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(54) **ELECTROLUMINESCENT MATERIALS COMPRISING FLUORENE DERIVATIVES**

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C07C 59/72	(2006.01)
C07D 403/14	(2006.01)
C07D 487/04	(2006.01)

(52) **U.S. Cl.**

CPC ***H01L 51/0069*** (2013.01); ***C07D 403/14*** (2013.01); ***C07D 471/22*** (2013.01); ***C07D 249/08*** (2013.01); ***C07D 487/04*** (2013.01); ***C07D 495/04*** (2013.01); ***C07D 333/16*** (2013.01); ***C07C 59/72*** (2013.01); ***C07C 43/215*** (2013.01); ***H01L 51/0067*** (2013.01); ***H01L 51/005*** (2013.01); ***H01L 51/0068*** (2013.01)

(57) **ABSTRACT**

OLED compounds of the general structure:

B-S-A-S-B

in which rod-like nuclei A comprise a condensed aromatic ring structure in turn comprising fluorene ring structures condensed with at least one additional fluorene ring structures wherein the fluorene ring systems comprised by the condensed aromatic structure are substituted at the 9-position, and in which the 9-positions of the fluorenes are not susceptible to oxidation.

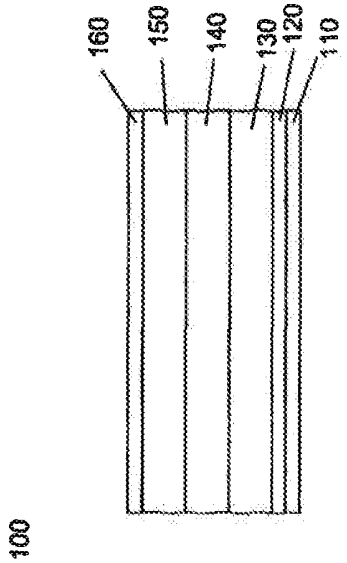


Figure 1

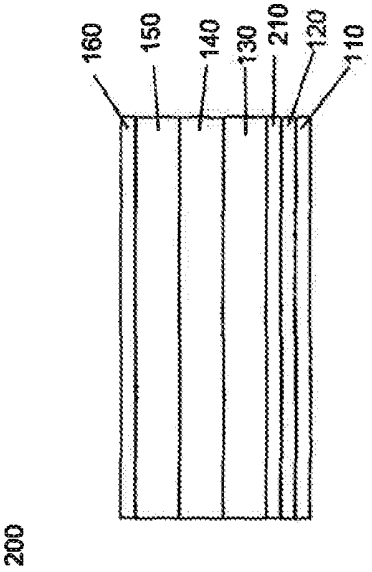


Figure 2

ELECTROLUMINESCENT MATERIALS COMPRISING FLUORENE DERIVATIVES

[0001] This invention relates to electroluminescent materials.

[0002] It is known that some reactive mesogens (liquid crystalline materials capable of being chemically crosslinked into a polymer matrix) of the general formula:

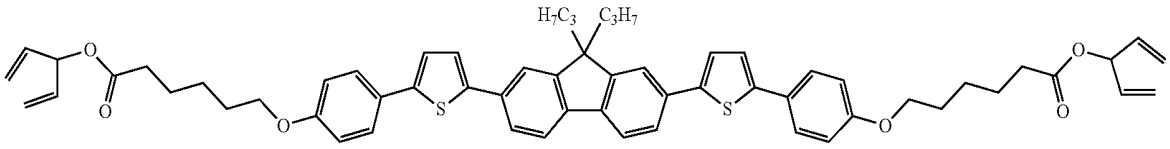
B-S-A-S-B

where A represents a linear aromatic molecular core, S represents flexible spacer units and B represents crosslinking groups such as methacrylate groups, may be useful in the fabrication of organic electronic devices. This is particularly the case if B represents photocrosslinkable groups, since then the materials function essentially as photoresists, which is to say, thin layers of these materials may be patterned into useful electronic structures by patterned exposure to light, particularly UV light.

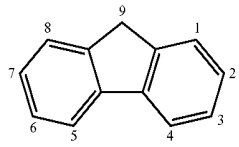
[0003] Further, if the linear aromatic core A is luminescent in nature, these reactive mesogen materials may be patterned into the active light emitting layers in electroluminescent devices such as organic light emitting diodes (OLEDS) and organic diode lasers.

[0004] One example of such a material is represented by the structure:

Structure 1



[0005] Here, the core aromatic structure A is a fluorene ring system:



substituted at the 2 and 7 ring positions with aromatic (phenylthienyl) groups and at the two 9 positions with alkyl groups (in this case, n-propyl groups). The B groups are penta-1,4-diene-3-yl groups useful for crosslinking the materials.

[0006] All working OLED devices produced to date of materials of the general structure

B-S-A-S-B

in which A contained 9,9-dialkylfluorene structures have had disappointingly low lifetimes.

[0007] The present invention provides materials of that general structure that have commercially useful lifetimes.

[0008] The invention comprises OLED compounds of the general structure:

B-S-A-S-B

in which rod-like nuclei A comprise a condensed aromatic ring structure in turn comprising fluorene ring structures condensed with at least one additional fluorene ring structures wherein the fluorene ring systems comprised by the condensed aromatic structure are substituted at the 9-position, and in which the 9-positions of the fluorenes are not susceptible to oxidation.

[0009] There are preferably no hydrogens α to the 9-position of the fluorene ring system or any of the fluorene ring systems.

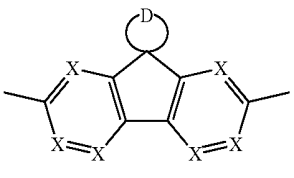
[0010] The additional fluorine ring systems may comprise benzene, naphthalene, indene, or other fluorene ring systems.

[0011] In these materials S may represent a flexible spacer comprising a chain of single bonded atoms. The chain may comprise an alkyl chain. The alkyl chain may contain one or more hetero atoms.

[0012] B may represent a crosslinking chemical group, which may be a methacrylate group, a 1,4-pentadien-3-yl group, an ethacrylate group, a vinyloxy group, an alkylvinyloxy group, an ethylmaleato group, an ethylfumarato group, an N-maleimido group, a vinylmaleato group, a vinylfumarato group, or a N-(2-vinyloxymaleimido) group.

[0013] A may represent a substantially linear, covalently bonded chain, which may be a chain of aromatic or heteroaromatic diradicals represented by the general formula:

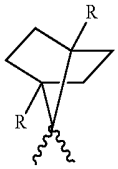
Wherein the Ar may each be independently chosen from an aromatic or heteroaromatic diradical, and may comprise a 1,4-phenylene, a biphenyl-4,4'-diyl, a terphen-4,4"-diyl, a naphthalene-1,4-diyl, a thiophene-2,5-diyl, a pyrimidine-2,5-diyl, a perylene-3,10-diyl, a pyrene-2,7-diyl, a 2,2'-dithiophen-5,5'-diyl, an oxazole-2,5-diyl, a thieno[3,2-b]thiophene-2,5-diyl, a dithieno[3,2-b:2',3'-d]thiophene-2,6-diyl, a thiazolo[5,4-d]thiazole-2,5-diyl, an oxazolo[5,4-d]oxazole-2,5-diyl, a thiazolo[5,4-d]oxazole-2,5-diyl, a thiazolo[4,5-d]thiazole-2,5-diyl, an oxazolo[4,5-d]oxazole-2,5-diyl, a thiazolo[4,5-d]oxazole-2,5-diyl, 2,1,3-benzothiadiazol-4,7-diyl, or an imidazo[4,5-d]imidazole-2,5-diyl diradical, a single bond, a diradical with the formula:



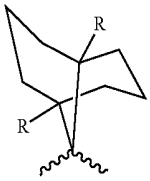
wherein the substituent

may be independently selected for each occurrence of this structure from one of the following spiro or bicyclospiro groups:

Structure 10



Structure 11



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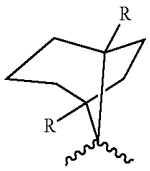

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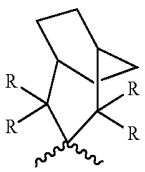

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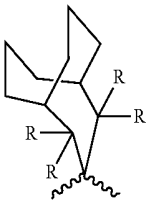

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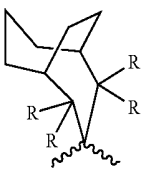
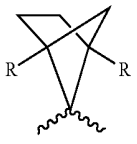


Structure 16



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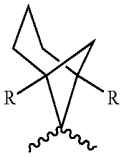
Structure 17



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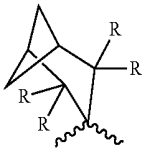

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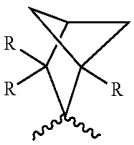

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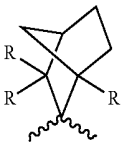

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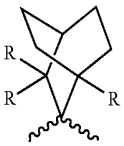

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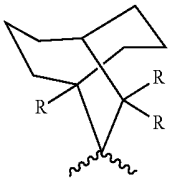

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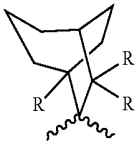

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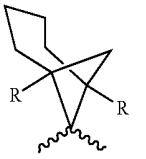
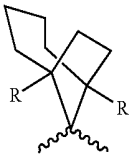


Structure 19



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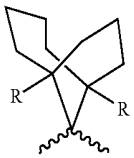
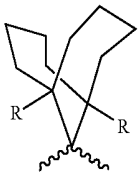
Structure 20



Structure 21



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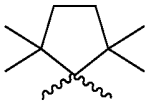

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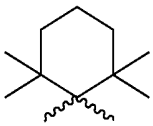

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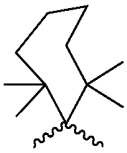

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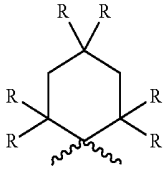
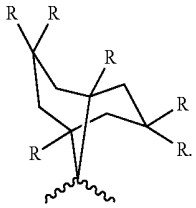


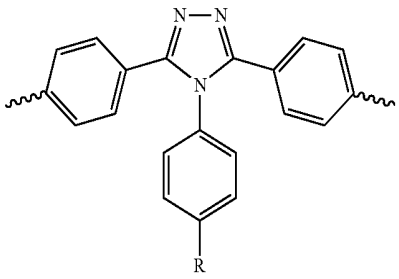
Structure 26



[0014] In these spirobicyclo and spiro substituents R is an alkyl group and may be chosen from methyl, ethyl, propyl, butyl, isopropyl, sec-butyl, isobutyl, tert-butyl, 2-amyl, 3-amyl, 2-methyl-2-butyl, 3-methyl-3-amyl, 3-ethyl-3-amyl, or neo-pentyl, and X may be independently selected from ═CH—, ═N—.

[0015] Ar may also be selected from the diradicals:

Structure 27



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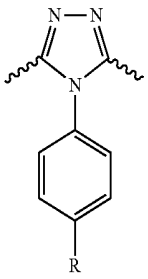
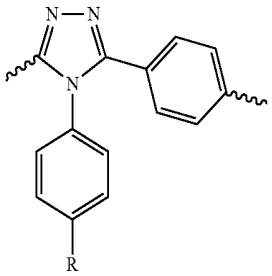


Structure 29



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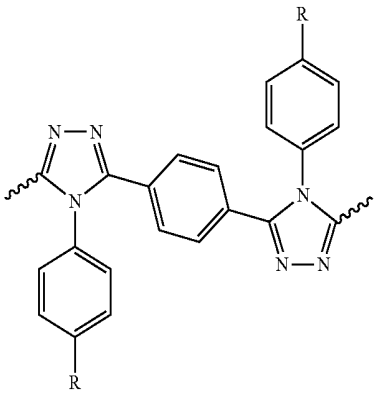

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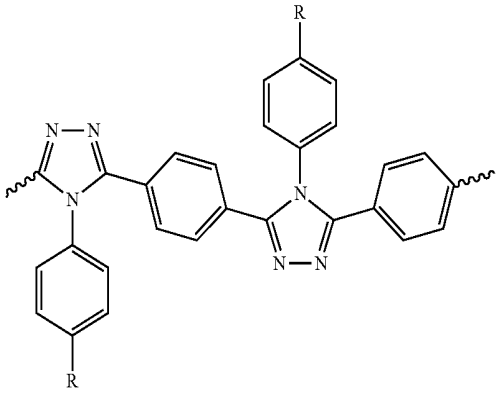

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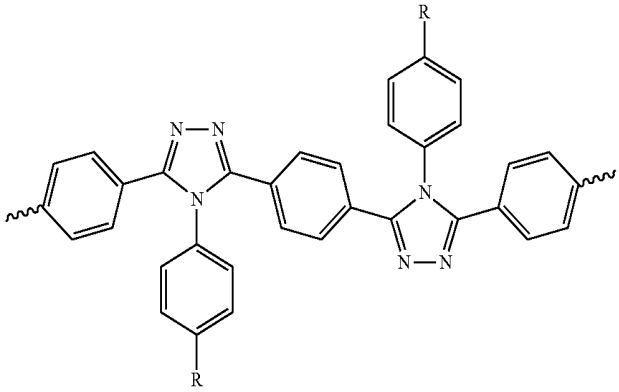

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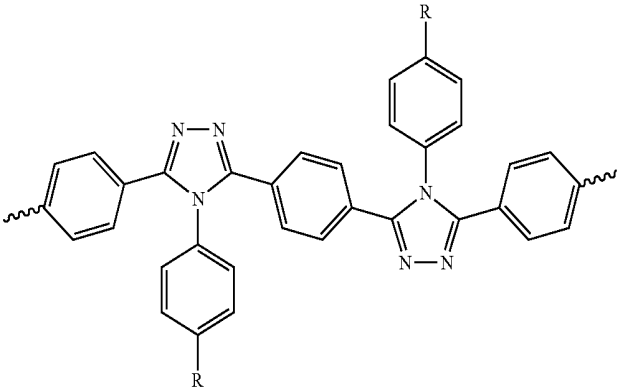

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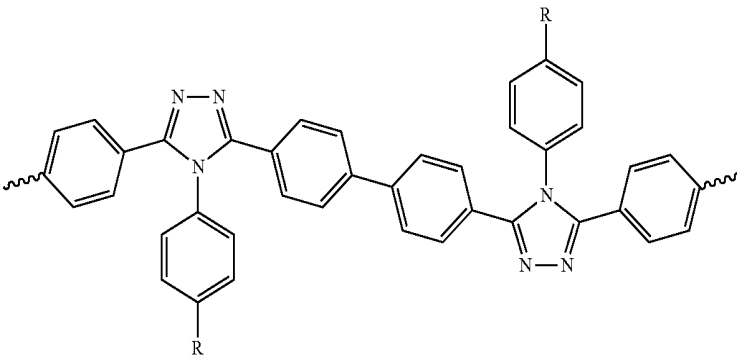

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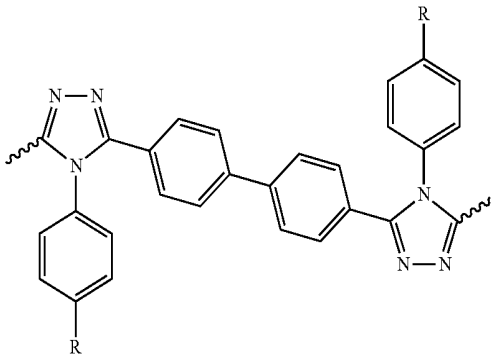

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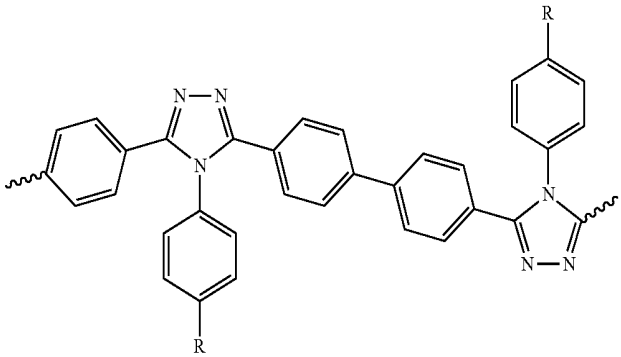

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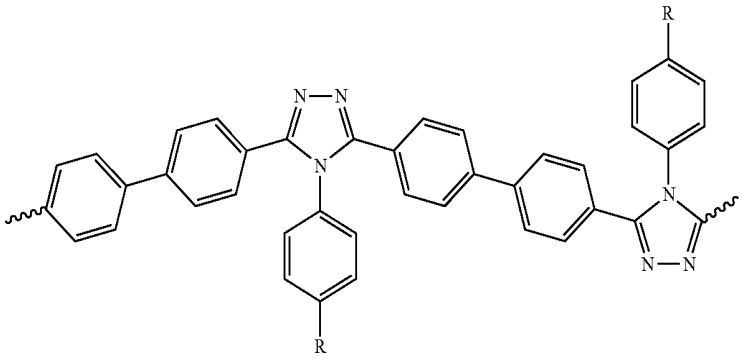

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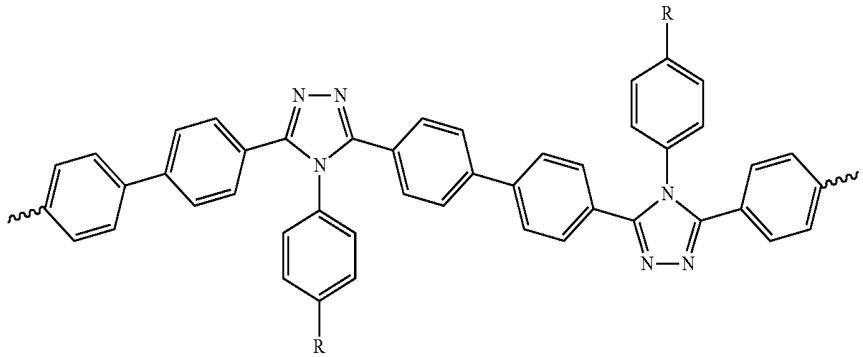

