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(54) USE OF PI-CONJUGATED ORGANOBORON POLYMERS IN THIN-FILM ORGANIC POLYMER ELECTRONIC DEVICES

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(57) ABSTRACT

Pi-conjugated organoboron polymers for use in thin-film organic polymer electronic devices. The polymers contain aromatic and or unsaturated repeat units and boron atoms. The vacant p-orbital of the boron atoms conjugate with the pi-conjugated orbital system of the aromatic or unsaturated monomer units extending the pi-conjugation length of the polymer across the boron atoms. The pi-conjugated organoboron polymers are electron-deficient and, therefore, exhibit n-type semiconducting properties, photoluminescence, and electroluminescence. The invention provides thin-film organic polymer electronic devices, such as organic photovoltaic cells (OPVs), organic diodes, organic photodiodes, organic thin-film transistors (TFTs), organic field-effect transistors (OFETs), printable or flexible electronics, such as radio-frequency identification (RFID) tags, electronic papers, and printed circuit elements, organic light-emitting diodes (OLEDs), polymer light-emitting diodes (PLEDs), and energy storage devices employing the pi-conjugated organoboron polymers. In OLED and PLED applications these materials are used as the electron transport layer (ETL) to improve device efficiency. The polymers which exhibit photo- and electroluminescence are also useful as light-emitting material in PLEDs.

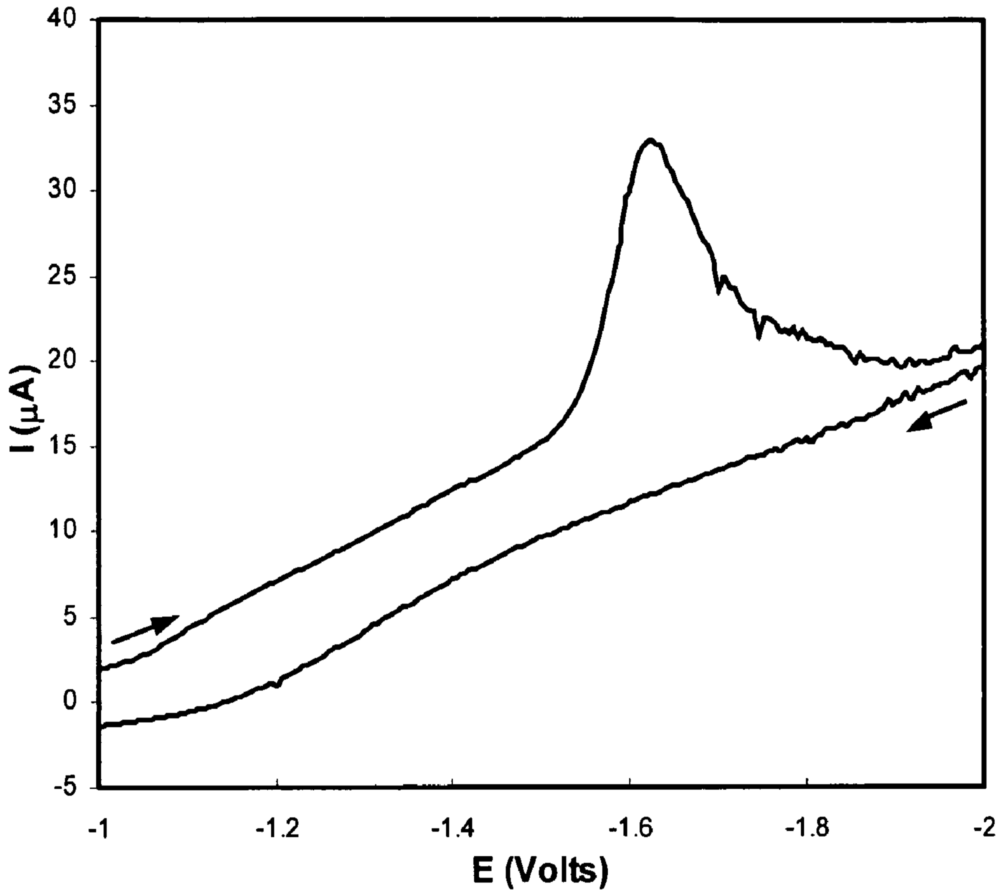


Fig. 1

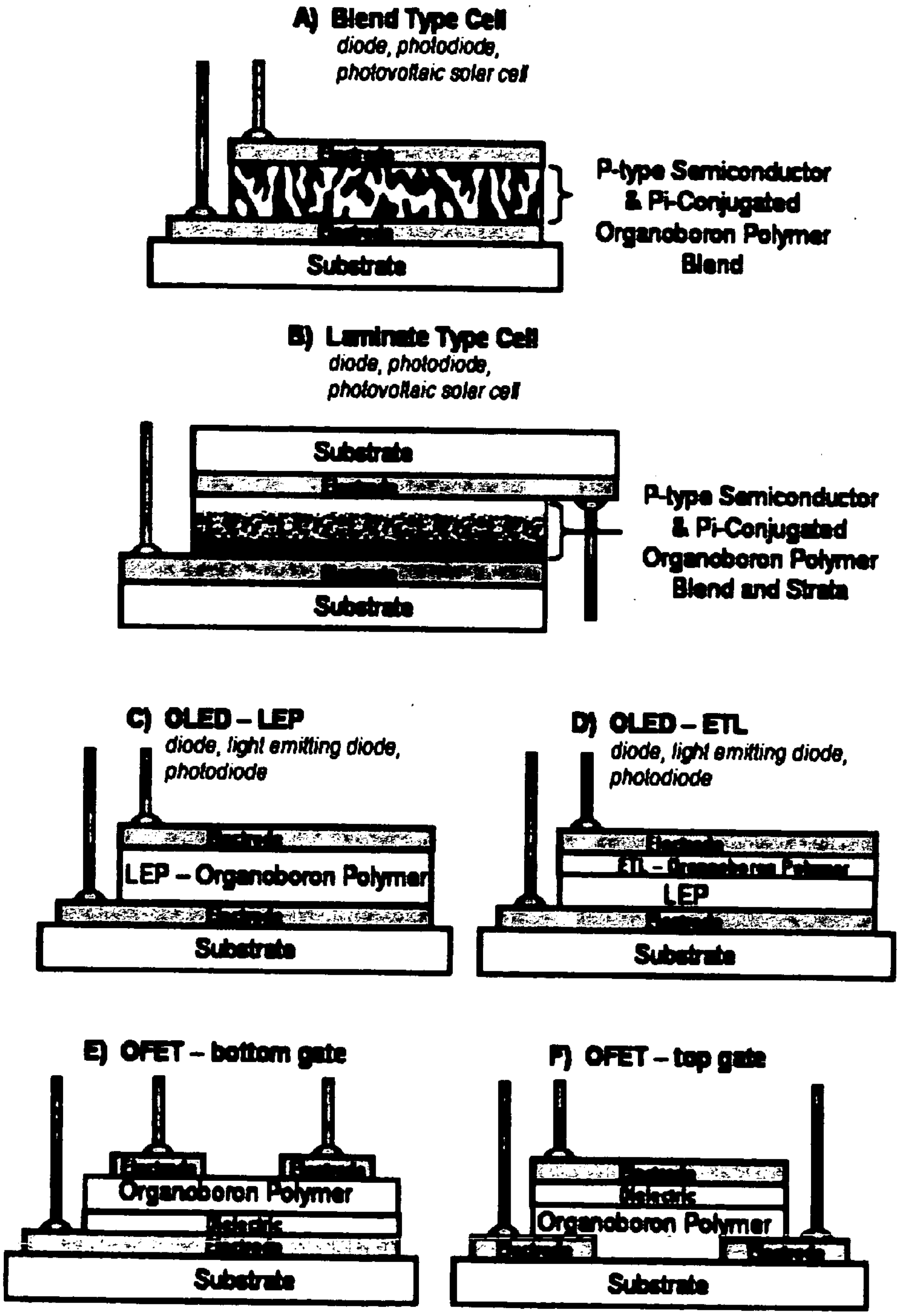

A) Blend Type Cell
diode, photodiode,
photovoltaic solar cell
Electrode
Electrode
Substrate
P-type Semiconductor
& Pi-Conjugated
Organoboron Polymer
Blend
B) Laminate Type Cell
diode, photodiode,
photovoltaic solar cell
Substrate
Electrode
Electrode
Substrate
P-type Semiconductor
& Pi-Conjugated
Organoboron Polymer
Blend and Strata
C) OLED – LEP
diode, light emitting diode,
photodiode
Electrode
LEP – Organoboron Polymer
Electrode
Substrate
D) OLED – ETL
diode, light emitting diode,
photodiode
Electrode
ETL – Organoboron Polymer
LEP
Electrode
Substrate
E) OFET – bottom gate
Electrode
Electrode
Organoboron Polymer
Dielectric
Electrode
Substrate
F) OFET – top gate
Electrode
Dielectric
Organoboron Polymer
Electrode
Electrode
Substrate

FIG. 2

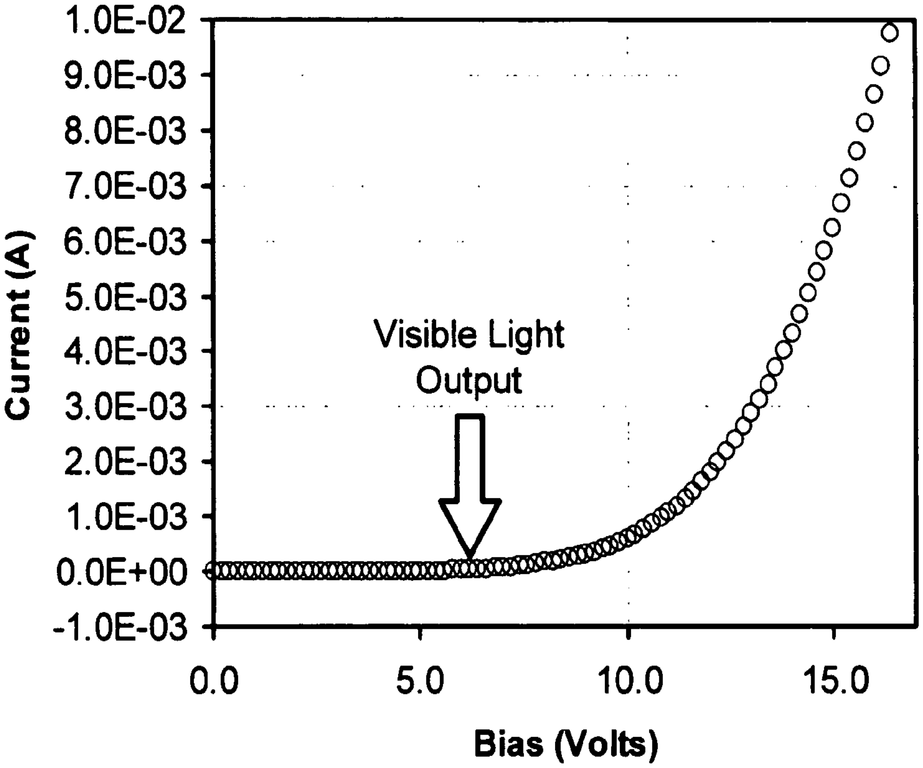

1.0E-02
9.0E-03
8.0E-03
7.0E-03
6.0E-03
5.0E-03
4.0E-03
3.0E-03
2.0E-03
1.0E-03
0.0E+00
-1.0E-03
Current (A)
Visible Light Output
0.0
5.0
10.0
15.0
Bias (Volts)

Fig. 3

USE OF PI-CONJUGATED ORGANOBORON POLYMERS IN THIN-FILM ORGANIC POLYMER ELECTRONIC DEVICES

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0001] This invention was made, at least in part, with funding from National Science Foundation contract DMI-0319320. The United States government has certain rights in the invention.

FIELD OF THE INVENTION

[0002] This invention relates to the use of pi-conjugated (or π-conjugated) organoboron polymers in thin film electronic devices and methods for the fabrication of such devices.

BACKGROUND OF THE INVENTION

[0003] The specific functions of many electronic components and devices arise from the unique interactions existing between p-type and n-type conducting and semiconducting materials. Until a few years ago, inorganic conductors and semiconductors entirely dominated the electronic industry. In recent years there has been a major worldwide research effort to develop conducting and semiconducting organic compounds and polymers, and to use them to fabricate plastic electronic devices, such as organic thin film transistors (TFTs), organic light emitting diodes (OLEDs), printable circuits, organic supercapacitors and organic photovoltaic devices. Plastic electronic components offer several potential advantages over traditional devices made of inorganic materials; they are flexible and can be manufactured by inexpensive ink-jet printing or roll-to-roll coating technologies.

[0004] Intrinsically conducting polymers (ICPs) are polymers with extended π conjugation along the molecular backbone, and their conductivity can be changed by several orders of magnitude by doping. P-doping is the partial oxidation of the polymer by a chemical oxidant or an electrode which causes depopulation of the bonding π orbital (HOMO) with the injection of "holes". N-doping is the partial reduction of the polymer by a chemical reducing agent or electrode with the injection of electrons in the antibonding π system (LUMO, MacDiarmid A., *Angew. Chem. Int. Ed.,* 40, 2581-2590, 2001). The doping process incorporates charge carriers (either electrons or holes) into the polymer backbone, and as a result the polymer becomes electrically conducting to a level that is commensurate with its doping level.

[0005] An equally important class of electronic polymers is the conjugated semiconducting polymers. These polymers, like ICPs, are able to support the injection of p-type or n-type charge carriers; however the charge carriers are often few in number and are transient species that ultimately decay or are transferred to a different material. Some ICPs function as semiconducting polymers in their undoped state, however other ICPs are not stable in their semiconducting state. Electrical conductivity and work function are the key parameters for characterizing ICPs, while charge carrier density and mobility, and energy levels are the key parameters for characterizing semiconducting polymers. One special class of semiconducting polymers is the group of light emitting polymers. These polymers are also able to support the injection and transport of both positive and negative charges (although one carrier is often preferred). When holes and electrons recombine within the electroluminescent material, a neutral excited species (termed an exciton) forms that decays to the ground state, liberating energy in the form of light (Salaneck, W. R. et al., *Nature,* 397,121-128,1999).

[0006] Thus, certain pi-conjugated polymers are well known to possess semiconducting properties which are due to the formation of interconnected molecular orbitals along the pi-bonding and pi-antibonding structure of the conjugated backbone. Charges that are introduced onto such polymer chains (either by addition or removal of an electron) are free to travel over a certain distance along the polymer chain giving rise to semiconducting properties. The number of charges that can be injected, the ease of introducing charges, the distance that a charge can travel (mobility), and the type of charge (positive holes or negative electrons) that is more favorable depends upon the electronic properties of the polymer. By careful design of the structure of the polymer, a structure that favors electrons (called an n-type semiconductor) or holes (called a p-type semiconductor) as the dominant form of charge carrier can be selected. This is done through introduction into the polymer of selected atoms, organic groups and/or substituent groups on the basis of their electron-donating or electron-withdrawing properties. Appropriate selections of atoms or groups for introduction into the polymer structure lead to a conjugated polymer structure that is either electron-rich or electron-deficient. Electron-rich polymer structures have p-type semiconducting properties and electron-deficient polymer structures have n-type semiconducting properties.

