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C07D 487/04 *(2006.01)* ***C07D 207/452*** *(2006.01)*
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(54) ELECTROLUMINESCENT MATERIALS COMPRISING FLUORENE DERIVATIVES

ELEKTROLUMINESZENTE MATERIALIEN MIT FLUORENDERIVATEN

MATÉRIAUX ÉLECTROLUMINESCENTS COMPRENANT DES DÉRIVÉS DE FLUORÈNE

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(56) References cited:
WO-A2-2007/064721
GB-A- 2 456 298
US-A1- 2006 046 092

EP 2 483 368 B1

Description

[0001] This invention relates to electroluminescent materials.

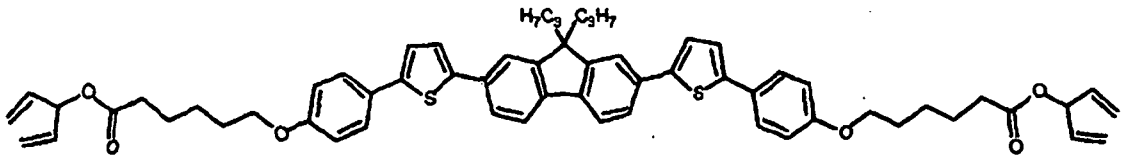
[0002] It is known that some reactive mesogens (liquid crystalline materials capable of being chemically crosslinked into a polymer matrix) of the general formula:

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.

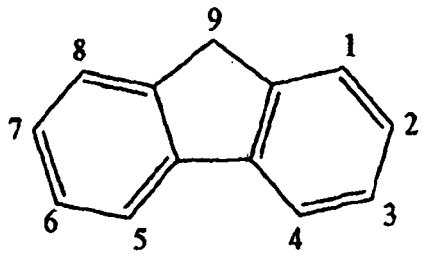
[0003] Further, if the linear aromatic core A is luminescent in nature, these reactive mesogen materials may be patterned into the active light emitting layers in electroluminescent devices such as organic light emitting diodes (OLEDS) and organic diode lasers.

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



Structure1

[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] Materials related to structure 1 with a fluorene bearing a spiroalkyl substituent at C-9 have been reported by (Newman et al, GB2456298 A). Indenofluorene derivatives have been used as luminescent components in polymeric materials (Towns et al, US 2006/046092 A1) and in liquid crystalline materials (Aldred et al, WO 2007/064721 A2).

[0007] 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.

[0008] Described herein are materials of that general structure that have commercially useful lifetimes.

[0009] The present invention provides OLED compounds of the general structure:

B-S-A-S-B

in which A is a substantially linear covalently bonded chain comprising a condensed aromatic ring structure in turn comprising fluorene ring structures condensed with at least one additional fluorene ring structure, S is a spacer group comprising an alkyl chain optionally containing one or more heteroatoms, and B is a crosslinking chemical group, wherein the fluorene ring systems comprised by the condensed aromatic structure are substituted at the 9-position, and in which there are no hydrogen substituents α- to the 9-position of the fluorene ring system or any of the fluorene ring systems.

[0010] Described herein are 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 fluorine ring structures condensed with at least one additional fluorine ring structures wherein the fluorine 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.

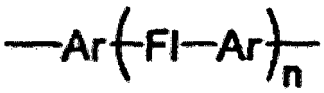
[0011] There are preferably no hydrogens α to the 9-position of the fluorine ring system or any of the fluorine ring systems.

[0012] The additional fluorine ring systems may comprise benzene, naphthalene, indene, or other fluorine ring systems.

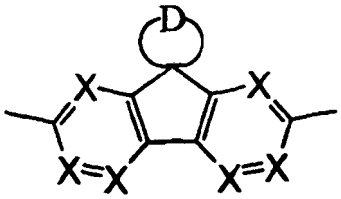
[0013] In these materials S may represent a flexible spacer comprising an alkyl chain. The alkyl chain may contain one or more hetero atoms.

[0014] 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.

[0015] A may represent a substantially linear, covalently bonded chain, which may be a chain of aromatic or heteroaromatic diradicals represented by the general formula:

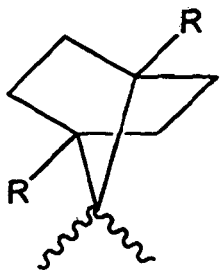


[0016] Wherein the Ar may each be independently chosen from an aromatic or heteroaromatic diradical, and may comprise a 1,4-phenylene, a biphenyl-4,4'-diyl, a terphen-4,4"-diyl, a naphthalene-1,4-diyl, a thiophene-2,5-diyl, a pyrimidine-2,5-diyl, a perylene-3,10-diyl, a pyrene-2,7-diyl, a 2,2'-dithiophen-5,5'-diyl, 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:



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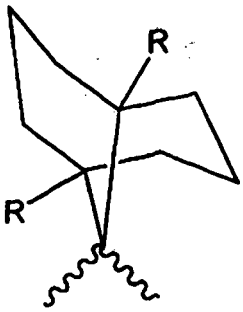

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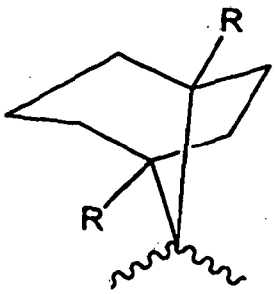

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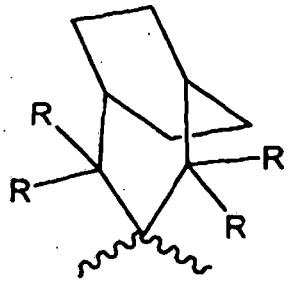

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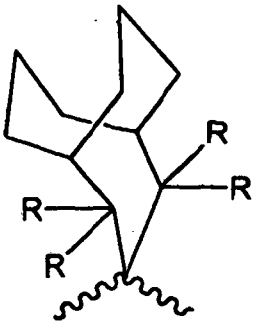

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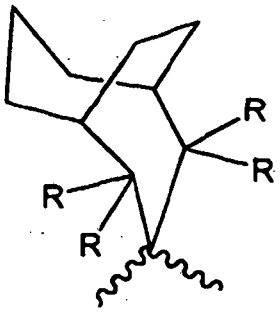

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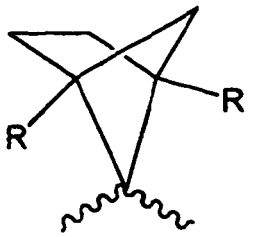

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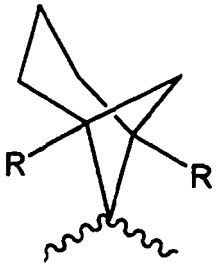

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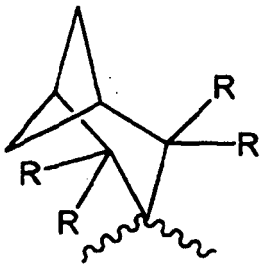

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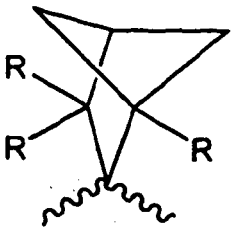

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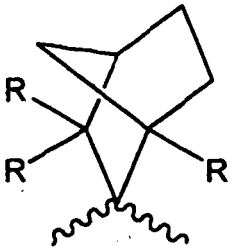

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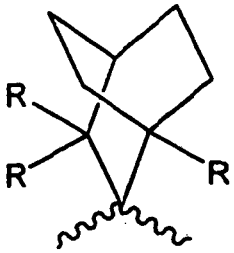

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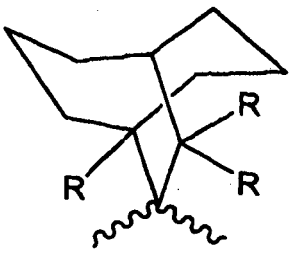

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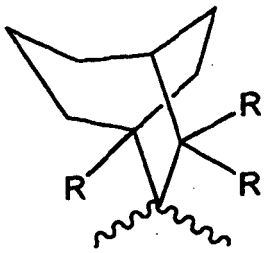

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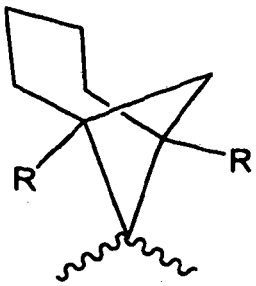

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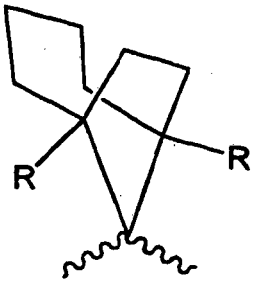

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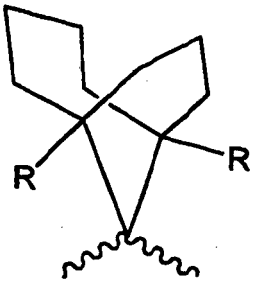

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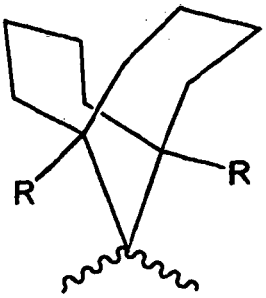
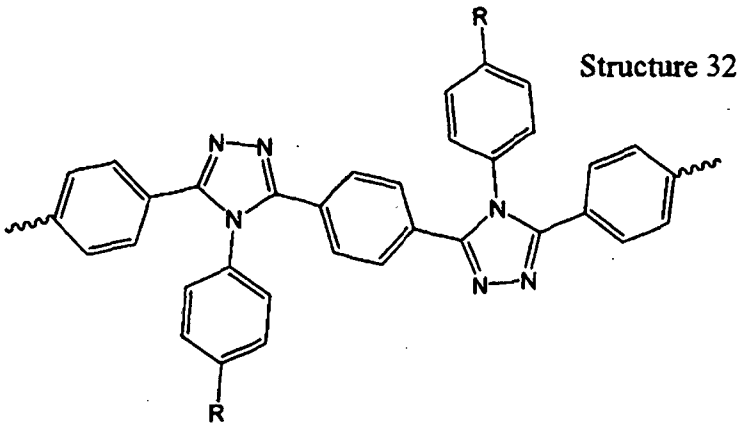


Structure 21

Structure 32



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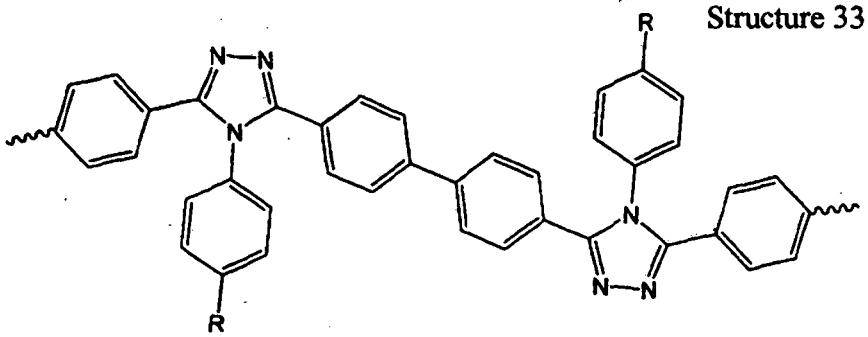

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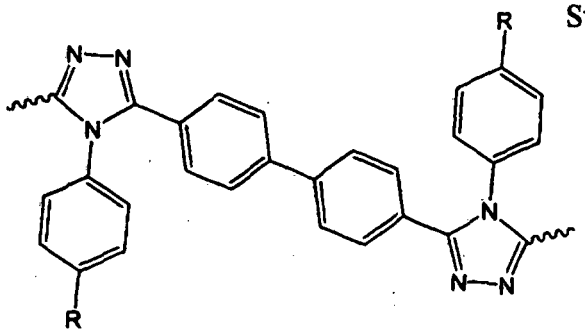

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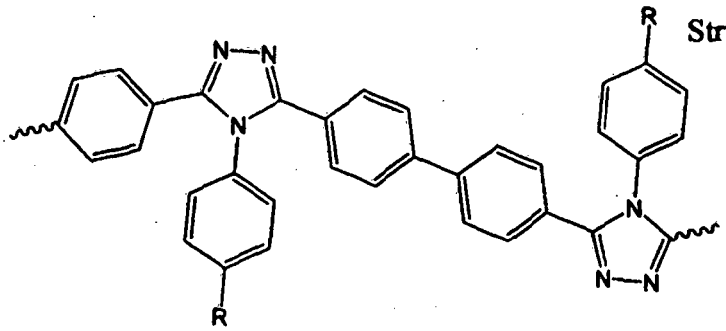

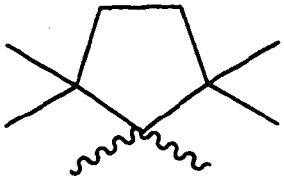

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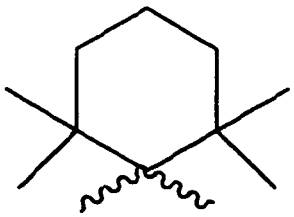

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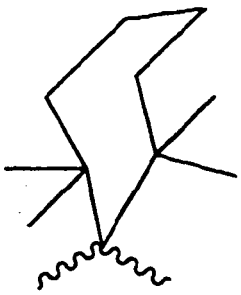

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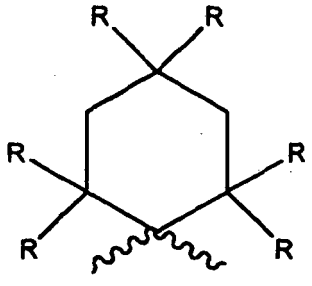

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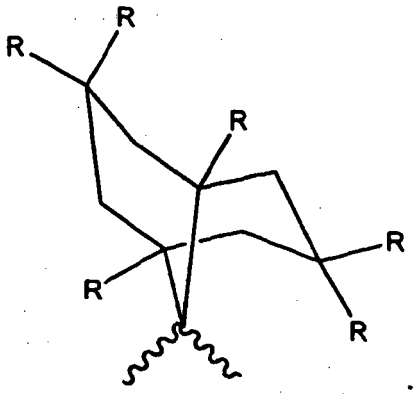
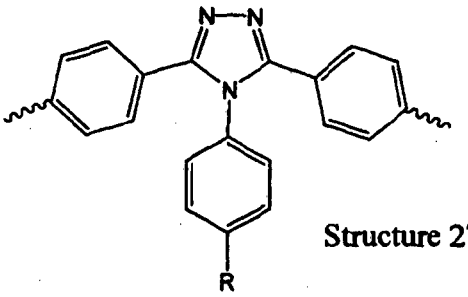


Structure 26

[0017] 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 neopentyl, and X may be independently selected from =CH-, =N-.

[0018] Ar may also be selected from the diradicals:



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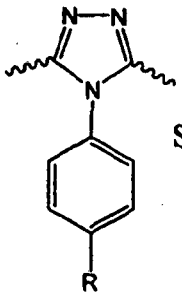

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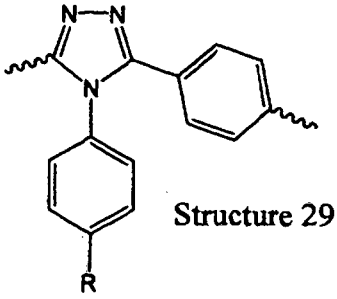

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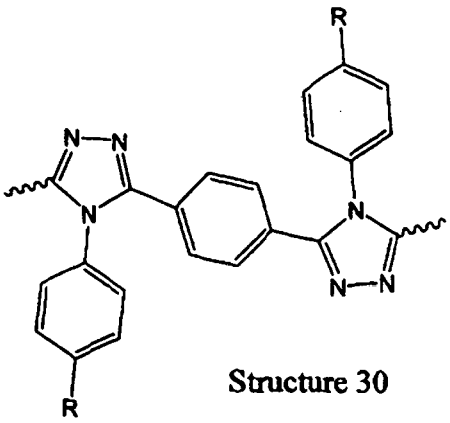

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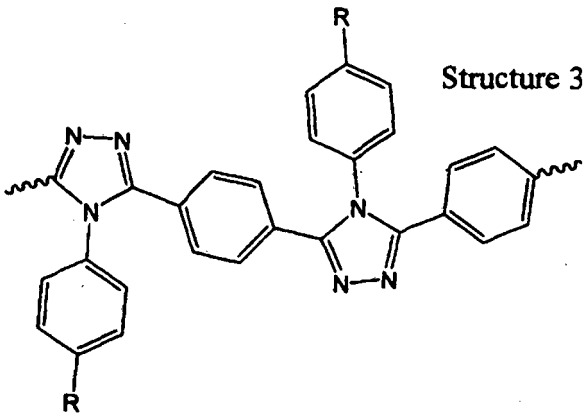

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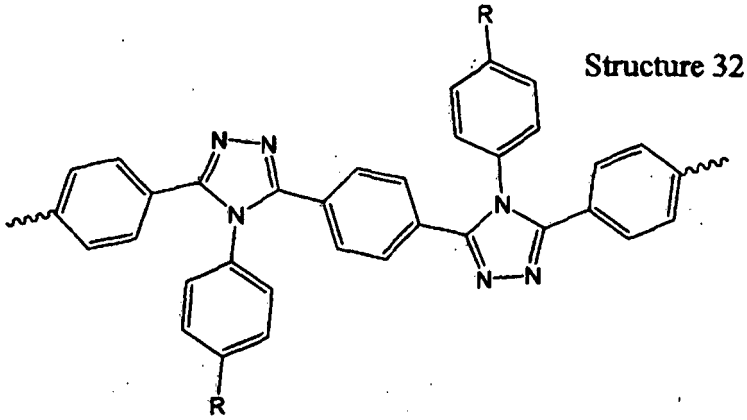

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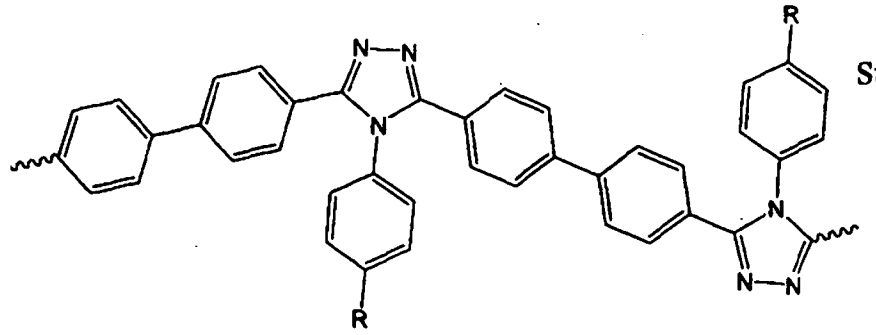

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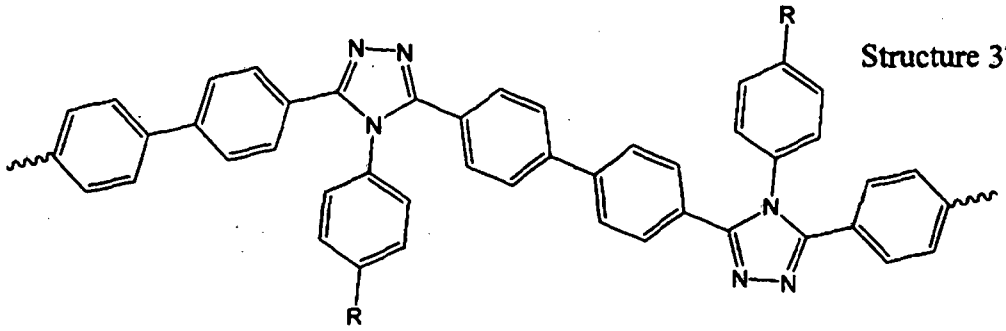

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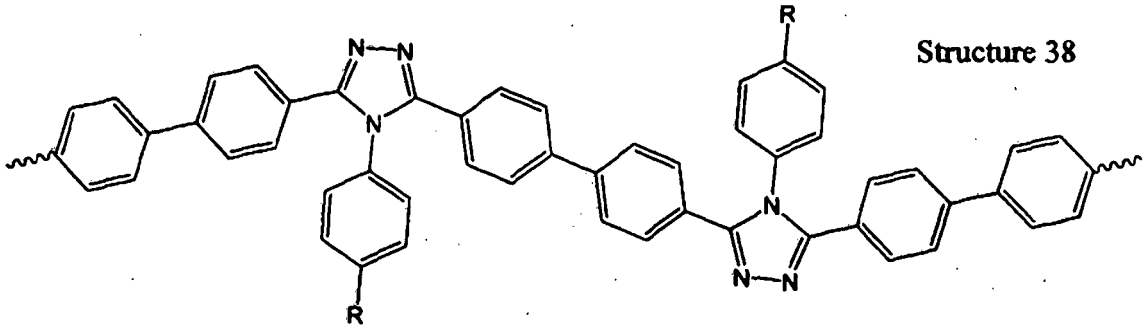

