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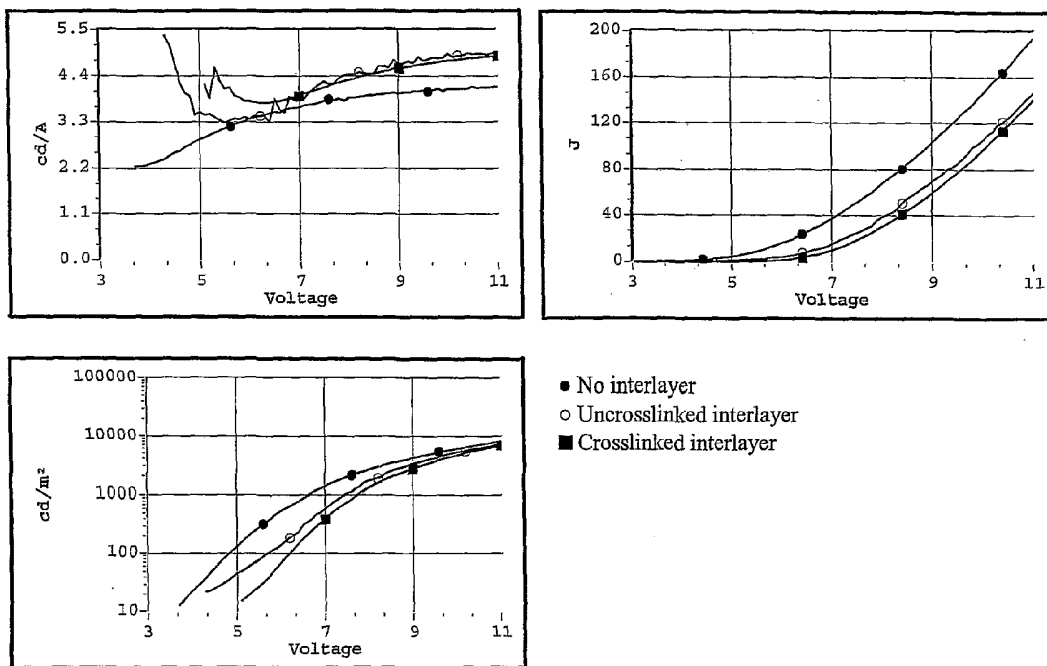
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(54) Title: CROSSLINKABLE ARYLAMINE COMPOUNDS AND CONJUGATED OLIGOMERS OF POLYMERS BASED THEREON



(57) Abstract: Crosslinkable arylamine compounds; oligomers and polymers prepared from such crosslinkable arylamine compounds; films and coatings; and multilayer electronic devices comprising such films are disclosed.

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CROSSLINKABLE ARYLAMINE COMPOUNDS AND CONJUGATED OLIGOMERS OR
POLYMERS BASED THEREON

Background of the Invention

5 This invention relates to novel crosslinkable arylamine compounds and methods for their preparation. The invention further relates to oligomers and polymers of such compounds, including crosslinked derivatives thereof, as well as films and coatings prepared from such compounds, oligomers or polymers, processes for preparing such films and coatings, and electronic devices, especially electroluminescent devices, comprised of one or more layers of such
10 polymer films.

USP's 6,605,373, 6,362,310, 6,255,449, 6,255,447, 6,169,163, 5,962,631 and related patents disclosed certain crosslinkable substituted fluorene compounds and oligomers and polymers therefrom. USP 5,929,194 disclosed the synthesis of polyarylpolyamines by crosslinking of certain small molecule amines containing two reactive groups. Related disclosures
15 are also found in USP 5,728,801.

Macromolecular Rapid Communication 21, 583-589(2000) described the synthesis of arylamine containing crosslinkable hole transport materials containing a crosslinkable oxetane group. Macromolecular Rapid Communication 20, 224-228 (1999) described the synthesis of triarylamine small molecules with crosslinkable oxetane groups that can be spin-coated and
20 crosslinked as films. The foregoing references, to the extent crosslinked polymers are disclosed, lack a conjugated polymer backbone, and have only restricted charge transport ability.

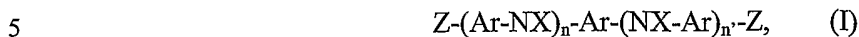
Recent advances in photodisplay technology have resulted in improved compounds and fabrication techniques for electroluminescent devices such as light-emitting diodes (LED's). High luminosity materials are now available for a large portion of the visible light spectrum, including
25 blue light emitting compounds. Recently it has been discovered that improved lifetimes and efficiencies of the active or light emitting layer of a multilayer LED can be obtained by incorporation of a charge transport layer into a multilayer LED between the active or light emitting layer and the anode. Such layers may also be referred to as a hole injection and/or hole transport layer where the purpose is to improve hole injection into the light emitting layer and to
30 provide a buffer layer between the anode and the light emitting layer. In other applications, such an inter layer between the hole transport layer and light emitting layer has been shown to provide improved device efficiency and lifetime.

The present invention is directed to novel compounds for use in various layers of a multilayer LED, such as hole transport layers and interlayers of a multilayer LED, as well as in

other electronic devices such as field effect transistors (FET's), photovoltaic cells, and even for integrated circuits or printed circuit boards.

Summary of the Invention

In one aspect, this invention is an arylamine compound of the formula:



wherein,

Ar independently each occurrence is a group comprising one or more divalent aromatic groups, and optionally two Ar groups separated by a single NX group may be joined together by a second covalent bond or by a bridging group, thereby forming a fused multiple ring system;

10 X is an inert substituent or a cross-linkable group, with the proviso that in at least one occurrence in said compound, X is a crosslinkable group;

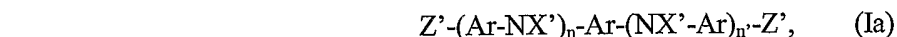
Z independently each occurrence is hydrogen or a leaving group,

n is 1 or 2; and

n' is 0, 1 or 2.

15 Due to the pendant nature of the crosslinkable group, X, the compounds of the present invention are capable of forming oligomers and polymers containing relatively large amounts of conjugated unsaturation, thereby resulting in improved charge transport properties. Oligomers and polymers, including copolymers, resulting from crosslinking compositions comprising the foregoing compounds advantageously are characterized by reduced ionization potential and
20 improved conductivity. Moreover, the compounds are capable of forming crosslinked, solvent resistant films that are well suited for use as interlayers in electroluminescent devices.

Accordingly, in a second aspect, this invention is a composition comprising oligomers, polymers, or crosslinked derivatives thereof having one or more repeating groups of the formula:



where X' is X or a divalent crosslinked remnant formed by addition polymerization of a crosslinkable X group, preferably such a group that forms conjugated unsaturation upon crosslinking;

Z' is Z, a covalent bond, or a terminal group formed by replacement or reaction of a leaving group; and

30 Ar, X, Z, n and n' are as previously defined with respect to compounds of formula (I).

In a third aspect, this invention is a process for preparing oligomers, polymers, including copolymers, and crosslinked derivatives thereof comprising one or more groups of formula (Ia), which process comprises heating one or more compounds of formula (I) or a composition comprising the same, such as a mixture thereof with one or more addition polymerizable

monomers, optionally in the presence of any other noninterfering compound, under reaction conditions sufficient to form an oligomer or polymer having one or more repeating groups of Formula (Ia).

In a fourth aspect, this invention is a film comprising one or more of the oligomers or polymers of the second embodiment of this invention or preparable according to the third embodiment of this invention.

In a fifth aspect, this invention is an electroluminescent device comprising one or more layers of polymer films, at least one of which comprises a film according to the fourth aspect of the invention.

The foregoing compounds, oligomers and polymers have been discovered to possess especially efficient hole injecting/transporting or electron blocking properties when used to form interlayers in electronic devices, and advantageously are characterized by reduced ionization potential and improved conductivity. Moreover, the compounds are capable of forming crosslinked, solvent resistant films that are well suited for use as such interlayers in electronic devices such as LEDs.

Brief Description of the Drawings

Figure 1 contains electrical properties of the light emitting devices of Example 6.

Figures 2 and 3 are DSC scans of the compound of Example 3A.

Detailed Description of the Invention

For purposes of United States patent practice, the contents of any patent, patent application or publication referenced herein is hereby incorporated by reference in its entirety herein, especially with respect to its disclosure of monomer, oligomer or polymer structures, synthetic techniques and general knowledge in the art. If appearing herein, the term "comprising" and derivatives thereof is not intended to exclude the presence of any additional component, step or procedure, whether or not the same is disclosed herein. In order to avoid any doubt, all compositions claimed herein through use of the term "comprising" may include any additional additive, adjuvant, or compound, unless stated to the contrary. In contrast, the term, "consisting essentially of" if appearing herein, excludes from the scope of any succeeding recitation any other component, step or procedure, excepting those that are not essential to operability. The term "consisting of", if used, excludes any component, step or procedure not specifically delineated or listed. The term "or", unless stated otherwise or apparent from the context, refers to the listed members individually as well as in any combination.

As used herein the term "aromatic" refers to a polyatomic, cyclic, ring system containing $(4\delta+2)$ π -electrons, wherein δ is an integer greater than or equal to 1. The term "fused" as used herein with respect to a ring system containing two or more polyatomic, cyclic rings means that with respect to at least two rings thereof, at least one pair of adjacent atoms is included in both
5 rings.

"B-Staged" refers to the oligomeric mixture or low molecular weight polymeric mixture resulting from partial polymerization of a monomer. Unreacted monomer may be included in the mixture.

"Conjugation" refers to full or partial overlap of adjacent π -, p- or d-orbital electrons associated with atoms in the polymer chain of interest. Conjugation is presumed to exist between
10 two entities containing atoms possessing delocalized charges, such as double or triple bonds, which are joined to one another by a covalent bond or by a -S-, -O-, -NR-, -PR-, -BR-, or -SiR₂- group.

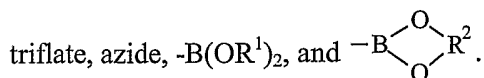
"Crosslinkable" means a functional group that is capable of being irreversibly cured or
15 polymerized, thereby forming a material that cannot be reshaped or reformed. Crosslinking may be assisted by heat or by UV, microwave, x-ray, or e-beam irradiation. The term is often used interchangeably with "thermosettable" when the crosslinking is done thermally.

"Hydrocarbyl" refers to a univalent moiety containing only carbon and hydrogen atoms.

"Hydrocarbylene" refers to a divalent moiety containing only carbon and hydrogen atoms.

"Inert substituent" means a substituent group which does not interfere with any
20 subsequent desirable coupling or polymerization reaction of the monomer or oligomer but may include further polymerizable moieties as disclosed herein. Suitable inert non-polymerizable substituents include hydrogen, C₁₋₂₀ hydrocarbyl and tri(C₁₋₂₀hydrocarbyl)silyl groups.

