



(11) **EP 2 403 657 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:  
**28.12.2016 Bulletin 2016/52**

(21) Application number: **10749289.4**

(22) Date of filing: **03.03.2010**

(51) Int Cl.:  
**B82Y 10/00** <sup>(2011.01)</sup> **G03G 5/05** <sup>(2006.01)</sup>  
**G03G 5/06** <sup>(2006.01)</sup> **G03G 5/147** <sup>(2006.01)</sup>  
**G03G 15/00** <sup>(2006.01)</sup> **H01L 51/00** <sup>(2006.01)</sup>  
**H01L 51/05** <sup>(2006.01)</sup> **B82Y 30/00** <sup>(2011.01)</sup>  
**H01L 51/50** <sup>(2006.01)</sup> **H01L 51/52** <sup>(2006.01)</sup>

(86) International application number:  
**PCT/US2010/026100**

(87) International publication number:  
**WO 2010/102043 (10.09.2010 Gazette 2010/36)**

(54) **PROCESS FOR PREPARING STRUCTURED ORGANIC FILMS (SOFS) VIA A PRE-SOF**

VERFAHREN ZUR HERSTELLUNG STRUKTURIERTER ORGANISCHER FILME (SOF) MITHILFE EINES PRÄ-SOFS

PROCÉDÉ POUR PRÉPARER DES FILMS ORGANIQUES STRUCTURÉS (FOS) VIA UN PRÉ-FOS

(84) Designated Contracting States:  
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO SE SI SK SM TR**

(30) Priority: **04.03.2009 US 157411 P**

(43) Date of publication of application:  
**11.01.2012 Bulletin 2012/02**

(73) Proprietor: **Xerox Corporation**  
**Norwalk, CT 06856-4505 (US)**

(72) Inventors:  
• **HEUFT, Matthew A.**  
**Oakville**  
**Ontario L6L 6X4 (CA)**  
• **COTE, Adrien Pierre**  
**Clarkson**  
**Ontario L5J 4J7 (CA)**  
• **MCGUIRE, Gregory M.**  
**Oakville**  
**Ontario L6M 5J6 (CA)**  
• **GAGNON, Yvan**  
**Mississauga**  
**Ontario L5L 1K2 (CA)**

(74) Representative: **Grünecker Patent- und Rechtsanwälte**  
**PartG mbB**  
**Leopoldstraße 4**  
**80802 München (DE)**

(56) References cited:  
**WO-A2-2007/098263 JP-A- 9 087 849**  
**KR-B1- 100 832 309 US-A- 5 231 162**  
**US-A1- 2002 098 346 US-A1- 2006 097 393**  
**US-A1- 2008 132 669 US-A1- 2008 268 135**  
**US-B1- 6 248 686**

- **ZWANEVELDET AL.:** 'Organized Formation of 2D Extended Covalent Organic Frameworks at Surfaces.' **J. AM. CHEM. SOC.** vol. 130, 28 May 2008, pages 6678 - 6679, XP055033538
- **R. J. JENG ET AL.:** "Low loss second-order nonlinear optical polymers based on all organic sol-gel materials", **JOURNAL OF APPLIED POLYMER SCIENCE**, vol. 55, no. 2, 10 January 1995 (1995-01-10), pages 209-214, XP055057608, ISSN: 0021-8995, DOI: 10.1002/app.1995.070550203

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

**EP 2 403 657 B1**

**Description**

**[0001]** Materials whose chemical structures are comprised of molecules linked by covalent bonds into extended structures may be placed into two classes: (1) polymers and cross-linked polymers, and (2) covalent organic frameworks (also known as covalently linked organic networks).

**[0002]** The first class, polymers and cross-linked polymers, is typically embodied by polymerization of molecular monomers to form long linear chains of covalently-bonded molecules. Polymer chemistry processes can allow for polymerized chains to, in turn, or concomitantly, become 'cross-linked.' The nature of polymer chemistry offers poor control over the molecular-level structure of the formed material, i.e. the organization of polymer chains and the patterning of molecular monomers between chains is mostly random. Nearly all polymers are amorphous, save for some linear polymers that efficiently pack as ordered rods. Some polymer materials, notably block co-polymers, can possess regions of order within their bulk. In the two preceding cases the patterning of polymer chains is not by design, any ordering at the molecular-level is a consequence of the natural intermolecular packing tendencies.

**[0003]** The second class, covalent organic frameworks (COFs), differs from the first class (polymers/cross-linked polymers) in that COFs are intended to be highly patterned. In COF chemistry molecular components are called molecular building blocks rather than monomers. During COF synthesis molecular building blocks react to form two- or three-dimensional networks. Consequently, molecular building blocks are patterned throughout COF materials and molecular building blocks are linked to each other through strong covalent bonds.

**[0004]** COFs developed thus far are typically powders with high porosity and are materials with exceptionally low density. COFs can store near-record amounts of argon and nitrogen. While these conventional COFs are useful, there is a need, addressed by embodiments of the present invention, for new materials that offer advantages over conventional COFs in terms of enhanced characteristics.

**[0005]** The properties and characteristics of conventional COFs are described in US 7,582,798.

**[0006]** WO 2007/098263 discloses a process for forming a boronate linked porous network comprising: reacting a polyboronic acid or an acrylic boronate ester thereof with a polydiol to form a covalently bonded polymeric or oligomeric porous network of boronate linkages.

**[0007]** US 2006/097393 A1 relates to an insulating material used in insulating layers between electric wirings, comprising a borazine-silicon polymer obtained by hydrosilylation polymerization of a specific borazine compound and a specific silicon compound.

**[0008]** US-A-5231162 discloses a polyamic acid having a three-dimensional network molecular structure produced by a gel forming ring-opening polyaddition reaction in an organic solvent of the reaction components comprising (A) an acid component consisting of at least one tetracarboxylic acid dianhydride; (B) at least one aromatic diamine; and (C) at least one polyamino compound.

**[0009]** R.J. Jeng et al., "how Cross Second-Order Nonlinear Optical Polymers Based on All Organic Sol-Gel Materials", Journal of Applied Polymer Science, vol. 55, no. 2 (10.1.1995) pp. 209-214, relates to a new class of all organic sol-gel second order nonlinear optical materials based on hexa(methoxymethyl)melamine.

**SUMMARY OF THE DISCLOSURE**

**[0010]** There is provided a process for preparing a structured organic film (SOF) according to claim 1. The SOF comprises a plurality of segments and a plurality of linkers arranged as a covalent organic framework, wherein at a macroscopic level the covalent organic framework is a film. Further preferred embodiments are disclosed in the dependent claims 2 to 15.

**BRIEF DESCRIPTION OF THE DRAWING**

**[0011]** Other aspects of the present disclosure will become apparent as the following description proceeds and upon reference to the following figures which represent illustrative embodiments:

FIG. 1 represents a simplified side view of an exemplary photoreceptor that incorporates an SOF of the present disclosure.

FIG. 2 represents a simplified side view of a second exemplary photoreceptor that incorporates an SOF of the present disclosure.

FIG. 3 represents a simplified side view of a third exemplary photoreceptor that incorporates an SOF of the present disclosure.

FIG. 4 represents a simplified side view of a first exemplary thin film transistor that incorporates an SOF of the present disclosure.

FIGS 5 is a graphic representation that compares the Fourier transform infrared spectra of the products of control

experiments mixtures, wherein only N4,N4,N4',N4'-tetrakis(4-(methoxymethyl)phenyl)biphenyl-4,4'-diamine is added to the liquid reaction mixture (top), wherein only benzene-1,4-dimethanol is added to the liquid reaction mixture (middle), and wherein the necessary components needed to form a patterned Type 2 SOF are included into the liquid reaction mixture (bottom).

FIG. 6 is a graphic representation of a Fourier transform infrared spectrum of a free standing SOF comprising N4,N4,N4',N4'-tetra-p-tolylbiphenyl-4,4'-diamine segments, p-xylyl segments, and ether linkers.

FIG. 7 is a graphic representation of a Fourier transform infrared spectrum of a free standing SOF comprising N4,N4,N4',N4'-tetra-p-tolylbiphenyl-4,4'-diamine segments, n-hexyl segments, and ether linkers.

FIG. 8 is a graphic representation of a Fourier transform infrared spectrum of a free standing SOF comprising N4,N4,N4',N4'-tetra-p-tolylbiphenyl-4,4'-diamine segments, 4,4'-(cyclohexane-1,1-diyl)diphenyl segments, and ether linkers.

FIG. 9 is a graphic representation of a Fourier transform infrared spectrum of a free standing SOF comprising triphenylamine segments and ether linkers.

FIG. 10 is a graphic representation of a Fourier transform infrared spectrum of a free standing SOF comprising triphenylamine segments, benzene segments, and imine linkers.

FIG. 11 is a graphic representation of a Fourier transform infrared spectrum of a free standing SOF comprising triphenylamine segments, and imine linkers.

FIG. 12 is a graphic representation of a photo-induced discharge curve (PIDC) illustrating the photoconductivity of a Type 1 structured organic film overcoat layer.

FIG. 13 is a graphic representation of a photo-induced discharge curve (PIDC) illustrating the photoconductivity of a Type 1 structured organic film overcoat layer containing wax additives.

FIG. 14 is a graphic representation of a photo-induced discharge curve (PIDC) illustrating the photoconductivity of a Type 2 structured organic film overcoat layer.

FIG. 15 is a graphic representation of two-dimensional X-ray scattering data for the SOFs produced in illustrative Examples 26 and 55.

**[0012]** Unless otherwise noted, the same reference numeral in different Figures refers to the same or similar feature.

#### DETAILED DESCRIPTION

**[0013]** "Structured organic film" (SOF) is a new term introduced by the present disclosure to refer to a COF that is a film at a macroscopic level. The term "SOF" refers to a covalent organic framework (COF) that is a film at a macroscopic level. The phrase "macroscopic level" refers, for example, to the naked eye view of the present SOFs. Although COFs area network at the "microscopic level" or "molecular level" (requiring use of powerful magnifying equipment or as assessed using scattering methods), the present SOF is fundamentally different at the "macroscopic level" because the film is for instance orders of magnitude larger in coverage than a microscopic level COF network. SOFs described herein have macroscopic morphologies much different than typical COFs previously synthesized. COFs previously synthesized were typically obtained as polycrystalline or particulate powders wherein the powder is a collection of at least thousands of particles (crystals) where each particle (crystal) can have dimensions ranging from nanometers to millimeters. The shape of the particles can range from plates, spheres, cubes, blocks, prisms, etc. The composition of each particle (crystal) is the same throughout the entire particle while at the edges, or surfaces of the particle, is where the segments of the covalently-linked framework terminate. The SOFs described herein are not collections of particles. Instead, the SOFs of the present disclosure are at the macroscopic level substantially defect-free SOFs or defect-free SOFs having continuous covalent organic frameworks that can extend over larger length scales such as for instance much greater than a millimeter to lengths such as a meter and, in theory, as much as hundreds of meters. It will also be appreciated that SOFs tend to have large aspect ratios where typically two dimensions of a SOF will be much larger than the third. SOFs have markedly fewer macroscopic edges and disconnected external surfaces than a collection of COF particles.

**[0014]** In embodiments, a "substantially defect-free SOF" or "defect-free SOF" may be formed from a reaction mixture deposited on the surface of an underlying substrate. The term "substantially defect-free SOF" refers, for example, to an SOF that may or may not be removed from the underlying substrate on which it was formed and contains substantially no pinholes, pores or gaps greater than the distance between the cores of two adjacent segments per square cm; such as, for example, less than 10 pinholes, pores or gaps greater than 250 nanometers in diameter per cm<sup>2</sup>, or less than 5 pinholes, pores or gaps greater than 100 nanometers in diameter per cm<sup>2</sup>. The term "defect-free SOF" refers, for example, to an SOF that may or may not be removed from the underlying substrate on which it was formed and contains no pinholes, pores or gaps greater than the distance between the cores of two adjacent segments per 1.10<sup>-8</sup> cm<sup>2</sup> (micron<sup>2</sup>), such as no pinholes, pores or gaps greater than 10 nm (100 Angstroms) in diameter per 1.10<sup>-8</sup> cm<sup>2</sup> (micron<sup>2</sup>), no pinholes, pores or gaps greater than 5 nm (50 Angstroms) in diameter per 1.10<sup>-8</sup> cm<sup>2</sup> (micron<sup>2</sup>), or no pinholes, pores or gaps greater than 2 nm (20 Angstroms) in diameter per 1.10<sup>-8</sup> cm<sup>2</sup> (micron<sup>2</sup>).

[0015] In embodiments, the SOF comprises at least one atom of an element that is not carbon, such as at least one atom selected from the group consisting of hydrogen, oxygen, nitrogen, silicon, phosphorous, selenium, fluorine, boron, and sulfur. In further embodiments, the SOF is a boroxine-, borazine-, borosilicate-, and boronate ester-free SOF.

## 5 **Molecular Building Block**

[0016] The SOFs of the present disclosure comprise molecular building blocks having a segment (S) and functional groups (Fg). Molecular building blocks require at least two functional groups ( $x \geq 2$ ) and may comprise a single type or two or more types of functional groups. Functional groups are the reactive chemical moieties of molecular building blocks that participate in a chemical reaction to link together segments during the SOF forming process. A segment is the portion of the molecular building block that supports functional groups and comprises all atoms that are not associated with functional groups. Further, the composition of a molecular building block segment remains unchanged after SOF formation.

## 15 **Functional Group**

[0017] Functional groups are the reactive chemical moieties of molecular building blocks that participate in a chemical reaction to link together segments during the SOF forming process. Functional groups may be composed of a single atom, or functional groups may be composed of more than one atom. The atomic compositions of functional groups are those compositions normally associated with reactive moieties in chemical compounds. Non-limiting examples of functional groups include halogens, alcohols, ethers, ketones, carboxylic acids, esters, carbonates, amines, amides, imines, ureas, aldehyde, isocyanates, tosylates, alkenes, alkynes and the like.

[0018] Molecular building blocks contain a plurality of chemical moieties, but only a subset of these chemical moieties are intended to be functional groups during the SOF forming process. Whether or not a chemical moiety is considered a functional group depends on the reaction conditions selected for the SOF forming process. Functional groups (Fg) denote a chemical moiety that is a reactive moiety, that is, a functional group during the SOF forming process.

[0019] In the SOF forming process the composition of a functional group will be altered through the loss of atoms, the gain of atoms, or both the loss and the gain of atoms; or, the functional group may be lost altogether. In the SOF, atoms previously associated with functional groups become associated with linker groups, which are the chemical moieties that join together segments. Functional groups have characteristic chemistries and those of ordinary skill in the art can generally recognize in the present molecular building blocks the atom(s) that constitute functional group(s). It should be noted that an atom or grouping of atoms that are identified as part of the molecular building block functional group may be preserved in the linker group of the SOF. Linker groups are described below.

## 35 **Segment**

[0020] A segment is the portion of the molecular building block that supports functional groups and comprises all atoms that are not associated with functional groups. Further, the composition of a molecular building block segment remains unchanged after SOF formation. In embodiments, the SOF may contain a first segment having a structure the same as or different from a second segment. In other embodiments, the structures of the first and/or second segments may be the same as or different from a third segment, fourth segment, fifth segment, etc. A segment is also the portion of the molecular building block that can provide an inclined property. Inclined properties are described later in the embodiments.

[0021] In specific embodiments, the segment of the SOF comprises at least one atom of an element that is not carbon, such as at least one atom selected from the group consisting of hydrogen, oxygen, nitrogen, silicon, phosphorous, selenium, fluorine, boron, and sulfur.

[0022] Illustrated below are examples of molecular building blocks. In each example the portion of molecular building block identified as the segment (S) and functional groups (Fg) is indicated.

### ***Molecular building block with one type of functional group.***

50 [0023]

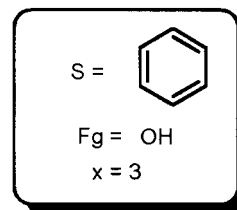
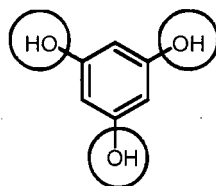
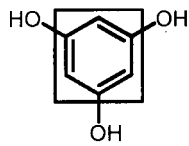
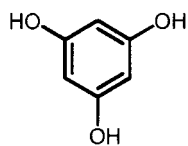
55

molecular building block

segment (S)  
(phenyl ring denoted in square)

functional groups (Fg)  
(three circled OH groups)

5



10

*Molecular building block with two types of functional groups.*

15

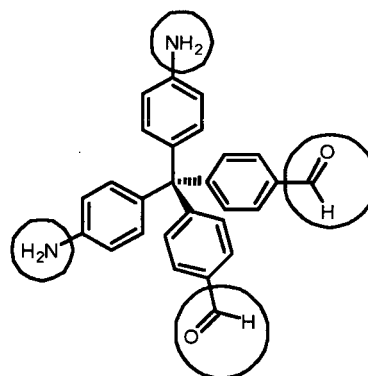
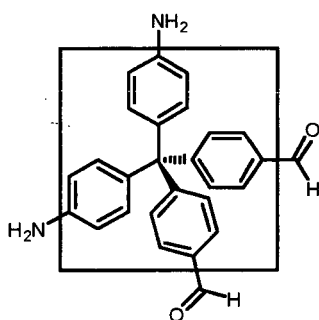
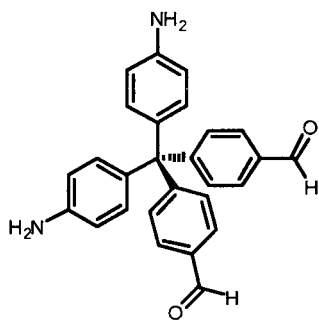
[0024]

molecular building block

segment (S)  
(tetraphenylmethane group denoted in square)

functional groups (Fg)  
(two circled NH<sub>2</sub> groups, and two circled CHO groups)

20

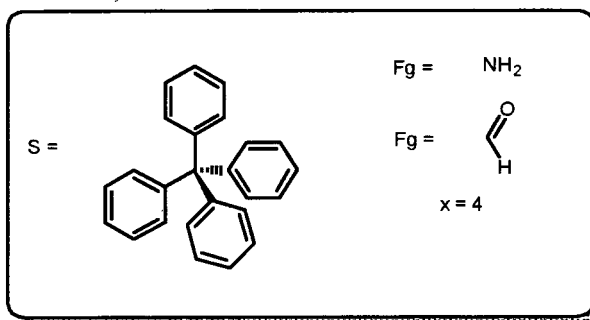


25

30

35

40



45

*Molecular building block with two types of functional groups.*

[0025]

50

55

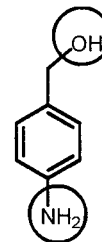
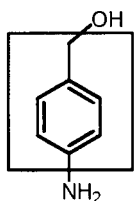
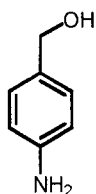
molecular building block

segment (S)  
(tolyl group outlined  
by solid box)

functional groups (Fg)  
(circled amino and circled hydroxyl groups)

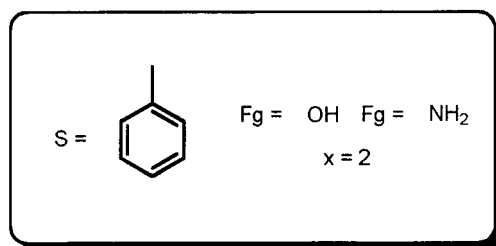
5

10



15

20



Linker

25

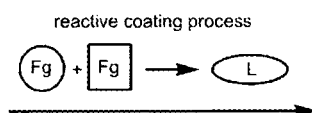
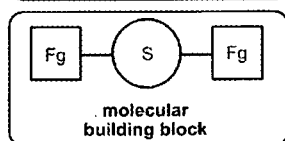
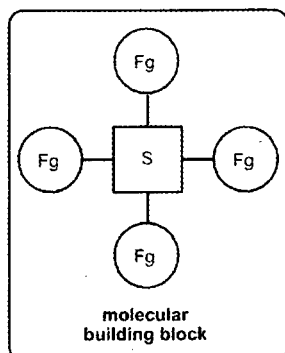
**[0026]** A linker is a chemical moiety that emerges in an SOF upon chemical reaction between functional groups present on the molecular building blocks (illustrated below).