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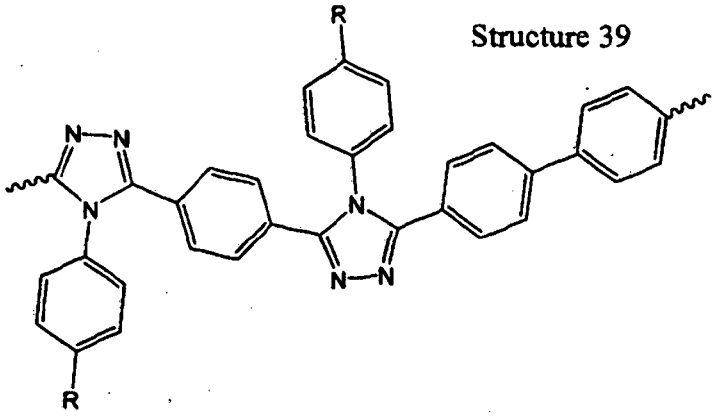
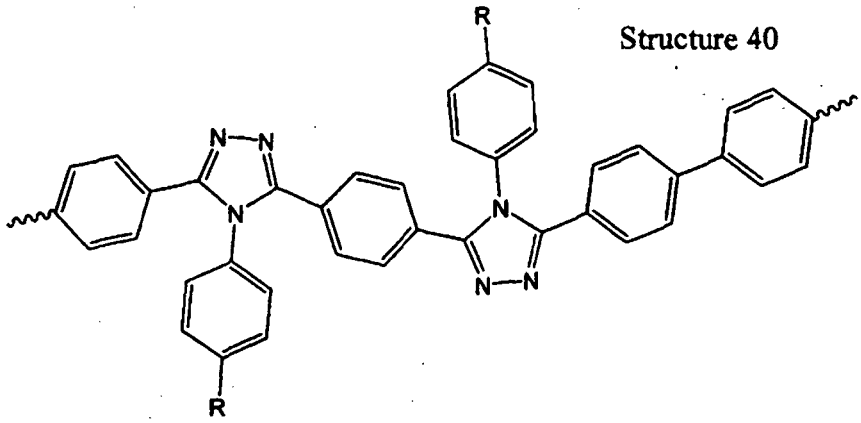


Structure 39

Structure 40



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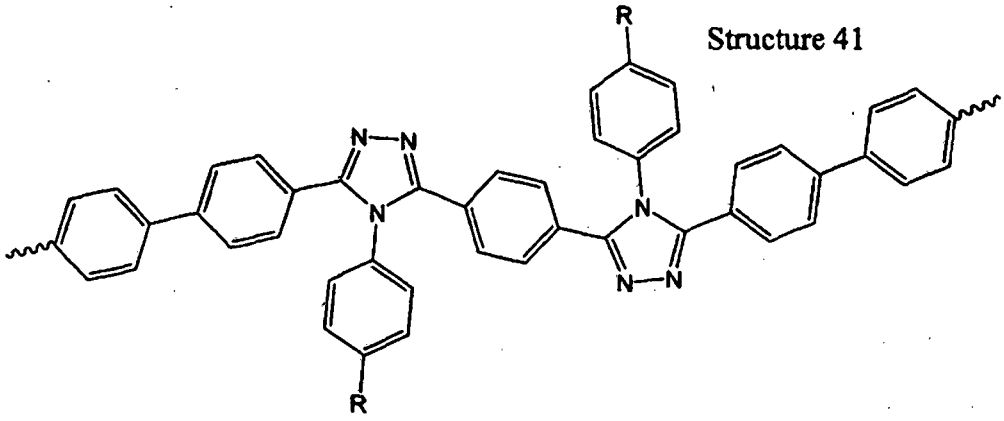
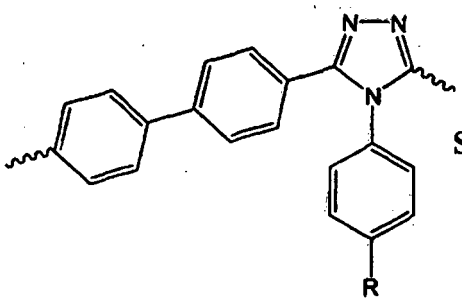
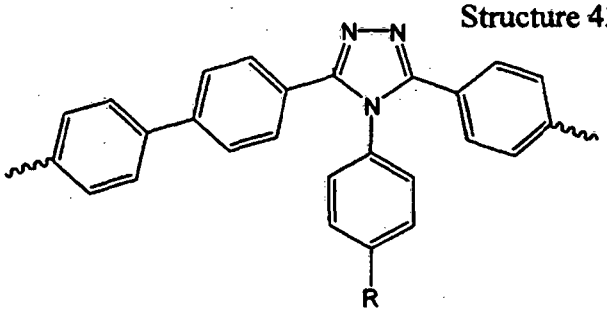


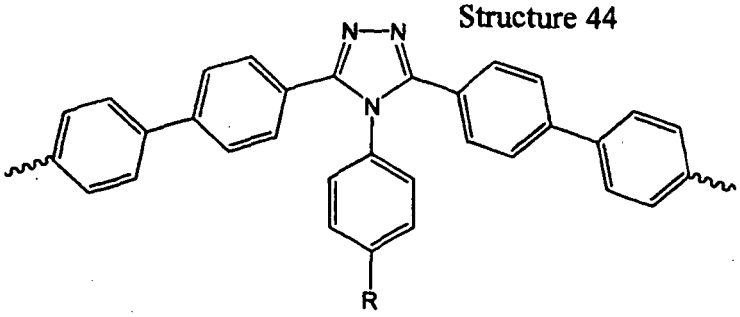


Structure 42

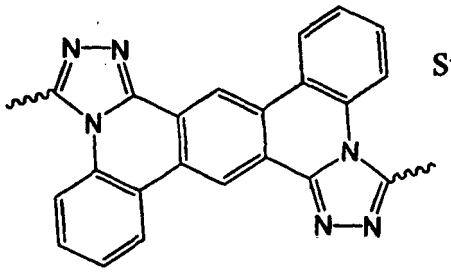
Structure 43



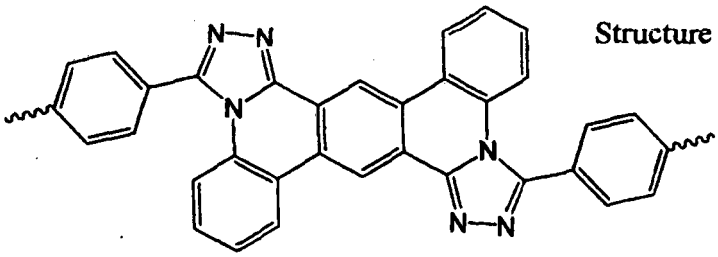
Structure 44



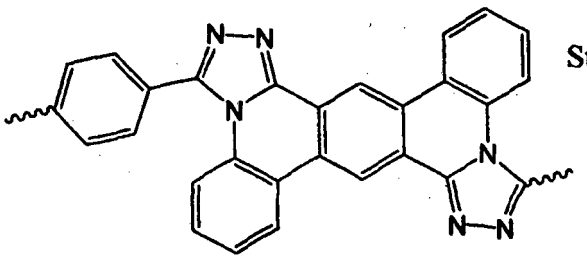
Structure 45



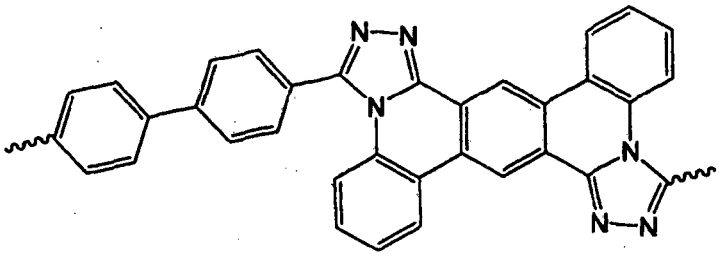
Structure 46



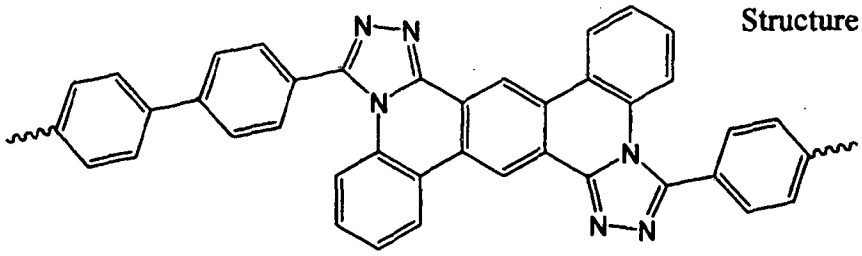
Structure 47



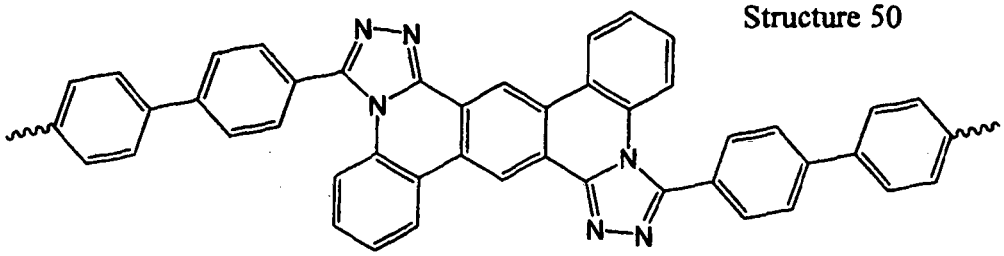
Structure 48



Structure 49

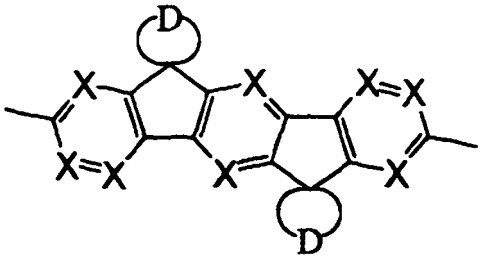


Structure 50

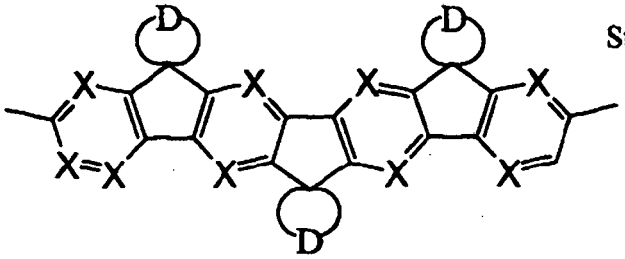


wherein each Fl may be independently chosen from:

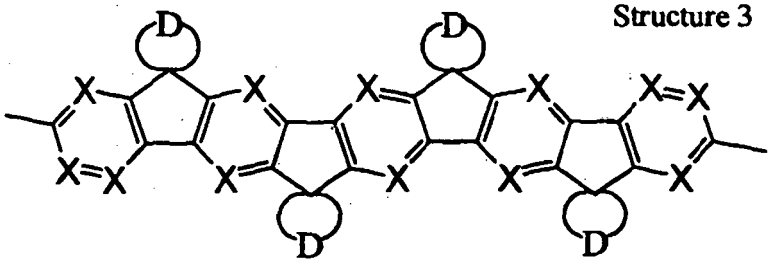
Structure 1



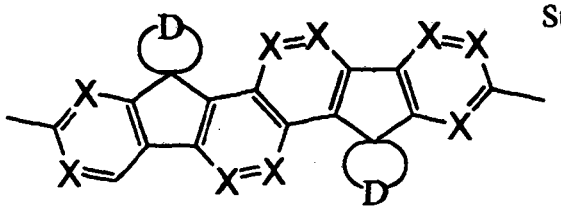
Structure 2



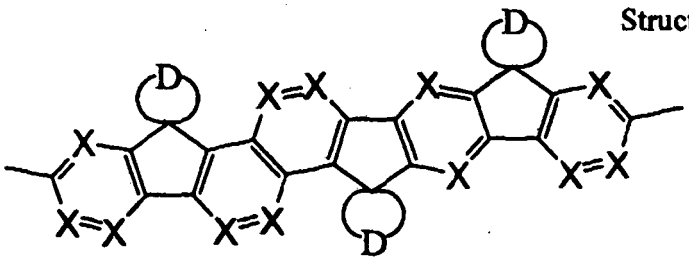
Structure 3



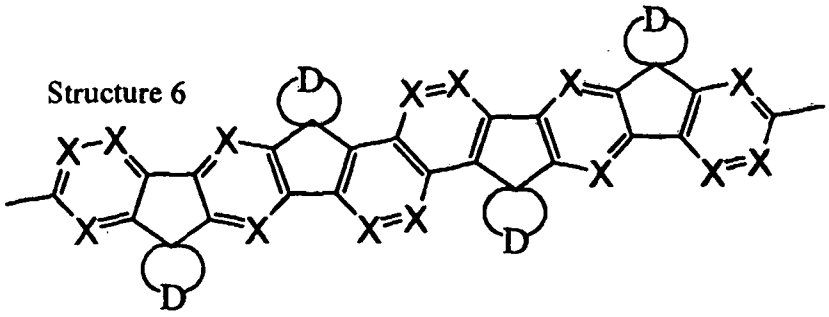
Structure 4



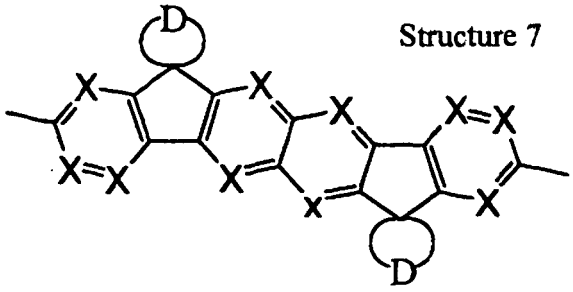
Structure 5



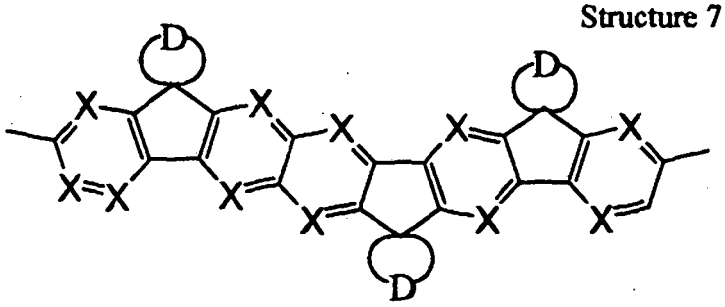
Structure 6



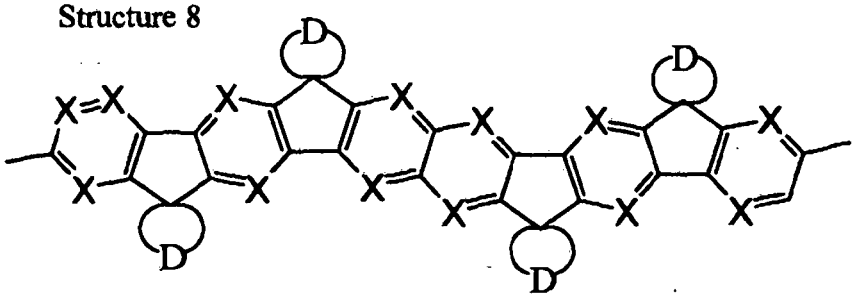
Structure 7



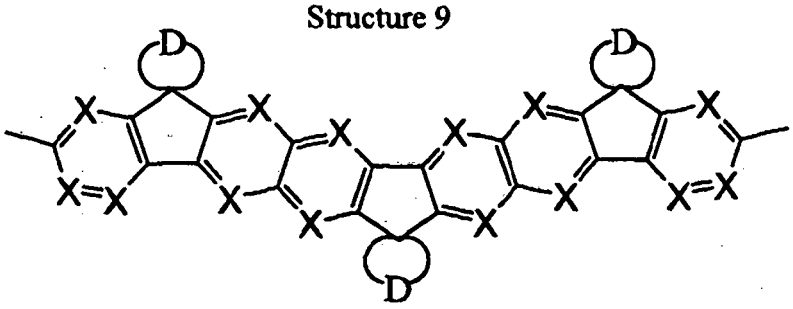
Structure 7



Structure 8



Structure 9



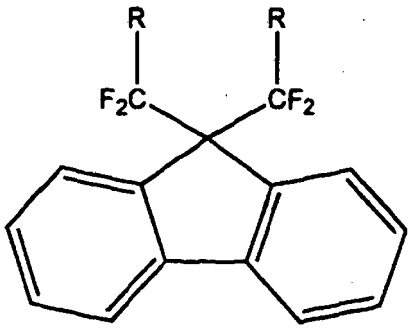
wherein the substituents

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

[0019] 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.

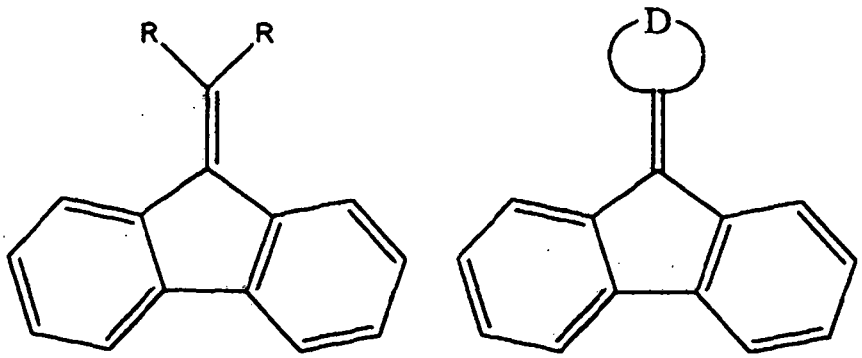
[0020] Preferably, the n subscript in the formula for A may be between 1 and 6 and preferably is from 3 to 6 and X may be chosen from =CH- or =N-.

[0021] 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.

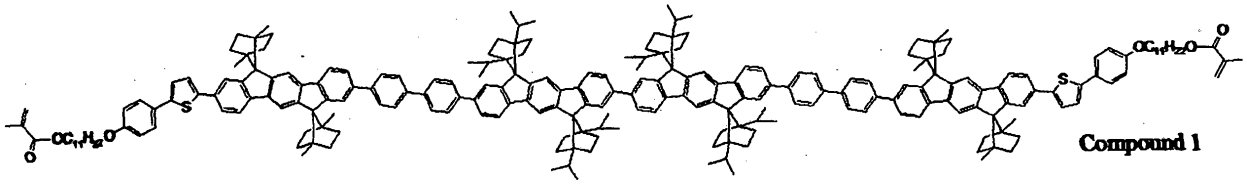
[0022] Alternatively, one or more of the fluorene ring residues in the condensed aromatic ring system may be substituted as shown in the two examples shown below:

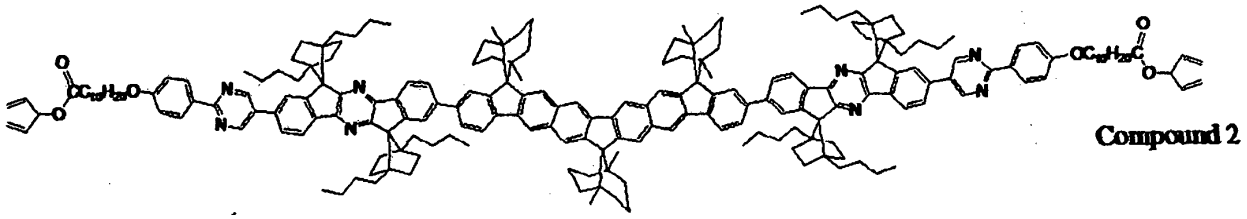


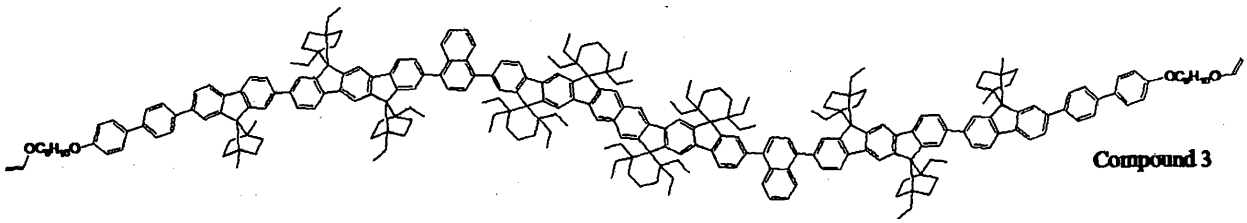
wherein R is alkyl, fluorene substituted alkyl, branched alkyl, cycloalkyl, or alkyl in which one or more carbons are substituted by hetero atoms, and

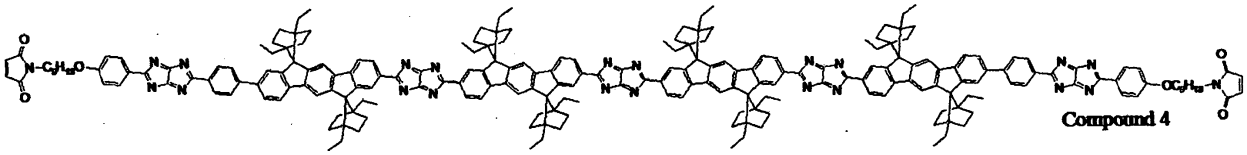
has the same meaning as the examples shown above.