"Leaving group" means a substituent that is readily displaced or eliminated from
25 the molecule under coupling conditions. Examples of suitable leaving groups include halo, cyano, triflate, azide, -B(OR¹)₂, and



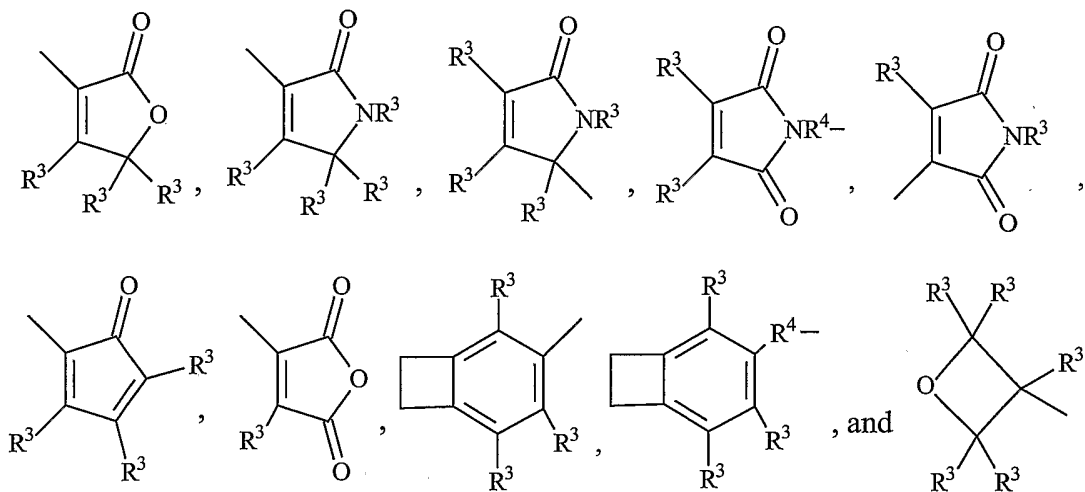
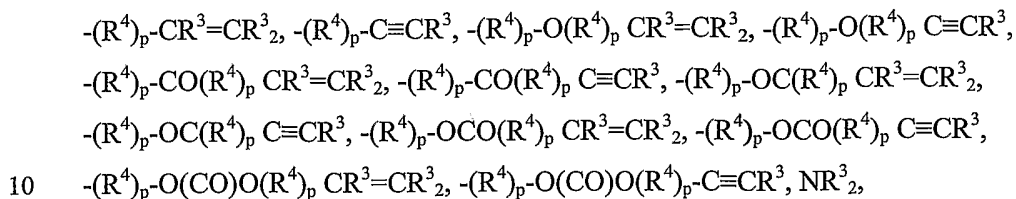
wherein R¹, independently in each occurrence, is hydrogen or a C₁₋₁₀ alkyl group, and

R², independently each occurrence, is a C₂₋₁₀ alkylene group. A preferred leaving group is
bromo.

30 Examples of crosslinkable X groups are moieties containing a double bond, a triple bond, a precursor capable of in situ formation of a double bond, or a heterocyclic, addition polymerizable group. Preferred crosslinkable X groups include benzocyclobutanyl groups and substituted C₆₋₁₂ arylene groups containing one or more substituents selected from the group

consisting of benzocyclobutane, azide, oxirane, di(hydrocarbyl)amino, cyanate ester, hydroxy, glycidyl ether, C₁₋₁₀ alkylacrylate, C₁₋₁₀ alkylmethacrylate, ethenyl, ethenyloxy, perfluoroethenyloxy, ethynyl, maleimide, nadimide, tri(C₁₋₄)-alkylsiloxy, tri(C₁₋₄)alkylsilyl, and halogenated derivatives thereof. Most preferred crosslinkable X groups are 1-benzo-3,4-cyclobutane and 4-phenyl-1-(benzo-3,4-cyclobutane).

5 Specific examples of suitable crosslinkable X groups include:



where

R³ is hydrogen, halogen, C₁₋₂₀ hydrocarbyl, C₁₋₂₀ halohydrocarbyl, or C₁₋₂₀ halocarbyl;
 15 R⁴ is C₁₋₂₀ hydrocarbylene, C₁₋₂₀ halohydrocarbylene, or C₁₋₂₀ halocarbylene; and
 p is 0 or 1.

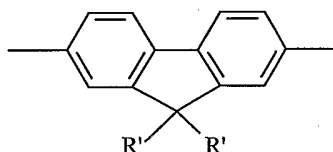
In like vein, X' is either X or a crosslinked remnant of X. It will be understood by the skilled artisan, that crosslinking of an X functional group involves a reaction between two or more X groups in two or more different compounds, oligomers or polymers, or a reaction of an X group with a separately added polymerizable comonomer, thereby joining said molecules into a single chemical entity.

In one preferred embodiment of the invention, X groups comprise an aromatic moiety, preferably a moiety of the formula ArX'', wherein Ar is as previously defined and X'' is a crosslinkable group having at least one of the crosslink forming atoms thereof covalently bound to an atom of Ar bearing delocalized electronic charge. That is, the X'' group is directly attached to an aromatic group comprising Ar. Especially suited X'' groups in this embodiment include 1-

ethenyl or benzo-3,4-cyclobutan-1-yl groups, and inertly substituted derivatives thereof. In yet another preferred embodiment, the X'' groups are self-crosslinkable, meaning that no initiator, such as an acid, base or peroxide compound, is needed to initiate crosslinking involving said X'' group, it being understood that copolymerizable comonomers, especially addition polymerizable comonomers such as ethylenically unsaturated compounds, may additionally be present. In this embodiment, the absence of an acid, base or peroxide initiator, reduces corrosion of the cathode or other components of the resulting electronic device and eliminates problems due to proton migration within the interlayer.

Suitable inert, non-crosslinkable, X groups include C₁₋₂₀ hydrocarbyl and halogenated C₁₋₂₀ hydrocarbyl groups, especially aryl and alkaryl groups. Preferred non-crosslinkable X groups include phenyl and C₁₋₁₀ alkylphenyl, especially p-n-butylphenyl.

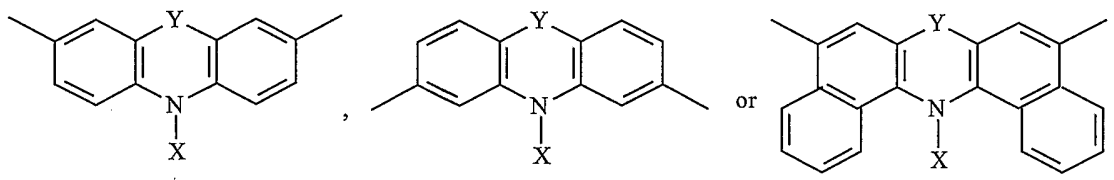
Suitable Ar groups include phenylene, biphenylene, naphthalenediyl, anthracenediyl, stilbenediyl, and fluorenediyl groups, inertly substituted derivatives thereof, and combinations of the foregoing groups. Preferred fluorenediyl groups correspond to the formula:



15

where R', independently each occurrence, is an inert substituent, X or X'.

As previously mentioned, two Ar groups separated by a single -NX- group may form a fused aromatic ring system. Examples include groups corresponding to the formulas:



20

where, X is as previously defined;

Y is a covalent bond, O, S or NR; where

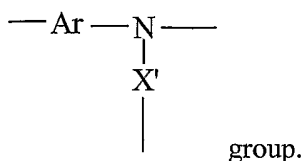
R independently in each occurrence is i) hydrogen; ii) halogen; iii) a C₁₋₂₀ hydrocarbyl group; iv) a hydrocarbyl group substituted with one or more heteroatom containing groups containing up to 20 atoms not counting hydrogen and wherein the heteroatom is selected from S, N, O, P, B or Si; v) a halogenated derivative of iii) or iv); or vi) a substituted derivative of iii) or iv) wherein the substituent is a crosslinkable X group.

25

Preferred substituents, R, include C₁₋₄₀ hydrocarbyl groups or C₁₋₄₀ hydrocarbyl groups containing one or more S, N, O, P, or Si heteroatoms, and the foregoing C₁₋₄₀ hydrocarbyl or C₁₋₄₀

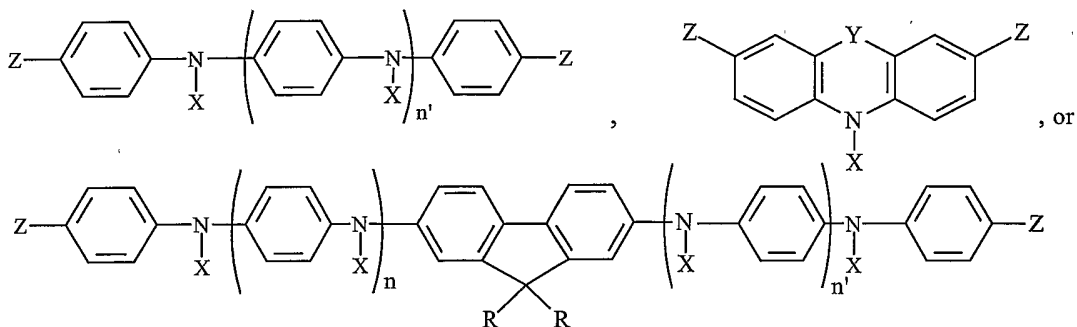
heteroatom containing groups substituted by a crosslinkable X group. In a more preferred embodiment, R is a C₁₋₁₀ alkyl group.

The monomers, oligomers and polymers of the invention preferably are highly conjugated, if not completely conjugated, along the backbone defined by $-(Ar-NX')_n-Ar-(NX'-Ar)_{n'}$. In a further preferred embodiment, they comprise difunctional derivatives of both fluorene and triarylamines in this backbone. More preferably still, the crosslinked oligomers and polymers of the invention are also highly conjugated, if not completely conjugated, along the crosslinked structure defined by at least one:



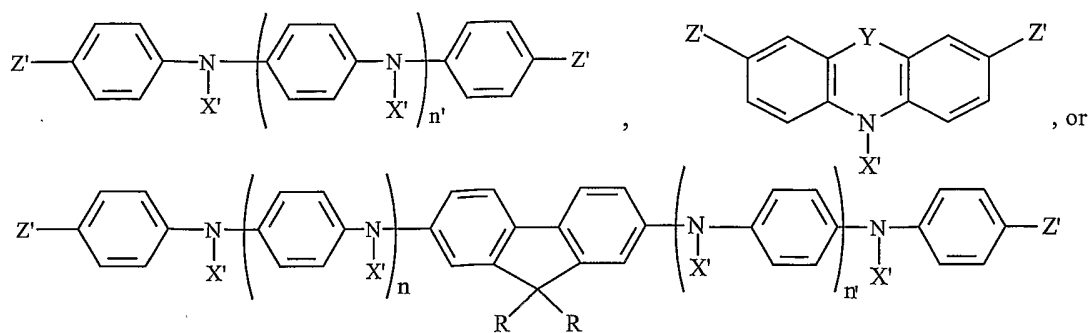
Highly preferred embodiments of the foregoing compounds are those wherein Ar each occurrence is 1,4-phenylene, 9,9-di(C₁₋₂₀alkyl)fluoren-2,7-diyl, or a combination thereof; X is 3,4-benzocyclobutan-1-yl, ethenyl or p-ethenylphenyl; Z is bromine or hydrogen; n is 1 or 2; and n' is 0 or 1. Further preferred amongst these compounds are those wherein Ar each occurrence is phenylene; each X group is 3,4-benzocyclobutan-1-yl; Z each occurrence is bromine; n is 1 or 2; and n' is 0. Highly preferably, within the foregoing compounds n is 1.

Specific examples of the compounds of formula I) according to the present invention are those having the following structures:



where n, n', R, X, Y and Z are as previously defined.

