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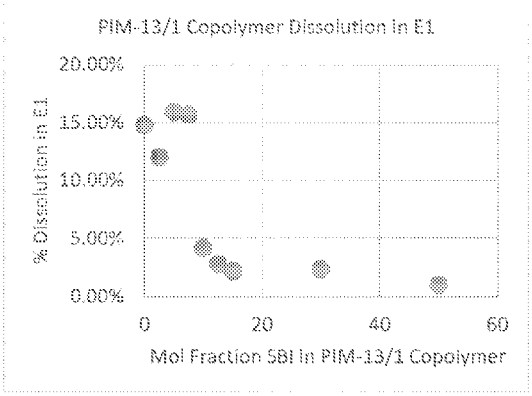
(54) Title: SPIROBISINDANE COPOLYMERS AND METHODS OF MAKING

(57) Abstract: The invention describes spirobisindane and spirobischromane copolymers of intrinsic microporosity for use in separators in electrochemical cells.

FIG. 1



WO 2025/006736 A2

SPIROBISINDANE COPOLYMERS AND METHODS OF MAKING

CROSS-REFERENCES TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Application No. 63/510,978, filed June 29, 2023, which is incorporated herein in its entirety for all purposes.

BACKGROUND OF THE INVENTION

[0002] Over the past decades, lithium-ion batteries (Li-ion batteries) have developed as the dominant high-energy chemistry due to their uniquely high energy density while maintaining high power and cyclability at acceptable prices. The energy density of current commercial Li-ion battery chemistries is however approaching the technology's theoretical limit, whereas demand for higher energy density batteries at lower unit cost is increasing with the rapid trend towards electrification of the transport and energy industries. There is indeed a need for batteries with improved capacity, long cycle life and high stability. Replacing graphite anodes in Li-ion with lithium metal anodes provides an opportunity to significantly increase the energy density of lithium batteries. However, after repetitive charge-discharge cycles, lithium metal batteries suffer from irreversible capacity loss driven by electrolyte depletion and loss of lithium inventory due to parasitic reactivity between the highly reactive lithium metal anode and the electrolyte components. This process contributes to local non-uniformities in the lithium anode surface, propagating further uneven plating and stripping and resulting in physically isolated "dead" lithium. Further, uneven lithium plating increases the risk of dendrite formation, which can cause thermal runaway resulting in catastrophic cell failure, posing a significant hurdle to the commercialization of lithium metal batteries. Mitigation of dendrite formation in lithium metal batteries is critical to enabling their safe, stable use in commercial applications.

[0003] Battery separators are a critical component of Li-ion batteries since they isolate the electrodes, providing ion transport through large pores filled with electrolyte and insulating electronic conductivity that would otherwise induce a short circuit. Whereas separators are not involved directly in cell reactions, their physical properties play an important role in determining the performance of the battery including energy density, power density, and safety. Importantly, separators' mechanical integrity throughout the entire lifetime of the battery cell is critical for prevention of internal short circuit.

[0004] Several porous membrane separator materials and composites are currently utilized in Li-ion batteries, such as separators made of made of polyolefin, for example polyethylene

(PE), polypropylene (PP) and polypropylene-polyethylene-polypropylene (PP/PE/PP), as well as ceramic-coated separators, which include PP, PE or multilayer porous substrates with at least one surface coated with a ceramic composite layer. As described in US 6,432,583 (Celgard Inc.), the ceramic composite layer is intended to block dendrite growth and to prevent electronic shorting. Although ceramic coated separators have been successfully utilized in Li-ion batteries to improve mechanical properties, their utility is limited in lithium metal batteries due to parasitic reactions induced at the anode by the binding materials which host the ceramic coatings.

[0005] WO 2018/106957 (Sepion Technologies, Inc et al.) describes the application of porous polymers (10-40% porosity, 0.5-2.0 nm pores) as templates that deliver solution-processed precursors of solid-state plus halide containing salts as a conformal coating between the Li-metal surface and the separator surface, in order to increase separator wettability and to increase Li-ion concentration and mobility at the separator-anode interface. The document also describes electrochemical cells including separators comprising several layers: a first polymer layer, comprising a planar species and a linker. The separator may also comprise a porous support made of PP or PE, laminated to the first polymer layer. The separator may also comprise a second membrane layer laminated to the porous support, such second layer comprising a ceramic material.

[0006] The use of Polymers of Intrinsic Microporosity (PIMs) as a selective battery membrane has been investigated. PIMs are composed of fused rings providing rigidity and sites of contortion, which may be provided by spiro-centers, by bent or bridged ring moieties, or by similar structural components which serve as a barrier preventing conformational relaxation of polymer chains. PIMs have been described and studied since 2006, as they create continuous networks of interconnected voids used as gas separation membranes, hydrogen storage materials, adsorbents and heterogeneous catalysts. The intrinsic microporosity of PIMs is defined as a continuous network of interconnected intermolecular voids, which form as a direct consequence of the shape and rigidity of the component macromolecules. Notably, the article of Li et al. (Nano Lett. 2015, 15, 5724-5729) describes the use of PIMs as a membrane platform for achieving high-flux, ion-selective transport in nonaqueous electrolytes.

[0007] As lithium metal is highly reactive, a solid-electrolyte-interphase (SEI) forms at the interface of the electrode and the adjacent electrolyte-filled separator. The composition and

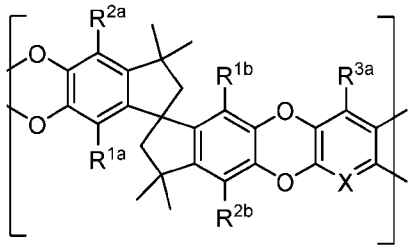
morphology of the SEI impacts the performance of the electrochemical cell. On one hand, the consumption of part of the lithium inventory inherent to the in situ SEI formation process reduces the coulombic efficiency of the electrochemical cell. On the other hand, optimal SEI limits the further decomposition of electrolyte components and improves lithium-ion transport at the electrode-separator interface, improving the cycling performance and service life of the batteries.

[0008] Artificial SEI layers have been investigated in order to limit lithium inventory and electrolyte component depletion processes at the surface of anode materials. One of the approaches is based on the use of a layer of PIMs which is coated on porous supports. Notably, WO 2020/037246 A1 (The Regents of the University of California) describes microporous ladder polymer according to the formula -[A-AB-B]- containing amine-functionalized monomer segments, amidoxime functionalized monomer segments, or a combination thereof, such microporous polymers being used in the separator which may comprise one or more support material such as glass fibers. Thin films of microporous polymers on porous supports, such as a polyolefin battery separator (e.g., Celgard) are described in the examples. The article of Chengyin Fu et al. (Nature Materials, April 2020) describes a lithium electrode laminated with a TBAF@PIM-1 coated polyolefin separator, i.e., a separator coated with microporous polymer host (e.g., PIM-1) in combination with tetrabutylammonium fluoride (TBAF), with the separator (Celgard 2325). The coated separator was then assembled in either Li–Li or Li–NMC-622 cells along with a carbonate electrolyte containing an ionizable lithium salt (e.g., LiPF6). The composites are described to act as dendrite-suppressing solid-ion conductors (SICs) in lithium metal batteries. What is needed are new polymers for separator coatings. Surprisingly, the present invention meets this and other needs.

BRIEF SUMMARY OF THE INVENTION

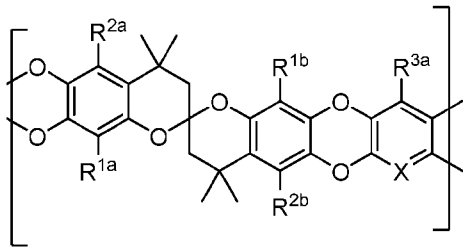
[0009] In one embodiment, the present invention provides a copolymer comprising a plurality of repeat units A and B, wherein

A and B are each independently a repeat unit having a structure of Formula I:



(I) ,

or a structure of Formula II:



(II) ,

wherein

A and B are each different;

R^{1a} and R^{1b} are each independently hydrogen, C_{1-6} alkyl, halogen, C_{1-6} haloalkyl, $-CH_2R^{1c}$ or $NR^{1a1}R^{1b1}$;

each R^{1a1} and R^{1b1} are independently hydrogen, C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, C_{1-6} alkyl-$NR^{1a2}R^{1b2}$, C_{3-10} cycloalkyl, or C_{1-6} alkyl-C_{3-10} cycloalkyl;

each R^{1a2} and R^{1b2} is independently hydrogen or C_{1-6} alkyl;

each R^{1c} is independently $NR^{1a1}R^{1b1}$, a 5-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 5-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S, wherein the heterocycloalkyl and heteroaryl are each independently substituted with 0, 1, 2, 3, 4 or 5 R^{1d} groups;

each R^{1d} is independently C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, halogen, C_{1-6} haloalkyl, -OH, =O, =NH, –CN, $–NO_2$, –C(O)H, $–C(O)R^{1e}$, $–C(O)OR^{1e}$, $–S(O)_2R^{1e}$, –C_{1-6} alkyl–(SO_3^-), $–OP(=O)(OR^{1e})_2$, a 3-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 3-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S;

R^{1e} is C_{1-6} alkyl or C_{1-6} hydroxyalkyl;

R^{2a} and R^{2b} are each independently hydrogen, C_{1-6} alkyl, halogen, C_{1-6} haloalkyl, $-CH_2R^{2c}$ or $NR^{2a1}R^{2b1}$;

each R^{2a1} and R^{2b1} are independently hydrogen, C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, C_{1-6} alkyl-$NR^{2a2}R^{2b2}$, C_{3-10} cycloalkyl, or C_{1-6} alkyl-C_{3-10} cycloalkyl;

each R^{2a2} and R^{2b2} is independently hydrogen or C_{1-6} alkyl;

each R^{2c} is independently $NR^{2a1}R^{2b1}$, a 5-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 5-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S, wherein the heterocycloalkyl and heteroaryl are each independently substituted with 0, 1, 2, 3, 4 or 5 R^{2d} groups;

each R^{2d} is independently C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, halogen, C_{1-6} haloalkyl, -OH, =O, =NH, –CN, $–NO_2$, –C(O)H, $–C(O)R^{2e}$, $–C(O)OR^{2e}$, $–S(O)_2R^{2e}$, $–C_{1-6}$ alkyl–(SO_3^-), $–OP(=O)(OR^{2e})_2$, a 3-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 3-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S;

R^{2e} is C_{1-6} alkyl or C_{1-6} hydroxyalkyl;

X is –N= or $–C(R^{3b})=$;

each R^{3a} and R^{3b} is independently hydrogen, C_{1-6} alkyl, halogen, C_{1-6} haloalkyl, –CN, or $–S(O)_2R^{3c}$; and

each R^{3c} is independently C_{1-6} alkyl, C_{1-6} haloalkyl, or C_{6-12} aryl, wherein each aryl is independently substituted with 0, 1, 2, 3, 4 or 5 groups each independently C_{1-6} alkyl or C_{1-6} haloalkyl.

[0010] In another embodiment, the present invention provides a coated separator comprising a porous membrane support; and a membrane layer on the porous membrane support comprising a copolymer of the present invention.

[0011] In another embodiment, the present invention provides an electrochemical cell comprising an anode; a cathode; a separator of the present invention; and an electrolyte.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] FIG. 1 shows the impact of copolymer composition on the percentage of polymer dissolved into E1 electrolyte from a 14 mg/mL mixture of that polymer in E1.

[0013] FIG. 2A and FIG. 2B shows the coated separator and multi-layer coated separator of the present invention.

[0014] FIG. 3A and FIG. 3B shows electrochemical cells of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

I. DEFINITIONS

[0015] The abbreviations used herein have their conventional meaning within the chemical and biological arts.

[0016] Where substituent groups are specified by their conventional chemical formulae, written from left to right, they equally encompass the chemically identical substituents that would result from writing the structure from right to left, e.g., $–CH_2O–$ is equivalent to $–OCH_2–$.

[0017] "Copolymer" refers to a polymer containing at least two distinct repeat units. The two distinct repeat units can be randomly distributed in the polymer chain to form a random copolymer where the repeat units are randomly located in the polymer chain, or organized into distinct blocks of the repeat units to form a block copolymer (e.g., AAAABBBBBAAA). Copolymer also includes an alternating copolymer where the repeat units are organized in an alternating fashion in the copolymer chain: ABABABABAB.

[0018] "Molecular weight" refers to the molecular weight of the polymer as determined by Size Exclusion Chromatograph (SEC), laser-light scattering, MALDI-TOF, or other methods. The molecular weight can be measured by the weight average or the number average. "Number average molecular weight" (M_N) refers to the mole fraction of molecules in the polymer sample, i.e., the total weight of polymer divided by the total number of molecules, or the arithmetic mean. "Weight average molecular weight" (M_W) refers to the weight fraction of molecules in the polymer sample, emphasizing the weight of the individual molecules such that the M_W is greater than the M_N. The ratio of the M_W/M_N, the polydispersity index, represents the distribution of molecular weights in the polymer.

[0019] "Alkyl" refers to a straight or branched, saturated, aliphatic radical having the number of carbon atoms indicated (i.e., C_{1-6} means one to six carbons). Alkyl can include any number of carbons, such as C_{1-2}, C_{1-3}, C_{1-4}, C_{1-5}, C_{1-6}, C_{1-7}, C_{1-8}, C_{1-9}, C_{1-10}, C_{2-3}, C_{2-4},

C_{2-5}, C_{2-6}, C_{3-4}, C_{3-5}, C_{3-6}, C_{4-5}, C_{4-6} and C_{5-6}. C_{1-6} alkyl includes, but is not limited to, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, isopentyl, hexyl, etc.

[0020] "Alkenyl" refers to a straight chain or branched hydrocarbon having at least 2 carbon atoms and at least one double bond and having the number of carbon atom indicated (i.e., C_{2-6} means to two to six carbons). Alkenyl can include any number of carbons, such as C_2, C_{2-3}, C_{2-4}, C_{2-5}, C_{2-6}, C_{2-7}, C_{2-8}, C_{2-9}, C_{2-10}, C_3, C_{3-4}, C_{3-5}, C_{3-6}, C_4, C_{4-5}, C_{4-5}, C_5, C_{5-6}, and C_6. Alkenyl groups can have any suitable number of double bonds, including, but not limited to, 1, 2, 3, 4, 5 or more. Examples of C_{2-4} alkenyl groups include, but are not limited to, vinyl (ethenyl), propenyl, isopropenyl, 1-butenyl, 2-butenyl, isobutenyl, or butadienyl.

[0021] "Alkynyl" refers to either a straight chain or branched hydrocarbon having at least 2 carbon atoms and at least one triple bond and having the number of carbon atom indicated (i.e., C_{2-6} means to two to six carbons). Alkynyl can include any number of carbons, such as C_2, C_{2-3}, C_{2-4}, C_{2-5}, C_{2-6}, C_{2-7}, C_{2-8}, C_{2-9}, C_{2-10}, C_3, C_{3-4}, C_{3-5}, C_{3-6}, C_4, C_{4-5}, C_{4-6}, C_5, C_{5-6}, and C_6. Examples of C_{2-4} alkynyl groups include, but are not limited to, acetylenyl, propynyl, 1-butynyl, 2-butynyl, isobutynyl, sec-butynyl, or butadiynyl.

[0022] "Hydroxyalkyl" or "alkylhydroxy" refers to an alkyl group, as defined above, where at least one of the hydrogen atoms is replaced with a hydroxy group. As for the alkyl group, hydroxyalkyl or alkylhydroxy groups can have any suitable number of carbon atoms, such as C_{1-6}. Exemplary C_{1-4} hydroxyalkyl groups include, but are not limited to, hydroxymethyl, hydroxyethyl (where the hydroxy is in the 1- or 2-position), hydroxypropyl (where the hydroxy is in the 1-, 2- or 3-position), hydroxybutyl (where the hydroxy is in the 1-, 2-, 3- or 4-position), 1,2-dihydroxyethyl, and the like.

[0023] "Alkyl-Alkoxy" or "alkoxyalkyl" refers to a radical having an alkyl component and an alkoxy component, where the alkyl component links the alkoxy component to the point of attachment. The alkyl component is as defined above, except that the alkyl component is at least divalent, an alkylene, to link to the alkoxy component and to the point of attachment. The alkyl component can include any number of carbons, such as C_{0-6}, C_{1-2}, C_{1-3}, C_{1-4}, C_{1-5}, C_{1-6}, C_{2-3}, C_{2-4}, C_{2-5}, C_{2-6}, C_{3-4}, C_{3-5}, C_{3-6}, C_{4-5}, C_{4-6} and C_{5-6}. In some instances, the alkyl component can be absent. The alkoxy component is as defined above. Examples of the alkyl-alkoxy group include, but are not limited to, 2-ethoxy-ethyl and methoxymethyl.

[0024] "Halogen" refers to fluorine, chlorine, bromine and iodine.

[0025] "Haloalkyl" refers to alkyl, as defined above, where some or all of the hydrogen atoms are replaced with halogen atoms. As for alkyl group, haloalkyl groups can have any suitable number of carbon atoms, such as C_{1-6}. For example, haloalkyl includes trifluoromethyl, fluoromethyl, 2,2,2-trifluoroethyl, etc. In some instances, haloalkyl includes the term "fluoroalkyl" that can be used to define an alkyl group where one or more hydrogen is replaced with fluorine.

[0026] "Cycloalkyl" refers to a saturated or partially unsaturated, monocyclic, fused bicyclic or bridged polycyclic ring assembly containing from 3 to 12 ring atoms, or the number of atoms indicated. Cycloalkyl can include any number of carbons, such as C_{3-6}, C_{4-6}, C_{5-6}, C_{3-8}, C_{4-8}, C_{5-8}, C_{6-8}, C_{3-9}, C_{3-10}, C_{3-11}, and C_{3-12}. Saturated monocyclic cycloalkyl rings include, for example, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, and cyclooctyl. Saturated bicyclic and polycyclic cycloalkyl rings include, for example, norbornane, [2.2.2] bicyclooctane, decahydronaphthalene and adamantane. Cycloalkyl groups can also be partially unsaturated, having one or more double or triple bonds in the ring. Representative cycloalkyl groups that are partially unsaturated include, but are not limited to, cyclobutene, cyclopentene, cyclohexene, cyclohexadiene (1,3- and 1,4-isomers), cycloheptene, cycloheptadiene, cyclooctene, cyclooctadiene (1,3-, 1,4- and 1,5-isomers), norbornene, and norbornadiene. When cycloalkyl is a saturated monocyclic C_{3-8} cycloalkyl, exemplary groups include, but are not limited to cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl. When cycloalkyl is a saturated monocyclic C_{3-6} cycloalkyl, exemplary groups include, but are not limited to cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl. Cycloalkyl groups can be substituted or unsubstituted.

[0027] "Alkyl-cycloalkyl" refers to a radical having an alkyl component and a cycloalkyl component, where the alkyl component links the cycloalkyl component to the point of attachment. The alkyl component is as defined above, except that the alkyl component is at least divalent, an alkylene, to link to the cycloalkyl component and to the point of attachment. In some instances, the alkyl component can be absent. The alkyl component can include any number of carbons, such as C_{1-6}, C_{1-2}, C_{1-3}, C_{1-4}, C_{1-5}, C_{2-3}, C_{2-4}, C_{2-5}, C_{2-6}, C_{3-4}, C_{3-5}, C_{3-6}, C_{4-5}, C_{4-6} and C_{5-6}. The cycloalkyl component is as defined within. Exemplary alkyl-cycloalkyl groups include, but are not limited to, methyl-cyclopropyl, methyl-cyclobutyl, methyl-cyclopentyl and methyl-cyclohexyl.

[0028] "Heterocycle" or "heterocycloalkyl" refers to a saturated ring system having from 3 to 12 ring members and from 1 to 4 heteroatoms of N, O and S. The heteroatoms can also be oxidized, such as, but not limited to, -S(O)- and -$S(O)_2$-. Heterocycloalkyl groups can include any number of ring atoms, such as, 3 to 6, 4 to 6, 5 to 6, 3 to 8, 4 to 8, 5 to 8, 6 to 8, 3 to 9, 3 to 10, 3 to 11, or 3 to 12 ring members. Any suitable number of heteroatoms can be included in the heterocycloalkyl groups, such as 1, 2, 3, or 4, or 1 to 2, 1 to 3, 1 to 4, 2 to 3, 2 to 4, or 3 to 4. The heterocycloalkyl group can include groups such as aziridine, azetidine, pyrrolidine, piperidine, azepane, azocane, quinuclidine, pyrazolidine, imidazolidine, piperazine (1,2-, 1,3- and 1,4-isomers), oxirane, oxetane, tetrahydrofuran, oxane (tetrahydropyran), oxepane, thiirane, thietane, thiolane (tetrahydrothiophene), thiane (tetrahydrothiopyran), oxazolidine, isoxazolidine, thiazolidine, isothiazolidine, dioxolane, dithiolane, morpholine, thiomorpholine, dioxane, or dithiane. The heterocycloalkyl groups can also be fused to aromatic or non-aromatic ring systems to form members including, but not limited to, indoline. Heterocycloalkyl groups can be unsubstituted or substituted. For example, heterocycloalkyl groups can be substituted with C_{1-6} alkyl or oxo (=O), among many others.