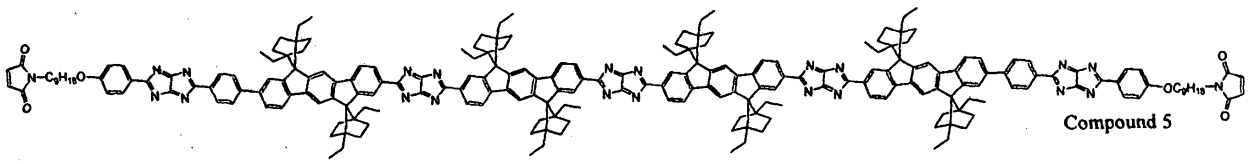
[0023] Example structures of these materials of the invention are:



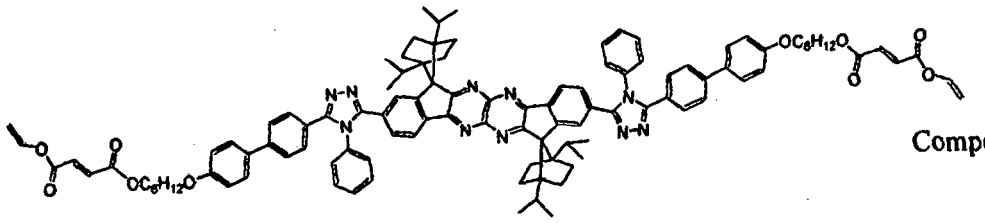




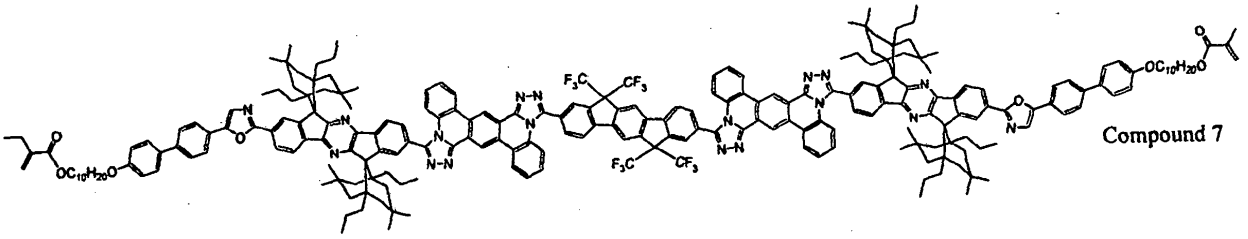




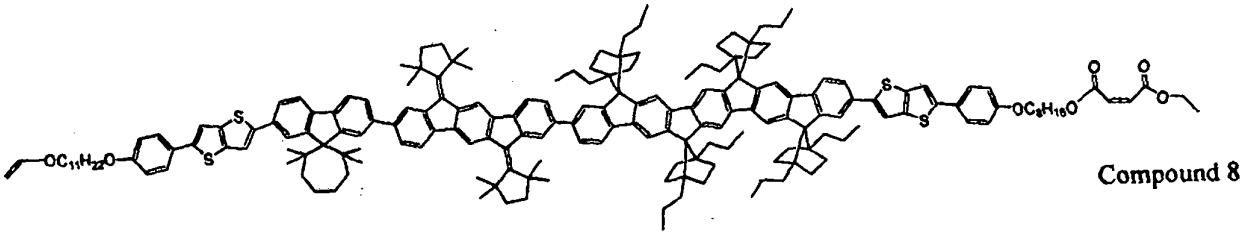
Compound 5



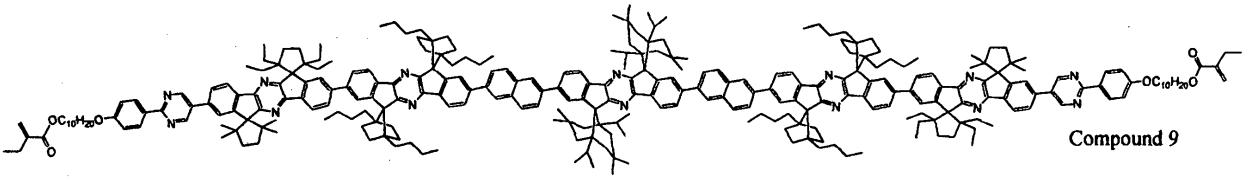
Compound 6



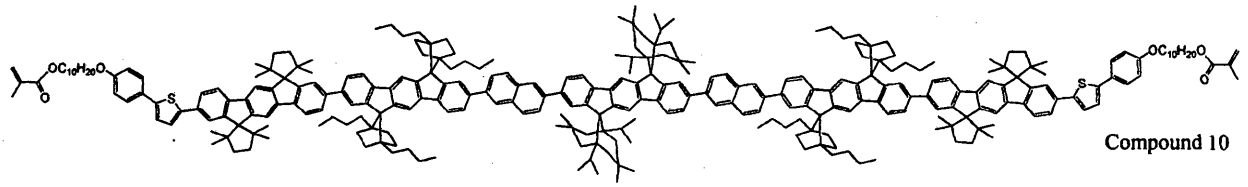
Compound 7



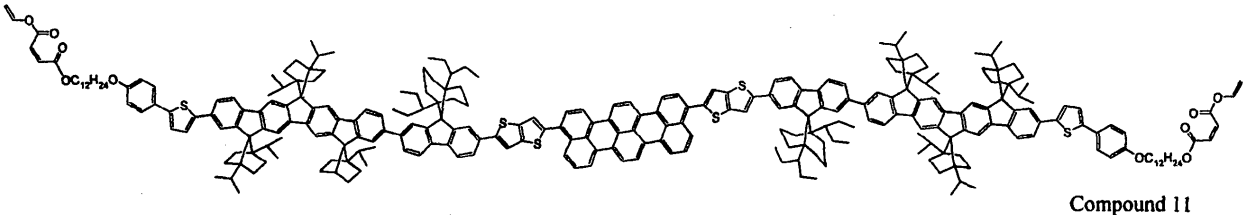
Compound 8



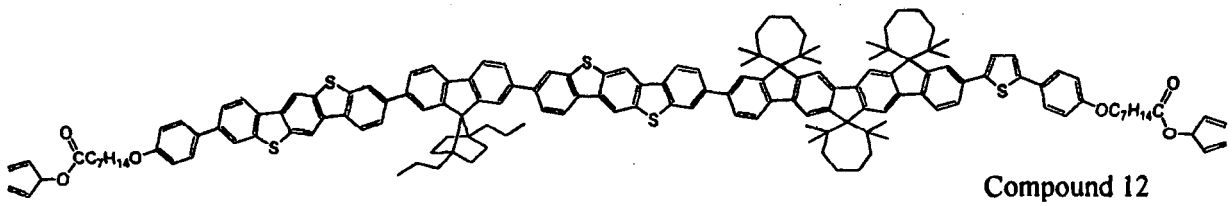
Compound 9



Compound 10



Compound 11

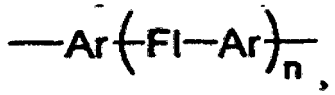


Compound 12

[0024] Also described herein are light emitting or charge transporting materials 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.

[0025] The material may be liquid crystalline.

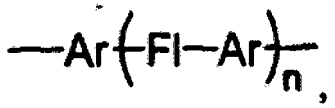
[0026] 'n' may be between 1 and 10.

[0027] The material may be a polymer.

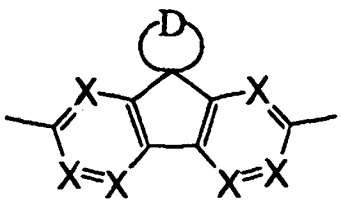
[0028] Also described herein are light emitting or charge transporting polymers of the general structure:

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:

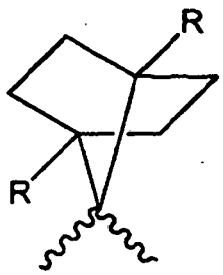


Wherein the Ar may each be independently chosen from an aromatic or heteroaromatic diradical, and may comprise a 1,4-phenylene, a biphenyl-4,4'-diyl, a terphen-4,4"-diyl, a naphthalene-1,4-diyl, a thiophene-2,5-diyl, a pyrimidine-2,5-diyl, a perylene-3,10-diyl, a pyrene-2,7-diyl, a 2,2'-dithiophen-5,5'-diyl, an oxazole-2,5-diyl, a thieno[3,2-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:

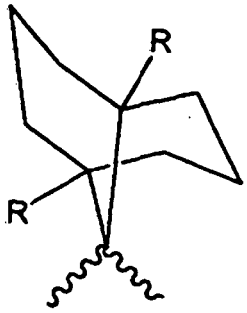


wherein the substituent

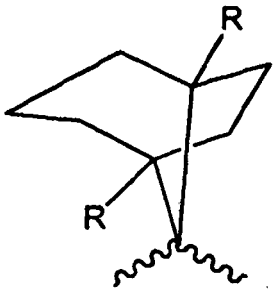
may be independently selected for each occurrence of this structure from one of the following spiro or bicyclospiro groups:



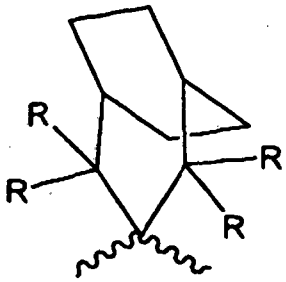
Structure 10



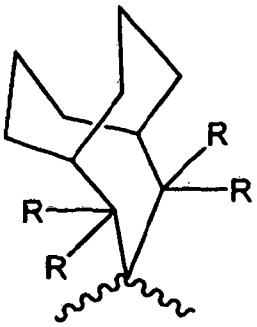
Structure 11



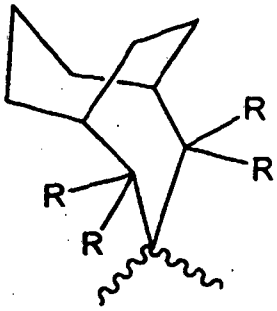
Structure 12



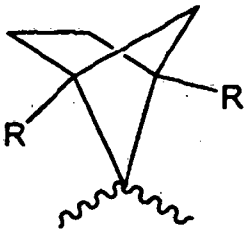
Structure 13



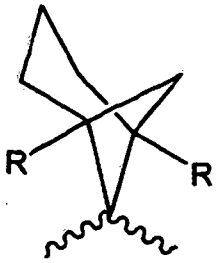
Structure 14



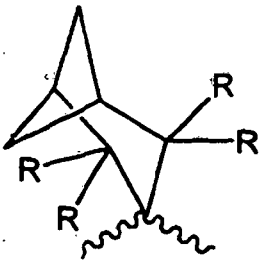
Structure 15



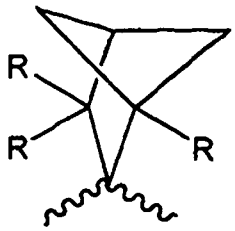
Structure 16



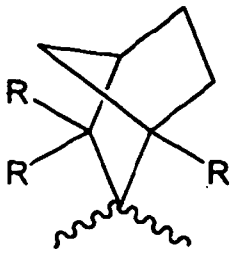
Structure 17



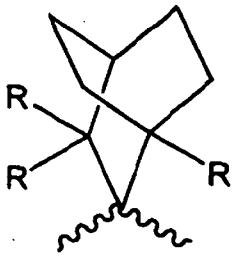
Structure 18



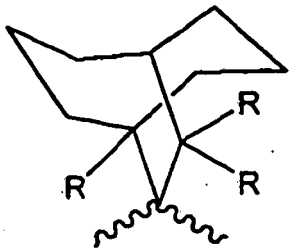
Structure 19



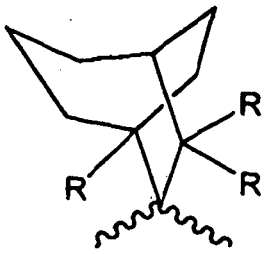
Structure 20



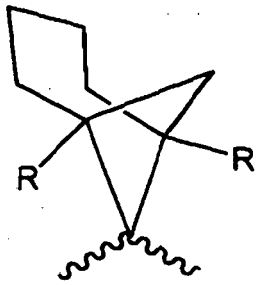
Structure 21



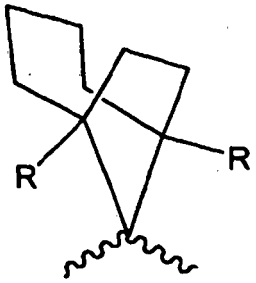
Structure 16



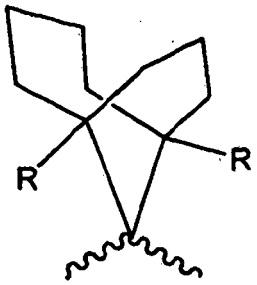
Structure 17



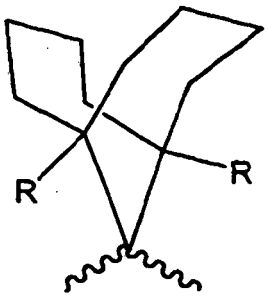
Structure 18



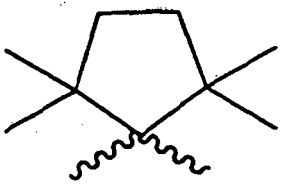
Structure 19



Structure 20



Structure 21



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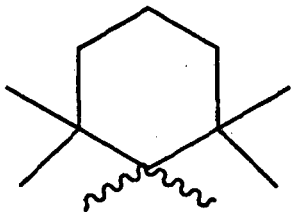

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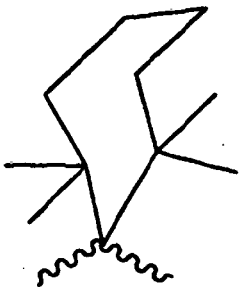

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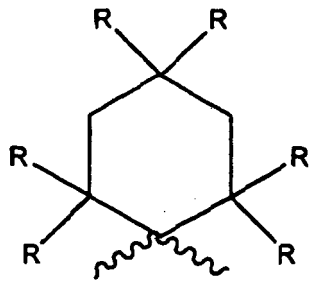

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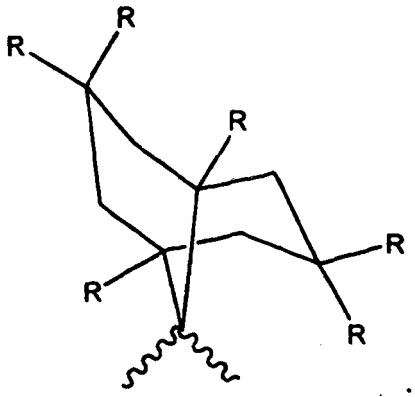
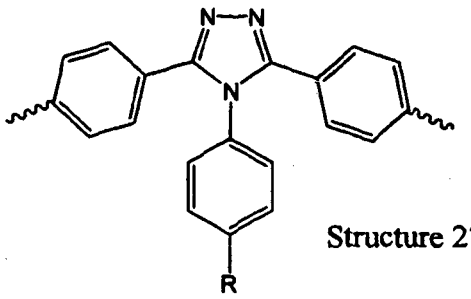


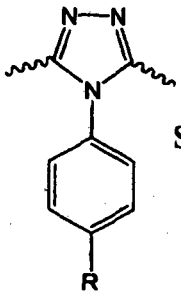
Structure 26

[0029] 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-.

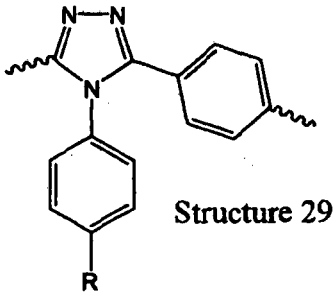
[0030] Ar may also be selected from the diradicals:



Structure 27



Structure 28



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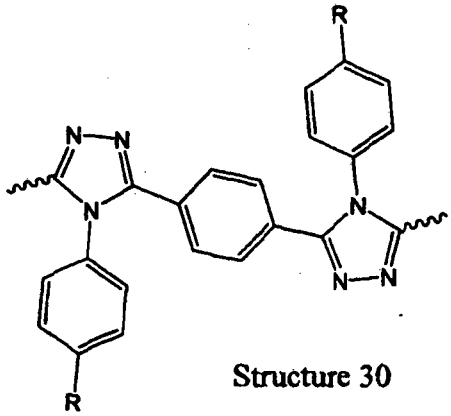
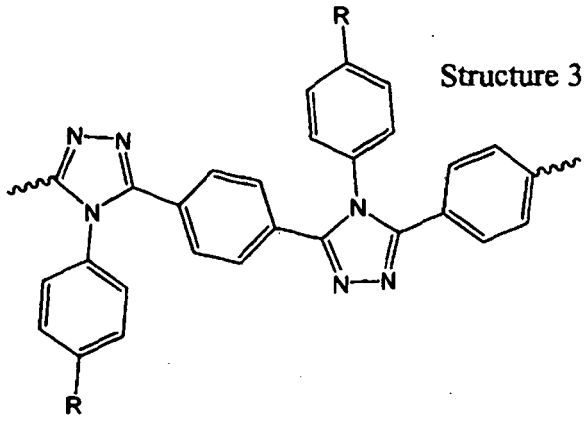


Structure 30

Structure 31



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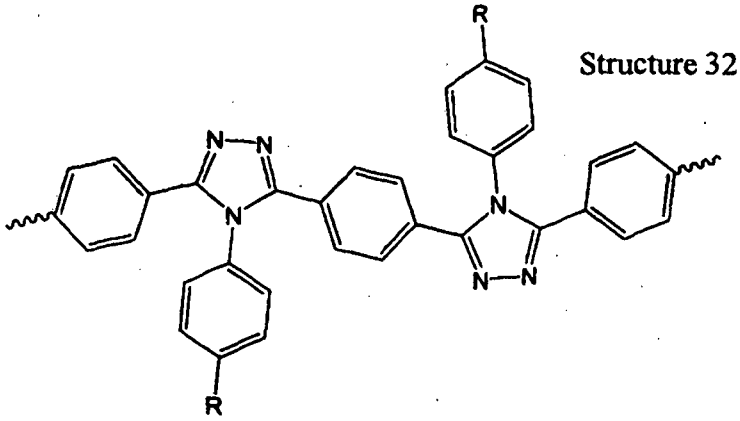

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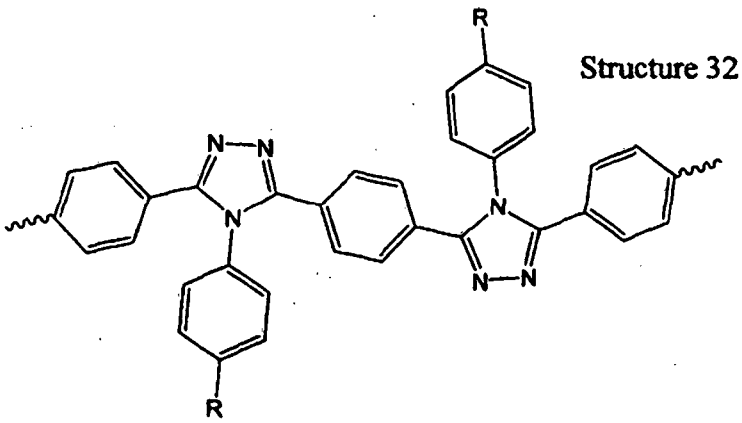

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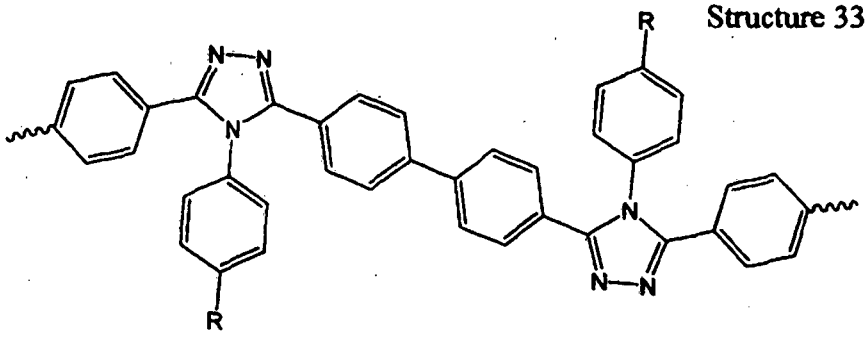

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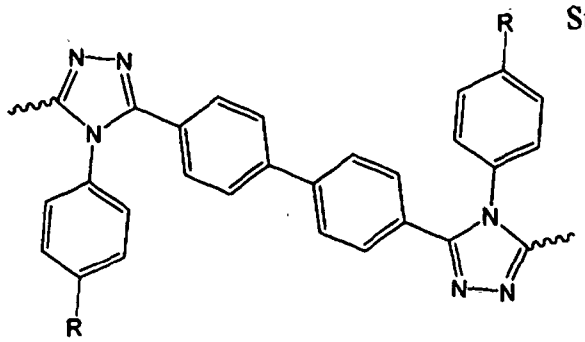

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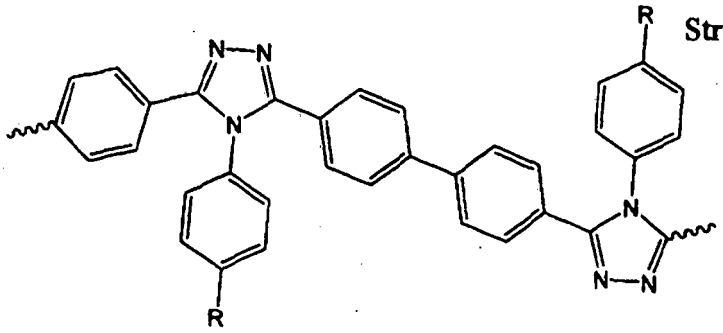