Specific examples of the oligomers and polymers of formula Ia) according to the present invention are those having the following structures:

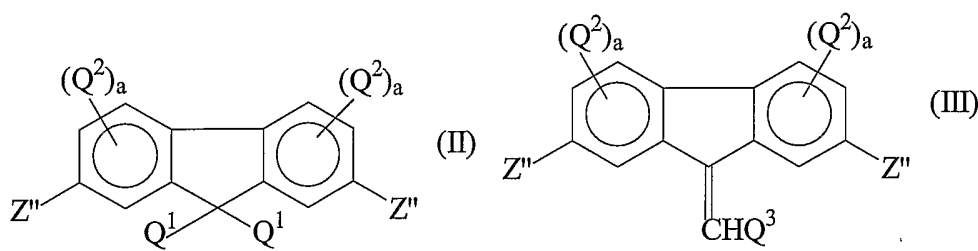


where n , n' , R , X' , Y and Z' are as previously defined. Such oligomers and polymers are readily prepared using conventional synthetic techniques to cause loss or polymerization of the leaving group, Z , and formation of the remnant, Z' . Suitable techniques include the well known
 5 Buchwald or half-Buchwald reaction, Suzuki coupling reactions, or similar techniques.

The oligomers and polymers are highly suited for use in the preparation of both hole transport films and interlayer films in electroluminescent devices.

Crosslinking of Monomers

10 The arylamine compounds of formula I) or Ia) of the invention are readily polymerized to form crosslinked oligomers or polymers by heating a composition comprising such compound at an elevated temperature for a time sufficient to result in addition polymerization or other crosslinking reaction of at least some X functionality. In one embodiment the compounds are copolymerized with one or more copolymerizable monomers capable of forming divalent
 15 crosslinking moieties. Preferred copolymerizable compounds for use herein correspond to the formulas (II) or (III):



wherein Q^1 is independently in each occurrence C_{1-20} hydrocarbyl or C_{1-20} hydrocarbyl containing one or more S, N, O, P or Si atoms, C_{4-16} hydrocarbyl carbonyloxy, C_{4-16}
 20 aryl(trialkylsiloxy) or both Q^1 may form with the 9-carbon on the fluorene ring a C_{5-20} ring structure or a C_{4-20} ring structure containing one or more of S, N or O;

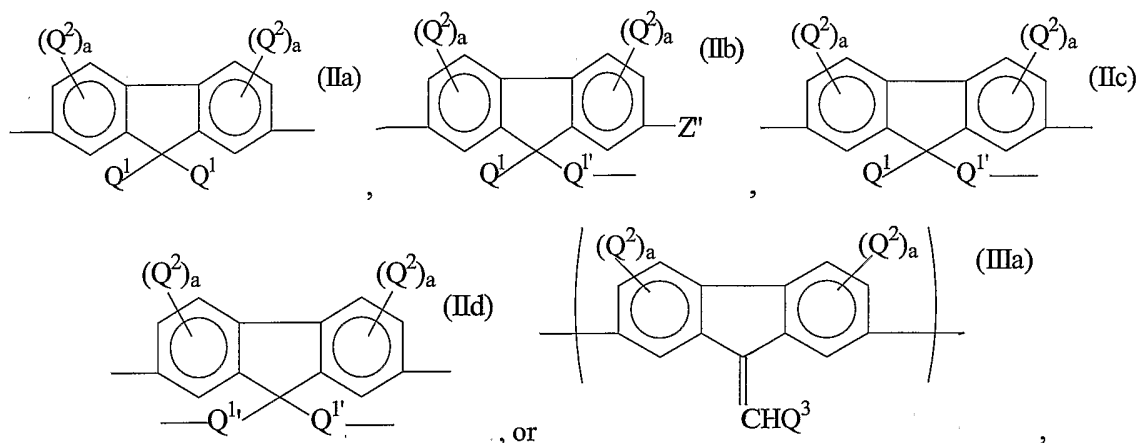
Q^2 is independently in each occurrence C_{1-20} hydrocarbyl, C_{1-20} hydrocarbyloxy, C_{1-20} thioether, C_{1-20} hydrocarbylcarbonyloxy or cyano;

Q^3 is independently in each occurrence C_{1-20} hydrocarbyl or C_{1-20} hydrocarbyl substituted with di(C_{1-20} alkyl)amino, C_{1-20} hydrocarbyloxy or C_{1-20} hydrocarbyl or tri(C_{1-10} alkyl)siloxy;

a is independently in each occurrence 0 or 1; and

Z'' is a leaving group, especially bromo.

5 In a preferred embodiment, the oligomers and polymers of the invention comprise from 1 to 99 percent, more preferably from 2 to 50 percent, and most preferably from 2 to 10 percent of repeat units of formula Ia) and 99 to 1 percent, more preferably 98 to 50 percent, most preferably 98 to 90 percent of repeat units of the formula:



10

wherein $Q^{1'}$ is a covalent bond or the divalent remnant of Q^1 .

The monomers and oligomers or b-staged derivatives of the invention are readily soluble in common organic solvents. They are processible into thin films or coatings by conventional techniques, particularly solution spin coating or ink-jet printing, with or without the use of a solvent.

15

The oligomers or polymers of this invention preferably have a weight average molecular weight of 1000 Daltons or greater, more preferably 5000 Daltons or greater, even more preferably 10,000 Daltons or greater, highly preferably 15,000 Daltons or greater and most preferably 20,000 Daltons or greater; preferably 1,000,000 Daltons or less, more preferably 500,000 Daltons or less and most preferably 200,000 Daltons or less. Molecular weights are determined by use of gel permeation chromatography using polystyrene standards. The degree of polymerization of the polymers of the invention as measured by the number of repeat units therein is preferably at least 2, more preferably at least 3. Preferably, the oligomers or polymers demonstrate a polydispersity (M_w/M_n) of 5.0 or less, more preferably 3.0 or less, and most preferably 2.0 or less.

25

Processes for Preparing Oligomers or Polymers

The compounds, oligomers and polymers of the invention are prepared by any suitable process, including a condensation reaction of an aromatic boronate and a bromide, commonly referred to as the "Suzuki reaction", as reported by N. Miyaura and A. Suzuki in Chemical Reviews, Vol. 95, pp. 457-2483 (1995). This palladium catalyzed reaction can be applied to preparing high molecular weight polymers and copolymers with addition of a phase transfer catalyst as taught in US-A-5,777,070. The reaction is typically conducted from 70°C to 120°C in suitable solvent or diluent. Preferred solvents include aromatic hydrocarbons, such as toluene or diethylbenzene, or aliphatic or aromatic ethers, esters, or carbamates, such as tetrahydrofuran or dimethylformamide. Mixtures of the foregoing solvents or diluents may be employed as well. A most preferred solvent is toluene. An aqueous base, preferably sodium carbonate or bicarbonate, is used as a scavenger for the reaction product of the leaving group, generally HBr. Depending on the reactivities of the reagents and the molecular weight of the desired product, a polymerization reaction may take from 1 minute to 100 hours. A monofunctional aryl halide or an aryl boronate compound may be added as a chain-terminator in such reactions, thereby resulting in the formation of a terminal aryl group.

Polymerization processes involving only dihalo-functional reactants used in the formation of compounds according to the present invention may also be carried out using nickel catalyzed coupling reactions. One such coupling reaction was described by Colon et al. in Journal of Polymer Science, Part A, Polymer Chemistry Edition, Vol. 28, p. 367 (1990), incorporated herein by reference, and by Colon et al. in Journal of Organic Chemistry, Vol. 51, p. 2627 (1986). The reaction is typically conducted in a polar aprotic solvent (e.g., dimethylacetamide) with a catalytic amount of nickel salt, a substantial amount of triphenylphosphine and a large excess of zinc dust. A variant of this process is described by Ioyda et al. in Bulletin of the Chemical Society of Japan, Vol. 63, p. 80 (1990) wherein an organo-soluble iodide was used as an accelerator. Another nickel-catalyzed coupling reaction was disclosed by Yamamoto in Progress in Polymer Science, Vol. 17, p. 1153 (1992) wherein a mixture of dihaloaromatic compounds were treated with an excess amount of nickel (1,5-cyclooctadiene) complex in an inert solvent. All nickel-catalyzed coupling reactions when applied to reactant mixtures of two or more aromatic dihalides yield essentially random copolymers. Such polymerization reactions may be terminated by the addition of small amounts of water to the polymerization reaction mixture, thereby replacing the terminal halogen groups with hydrogen groups. Alternatively, a monofunctional aryl halide may be used as a chain-terminator, resulting in the formation of a terminal aryl group.

Copolymers Containing Other Conjugated Groups

The polymers of the invention desirably contain conjugated unsaturated groups. "Conjugated groups" refers to moieties containing two or more double bonds, triple bonds and/or aromatic rings, separated by a single covalent bond. The incorporation of such groups into the polymer may be used to modify the light absorption, ionization potential, and/or electronic properties of the polymer. Preferred unsaturated groups present in the conjugated unsaturated group-containing comonomers for use herein include divalent derivatives of hydrocarbons such as divalent derivatives of benzene, naphthalene, acenaphthene, phenanthrene, anthracene, fluorene, pyrene, rubrene, and chrysene, as well as unsaturated heterocyclic groups, such as divalent derivatives of furan, thiophene, pyrrole, oxazole, isooxazole, thiazole, isothiazole, imidazole, oxadiazoles, thiadiazole, pyrazole, pyridine, pyridazine, pyrimidine, pyrazine, triazine, tetrazene; benzoxazole, benzothiazole, benzimidazole, quinoline, isoquinoline, cinnoline, quinazoline, quinoxaline, phthalazine, benzothiadiazole, benzotriazine, phenazine, phenanthridine, acridine, carbazole, and diphenylene oxide. Highly desirable copolymerizable conjugated unsaturated groups include 9,9-disubstituted fluorenyl groups and triarylamine groups.

It is possible to control the sequencing of the monomeric units in the resulting copolymers by controlling the order and composition of monomer feeds, especially when employing a Suzuki reaction. For instance, a high molecular weight copolymer comprising mainly large blocks of polyfluorenyl homopolymers connected to short blocks of alternating diarylamine-comonomer oligomers may be made by first introducing into the reaction suitable reactants in the appropriate ratio to make the alternating fluorenyl-comonomer oligomers followed by the remainder of diarylamine monomers so long as there is an overall stoichiometric balance of the reagents, that is, the boron and bromine containing reagents.

Examples of diarylamine groups that may be additionally incorporated into the copolymers of the invention are tertiary aromatic amines containing two reactive substituents. Such compounds result in the inclusion of the corresponding triarylamine remnant into the copolymer. Examples of suitable tertiary aromatic amines include, triphenyl amine, alkyldiaryl amines, N,N,N',N'-tetraphenylbenzidine, and N,N,N',N'-tetraphenyl-1,4-phenylenediamine.

In general, copolymerizable, conjugated compounds containing up to 60 carbons are useful for the present purpose. They may be substituted optionally with one or more substituents that are not deleterious to the photoluminescent properties of the polymer compositions. Examples of suitable substituents include C₁-C₂₀ hydrocarbyl radicals, C₁-C₂₀ (thio)alkoxy radicals, C₁-C₂₀ (thio)aryloxy radicals, cyano, fluoro, chloro, C₁-C₂₀ alkoxycarbonyl, C₁-C₂₀ aryloxy carbonyl, C₁-C₂₀ carboxyl and alkyl(aryl)sulfonyl radicals. Substituents which are known

photoluminescent quenchers, such as arylcarbonyl and nitro groups, are undesirable and should be avoided.