[0029] "Alkyl-heterocycloalkyl" refers to a radical having an alkyl component and a heterocycloalkyl component, where the alkyl component links the heterocycloalkyl component to the point of attachment. The alkyl component is as defined above, except that the alkyl component is at least divalent, an alkylene, to link to the heterocycloalkyl component and to the point of attachment. The alkyl component can include any number of carbons, such as C_{0-6}, C_{1-2}, C_{1-3}, C_{1-4}, C_{1-5}, C_{1-6}, C_{2-3}, C_{2-4}, C_{2-5}, C_{2-6}, C_{3-4}, C_{3-5}, C_{3-6}, C_{4-5}, C_{4-6} and C_{5-6}. In some instances, the alkyl component can be absent. The heterocycloalkyl component is as defined above. Alkyl-heterocycloalkyl groups can be substituted or unsubstituted.

[0030] "Aryl" refers to an aromatic ring system having any suitable number of ring atoms and any suitable number of rings. Aryl groups can include any suitable number of ring atoms, such as, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15 or 16 ring atoms, as well as from 6 to 10, 6 to 12, or 6 to 14 ring members. Aryl groups can be monocyclic, fused to form bicyclic or tricyclic groups, or linked by a bond to form a biaryl group. Representative aryl groups include phenyl, naphthyl and biphenyl. Other aryl groups include benzyl, having a methylene linking group. Some aryl groups have from 6 to 12 ring members, such as phenyl, naphthyl or biphenyl. Other aryl groups have from 6 to 10 ring members, such as phenyl or naphthyl.

Some other aryl groups have 6 ring members, such as phenyl. Aryl groups can be substituted or unsubstituted.

[0031] "Alkyl-aryl" refers to a radical having an alkyl component and an aryl component, where the alkyl component links the aryl component to the point of attachment. The alkyl component is as defined above, except that the alkyl component is at least divalent, an alkylene, to link to the aryl component and to the point of attachment. The alkyl component can include any number of carbons, such as C_{0-6}, C_{1-2}, C_{1-3}, C_{1-4}, C_{1-5}, C_{1-6}, C_{2-3}, C_{2-4}, C_{2-5}, C_{2-6}, C_{3-4}, C_{3-5}, C_{3-6}, C_{4-5}, C_{4-6} and C_{5-6}. In some instances, the alkyl component can be absent. The aryl component is as defined above. Examples of alkyl-aryl groups include, but are not limited to, benzyl and ethyl-benzene. Alkyl-aryl groups can be substituted or unsubstituted.

[0032] "Heteroaryl" refers to a monocyclic or fused bicyclic or tricyclic aromatic ring assembly containing 5 to 16 ring atoms, where from 1 to 5 of the ring atoms are a heteroatom such as N, O or S. The heteroatoms can also be oxidized, such as, but not limited to, N-oxide, -S(O)- and $-S(O)_2-$. The nitrogen atom(s) can also be quaternized. Heteroaryl groups can include any number of ring atoms, such as, 5 to 6, 5 to 8, 6 to 8, 5 to 9, 5 to 10, 5 to 11, or 5 to 12 ring members. Any suitable number of heteroatoms can be included in the heteroaryl groups, such as 1, 2, 3, 4, or 5, or 1 to 2, 1 to 3, 1 to 4, 1 to 5, 2 to 3, 2 to 4, 2 to 5, 3 to 4, or 3 to 5. Heteroaryl groups can have from 5 to 10 ring members and from 1 to 4 heteroatoms, from 5 to 8 ring members and from 1 to 4 heteroatoms, or from 5 to 8 ring members and from 1 to 3 heteroatoms, or from 5 to 6 ring members and from 1 to 4 heteroatoms, or from 5 to 6 ring members and from 1 to 3 heteroatoms. The heteroaryl group can include groups such as pyrrole, pyridine, imidazole, pyrazole, triazole, tetrazole, pyrazine, pyrimidine, pyridazine, triazine (1,2,3-, 1,2,4- and 1,3,5-isomers), thiophene, furan, thiazole, isothiazole, oxazole, and isoxazole. The heteroaryl groups can also be fused to aromatic ring systems, such as a phenyl ring, to form members including, but not limited to, benzopyrroles such as indole and isoindole, benzopyridines such as quinoline and isoquinoline, benzopyrazine (quinoxaline), benzopyrimidine (quinazoline), benzopyridazines such as phthalazine and cinnoline, benzothiophene, and benzofuran. Other heteroaryl groups include heteroaryl rings linked by a bond, such as bipyridine.

[0033] The heteroaryl groups can be linked via any position on the ring. For example, pyrrole includes 1-, 2- and 3-pyrrole, pyridine includes 2-, 3- and 4-pyridine, imidazole

includes 1-, 2-, 4- and 5-imidazole, pyrazole includes 1-, 3-, 4- and 5-pyrazole, triazole includes 1-, 4- and 5-triazole, tetrazole includes 1- and 5-tetrazole, pyrimidine includes 2-, 4-, 5- and 6- pyrimidine, pyridazine includes 3- and 4-pyridazine, 1,2,3-triazine includes 4- and 5-triazine, 1,2,4-triazine includes 3-, 5- and 6-triazine, 1,3,5-triazine includes 2-triazine, thiophene includes 2- and 3-thiophene, furan includes 2- and 3-furan, thiazole includes 2-, 4- and 5-thiazole, isothiazole includes 3-, 4- and 5-isothiazole, oxazole includes 2-, 4- and 5-oxazole, isoxazole includes 3-, 4- and 5-isoxazole, indole includes 1-, 2- and 3-indole, isoindole includes 1- and 2-isoindole, quinoline includes 2-, 3- and 4-quinoline, isoquinoline includes 1-, 3- and 4-isoquinoline, quinazoline includes 2- and 4-quinoazoline, cinnoline includes 3- and 4-cinnoline, benzothiophene includes 2- and 3-benzothiophene, and benzofuran includes 2- and 3-benzofuran.

[0034] Some heteroaryl groups include those having from 5 to 10 ring members and from 1 to 3 ring atoms including N, O or S, such as pyrrole, pyridine, imidazole, pyrazole, triazole, pyrazine, pyrimidine, pyridazine, triazine (1,2,3-, 1,2,4- and 1,3,5-isomers), thiophene, furan, thiazole, isothiazole, oxazole, isoxazole, indole, isoindole, quinoline, isoquinoline, quinoxaline, quinazoline, phthalazine, cinnoline, benzothiophene, and benzofuran. Other heteroaryl groups include those having from 5 to 8 ring members and from 1 to 3 heteroatoms, such as pyrrole, pyridine, imidazole, pyrazole, triazole, pyrazine, pyrimidine, pyridazine, triazine (1,2,3-, 1,2,4- and 1,3,5-isomers), thiophene, furan, thiazole, isothiazole, oxazole, and isoxazole. Some other heteroaryl groups include those having from 9 to 12 ring members and from 1 to 3 heteroatoms, such as indole, isoindole, quinoline, isoquinoline, quinoxaline, quinazoline, phthalazine, cinnoline, benzothiophene, benzofuran and bipyridine. Still other heteroaryl groups include those having from 5 to 6 ring members and from 1 to 2 ring atoms including N, O or S, such as pyrrole, pyridine, imidazole, pyrazole, pyrazine, pyrimidine, pyridazine, thiophene, furan, thiazole, isothiazole, oxazole, and isoxazole.

[0035] Some heteroaryl groups include from 5 to 10 ring members and only nitrogen heteroatoms, such as pyrrole, pyridine, imidazole, pyrazole, triazole, pyrazine, pyrimidine, pyridazine, triazine (1,2,3-, 1,2,4- and 1,3,5-isomers), indole, isoindole, quinoline, isoquinoline, quinoxaline, quinazoline, phthalazine, and cinnoline. Other heteroaryl groups include from 5 to 10 ring members and only oxygen heteroatoms, such as furan and benzofuran. Some other heteroaryl groups include from 5 to 10 ring members and only sulfur heteroatoms, such as thiophene and benzothiophene. Still other heteroaryl groups include from 5 to 10 ring members and at least two heteroatoms, such as imidazole, pyrazole,

triazole, pyrazine, pyrimidine, pyridazine, triazine (1,2,3-, 1,2,4- and 1,3,5-isomers), thiazole, isothiazole, oxazole, isoxazole, quinoxaline, quinazoline, phthalazine, and cinnoline.

[0036] "Alkyl-heteroaryl" refers to a radical having an alkyl component and a heteroaryl component, where the alkyl component links the heteroaryl component to the point of attachment. The alkyl component is as defined above, except that the alkyl component is at least divalent, an alkylene, to link to the heteroaryl component and to the point of attachment. The alkyl component can include any number of carbons, such as C_{0-6}, C_{1-2}, C_{1-3}, C_{1-4}, C_{1-5}, C_{1-6}, C_{2-3}, C_{2-4}, C_{2-5}, C_{2-6}, C_{3-4}, C_{3-5}, C_{3-6}, C_{4-5}, C_{4-6} and C_{5-6}. In some instances, the alkyl component can be absent. The heteroaryl component is as defined within. Alkyl-heteroaryl groups can be substituted or unsubstituted.

[0037] "Salt" refers to acid or base salts of the compounds used in the methods of the present invention. Salts of the basic compounds of the present invention are salts formed with acids, such as mineral acids, organic carboxylic, and organic sulfonic acids. Namely examples of salts include, but are not limited to, halogen salts, such as fluoride, chloride, bromide, and iodide salts, oxanion salts, such as chlorate, bromate, iodate, carbonate, nitrate, sulfate, or phosphate salts, carboxylic salts, such as fumerate or acetate salts, and sulfonate salts, such as trifluoromethylsulfonate salts

[0038] Also included are base addition salts such as sodium, potassium, calcium, ammonium, organic amino, or magnesium salt, or a similar salt, provided an acidic group consititutes part of the structure. Illustrative examples of salts are mineral acid (hydrochloric acid, hydrobromic acid, phosphoric acid, and the like) salts, organic acid (acetic acid, propionic acid, glutamic acid, citric acid and the like) salts, quaternary ammonium (methyl iodide, ethyl iodide, and the like) salts.

[0039] "Sulfonate" refers to a compound comprising $-S(O)_3^-$. Examples of sulfonates include, but are not limited to, $H_3C-S(O)_3^-$, $H_3CCH_2-S(O)_3^-$, or $F_3C-S(O)_3^-$. Sulfonates can include any chemical group attached to $-S(O)_3^-$ by a single bond.

[0040] "Carbonate" refers to a compound of the formula R'OC(O)OR", where R' and R" can be the same or different, or combined to form a cyclic structure. R' and R" can be alkyl, haloalkyl, or combined to form an alkylene that is optionally substituted with halogen. Representative carbonates include, but are not limited to, dimethyl carbonate (DMC) and fluoroethylene carbonate (FEC).

[0041] "Forming a reaction mixture" refers to the process of bringing into contact at least two distinct species such that they mix together and can react. It should be appreciated, however, that the resulting reaction product can be produced directly from a reaction between the added reagents or from an intermediate from one or more of the added reagents which can be produced in the reaction mixture.

[0042] "Solvent" refers to a substance, such as a liquid, capable of dissolving a solute. Solvents can be polar or non-polar, protic or aprotic. Polar solvents typically have a dielectric constant greater than about 5 or a dipole moment below about 1.0. Protic solvents are characterized by having a proton available for removal, such as by having a hydroxyl or carboxy group. Aprotic solvents lack such a group. Representative polar protic solvents include alcohols (methanol, ethanol, propanol, isopropanol, etc.), acids (formic acid, acetic acid, etc.) and water. Representative polar aprotic solvents include dichloromethane, chloroform, tetrahydrofuran, diethyl ether, acetone, ethyl acetate, dimethylformamide, dimethylacetamide, acetonitrile, and dimethyl sulfoxide. Representative non-polar solvents include alkanes (pentanes, hexanes, etc.), benzene, toluene, and 1,4-dioxane. Other solvents are useful in the present invention.

[0043] "Electrode" refers to an electrically conductive material in a circuit that is in contact with a nonmetallic part of the circuit, such as the electrolyte. The electrode can be a positive electrode or cathode, the electrode where reduction occurs. The electrode can be a negative electrode or anode, the electrode where oxidation occurs.

[0044] "Anode" refers to a negative electrode, as described above.

[0045] "Cathode" refers to a positive electrode, as described above.

[0046] "Electrolyte" refers to a solution of the electrochemical cell that includes ions, such as metal ions and protons as well as anions, that provides ionic communication between the positive and negative electrodes.

[0047] "Electrolyte Solvent" refers to the molecules solvating ions in the liquid electrolyte, such as small organic carbonates or ethereal molecules, that enable diffusion of ions in the electrolyte. The Electrolyte Solvent may also be an ionic liquid or a gas at standard temperature and pressure.

[0048] "Separator" refers to an electrically insulating membrane between the positive and negative electrodes to prevent electrical shorts, i.e., provides electronic isolation. The

separator also allows the ions to move between the positive and anode electrodes. The separator can include any suitable polymeric or inorganic material that is electrically insulating. The separator can include several layers including one or more membrane layers, and a porous support material for the membrane layers.

[0049] "First polymer layer" refers to a layer of the separator that is permeable to a first species of the electrolyte while substantially impermeable to liquid electrolyte. The membrane layer can be of any suitable material that can provide the selective permeability, such as composites of microporous polymers and inorganic materials. "Substantially impermeable" refers to less than 10% of the electrolyte solvent passing through the membrane layer, or less than 1%, or less than 0.1%, or less than 0.01%, or less than 0.001% of the liquid electrolyte passing through the membrane layer.

[0050] "Oxide" refers to a chemical compound having an oxygen, such as metal oxides or molecular oxides.

[0051] "Pore size" or "pore diameter" refers to the average diameter of interstitial space not occupied by the pore forming material. This may include, but is not limited to, the space remaining between polymer chains due to inefficient packing, the space remaining between organic linkers and metal ions in a metal-organic framework, the space between layers and within the holes of stacked 2D material, and the space left in an amorphous or semi-crystalline carbon due to unaligned covalent bonding. The pore size may also change once wetted with electrolyte or it may stay the same.

[0052] "Surface area" refers to the surface area of a porous material as measured by a variety of methods, such as nitrogen adsorption BET.

[0053] "Microporous polymer" refers to an amorphous glassy polymer having interconnected pores with an average diameter of less than 10 nm, or less than 5, 4, 3, 2, or less than 1 nm.

[0054] "Microporosity" refers to a layer of the membrane comprising pores of less than or equal to 2 nm in size.

[0055] "Intrinsic microporosity" refers to a polymer providing a continuous network of interconnected intermolecular voids (suitably of less than or equal to 4 nm in size), which forms as a direct consequence of the shape and rigidity of at least a proportion of the component monomers of the polymer. As will be appreciated by a person skilled in the art,

intrinsic microporosity arises due to the structure of the monomers used to form the polymer and, as the term suggests, it is an intrinsic property of a polymer formed from such monomers.

[0056] It is understood that the network polymers disclosed herein have a certain property (i.e. intrinsic microporosity). Disclosed herein are certain structural requirements in the monomers used for giving a polymer performing the disclosed function, and it is understood that there are a variety of structures that can perform the same function that are related to the disclosed monomer structures, and that these structures will typically achieve the same result.

[0057] "Metal" refers to elements of the periodic table that are metallic and that can be neutral, or negatively or positively charged as a result of having more or fewer electrons in the valence shell than is present for the neutral metallic element. Metals useful in the present invention include the alkali metals, alkali earth metals, transition metals and post-transition metals. Alkali metals include Li, Na, K, Rb and Cs. Alkaline earth metals include Be, Mg, Ca, Sr and Ba. Transition metals include Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg and Ac. Post-transition metals include Al, Ga, In, Tl, Ge, Sn, Pb, Sb, Bi, and Po. Rare earth metals include Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. One of skill in the art will appreciate that the metals described above can each adopt several different oxidation states, all of which are useful in the present invention. In some instances, the most stable oxidation state is formed, but other oxidation states are useful in the present invention.

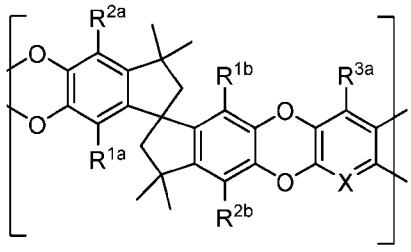
[0058] "Porous support" refers to any suitable material that is capable of supporting the membrane layer of the present invention, and is permeable to the electrolyte.

[0059] "Laminated" refers to the deposition of one layer on another, such as the microporous polymer layer or first polymer layer onto the porous support.

II. COPOLYMERS

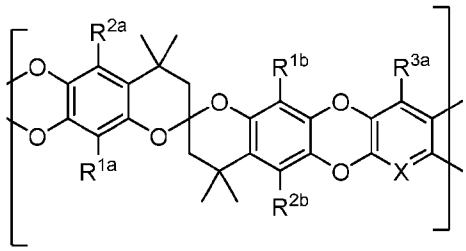
[0060] The present invention provides copolymers of spiro-bisindane and/or spiro-bischromane monomer repeat units. In some embodiments, the present invention provides a copolymer comprising a plurality of repeat units A and B, wherein

A and B are each independently a repeat unit having a structure of Formula I:



(I) ,

or a structure of Formula II:



(II) ,

wherein

A and B are each different;

R^{1a} and R^{1b} are each independently hydrogen, C_{1-6} alkyl, halogen, C_{1-6} haloalkyl, $-CH_2R^{1c}$ or $NR^{1a1}R^{1b1}$;

each R^{1a1} and R^{1b1} are independently hydrogen, C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, C_{1-6} alkyl-$NR^{1a2}R^{1b2}$, C_{3-10} cycloalkyl, or C_{1-6} alkyl-C_{3-10} cycloalkyl;

each R^{1a2} and R^{1b2} is independently hydrogen or C_{1-6} alkyl;

each R^{1c} is independently $NR^{1a1}R^{1b1}$, a 5-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 5-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S, wherein the heterocycloalkyl and heteroaryl are each independently substituted with 0, 1, 2, 3, 4 or 5 R^{1d} groups;

each R^{1d} is independently C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, halogen, C_{1-6} haloalkyl, -OH, =O, =NH, –CN, $–NO_2$, –C(O)H, $–C(O)R^{1e}$, $–C(O)OR^{1e}$, $–S(O)_2R^{1e}$, –C_{1-6} alkyl–(SO_3^-), $–OP(=O)(OR^{1e})_2$, a 3-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 3-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S;

R^{1e} is C_{1-6} alkyl or C_{1-6} hydroxyalkyl;

R^{2a} and R^{2b} are each independently hydrogen, C_{1-6} alkyl, halogen, C_{1-6} haloalkyl, $-CH_2R^{2c}$ or $NR^{2a1}R^{2b1}$;

each R^{2a1} and R^{2b1} are independently hydrogen, C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, C_{1-6} alkyl-$NR^{2a2}R^{2b2}$, C_{3-10} cycloalkyl, or C_{1-6} alkyl-C_{3-10} cycloalkyl;

each R^{2a2} and R^{2b2} is independently hydrogen or C_{1-6} alkyl;

each R^{2c} is independently $NR^{2a1}R^{2b1}$, a 5-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 5-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S, wherein the heterocycloalkyl and heteroaryl are each independently substituted with 0, 1, 2, 3, 4 or 5 R^{2d} groups;

each R^{2d} is independently C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, halogen, C_{1-6} haloalkyl, -OH, =O, =NH, –CN, $–NO_2$, –C(O)H, $–C(O)R^{2e}$, $–C(O)OR^{2e}$, $–S(O)_2R^{2e}$, $–C_{1-6}$ alkyl–(SO_3^-), $–OP(=O)(OR^{2e})_2$, a 3-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 3-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S;

R^{2e} is C_{1-6} alkyl or C_{1-6} hydroxyalkyl;

X is –N= or $–C(R^{3b})=$;

each R^{3a} and R^{3b} is independently hydrogen, C_{1-6} alkyl, halogen, C_{1-6} haloalkyl, –CN, or $–S(O)_2R^{3c}$; and

each R^{3c} is independently C_{1-6} alkyl, C_{1-6} haloalkyl, or C_{6-12} aryl, wherein each aryl is independently substituted with 0, 1, 2, 3, 4 or 5 groups each independently C_{1-6} alkyl or C_{1-6} haloalkyl.

[0061] The copolymer can be a random copolymer, an alternating copolymer or a block copolymer. In some embodiments, the copolymer is a random copolymer.

[0062] The copolymers of the present invention can include additional repeat unit C, where repeat unit C is different from repeat units A and B. The copolymers of the present invention can include additional repeat unit D, where repeat unit D is different from repeat units A, B and C. The copolymers of the present invention can include additional repeat unit E, where repeat unit E is different from repeat units A, B, C and D. The copolymers of the present invention can include additional repeat unit F, where repeat unit F is different from repeat

units A, B, C, D and E. Additional repeat units can be present in the copolymers of the present invention.

[0063] In some embodiments, the copolymer of the present invention is the copolymer having the structure of Formula J:

$$[A]_x\text{-}[B]_y\text{-}[C]_{z1}\text{-}[D]_{z2}\text{-}[E]_{z3}\text{-}[F]_{z4} \quad (J) \quad ,$$

wherein: repeat units A, B, C, D, E and F are each independently the structure of Formula I or the structure of Formula II, wherein A, B, C, D, E and F are each different; subscript x and y are each independently an integer from 1 to 1000; and each subscript z1, z2, z3 and z4 is independently an integer from 0 to 1000.