[0007] Most pi-conjugated hydrocarbon polymers such as polyacetylene, poly(phenylenevinylene), poly(paraphenylene), polyfluorenes and their derivatives readily support the injection of both electrons and holes (the respective n-type and p-type charge carriers). In fact, theoretical calculations show that for certain hydrocarbon conjugated polymers such as poly(paraphenylene) there is a perfect electron-hole symmetry [i.e. the frontier orbitals of positively and negatively charged carriers are fully symmetrical], indicating that electron and hole conduction are equally favorable processes (Kertesz, M. in *Handbook of Organic Conductive Molecules and Polymers, Vol.* 4, Ed. Hari Singh Nalwa, J. Wiley & Sons, Chichester, UK, p. 163, 1997). This symmetry can be broken by introducing atoms other than carbon (heteroatoms), organic groups and/or substituent groups that are either electron-rich or electron-deficient, thus favoring either the injection of holes or electrons, respectively. It is generally easier to design electron-rich conjugated polymers than electron-deficient conjugated polymers. An electron-rich polymer can be created by appropriate introduction of an electro-negative heteroatom such as sulfur, nitrogen or oxygen into the conjugated polymer. A variety of chemistries are available in the art for introducing electro-negative heteroatoms into such polymers. As a result a large number of p-type conducting polymers have been developed and characterized over the past two decades. Furthermore, many p-type conducting and semiconducting polymers have been used in commercial devices and are successfully competing with conventional inorganic semiconductors and conductors.

[0008] In contrast, it is more difficult to design electron-deficient conjugated polymer systems. Most of the polymers currently used as n-type semiconductors are hydrocarbon-based polymers [especially poly(phenylenevinylene)] carrying electron-withdrawing substituents such as cyano or nitro groups (Friend, R. H. et al. *Nature,* 395, 257-259, 1998; Holmes et al. *Angew. Chemie. In. Ed.,* 37, 402-428, 1998), polymers containing oxadiazole, quinoxaline, or pyridine units (Bradley, et al. *Appl. Phys. Left.,* 69, 881-883, 1996; Holmes et al. *Angew. Chemie. In. Ed.,* 37, 402-428, 1998; Andersson et al. *Macromolecules,* 35, 1638-1643, 2002), and a few ladder polymers such as BBL ({poly(7-oxo, 10H-benz[de]imidazo[4',5:5,6]-benzimidazo[2,1-a]isoquinoline-3,4:10,11-tetrayl)-10-carbonyl}) (Sherf, U. "Conjugated Ladder-Type Structures," in *Handbook of Conducting Polymers,* 2nd Ed.", Ed. T. A. Skotheim, R L Elsenbauer, J. R. Reynolds, Marcel Dekker, New York, 363-379, 1998). Unfortunately, current n-type semiconducting polymers have generally poor properties, including low charge carrier density and low carrier mobility. Furthermore, most of these materials are difficult to process, and some of them are difficult to synthesize.

[0009] In some cases, n-type semiconducting non-polymeric species, such as functionalized fullerenes, molecular glasses and metal complexes, are used instead of polymers (Strohriegl, P. et. Al, *Advanced Materials,* 14, 1439-1451, 2002; Shaheen, S. et. al., *Appl. Phys. Lett.,* 78, 841-843, 2001). The disadvantage of these non-polymeric semiconducting species is the low charge carrier mobility due to the limited conjugation (due to low molecular weight), and the fact that they often need to be processed by vacuum deposition techniques. Thus, there is a significant need in the art for new n-type conducting and semiconducting materials that have improved charge carrier mobility, which are more readily processed and synthesized. The present invention provides n-type semiconducting polymers which provide such improvements.

[0010] There are two basic ways to make a pi-conjugated polymer structure that is electron deficient. First, as noted above, the conjugated backbone of the polymer can be chemically modified by substitution with electron withdrawing substituent groups, such as cyano or nitro groups. Such pendant modification is effective to impart some electron deficiency to the pi-conjugated polymer. For example, poly(para-phenylene vinylene) has been modified with cyano and other pendant groups to produce a pi-conjugated semiconducting polymer with n-type properties (Granstrom et al. *Nature* 395, 257-260, 1998). A second and more effective way to impart n-type semiconducting properties is to directly modify the backbone of the polymer with electron deficient atoms or organic structures. Holmes et al. prepared pi-conjugated oxadiazole-containing polymers that exhibited n-type semiconducting properties and photoluminescence (Li et al. *J. Chem. Soc. Chem. Commun.* 2211-2212, 1995). Yamamoto et al. prepared pi-conjugated quinoxaline-containing polymers that also exhibited n-type semiconducting properties, photoluminescence, and electroluminescence. Both the oxadiazole and quinoxaline structures are known to impart electron deficiency in molecules. Similarly, Babel and Jenekhe. prepared pi-conjugated polymers incorporating regioregular dioctylbithiophene and bis(phenylquinoline) units in the backbone of the polymer and demonstrated both PLED(polymer light-emitting diodes and OFET (organic field-effect transistors) prototype devices utilizing these materials (Babel, A., Jenekhe, S. A. *Adv. Mater.,* 14, 371-374, 2002).

[0011] Certain non-polymeric, pi-conjugated, organoboron molecules have been observed to be electron deficient (Noda et al. *J. Am. Chem. Soc.* 120, 9714-9715, 1998; Matsumi et al. *Polymer Bulletin* 50, 259-264, 2003). This is due to the valence electronic structure of the boron atom and its ability to form multiple stable bonds with carbon atoms. The empty p-orbital of boron can join in the pi-conjugated system without any added electron density (Zweifel et al. *J. Organomet. Chem.* 117, 303-312, 1976). The possibility of delocalization of pi electrons between the vacant p orbital of boron and the pi orbitals of conjugated organic substituents has been extensively studied on mono- and di-vinylhaloboranes and trivinylborane. These molecules exist only in a planar conformation, suggesting that there is, in fact, delocalization of the vinyl pi electrons over the boron atom (Pelter, A., and Smith, K. "Triorganylboranes," in *Comprehensive Organometallic Chemistry,* Vol 3, 792-795, 1979). Theoretical calculations performed with the LCAO and self-consistent field methods (Good, C. D., and Ritter, D. M. *J. Am. Chem. Soc.,* 84, 1162-1165, 1962) as well as ^{13}C-NMR studies (Yamamoto, Y. and Moritani, I. *J. Org. Chem.,* 40, 3434-3437, 1975) also predict considerable delocalization of the vinyl pi electrons over the carbon-boron bonds. Marder et al. reports that three-coordinate boron species are equivalent to carbonium ions, and are thus extremely electron-deficient systems. However, if the boron is sterically protected, for example, with bulky trimethylphenyl groups, the resultant materials are air-stable (Marder et al. *J. of Solid State Chemistry,* 154, 5-12, 2000). Kaim and co-workers report that low molecular weight, non-polymeric, pi-conjugated organoboron compounds have redox properties that are analogous to nitrogen-containing pi-conjugated molecules. In fact, under chemical or electrochemical reduction, organoboron compounds form a series of anions of the type: $—BR_2$, $—BR_2^{\bullet -}$, $=BR_2^{-}$, while nitrogen-containing compounds upon oxidation form the series of cations: $—NR_2$, $—NR_2^{\bullet +}$, $=NR_2^{+}$ (Fiedler et al. *Inorg. Chem.,* 35, 3039-3043, 1996). This indicates that pi-conjugated organoboron compounds are redox active and are effectively easy to reduce. The use of certain organoboron, non-polymeric pi-conjugated molecules as an electron transport layer (ETL) in molecular organic light-emitting diodes is reported by Shirota and Noda. These authors report an improvement in maximum luminescence by a factor of 1.6 to 1.8 compared to an identical single layer device that does not contain the organoboron ETL (Shirota Y. and T. Noda *J. Am. Chem. Soc.,* 120, 9714-9715, 1998). The organoboron ETL materials of Shirota and Noda are non-polymeric molecules of defined structure having a specific molecular weight and are not pi-conjugated organoboron polymers.

[0012] Chujo et al. have reported non-conjugated, organoboron polymers in which sterically bulky organic groups are appended to the boron atoms adjacent to the polymer chain. The authors concluded that the bulky protecting groups on boron led to stable non-conjugated polymers with weight average molecular weights that remained stable with constant exposure to air for two weeks (Chujo et al. *Polymer* 41, 5047-5051, 2000). Chujo and co-workers have also reported a number of pi-conjugated, organoboron polymers that make use of bulky protecting groups (Matsumi et al. *J. Am. Chem. Soc.,* 120, 10776-10777, 1998; Matsumi et al. *J.*

Am. Chem. Soc., 120, 5112-5113, 1998; Miyata et al. *Polymer Bulletin,* 42, 505-510, 1999; Matsumi et al. *Macromolecules,* 32, 4467-4469, 1999; Matsumi et al. *Polymer Bulletin,* 44, 431-436, 2002). These polymers have absorption maxima in the visible region and are highly fluorescent when irradiated with UV light, suggesting the existence of an extended π-conjugation across the boron atoms. The polymers are also soluble in common organic solvents and stable in air and moisture in the pristine (undoped) state. Chujo and co-workers have also reported the n-doping of a pi-conjugated, organoboron polymer with triethylamine to a conductivity of 10^{-6} S/cm (Kobayashi et al. *Synthetic Metals,* 135-136, 393-394, 2003). The n-type semiconducting properties and photoluminescence of these materials have been reported, but the materials were not shown to be useful in thin film, organic polymer electronic devices, such as OPVs (organic photovoltaics), PLEDs, or OFETs.

[0013] Jäkle studied multiborylated polythiophenes for use in chemical sensors (Sundararraman., et al., JACS, 127, 13748-13749, 2005) and Siebert and co-workers reported the synthesis of certain pi-conjugated organoboron polymers containing thiophene units by hydroboration polymerization (Corriu et al., *Chem. Commun.,* 963-964 1998)

[0014] U.S. Pat. Nos. 3,269,992, 3,203,909, 3,203,930, 3,203,929, 3,166,522, and 3,109,031 report the preparation of certain organoboron polymers. U.S. Pat. No. 6,025,453 reports the composition of polymers containing at least an alkynyl group, at least one silyl group and at least one boranyl group and their use for making high temperature oxidatively stable thermosetting plastics.

SUMMARY OF THE INVENTION

[0015] This invention relates to the use of certain pi-conjugated polymers in thin-film organic polymer electronic devices. These polymers all contain boron atoms in the pi-conjugated backbone of the polymer and therefore are electron-deficient and exhibit n-type semiconducting properties, photoluminescence, and/or electroluminescence.

[0016] The invention provides thin-film, organic polymer electronic devices which comprise at least one active layer containing a thin film of a pi-conjugated organoboron polymer and at least two electrodes in contact with the active layer. The thin film of the pi-conjugated organoboron polymer can be 100 angstroms to 10000 angstroms in thickness. Preferably the thin film of the pi-conjugated organoboron polymer is 100 angstroms to 3000 angstroms in thickness.

[0017] The devices of this invention include those which exhibit current rectification or diode-like properties. The devices of this invention include those wherein the thin film comprises a pi-conjugated organoboron polymer that emits light under a voltage bias.

[0018] The invention also provides devices wherein the active layer of the device contains, in addition to the thin film of the pi-conjugated organoboron polymer, a light-emitting thin film which comprises a light-emitting polymer which is not a pi-conjugated organoboron polymer, a light-emitting non-polymeric molecule, or an inorganic light emitting compound.

[0019] The invention further provides devices having an active layer which comprises at least one thin film that in turn comprises one or more pi-conjugated organoboron polymers blended with one or more light-emitting molecules, or polymers or an inorganic compound. The invention provides devices having an active layer comprising at least one thin film of a pi-conjugated organoboron polymer blended with a different organic or inorganic conducting or semiconducting material. This organic or inorganic conducting or semiconducting material may be one or more polymers, one or more non-polymeric molecules, one or more inorganic compounds, or a mixture thereof. More particularly, the active layer of the devices herein can comprise at least one thin film containing a p-type conducting or semiconducting polymer that is not a pi-conjugated organoboron polymer blended with a pi-conjugated organoboron polymer. In other embodiments, the active layer of the devices herein comprises at least one thin film containing inorganic p-type semiconducting particles mixed with a pi-conjugated organoboron polymer. More specifically, inorganic p-type semiconducting particles having at least one dimension less than 1000 angstroms can be employed in active layers herein. Regioregular poly(n-alkyl thiophene)s are examples of organic p-type semiconducting materials and boron-doped silicon, p-type gallium arsenide and p-type zinc telluride are examples of inorganic p-type semiconductors that can be used in this invention.

[0020] Devices of this invention further include those wherein the active layer further comprises an additional thin film of a dielectric material that is in contact with one or more additional electrodes. The layer of dielectric insulating material is usually in contact with one of the electrodes as exemplified in FIGS. **2**E and **2**F.

[0021] Representative structures of organoboron polymer compositions useful in the devices of this invention are shown in Scheme 1, formulas a-j. More specific structures of organoboron polymers of this invention are shown in Scheme 2, formulas A-I. Representative synthetic methods are shown in Examples 1, 2 and 7.

[0022] The invention also provides certain novel pi-conjugated organoboron polymers and oligomers which exhibit beneficial properties for application in thin-film organic polymer electronic devices.

[0023] Novel polymers of this invention include pi-conjugated organoboron polymers and oligomers that do not contain an aromatic ring in the polymer backbone. However, the novel polymers of this invention may contain one or/more aromatic rings in a side chain, as substituents on the boron atoms or as substituents of the unsaturated carbon atoms of the polymer backbone. The novel polymers of this invention include, among others, poly(vinylborane)s, poly(acetylenylborane)s, poly(divinylborane)s, poly(vinyl acetylenylborane)s, and poly(polyenylborane)s. Representative structures of these novel organoboron polymer compositions useful in the devices of this invention are shown in Scheme 1, formulas a, f and g. More specific structures of novel organoboron polymers of this invention are shown in Scheme 2, formulas D. Representative synthetic methods of these novel polymers are shown in Example 2. Novel polymers of this invention can exhibit improved properties over prior art polymers, particularly those reported by Chujo and coworkers, because the higher density of boron atoms can provide higher electron-deficiency.