Polymer Blends

5 The oligomers and polymers of invention may be used in forming a blend of at least two polymers. If desired, one or more of the oligomers or polymers of the blend may be a light-emitting polymer. Suitably the blend is composed of one or more polymeric materials selected from polystyrene, polybutadiene, poly(methyl methacrylate), poly(ethylene oxide), phenoxy resins, polycarbonates, polyamides, polyesters, polyurethanes, polyimides, crosslinked epoxy
10 resins, crosslinked phenolic resins, crosslinked acrylate resins, and crosslinked urethane resins. Examples of these polymers may be found in Preparative Methods of Polymer Chemistry, W. R. Sorenson and T. W. Campbell, Second Edition, Interscience Publishers (1968). Preferably the blends comprising a crosslinked polymer are formed by blending the uncrosslinked components and later crosslinking the components in situ.

15 Preferably the blend comprises at least two light emitting polymers and the maximum emission wavelength of one of the polymers in the blend is within 25 nm of the maximum absorption wavelength of at least one other polymer in the blend. Highly desirably the blend comprises a mixture of two polymers each corresponding to the present invention in the range from 0.1 to 99.9 and 99.9 to 0.1 percent respectively.

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Polymer Applications

 The primary use for the oligomers and polymers of the invention is in the formation of films. Such films can be used in preparing photoluminescent or fluorescent coatings as well as interlayers, protective coating, and hole transport layers in electronic devices such as organic light
25 emitting diodes, especially polymeric light-emitting diodes, photovoltaic cells, lighting, photodiodes, sensors, thin film transistors, and other devices. The thickness of the coating or film is dependent upon the ultimate use. Generally, such thickness can be from 0.01 to 200 micrometers. When used as a fluorescent coating, the film thickness is desirably from 50 to 200 micrometers. When used as electronic protective layers, the film thickness is desirably from 5
30 to 20 micrometers. When used as a layer in a polymeric light-emitting diode, the film thickness is desirably from 0.001 to 2 micrometers. The oligomers or polymers of the invention form films that are substantially lacking in pinholes and other defects. Such films can be prepared by means well known in the art including spin-coating, spray-coating (including ink-jet spraying), dip-coating and roller-coating. Such coatings are prepared by a process wherein a composition

comprising the present compounds, oligomers or polymers is applied to a substrate and exposed to conditions such that a film is formed, generally by means of a crosslinking reaction. The conditions which form a film depend upon the application technique and the reactive end groups of the film forming moieties. Preferably, the solution contains from 0.1 to 10 weight percent of the oligomers or polymers of the invention, and the remainder solvent. For thin coatings, it is preferred that the composition contains from 0.5 to 5.0 percent by weight of the compounds, oligomers or polymers. This composition is then applied to the appropriate substrate by the desired method and the solvent is allowed to evaporate. Residual solvent may be removed by vacuum and/or by heat. If the solvent is low boiling, then low solution concentrations, for example, 0.1 to 2 percent, are desired. If the solvent is high boiling, then high concentrations, for example, 3 to 10 percent, are desired. After removal of the solvent, the coating is then exposed to the necessary conditions to cure the film, if needed, thereby preparing a film having high solvent and heat resistance. The films are preferably substantially uniform in thickness and substantially free of pinholes. Preferably, the films are cured when exposed to temperatures of 100°C or greater, more preferably 150°C or greater and most preferably 200°C or greater. Preferably, the films cure at a temperature of 300°C or less.

In the preparation of the films, the composition may further comprise a catalyst suitable to facilitate or initiate the crosslinking process. Such catalysts are well known in the art, for instance, for materials having ethylenic unsaturation, a free radical catalyst may be used. For aryl moieties with glycidyl ethers as end-groups, ureas or imidazoles may be used. In the preparation of films from fluorenes with glycidyl ether substituted aryl groups as terminal moieties, the materials may be reacted with commonly known curing agents which facilitate crosslinking. Among preferred curing agents are tetrahydrophthalic anhydride, methylbicyclo[2.2.1]heptane-2,3-dicarboxylic anhydride (nadic anhydride), and maleic anhydride.

In another desirable embodiment, the monomers and oligomers may be partially cured or B-staged prior to forming the film. In such embodiment, the composition is exposed to conditions such that a portion of the reactive materials cure and a portion of the reactive materials do not cure. This is commonly used to improve the handleability of composition and can facilitate the preparation of films. Such B-staged material can thereafter be used to prepare coatings by the means disclosed above. Preferably, from 10 to 50 percent of the reactive moieties are reacted during B-staging.

Yet another aspect of the invention relates to organic electroluminescent (EL) devices comprising a film of the polymers of this invention. An organic EL device typically consists of an organic film located between an anode and a cathode in electrical contact therewith, such that

when a positive bias is applied to the device, holes are injected into the organic film from the anode, and electrons are injected into the organic film from the cathode. The subsequent combination of a hole with an electron may give rise to an exciton which may undergo radiative decay to the ground state by liberating a photon. In practice the anode is commonly a mixed oxide of indium and tin (ITO), employed for its high conductivity and transparency. The mixed oxide is normally deposited on a transparent substrate such as glass or plastic so that the light emitted by the organic film may be observed. The organic film may be the composite of several individual layers each designed for a distinct function or purpose. Since holes are injected from the anode, the layer next to the anode desirably has suitable functionality for transporting holes. Similarly, the layer next to the cathode desirably has suitable functionality for transporting electrons. In many instances, the hole or electron transporting layer also acts as the emitting layer. In some instances, one layer performs the combined functions of hole transport, electron transport, and light emission. Generally, films comprising the polymers of the present invention act as buffer layers or hole transport layers in an electronic device. In addition to the foregoing polymeric film layers, films of small molecules deposited by thermal evaporation may be incorporated into the electronic device, if desired. It is preferred that the total thickness of the organic film be less than 1000 nm, more preferably less than 500 nm, most preferably less than 300 nm. One embodiment of the instant invention is an EL device in which the organic film comprises at least one of the polymeric compositions of this invention.

The ITO surface which serves as the anode may be coated with a film according to the invention usually after first cleaning the exposed surface with an aqueous detergent solution, an organic solvent, and/or a UV or plasma generated ozone treatment. It may also be coated with a thin layer of a conducting substance to facilitate hole injection if desired. Suitable conducting substances include copper phthalocyanine, polyaniline and poly(3,4-ethylenedioxy-thiophene) (PEDT); the last two of which in their conductive forms are prepared by doping with a strong organic acid, for example, poly(styrenesulfonic acid). It is preferred that the thickness of the conducting layer, when used, be 200 nm or less; more preferably 100 nm or less.

The present compounds may be used in the preparation of interlayers in a multilayer device or as one component of a mixture of compounds forming a hole transporting polymer layer or as a separate hole transporting layer in a multilayer electronic device, especially an electroluminescent device. In the case where a hole-transporting polymer other than the present invention is used, known hole-conducting polymers, such as polyvinylcarbazole, or the polymeric aryl amines disclosed in USP's 5,728,801 or 5,929,194 may be employed. The resistance of this layer to erosion by the solution of the copolymer film which is to be applied next is obviously

critical to the successful fabrication of multi-layer devices. Accordingly the copolymers of this invention are normally applied from solutions in organic solvents such as xylene or toluene in which the hole-transporting layer is insoluble. By covering or protecting the hole-transporting polymer with an interlayer comprising a crosslinked polymer according to the present invention, the hole-transporting polymer can be protected from subsequent reagents or solvents employed in manufacture of the electronic device. The thickness of the hole-transporting layer or interlayer according to the invention is desirably 500 nm or less, preferably 300 nm or less, most preferably 150 nm or less.

A suitable electron-transporting layer, if used, may be applied either by thermal evaporation of a low molecular weight material or by solution coating of a polymer, such as a polymer according to the present invention, using a solvent that does not significantly damage any previously deposited film layer. Examples of low molecular weight materials conventionally used in forming electron-transporting layers include metal complexes of 8-hydroxyquinoline (as described by Burrows et al. in Applied Physics Letters, Vol. 64, pp. 2718-2720 (1994)), metallic complexes of 10-hydroxybenzo(h)quinoline (as described by Hamada et al. in Chemistry Letters, pp. 906-906 (1993)), 1,3,4-oxadiazoles (as described by Hamada et al. in Optoelectronics - Devices and Technologies, Vol. 7, pp. 83-93 (1992)), 1,3,4-triazoles (as described by Kido et al. in Chemistry Letters, pp. 47-48 (1996)), and dicarboximides of perylene (as described by Yoshida et al. in Applied Physics Letters, Vol. 69, pp. 734-736 (1996)).

Polymeric electron-transporting materials in addition to those of the present invention are exemplified by 1,3,4-oxadiazole-containing polymers (as described by Li et al. in Journal of Chemical Society, pp. 2211-2212 (1995), by Yang and Pei in Journal of Applied Physics, Vol 77, pp. 4807-4809 (1995)), 1,3,4-triazole-containing polymers (as described by Strukelj et al. in Science, Vol. 267, pp. 1969-1972 (1995)), quinoxaline-containing polymers (as described by Yamamoto et al. in Japan Journal of Applied Physics, Vol. 33, pp. L250-L253 (1994), O'Brien et al. in Synthetic Metals, Vol. 76, pp. 105-108 (1996)), and cyano-PPV (as described by Weaver et al. in Thin Solid Films, Vol. 273, pp. 39-47 (1996)). The thickness of this layer may be 500 nm or less, preferably 300 nm or less, most preferably 150 nm or less.

The final layer in the electronic device is normally the cathode, which may be formed from any conductive material, preferably a metal. Examples of suitable metals include lithium, calcium, magnesium, indium, silver, aluminum, or blends and alloys of the above. A metallic cathode may be deposited either by thermal evaporation or by sputtering, according to known techniques. The thickness of the cathode may be from 100 nm to 10,000 nm. The preferred metals are calcium, magnesium, indium, and aluminum. Alloys of these metals may also be used.

Alloys of aluminum containing 1 to 5 percent of lithium and alloys of magnesium containing at least 80 percent magnesium are highly preferred.

The EL devices of this invention emit light when subjected to an applied voltage of 50 volts or less with luminance efficiency as high as 3.5 Cd/A. If desired, an encapsulating or
5 protecting coating may be applied to one or more exposed surfaces of the finished device.

In a preferred embodiment, the electroluminescent device comprises at least one hole-transporting polymer film and a light-emitting polymer film at least one of which is comprised of a polymer of the invention, arranged between an anode material and a cathode material such that under an applied voltage, holes are injected from the anode material into the hole-transporting
10 polymer film and electrons are injected from the cathode material into the light-emitting polymer films when the device is forward biased, resulting in light emission from the light-emitting layer. In another preferred embodiment, layers of hole-transporting polymers are arranged so that the layer closest to the anode has the lower oxidation potential, with the adjacent layers having progressively higher oxidation potentials. By these methods, electroluminescent devices having
15 relatively high light output per unit voltage may be prepared.