30

35

40

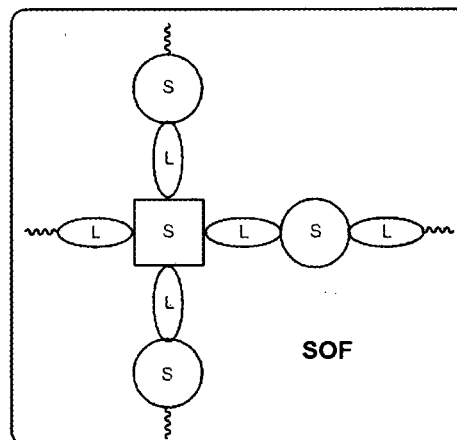
45



**S = segment**  
(portion of the molecular building block conserved in SOF)

**Fg = functional group**  
(reactive portion of the molecular building block)

**L = linker**  
(connects segments moieties in SOF)



**[0027]** A linker may comprise a covalent bond, a single atom, or a group of covalently bonded atoms. The former is defined as a covalent bond linker and may be, for example, a single covalent bond or a double covalent bond and emerges when functional groups on all partnered building blocks are lost entirely. The latter linker type is defined as a chemical moiety linker and may comprise one or more atoms bonded together by single covalent bonds, double covalent bonds, or combinations of the two. Atoms contained in linking groups originate from atoms present in functional groups on molecular building blocks prior to the SOF forming process. Chemical moiety linkers may be well-known chemical groups such as, for example, esters, ketones, amides, imines, ethers, urethanes, carbonates, and the like, or derivatives thereof.

**[0028]** For example, when two hydroxyl (-OH) functional groups are used to connect segments in an SOF via an oxygen atom, the linker would be the oxygen atom, which may also be described as an ether linker. In embodiments, the SOF may contain a first linker having a structure different from a second linker. In other embodiments, the structures of the first and/or second linkers may be different from a third linker, etc.

[0029] In specific embodiments, the linker comprises at least one atom of an element that is not carbon, such as at least one atom selected from the group consisting of hydrogen, oxygen, nitrogen, silicon, phosphorous, selenium, fluorine, boron, and sulfur.

5 SOF Types

[0030] Three exemplary types of SOF are described below. These SOF types are expressed in terms of segment and linker combinations. The naming associated with a particular SOF type bears no meaning toward the composition of building blocks selected, or procedure used to synthesize an SOF, or the physical properties of the SOF.

10

Type 1 SOF: comprises one segment type and one linker type.

Type 2 SOF: comprises two segment types and one linker type.

Type 3 SOF : comprises a plurality of segment types and a plurality of linker types or comprises one segment type and a plurality of linker types.

15

[0031] In embodiments, a plurality of building block types may be employed in a single process to generate an SOF, which in turn would contain a plurality of segment types so long as the reactivity between building block functional groups remains compatible. An SOF comprising a plurality of linker types is described as a Type 3 SOF.

20

[0032] For example, among the various possibilities for Type 3 SOFs, a Type 3 SOF may comprise a plurality of linkers including at least a first linker and a second linker (and optionally a third, fourth, or fifth, etc., linker) that are different in structure, and a plurality of segments including at least a first segment and a second segment (and optionally a third, fourth, or fifth, etc., segment) that are different in structure, where the first segment, when it is not at the edge of the SOF, is connected to at least three other segments (such as three of the second segments being connected via linkers to a first segment), wherein at least one of the connections is via the first linker and at least one of the connections is via the second linker; or a Type 3 SOF may comprise a plurality of linkers including at least a first linker and a second linker (and optionally a third, fourth, or fifth, etc., linker) that are different in structure, and a plurality of segments consisting of segments having an identical structure, where the segments that are not at the edges of the SOF are connected by linkers to at least three other segments, where at least one of the connections is via the first linker, and at least one of the connections is via the second linker.

25

30

### Illustration of SOF Types

35

[0033] Described below are non-limiting examples for strategies to synthesize a specific SOF type with exemplary chemical structures. From the illustrations below, it is made clear here that it is possible that the same SOF type may be synthesized using different sets of molecular building blocks. In each of the strategies provided below only a fragment of the chemical structure of the SOF is displayed.

[0034] **Strategy 1: Production of a Type 1 SOF using one type of molecular building block. This SOF contains an ethylene (two atom) linker type.**

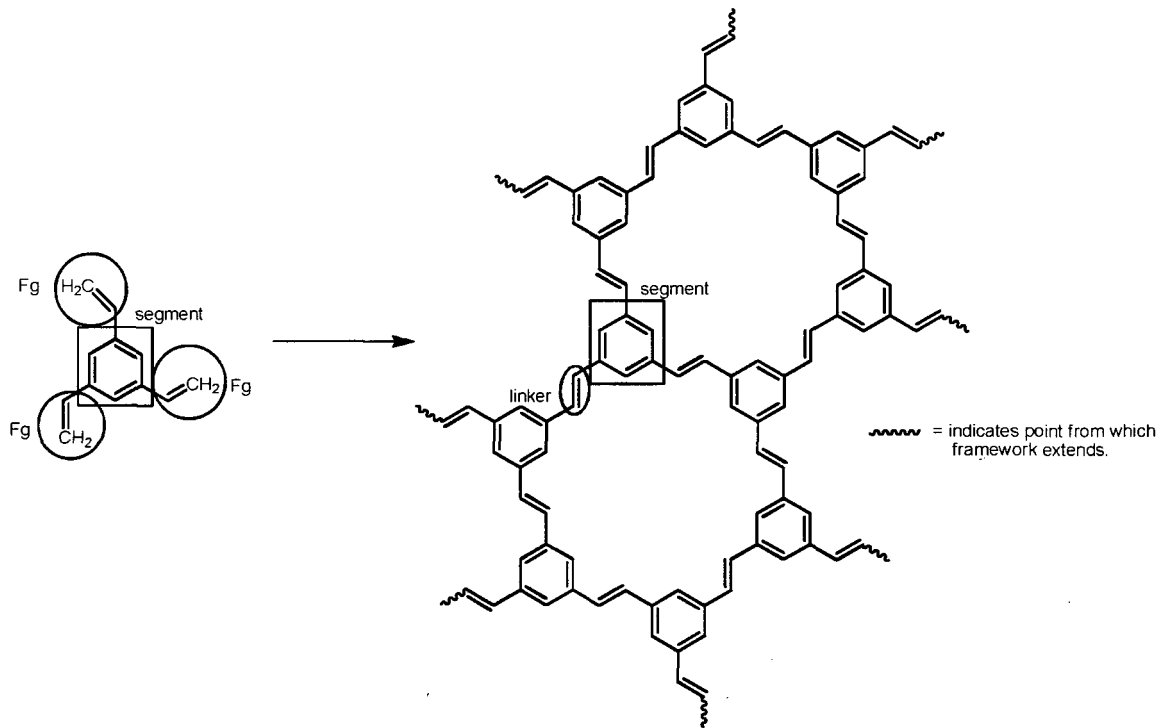
40

45

50

55

5  
10  
15  
20  
25  
30  
35  
40  
45  
50  
55

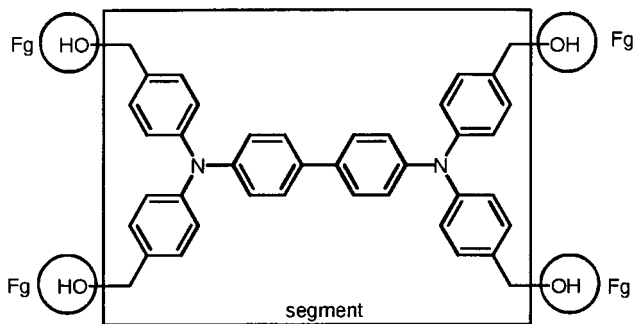


**[0035] Strategy 2: Production of a Type 1 SOF using one type of molecular building block. This SOF contains a single atom linker type.**



5

10



15



20

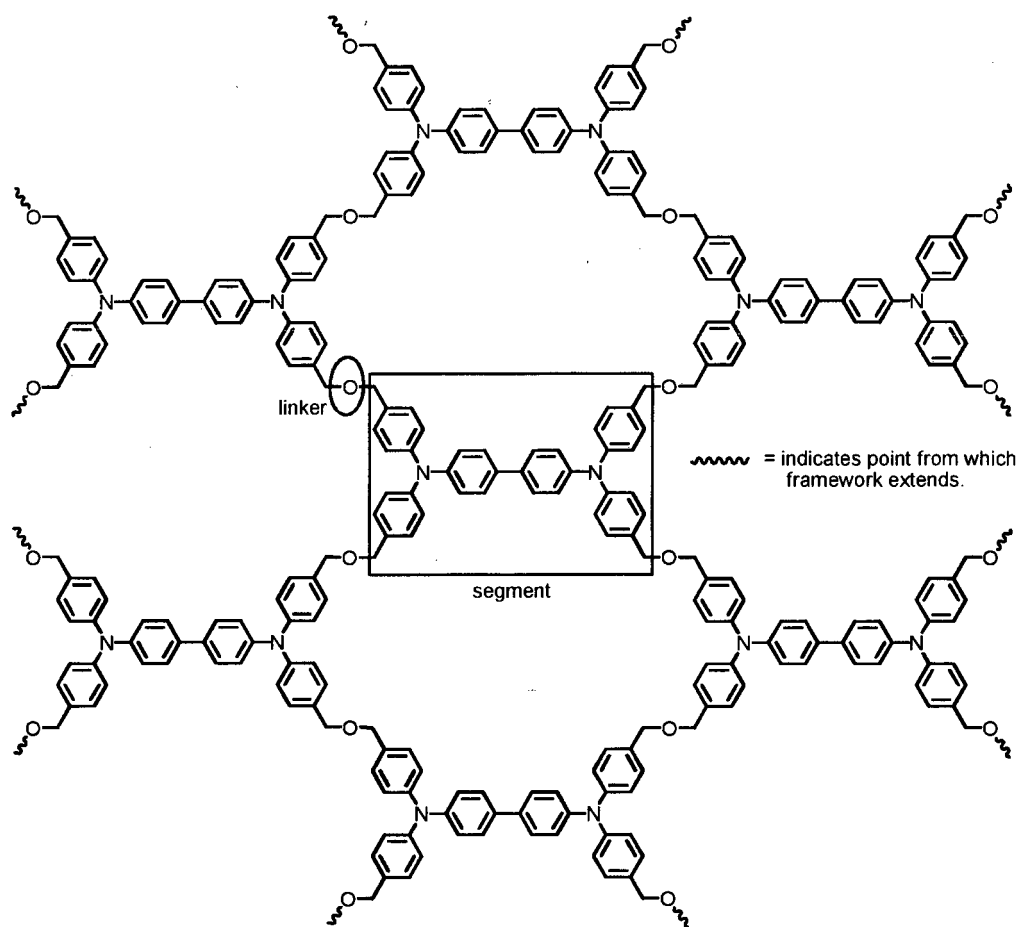
25

30

35

40

45



50

**[0036] Strategy 3: Production of a Type 1 SOF using two types of molecular building blocks wherein the segments are the same. This SOF contains an imine (two atom) linker type.**

55

5

10

15

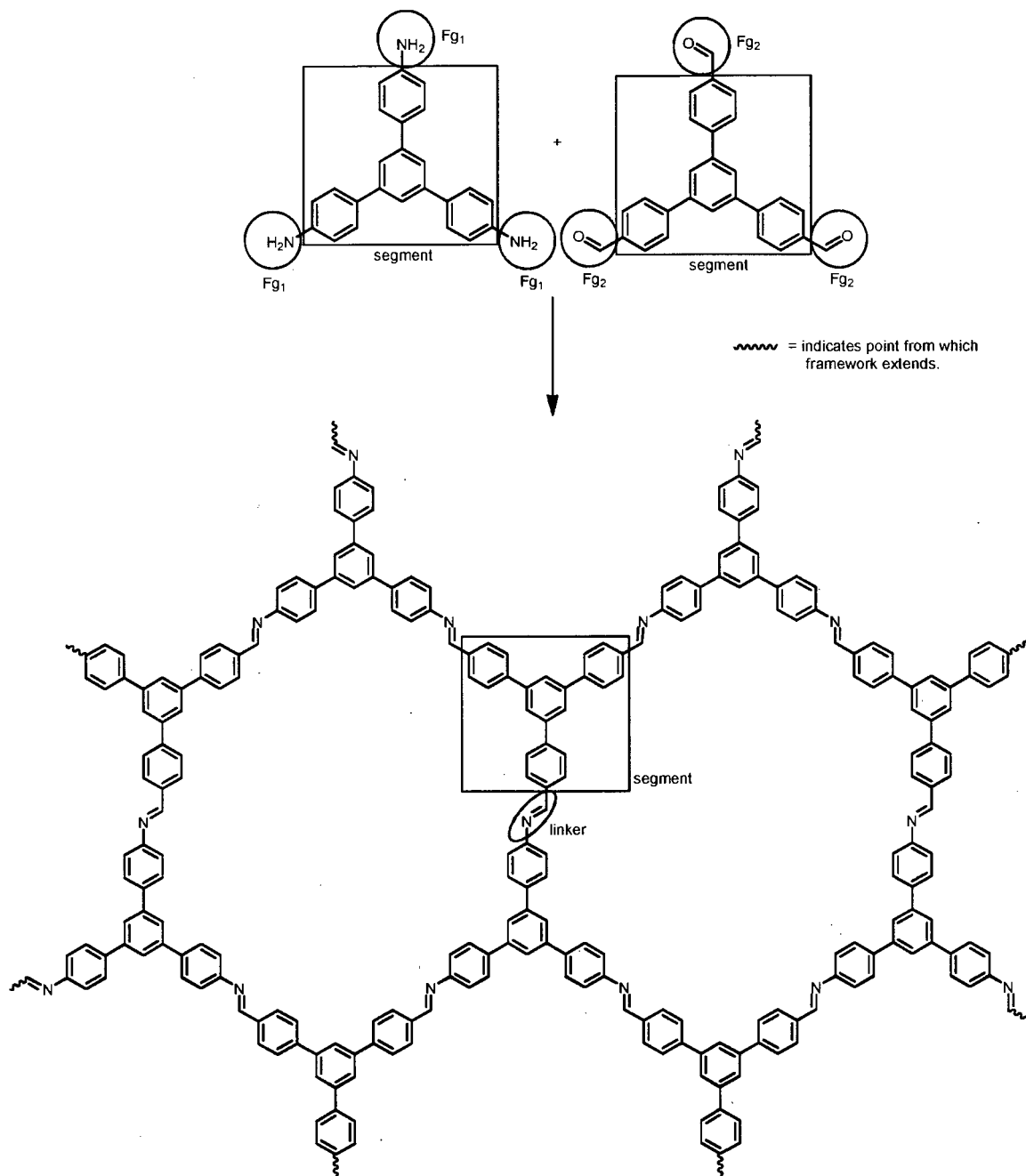
20

25

30

35

40



45 **[0037]** Strategy 4: Production of a Type 2 SOF using two types of molecular building blocks This SOF contains **two segment types** and a **single linker type (amide, four atoms)**

50

55

5

10

15

20

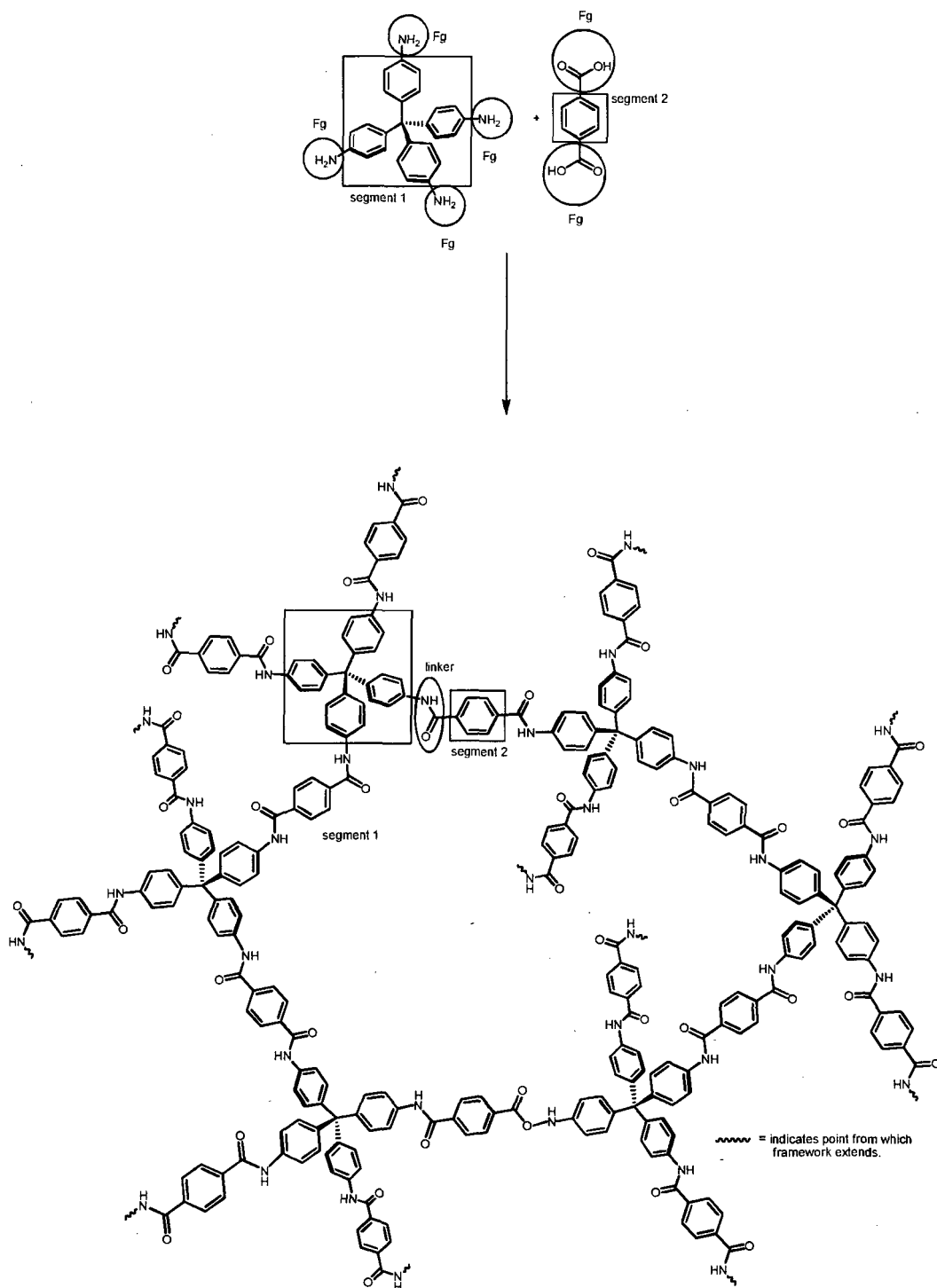
25

30

35

40

45



50

**[0038] Strategy 5: Production of a Type 3 SOF using two types of molecular building blocks. In this cases the number of segments is two and the number of linker types is two. In addition, the SOF has patterned segments linked by imine (three atoms) and amide (four atoms) linkers.**

55



circle goniometers equipped with point, line, or area detection systems capable of detecting scattering (electromagnetic and/or subatomic) in 1-, 2-, or 3-dimensions, imaging tools such as, but are not limited to, electron microscopes equipped to detect scattered electrons from materials.

5 [0044] Alternatively, imaging methods capable of mapping structures at micron and submicron scales may be employed to assess the periodicity of an SOF. Such methods include, but are not limited to, scanning electron microscopy, tunneling electron microscopy, and atomic force microscopy.

### Multilayer SOFs

10 [0045] An SOF may comprise a single layer or a plurality of layers (that is, two, three or more layers). SOFs that are comprised of a plurality of layers may be physically joined (e.g., dipole and hydrogen bond) or chemically joined. Physically attached layers are characterized by weaker interlayer interactions or adhesion; therefore physically attached layers may be susceptible to delamination from each other. Chemically attached layers are expected to have chemical bonds (e.g., covalent or ionic bonds) or have numerous physical or intermolecular (supramolecular) entanglements that strongly link adjacent layers.