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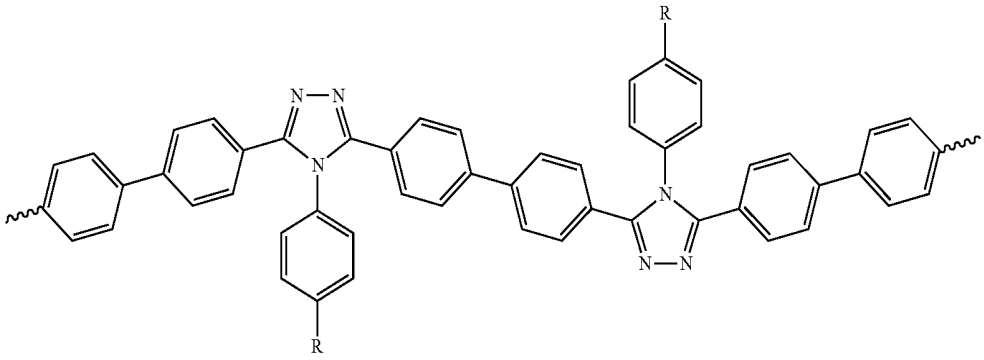

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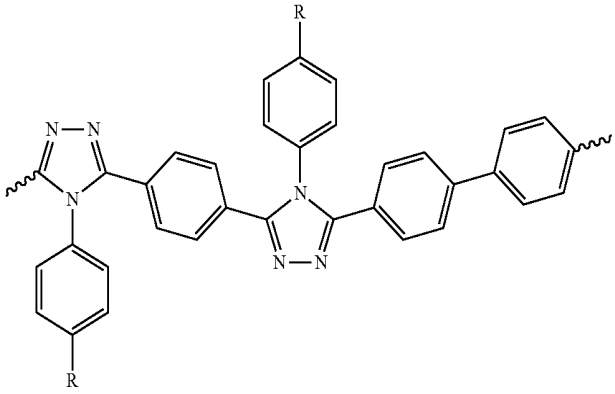

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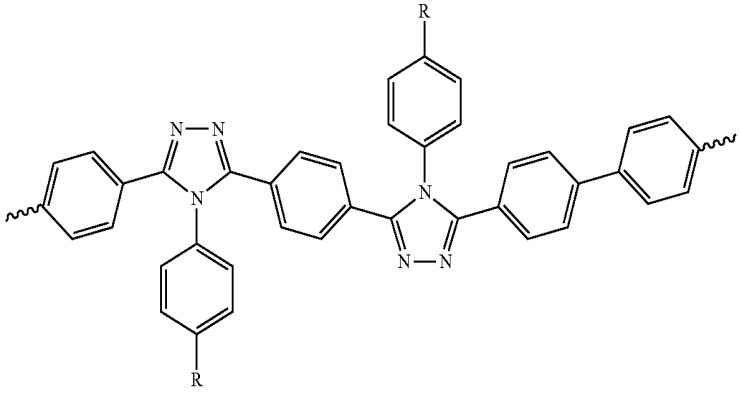

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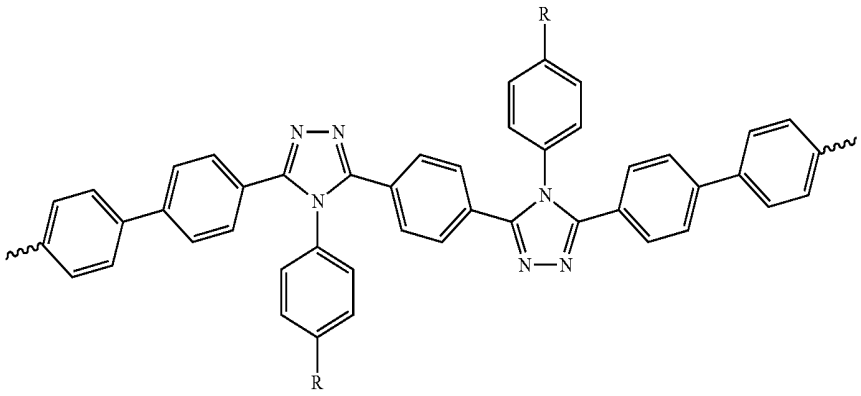

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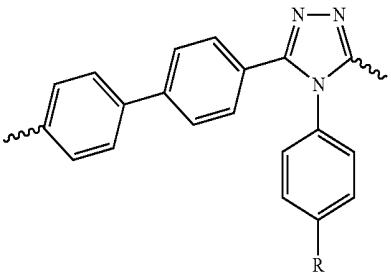
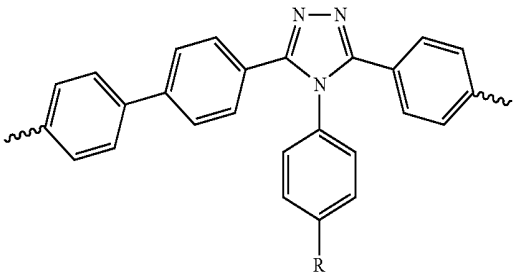
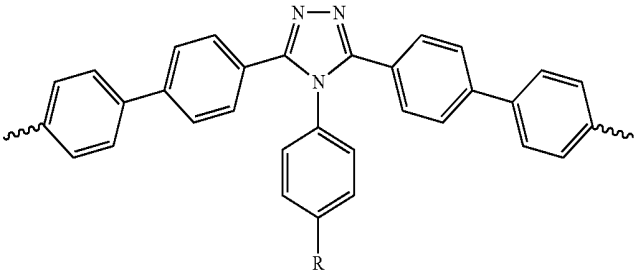
Structure 42



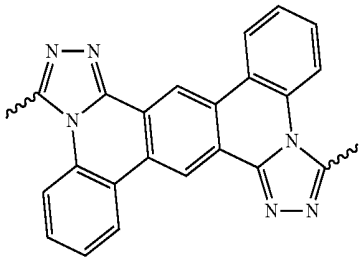
Structure 43



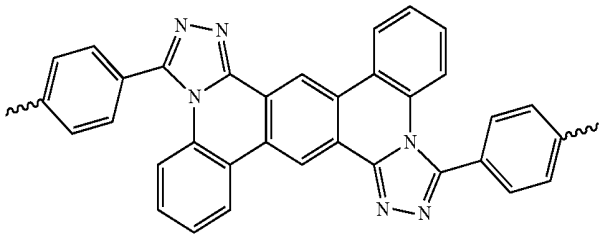
Structure 44



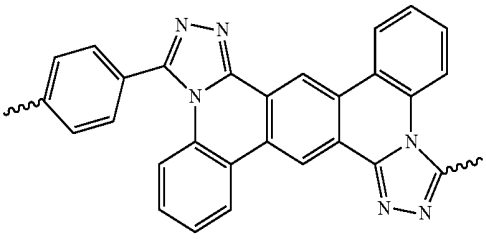
Structure 45



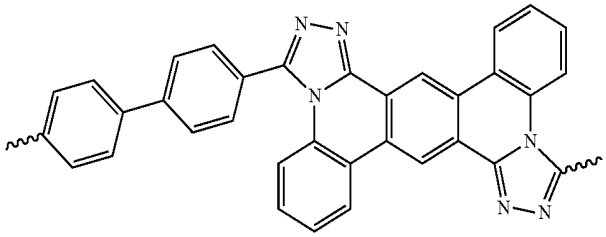
Structure 46



Structure 47



Structure 48



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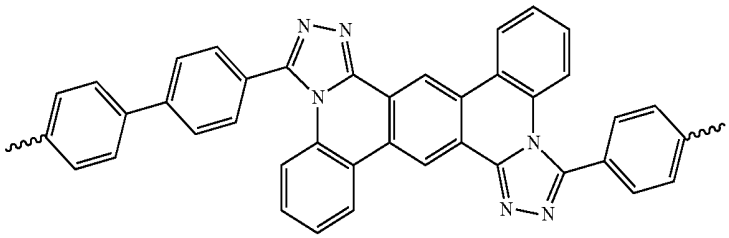
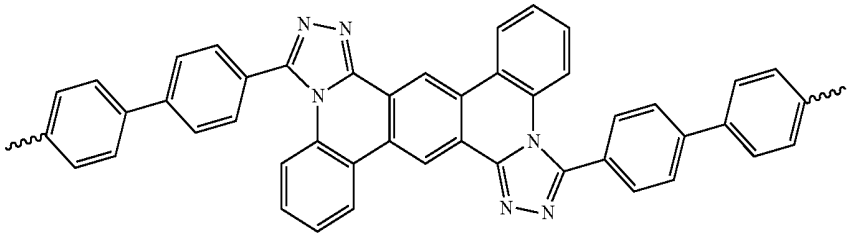
Structure 49

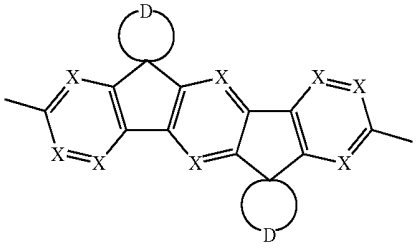


Structure 50

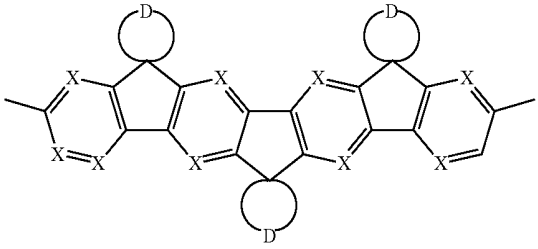


wherein each Fl may be independently chosen from:

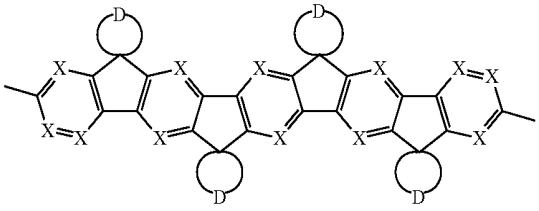
Structure 1



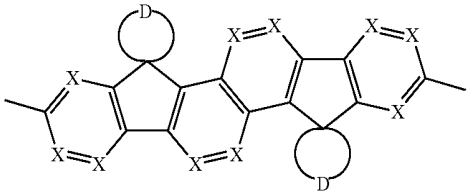
Structure 2



Structure 3



Structure 4



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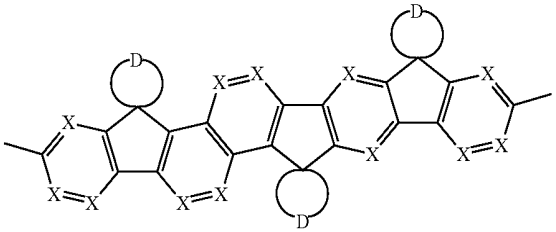
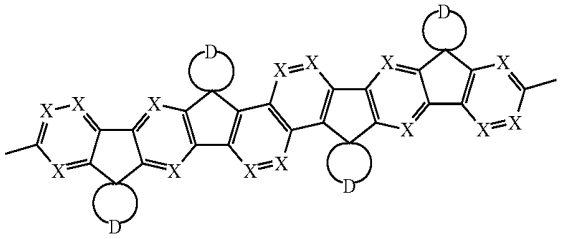
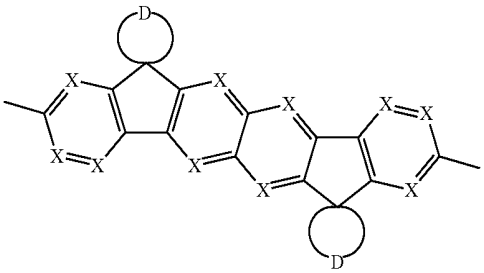
Structure 5



Structure 6



Structure 7



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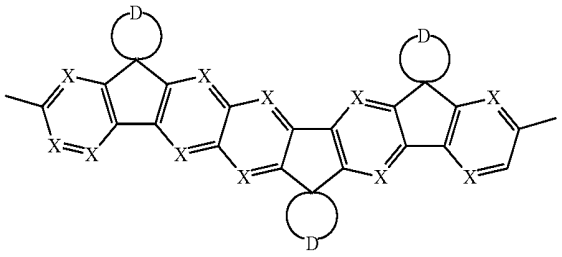
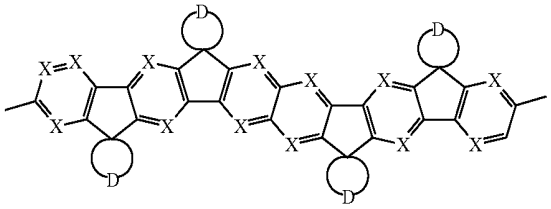
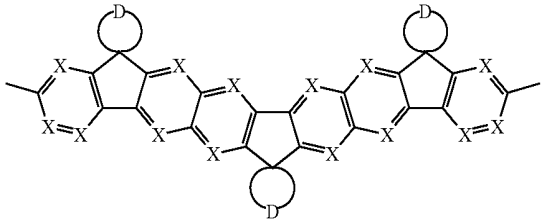
Structure 7



Structure 8



Structure 9



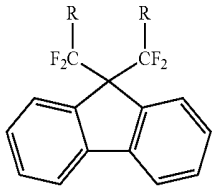
wherein the substituents

may independently be one of structures 10 through 26 from above.

[0016] In these spirobicyclo and spiro materials R is an alkyl group and may be chosen from methyl, ethyl, propyl, butyl, isopropyl, sec-butyl, isobutyl, tert-butyl, 2-amyl, 3-amyl, 2-methyl-2-butyl, 3-methyl-3-amyl, 3-ethyl-3-amyl, or neo-pentyl.

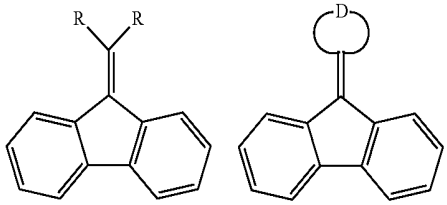
[0017] Preferably, the n subscript in the formula for A may be between 1 and 6 and preferably is from 3 to 6 and X may be chosen from ═CH— or ═N—.

[0018] While the spiro and spirobicyclo structures shown above are preferred other substituents that meet this criterion are possible. For instance, one or more of the fluorene ring residues in the condensed aromatic ring system may be substituted as shown below:



wherein R is fluoro (yielding trifluoromethyl substituents), branched, cyclo, or straight chained alkyl groups, alkyl groups substituted with some number of fluorine groups or alkyl groups in which one or more carbons are substituted with hetero atoms.

[0019] Alternatively, one or more of the fluorene ring residues in the condensed aromatic ring system may be substituted as shown in the two examples shown below:

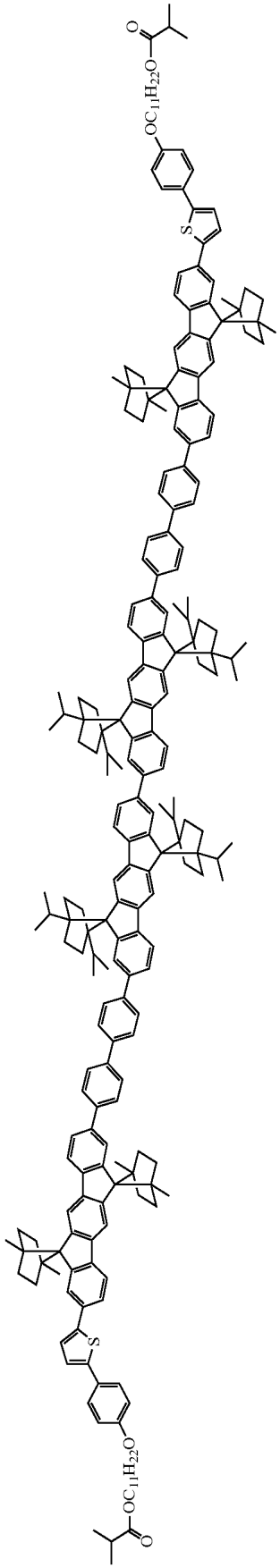


wherein R is alkyl, fluorene substituted alkyl, branched alkyl, cycloalkyl, or alkyl in which one or more carbons are substituted by hetero atoms, and

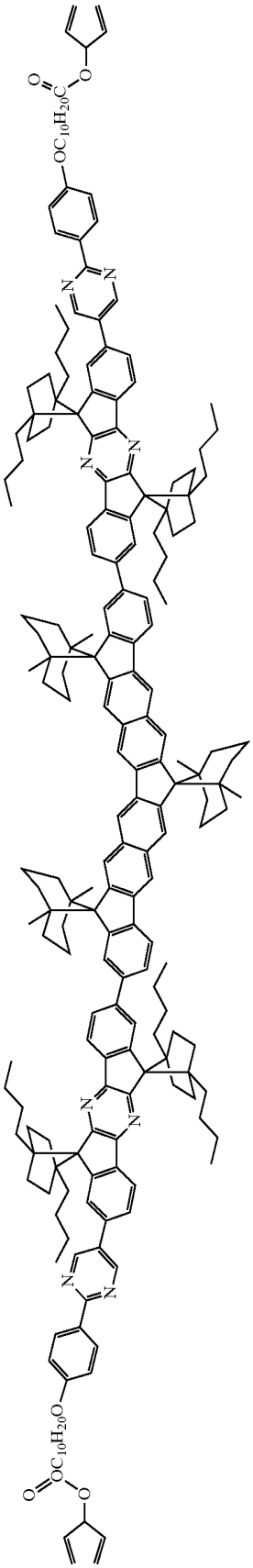
has the same meaning as the examples shown above.

