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DIODE (OLED) MATERIALS CONTAINING
MULTIPLE CROSSLINKING FUNCTIONS****Publication Classification**(51) **Int. Cl.**
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C07C 69/52 (2006.01)(71) Applicant: **LOMOX LIMITED**, Abercynon (GB)(72) Inventor: **Gene Carl Koch**, Bishop Auckland (GB)(52) **U.S. Cl.**
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(2013.01)(21) Appl. No.: **14/399,296**(22) PCT Filed: **May 9, 2013**(86) PCT No.: **PCT/GB2013/000201**

§ 371 (c)(1),

(2) Date: **Nov. 6, 2014**(57) **ABSTRACT**(30) **Foreign Application Priority Data**

May 9, 2012 (GB) 1208115.4

OLED materials having the formula: T-A(-S-B(-P-B)m-S-A)
n-T where A are independently selected rod-shaped, rigid
molecular core units, S are independently selected flexible
spacer units, B are polymerisable crosslinking groups inde-
pendently selected, P are spacer groups independently
selected, T are independently selected end groups, m are
independently selected from values of from 1 to 4, n is equal
to 1 to 3.

OLIGOMERIC ORGANIC LIGHT EMITTING DIODE (OLED) MATERIALS CONTAINING MULTIPLE CROSSLINKING FUNCTIONS

[0001] OLED materials are known from U.S. Pat. No. 6,867,243 having the generic structure:



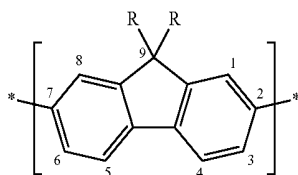
where A is a rigid, rod or lathe-like molecular nucleus, S are flexible spacers, and B are crosslinking groups.

[0002] In these materials the central core (A), generally a highly conjugated aromatic ring system, confers the desired light emitting or charge transporting properties on the materials, and the crosslinking groups (B) allow the materials to be crosslinked, usually through exposure to UV radiation, into an insoluble, polymer matrix film. Thus, the materials can be solvent cast onto electronic substrates and photopatterned much as one would do with a photoresist.

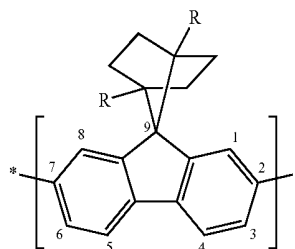
[0003] The flexible spacers serve to mechanically and electronically insulate the molecular nuclei (A) from the crosslink connections into the polymer matrix formed through UV exposure. Without this isolation, energy of excitation produced in the molecular nuclei to, for instance, initiate light emission would be drained off into the polymer matrix destroying the desired optoelectronic effect. The spacers (B) are also necessary, in combination with the rod-like shape of the molecular nuclei, to promote liquid crystalline behaviour in the uncrosslinked materials. It has been found that liquid crystalline order is highly desirable in these materials, both to increase desirable properties such as carrier mobilities, and also to allow the materials to be cast in highly ordered films with no disruptive defects such as the defects that occur in polycrystalline organic films.

[0004] It has further been found that it is highly desirable to incorporate one or more 9,9-disubstituted fluorene aromatic units into molecular nucleus (A). If the substituent(s) at the 9-position on the fluorene ring are sufficiently bulky, this substitution serves a threefold purpose. First, it increases the solvent solubilities of the materials so that they may be solvent processed. Second, this substitution promotes the thermodynamic stability of the nematic liquid crystalline phase over the crystalline or smectic phases that might also occur in these materials making it possible to cast films with nematic ordering. And third, this substitution provides sufficient separation between adjacent molecular nuclei to limit unwanted intermolecular mechanical and electronic interactions that would drain off energy of excitation.

[0005] Fluorene functional units that have been used in this respect are, for instance,



where R represents n-alkyl groups substituted at the 9 positions. (See U.S. Pat. No. 6,867,2430.) Further examples are spirocycloalkylfluorenes such as



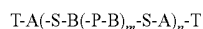
where R represents alkyl groups. (See WO2009087364.) In both these case substitution of the fluorene units into the molecular nucleus occurs at the 2 and 7 positions so as to maintain the nucleus' linear nature.

[0006] The materials described above have proven useful for use in OLEDs both as light emitters and as charge transporting materials. An important aspect of their application is their film forming properties since they can only be formed into useful structures if they can be applied to a surface in a uniform layer. Since the material layers in OLED devices are in general quite thin, these materials must be applied by spin coating, ink jet printing, or coating from a slot die in quite dilute solution. The low viscosity of these materials in dilute solution makes it difficult to form uniform films using the above techniques.

[0007] An approach to increasing the viscosity of solutions of the B-S-A-S-B materials is to increase the length of the molecular cores of the materials. Molecular cores (A) have been produced containing up to five fluorene units yielding molecules having molecular weights in excess of 2000. While these molecules do have better film forming properties and also give superior light emission efficacies, they are expensive to produce and are best suited as dopants in a polymer matrix formed from lower cost materials.

[0008] The present invention provides liquid crystalline, photopolymerisable host materials having suitable electronic properties, but which are relatively inexpensive to make

[0009] The invention, in one aspect, comprises materials having the formula:



where

[0010] A are independently selected rod-shaped, rigid molecular core units,

[0011] S are independently selected flexible spacer units,

[0012] B are polymerisable crosslinking groups independently selected,

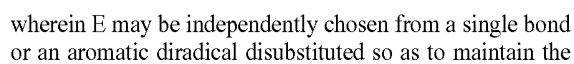
[0013] P are spacer groups independently selected,

[0014] T are independently selected end groups,

[0015] m are independently selected from values of from 1 to 4,

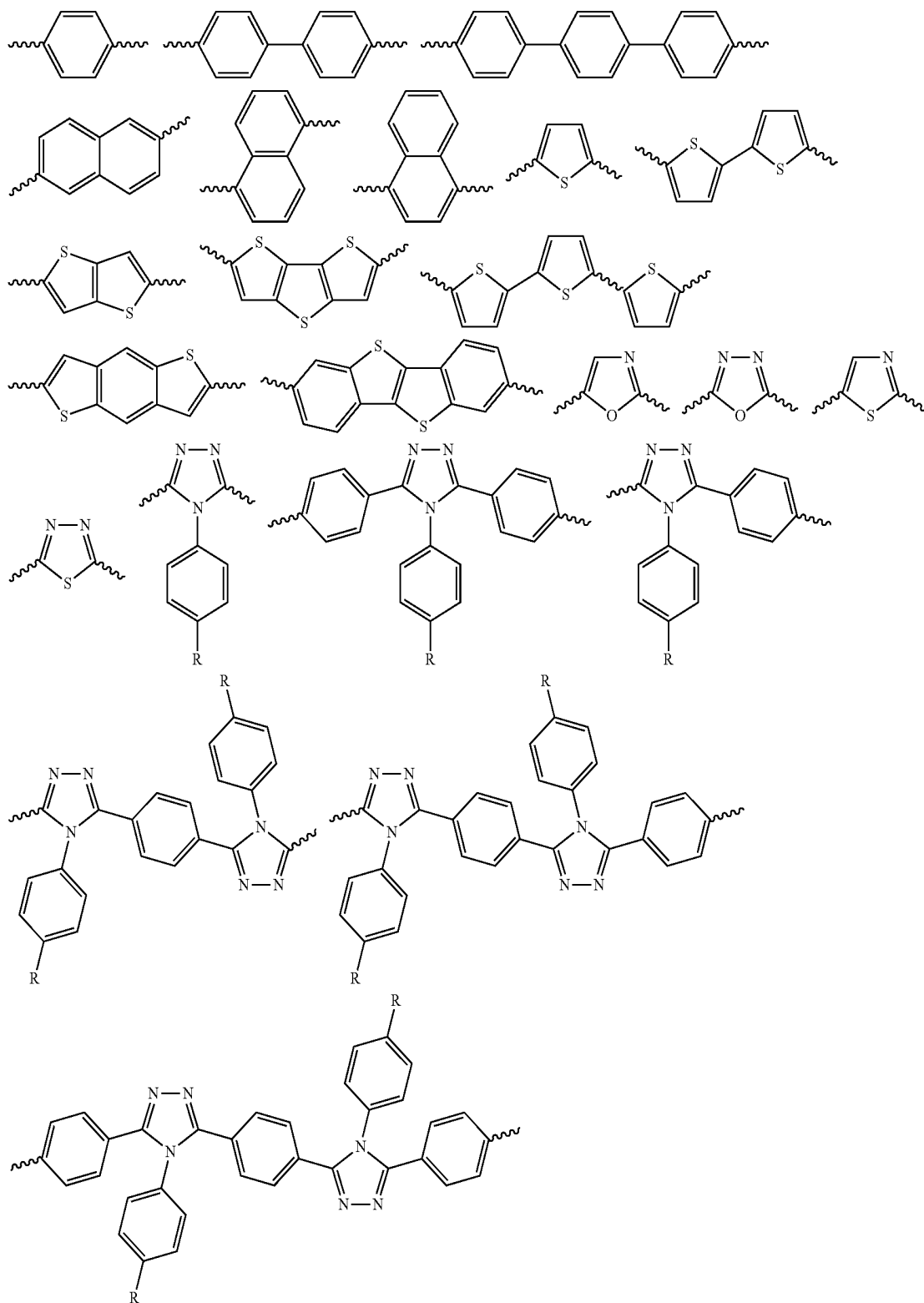
[0016] n is equal to 1 to 3.

[0017] The crosslinking groups may be chosen so as to allow the molecules to be polymerised into a polymer matrix, particularly by exposure to UV. The molecular nucleus or core units and also the spacer units may be chosen such that the material displays liquid crystalline order and most preferably that it displays nematic order. It is also preferred that the core units are chosen so as to promote either light emitting or charge transporting properties, or both, in the product polymer matrix.

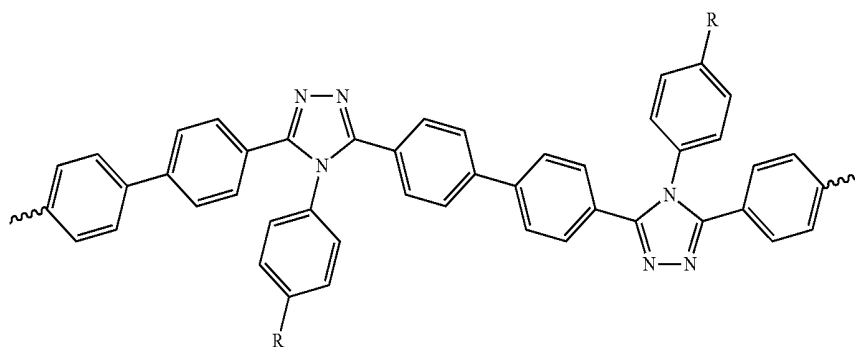
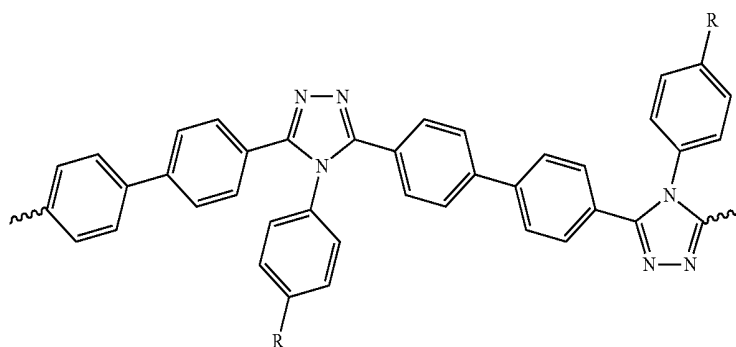
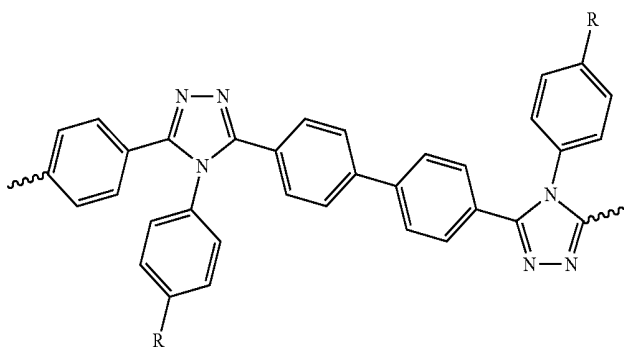
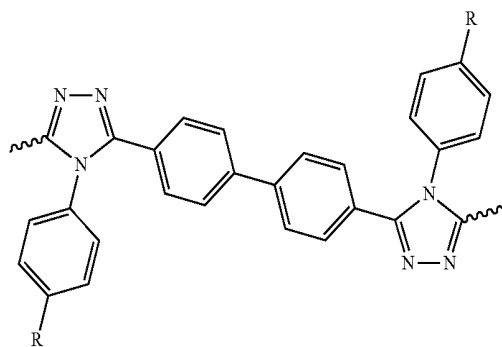
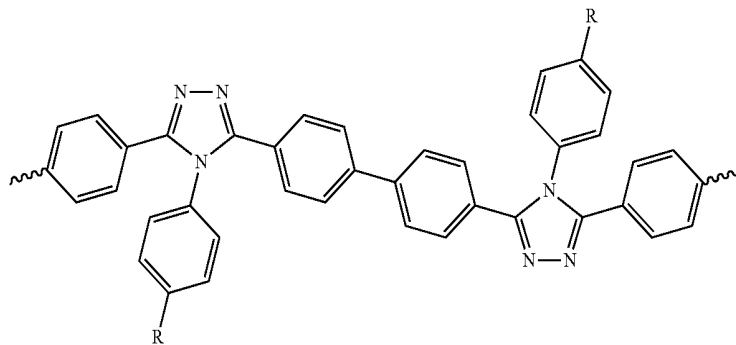


linear nature of rigid molecular core A, and wherein F is a diradical containing a fluorene, azafluorene or polyazafluorene aromatic ring system and which is disubstituted so as to maintain the linear nature of the rigid molecular core A, and wherein n is between 0 and 7, preferably between 0 and 4.

