or more carbons has been replaced by sulfur or nitrogen, respectively. Examples include ethylaminoethyl and methylthiopropyl.

[0035] Silyl means an alkyl residue in which one to three of the carbons is replaced by tetravalent silicon and which is attached to the parent structure through a silicon atom. Siloxy is an alkoxy residue in which both of the carbons are replaced by tetravalent silicon that is endcapped with an alkyl residue, aryl residue or a cycloalkyl residue, and which is attached to the parent structure through an oxygen atom.

[0036] As used herein, the term "aromatic radical" refers to an array of atoms having a valence of at least one comprising at least one aromatic group. The array of atoms having a valence of at least one comprising at least one aromatic group may include heteroatoms such as nitrogen, sulfur, selenium, silicon and oxygen, or may be composed exclusively of carbon and hydrogen. As used herein, the term "aromatic radical" includes but is not limited to phenyl, pyridyl, furanyl, thienyl, naphthyl, phenylene, and biphenyl radicals. As noted, the aromatic radical contains at least one aromatic group. The aromatic group is invariably a cyclic structure having $4n+2$ "delocalized" electrons where "n" is an integer equal to 1 or greater, as illustrated by phenyl groups ($n = 1$), thienyl groups ($n = 1$), furanyl groups ($n = 1$), naphthyl groups ($n = 2$), azulenyl groups ($n = 2$), anthracenyl groups ($n = 3$) and the like. The aromatic radical may also include nonaromatic components. For example, a benzyl group is an aromatic radical which comprises a phenyl ring (the aromatic group) and a methylene group (the nonaromatic component). Similarly a tetrahydronaphthyl radical is an aromatic radical comprising an aromatic group (C_6H_3) fused to a nonaromatic component $-(CH_2)_4-$. For convenience, the term "aromatic radical" is defined herein to encompass a wide range of functional groups such as alkyl groups, alkenyl groups, alkynyl groups, haloalkyl groups, haloaromatic groups, conjugated dienyl groups, alcohol groups, ether groups, aldehydes groups, ketone groups, carboxylic acid groups, acyl groups (for example carboxylic acid derivatives such as esters and amides), amine groups, nitro groups, and the like. For example, the 4-methylphenyl radical is a C_7 aromatic radical comprising a methyl group, the methyl group being a functional group which is an alkyl group. Similarly, the 2-nitrophenyl group is a C_6 aromatic radical comprising a nitro group, the nitro group being a functional group. Aromatic radicals include halogenated aromatic radicals such as

4-trifluoromethylphenyl, hexafluoroisopropylidenebis(4-phen-1-yloxy) (i.e., -OPhC(CF₃)₂PhO-), 4-chloromethylphen-1-yl, 3-trifluorovinyl-2-thienyl, 3-trichloromethylphen-1-yl (i.e., 3-CCl₃Ph-), 4-(3-bromoprop-1-yl)phen-1-yl (i.e., 4-BrCH₂CH₂CH₂Ph-), and the like. Further examples of aromatic radicals include 4-allyloxyphen-1-yl, 4-aminophen-1-yl (i.e., 4-H₂NPh-), 3-aminocarbonylphen-1-yl (i.e., NH₂COPh-), 4-benzoylphen-1-yl, dicyanomethylidenebis(4-phen-1-yloxy) (i.e., -OPhC(CN)₂PhO-), 3-methylphen-1-yl, methylenebis(4-phen-1-yloxy) (i.e., -OPhCH₂PhO-), 2-ethylphen-1-yl, phenylethenyl, 3-formyl-2-thienyl, 2-hexyl-5-furanyl, hexamethylene-1,6-bis(4-phen-1-yloxy) (i.e., -OPh(CH₂)₆PhO-), 4-hydroxymethylphen-1-yl (i.e., 4-HOCH₂Ph-), 4-mercaptomethylphen-1-yl (i.e., 4-HSCH₂Ph-), 4-methylthiophen-1-yl (i.e., 4-CH₃SPh-), 3-methoxyphen-1-yl, 2-methoxycarbonylphen-1-yloxy (e.g. methyl salicyl), 2-nitromethylphen-1-yl (i.e., 2-NO₂CH₂Ph), 3-trimethylsilylphen-1-yl, 4-t-butyltrimethylsilylphen-1-yl, 4-vinylphen-1-yl, vinylidenebis(phenyl), and the like. The term "a C₃ – C₁₀ aromatic radical" includes aromatic radicals containing at least three but no more than 10 carbon atoms. The aromatic radical 1-imidazolyl (C₃H₂N₂-) represents a C₃ aromatic radical. The benzyl radical (C₇H₇-) represents a C₇ aromatic radical.