[0020] Example structures of these materials of the invention are:

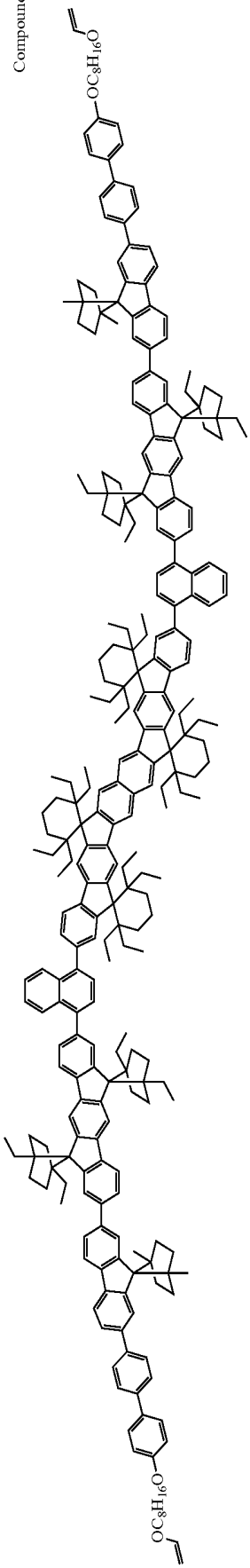
Compound 1



Compound 2



Compound 3



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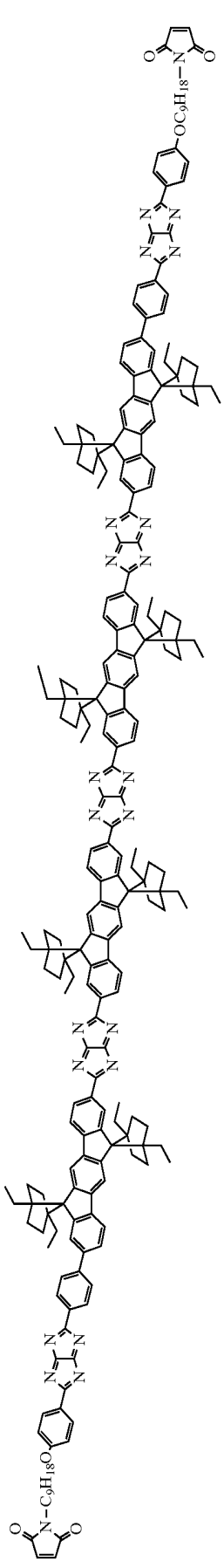
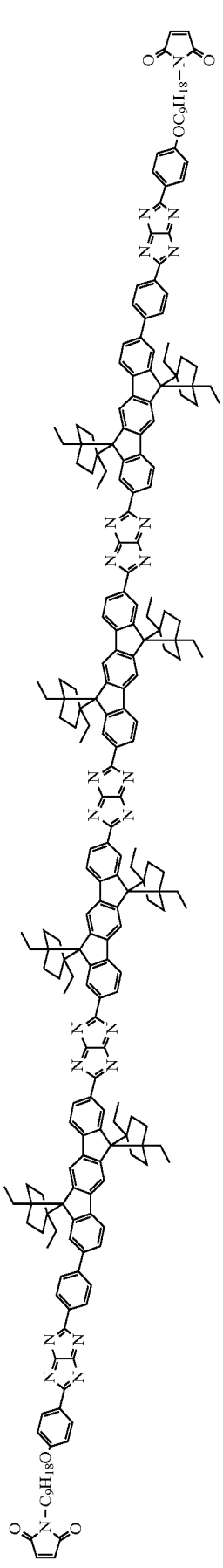
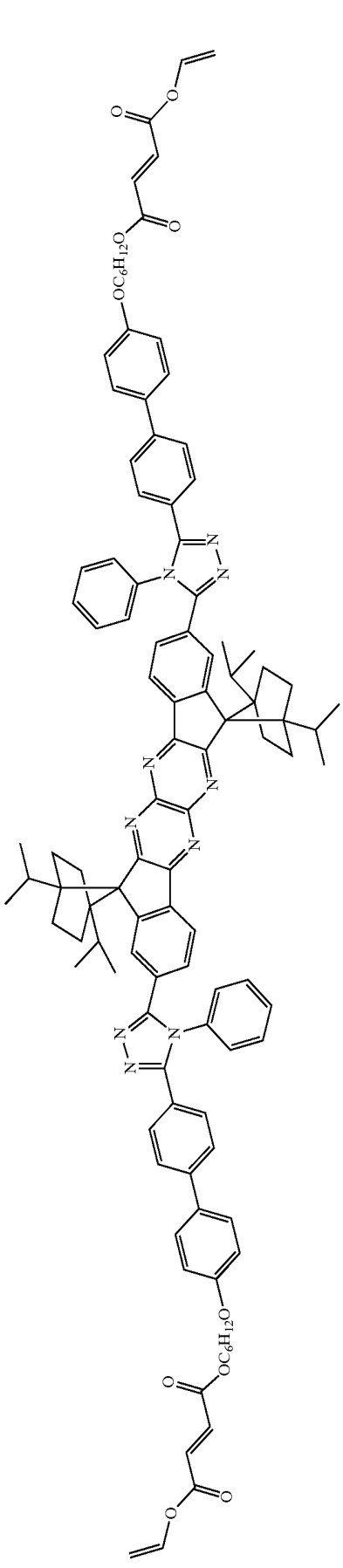
Compound 4



Compound 5

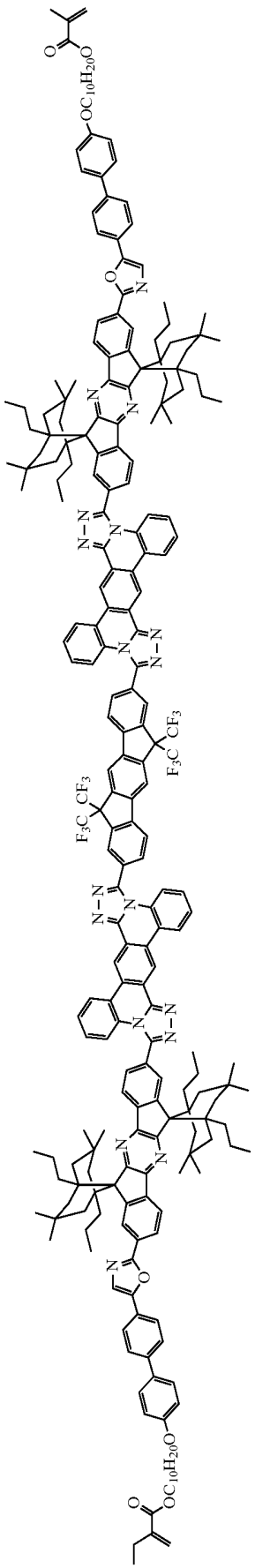


Compound 6

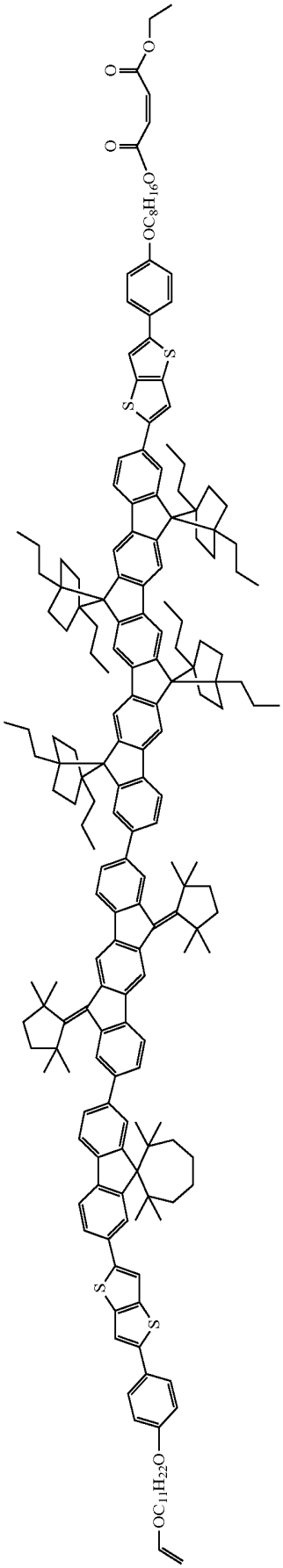


-continued

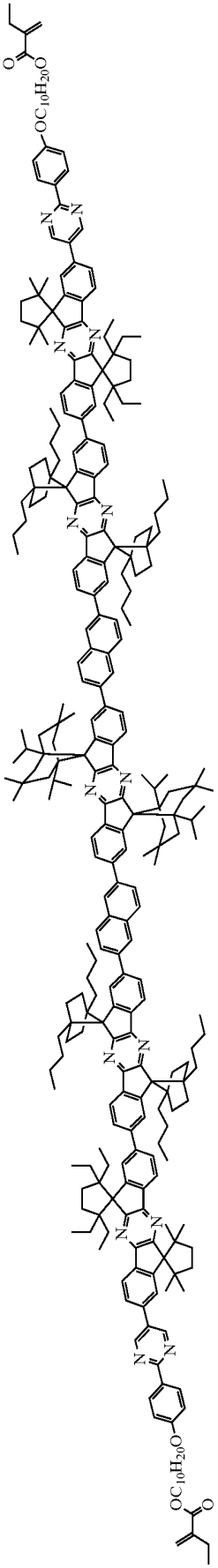
Compound 7



Compound 8



Compound 9



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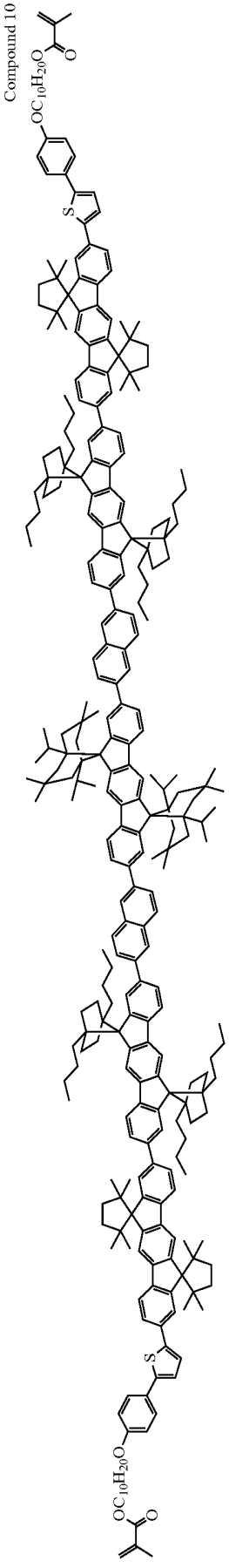
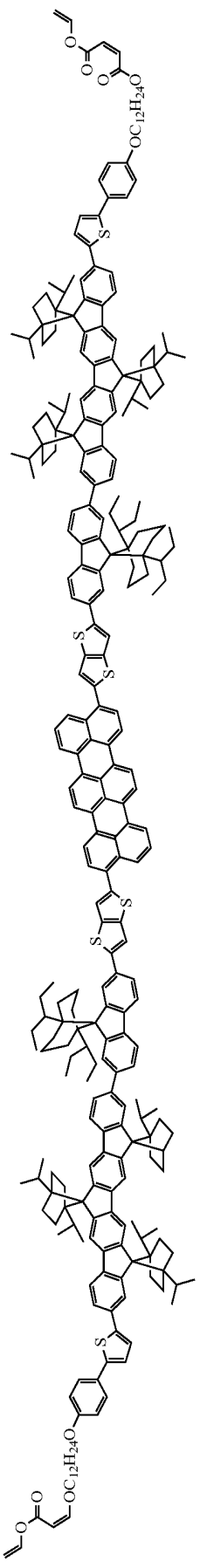
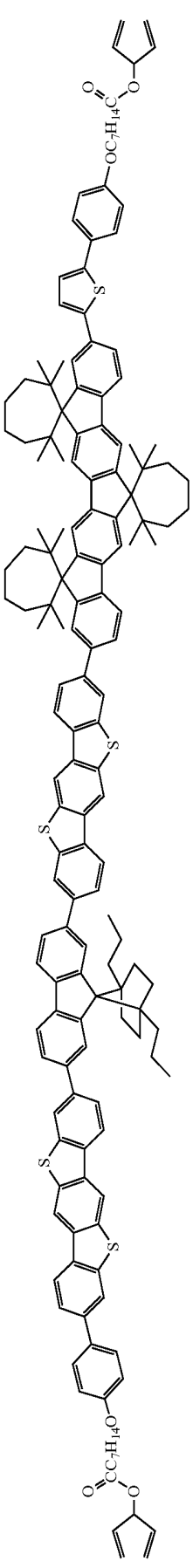
Compound 10



Compound 11



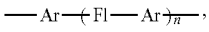
Compound 12



[0021] The invention also comprises a light emitting or charge transporting material of the general structure:

S-A-S,

wherein A is a substantially rigid, rod-shaped molecular core comprising a chain of aromatic or heteroaromatic diradicals represented by the general formula:



wherein Fl comprises a fluorene-2,7-diyl diradical spiro substituted at the 9 position on the fluorene ring with an alicyclic ring system, wherein the alicyclic substituent has no hydrogen substituted on the two carbon atoms immediately adjacent the carbon atom at position **9** in the fluorene ring system, wherein Ar is chosen independently from aromatic or heteroaromatic diradicals or single bonds, and wherein S are flexible spacer units.

[0022] The material may be liquid crystalline.

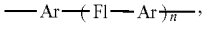
[0023] 'n' may be between 1 and 10.

[0024] The material may be a polymer.

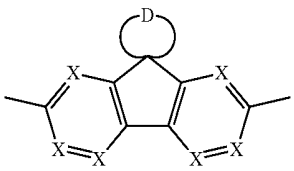
[0025] The invention also comprises a light emitting or charge transporting polymer of the general structure:

T-A-T,

wherein A is a substantially linear, covalently bonded chain comprising a chain of aromatic or heteroaromatic diradicals represented by the general formula:



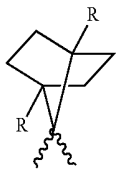
Wherein the Ar may each be independently chosen from an aromatic or heteroaromatic diradical, and may comprise a 1,4-phenylene, a biphenyl-4,4'-diyl, a terphen-4,4"-diyl, a naphthalene-1,4-diyl, a thiophene-2,5-diyl, a pyrimidine-2,5-diyl, a perylene-3,10-diyl, a pyrene-2,7-diyl, a 2,2'-dithiophen-5,5'-diyl, an oxazole-2,5-diyl, a thieno[3,2-1)] thiophene-2,5-diyl, a dithieno[3,2-b:2',3'-d]thiophene-2,6-diyl, a thiazolo[5,4-d]thiazole-2,5-diyl, an oxazolo[5,4-d] oxazole-2,5-diyl, a thiazolo[5,4-d]oxazole-2,5-diyl, a thiazolo[4,5-d]thiazole-2,5-diyl, an oxazolo[4,5-d]oxazole-2,5-diyl, a thiazolo[4,5-d]oxazole-2,5-diyl, 2,1,3-benzothiadiazol-4,7-diyl, or an imidazo[4,5-d]imidazole-2,5-diyl diradical, a single bond, a diradical with the formula:



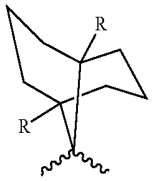
wherein the substituent

may be independently selected for each occurrence of this structure from one of the following spiro or bicyclospiro groups:

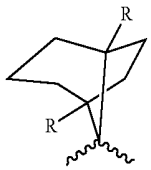
Structure 10



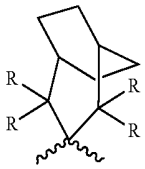
Structure 11



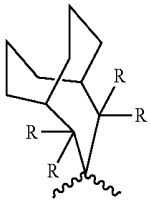
Structure 12



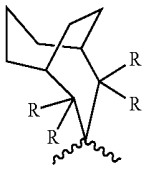
Structure 13



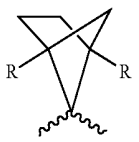
Structure 14



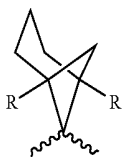
Structure 15



Structure 16



Structure 17



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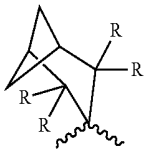
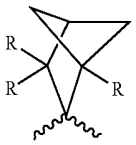
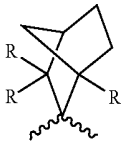
Structure 18



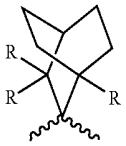
Structure 19



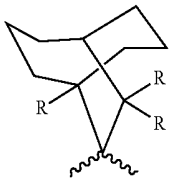
Structure 20



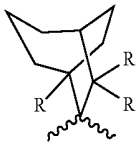
Structure 21



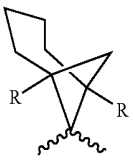
Structure 16



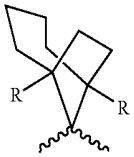
Structure 17



Structure 18



Structure 19



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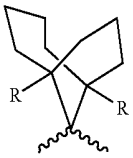
Structure 20



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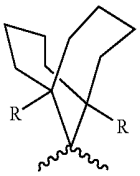

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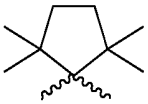

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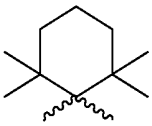

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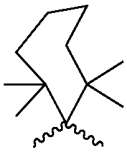

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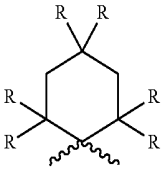

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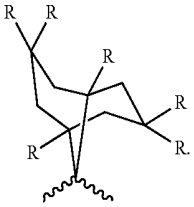
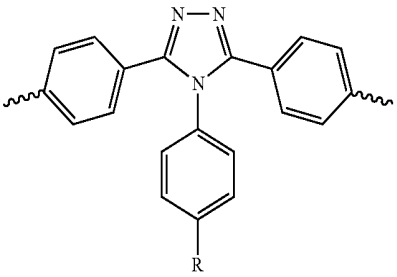


[0026] In these spirobicyclo and spiro substituents R is an alkyl group and may be chosen from methyl, ethyl, propyl, butyl, isopropyl, sec-butyl, isobutyl, tert-butyl, 2-amyl, 3-amyl, 2-methyl-2-butyl, 3-methyl-3-amyl, 3-ethyl-3-amyl, or neo-pentyl, and X may be independently selected from ═CH—, ═N—.