15 [0046] Therefore, delamination of chemically attached layers is much more difficult. Chemical attachments between layers may be detected using spectroscopic methods such as focusing infrared or Raman spectroscopy, or with other methods having spatial resolution that can detect chemical species precisely at interfaces. In cases where chemical attachments between layers are different chemical species than those within the layers themselves it is possible to detect these attachments with sensitive bulk analyses such as solid-state nuclear magnetic resonance spectroscopy or by using other bulk analytical methods.

20 [0047] In the embodiments, the SOF may be a single layer (mono-segment thick or multi-segment thick) or multiple layers (each layer being mono-segment thick or multi-segment thick). "Thickness" refers, for example, to the smallest dimension of the film. As discussed above, in an SOF, segments are molecular units that are covalently bonded through linkers to generate the molecular framework of the film. The thickness of the film may also be defined in terms of the number of segments that is counted along that axis of the film when viewing the cross-section of the film. A "monolayer" SOF is the simplest case and refers, for example, to where a film is one segment thick. An SOF where two or more segments exist along this axis is referred to as a "multi-segment" thick SOF.

25 [0048] An exemplary method for preparing physically attached multilayer SOFs includes: (1) forming a base SOF layer that may be cured by a first curing cycle, and (2) forming upon the base layer a second reactive wet layer followed by a second curing cycle and, if desired, repeating the second step to form a third layer, a fourth layer and so on. The physically stacked multilayer SOFs may have thicknesses greater than 2 nm (20 Angstroms) such as, for example, the following illustrative thicknesses: 2 nm (20 Angstroms) to 10 cm, such as 1 nm to 10 mm, or 0.1 mm to 5 mm. In principle there is no limit with this process to the number of layers that may be physically stacked.

30 [0049] In embodiments, a multilayer SOF is formed by a method for preparing chemically attached multilayer SOFs by: (1) forming a base SOF layer having functional groups present on the surface (or dangling functional groups) from a first reactive wet layer, and (2) forming upon the base layer a second SOF layer from a second reactive wet layer that comprises molecular building blocks with functional groups capable of reacting with the dangling functional groups on the surface of the base SOF layer. If desired, the formulation used to form the second SOF layer should comprise molecular building blocks with functional groups capable of reacting with the dangling functional groups from the base layer as well as additional functional groups that will allow for a third layer to be chemically attached to the second layer. The chemically stacked multilayer SOFs may have thicknesses greater than 2 nm (20 Angstroms) such as, for example, the following illustrative thicknesses: 2 nm (20 Angstroms) to 10 cm, such as 1 nm to 10 mm, or 0.1 mm to 5 mm. In principle there is no limit with this process to the number of layers that may be chemically stacked.

35 [0050] In embodiments, the method for preparing chemically attached multilayer SOFs comprises promoting chemical attachment of a second SOF onto an existing SOF (base layer) by using a small excess of one molecular building block (when more than one molecular building block is present) during the process used to form the SOF (base layer) whereby the functional groups present on this molecular building block will be present on the base layer surface. The surface of the base layer may be treated with an agent to enhance the reactivity of dangling functional groups or to create an increased number of dangling functional groups.

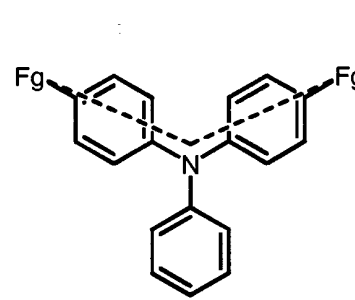
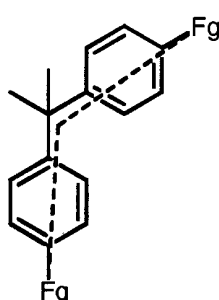
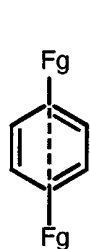
40 [0051] In an embodiment the dangling functional groups present on the surface of an SOF may be altered to increase the propensity for covalent attachment (or, alternatively, to disfavor covalent attachment) of particular classes of molecules or individual molecules, such as SOFs, to a base layer or any additional substrate or SOF layer. For example, the surface of a base layer, such as an SOF layer, which may contain reactive dangling functional groups, may be rendered pacified through surface treatment with a capping chemical group. For example, an SOF layer having dangling hydroxyl alcohol groups may be pacified by treatment with trimethylsilylchloride thereby capping hydroxyl groups as stable trimethylsilyl ethers. Alternatively, the surface of the base layer may be treated with a non-chemically bonding agent, such as a wax, to block reaction with dangling functional groups from subsequent layers.

## Molecular Building Block Symmetry

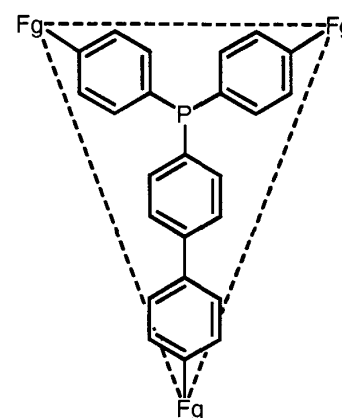
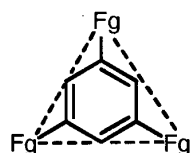
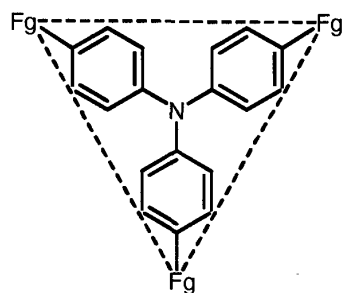
**[0052]** Molecular building block symmetry relates to the positioning of functional groups (Fgs) around the periphery of the molecular building block segments. Without being bound by chemical or mathematical theory, a symmetric molecular building block is one where positioning of Fgs may be associated with the ends of a rod, vertexes of a regular geometric shape, or the vertexes of a distorted rod or distorted geometric shape. For example, the most symmetric option for molecular building blocks containing four Fgs are those whose Fgs overlay with the corners of a square or the apexes of a tetrahedron.

**[0053]** Use of symmetrical building blocks is practiced in embodiments of the present disclosure for two reasons: (1) the patterning of molecular building blocks may be better anticipated because the linking of regular shapes is a better understood process in reticular chemistry, and (2) the complete reaction between molecular building blocks is facilitated because for less symmetric building blocks errant conformations/orientations may be adopted which can possibly initiate numerous linking defects within SOFs.

**[0054]** Drawn below are building blocks whose symmetrical elements are outlined. Such symmetrical elements are found in building blocks used in the present disclosure.



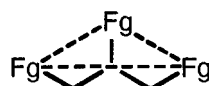
ideal rod building block    ideal rod building block    ,    distorted rod building block    ,    distorted rod building block



ideal triangular building block

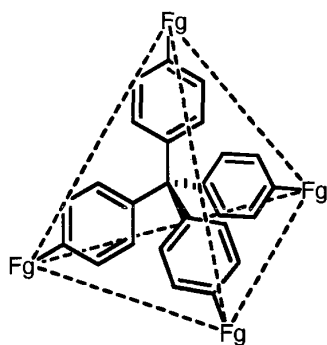
ideal triangular building block

distorted triangular building block

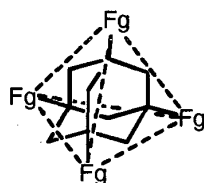


distorted triangular building block

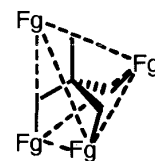
5  
10  
15  
20  
25  
30  
35  
40  
45  
50  
55



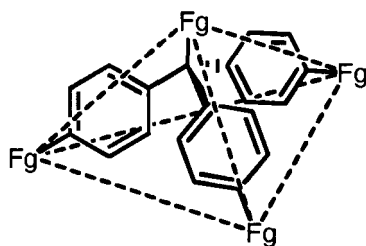
ideal tetrahedral building block



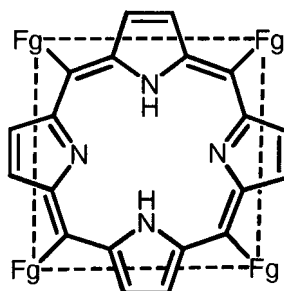
ideal tetrahedral building block



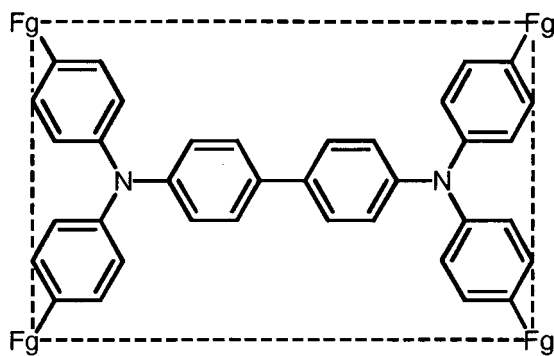
distorted tetrahedral building block



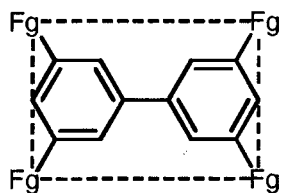
distorted tetrahedral building block



ideal square building block



distorted square/tetrahedral building block



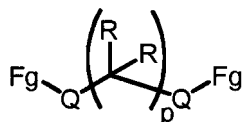
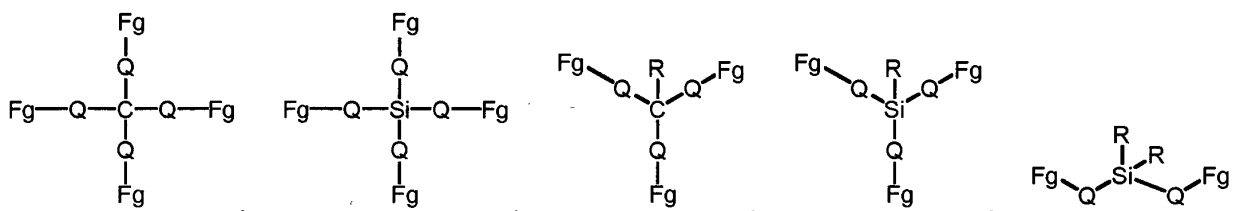
distorted square/tetrahedral building block

5  
10 [0055] Type 1 SOFs contain segments, which are not located at the edges of the SOF, that are connected by linkers to at least three other segments. For example, the SOF comprises at least one symmetrical building block selected from the group consisting of ideal triangular building blocks, distorted triangular building blocks, ideal tetrahedral building blocks, distorted tetrahedral building blocks, ideal square building blocks, and distorted square building blocks. Type 2 and 3 SOFs contains one segment type or at least two segment types, which are not located at the edges of the SOF, that are connected by linkers to at least three other segments. For example, the SOF comprises at least one symmetrical building block selected from the group consisting of ideal triangular building blocks, distorted triangular building blocks, ideal tetrahedral building blocks, distorted tetrahedral building blocks, ideal square building blocks, and distorted square building blocks.

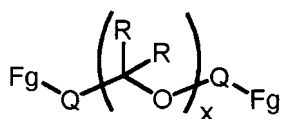
### 20 Molecular Building Block Enumeration

[0056] Illustrated below is a list of classes of exemplary molecular entities and examples of members of each class that may serve as molecular building blocks for SOFs of the present disclosure.

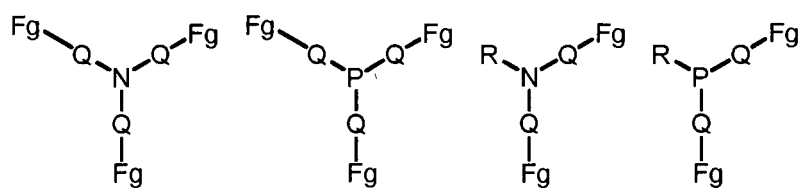
[0057] Building blocks containing a carbon or silicon atomic core:



40 Building blocks containing an alkoxy core:



Building blocks containing a nitrogen or phosphorous atomic core:

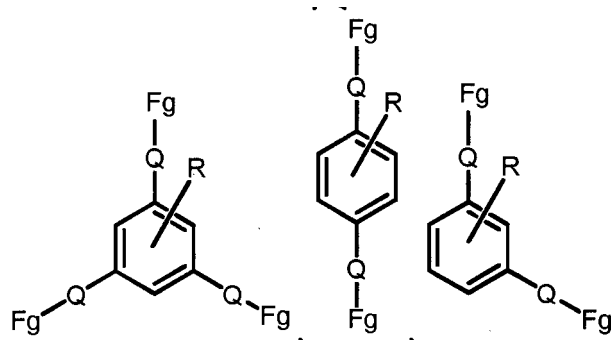


Building blocks containing an aryl core:



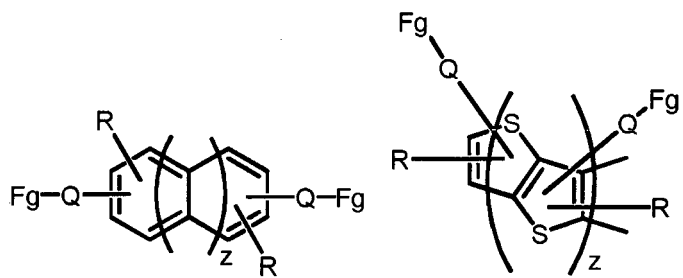
5

10



15

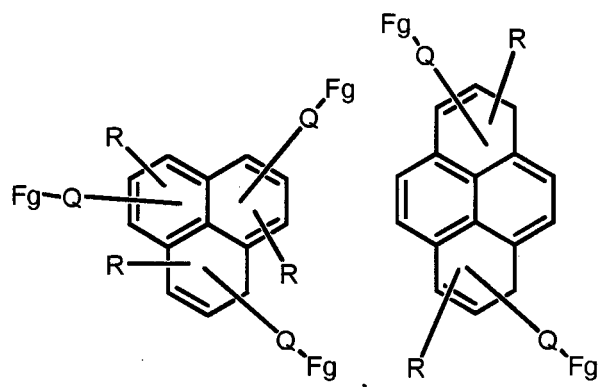
20



25

30

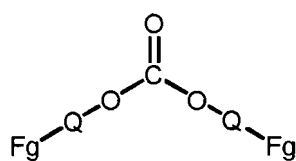
35



Building blocks containing a carbonate core:

40

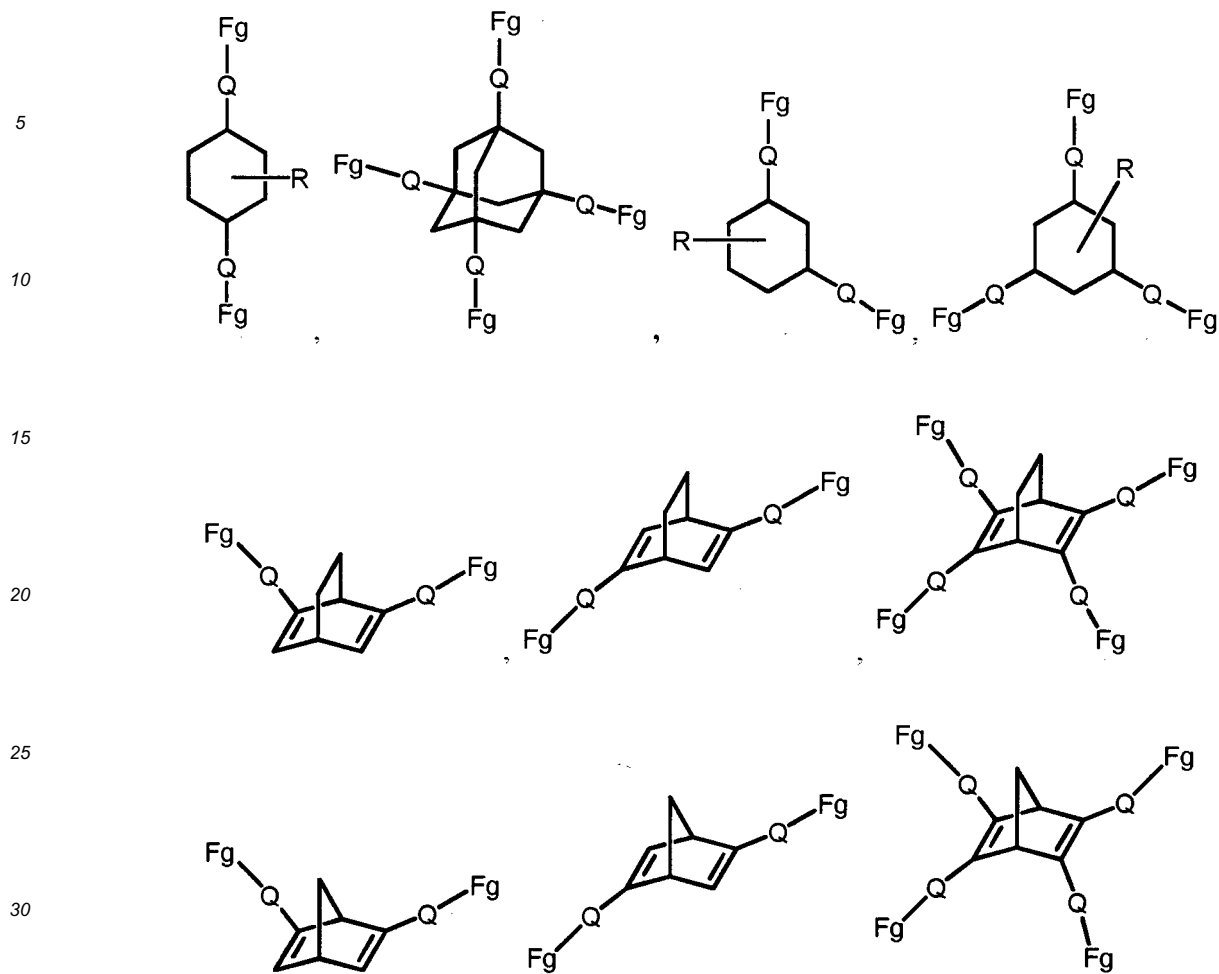
45



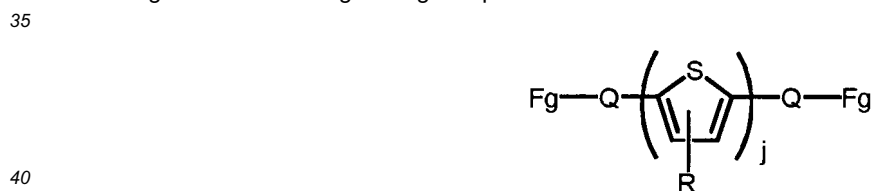
Building blocks containing a carbocyclic-, carbobicyclic-, or carbotricyclic core:

50

55



Building blocks containing an oligothiophene core:



**[0058]** Where Q may be independently selected from:

- 45
- 50
- 55
- Aryl, biaryl, triaryl, and naphthyl, optionally substituted with C1-C8 branched and unbranched alkyl, branched and unbranched C1-C8 perfluoroalkyl, C1-C6 carbocyclic, amino, hydroxyl, halogen, cyano, nitro, ketone, carboxylic acid, carboxylic ester, mercaptyl, thioether;
  - Aryl, biaryl, triaryl, and naphthyl, containing 1-3 heteroatoms per ring, optionally substituted with C1-C8 branched and unbranched alkyl, branched and unbranched C1-C8 perfluoroalkyl, C1-C6 carbocyclic, amino, hydroxyl, halogen, cyano, nitro, carboxylic acid, carboxylic ester, mercaptyl, thioether;
  - branched and unbranched C1-C8 perfluoroalkyl, C1-C6 carbocyclic, amino, hydroxyl, halogen, cyano, nitro, carboxylic acid, ketone, carboxylic ester, mercaptyl, thioether, alkyl ether, aryl ether,
  - C 1-C12 branched and unbranched alkyl;
  - C1-C12 branched an unbranched perfluoroalkyl; and
  - oligoether containing as many as 12 C-O units;
  - with p of the Group IV atomic core ranging from 1 to 24, such as from 12 to 24 x of the alkoxy core ranging from 1 to 12, such as from 6 to 12; z ranging from 1 to 4, such as from 2 to 4; and j ranging from 1 to 12.