[0037] As used herein the term "cycloaliphatic radical" refers to a radical having a valence of at least one, and comprising an array of atoms which is cyclic but which is not aromatic. As defined herein a "cycloaliphatic radical" does not contain an aromatic group. A "cycloaliphatic radical" may comprise one or more noncyclic components. For example, a cyclohexylmethyl group (C₆H₁₁CH₂-) is an cycloaliphatic radical which comprises a cyclohexyl ring (the array of atoms which is cyclic but which is not aromatic) and a methylene group (the noncyclic component). The cycloaliphatic radical may include heteroatoms such as nitrogen, sulfur, selenium, silicon and oxygen, or may be composed exclusively of carbon and hydrogen. For convenience, the term "cycloaliphatic radical" is defined herein to encompass a wide range of functional groups such as alkyl groups, alkenyl groups, alkynyl groups, haloalkyl groups, conjugated dienyl groups, alcohol groups, ether groups, aldehyde groups, ketone groups, carboxylic acid groups, acyl groups (for example carboxylic acid derivatives such as esters and amides), amine groups, nitro groups, and the like. For example, the 4-methylcyclopent-1-yl radical is a C₆ cycloaliphatic radical comprising a methyl group, the methyl group being a functional group which is an alkyl group. Similarly, the 2-nitrocyclobut-1-yl radical is a C₄

cycloaliphatic radical comprising a nitro group, the nitro group being a functional group. A cycloaliphatic radical may comprise one or more halogen atoms which may be the same or different. Halogen atoms include, for example; fluorine, chlorine, bromine, and iodine. Cycloaliphatic radicals comprising one or more halogen atoms include 2-trifluoromethylcyclohex-1-yl, 4-bromodifluoromethylcyclooct-1-yl, 2-chlorodifluoromethylcyclohex-1-yl, hexafluoroisopropylidene-2,2-bis (cyclohex-4-yl) (i.e., $-\text{C}_6\text{H}_{10}\text{C}(\text{CF}_3)_2\text{C}_6\text{H}_{10}-$), 2-chloromethylcyclohex-1-yl, 3-difluoromethylene cyclohex-1-yl, 4-trichloromethylcyclohex-1-yloxy, 4-bromodichloromethyl cyclohex-1-ylthio, 2-bromoethylcyclopent-1-yl, 2-bromopropylcyclohex-1-yloxy (e.g. $\text{CH}_3\text{CHBrCH}_2\text{C}_6\text{H}_{10}\text{O}-$), and the like. Further examples of cycloaliphatic radicals include 4-allyloxycyclohex-1-yl, 4-aminocyclohex-1-yl (i.e., $\text{H}_2\text{NC}_6\text{H}_{10}-$), 4-aminocarbonylcyclopent-1-yl (i.e., $\text{NH}_2\text{COC}_5\text{H}_8-$), 4-acetyloxycyclohex-1-yl, 2,2-dicyanoisopropylidenebis(cyclo-hex-4-yloxy) (i.e., $-\text{OC}_6\text{H}_{10}\text{C}(\text{CN})_2\text{C}_6\text{H}_{10}\text{O}-$), 3-methylcyclohex-1-yl, methylenebis(cyclohex-4-yloxy) (i.e., $-\text{OC}_6\text{H}_{10}\text{CH}_2\text{C}_6\text{H}_{10}\text{O}-$), 1-ethylcyclobut-1-yl, cyclopropylethenyl, 3-formyl-2-terahydrofuranyl, 2-hexyl-5-tetrahydrofuranyl, hexamethylene-1,6-bis(cyclohex-4-yloxy) (i.e., $-\text{OC}_6\text{H}_{10}(\text{CH}_2)_6\text{C}_6\text{H}_{10}\text{O}-$), 4-hydroxymethylcyclohex-1-yl (i.e., $4\text{-HOCH}_2\text{C}_6\text{H}_{10}-$), 4-mercaptomethylcyclohex-1-yl (i.e., $4\text{-HSCH}_2\text{C}_6\text{H}_{10}-$), 4-methylthiocyclohex-1-yl (i.e., $4\text{-CH}_3\text{SC}_6\text{H}_{10}-$), 4-methoxycyclohex-1-yl, 2-methoxycarbonylcyclohex-1-yloxy ($2\text{-CH}_3\text{OCOC}_6\text{H}_{10}\text{O}-$), 4-nitromethylcyclohex-1-yl (i.e., $\text{NO}_2\text{CH}_2\text{C}_6\text{H}_{10}-$), 3-trimethylsilylcyclohex-1-yl, 2-t-butyl dimethylsilylcyclopent-1-yl, 4-trimethoxysilylethylcyclohex-1-yl (e.g. $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{C}_6\text{H}_{10}-$), 4-vinylcyclohexen-1-yl, vinylidenebis(cyclohexyl), and the like. The term “a $\text{C}_3 - \text{C}_{10}$ cycloaliphatic radical” includes cycloaliphatic radicals containing at least three but no more than 10 carbon atoms. The cycloaliphatic radical 2-tetrahydrofuranyl ($\text{C}_4\text{H}_7\text{O}-$) represents a C_4 cycloaliphatic radical. The cyclohexylmethyl radical ($\text{C}_6\text{H}_{11}\text{CH}_2-$) represents a C_7 cycloaliphatic radical.