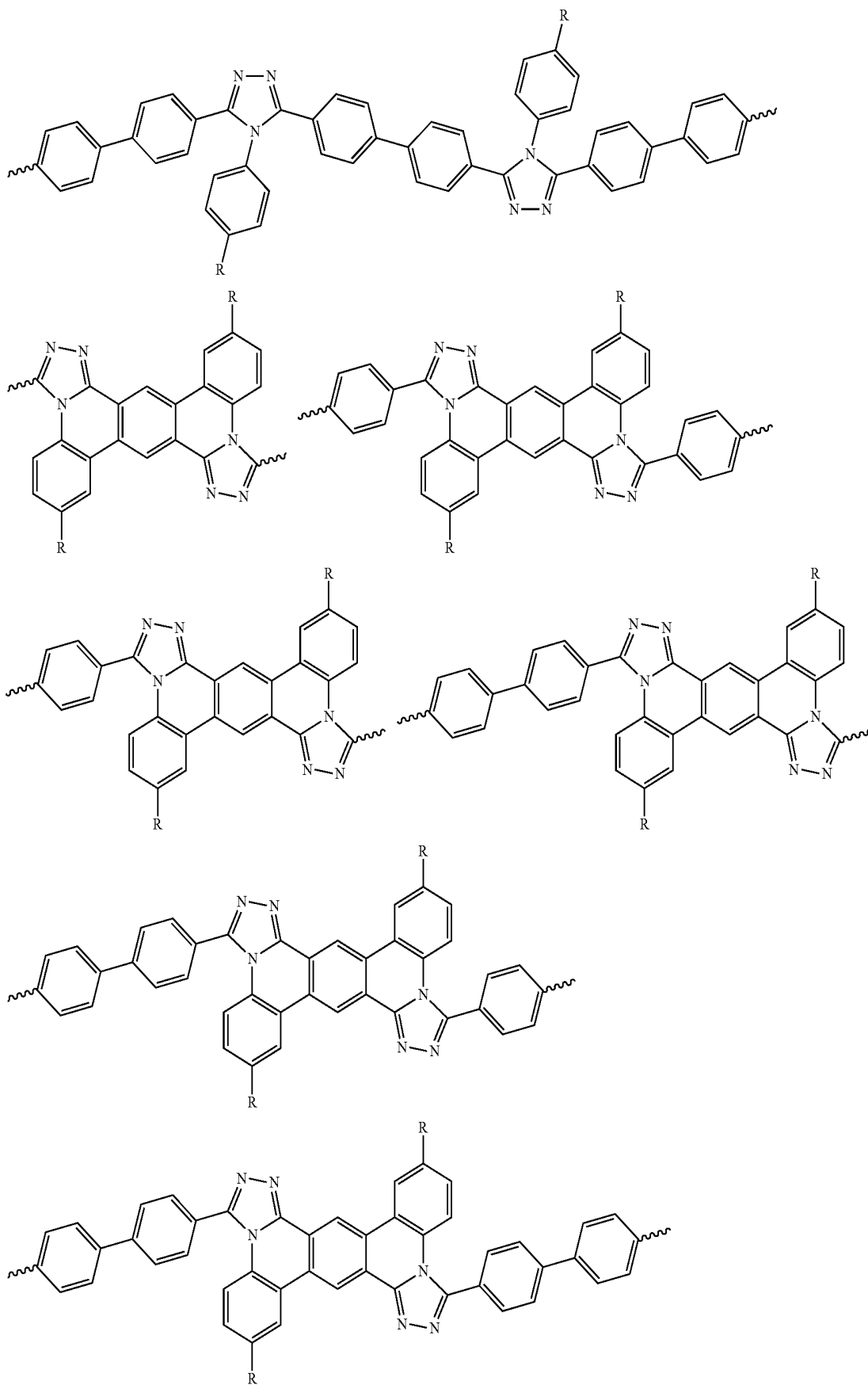
[0019] Examples of E sub-units are:



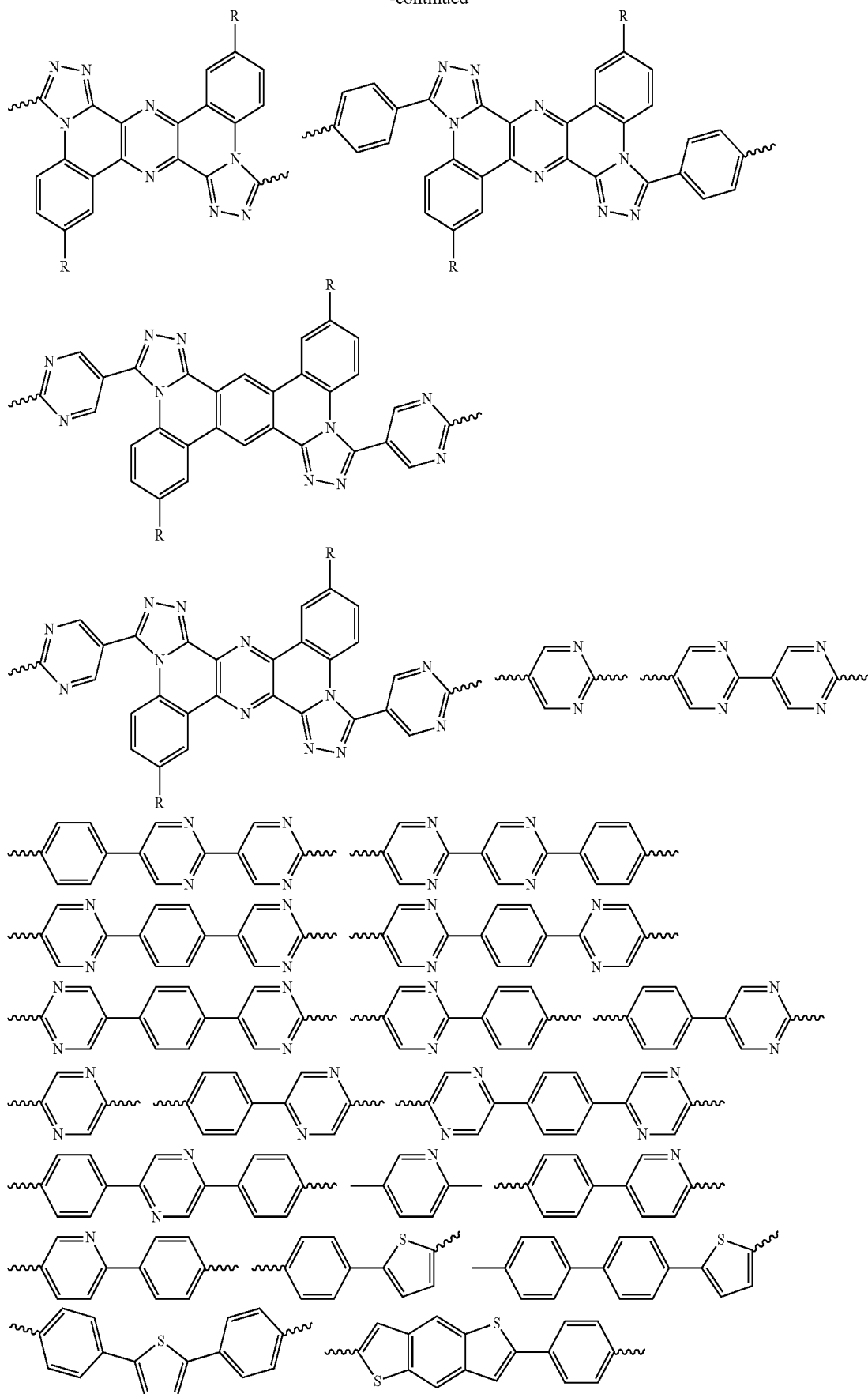
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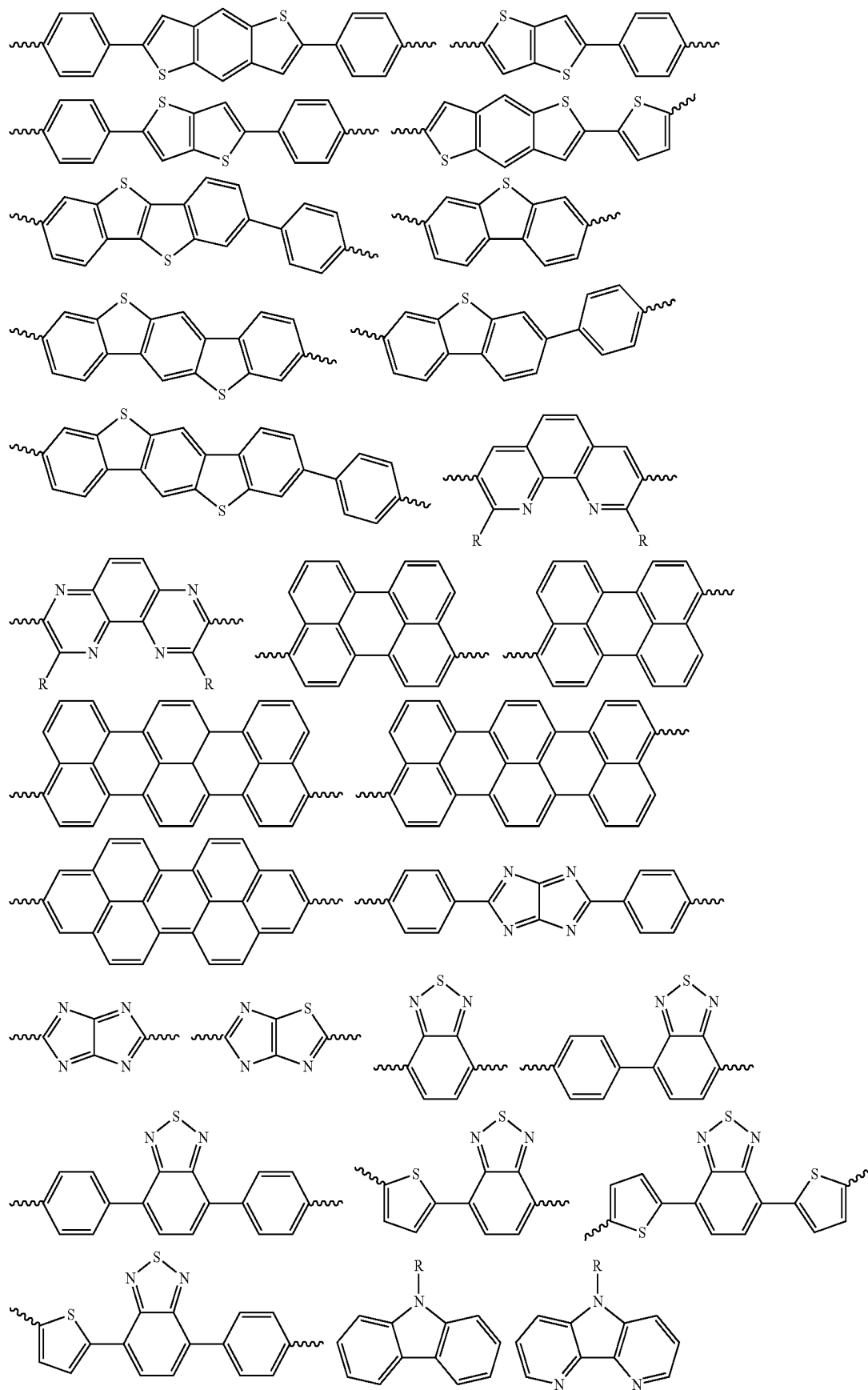
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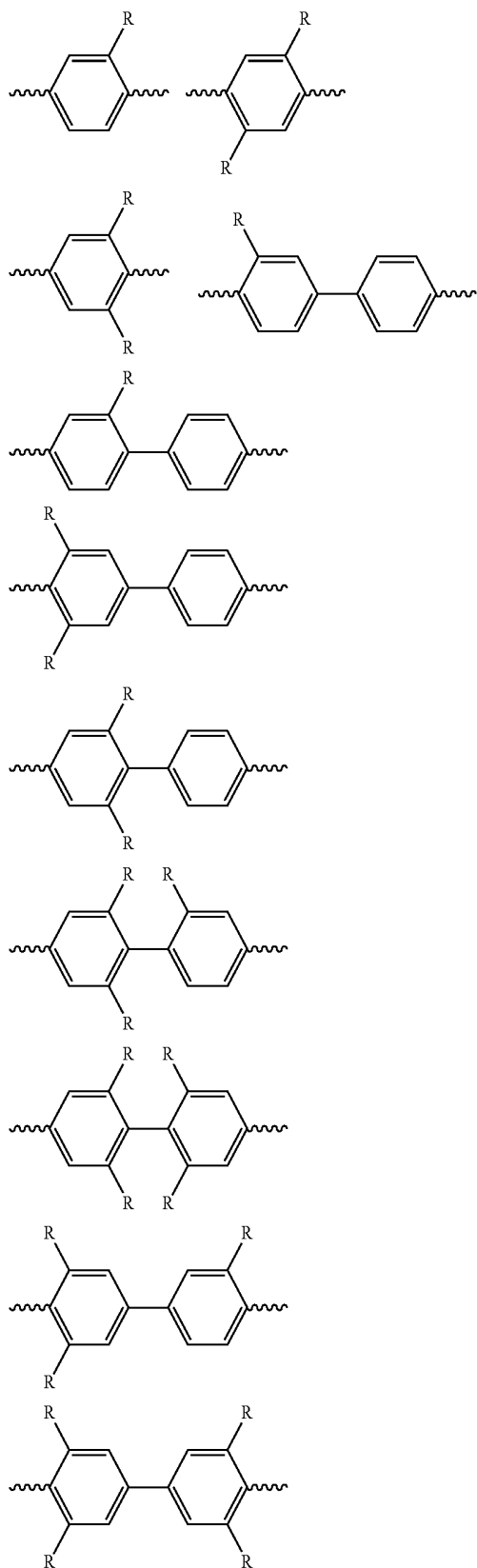
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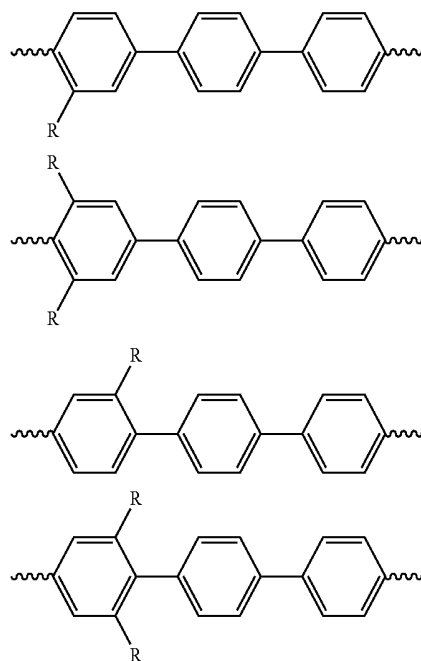
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wherein R may be hydrogen, alkyl or fluoroalkyl. Further examples of E sub-units are:

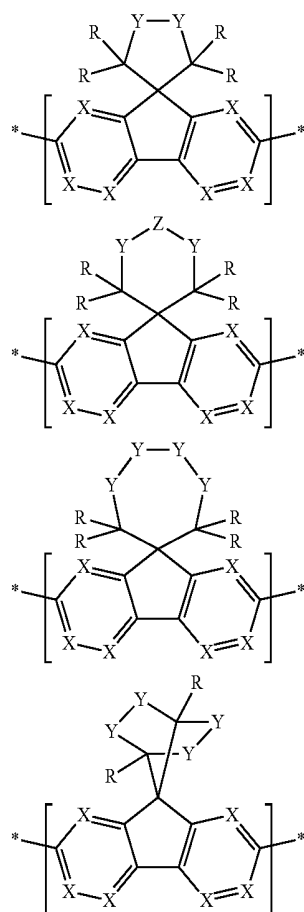


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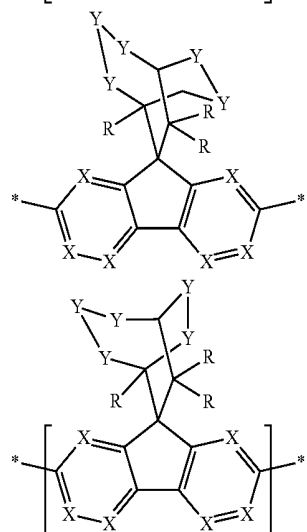
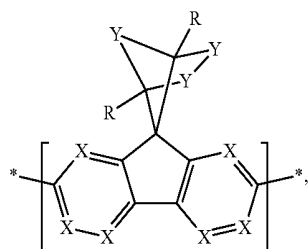
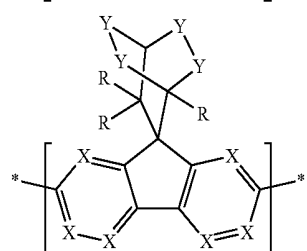
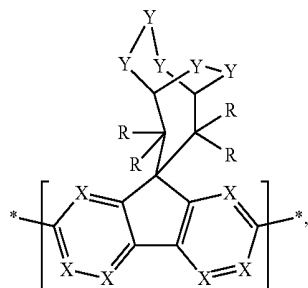
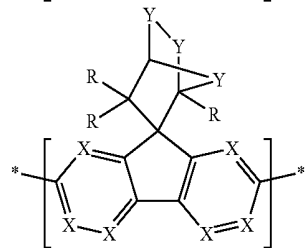
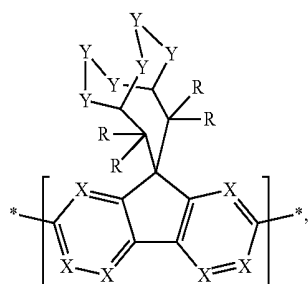
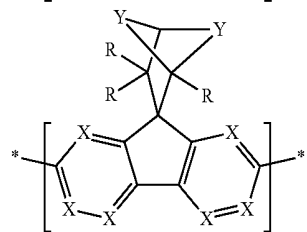
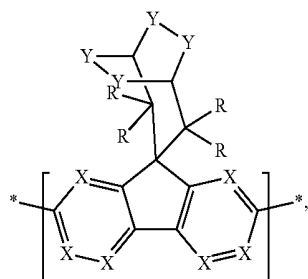
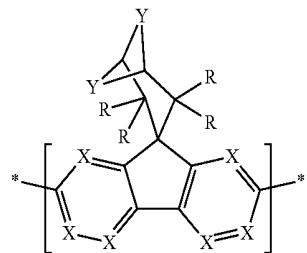
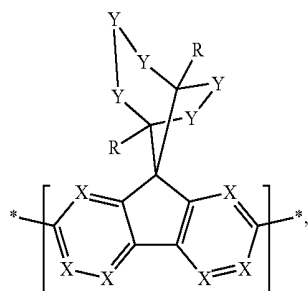
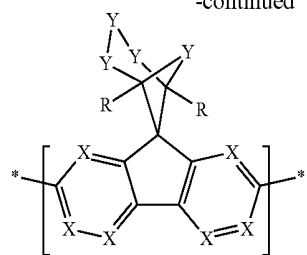


wherein R may be an alkyl or fluorinated alkyl group.

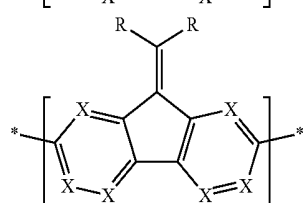
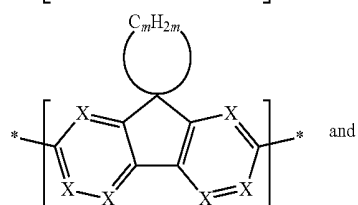
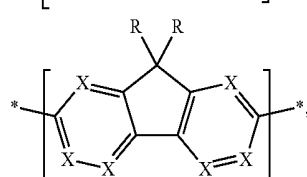
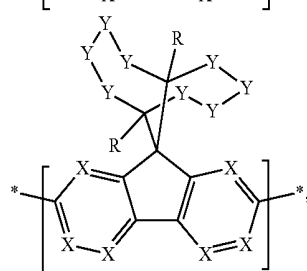
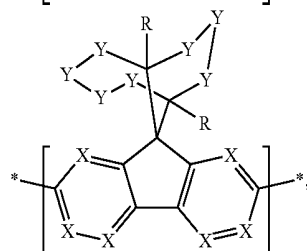
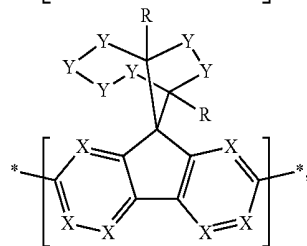
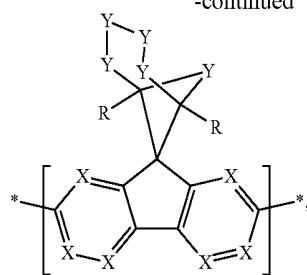
[0020] Examples of F sub-units are:



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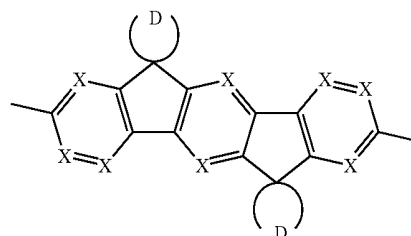


wherein X are chosen independently from CH, N, CR', or CF, and R' = C_nH_{2n+1} where n has a value chosen independently from 1 to 5; Y and Z are chosen independently from CH_2 , CHR'' , CR''_2 , NH , NR'' , O, S, $S=O$, $O=S=O$, and $C=O$ and R'' = C_nH_{2n+1} where n has a value chosen independently

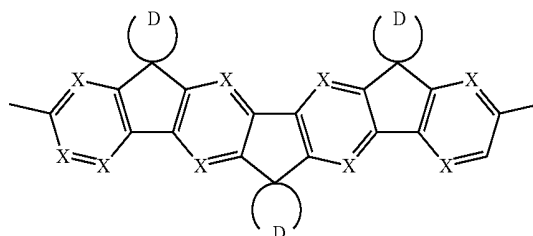
from 1 to 5; R are independently chosen from H or C_nH_{2n+1} where n has a value chosen independently from 1 to 10, and m has a value between 3 and 7.

[0021] Other examples of F sub-units are:

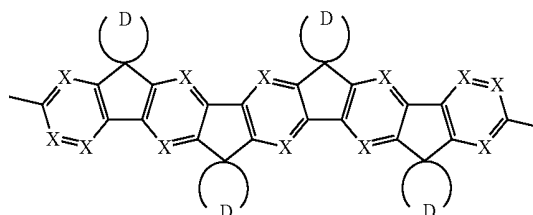
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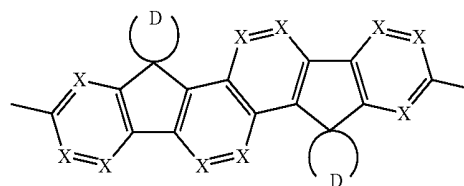
Structure 2



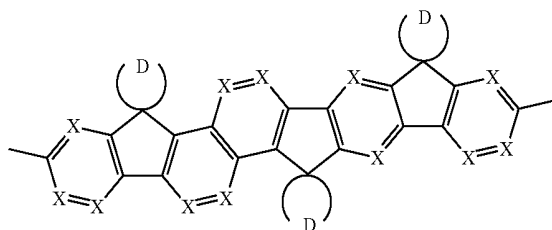
Structure 3



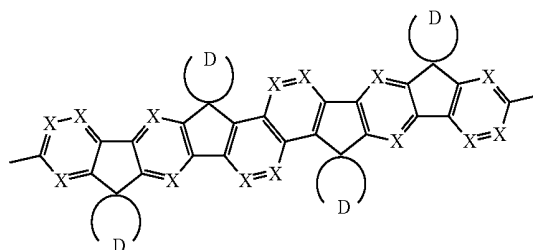
Structure 4



Structure 5

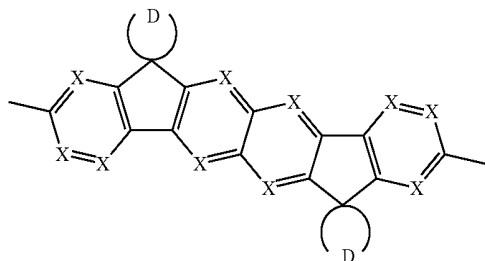


Structure 6

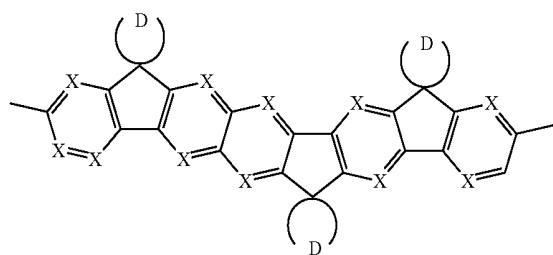


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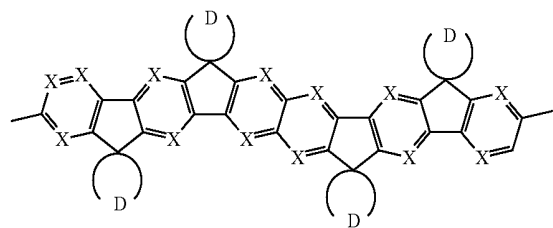
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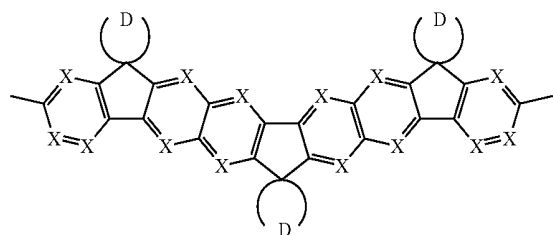
Structure 7



Structure 8

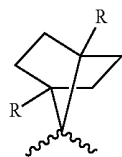


Structure 9

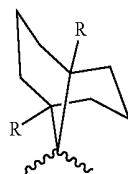


wherein the substituents $\oplus$ may independently be one of structures:

Structure 10

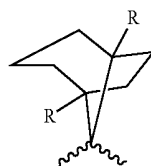


Structure 11

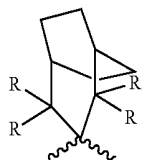


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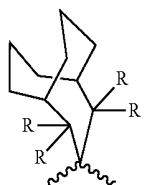
Structure 12