The term "hole-transporting polymer film" as used herein refers to a layer of a film of a polymer which when disposed between two electrodes to which a field is applied and holes are injected from the anode, permits adequate transport of holes into the emitting polymer. The term
20 "light-emitting polymer film" as used herein refers to a layer of a film of a polymer whose excited states can relax to the ground state by emitting photons, preferably corresponding to wavelengths in the visible light range. The term "anode material" as used herein refers to a semi-transparent, or transparent, conducting film with a work function between 4.5 electron volts (eV) and 5.5 eV. Examples are gold and oxides and mixed oxides of indium and tin. The term "cathode material"
25 as used herein refers to a conducting film desirably having a work function between 2.5 eV and 4.5 eV.

It is expressly intended that the foregoing disclosure of preferred or desired, more preferred or more desired, highly preferred or highly desired, or most preferred or most desired substituents, ranges, end uses, processes, or combinations with respect to any one of the
30 embodiments of the invention is applicable as well to any other of the preceding or succeeding embodiments of the invention, independently of the identity of any other specific substituent, range, use, process, or combination.

The following specific embodiments of the invention are especially desirable and hereby delineated in order to provide a detailed disclosure for the appended claims.

1. An arylamine compound of the formula:



wherein,

Ar independently each occurrence is a group comprising one or more divalent aromatic groups, and optionally two Ar groups separated by a single NX group may be joined together by a second covalent bond or by a bridging group, thereby forming a fused multiple ring system;

X is an inert substituent or a cross-linkable group, with the proviso that in at least one occurrence in said compound, X is a crosslinkable group;

Z independently each occurrence is hydrogen or a leaving group,

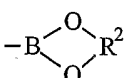
n is 1 or 2; and

n' is 0, 1 or 2.

2. A compound according to embodiment 1 wherein X in at least one occurrence is a moiety containing a double bond, a triple bond, a precursor capable of in situ formation of a double bond, or a heterocyclic, addition polymerizable group.

3. A compound according to embodiment 1 wherein X in at least one occurrence is selected from the group consisting of benzocyclobutanyl groups and substituted C₆₋₁₂ arylene groups containing one or more substituents selected from the group consisting of benzocyclobutane, azide, oxirane, di(hydrocarbyl)amino, cyanate ester, hydroxy, glycidyl ether, C₁₋₄ alkylacrylate, C₁₋₄ alkylmethacrylate, ethenyl, ethenyloxy, perfluoroethenyloxy, ethynyl, maleimide, nadimide, tri(C₁₋₄)-alkylsiloxy, tri(C₁₋₄)alkylsilyl, and halogenated derivatives thereof.

4. A compound according to embodiment 1 wherein X in at least one occurrence is 1-benzo-3,4-cyclobutane or 4-phenyl-1-(benzo-3,4-cyclobutane).

5. A compound according to embodiment 1 wherein Z each occurrence is halo, cyano, triflate, azide, -B(OR¹)₂, or .

wherein R¹, independently in each occurrence, is hydrogen or a C₁₋₁₀ alkyl group, and R², independently each occurrence, is a C₂₋₁₀ alkylene group.

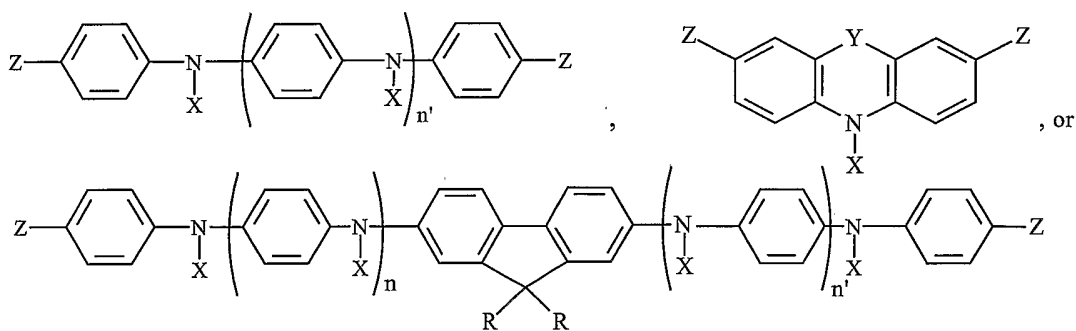
6. A compound according to embodiment 1 wherein Ar each occurrence is phenylene, 9,9-di(C₁₋₂₀alkyl)fluorenyl, or a combination thereof; X is 3,4-benzocyclobutan-1-yl, ethenyl or p-ethenylphenyl; Z is bromine or hydrogen; n is 1 or 2; and n' is 0 or 1.

5 7. A compound according to embodiment 6 wherein Ar each occurrence is phenylene; each X group is 3,4-benzocyclobutan-1-yl; Z each occurrence is bromine; n is 1 or 2; and n' is 0.

8. A compound according to embodiment 7 wherein n is 1.

10

9. A compound according to embodiment 1 having the formula:



wherein Y is a covalent bond, O, S or NR; where

15 R independently each occurrence is i) hydrogen; ii) halogen; iii) a C₁₋₂₀ hydrocarbyl group; iv) a hydrocarbyl group substituted with one or more heteroatom containing groups containing up to 20 atoms not counting hydrogen and wherein the heteroatom is selected from S, N, O, P, B or Si; v) a halogenated derivative of iii) or iv); or vi) a substituted derivative of iii) or iv) wherein the substituent is a crosslinkable X group; and

(n, n', X, and Z are as previously defined in embodiment 1.

20

10. An oligomer or polymer having one or more repeating groups of the formula:



where X' is X or a divalent crosslinked remnant formed by addition polymerization of a crosslinkable X group;

25 Z' is Z, a covalent bond, or a terminal group formed by replacement or reaction of a leaving group;

Ar independently each occurrence is a divalent aromatic group, and optionally two Ar groups separated by a single NX group may be joined together by a second covalent bond or by a bridging group, thereby forming a fused multiple ring system;

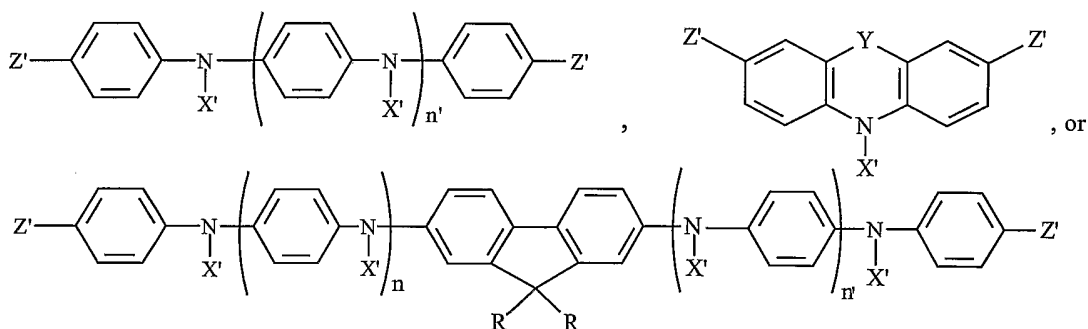
X is an inert substituent, with the proviso that in at least one occurrence in said
5 compound, X is a crosslinkable group;

Z independently each occurrence is hydrogen or a leaving group,

n is 1 or 2; and

n' is 0, 1 or 2.

10 11. An oligomer or polymer according to embodiment 10 having one or more repeating groups Ia) of the formula:



where X' is X or a divalent crosslinked remnant formed by addition polymerization of a crosslinkable X group;

15 X is an inert substituent or a group capable of forming crosslinking functionality;

Y is O, S or NR';

R independently each occurrence is i) hydrogen; ii) halogen; iii) a C₁₋₂₀ hydrocarbyl group; iv) a hydrocarbyl group substituted with one or more heteroatom containing groups containing up to 20 atoms not counting hydrogen and wherein the heteroatom is selected from S,
20 N, O, P, B or Si; v) a halogenated derivative of iii) or iv); or vi) a substituted derivative of iii) or iv) wherein the substituent is a crosslinkable X group;

Z' is Z, a covalent bond or a terminal group formed by replacement or reaction of a leaving group;

n is 1 or 2; and

25 n' is 0, 1 or 2.

12. A crosslinked polymer according to embodiment 10 or 11 wherein X' in at least one occurrence is a divalent crosslinked remnant formed by addition polymerization of a crosslinkable X group.

5 13. A crosslinked polymer according to embodiment 12, wherein X' comprises conjugated unsaturation.

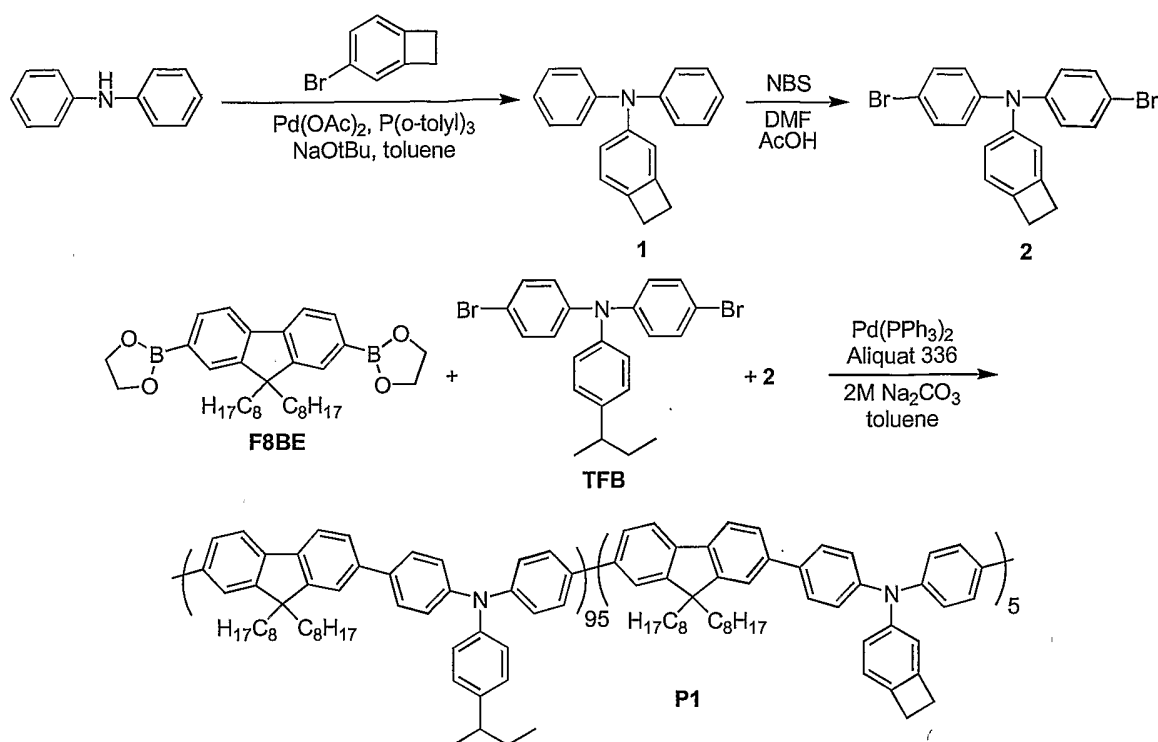
14. A process for preparing oligomers or polymers according to embodiment 10, which comprises heating a composition comprising a compound according to embodiment 1 under
10 reaction conditions sufficient to form an oligomer or polymer.