[0038] As used herein the term “aliphatic radical” refers to an organic radical having a valence of at least one consisting of a linear or branched array of atoms which is not cyclic. Aliphatic radicals are defined to comprise at least one carbon atom. The array of atoms comprising the aliphatic radical may include heteroatoms such as nitrogen, sulfur, silicon, selenium and oxygen or may be composed exclusively of carbon and hydrogen. For convenience, the term “aliphatic radical” is defined herein to encompass, as part of the “linear or branched array of atoms which is not cyclic”

organic radicals substituted with a wide range of functional groups such as alkyl groups, alkenyl groups, alkynyl groups, haloalkyl groups, conjugated dienyl groups, alcohol groups, ether groups, aldehyde groups, ketone groups, carboxylic acid groups, acyl groups (for example carboxylic acid derivatives such as esters and amides), amine groups, nitro groups, and the like. For example, the 4-methylpent-1-yl radical is a C₆ aliphatic radical comprising a methyl group, the methyl group being a functional group which is an alkyl group. Similarly, the 4-nitrobut-1-yl group is a C₄ aliphatic radical comprising a nitro group, the nitro group being a functional group. An aliphatic radical may be a haloalkyl group which comprises one or more halogen atoms which may be the same or different. Halogen atoms include, for example; fluorine, chlorine, bromine, and iodine. Aliphatic radicals comprising one or more halogen atoms include the alkyl halides trifluoromethyl, bromodifluoromethyl, chlorodifluoromethyl, hexafluoroisopropylidene, chloromethyl, difluorovinylidene, trichloromethyl, bromodichloromethyl, bromoethyl, 2-bromotrimethylene (e.g. -CH₂CHBrCH₂-), and the like. Further examples of aliphatic radicals include allyl, aminocarbonyl (i.e., -CONH₂), carbonyl, 2,2-dicyanoisopropylidene (i.e., -CH₂C(CN)₂CH₂-), methyl (i.e., -CH₃), methylene (i.e., -CH₂-), ethyl, ethylene, formyl (i.e., -CHO), hexyl, hexamethylene, hydroxymethyl (i.e., -CH₂OH), mercaptomethyl (i.e., -CH₂SH), methylthio (i.e., -SCH₃), methylthiomethyl (i.e., -CH₂SCH₃), methoxy, methoxycarbonyl (i.e., CH₃OCO-) , nitromethyl (i.e., -CH₂NO₂), thiocarbonyl, trimethylsilyl (i.e., (CH₃)₃Si-), t-butyl dimethylsilyl, 3-trimethyloxysilylpropyl (i.e., (CH₃O)₃SiCH₂CH₂CH₂-), vinyl, vinylidene, and the like. By way of further example, a C₁ – C₁₀ aliphatic radical contains at least one but no more than 10 carbon atoms. A methyl group (i.e., CH₃-) is an example of a C₁ aliphatic radical. A decyl group (i.e., CH₃(CH₂)₉-) is an example of a C₁₀ aliphatic radical.

Examples

Example 1 Preparation of oligofluorenes

[0039] A general procedure for the preparation of oligofluorenes is exemplified by the synthesis of 392-59: A 200 ml 2-neck flask fitted with a condenser, gas inlet tube and Teflon magnetic stir bar was charged with 9,9-bis-(4-hexyloxyphenyl)-2,7-dibromofluorene, 2.028g (3.00 mmol), 9,9-dioctyl-2-ethylenedioxyborane, 3.132g (6.24 mmol), dicyclohexyl-2-(2',6'-di-methoxyphenyl)phenylphosphine, 0.129g (0.32

mmol) and toluene, 60ml. The solution was degassed with argon for 15 minutes and palladium acetate, 0.20g (0.09 mmol) followed by a degassed solution of tetraethylammonium hydroxide, 2.2g (15 mmol) in water 22g. The solution was immersed in a 70°C oil bath and stirred under a nitrogen blanket for 16hr. The cooled mixture was diluted with toluene, 50 ml, and water, 25 ml, filtered through a pad of Celite and transferred to a separatory funnel. The aqueous phase was discarded and the organic phase was washed successively with water (2x100 ml) and brine (1x100ml) then passed through a cone of Drierite. The solution was stirred at room temperature with sodium borohydride ~ 25 mg then concentrated under vacuum and the residual oil was chromatographed on 120g of silica gel eluted with 0-30% ethyl acetate in hexane to afford 2.3g of a colorless oil: ^1H nmr (CDCl_3) δ 8.0-7.3 (m, 20, fluorene-H), 7.3-6.8 (AB quartet, 8, phenol ether Ar-H), 3.96 (t, 4, ArOCH_2), 2.04 (t, 8, $\text{C}_9\text{-CH}_2$), and 1.8-0.6 ppm (m, 60, octyl-H).