[0064] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, wherein A, B, C, D, E and F are each independently a repeat unit having the structure of Formula I.

[0065] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, having the structure of Formula J-1:

$$[A]_x\text{-}[B]_y\text{-}[C]_{z1} \quad (J\text{-}1)$$

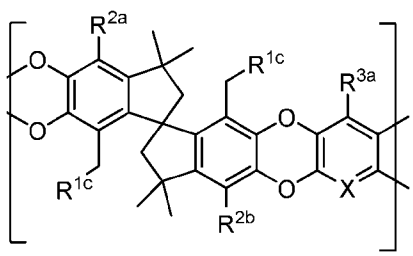
wherein A, B and C are each different; subscript x and y are each independently an integer from 1 to 1000; and subscript z1 is independently an integer from 0 to 1000.

[0066] In some embodiments, the copolymer of the present invention is the copolymer of Formula J or J-1, having the structure of Formula J-2:

$$[A]_x\text{-}[B]_y \quad (J\text{-}2)$$

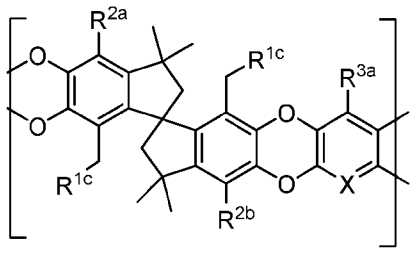
wherein A, B and C are each different; and subscript x and y are each independently an integer from 1 to 1000.

[0067] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein A is a repeat unit having the structure of Formula Ia:



(Ia) .

[0068] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein each repeat unit of Formula I independently has the structure of Formula Ia:



(Ia) .

[0069] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein each R^{1c} is independently $NR^{1a1}R^{1b1}$, or a 5- or 6- membered heterocycloalkyl having 1 or 2 heteroatoms each independently N, O or S, wherein the heterocycloalkyl is independently substituted with 0 or 1 R^{1d} groups.

[0070] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein each R^{1c} is independently a 5- or 6- membered heterocycloalkyl having 1 or 2 heteroatoms each independently N, O or S, wherein the heterocycloalkyl is independently substituted with 0 or 1 R^{1d} groups. In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein each R^{1c} is independently a 6-membered heterocycloalkyl having 1 or 2 heteroatoms each independently N, O or S. In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein each R^{1c} is morpholine, thiomorpholine, or piperazine, each independently substituted with 0 or 1 R^{1d} groups. In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein each R^{1c} is morpholine, or thiomorpholine.

[0071] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein each R^{1c} is independently $NR^{1a1}R^{1b1}$.

[0072] In some embodiments, the copolymer of the present invention is the copolymer of J, J-1, or J-2, wherein each R^{1a1} and R^{1b1} are independently hydrogen, C_{1-6} alkyl, C_{2-6} alkenyl, or C_{2-6} alkynyl. In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein each R^{1a1} and R^{1b1} are independently C_{1-3} alkyl or C_{2-4} alkenyl. In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein each R^{1a1} and R^{1b1} are independently methyl, ethyl, or n-propyl. In some embodiments, the copolymer of the present invention is the

copolymer of Formula J, J-1, or J-2, wherein each R^{1a1} and R^{1b1} are independently ethenyl, propenyl, n-butenyl, s-butenyl, or isobutenyl. In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein each R^{1a1} and R^{1b1} are independently methyl or propenyl. In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein each R^{1c} is independently methylallylamine or diallylamine.

[0073] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein each R^{1d} is independently C_{1-6} alkyl, $-C(O)R^{1e}$, $-C(O)OR^{1e}$, $-S(O)_2R^{1e}$, $-C_{1-6}$ alkyl$-(SO_3^-)$, or $-OP(=O)(OR^{1e})_2$. In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein each R^{1d} is independently C_{1-6} alkyl, $-S(O)_2R^{1e}$, or $-C_{1-6}$ alkyl$-(SO_3^-)$. In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein each R^{1d} is independently $-S(O)_2R^{1e}$.

[0074] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein R^{1e} is C_{1-6} alkyl. In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein R^{1e} is C_{1-3} alkyl. In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein R^{1e} is methyl, ethyl, or n-propyl.

[0075] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein each R^{1d} is independently $-S(O)_2-C_{1-3}$ alkyl.

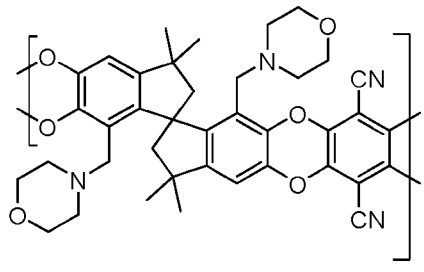
[0076] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein R^{2a} and R^{2b} are each hydrogen.

[0077] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein R^{3a} is –CN.

[0078] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein X is $-C(R^{3b})=$. In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein R^{3b} is –CN.

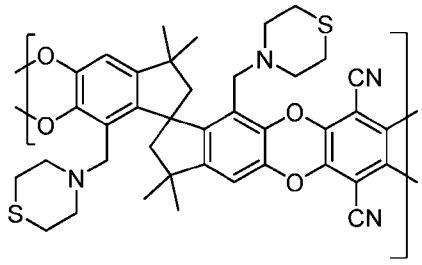
[0079] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein A is

PIM-13 having the structure:

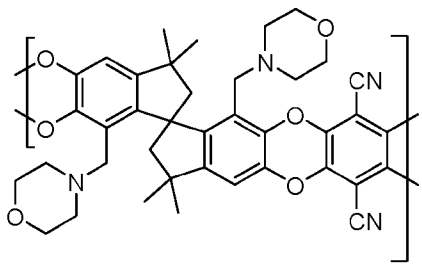


, or

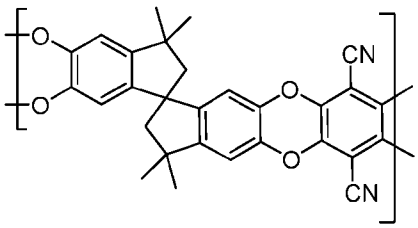
PIM-13S having the structure:



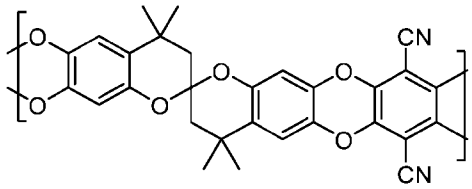
[0080] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein A is PIM-13 having the structure:



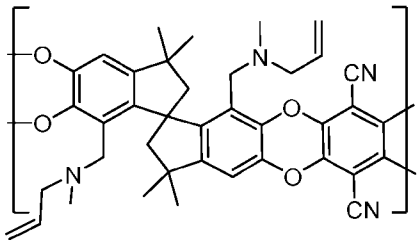
[0081] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein B is PIM-1:



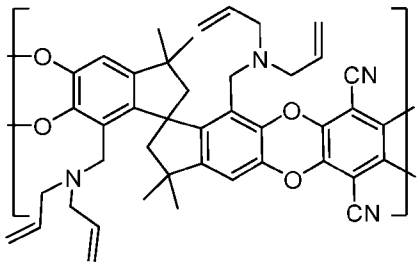
[0082] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein B is SBC:



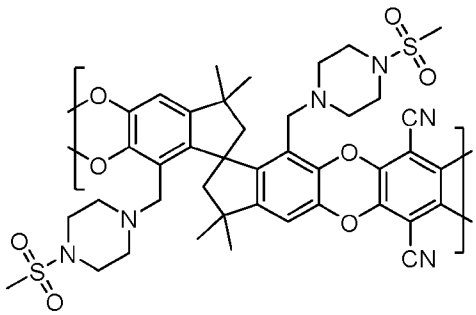
[0083] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein B is PIM-MAA:



[0084] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein B is PIM-DAA:



[0085] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein C is PzMeSO2 having the structure:



[0086] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein: subscript x is an integer from 10 to 500, subscript y is an integer from 1 to 200, and each subscript z1, z2, z3 and z4 is independently is an integer from 0 to 100. In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein subscript x is an integer from 10 to 300, subscript y is an

integer from 1 to 200, and each subscript z1, z2, z3 and z4 is independently is an integer from 0 to 100.

[0087] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein each subscript z1, z2, z3 and z4 is 0. In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein each subscript z1, z2, z3 and z4 is independently an integer from 1 to 100.

[0088] The copolymer of the present invention can have a molar ratio of subscript x to subscript y is from about 10:90 to about 99:1, or about 20:80 to about 98:2, about 25:75 to about 98:2, about 30:70 to about 97.5:2.5, about 50:50 to about 97.5:2.5, about 50:50 to about 95:5, or about 50:50 to about 90:10. Other molar ratios of subscript x to subscript y is about 99:1, or about 98.5:1.5, 98:2, 97.5:2.5, 97:3, 96.5:3.5, 96:4, 95.5:4.5, 95:5, 94:6, 93:7, 92:8, 91:9, 90:10, 87.5:12.5, 85:15, 82.5:17.5, 80:20, 75:25, 70:30, 65:35, 60:40, 55:45, 50:50, 45:55, 40:60, 35:65, 30:70, 25:75, 20:80, 15:85, 10:90, 5:95, or about 1:99. In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein the molar ratio of subscript x to subscript y is from about 10:90 to about 99:1.

[0089] The copolymers of the present invention can have a weight average molecular weight (M_w) or number average molecular weight of from 1 kg/mol to 1000 kg/mol, or 1 kDa to 1000 kDa. The copolymers can have a weight average molecular weight (M_w) or number average molecular weight of from 10 kg/mol to 500 kg/mol, or from 20 kg/mol to 400 kg/mol, or from 30 kg/mol to 300 kg/mol, or from 40 kg/mol to 200 kg/mol, or from 50 kg/mol to 175 kg/mol, or from 50 kg/mol to 150 kg/mol. In some embodiments, the copolymer of the present invention is the copolymer wherein the weight average molecular weight (M_w) of the copolymer is from 1 kg/mol to 1000 kg/mol. In some embodiments, the copolymer of the present invention is the copolymer wherein the weight average molecular weight (M_w) of the copolymer is from 10 kg/mol to 500 kg/mol. In some embodiments, the copolymer of the present invention is the copolymer wherein the weight average molecular weight (M_w) of the copolymer is from 35 kg/mol to 160 kg/mol. In some embodiments, the copolymer of the present invention is the copolymer wherein the weight average molecular weight (M_w) of the copolymer is from 55 kg/mol to 150 kg/mol. The molecular weight of the polymer can be calculated by a variety of methods including, but not limited to, size exclusion chromatography (SEC), laser light scattering, MALDI-TOF, and others. Molecular weight determination of the polymers in the present invention is made using a Waters APC

SEC (Size Exclusion Chromatograph) system with RI detector compared against polystyrene standards for relative molecular weight, or a Malvern OMNISEC GPC with triple detector for absolute molecular weight determination.

[0090] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein the weight average molecular weight (M_w) of the copolymer is from 1 kg/mol to 1000 kg/mol. In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein the weight average molecular weight (M_w) of the copolymer is from 10 kg/mol to from 500 kg/mol. In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein the weight average molecular weight (M_w) of the copolymer is from 35 kg/mol to 160 kg/mol. In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein the weight average molecular weight (M_w) of the copolymer is from 55 kg/mol to 150 kg/mol.

[0091] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein A is PIM-13, and B is PIM-1. In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein A is PIM-13S, and B is PIM-1. In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein A is PIM-13, and B is SBC.

[0092] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein A is PIM-13, and B is PIM-MAA. In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein A is PIM-13, and B is PIM-DAA.

[0093] In some embodiments, the copolymer of the present invention is the copolymer of Formula J or J-1, wherein A is PIM-13, B is PIM-1, and C is $PzMeSO_2$.

[0094] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, having the structure:

$[PIM\text{-}13]_x\text{-}[PIM\text{-}1]_y$,

$[PIM\text{-}13S]_x\text{-}[PIM\text{-}1]_y$,

$[PIM\text{-}13]_x\text{-}[SBC]_y$,

$[PIM\text{-}13]_x\text{-}[PIM\text{-}MAA]_y$,

$[PIM\text{-}13]_x\text{-}[PIM\text{-}DAA]_y$, or

$[PIM\text{-}13]_x\text{-}[PIM\text{-}1]_y\text{-}[PzMeSO_2]_{z1}$.

[0095] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, having the structure:

$[PIM\text{-}13]_x\text{-}[PIM\text{-}1]_y$,

$[PIM\text{-}13S]_x\text{-}[PIM\text{-}1]_y$,

$[PIM\text{-}13]_x\text{-}[SBC]_y$, or

$[PIM\text{-}13]_x\text{-}[PIM\text{-}1]_y\text{-}[PzMeSO2]_{z1}$.

[0096] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, having the structure:

$[PIM\text{-}13]_x\text{-}[PIM\text{-}1]_y$,

wherein subscript x is from about 30 to about 150; and subscript y is from about 1 to about 120.

[0097] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, having the structure:

$[PIM\text{-}13S]_x\text{-}[PIM\text{-}1]_y$,

wherein subscript x is from about 50 to about 200; and subscript y is from about 1 to about 60.

[0098] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein the copolymer is a random copolymer having the structure:

a) $[PIM\text{-}13]_x\text{-}[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 97.5:2.5, and
the weight average molecular weight (M_w) of the random copolymer is about 68 kg/mol,

b) $[PIM\text{-}13]_x\text{-}[PIM\text{-}1]_y$, wherein
wherein the ratio of subscript x to subscript y is about 95:5, and
the weight average molecular weight (M_w) of the random copolymer is about 67 kg/mol,

c) $[PIM\text{-}13]_x\text{-}[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 92.5:7.5, and
the weight average molecular weight (M_w) of the random copolymer is about 76 kg/mol,

d) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 90:10, and
the weight average molecular weight (M_w) of the random copolymer is about 65 kg/mol,

e) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 87.5:12.5, and
the weight average molecular weight (M_w) of the random copolymer is about 80 kg/mol,

f) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 85:15, and
the weight average molecular weight (M_w) of the random copolymer is about 95 kg/mol,

g) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 82.5:17.5, and
the weight average molecular weight (M_w) of the random copolymer is about 73 kg/mol,

h) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 80:20, and
the weight average molecular weight (M_w) of the random copolymer is about 80 kg/mol,

i) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 70:30,

j) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 50:50, and
the weight average molecular weight (M_w) of the random copolymer is about 101 kg/mol,

k) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 30:70, and
the weight average molecular weight (M_w) of the random copolymer is about 78 kg/mol,

l) $[PIM\text{-}13S]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 90:10, and
the weight average molecular weight (M_w) of the random copolymer is about 61 kg/mol,

m) $[PIM\text{-}13S]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 85:15, and
the weight average molecular weight (M_w) of the random copolymer is about 116 kg/mol,

n) $[PIM\text{-}13S]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 80:20, and
the weight average molecular weight (M_w) of the random copolymer is about 144 kg/mol,

o) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$-$[PzMeSO_2]_{z1}$, wherein
the ratio of subscript x to subscript y to subscript z1 is about 80:10:10, and
the weight average molecular weight (M_w) of the random copolymer is about 60 kg/mol,

p) $[PIM\text{-}13]_x$-$[SBC]_y$, wherein
the ratio of subscript x to subscript y is about 90:10, and
the weight average molecular weight (M_w) of the random copolymer is about 85 kg/mol,

q) $[PIM\text{-}13]_x$-$[SBC]_y$, wherein
the ratio of subscript x to subscript y is about 70:30, and
the weight average molecular weight (M_w) of the random copolymer is about 156 kg/mol,

r) $[PIM\text{-}13]_x$-$[SBC]_y$, wherein
the ratio of subscript x to subscript y is about 50:50, and
the weight average molecular weight (M_w) of the random copolymer is about 99 kg/mol,

s) $[PIM\text{-}13]_x$-$[PIM\text{-}MAA]_y$, wherein
the ratio of subscript x to subscript y is about 50:50, and
the weight average molecular weight (M_w) of the random copolymer is about 95 kg/mol,

t) $[PIM\text{-}13]_x$-$[PIM\text{-}DAA]_y$, wherein
the ratio of subscript x to subscript y is about 95:5, and
the weight average molecular weight (M_w) of the random copolymer is about 57 kg/mol,

u) $[PIM\text{-}13]_x$-$[PIM\text{-}DAA]_y$, wherein
the ratio of subscript x to subscript y is about 90:10, and
the weight average molecular weight (M_w) of the random copolymer is about 63 kg/mol,

v) $[PIM\text{-}13]_x$-$[PIM\text{-}DAA]_y$, wherein
the ratio of subscript x to subscript y is about 70:30, and
the weight average molecular weight (M_w) of the random copolymer is about 40 kg/mol,

w) $[PIM\text{-}13]_x$-$[PIM\text{-}DAA]_y$, wherein
the ratio of subscript x to subscript y is about 50:50, and
the weight average molecular weight (M_w) of the random copolymer is about 61 kg/mol,

x) $[PIM\text{-}13]_x$-$[PIM\text{-}DAA]_y$, wherein
the ratio of subscript x to subscript y is about 30:70, and
the weight average molecular weight (M_w) of the random copolymer is about 56.6 kg/mol,

y) $[PIM\text{-}13]_x$-$[PIM\text{-}DAA]_y$, wherein
the ratio of subscript x to subscript y is about 20:80, and
the weight average molecular weight (M_w) of the random copolymer is about 113 kg/mol, or

z) $[PIM\text{-}13]_x$-$[PIM\text{-}DAA]_y$, wherein
the ratio of subscript x to subscript y is about 10:90, and
the weight average molecular weight (M_w) of the random copolymer is about 90.5 kg/mol

[0099] In some embodiments, the copolymer of the present invention is the copolymer of Formula J, J-1, or J-2, wherein the copolymer is a random copolymer having the structure:

a) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is 97.5:2.5, and
the weight average molecular weight (Mw) of the random copolymer is about 68 kg/mol,

b) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$, wherein
wherein the ratio of subscript x to subscript y is about 95:5, and
the weight average molecular weight (Mw) of the random copolymer is about 67 kg/mol,

c) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 92.5:7.5, and
the weight average molecular weight (Mw) of the random copolymer is about 76 kg/mol,

d) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 90:10, and
the weight average molecular weight (Mw) of the random copolymer is about 65 kg/mol,

e) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 87.5:12.5, and
the weight average molecular weight (Mw) of the random copolymer is about 80 kg/mol,

f) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 85:15, and
the weight average molecular weight (Mw) of the random copolymer is about 95 kg/mol,

g) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 82.5:17.5, and
the weight average molecular weight (Mw) of the random copolymer is about 73 kg/mol,

h) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 80:20, and
the weight average molecular weight (Mw) of the random copolymer is about 80 kg/mol,

i) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 70:30,

j) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 50:50, and
the weight average molecular weight (Mw) of the random copolymer is about 101 kg/mol,

k) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 30:70, and
the weight average molecular weight (Mw) of the random copolymer is about 78 kg/mol,

l) $[PIM\text{-}13S]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 90:10, and
the weight average molecular weight (Mw) of the random copolymer is about 61 kg/mol,

m) $[PIM\text{-}13S]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 85:15, and
the weight average molecular weight (Mw) of the random copolymer is about 116 kg/mol,

n) $[PIM\text{-}13S]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 80:20, and
the weight average molecular weight (Mw) of the random copolymer is about 144 kg/mol,

o) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$-$[PzMeSO_2]_{z1}$, wherein
the ratio of subscript x to subscript y to subscript z1 is about 80:10:10, and
the weight average molecular weight (M_w) of the random copolymer is about 60 kg/mol,

p) $[PIM\text{-}13]_x$-$[SBC]_y$, wherein
the ratio of subscript x to subscript y is about 90:10, and
the weight average molecular weight (M_w) of the random copolymer is about 85 kg/mol,

q) $[PIM\text{-}13]_x\text{-}[SBC]_y$, wherein
the ratio of subscript x to subscript y is about 70:30, and
the weight average molecular weight (M_w) of the random copolymer is about 156 kg/mol, or

r) $[PIM\text{-}13]_x\text{-}[SBC]_y$, wherein
the ratio of subscript x to subscript y is about 50:50, and
the weight average molecular weight (M_w) of the random copolymer is about 99 kg/mol.

[0100] The copolymers of the present invention can be prepared by a variety of methods. For example, spirobisindane and spirobischromane monomers can be condensed with tetrafluoroterephthalonitrile, or other phthalonitriles, with potassium carbonate or other suitable bases. Bases useful in the method for preparing the copolymers include, but are not limited to, sodium carbonate, potassium carbonate, and cesium carbonate.

[0101] The copolymer of the present invention can be used as a membrane. In some embodiments, the present invention provides a membrane comprising a copolymer of the present invention. The copolymer membrane can include a variety of additional components.