15. A film comprising one or more of the oligomers or polymers according to embodiment 10 or preparable according to embodiment 14.

15 16. An electronic device comprising one or more layers of polymer films, at least one of which comprises a film according to embodiment 15.

The following examples are included for illustrative purposes only and are not intended to limit the scope of the claims. Unless otherwise stated, implicit from the context or conventional in
20 the art, all parts and percentages herein are based on weight. It is understood that the present invention is operable in the absence of any component which has not been specifically disclosed. The term "overnight", if used, refers to a time of approximately 16-18 hours and "room temperature", if used, refers to a temperature of about 20-25 °C.

The following reaction scheme 1 discloses the preparation of a triaryl amine compound
25 with a crosslinkable benzocyclobutane group and its use in a polymerization reaction to make a crosslinkable amine copolymer according to the invention containing 5 mole percent crosslinkable conjugated diaryl amine functionality and 95 mole percent noncrosslinkable diarylamine functional units.



where F8BE is 2,7-bis(1,3,2-dioxaborole)-9,9-di(1-octyl)fluorene and TFB is N,N-di(p-bromophenyl)-N-(4-(butan-2-yl)phenyl)amine.

5 Example 1

A) Synthesis of diphenyl benzocyclobutane amine (1)

To a 500 ml, 3-neck round bottom flask equipped with a mechanical stirrer, nitrogen inlet, and reflux condenser (with nitrogen outlet), palladium (II) acetate (196 mg, 1.20 mmol) and tri(o-tolyl)phosphine (731 mg, 2.40 mmol) are added to 100 ml toluene. The mixture is stirred at room temperature under nitrogen until the palladium catalyst dissolves and the solution turns yellow. Diphenyl amine (20.0 g, 118 mmol), bromo benzocyclobutane (23.8 g, 130 mmol) and 400 ml toluene are added, followed by sodium t-butoxide (22.8 g, 237 mmol). Upon addition of the sodium t-butoxide the reaction turns black. The reaction is heated to reflux under nitrogen for 22 hours. The reaction is quenched by addition of 30 ml of aqueous 1 M HCl. The toluene layer is washed with 2M Na₂CO₃ (100 ml) then the toluene solution is passed through basic alumina. Evaporation of the toluene gives a yellow oil. The product is precipitated by stirring the oil with isopropanol. The solids are collected and recrystallized from hot isopropanol. ¹H NMR (CDCl₃-d) δ: 7.3-6.8 (m, 13H, Ar), 3.12 (d, 4H, -CH₂CH₂-).

B) Synthesis of di(4-bromophenyl) benzocyclobutane amine (2)

To a 250 ml round bottom flask, diphenyl benzocyclobutane amine (8.00 g, 29.5 mmol) is added to 100 ml dimethylformamide (DMF) containing 5 drops of glacial acetic acid. To the stirring solution, N-bromosuccinimide (NBS, 10.5 g, 60.7 mmol, 1.97 eq.) is added. After stirring for 5 hours, the reaction is quenched by pouring the reaction mixture into 600 ml of methanol/water (1:1 by vol). A gray solid is recovered by filtration and recrystallized from isopropanol. ¹H NMR (CDCl₃-d) δ: 7.3 (d, 4H, Ar), 7.0 (d, 4H, Ar), 6.95 (t, Ar), 6.8 (s, Ar), 3.12 (d, 4H, -CH₂CH₂-).

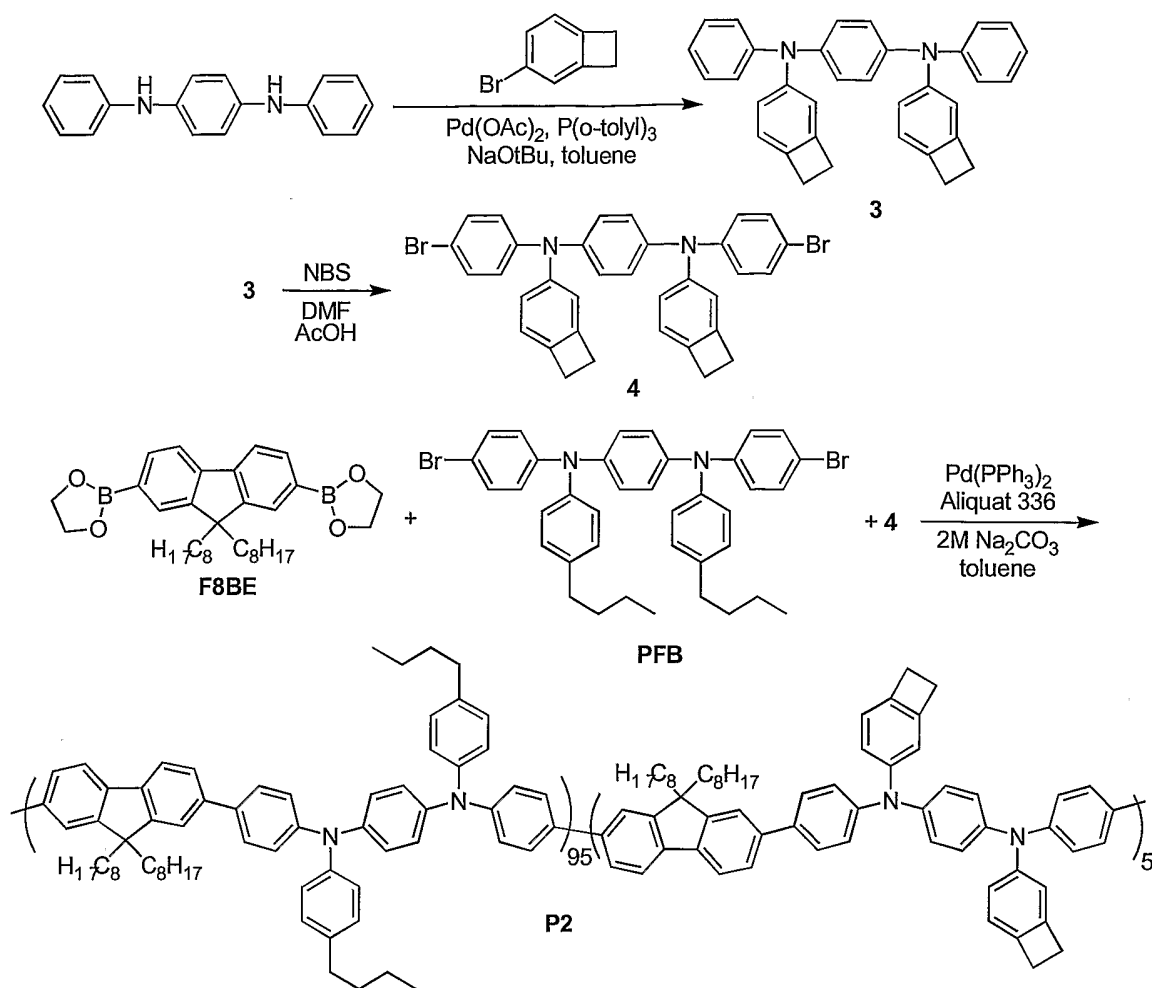
10 Example 2

A) Synthesis of Fluorene/Triarylamine Containing Polymer with BCB (P1)

To a 1-liter, 3-neck round bottom flask equipped with reflux condenser and an overhead stirrer, the following monomers are added: F8BE (3.863 g, 7.283 mmol), TFB (3.177 g, 6.919 mmol), and compound 2 (156.3 mg, 0.364 mmol). A 0.74 M toluene solution of a quaternary ammonium chloride catalyst (Aliquat™ 336, available from Sigma-Aldrich Corporation, 3.1 ml) is added followed by 50 ml of toluene. After addition of the PdCl₂(PPh₃)₂ catalyst (4.9 mg), the mixture is stirred in an oil bath (105 °C) until all of the monomer is dissolved (about 15 min). An aqueous solution of sodium carbonate (2.0 M, 14 ml) is added and the reaction stirred in an oil bath (105 °C) for 16.5 hours. Phenylboronic acid (0.5 g) is then added and the reaction stirred for 20 7 hours. The aqueous layer is removed and the organic layer washed with 50 ml of water. The organic layer is placed back in the reaction flask, and 0.75 g of sodium diethyldithiocarbamate and 50 ml water are added. The reaction is stirred in an oil bath (85 °C) for 16 h. The aqueous layer is removed, the organic layer is washed with water (3 x 100 ml) and then passed through a column of silica gel and basic alumina. The toluene/polymer solution is then precipitated into methanol 25 (twice), and the polymer dried under vacuum at 60 °C. Yield = 4.2 g (82 percent) Mw = 124,000; Mw/Mn = 2.8

Example 3

Scheme 2 shows the synthesis of a phenylenediamine monomer with a crosslinkable benzocyclobutane group, and the polymerization reaction used to make a fluorene/amine copolymer containing 5 mole percent of crosslinkable moieties able to achieve conjugated crosslinks.



A) Synthesis of *N,N'*-diphenyl-*N,N'*-dibenzocyclobutane-1,4-phenylenediamine (3)

To a 500 ml, 3-neck round bottom flask equipped with a mechanical stirrer, nitrogen inlet, and reflux condenser (with nitrogen outlet), palladium (II) acetate (173 mg, 0.80 mmol) and tri(*o*-tolyl)phosphine (486 mg, 1.60 mmol) are added to 50 ml toluene. The mixture is stirred at room temperature under nitrogen until the palladium catalyst dissolves and the solution turns yellow. *N,N'*-diphenyl-1,4-phenylenediamine (10.0 g, 38.4 mmol), bromobenzocyclobutane (15.5 g, 76.8 mmol) and 200 ml toluene are added, followed by sodium *t*-butoxide (7.37 g, 76.8 mmol). Upon addition of the sodium *t*-butoxide the reaction turns black. The reaction is heated to reflux under nitrogen for 22 hours. The reaction is quenched by addition of 30 ml of 1 M aqueous HCl. The toluene solution is passed through basic alumina and the crude product is purified by recrystallization from a toluene/hexanes/methanol mixture. Yield = 9.43 g (53 percent). ¹H NMR (THF-*d*8) δ: 7.15 (t, 4H, Ar), 6.80-7.01 (m, 16H, Ar) 3.09 (s, 8H, -CH₂CH₂-) ¹³C-NMR (THF-*d*8)

δ : 149.72, 148.26, 147.34, 144.18, 141.50, 129.92, 125.82, 125.76, 124.35, 123.61, 122.45, 121.06, 29.78.

B) Synthesis of di(4-bromophenyl) benzocyclobutane amine (4)

5 To a 500 ml round bottom flask, compound 3 (7.42 g, 16.0 mmol) is added to 200 ml DMF and 150 mL of THF containing 5 drops of glacial acetic acid. To the stirring solution, N-bromosuccinimide (NBS, 5.57 g, 31.5 mmol) is added. After stirring for 18 hours, the product precipitates from the reaction mixture. The product is collected by filtration and recrystallized three times from toluene. Yield = 4.44 g (45 percent).