Example 2 Multiple layer Structure

[0040] The materials of this invention are soluble in common alcohols such as 1-butanol and 1 hexanol. For example, we have found that materials such as JC392-59 and 392-38 may be readily dissolved by 1-hexanol and 1-butanol at a concentration of approximately 10 mg/ml. Once cooled to room temperature, this material can be deposited via spin casting directly from solution onto a poly-fluorene polymer layer that is not dissolved by alcohol solvents. We have found that spin coating a ~10 mg/ml alcoholic solution at ~1000 rpm onto a polyfluorene coated glass slide results in an additional film thickness of ~20nm, which we assigned to an additional layer of the trimer type material. We have found that it is possible to follow the formation of this bilayer structure both through mechanical and optical thickness measurements of the polymer films on glass. The mechanical measurements are performed by first using a sharp edge to scratch the film, followed by measuring the distance between the top of the film and the glass using a profilometer. (in this case a Tencor P1) The optical measurements are performed by taking advantage of the fact that polyfluorene materials exhibit a peak in their optical absorption at ~390 nm and are much less absorbing at ~357 nm, where the peak absorption of many of the trimer species of this invention absorb. Thus it is possible to deconvolute the

combined by layer absorption into two components, one corresponding to the polyfluorene the other corresponding to the oligomers of this invention. Since the optical absorbance (in OD units) is linearly related to the average thickness, this provides additional support for existence of a bilayer structure.

Example 3: OLED Incorporating Multilayer Structure

[0041] It is possible to use the advantageous solubility properties of these materials to fabricate an OLED device. To fabricate the device, a layer of PEDOT/PSS (Baytron P VP 8000, a poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) obtained as a solution from HC Starck, Inc.) or other hole injecting material having a thickness of about 60nm can be by spin-coating onto clean, UV-Ozone treated, 2.5cm x 2.5cm ITO patterned glass substrates. The coated substrates can then be baked on a hot plate in air for 30 minutes at 160°C. A layer of F8-TFB (an octylfluorene-triarylamine copolymer obtained from Sumation, Inc.) hole transporter layer having a thickness of about 10-20 nm can be deposited via spin-coating atop the PEDOT/PSS coated substrates. The F8-TFB-PEDOT/PSS coated substrates can then be baked on a hot plate in argon for 30 minutes at 160°C. A layer comprised of a non alcohol soluble polyfluorene material (obtained from Sumation chemical or American Dye Source) can then be dissolved in a solvent such as xylene and deposited solution atop the F8-TFB layer as an emissive layer. This emissive layer can vary in thickness up to 200nm, but a thickness of 5nm-40 nm is preferred. A final layer of layer of the trimer material can be deposited from an alcohol (example 1-butanol, 1-hexanol) solution with a preferred thickness in the range of 10nm-50nm.

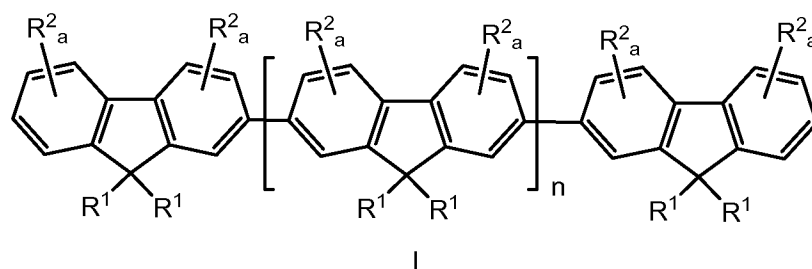
[0042] The coated substrates can then be placed into a bell jar evaporator, and the system was pumped until a pressure of about 1×10^{-6} torr was obtained. A layer of sodium fluoride about 7 nm thick (as measured via a calibrated quartz crystal microbalance) can then be deposited atop the final layer of the coated substrates by physical vapor deposition. Subsequently, a layer of aluminum metal about 130 nm thick can be deposited atop the sodium fluoride layer by vapor deposition under vacuum to form the cathode component of the OLED.

[0043] While only certain features of the invention have been illustrated and described herein, many modifications and changes will occur to those skilled in the

art. It is, therefore, to be understood that the appended claims are intended to cover all such modifications and changes as fall within the true spirit of the invention.

CLAIMS:

1. A compound of formula I



wherein

R^1 is, independently at each occurrence, C_{1-20} hydrocarbyl and at least one of R^1 is R^3 ;

R^2 is independently at each occurrence C_{1-20} hydrocarbyl, C_{1-20} hydrocarbyloxy, C_{1-20} thioether, C_{1-20} hydrocarbylcarbonyloxy or cyano;

R^3 is $-R^4XR^5$;

R^4 is a direct bond, C_{1-20} aryl, C_{1-20} arylalkyl, C_{1-20} alkylaryl, C_{1-20} substituted aryl, C_{1-20} substituted arylalkyl, or C_{1-20} substituted alkylaryl;

R^5 is C_{1-20} hydrocarbyl or C_{1-20} hydrocarbyl containing at least one S, N, O or P atom between carbon atoms;

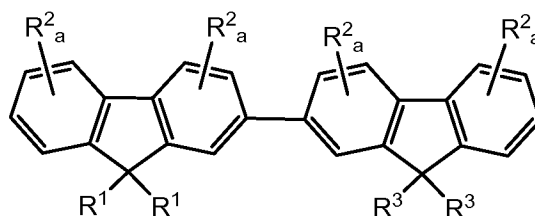
R^6 is C_{1-20} alkyl or C_{1-20} substituted alkyl;