Where Fg is a functional group, as defined earlier in the embodiments, and which may be independently selected from:

-alcohol, alkyl or aryl ether, cyano, amino, halogen, ketone, carboxylic acid, carboxylic acid ester, carboxylic acid chloride, aryl or alkyl sulfonyl, formyl, hydrogen, and isocyanate.

[0059] Where R is independently selected from:

- 5 - Aryl, biaryl, triaryl, and naphthyl, optionally substituted with C1-C8 branched and unbranched alkyl, branched and unbranched C1-C8 perfluoroalkyl, C1-C6 carbocyclic, amino, hydroxyl, halogen, cyano, nitro, ketone, carboxylic acid, carboxylic ester, mercaptlyl, thioether,
- Aryl, biaryl, triaryl, and naphthyl, containing 1-3 heteratoms per ring optionally substituted with C1-C8 branched and unbranched alkyl, branched and unbranched C1-C8 perfluoroalkyl, C1-C6 carbocyclic, amino, hydroxy, halogen,
- 10 - branched and unbranched C1-C8 perfluoroalkyl, C1-C6 carbocyclic, amino, hydroxyl, halogen, cyano, nitro, ketone, carboxylic acid, carboxylic ester, mercaptlyl, thioether, C1-C12 branched and unbranched alkyl;
- C 1-C12 branched an unbranched perfluoroalkyl;
- 15 - oligoether containing as many as 12 C-O units; and
- alcohol, alkyl or aryl ether, cyano, amino, halogen, carboxylic acid, carboxylic acid ester, ketone, carboxylic acid chloride, aryl or alkyl sulfonyl, formyl, hydrogen, isocyanate and the like.

### Practice of Linking Chemistry

20 [0060] In embodiments linking chemistry may occur wherein the reaction between functional groups produces a volatile byproduct that may be largely evaporated or expunged from the SOF during or after the film forming process or wherein no byproduct is formed. Linking chemistry may be selected to achieve an SOF for applications where the presence of linking chemistry byproducts is not desired. Linking chemistry reactions may include, for example, condensation, addition/elimination, and addition reactions, such as, for example, those that produce esters, imines, ethers, carbonates, urethanes, amides, acetals, and silyl ethers.

25 [0061] In embodiments the linking chemistry may occur via a reaction between functional groups producing volatile byproduct that largely remains incorporated within the SOF after the film forming process. Linking chemistry in embodiments may be selected to achieve an SOF for applications where the presence of linking chemistry byproducts does not impact the properties or for applications where the presence of linking chemistry byproduct may alter the properties of an SOF (such as, for example, the electroactive, hydrophobic or hydrophilic nature of the SOF). Linking chemistry reactions may include, for example, substitution, metathesis, and metal catalyzed coupling reactions, such as those that produce carbon-carbon bonds.

30 [0062] For all linking chemistry the ability to control the rate and extent of reaction between building blocks via the chemistry between building block functional groups is an important aspect of the present disclosure. Reasons for controlling the rate and extent of reaction may include adapting the film forming process for different coating methods and tuning the microscopic arrangement of building blocks to achieve a periodic SOF, as defined in earlier embodiments.

### Innate Properties of COFs

40 [0063] COFs have innate properties such as high thermal stability (typically higher than 400 °C under atmospheric conditions); poor solubility in organic solvents (chemical stability), and porosity (capable of reversible guest uptake). In embodiments, SOFs may also possess these innate properties.

### Added Functionality of SOFs

45 [0064] Added functionality denotes a property that is not inherent to conventional COFs and may occur by the selection of molecular building blocks wherein the molecular compositions provide the added functionality in the resultant SOF. Added functionality may arise upon assembly of molecular building blocks having an "inclined property" for that added functionality. Added functionality may also arise upon assembly of molecular building blocks having no "inclined property" for that added functionality but the resulting SOF has the added functionality as a consequence of linking segments (S) and linkers into an SOF. Furthermore, emergence of added functionality may arise from the combined effect of using molecular building blocks bearing an "inclined property" for that added functionality whose inclined pproperty is modified or enhanced upon linking together the segments and linkers into an SOF.

### An Inclined Property of a Molecular Building Block

55 [0065] The term "inclined property" of a molecular building block refers, for example, to a property known to exist for

certain molecular compositions or a property that is reasonably identifiable by a person skilled in art upon inspection of the molecular composition of a segment. As used herein, the terms "inclined property" and "added functionality" refer to the same general property (e.g., hydrophobic, electroactive, etc.) but "inclined property" is used in the context of the molecular building block and "added functionality" is used in the context of the SOF.

5 **[0066]** The hydrophobic (superhydrophobic), hydrophilic, lipophobic (superlipophobic), lipophilic, photochromic and/or electroactive (conductor, semiconductor, charge transport material) nature of an SOF are some examples of the properties that may represent an "added functionality" of an SOF. These and other added functionalities may arise from the inclined properties of the molecular building blocks or may arise from building blocks that do not have the respective added functionality that is observed in the SOF.

10 **[0067]** The term hydrophobic (superhydrophobic) refers, for example, to the property of repelling water, or other polar species such as methanol, it also means an inability to absorb water and/or to swell as a result. Furthermore, hydrophobic implies an inability to form strong hydrogen bonds to water or other hydrogen bonding species. Hydrophobic materials are typically characterized by having water contact angles greater than 90° and superhydrophobic materials have water contact angles greater than 150° as measured using a contact angle goniometer or related device.

15 **[0068]** The term hydrophilic refers, for example, to the property of attracting, adsorbing, or absorbing water or other polar species, or a surface that is easily wetted by such species. Hydrophilic materials are typically characterized by having less than 20° water contact angle as measured using a contact angle goniometer or related device. Hydrophilicity may also be characterized by swelling of a material by water or other polar species, or a material that can diffuse or transport water, or other polar species, through itself. Hydrophilicity, is further characterized by being able to form strong or numerous hydrogen bonds to water or other hydrogen bonding species.

20 **[0069]** The term lipophobic (oleophobic) refers, for example, to the property of repelling oil or other non-polar species such as alkanes, fats, and waxes. Lipophobic materials are typically characterized by having oil contact angles greater than 90° as measured using a contact angle goniometer or related device.

25 **[0070]** The term lipophilic (oleophilic) refers, for example, to the property of attracting oil or other non-polar species such as alkanes, fats, and waxes or a surface that is easily wetted by such species. Lipophilic materials are typically characterized by having a low to nil oil contact angle as measured using, for example, a contact angle goniometer. Lipophilicity can also be characterized by swelling of a material by hexane or other non-polar liquids.

30 **[0071]** The term photochromic refers, for example, to the ability to demonstrate reversible color changes when exposed to electromagnetic radiation. SOF compositions containing photochromic molecules may be prepared and demonstrate reversible color changes when exposed to electromagnetic radiation. These SOFs may have the added functionality of photochromism. The robustness of photochromic SOFs may enable their use in many applications, such as photochromic SOFs for erasable paper, and light responsive films for window tinting/shading and eye wear. SOF compositions may contain any suitable photochromic molecule, such as difunctional photochromic molecules as SOF molecular building blocks (chemically bound into SOF structure), monofunctional photochromic molecules as SOF capping groups (chemically bound into SOF structure), or unfunctionalized photochromic molecules in a composite SOF (not chemically bound into SOF structure). Photochromic SOFs may change color upon exposure to selected wavelengths of light and the color change may be reversible.

35 **[0072]** SOF compositions containing photochromic molecules that chemically bond to the SOF structure are exceptionally chemically and mechanically robust photochromic materials. Such photochromic SOF materials demonstrate many superior properties, such as a high number of reversible color change processes, to available polymeric alternatives.

40 **[0073]** The term electroactive refers, for example, to the property to transport electrical charge (electrons and/or holes). Electroactive materials include conductors, semiconductors, and charge transport materials. Conductors are defined as materials that readily transport electrical charge in the presence of a potential difference Semiconductors are defined as materials that do not inherently conduct charge but may become conductive in the presence of a potential difference and applied stimuli, such as, for example, an electric field, electromagnetic radiation, heat, and the like. Charge transport materials are defined as materials that can transport charge when charge is injected from another material such as, for example, a dye, pigment, or metal in the presence of a potential difference.

45 **[0074]** Conductors may be further defined as materials that give a signal using a potentiometer from 0.1 to 10<sup>7</sup> S/cm.

50 **[0075]** Semiconductors may be further defined as materials that give a signal using a potentiometer from 10<sup>-6</sup> to 10<sup>4</sup> S/cm in the presence of applied stimuli such as, for example an electric field, electromagnetic radiation, heat, and the like. Alternatively, semiconductors may be defined as materials having electron and/or hole mobility measured using time-of-flight techniques in the range of 10<sup>-10</sup> to 10<sup>6</sup> to 10<sup>6</sup>cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> when exposed to applied stimuli such as, for example an electric field, electromagnetic radiation, heat, and the like.

55 **[0076]** Charge transport materials may be further defined as materials that have electron and/or hole mobility measured using time-of-flight techniques in the range of 10<sup>-10</sup> to 10<sup>6</sup> cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. It should be noted that under some circumstances charge transport materials may be also classified as semiconductors.

**[0077]** SOFs with hydrophobic added functionality may be prepared by using molecular building blocks with inclined hydrophobic properties and/or have a rough, textured, or porous surface on the sub-micron to micron scale. A paper

describing materials having a rough, texture, or porous surface on the sub-micron to micron scale being hydrophobic was authored by Cassie and Baxter (Cassie, A. B. D.; Baxter, S. *Trans. Faraday Soc.*, 1944, 40, 546).

**[0078]** Molecular building blocks comprising or bearing highly-fluorinated segments have inclined hydrophobic properties and may lead to SOFs with hydrophobic added functionality. Highly-fluorinated segments are defined as the number of fluorine atoms present on the segment(s) divided by the number of hydrogen atoms present on the segment(s) being greater than one. Fluorinated segments, which are not highly-fluorinated segments may also lead to SOFs with hydrophobic added functionality.

**[0079]** The above-mentioned fluorinated segments may include, for example, tetrafluorohydroquinone, perfluoroadipic acid hydrate, 4,4'-(hexafluoroisopropylidene)diphthalic anhydride, 4,4'-(hexafluoroisopropylidene)diphenol, and the like.

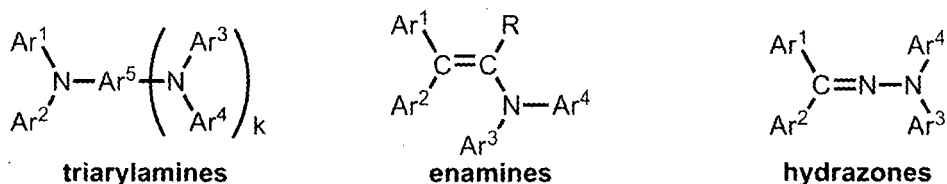
**[0080]** SOFs having a rough, textured, or porous surface on the sub-micron to micron scale may also be hydrophobic. The rough, textured, or porous SOF surface can result from dangling functional groups present on the film surface or from the structure of the SOF. The type of pattern and degree of patterning depends on the geometry of the molecular building blocks and the linking chemistry efficiency. The feature size that leads to surface roughness or texture is from 100 nm to 10  $\mu\text{m}$ , such as from 500 nm to 5  $\mu\text{m}$ .

**[0081]** SOFs with hydrophilic added functionality may be prepared by using molecular building blocks with inclined hydrophilic properties and/or comprising polar linking groups.

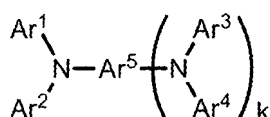
**[0082]** Molecular building blocks comprising segments bearing polar substituents have inclined hydrophilic properties and may lead to SOFs with hydrophilic added functionality. The term polar substituents refers, for example, to substituents that can form hydrogen bonds with water and include, for example, hydroxyl, amino, ammonium, and carbonyl (such as ketone, carboxylic acid, ester, amide, carbonate, urea).

**[0083]** SOFs with electroactive added functionality may be prepared by using molecular building blocks with inclined electroactive properties and/or be electroactive resulting from the assembly of conjugated segments and linkers. The following sections describe molecular building blocks with inclined hole transport properties, inclined electron transport properties, and inclined semiconductor properties.

**[0084]** SOFs with hole transport added functionality may be obtained by selecting segment cores such as, for example, triaryl amines, hydrazones (U.S. Patent No. 7,202,002 B2 to Tokarski et al.), and enamines (U.S. Patent No. 7,416,824 B2 to Kondoh et al.) with the following general structures:



The segment core comprising a triaryl amine being represented by the following general formula:

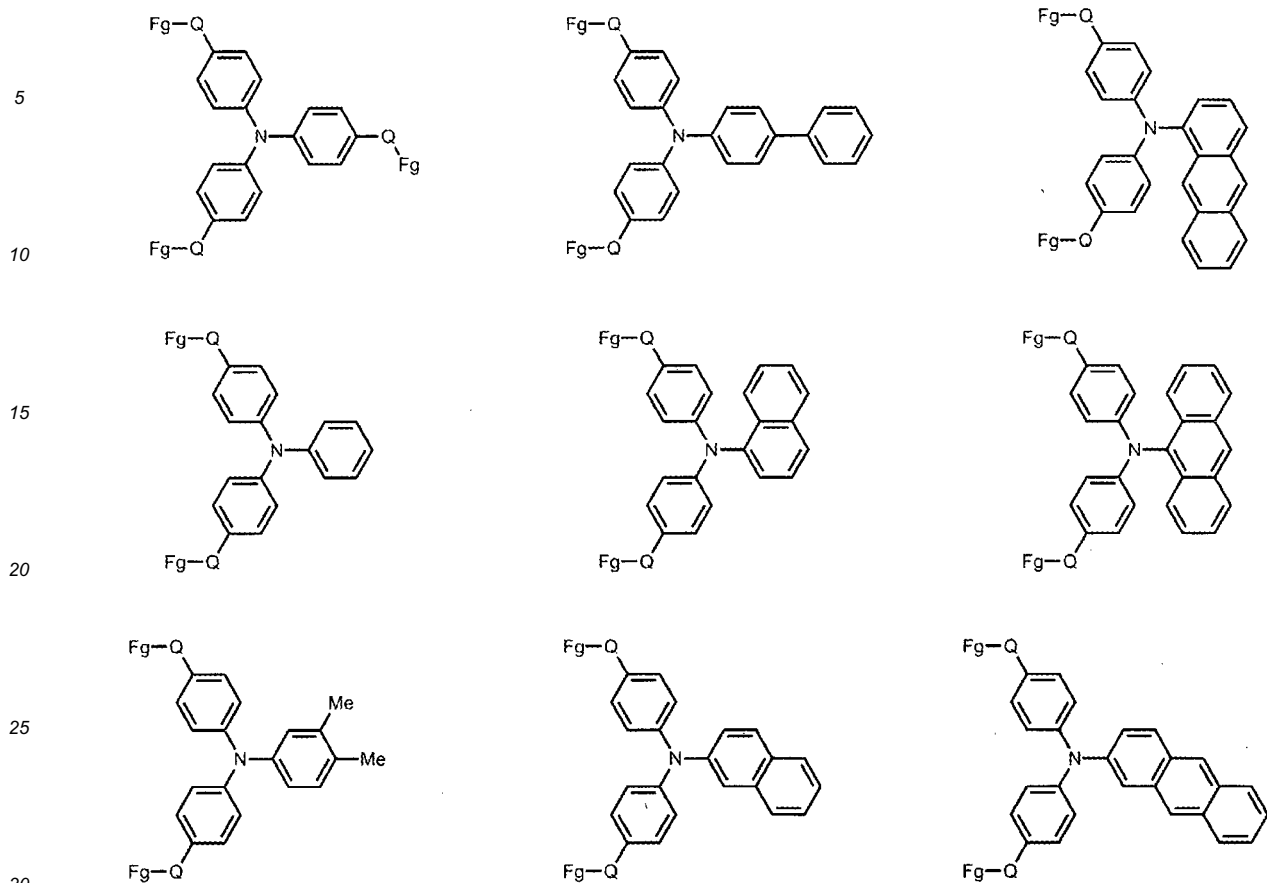


wherein Ar<sup>1</sup>, Ar<sup>2</sup>, Ar<sup>3</sup>, Ar<sup>4</sup> and Ar<sup>5</sup> each independently represents a substituted or unsubstituted aryl group, or Ar<sup>5</sup> independently represents a substituted or unsubstituted arylene group, and k represents 0 or 1, wherein at least two of Ar<sup>1</sup>, Ar<sup>2</sup>, Ar<sup>3</sup>, Ar<sup>4</sup> and Ar<sup>5</sup> comprises a Fg (previously defined). Ar<sup>5</sup> may be further defined as, for example, a substituted phenyl ring, substituted/unsubstituted phenylene, substituted/unsubstituted monovalently linked aromatic rings such as biphenyl, terphenyl, and the like, or substituted/unsubstituted fused aromatic rings such as naphthyl, anthranyl, phenanthryl, and the like.

**[0085]** Segment cores comprising aryl amines with hole transport added functionality include, for example, aryl amines such as triphenylamine, N,N,N',N'-tetraphenyl-(1,1'-biphenyl)-4,4'-diamine, N,N'-diphenyl-N,N'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine, N,N'-bis(4-butylphenyl)-N,N'-diphenyl-[p-terphenyl]-4,4''-diamine; hydrazones such as N-phenyl-N-methyl-3-(9-ethyl)carbazyl hydrazone and 4-diethyl amino benzaldehyde-1,2-diphenyl hydrazone; and oxadiazoles such as 2,5-bis(4-N,N'-diethylaminophenyl)-1,2,4-oxadiazole, stilbenes, and the like.