10

Example 4

Synthesis of fluorene/phenylenediamine polymer containing BCB (P2)

To a 250 mL 3-neck round bottom flask equipped with reflux condenser and an overhead stirrer, the following monomers are added: F8BE (2.922 g, 5.504 mmol), PFB (3.583 g, 5.229
15 mmol), compound 4 (175 mg, 0.275 mmol), Aliquat™ 336 (available from Sigma-Aldrich Corporation, 0.8 g), and toluene (50 mL). After addition of the PdCl₂(PPh₃)₂ catalyst (3.8 mg), the mixture is stirred in an oil bath (105 °C) until all of the monomer is dissolved (about 15 min). An aqueous solution of sodium carbonate (2.0 M, 12 ml) is added and the reaction stirred while heating in an oil bath (105 °C) for 22 hours. Phenylboronic acid (0.5 g) is then added and the
20 reaction stirred for 24 hours. The aqueous layer is removed and the organic layer washed with water (50 ml). The organic layer is placed back in the reaction flask, and 0.75 g of sodium diethyldithiocarbamate and 50 ml water are added. The reaction is stirred in an oil bath (85 °C) for 16 hours. The aqueous layer is removed, the organic layer washed with water (3 x 100 ml), then
25 precipitated into methanol (twice), and the polymer dried under vacuum at 60 °C. Yield = 3.9 g (78 percent) Mw = 61,348; Mw/Mn = 2.8

Example 5

Crosslinked Films

30 A) The crosslinkable monomers of Examples 2 and 4 are dissolved in 4 ml of mixed xylenes. The solutions are shaken at room temperature overnight and then filtered through a 0.45 μ m nylon syringe filter. On a cleaned glass substrate, a cured film of about 80 nm thickness is deposited by spin-coating each solution at 4000 rpm. The films are then heated in a nitrogen-filled oven at 250 °C for 30 min. to create crosslinking in the film. The UV-Vis absorption

spectra of the films are measured. The films are then rinsed with toluene, rinsed and dried and the absorption spectra remeasured. Finally, the films are soaked in toluene for 30 minutes, rinsed and dried and the absorption spectra remeasured. Only slight variation in the absorption spectra is observed, indicating that the cured film is essentially unaffected by exposure to toluene.

5 B) A 16.0 mg sample of crosslinkable monomer N,N'-diphenyl-N,N'-dibenzocyclobutane-1,4-phenylenediamine (Example 3A) is analyzed by differential scanning calorimetry (DSC). The initial heating rate is 5 °C/min starting from 25 °C to 325 °C. In the first heat, (Figure 2) the compound's melting point is seen at 126 °C and a large exotherm with peak maximum at 246 °C due to the crosslinking reaction between the pendant benzocyclobutane
10 groups is observed. Subsequent heating (Figure 3) shows the disappearance of both the melting point and the crosslinking exotherm, confirming the formation of a stable crosslinked material has occurred.

Example 6

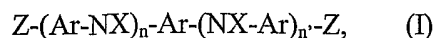
15 Light emitting device using crosslinked and uncrosslinked films as interlayers

A conventional hole transport layer polymer (Baytron P™, available from Sigma-Aldrich Corporation) is spin coated on a cleaned ITO substrate to a thickness of 80 nm and cured in air at 200 °C for 15 minutes. A filler layer of the crosslinkable polymer from Example 2 is similarly
20 deposited from xylenes (0.5 % w/v) and cured (crosslinked) for 30 minutes at 250 °C in a nitrogen atmosphere. Next, a light emitting polymer prepared substantially according to the teachings of USP 6,353,083 is spin-coated from a solution in xylenes (1.5 % w/v) and cured at a temperature of 130 °C. The cathode metals (Ca, 10 nm and Al, 150 nm) are vapor deposited over the resulting polymer film.

The foregoing procedures are substantially repeated to produce light emitting diodes
25 having no interlayer (comparative) and a dried but uncured (uncrosslinked) interlayer. Electroluminescent properties of the light emitting diodes are then tested. Results are reported in Figure 1.

WHAT IS CLAIMED IS:

1. An arylamine compound of the formula:



wherein,

- 5 Ar independently each occurrence is a group comprising one or more divalent aromatic groups, and optionally two Ar groups separated by a single NX group may be joined together by a second covalent bond or by a bridging group, thereby forming a fused multiple ring system;

X is an inert substituent or a cross-linkable group, with the proviso that in at least one occurrence in said compound; X is a crosslinkable group;

- 10 Z independently each occurrence is hydrogen or a leaving group,

n is 1 or 2; and

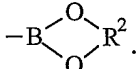
n' is 0, 1 or 2.

2. A compound according to claim 1 wherein X in at least one occurrence is a
15 moiety containing a double bond, a triple bond, a precursor capable of in situ formation of a double bond, or a heterocyclic, addition polymerizable group.

3. A compound according to claim 1 wherein X in at least one occurrence is selected
20 from the group consisting of benzocyclobutanyl groups and substituted C₆₋₁₂ arylene groups containing one or more substituents selected from the group consisting of benzocyclobutane, azide, oxirane, di(hydrocarbyl)amino, cyanate ester, hydroxy, glycidyl ether, C₁₋₄ alkylacrylate, C₁₋₄ alkylmethacrylate, ethenyl, ethenyloxy, perfluoroethenyloxy, ethynyl, maleimide, nadimide, tri(C₁₋₄)-alkylsiloxy, tri(C₁₋₄)-alkylsilyl, and halogenated derivatives thereof.

- 25 4. A compound according to claim 1 wherein X in at least one occurrence is 1-benzo-3,4-cyclobutane or 4-phenyl-1-(benzo-3,4-cyclobutane).

5. A compound according to claim 1 wherein Z each occurrence is halo, cyano,

triflate, azide, -B(OR¹)₂, or 

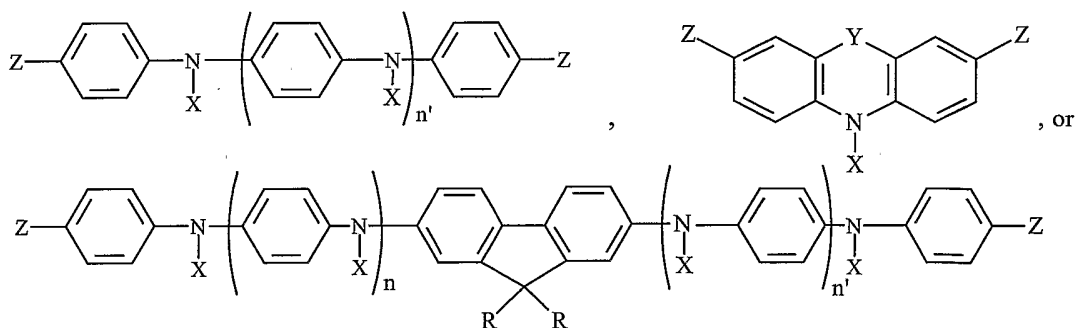
- 30 wherein R¹, independently in each occurrence, is hydrogen or a C₁₋₁₀ alkyl group, and R², independently each occurrence, is a C₂₋₁₀ alkylene group.

6. A compound according to claim 1 wherein Ar each occurrence is phenylene, 9,9-di(C₁₋₂₀alkyl)fluorenyl, or a combination thereof; X is 3,4-benzocyclobutan-1-yl, ethenyl or p-ethenylphenyl; Z is bromine or hydrogen; n is 1 or 2; and n' is 0 or 1.

7. A compound according to claim 6 wherein Ar each occurrence is phenylene; each X group is 3,4-benzocyclobutan-1-yl; Z each occurrence is bromine; n is 1 or 2; and n' is 0.

8. A compound according to claim 7 wherein n is 1.

9. A compound according to claim 1 having the formula:



wherein Y is a covalent bond, O, S or NR; where

R independently each occurrence is i) hydrogen; ii) halogen; iii) a C₁₋₂₀ hydrocarbyl group; iv) a hydrocarbyl group substituted with one or more heteroatom containing groups containing up to 20 atoms not counting hydrogen and wherein the heteroatom is selected from S, N, O, P, B or Si; v) a halogenated derivative of iii) or iv); or vi) a substituted derivative of iii) or iv) wherein the substituent is a crosslinkable X group; and

n, n', X, and Z are as previously defined in claim 1.

10. An oligomer or polymer having one or more repeating groups of the formula:



where X' is X or a divalent crosslinked remnant formed by addition polymerization of a crosslinkable X group;

Z' is Z, a covalent bond, or a terminal group formed by replacement or reaction of a leaving group;

Ar independently each occurrence is a divalent aromatic group, and optionally two Ar groups separated by a single NX group may be joined together by a second covalent bond or by a bridging group, thereby forming a fused multiple ring system;

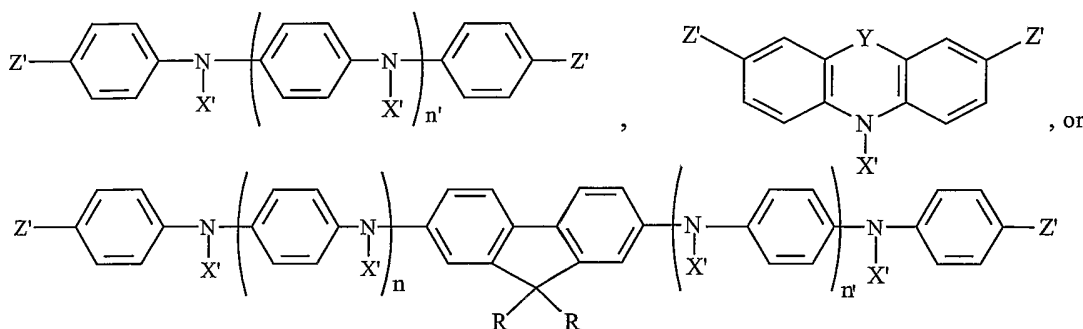
X is an inert substituent, with the proviso that in at least one occurrence in said compound, X is a crosslinkable group;

Z independently each occurrence is hydrogen or a leaving group,

n is 1 or 2; and

5 n' is 0, 1 or 2.

11. An oligomer or polymer according to claim 10 having one or more repeating groups Ia) of the formula:



10 where X' is X or a divalent crosslinked remnant formed by addition polymerization of a crosslinkable X group;

X is an inert substituent or a group capable of forming crosslinking functionality;

Y is O, S or NR';

15 R independently each occurrence is i) hydrogen; ii) halogen; iii) a C₁₋₂₀ hydrocarbyl group; iv) a hydrocarbyl group substituted with one or more heteroatom containing groups containing up to 20 atoms not counting hydrogen and wherein the heteroatom is selected from S, N, O, P, B or Si; v) a halogenated derivative of iii) or iv); or vi) a substituted derivative of iii) or iv) wherein the substituent is a crosslinkable X group;

20 Z' is Z, a covalent bond or a terminal group formed by replacement or reaction of a leaving group;

n is 1 or 2; and

n' is 0, 1 or 2.

12. A crosslinked polymer according to claim 10 or 11 wherein X' in at least one occurrence is a divalent crosslinked remnant formed by addition polymerization of a crosslinkable X group.

25

13. A crosslinked polymer according to claim 12, wherein X' comprises conjugated unsaturation.

14. A process for preparing oligomers or polymers according to claim 10, which
5 comprises heating a composition comprising a compound according to claim 1 under reaction conditions sufficient to form an oligomer or polymer.

15. A film comprising one or more of the oligomers or polymers according to claim
10 or preparable according to claim 14.