III. COATED SEPARATOR

[0102] In some embodiments, the present invention provides a coated separator comprising a porous membrane support; and a membrane layer on the porous membrane support comprising a copolymer of the present invention.

[0103] FIG. 2A shows coated separator **100**, having porous support **110** having a first surface **111** and a second opposing surface **112**, and a copolymer layer **130**.

[0104] The separator can include the polymer of the present invention alone or in combination with other components. In some embodiments, the present invention provides a multi-layer coated separator, comprising:

a porous support having a first surface and a second opposing surface;
a first polymer layer; and
a copolymer layer comprising a copolymer of the present invention,
wherein the first polymer layer is coated on the first surface of the porous support, and the copolymer layer is coated on the first polymer layer.

[0105] FIG. 2B shows multi-layer coated separator **150**, having porous support **110** having a first surface **111** and a second opposing surface **112**, a first polymer layer **120**, and a copolymer layer **130**.

Porous support

[0106] In some embodiments, the pore size of porous support is between about 0.01 micrometers and 5 micrometers or more specifically between about 0.02 micrometers and 0.5 micrometers. The porosity of porous support may be between about 20% and 85%, or more specifically, between about 30% and 60%. One having ordinary skills in the art would understand that pore sizes may be effected by the composition of electrolyte that is provided in the pores of separator. For example, some components of separator (e.g., porous support or first polymer layer) may swell when come in contact with some materials of electrolyte causing the pore size to change. Unless specifically noted, the pore size and other like parameter refer to components of separator before they come in contact with electrolyte.

[0107] Larger pore sizes allow using porous support that is much thicker than first polymer layer without significantly undermining the overall permeability of separator to first species. In some embodiments, the thickness of porous support is between about 5 micrometers and 500 micrometers, or in specific embodiment between about 5 micrometers and 50 micrometers, or more specifically between about 10 micrometers and 30 micrometers. In the same or other embodiments, the thickness of porous support may be between about 1 to 50 times greater than the thickness of first polymer layer or, more specifically, between about 5 and 25 times greater.

[0108] Some examples of suitable materials for porous support include, but are not limited, fluoro-polymeric fibers of poly(ethylene-co-tetrafluoroethylene (PETFE) and poly(ethylenechloro-co-trifluoroethylene) (e.g., a fabric woven from these used either by itself or laminated with a fluoropolymeric microporous film), polyvinylidene difluoride, polytetrafluoroethylene (PTFE), polystyrenes, polyarylether sulfones, polyvinyl chlorides, polypropylene, polyethylene (including LDPE, LLDPE, HDPE, and ultrahigh molecular weight polyethylene), polyamides, polyimides, polyacrylics, polyacetals, polycarbonates, polyesters, polyetherimides, polyimides, polyketones, polyphenylene ethers, polyphenylene sulfides, polymethylpentene, polysulfones non-woven glass, glass fiber materials, ceramics, metal oxides, composites of organic and inorganic species, and a polypropylene membrane. Porous support may also be supplied with an additional coating of a second suitable material

including, but not limited to, PTFV, PVDF, and PETFE. These examples of porous support may or may not be commercially available under the designation CELGARD from Celanese Plastic Company, Inc. in Charlotte, N.C., USA, as well as Asahi Kasei Chemical Industry Co. in Tokyo, Japan, Tonen Corporation, in Tokyo, Japan, Ube Industries in Tokyo, Japan, Nitto Denko K.K. in Osaka, Japan. Nippon Kodoshi Corporation, in Kochi, Japan, Entek in Lebanon, Oregon, USA, SK Innovation in Jongro-Gu, Korea, Sumitomo Corporation, in Tokyo, Japan, Toray Industries in Tokyo, Japan, Dupont USA, in Wilmington, DE, USA, W-Scope in Japan, and Parker Hannifin Filtration Group, in Carson, CA, USA.

[0109] In some embodiments, the multi-layer coated separator is the separator wherein the porous support comprises polyethylene, polypropylene, poly(tetrafluoroethylene) (PTFE), poly(vinyl chloride) (PVC), poly(vinylidene difluoride) (PVDF), cellulose, a ceramic, or combinations thereof. In some embodiments, the multi-layer coated separator is the separator wherein the porous support comprises polyethylene.

[0110] The porous support may have a thickness of between about 3 micrometers and 200 micrometers, or between about 5 micrometers and 100 micrometers, or between about 10 micrometers and 50 micrometers, or between about 9 micrometers and 25 micrometers, or between about 10 micrometers and 20 micrometers, or more specifically between about 15 micrometers and 30 micrometers. The porous support can have a thickness of about 5 micrometers, or about 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or about 20 micrometers.

First Polymer Layer

[0111] Selective blocking characteristics of one or more polymer layers used in a separator come from the composition or specific pore architectures of these layers. For purposes of this disclosure, the term "blocking" is referred to as sieving, selecting, or excluding. In some embodiments, the pore architectures of polymer layer manifest as networks of interconnected pores with small pore sizes, narrow pore-size distribution, high surface area, and high porosity as further described below. In some embodiments, the pore architectures of polymer layer manifest as an array of channels with small pore sizes, narrow pore-size distribution, high surface area, and high porosity as further described below. In addition to these blocking properties, the first polymer layer possesses various other properties making them suitable for electrochemical cell applications, such as chemical and electrochemical stability, wettability, thickness, thermal stability, and the like.

[0112] The blocking mechanism is based on chemical exclusion (non-wettable) or a size-exclusion effect transpired at a nanometer to sub-nanometer scale where tortuous, ionically percolating, pathways are established in polymer layers. For example, a polymer layer may allow Li-ions (or other like species described below) to pass while blocking larger electrolyte solvent or the like. The membrane may be formed from a ladder polymer with angular spiro centers and absence of rotatable bonds in the polymer backbone or bonds in the backbone with restricted bond rotation. These characteristics provide inefficient solid-state packing with porosity of between about 10% and 40% or, more specifically, between about 20% and 30% of the bulk powder. The pores may then be filled with an inorganic component leaving a non-porous or partially porous polymer layer.

[0113] The first polymer layer can include any suitable polymer. In some embodiments, the multi-layer coated separator is the separator wherein the first polymer layer is substantially insoluble in carbonate electrolytes. Representative carbonate electrolytes are described within. For example, the first polymer layer can be more than 50% insoluble in the carbonate electrolyte, or more than 55, 60, 65, 70, 75, 80, 85, 90, 95, 96, 97, 98, or more than 99% insoluble in the carbonate electrolyte.

[0114] In some embodiments, the multi-layer coated separator is the separator wherein the first polymer layer is substantially insoluble in electrolytes comprising one or more lithium salts. Representative electrolytes comprising one or more lithium salts are described within. For example, the first polymer layer can be more than 50% insoluble in the electrolyte comprising one or more lithium salts, or more than 55, 60, 65, 70, 75, 80, 85, 90, 95, 96, 97, 98, or more than 99% insoluble in the electrolyte comprising one or more lithium salts.

[0115] The first polymer layer can include one or more different polymer layers. For example, the first polymer layer can include a first polymer layer, a second polymer layer, or more polymer layers. In some embodiments, the multi-layer coated separator is the separator wherein the first polymer layer comprises polyacrylonitrile, poly(acrylonitrile-methyl acrylate), poly(acrylonitrile-co-methacrylic acid), poly(acrylonitrile-acrylic acid), poly(acrylonitrile-itaconic acid), poly(acrylonitrile-methyl methacrylate), poly(acrylonitrile-itaconic acid-methyl acrylate), poly(acrylonitrile-methacrylic acid-methyl acrylate), poly(acrylonitrile-vinyl pyridine), poly(acrylonitrile-vinyl chloride), poly(acrylonitrile-vinyl acetate), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), a second polymer of intrinsic microporosity different from the first polymer of intrinsic microporosity, or

combinations thereof. In some embodiments, the multi-layer coated separator is the separator wherein the first polymer layer comprises poly(acrylonitrile-co-methyl acrylate), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), the second polymer of intrinsic microporosity different from the first polymer of intrinsic microporosity, or combinations thereof.

PIM Polymer Layer

[0116] Polymers of intrinsic microporosity useful in the electrochemical device of the present invention include those described in U.S. Patent Nos. 10,710,065, and 11,394,082, U.S. Publication No. 2021/0309802, and 2019/0326578, each of which is incorporated herein by reference in its entirety. In some embodiments, the copolymer layer is a copolymer of the present invention.

[0117] To achieve very high ion transport required to enable fast charge and high power applications, high free volume and microporosity are sought after. Polymers presenting these properties are so-called high free volume polymers. These highly permeable polymers have been applied mostly to gas separations. Some examples include certain substituted polyacetylenes (e.g. PTMSP), some perfluoropolymers (e.g. Teflon AF), certain poly(norbornene)s, polymers of intrinsic microporosity, and some polyimides. Their microporosity has been demonstrated by molecular modelling and positron lifetime spectroscopy (PALS). Highly permeable polyacetylenes have bulky side groups that inhibit conformational change and force the backbone into a twisted shape. These rigid polymer macromolecules cannot pack properly in the solid state, resulting in high free volume. The free volume distribution comprises disconnected elements as in glassy polymers and continuous microvoids. In Teflon perfluoropolymers their high free volume is due to a high barrier to rotation between neighbouring dioxolane rings, coupled with weak interchain interactions, which are well known for fluoropolymers, leading to low packing density and hence high permeability. In the case of poly(norborene)s and PTMSP, the presence of bulky trimethylsilyl groups on the ring greatly restricts the freedom of the polymer to undergo conformational change. In polymers of intrinsic microporosity (PIMs), molecular linkers containing points of contortion are held in non-coplanar orientation by rigid molecules, which do not allow the resulting polymers to pack closely and ensure high microporosity. The PIMs concept has been reported for polymides [P M Budd and N B McKeown, "Highly permeable polymers for gas separation membranes, Polymer Chemistry, 1, 63-68, 2010].

[0118] There are two different types of PIMs, i) non-network (linear) polymers which may be soluble in organic solvents, and ii) network polymers which are generally insoluble, depending on the monomer choice. PIMs possess internal molecular free volume (IMFV), which is a measure of concavity and is defined by Swager as the difference in volume of the concave unit as compared to the non-concave shape [T M Long and T M Swager, "Minimization of Free Volume: Alignment of Triptycenes in Liquid Crystals and Stretched Polymers", Adv. Mater, 13, 8, 601-604, 2001]. While the intrinsic microporosity in linear PIMs is claimed to derive from the impenetrable concavities given by their contorted structures, in network PIMs, microporosity is also claimed to derive from the concavities associated with macrocycles. In non-network PIMs, rotation of single bonds has to be avoided, whereas the branching and crosslinking in network PIMs is thought to avoid structural rearrangement that may result in the loss of microporosity (McKeown, 2010), so that single bonds can be present without loss of microporosity. In general, it has been observed that network PIMs possess greater microporosity than non-network PIMs due to their macrocyclization [N B McKeown, P M Budd, "Exploitation of Intrinsic Microporosity in Polymer-Based materials", Macromolecules, 43, 5163-5176, 2010]. However, since prior art network PIMs are not soluble, they can only be incorporated into a membrane if mixed as fillers with microporous soluble materials, which include soluble PIMs or other soluble polymers. There is a strict requirement in non-network PIMs that there are no single bonds in the polymer backbone, to prevent rotational freedom and so provide intrinsic microporosity. Highly rigid and contorted molecular structures are required, providing awkward macromolecular shapes that cannot pack efficiently in space. Molecules with awkward shapes are those that pose packing problems due to their concavities. However, in order to have microporosity in non-network PIMs, concave shape molecules are not sufficient as the voids must be sufficiently interconnected for transport to occur with minimal energy (i.e. intrinsic microporosity) [N B McKeown, P M Budd, "Exploitation of Intrinsic Microporosity in Polymer-Based materials", Macromolecules, 43, 5163-5176, 2010]. Non-network PIMs may be soluble, and so suitable for casting a membrane by phase inversion, or for use coating a support membrane to make a thin film composite. However, their solubility in a range of solvents restricts their applications in organic solvent nanofiltration [Ulbricht M, Advanced functional polymer membranes. Single Chain Polymers, 47, 2217-2262, 2006].

[0119] U.S. Pat. No. 7,690,514 B2 describes materials of intrinsic microporosity comprising organic macromolecules comprised of a first generally planar species connected

by linkers having a point of contortion such that two adjacent first planar species connected by a linker are held in non-coplanar orientation. Preferred points of contortion are spiro groups, bridged ring moieties and sterically congested bonds around which there is restricted rotation. These non-network PIMs may be soluble in common organic solvents, allowing them to be cast into membranes, or coated onto other support membranes to make a thin film composite.

[0120] PIM-1 (soluble PIM) membranes exhibit gas permeabilities which are exceeded only by very high free volume polymers such as Teflon AF2400 and PTMSP, presenting selectivities above Robeson's 1991 upper bound for gas pairs such as CO_2/CH_4 and O_2/N_2. Studies have shown that permeability is enhanced by methanol treatment, helping flush out residual casting solvent and allowing relaxation of the chains [P M Budd and N B McKeown, D Fritsch, "Polymers of Intrinsic Microporosity (PIMs): High free volume polymers for membrane applications", Macromol Symp, 245-246, 403-405, 2006].

[0121] A range of polyimides with characteristics similar to a microporous polymer (PIM) were prepared by Ghanem et al. and membrane gas permeation experiments showed these PIM-Polyimides to be among the most permeable of all polyimides and to have selectivity close to the upper bound for several important gas pairs [B G Ghanem, N B McKeown, P M Budd, N M Al-Harbi, D Fritsch, K Heinrich, L Starannikova, A Tokarev and Y Yampolskii, "Synthesis, characterization, and gas permeation properties of a novel group of polymers with intrinsic micro porosity: PIM-polyimides", Macromolecules, 42, 7781-7888, 2009].

[0122] U.S. Pat. No. 7,410,525 B1, describes polymer/polymer mixed matrix membranes incorporating soluble polymers of intrinsic microporosity as microporous fillers for use in gas separation applications.

[0123] International Patent Publication No. WO 2005/113121 (PCT/GB2005/002028) describes the formation of thin film composite membranes from PIMs by coating a solution of PIMs in organic solvent onto a support membrane, and then optionally crosslinking this PIM film to enhance its stability in organic solvents.

[0124] In order to improve the stability of soluble-PIMs membranes U.S. Pat. No. 7,758,751 B1, describes high performance UV-crosslinked membranes from polymers of intrinsic microporosity (PIMs) and their use in both gas separations, and liquid separations involving organic solvents such as olefin/paraffin, deep desulfurization of gasoline and diesel fuels, and ethanol/water separations.

[0125] In some embodiments, a copolymer layer comprises a polymer having a chain comprised of repeating units bonded to each other. Each unit may include a first generally planar species comprising at least one aromatic ring and also comprising a rigid linker having a site of contortion, which is a spiro group, a bridged ring moiety, or a sterically congested single covalent bond. The rigid linker restricts rotation of the first planar species in a non-coplanar orientation. In some embodiments, at least 50% by mole (or 70%, 80%, or even 90%) of the first planar species in the chain are connected by the rigid linkers to a maximum of two other planar species and being such that it does not have a cross-linked, covalently bonded 3-dimensional structure. As such, this polymer may include rigid linkers having a site of contortion. Since these polymer chains do not pack together by virtue of their rigid contorted structure, the copolymer layer possesses intrinsic microporosity and, in some cases, nanoporosity. As such, this combination of non-packed and non-crosslinked polymer chains extends in three dimensions. It may be also considered as a non-network polymer. Cross-linked polymers are also within the scope.

[0126] In some embodiments, the surface area of the PIM polymer layer (as measured by nitrogen adsorption or a related technique of the dry powder prior to membrane processing) prior to infilling with an inorganic component may be at least 200 m^2/g or at least 500 m^2/g such as between 200 m^2/g and 2200 m^2/g or more specifically between 600 m^2/g and 900 m^2/g. Representative methods for measuring surface area include nitrogen adsorption BET. The surface area is directly related to the porosity, essential for efficient transport of supporting electrolyte between electrodes and higher power cell operation. Typical porosities range from 20% to 70% or more specifically 30% to 60%. The surface area of the PIM polymer layer can be from 100 m^2/g to 3000 m^2/g, such as 100 m^2/g, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200, 1300, 1400, 1500, 1600, 1700, 1800, 1900, 2000, 2100, 2200, 2300, 2400, 2500, 2600, 2700, 2800, 2900, or 3000 m^2/g. In some embodiments, the multi-layer coated separator is the separator wherein the copolymer layer has a surface area of from 100 m^2/g to 3000 m^2/g, as measured by nitrogen adsorption BET.

[0127] In some embodiments, the multi-layer coated separator is the separator wherein the average pore diameter of the copolymer layer prior to infilling with an inorganic component is of less than 100 nm, or from about 0.1 nm to about 20 nm, or from about 0.1 nm to about 10 nm, or from about 0.1 nm to about 5 nm, or from about 0.1 nm to about 2 nm, or from about 0.1 nm to about 1 nm. For example, the average pore diameter of the copolymer layer can be less than about 10 nm, or less than about 9, 8, 7, 6, 5, 4, 3, 2, or 1 nm. For example,

the average pore diameter of the copolymer layer can be about 10 nm, or about 9, 8, 7, 6, 5, 4, 3, 2, or 1 nm. This pore diameter ensures that some materials (e.g., materials that have unit sizes greater than the pore diameter) are blocked by the copolymer layer, while other materials are allowed to pass (e.g., materials with smaller unit sizes). In some embodiments, the multi-layer coated separator is the separator wherein the copolymer layer has an average pore diameter of from 0.1 nm to 10 nm. In some embodiments, the multi-layer coated separator is the separator wherein the copolymer layer has an average pore diameter of from 0.1 nm to 2 nm. In some embodiments, the multi-layer coated separator is the separator wherein the copolymer layer has an average pore diameter of from 0.1 nm to 1 nm.

[0128] In some embodiments, the multi-layer coated separator is the separator wherein the number average molecular weight (M_n) of the copolymer layer is between $1x10^3$ and $2000x10^3$ kg/mol or, more specifically, between $15x10^3$ and $500x10^3$ kg/mol or between $20x10^3$ and $200x10^3$ kg/mol. Larger number average molecular weight polymers contribute to enhanced mechanical properties of the formed membrane.

[0129] The copolymer layer can be a film cast, sprayed or coated from solution (e.g., onto the porous support), a composite comprised of a plurality of individual membrane layers, a free-standing film, or a supported film (e.g., by a porous support).

[0130] In some embodiments, the multi-layer coated separator is the separator wherein the copolymer layer has a thickness of between about 5 nanometers and 20 micrometers, or between about 100 nanometers and 10 micrometers, or more specifically between about 500 nanometers and 5 micrometers.

[0131] The microporosity of a polymer layer is demonstrated by its high surface area (approximately 680 – 850 m^2/g) determined using nitrogen adsorption measurements (BET calculation). The presence of the cyano and methyl groups is optional, they may be omitted or replaced with other simple substituents. Each phenyl goup may contain one or more substituents. Additionally, the nature and arrangement of substituents on the spiro-indane moiety may be chosen to provide any desirable configuration around the carbon atom common to both 5-membered rings.

IV. ELECTROLYTE

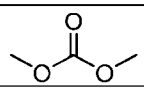
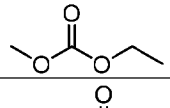
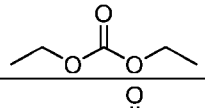
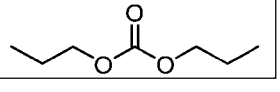
[0132] The electrochemical cell of the present invention also includes an electrolyte, such as a carbonate-based electrolyte. The electrolyte can have a variety of components, such as

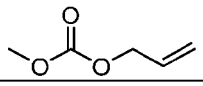
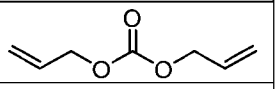
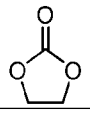
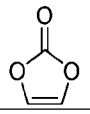
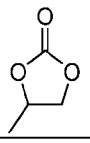
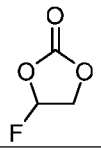
an alkyl carbonate, a fluorinated carbonate, a diisocyanate, a lithium salt, or combinations thereof. The present invention also includes an electrolyte having an alkyl carbonate, a fluorinated carbonate, a diisocyanate, and a lithium salt.

[0133] In some embodiments, the present invention provides an electrolyte comprising an alkyl carbonate, a fluorinated carbonate, a diisocyanate, and a first lithium salt. In some embodiments, the electrolyte comprises a second lithium salt different from the first lithium salt.