[0027] Ar may also be selected from the diradicals:

Structure 27



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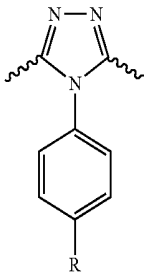

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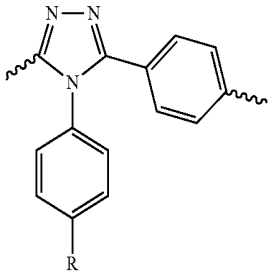

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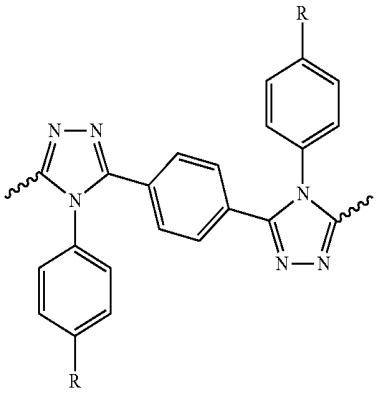

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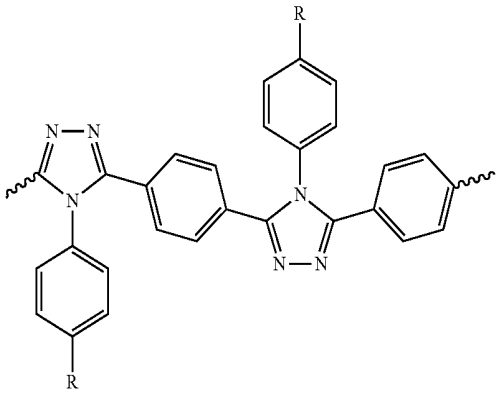

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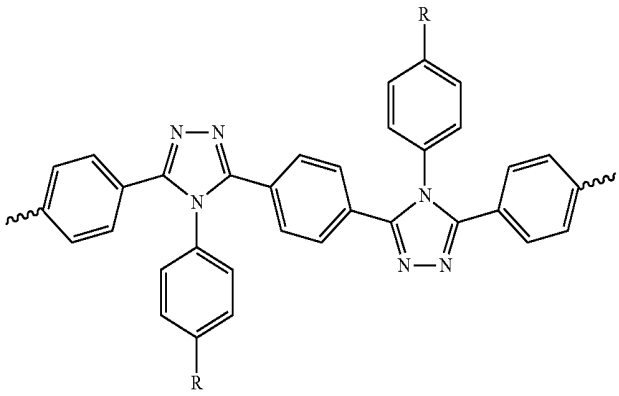

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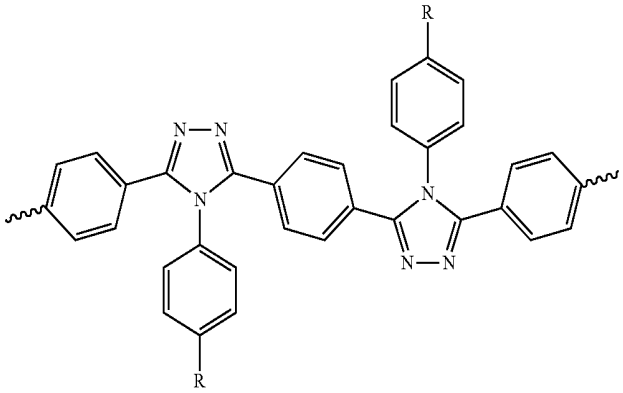

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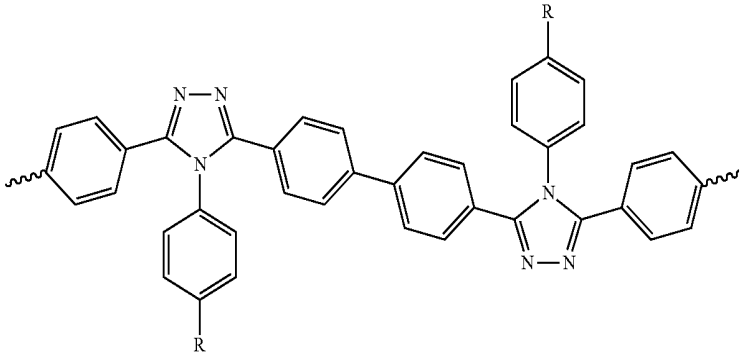

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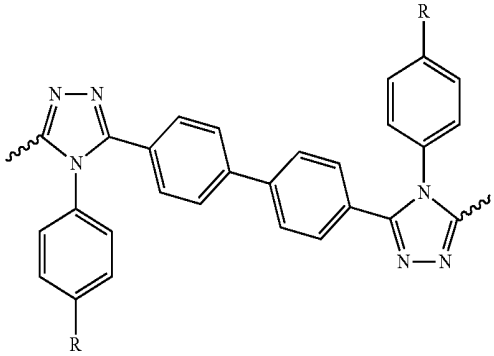

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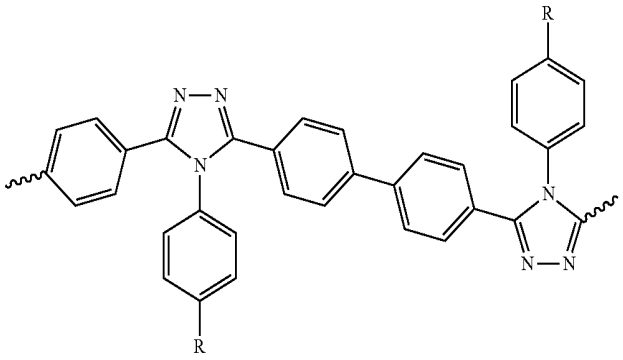

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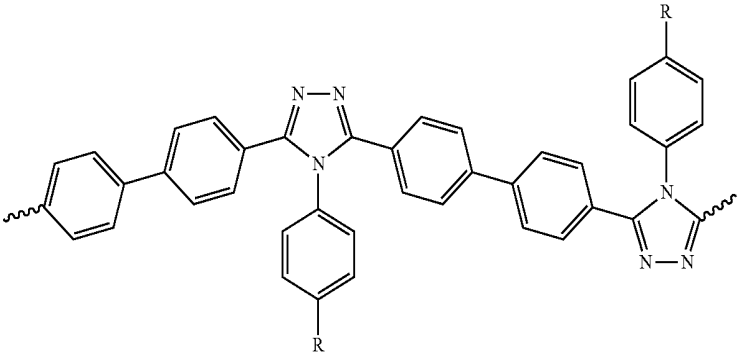

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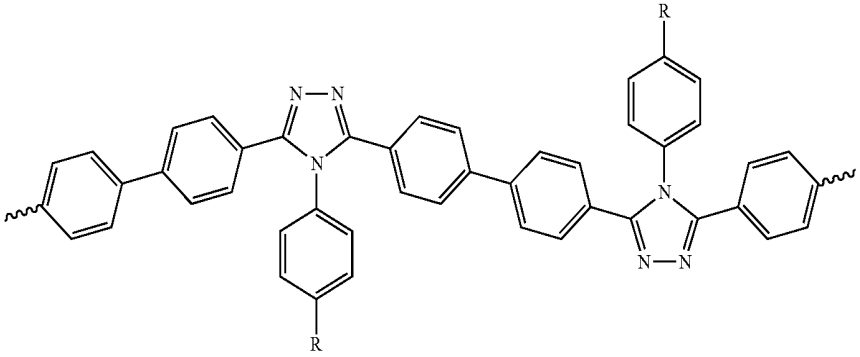

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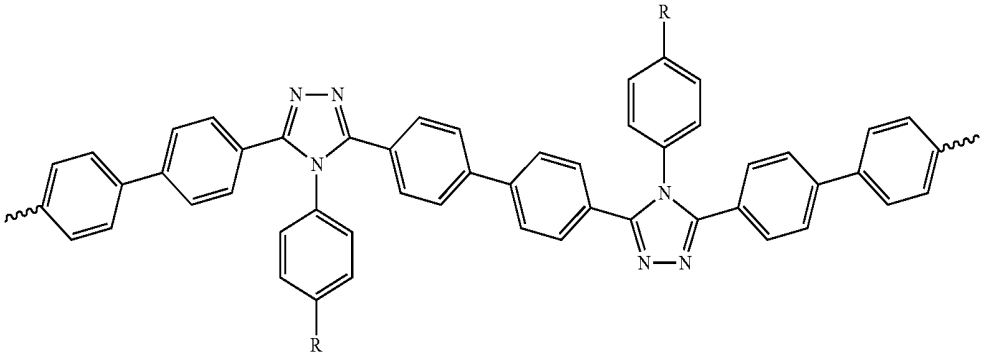

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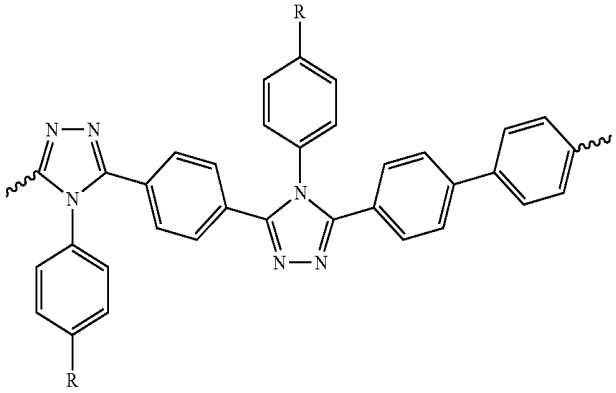

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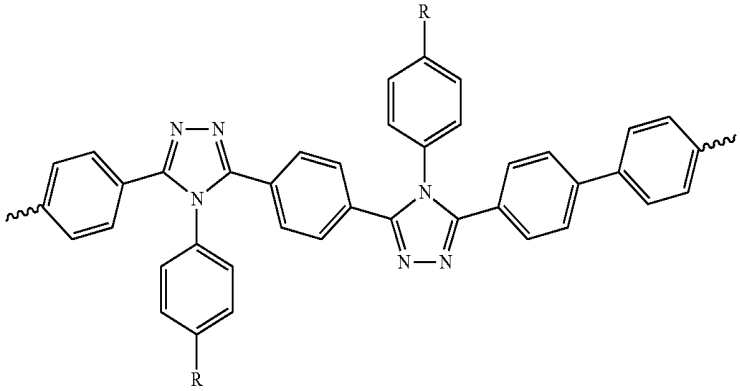

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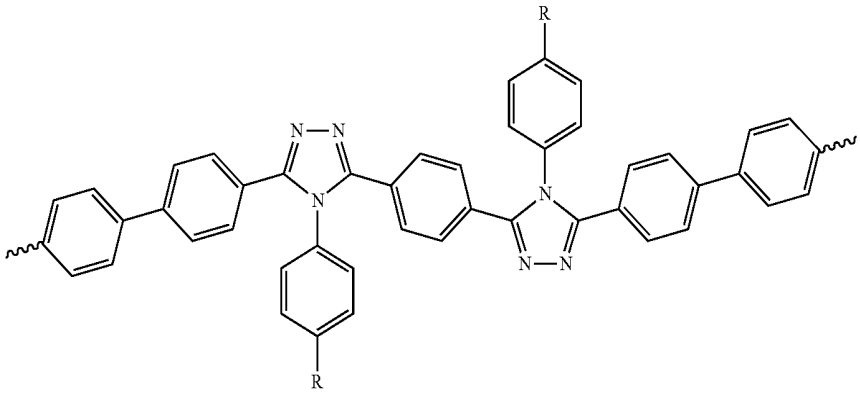

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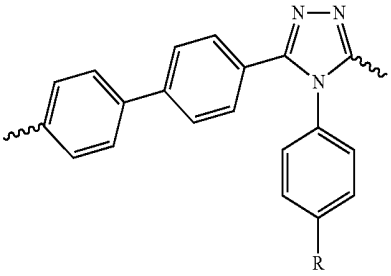

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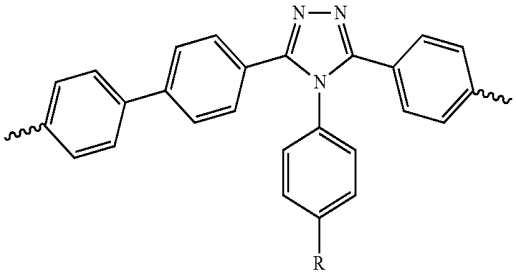

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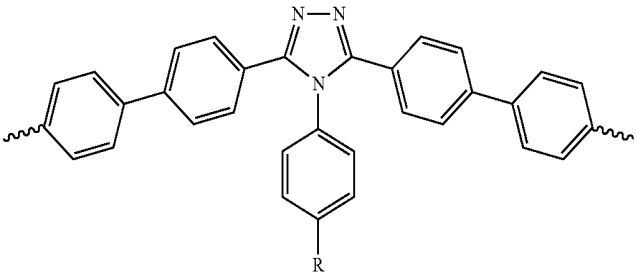

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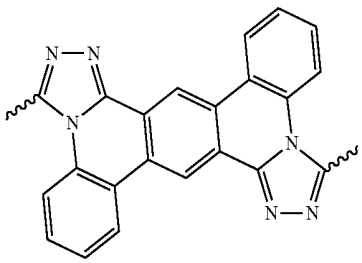

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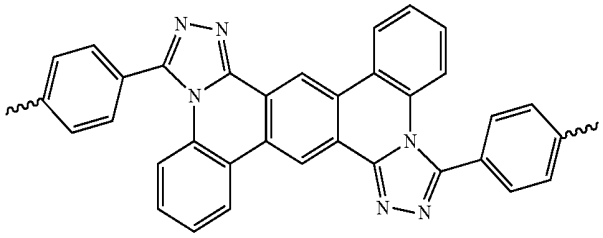

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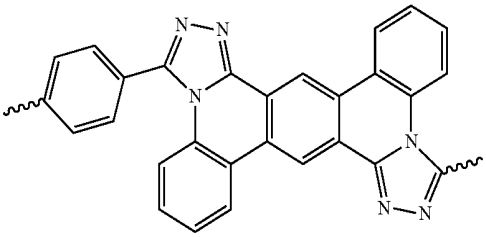

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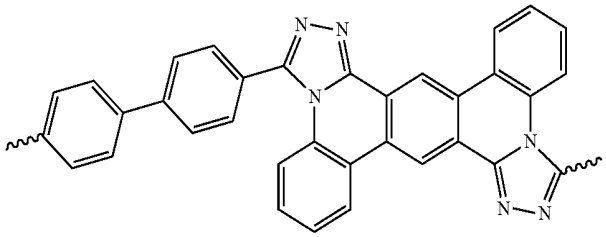

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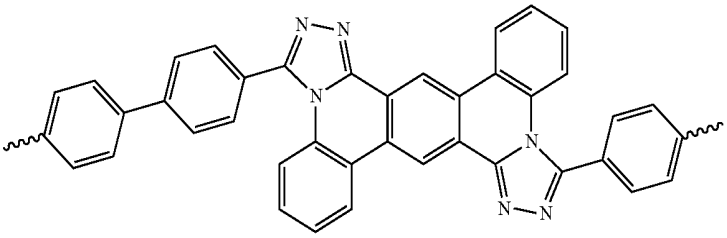

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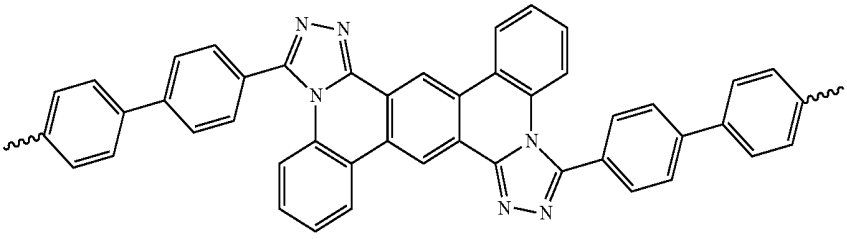

wherein each Fl may be independently chosen from:

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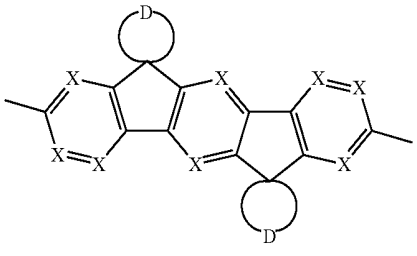
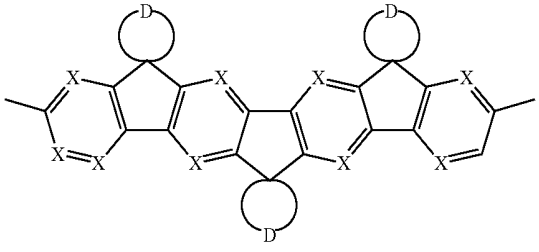
Structure 1



Structure 2



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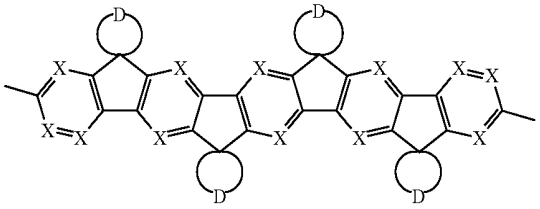

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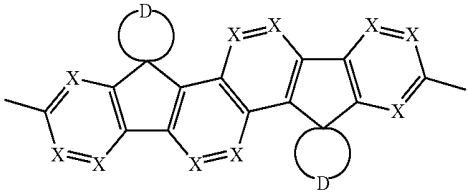

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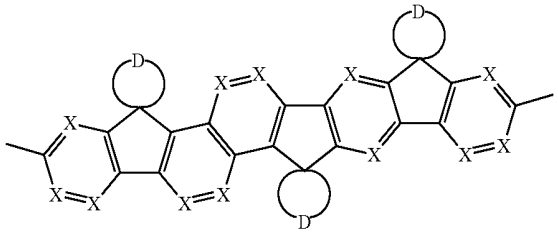

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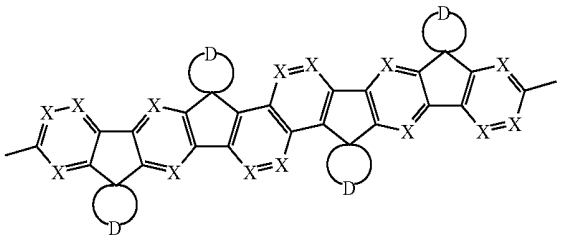

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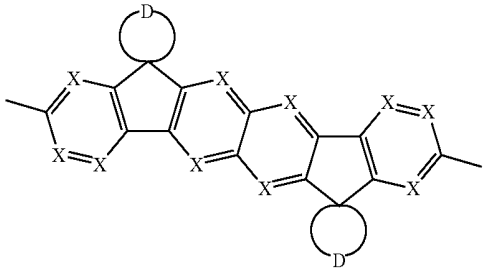
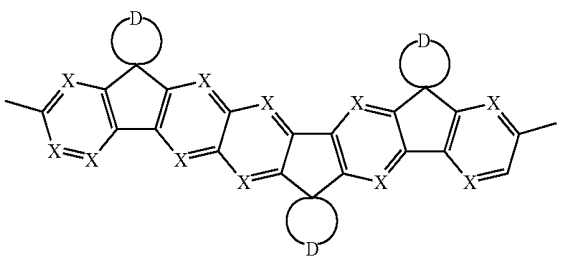


Structure 7



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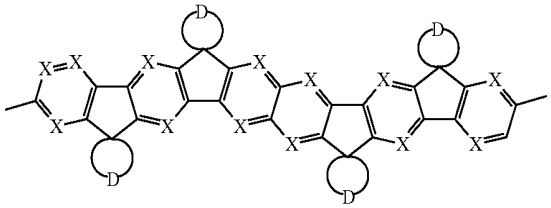
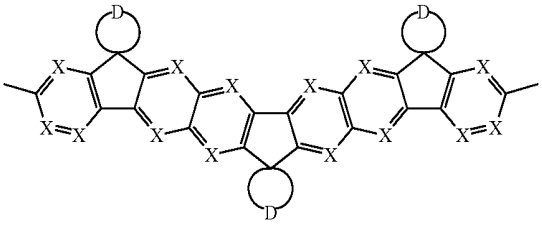
Structure 8



Structure 9



wherein the substituents

may independently be one of structures 10 through 26 from above.