X is $-O-$, $-S-$, $-COO-$, $-OOC-$, $-CSS-$, $-SSC-$, NR^6 or PR^6 ;

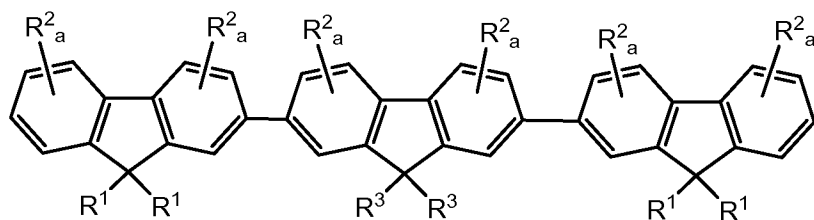
a is independently at each occurrence 0, 1 or 2; and

n is 0 or 1.

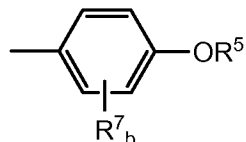
2. A compound according to claim 1, of formula



3. A compound according to claim 1, of formula



4. A compound according to claim 1, wherein R^3 is

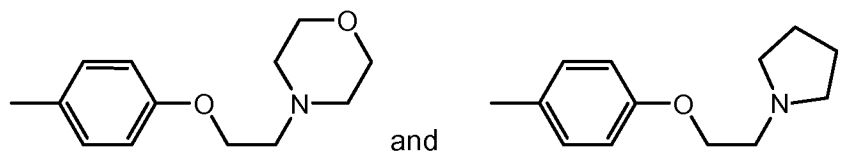


wherein

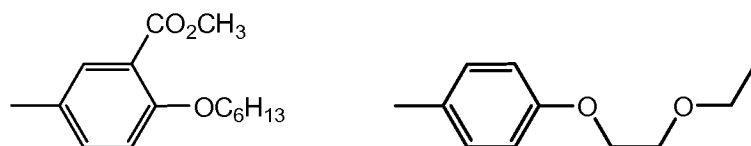
R^7 is C_{1-20} hydrocarbyl, C_{1-20} hydrocarbyloxy, C_{1-20} thioether, C_{1-20} hydrocarbylcarbonyloxy or cyano; and
b is 0, 1 or 2.

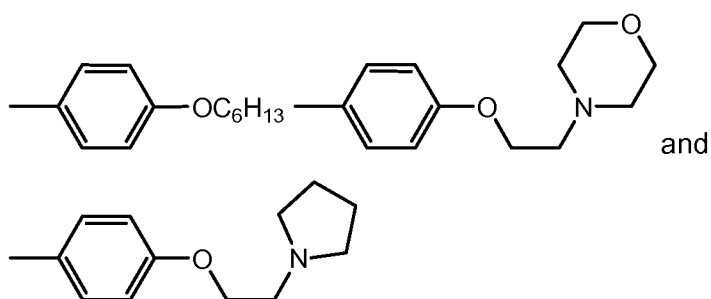
5. A compound according to claim 1, wherein R^1 is, independently at each occurrence, alkyl or R^3 .
6. A compound according to claim 1, wherein R^3 is $-O(CH_2CH_2O)_mCH_2CH_2NR^6$; and m is 0 or an integer from 0 to about 20.
7. A compound according to claim 1, wherein R^5 is morpholinyl or pyrrolidinyl.