16. An electronic device comprising one or more layers of polymer films, at least one
of which comprises a film according to claim 15.

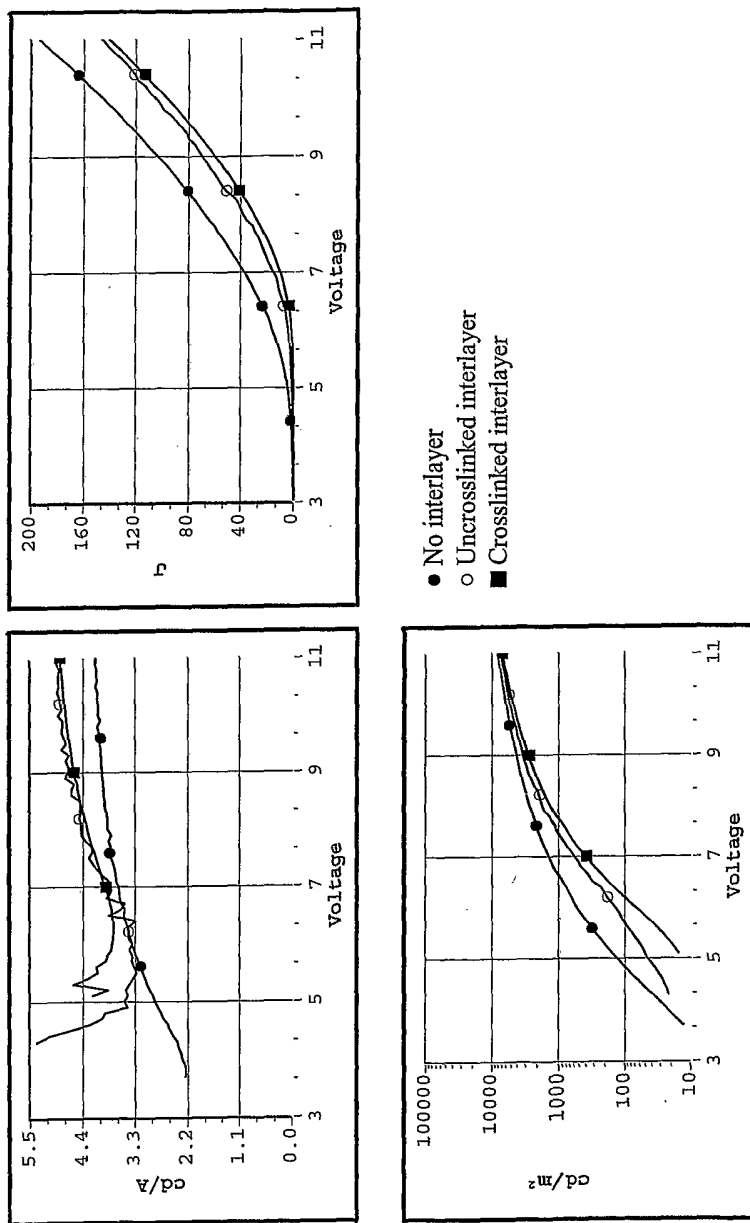


Fig. 1

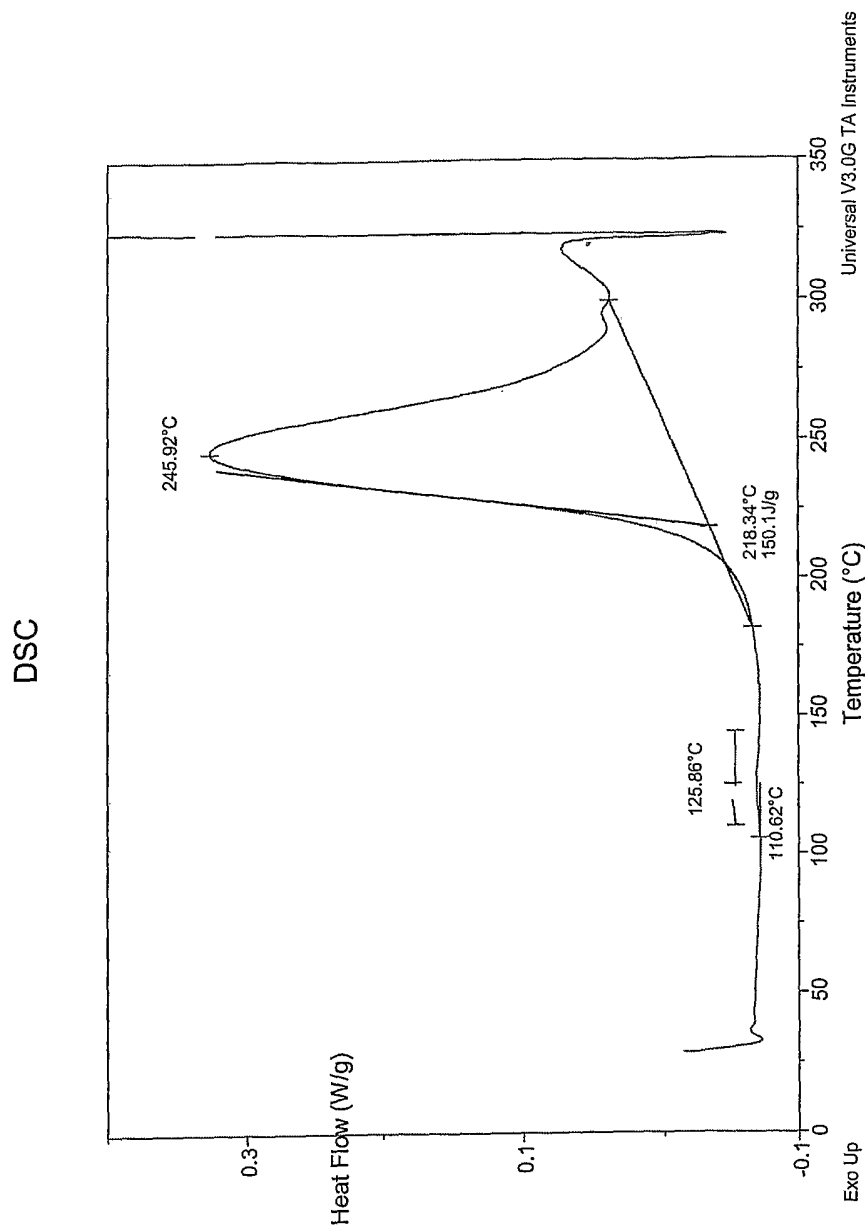


Fig. 2

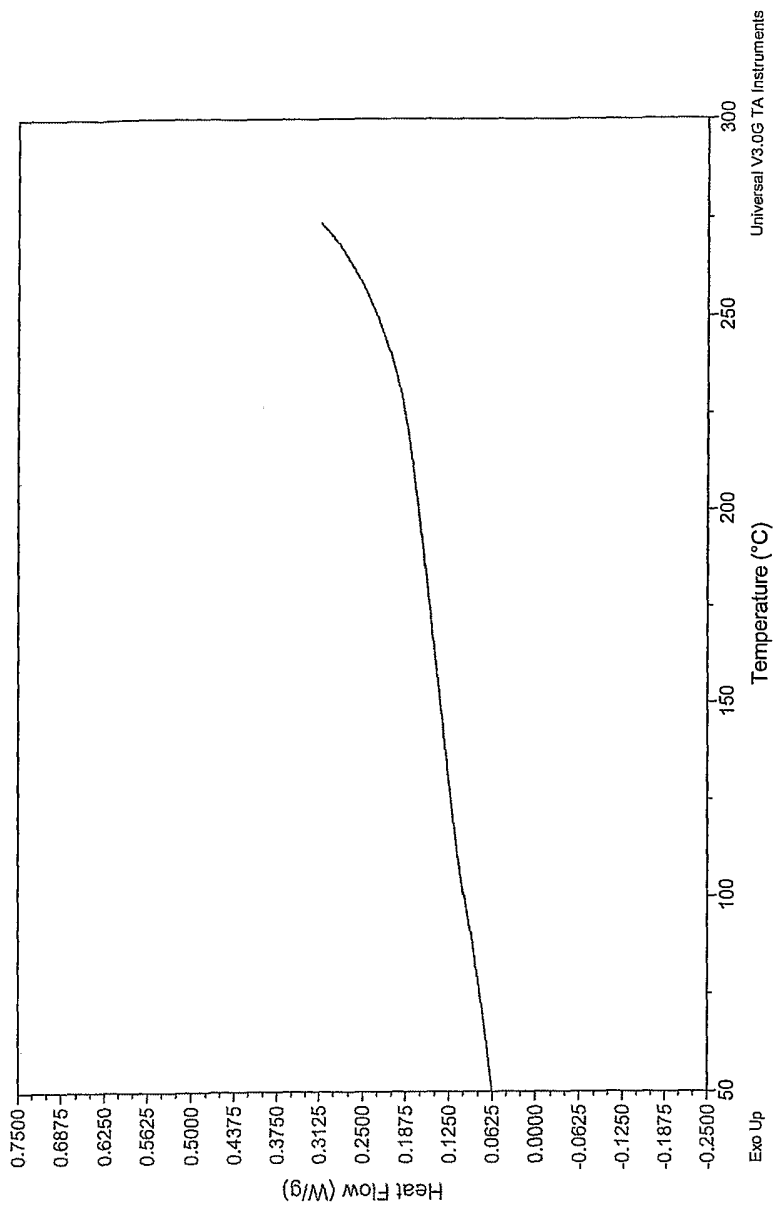


Fig. 3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/035221

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C08G73/02 C09K11/06 H01L51/30 C07C211/60

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 C08G C09K H01L C07C

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
 EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-------------------------|
| X | BAYERL M S: "Crosslikable hole-transport materials for preparation of multilayer organic light emitting devices by spin-coating" MACROMOLECULAR: RAPID COMMUNICATIONS, WILEY VCH, WEINHEIM, DE, vol. 20, no. 4, 1999, pages 224-228, XP002193426 ISSN: 1022-1336 cited in the application | 1-3, 10-12, 14,15 |
| A | compounds 4,7 <div style="text-align: center; margin-top: 10px;"> ----- -/-- </div> | 16 |

Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

| | |
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| <p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document but published on or after the international filing date</p> <p>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p> | <p>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>*Z* document member of the same patent family</p> |
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| Date of the actual completion of the international search | Date of mailing of the international search report |
| 25 February 2005 | 08/03/2005 |

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| Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016 | Authorized officer <p style="text-align: center;">Diederens, J</p> |
|--|---|

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/035221

| C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|--|--|-----------------------|
| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| X | BRAIG T: "Crosslinkable hole-transporting polymers by palladium catalyzed C-N-coupling reaction" MACROMOLECULAR: RAPID COMMUNICATIONS, WILEY VCH, WEINHEIM, DE, vol. 21, no. 9, June 2000 (2000-06), pages 583-589, XP002193425 ISSN: 1022-1336 cited in the application | 10-12, 14,15 |
| A | Scheme 3 ----- | 16 |
| X | US 5 929 194 A (WOO ET AL) 27 July 1999 (1999-07-27) cited in the application Column 19-20, 1st structure ----- | 1-4 |

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Information on patent family members

International Application No
PCT/US2004/035221

| Patent document cited in search report | | Publication date | | Patent family member(s) | Publication date |
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| | | | WO | 9733193 A2 | 12-09-1997 |