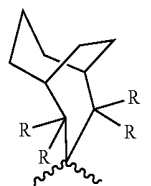
Structure 13



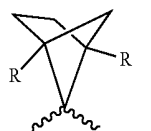
Structure 14



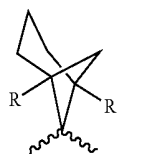
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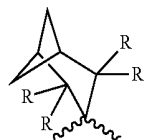
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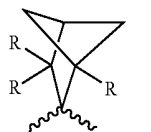
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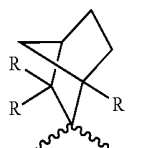
Structure 18



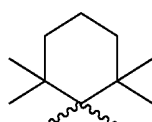
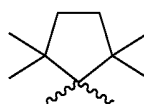
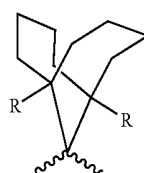
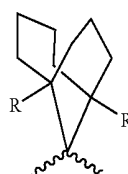
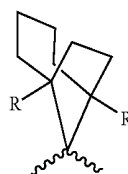
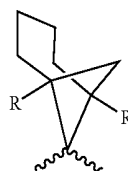
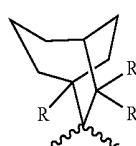
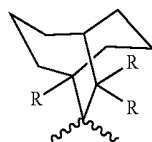
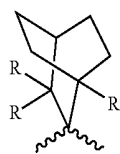
Structure 19



Structure 20



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Structure 21

Structure 16

Structure 17

Structure 18

Structure 19

Structure 20

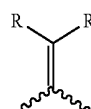
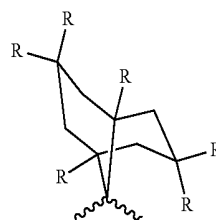
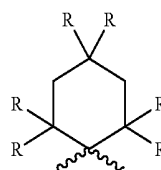
Structure 21

Structure 22

Structure 23

Structure 24

-continued



Structure 25

Structure 26

Structure 27

Structure 28

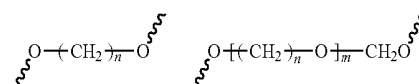
and wherein R is an alkyl group and may be chosen from methyl, ethyl, propyl, butyl, isopropyl, sec-butyl, isobutyl, tert-butyl, 2-amyl, 3-amyl, 2-methyl-2-butyl, 3-methyl-3-amyl, 3-ethyl-3-amyl, neo-pentyl, hexyl, heptyl, octyl, nonyl, or decyl and X may be independently selected from =CH- , =N- , CR' , or CF , and $\text{R}^1=\text{C}_n\text{H}_{2n+1}$ where n has a value chosen independently from 1 to 5.

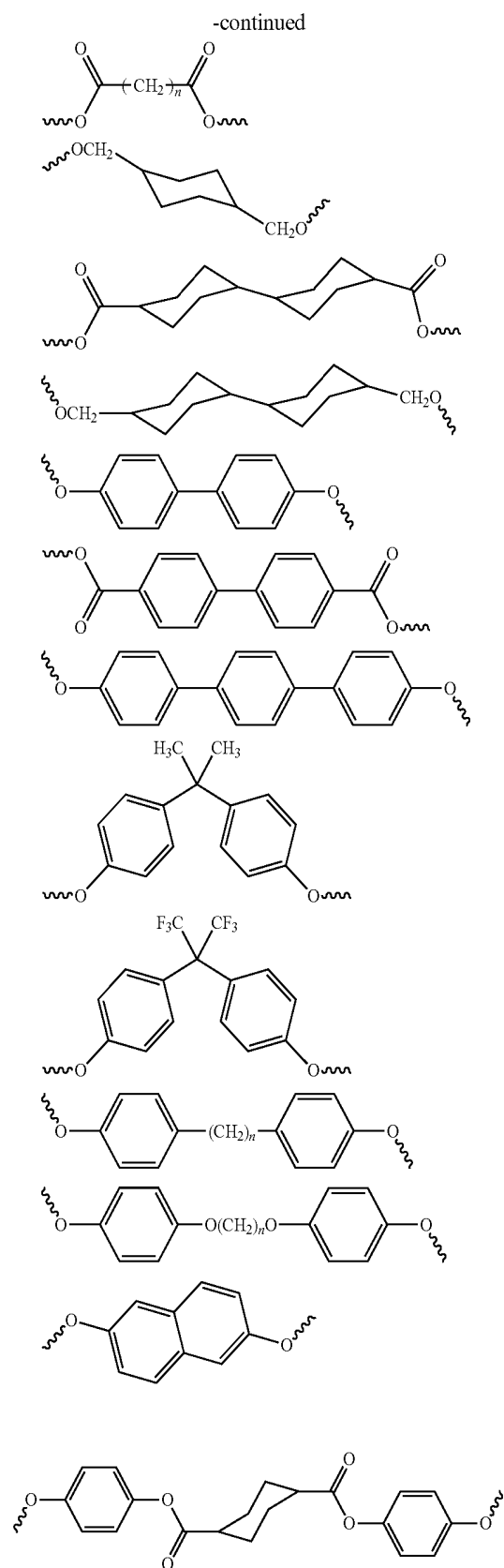
[0022] The flexible spacer units S may be branched, straight chain, or cyclic alkyl groups with 3 to 12 carbon atoms, which are unsubstituted, or mono- or poly-substituted by F, Cl, Br, I, or CN or wherein one or more nonadjacent CH_2 groups are replaced by —O— , —S— , —NH— , —NR— , —SiRR— , —CO— , —COO— , —OCO— , —OCO—O— , —S—CO— , —CO—S— , —CH=CH— , —C=C— such that O and S atoms are not directly linked to other O or S atoms.

[0023] The spacer units P separate the crosslinking groups B from each other and help determine the stiffness of the polymer matrix formed after the molecules have been crosslinked. More rigid P units, for instance those composed of aromatic rings, will lead to a stiffer, more rigid polymer. More flexible P spacers, for instance simple alkyl chains, will result in a softer more deformable polymer matrix. Altering the characteristics of the P spacers can be used to “tune” the characteristic of the resulting polymer matrix film.

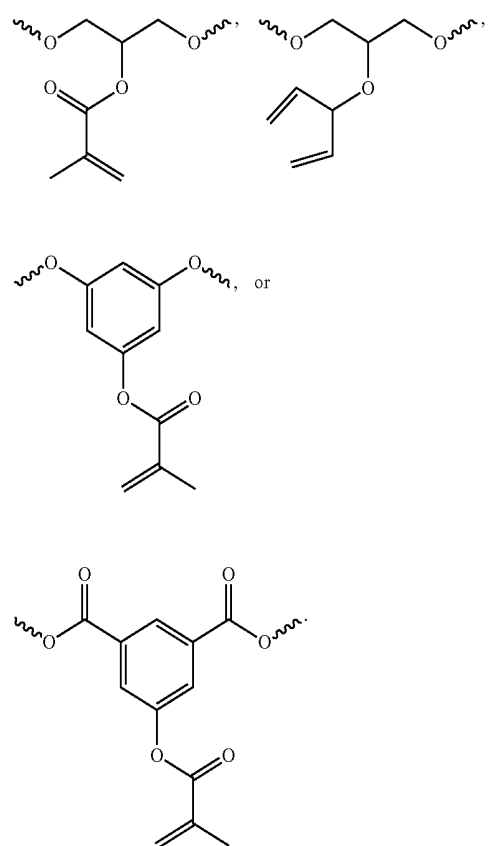
[0024] A further aspect of the invention is that mixtures of materials with varying length spacers may be used to destabilise the more highly ordered smectic phases in favour of the nematic phase if that is desired.

[0025] Examples of spacer groups (P) are:



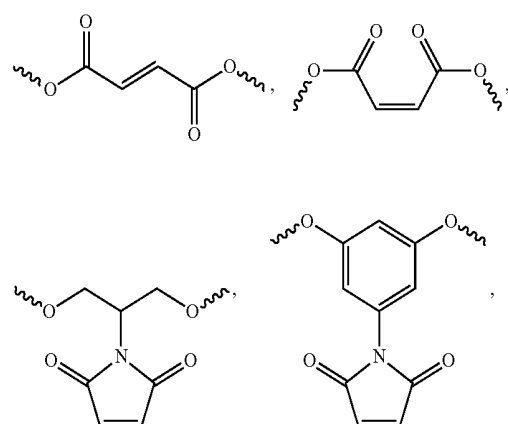


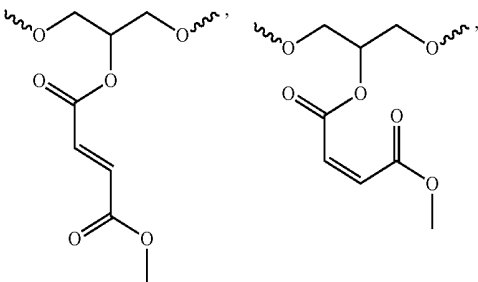
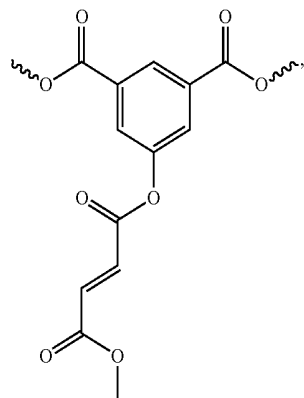
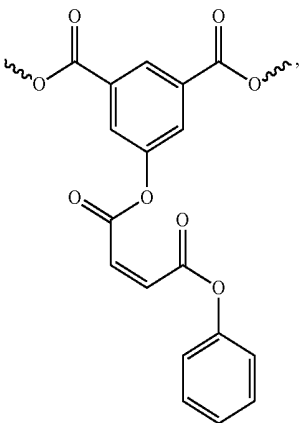
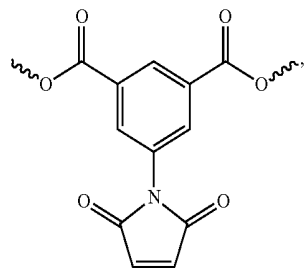
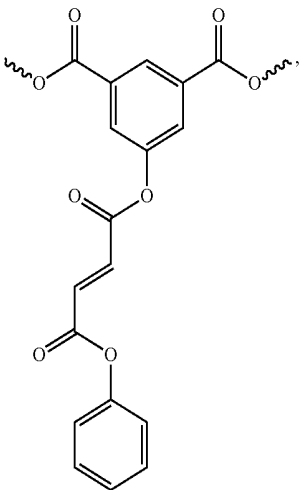
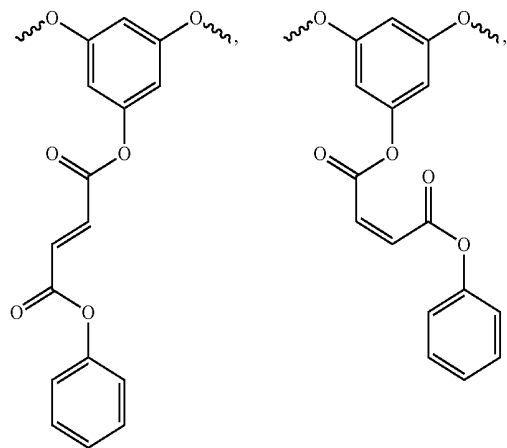
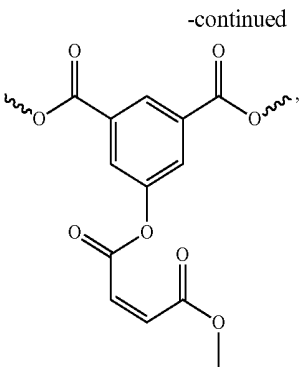
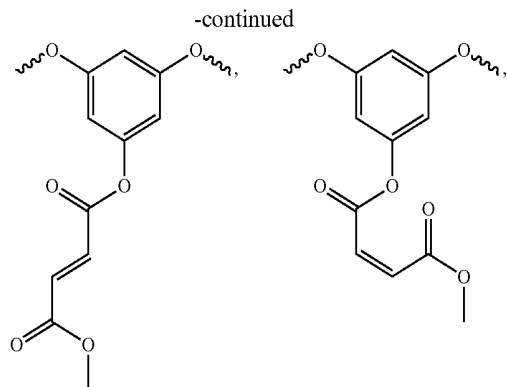
[0026] Crosslinking group (B) may be any crosslinking group so long as it is difunctionalised such that it may be incorporated in the backbone of the molecule, for instance:

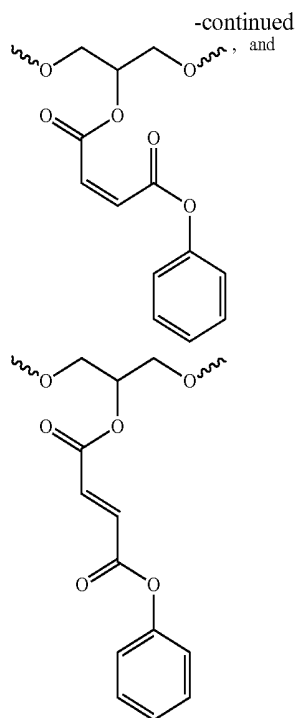


[0027] Mixtures may be used of two or more molecules in at least one of which the crosslinking units are electron deficient and in at least another one of which the crosslinking units are electron rich. In mixtures of this type crosslinking proceeds by way of electron transfer polymerization. Crosslinking liquid crystalline materials using this technique for use in OLEDs and other organic electronics has previously been described in patent application WO2007064721.