[0028] In these spirobicyclo and spiro materials R is an alkyl group and may be chosen from methyl, ethyl, propyl, butyl, isopropyl, sec-butyl, isobutyl, tert-butyl, 2-amyl, 3-amyl, 2-methyl-2-butyl, 3-methyl-3-amyl, 3-ethyl-3-amyl, or neo-pentyl.

[0029] Preferably, the n subscript in the formula for A may be between 1 and 6 and preferably is from 3 to 6 and X may be chosen from ═CH— or ═N—.

[0030] and wherein T are polymer chain terminating units.

[0031] T may be independently selected from hydrogen, halogen, aryl, or aryl substituted with a cyano, hydroxyl, glycidyl ether, acrylate ester, methacrylate ester, ethenyl, ethynyl, maleimide, nadimide, trialkylsiloxy, or trifluorovinyl ether moieties.

[0032] Three-dimensional models of the materials described above show them to be no more bulky than similar material in which the fluorene 9-positions are substituted with straight chain alkyl groups. Therefore, the nematic phase in these materials should be just as stable as in the previous materials.

[0033] The preferred embodiment of the above materials is one in which all of the R groups are alkyls. This is because these materials have no hydrogen substituents α to the fluorene ring system. Hydrogens in these positions are at least partially benzylic in character and are thought to be implicated in oxidation at the nine position. Also, in these preferred completely alkyl-substituted materials the 9-position has the greatest steric shielding from attack by reactive species.

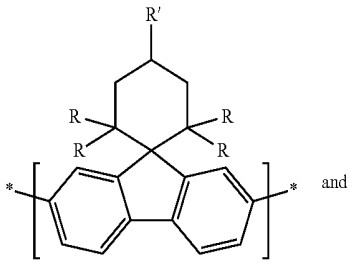
[0034] It is also preferable that the spiro[cyclopentane-1,9'-fluorene]-2',7'diyl (Structure 22), spiro[cyclohexane-1,9'-fluorene]-2',7'diyl (Structure 23), spiro[cycloheptane-1,9'-fluorene]-2',7'diyl (Structure 24), spiro[bicyclo[2,2,1]heptane-7,9'-fluorene]-2',7'diyl (Structure 10), or spiro[bicyclo[3,3,1]nonane-9,9'-fluorene]-2',7'diyl (Structure 11)

diradicals are chosen as the Fl units in the general formula of the invention because of their symmetry and ease of synthesis.

[0035] Still further, it is preferable that all the R substituents are the same. This is because molecules in which the R substituents are different will show positional or stereoisomerism that will complicate the electronic level purification required for these materials.

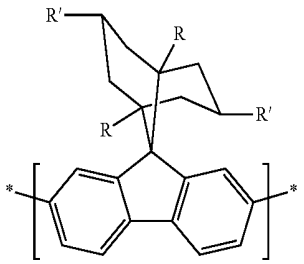
[0036] The compounds of the invention containing diradicals Fl with structures 10 through 26 may be further substituted at positions (other than those that are substituted already with R groups) on the cycloaliphatic and bicycloaliphatic rings that are joined to the fluorene ring structures at their 9-positions. However, compounds with substituents at these other positions are less preferred because of the potential for geometrical or stereoisomerism that will complicate their purification. An exception is that compounds with structures

Structure 23



and

Structure 24



wherein R is as above and R' are preferably selected from alkyls ranging from CH_3— to C_5H_{11}— in chain length, are useful.

[0037] Emitter materials of the invention in which the n subscript in the formula for A is equal to between 3 and 6 are preferred. Lower n values lead to molecules with lower light emission efficiency. Higher n values lead to molecules that are more difficult to synthesise and/or more difficult to purify.

[0038] Materials according to this invention may be mixed together to form liquid crystalline mixtures. This can be very advantageous from the standpoint of optimising the properties of the materials. For instance, individual compounds of the invention may have liquid crystal to isotropic liquid transition temperature far below their melting points (monotropic liquid crystalline phases). In device fabrication applications this can lead to glassy or supercooled liquid films of the materials that are sufficiently thermodynamically unstable so as to lead to the danger of crystallisation within the film and subsequent destruction of useful electronic properties. Mixing multiple component compounds together can depress the melting point of the resulting mixtures below the liquid crystal to isotropic liquid transition temperatures or at least sufficiently suppress crystallisation so as to eliminate this problem.

[0039] Another advantage of using mixtures of the materials of the invention is that it may allow materials with otherwise highly useful device application properties to be used even though they a have a particular property that renders them unusable as a pure material. For instance it may be desired to prepare a light emitting polymer film having a nematic liquid crystalline structure. A compound of the invention may be a light emitting material of very high efficiency and possess other useful properties, but at the same time may be found to possess a smectic rather than a nematic liquid crystalline phase. By dissolving said desirable compound into a mixture of other compounds of the invention that have nematic phases, a mixture having the light emission properties of the first highly desirable material combined with a nematic phase structure may result.

[0040] It is often also desirable to reduce the self-absorption of emitted light by organic luminescent materials. This self-absorption occurs because the spectral absorbance and emission bands of organic luminescent materials overlap to a greater or lesser extent in various materials. A solution to this problem well known, for instance, in the field of dye lasers is to dissolve the luminescent material in a host with that absorbs light at a shorter wavelength than the luminescent solute. If the solution is dilute, for instance one to two percent, the self-absorption of the luminescent solute is nearly completely suppressed. The facile mutual miscibility of the various compounds of this invention makes the preparation of solutions of this type very easy.

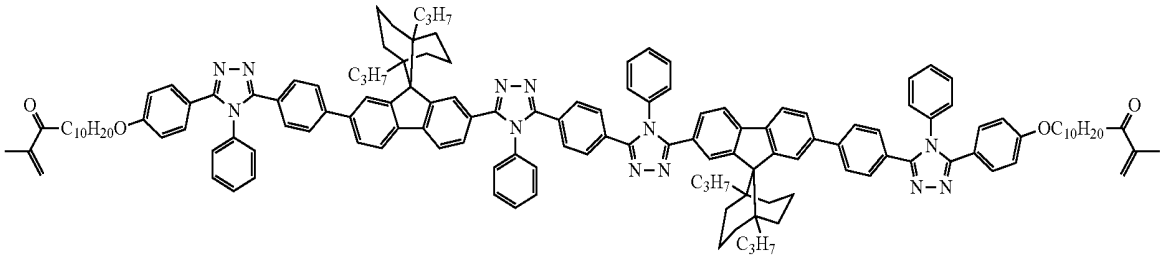
[0041] In organic light emitting device applications it is necessary that there be facile excitation energy transfer from the host material to the solute luminescent material. This is because charge carriers (electrons and holes) must be transported through the host medium to recombine to form the excitons (electrically excited molecular orbital states) that radiate light. In a mixture composed mainly of component host molecules this recombination and exciton formation will mainly occur in the host molecules. The excitation energy then needs to be transferred from the host molecules into the luminescent solute molecules. It is a requirement for this energy transfer that the spectral luminescent emission band (s) of the host material overlap the absorption band of the luminescent solute. Thus an important aspect of the invention is the preparation of mixtures of the compounds of the invention that have this spectral relationship between the constituent components. For instance, compound 28, which emits in the blue region of the spectrum, can serve as a host for compound 27, which is a green light emitter. A polymer film prepared by the UV induced crosslinking of a solution of 5% compound 27 in compound 28 will exhibit considerably less self-absorption of the green light emitted by 27 than will a film prepared by UV crosslinking of pure 27.

[0042] Another aspect of the invention relates to the balanced transport and insertion of positive and negative charge carriers into the electrically active regions or layers of devices. As an example, a typical (prior art) OLED configuration is shown in FIG. **1**. This device contains an anode **110** usually prepared as a conductive indium-tin oxide film on a glass substrate, a hole injection layer **120** that supports facile injection of holes into the hole transporting layer **130**. The hole-transporting layer **130** in the case of this invention is a polymerised film of a compound or a mixture of compounds of the invention that is chosen for its high mobility for holes. The device further consists of a cathode **160** that injects electrons into electron transporting layer **150**. There may be

an optional electron injection layer (not shown) between cathode **160** and electron transporting layer **150**. Electron transporting layer **150** and hole transporting layer **130** insert respectively electrons and holes into light emitting layer **140** where they recombine to form excitons and then light. The electron-transporting layer **150** of this invention is a polymerised film of a compound or mixture of compounds of the invention that is chosen for its high mobility for electrons. The light-emitting layer of this invention is also a polymerised film of a compound or mixture of compounds of the invention.

[0043] A further function of electron transporting layer **150** is to prevent holes injected into **140** from continuing onward out the other side of **140** and eventually recombining with electrons at the surface of the cathode in a non-light emissive event. To effect this the material(s) of **150** are chosen so as to have a HOMO (highest occupied molecular orbital) energy level that is quite low as compared to the HOMO energy level of the light emitting layer **140**. Usually around 6.5 electron volts below vacuum as opposed to around 5.25 ev below vacuum for the material of **140**. The result is that that there is a very high-energy barrier that prevents holes from entering **150**. Electron transporting layer materials of this type are said to be hole blocking. A hole blocking, electron transporting reactive mesogen material of the invention is

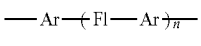
Structure 37



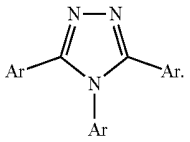
[0044] It can be seen that this material is of the type

B-S-A-S-B

with A having the structure



as above, but with Ar now comprising a 3,4,5-triaryl substituted 1,2,4-triazole,

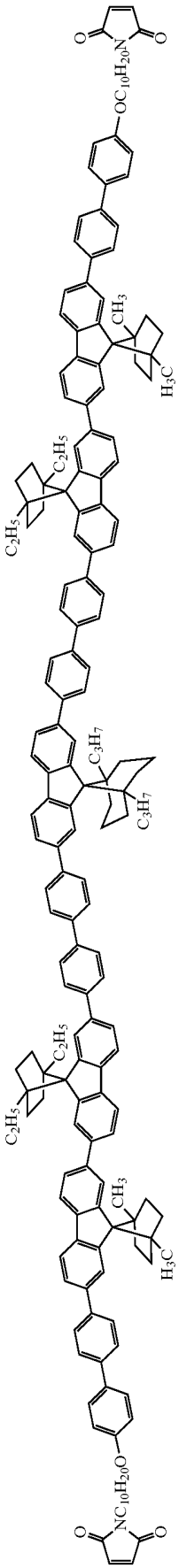


[0045] The light-emitting layer **140** of device **100** will perform optimally if electron and hole mobilities in the material are approximately the same. Unfortunately most of the best light emitting materials according to the invention have considerably higher hole mobilities than electron mobilities. However, the ability to produce mixtures of the materials of the invention allows compound 37 and similar compounds to be blended into the light emitting materials of the invention to form mixtures with substantially equal hole and electron mobilities. These mixtures can then be polymerised by UV exposure to form optimised light emitting layers.

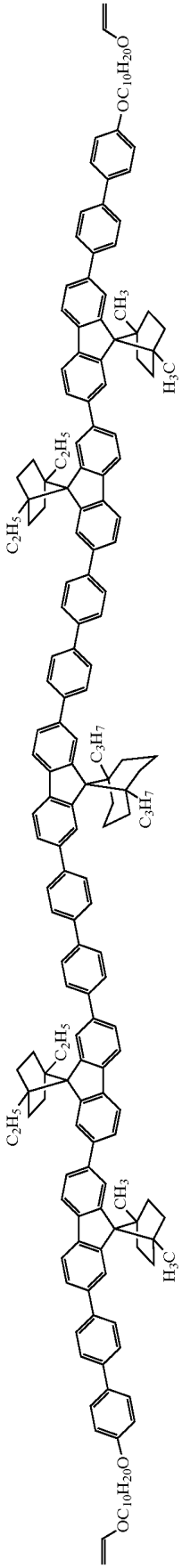
[0046] Yet another advantage of using mixtures of the materials of the invention is that it allows the use of mixtures of reactive mesogen materials in which photoinitiated electron donor-acceptor interactions as opposed to ionic or free radical initiation are used to initiate polymerization. This may result in much more stable (in terms of shelf-life) reactive mesogen materials than in methacrylate-based systems, while at the same time maintaining low UV crosslinking fluences. In these mixtures at least one of the reactive mesogen materials is substituted with electron-rich crosslinking groups while at least one other component reactive mesogen material is substituted with electron-deficient crosslinking groups. Ultraviolet radiation incident on the material promotes the electron-deficient crosslinking groups on some reactive mesogen molecules into electronically excited states. The excited state, electron-deficient crosslinking groups then abstract electrons from the electron-rich (electron donor) crosslinking groups on other reactive mesogen molecules initiating the copolymerization crosslinking reaction. Descriptions of this mode of photopolymerization may be found in, for example, "Photoinitiated radical polymerization of vinyl ether-maleate systems", *Polymer* 38, (9) pp. 2229-37 (1997); and "Co-Polymerization of Maleimides and Vinyl Ethers: A Structural Study", *Macromolecules* 1998, (31) pp. 5681-89.

[0047] Electron-deficient crosslinking groups include maleimides, maleates, fumarates, and other unsaturated esters. Electron donor groups include vinyl ethers, 1-propenyl ethers and other similar alkenyl ethers. Mixtures like these are advantageous in that the individual components are thermally and photochemically stable with excellent shelf-lives. However, when the materials are combined, the mixture has high photochemical sensitivity and requires only a relatively small UV dose for crosslinking. An examples of reactive mesogen mixtures of the invention containing both electron-deficient and electron donor crosslinking groups is a 50:50 mixture of compounds 38 and 39. Mixtures of this type need not contain components having the same molecular core structure as is the case in this example.

Structure 38



Structure 39

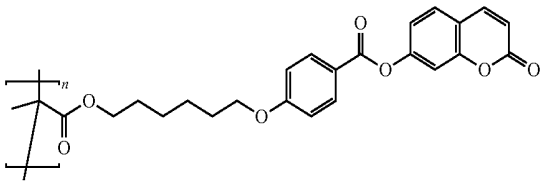


[0048] The exemplary OLED device **100** may be fabricated as follows. A substrate of indium-tin oxide coated glass (30 ohms/square) is patterned into a pixel or multipixel pattern a standard process of coating photoresist onto the substrate, patterning it with a UV light exposure through a photomask, developing the material, and then etching the ITO with 20% HCl/5% HNO_3. The photoresist is stripped from the ITO; the ITO is rinsed with D.I. water and then cleaned with an oxygen plasma. Hole injection layer **120** is formed by spin coating a 1.6% aqueous solution of Baytron P(AI 4083) polyethylene dioxythiophene polystyrene sulfonate (PEDT/PSS) available from H.C. Starck GmbH. onto the substrate glass over the patterned ITO. The substrate is then baked at 120° C. Next a 0.75% solution of compound 34 in chloroform is spin coated over the PEDT/PSS to form hole-transporting layer **130**. The material is dried at 50° C. for 30 minutes and annealed at 90° C. for a minute. The material is then photocured using 351 nm. radiation from an argon ion laser at a fluence of 30 joules/cm^2. Then the light emitting layer **140** is formed by spin coating a chloroform solution consisting of 0.40% compound 37, 0.35% compound 35 and 0.05% compound 36 over layer **130**. This layer dried and exposed to crosslinking UV exposure in the same way as was layer **130**. Next electron transporting layer **150** is formed by spin coating a 0.75% chloroform solution of compound 37 over layer **140**. This layer is then dried and photocured in the same way as were the previous layers. Finally an aluminium cathode is vacuum deposited over layer **150** yielding the device **100** represented in the drawing.

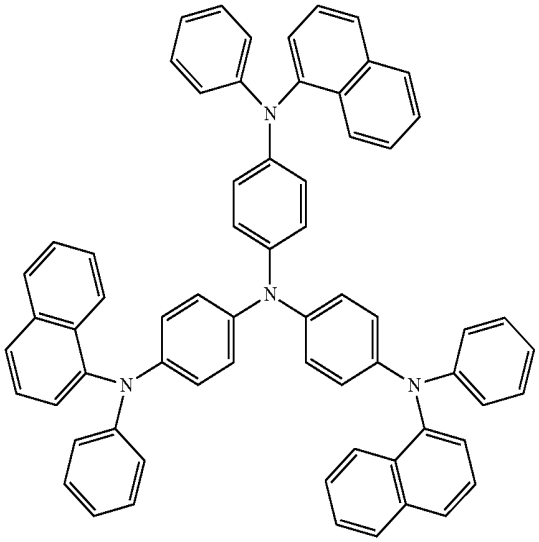
[0049] By using prior art techniques it is possible to insert a liquid crystal photoalignment material into device **100** as is shown in FIG. **2**. In this new device **200** the hole transporting photoalignment layer **210** aligns the molecular long axes of the molecules in the spin coated liquid crystal layer from which hole injection layer **130** is formed by photocrosslinking. The alignment within **130** is such that the long axes of the liquid crystalline molecular core units within the polymer matrix forming the layer are parallel to each other and to the device substrate surface. The uniform alignment of the molecular cores in **130** aligns the long molecular axes of the liquid crystal molecules from which the light-emitting layer **140** is formed by acting as an alignment template. Similarly, the alignment of layer **140** acts as a template for the alignment of the liquid crystal molecules from which the electron-transporting layer **150** is formed. Thus, all three liquid crystal polymer layers, **130**, **140**, and **150**, end up being uniformly aligned by the insertion of the alignment layer **210** forming the new device **200**.