[0024] Novel polymers of this invention also include poly(9,9-dialkylfluorenylborane)s. Examples of these polymers include polymers 3dx, 3dy, 3ex, 3ey, and 3gx of Scheme 4. Representative synthetic methods of these novel polymers are given in Example 1. These novel polymers can provide improved properties compared to known polymers because of their specific light emitting properties (color and intensity).

[0025] Novel polymers of this invention also include structures E, F, G, H, and I of Scheme 2. Representative synthetic methods of these novel polymers are given in Example 7. These novel polymers can provide improved properties compared to known polymers because of the higher electron deficiency of the aromatic unit.

[0026] Methods or improved methods for synthesis of certain pi-conjugated organoboron polymers are also provided. A significant improvement of the method of preparation of poly(arylborane)s polymers 3a-3e over prior art methods is the use of an organolithium derivative rather than a Grignard reagent and the use of cyclohexane (a cyclic hydrocarbon) rather than tetrahydrofurane (THF) or other oxygenated solvent. The improved methods provide polymers having boron atoms that are free from coordination, while prior art methods provide polymers having the boron atoms coordinated to the solvent. Coordination with the solvent partially fills the empty p orbital of the boron atoms and decreases the electron-deficiency of the polymer.

[0027] The invention further provides methods for making thin films containing pi-conjugated organoboron polymers for use in thin-film organic polymer electronic devices and methods for making such devices employing thin films containing pi-conjugated organoboron polymers.

[0028] The invention additionally provides methods employing thin-film organic polymer electronic devices that contain an active layer comprising one or more pi-conjugated organoboron polymers as photovoltaic cells, diodes, photodiodes, TFTs, OFETs, printable or flexible electronics like radio-frequency identification (RFID) tags, electronic papers, printed circuit elements, organic light emitting diodes (OLED)s, PLEDs, and energy storage devices.

BRIEF DESCRIPTION OF THE DRAWINGS

[0029] FIG. **1**. Cyclic voltammetry of a thin film of polymer 3ay. Arrows indicate direction of the voltage sweep.

[0030] FIG. **2**. Exemplary configurations of various thin-film organic polymer electronic devices containing a layer of a pi-conjugated organoboron polymer.

[0031] FIG. **3**. Current versus voltage response of a MEH-PPV diode with a 3by layer acting to transport electrons.

DETAILED DESCRIPTION OF THE INVENTION

[0032] This invention relates to the use of pi-conjugated polymers comprising both organic conjugated repeat units and organoboron units in thin-film, organic polymer, electronic devices.

[0033] An individual polymer molecule is a molecule comprising a plurality of repeating units. For clarity herein, a polymer molecule is defined as containing four or more repeating units of the same type, or four or more repeating units of at least one type of repeating unit, if different repeating units are presents. The four repeating units in a polymer molecule need not be contiguous in the molecule. Individual molecules containing two or three contiguous or non-contiguous repeating units of the same type are defined herein as oligomer molecules. Different repeating units can be distributed in an ordered or random (non-ordered) fashion in the polymer or oligomer molecule. Polymer molecules and oligomer molecules are thus distinguished from non-polymeric molecules which do not contain repeating units. A polymer molecule may comprise a linear chain of four or more repeating units or may comprise branched chains of four or more repeating units. Similarly, oligomers may be linear or branched. Polymer and oligomer molecules optionally contain end groups that differ in structure and chemistry from the repeating units.

[0034] In general, because of the way that they are prepared, polymers are a mixture of polymer molecules comprising a statistical distribution of individual polymer molecules which contain a different number of repeating units, or a different ordering of more than one repeating unit. Each individual polymer molecule in the polymer has a specific chemical structure and molecular weight. However, the polymer is a mixture of individual polymer molecules. Unless otherwise specified herein the term polymer refers to such mixtures of individual polymer molecules. Polymers may also contain a mixture of oligomer molecules. Like polymers, oligomers can be prepared as a mixture of individual oligomer molecules with different numbers of repeating units or a different order of repeating units if more than one repeating unit is present. Because oligomers contain fewer repeating units the diversity of structures present in a mixture of oligomers is less than in polymers.

[0035] Therefore polymers (mixtures of individual polymer molecules) are characterized by their "weight average molecular weight," also called "weight average molar mass" that is defined as:

$$<M>_w=(\Sigma w_i M_i)/(\Sigma w_i),$$

where < > indicates that it is an average,

$$w_i=N_iM_i/N_A,$$

where N_i is the number of molecules of the polymer i having molar mass M_i. [J. M. G. Cowie, "Polymers: Chemistry & Physics of Modern Materials", 2nd Edition, Blackie Academic & Professional, Great Britain, (1993), pages 8-9]. The weight average molecular weight is typically measured by Gel Permeation Chromatography (also called size exclusion chromatography) using either a light scattering or a refractive index detector, using appropriate standards of known mass [J. M. G. Cowie, "Polymers: Chemistry & Physics of Modern Materials", 2nd Edition, Blackie Academic & Professional, Great Britain, (1993), pages 210-214]. The chain length of polymers can also be described by the "average degree of polymerization x_w" where $x=<M>_w/M_0$, where M_0 is the molar mass of a monomer (repeating unit) and $<M>_w$ is the weight average molar mass as defined above. As known in the art, polymers may also be characterized by a "number average molecular weight" or the "z-average" both of which are terms that are well-known in the art.

[0036] According to this invention polymers encompass oligomeric and telomeric compounds and any mixtures containing a distribution of polymer molecules having the same four or more repeating units, but having different molecular weights or having a different ordering of repeating units. In specific embodiments, polymers of this invention include those in which the average degree of polymerization is 10 or more. In other specific embodiments, polymers of this invention include those in which the average degree of polymerization is 20 or more. In other specific embodiments, polymers of this invention include those in which the average degree of polymerization is 50 or more.

[0037] The term "organic" refers to a chemical species, i.e., a molecule, moiety, radical, or functional or substituent group, which contains a single carbon atom (substituted with hydrogen or other substituent group, e.g., CH_3—, CF_3—, CH_3—NH—CH_2—) or contains covalently bonded carbon atoms and optionally contains various other atoms in addition to carbon and hydrogen. The bonds between carbons may be single, double, triple or aromatic (as in benzene). Carbons may be bonded in a linear chain, a branched chain, or a ring which may be an aromatic ring.

[0038] The term organic polymer refers to a polymer comprising organic polymer molecules in which at least one of the repeating units is an organic moiety which contains covalently bonded carbon atoms and optionally contains various other atoms. Typically an organic moiety contains a carbon-carbon bonded backbone or ring structure which may be substituted with various substituents (other than hydrogen) containing various atoms or in which the backbone remains predominantly composed of carbon, but may contain other atoms (e.g., O, S, N, etc.). Organic polymers may be formed having more than one repeat unit that are different in structure from each other, and are distributed along the polymer chain in any ordered or random arrangement or sequence. Therefore, the term polymer herein encompasses also random, alternated and block copolymers.

[0039] A monovalent organic radical (or simply a monovalent radical) is a group of atoms (molecular fragment) derived formally by removal of a single hydrogen atom from an organic molecule. Examples of monovalent organic radicals include, among others, CH_3— (methyl radical), CH_3—CH_2—, OH—CH_2—CH_2—, C_6H_5—CH_2—, and CH_3—CH═CH—. Additional organic radicals are species derived formally by removal of a single hydrogen atom from a non-carbon atom (e.g., O, N, S, Si) in the organic molecule, such as alkoxide radicals (R—O—, where R is an alkyl or other organic group), which is derived by removal of hydrogen from an alcohol, an amine radical (RR'—N—, where one of R or R' is an alkyl or other organic group), or a silyl radical (R_3Si—, where R is an alkyl or other organic group).

[0040] A divalent organic radical (or simply a divalent radical) is a group of atoms (molecular fragment) derived formally by removal of two hydrogen atoms from an organic molecule where both hydrogens may be removed from the same atom in the organic molecule or two different atoms in the organic molecule. Exemplary divalent organic radicals are: —CR_2—, —CF_2—, —C_6R_4— (a phenylene radical), —$(CR_2)_n$—, —$(CR_2)_n$—X—$(CR_2)_m$—, —X—(CH_2)—, —NR"—, where n and m are integers, each R, independent of other R's is hydrogen, halogen, alkyl or other organic group, R" is an organic group and X is O, S, NR, CO, CS, NRCO, COO, double bond, triple bond, or phenylene, among others.

[0041] A multivalent organic radical (or simply a multivalent radical) is a group of atoms (molecular fragment) derived formally by removal of three or more hydrogen atoms from an organic molecule. Examples of multivalent radicals include —(R)C<, —$(CR_2)_n$—CR<, —$(CR_2)_n$—X<, —$(CR_2)_n$—X(−)-$(CR_2)_m$—Y—, —$(CR_2)_n$—X(−)-$(CR_2)_m$—, where n and m are integers, each R, independent of other R's is hydrogen, halogen, alkyl or other organic group, X is N, CR, N—CO, and Y is CR_2, CO, COO, CS, O, S, NR, NR—CO, and phenyl (C_6R_4),

[0042] Organic radicals can contain linear or branched carbon chains or rings containing carbon and other atoms (e.g., O, S, N). Organic radicals can contain double bonded carbons, triple bonded carbons, non-aromatic or aromatic rings. Carbons in organic radicals can be substituted with one or more various non-hydrogen substituents, including halogens, amino group, alkoxide or hydroxide groups, alkyl thiols or thiols, oxygen or sulfur (to form CO or CS groups).

[0043] A functional group is a combination of atoms (or in the case of halides a single atom) that when attached to an organic radical has either a specific reactivity or imparts to the molecule a specific character, for example, by electron withdrawing or electron donating action. Hydrogen is not a functional group.

[0044] Typical functional groups include halogen atoms, nitro groups, cyano groups, cyanate groups, thiocyanate groups, isocyanate groups, thioisocyanate groups, alcohol groups (e.g. organic groups with one or more OH groups), polyol groups (e.g., organic groups with more than one and more typically a plurality of OH groups), alkoxide groups, ether groups (e.g., alkyl or other organic groups containing one or more C—O—C linkages), thiols, thioether groups (e.g., alkyl or other organic groups containing one or more C—S—C linkages), silyl (e.g., R_3Si—, where R is various substituents or organic groups), siloxy (e.g., R_2—Si(OR)—), aldehyde groups (organic radicals containing a —COH moiety), ketone groups (organic radicals containing a CO moiety), carboxylic acids (organic radicals containing —COOH groups or —COO^- groups, carboxylic ester groups (organic groups containing —COOR" groups, where R" is an alkyl group or other organic group), acyl halide groups (organic groups containing —COX groups where X is a halide), anhydride groups (an organic group containing an anhydride group), groups containing other carboxylic acid derivatives, amino groups, alkyl amino groups, amino oxide groups and groups containing other derivatives of amino groups, diazo groups, azide groups, phosphoric acid ester groups, alkyl phosphate groups and groups containing other phosphoric acid derivatives, phosphinic acid groups, and groups containing phosphinic acid derivatives, phosphine groups, groups containing phosphonium salts, sulfuric acid ester groups, sulfate groups, sulfonate groups, groups containing sulfinic acid derivatives, groups containing sulfonium salts, groups containing oxonium salts, groups containing carbon-carbon double bonds (e.g., alkenyl groups) and groups containing carbon-carbon triple bonds (e.g., alkynyl groups), and combinations thereof. Functional groups include organic functional groups.

[0045] Many other functional groups are known in the art. Aldehyde groups, halogen atoms, isocyanate groups and acyl halide groups are examples, among many others, of functional groups that may be used to impart a desired reactivity to a molecule or polymer. Nitro groups, cyano groups, chlorine and bromine atoms, and carboxylic acid derivatives are examples, among many others, of functional groups with electron-withdrawing properties. Alcohol groups, alkoxide groups, thiol groups, mercapto groups, and amino groups are examples, among many others, of groups with electro-donating properties. The terms "electron-withdrawing group: and "electron-donating group" are terms that are well known in the art of chemistry. Many groups are known in the art which are classified into one of these groupings. These terms are used herein to have their broadest meaning in the art. One of ordinary skill in the art understands the meaning of these terms and knows how to select functional groups which will function as an electron-withdrawing group or an electron-donating group in a particular molecular structure.

[0046] A conjugated compound is a compound that contains one or more bonding orbitals that are not restricted to two atoms, but they are spread (or delocalized) over three or more atoms. A pi-conjugated (or π-conjugated) compound is a compound in which the delocalized molecular orbitals are made by overlap of atomic p orbitals such as the remaining (non hybridized) p orbital of an sp^2 hybridized carbon atom (M. B. Smith and J March, "March's Advanced organic Chemistry, Delocalized Chemical Bonding" 5th Ed. John Wiley and Sons, 2001, p 32-33). This continuum of pi bonds defines pi-conjugation, often referred to simply as conjugation, and is most commonly observed in unsaturated or aromatic organic molecules. Chemical species other than molecules, including radicals, moieties and groups may be conjugated.

[0047] Organic molecules include saturated, unsaturated and aromatic organic molecules. Chemical species other than molecules, including radicals, moieties and groups may be saturated, unsaturated or aromatic or contain portions that are saturated, unsaturated or aromatic. In a saturated organic molecule, each carbon has four bonds to other carbons, hydrogens, non-hydrogen substituents, or functional groups (that do not contain double or triple bonds). Exemplary saturated organic groups are alkyl groups which may be straight-chain, branched or cyclic alkyl groups, and which are optionally substituted with one or more non-hydrogen substituents, such as halogens, hydroxide groups, alkoxide groups, thiol groups, thioalkyl groups, ether groups, thioether groups, silyl groups (e.g., R_3Si- groups) and/or amino groups, among others.

[0048] Unsaturated organic molecules are molecules containing at least one carbon-carbon or carbon-heteroatom double bond (e.g., C═O, C═S, C═N). Exemplary unsaturated organic groups are alkenyl groups and alkynyl groups which may be straight-chain, branched or contain one or more rings groups, and which are optionally substituted with one or more non-hydrogen substituents, such as halogen atoms, or unsaturated functional groups (e.g., as listed above) and alkyl groups which are substituted with unsaturated functional groups, such as aldehyde and/or ketone groups (containing —COH or —CO—), carboxylic acid, carboxylate or carboxylic ester groups (containing —CO—O—), acyl halide groups, cyanide groups, isocyanide groups, among many others. Chemical species other than molecules, including radicals, moieties and groups may be unsaturated.

[0049] Aromatic organic molecules are defined in M. B. Smith and J March, "March's Advanced organic Chemistry, Delocalized Chemical Bonding" 5th Ed. John Wiley and Sons, 2001, p 46-48). Aromatic molecules may carry additional substituents including, halogens, organic functional groups, and organic radicals (substituents may be saturated and/or unsaturated groups). Chemical species other than molecules, including radicals, moieties and groups may be aromatic or contain portions that are aromatic. Aromatic organic radicals are molecular fragments formally obtained by removal of a hydrogen atom from the aromatic portion of an aromatic molecule.