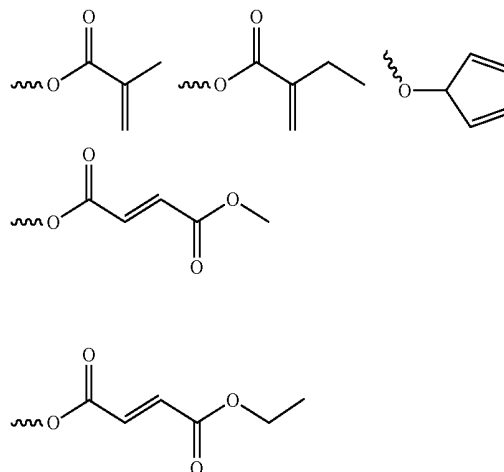
[0028] Examples of electron deficient crosslinking groups that may serve as the B group in the invention are:



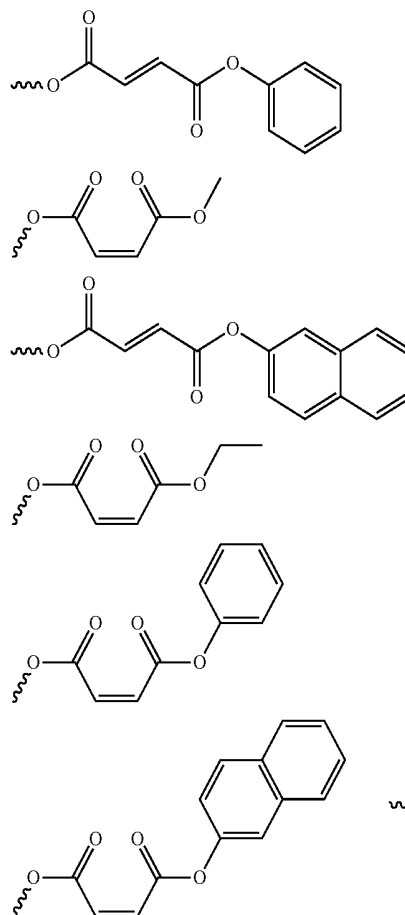
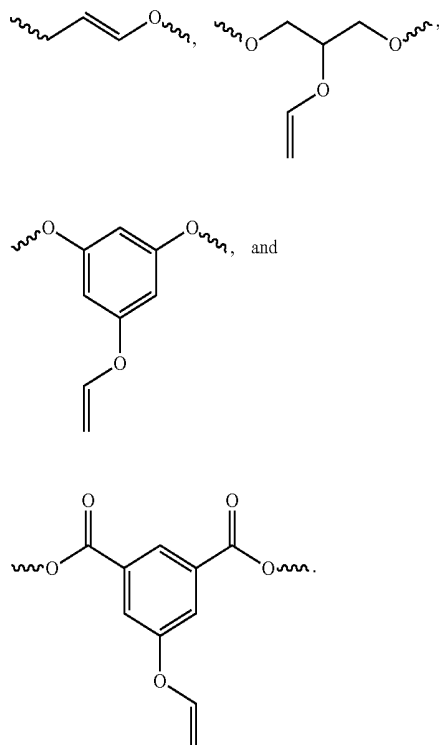




or CN or wherein one or more nonadjacent CH₂ groups are replaced by —O—, —S—, —NH—, —NR—, —SiRR—, —CO—, —COO—, —OCO—, —OCO—O—, —S—CO—, —CO—S—, —CH=CH—, —C≡C— such that O and S atoms are not directly linked to other O or S atoms. The alkyl or alkoxy chains may be terminated with crosslinking groups. Examples of these terminal crosslinking groups are:

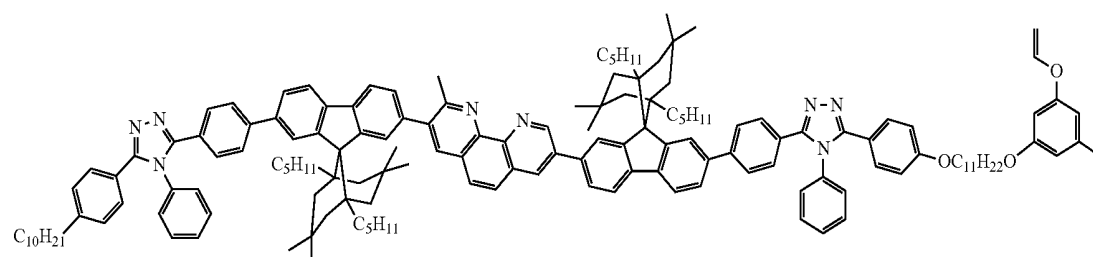
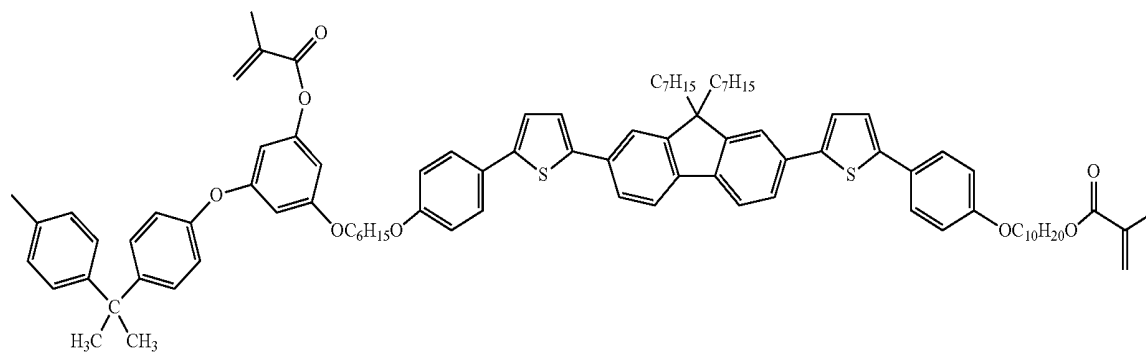
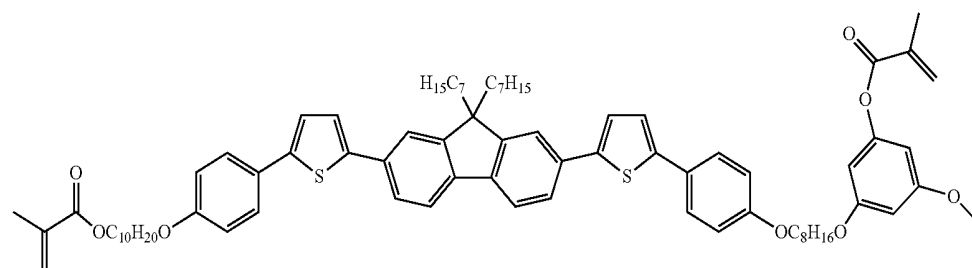
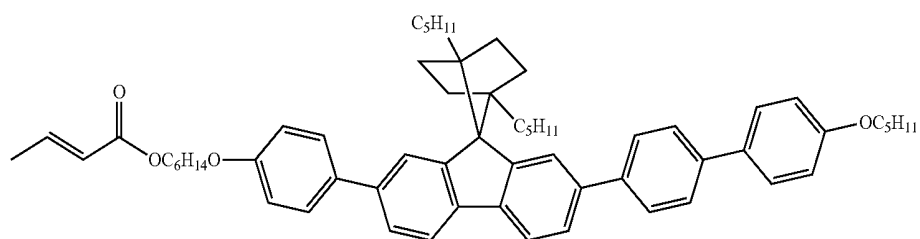
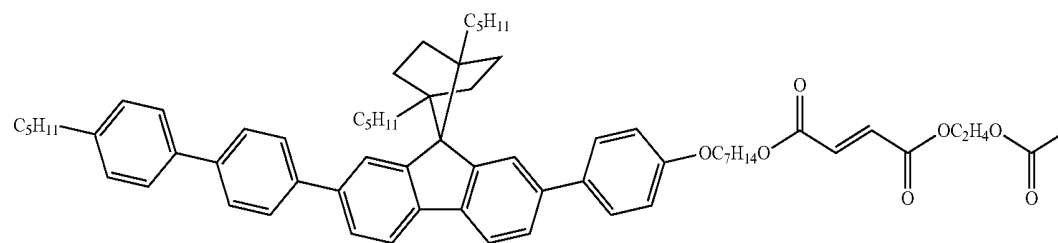


[0029] Examples of electron rich crosslinking groups that may serve as the B group in the invention are:

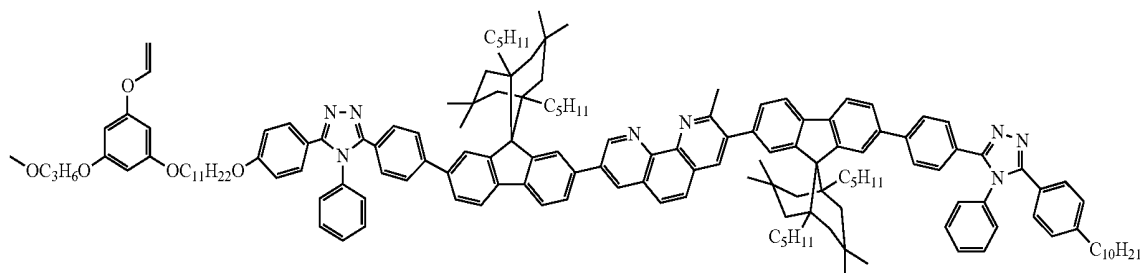


[0030] The end groups T may be chosen from hydrogen, an alkyl chain, an alkoxy chain, a cyano group or a fluorine. The alkyl and alkoxy chains may comprise branched, straight chain, or cyclic alkyl groups with 1 to 12 carbon atoms, which are unsubstituted, or mono- or poly-substituted by F, Cl, Br, I,

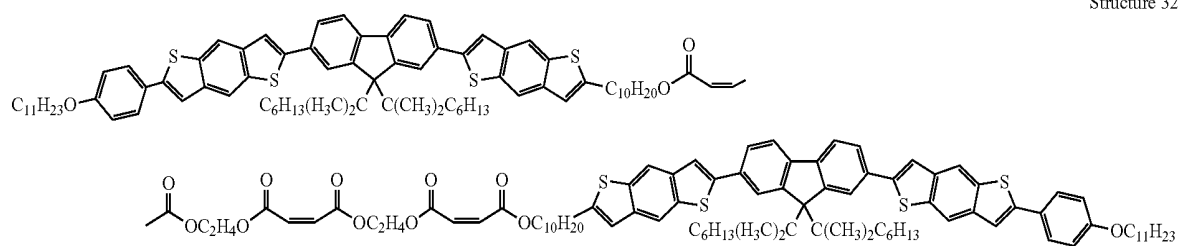
[0031] Examples of molecular structures of the inventive materials are:



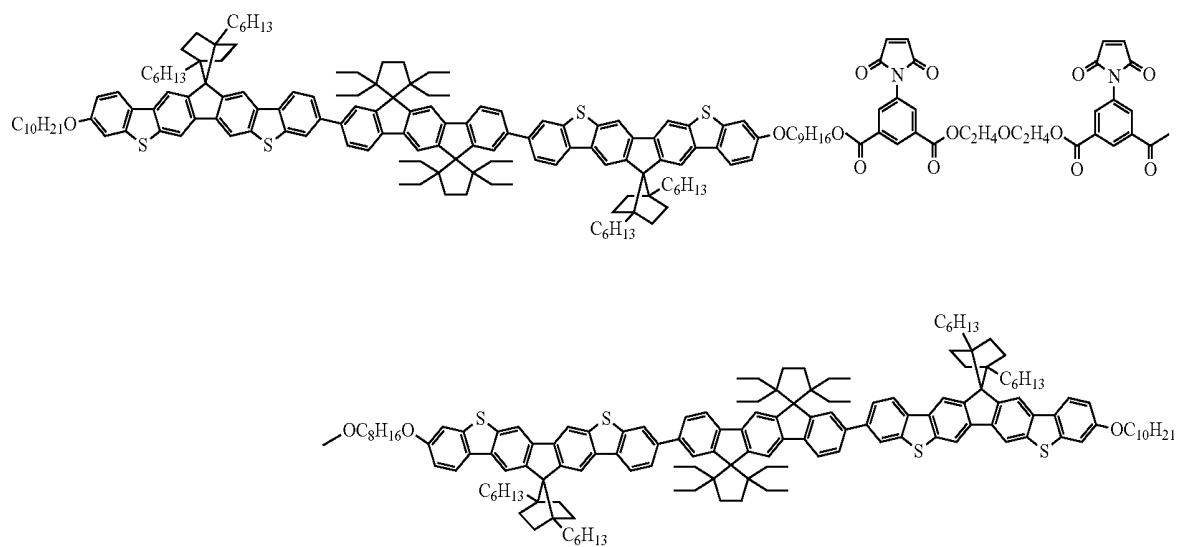
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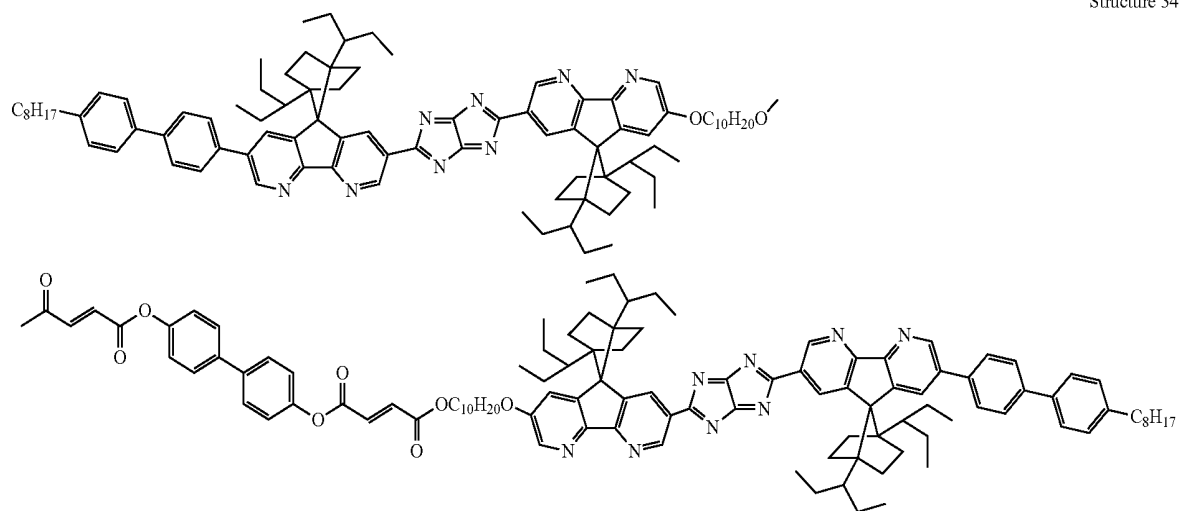
Structure 32