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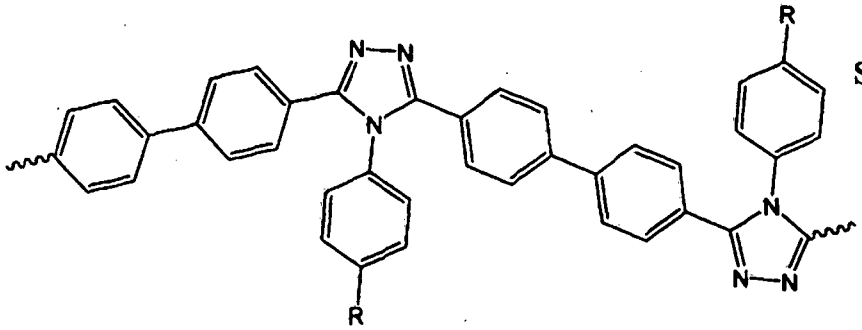
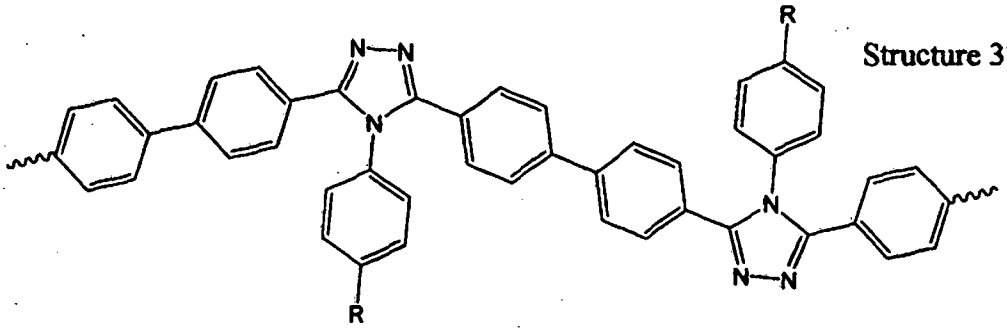


Structure 37



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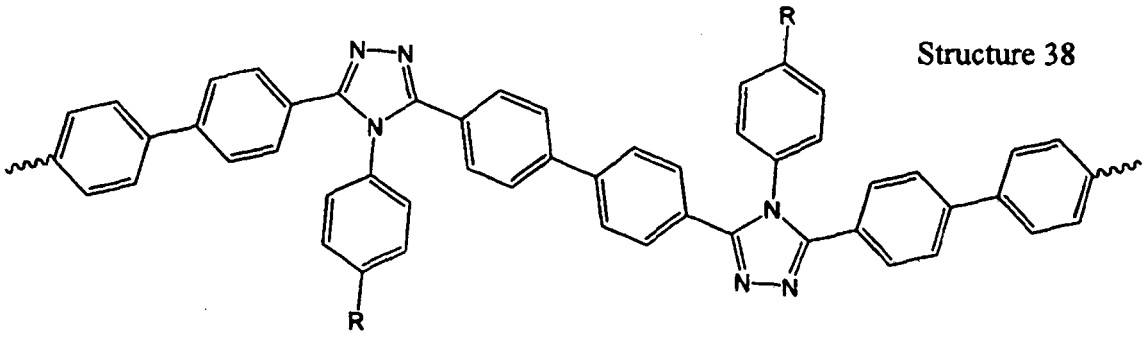

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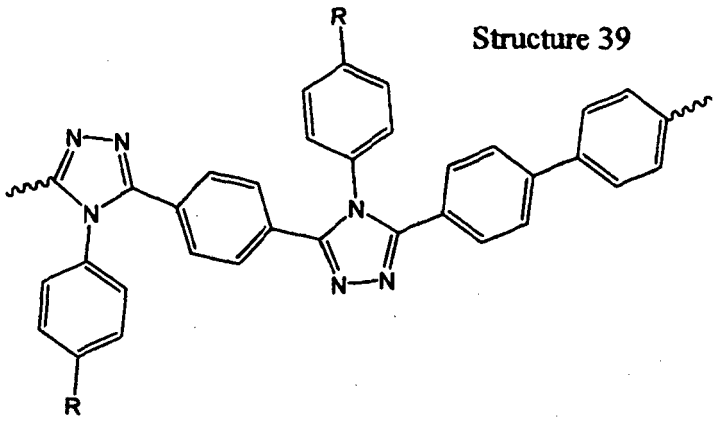

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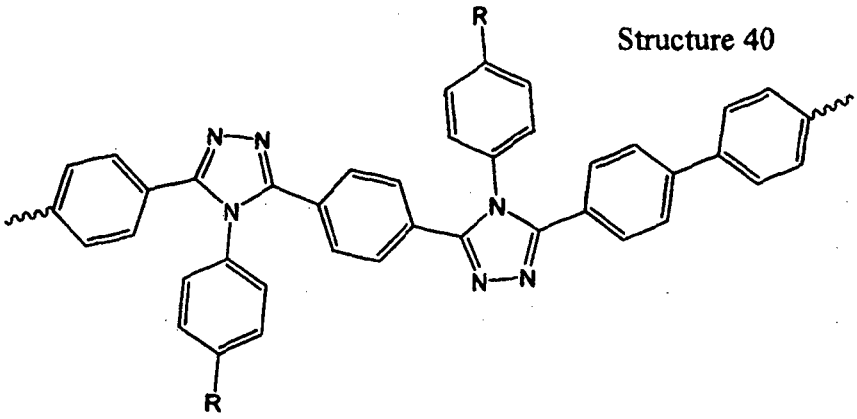

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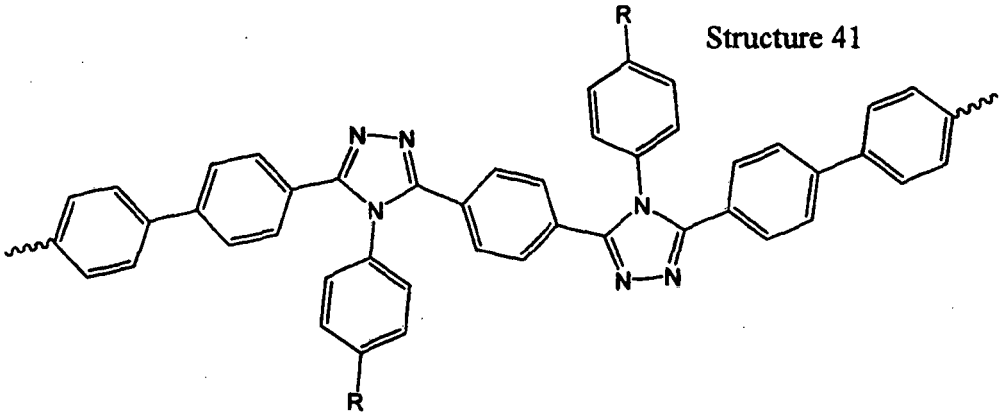

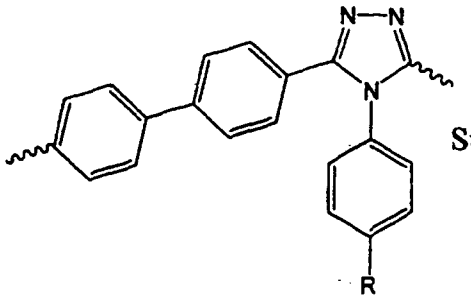

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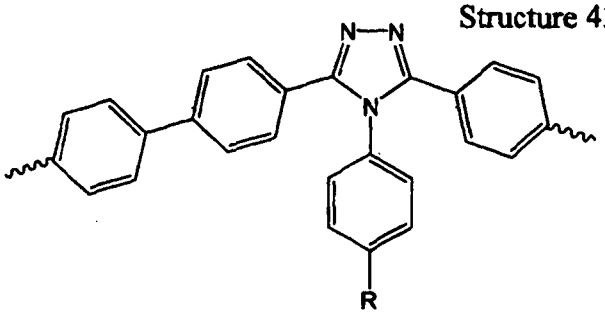

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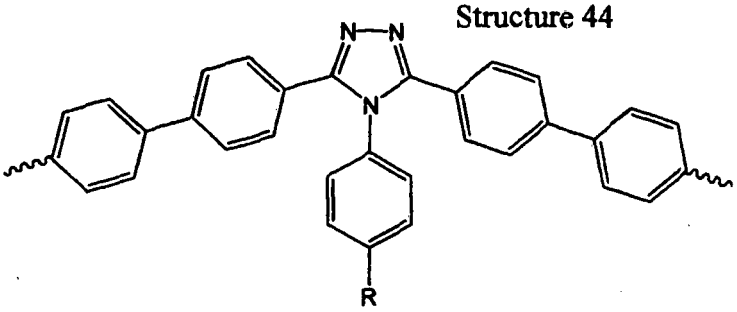

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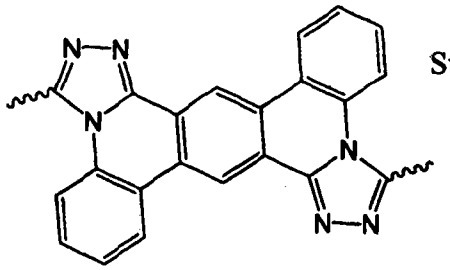

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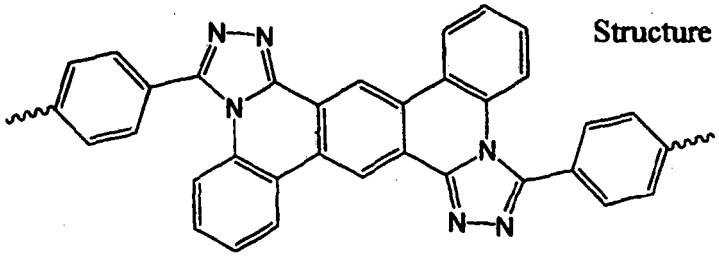

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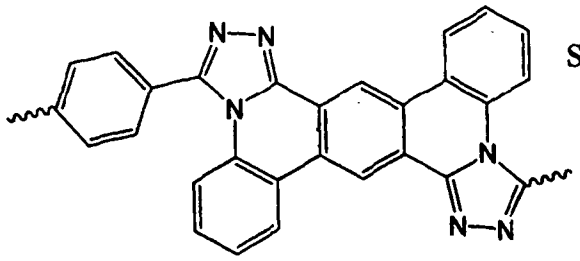

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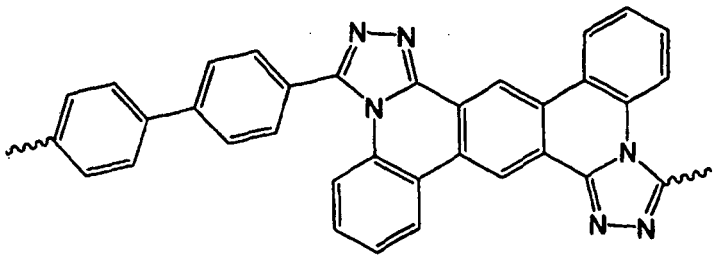

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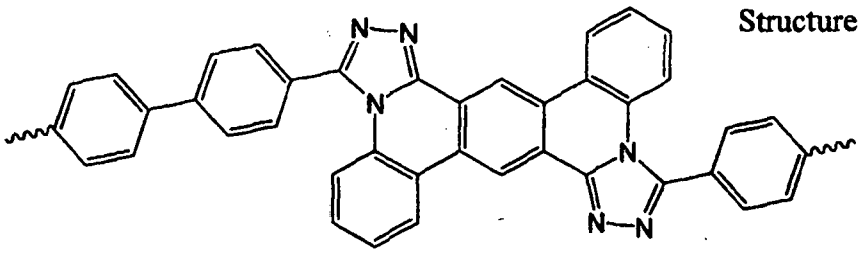

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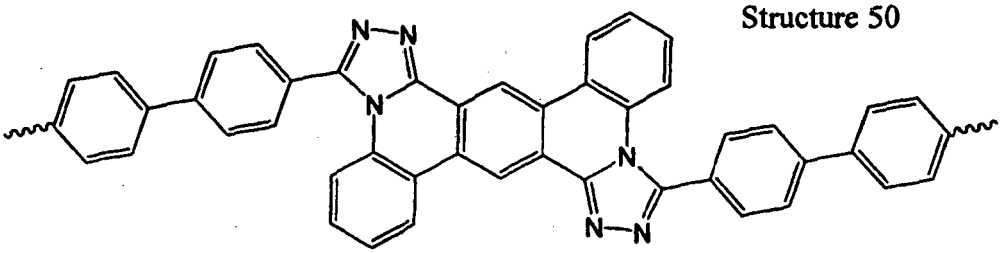
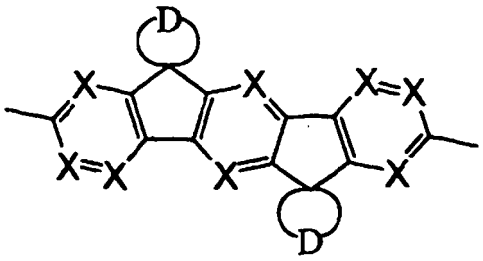


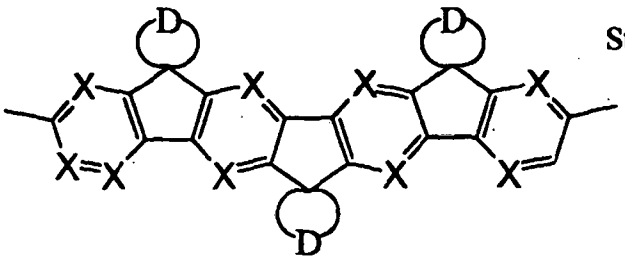
Structure 50

wherein each Fl may be independently chosen from:

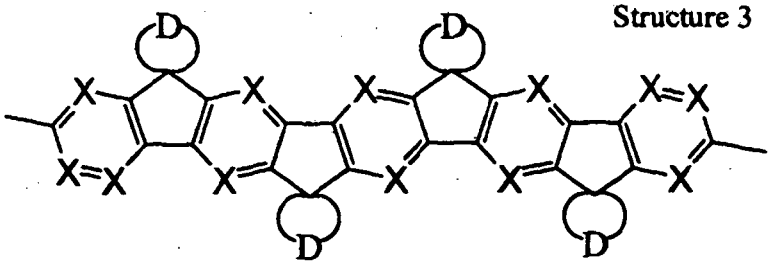


Structure 1

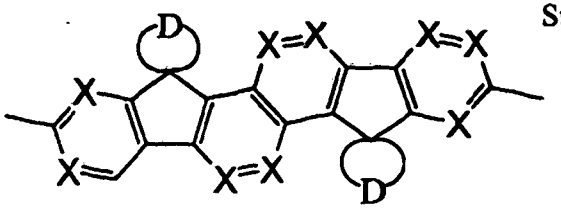
Structure 2



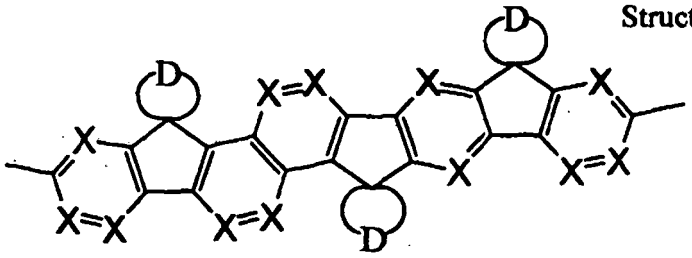
Structure 3



Structure 4

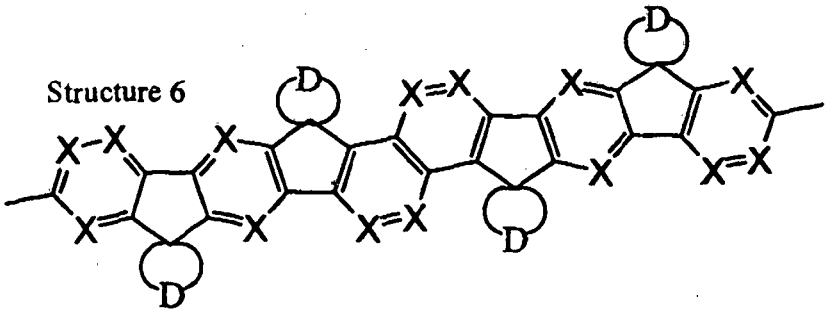


Structure 5

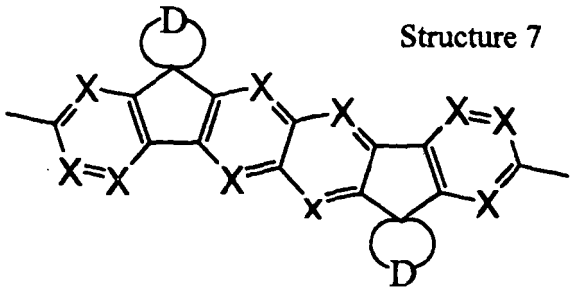


fromrom:

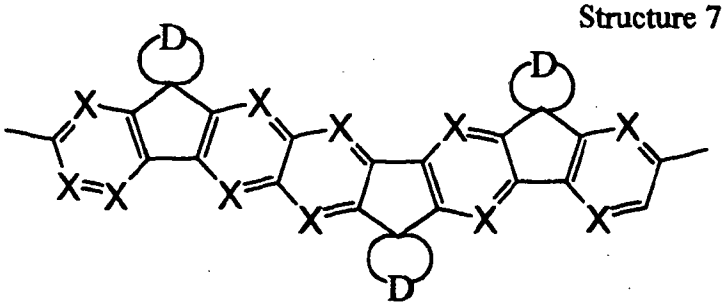
Structure 6



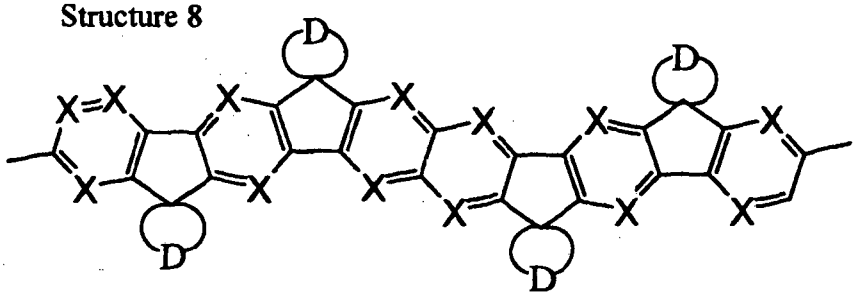
Structure 7



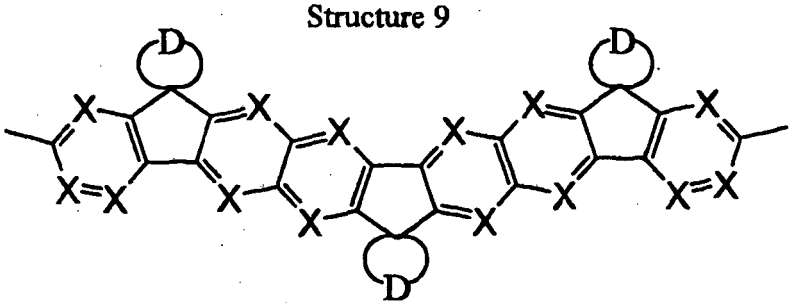
Structure 7



Structure 8



Structure 9



wherein the substituents

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

[0031] 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 neopentyl.

[0032] 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-.

and wherein T are polymer chain terminating units.

[0033] 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.

[0034] Three-dimentional models of the materials described above show them to be no more bulky than similar material in which the fluorine 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.

[0035] The preferred embodiment of the materials of the invention is one in which all of the R groups are alkyls. This is because these materials have no hydrogen substituents α to the fluorine 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.

[0036] 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[bicycle[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 F1 units in the general formula of the invention because of their symmetry and ease of synthesis.

[0037] Still further, it is preferable that all the R substituents in the materials of the invention 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.

[0038] The compounds of the invention containing diradicals F1 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 fluorine 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.

[0039] 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.

[0040] 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

[0041] (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.

[0042] 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.

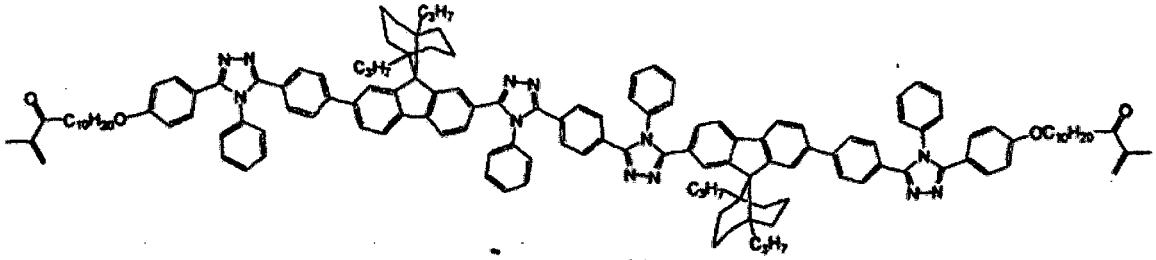
[0043] It is often also desirable to reduce the self-absorption of emitted light by organic luminescent materials. This self-absorption occurs because the spectral absorbance and emission bands of organic luminescent materials overlap to a greater or lesser extent in various materials. A solution to 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.