8. A compound according to claim 1, wherein R^5 is selected from

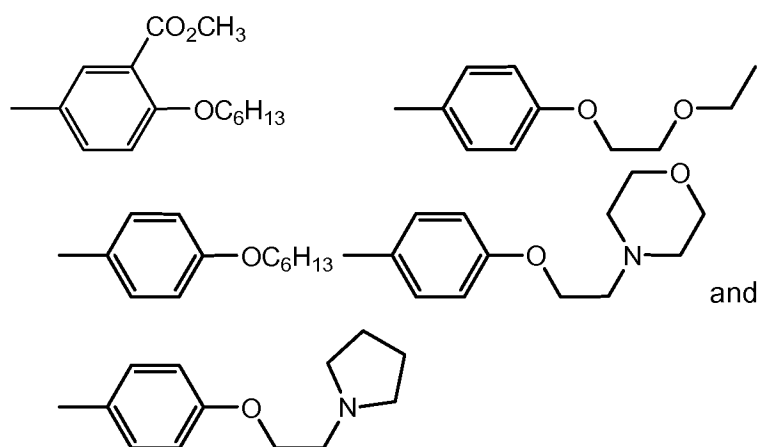


9. A compound according to claim 1, wherein R^3 is selected from

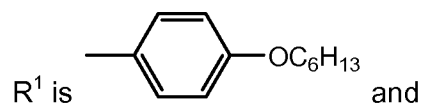




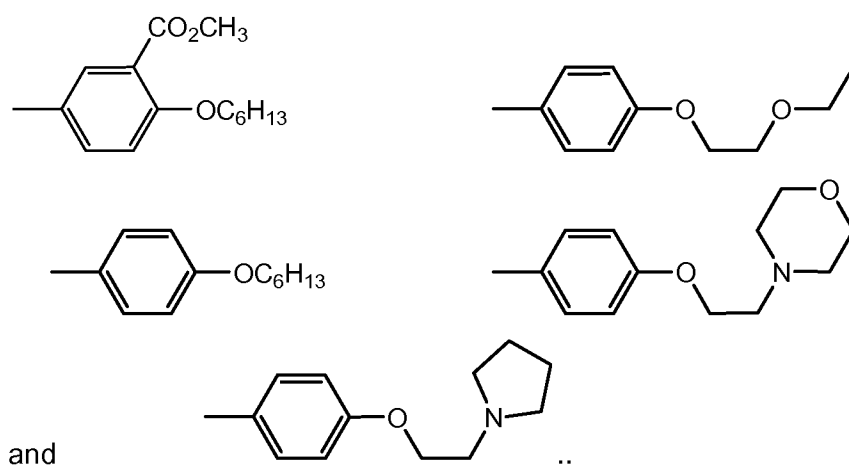
10. A compound according to claim 3, wherein R^1 is C_8H_{17} and R^3 is selected from



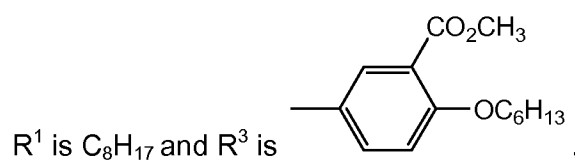
11. A compound according to claim 3, wherein



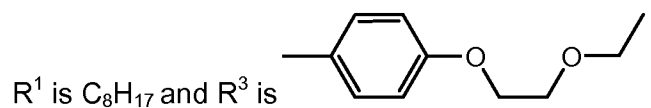
R^3 is selected from



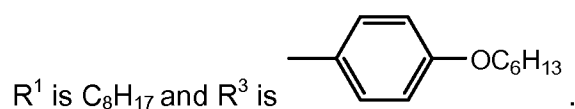
12. A compound according to claim 3, wherein



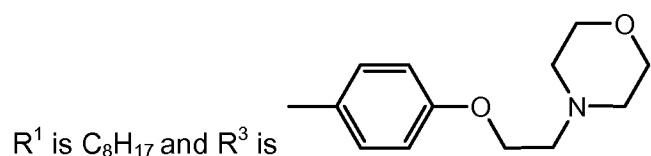
13. A compound according to claim 3, wherein



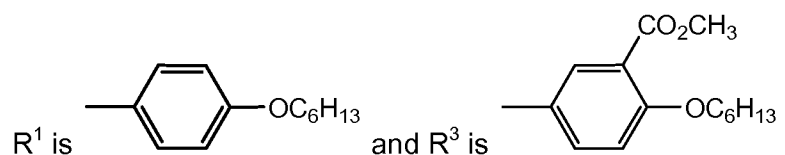
14. A compound according to claim 3, wherein



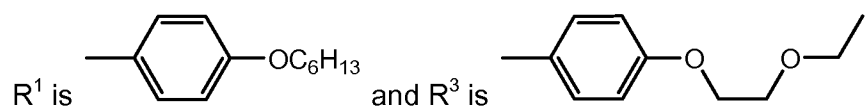
15. A compound according to claim 3, wherein



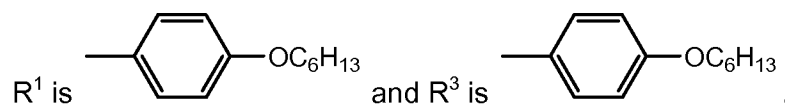
16. A compound according to claim 3, wherein



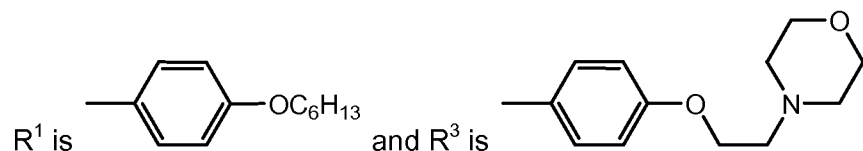
17. A compound according to claim 3, wherein



18. A compound according to claim 3, wherein



19. A compound according to claim 3, wherein



20. An optoelectronic device comprising a compound according to claim 1.

21. An optoelectronic device comprising

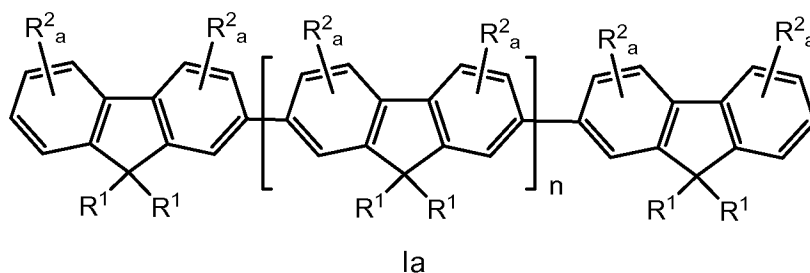
a cathode;

an anode;

an electroluminescent layer disposed between the cathode and the anode;

and

a layer disposed between the electroluminescent layer and the cathode, and comprising a compound of formula Ia