[0134] In some embodiments, the electrolyte comprises a carbonate electrolyte. A carbonate electrolyte can have the formula R'-OC(O)O-R", where R' and R" are each independently C_{1-6} alkyl, C_{2-6} alkenyl, C_{1-6} haloalkyl, C_{3-6} cycloalkyl, or C_{6-12} aryl, wherein each aryl can be substituted with 1, 2, 3, 4, or 5 halogens, alternatively R' and R" can be combined to form a 5 to 6 membered heterocycloalkyl that can be substituted with 0, 1, 2, 3, 4, or 5 halogens. In some embodiments, the carbonate electrolyte can have the formula R'-OC(O)O-R", where R' and R" are each independently C_{1-6} alkyl, C_{2-6} alkenyl, or C_{1-6} haloalkyl, alternatively R' and R" can be combined to form a 5 membered heterocycloalkyl that can be substituted with 0, 1, or 2 halogens. In some embodiments, the carbonate electrolyte can have the formula R'-OC(O)O-R", where R' and R" are each independently C_{1-3} alkyl, or C_{1-4} haloalkyl, alternatively R' and R" can be combined to form a 5 membered heterocycloalkyl that can be substituted with 0, 1, or 2 halogens. The carbonate electrolyte can be an alkyl carbonate of the formula R'-OC(O)O-R", where R' and R" are each independently C_{1-6} alkyl. The carbonate electrolyte can be a fluorinated carbonate of the formula R'-OC(O)O-R", where R' is C_{1-6} alkyl, or C_{1-6} haloalkyl, and R" is C_{1-6} haloalkyl, wherein each haloalkyl is a fluoroalkyl, alternatively R' and R" can be combined to form a 5 to 6 membered heterocycloalkyl that can be substituted with 0, 1, 2, 3, 4, or 5 fluorine.

[0135] Representative alkyl carbonates of the electrolyte include, but are not limited to:

Dimethyl carbonate	
Ethyl methyl carbonate	
Diethyl carbonate	
Dipropyl carbonate	

Allyl methyl carbonate	
Diallyl carbonate	
Ethylene carbonate	
Vinylene carbonate	
Propylene carbonate	
Fluoroethylene carbonate	

[0136] In some embodiments, the alkyl carbonate is dimethyl carbonate.

[0137] Representative fluorinated carbonates of the electrolyte include, but are not limited to, fluoroethylene carbonate, $CH_3OC(O)OCH_2CF_3$, $CH_3OC(O)OCH_2CF_2CHF_2$, $CH_3OC(O)OCH_2CF_2CHF_2$, $CF_3CH_2OC(O)OCH_2CF_3$, $CH_3OC(O)OCH_2CF_2CF_2CF_3$, $CH_3CH_2OC(O)OCH_2CF_2CF_3$, $CH_3CH_2OC(O)OCH_2CF_2CHF_2$, or $CH_3OC(O)OCH_2CF_2CF_2CF_3$.

[0138] Representative diisocyanates of the electrolyte include, but are not limited to, tolylene-2,4-diisocyanate, or tolylene-2,6-diisocyanate.

[0139] The lithium salt of the electrolyte compositions of the present invention can be any suitable lithium salt. For example, suitable lithium salts include, but are not limited to, lithium bis(fluorosulfonyl)imide, lithium hexafluorophosphate, lithium 4,5-dicyano-2-(trifluoromethyl)imidazolium, lithium difluoro(oxalato)borate, lithium bis(trifluoromethanesulfonyl)imide, lithium difluorophosphate, lithium nitrate, lithium perchlorate, lithium tetrafluoroborate, lithium trifluoromethanesulfonate, or combinations thereof. In some embodiments, the lithium salt can be lithium bis(fluorosulfonyl)imide, lithium hexafluorophosphate, lithium 4,5-dicyano-2-(trifluoromethyl)imidazolium, lithium difluoro(oxalato)borate, lithium bis(trifluoromethanesulfonyl)imide, lithium

difluorophosphate, lithium nitrate, lithium perchlorate, lithium tetrafluoroborate, lithium trifluoromethanesulfonate, or combinations thereof.

[0140] In some embodiments, the electrolyte composition is the electrolyte composition wherein the first lithium salt includes lithium bis(fluorosulfonyl)imide (LiFSi), lithium hexafluorophosphate, or combinations thereof. In some embodiments, the electrolyte composition is the electrolyte composition wherein the first lithium salt includes lithium bis(fluorosulfonyl)imide (LiFSi).

[0141] The first lithium salt can be present in the electrolyte composition in any suitable amount. For example, the first lithium salt can be present in the electrolyte composition in an amount of from 0.1 to 20 mol%, from 0.1 to 20 mol%, from 1 to 20 mol%, from 5 to 20 mol%, from 5 to 15 mol%, from 8 to 12 mol%, or from 9 to 11 mol%. Representative amounts of the first lithium salt in the electrolyte compositions of the present invention include, but are not limited to, about 5 mol%, or about 6, 7, 8, 9, 10, 11, 12, 13, 14, or about 15 mol%.

[0142] The electrolyte composition of the present invention can include one or more lithium salts. For example, the electrolyte composition can include 1, 2, 3, 4, or more different lithium salts as defined above. In some embodiments, the electrolyte composition is the electrolyte composition comprising a single lithium salt. In some embodiments, the electrolyte composition is the electrolyte composition comprising two different lithium salts. In some embodiments, the electrolyte composition is the electrolyte composition comprising three different lithium salts.

[0143] The electrolyte compositions of the present invention can also include a second lithium salt that is different from the first lithium salt. In some embodiments, the electrolyte composition is the electrolyte composition including a second lithium salt that is different from the first lithium salt.

[0144] In some embodiments, the electrolyte composition is the electrolyte composition wherein the second lithium salt comprises lithium 4,5-dicyano-2-(trifluoromethyl)imidazolium, lithium difluoro(oxalato)borate, lithium bis(trifluoromethanesulfonyl)imide, lithium difluorophosphate, lithium nitrate, lithium perchlorate, lithium tetrafluoroborate, lithium trifluoromethanesulfonate, or combinations thereof. In some embodiments, the electrolyte composition is the electrolyte composition wherein the second lithium salt comprises lithium 4,5-dicyano-2-

(trifluoromethyl)imidazolium, lithium difluoro(oxalato)borate, or combinations thereof. In some embodiments, the electrolyte composition is the electrolyte composition wherein the second lithium salt comprises lithium 4,5-dicyano-2-(trifluoromethyl)imidazolium. In some embodiments, the electrolyte composition is the electrolyte composition wherein the second lithium salt comprises lithium difluoro(oxalato)borate. In some embodiments, the electrolyte composition is the electrolyte composition wherein the second lithium salt comprises lithium nitrate.

[0145] The second lithium salt can be present in the electrolyte composition in any suitable amount. For example, the second lithium salt can be present in the electrolyte composition in an amount of from 0.1 to 10 mol%, from 0.1 to 5 mol%, from 0.5 to 5 mol%, from 0.5 to 4 mol%, from 0.5 to 3.5 mol%, from 1 to 3 mol%, from 1.0 to 2.5 mol%, or from 1.5 to 2.5 mol%. Representative amounts of the second lithium salt in the electrolyte compositions of the present invention include, but are not limited to, about 1.5 mol%, or about 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, or about 2.5 mol%.

[0146] In some embodiments, the electrolyte composition is the electrolyte composition wherein the second lithium salt is present in the electrolyte composition in an amount of from 0.1 to 5 mol%. In some embodiments, the electrolyte composition is the electrolyte composition wherein the second lithium salt is present in the electrolyte composition in an amount of from 0.5 to 3.5 mol%. In some embodiments, the electrolyte composition is the electrolyte composition wherein the second lithium salt is present in the electrolyte composition in an amount of 1 to 3 mol%. In some embodiments, the electrolyte composition is the electrolyte composition wherein the second lithium salt is present in the electrolyte composition in an amount of from 1.5 to 2.5 mol%.

[0147] In some embodiments, the present invention provides an electrolyte comprising:

dimethyl carbonate in an amount of of from 25% to 75% (mol/mol);
fluoroethylene carbonate in an amount of from 20% to 65% (mol/mol);
tolylene-2,6-diisocyanate in an amount of from 0.1% to 10% (mol/mol);
lithium bis(fluorosulfonyl)imide in an amount of from 1% to 20% (mol/mol); and
lithium difluoro(oxalato)borate in an amount of from 0.1% to 10% (mol/mol).

[0148] In some embodiments, the present invention provides an electrolyte comprising:

dimethyl carbonate in an amount of about 48% (mol/mol);
fluoroethylene carbonate in an amount of about 39% (mol/mol);

tolylene-2,6-diisocyanate in an amount of about 1% (mol/mol);
lithium bis(fluorosulfonyl)imide in an amount of about 10% (mol/mol); and
lithium difluoro(oxalato)borate in an amount of about 2% (mol/mol).

V. ELECTROCHEMICAL CELL

[0149] In some embodiments, the present invention provides an electrochemical cell comprising an anode; a cathode; a separator of the present invention; and an electrolyte.

[0150] In some embodiments, the electrochemical device is an electrochemical cell. In some embodiments, an electrochemical cell includes a positive electrode, a negative electrode, a separator, and an electrolyte.

[0151] In some embodiments, the present invention provides an electrochemical cell comprising: an anode; a cathode; a coated separator of the present invention; and an electrolyte. FIG. 3A shows the electrochemical cell **200**, having anode **210**, cathode **220**, and the coated separator **100**. The separator **100** is disposed between the anode **210** and the cathode **220**. The separator provides electronic isolation between the anode and the cathode. At least a portion of the electrolyte is disposed within the separator.

[0152] In some embodiments, the present invention provides an electrochemical cell comprising: an anode; a cathode; a multi-layer coated separator of the present invention; and an electrolyte. FIG. 3B shows the electrochemical cell **200**, having anode **210**, cathode **220**, and the multi-layer coated separator **150**. The separator **100** is disposed between the anode **210** and the cathode **220**. The separator provides electronic isolation between the anode and the cathode. At least a portion of the electrolyte is disposed within the separator.

[0153] In some embodiments, the electrochemical cell is the electrochemical cell wherein the multi-layer coated separator is between the anode and the cathode. In some embodiments, the electrochemical cell is the electrochemical cell wherein the multi-layer coated separator is oriented such that the first surface of the support material is oriented towards the anode.

[0154] In some embodiments, the electrochemical cell of the present invention is the electrochemical cell wherein the electrolyte is an electrolyte of the present invention. In some embodiments, the electrolyte can comprise one or more lithium salts. In some embodiments, the electrolyte can be a carbonate electrolyte.

[0155] In some embodiments, the electrochemical cell of the present invention is the electrochemical cell wherein the electrolyte comprises a first lithium salt. In some embodiments, the electrochemical cell of the present invention is the electrochemical cell wherein the electrolyte comprises a second lithium salt different from the first lithium salt.

[0156] In some embodiments, the electrochemical cell of the present invention is the electrochemical cell wherein the electrolyte comprises lithium bis(fluorosulfonyl)imide, lithium difluoro(oxalato)borate, or lithium hexafluorophosphate.

[0157] In some embodiments, the electrochemical cell of the present invention is the electrochemical cell wherein the electrolyte is E1, E2, LP40, LP57, LP57.2, or LP71.

[0158] In some embodiments, the electrochemical cell of the present invention is the electrochemical cell wherein the electrolyte comprises:

dimethyl carbonate in an amount of from 25% to 75% (mol/mol);
fluoroethylene carbonate in an amount of from 20% to 65% (mol/mol);
tolylene-2,6-diisocyanate in an amount of from 0.1% to 10% (mol/mol);
lithium bis(fluorosulfonyl)imide in an amount of from 1% to 20% (mol/mol); and
lithium difluoro(oxalato)borate in an amount of from 0.1% to 10% (mol/mol).

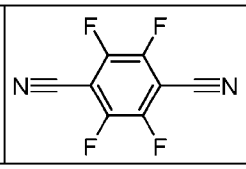
[0159] In some embodiments, the electrochemical cell of the present invention is the electrochemical cell wherein the electrolyte comprises:

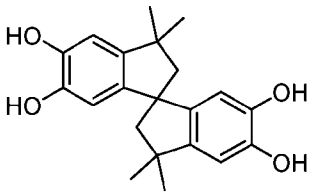
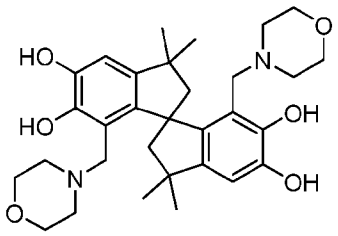
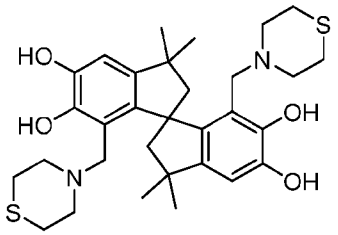
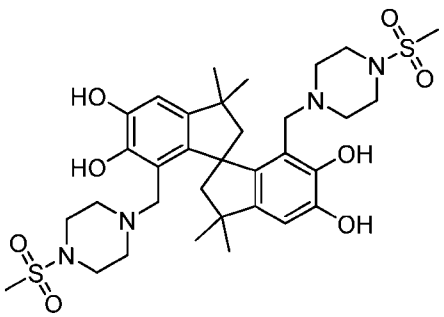
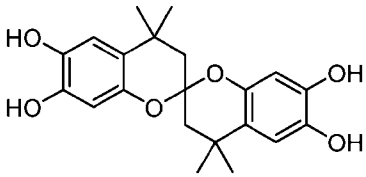
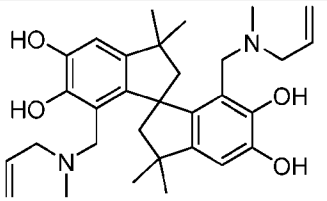
dimethyl carbonate in an amount of about 48% (mol/mol);
fluoroethylene carbonate in an amount of about 39% (mol/mol);
tolylene-2,6-diisocyanate in an amount of about 1% (mol/mol);
lithium bis(fluorosulfonyl)imide in an amount of about 10% (mol/mol); and
lithium difluoro(oxalato)borate in an amount of about 2% (mol/mol).

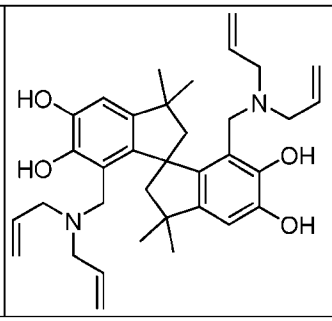
[0160] In some embodiments, the electrochemical device is a lithium-ion battery with a carbon-based, metallic, or metalloid anode and a metal oxide or conversion cathode.

VI. EXAMPLES

[0161] The following raw materials were used:

tetrafluoroterephthalonitrile	

SBI monomer	
SBI-morpholine monomer	
SBI-thiomorpholine monomer	
SBI-piperizine-$MeSO_2$ monomer	
SBC monomer	
SBI-methylallylamine (SBI-MAA)	

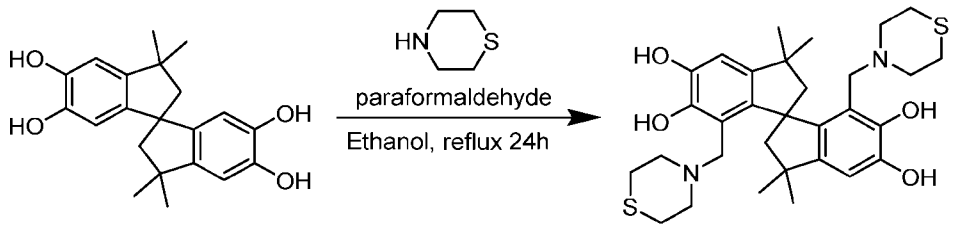
SBI-diallylamine (SBI-DAA)	

[0162] Additional molecular weight determination is made using a Waters APC SEC (Size Exclusion Chromatograph) system with RI detector compared against polystyrene standards for relative MW, or a Malvern OMNISEC GPC with triple detector for absolute MW determination.

[0163] Molecular weight information for PIM-13 and copolymers was determined using a Waters Acquity advanced Polymer Chromatography system equipped with a refractive index detector and using chloroform as the mobile phase. Relative molecular weights were determined using a calibration curve produced from polystyrene standards ranging in molecular weight from 0.266 to 1760 kg/mol.

A. Intermediates

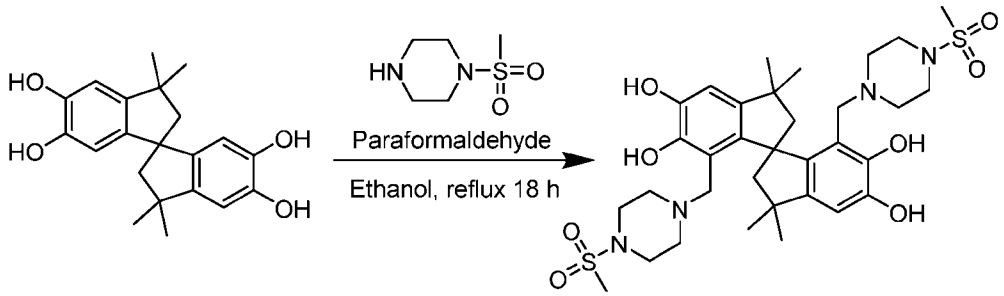
Intermediate 1: SBI-thiomorpholine (1)



[0164] To a 1L two-neck round bottom flask equipped with a reflux condenser was added paraformaldehyde (4.41 g, 147 mmol, 2.5 eq), thiomorpholine (14.71 mL, 147 mmol, 2.5 eq), and ethanol (300 mL). The reaction mixture was purged with argon for 25 minutes, then heated to reflux for one hour. After heating for one hour, 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane (20 g, 58.8 mmol, 1 eq) was added and the reaction mixture stirred at reflux under argon for 24 hours after which a white precipitate was observed. The reaction was then cooled to room temperature, poured into heptane (700 mL), and cooled to 0°C. The reaction mixture was then filtered, washed with heptane (2 x 50 mL), and dried in

vacuo to yield SBI-morpholine (5.23 g, 15.6% yield). ^{1}H-NMR (400 MHz, DMSO-*d6*, δ): δ 10.98 (s, 2H), 8.36 (s, 2H), 6.52 (s, 2H), 3.09 (dd, 4H), 2.52 (m, 16H), 2.15 (dd, 4H), 1.30 (s, 6H), 1.20 (s, 6H).

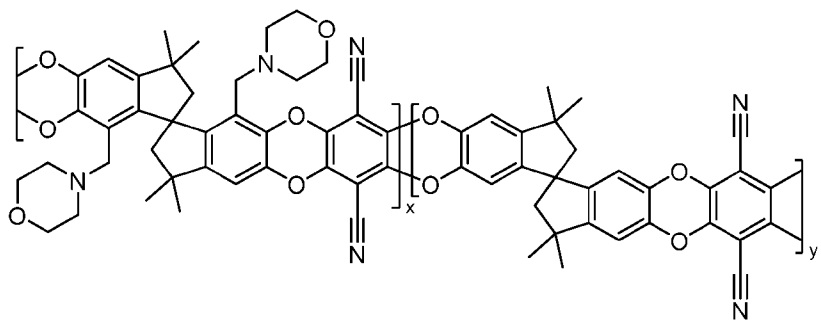
Intermediate 2: SBI-Piperizine-MeSO$_2$ (2)



[0165] To a 250L two-neck round bottom flask equipped with a reflux condenser was added paraformaldehyde (1.10 g, 36.7 mmol, 2.5 eq), Piperizine methylsulfate (6.03 g, 36.7 mmol, 2.5 eq), and ethanol (75 mL). The reaction mixture was purged with argon for 25 minutes, then heated to reflux for one hour. After heating for one hour, 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane (5 g, 14.7 mmol, 1 eq) was added and the reaction mixture stirred at reflux under argon for 24 hours after which a white precipitate was observed. The reaction was then cooled to room temperature, solvent removed by rotary evaporation, and the resulting solids purified using column chromatography on a silica column with an ethyl acetate and hexane mixture mobile phase and dried *in vacuo* to yield SBI-piperizine-MeSO$_2$ (1.29 g, 12.6% yield). ^{1}H-NMR (400 MHz, DMSO-*d6*, δ): δ 10.52 (2H, s), 8.31 (2H, s), 6.53 (2H, s), 3.12 (12H, m), 2.25 (12H, m), 1.32 (6H, s), 1,18 (6H, s).

B. Copolymers

Example 1: PIM-13/1 (97.5/2.5) (3)



[0166] To a dry 20 mL scintillation vial was added tetrafluoroterephthalonitrile (0.300 g, 1.50 mmol, 1 eq), SBI-morpholine (0.772 g, 1.433 mmol, 0.956 eq), SBI (0.013 g, 0.037 mmol, 0.025 eq), and anhydrous DMF (16 mL). This reaction mixture was heated to 65°C, dry potassium carbonate (0.846 g, 6.12 mmol, 4.08 eq) added, and stirred overnight under argon. The reaction mixture was then cooled to room temperature, precipitated into water (100 mL), filtered, and washed with additional water (50 mL) and ethanol (100 mL). This solid was then dried and stirred at 25 mg/mL in methyl ethyl ketone for 24 h to remove oligomeric impurities, filtered, and dried *in vacuo* to yield PIM-13/1 (97.5/2.5) (0.775 g, 81%, M_w = 67.8 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.81 (1H, s), 6.44 (0.03H, s), 3.54 (4H, s), 2.99 (3H, m), 2.24 (5H, m), 1.36 (6H, d).