[0050] The formation of hole transporting, photoalignment layers like **210** is described in U.S. Pat. No. 7,118,787. These layers are formed by solvent casting, for instance from a 0.5% solution in cyclopentanone, a blend of a commercial photoalignment polymer, for instance a coumarin substituted polymethyl methacrylate like the material with structure 40, and a commercially available hole transporting material, for instance the triaryl substituted amine material (structure 41). The layer **210** is formed over the electron injection layer by solvent casting and the surface energy bias necessary to align the liquid crystal molecules is of the subsequent layers is induced by exposure to polarised UV light, for instance from the 300 nm spectral line of an argon ion laser.

Formula 40



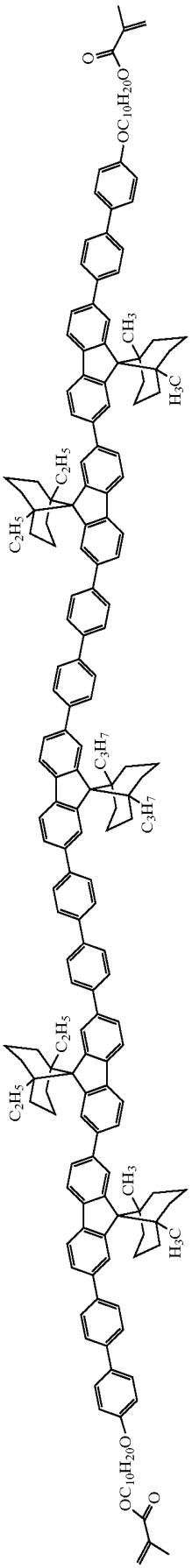
Formula 41



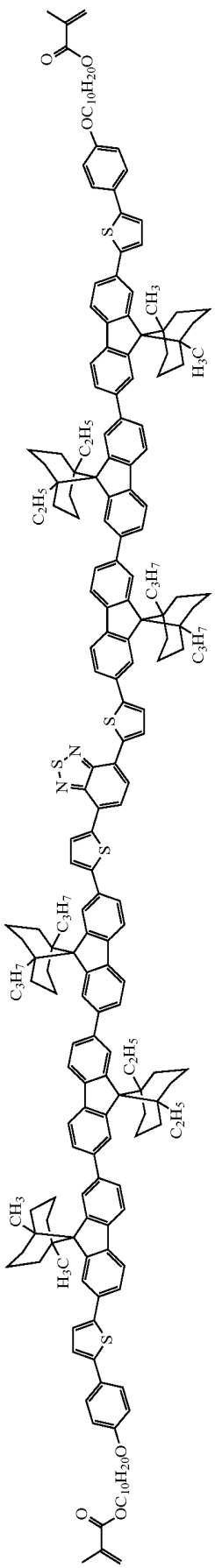
[0051] Devices like device **200** are useful because the light emitting, liquid crystalline polymer layers of the invention like **140** emit highly polarised light if they have their luminescent molecular cores uniformly aligned as they are in device **200**. As a result, device **200** is an OLED that emits highly polarised light. OLEDs like **200** can find use as liquid crystal display backlights, in 3-dimensional displays, and in any other applications where the efficient emission of highly polarised light is advantageous. Aligned light emitting liquid crystalline layers of the types used in device **200** may also be advantageously used in other devices, for instance, photoluminescent polarisers.

[0052] Because the light emitting and charge transporting materials of the invention can be photopatterned like ordinary photoresists, they can easily and cost effectively be used to produce multicolour pixelated devices. For instance, a matrix array of green light emitting elements each having the structure of discrete device **100** may be fabricated on a glass substrate. Then a second array of the same number of blue light emitting elements may be fabricated with the same structure as **100**, but by forming layer **140** by spin coating a chloroform solution consisting of 0.40% compound 37, 0.35% compound 42 and 0.05% compound 35 over layer **130** rather than using the formulation for layer **140** as in the example above. Finally an array of red light emitting elements equal in number to the green light emitting pixels may be fabricated with the same structure as **100**, but by forming layer **140** by spin coating a chloroform solution consisting of 0.40% compound 37, 0.35% compound 35 and 0.05% compound 43 over layer **130**. The arrays of the three different coloured light emitting elements may be arranged such that groups of one green emitting, one blue emitting, and one red light emitting element form a full-colour pixel group as is used in colour flat panel displays. It should be obvious that some device layers such as the hole injecting layer **120**, the hole transporting, photoalignment layer **210**, and the cathode **160** may be common to light emitting elements of all three colours.

Structure 42



Structure 43



[0053] A further advantage of the materials described in this invention over more conventional OLED emitter and charge transporting materials is the ability for multiple layers to be cast then photocured into insoluble, immobile liquid crystalline polymer materials one over the other. Other polymeric OLED emitters and charge transporting materials remain solvent soluble after deposition onto device substrates with the result that subsequent material depositions from solvent would wash them away. This renders the fabrication of multilayer structures as in device **100** impossible. It should be obvious that devices with even more layers than device **100** can be easily fabricated by adding more deposition and curing steps.

[0054] The ability to cheaply and economically produce multilayer devices in which adjoining layers have different highest occupied or lowest unoccupied molecular orbital (HOMO and LUMO) energy levels as well as different charge carrier mobilities is of general utility in plastic electronics. For instance, the equivalent of p-n junctions may be formed using the materials and processes of this invention and these may find utility in diodes, transistors, and photovoltaic devices. The capability of the materials of the invention to be photolithographically patterned allows large arrays of plastic electronic devices of virtually any size and description to be fabricated.

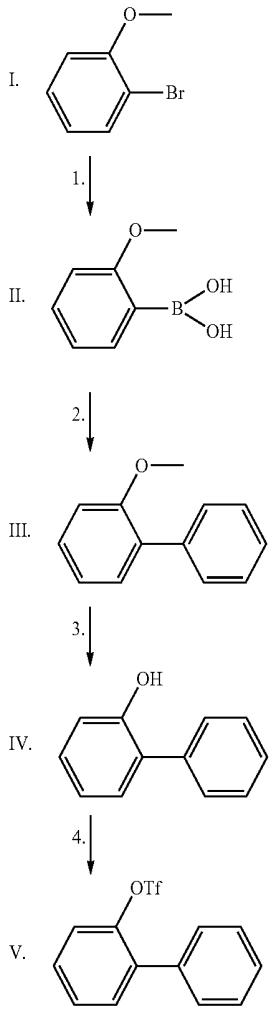
[0055] The synthesis of the oxidation resistant materials of the invention proceeds through keto diester derivatives of alicyclic and bicyclic compounds such as VIII, XVIII, and XXVII in the following. These materials are produced by the alkylation of the enols of acetonedicarboxylic acid esters (VI and XVI). The keto componds are then converted to the corresponding bromo compounds (X, XX, and XXIX). The bromides then undergo the Miyaura borylation reaction to yield the alkylboronic acid pinacol esters (XI, XXI, and XXX). These compounds are then coupled to the appropriate biphenyl derivative V. The Suzuki coupling reaction is not usually successful using boronates of this type because of the competing β-elimination reaction. However, because the boronates in this case have no β-substituted hydrogens, the competing reaction is not possible. The resulting intermediates are then ring-closed to the corresponding 9-spiro-substituted fluorenes diesters (XIV, XXIV, and XXXIII). The dieters may be converted to the desired alkyl substituted ring systems (for instance, XVII, XXVI, or XXXVI) by either reduction, or reaction with Grignard or alkyl lithium reagents followed by reduction.

[0056] The spiro-substituted fluorenes are the dihalogenated (Scheme 5) to ready them for incorporation into the reactive mesogen backbones. Schemes 6, 8, 7, and 9 portray the synthesis of reactive mesogen LVII using a series of Stille and Suzuki coupling reactions.

[0057] The synthesis of the oxidation resistant materials of the invention proceeds through keto diester derivatives of alicyclic and bicyclic compounds such as VIII, XVIII, and XXVII in the following. These materials are produced by the alkylation of the enols of acetonedicarboxylic acid esters (VI and XVI). The keto componds are then converted to the corresponding bromo compounds (X, XX, and XXIX). The bromides then undergo the Miyaura borylation reaction to yield the alkylboronic acid pinacol esters (XI, XXI, and XXX). These compounds are then coupled to the appropriate biphenyl derivative V. The Suzuki coupling reaction is not usually successful using boronates of this type because of the competing β-elimination reaction. However, because the boronates in this case have no β-substituted hydrogens, the competing reaction is not possible. The resulting intermediates are then ring-closed to the corresponding 9-spiro-substituted fluorenes diesters (XIV, XXIV, and XXXIII). The diesters may be converted to the desired alkyl substituted ring systems (for instance, XVII, XXVI, or XXXVI) by either reduction, or reaction with Grignard or alkyl lithium reagents followed by reduction.

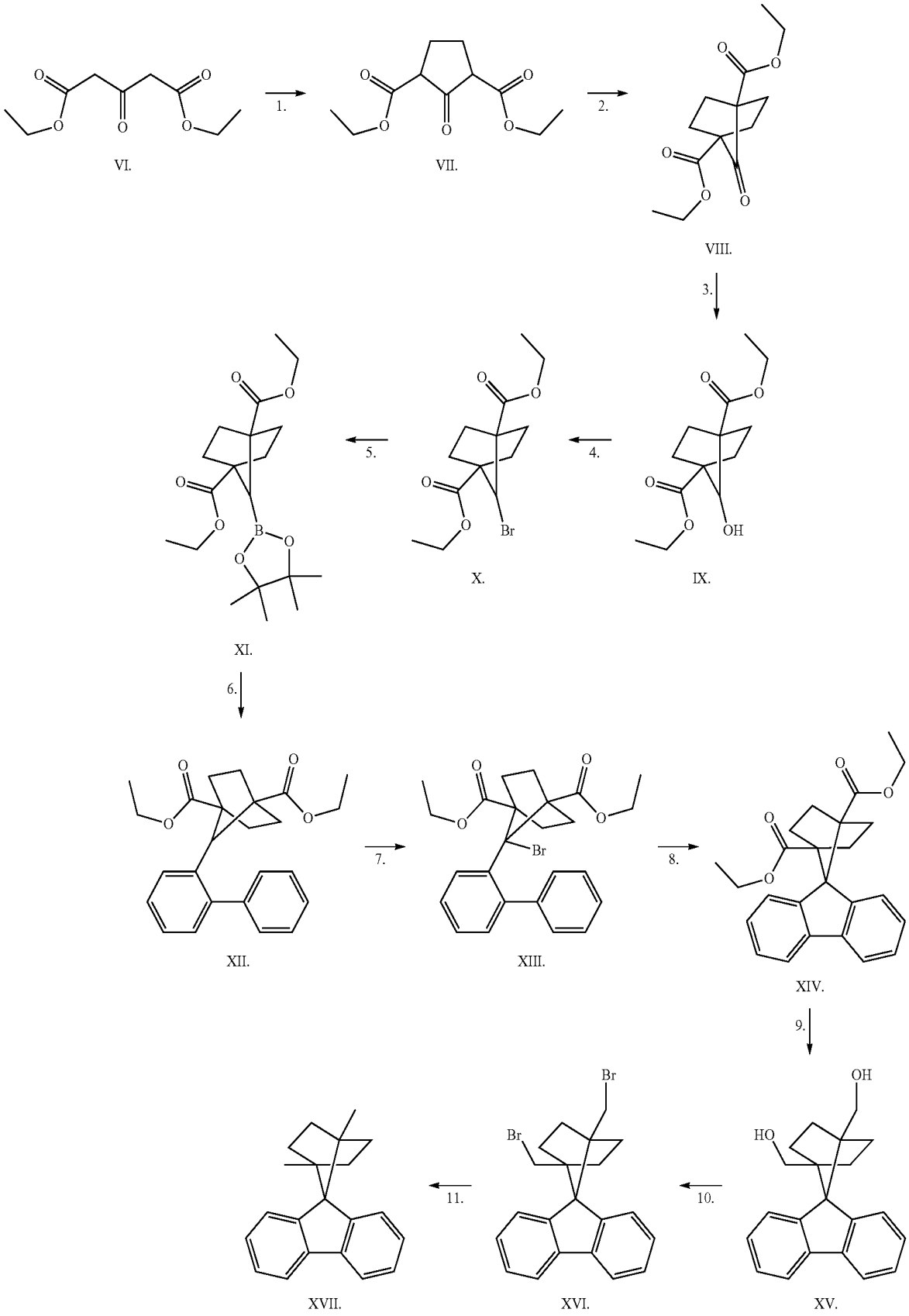
[0058] The spiro-substituted fluorenes are then dihalogenated (Scheme 5) to ready them for incorporation into the reactive mesogen backbones. Schemes 6, 8, 7, and 9 portray the synthesis of reactive mesogen LVII using a series of Stille and Suzuki coupling reactions.

Scheme 1: Synthesis of Biphenyl-2-yl Triflate



1. a. Mg, Et_2O; b. $B(OMe)_3$, THF;
2. Bromobenzene, 2 equiv. aqueous K_2CO_3, 3 mole % $Pd(PPh_3)_4$;
3. BBr_3, CH_2Cl_2, -80° C.;
4. $(CF_3SO_2)_2O$, pyridine.

Scheme 2: Synthesis of 1,4-dimethyl spiro[bicyclo[2,2,1]heptane-7,9′-fluorene]



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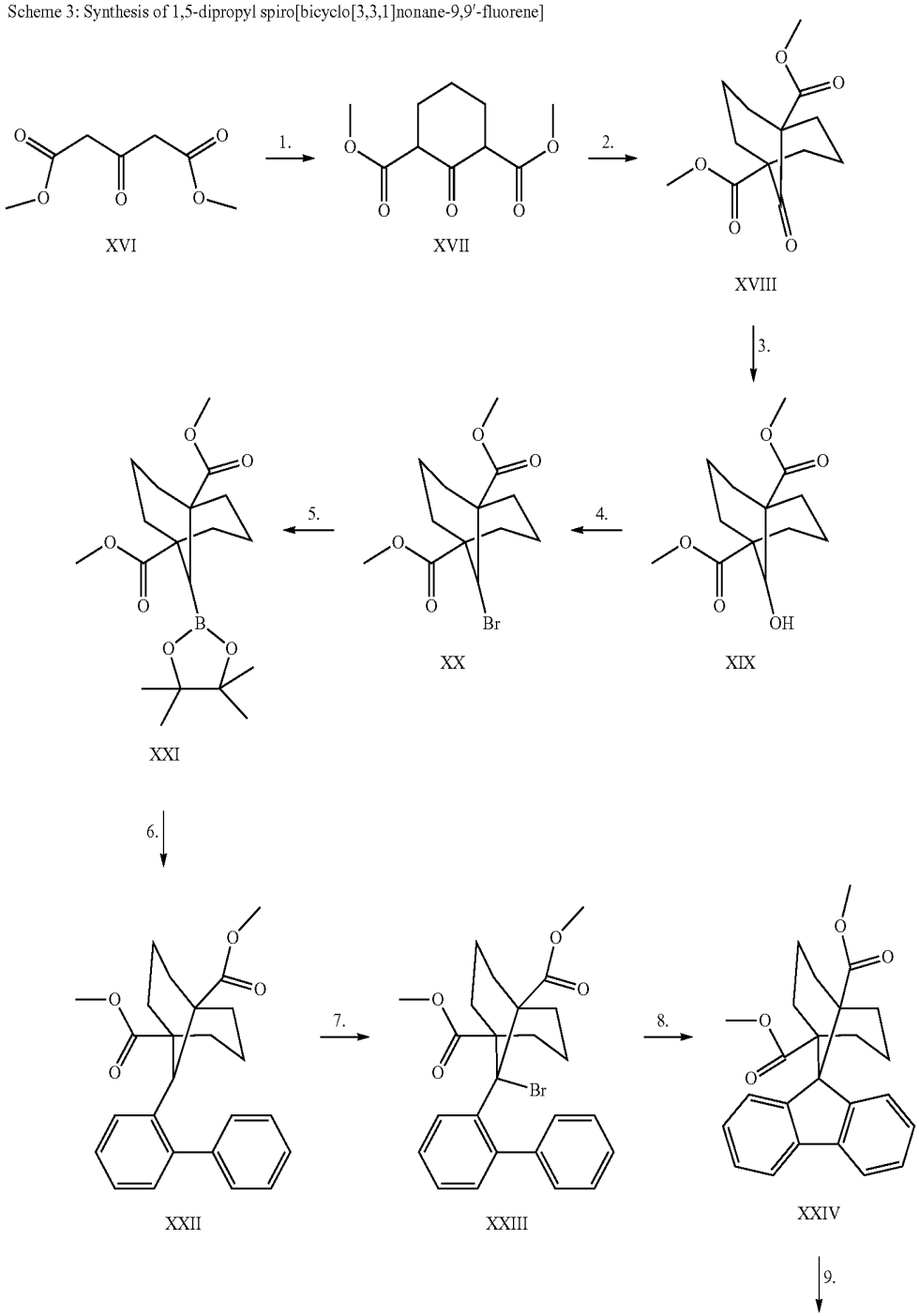
1. a. lithium diisopropylamide, THF; b. 1,2-dibromoethane, c. NaH, THF; 2. a. lithium diisopropylamide, THF; b. 1,2-dibromoethane, c. NaH, THF; 3. $NaBH_4$, CH_3OH; 4. Ph_3PBr_2, CH_3CN; 5. Bis(pinacolato)diboron, $PdCl_2(dppf)$, aqueous KOAc, dioxane; 6. Compound V, $Pd(PPh_3)_4$, toluene, aqueous Na_2CO_3; 7. Br_2, CCl_4, dibenzoyl peroxide, UV light; 8. Boron trifluoride etherate, THF; 9. $LiEt_3BH$, THF; 10. Ph_3PBr_2, CH_3CN; 11. $LiEt_3BH$, THF.