R^1 is, independently at each occurrence, C_{1-20} hydrocarbyl and at least one of R^1 is R^{3a} ;

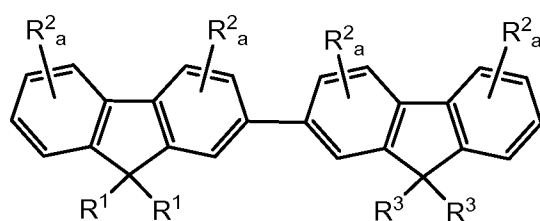
R^2 is independently at each occurrence C_{1-20} hydrocarbyl, C_{1-20} hydrocarbyloxy, C_{1-20} thioether, C_{1-20} hydrocarbylcarbonyloxy or cyano;

R^{3a} is C_{1-20} hydrocarbyl containing at least one S, N, O or P atom between carbon atoms;

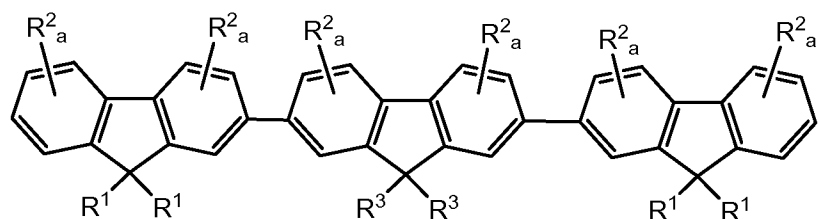
a is independently at each occurrence 0, 1 or 2; and

n is 0 or 1.

22. An optoelectronic device according to claim 22, wherein the compound of formula Ia is



23. An optoelectronic device according to claim 22, wherein the compound of formula Ia is



24. An optoelectronic device according to claim 22, wherein R^{3a} is C_{1-20} hydrocarbyl containing at least one ether, thioether, ester, thioester, or alkylamino group.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2010/025718

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09K11/06

ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09K C07C C07D C09B

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2004/106458 A1 (DOW GLOBAL TECHNOLOGIES INC [US]; KRAM SHARI L [US]; MARSHALL WILLIAM) 9 December 2004 (2004-12-09) page 3, line 1 - line 6 page 5, line 1 - line 5	1-24
X	WO 2005/049546 A1 (DOW GLOBAL TECHNOLOGIES INC [US]; HUDACK MICHELLE L [US]; YU WANGLIN []) 2 June 2005 (2005-06-02) page 8, line 12 - line 19	1-24
A	WO 2007/072742 A1 (CANON KK [JP]; IGAWA SATOSHI [JP]; OKADA SHINJIRO [JP]; TAKIGUCHI TAKA) 28 June 2007 (2007-06-28) claim 1	1-24

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

10 September 2010

Date of mailing of the international search report

16/09/2010

Name and mailing address of the ISA/

European Patent Office, P.B. 5618 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Ziegler, Jan

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2010/025718

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2006/121312 A1 (YAMADA NAOKI [JP] ET AL) 8 June 2006 (2006-06-08) claim 1 -----	1-24
A	WO 2008/147110 A2 (CHEIL IND INC [KR]; YU EUN-SUN [KR]; KIM NAM-SOO [KR]; KIM YOUNG-HOON) 4 December 2008 (2008-12-04) claim 1 -----	1-24
A	WO 02/05971 A1 (CANON KK [JP]; SELLINGER ALAN [US]; LAINE RICHARD M [US]) 24 January 2002 (2002-01-24) claim 7 -----	1-24
A	WO 2006/096399 A2 (SUMITOMO CHEMICAL CO [JP]; YU WANGLIN [US]; WU WEISHI [US]; HUDACK MIC) 14 September 2006 (2006-09-14) page 43 -----	1-24
A	WO 2008/071376 A1 (SENSIENT IMAGING TECHNOLOGIES [DE]; CSUK RENE [DE]; MATTERSTEIG GUNTER) 19 June 2008 (2008-06-19) claim 1 -----	1-24
A	JP 2001 039933 A (MITSUI CHEMICALS INC) 13 February 2001 (2001-02-13) compounds G8, H8 -----	1-24
X	US 6 169 163 B1 (WOO EDMUND P [US] ET AL) 2 January 2001 (2001-01-02) table 1; compounds M7-M10 claims 1,4,10 -----	1-24
X	US 2009/023877 A1 (LIAW DER-JANG [TW] ET AL) 22 January 2009 (2009-01-22) paragraph [0042] - paragraph [0045] -----	1-24
X	US 2008/200736 A1 (KOSUGE TETSUYA [JP] ET AL) 21 August 2008 (2008-08-21) paragraph [0087]; compound D02 paragraph [0119]; compound FL claims 1,2,4,5 -----	1-24
A	HOLMES A B ET AL: "A NEW FAMILY OF POLYFLUORENE COPOLYMERS FOR LIGHT EMITTING DEVICES" PROCEEDINGS OF THE SPIE, SPIE, US LNKD-DOI:10.1117/12.457502, vol. 4464, 30 July 2002 (2002-07-30), pages 42-48, XP008010995 ISSN: 0277-786X scheme 3compound 13 -----	1-24
	-/--	