Example 2: PIM-13/1 (95/5) (4)

[0167] To a dry 20 mL scintillation vial was added tetrafluoroterephthalonitrile (0.300 g, 1.50 mmol, 1 eq), SBI-morpholine (0.752 g, 1.397 mmol, 0.931 eq), SBI (0.025 g, 0.074 mmol, 0.049 eq), and anhydrous DMF (16 mL). This reaction mixture was heated to 65°C, dry potassium carbonate (0.846 g, 6.12 mmol, 4.08 eq) added, and stirred overnight under argon. The reaction mixture was then cooled to room temperature, precipitated into water (100 mL), filtered, and washed with additional water (50 mL) and ethanol (100 mL). This solid was then dried and stirred at 25 mg/mL in methyl ethyl ketone for 24 h to remove oligomeric impurities, filtered, and dried *in vacuo* to yield PIM-13/1 (95/5) (0.848 g, 89.2%, M_w = 66.9 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.81 (1H, s), 6.44 (0.05H, s), 3.54 (4H, s), 2.99 (3H, m), 2.24 (5H, m), 1.36 (6H, d).

Example 3: PIM-13/1 (92.5/7.5) (5)

[0168] To a dry 20 mL scintillation vial was added tetrafluoroterephthalonitrile (0.300 g, 1.50 mmol, 1 eq), SBI-morpholine (0.733 g, 1.360 mmol, 0.907 eq), SBI (0.038 g, 0.110 mmol, 0.074 eq), and anhydrous DMF (16 mL). This reaction mixture was heated to 65°C, dry potassium carbonate (0.846 g, 6.12 mmol, 4.08 eq) added, and stirred overnight under argon. The reaction mixture was then cooled to room temperature, precipitated into water (100 mL), filtered, and washed with additional water (50 mL) and ethanol (100 mL). This solid was then dried and stirred at 25 mg/mL in methyl ethyl ketone for 24 h to remove oligomeric impurities, filtered, and dried *in vacuo* to yield PIM-13/1 (92.5/7.5) (0.807 g, 85.5%, M_w = 76.0 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.81 (1H, s), 6.44 (0.07H, s), 3.54 (4H, s), 2.99 (3H, m), 2.24 (5H, m), 1.36 (6H, d).

Example 4: PIM-13/1 (90/10) (6)

[0169] To a dry 500 mL two-neck round bottom flask equipped with a vacuum adapter and septum was added tetrafluoroterephthalonitrile (2.106 g, 10.52 mmol, 1 eq), SBI-morpholine (5.00 g, 9.28 mmol, 0.882 eq), SBI (0.351 g, 1.03 mmol, 0.098 eq), and anhydrous DMF (110 mL). This reaction mixture was heated to 65°C, dry potassium carbonate (5.93 g, 42.94 mmol, 4.08 eq) added, and stirred overnight under argon. The reaction mixture was then cooled to room temperature, precipitated into water (300 mL), filtered, and washed with additional water (100 mL) and ethanol (200 mL). This solid was then dried and stirred at 25 mg/mL in methyl ethyl ketone for 24 h to remove oligomeric impurities, filtered, and dried *in vacuo* to yield PIM-13/1 (90/10) (5.86 g, 88.9%, M_w = 64.8 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.81 (1H, s), 6.44 (0.13H, s), 3.54 (4H, s), 2.99 (3H, m), 2.24 (5H, m), 1.36 (6H, d).

Example 5: PIM-13/1 (87.5/12.5) (7)

[0170] To a dry 20 mL scintillation vial was added tetrafluoroterephthalonitrile (0.300 g, 1.50 mmol, 1 eq), SBI-morpholine (0.693 g, 1.286 mmol, 0.858 eq), SBI (0.063 g, 0.184 mmol, 0.122 eq), and anhydrous DMF (16 mL). This reaction mixture was heated to 65°C, dry potassium carbonate (0.846 g, 6.12 mmol, 4.08 eq) added, and stirred overnight under argon. The reaction mixture was then cooled to room temperature, precipitated into water (100 mL), filtered, and washed with additional water (50 mL) and ethanol (100 mL). This solid was then dried and stirred at 25 mg/mL in methyl ethyl ketone for 24 h to remove oligomeric impurities, filtered, and dried *in vacuo* to yield PIM-13/1 (87.5/12.5) (0.783 g 84.3%, M_w = 79.5 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.81 (1H, s), 6.44 (0.12H, s), 3.54 (4H, s), 2.99 (3H, m), 2.24 (5H, m), 1.36 (6H, d).

Example 6: PIM-13/1 (85/15) (8)

[0171] To a dry 20 mL scintillation vial was added tetrafluoroterephthalonitrile (0.300 g, 1.50 mmol, 1 eq), SBI-morpholine (0.673 g, 1.250 mmol, 0.833 eq), SBI (0.075 g, 0.221 mmol, 0.147 eq), and anhydrous DMF (16 mL). This reaction mixture was heated to 65°C, dry potassium carbonate (0.846 g, 6.12 mmol, 4.08 eq) added, and stirred overnight under argon. The reaction mixture was then cooled to room temperature, precipitated into water (100 mL), filtered, and washed with additional water (50 mL) and ethanol (100 mL). This solid was then dried and stirred at 25 mg/mL in methyl ethyl ketone for 24 h to remove

oligomeric impurities, filtered, and dried *in vacuo* to yield PIM-13/1 (85/15) (0.785 g, 85.1%, M_w = 95.0 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.81 (1H, s), 6.44 (0.14H, s), 3.54 (4H, s), 2.99 (3H, m), 2.24 (5H, m), 1.36 (6H, d).

Example 7: PIM-13/1 (82.5/17.5) (9)

[0172] To a dry 20 mL scintillation vial was added tetrafluoroterephthalonitrile (0.300 g, 1.50 mmol, 1 eq), SBI-morpholine (0.653 g, 1.213 mmol, 0.809 eq), SBI (0.088 g, 0.257 mmol, 0.172 eq), and anhydrous DMF (16 mL). This reaction mixture was heated to 65°C, dry potassium carbonate (0.846 g, 6.12 mmol, 4.08 eq) added, and stirred overnight under argon. The reaction mixture was then cooled to room temperature, precipitated into water (100 mL), filtered, and washed with additional water (50 mL) and ethanol (100 mL). This solid was then dried and stirred at 25 mg/mL in methyl ethyl ketone for 24 h to remove oligomeric impurities, filtered, and dried *in vacuo* to yield PIM-13/1 (82.5/17.5) (0.809 g, 88.4%, M_w = 73.0 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.81 (1H, s), 6.44 (0.16H, s), 3.54 (4H, s), 2.99 (3H, m), 2.24 (5H, m), 1.36 (6H, d).

Example 8: PIM-13/1 (80/20) (10)

[0173] To a dry 500 mL two-neck round bottom flask equipped with a vacuum adapter and septum was added tetrafluoroterephthalonitrile (2.104 g, 10.52 mmol, 1 eq), SBI-morpholine (4.44 g, 8.245 mmol, 0.784 eq), SBI (0.702 g, 2.061 mmol, 0.196 eq), and anhydrous DMF (110 mL). This reaction mixture was heated to 65°C, dry potassium carbonate (5.93 g, 42.94 mmol, 4.08 eq) added, and stirred overnight under argon. The reaction mixture was then cooled to room temperature, precipitated into water (300 mL), filtered, and washed with additional water (100 mL) and ethanol (200 mL). This solid was then dried and stirred at 25 mg/mL in methyl ethyl ketone for 24 h to remove oligomeric impurities, filtered, and dried *in vacuo* to yield PIM-13/1 (80/20) (5.86 g, 88.9%, M_w = 79.6 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.81 (1H, s), 6.44 (0.2H, s), 3.54 (4H, s), 2.99 (3H, m), 2.24 (5H, m), 1.36 (6H, d).

Example 9: PIM-13/1 (70/30) (11)

[0174] To a dry 20 mL scintillation vial was added tetrafluoroterephthalonitrile (0.300 g, 1.50 mmol, 1 eq), SBI-morpholine (0.554 g, 1.029 mmol, 0.686 eq), SBI (0.150 g, 0.441 mmol, 0.294 eq), and anhydrous DMF (16 mL). This reaction mixture was heated to 65C, dry potassium carbonate (0.846 g, 6.12 mmol, 4.08 eq) added, and stirred overnight under argon.

The reaction mixture was then cooled to room temperature, precipitated into water (100 mL), filtered, and washed with additional water (50 mL) and ethanol (100 mL). This solid was then dried and stirred at 25 mg/mL in methyl ethyl ketone for 24 h to remove oligomeric impurities, filtered, and dried *in vacuo* to yield PIM-13/1 (70/30) (701 mg, 79.6%) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.81 (1H, s), 6.44 (0.31H, s), 3.54 (4H, s), 2.99 (3H, m), 2.24 (5H, m), 1.36 (6H, d).

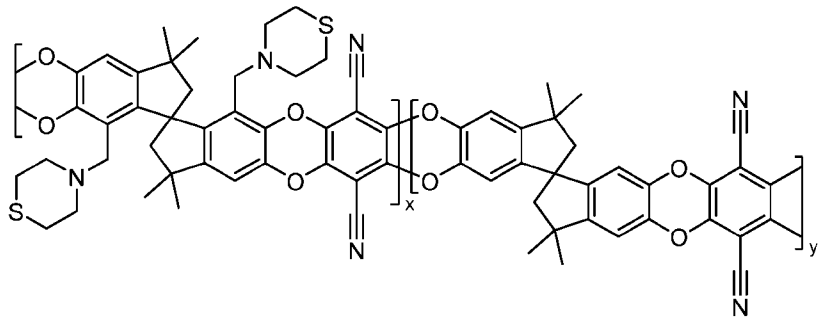
Example 10: PIM-13/1 (50/50) (12)

[0175] To a dry 20 mL scintillation vial was added tetrafluoroterephthalonitrile (0.300 g, 1.50 mmol, 1 eq), SBI-morpholine (0.396 g, 0.735 mmol, 0.490 eq), SBI (0.250 g, 0.735 mmol, 0.490 eq), and anhydrous DMF (16 mL). This reaction mixture was heated to 65C, dry potassium carbonate (0.846 g, 6.12 mmol, 4.08 eq) added, and stirred overnight under argon. The reaction mixture was then cooled to room temperature, precipitated into water (100 mL), filtered, and washed with additional water (50 mL) and ethanol (100 mL). This solid was then dried and stirred at 25 mg/mL in methyl-ethyl ketone for 24 h to remove oligomeric impurities, filtered, and dried *in vacuo* to yield PIM-13/1 (50/50) (0.699 g, 85%, Mw = 101 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.80 (1H, s), 6.43 (0.48H, s), 1.87 (3.54H, s), 2.99 (1.44H, m), 2.28 (3.17H, s), 1.35 (6H, d).

Example 11: PIM-13/1 (30/70) (13)

[0176] To a dry 20 mL scintillation vial was added tetrafluoroterephthalonitrile (0.300 g, 1.50 mmol, 1 eq), SBI-morpholine (0.238 g, 0.441 mmol, 0.294 eq), SBI (0.350 g, 1.029 mmol, 0.686 eq), and anhydrous DMF (16 mL). This reaction mixture was heated to 65C, dry potassium carbonate (0.846 g, 6.12 mmol, 4.08 eq) added, and stirred overnight under argon. The reaction mixture was then cooled to room temperature, precipitated into water (100 mL), filtered, and washed with additional water (50 mL) and ethanol (100 mL). This solid was then dried and stirred at 25 mg/mL in 1,4-dioxane for 24 h to remove oligomeric impurities, filtered, and dried *in vacuo* to yield PIM-13/1 (30/70) (0.650 g, 85%, M_w = 78.2 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.80 (1H, s), 6.43 (0.48H, s), 1.87 (3.54H, s), 2.99 (1.44H, m), 2.28 (3.17H, s), 1.35 (6H, d).

Example 12: PIM-13S/1 (90/10) (14)



[0177] To a dry 20 mL scintillation vial was added tetrafluoroterephthalonitrile (0.300 g, 1.50 mmol, 1 eq), SBI-thiomorpholine (753 mg, 1.32 mmol, 0.88 eq), SBI (51 mg, 0.150 mmol, 0.10 eq), and anhydrous DMF (16 mL). This reaction mixture was heated to 65°C, dry potassium carbonate (0.846 g, 6.12 mmol, 4.08 eq) added, and stirred overnight under argon. The reaction mixture was then cooled to room temperature, precipitated into water (100 mL), filtered, and washed with additional water (50 mL) and ethanol (100 mL). This solid was then dried and stirred at 25 mg/mL in methyl ethyl ketone for 24 h to remove oligomeric impurities, filtered, and dried *in vacuo* to yield PIM-13S/1 (90/10) (826 mg, 84.1%, M_w = 61.1 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.82 (1H, s), 6.44 (0.09H, s), 2.7 (10H, m), 1.35 (6H, d).

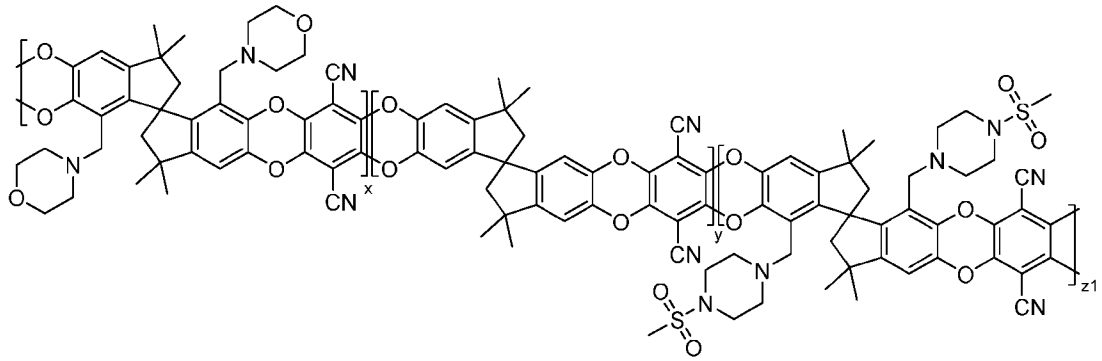
Example 13: PIM-13S/1 (85/15) (15)

[0178] To a dry 20 mL scintillation vial was added tetrafluoroterephthalonitrile (0.300 g, 1.50 mmol, 1 eq), SBI-thiomorpholine (713 mg, 1.25 mmol, 0.83 eq), SBI (75.0 mg, 0.220 mmol, 0.15 eq), and anhydrous DMF (16 mL). This reaction mixture was heated to 65°C, dry potassium carbonate (0.846 g, 6.12 mmol, 4.08 eq) added, and stirred overnight under argon. The reaction mixture was then cooled to room temperature, precipitated into water (100 mL), filtered, and washed with additional water (50 mL) and ethanol (100 mL). This solid was then dried and stirred at 25 mg/mL in methyl ethyl ketone for 24 h to remove oligomeric impurities, filtered, and dried *in vacuo* to yield PIM-13S/1 (85/15) (656 mg, 67.9%, M_w = 116 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.82 (1H, s), 6.44 (0.12H, s), 2.7 (10H, m), 1.35 (6H, d).

Example 14: PIM-13S/1 (80/20) (16)

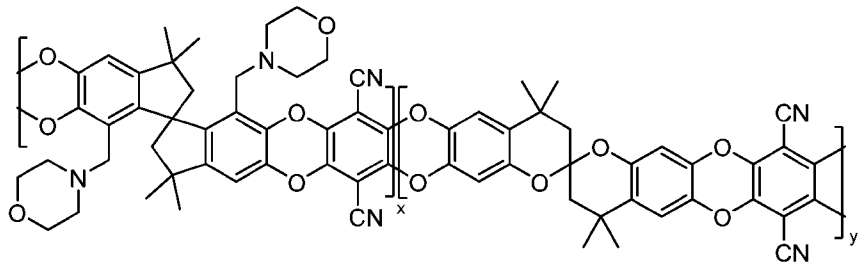
[0179] To a dry 20 mL scintillation vial was added tetrafluoroterephthalonitrile (0.300 g, 1.50 mmol, 1 eq), SBI-thiomorpholine (671 mg, 1.18 mmol, 0.78 eq), SBI (102 mg, 0.300 mmol, 0.20 eq), and anhydrous DMF (16 mL). This reaction mixture was heated to 65°C, dry potassium carbonate (0.846 g, 6.12 mmol, 4.08 eq) added, and stirred overnight under argon. The reaction mixture was then cooled to room temperature, precipitated into water (100 mL), filtered, and washed with additional water (50 mL) and ethanol (100 mL). This solid was then dried and stirred at 25 mg/mL in methyl ethyl ketone for 24 h to remove oligomeric impurities, filtered, and dried *in vacuo* to yield PIM-13S/1 (80/20) (696 g, 73.3%, M_w = 144 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.82 (1H, s), 6.44 (0.16H, s), 2.7 (10H, m), 1.35 (6H, d).

Example 15: PIM-13/1/PzMeSO$_2$ (80/10/10) (17)



[0180] To a dry 20 mL scintillation vial was added tetrafluoroterephthalonitrile (0.300 g, 1.50 mmol, 1 eq), SBI-morpholine (633 mg, 1.18 mmol, 0.78 eq), SBI (50 mg, 0.15 mmol, 0.10 eq), SBI-piperizine-MeSO$_2$ (102 mg, 0.15 mmol, 0.1 eq) and anhydrous DMF (16 mL). This reaction mixture was heated to 65°C, dry potassium carbonate (0.846 g, 6.12 mmol, 4.08 eq) added, and stirred overnight under argon. The reaction mixture was then cooled to room temperature, precipitated into water (100 mL), filtered, and washed with additional water (50 mL) and ethanol (100 mL). This solid was then dried and stirred at 25 mg/mL in methyl ethyl ketone for 24 h to remove oligomeric impurities, filtered, and dried *in vacuo* to yield PIM-13/1/PzMeSO$_2$ (80/10/10) (0.805 g, 84%, M_w = 59.8 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.81 (1H, s), 6.44 (0.1H, s), 3.54 (2.95H, s), 3.00 (3.13H, m), 2.24 (4.45H, s), 1.36 (6H, d).

Example 16: PIM-13/SBC (90/10):



[0181] To a dry 20 mL scintillation vial was added tetrafluoroterephthalonitrile (0.300 g, 1.50 mmol, 1 eq), SBI-morpholine (0.712 g, 1.322 mmol, 0.882 eq), 6,6',7,7'-Tetrahydroxy-4,4,4',4'-tetramethyl-2,2'-spirobichroman (0.055 g, 0.147 mmol, 0.098 eq), and anhydrous DMF (16 mL). This reaction mixture was heated to 65°C, dry potassium carbonate (0.846 g, 6.12 mmol, 4.08 eq) added, and stirred overnight under argon. The reaction mixture was then cooled to room temperature, precipitated into water (100 mL), filtered, and washed with additional water (50 mL) and ethanol (100 mL). This solid was then dried and stirred at 25 mg/mL in methyl ethyl ketone for 24 h to remove oligomeric impurities, filtered, and dried *in vacuo* to yield PIM-13/SBC (90/10) (0.84 g, 89%, M_w = 84.9 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.97 (0.11H, s), 6.81 (1H, s), 6.33 (0.11H, s), 3.54 (4H, s), 3.08 (3H, m), 2.25 (5H, m), 2.03 (0.22H, d), 1.59 (0.66H, d), 1.36 (6H, d).

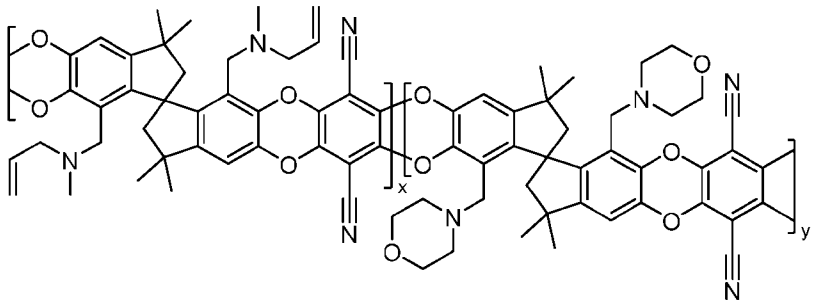
Example 17: PIM-13/SBC (70/30):

[0182] To a dry 20 mL scintillation vial was added tetrafluoroterephthalonitrile (0.300 g, 1.50 mmol, 1 eq), SBI-morpholine (0.554 g, 1.029 mmol, 0.686 eq), 6,6',7,7'-Tetrahydroxy-4,4,4',4'-tetramethyl-2,2'-spirobichroman (0.164 g, 0.441 mmol, 0.294 eq), and anhydrous DMF (16 mL). This reaction mixture was heated to 65°C, dry potassium carbonate (0.846 g, 6.12 mmol, 4.08 eq) added, and stirred overnight under argon. The reaction mixture was then cooled to room temperature, precipitated into water (100 mL), filtered, and washed with additional water (50 mL) and ethanol (100 mL). This solid was then dried and stirred at 25 mg/mL in methyl ethyl ketone for 24 h to remove oligomeric impurities, filtered, and dried *in vacuo* to yield PIM-13/SBC (70/30) (0.74 g, 83%, M_w = 156 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.97 (0.44H, s), 6.81 (1H, s), 6.33 (0.44H, s), 3.54 (4H, s), 3.08 (3H, m), 2.25 (5H, m), 2.03 (0.88H, d), 1.59 (2.64H, d), 1.36 (6H, d).