[0050] A pi-conjugated polymer is an organic polymer comprising pi-conjugated repeat units in which one or more bonding orbitals are delocalized over at least two repeat units. A pi-conjugated organoboron polymer is a polymer made of repeat units that comprise both unsaturated and/or aromatic units and boron atoms, wherein the vacant p-orbital of the boron atoms conjugate with the pi-conjugated orbital system of the aromatic and/or unsaturated units. In a preferred embodiment the boron atoms are trivalent (i.e. carry three substituents) and are sp^2 hybridized. Repeating units of these polymers optionally contain one or more hydrogen substituents, including halogens or organic functional groups.

[0051] A semiconductor is a material in which the uppermost band of occupied electron energy states is completely full at the temperature of 0 K (and without excitations). It is well-known from solid-state physics that electrical conduction in solids occurs only via electrons in partially-filled bands, so conduction in pure semiconductors occurs only when electrons have been excited-thermally, optically, or by other known means, into higher unfilled bands. At room temperature, a proportion (generally very small, but not negligible) of electrons in a semiconductor have been thermally excited from the "valence band," to the "conduction band." Semiconductors generally have bandgaps of approximately a few electron-volts, while insulators have bandgaps several times greater.

[0052] An n-type semiconductor is a semiconductor in which the conduction electron density exceeds the hole density and in which the electrical conduction is mainly due to the movement of these excess electrons.

[0053] A thin-film is defined as a continuous stratum of any material that is between 1 angstrom and 10,000 angstroms thick, and more preferably 100 to 10,000 angstroms thick.

[0054] A thin-film, organic electronic device is defined as a device comprising an active layer made of at least one thin-film comprising a semiconducting or conducting organic molecule or organic polymer in contact with two or more conducting materials acting as electrodes to which a current or voltage is applied or from which a current or voltage is obtained. Examples of thin-film organic electronic devices include, but are not limited to OPVs, organic diodes, organic photodiodes, organic TFTs, OFETs, printable or flexible electronics like RFID tags, electronic papers, printed circuit elements, OLEDs, PLEDs, thin-film capacitors and other energy storage devices. When the device is turned on the active layer exchanges charge carriers with one or more of the electrodes.

[0055] A thin-film, organic polymer, electronic device is defined as a device comprising an active layer made of at least one thin-film comprising a semiconducting or conducting organic polymer in contact with two or more conducting materials acting as electrodes to which a current or voltage is applied or from which a current or voltage is obtained. The terms conducting, conduction, and conductivity all refer to electronic or electrical conductivity and are not intended to refer to or imply ionic or thermal conductivity. As known by those of ordinary skill in the art, the active layer of a thin-film, organic polymer, electronic device may contain more than one stratum, typically a plurality of strata, of thin films of other materials or blends of materials, including but not limited to organic or inorganic molecules and polymers that have semiconducting, conducting or non-conducting properties. These additional strata may play different roles in the device including, but not limited to: hole transporting layers (HTL), hole injecting layers (HIL), electron transporting layers (ETL), electron injecting layers (EIL), singlet light-emitting layers, triplet light-emitting layers, electron blocking layers, hole blocking layers, flattening layers, photon absorbing layers, barrier layers, charge separating layers, and dielectric layers.

[0056] An active layer of an electronic device is a layer comprising one or more thin films of semiconducting, conducting, or non-conducting materials and blends thereof. An active layer has a function in the electronic device other than providing mechanical strength to the device or acting as a substrate to carry an active layer. For example, the active layer may have one or more of the following functions: hole transporting, hole injecting, electron transporting, electron injecting, singlet light emission, triplet light emission, electron blocking, hole blocking, surface flattening function, photon absorption, barrier function, charge separation, and dielectric function.

[0057] In one embodiment of this invention the active layer comprises a single thin-film of a pi-conjugated organoboron polymer. In another embodiment, the active layer comprises a single thin-film made of a blend or mixture of materials, at least one of which is a pi-conjugated organoboron polymer. In yet another embodiment of this invention the active layer of the device comprises two or more thin films of semiconducting materials, at least one of which is a pi-conjugated organoboron polymer or a blend containing a pi conjugated organoboron polymer. When two or more thin-films are present in the active layer, these thin-films are in contact with any adjacent thin-films and electrodes.

[0058] The devices of this invention include those which exhibit current rectification or diode-like properties. Current rectification is the conversion of alternating current into direct current. A diode is a device that preferably allows current to flow in one direction and not in the other. The devices of this invention include those wherein the thin film comprising a pi-conjugated organoboron polymer which emits light under a voltage bias.

[0059] This invention relates to the use of a new type of pi-conjugated polymer in thin-film organic polymer electronic devices. These polymers all contain boron atoms in the pi-conjugated backbone of the polymer and preferably exhibit one or more of the following properties: n-type semiconducting properties, photoluminescence, and electroluminescence.

[0060] Pi-conjugated organoboron polymers of this invention are made of repeat units that comprise at least one boron atom and at least an aromatic or unsaturated fragment, such that conjugation of bonding orbitals extends over more than one repeat unit of the polymer and across the vacant p-orbital of the boron.

[0061] The preferred pi-conjugated organoboron polymers have a conjugated backbone comprised of unsaturated organic portions (or fragments) or aromatic organic portions (or fragments), or a mixture thereof and boron atoms which may be additionally substituted with a hydrogen, deuterium, halogen atoms, an organic functional group or an organic radical. Exemplary pi-conjugated organoboron polymers, represented by repeating units in brackets, are illustrated in Scheme 1, where each R, independent of other R's in the repeating unit, and R_1, independent of any R's, can be hydrogen, deuterium, a halogen atom, or an organic radical, Ar represents a divalent aromatic radical which may optionally carry one or more other organic radical groups, substituent groups, and/or functional groups described herein and "n", "m" and "p" are integers indicating either the number of moieties present in a given repeating unit or the average degree of polymerization of the polymer dependent upon the structure illustrated. In Scheme 1, R_1 is a substituent on the boron atom.

[0062] The preferred unsaturated portions of the pi-conjugated organoboron polymers are vinylene, ethynylene, 1,3-butadienylene, and other divalent radicals comprising more than one conjugated carbon-carbon double bond, carbon carbon-triple bond, carbon-heteroatom double bond, carbon heteroatom triple bond, and mixtures thereof. More preferred are vinylene, ethynylene, and 1,3-butadienylene. Most preferred is vinylene. Additional unsaturated fragments may be oligomeric species comprising one or more of the repeat units listed above. The unsaturated fragment may optionally carry one or more substituent group including hydrogen, deuterium, halogens, any organic functional groups, or any monovalent, divalent or multivalent organic radicals.

[0063] The preferred aromatic portions (or fragments) are divalent radicals resulting from the removal of two hydrogen atoms from benzene (such as 1,4 phenylene, 1,3-phenylene, and 1,2-phenylene), napthalene, diphenyl, pyridine, pyrimidine, triazine, pyrrole, N-alkylpyrroles, N-substituted pyrroles, 3-substituted pyrroles, furan, tetrazole, indole, purine, oxadiazole, 1,5-diphenyl-oxadiazole, quinoxaline, phenazine, N,N'-dialkylphenazines, phenothiazine, N-alkylphenothiazines, carbazole, N-alkylcarbazoles, thiophene, 3-alkylthiophenes, 3-substituted thiophenes, 3,4-disubstituted thiophenes, thienothiophene, substituted thienothiophenes, bithiophene, terthiophene, quaterthiophene, dialkyloxybenzenes, oxazole, fluorene, 9,9-dialkylfluorenes and their substituted derivatives. These aromatic fragments are optionally substituted with one or more non-hydrogen substituents and/or functional groups as described herein. More preferred fragments are divalent radical fragments resulting from the removal of two hydrogen atoms from benzene, thiophene, 3-alkylthiophenes, bithiophene, terthiophene, quaterthiophene, dialkyloxybenzene, fluorene, 9,9-dialkylfluorenes and derivatives thereof. Additionally, the aromatic fragments may be oligomeric species comprising one or more of the repeating unit listed above and their mixtures.

[0064] Additionally a combination of one or more unsaturated fragment and one or more aromatic fragment can be used (Scheme 1, formulas c,d,e,g, and j). The aromatic fragment may optionally carry one or more substituents including hydrogen, deuterium, halogens, any organic functional groups, or any monovalent, divalent or multivalent organic radicals.

[0065] It is preferred that the R_1 group (referring to Scheme 1) on the boron atom is a bulky group that provides steric hindrance to the boron atoms and protects it from the attack by nucleophiles and radicals, such as water and oxygen. Steric hindrance occurs when functional groups on a molecule (or molecules individually) that would normally react with each other or be attracted to one another cannot interact due to their special relationship because the bulkiness of a side chains physically covers the reactive site or because, due to the shape or stiffness of a molecule, the reactive groups cannot come into contact. The preferred organic groups "R_1" on the boron atoms are any aliphatic or aromatic radicals including, but not limited to, methyl, trifluoromethyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, t-butyl, thexyl, perfluorinated alkyls, phenyl, perfluorophenyl, alkyl-substituted phenyl, linear and branched alkyl groups, which optionally may carry additional functional groups such as carbon-carbon double or triple bonds, ester groups, cyano groups, nitro groups, halogens, alcohols, amines, ethers, aryl groups, which optionally may carry additional substituents such as alkyl groups and or functional groups such as carbon-carbon double or triple bonds, ester groups, cyano groups, nitro groups, halogens, alcohols, amines, ethers, and any other known organic functional group or organic radical. More preferred sterically bulky, organic groups are pentafluorophenyl, di(trifluoromethyl)phenyl, thexyl, 2-ethylhexyl, 1,3,5-trimethylphenyl(mesityl), and 1,3,5-triisopropylphenyl(tripyl) groups.

[0066] Selected structures of preferred pi-conducting organoboron polymers are shown in Scheme 2, wherein R_1, independent of other R_1 in the repeating unit and R_2, and R_2, and R_3, independent of any R_1, are hydrogens, deuterium atoms, halogen atoms, or linear or branched alkyl radicals, particularly alkyl radicals having 1-20 carbon atoms, which can be optionally substituted with one or more non-hydrogen substituents or functional groups as defined herein; R_3 is hydrogen, deuterium atom, halogen atom, or an alkoxide or mercapto group, particularly wherein the group has 1-20 carbon atoms, and which can optionally carry one or more additional non-hydrogen substituents or functional groups as defined herein; R_4 is an aliphatic radical (a saturated or unsaturated organic radical) particularly one which contains 1-20 carbon atoms, or an aromatic radical, such as a phenyl or substituted phenyl group, n is an integer number and m is a small integer number preferably 1 to 6, and most preferably 1 to 3. In the formulas B, C, F and G, R_2 and R_3 can also represent multiple independent substituent and/or functional groups on the rings shown. Additionally R_2 and R_3 can represent groups that link two ring positions, such as alkylene, ether or thioether linkages between two ring positions. The wavy line to the R_2 and R_3 groups indicates, as is understood in the art, that these groups may be attached at any ring positions in place of hydrogens. Note that in formulas shown herein, as is conventional in the art, hydrogen substituents are not shown. Further any one or more hydrogen substituents on the aromatic rings in the formulas of Scheme 2 can optionally be substituted with a non-hydrogen substituent or functional groups as described herein. In particular, any hydrogen substituent in the formulas can be replaced with a halogen, e.g., a fluorine atom, or an alkyl group having 1 to 3 carbon atoms.

[0067] In specific embodiments, pi-conjugated organoboron polymers include those of formula A in Scheme 2 wherein R_1 is an alkyl group having 1 to 6 carbon atoms which is optionally substituted with one or more non-hydrogen substituents, particularly one or more halogens, such as fluorine, and R_2 is an alkyl group having 3 to 20 carbon atoms which is optionally substituted with one or more non-hydrogen substituents, particularly one or more halogens, such as fluorine. In specific embodiments, pi-conjugated organoboron polymers include those of formula A in Scheme 2 wherein R_1 is a straight-chain or branched alkyl group having 1 to 6 carbon atoms and R_2 is a straight-chain or branched alkyl group having 6 to 12 carbon atoms. In more specific embodiments, pi-conjugated organoboron polymers include those of formula A in Scheme 2 wherein R_1 is a methyl or propyl group, particularly an isopropyl group and R_2 is a straight-chain or branched alkyl group having 6 to 12 carbon atoms. In more specific embodiments, pi-conjugated organoboron polymers include those of formula A in Scheme 2 wherein R_1 is a straight-chain or branched alkyl group having 1-6 carbon atoms and R_2 is a straight-chain alkyl group having 6-16 carbon atoms, and more specifically a straight-chain alkyl group having 6 or 12 carbons atoms or R_2 is a branched alkyl group having 6 to 16 carbon atoms and more specifically a branched alkyl group having 8-12 carbon atoms.

[0068] A preferred method of preparing pi-conjugated organoboron polymers is by reacting the respective dibrominated unsaturated or aromatic compounds with dimethoxymesitylborane or dimethoxytripylborane in the presence of magnesium via the formation of the Grignard reagent (as exemplified in Example 1). Yet another preferred method of preparing pi-conjugated organoboron polymers is by reacting di-lithiated unsaturated or aromatic compounds with dimethoxymesitylborane, dimethoxytripyl-borane, dichlorophenylborane or dichloro-t-hexylborane (as exemplified in Example 3 and 4). Other organometallic coupling reagents may be used for this application in place of the Grignard reagent or lithium derivatives, including copper derivatives, tin derivatives, nickel derivatives, and silyl derivatives. These methods can be used to prepare, for example, compounds of the type of formula a, b f and i in Scheme 1.

[0069] Compounds of the type g and h in Scheme 1 can be prepared by reacting the dibromo derivative of an oligomeric or telechelic species of the unsaturated or aromatic monomer with a borane reagent. Oligomerization of the aromatic or unsaturated compound and coupling with the borane reagent may occur in a single step if the proper organometallic intermediate and the proper reaction conditions are used. Preferred borane reagents are compounds containing a trivalent boron atom that is substituted with an alkyl or aryl group and two reactive groups such as alkoxy groups or halogen atoms. Dimethoxymesitylborane, dimethoxytripylborane, dichlorohexylborane and dichlorophenylborane are examples of borane reagents.

[0070] Another preferred method to prepare pi-conjugated organoboron polymers is by the hydroboration or dihydrobromination of dialkynes (Chujo et al. *J. Am. Chem. Soc.,* 120, 5112-5113, 1998; Chujo et al. *Polymer Bulletin,* 42, 505-510, 1999). This method can be used, for example, to prepare compounds of the type of formulas e, g and j in Scheme 1.