Structure 33



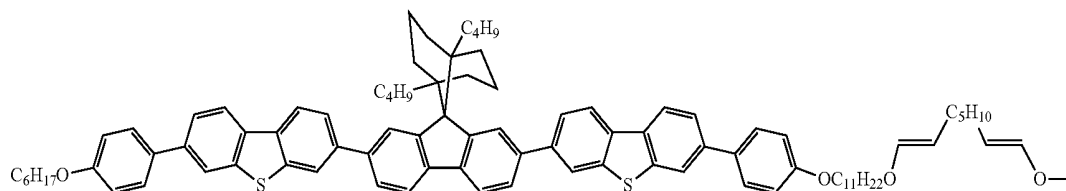
Structure 34



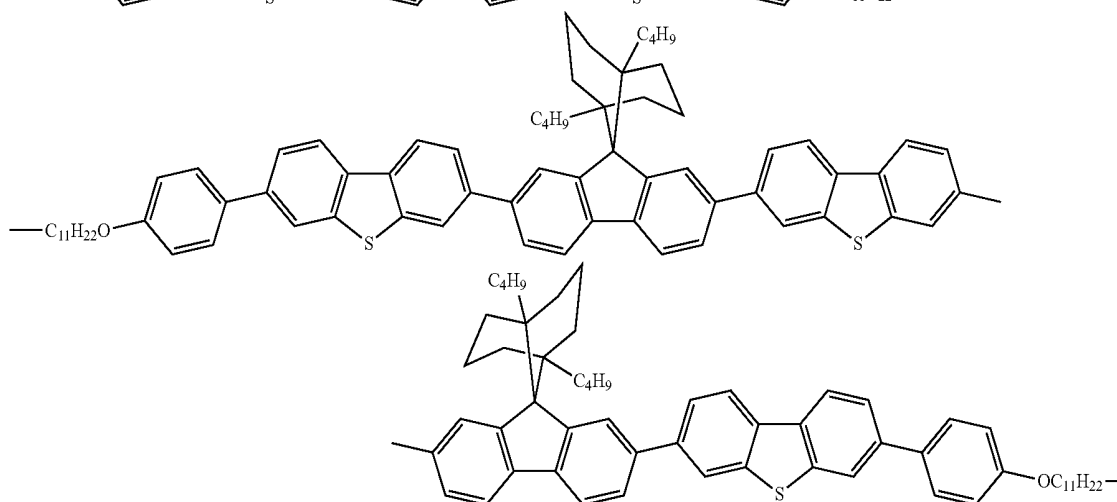
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Structure 35 = (A)₂B
wherein:

A =



B =

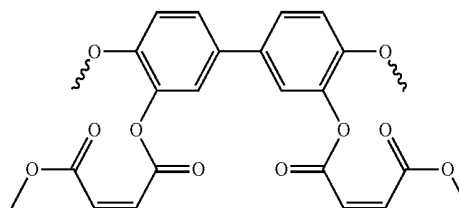
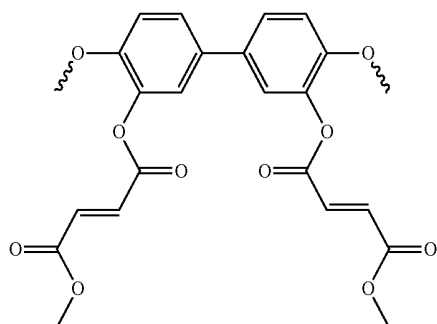
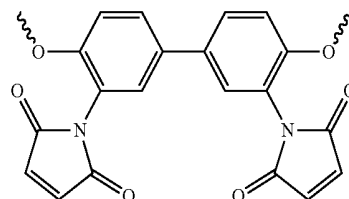
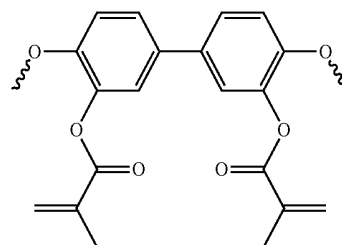


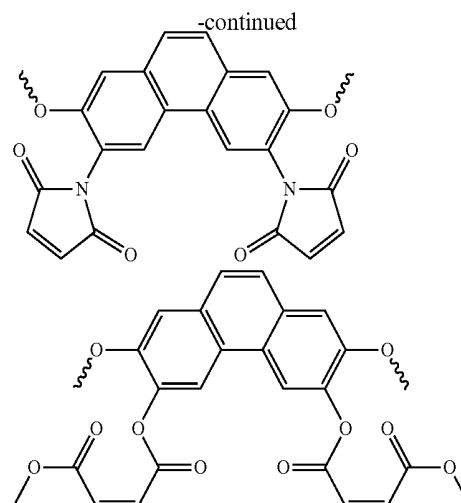
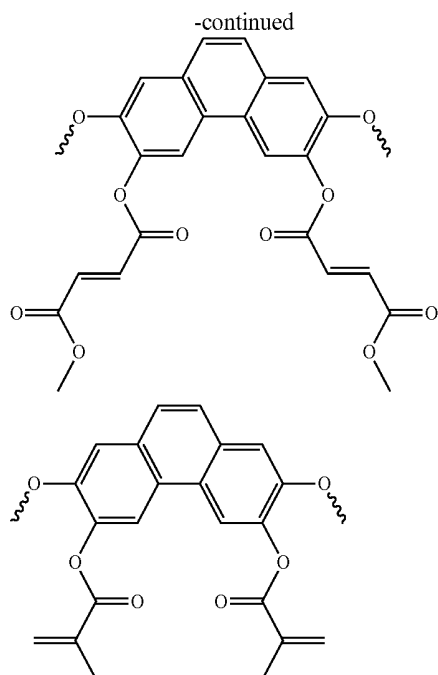
[0032] Compounds with structures 29, 30, 31, 33, and 34 in which $m=n=1$ are, in general preferred because they are simpler and less expensive to prepare.

[0033] Since the -S-B-P-B-S- structure will, in general, be easily prepared and therefore less expensive than adding on additional aromatic rings in the molecular core units, the inventive compounds provide a method to increase molecular weight and to enhance the film forming characteristics of solutions of the materials with minimal impact to the cost of manufacture. In addition, the length of the molecule is increased without substantially altering chromophoric properties of the molecular core. The capability can prove most useful when developing host materials that require relatively short wavelength luminescence bands to be compatible with guest emitter materials.

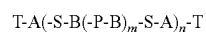
[0034] In another embodiment of the invention the crosslinking (B) and spacer (P) functionalities can be combined in a single structural sub-unit of the molecule. Some examples of these sorts of structures are:

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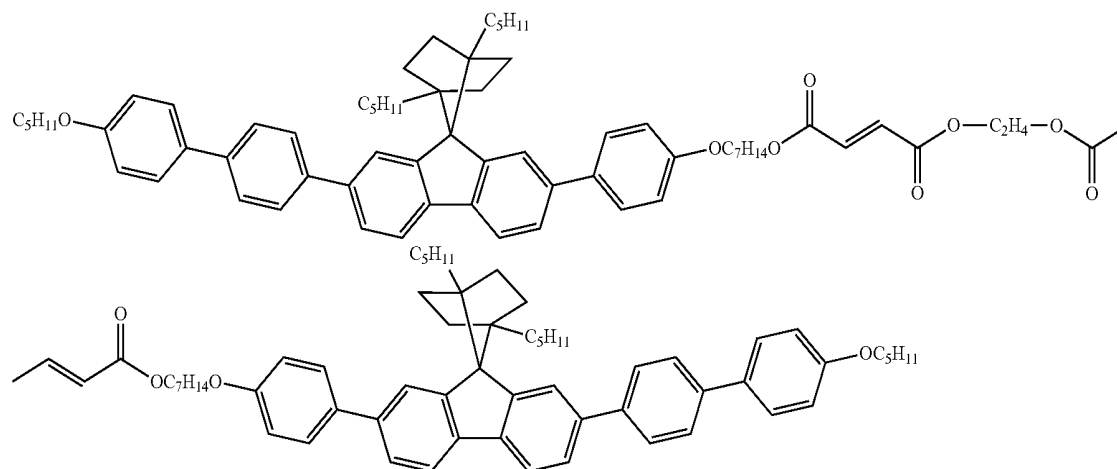


[0035] In another embodiment of the invention, materials having the formula:

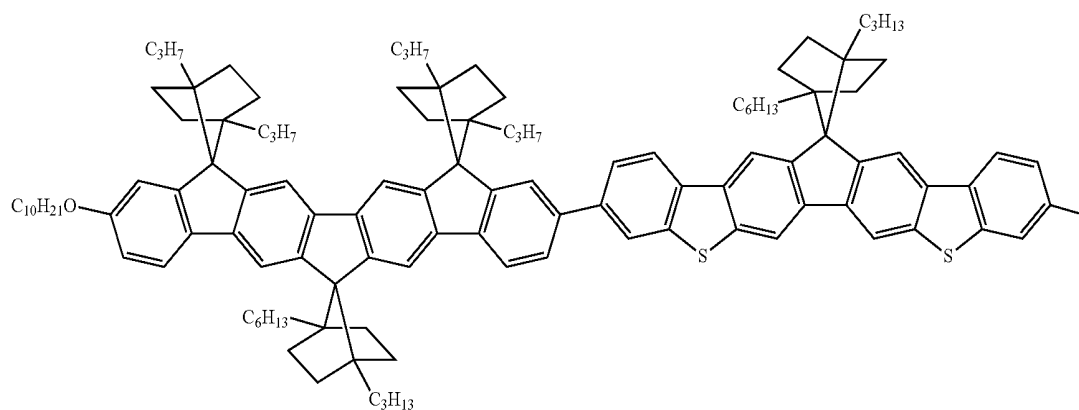


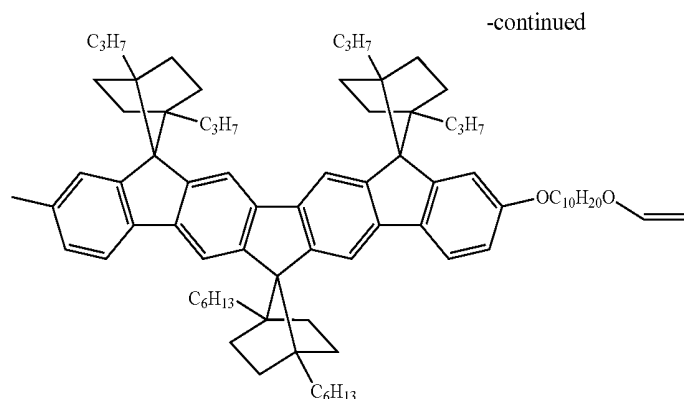
may be mixed with the prior art materials having the formulae B-S-A-S or B-S-A-S-B.

[0036] For instance one equivalent of material having the structure 29 from above:

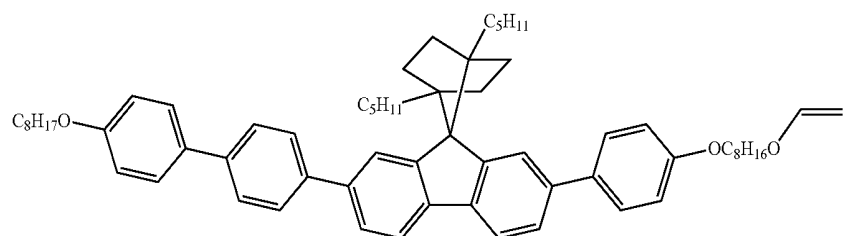


could be mixed with two equivalents of material consisting of 3 mole % of a compound with formula:



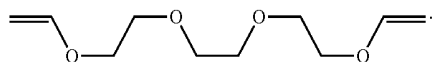


and 97 mole % of a compound with formula:



[0037] The material is then coated down and polymerized to form the copolymer.