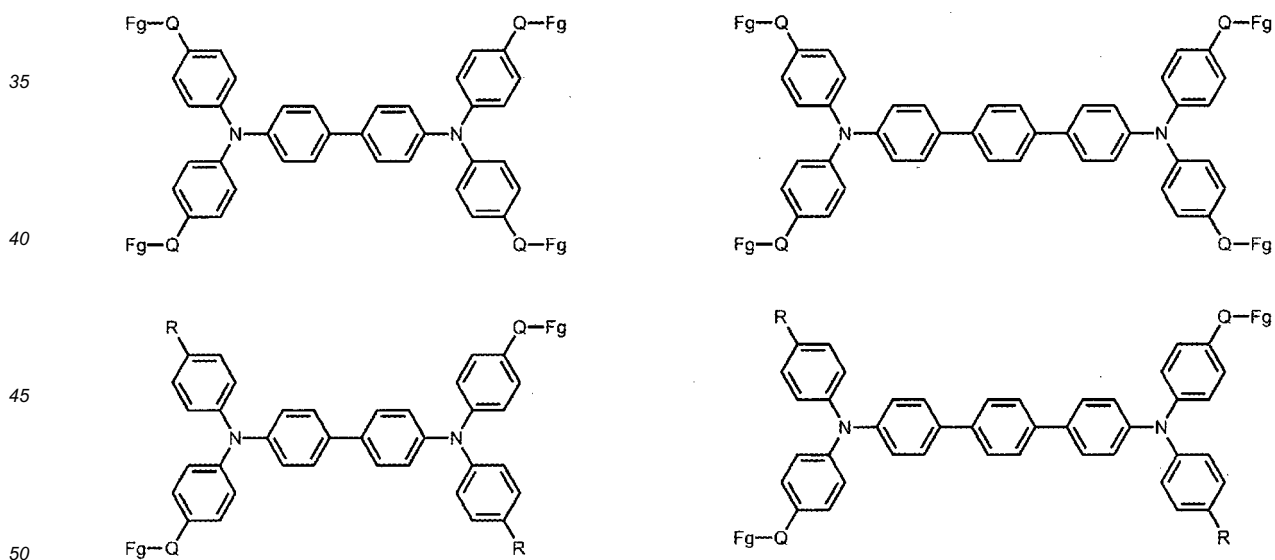
**[0086]** Molecular building blocks comprising triaryl amine core segments with inclined hole transport properties may be derived from the list of chemical structures including, for example, those listed below:

triarylamine cores



tetraarylbiphenylenediamine (TBD) cores

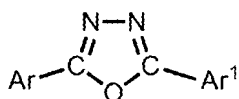
tetraarylterphenylenediamine (TER) cores



[0087] The segment core comprising a hydrazone being represented by the following general formula:



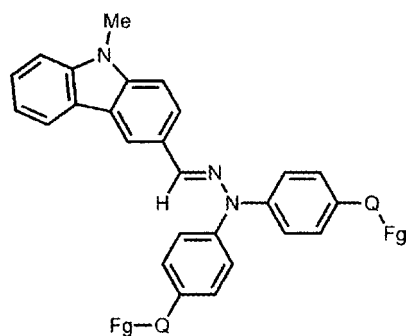
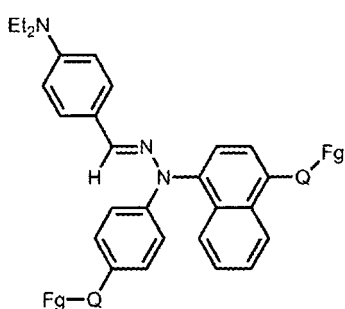
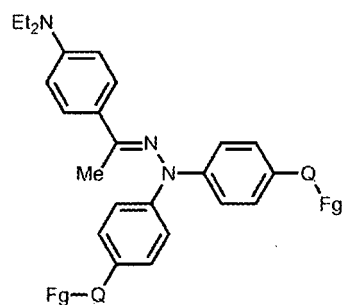
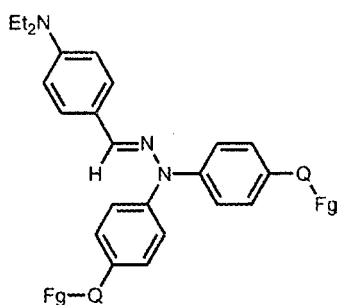
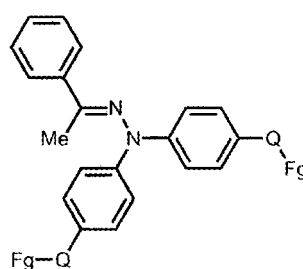
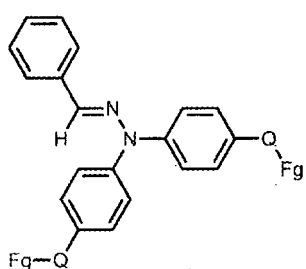
wherein Ar<sup>1</sup>, Ar<sup>2</sup>, and Ar<sup>3</sup> each independently represents an aryl group optionally containing one or more substituents, and R represents a hydrogen atom, an aryl group, or an alkyl group optionally containing a substituent; wherein at least two of Ar<sup>1</sup>, Ar<sup>2</sup>, and Ar<sup>3</sup> comprises a Fg (previously defined); and a related oxadiazole being represented by the following general formula:



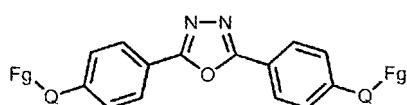
wherein Ar and Ar<sup>1</sup> each independently represent an aryl group that comprises a Fg (previously defined).

**[0088]** Molecular building blocks comprising hydrazone and oxadiazole core segments with inclined hole transport properties may be derived from the list of chemical structures including, for example, those listed below:

#### hydrazone cores



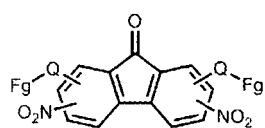
#### oxadiazole cores



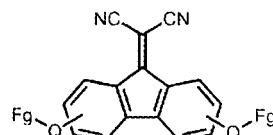
**[0089]** The segment core comprising an enamine being represented by the following general formula:



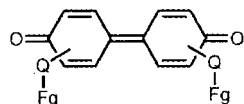




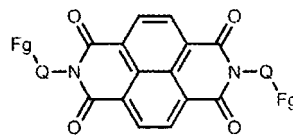
nitrofluorenones



9-fluorenylidene malonitriles



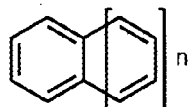
diphenoquinones



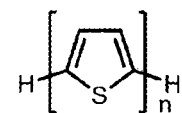
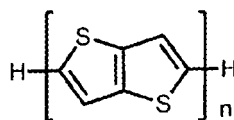
naphthalenetetracarboxylic diimides

15 It should be noted that the carbonyl groups of diphenylquinones could also act as Fgs in the SOF forming process.

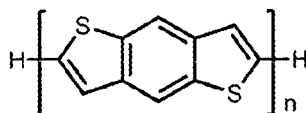
**[0092]** SOFs with semiconductor added functionality may be obtained by selecting segment cores such as, for example, acenes, thiophenes/oligothiophenes/fused thiophenes, perylene bisimides, or tetrathiofulvalenes, and derivatives thereof with the following general structures:



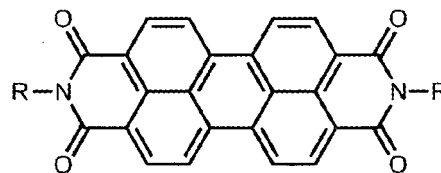
acenes



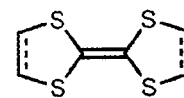
oligothiophenes



fused thiophenes



perylene bisimides

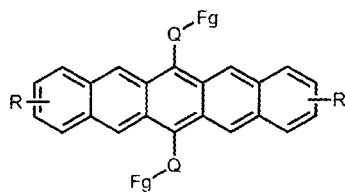


tetrathiofulvalenes

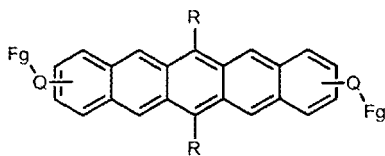
40 **[0093]** The SOF may be a p-type semiconductor, n-type semiconductor or ambipolar semiconductor. The SOF semiconductor type depends on the nature of the molecular building blocks. Molecular building blocks that possess an electron donating property such as alkyl, alkoxy, aryl, and amino groups, when present in the SOF, may render the SOF a p-type semiconductor. Alternatively, molecular building blocks that are electron withdrawing such as cyano, nitro, fluoro, fluorinated alkyl, and fluorinated aryl groups may render the SOF into the n-type semiconductor.

45 **[0094]** Molecular building blocks comprising acene core segments with inclined semiconductor properties may be derived from the list of chemical structures including, for example, those listed below:

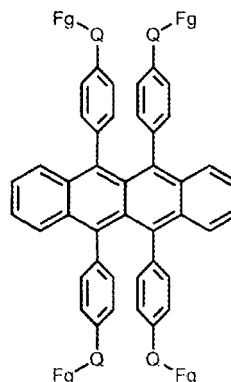
5



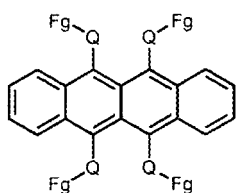
10



15

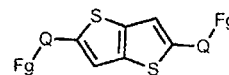
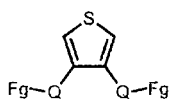
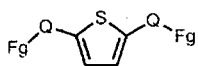


20

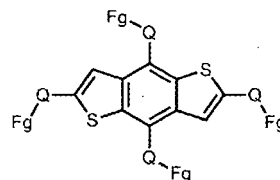
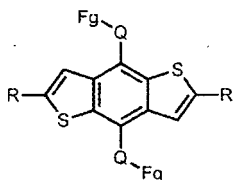
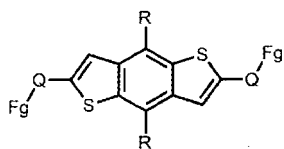


**[0095]** Molecular building blocks comprising thiophene/oligothiophene/fused thiophene core segments with inclined semiconductor properties may be derived from the list of chemical structures including, for example, those listed below:

25



30



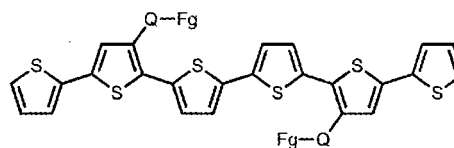
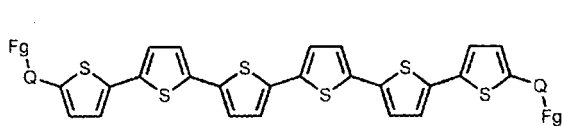
35

(or isomer and mixtures)

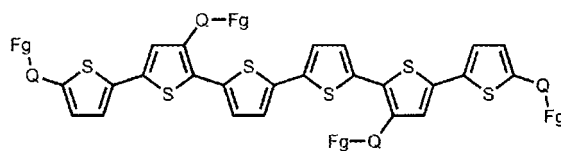
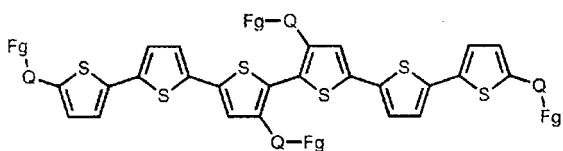
(or isomer and mixtures)

(or isomer and mixtures)

40



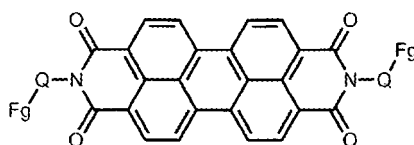
45



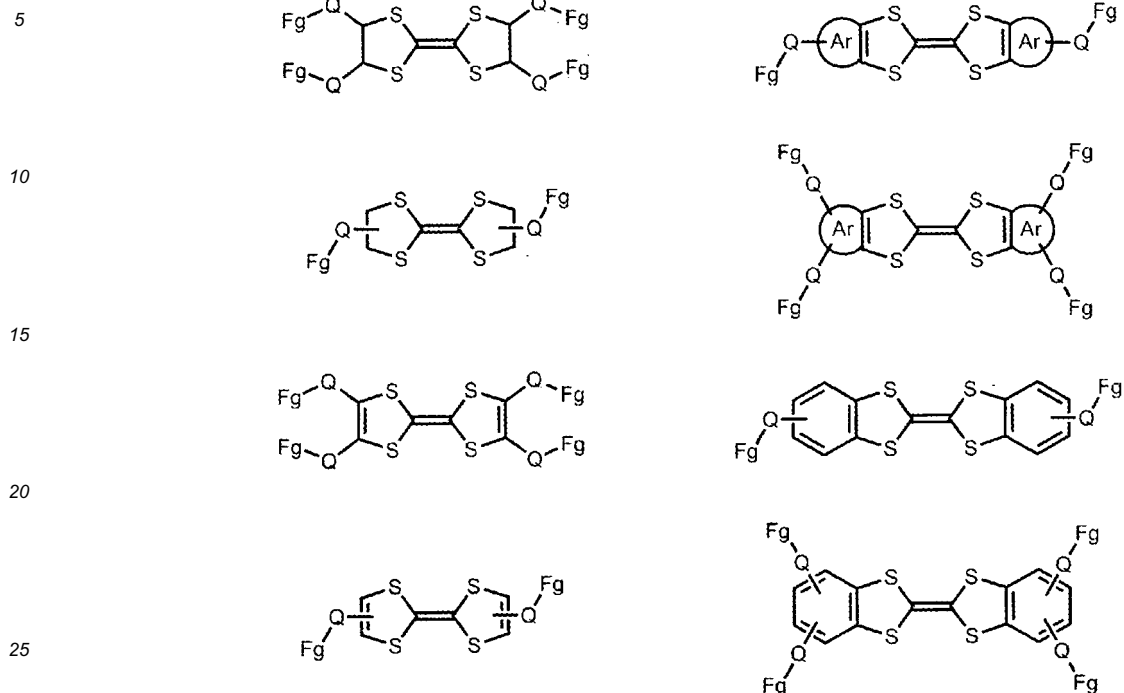
50

**[0096]** Examples of molecular building blocks comprising perylene bisimide core segments with inclined semiconductor properties may be derived from the chemical structure below:

55



**[0097]** Molecular building blocks comprising tetrathiofulvalene core segments with inclined semiconductor properties may be derived from the list of chemical structures including, for example, those listed below:



wherein Ar each independently represents an aryl group that optionally contains one or more substituents or a heterocyclic group that optionally contains one or more substituents.

**[0098]** Similarly, the electroactivity of SOFs prepared by these molecular building blocks will depend on the nature of the segments, nature of the linkers, and how the segments are orientated within the SOF. Linkers that favor preferred orientations of the segment moieties in the SOF are expected to lead to higher electroactivity.

### Process for Preparing a Structured Organic Film

**[0099]** The process for making SOFs typically comprises a number of activities or steps (set forth below) that may be performed in any suitable sequence or where two or more activities are performed simultaneously or in close proximity in time.

A process for preparing a structured organic film comprises:

- (a) preparing a liquid-containing reaction mixture comprising a plurality of molecular building blocks each comprising a segment and a number of functional groups, and a pre-SOF;
- (b) depositing the reaction mixture as a wet film;
- (c) promoting a change of the wet film including the molecular building blocks to a dry film comprising the SOF comprising a plurality of the segments and a plurality of linkers arranged as a covalent organic framework, wherein at a macroscopic level the covalent organic framework is a film;
- (d) optionally removing the SOF from the coating substrate to obtain a free-standing SOF;
- (e) optionally processing the free-standing SOF into a roll;
- (f) optionally cutting and seaming the SOF into a belt; and
- (g) optionally performing the above SOF formation process(es) upon an SOF (which was prepared by the above SOF formation process(es)) as a substrate for subsequent SOF formation process(es).

**[0100]** The above activities or steps may be conducted at atmospheric, super atmospheric or subatmospheric pressure. The term "atmospheric pressure" as used herein refers to a pressure or  $1.10^5$  Pa (760 torr). The term "super atmospheric" refers to pressures greater than atmospheric pressure, but less than  $2.10^6$  Pa (20 atm). The term "subatmospheric pressure" refers to pressures less than atmospheric pressure. In an embodiment, the activities or steps may be conducted at or near atmospheric pressure. Generally, pressures of from  $1.10^4$  to  $2.10^5$  Pa (0.1 atm to 2 atm), such as from  $5.10^4$  to  $1.5.10^5$  Pa (0.5 atm to 1.5 atm) or  $8.10^4$  to  $1.2.10^5$  Pa (0.8 atm to 1.2 atm) may be conveniently employed.

**Process Action A: Preparation of the Liquid-Containing Reaction Mixture**

5 [0101] The reaction mixture comprises a plurality of molecular building blocks that are dissolved, suspended, or mixed in a liquid. The plurality of molecular building blocks may be of one type or two or more types. When one or more of the molecular building blocks is a liquid, the use of an additional liquid is optional. Catalysts may optionally be added to the reaction mixture to enable pre-SOF formation and/or modify the kinetics of SOF formation during Action C described above. The term "pre-SOF" may refer to, for example, at least two molecular building blocks that have reacted and have a molecular weight higher than the starting molecular building blocks and contain multiple functional groups capable of undergoing further reactions with functional groups of other molecular building blocks or pre-SOFs to obtain an SOF, which may be a substantially defect-free or defect-free SOF, and/or the 'activation' of molecular building block functional groups that imparts enhanced or modified reactivity for the film forming process. Activation may include dissociation of a functional group moiety, pre-association with a catalyst, association with a solvent molecule, liquid, second solvent, second liquid, secondary component, or with any entity that modifies functional group reactivity. Pre-SOF formation includes the partial reaction between molecular building blocks or the 'activation' of molecular building block functional groups, or a combination of the two. The formation of the "pre-SOF" may be achieved in a number of ways, such as heating the reaction mixture, exposure of the reaction mixture to UV radiation, or any other means of partially reacting the molecular building blocks and/or activating functional groups in the reaction mixture prior to deposition of the wet layer on the substrate. Additives or secondary components may optionally be added to the reaction mixture to alter the physical properties of the resulting SOF.

20 [0102] The reaction mixture components (molecular building blocks, optionally a liquid, optionally catalysts, and optionally additives) are combined in a vessel. The order of addition of the reaction mixture components may vary; however, typically when a process for preparing an SOF includes a pre-SOF or formation of a pre-SOF, the catalyst, when present, may be added to the reaction mixture before depositing the reaction mixture as a wet film. In embodiments, the molecular building blocks may be reacted actinically, thermally, chemically or by any other means with or without the presence of a catalyst to obtain a pre-SOF. The pre-SOF and the molecular building blocks formed in the absence of a catalyst may be heated in the liquid in the absence of the catalyst to aid the dissolution of the molecular building blocks and pre-SOFs. In embodiments, the pre-SOF and the molecular building blocks formed in the presence of a catalyst may be heated at a temperature that does not cause significant further reaction of the molecular building blocks and/or the pre-SOFs to aid the dissolution of the molecular building blocks and pre-SOFs. The reaction mixture may also be mixed, stirred, milled, or the like, to ensure even distribution of the formulation components prior to depositing the reaction mixture as a wet film.

35 [0103] In embodiments, the reaction mixture may be heated prior to being deposited as a wet film. This may aid the dissolution of one or more of the molecular building blocks and/or increase the viscosity of the reaction mixture by the partial reaction of the reaction mixture prior to depositing the wet layer to form pre-SOFs. For example, the weight percent of molecular building blocks in the reaction mixture that are incorporated into pre-reacted molecular building blocks and pre-SOFs may be less than 20%, such as 15% to 1%, or 10% to 5%. In embodiments, the molecular weight of 95% pre-SOF molecules is less than 5,000 daltons, such as 2,500 daltons, or 1,000 daltons. The preparation of pre-SOFs may be used to increase the loading of the molecular building blocks in the reaction mixture.

40 [0104] In the case of pre-SOF formation via functional group activation, the molar percentage of functional groups that are activated may be less than 50 %, such as 30 % to 10 %, or 10 % to 5 %.

45 [0105] The two methods of pre-SOF formation (pre-SOF formation by the partial reaction between molecular building blocks or pre-SOF formation by the 'activation' of molecular building block functional groups) may occur in combination and the molecular building blocks incorporated into pre-SOF structures may contain activated functional groups. Pre-SOF formation by the partial reaction between molecular building blocks and pre-SOF formation by the 'activation' of molecular building block functional groups may occur simultaneously.

[0106] In embodiments, the duration of pre-SOF formation lasts 10 seconds to 48 hours, such as 30 seconds to 12 hours, or 1 minute to 6 hours.

50 [0107] In particular embodiments, the reaction mixture needs to have a viscosity that will support the deposited wet layer. Reaction mixture viscosities range from 0.01 to 50 Pa·s (10 to 50,000 cps), such as from 0.025 to 25 Pa·s (25 to 25,000 cps) or from 0.05 to 1 Pa·s (50 to 1000 cps).

55 [0108] The molecular building block loading or "loading" in the reaction mixture is defined as the total weight of the molecular building blocks and optionally the catalysts divided by the total weight of the reaction mixture. Building block loadings may range from 3 to 100%, such as from 5 to 50%, or from 15 to 40%. In the case where a liquid molecular building block is used as the only liquid component of the reaction mixture (i.e. no additional liquid is used), the building block loading would be 100%.

[0109] In embodiments, the pre-SOF may be made from molecular building blocks with one or more of the added functionality selected from the group consisting of hydrophobic added functionality, superhydrophobic added functionality, hydrophilic added functionality, lipophobic added functionality, superlipophobic added functionality, lipophilic added

functionality, photochromic added functionality, and electroactive added functionality. In embodiments, the inclined property of the molecular building blocks is the same as the added functionality of the pre-SOF. In embodiments, the added functionality of the SOF is not an inclined property of the molecular building blocks.

**[0110]** Liquids used in the reaction mixture may be pure liquids, such as solvents, and/or solvent mixtures. Liquids are used to dissolve or suspend the molecular building blocks and catalyst/modifiers in the reaction mixture. Liquid selection is generally based on balancing the solubility/dispersion of the molecular building blocks and a particular building block loading, the viscosity of the reaction mixture, and the boiling point of the liquid, which impacts the promotion of the wet layer to the dry SOF. Suitable liquids may have boiling points from 30 to 300 °C, such as from 65 °C to 250 °C, or from 100 °C to 180 °C.