Scheme 3: Synthesis of 1,5-dipropyl spiro[bicyclo[3,3,1]nonane-9,9′-fluorene]



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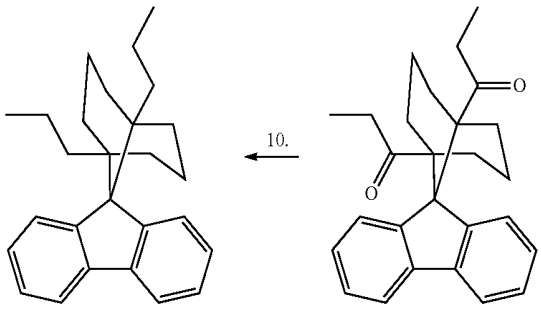
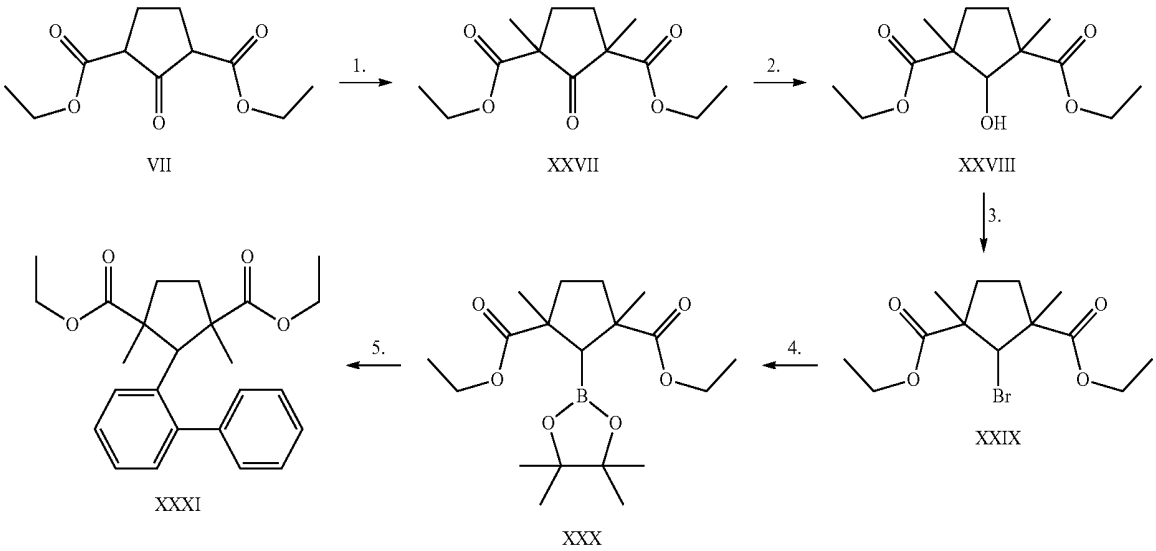


XXVI XXV

1. a. lithium diisopropylamide, THF; b. 1,3-dibromopropane, c. NaH, THF; 2. a. lithium diisopropylamide, THF; b. 1,3-dibromopropane, c. NaH, THF; 3. $NaBH_4$, CH_3OH; 4. Ph_3PBr_2, CH_3CN; 5. Bis(pinacolato)diboron, $PdCl_2(dppf)$, aqueous KOAc, dioxane; 6. Compound V, $Pd(PPh_3)_4$, toluene, aqueous Na_2CO_3; 7. Br_2, CCl_4, dibenzoyl peroxide, UV light; 8. Boron trifluoride etherate, THF; 9. C_2H_5MgBr, THF, b. dilute HCl; 10. a. $H_2NNH_2 \cdot H_2O$, $N(C_2H_5OH)_3$, reflux, b. KOH, reflux.

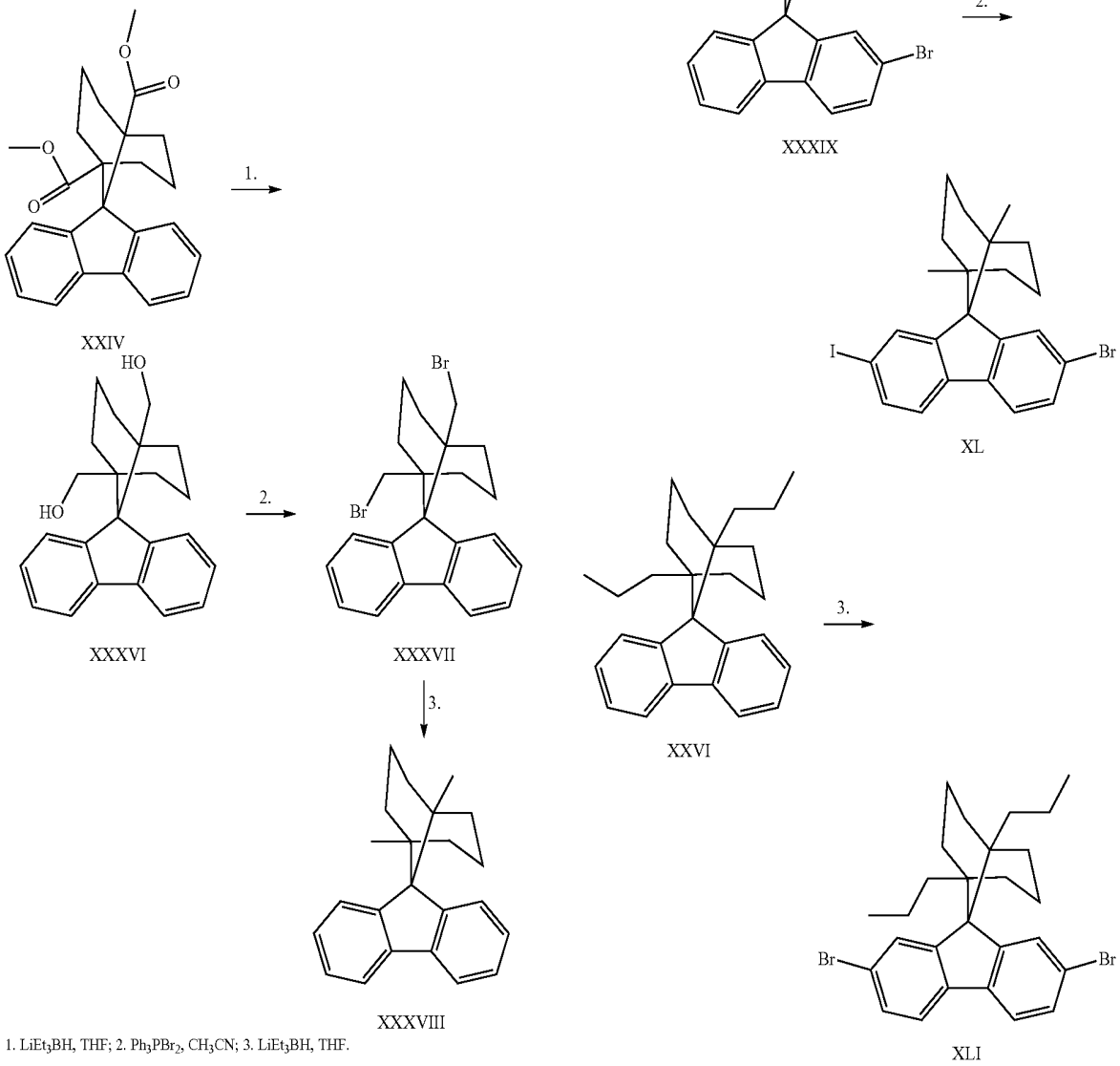
Scheme 4: Synthesis of 2,2,5,5-tetramethyl spiro[cyclopentane-1,9′-fluorene]



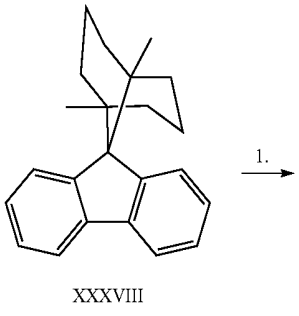
VII XXVII XXVIII XXIX XXX XXXI XXXII XXXIII XXXIV XXXV XXXVI

1. a. lithium diisopropylamide, THF; b. methyl iodide, 2. $NaBH_4$, CH_3OH; 3. Ph_3PBr_2, CH_3CN; 4. Bis(pinacolato)diboron, $PdCl_2(dppf)$, aqueous KOAc, dioxane; 5. Compound V, $Pd(PPh_3)_4$, toluene, aqueous Na_2CO_3; 6. Br_2, CCl_4, dibenzoyl peroxide, UV light; 7. Boron trifluoride etherate, THF; 8. $LiEt_3BH$, THF; 9. Ph_3PBr_2, CH_3CN; 10. $LiEt_3BH$, THF.

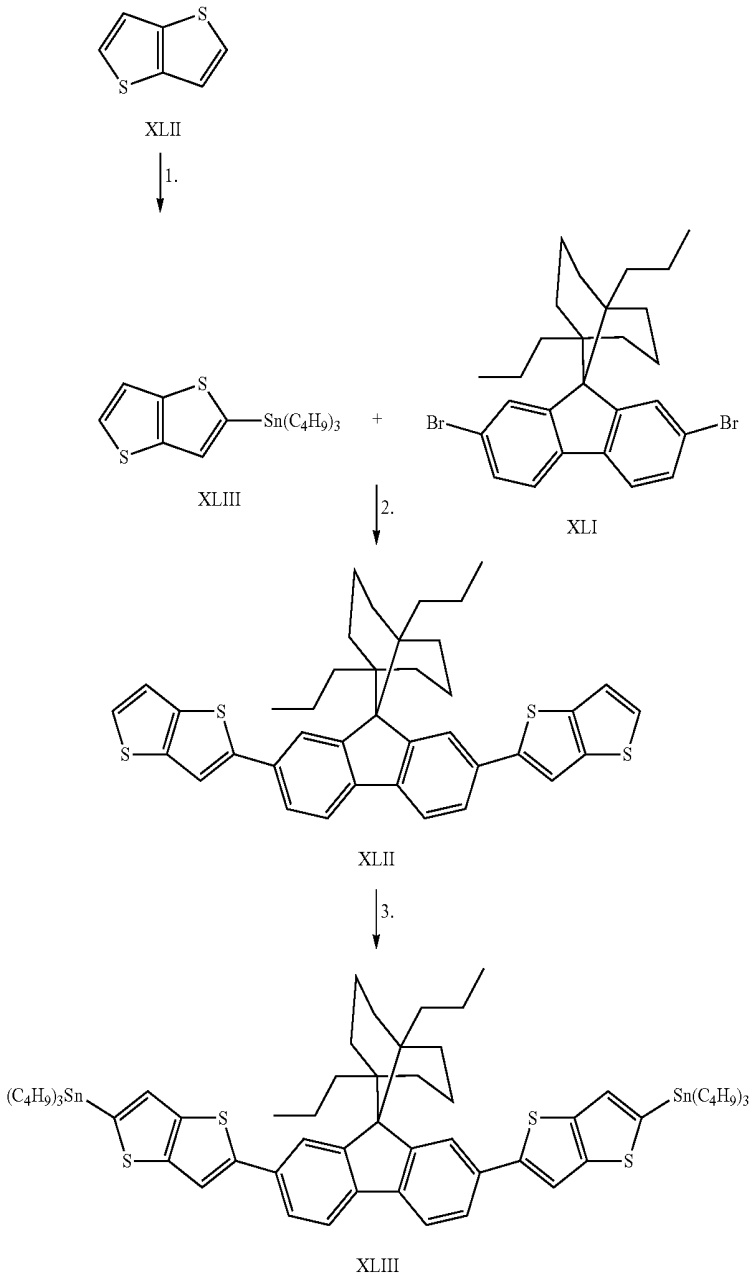
Scheme 5: Synthesis of 1,5-dimethyl spiro[bicyclo[3,3,1] nonane-9,9′-fluorene]



Scheme 5: Synthesis of dihalofluorenes

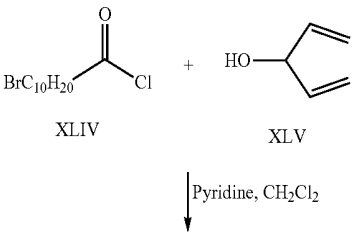


Scheme 6: Synthesis of Key Intermediate, 2′,7′-bis(2,5-di[tri-n-butylstannyl]thieno[4,5-b]thienyl)-1,5-dipropyl spiro[bicyclo[3,3,1]nonane-9,9′-fluorene]



1. a. C_4H_9Li, THF (dry), -78° C., b. $ClSn(C_4H_9)_3$ (room temp.) 2. $Pd(PPh_3)_4$, DMF, 80° C. 3. a. C_4H_9Li, THF (dry), -78° C., b. $ClSn(C_4H_9)_3$ (room temp.)

Scheme 7: Synthesis of Spacer/Crosslinker



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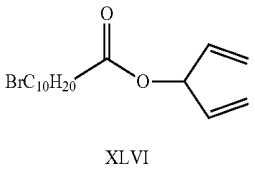
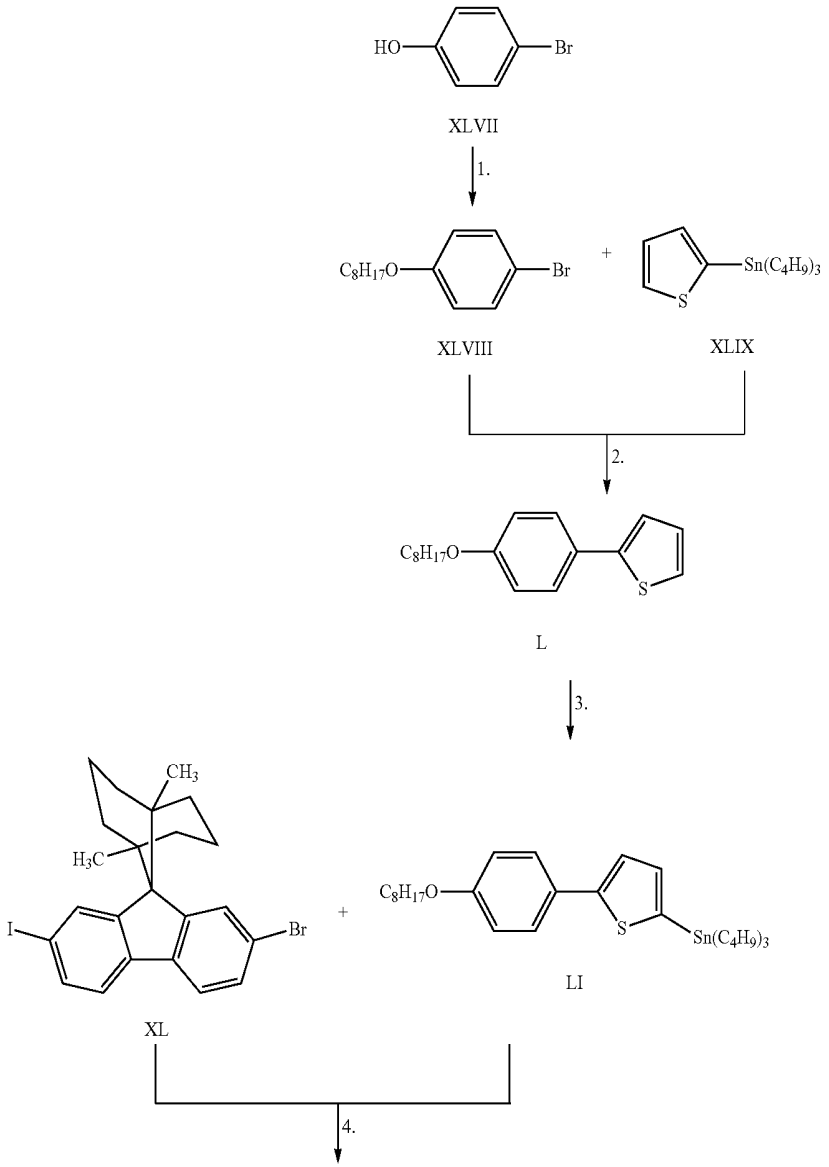


Scheme 8: Synthesis of Key Intermediate 7-([4-octyloxyphenyl]thien-2-yl) 2-(7-bromo{1,5-dimethyl spiro[bicyclo[3,3,1]nonane-9,9′-fluorene]}-2′-yl) spiro[bicyclo[3,3,1]nonane-9,9′-fluorene]