Example 18: PIM-13/SBC (50/50):

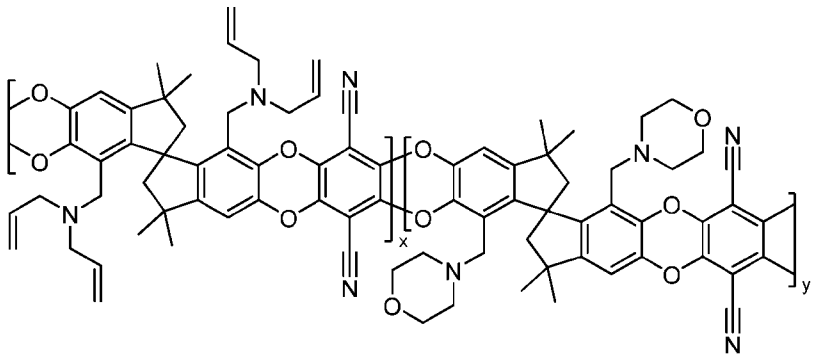
[0183] To a dry 20 mL scintillation vial was added tetrafluoroterephthalonitrile (0.300 g, 1.50 mmol, 1 eq), SBI-morpholine (0.396 g, 0.735 mmol, 0.490 eq), 6,6',7,7'-Tetrahydroxy-4,4,4',4'-tetramethyl-2,2'-spirobichroman (0.274 g, 0.735 mmol, 0.490 eq), and anhydrous DMF (16 mL). This reaction mixture was heated to 65°C, dry potassium carbonate (0.846 g, 6.12 mmol, 4.08 eq) added, and stirred overnight under argon. The reaction mixture was then cooled to room temperature, precipitated into water (100 mL), filtered, and washed with additional water (50 mL) and ethanol (100 mL). This solid was then dried and stirred at 25 mg/mL in methyl ethyl ketone for 24 h to remove oligomeric impurities, filtered, and dried *in vacuo* to yield PIM-13/SBC (50/50) (0.74 g, 87%, M_w = 99.3 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.97 (1H, s), 6.81 (1H, s), 6.33 (1H, s), 3.54 (4H, s), 3.08 (3H, m), 2.25 (5H, m), 2.03 (2H, d), 1.59 (6H, d), 1.36 (6H, d).

Example 19: PIM-13/MAA (50/50) (22):



[0184] To a 250 mL, two neck round bottom flask equipped with a vacuum adapter and septum was added tetrafluoroterephthalonitrile (3 g, 15 mmol, 1 eq), SBI-methylallylamine (3, 3.724 g, 7.35 mmol, 0.49 eq.), SBI-morpholine (3.959 g, 7.35 mmol, 0.49 eq) and anhydrous DMAc (135 mL). The reaction mixture was then heated to 120 °C and anhydrous potassium carbonate (8.46 g, 61.2, 4.08 eq) added. The reaction mixture was stirred under nitrogen at 120°C for 2 hours, after which it was precipitated into water (500 mL), vacuum filtered, washed with additional water (250 mL) and ethanol (250 mL), and dried *in-vacuo*. This crude product was further purified by stirring the crude solid with 60/40 (vol/vol) methyl-ethyl ketone and ethanol at a concentration of 25 mg/mL for 24 hours and filtering to yield PIM-13/MAA (50/50) (8.86 g, 94%, M_w = 95.0 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.79 (1H, s), 5.59 (0.5H, s), 5.00 (1H, d), 2.99 (9H, m), 1.85 (1.5H, s), 1.34 (6H, d).

Example 20: PIM-13/DAA (95/5):



[0185] To a dry 20 mL scintillation vial was added tetrafluoroterephthalonitrile (0.300 g, 1.50 mmol, 1 eq), SBI-DAA (18, 41 mg, 0.074 mmol, 0.049 eq), SBI-morpholine (752 mg, 1.397 mmol, 0.931 eq), and anhydrous DMF (16 mL). This reaction mixture was heated to 65°C, dry potassium carbonate (0.846 g, 6.12 mmol, 4.08 eq) added, and stirred overnight under argon. The reaction mixture was then cooled to room temperature, precipitated into water (100 mL), filtered, and washed with additional water (50 mL) and ethanol (100 mL). This solid was then dried and stirred at 25 mg/mL in methyl ethyl ketone for 24 h to remove oligomeric impurities, filtered, and dried *in vacuo* to yield PIM-13/DAA (95/5) (0.97g, ~100%, M_w = 56.7 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.81 (2H, s), 5.51 (0.09H, s), 4.98 (0.26H, d), 3.25 (14.96H, m), 2.24 (9.12H, s), 1.40 (6H, s), 1.32 (6H, s).

Example 21: PIM-13/DAA (90/10):

[0186] To a 250 mL, two neck round bottom flask equipped with a vacuum adapter and septum was added tetrafluoroterephthalonitrile (3 g, 15 mmol, 1 eq), SBI-DAA (18, 0.820 g, 1.47 mmol, 0.098 eq.), SBI-morpholine (7.13 g, 13.23 mmol, 0.882 eq) and anhydrous DMF (160 mL). The reaction mixture was then heated to 65 °C and anhydrous potassium carbonate (8.46 g, 61.2, 4.08 eq) added. The reaction mixture was stirred under nitrogen at 65°C for 2 hours, after which it was precipitated into water (500 mL), vacuum filtered, washed with additional water (250 mL) and ethanol (250 mL), and dried *in-vacuo*. This crude product was further purified by stirring the crude solid with methyl-ethyl ketone at a concentration of 25 mg/mL for 24 hours and filtering to yield PIM-13/DAA (90/10) (7.43 g, 67.5%, M_w = 63.2 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.81 (2H, s), 5.51 (0.27H, s), 4.98 (0.61H, d), 3.25 (13.6H, m), 2.24 (8.59H, s), 1.40 (6H, s), 1.32 (6H, s).

Example 22: PIM-13/DAA (70/30):

[0187] To a dry 20 mL scintillation vial was added tetrafluoroterephthalonitrile (0.300 g, 1.50 mmol, 1 eq), SBI-DAA (**18**, 249 mg, 0.446 mmol, 0.297 eq), SBI-morpholine (560 mg, 1.404 mmol, 0.693 eq), and anhydrous DMF (16 mL). This reaction mixture was heated to 65°C, dry potassium carbonate (0.846 g, 6.12 mmol, 4.08 eq) added, and stirred overnight under argon. The reaction mixture was then cooled to room temperature, precipitated into water (100 mL), filtered, and washed with additional water (50 mL) and ethanol (100 mL). This solid was then dried and stirred at 25 mg/mL in 1:1 (vol/vol) methyl ethyl ketone/ethanol for 24 h to remove oligomeric impurities, filtered, and dried *in vacuo* to yield PIM-13/DAA (70/30) (0.963g, ~94%, M_w = 39.6 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.81 (2H, s), 5.51 (1.06H, s), 4.98 (2.15H, d), 3.25 (13.7H, m), 2.24 (7.51H, s), 1.40 (6H, s), 1.32 (6H, s).

Example 23: PIM-13/DAA (50/50):

[0188] To a 100 mL, two neck round bottom flask equipped with a vacuum adapter and septum was added tetrafluoroterephthalonitrile (0.600 g, 3 mmol, 1 eq), SBI-DAA (**18**, 0.830 g, 1.486 mmol, 0.495 eq.), SBI-morpholine (0.800 g, 1.486 mmol, 0.495 eq) and anhydrous DMAc (27 mL). The reaction mixture was then heated to 120 °C and anhydrous potassium carbonate (1.692 g, 12.24, 4.08 eq) added. The reaction mixture was stirred under nitrogen at 120°C for 2 hours, after which it was precipitated into water (200 mL), vacuum filtered, washed with additional water (100 mL) and ethanol (100 mL), and dried *in-vacuo*. This solid was then dried and stirred at 25 mg/mL in 60/40 (vol/vol) methyl ethyl ketone/ethanol for 24 h to remove oligomeric impurities, filtered, and dried *in vacuo* to yield PIM-13/DAA (50/50) (1.07 g, 55%, M_w = 61.0 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.83 (2H, s), 5.51 (1.90H, s), 4.98 (3.41H, d), 3.25 (12.51H, m), 2.24 (7.10H, s), 1.38 (6H, s), 1.32 (6H, s).

Example 24: PIM-13/DAA (30/70):

[0189] To a 250 mL, two neck round bottom flask equipped with a vacuum adapter and septum was added tetrafluoroterephthalonitrile (3 g, 15 mmol, 1 eq), SBI-DAA (18, 5.984 g, 10.71 mmol, 0.714 eq.), SBI-morpholine (2.473 g, 4.59 mmol, 0.306 eq) and anhydrous DMF (160 mL). The reaction mixture was then heated to 65 °C and anhydrous potassium carbonate (8.46 g, 61.2 mmol, 4.08 eq) added. The reaction mixture was stirred under nitrogen at 65°C

overnight, after which it was precipitated into water (500 mL), vacuum filtered, washed with additional water (250 mL) and ethanol (250 mL), and dried *in-vacuo*. This crude product was further purified by stirring the crude solid with 60/40 (vol/vol) methyl-ethyl ketone and ethanol at a concentration of 25 mg/mL for 24 hours and filtering to yield PIM-13/DAA (30/70) (8.18 g, 81%, M_w = 56.6 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.83 (2H, s), 5.51 (2.70H, s), 5.01(5.28H, d), 3.11 (13.52H, m), 2.22 (4.12H, s), 1.39 (6H, s), 1.33 (6H, s).

Example 25: PIM-13/DAA (20/80):

[0190] To a 250 mL, two neck round bottom flask equipped with a vacuum adapter and septum was added tetrafluoroterephthalonitrile (3 g, 15 mmol, 1 eq), SBI-DAA (**18**, 6.839 g, 12.24 mmol, 0.816 eq.), SBI-morpholine (1.648 g, 3.06 mmol, 0.204 eq) and anhydrous DMF (160 mL). The reaction mixture was then heated to 65 °C and anhydrous potassium carbonate (8.46 g, 61.2, 4.08 eq) added. The reaction mixture was stirred under nitrogen at 65°C for 2 hours, after which it was precipitated into water (500 mL), vacuum filtered, washed with additional water (250 mL) and ethanol (250 mL), and dried *in-vacuo*. This crude product was further purified by stirring the crude solid with 60/40 (vol/vol) methyl-ethyl ketone and ethanol at a concentration of 25 mg/mL for 24 hours and filtering to yield PIM-13/DAA (20/80) (8.07 g, 80%, M_w = 113 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): δ 6.83 (2H, s), 5.51 (3.18H, s), 4.98 (6.24H, d), 3.25 (13.72H, m), 2.24 (3.43H, s), 1.38 (6H, s), 1.33 (6H, s).

Example 26: PIM-13/DAA (10/90):

[0191] To a 250 mL, two neck round bottom flask equipped with a vacuum adapter and septum was added tetrafluoroterephthalonitrile (3 g, 15 mmol, 1 eq), SBI-DAA (**18**, 7.694 g, 13.77 mmol, 0.918 eq.), SBI-morpholine (0.824 g, 1.53 mmol, 0.102 eq) and anhydrous DMF (160 mL). The reaction mixture was then heated to 65 °C and anhydrous potassium carbonate (8.46 g, 61.2, 4.08 eq) added. The reaction mixture was stirred under nitrogen at 65°C for 2 hours, after which it was precipitated into water (500 mL), vacuum filtered, washed with additional water (250 mL) and ethanol (250 mL), and dried *in-vacuo*. This crude product was further purified by stirring the crude solid with 60/40 (vol/vol) methyl-ethyl ketone and ethanol at a concentration of 25 mg/mL for 24 hours and filtering to yield PIM-13/DAA (10/90) (8.26 g, 81%, M_w = 90.5 kg/mol) as a bright yellow solid. ^{1}H-NMR (400 MHz,

$CDCl_3$, δ): δ 6.83 (2H, s), 5.51 (3.72H, s), 4.98 (7.13H, d), 3.25 (13.97H, m), 2.24 (2.77H, s), 1.38 (6H, s), 1.33 (6H, s).

C. Dissolution Examples

Example 1: Dissolution Study in Lithium ion Electrolyte

Preparation of electrolytes

[0192] E1: 1.2 mol/kg lithium bis(fluorosulfonyl)imide and 0.2 mol/kg lithium(difluorooxalatoborate) in dimethylcarbonate:fluoroethylene carbonate (50:48 wt/wt) and 2 wt% tolylene-2-6-diisocyanate

[0193] E2: 3.0 mol/kg lithium bis(fluorosulfonyl)imide and 0.2 mol/kg lithium (difluorooxalatoborate) in 1,2-dimethoxyethane:1H,1H,5H-octafluoropentyl 1,1,2,2-tetrafluoroethyl ether (OFE):1,1,2,2-tetrafluoroethyl 2,2,2,3-tetrafluoropropyl ether (TTE) (44:28:27 wt/wt/wt) and 2 wt% of ethoxy(pentafluoro)triphosphazine

[0194] LP40: 1.0 M lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate:diethyl carbonate (1:1 wt/wt)

[0195] LP57: 1.0 M $LiPF_6$ in ethylene carbonate:ethyl methyl carbonate (3:7 wt/wt)

[0196] LP57.2: 1.0 M $LiPF_6$ in ethylene carbonate:ethyl methyl carbonate (3:7 wt/wt) with 2% w/w vinylene carbonate

[0197] LP71: 1.0 M $LiPF_6$ in ethylene carbonate:diethyl carbonate:dimethyl carbonate (1:1:1 wt/wt/wt)

Dissolution Study in Lithium ion Electrolyte:

[0198] In a lean liquid electrolyte lithium ion battery cell design wherein there is a roughly 2 g/Ah electrolyte to cathode nominal capacity ratio with a 1 um coating layer across the battery separator surface, the ratio of polymer material to total liquid electrolyte content is roughly 14 mg polymer/mL lithium ion electrolyte. Thus, to measure the intrinsic solubility of various homopolymer and copolymer formulations in lithium ion battery electrolyte, 14 mg/mL mixtures of each polymer were prepared in a representative lithium ion battery electrolyte (E1). The solutions were stirred vigorously for 24 hours, syringe filtered to remove undissolved polymer fractions, then diluted 6-fold in additional E1 for spectroscopic analysis. The total content of dissolved polymer in each sample was measured by UV-Visible

spectroscopy. Table 1 shows copolymers that exhibit reductions in solubility relative to PIM-13, which is entirely soluble in E1 at this concentration. By tuning the content of PIM-1 monomer, the copolymer solubility can be reduced to undetectable concentrations.

Table 1. Impact of copolymer composition on the percentage of polymer dissolved into E1 electrolyte from a 14 mg/mL mixture of that polymer in E1.

Example	Polymer	Concentration in filtered sample (mg/mL)	% Dissolved
	PIM-1	Below LOD	Below LOD, <1%
	PIM-13	2.08	14.8%
1	PIM-13/1 (97.5/2.5)	1.68	12.0%
2	PIM-13/1 (95/5)	2.22	15.9%
3	PIM-13/1 (92.5/7.5)	2.20	15.7%
4	PIM-13/1 (90/10)	0.58	4.2%
5	PIM-13/1 (87.5/12.5)	0.40	2.8%
6	PIM-13/1 (85/15)	0.31	2.2%
9	PIM-13/1 (70/30)	0.33	2.37 %
10	PIM-13/1 (50/50)	0.14	1.0 %
11	PIM-13/1 (30/70)	Below LOD	Below LOD, <1%

High Dilution Dissolution Study in Lithium Ion Electrolytes:

[0199] A 14mm diameter punch of polyethylene battery separator coated with copolymer at a coat weight of 1 g/m^2 was immersed in an excess (1 mL) of E1, E2, or LP57 electrolyte for 24 hours, after which solutions were observed for evidence of polymer dissolution indicated by a yellow color in solution. Results are divided into three categories:

Near complete dissolution of coating (A)

Yellow color observed in electrolyte solution but coating remains intact (B)

No discoloration of solution (C)

Table 2: Qualitative high-dilution solubility test of copolymers in various electrolytes

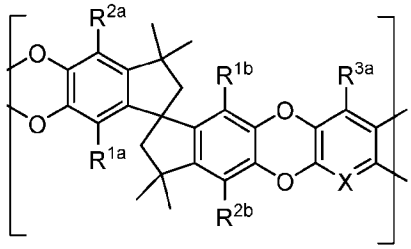
Example	Polymer	E1 Observation	LP57 Observation	E2 Observation
	PIM-1	C	C	C
	PIM-13	A		C
1	PIM-13/1 (97.5/2.5)	A		C
2	PIM-13/1 (95/5)	A		C
3	PIM-13/1 (92.5/7.5)	A		C

Example	Polymer	E1 Observation	LP57 Observation	E2 Observation
4	PIM-13/1 (90/10)	A		C
5	PIM-13/1 (87.5/12.5)	A		C
6	PIM-13/1 (85/15)	A		C
8	PIM-13/1 (80/20)	A		C
9	PIM-13/1 (70/30)	A	A	
10	PIM-13/1 (50/50)	B	A	
11	PIM-13/1 (30/70)	C	C	
15	PIM-13/1/PzMeSO$_2$ (80/10/10)	A		
17	PIM-13/SBC (70/30)			C
18	PIM-13/SBC (50/50)			C

[0200] Although the foregoing invention has been described in some detail by way of illustration and example for purposes of clarity of understanding, one of skill in the art will appreciate that certain changes and modifications may be practiced within the scope of the appended claims. In addition, each reference provided herein is incorporated by reference in its entirety to the same extent as if each reference was individually incorporated by reference. Where a conflict exists between the instant application and a reference provided herein, the instant application shall dominate.

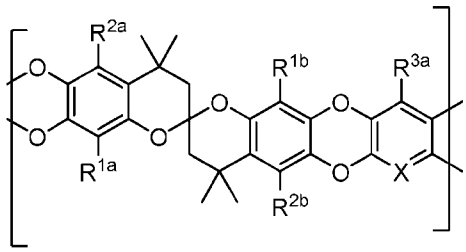
WHAT IS CLAIMED IS:

1. A copolymer comprising a plurality of repeat units A and B, wherein A and B are each independently a repeat unit having a structure of Formula I:



(I) ,

or a structure of Formula II:



(II) ,

wherein

A and B are each different;

R^{1a} and R^{1b} are each independently hydrogen, C_{1-6} alkyl, halogen, C_{1-6} haloalkyl, $-CH_2R^{1c}$ or $NR^{1a1}R^{1b1}$;

each R^{1a1} and R^{1b1} are independently hydrogen, C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, C_{1-6} alkyl-$NR^{1a2}R^{1b2}$, C_{3-10} cycloalkyl, or C_{1-6} alkyl-C_{3-10} cycloalkyl;

each R^{1a2} and R^{1b2} is independently hydrogen or C_{1-6} alkyl;

each R^{1c} is independently $NR^{1a1}R^{1b1}$, a 5-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 5-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S, wherein the heterocycloalkyl and heteroaryl are each independently substituted with 0, 1, 2, 3, 4 or 5 R^{1d} groups;

each R^{1d} is independently C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, halogen, C_{1-6} haloalkyl, -OH, =O, =NH, –CN, $–NO_2$, –C(O)H, $–C(O)R^{1e}$, $–C(O)OR^{1e}$, $–S(O)_2R^{1e}$, $–C_{1-6}$ alkyl–(SO_3^-), $–OP(=O)(OR^{1e})_2$, a 3-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O

or S, or a 3-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S;

R^{1e} is C_{1-6} alkyl or C_{1-6} hydroxyalkyl;

R^{2a} and R^{2b} are each independently hydrogen, C_{1-6} alkyl, halogen, C_{1-6} haloalkyl, $-CH_2R^{2c}$ or $NR^{2a1}R^{2b1}$;

each R^{2a1} and R^{2b1} are independently hydrogen, C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, C_{1-6} alkyl-$NR^{2a2}R^{2b2}$, C_{3-10} cycloalkyl, or C_{1-6} alkyl-C_{3-10} cycloalkyl;

each R^{2a2} and R^{2b2} is independently hydrogen or C_{1-6} alkyl;

each R^{2c} is independently $NR^{2a1}R^{2b1}$, a 5-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 5-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S, wherein the heterocycloalkyl and heteroaryl are each independently substituted with 0, 1, 2, 3, 4 or 5 R^{2d} groups;

each R^{2d} is independently C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} hydroxyalkyl, C_{2-6} alkoxyalkyl, halogen, C_{1-6} haloalkyl, -OH, =O, =NH, –CN, $–NO_2$, –C(O)H, $–C(O)R^{2e}$, $–C(O)OR^{2e}$, $–S(O)_2R^{2e}$, $–C_{1-6}$ alkyl–(SO_3^-), $–OP(=O)(OR^{2e})_2$, a 3-10 membered heterocycloalkyl having 1-4 heteroatoms each independently N, O or S, or a 3-10 membered heteroaryl having 1-4 heteroatoms each independently N, O or S;

R^{2e} is C_{1-6} alkyl or C_{1-6} hydroxyalkyl;

X is –N= or $–C(R^{3b})$=;

each R^{3a} and R^{3b} is independently hydrogen, C_{1-6} alkyl, halogen, C_{1-6} haloalkyl, –CN, or $–S(O)_2R^{3c}$; and

each R^{3c} is independently C_{1-6} alkyl, C_{1-6} haloalkyl, or C_{6-12} aryl, wherein each aryl is independently substituted with 0, 1, 2, 3, 4 or 5 groups each independently C_{1-6} alkyl or C_{1-6} haloalkyl.