[0071] Compounds of the type of formulas c and d in Scheme 1 can be prepared by coupling of borane reagents with asymmetric organometallic compounds or via more complex synthesis comprising multiple steps or hydroboration and coupling.

[0072] Polymers of this invention, including those illustrated in Schemes 1 and 2, can be readily prepared in view of the description herein and methods that are well-known in the art. Those of ordinary skill in the art will appreciate that methods other than those specifically exemplified herein can be used to prepare the desired pi-conjugated organoboron polymers.

[0073] Preferred pi-conjugated organoboron polymers comprise at least two repeating units and have weight average molecular weights ranging from 50 Dalton to one million Dalton as determined by Gel Permeation Chromatography (GPC). More preferred polymers have weight average molecular weights ranging from 500 to 100,000, and most preferably from 3,000 to 30,000.

[0074] In a preferred embodiment the pi-conjugated organoboron polymers are N-type semiconductors and have a non-negligible (i.e., measurable with current state-of-the art equipment) mobility of charge carriers, preferably where the charge carriers are negative charge carriers. Preferred charge carrier mobilities are greater than 10^{-5} $cm^2/V \cdot s$ with more preferred mobility being greater than 10^{-3} $cm^2/V \cdot s$. Preferred carrier densities are greater than 10^6 cm^{-2} with more preferred carrier densities greater than 10^9 cm^{-2}. Charge carrier type, density, and mobility can be measured by carrying out Hall probe measurements or by using a time of flight laser excitation technique (ASTM F76 from the ASTM book of Standards Version 10.05, 2000). These properties are required when the pi-conjugated organoboron polymers are used for the fabrication of transistors, solar cells and for the electron transport layer of an OLED.

[0075] In another preferred embodiment the pi-conjugated organoboron polymers of this invention are fluorescent, electroluminescent and/ or emit light under applied bias. Typical fluorescence is green- and/or blue. These properties are required when the pi-conjugated organoboron polymer is the light emitter (Example 5), for example, in a PLED.

[0076] In yet another embodiment the pi-conjugated organoboron polymers of this invention are doped to a conducting state. This can be achieved, for example, by reaction with a reducing agent such as an alkali metal hydride, or a solution of sodium naphthalenide, by ion implantation or by electrochemical methods (Antoun, S., and R. D. Gagnon, J. D. Capistran, F. E. Karask, R. W. Lenz., (1987). "Synthesis, doping, and electrical properties of high molecular weight poly(p-phenylenevinylene),"*Polymer,* 28, 587-573, Moliton, A. (1998) "Ion Implantation Doping of Electroactive Polymers and Device Fabrication," in *Handbook of Conducting Polymers,* 2nd Ed." Ed. T. A. Skotheim, R L Elsenbauer, J. R. Reynolds, Marcel Dekker, New York, p-589-638, Shacklette, L. W., and J. E. Toth, N. S. Murthy, R. B. Baughman, (1985) "Polyacetylene and Polyphenylene as Anode Materials for Non-aqueous Secondary Batteries,"*J. Electrochem. Soc.,* 132, 1529-1535). Preferred conductivities are higher than 10^{-6} S/cm and most preferred are higher than 10^{-3} S/cm. Most preferably, the doping process is reversible and stable (Example 4).

[0077] Preferred pi-conjugated organoboron polymers are soluble in common organic solvents at 0.1 g/L or more and more preferably at 1 g/L or more. In an embodiment of this invention, coating solutions of pi-conjugated organoboron polymers are prepared by dissolving the polymers in an appropriate solvent at an appropriate concentration. Preferred solvents are alkanes, aromatic hydrocarbons, ethers, alcohols, ketones, esters, nitrites, lactones, nitroalkanes, halogenated alkanes, and supercritical carbon dioxide. The most preferred solvents are benzene, toluene, xylenes, pentane, hexanes, cyclohexane, tetrahydrofuran, dimethylformamide, dimethylsulfoxide, N-methylpyrrolidone, dimethylcarbonate, acetonitrile, chloroform, dichloromethane, dichloroethane. The concentration of a coating solution is in the range of greater than 0 to 40% solids by weight, e.g., 0.01% to 10%, but preferably is 0.1% to 5% solids by weight. Common coatings additives such as rheology modifiers, surfactants, wetting agents, anti-foaming agents, and crosslinkers may be added to coating solutions as an embodiment of this invention. These coating solutions may be used to prepare coatings, patterned coatings, printed circuitry elements, and other device elements or features.

[0078] The preferred solubility properties of a given boron-containing conjugated polymer depend on the device design in which the polymer will be used (FIG. **2**). In order to construct layered materials, polymers for use in adjacent layers are selected so that their solubility is either orthogonal to each other or similar to each other. The term "orthogonal" with respect to solubility is used to describe the situation where there exists at least one solvent in which one of the two different polymers used in adjacent layers is substantially more soluble than the second polymer under selected conditions (temperature, contact time, etc.) The term "similar" with respect to solubility is used to describe the situation where there exists at least one solvent in which both of the two different polymers are substantially soluble under selected conditions. If polymers for use in adjacent layers have substantially similar solubility in a given solvent, partial or complete mixing of the two layers at the interface can occur during spin casting. The different polymers need not exhibit the same level of solubility in the given solvent under the selected conditions. They need only have sufficient solubility in the solvent to obtain the level of mixing desired. If the solubility of the polymers for use in adjacent layers is substantially orthogonal, then no significant level of mixing occurs in a given solvent under selected conditions.

[0079] Again dependent upon device design and application, mixing of the adjacent layers may be a desirable property (e.g., laminate cell device of FIG. **2**B) or a highly undesirable property (e.g., cell devices of FIG. **2**C-F). In these cases the underlying layers are cast from polar or aqueous solvents and therefore the organoboron polymer is preferred to be soluble in non-polar solvents. For these reasons it is desirable to control and change the solubility properties of organoboron polymers for use in device applications herein. This is achieved by selecting the nature of the polymer side chains, by selecting functional groups for inclusion on the polymer side chains and by selecting the average molecular weight of the polymer itself. Tunable solubility properties of polymers also facilitate the preparation of ideal blends of the n-type boron-containing conjugated polymers with other p-type conjugated polymers for use in photodiodes and photovoltaic solar cells. Ideal blends contain phase separated domains of the p-type and n-type materials, wherein the domains of each phase are preferably small and have a fractal surface to maximize the surface area (interface) that separates the two materials. Maximizing the interface in such devices can be beneficial because light generation (in OLEDs and PLEDs) and charge separation (i.e. creation of current in photovoltaic devices) occur at the interface.

[0080] In a preferred embodiment of this invention, coating solutions may contain more than one polymer, for example they may contain two or more pi-conjugated organoboron polymers or a mixture of a pi-conjugated organoboron polymer with one or more other pi-conjugated, conducting or semiconducting polymers (that are not organoboron polymers) or non-polymeric molecules. In a more preferred embodiment of this invention a coating solution may be prepared with one or more pi-conjugated organoboron polymer and one or more p-type conducting or semiconducting polymers that are not organoboron polymers, p-type conducting or semiconducting non-polymeric molecules, or p-type conducting or semiconducting particulate solids. P-type conducting or semiconducting particulate solids with physical dimensions smaller than 10 microns are preferred. Regioregular poly(n-alkyl thiophene)s are examples of organic p-type semiconducting polymers, zinc phthalocyanine and hexathiophene are examples of p-type molecules and nano-crystalline boron-doped silicon, p-type gallium arsenide and p-type zinc telluride are example of inorganic p-type semiconductors.

[0081] Thin-films of this invention can contain polymer blends. Polymer blends are macroscopically homogenous mixtures of two or more measurably different polymers (noting that polymers themselves are mixtures of polymer molecules). The polymers may be miscible, but need not be miscible. Blends may contain different phase domains in contrast to miscible polymer mixtures that contain a single phase.

[0082] In an embodiment of this invention a thin film of a pi-conjugated organoboron polymer or containing such a polymer is formed by application of a coating solution to a substrate material by appropriate means. Preferred methods include spin coating, dip coating, contact printing, ink-jetting, screen printing, and airbrushing. Removal of the coating solution solvent is preferably carried out by evaporation with heating of the film to a temperature in the range from room temperature to 250 degrees Celsius and more preferably from 50 to 150 degrees Celsius for 5 to 30 minutes. Most preferably the thin film is annealed at 80 to 110 degrees Celsius for 5 to 10 minutes. If supercritical fluids are employed as the solvent, temperatures below room temperature may be used. Drying and annealing can be accomplished in air, but more preferably is carried out under a flow of dry nitrogen or argon. Dried thin films have a preferred thickness of 10 to 10,000 angstroms and a most preferred thickness of 100 to 5,000 angstroms.

[0083] In a preferred embodiment of this invention, thin films are prepared on a substrate, which can be a glass, ceramic, plastic, paper, textile, or metal substrate. These substrates can be of any useful thickness and surface roughness. Preferred plastic substrates are polyethylene, polypropylene, other polyolefins, polyesters, polyacrylates, polycarbonates, polyvinylchloride, polyvinylalcohol, polyvinylacetate, other vinyl polymers and copolymers, polysulfones, polyamides, polyimides, polyolefins, cellulose, cellulose acetate, Kapton, Kevlar, and perfluorinated polymers. Optionally these substrates may be coated with any useful thickness of films of metals, metal oxides, semiconductors, dielectric materials, conducting polymers, or semiconducting polymers. These films may be applied by any known means and completely cover the substrate or be patterned by any known means so as to provide the proper electrical properties and connections for the operation of devices of this invention. In a preferred embodiment of this invention the substrate may itself act as one or more electrodes for the operation of devices of this invention. In a preferred embodiment of this invention the substrate is glass or plastic coated with a transparent, conducting oxide film comprising tin-doped indium oxide or fluorine-doped tin oxide. In another preferred embodiment of this invention the substrate is glass or plastic coated with a transparent, conducting polymer comprising polythiophene, polypyrrole, polyaniline, or derivatives thereof (see Orgacon products by Agfa, Ormecon products by Ormecon, or Baytron products by H. C. Starck).

[0084] Objects of this invention include thin-film, organic polymer electronic devices that comprise one or more active layers and at least two electrodes in contact with the active layer or layers, wherein the electrodes provide a means by which a current or a voltage is either applied to or derived from the active layer or layers. The active layer or layers comprise at least one thin film of an organic polymer. When only one active layer exists, that layer comprises a pi-conjugated organoboron polymer. When the active layers comprise more than one layer, then at least one of the active layers is a pi-conjugated organoboron polymer. Examples of various organic polymer electronic devices containing an active layer of a pi-conjugated organoboron polymer are in FIGS. **2**A-F.

[0085] FIGS. **2**A and B schematically illustrate device configurations useful particularly for diodes, photodiodes or photovoltaic solar cells. FIG. **2**A is a bended cell type device configuration (**10***a*) in which the active layer **5** is a thin film of a polymer blend, e.g., a p-type semiconductor polymer and a pi-conjugated organoboron polymer blend. The active layer (**5**) is positioned between and separating two electrode layers (**7***a* and **7***b*) which are in electrical communication with two contacts (**9***a*, **9***b*). FIG. **2**A illustrates a device constructed with a single substrate layer (**11***a*).

[0086] FIG. **2**B illustrates a laminated-type cell device configuration in which the active layer **5** comprises one or more thin-film layers (multiple strata). This device configuration contains two substrates (**11***a* and **11***b*). Again the active layer separates two electrodes (**7***a* and **7***b*) each of which is in electrical communication with contacts (**8***a* and **8***b*) respectively.

[0087] FIGS. **2**C and D illustrate exemplary device configurations useful for diodes, light-emitting diodes and photodiodes. In FIG. **2**C, the device is constructed with a single substrate (**11***a*), the active layer (**5**) is a light-emitting polymer layer which comprises a pi-conjugated organoborane polymer that is light-emitting. The active layer separates two electrodes (*7a* and *7b*). The electrodes are in electrical communication with two electrical contacts (**8***a* and **8***b*), respectively. In FIG. **2**D, a two substrate device configuration is illustrates. The active layer **5** comprises multiple layers, including an electron transfer layer (**15**) which comprises a pi-conjugated organoborane polymer and a light-emitting polymer layer (**17**) comprising a light-emitting species, e.g., a light emitting polymer (this polymer may or may not comprise or be a pi-conjugated organoborane polymer.)

[0088] FIG. **2**E illustrates a device configuration for an OFET-bottom gate. Both configurations contain two substrates (**11***a* and **11***b*). The active layer **5** is positioned between a bottom electrode (*7a*) and two separate top electrodes (*7b* and *7c*). The configuration has three contacts (**8***a*, **8***b* and **8***c*) in electrical communication with each electrode, respectively. The active layer **5** comprises a dielectric layer (**19**) adjacent the bottom electrode and a pi-conjugated organoboron polymer comprising layer (**21**) between the dielectric layer and in contact with top electrodes (*7b* and *7c*).

[0089] FIG. **2**F illustrates a device configuration for an OFET-top gate. The active layer **5** is positioned between a top electrode (*7a*) and two separate bottom electrodes (*7b* and *7c*). The active layer **5** comprises a dielectric layer (**19**) adjacent the top electrode and a pi-conjugated organoboron polymer comprising layer (**21**) between the dielectric layer and in contact with bottom electrodes (*7b* and *7c*).

[0090] It will be appreciated by those of ordinary skill in the art that the pi-conjugated organoboron polymers and thin films comprising them can be employed in additional device configurations.

[0091] A more preferred object of this invention is a thin film, organic polymer electronic device that is comprised of at least one p-type semiconducting organic polymer layer and at least one n-type, pi-conjugated organoboron polymer (as exemplified in FIGS. **2**A and B). One or more electrode may constitute the substrate onto which the organic polymer thin films are applied, or may be applied as a layer on top of the thin film, organic polymer layers. In a preferred embodiment of this invention, electrodes comprise metals, metal oxides, semiconductors, conducting polymers, semiconducting polymers or mixtures thereof. These electrode contacts may be applied by any known means and completely cover the organic polymer layers or be patterned by any known means so as to provide the proper electrical properties and connections for the operation of devices of this invention. In a more preferred embodiment of this invention the electrode contacts are applied by thermal or physical vapor phase deposition of aluminum, aluminum fluoride, copper, nickel, gold, silver, magnesium, calcium, barium, zinc, titanium, titanium oxide, fluorine-doped tin oxide, antimony-doped tin oxide, tin-doped indium oxide, aluminum doped zinc oxide, or mixtures thereof.