**[0111]** Liquids can include molecule classes such as alkanes (hexane, heptane, octane, nonane, decane, cyclohexane, cycloheptane, cyclooctane, decalin); mixed alkanes (hexanes, heptanes); branched alkanes (isooctane); aromatic compounds (toluene, *o*-, *m*-, *p*-xylene, mesitylene, nitrobenzene, benzonitrile, butylbenzene, aniline); ethers (benzyl ethyl ether, butyl ether, isoamyl ether, propyl ether); cyclic ethers (tetrahydrofuran, dioxane), esters (ethyl acetate, butyl acetate, butyl butyrate, ethoxyethyl acetate, ethyl propionate, phenyl acetate, methyl benzoate); ketones (acetone, methyl ethyl ketone, methyl isobutylketone, diethyl ketone, chloroacetone, 2-heptanone), cyclic ketones (cyclopentanone, cyclohexanone), amines (1°, 2°, or 3° amines such as butylamine, diisopropylamine, triethylamine, diisopropylethylamine; pyridine); amides (dimethylformamide, *N*-methylpyrrolidinone, *N,N*-dimethylformamide); alcohols (methanol, ethanol, *n*-, *i*-propanol, *n*-, *i*-, *t*-butanol, 1-methoxy-2-propanol, hexanol, cyclohexanol, 3-pentanol, benzyl alcohol); nitriles (acetonitrile, benzonitrile, butyronitrile), halogenated aromatics (chlorobenzene, dichlorobenzene, hexafluorobenzene), halogenated alkanes (dichloromethane, chloroform, dichloroethylene, tetrachloroethane); and water.

**[0112]** Mixed liquids comprising a first solvent, second solvent, third solvent, and so forth may also be used in the reaction mixture. Two or more liquids may be used to aid the dissolution/dispersion of the molecular building blocks; and/or increase the molecular building block loading; and/or allow a stable wet film to be deposited by aiding the wetting of the substrate and deposition instrument; and/or modulate the promotion of the wet layer to the dry SOF. In embodiments, the second solvent is a solvent whose boiling point or vapor-pressure curve or affinity for the molecular building blocks differs from that of the first solvent. In embodiments, a first solvent has a boiling point higher than that of the second solvent. In embodiments, the second solvent has a boiling point equal to or less than 100 °C, such as in the range of from 30 °C to 100 °C, or in the range of from 40 °C to 90 °C, or 50 °C to 80 °C.

**[0113]** In embodiments, the first solvent, or higher boiling point solvent, has a boiling point equal to or greater than 65 °C, such as in the range of from 80 °C to 300 °C, or in the range of from 100 °C to 250 °C, or 100 °C to 180 °C. The higher boiling point solvent may include, for example, the following (the value in parentheses is the boiling point of the compound): hydrocarbon solvents such as amylbenzene (202 °C), isopropylbenzene (152 °C), 1,2-diethylbenzene (183 °C), 1,3-diethylbenzene (181 °C), 1,4-diethylbenzene (184 °C), cyclohexylbenzene (239 °C), dipentene (177 °C), 2,6-dimethylnaphthalene (262 °C), *p*-cymene (177 °C), camphor oil (160-185 °C), solvent naphtha (110-200 °C), *cis*-decalin (196 °C), *trans*-decalin (187 °C), decane (174 °C), tetralin (207 °C), turpentine oil (153-175 °C), kerosene (200-245 °C), dodecane (216 °C), dodecylbenzene (branched), and so forth; ketone and aldehyde solvents such as acetophenone (201.7 °C), isophorone (215.3 °C), phorone (198-199 °C), methylcyclohexanone (169.0-170.5 °C), methyl *n*-heptyl ketone (195.3 °C), and so forth; ester solvents such as diethyl phthalate (296.1 °C), benzyl acetate (215.5 °C),  $\gamma$ -butyrolactone (204 °C), dibutyl oxalate (240 °C), 2-ethylhexyl acetate (198.6 °C), ethyl benzoate (213.2 °C), benzyl formate (203 °C), and so forth; diethyl sulfate (208 °C), sulfolane (285 °C), and halohydrocarbon solvents; etherified hydrocarbon solvents; alcohol solvents; ether/acetal solvents; polyhydric alcohol solvents; carboxylic anhydride solvents; phenolic solvents; water; and silicone solvents.

**[0114]** The ratio of the mixed liquids may be established by one skilled in the art. The ratio of liquids in a binary mixed liquid may be from 1:1 to 99:1, such as from 1:10 to 10:1, or 1:5 to 5:1, by volume. When *n* liquids are used, with *n* ranging from 3 to 6, the amount of each liquid ranges from 1% to 95% such that the sum of each liquid contribution equals 100%.

**[0115]** In embodiments, the mixed liquid comprises at least a first and a second solvent with different boiling points. In further embodiments, the difference in boiling point between the first and the second solvent may be from nil to 150 °C, such as from nil to 50 °C. For example, the boiling point of the first solvent may exceed the boiling point of the second solvent by 1 °C to 100 °C, such as by 5 °C to 100 °C, or by 10 °C to 50 °C. The mixed liquid may comprise at least a first and a second solvent with different vapor pressures, such as combinations of high vapor pressure solvents and/or low vapor pressure solvents. The term "high vapor pressure solvent" refers to, for example, a solvent having a vapor pressure of at least 1 kPa, such as 2 kPa, or 5 kPa. The term "low vapor pressure solvent" refers to, for example, a solvent having a vapor pressure of less than 1 kPa, such as 0.9 kPa, or 0.5 kPa. In embodiments, the first solvent may be a low vapor pressure solvent such as, for example, terpineol, diethylene glycol, ethylene glycol, hexylene glycol, *N*-methyl-2-pyrrolidone, and tri(ethylene glycol) dimethyl ether. A high vapor pressure solvent allows rapid removal of the solvent by drying and/or evaporation at temperatures below the boiling point. High vapor pressure solvents may include, for example, acetone, tetrahydrofuran, toluene, xylene, ethanol, methanol, 2-butanone and water.

**[0116]** In embodiments where mixed liquids comprising a first solvent, second solvent, third solvent, and so forth are

used in the reaction mixture, promoting the change of the wet film and forming the dry SOF may comprise, for example, heating the wet film to a temperature above the boiling point of the reaction mixture to form the dry SOF; or heating the wet film to a temperature above the boiling point of the second solvent (below the temperature of the boiling point of the first solvent) in order to remove the second solvent while substantially leaving the first solvent and then after substantially removing the second solvent, removing the first solvent by heating the resulting composition at a temperature either above or below the boiling point of the first solvent to form the dry SOF; or heating the wet film below the boiling point of the second solvent in order to remove the second solvent (which is a high vapor pressure solvent) while substantially leaving the first solvent and, after removing the second solvent, removing the first solvent by heating the resulting composition at a temperature either above or below the boiling point of the first solvent to form the dry SOF.

**[0117]** The term "substantially removing" refers to, for example, the removal of at least 90% of the respective solvent, such as 95% of the respective solvent. The term "substantially leaving" refers to, for example, the removal of no more than 2% of the respective solvent, such as removal of no more than 1% of the respective solvent.

**[0118]** These mixed liquids may be used to slow or speed up the rate of conversion of the wet layer to the SOF in order to manipulate the characteristics of the SOFs. For example, in condensation and addition/elimination linking chemistries, liquids such as water, or 1°, 2°, or 3° alcohols (such as methanol, ethanol, propanol, isopropanol, butanol, 1-methoxy-2-propanol, tert-butanol) may be used.

**[0119]** Optionally a catalyst may be present in the reaction mixture to assist the promotion of the wet layer to the dry SOF. Selection and use of the optional catalyst depends on the functional groups on the molecular building blocks. Catalysts may be homogeneous (dissolved) or heterogeneous (undissolved or partially dissolved) and include Brønsted acids (HCl (aq), acetic acid, p-toluenesulfonic acid, amine-protected p-toluenesulfonic acid such as pyridium p-toluenesulfonate, trifluoroacetic acid); Lewis acids (boron trifluoroetherate, aluminum trichloride); Brønsted bases (metal hydroxides such as sodium hydroxide, lithium hydroxide, potassium hydroxide; 1°, 2°, or 3° amines such as butylamine, diisopropylamine, triethylamine, diisopropylethylamine); Lewis bases (*N,N*-dimethyl-4-aminopyridine); metals (Cu bronze); metal salts (FeCl<sub>3</sub>, AuCl<sub>3</sub>); and metal complexes (ligated palladium complexes, ligated ruthenium catalysts). Typical catalyst loading ranges from 0.01 % to 25%, such as from 0.1 % to 5% of the molecular building block loading in the reaction mixture. The catalyst may or may not be present in the final SOF composition.

**[0120]** Optionally additives or secondary components, such as dopants, may be present in the reaction mixture and wet layer. Such additives or secondary components may also be integrated into a dry SOF. Additives or secondary components can be homogeneous or heterogeneous in the reaction mixture and wet layer or in a dry SOF. The terms "additive" or "secondary component," refer, for example, to atoms or molecules that are not covalently bound in the SOF, but are randomly distributed in the composition. In embodiments, secondary components such as conventional additives may be used to take advantage of the known properties associated with such conventional additives. Such additives may be used to alter the physical properties of the SOF such as electrical properties (conductivity, semiconductivity, electron transport, hole transport), surface energy (hydrophobicity, hydrophilicity), tensile strength, and thermal conductivity; such additives may include impact modifiers, reinforcing fibers, lubricants, antistatic agents, coupling agents, wetting agents, antifogging agents, flame retardants, ultraviolet stabilizers, antioxidants, biocides, dyes, pigments, odorants, deodorants, nucleating agents and the like.

**[0121]** In embodiments, the SOF may contain antioxidants as a secondary component to protect the SOF from oxidation. Examples of suitable antioxidants include (1) *N,N'*-hexamethylene bis(3,5-di-*tert*-butyl-4-hydroxy hydrocinnamamide) (IRGANOX 1098, available from Ciba-Geigy Corporation), (2) 2,2-bis(4-(2-(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamoyloxy))ethoxyphenyl) propane (TOPANOL-205, available from ICI America Corporation), (3) tris(4-*tert*-butyl-3-hydroxy-2,6-dimethyl benzyl) isocyanurate (CYANOX 1790, Aldrich 41,322-4, LTDP, Aldrich D12,840-6), (4) 2,2'-ethylidene bis(4,6-di-*tert*-butylphenyl) fluoro phosphonite (ETHANOX-398, available from Ethyl Corporation), (5) tetrakis(2,4-di-*tert*-butylphenyl)-4,4'-biphenyl diphosphonite (ALDRICH 46,852-5; hardness value 90), (6) pentaerythritol tetrastearate (TCI America #PO739), (7) tributylammonium hypophosphite (Aldrich 42,009-3), (8) 2,6-di-*tert*-butyl-4-methoxyphenol (Aldrich 25,106-2), (9) 2,4-di-*tert*-butyl-6-(4-methoxybenzyl) phenol (Aldrich 23,008-1), (10) 4-bromo-2,6-dimethylphenol (Aldrich 34,951-8), (11) 4-bromo-3,5-dimethylphenol (Aldrich B6,420-2), (12) 4-bromo-2-nitrophenol (Aldrich 30,987-7), (13) 4-(diethyl aminomethyl)-2,5-dimethylphenol (Aldrich 14,668-4), (14) 3-dimethylaminophenol (Aldrich D14,400-2), (15) 2-amino-4-*tert*-amylphenol (Aldrich 41,258-9), (16) 2,6-bis(hydroxymethyl)-*p*-cresol (Aldrich 22,752-8), (17) 2,2'-methylenediphenol (Aldrich B4,680-8), (18) 5-(diethylamino)-2-nitrosophenol (Aldrich 26,951-4), (19) 2,6-dichloro-4-fluorophenol (Aldrich 28,435-1), (20) 2,6-dibromo fluoro phenol (Aldrich 26,003-7), (21) a trifluoro-*o*-cresol (Aldrich 21,979-7), (22) 2-bromo-4-fluorophenol (Aldrich 30,246-5), (23) 4-fluorophenol (Aldrich F 1,320-7), (24) 4-chlorophenyl-2-chloro-1,1,2-trifluoroethyl sulfone (Aldrich 13,823-1), (25) 3,4-difluoro phenylacetic acid (Aldrich 29,043-2), (26) 3-fluorophenylacetic acid (Aldrich 24,804-5), (27) 3,5-difluoro phenylacetic acid (Aldrich 29,044-0), (28) 2-fluorophenylacetic acid (Aldrich 20,894-9), (29) 2,5-bis (trifluoromethyl) benzoic acid (Aldrich 32,527-9), (30) ethyl-2-(4-(4-(trifluoromethyl) phenoxy) phenoxy) propionate (Aldrich 25,074-0), (31) tetrakis (2,4-di-*tert*-butyl phenyl)-4,4'-biphenyl diphosphonite (Aldrich 46,852-5), (32) 4-*tert*-amyl phenol (Aldrich 15,384-2), (33) 3-(2H-benzotriazol-2-yl)-4-hydroxy phenethylalcohol (Aldrich 43,071-4), NAUGARD 76, NAUGARD 445, NAUGARD 512, and NAUGARD 524 (manufactured by

Uniroyal Chemical Company), and the like, as well as mixtures thereof. The antioxidant, when present, may be present in the composite SOF in any desired or effective amount, such as from 0.25 percent to 10 percent by weight of the SOF or from 1 percent to 5 percent by weight of the SOF.

**[0122]** In embodiments, the SOF may further comprise any suitable polymeric material known in the art as a secondary component, such as polycarbonates, acrylate polymers, vinyl polymers, cellulose polymers, polyesters, polysiloxanes, polyamides, polyurethanes, polystyrenes, polystyrene, polyolefins, fluorinated hydrocarbons (fluorocarbons), and engineered resins as well as block, random or alternating copolymers thereof. The composite SOF may comprise homopolymers, higher order polymers, or mixtures thereof, and may comprise one species of polymeric material or mixtures of multiple species of polymeric material, such as mixtures of two, three, four, five or more multiple species of polymeric material. In embodiments, suitable examples of the polymers include, for example, crystalline and amorphous polymers, or mixtures thereof. In embodiments, the polymer is a fluoroelastomer.

**[0123]** Suitable fluoroelastomers are those described in detail in U.S. Patents Nos. 5,166,031, 5,281,506, 5,366,772, 5,370,931, 4,257,699, 5,017,432 and 5,061,965. The amount of fluoroelastomer compound present in the SOF, in weight percent total solids, is from 1 to 50 percent, or from 2 to 10 percent by weight of the SOF. Total solids, as used herein, includes the amount of secondary components and SOF.

**[0124]** In embodiments, examples of styrene-based monomers and acrylate-based monomers include, for example, poly(styrene-alkyl acrylate), poly(styrene-1,3-diene), poly(styrene-alkyl methacrylate), poly(styrene-alkyl acrylate-acrylic acid), poly(styrene-1,3-diene-acrylic acid), poly(styrene-alkyl methacrylate-acrylic acid), poly(alkyl methacrylate-alkyl acrylate), poly(alkyl methacrylate-aryl acrylate), poly(aryl methacrylate-alkyl acrylate), poly(alkyl methacrylate-acrylic acid), poly(styrene-alkyl acrylate-acrylonitrile-acrylic acid), poly(styrene-1,3-diene-acrylonitrile-acrylic acid), poly(alkyl acrylate-acrylonitrile-acrylic acid), poly(styrene-butadiene), poly(methylstyrene-butadiene), poly(methyl methacrylate-butadiene), poly(ethyl methacrylate-butadiene), poly(propyl methacrylate-butadiene), poly(butyl methacrylate-butadiene), poly(methyl acrylate-butadiene), poly(ethyl acrylate-butadiene), poly(propyl acrylate-butadiene), poly(butyl acrylate-butadiene), poly(styrene-isoprene), poly(methylstyrene-isoprene), poly(methyl methacrylate-isoprene), poly(ethyl methacrylate-isoprene), poly(propyl methacrylate-isoprene), poly(butyl methacrylate-isoprene), poly(methyl acrylate-isoprene), poly(ethyl acrylate-isoprene), poly(propyl acrylate-isoprene), and poly(butyl acrylate-isoprene); poly(styrene-propyl acrylate), poly(styrene-butyl acrylate), poly(styrene-butadiene-acrylic acid), poly(styrene-butadiene-methacrylic acid), poly(styrene-butadiene-acrylonitrile-acrylic acid), poly(styrene-butyl acrylate-acrylic acid), poly(styrene-butyl acrylate-methacrylic acid), poly(styrene-butyl acrylate-acrylonitrile), poly(styrene-butyl acrylate-acrylonitrile-acrylic acid), and other similar polymers.

**[0125]** Further examples of the various polymers that are suitable for use as a secondary component in SOFs include polyethylene terephthalate, polybutadienes, polysulfones, polyarylethers, polyarylsulfones, polyethersulfones, polycarbonates, polyethylenes, polypropylenes, polydecene, polydodecene, polytetradecene, polyhexadecene, polyoctadene, and polycyclododecene, polyolefin copolymers, mixtures of polyolefins, functional polyolefins, acidic polyolefins, branched polyolefins, polymethylpentenes, polyphenylene sulfides, polyvinyl acetates, polyvinylbutyrals, polysiloxanes, polyacrylates, polyvinyl acetals, polyamides, polyimides, polystyrene and acrylonitrile copolymers, polyvinylchlorides, polyvinyl alcohols, poly-N-vinylpyrrolidinone)s, vinylchloride and vinyl acetate copolymers, acrylate copolymers, poly(amideimide), styrene-butadiene copolymers, vinylidenechloride-vinylchloride copolymers, vinylacetate-vinylidenechloride copolymers, polyvinylcarbazoles, polyethylene-terephthalate, polypropylene-terephthalate, polybutylene-terephthalate, polypentylene-terephthalate, polyhexalene-terephthalate, polyheptadene-terephthalate, polyoctalene-terephthalate, polyethylene-sebacate, polypropylene sebacate, polybutylene-sebacate, polyethylene-adipate, polypropylene-adipate, polybutylene-adipate, polypentylene-adipate, polyhexalene-adipate, polyheptadene-adipate, polyoctalene-adipate, polyethylene-glutarate, polypropylene-glutarate, polybutylene-glutarate, polypentylene-glutarate, polyhexalene-glutarate, polyheptadene-glutarate, polyoctalene-glutarate polyethylene-pimelate, polypropylene-pimelate, polybutylene-pimelate, polypentylene-pimelate, polyhexalene-pimelate, polyheptadene-pimelate, poly(propoxylated bisphenol-fumarate), poly(propoxylated bisphenol-succinate), poly(propoxylated bisphenol-adipate), poly(propoxylated bisphenol-glutarate), SPAR™ (Dixie Chemicals), BECKOSOL™ (Reichhold Chemical Inc), ARAKOTE™ (Ciba-Geigy Corporation), HETRON™ (Ashland Chemical), PARAPLEX™ (Rohm & Hass), POLYLITE™ (Reichhold Chemical Inc), PLASTHALL™ (Rohm & Hass), CYGAL™ (American Cyanamide), ARMCO™ (Armco Composites), ARPOL™ (Ashland Chemical), CELANEX™ (Celanese Eng), RYNITE™ (DuPont), STYPOL™ (Freeman Chemical Corporation), mixtures thereof and the like.

**[0126]** In embodiments, the secondary components, including polymers may be distributed homogeneously, or heterogeneously, such as in a linear or nonlinear gradient in the SOF. In embodiments, the polymers may be incorporated into the SOF in the form of a fiber, or a particle whose size may range from 50 nm to 2 mm. The polymers, when present, may be present in the composite SOF in any desired or effective amount, such as from 1 percent to 50 percent by weight of the SOF or from 1 percent to 15 percent by weight of the SOF.

**[0127]** In embodiments, the SOF may further comprise carbon nanotubes or nanofiber aggregates, which are microscopic particulate structures of nanotubes, as described in U.S. Patent Nos. 5,165,909; 5,456,897; 5,707,916; 5,877,110;

5,110,693; 5,500,200 and 5,569,635.