[0038] In yet a further embodiment of the invention, material having structure 29, for example, may be copolymerised with a non-liquid crystalline monomer, for instance:

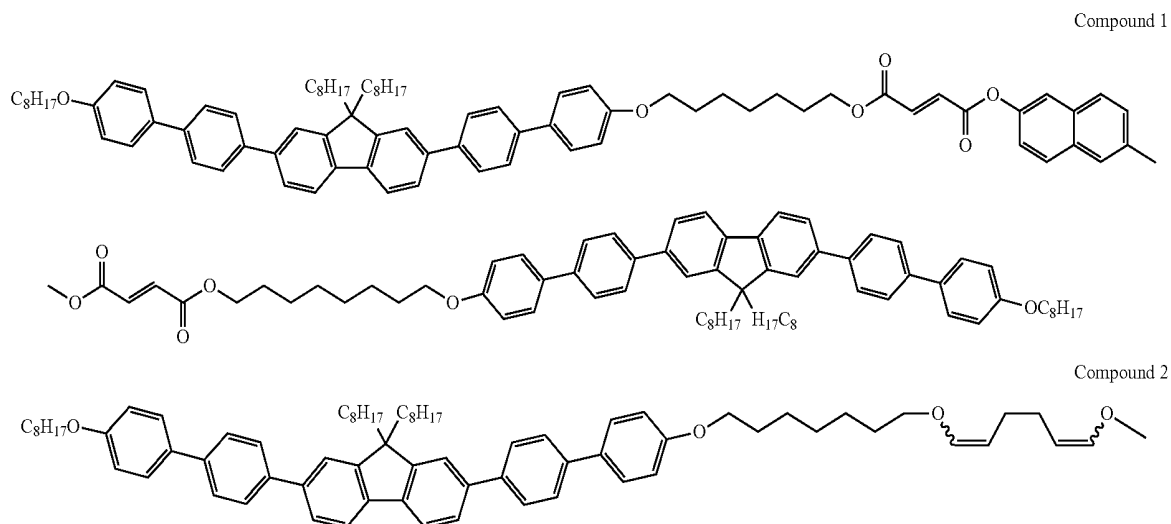


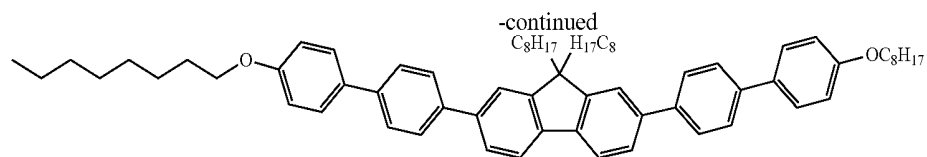
[0039] This provides a method of producing a polymer matrix film by the electron transfer polymerization method while only using only single liquid crystalline material of the invention.

[0040] An exemplary synthesis follows:

Compounds Used for Exemplary Synthesis

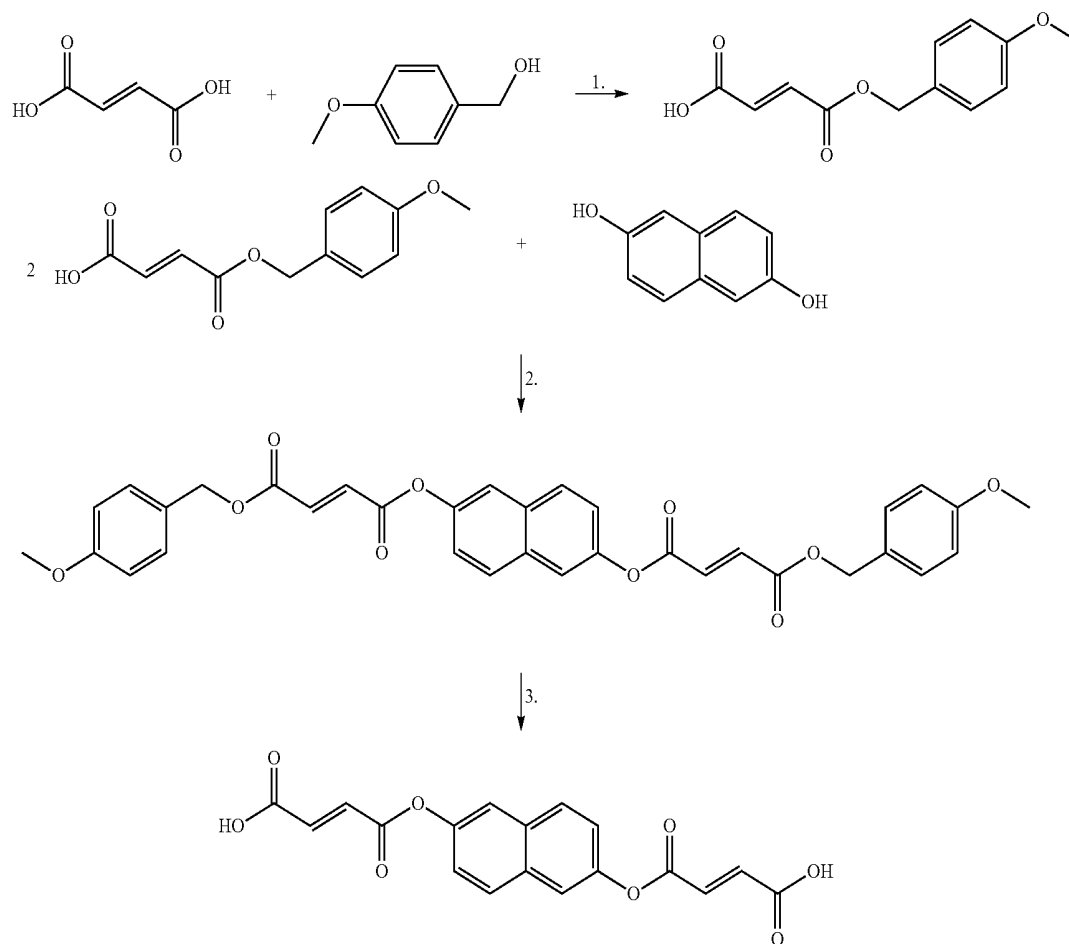
[0041]



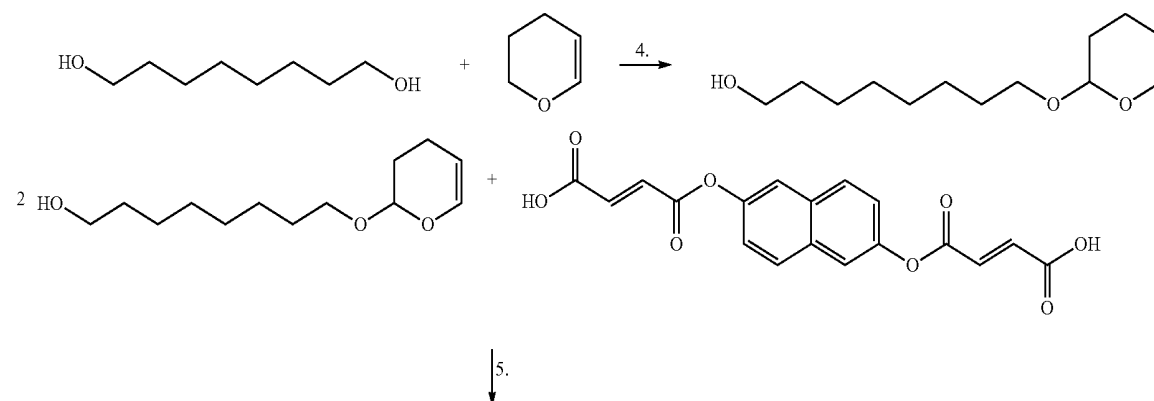


Synthesis of Compound 1

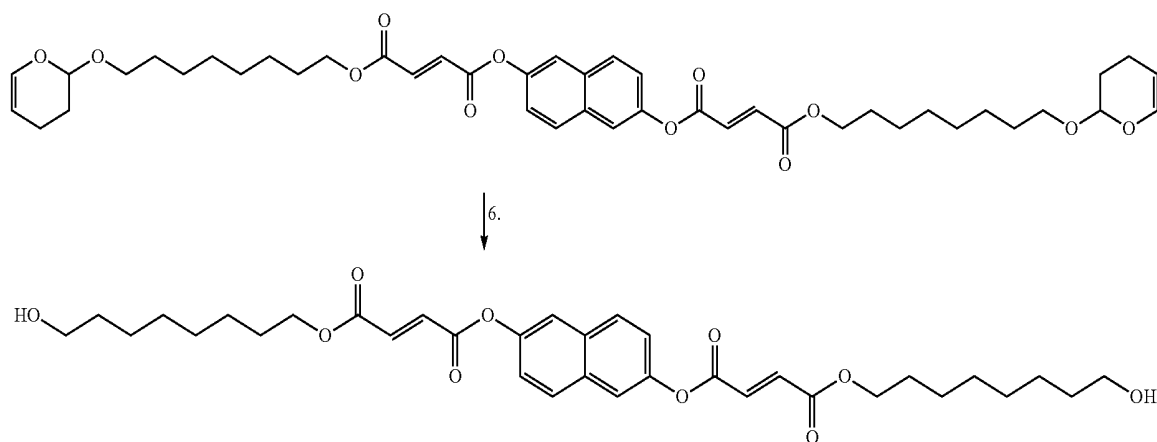
[0042]



1. Dicyclohexylcarbodiimide and catalytic 4-dimethylaminopyridine in dimethylformamide solvent overnight at room temperature,
2. Dicyclohexylcarbodiimide and catalytic 4-dimethylaminopyridine in dimethylformamide solvent overnight at room temperature,
3. Equimolar trifluoroacetic acid in phenol as the solvent at 45 degrees C. for one hour



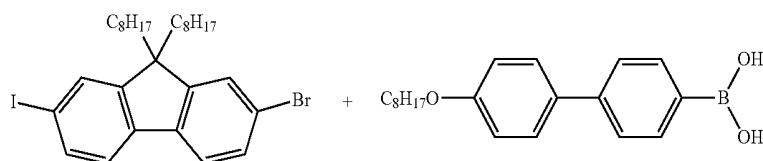
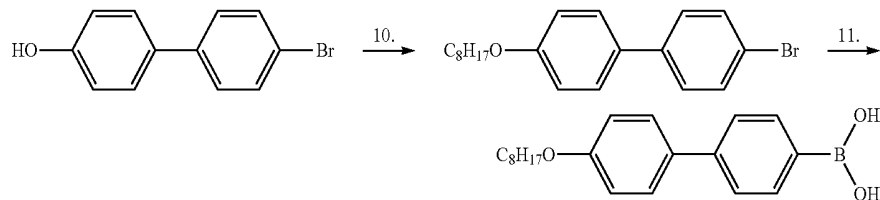
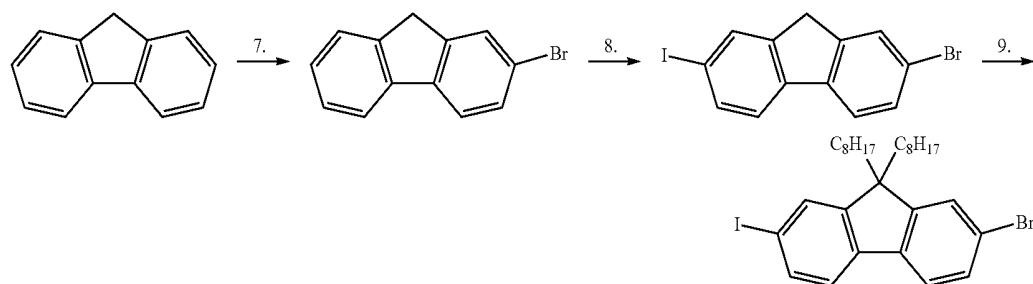
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4. Excess dihydropyran with catalytic camphorsulfonic acid at 65 degrees C. for 3.5 hours

5. Dicyclohexylcarbodiimide and catalytic 4-dimethylaminopyridine in dimethylformamide solvent overnight at room temperature

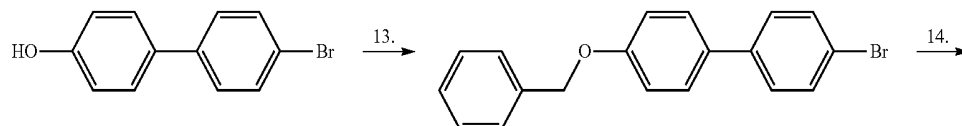
6. 95% acetic acid/5% water for six hours