[0092] In one embodiment of this invention a thin-film of the pi-conjugated organoboron polymer layer is used as the ETL in OLEDs, PLEDs and other light emitting diodes to control the current of injected electrons (from the cathode) such that they are balanced with the current of injected holes (from the anode) under forward bias (FIG. **2**D). During such use of the pi-conjugated organoboron polymer layer as an ETL, the device design may additionally allow for light emission to occur (by singlet recombination of electrons and holes) in this same layer. Therefore the pi-conjugated organoboron polymer layer may be used as both an ETL and a light-emitting polymer layer for PLEDs (FIG. **2**D). In another embodiment of this invention a thin film of the pi-conjugated organoboron polymer is used as the light-emitting layer of a PLED optionally in combination with a layer of a different material that acts as the ETL (FIG. **2**D).

[0093] In other embodiments of this invention, the pi-conjugated organoboron polymer layer is similarly useful as the n-type semiconductor and/or ETL in photodiodes. Such devices are similar in design to PLEDs, but are typically operated under reverse bias where photons produce a measurable induced photocurrent (by photo-induced charge transfer and separation at the interface of the p-type and an n-type semiconductor layers).

[0094] In additional embodiments of this invention, the pi-conjugated organoboron polymer layer is similarly useful as the n-type semiconductor and/or ETL in OPVs. Such devices are similar in design to diodes, but are more preferably constructed with active layers from blends of p-type and n-type semiconducting polymers rather than separate layers of the p-type and n-type semiconducting polymers. This blended active layer maximizes the surface-to-volume ratio of the interface between p-type and n-type semiconducting polymers where photo-induced charge transfer and separation occurs, which is responsible for the generation of power in these devices (FIG. **2**A and B).

[0095] In further embodiments of this invention, the pi-conjugated organoboron polymer layer is similarly useful as the n-type semiconductor for the active layer in TFTs and OFETs (FIGS. **2**E and F). TFTs and OFETs may comprise a single semiconductor (n- or p-type) or multiple semiconductors as in patterned p-n-p or n-p-n junctions. Additional uses of n-type semiconductors in thin film electronic devices are known by those skilled in the art. Pi-conjugated organoborane polymers having n-type semiconductor properties of this invention can be employed in all such applications.

[0096] When a group of substituents is disclosed herein, it is understood that all individual members of that group and all subgroups, including any isomers, enantiomers, diastereomers, and epimers of the group members, are disclosed separately. When Markush groups or other groupings are used herein, all individual members of the group and all combinations and subcombinations possible of the various individual members of the various groups are intended to be individually included in the disclosure and useful in the practice of the invention. When a compound is described herein such that a particular isomer, enantiomer, diastereomer or epimer of the compound is not specified, for example, in a formula or in a chemical name, that description is intended to include each isomers and enantiomer of the compound described individual or in any combination. Additionally, unless otherwise specified, all isotopic variants of compounds disclosed herein are intended to be encompassed by the disclosure. For example, it will be understood that any one or more hydrogens in a molecule disclosed can be replaced with deuterium or tritium. Isotopic variants of a molecule are generally useful as standards in assays for the molecule and in chemical research related to the molecule or its use. Isotopic variants of molecules (or mixtures thereof) can exhibit distinct properties in certain applications. Methods for making such isotopic variants are known in the art. Specific names of compounds are intended to be exemplary, as it is known that one of ordinary skill in the art can name the same compounds differently.

[0097] Formulas of polymeric species disclosed herein may contain one or more ionizable groups [groups from which a proton can be removed (e.g., —COOH) or added (e.g., amines) or which can be quaternized (e.g., amines)]. All possible ionic forms of such molecules and salts thereof are intended to be included individually in the disclosure herein. With regard to salts of the compounds herein, one of ordinary skill in the art can select from among a wide variety of available counterions those that are appropriate for preparation of salts of this invention for a given application.

[0098] Every formulation or combination of components described or exemplified herein can be used to practice the invention, unless otherwise stated.

[0099] Whenever a range is given in the specification, for example, a temperature range, a time range, or a composition or concentration range, all intermediate ranges and subranges, as well as all individual values included in the ranges given are intended to be included in the disclosure. It will be understood that any subranges or individual values in a range or subrange that are included in the description herein can be excluded from the claims herein.

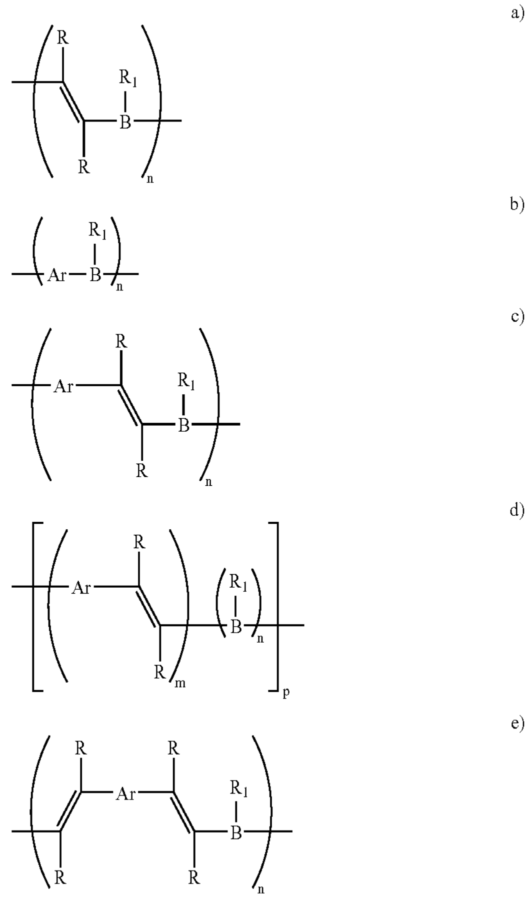
[0100] All patents and publications mentioned in the specification are indicative of the levels of skill of those skilled in the art to which the invention pertains. References cited herein are incorporated by reference herein in their entirety to indicate the state of the art as of their publication or filing date and it is intended that this information can be employed herein, if needed, to exclude specific embodiments that are in the prior art. For example, when a compound is claimed, it should be understood that compounds known and available in the art prior to Applicant's invention, including compounds for which an enabling disclosure is provided in the references cited herein, are not intended to be included in claims to compounds herein. However, certain compositions claimed herein may contain components which are in the prior art.

[0101] As used herein, "comprising" is synonymous with "including,""containing," or "characterized by," and is inclusive or open-ended and does not exclude additional, unrecited elements or method steps. As used herein, "consisting of" excludes any element, step, or ingredient not specified in the claim element. As used herein, "consisting essentially of" does not exclude materials or steps that do not materially affect the basic and novel characteristics of the claim. In each instance herein any of the terms "comprising", "consisting essentially of" and "consisting of" may be replaced with either of the other two terms. The invention illustratively described herein suitably may be practiced in the absence of any element or elements, limitation or limitations which is not specifically disclosed herein.

[0102] One of ordinary skill in the art will appreciate that starting materials, reagents, synthetic methods, purification methods, analytical methods, assay methods, methods for coating, methods for preparation of thin films, methods for preparation of devices, device configurations and methods for testing device configurations other than those specifically exemplified can be employed in the practice of the invention without resort to undue experimentation. All art-known functional equivalents, of any such materials and methods are intended to be included in this invention. The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention that in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims.

[0103] All references cited herein are hereby incorporated by reference to the extent that there is no inconsistency with the disclosure of this specification. Some references provided herein are incorporated by reference to provide details concerning sources of starting materials, additional starting materials, additional reagents, additional methods of synthesis, additional methods of analysis, device configurations, methods for use of devices and additional uses of the invention.

Scheme 1



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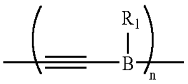

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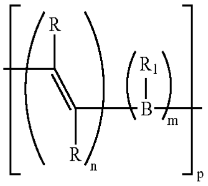
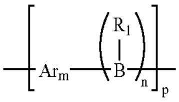


g)



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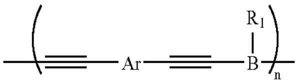

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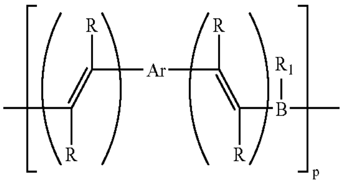
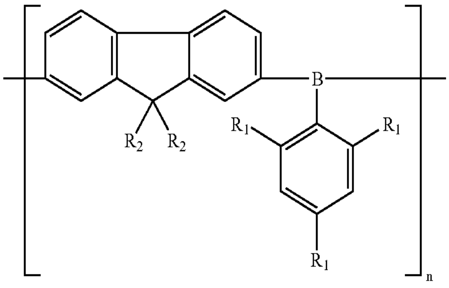


j)

Scheme 2



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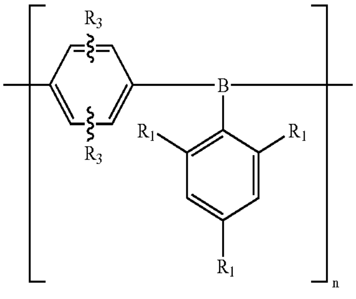

B)

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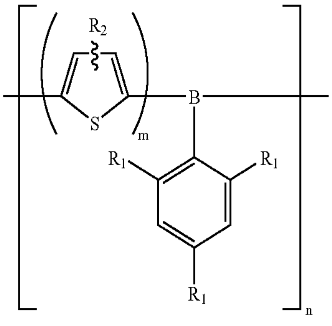
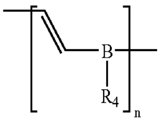


C)



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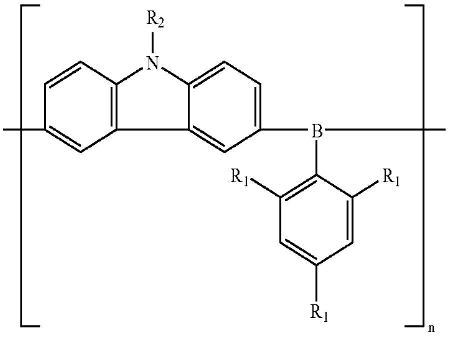

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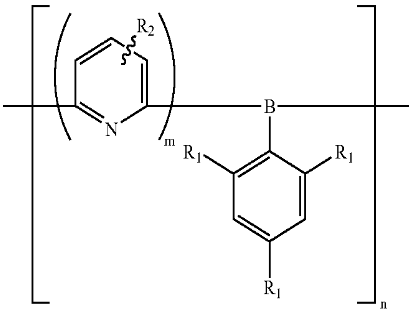
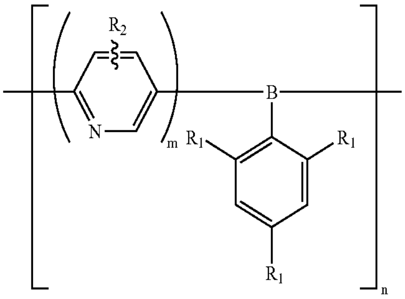


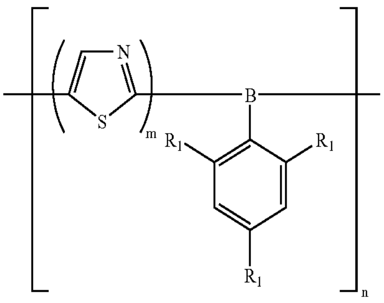
F)



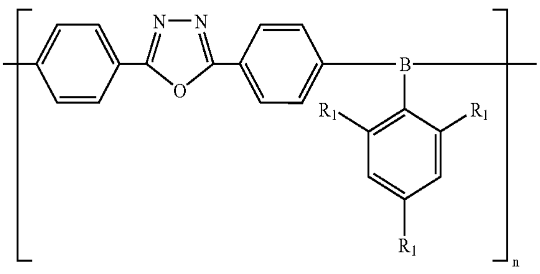
G)

-continued

H)



I)



EXAMPLES

Example 1

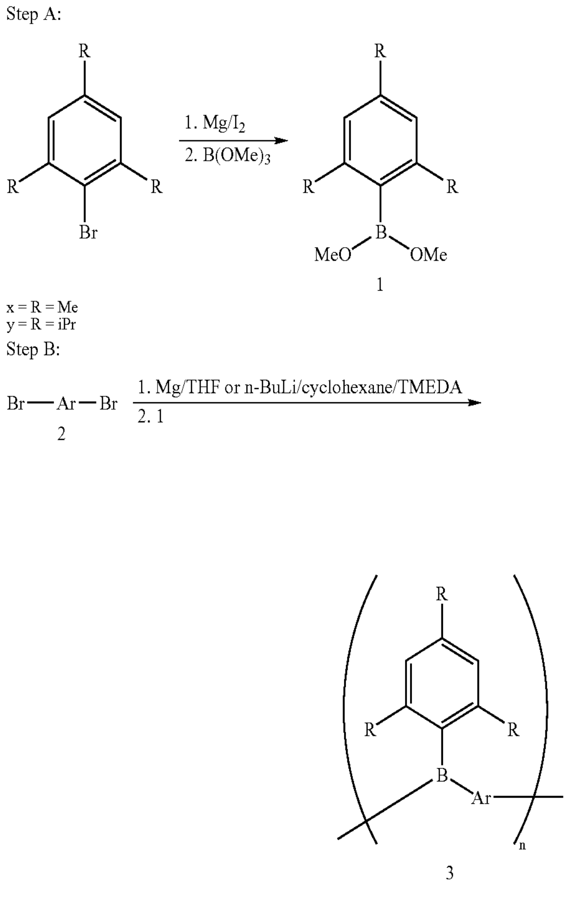
Synthesis of Poly(arylboranes)

[0104] Poly(arylborane)s were prepared in a two-step synthesis from commercially available starting materials according as illustrated in Scheme 3; first two different borane reagents were prepared with a mesityl or tripyl group (step A), then the borane reagent was polymerized with an aromatic dibromo compound after transforming it into its Grignard reagent (step B). Representative syntheses are given below.