**[0128]** In embodiments, the SOF may further comprise metal particles as a secondary component; such metal particles include noble and non-noble metals and their alloys. Examples of suitable noble metals include, aluminum, titanium, gold, silver, platinum, palladium and their alloys. Examples of suitable non-noble metals include, copper, nickel, cobalt, lead, iron, bismuth, zinc, ruthenium, rhodium, rubidium, indium, and their alloys. The size of the metal particles may range from 1 nm to 1 mm and their surfaces may be modified by stabilizing molecules or dispersant molecules or the like. The metal particles, when present, may be present in the composite sof in any desired or effective amount, such as from 0.25 percent to 70 percent by weight of the SOF or from 1 percent to 15 percent by weight of the SOF.

**[0129]** In embodiments, the SOF may further comprise oxides and sulfides as secondary components. Examples of suitable metal oxides include, titanium dioxide (titania, rutile and related polymorphs), aluminum oxide including alumina, hydrated alumina, and the like, silicon oxide including silica, quartz, cristobalite, and the like, aluminosilicates including zeolites, talcs, and clays, nickel oxide, iron oxide, cobalt oxide. Other examples of oxides include glasses, such as silica glass, borosilicate glass, aluminosilicate glass and the like. Examples of suitable sulfides include nickel sulfide, lead sulfide, cadmium sulfide, tin sulfide, and cobalt sulfide. The diameter of the oxide and sulfide materials may range from 50 nm to 1 mm and their surfaces may be modified by stabilizing molecules or dispersant molecules or the like. The oxides, when present, may be present in the composite SOF in any desired or effective amount, such as from 0.25 percent to 20 percent by weight of the SOF or from 1 percent to 15 percent by weight of the SOF.

**[0130]** In embodiments, the SOF may further comprise metalloid or metal-like elements from the periodic table. Examples of suitable metalloid elements include, silicon, selenium, tellurium, tin, lead, germanium, gallium, arsenic, antimony and their alloys or intermetallics. The size of the metal particles may range from 10 nm to 1 mm and their surfaces may be modified by stabilizing molecules or dispersant molecules or the like. The metalloid particles, when present, may be present in the composite SOF in any desired or effective amount, such as from 0.25 percent to 10 percent by weight of the SOF or from 1 percent to 5 percent by weight of the SOF.

**[0131]** In embodiments, the SOF may further comprise hole transport molecules or electron acceptors as a secondary component, such charge transport molecules include for example a positive hole transporting material selected from compounds having in the main chain or the side chain a polycyclic aromatic ring such as anthracene, pyrene, phenanthrene, coronene, and the like, or a nitrogen-containing hetero ring such as indole, carbazole, oxazole, isoxazole, thiazole, imidazole, pyrazole, oxadiazole, pyrazoline, thiadiazole, triazole, and hydrazone compounds. Typical hole transport materials include electron donor materials, such as carbazole; N-ethyl carbazole; N-isopropyl carbazole; N-phenyl carbazole; tetraphenylpyrene; 1-methyl pyrene; perylene; chrysene; anthracene; tetraphene; 2-phenyl naphthalene; azopyrene; 1-ethyl pyrene; acetyl pyrene; 2,3-benzochrysene; 2,4-benzopyrene; 1,4-bromopyrene; poly(N-vinylcarbazole); poly(vinylpyrene); poly(vinyltetraphene); poly(vinyltetracene) and poly(vinylperylene). Suitable electron transport materials include electron acceptors such as 2,4,7-trinitro-9-fluorenone; 2,4,5,7-tetranitro-fluorenone; dinitroanthracene; dinitroacridene; tetracyanopyrene; dinitroanthraquinone; and butylcarbonylfluorene-malononitrile, see U.S. Patent No. 4,921,769. Other hole transporting materials include arylamines described in U.S. Patent No. 4,265,990, such as N,N'-diphenyl-N,N'-bis(alkylphenyl)-(1,1'-biphenyl)-4,4'-diamine wherein alkyl is selected from the group consisting of methyl, ethyl, propyl, butyl, hexyl, and the like. Hole transport molecules of the type described in, for example, U.S. Patents Nos. 4,306,008; 4,304,829; 4,233,384; 4,115,116; 4,299,897; 4,081,274, and 5,139,910. Other known charge transport molecules may be selected, reference for example U.S. Patent Nos. 4,921,773 and 4,464,450. The hole transport molecules or electron acceptors, when present, may be present in the composite SOF in any desired or effective amount, such as from 0.25 percent to 50 percent by weight of the SOF or from 1 percent to 20 percent by weight of the SOF.

**[0132]** In embodiments, the SOF may further comprise biocides as a secondary component. Biocides may be present in amounts of from 0.1 to 1.0 percent by weight of the SOF. Suitable biocides include, for example, sorbic acid, 1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride, commercially available as DOWICIL 200 (Dow Chemical Company), vinylene-bis thiocyanate, commercially available as CYTOX 3711 (American Cyanamid Company), disodium ethylenebis-dithiocarbamate, commercially available as DITHONE D 14 (Rohm & Haas Company), bis(trichloromethyl)sulfone, commercially available as BIOCIDE N-1386 (Stauffer Chemical Company), zinc pyridinethione, commercially available as zinc omadine (Olin Corporation), 2-bromo-t-nitropropane-1,3-diol, commercially available as ONYXIDE 500 (Onyx Chemical Company), BOSQUAT MB50 (Louza, Inc.), and the like.

**[0133]** In embodiments, the SOF may further comprise small organic molecules as a secondary component; such small organic molecules include those discussed above with respect to the first and second solvents. The small organic molecules, when present, may be present in the SOF in any desired or effective amount, such as from 0.25 percent to 50 percent by weight of the SOF or from 1 percent to 10 percent by weight of the SOF.

**[0134]** When present, the secondary components or additives may each, or in combination, be present in the composition in any desired or effective amount, such as from 1 percent to 50 percent by weight of the composition or from 1 percent to 20 percent by weight of the composition.

**[0135]** SOFs may be modified with secondary components (dopants and additives, such as, hole transport molecules (mTBD), polymers (polystyrene), nanoparticles (C60 Buckminster fullerene), small organic molecules (biphenyl), metal



particles (copper micropowder), and electron acceptors (quinone)) in this may to give composite structured organic films. Secondary components may be introduced to the liquid formulation that is used to generate a wet film in which a change is promoted to form the SOF. Secondary components (dopants, additives, etc.) may either be dissolved or undissolved (suspended) in the reaction mixture. Secondary components are not bonded into the network of the film. For example, a secondary component may be added to a reaction mixture that contains a plurality of building blocks having four methoxy groups (-OMe) on a segment, such as N4,N4,N4',N4'-tetra-*p*-tolylbiphenyl-4,4'-diamine, which upon promotion of a change in the wet film, exclusively react with the two alcohol (-OH) groups on a building block, such as 1,4-benzenedimethanol, which contains a *p*-xylyl segment. The chemistry that is occurring to link building blocks is an acid catalyzed transesterification reaction. Because -OH groups will only react with -OMe groups (and vice versa) and not with the secondary component, these molecular building blocks can only follow one pathway. Therefore, the SOF is programmed to order molecules in a way that leaves the secondary component incorporated within and/or around the SOF structure. This ability to pattern molecules and incorporate secondary components affords superior performance and unprecedented control over properties compared to conventional polymers and available alternatives.

**[0136]** In embodiments, the secondary components may have similar or disparate properties to accentuate or hybridize (synergistic effects or ameliorative effects as well as the ability to attenuate inherent or inclined properties of the SOF) the intended property of the SOF to enable it to meet performance targets. For example, doping the SOFs with antioxidant compounds will extend the life of the SOF by preventing chemical degradation pathways.

**[0137]** Additionally, additives may be added to improve the morphological properties of the SOF by tuning the reaction occurring during the promotion of the change of the reaction mixture to form the SOF.

### Process Action B: Depositing the Reaction Mixture as a Wet Film

**[0138]** The reaction mixture may be applied as a wet film to a variety of substrates using a number of liquid deposition techniques. The thickness of the SOF is dependant on the thickness of the wet film and the molecular building block and/or pre-SOF loading in the reaction mixture. The thickness of the wet film is dependent on the viscosity of the reaction mixture and the method used to deposit the reaction mixture as a wet film. In embodiments, the thickness of the wet layer may be greater than 100 nm, such as in the range from 200 nm to 5 mm, or 500 nm to 50  $\mu\text{m}$  (50 microns).

**[0139]** Substrates include, for example, polymers, papers, metals and metal alloys, doped and undoped forms of elements from Groups III-VI of the periodic table, metal oxides, metal chalcogenides, and previously prepared SOF films. Examples of polymer film substrates include polyesters, polyolefins, polycarbonates, polystyrenes, polyvinylchloride, block and random copolymers thereof, and the like. Examples of metallic surfaces include metallized polymers, metal foils, metal plates; mixed material substrates such as metals patterned or deposited on polymer, semiconductor, metal oxide, or glass substrates. Examples of substrates comprised of doped and undoped elements from Groups III-VI of the periodic table include, aluminum, silicon, silicon n-doped with phosphorous, silicon p-doped with boron, tin, gallium arsenide, lead, gallium indium phosphide, and indium. Examples of metal oxides include silicon dioxide, titanium dioxide, indium tin oxide, tin dioxide, selenium dioxide, and alumina. Examples of metal chalcogenides include cadmium sulfide, cadmium telluride, and zinc selenide. Additionally, it is appreciated that chemically treated or mechanically modified forms of the above substrates remain within the scope of surfaces which may be coated with the reaction mixture.

**[0140]** In embodiments, the substrate may be composed of, for example, silicon, glass plate, plastic film or sheet. For structurally flexible devices, a plastic substrate such as polyester, polycarbonate, polyimide sheets and the like may be used. The thickness of the substrate may be from around 10 micrometers to over 10 millimeters with an exemplary thickness being from 50 to 100 micrometers, especially for a flexible plastic substrate, and from 1 to 10 millimeters for a rigid substrate such as glass or silicon.

**[0141]** The reaction mixture may be applied to the substrate using a number of liquid deposition techniques including, for example, spin coating, blade coating, web coating, dip coating, cup coating, rod coating, screen printing, ink jet printing, spray coating, stamping and the like. The method used to deposit the wet layer depends on the nature, size, and shape of the substrate and the desired wet layer thickness. The thickness of the wet layer can range from 10 nm to 5 mm, such as from 100 nm to 1 mm, or from 1  $\mu\text{m}$  to 500  $\mu\text{m}$ .

**[0142]** In embodiments, the secondary component may be introduced following completion of the above described process action B. The incorporation of the secondary component in this way may be accomplished by any means that serves to distribute the secondary component homogeneously, heterogeneously, or as a specific pattern over the wet film. Following introduction of the secondary component subsequent process actions may be carried out resuming with process action C.

**[0143]** For example, following completion of process action B (i.e., after the reaction mixture may be applied to the substrate), secondary components (dopants, additives, etc.) may be added to the wet layer by any suitable method, such as by distributing (e.g., dusting, spraying, pouring, sprinkling, etc. depending on whether the secondary component is a particle, powder or liquid) the secondary component on the top of the wet layer. The secondary components may be applied to the formed wet layer in a homogeneous or heterogeneous manner, including various patterns, wherein

the concentration or density of the secondary component is reduced in specific areas, such as to form a pattern of alternating bands of high and low concentrations of the secondary component of a given width on the wet layer. In embodiments, the application of the secondary component to the top of the wet layer may result in a portion of the secondary component diffusing or sinking into the wet layer and thereby forming a heterogeneous distribution of secondary component within the thickness of the SOF, such that a linear or nonlinear concentration gradient may be obtained in the resulting SOF obtained after promotion of the change of the wet layer to a dry SOF. In embodiments, a secondary component may be added to the top surface of a deposited wet layer, which upon promotion of a change in the wet film, results in an SOF having a heterogeneous distribution of the secondary component in the dry SOF. Depending on the density of the wet film and the density of the secondary component, a majority of the secondary component may end up in the upper half (which is opposite the substrate) of the dry SOF or a majority of the secondary component may end up in the lower half (which is adjacent to the substrate) of the dry SOF.

**Process Action C: Promoting the Change of Wet Film to the Dry SOF**

**[0144]** The term "promoting" refers, for example, to any suitable technique to facilitate a reaction of the molecular building blocks and/or pre-SOFs, such as a chemical reaction of the functional groups of the building blocks and/or pre-SOFs. In the case where a liquid needs to be removed to form the dry film, "promoting" also refers to removal of the liquid. Reaction of the molecular building blocks and/or pre-SOFs and removal of the liquid can occur sequentially or concurrently. In certain embodiments, the liquid is also one of the molecular building blocks and is incorporated into the SOF. The term "dry SOF" refers, for example, to substantially dry SOFs, for example, to a liquid content less than 5% by weight of the SOF, or to a liquid content less than 2% by weight of the SOF.

**[0145]** Promoting the wet layer to form a dry SOF may be accomplished by any suitable technique. Promoting the wet layer to form a dry SOF typically involves thermal treatment including, for example, oven drying, infrared radiation (IR), and the like with temperatures ranging from 40 to 350°C and from 60 to 200°C and from 85 to 160°C. The total heating time can range from four seconds to 24 hours, such as from one minute to 120 minutes, or from three minutes to 60 minutes.

**[0146]** IR promotion of the wet layer to the dry SOF may be achieved using an IR heater module mounted over a belt transport system. Various types of IR emitters may be used, such as carbon IR emitters or short wave IR emitters (available from Heraeus). Additional exemplary information regarding carbon IR emitters or short wave IR emitters is summarized in the following Table (1 micron corresponds to 1 μm).

IR lamp	Peak Wavelength	Number of lamps	Module Power (kW)
Carbon	2.0 micron	2 - twin tube	4.6
Short wave	1.2 - 1.4 micron	3 - twin tube	4.5

**Process Action D: Optionally removing the SOF from the coating substrate to obtain a free-standing SOF**

**[0147]** In embodiments, a free-standing SOF is desired. Free-standing SOFs may be obtained when an appropriate low adhesion substrate is used to support the deposition of the wet layer. Appropriate substrates that have low adhesion to the SOF may include, for example, metal foils, metalized polymer substrates, release papers and SOFs, such as SOFs prepared with a surface that has been altered to have a low adhesion or a decreased propensity for adhesion or attachment. Removal of the SOF from the supporting substrate may be achieved in a number of ways by someone skilled in the art. For example, removal of the SOF from the substrate may occur by starting from a corner or edge of the film and optionally assisted by passing the substrate and SOF over a curved surface.

**Process Action E: Optionally processing the free-standing SOF into a roll**

**[0148]** Optionally, a free-standing SOF or an SOF supported by a flexible substrate may be processed into a roll. The SOF may be processed into a roll for storage, handling, and a variety of other purposes. The starting curvature of the roll is selected such that the SOF is not distorted or cracked during the rolling process.

**Process Action F: Optionally cutting and seaming the SOF into a shape, such as a belt**

**[0149]** The method for cutting and seaming the SOF is similar to that described in U.S. Patent No. 5,455,136 issued on October 3<sup>rd</sup>, 1995 (for polymer films). An SOF belt may be fabricated from a single SOF, a multi layer SOF or an SOF sheet cut from a web. Such sheets may be rectangular in shape or any particular shape as desired. All sides of the SOF(s) may be of the same length, or one pair of parallel sides may be longer than the other pair of parallel sides.

The SOF(s) may be fabricated into shapes, such as a belt by overlap joining the opposite marginal end regions of the SOF sheet. A seam is typically produced in the overlapping marginal end regions at the point of joining. Joining may be affected by any suitable means. Typical joining techniques include, for example, welding (including ultrasonic), glueing, taping, pressure heat fusing and the like. Methods, such as ultrasonic welding, are desirable general methods of joining flexible sheets because of their speed, cleanliness (no solvents) and production of a thin and narrow seam.

#### Process Action G: Optionally Using an SOF as a Substrate for Subsequent SOF Formation Processes

**[0150]** An SOF may be used as a substrate in the SOF forming process to afford a multi-layered structured organic film. The layers of a multi-layered SOF may be chemically bound in or in physical contact. Chemically bound, multi-layered SOFs are formed when functional groups present on the substrate SOF surface can react with the molecular building blocks present in the deposited wet layer used to form the second structured organic film layer. Multi-layered SOFs in physical contact may not chemically bound to one another.

**[0151]** An SOF substrate may optionally be chemically treated prior to the deposition of the wet layer to enable or promote chemical attachment of a second SOF layer to form a multi-layered structured organic film.

**[0152]** Alternatively, an SOF substrate may optionally be chemically treated prior to the deposition of the wet layer to disable chemical attachment of a second SOF layer (surface pacification) to form a physical contact multi-layered SOF.

**[0153]** Other methods, such as lamination of two or more SOFs, may also be used to prepare physically contacted multi-layered SOFs.

#### Applications of SOFs

**[0154]** SOFs may be used in for instance electronic devices such as solar cells, radio frequency identification tags, organic light emitting devices, photoreceptors, thin film transistors and the like.

#### Application A: SOFs in Photoreceptor Layers

**[0155]** Representative structures of an electrophotographic imaging member (e.g., a photoreceptor) are shown in FIGS. 1-3.

**[0156]** As seen in the figures, in fabricating a photoreceptor, a charge generating material (CGM) and a charge transport material (CTM) may be deposited onto the substrate surface either in a laminate type configuration where the CGM and CTM are in different layers (e.g., FIGS. 1 and 2) or in a single layer configuration where the CGM and CTM are in the same layer (e.g., FIG. 3). In embodiments, the photoreceptors may be prepared by applying over the electrically conductive layer the charge generation layer 6 and, optionally, a charge transport layer 7. In embodiments, the charge generation layer and, when present, the charge transport layer, may be applied in either order.

#### Anti Curl Layer

**[0157]** For some applications, an optional anti-curl layer 1, which comprises film-forming organic or inorganic polymers that are electrically insulating or slightly semi-conductive, may be provided. The anti-curl layer provides flatness and/or abrasion resistance. Anti-curl layer 1 may be formed at the back side of the substrate 2, opposite the imaging layers.

**[0158]** An intermediate layer 5 between the blocking layer and the charge generating layer may, if desired, be provided to promote adhesion. However, in embodiments, a dip coated aluminum drum may be utilized without an adhesive layer.

**[0159]** The imaging layer refers to a layer or layers containing charge generating material, charge transport material, or both the charge generating material and the charge transport material.

**[0160]** FIG. 4 schematically illustrates a thin film transistor (TFT) configuration 30 comprised of a substrate 36, a gate electrode 38, a source electrode 40 and a drain electrode 42, an insulating layer 34, and an organic semiconductor layer 32.

**[0161]** The substrate may be composed of for instance silicon wafer, glass plate, metal sheet, plastic film or sheet. For structurally flexible devices, plastic substrate, such as for example polyester, polycarbonate, polyimide sheets and the like may be used. The thickness of the substrate may be from 10 micrometers to over 10 millimeters with an exemplary thickness being from 50 micrometers to 2 millimeters, especially for a flexible plastic substrate and from 0.4 to 10 millimeters for a rigid substrate such as glass or silicon. Examples

**[0162]** A number of examples of the process used to make SOFs are set forth herein and are illustrative of the different compositions, conditions and techniques that may be utilized. Identified within each example are the nominal actions associated with the example. The sequence and number of actions along with operational parameters, such as temperature, time, coating method, and the like, are not limited by the following examples. All proportions are by weight unless otherwise indicated. The term "rt" refers, for example, to temperatures ranging from 20 °C to 25 °C. Mechanical measurements were measured on a TA Instruments DMA Q800 dynamic mechanical analyzer using methods standard in

the art. Differential scanning calorimetry was measured on a TA Instruments DSC 2910 differential scanning calorimeter using methods standard in the art. Thermal gravimetric analysis was measured on a TA Instruments TGA 2950 thermal gravimetric analyzer using methods standard in the art. FR-IR spectra were measured on a Nicolet Magna 550 spectrometer using methods standard in the art. Thickness measurements 1  $\mu\text{m}$  (1 micron) were measured on a Dektak 6m Surface Profiler. Surface energies were measured on a Fibro DAT 1100 (Sweden) contact angle instrument using methods standard in the art. Unless otherwise noted, the SOFs produced in the following examples were either defect-free SOFs or substantially defect-free SOFs.

[0163] The SOFs coated onto Mylar were delaminated by immersion in a room temperature water bath. After soaking for 10 minutes the SOFs generally detached from the Mylar substrate. This process is most efficient with an SOF coated onto substrates known to have high surface energy (polar), such as glass, mica, salt, and the like.