[0044] 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.

[0045] Also described is 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 Figure 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 hold 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 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 is also a polymerised film of a compound or mixture of compounds of the invention.

[0046] 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 is

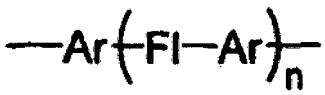


Structure 37

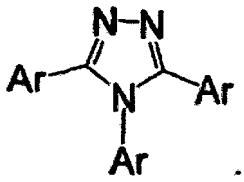
[0047] It can be seen that this material is of the type

B-S-A-S-B

with A having the structure



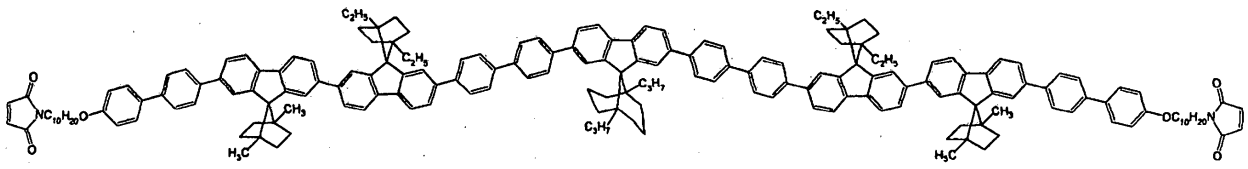
as above, but with Ar now comprising a 3,4,5-triaryl substituted 1,2,4-triazole,



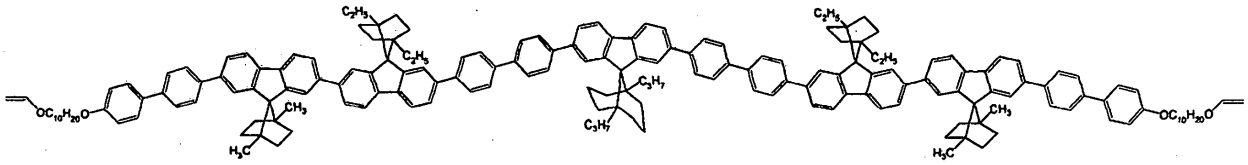
[0048] The light-emitting layer 140 of device 100 will perform optimally if electron and hole mobilities in the material are approximately the same. Unfortunately most of the best light emitting materials according to the invention have considerably higher hole mobilities than electron mobilities. However, 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.

[0049] 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 either-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.

[0050] 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 example of reactive mesogen mixtures 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



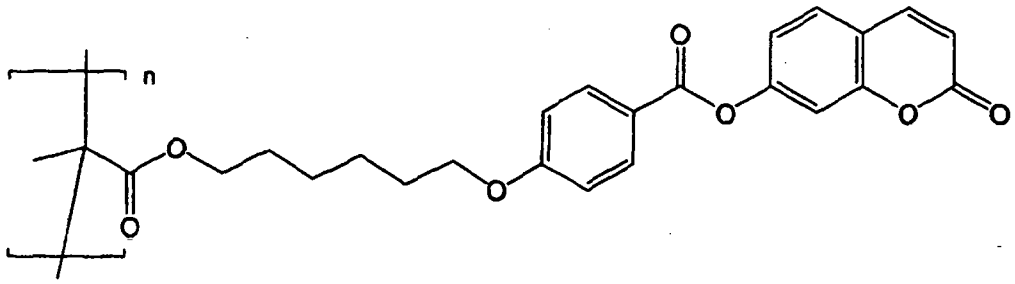
Structure 39

[0051] An 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(Al 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.

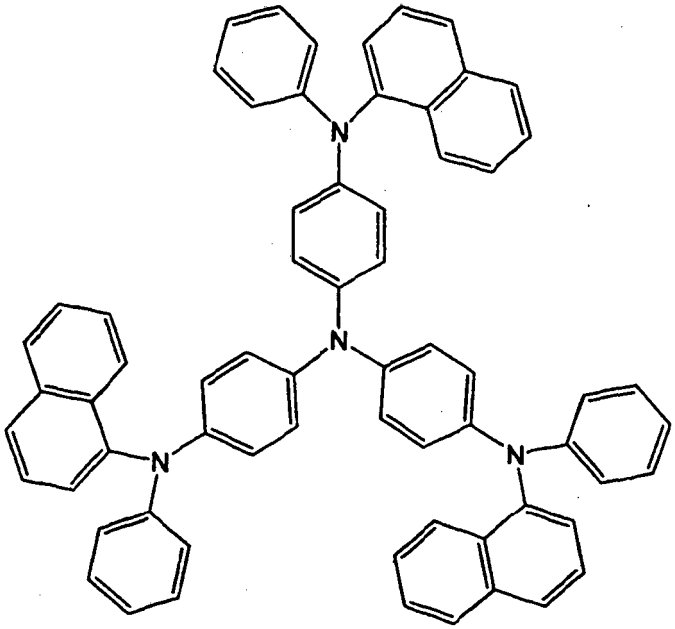
[0052] By using prior art techniques it is possible to insert a liquid crystal photoalignment material into device 100 as is shown in Figure 2. In this new device 200 the hole transporting photoalignment layer 210 aligns the molecular long axes of the molecules in the spin coated liquid crystal layer from which hold injection layer 130 is formed by photo-crosslinking. 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.

[0053] The formation of hole transporting, photoalignment layers like 210 is described in US Patent 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

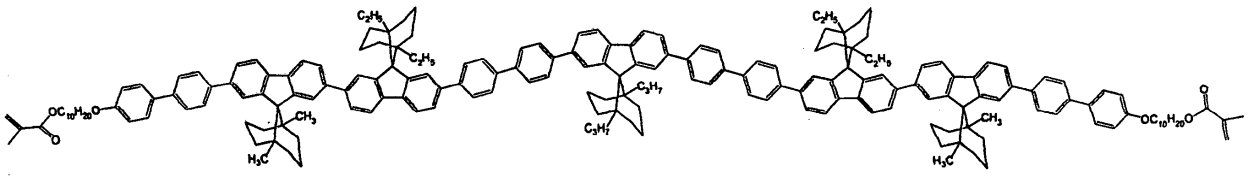


Formula 41

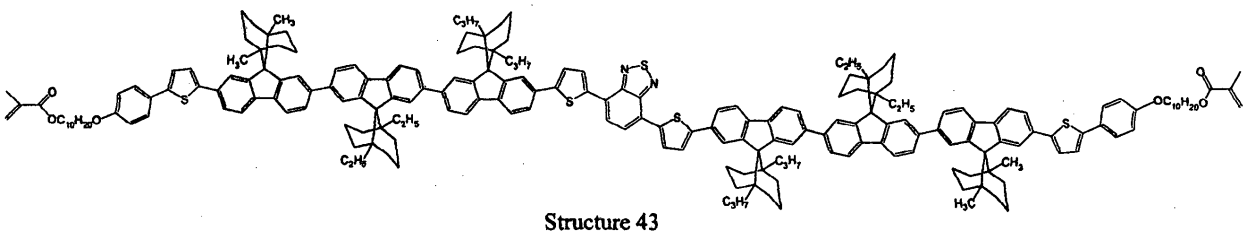
[0054] Devices like device 200 are useful because the light emitting, liquid crystalline polymer layers of the invention like 140 emit highly polarised light if they have their luminescent molecular cores uniformly aligned as they are in device 200. As a result, device 200 is an OLED that emits highly 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.

[0055] Because the light emitting and charge transporting materials of the invention can be photopattemed 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

[0056] 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.

[0057] 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.

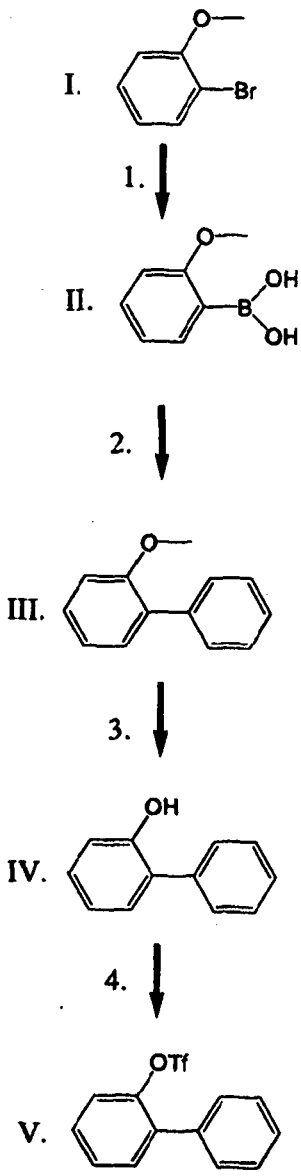
[0058] The synthesis of the oxidation resistant materials proceeds through the keto diester derivatives of alicyclic and bycyclic compounds such as VIII, XVIII, and XXVII in the following. These materials are produced by the alkylation of the enols of acetonedicarboxylic acid esters (VI and XVI). The keto compounds 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.

[0059] 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.

[0060] The synthesis of the oxidation resistant materials 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 compounds are then converted to the corresponding bromo compounds (X, X, 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.

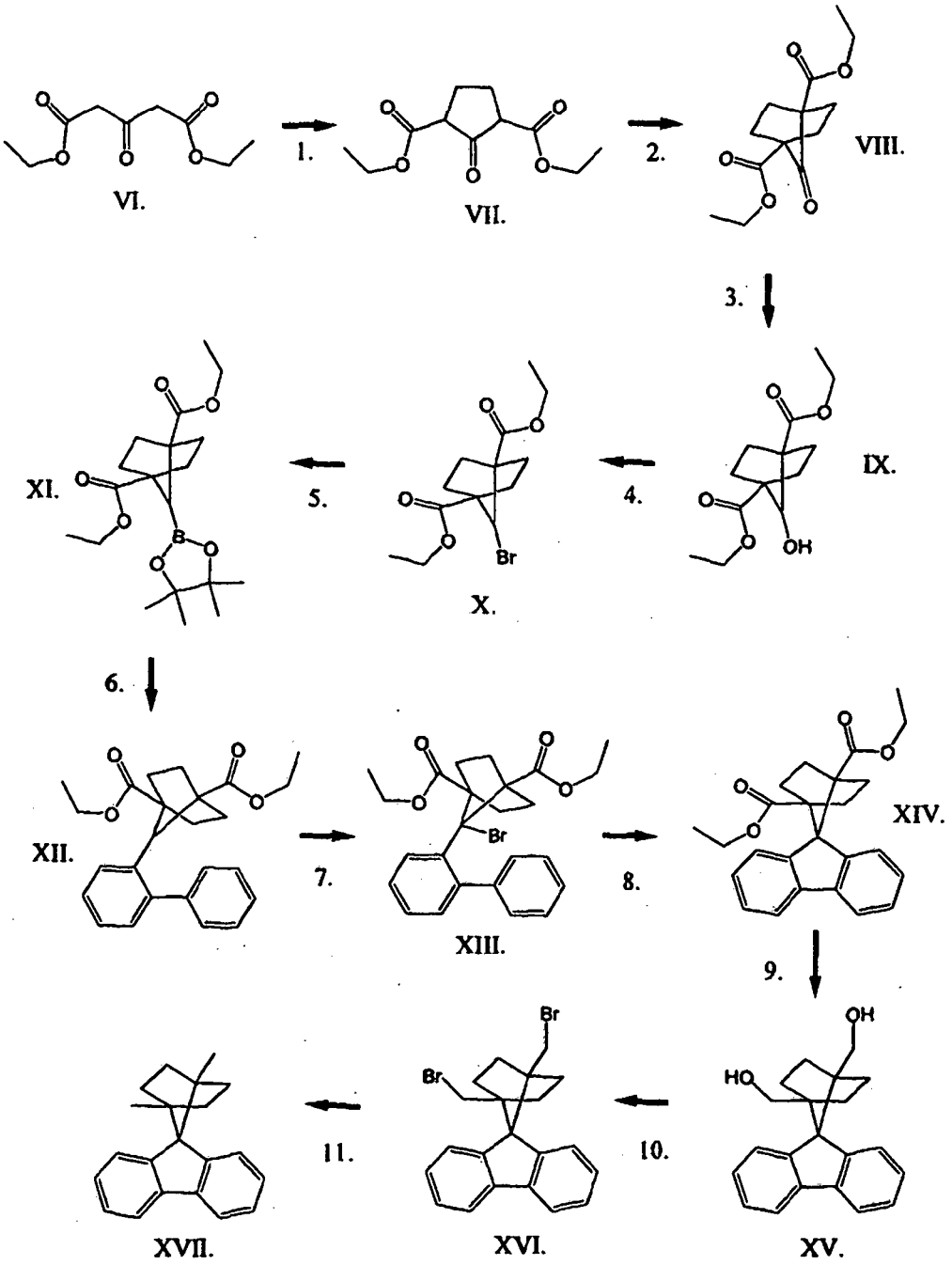
[0061] The spiro-substituted fluorenes are then dihalogenated (Scheme 5) to ready them for incorporation into the reactive mesogen backbones. Schemes 6, 8, 7, and 9 portray the synthesis of reactive mesogen LVII using a series of Stille and Suzuki coupling reactions.

Scheme 1: Synthesis of Biphenyl-2-yl Triflate



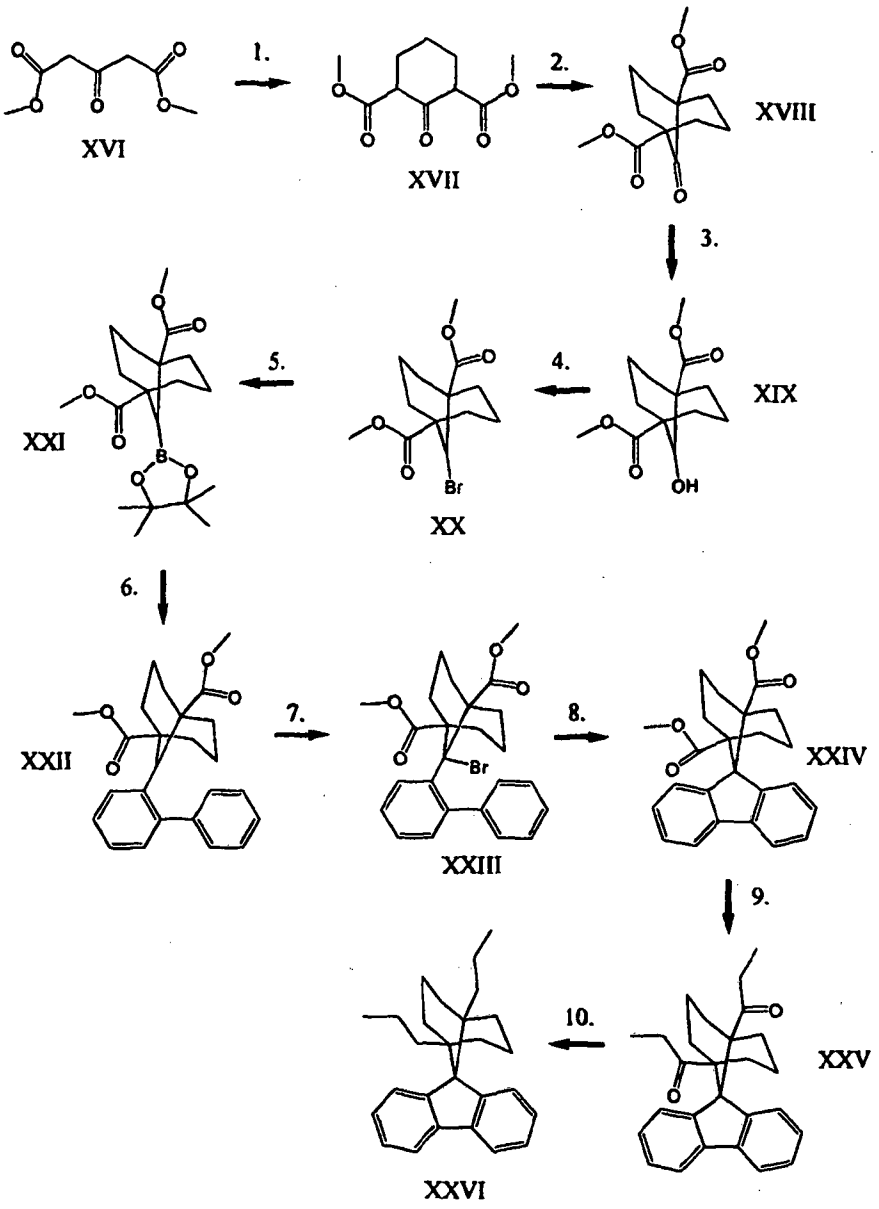
1. a. Mg, Et_2O; b. $B(OMe)_3$, THF; 2. Bromobenzene, 2 equiv. aqueous K_2CO_3, 3 mole % $Pd(PPh_3)_4$; 3. BBr_3, CH_2Cl_2, -80°C; 4. $(CF_3SO_2)_2O$, pyridine.

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



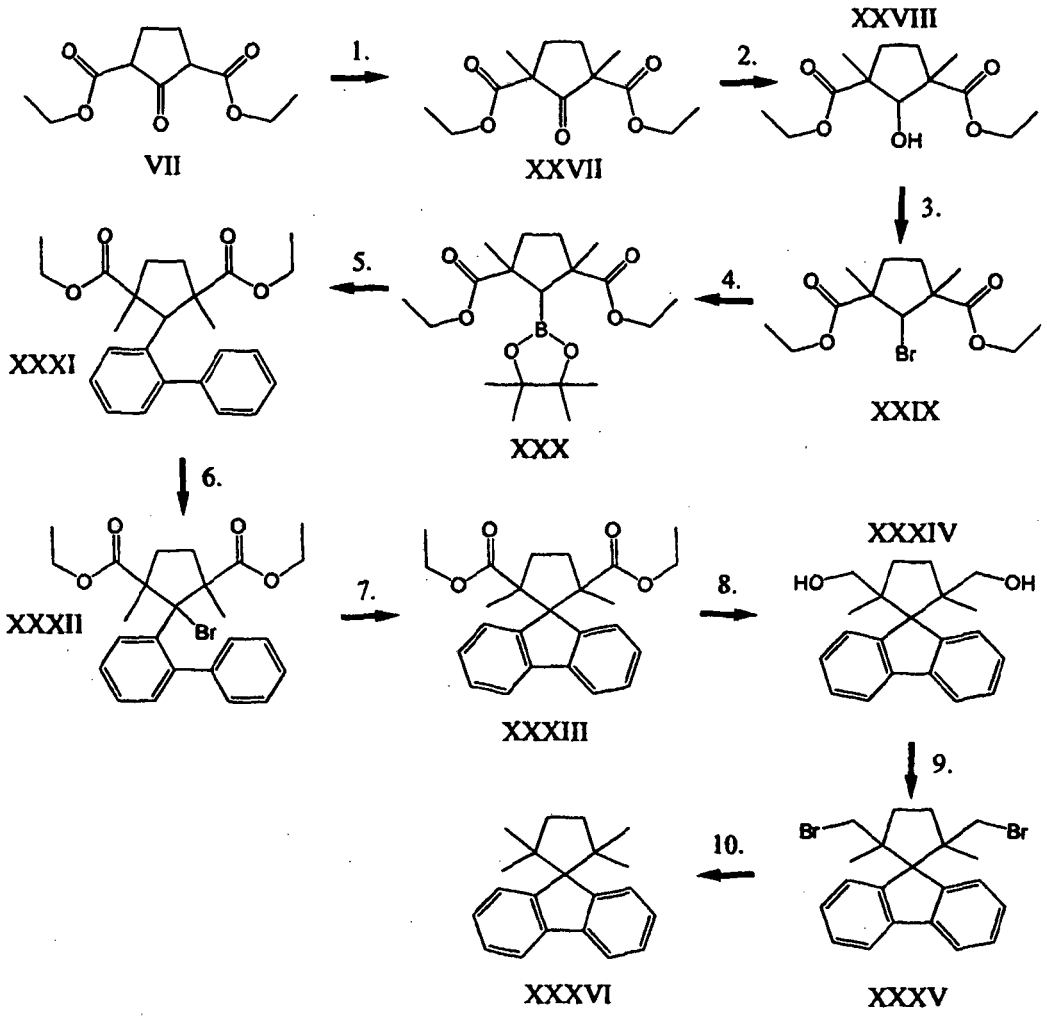
1. a. lithium diisopropylamide, THF; b. 1,2-dibromoethane, c. NaH, THF; 2. a. lithium diisopropylamide, THF; b. 1,2-dibromoethane, c. NaH, THF; 3. $NaBH_4$, CH_3OH; 4. Ph_3PBr_2, CH_3CN; 5. Bis(pinacolato)diboron, $PdCl_2(dppf)$, aqueous KOAc, dioxane; 6. Compound V, $Pd(PPh_3)_4$, toluene, aqueous Na_2CO_3;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