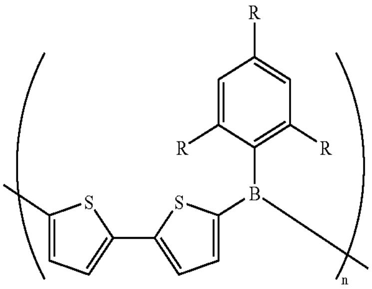
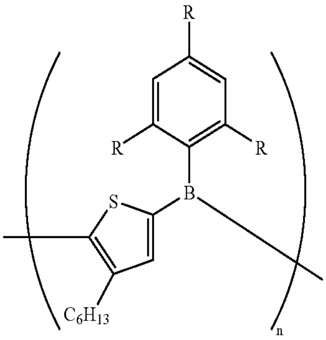
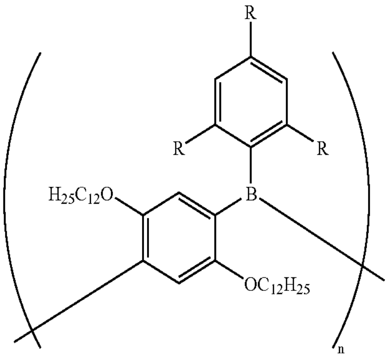
[0105] Scheme 4 shows the structure of the polymers prepared in this way, six with mesityl substituents on the boron atoms (x series) and seven with tripyl substituents (y series). Seven different dibromo-aromatic compounds were used as the starting materials: 5,5'-dibromobithiophene (polymers 3a), 2,5-dibromo-3-hexyl-thiophene (polymers 3b), 1,4-dibromo-2,5-bis(decyloxy)benzene (polymers 3c), 9,9-dihexyl-2,7-dibromofluorene (polymers 3d), 9,9-di-dodecyl-2,7-dibromofluorene (polymers 3e), 2,5-dibromo-3-dodecyl-thiophene (polymers 3f), and 9,9-diisooctyl-2,7-dibromofluorene (polymers 3g). The structures of all the intermediates and polymers were confirmed by ^{1}H-NMR analysis. The occurrence of the coupling reaction (step 2) was confirmed by the disappearance of the ^{1}H-NMR signal corresponding to the methoxy protons of the borane reagent at 3.6 ppm. The ^{1}H-NMR spectra of some of the polymers showed the presence of tetrahydrofuran (THF, the solvent used in the polymerization) in about one molar equivalent with respect to boron atoms suggesting that a significant fraction of the boron atoms of the polymers are coordinated to a molecule of solvent. Gel permeation chromatography results indicated that these materials have a broad molecular weight distribution ranging from a few repeat units to greater than 60 repeat units.

[0106] All of the prepared polymers were colored viscous oils with the exception of 3ay and 3by which were colored powdery solids. The polymers were at least partially soluble in THF and chloroform with exception of polymer 3dx, which was insoluble in these solvents. The fluorene derivatives 3dx, 3dy, 3ex, 3ey and 3gy were soluble in toluene or ortho-xylene and the thiophene derivatives were soluble in THF, acetonitrile and chloroform. All the prepared polymers were found to be air stable for an extended period of time (at least three months).

Scheme 3. Synthesis of poly(arylborane)s.



Scheme 4: Structure and properties of pi-conjugated organoboron polymers produced by the methods in Examples 3 and 4.

Structure	Mesityl derivative (3?x)	Tripyl Derivative (3?y)
 3ax (R = Me) 3ay (R = iPr)	Brown viscous oil Green fluoroscence	Brown powder Green fluorescence
 3bx (R = Me) 3by (R = iPr)	Brown viscous oil Blue-green fluorescence	Yellow-brown powder Green fluorescence
 3cx (R = Me) 3cy (R = iPr)	Brown viscous oil Blue-green fluorescence	Brown viscous oil Blue-green fluorescence

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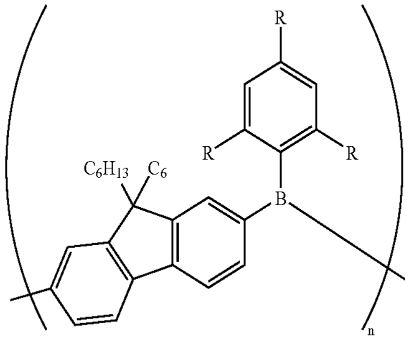
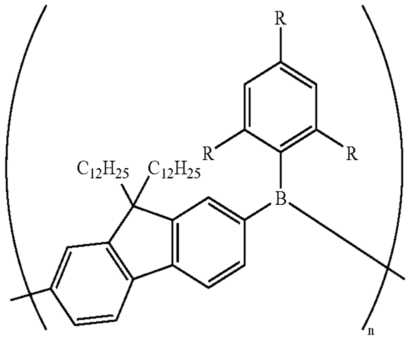
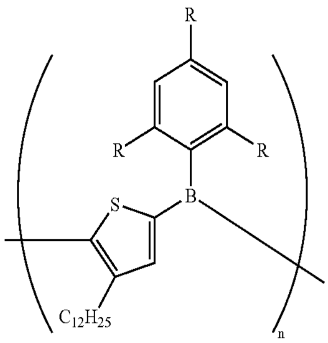
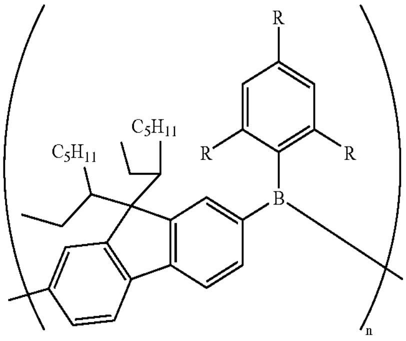
Scheme 4: Structure and properties of pi-conjugated organoboron polymers produced by the methods in Examples 3 and 4.

Structure	Mesityl derivative (3?x)	Tripyl Derivative (3?y)
 3dx (R = Me) 3dy (R = iPr)	Yellow viscous oil Blue fluorescence	Yellow viscous oil Blue fluorescence
 3ex (R = Me) 3ey (R = iPr)	Yellow viscous oil Blue fluorescence	Yellow viscous oil Blue fluorescence
 3fx (R = Me) 3fy (R = iPr)	Brown viscous oil Blue-green fluorescence	Brown viscous oil Blue-green fluorescence

-continued

Scheme 4: Structure and properties of pi-conjugated organoboron polymers produced by the methods in Examples 3 and 4.

Structure	Mesityl derivative (3?x)	Tripyl Derivative (3?y)
 3gx (R = Me) 3gy (R = iPr)		Yellow viscous oil Blue fluorescence

[0107] Elemental analysis data combined with ^{1}H-NMR data confirmed that all the polymers with the exception of 3by contained alternating aromatic and boron repeat units (i.e. had structure of the type of Scheme 1, formula b) and that the aromatic unit terminated the polymer at least on one side. Elemental analysis indicated that polymer 3by contained an excess of sulfur indicating that this polymer may contain short segments of homopolymerized 3-hexylthiophene (Scheme 1, formula h, with n equal to about 1 and m equal to about 3).

[0108] The photoluminescence emission spectra were recorded for each polymer using an excitation wavelength of 230 nm with a Shimadzu RF-1501 Spectrofluorometer in chloroform, THF, cyclohexane or dimethylsulfoxide (DMSO). The emission maxima in chloroform are given in Table 1. The location of the emission maxima were independent of the excitation wavelength, but showed a strong dependence on solvent polarity. For instance, 3by exhibited a blue shifted emission (lambda$_{max}$=492 nm) in less polar THF and red shifted emission in polar DMSO (lambda$_{max}$ 533 nm).

TABLE 1

Optical properties of organoboron polymers in chloroform.

	Absorbance (λ_{max})	Emission (λ_{max})
3ax	330, 440	394, 774
3ay	455, 477	481
3bx	340	443
3by	240, 300, 402	337, 431, 672, 859
3cx	230, 360	302, 464
3cy	450, 479	465
3dx	230, 320	419, 791

Synthesis of the Borane Reagents (1x,y)

[0109] Dimethoxymesitylborane (1x): To a stirred solution of magnesium turnings (3.11 g, 0.128 mol) and a crystal of iodine, 2-bromomesitylene (23.40 g, 0.118 mol) in THF (80 cm^3) was added dropwise at room temperature. The reaction was allowed to reflux for 3 hours. After the reaction mixture was cooled, it was added dropwise to an ether solution (80 cm^3) of trimethoxyborane (26 cm^3, 0.229 mol) at −15° C. The reaction was stirred at −15° C. for 3 hours, was warmed to room temperature, and left to stir overnight. The solution was then filtered under argon and the precipitated salts were washed with dry pentane (20 cm^3). The filtrates were combined, concentrated and distilled under vacuum to give dimethoxymesitylborane 1x. ^{1}H NMR (200 MHz, $CDCl_3$) 2.28 ppm (s, 6H), 2.30 ppm (s, 3H), 3.58 ppm (s, 6H), 6.84 ppm (s, 2H).

Synthesis of Polymers (3a-3e) in THF

[0110] To a clean dry round bottom flask, the borane reagent 1 (2 mmol, 1 eq.), the commercially available aromatic dibromide 2 (2 mmol,1 eq.) and magnesium turnings (4 mmol, 2 eq.) were added to 15 cm^3 of THF. The reaction was allowed to reflux for 24 to 72 hours depending on the substrates. Color change and photoluminescence generally indicated the completion of the reaction. The reaction was cooled to room temperature and a few drops of methanol were added. The solvent was removed and the obtained gum was dissolved in a minimal amount of chloroform and then precipitated in methanol. The insoluble part was centrifuged down and washed repeatedly with methanol. The solvent was removed in vacuo.

Synthesis of polymers (3a-3e) in cyclohexane

[0111] To a stirred solution of the commercially available dibromide 2 in anhydrous cyclohexane (dried over calcium hydride) 1 eq. of n-butyllithium (n-BuLi) and 1 eq. of tetramethylethylenediamine (TMEDA) were added at −15° C. The mixture was warmed to room temperature for 15 minutes (to ensure the formation of the lithio compound) and then cooled back to −15° C. A solution of the borane reagent 1 in cyclohexane was added to the reaction mixture dropwise over 30 minutes. The reaction was stirred at room temperature for 48 hours. Color change and photoluminescence indicated the completion of the reaction. Methanol (~10 cm^3) was added to quench the reaction. The solution was gravity filtered to remove all the precipitated salts. The solvent was removed in vacuo. ^{1}H-NMR showed no methanol in the sample, suggesting that the boron is free from coordination.

Synthesis of 3f and 3g in THF via lithio compound

[0112] To a stirred solution of the commercially available aromatic dibromide 2 in anhydrous THF was added 2 eq. of n-butyllithium (n-BuLi) at −78° C. The mixture was warmed to room temperature for 15 minutes (to ensure the formation of the di-lithiated compound) and then cooled back to ~78° C.

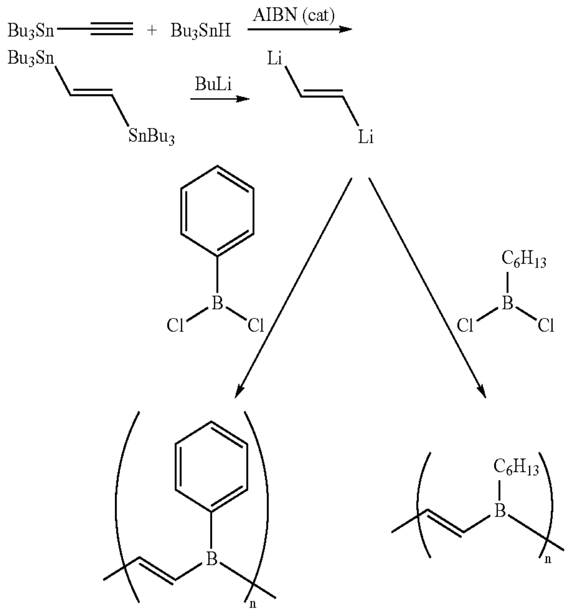
[0113] A solution of the borane reagent 1 in THF was added to the reaction mixture dropwise over 5 minutes. The reaction was stirred at room temperature for 48 hours. Color change and photoluminescence indicated the completion of the reaction. Methanol (~10 cm^3) was added to quench the reaction. The solution was gravity filtered to remove all the precipitated salts. The solvent was removed in vacuum. 3fx and 3fy were both brown gums and had blue-green photoluminescence. 3gy was a yellow gum and had blue photoluminescence.

Example 2

Synthesis of Poly(vinylborane)s

[0114] Poly(vinylborane)s were synthesized by reacting trans-1,2-bis(tributyltin)ethene with dichloroboranes (Scheme 5). ^{1}H-NMR and elemental analysis indicated that the desired products were formed.

Scheme 5



3h 3i

Synthesis of trans-1,2-bis(tributyltin)ethene

[0115] Tribuytyltin hydride (3.15 g, 10.8 mmol) and ethynyltributylstannane (3.4 g 10.8 mmol) and a catalytic amount of azobisisobutyronitrile (AIBN) were heated at 90° C. for 10 hours under an inert argon atmosphere. The reaction was vacuum distilled and the product was obtained in 95% yield.

Synthesis of Dichlorohexylborane

[0116] A solution of 1.91 g (16.25 mmol) of boron trichloride and 1.37 g (2.03 mL, 16.25 mmol) of 1-hexene in 5 cm^3 of pentane was stirred under argon at −78° C. for 15 minutes. Tributylsilane (3.26 g, 16.25 mmol) was added dropwise to the stirred reaction mixture and left to stir overnight at room temperature. Vacuum distillation yielded dichlorohexylborane in 90% yield.

Synthesis of 3i and 3h

[0117] To a stirred solution of the trans-1,2-bis(tributyltin)ethene in anhydrous THF was added 2 eq. of n-butyllithium (n-BuLi) at −78° C. The mixture was warmed to room temperature for 15 minutes (to ensure the formation of the di-lithiated compound) and then cooled back to −78° C. A solution of the dichloroborane reagent in THF was added to the reaction mixture dropwise over 5 minutes. The reaction was stirred at room temperature for 48 hours. Color change indicated the completion of the reaction. Methanol (~10 cm^3) was added to quench the reaction. The solution was gravity filtered to remove all the precipitated salts. The product was washed with chloroform and the solvent was removed in vacuum.

Example 3

Electrochemical Doping

[0118] To identify the n-type semiconducting behavior of these polymers, we cast thin films onto a platinum working electrode and subjected these films to cyclic voltammetry. FIG. **1** shows the reduction of the 3ay polymer under an argon atmosphere. N-type behavior is generally indicated by a facile reduction process (electron injection) of the film on the electrode surface. We observe a reduction process in our materials, however, this reduced or n-doped form of the material is unstable or highly soluble because no film remains on the electrode after reducing the film.

Example 4

Doping with Sodium Naphthalenide (NaNp)

[0119] To a solution of naphthalene (150 mg, 1.17 mmol) in anhydrous THF (~40 cm^3), was added sodium metal (30 mg, 1.3 mmol) at room temperature under an argon atmosphere. The mixture was allowed to stir for 2 hours. The resulting dark green solution was added dropwise via cannula to the stirred polymer in THF. The solution was allowed to stir for 30 minutes at room temperature.

[0120] The polymers 3cy, 3dx, 3ex, and 3ey dramatically changed color upon adding sodium naphthalenide from a pale yellow to a dark purple-black or greenish-black color and lost their characteristic photoluminescence, indicating that reduction of the polymers has occurred, presumably by formation of a radical anion. Upon exposing the polymers to air (even in trace amounts) the polymers returned to their original colors and regained their photoluminescence, confirming that the reduction is a reversible process, i.e. that this is effectively a doping process and not an irreversible chemical reduction of the polymer chain.