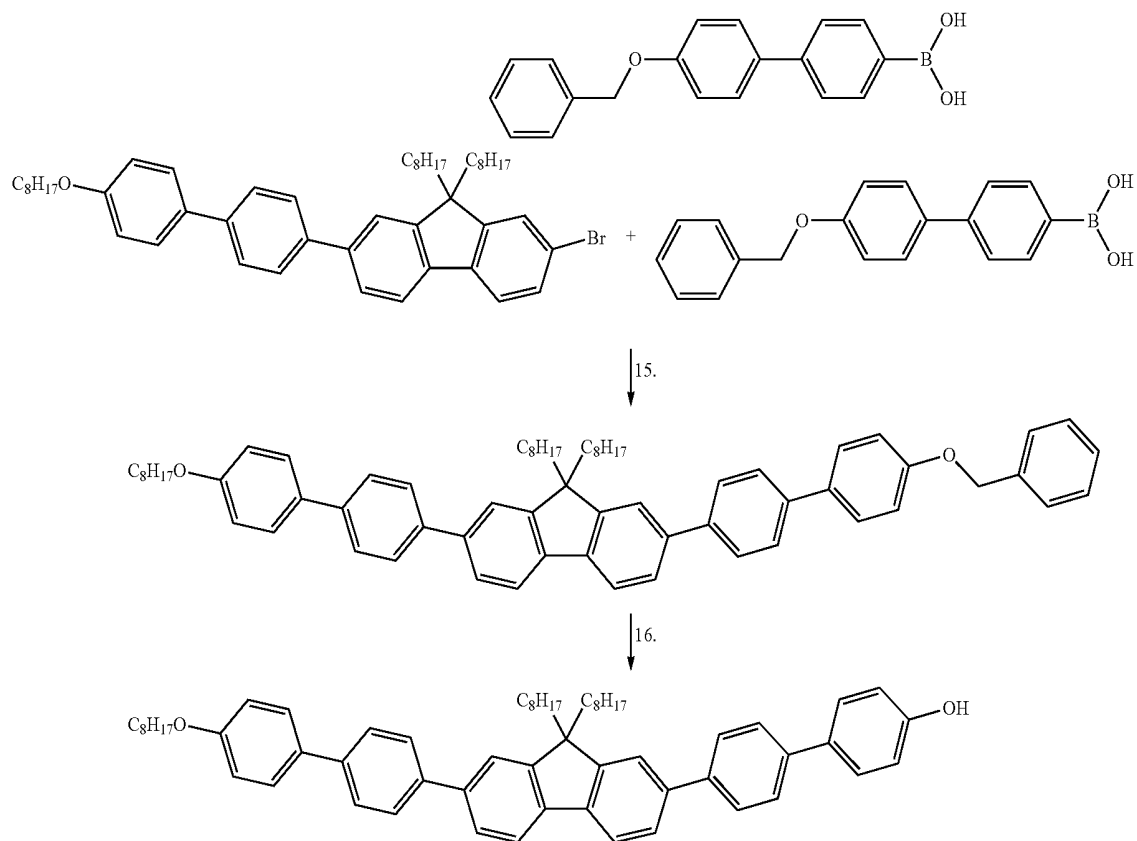
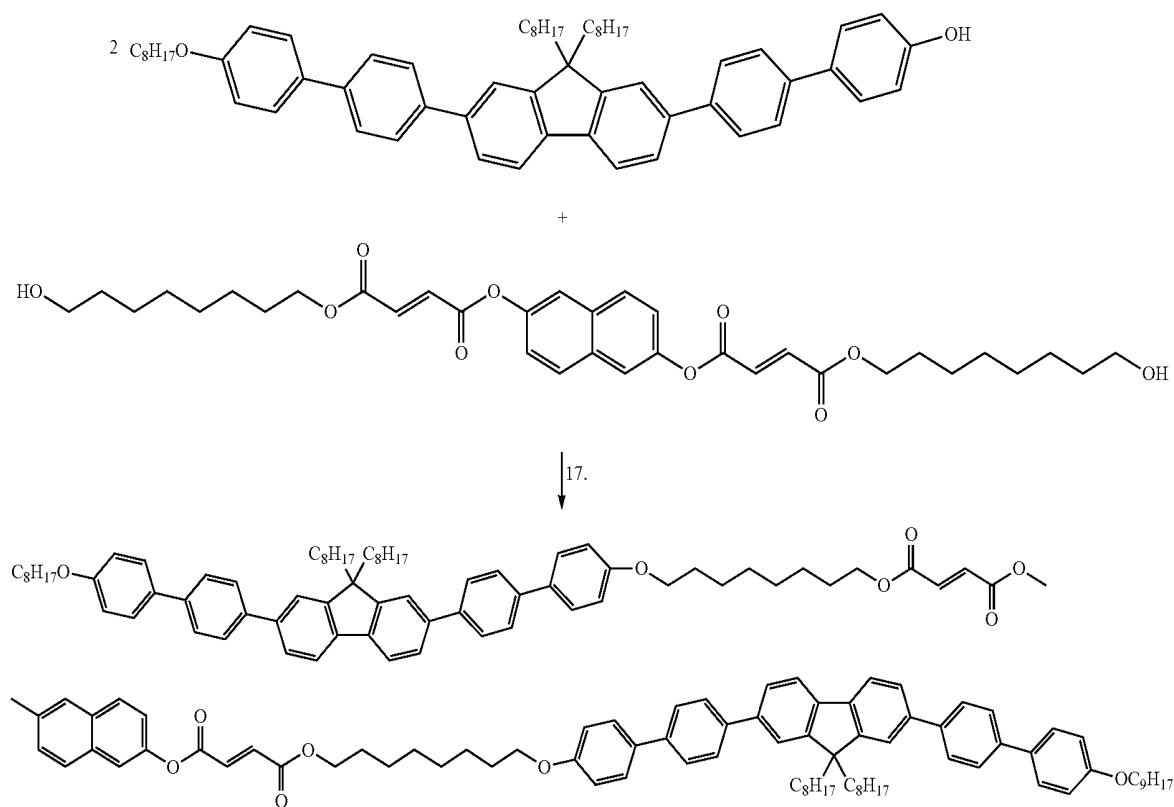
7. Equimolar bromine in chloroform solvent at room temperature under nitrogen for one hour

8. Iodine, potassium iodate, acetic acid, H₂O9. i. KOH in DMSO solvent at 5-10 degrees C. for two hours, ii. C₈H₁₇Br overnight at 5-10 degrees C.10. C₈H₁₇Br, K₂CO₃, catalytic tetrabutylammonium bromide in 2-butanone refluxed overnight

11. i. n-Butyl lithium in dry THF solvent for one hour at -78 degrees C., ii. Trimethyl borate at -78 degrees C., warm to RT overnight

12. K₂CO₃, Pd(PPh₃)₄, toluene:H₂O (2:1)

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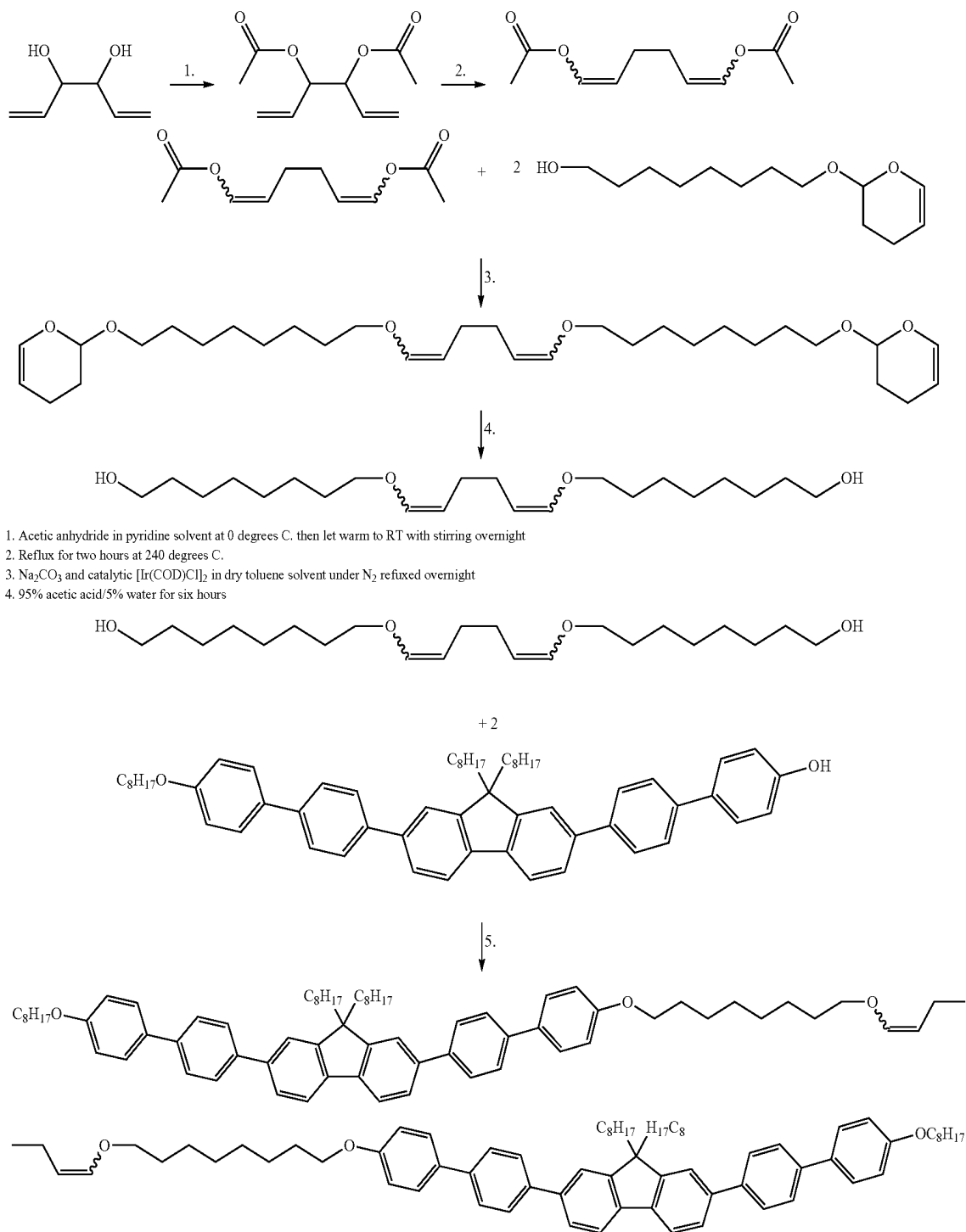
13. Benzyl bromide, K_2CO_3 , catalytic tetrabutylammonium bromide in 2-butanone refluxed overnight14. i. n-Butyl lithium in dry THF solvent for one hour at -78 degrees C., ii. Trimethyl borate at -78 degrees C., warm to RT overnight15. K_2CO_3 , $Pd(PPh_3)_4$, toluene: H_2O (2:1)16. 5% Pd/H_2 on carbon in THF solvent overnight

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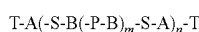
17. $\text{C}_8\text{H}_{17}\text{Br}$, K_2CO_3 , catalytic tetrabutylammonium bromide in 2-butanone refluxed overnight

Synthesis of Compound 2

[0043]



1. OLED materials having the formula:



where

A are independently selected rod-shaped, rigid molecular core units,

S are independently selected flexible spacer units,

B are polymerisable crosslinking groups independently selected,

P are spacer groups independently selected,

T are independently selected end groups,

m are independently selected from values of from 1 to 4, n is equal to 1 to 3.

2. Materials according to claim 1, in which the crosslinking groups are chosen so as to allow the molecules to be polymerised into a polymer matrix, particularly by exposure to UV.

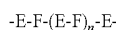
3. Materials according to claim 2, in which the molecular nucleus or core units and also the spacer units are chosen such that the material displays liquid crystalline order.

4. Materials according to claim 3, in which the units are chosen so that the material displays nematic order.

5. Materials according to claim 4, in which the core units are chosen so as to promote either light emitting or charge transporting properties, or both, in the product polymer matrix.

6. Materials according to claim 5, in which the rod-shaped, rigid molecular core units (A) comprise any conjugated aromatic ring systems.

7. Materials according to claim 6, in which the rod-shaped, rigid molecular core units (A) have the general structure:



wherein E is independently chosen from a single bond or an aromatic diradical disubstituted so as to maintain the linear nature of rigid molecular core A, and wherein F is a diradical containing a fluorene, azafluorene or polyazafluorene aromatic ring system and which is disubstituted so as to maintain the linear nature of the rigid molecular core A, and wherein n is between 0 and 7.

8. Materials according to claim 7, in which n is between 0 and 4.

9. Materials according to claim 8, in which the flexible spacer units S are branched, straight chain or cyclic alkyl groups with 3 to 12 carbon atoms, which are unsubstituted, or mono- or poly-substituted by F, Cl, Br, I, or CN or wherein one or more nonadjacent CH₂ groups are replaced by —O—, —S—, —NH— —NR—, —SiRR~—, —CO—, —COO—, —OCO—, —OCO—O—, —S—CO—, —CO—S—, —CH=CH—, —C≡C— such that O and S atoms are not directly linked to other O or S atoms.

10. Materials according to claim 9, in which the spacer units P separate the crosslinking groups B from each other and help determine the stiffness of the polymer matrix formed after the molecules have been crosslinked.

11. Materials according to claim 10, in which more rigid P units, for instance those composed of aromatic rings, are used, leading to a stiffer, more rigid polymer.

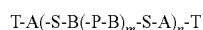
12. Materials according to claim 10, in which more flexible P spacers, for instance simple alkyl chains, result in a softer more deformable polymer matrix.

13. Materials according to claim 12, comprising mixtures of materials with varying length spacers destabilising the more highly ordered smectic phases in favour of the nematic phase.

14. Materials according to claim 13, comprising mixtures of two or more molecules in at least one of which the crosslinking units are electron deficient and in at least another one of which the crosslinking units are electron rich.

15. Materials according to claim 14, in which the crosslinking (B) and spacer (P) functionalities are combined in a single structural sub-unit of the molecule.

16. Materials according to claim 15, in which materials having the formula:



are mixed with the prior art materials having the formulae B-S-A-S or B-S-A-S-B.

* * * * *

专利名称(译)	含有多种交联功能的低聚有机发光二极管 (OLED) 材料		
公开(公告)号	US20150097145A1	公开(公告)日	2015-04-09
申请号	US14/399296	申请日	2013-05-09
[标]申请(专利权)人(译)	洛马克斯有限公司		
申请(专利权)人(译)	LOMOX有限公司		
当前申请(专利权)人(译)	LOMOX有限公司		
[标]发明人	KOCH GENE CARL		
发明人	KOCH, GENE CARL		
IPC分类号	H01L51/00 C07C43/215 C07C69/52		
CPC分类号	H01L51/0039 H01L51/50 C07C43/215 C07C69/52 C09K11/06 C09K2211/1416 C09K2211/1425 C09K2211/1433 C09K2211/1458 C09K2211/1466 C09K2211/1483 H01L51/005 H01L51/5012 H01L51/5048 H05B33/14		
优先权	2012008115 2012-05-09 GB		
其他公开文献	US9761804		
外部链接	Espacenet USPTO		

摘要(译)

具有下式的OLED材料：TA (-SB (-PB) mSA) nT其中A是独立选择的棒状，刚性分子核心单元，S是独立选择的柔性间隔单元，B是独立选择的可聚合交联基团，P是间隔基团在独立选择的基团中，T是独立选择的端基，m独立地选自1至4的值，n等于1至3。