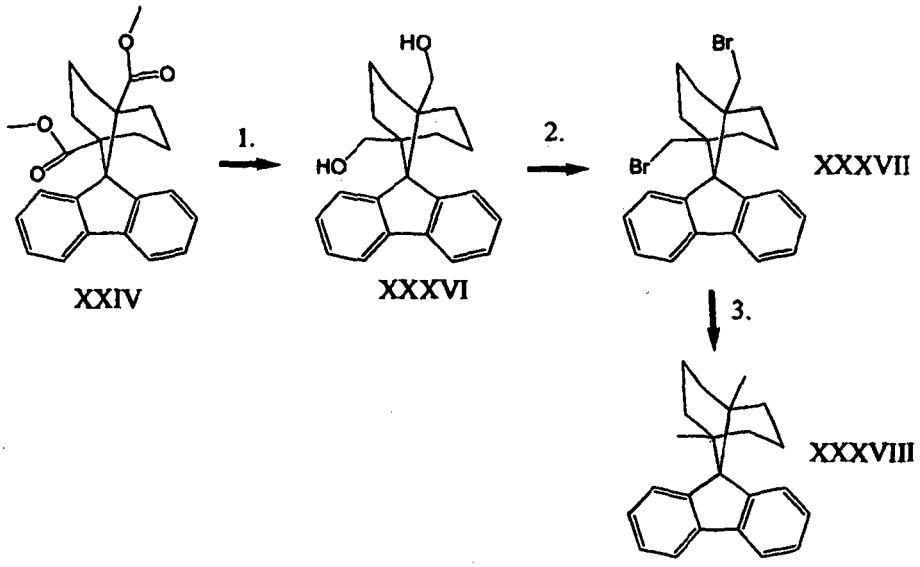
1. a. lithium diisopropylamide, THF; b. 1,3-dibromopropane, c. NaH, THF; 2. a. lithium diisopropylamide, THF; b. 1,3-dibromopropane, c. NaH, THF; 3. $NaBH_4$, CH_3OH; 4. Ph_3PBr_2, CH_3CN; 5. Bis(pinacolato)diboron, $PdCl_2(dppf)$, aqueous KOAc, dioxane; 6. Compound V, $Pd(PPh_3)_4$, toluene, aqueous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



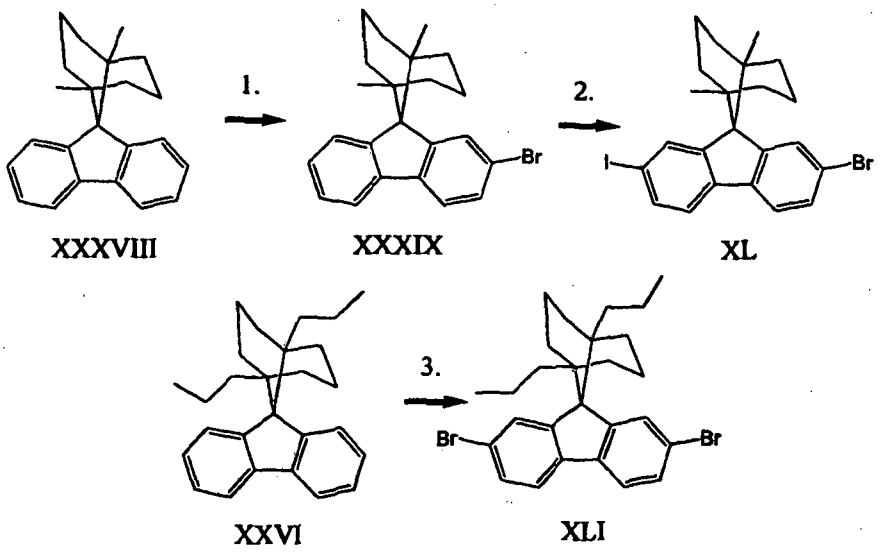
1. a. lithium diisopropylamide, THF; b. methyl iodide; 2. $NaBH_4$, CH_3OH; 3. Ph_3PBr_2, CH_3CN; 4. Bis(pinacolato)diboron, $PdCl_2$(dppf), aqueous KOAc, dioxane; 5. Compound V, $Pd(PPh_3)_4$, toluene, aqueous Na_2CO_3; 6. Br_2, CCl_4, dibenzoyl peroxide, UV light; 7. Boron triflouride etherate, THF;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



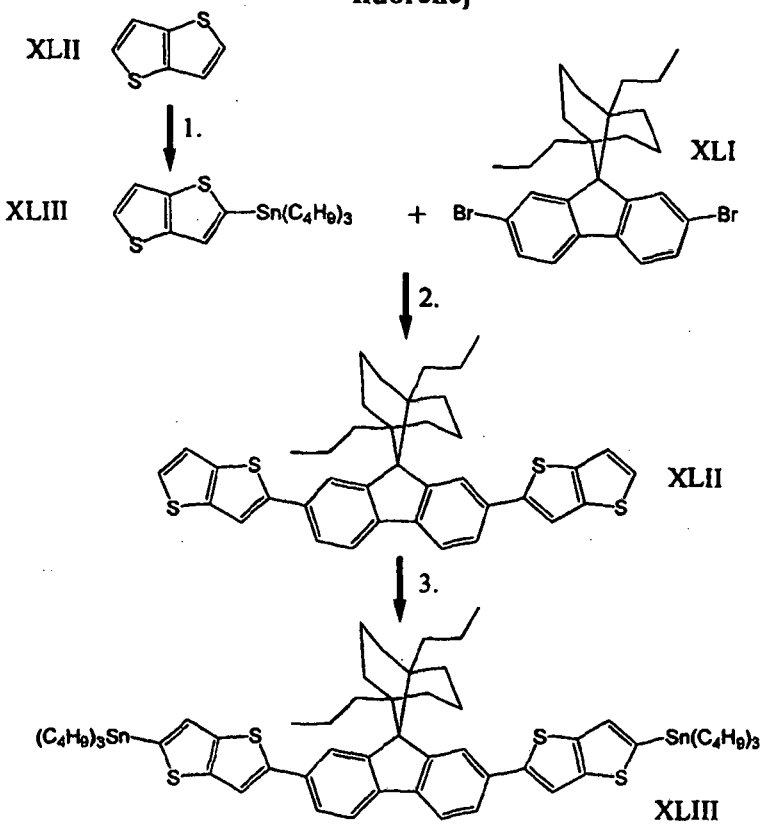
1. $LiEt_3BH$, THF; 2. Ph_3PBr_2, CH_3CN; 3. $LiEt_3BH$, THF.

Scheme 5: Synthesis of dihalofluorenes



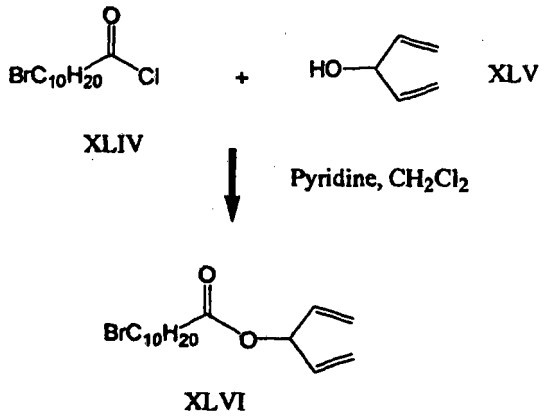
1. Br_2, $CHCl_3$; 2. I_2, HIO_4, CH_3COOH; 3. Br_2, $CHCl_3$

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]

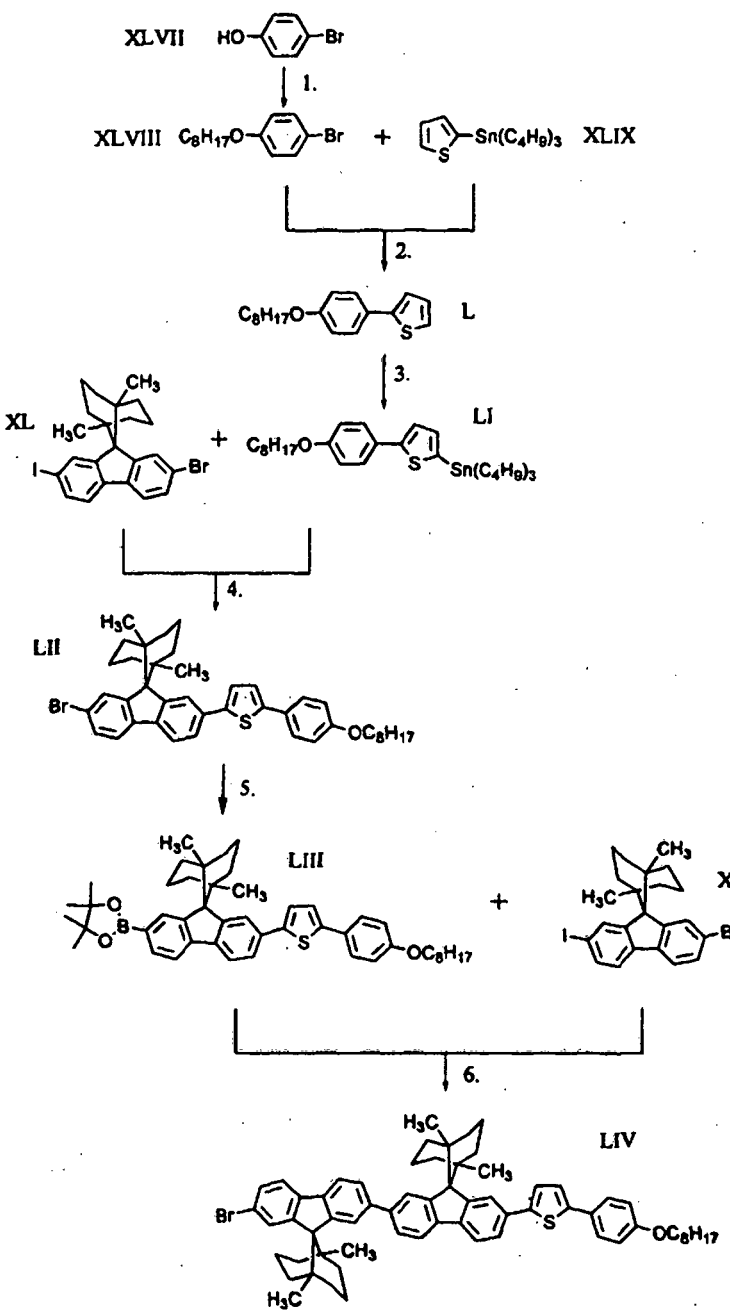


1. a. C_4H_9Li, THF (dry), -78°C, b. $ClSn(C_4H_9)_3$ (room temp.) 2. $Pd(PPh_3)_4$, DMF, 80°C
3. a. C_4H_9Li, THF (dry), -78°C, b. $ClSn(C_4H_9)_3$ (room temp.)

Scheme 7: Synthesis of Spacer / Crosslinker

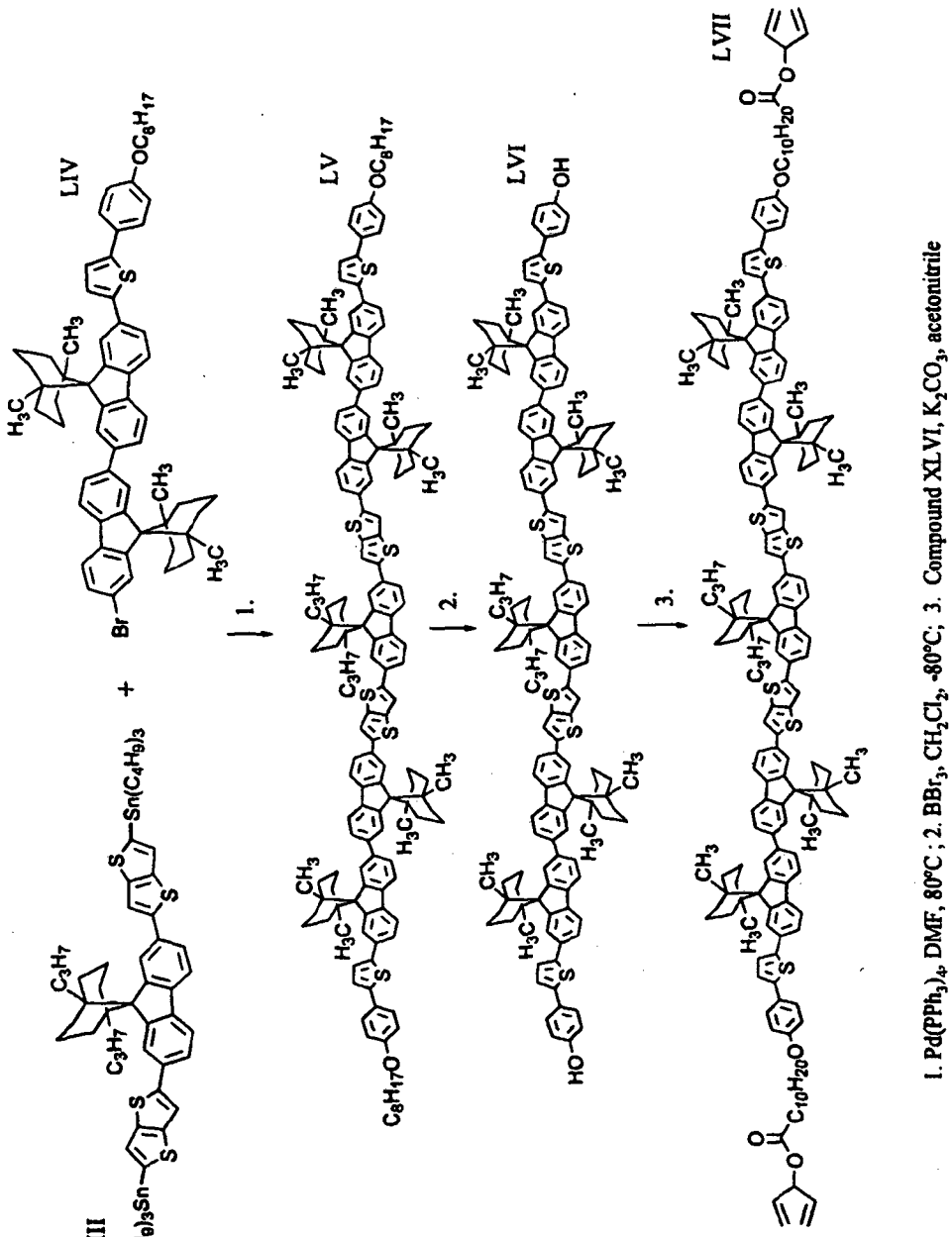


Scheme 8: Synthesis of Key Intermediate 7-([4-octyloxyphenyl]thien-2-yl) 2-(7-bromo{1,5-dimethyl spiro[bicyclo[3,3,1]nonane-9,9'-fluorene]}-2'-yl) spiro[bicyclo[3,3,1]nonane-9,9'-fluorene]

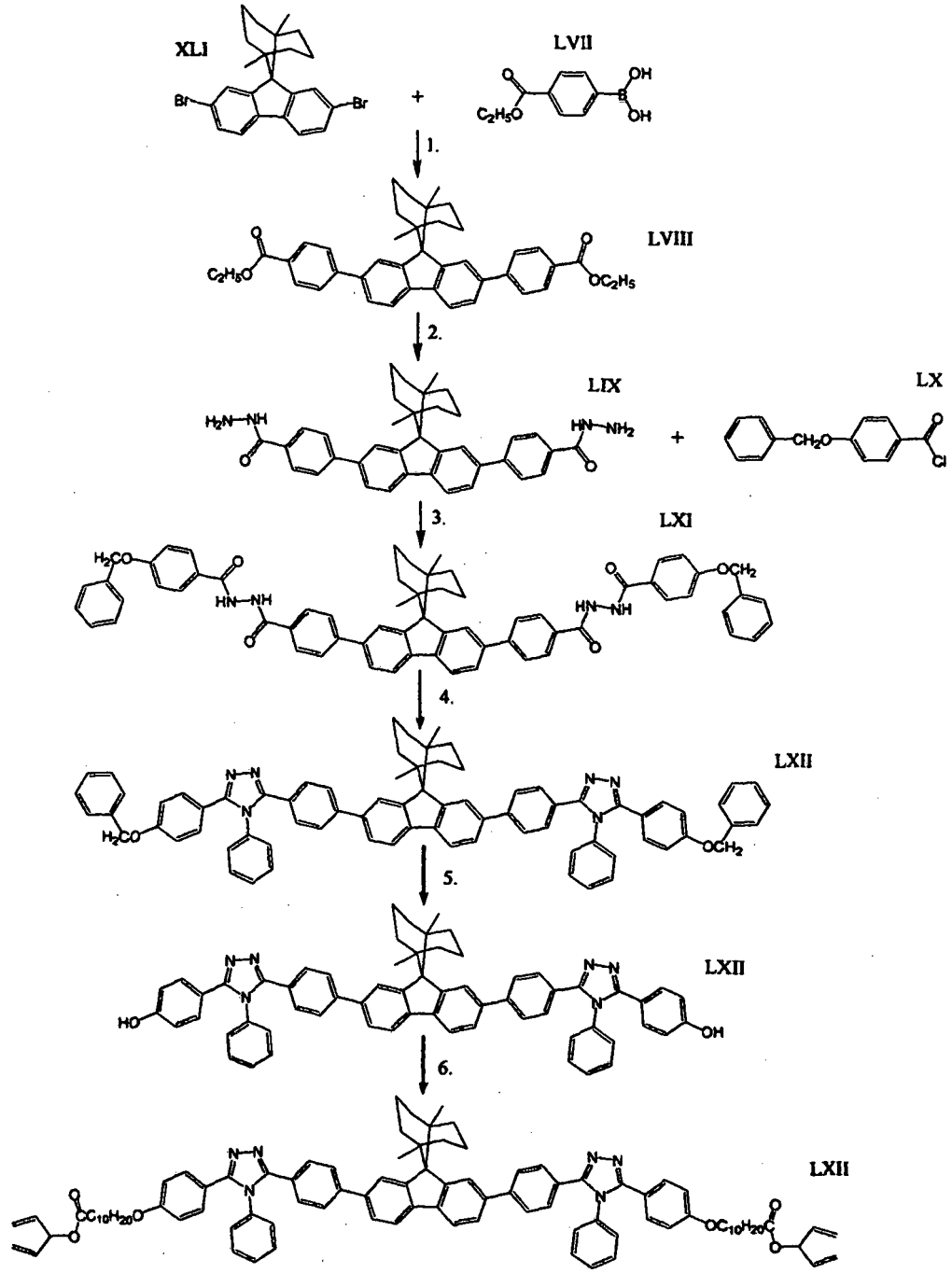


1. 1-bromooctane, K_2CO_3, butanone, reflux; 2. $Pd(PPh_3)_4$, DMF, 80°C ; 3. a. C_4H_9Li, THF (dry), -78°C, b. $ClSn(C_4H_9)_3$ (room temp.) 4. $Pd(PPh_3)_4$, DMF, 80°C ; 5. Bis(pinacolato)diboron, $PdCl_2$(dppf), aqueous KOAc, dioxane; 6. Compound XXXX, $Pd(PPh_3)_4$, toluene, aqueous Na_2CO_3;

Scheme 9: Synthesis of Electroluminescent Reactive Mesogen



Scheme 10: Synthesis of Electron Transporting Reactive Mesogen



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_3, acetonitrile

Claims

1. OLED compounds of the general structure:

B-S-A-S-B

in which:

A is a substantially linear covalently bonded chain comprising a condensed aromatic ring structure in turn comprising fluorene ring structures condensed with at least one additional fluorene ring structure;
S is a spacer group comprising an alkyl chain optionally containing one or more heteroatoms; and
B is a crosslinking chemical group;

wherein the fluorene ring systems comprised by the condensed aromatic structure are substituted at the 9-position, and in which there are no hydrogen substituents α- to the 9-position of the fluorene ring system or any of the fluorene ring systems.

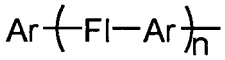
2. Compounds according to claim 1 in which the additional fluorene ring systems comprise at least one of benzene, naphthalene, indene, and other fluorene ring systems.

3. Compounds according to claim 1 or 2, wherein each B is independently selected from 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.

4. Compounds according to any preceding claim wherein B comprises a methacrylate group.

5. Compounds according to any preceding claim wherein B comprises a 1,4-pentadien-3-yl group.

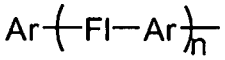
6. Compounds according to any preceding claim in which A represents a substantially linear, covalently bonded chain of aromatic or heteroaromatic diradicals of the general formula



wherein:

each Ar is individually selected from an aromatic or heteroaromatic diradical;
Fl comprises a fluorene-2,7-diyl diradical spiro substituted at the 9-position with an alicyclic ring system; and
n is an integer from 1 to 6.