Example 5

Device Fabrication and Testing

[0121] Poly(bithienyl-tripylborane) (polymer 3ay) was used for the fabrication of OLED prototypes. The device design is shown in FIG. **2**C and comprises a layer of patterned ITO as the anode, a thin film of PEDOT/PSS as the hole injecting layer, our pi-conjugated organoboron polymer, and an aluminum cathode. The devices were fabricated using a clean room facility. ITO was patterned according to well-known photolithographic masking and etching methods. A 50 nm layer of PEDOT/PSS was spin coated at 2000 RPM from a freshly filtered commercially available solution of this material (Baytron P, electronic grade VP Al 4083, H. C. Starck) as a hole injection layer. After annealing at 100 C for 30 minutes, a 200 nm layer of the pi-conjugated organoboron polymer was spin coated at 2000 RPM from freshly filtered chloroform solution. To complete the devices, a top layer of aluminum was deposited by thermal vapor deposition on top of the organoboron polymer. The operation and light output of devices of were tested by application of a supplied voltage and evaluated by visual inspection. The anode and cathode were connected to the outputs of a 30 V DC power supply. The voltage between the anode and cathode was increased manually until there was an observed output of light. The voltage at which this occurred was recorded at 6-7 V for a number of devices tested. The color of the light output was yellow-green light. The turn-on voltage of this un-optimized device in air was around 6-7 Volts. Those skilled in the art know that device optimization will result in a decrease of the turn-on voltage. As known in the art, quantification of the light output and lifetime of the device can be readily measured employing art known techniques, and standard instrumentation such as a direct current (DC) source coupled to a metering device, a photodiode, a photomultiplier, an integration sphere and laboratory software. Complete OLED/PLED test systems are now commercially available (for example the Eclipse test system from Cambridge Display technologies, LTD.http//www.cdtltd.co.uk/).

Example 6

Device Fabrication and Testing

[0122] To test the electron transport properties of these materials we constructed a diode with the structure illustrated in FIG. **2**D, using a known light emitting polymer, poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV). The device structure consisted of glass\ITO\Baytron P\MEH-PPV\organoboron polymer 3by\aluminum. The current-voltage characteristics of these devices were monitored and light output was visually confirmed. FIG. **3** shows the current versus voltage data obtained for a device containing a ca. 100 nm thick 3by ETL.

Example 7

Synthesis of Poly(thiazole-mesitylborane) by reaction of dibromothiazole and 1x (Scheme 3) in THF

[0123] To a clean dry round bottom flask, the borane reagent 1x (8.2 mmol, 1 eq.), the commercially available aromatic dibromide, 2,5-dibromothiazole (8.2 mmol,1 eq.) and magnesium turnings (16.4 mmol, 2 eq.) were added to 24 cm^3 of anhydrous THF. The reaction was allowed to reflux under an inert atmosphere for 72 hours. Color change and polymer precipitation generally indicated the completion of the reaction. The reaction was cooled to room temperature and a few drops of methanol were added. The solvent was removed and the brown polymer obtained was dissolved in a minimal amount of N,N-dimethylformamide and then precipitated in methanol. The insoluble precipitate was centrifuged down and washed repeatedly with methanol. The solvent was removed in vacuo to provide the poly(thiazole-mesitylborane).

We claim:

1. A thin film, organic polymer electronic device which comprises at least one active layer containing a first thin film of a pi-conjugated organoboron polymer and at least two electrodes in contact with the active layer.

2. The device of claim 1 wherein the first thin film of the pi-conjugated organoboron polymer is 100 angstroms to 10000 angstroms in thickness.

3. The device of claim 1 wherein the first thin film of the pi-conjugated organoboron polymer is 100 angstroms to 3000 angstroms in thickness.

4. The device of claim 3 that exhibits current rectification or diode-like properties.

5. The device of claim 4 wherein the first thin film of a pi-conjugated organoboron polymer emits light under a voltage bias.

6. The device of claim 4 wherein the active layer of the device contains a second thin film containing a light-emitting polymer that is not a pi-conjugated organoboron polymer.

7. The device of claim 4 wherein the device contains a second thin film containing a light-emitting non-polymeric molecule.

8. The device of claim 1 wherein the first thin film comprises a pi-conjugated organoboron polymer blended with a light-emitting non-polymeric molecule.

9. The device of claim 1 wherein the first thin film comprises a pi-conjugated organoboron polymer blended with an organic or inorganic conducting or semiconducting material.

10. The device of claim 1 wherein the first thin film comprises a p-type conducting or semiconducting polymer blended with a pi-conjugated organoboron polymer.

11. The device of claim 1 wherein the first thin film comprises a p-type conducting or semiconducting molecule blended with a pi-conjugated organoboron polymer.

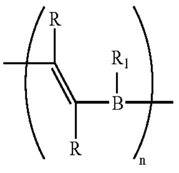
12. The device of claim 1 wherein the first thin film comprises inorganic p-type semiconducting particles mixed with a pi-conjugated organoboron polymer.

13. The device of claim 12 wherein the inorganic p-type semiconducting particles have at least one dimension less than 1000 angstroms.

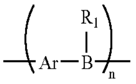
14. The device of claim 1 wherein the active layer comprises a second thin film of a dielectric material wherein the second thin film is in contact with one or more additional electrodes.

15. The device of claim 1 wherein the pi-conjugated organoboron polymer has any of the structures:

a)

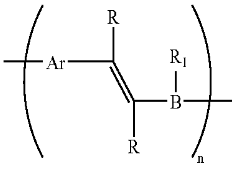


b)

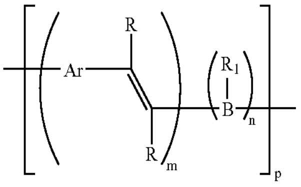


$\left(\mathrm{Ar}-\overset{R_1}{\overset{|}{B}}\right)_n$

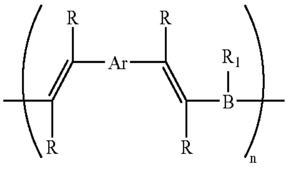
c)



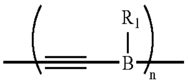
d)



e)

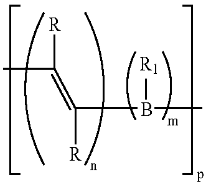


f)

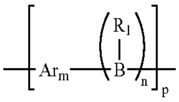


$\left(\equiv-\overset{R_1}{\overset{|}{B}}\right)_n$

g)

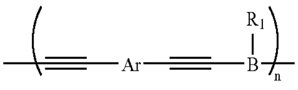


h)



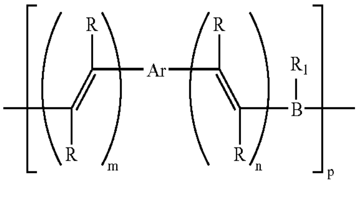
$\left[\mathrm{Ar}_m-\left(\overset{R_1}{\overset{|}{B}}\right)_n\right]_p$

i)



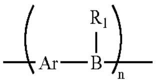
$\left(\equiv\mathrm{Ar}\equiv\overset{R_1}{\overset{|}{B}}\right)_n$

j)



wherein each R, independent of other R's in the repeating unit, and R_1, independent of any R's, can be hydrogen, deuterium, a halogen atom, or an organic radical, Ar represents a divalent aromatic radical which may optionally carry one or more other organic radical groups, substituent groups, and/or functional groups described herein and "n", "m" and "p" are integers representing the number of indicated moieties in a repeating unit or the average degree of polymerization of the polymer.

16. The device of claim 1 wherein the pi-conjugated organoboron polymer has the structure:



$\left(\mathrm{Ar}-\overset{R_1}{\overset{|}{B}}\right)_n$

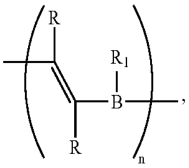
where:

Ar is a divalent radical resulting from the removal of two hydrogen atoms from benzene, naphthalene, diphenyl, pyridine, pyrimidine, triazine, pyrrole, N-alkylpyrroles, N-substituted pyrroles, 3-substituted pyrroles, furan, tetrazole, indole, purine, oxadiazole, quinoxaline, phenazine, N,N'-dialkylphenazines, phenothiazine, N-alkylphenothiazines, carbazole, N-alkylcarbazoles, thiophene, 3-alkylthiophenes, 3-substituted thiophenes, 3,4-disubstituted thiophenes, thienothiophene, substituted thienothiophenes, bithiophene, terthiophene, quaterthiophene, dialkyloxybenzenes, oxadiazole, fluorene, 9,9-dialkylfluorenes and their substituted derivatives;

R_1 is any aliphatic or aromatic radical; and

n is an integer.

17. The device of claim 1 wherein the pi-conjugated organoboron polymer has the structure:



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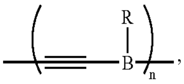
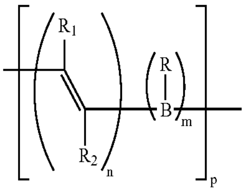


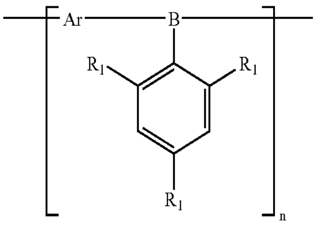
$\left(\equiv-\overset{R}{\overset{|}{B}}\right)_n$

, or



where each R, independent of other R's in the repeating unit, and R_1, independent of any R's, can be hydrogen, deuterium, a halogen atom, or an organic radical, and n, m and p are integer numbers indicating the average degree of polymerization of the polymer or the number of repeat units.

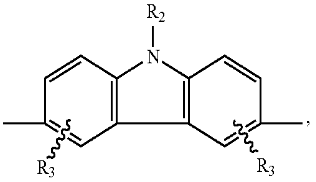
18. An organoboron polymer having the structure:



where Ar is a divalent radical resulting from the removal of two hydrogen atoms from, pyridine, pyrimidine, triazine, pyrrole, N-alkylpyrroles, N-substituted pyrroles, 3-substituted pyrroles, furan, tetrazole, indole, purine, oxadiazole, 1,5-diphenyl-oxadiazole, quinoxaline, phenazine, N,N'-dialkylphenazines, phenothiazine, N-alkylphenothiazines, carbazole, N-alkylcarbazoles, 3,4-disubstituted thiophenes, thienothiophene, substituted thienothiophenes, oxazole, fluorene, 9,9-dialkylfluorenes and their substituted derivatives; R_1, independent of other R_1 in the repeating unit are hydrogens, deuterium atoms, halogen atoms, linear or branched alkyl radicals which can be optionally substituted with one or more non-hydrogen substituents or functional groups; and n is an integer representing the average degree of polymerization of the polymer.

19. The polymer of claim 18 wherein Ar is selected from the group consisting of fluorenes, substituted fluorenes and 9,9, dialkylfluorenes.

20. The polymer of claim 18 wherein Ar is selected from the group consisting of



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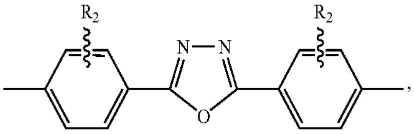

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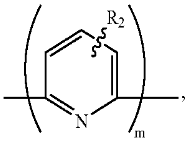

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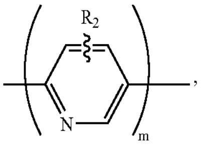
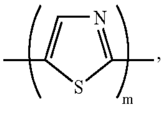


, and

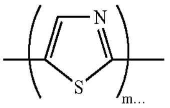


,

wherein R_2 and R_3, independently of each other, are hydrogens, deuterium atoms, halogen atoms, or linear or branched alkyl radicals, which can be optionally substituted with one or more non-hydrogen substituents or functional groups or R_2 represents an organic group that links two ring positions wherein R_2 can represent multiple independent substituents or functional groups on the rings and m is an integer ranging from 1 to 6.

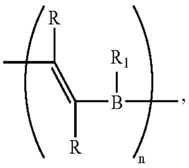
21. The polymer of claims **20** wherein m is an integer from 1 to 3.

22. The polymer of claims **20** wherein Ar is



23. The polymer of claim 20 wherein R_2 and R_3 are hydrogens, deuteriums or alkyl groups.

24. An organoboron polymer having structure:



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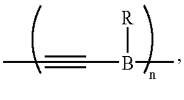
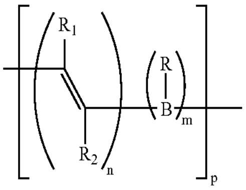
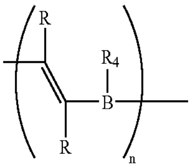


, or



where each R, R_1, R_2 independent of each other is a hydrogen, deuterium, a halogen atom, or an organic radical, and n, m and p are integer numbers indicating the average degree of polymerization of the polymer or the number of repeat units.

25. An organoboron polymer having the structure:



where R_4 is an optionally substituted saturated or unsaturated organic radical or an aromatic radical;

R, independent of other R's in the repeating unit, is hydrogen, deuterium, a halogen atom, a silyl radical, or an organic radical and n is an integer representing the average degree of polymerization of the polymer.

26. The polymer of claim 22 wherein each R is hydrogen or deuterium.

* * * * *

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公开(公告)号	US20070215864A1	公开(公告)日	2007-09-20
申请号	US11/378619	申请日	2006-03-17
[标]申请(专利权)人(译)	LUEBBEN SILVIAĐ SAPP SHAWN一个		
申请(专利权)人(译)	LUEBBEN SILVIAĐ SAPP SHAWN一个		
当前申请(专利权)人(译)	TDA研究公司.		
[标]发明人	LUEBBEN SILVIA DEVITO SAPP SHAWN A		
发明人	LUEBBEN, SILVIA DEVITO SAPP, SHAWN A.		
IPC分类号	H01L51/00 H01L51/54 C08G79/08		
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外部链接	Espacenet USPTO		

摘要(译)

Pi共轭有机硼聚合物，用于薄膜有机聚合物电子器件。聚合物含有芳族和/或不饱和重复单元和硼原子。硼原子的空的p-轨道与芳族或不饱和单体单元的π-共轭轨道系统共轭，使聚合物的π-共轭长度延伸穿过硼原子。 π-共轭的有机硼聚合物是缺电子的，因此表现出n型半导体特性，光致发光和电致发光。本发明提供薄膜有机聚合物电子器件，例如有机光伏电池（OPV），有机二极管，有机光电二极管，有机薄膜晶体管（TFT），有机场效应晶体管（OFET），可印刷或柔性电子器件，例如作为射频识别（RFID）标签，电子纸和印刷电路元件，有机发光二极管（OLED），聚合物发光二极管（PLED）和采用π共轭有机硼聚合物的能量存储装置。在OLED和PLED应用中，这些材料用作电子传输层（ETL）以提高器件效率。显示光电和电致发光的聚合物也可用作PLED中的发光材料。