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2010/025718

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 2 067 767 A1 (GRACEL DISPLAY INC [KR]) 10 June 2009 (2009-06-10) compounds H-110 claim 1 -----	1-24
A	US 2003/039838 A1 (CHEN SHAW H [US] ET AL) 27 February 2003 (2003-02-27) paragraphs [0048], [0227] -----	1-24
A	US 2007/257603 A1 (SUZUKI KOICHI [JP] ET AL) 8 November 2007 (2007-11-08) paragraph [0115] claim 1 -----	1-24

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2010/025718

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

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

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

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

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

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☒ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

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

1. claims: 1-24(partially)

fluoren compounds according to formula I, wherein X = -O-
and optoelectronic devices using this compound.

2. claims: 1-24(partially)

fluoren compounds according to formula I, wherein X = -S-
and optoelectronic devices using this compound.

3. claims: 1-24(partially)

fluoren compounds according to formula I, wherein X = -COO-
and optoelectronic devices using this compound.

4. claims: 1-24(partially)

fluoren compounds according to formula I, wherein X = -CSS-
and optoelectronic devices using this compound.

5. claims: 1-24(partially)

fluoren compounds according to formula I, wherein X = -SSC-
and optoelectronic devices using this compound.

6. claims: 1-24(partially)

fluoren compounds according to formula I, wherein X = -NR6-
and optoelectronic devices using this compound.

7. claims: 1-24(partially)

fluoren compounds according to formula I, wherein X = -PR6-
and optoelectronic devices using this compound.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2010/025718

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2004106458 A1	09-12-2004	CN 1791656 A DE 112004000838 T5 JP 4465484 B2 JP 2007505204 T KR 20060013664 A	21-06-2006 30-03-2006 19-05-2010 08-03-2007 13-02-2006
WO 2005049546 A1	02-06-2005	CN 1894199 A DE 112004002193 T5 GB 2422838 A JP 2007512249 T KR 20060107776 A US 2007126345 A1	10-01-2007 12-10-2006 09-08-2006 17-05-2007 16-10-2006 07-06-2007
WO 2007072742 A1	28-06-2007	EP 1863751 A1 JP 2007332127 A KR 20080081320 A US 2009079331 A1	12-12-2007 27-12-2007 09-09-2008 26-03-2009
US 2006121312 A1	08-06-2006	JP 4429149 B2 JP 2006151845 A	10-03-2010 15-06-2006
WO 2008147110 A2	04-12-2008	KR 20080104997 A US 2010187978 A1	03-12-2008 29-07-2010
WO 0205971 A1	24-01-2002	JP 3880518 B2 JP 2004506050 T TW 245793 B US 6517958 B1	14-02-2007 26-02-2004 21-12-2005 11-02-2003
WO 2006096399 A2	14-09-2006	CN 101495534 A DE 112006000531 T5 GB 2437899 A JP 2008531822 T KR 20070108392 A US 2009066224 A1	29-07-2009 17-01-2008 07-11-2007 14-08-2008 09-11-2007 12-03-2009
WO 2008071376 A1	19-06-2008	CN 101641321 A DE 102006059215 A1 EP 2118049 A1 US 2010094056 A1	03-02-2010 10-07-2008 18-11-2009 15-04-2010
JP 2001039933 A	13-02-2001	JP 4220624 B2	04-02-2009
US 6169163 B1	02-01-2001	CN 1376658 A CN 1192223 A DE 69608446 D1	30-10-2002 02-09-1998 21-06-2000
US 6169163 B1		DE 69608446 T2 EP 0842208 A1 JP 3865406 B2 JP 11510535 T JP 3970306 B2 JP 2006257094 A JP 2007224026 A TW 384295 B WO 9705184 A1	25-01-2001 20-05-1998 10-01-2007 14-09-1999 05-09-2007 28-09-2006 06-09-2007 11-03-2000 13-02-1997
US 2009023877 A1	22-01-2009	JP 2009024147 A	05-02-2009

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2010/025718

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 2008200736	A1	21-08-2008	JP	2008201716 A	04-09-2008
EP 2067767	A1	10-06-2009	CN	101575259 A	11-11-2009
			JP	2009185024 A	20-08-2009
			KR	20090058063 A	09-06-2009
			US	2009200926 A1	13-08-2009
US 2003039838	A1	27-02-2003	NONE		
US 2007257603	A1	08-11-2007	JP	2007204425 A	16-08-2007