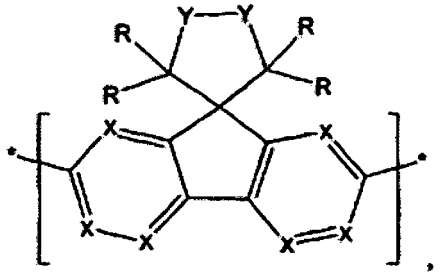
7. Compounds according to any of claims 1 to 5 in which A represents a substantially linear, covalently bonded chain of aromatic or heteroaromatic diradicals the general formula

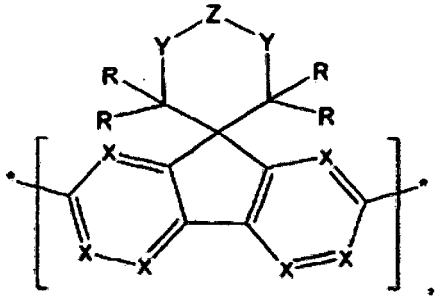


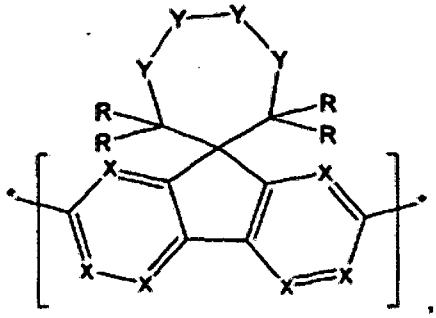
wherein:

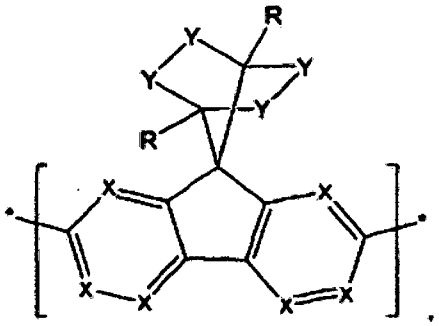
each Ar is independently selected from 1,4-phenylene, a biphenyl-4,4'-diyl, a terphen-4,4"-diyl, a naphthalene-1,4-diyl, a thiophene-2,5-diyl, a pyrimidine-2,5-diyl, a perylene-3,10-diyl, a pyrene-2,7-diyl, a 2,2'-dithiophen-5,5'-diyl, an oxazole-2,5-diyl, a thieno[3,2-b] thiophene-2,5-diyl, a dithieno[3,2-b:2',3'-d] thiophene-2,6-diyl, or an imidazo[4,5-d]imidazole-2,5-diyl diradical, or a single bond;
Fl comprises a fluorene-2,7-diyl diradical spiro substituted at the 9-position with an alicyclic ring system; and
n is an integer from 1 to 6.

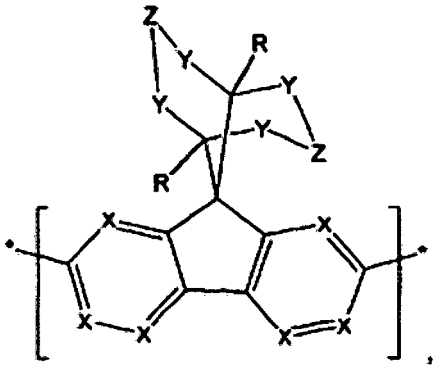
8. Compounds according to claim 6 or 7, wherein Fl comprises a diradical chosen from:

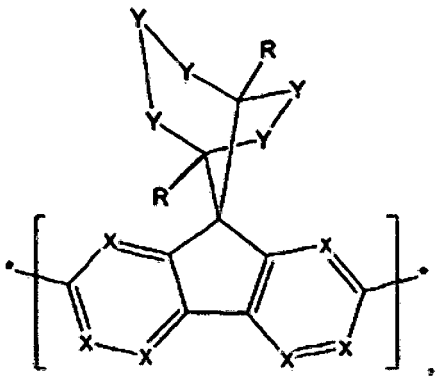


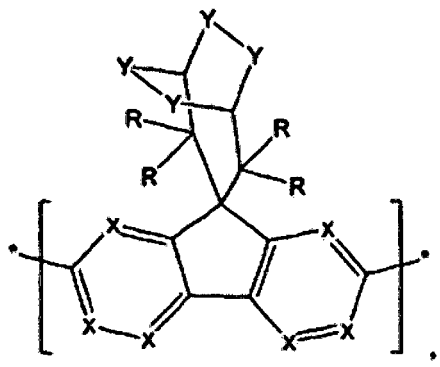


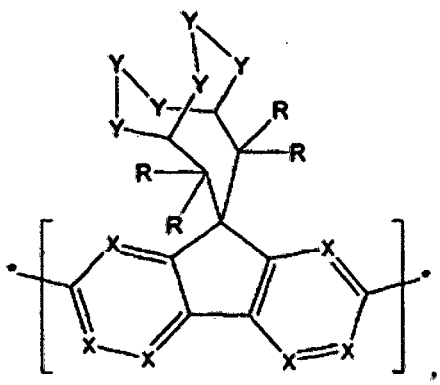


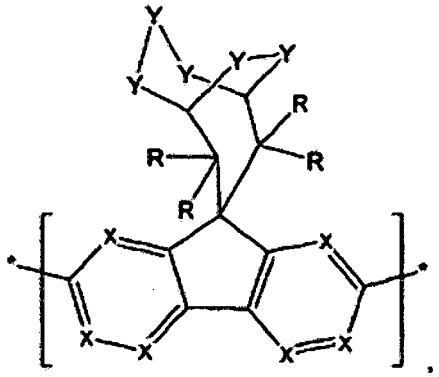


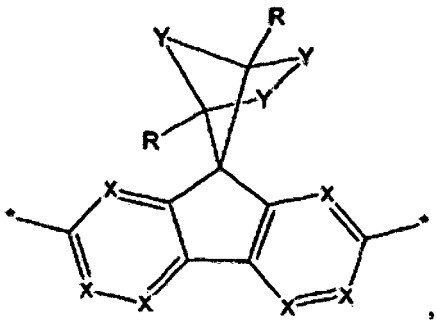


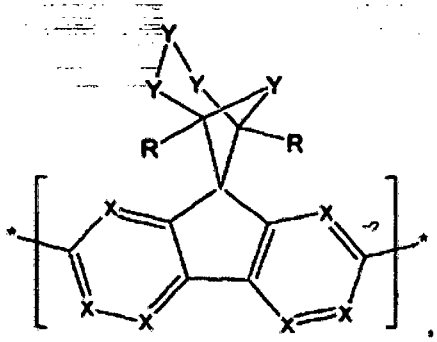


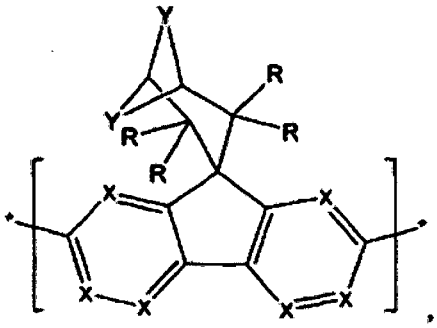


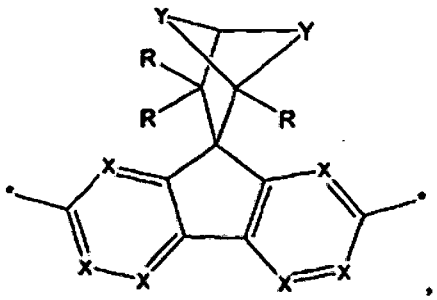


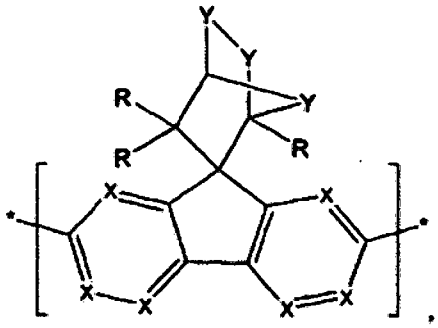


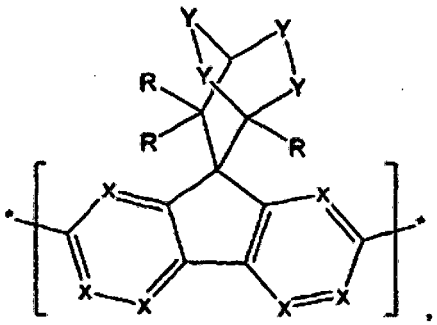


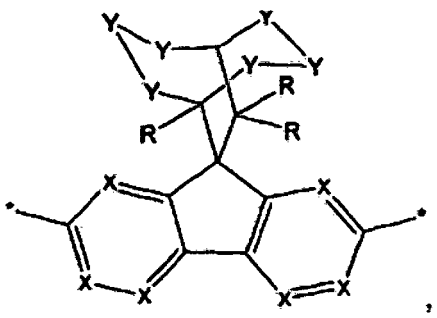


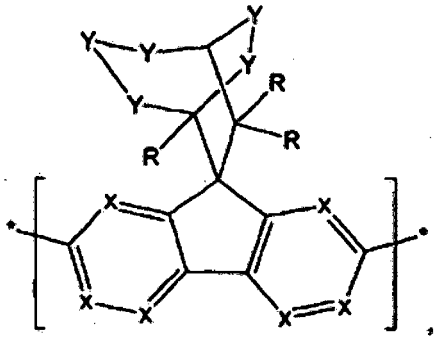


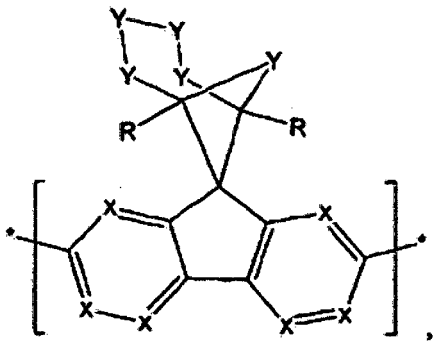


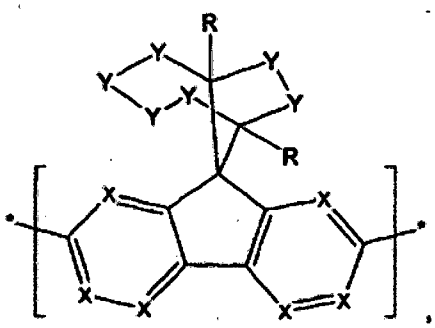


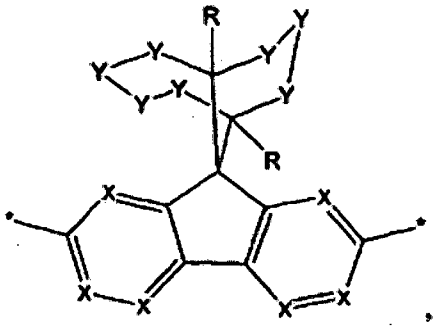




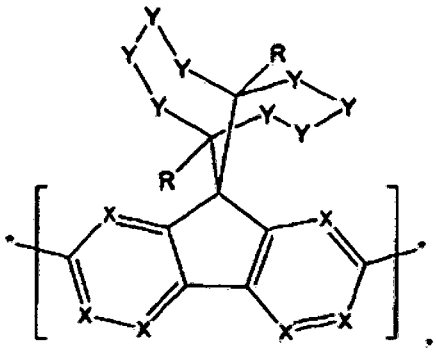








and



wherein:

X may be chosen independently from CH, N, CR', or CF, and R' = C_nH_{2n+1} where n may have values chosen independently from 1 to 5;
Y and Z are chosen independently from CH_2, CHR", $CR"_2$, NH, NR", O, S, S=O, O=S=O, and C=O and R" = C_nH_{2n+1} where n may have values chosen independently from 1 to 5; and
R are independently chosen from C_nH_{2n+1} where n may have values chosen independently from 1 to 5.

9. Compounds according to claim 8 wherein X = CH, Y = Z = CH_2 and each R is independently selected from methyl, ethyl and propyl.

10. Compounds according to claim 8 wherein X = CH; Y = CH_2; Z = CHR"; and each R and each R" are independently

selected from methyl, ethyl and propyl.

11. Compounds according to claims 8, 9 or 10 in which the R groups are the same.

12. Compounds according to claims 6 to 11 in which n is from 3 to 6.

Patentansprüche

1. OLED-Verbindungen der allgemeinen Struktur:

B-S-A-S-B

wobei:

A eine im Wesentlichen lineare Kette mit kovalenter Bindung ist, die eine kondensierte aromatische Ringstruktur umfasst, die wiederum Fluorenringstrukturen umfasst, die mit wenigstens einer weiteren Fluorenringstruktur kondensiert sind;
S eine Spacergruppe ist, die eine Alkylkette umfasst, die optional ein oder mehrere Heteroatome aufweist; und
B eine vernetzende chemische Gruppe ist;

wobei die Fluorenringsysteme, welches die kondensierte aromatische Struktur umfasst, an der 9-Position substituiert sind, und wobei keine Wasserstoffsubstituenten α zu der 9-Position des Fluorenringsystems oder eines der Fluorenringsysteme existieren.

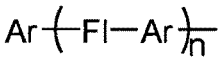
2. Verbindungen nach Anspruch 1, wobei die weiteren Fluorenringsysteme wenigstens eines der folgenden umfassen: Benzen-, Naphthalen-, Inden- und sonstige Fluorenringsysteme.

3. Verbindungen nach Anspruch 1 oder 2, wobei jedes B unabhängig ausgewählt ist aus einer Methacrylatgruppe, einer 1,4-Pentadien-3-yl-Gruppe, einer Ethacrylatgruppe, einer Vinyloxygruppe, einer Alkylvinyloxygruppe, einer Ethylmaleatogruppe, einer Ethylfumaratogruppe, einer N-Maleimidogruppe, einer Vinylmaleatogruppe, einer Vinylfumaratogruppe oder einer N-(2-Vinyloxymaleido)-Gruppe.

4. Verbindungen nach einem der vorstehenden Ansprüche, wobei B eine Methacrylatgruppe umfasst.

5. Verbindungen nach einem der vorstehenden Ansprüche, wobei B eine 1,4-Pentadien-3-yl-Gruppe umfasst.

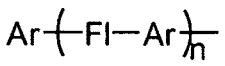
6. Verbindungen nach einem der vorstehenden Ansprüche, wobei A eine im Wesentlichen lineare Kette mit kovalenter Bindung aus aromatischen oder heteroaromatischen Diradikalen der folgenden allgemeinen Formel darstellt:



wobei:

jedes Ar individuell ausgewählt ist aus einem aromatischen oder heteroaromatischen Diradikal;
Fl eine Fluoren-2,7-Diyl-Diradikal-Spiroverbindung umfasst, die an der 9-Position mit einem alizyklischen Ringsystem substituiert ist; und
n eine ganze Zahl zwischen 1 und ist.

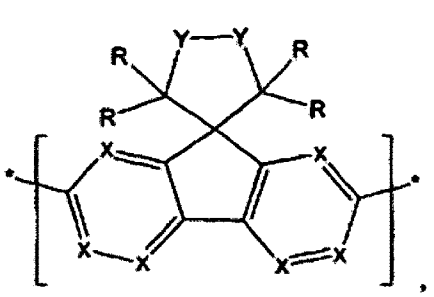
7. Verbindungen nach einem der Ansprüche 1 bis 5, wobei A eine im Wesentlichen lineare Kette mit kovalenter Bindung aus aromatischen oder heteroaromatischen Diradikalen der folgenden allgemeinen Formel darstellt:

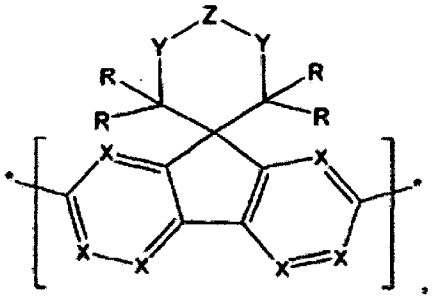


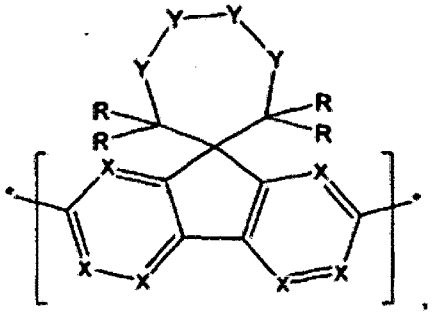
wobei:

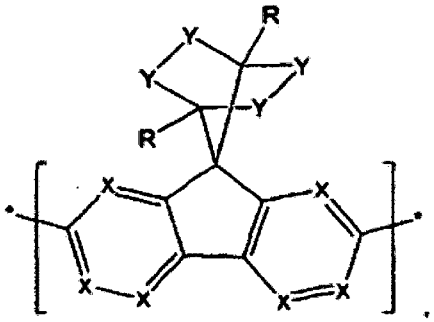
jedes Ar unabhängig ausgewählt ist aus 1,4-Phenylen, einem Biphenyl-4-4'-diyl, einem Terphen-4-4"-diyl, einem Naphthalen-1,4-diyl, einem Thiophen-2,5-diyl, einem Pyrimidin-2,5-diyl, einem Perylen-3,10-diyl, einem Pyren-2,7-diyl, einem 2,2'-Dithiophen-5,5'-diyl, einem Oxazol-2,5-diyl, einem Thieno[3,2-b]thiophen-2,5-diyl, einem Dithieno[3,2-b:2',3'-d]thiophen-2,6-diyl oder einem Imidazo[4,5-d]imidazol-2,5-diyl-Diradikal oder einer einzelnen Bindung;
Fl eine Fluoren-2,7-Diyl-Diradikal-Spiroverbindung umfasst, die an der 9-Position mit einem alizyklischen Ringsystem substituiert ist; und
n eine ganze Zahl zwischen 1 und ist.

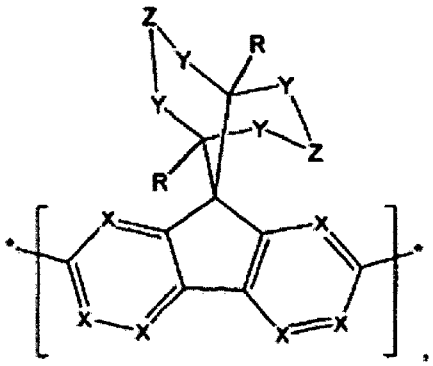
8. Verbindungen nach einem der Ansprüche 6 oder 7, wobei FL ein aus folgenden ausgewähltes Diradikal umfasst:

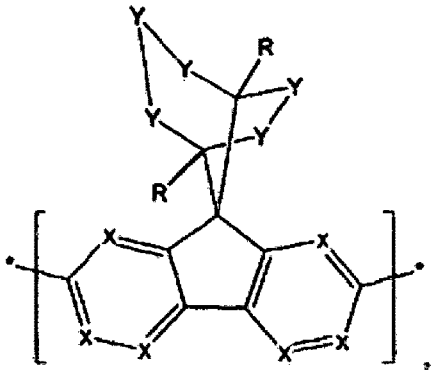


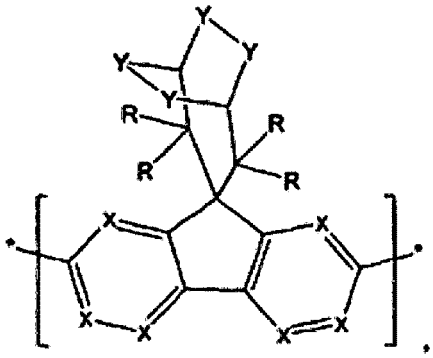


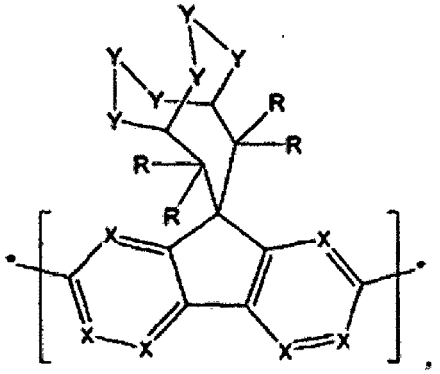


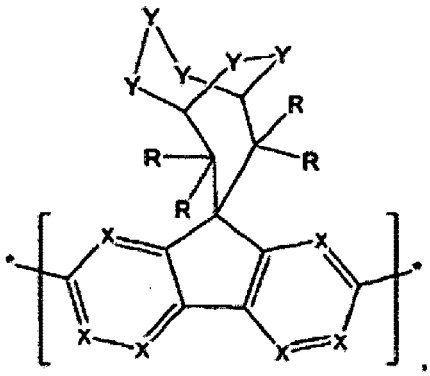


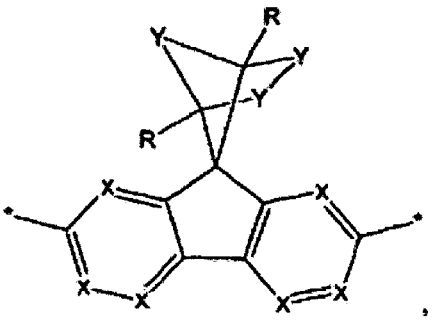


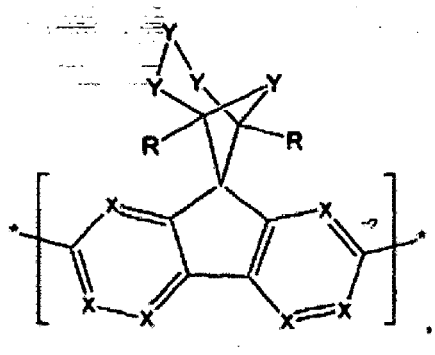


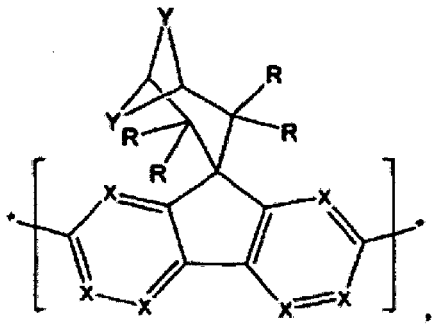


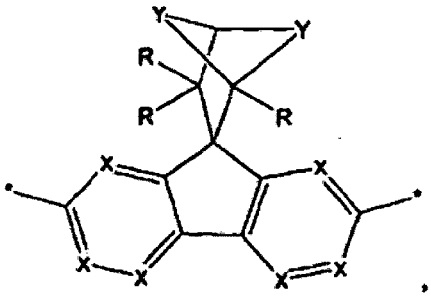


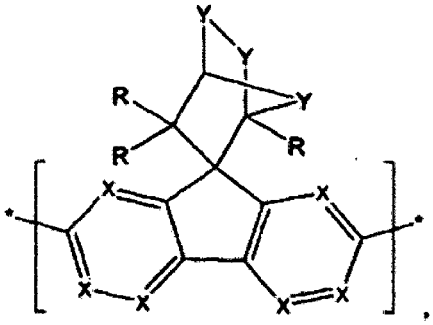


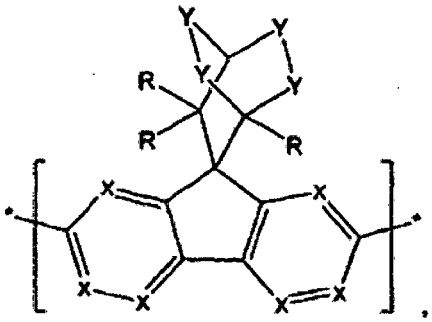


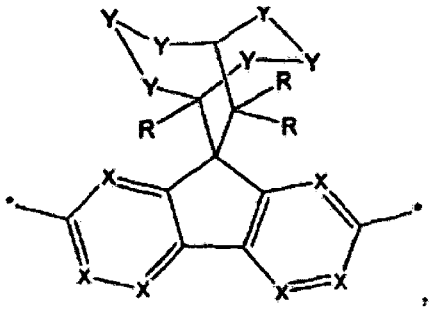


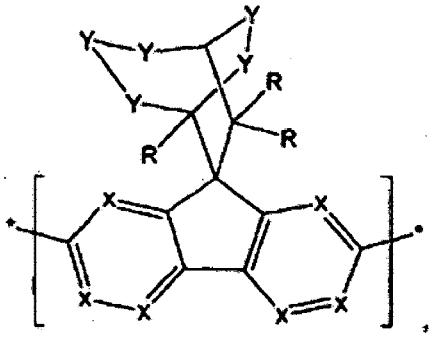


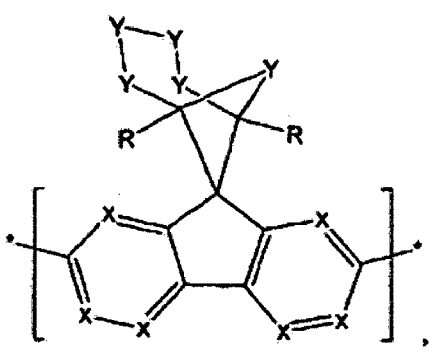


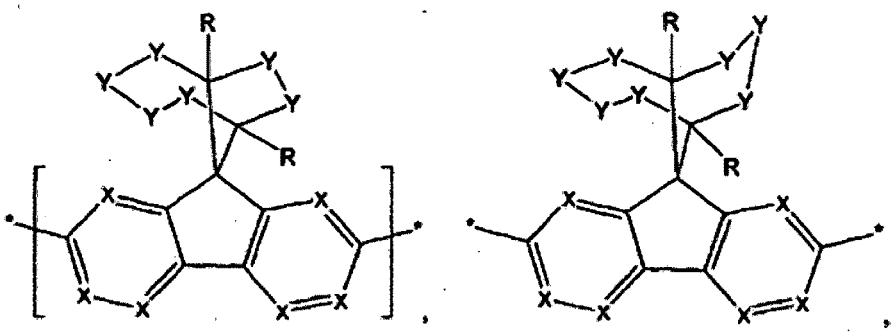












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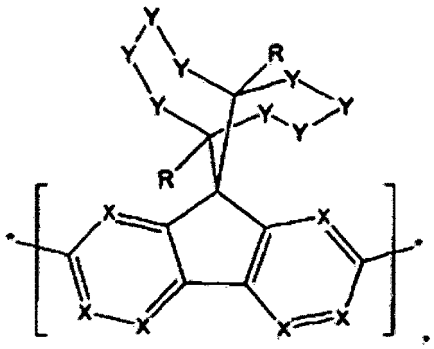


wobei:

X unabhängig ausgewählt werden kann aus CH, N, CR' oder CF, und wobei R' = C_nH2_{n+1}, wobei n unabhängig zwischen 1 und 5 ausgewählte Werte aufweisen kann;
Y und Z unabhängig ausgewählt werden aus CH_2, CHR", $CR"_2$, NH, NR", O, S, S=O, O=S=O und C=O und R" = C_nH_{2n+1}, wobei n unabhängig zwischen 1 und 5 ausgewählte Werte aufweisen kann; und wobei R unabhängig ausgewählt wird aus C_nH_{2n+1}, wobei n unabhängig zwischen 1 und 5 ausgewählte Werte aufweisen kann.

9. Verbindungen nach Anspruch 8, wobei X = CH, Y = Z = CH_2, und wobei jedes R unabhängig ausgewählt ist aus Methyl, Ethyl und Propyl.

10. Verbindungen nach Anspruch 8, wobei X = CH; Y = CH_2; Z = CHR"; und wobei jedes R und jedes R" unabhängig ausgewählt sind aus Methyl, Ethyl und Propyl.

11. Verbindungen nach Anspruch 8, 9 oder 10, wobei die R-Gruppen gleich sind.

12. Verbindungen nach einem der Ansprüche 6 bis 11, wobei n zwischen 3 und 6 liegt.

Revendications

1. Composés OLED de structure générale :

B-S-A-S-B

dans laquelle :

A est essentiellement une chaine linéaire liée de manière covalente comprenant une structure cyclique aromatique condensée, entre autre comprenant des structures fluorène cycliques condensées avec au moins une structure fluorène cyclique supplémentaire ;
S est un groupe espaceur comprenant une chaine alkyle éventuellement contenant un ou plusieurs hétéroatomes ; et
B est un groupe chimique réticulant ;

les systèmes fluorène cycliques constitués de la structure aromatique condensée étant substitués en position 9, et dans lesquels il n'y a pas de substituants hydrogène en α-de la position 9 du système fluorène cyclique ou de quelconque système fluorène cyclique.

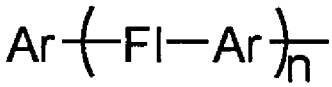
2. Composés selon la revendication 1 dans lesquels les systèmes fluorène cycliques supplémentaires comprennent au moins un parmi le benzène, le naphtalène, l'indène et d'autres systèmes fluorène cycliques.

3. Composés selon la revendication 1 ou la revendication 2, dans lesquels chaque B est indépendamment choisi parmi un groupe méthacrylate, un groupe 1,4-pentadiène-3-yl, un groupe éthacrylate, un groupe vinyloxy, un groupe alkylvinyloxy, un groupe éthylmaléato, un groupe éthylfumarato, un groupe N-maléimido, un groupe vinylmaléato, un groupe vinylfumarato, ou un groupe N-(2-vinyloxymaléimido).

4. Composés selon l'une quelconque des revendications précédentes dans lesquels B comprend un groupe méthacrylate.

5. Composés selon l'une quelconque des revendications précédentes dans lesquels B comprend un groupe 1,4-pentadiène-3-yl.

6. Composés selon l'une quelconque des revendications précédentes dans lesquels A représente une chaine de di-radicaux aromatiques ou hétéroaromatiques essentiellement linéaire, liée de manière covalente de formule générale



dans laquelle :

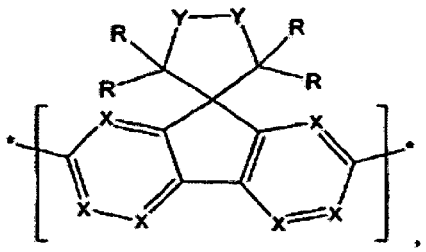
chaque Ar est individuellement choisi parmi un di-radical aromatique ou hétéroaromatique ;
FI comprend un di-radical spiro fluorène-2,7-diyle substitué en position 9 par un système aromatique alicyclique ; et
n est un entier valant de 1 à 6.

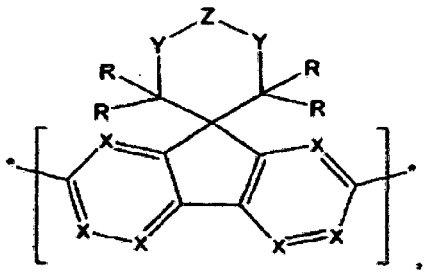
7. Composés selon l'une quelconque des revendications 1 à 5, dans lesquels A représente une chaine de di-radicaux aromatiques ou hétéroaromatiques essentiellement linéaire, liée de manière covalente de formule générale

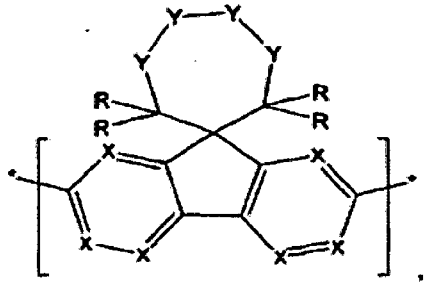
dans laquelle :

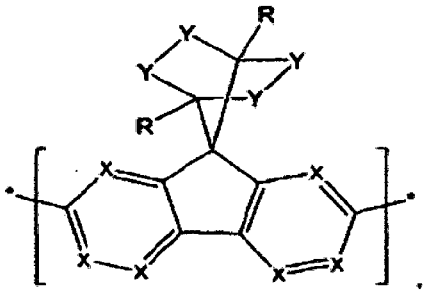
chaque Ar est individuellement choisi parmi 1,4-phénylène, un biphényl-4,4'-diyle, un terphén-4,4'-diyle, un naphtalène-1,4-diyle, un thiophène-2,5-diyle, un pyrimidine-2,5-diyle, un pérylène-3,10-diyle, un pyrene-2,7-diyle, un 2,2'-dithiophén-5,5'-diyle, un oxazole-2,5-diyle, un thiéno[3,2-b] thiophène-2,5-diyle, un dithiéno[3,2-b :2',3'-d] thiphene-2,6-diyle, ou un di-radical imidazo[4,5-d]imidazole-2,5-diyle, ou une liaison simple ;
FI comprend un di-radical spiro fluorène-2,7-diyle substitué en position 9 par un système aromatique alicyclique ; et
n est un entier valant de 1 à 6.

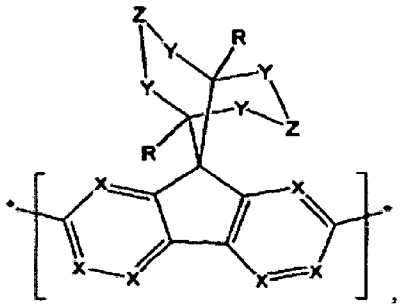
8. Composés selon l'une quelconque des revendications 6 ou 7, dans lesquels FI comprend un di-radical choisi parmi :

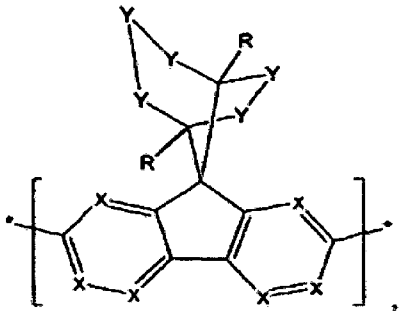


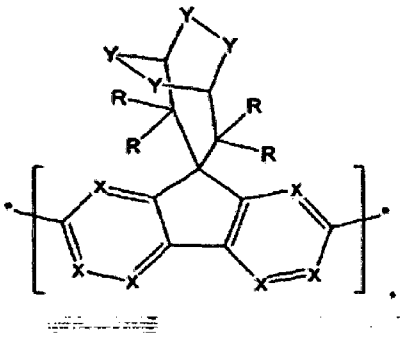


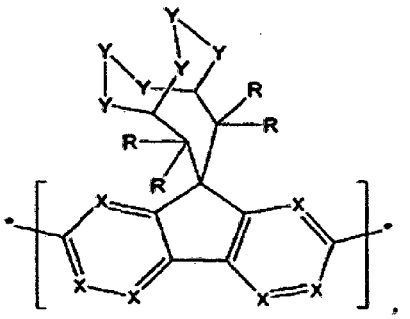


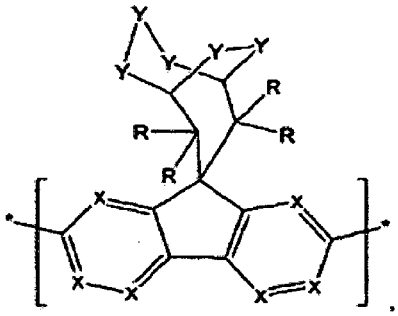


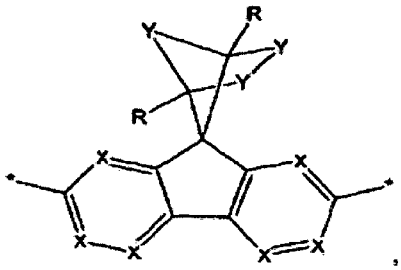


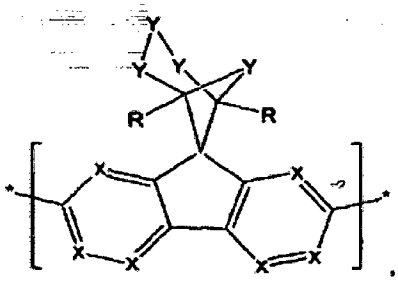


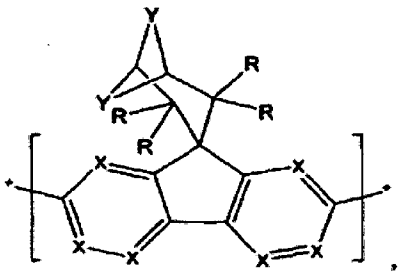


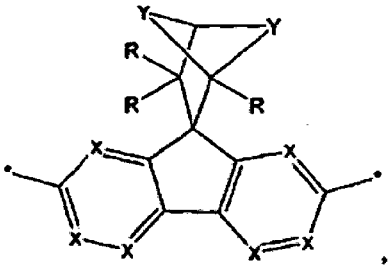


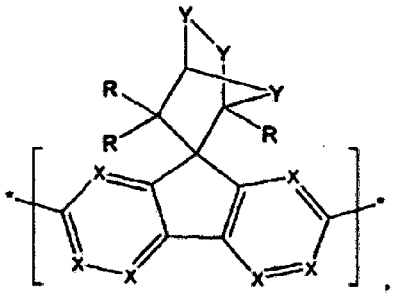


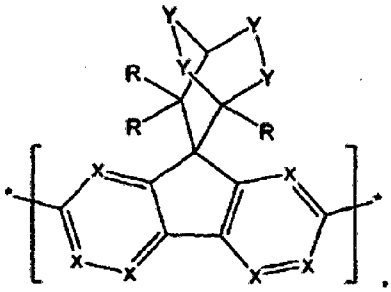


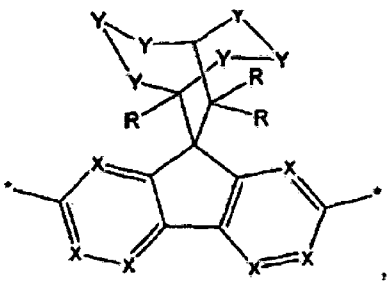


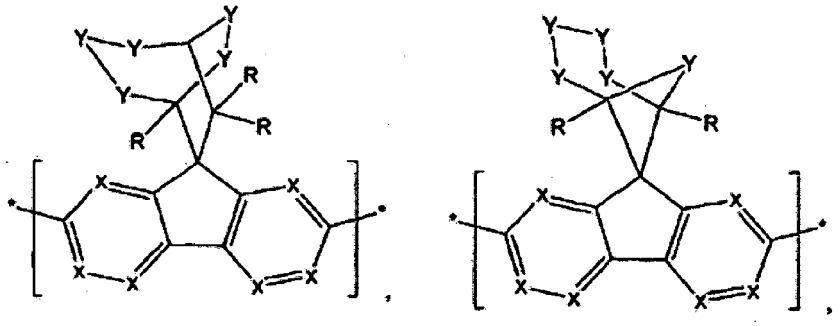


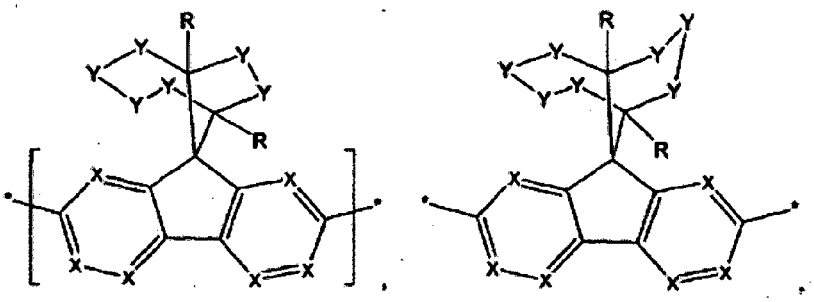




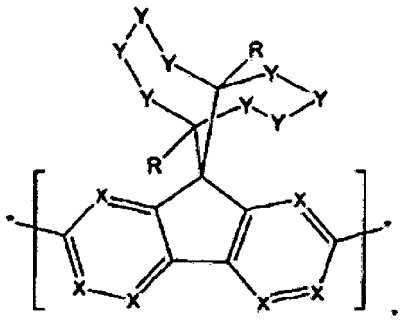








et



X pouvant être indépendamment choisi parmi CH, N, CR', ou CF et R' = C_nH_{2n+1}, où n peut indépendamment valoir de 1 à 5 ;
Y et Z étant indépendamment choisis parmi CH_2, CHR", $CR"_2$, NH, NR"', O, S, S=O, O=S=O et C=O, et R"' = C_nH_{2n+1}, où n peut indépendamment valoir de 1 à 5 ; et R étant indépendamment choisis parmi C_nH_{2n+1}, où n peut indépendamment valoir de 1 à 5.

9. Composés selon la revendication 8 dans lesquels X = CH, Y = Z = CH_2 et chaque R est indépendamment choisi parmi méthyle, éthyle et propyle.

10. Composés selon la revendication 8 dans lesquels X = CH, ;Y = CH_2 ; Z = CHR" ; et chaque R et chaque R" sont indépendamment choisis parmi méthyle, éthyle et propyle.

11. Composés selon les revendications 8, 9 ou 10 dans lesquels les groupes R sont identiques.

12. Composés selon les revendications 6 à 11, dans lesquels n vaut de 3 à 6.

Figure 1

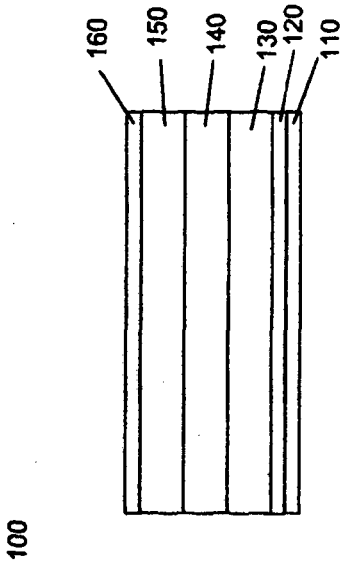
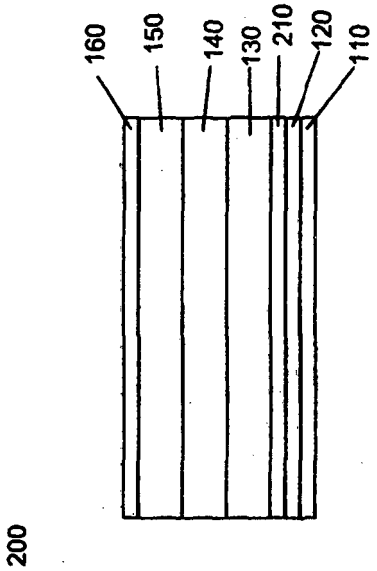


Figure 2



REFERENCES CITED IN THE DESCRIPTION

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专利名称(译)	包含芴衍生物的电致发光材料		
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[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 KARL		
发明人	KOCH, GENE KARL		
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优先权	2009017083 2009-09-30 GB		
其他公开文献	EP2483368A1		
外部链接	Espacenet		

摘要(译)

具有一般结构的OLED化合物：BS-A-S-B，其中棒状核A包含稠合芳环结构，其又包含与至少一个另外的芴环结构缩合的芴环结构，其中所述芴环系统包含芴环结构。缩合芳族结构在9位被取代，并且其中芴的9位不易氧化。