2. The copolymer of claim 1, wherein the copolymer is a random copolymer.

3. The copolymer of claim 1 or 2, having the structure of Formula J:

$$[A]_x\text{-}[B]_y\text{-}[C]_{z1}\text{-}[D]_{z2}\text{-}[E]_{z3}\text{-}[F]_{z4} \quad (J) \quad ,$$

wherein:

repeat units A, B, C, D, E and F are each independently the structure of Formula I or the structure of Formula II, wherein A, B, C, D, E and F are each different;
subscript x and y are each independently an integer from 1 to 1000; and
each subscript z1, z2, z3 and z4 is independently an integer from 0 to 1000.

4. The copolymer of claim 3, wherein A, B, C, D, E and F are each independently a repeat unit having the structure of Formula I.

5. The copolymer of claim 3 or 4, having the structure of Formula J-1:

$$[A]_x\text{-}[B]_y\text{-}[C]_{z1} \qquad \text{(J-1)}$$

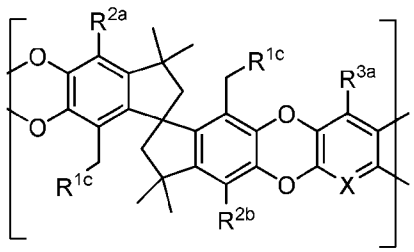
wherein
A, B and C are each different;
subscript x and y are each independently an integer from 1 to 1000; and
subscript z1 is independently an integer from 0 to 1000.

6. The copolymer of any one of claims 3 to 5, having the structure of Formula J-2:

$$[A]_x\text{-}[B]_y \qquad \text{(J-2)}$$

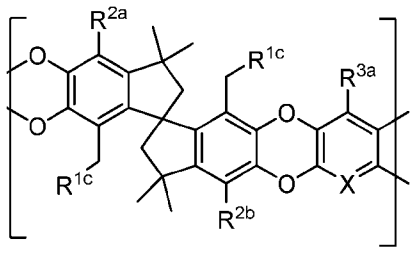
wherein
A and B are each different; and
subscript x and y are each independently an integer from 1 to 1000.

7. The copolymer of claim 1 or 6, wherein A is a repeat unit having the structure of Formula Ia:



(Ia) .

8. The copolymer of claim 1 or 6, wherein each repeat unit of Formula I independently has the structure of Formula Ia:



(Ia) .

9. The copolymer of any one of claims 1 to 8, wherein each R^{1c} is independently $NR^{1a1}R^{1b1}$, or a 5- or 6- membered heterocycloalkyl having 1 or 2 heteroatoms each independently N, O or S, wherein the heterocycloalkyl is independently substituted with 0 or 1 R^{1d} groups.

10. The copolymer of any one of claims 1 to 9, wherein each R^{1c} is independently a 6- membered heterocycloalkyl having 1 or 2 heteroatoms each independently N, O or S.

11. The copolymer of any one of claims 1 to 9 , wherein each R^{1a1} and R^{1b1} are independently C_{1-3} alkyl or C_{2-4} alkenyl.

12. The copolymer of claim 1 or 9, wherein each R^{1d} is independently –$S(O)_2$–C_{1-3} alkyl.

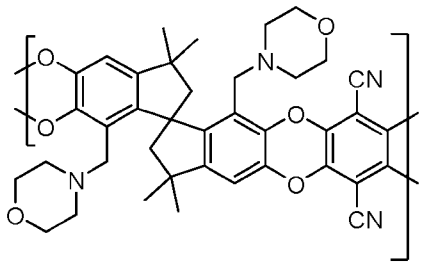
13. The copolymer of any one of claims 1 to 12, wherein R^{2a} and R^{2b} are each hydrogen.

14. The copolymer of any one of claims 1 to 13, wherein R^{3a} is –CN.

15. The copolymer of any one of claims 1 to 14, wherein X is $–C(R^{3b})=$.

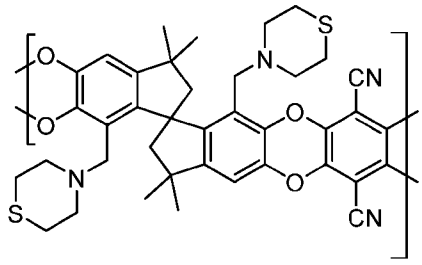
16. The copolymer of any one of claims 1 to 15, wherein R^{3b} is –CN.

17. The copolymer of any one of claims 1 to 16, wherein A is PIM-13 having the structure:



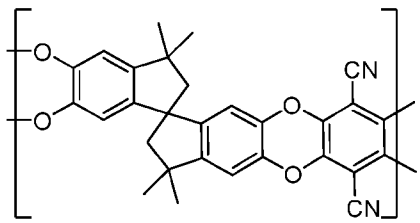
, or

PIM-13S having the structure:



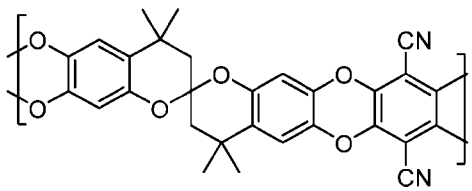
.

18. The copolymer of any one of claims 1 to 17, wherein B is PIM-1:



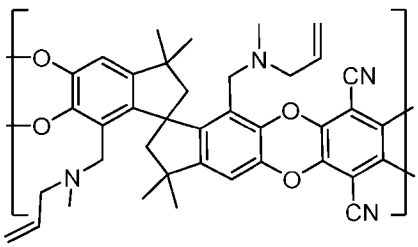
.

19. The copolymer of any one of claims 1 to 17, wherein B is SBC:



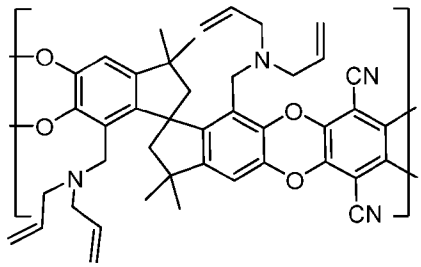
.

20. The copolymer of any one of claims 1 to 17, wherein B is PIM-MAA:



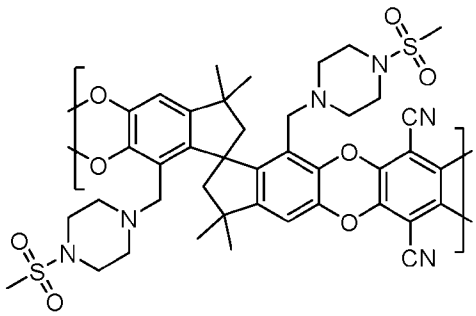
.

21. The copolymer of any one of claims 1 to 17, wherein B is PIM-DAA:



.

22. The copolymer of any one of claims 3 to 18, wherein C is $PzMeSO_2$ having the structure:



.

23. The copolymer of any one of claims 3 to 22, wherein:
subscript x is an integer from 10 to 500,
subscript y is an integer from 1 to 200, and
each subscript z1, z2, z3 and z4 is independently is an integer from 0 to 100.

24. The copolymer of any one of claims 3 to 23, wherein
subscript x is an integer from 10 to 300,
subscript y is an integer from 1 to 200, and
each subscript z1, z2, z3 and z4 is independently is an integer from 0 to 100.

25. The copolymer of any one of claims 3 to 24, wherein each subscript z1, z2, z3 and z4 is 0.

26. The copolymer of any one of claims 3 to 24, wherein each subscript z1, z2, z3 and z4 is independently an integer from 1 to 100.

27. The copolymer of any one of claims 1 to 26, wherein the molar ratio of subscript x to subscript y is from about 10:90 to about 99:1.

28. The copolymer of any one of claims 1 to 27, wherein the weight average molecular weight (M_w) of the copolymer is from 1 kg/mol to 1000 kg/mol.

29. The copolymer of any one of claims 1 to 28, wherein the weight average molecular weight (M_w) of the copolymer is from 10 kg/mol to 500 kg/mol.

30. The copolymer of any one of claims 1 to 29, wherein the weight average molecular weight (M_w) of the copolymer is from 35 kg/mol to 160 kg/mol.

31. The copolymer of any one of claims 17 to 30, having the structure:

$[PIM\text{-}13]_x\text{-}[PIM\text{-}1]_y$,

$[PIM\text{-}13S]_x\text{-}[PIM\text{-}1]_y$,

$[PIM\text{-}13]_x\text{-}[SBC]_y$, or

$[PIM\text{-}13]_x\text{-}[PIM\text{-}1]_y\text{-}[PzMeSO_2]_{z1}$.

32. The copolymer of any one of claims 17 to 31, having the structure:

$[PIM\text{-}13]_x\text{-}[PIM\text{-}1]_y$,

wherein

subscript x is from about 30 to about 150; and

subscript y is from about 1 to about 120.

33. The copolymer of any one of claims 17 to 31, having the structure:

$[PIM\text{-}13S]_x\text{-}[PIM\text{-}1]_y$,

wherein

subscript x is from about 50 to about 200; and

subscript y is from about 1 to about 60.

34. The copolymer of any one of claims 17 to 33, wherein the copolymer is a random copolymer having the structure:

a) $[PIM\text{-}13]_x\text{-}[PIM\text{-}1]_y$, wherein

the ratio of subscript x to subscript y is about 97.5:2.5, and

the weight average molecular weight (M_w) of the random copolymer is about 68 kg/mol,

b) $[PIM\text{-}13]_x\text{-}[PIM\text{-}1]_y$, wherein

wherein the ratio of subscript x to subscript y is about 95:5, and

the weight average molecular weight (M_w) of the random copolymer is about 67 kg/mol,

c) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 92.5:7.5, and
the weight average molecular weight (M_w) of the random copolymer is about 76 kg/mol,

d) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 90:10, and
the weight average molecular weight (M_w) of the random copolymer is about 65 kg/mol,

e) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 87.5:12.5, and
the weight average molecular weight (M_w) of the random copolymer is about 80 kg/mol,

f) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 85:15, and
the weight average molecular weight (M_w) of the random copolymer is about 95 kg/mol,

g) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 82.5:17.5, and
the weight average molecular weight (M_w) of the random copolymer is about 73 kg/mol,

h) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 80:20, and
the weight average molecular weight (M_w) of the random copolymer is about 80 kg/mol,

i) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 70:30,

j) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 50:50, and
the weight average molecular weight (M_w) of the random copolymer is about 101 kg/mol,

k) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 30:70, and

the weight average molecular weight (M_w) of the random copolymer is about 78 kg/mol,

l) $[PIM\text{-}13S]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 90:10, and
the weight average molecular weight (M_w) of the random copolymer is about 61 kg/mol,

m) $[PIM\text{-}13S]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 85:15, and
the weight average molecular weight (M_w) of the random copolymer is about 116 kg/mol,

n) $[PIM\text{-}13S]_x$-$[PIM\text{-}1]_y$, wherein
the ratio of subscript x to subscript y is about 80:20, and
the weight average molecular weight (M_w) of the random copolymer is about 144 kg/mol,

o) $[PIM\text{-}13]_x$-$[PIM\text{-}1]_y$-$[PzMeSO_2]_{z1}$, wherein
the ratio of subscript x to subscript y to subscript z1 is about 80:10:10, and
the weight average molecular weight (M_w) of the random copolymer is about 60 kg/mol,

p) $[PIM\text{-}13]_x$-$[SBC]_y$, wherein
the ratio of subscript x to subscript y is about 90:10, and
the weight average molecular weight (M_w) of the random copolymer is about 85 kg/mol,

q) $[PIM\text{-}13]_x$-$[SBC]_y$, wherein
the ratio of subscript x to subscript y is about 70:30, and
the weight average molecular weight (M_w) of the random copolymer is about 156 kg/mol,

r) $[PIM\text{-}13]_x$-$[SBC]_y$, wherein
the ratio of subscript x to subscript y is about 50:50, and
the weight average molecular weight (M_w) of the random copolymer is about 99 kg/mol,

s) $[PIM\text{-}13]_x$-$[PIM\text{-}MAA]_y$, wherein
the ratio of subscript x to subscript y is about 50:50, and
the weight average molecular weight (M_w) of the random copolymer is about 95 kg/mol,

t) $[PIM\text{-}13]_x$-$[PIM\text{-}DAA]_y$, wherein
the ratio of subscript x to subscript y is about 95:5, and
the weight average molecular weight (M_w) of the random copolymer is about 57 kg/mol,

u) $[PIM\text{-}13]_x$-$[PIM\text{-}DAA]_y$, wherein
the ratio of subscript x to subscript y is about 90:10, and
the weight average molecular weight (M_w) of the random copolymer is about 63 kg/mol,

v) $[PIM\text{-}13]_x$-$[PIM\text{-}DAA]_y$, wherein
the ratio of subscript x to subscript y is about 70:30, and
the weight average molecular weight (M_w) of the random copolymer is about 40 kg/mol,

w) $[PIM\text{-}13]_x$-$[PIM\text{-}DAA]_y$, wherein
the ratio of subscript x to subscript y is about 50:50, and
the weight average molecular weight (M_w) of the random copolymer is about 61 kg/mol,

x) $[PIM\text{-}13]_x$-$[PIM\text{-}DAA]_y$, wherein
the ratio of subscript x to subscript y is about 30:70, and
the weight average molecular weight (M_w) of the random copolymer is about 56.6 kg/mol,

y) $[PIM\text{-}13]_x$-$[PIM\text{-}DAA]_y$, wherein
the ratio of subscript x to subscript y is about 20:80, and
the weight average molecular weight (M_w) of the random copolymer is about 113 kg/mol, or

z) $[PIM\text{-}13]_x$-$[PIM\text{-}DAA]_y$, wherein
the ratio of subscript x to subscript y is about 10:90, and
the weight average molecular weight (M_w) of the random copolymer is about 90.5 kg/mol.

35. A coated separator comprising
a porous membrane support; and
a membrane layer on the porous membrane support comprising a copolymer of any one of claims 1 to 34.

36. An electrochemical cell comprising

an anode;

a cathode;

a separator of claim 35; and

an electrolyte.

37. The electrochemical cell in claim 36, wherein the electrolyte comprises one or more lithium salts.

38. The electrochemical cell in claim 36, wherein the electrolyte comprises a carbonate electrolyte.

39. The electrochemical cell in claim 36, wherein the carbonate electrolyte is E1, E2, LP40, LP57, LP57.2, or LP71.

40. The electrochemical cell in any one of claims 36 to 38, wherein the electrolyte comprises:

dimethyl carbonate in an amount of from 25% to 75% (mol/mol);

fluoroethylene carbonate in an amount of from 20% to 65% (mol/mol);

tolylene-2,6-diisocyanate in an amount of from 0.1% to 10% (mol/mol);

lithium bis(fluorosulfonyl)imide in an amount of from 1% to 20% (mol/mol); and

lithium difluoro(oxalato)borate in an amount of from 0.1% to 10% (mol/mol).

41. The electrochemical cell of any one of claims 36 to 40, wherein the electrolyte comprises:

dimethyl carbonate in an amount of about 48% (mol/mol);

fluoroethylene carbonate in an amount of about 39% (mol/mol);

tolylene-2,6-diisocyanate in an amount of about 1% (mol/mol);

lithium bis(fluorosulfonyl)imide in an amount of about 10% (mol/mol); and

lithium difluoro(oxalato)borate in an amount of about 2% (mol/mol).

FIG. 1

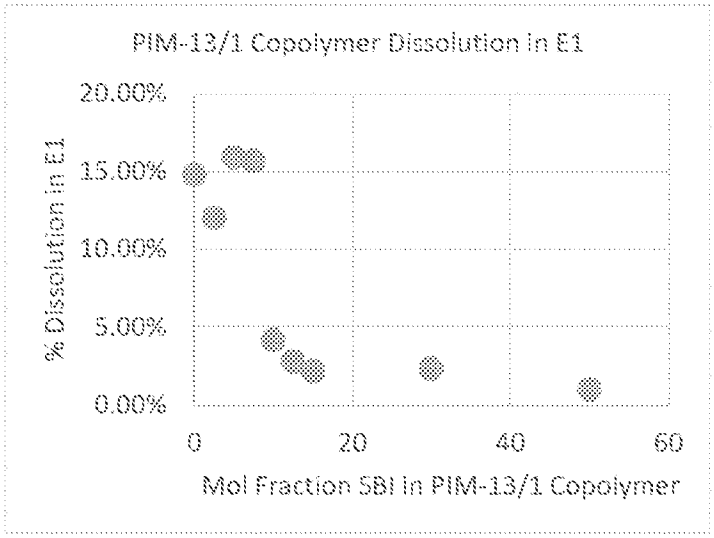

PIM-13/1 Copolymer Dissolution in E1
% Dissolution in E1
20.00%
15.00%
10.00%
5.00%
0.00%
0
20
40
60
Mol Fraction SBI in PIM-13/1 Copolymer

FIG. 2A

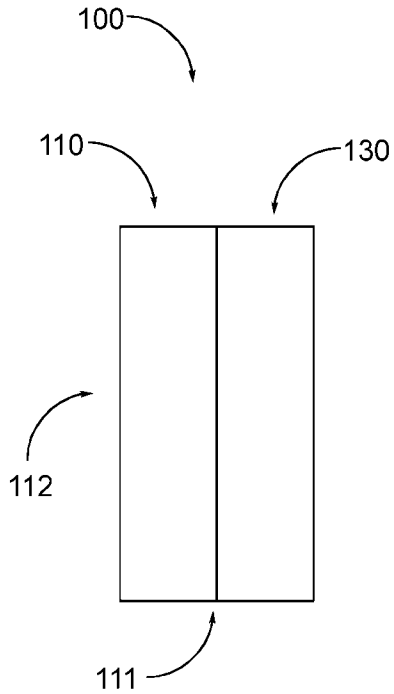


FIG. 2B

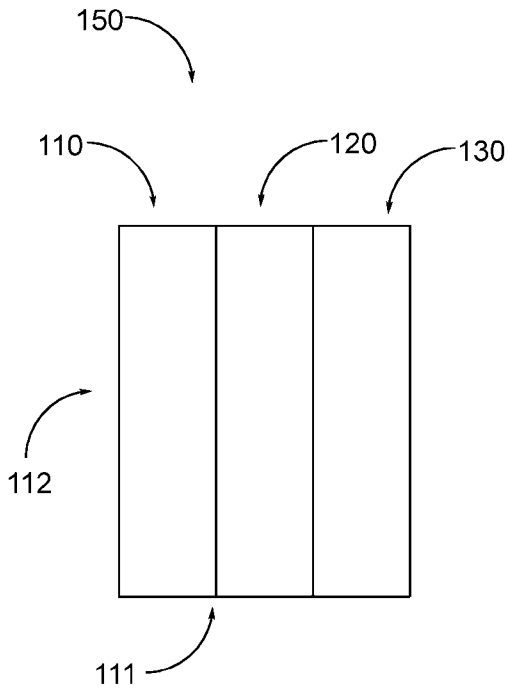


FIG. 3A

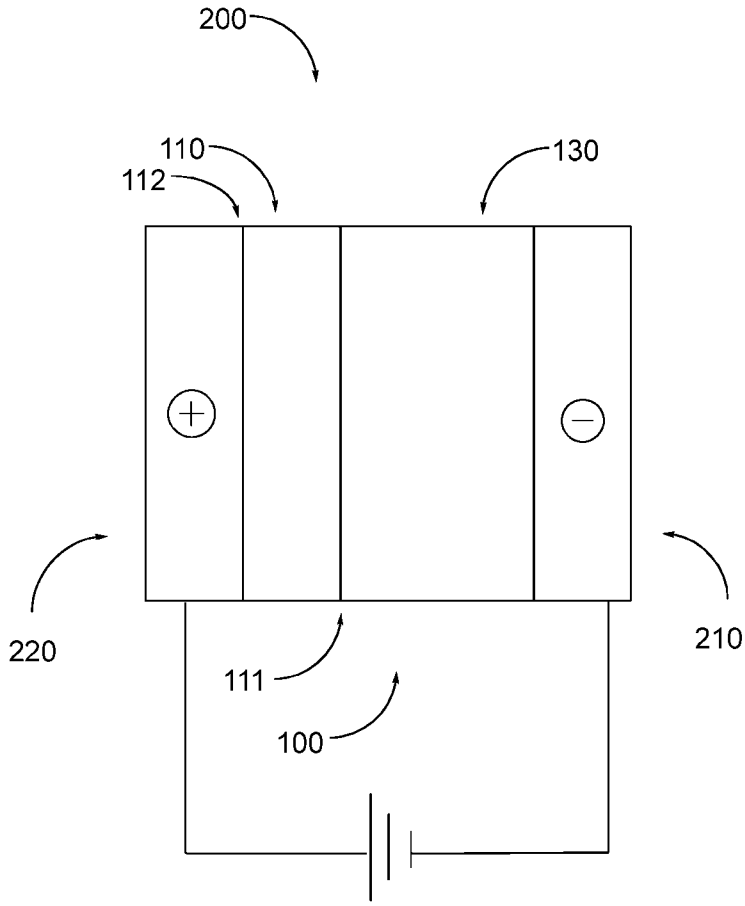


FIG. 3B