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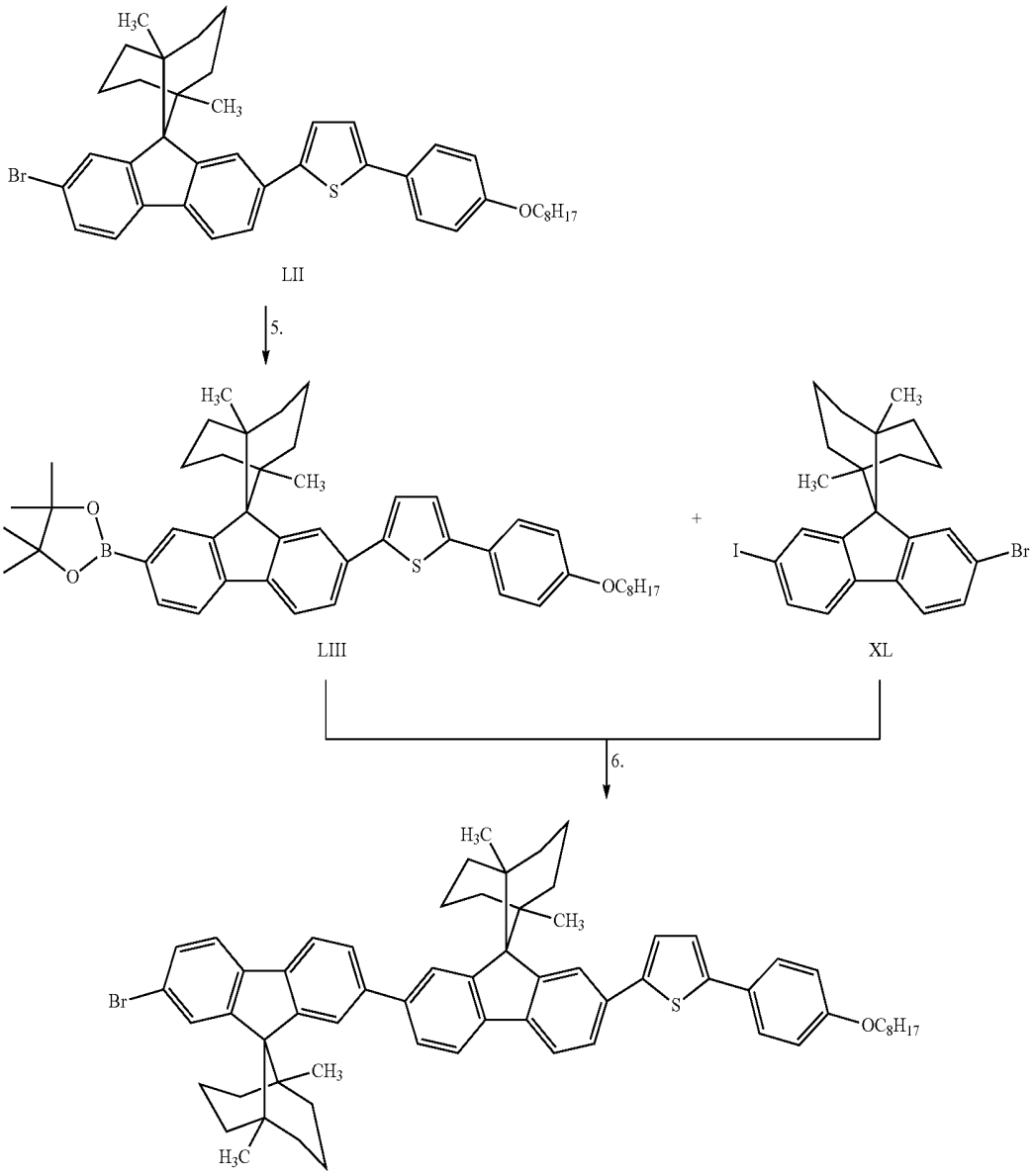
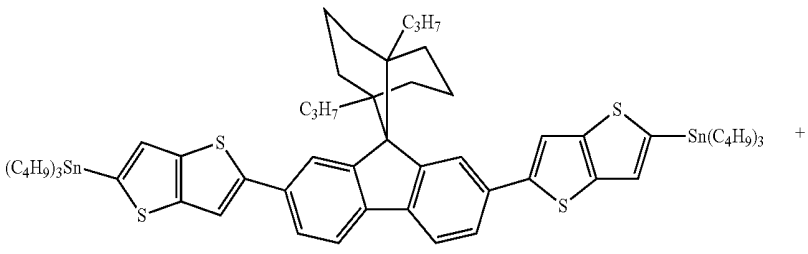


1. 1-bromooctane, K_2CO_3, butanone, reflux; 2. $Pd(PPh_3)_4$, DMF, 80° C.; 3. a. C_4H_9Li, THF (dry), -78° C., b. $ClSn(C_4H_9)_3$ (room temp.) 4. $Pd(PPh_3)_4$, DMF, 80°C.; 5 Bis(pinacolato)diboron, $PdCl_2$ (dppf), aqueous KOAc, dioxane; 6. Compound XXXX, $Pd(PPh_3)_4$, toluene, aqueous Na_2CO_3.

Scheme 9: Synthesis of Electroluminescent Reactive Mesogen



LIII

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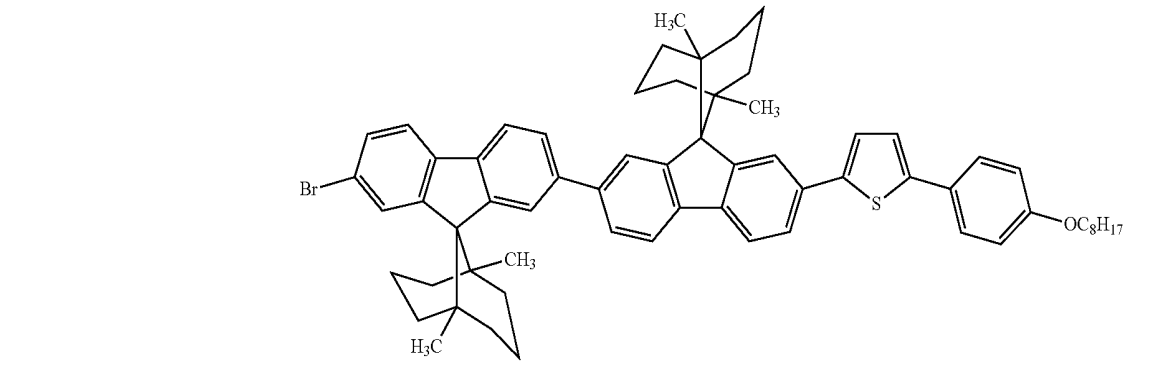
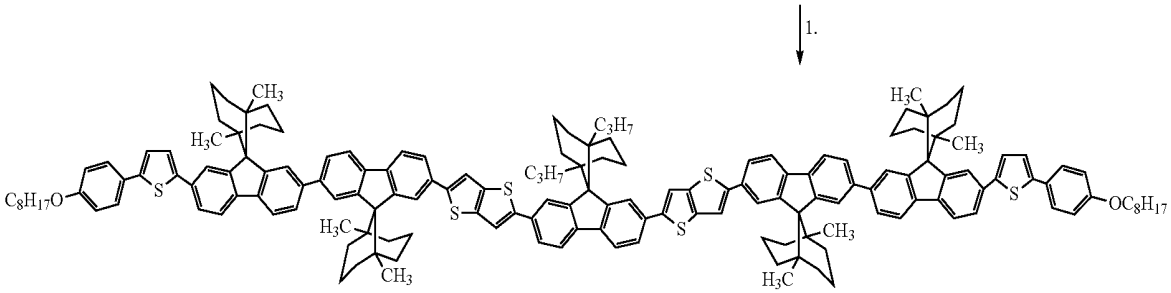
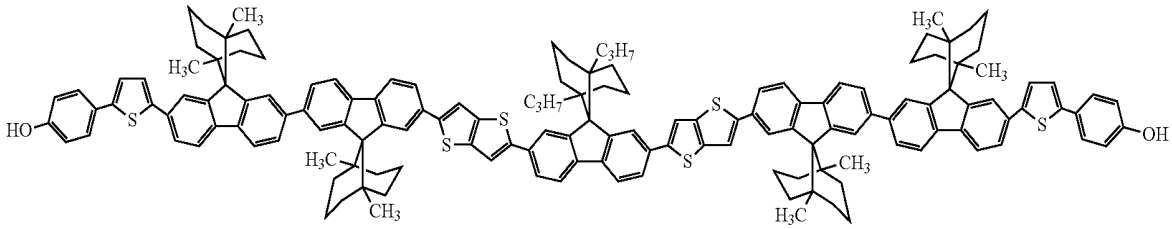


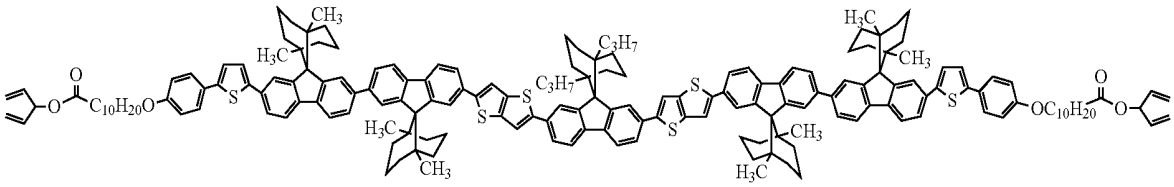
LIV



LV



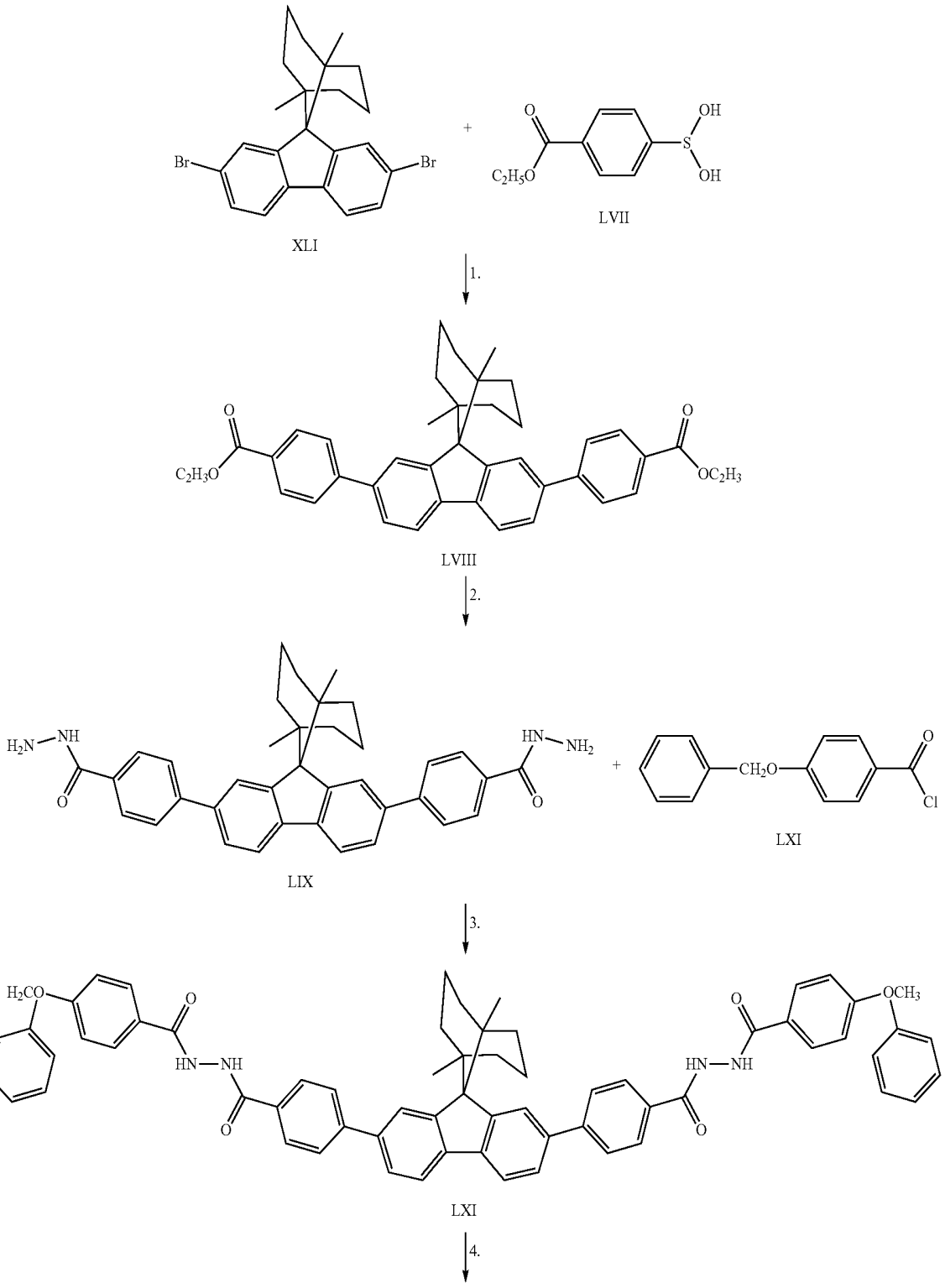
LVI



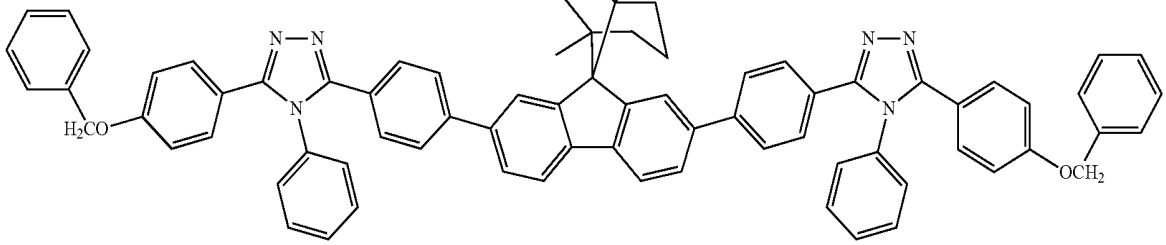
LVII

1. $Pd(PPh_3)_4$, DMF, 80° C.; 2. BBr_3, CH_2Cl_2, -80° C.; 3. Compound XLVI, K_2CO_3, acetonitrile

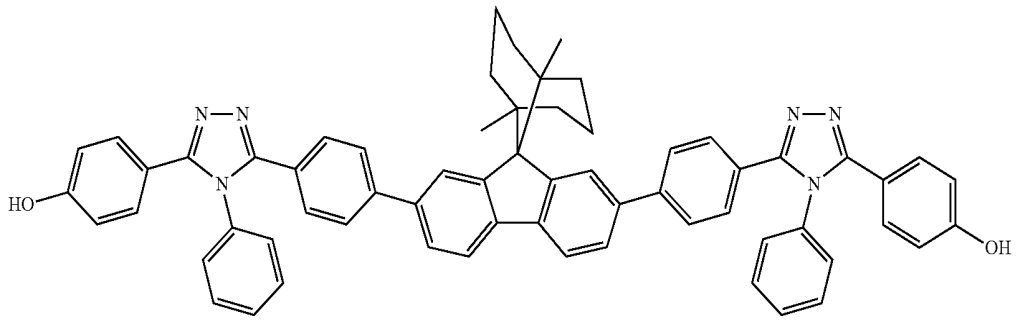
Scheme 10: Synthesis of Electron Transporting Reactive Mesogen



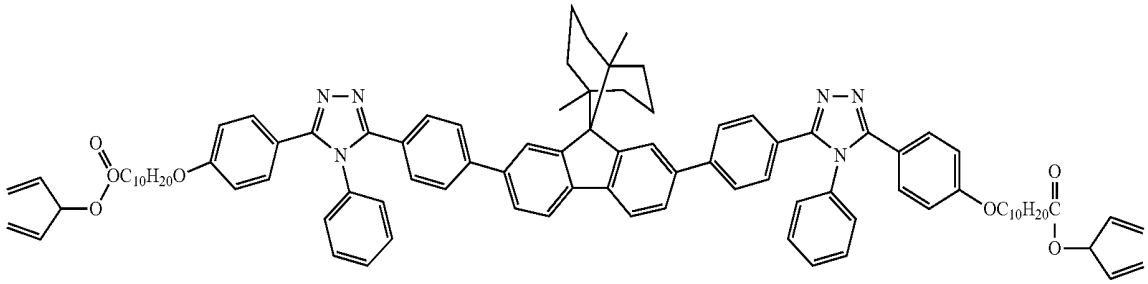
-continued



LXII



LXII



LXII

1. $Pd(PPh_3)_4$, toluene, aqueous Na_2CO_3; 2. H_2NNH_2, EtOH; 3. CH_2Cl_2, pyridine 4. Aniline, PCl_3, toluene; 5. H_2, Pd/C; 6. Compound XLVI, K_2CO_2, acetonitrile

BRIEF DESCRIPTION OF THE DRAWINGS

[0059] A full and enabling disclosure of the present disclosure is provided in the specification, including reference to the accompanying figures, in which:

[0060] FIG. **1** illustrates a prior art OLED configuration; and

[0061] FIG. **2** illustrates an OLED configuration in accordance with the present disclosure.

[0062] Repeat use of reference characters in the present specification and drawings is intended to represent the same or analogous features or elements of the present invention.

1-102. (canceled)

103. An OLED compound of the general structure:

B-S-A-S-B

in which rod-like nuclei A comprise a condensed aromatic ring structure in turn comprising a fluorene ring structure condensed with at least one additional fluorene ring structure wherein the fluorene ring systems comprised by the condensed aromatic structure are substituted at the 9-position and in which the 9-position of the fluorenes are not susceptible to oxidation.

* * * * *

专利名称(译)	包含芴衍生物的电致发光材料		
公开(公告)号	US20160056389A1	公开(公告)日	2016-02-25
申请号	US14/796383	申请日	2015-07-10
[标]申请(专利权)人(译)	洛马克斯有限公司		
申请(专利权)人(译)	LOMOX有限公司		
当前申请(专利权)人(译)	LOMOX有限公司		
[标]发明人	KOCH GENE CARL		
发明人	KOCH, GENE, CARL		
IPC分类号	H01L51/00 C07C43/215 C07C59/72 C07D249/08 C07D333/16 C07D403/14 C07D471/22 C07D487/04 C07D495/04		
CPC分类号	H01L51/0069 C07D403/14 C07D471/22 C07D249/08 C07D487/04 H01L51/0068 C07D333/16 C07C59/72 C07C43/215 H01L51/0067 H01L51/005 C07D495/04 C07C69/54 C07C2603/94 C07D207/452 C07D333/18 C07D417/14 C07D519/00 C09K11/06 C09K2211/1416 C09K2211/1425 C09K2211/1458 C09K2211/1466 C09K2211/1475 H01L51/0037 H01L51/0039 H01L51/004 H01L51/0058 H01L51/0072 H01L51/0074 H01L51/0508 H01L51/42 H01L51/5012 H01L51/5048 H01L51/5293 H01L2251/308 Y02E10/549 H01L51/0032		
优先权	2009017083 2009-09-30 GB 13/499039 2012-07-13 US PCT/GB2010/001818 2010-09-29 WO		
外部链接	Espacenet USPTO		

摘要(译)

OLED化合物的一般结构： B-S-A-S-B 其中棒状核A包含稠合芳环结构，其包含与至少一个另外的芴环结构缩合的芴环结构，其中由稠合芳族结构包含的芴环系统在9-位被取代，并且其中芴的9位不易氧化。