[0164] Given the examples below it will be apparent, that the compositions prepared by the methods of the present disclosure may be practiced with many types of components and may have many different uses in accordance with the disclosure above and as pointed out hereinafter.

### Embodiment of a Patterned SOF Composition

[0165] An embodiment of the disclosure is to attain an SOF wherein the microscopic arrangement of segments is patterned. The term "patterning" refers, for example, to the sequence in which segments are linked together. A patterned SOF would therefore embody a composition wherein, for example, segment A is only connected to segment B, and conversely, segment B is only connected to segment A. Further, a system wherein only one segment exists, say segment A, is employed is will be patterned because A is intended to only react with A. In principle a patterned SOF may be achieved using any number of segment types. The patterning of segments may be controlled by using molecular building blocks whose functional group reactivity is intended to compliment a partner molecular building block and wherein the likelihood of a molecular building block to react with itself is minimized. The aforementioned strategy to segment patterning is non-limiting. Instances where a specific strategy to control patterning has not been deliberately implemented are also embodied herein.

[0166] A patterned film may be detected using spectroscopic techniques that are capable of assessing the successful formation of linking groups in an SOF. Such spectroscopies include, for example, Fourier-transfer infrared spectroscopy, Raman spectroscopy, and solid-state nuclear magnetic resonance spectroscopy. Upon acquiring data by a spectroscopic technique from a sample, the absence of signals from functional groups on building blocks and the emergence of signals from linking groups indicate the reaction between building blocks and the concomitant patterning and formation of an SOF.

[0167] Different degrees of patterning are also embodied. Full patterning of an SOF will be detected by the complete absence of spectroscopic signals from building block functional groups. Also embodied are SOFs having lowered degrees of patterning wherein domains of patterning exist within the SOF. SOFs with domains of patterning, when measured spectroscopically, will produce signals from building block functional groups which remain unmodified at the periphery of a patterned domain.

[0168] It is appreciated that a very low degree of patterning is associated with inefficient reaction between building blocks and the inability to form a film. Therefore, successful implementation of the process of the present disclosure requires appreciable patterning between building blocks within the SOF. The degree of necessary patterning to form an SOF is variable and can depend on the chosen building blocks and desired linking groups. The minimum degree of patterning required is that required to form a film using the process described herein, and may be quantified as formation of 20 % or more of the intended linking groups, such as 40 % or more of the intended linking groups or 50 % or more of the intended linking groups; the nominal degree of patterning embodied by the present disclosure is formation of 60 % of the intended linking group, such as formation of 100 % of the intended linking groups. Formation of linking groups may be detected spectroscopically as described earlier in the embodiments.

### PRODUCTION OF A PATTERNED SOF

[0169] The following experiments demonstrate the development of a patterned SOF. The examples described below are non-limiting as it will be apparent that many types of approaches may be used to generate patterning in an SOF. All the examples described below fall outside the scope of the appended claims.

[0170] Illustrative EXAMPLE 1 describes the synthesis of a Type 2 SOF wherein components are combined such that etherification linking chemistry is promoted between two building blocks. The presence of an acid catalyst and a heating action yield an SOF with the method described in illustrative EXAMPLE 1.

#### Illustrative EXAMPLE 1: Type 2 SOF

[0171] (*Action A*) *Preparation of the liquid containing reaction mixture.* The following were combined: the building block

benzene-1,4-dimethanol [segment = p-xylyl; Fg = hydroxyl (-OH); (0.47 g, 3.4 mmol)] and a second Building block N4,N4,N4',N4'-tetrakis(4-(methoxymethyl)phenyl)biphenyl-4,4'-diamine [segment = N4,N4,N4',N4'-tetra-p-tolylbiphenyl-4,4'-diamine; Fg = methoxy ether (-OCH<sub>3</sub>); (1.12 g, 1.7 mmol)], and 17.9 g of 1-methoxy-2-propanol. The mixture was shaken and heated to 60 °C until a homogenous solution resulted. Upon cooling to room temperature, the solution was filtered through a 0.45 μm (0.45 micron) PTFE membrane. To the filtered solution was added an acid catalyst delivered as 0.31 g of a 10 wt % solution of p-toluenesulfonic acid in 1-methoxy-2-propanol to yield the liquid containing reaction mixture.

**[0172]** (Action B) *Deposition of reaction mixture as a wet film.* The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 0.2 mm (8 mil) gap.

**[0173]** (Action C) *Promotion of the change of the wet film to a dry SOF.* The metalized MYLAR™ substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 130 °C and left to heat for 40 min. These actions provided an SOF having a thickness ranging from 3 to 6 μm (3-6 microns), which may be delaminated from the substrate as a single free-standing SOF. The color of the SOF was green. The Fourier-transform infrared spectrum of a portion of this SOF is provided in FIG. 6

**[0174]** To demonstrate that the SOF prepared in illustrative EXAMPLE 1 comprises segments from the employed molecular building blocks that are patterned within the SOF, three control experiments were conducted. Namely, three liquid reaction mixtures were prepared using the same procedure as set forth in Action A in illustrative EXAMPLE 1; however, each of these three formulations were modified as follows:

(Control reaction mixture 1; illustrative EXAMPLE 2) the building block benzene-1,4-dimethanol was not included.

(Control reaction mixture 2; illustrative EXAMPLE 3) the building block N4,N4,N4',N4'-tetrakis(4-(methoxymethyl)phenyl)biphenyl-4,4'-diamine was not included.

(Control reaction mixture 3; illustrative EXAMPLE 4) the catalyst p-toluenesulfonic acid was not included

**[0175]** The full descriptions of the SOF forming process for the above described control experiments are detailed in illustrative EXAMPLES 2 - 4 below.

Illustrative EXAMPLE 2: (Control experiment wherein the building block benzene-1,4-dimethanol was not included)

**[0176]** (Action A) *Preparation of the liquid containing reaction mixture.* The following were combined: the building block N4,N4,N4',N4'-tetrakis(4-(methoxymethyl)phenyl)biphenyl-4,4'-diamine [segment = N4,N4,N4',N4'-tetra-p-tolylbiphenyl-4,4'-diamine; Fg = methoxy ether (-OCH<sub>3</sub>); (1.12 g, 1.7 mmol)], and 17.9 g of 1-methoxy-2-propanol. The mixture was shaken and heated to 60 °C until a homogenous solution resulted. Upon cooling to room temperature, the solution was filtered through 0.45 μm (0.45 micron) PTFE membrane. To the filtered solution was added an acid catalyst delivered as 0.31 g of a 10 wt % solution of p-toluenesulfonic acid in 1-methoxy-2-propanol to yield the liquid containing reaction mixture.

**[0177]** (Action B) *Deposition of reaction mixture as a wet film.* The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 0.2 mm (8 mil) gap.

**[0178]** (Action C) *Attempted promotion of the change of the wet film to a dry SOF.* The metalized MYLAR™ substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 130 °C and left to heat for 40 min. These actions did not provide a film. Instead, a precipitated powder of the building block was deposited onto the substrate.

**[0179]** Illustrative EXAMPLE 3: (Control experiment wherein the building block N4,N4,N4',N4'-tetrakis(4-(methoxymethyl)phenyl)biphenyl-4,4'-diamine was not included)

**[0180]** (Action A) *Preparation of the liquid containing reaction mixture.* The following were combined: the building block benzene-1,4-dimethanol [segment = p-xylyl; Fg = hydroxyl (-OH); (0.47 g, 3.4 mmol)] and 17.9 g of 1-methoxy-2-propanol. The mixture was shaken and heated to 60 °C until a homogenous solution resulted. Upon cooling to room temperature, the solution was filtered through a 0.45 μm (0.45 micron) PTFE membrane. To the filtered solution was added an acid catalyst delivered as 0.31 g of a 10 wt % solution of p-toluenesulfonic acid in 1-methoxy-2-propanol to yield the liquid containing reaction mixture.

**[0181]** (Action B) *Deposition of reaction mixture as a wet film.* The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having an 0.2 mm (8 mil) gap.

**[0182]** (Action C) *Attempted promotion of the change of the wet film to a dry SOF.* The metalized MYLAR™ substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 130 °C and left to heat for 40 min. These actions did not provide a film. Instead, a precipitated powder of the building block was deposited onto the

substrate.

Illustrative EXAMPLE 4: (Control experiment wherein the acid catalyst p-toluenesulfonic acid was not included)

5 **[0183]** (Action A) *Preparation of the liquid containing reaction mixture.* The following were combined: the building block benzene-1,4-dimethanol [segment = p-xylyl; Fg = hydroxyl (-OH); (0.47 g, 3.4 mmol)] and a second building block N4,N4,N4',N4'-tetrakis(4-(methoxymethyl)phenyl)biphenyl-4,4'-diamine [segment = N4,N4,N4',N4'-tetra-p-tolylbiphenyl-4,4'-diamine; Fg = methoxy ether (-OCH<sub>3</sub>); (1.12 g, 1.7 mmol)], and 17.9 g of 1-methoxy-2-propanol. The mixture was shaken and heated to 60 °C until a homogenous solution resulted. Upon cooling to room temperature, the solution was filtered through a 0.45 μm (0.45 micron) PTFE membrane to yield the liquid containing reaction mixture.

10 **[0184]** (Action B) *Deposittion of reaction mixture as a wet film.* The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 0.2 mm (8 mil) gap.

15 **[0185]** (Action C) *Attempted promotion of the change of the wet film to a dry SOF.* The metalized MYLAR™ substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 130 °C and left to heat for 40 min. These actions did not provide a film. Instead, a precipitated powder of the building blocks was deposited onto the substrate.

20 **[0186]** As described in Illustrative EXAMPLES 2-4, each of the three control reaction mixtures were subjected to Action B and Action C as outlined Illustrative in EXAMPLE 1. However, in all cases an SOF did not form; the building blocks simply precipitated on the substrate. It is concluded from these results that building blocks cannot react with themselves under the stated processing conditions nor can the building blocks react in the absence of a promoter (p-toluenesulfonic acid). Therefore, the activity described in illustrative EXAMPLE 1 is one wherein building blocks (benzene-1,4-dimethanol and N4,N4,N4',N4'-tetrakis(4-(methoxymethyl)phenyl)biphenyl-4,4'-diamine) can only react with each other when promoted to do so. A patterned SOF results when the segments p-xylyl and N4,N4,N4',N4'-tetra-p-tolylbiphenyl-4,4'-diamine connect only with each other. The Fourier-transform infrared spectrum, compared to that of the products of the control experiments (FIG. 5) of the SOF shows absence of functional groups (notably the absence of the hydroxyl band from the benzene-1,4-dimethanol) from the starting materials and further supports that the connectivity between segments has proceed as described above. Also, the complete absence of the hydroxy band in the spectrum for the SOF indicates that the patterning is to a very high degree.

25 **[0187]** Described below are further Examples of defect-free SOFs and/or substantially defect-free SOFs prepared in accordance with the present disclosure. In the following examples (Action A) is the *preparation of the liquid containing reaction mixture*; (Action B) is the *deposition of reaction mixture as a wet film*; and (Action C) is the *promotion of the change of the wet film to a dry SOF*.

30 Illustrative EXAMPLE 5: Type 2 SOF

35 **[0188]** (Action A) The following were combined: the building block benzene-1,3,5-trimethanol [segment = benzene-1,3,5-trimethyl; Fg = hydroxyl (-OH); (0.2 g, 1.2 mmol)] and a second building block N4,N4,N4',N4'-tetrakis(4-(methoxymethyl)phenyl)biphenyl-4,4'-diamine (segment= N4,N4,N4',N4'-tetra-p-tolylbiphenyl-4,4'-diamine; Fg = methoxy ether (-OCH<sub>3</sub>); (0.59 g, 0.8 mmol)], and 8.95 g of 1-methoxy-2-propanol. The mixture was shaken and heated to 60 °C until a homogenous solution resulted. Upon cooling to room temperature, the solution was filtered through a 0.45 μm (0.45 micron) PTFE membrane. To the filtered solution was added an acid catalyst delivered as 0.16 g of a 10 wt % solution of p-toluenesulfonic acid in 1-methoxy-2-propanol to yield the liquid containing reaction mixture. (Action B) The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 0.508 mm (20 mil) gap. (Action C) The metalized MYLAR™ substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 130 °C and left to heat for 40 min. These actions provided an SOF having a thickness ranging from 2-4 μm (2-4 microns) that could be delaminated from the substrate as a single free-standing SOF. The color of the SOF was green.

40 Illustrative EXAMPLE 6: Type 2 SOF

45 **[0189]** (Action A) The following were combined: the building block 1,6-n-hexanediol [segment = n-hexyl; Fg = hydroxyl (-OH); (0.21 g, 1.8 mmol)] and a second building block N4,N4,N4',N4'-tetrakis(4-(methoxymethyl)phenyl)biphenyl-4,4'-diamine [segment = N4,N4,N4',N4'-tetra-p-tolylbiphenyl-4,4'-diamine; Fg = methoxy ether (-OCH<sub>3</sub>); (0.58 g, 0.87 mmol)], and 8.95 g of 1-methoxy-2-propanol. The mixture was shaken and heated to 60 °C until a homogenous solution resulted. Upon cooling to room temperature, the solution was filtered through 0.45 μm (0.45 micron) PTFE membrane. To the filtered solution was added an acid catalyst delivered as 0.16 g of a 10 wt % solution of p-toluenesulfonic acid in 1-methoxy-2-propanol to yield the liquid containing reaction mixture. (Action B) The reaction mixture was applied to the

## EP 2 403 657 B1

reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 0.508 mm (20 mil) gap. (Action C) The metalized MYLAR™ substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 13 °C and left to heat for 40 min. These actions provided an SOF having a thickness ranging from 4-5 μm (4-5 microns) that could be delaminated from the substrate as a single free standing SOF. The color of the SOF was green. The Fourier-transform infrared spectrum of a portion of this SOF is provided in FIG 7.

### Illustrative EXAMPLE 7: Type 2 SOF

**[0190]** (Action A) The following were combined: the building block benzene-1,4-dimethanol [segment = p-xylyl; Fg = hydroxyl (-OH); (0.64 g, 4.6 mmol)] and a second building block N4,N4,N4',N4'-tetrakis(4-(methoxymethyl)phenyl)biphenyl-4,4'-diamine [segment = N4,N4,N4',N4'-tetra-p-tolylbiphenyl-4,4'-diamine; Fg = methoxy ether (-OCH<sub>3</sub>); (1.54 g, 2.3 mmol)], and 7.51 g of 1,4-dioxane. The mixture was shaken and heated to 60 °C until a homogenous solution resulted, which was then filtered through a 0.45 μm (0.45 micron) PTFE membrane. To the filtered solution was added an acid catalyst delivered as 0.28 g of a 10 wt % solution of p-toluenesulfonic acid in 1,4-dioxane to yield the liquid containing reaction mixture. (Action B) The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 0.25 mm (10 mil) gap. (Action C) The metalized MYLAR™ substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 130 °C and left to heat for 4 min. These actions provided an SOF having a thickness ranging from 8-12 μm (8-12 microns) that could be delaminated from the substrate as a single free-standing film. The color of the SOF was green.

### Illustrative EXAMPLE 8: Type 2 SOF

**[0191]** (Action A) The following were combined: the building block 1,6-n-hexanediol [segment = n-hexyl; Fg = hydroxyl (-OH); (0.57 g, 4.8 mmol)] and a second building block N4,N4,N4',N4'-tetrakis(4-(methoxymethyl)phenyl)biphenyl-4,4'-diamine [segment = N4,N4,N4',N4'-tetra-p-tolylbiphenyl-4,4'-diamine; Fg = methoxy ether (-OCH<sub>3</sub>); (1.61 g, 2.42 mmol)], and 7.51 g of 1,4-dioxane. The mixture was shaken and heated to 60 °C until a homogenous solution resulted. Upon cooling to rt, the solution was filtered through a 0.45 μm (0.45 micron) PTFE membrane. To the filtered solution was added an acid catalyst delivered as 0.22 g of a 10 wt % solution of p-toluenesulfonic acid in 1,4-dioxane to yield the liquid containing reaction mixture. (Action B) The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 0.25 mm (10 mil) gap. (Action C) The metalized MYLAR™ substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 130 °C and left to heat for 40 min. These actions provided an SOF having a thickness ranging from 12-20 μm (12-20 microns) that could be delaminated from the substrate as a single free-standing film. The color of the SOF was green.

### Illustrative EXAMPLE 9: Type 2 SOF

**[0192]** (Action A) The following were combined: the building block 4,4'-(cyclohexane-1,1-diyl)diphenol [segment = 4,4'-(cyclohexane-1,1-diyl)diphenyl; Fg = hydroxyl (-OH); (0.97 g, 6 mmol)] and a second building block N4,N4,N4',N4'-tetrakis(4-(methoxymethyl)phenyl)biphenyl-4,4'-diamine [segment = N4,N4,N4',N4'-tetra-p-tolylbiphenyl-4,4'-diamine; Fg = methoxy ether (-OCH<sub>3</sub>); (1.21 g, 1.8 mmol)] and 7.51 g of 1,4-dioxane. The mixture was shaken and heated to 60 °C until a homogenous solution resulted. Upon cooling to rt, the solution was filtered through a 0.45 μm (0.45 micron) PTFE membrane. To the filtered solution was added an acid catalyst delivered as 0.22 g of a 10 wt % solution of p-toluenesulfonic acid in 1,4-dioxane to yield the liquid containing reaction mixture. (Action B) The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 0.25 mm (10 mil) gap. (Action C) The metalized MYLAR™ substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 130 °C and left to heat for 40 min. These actions provided an SOF having a thickness ranging from 12-20 μm (12-20 microns) that could be delaminated from the substrate as a single free-standing film. The color of the SOF was green. The Fourier-transform infrared spectrum of SOF is provided in FIG 8.

### Illustrative EXAMPLE 10: Type 2 SOF

**[0193]** (Action A) The following were combined: the building block benzene-1,4-dimethanol [segment = p-xylyl; Fg = hydroxyl, (-OH); (0.52 g, 3.8 mmol)] and a second building block N4,N4,N4',N4'-tetrakis(4-(methoxymethyl)phenyl)biphenyl-4,4'-diamine [segment = N4,N4,N4',N4'-tetra-p-tolylbiphenyl-4,4'-diamine; Fg = methoxy ether (-OCH<sub>3</sub>); (1.26 g, 1.9 mmol)], and 6.3 g of 1,4-dioxane and 1.57 g of n-butyl acetate. The mixture was shaken and heated to 60 °C until

## EP 2 403 657 B1

a homogenous solution resulted, which was then filtered through a 0.45  $\mu\text{m}$  (0.45 micron) PTFE membrane. To the filtered solution was added an acid catalyst delivered as 0.28 g of a 10 wt % solution of p-toluenesulfonic acid in 1,4-dioxane to yield the liquid containing reaction mixture. (Action B) The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 0.254 mm (10 mil) gap. (Action C) The metalized MYLAR™ substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 130 °C and left to heat for 4 min. These actions provided an SOF having a thickness of 7-10  $\mu\text{m}$  (7-10 microns) that could be delaminated from the substrate as a single free-standing film. The color of the SOF was green.

### 10 Illustrative EXAMPLE 11: Type 2 SOF

**[0194]** (Action A) Same as illustrative EXAMPLE 7. (Action B) The reaction mixture was applied to a photoconductive layer, containing a pigment and polymeric binder, supported on metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 0.25 mm (10 mil) gap. (Action C) The supported wet layer was rapidly transferred to an actively vented oven preheated to 120 °C and left to heat for 20 min. These actions provided a uniformly coated multilayer device wherein the SOF had a thickness ranging from 9-10  $\mu\text{m}$  (9-10 microns).

### Illustrative EXAMPLE 12: Type 2 SOF

**[0195]** (Action A) The following were combined: the building block benzene-1,4-dimethanol [segment = p-xylyl; Fg = hydroxyl (-OH); (0.52 g, 3.8 mmol)] and a second building block N<sub>4</sub>,N<sub>4</sub>,N<sub>4</sub>',N<sub>4</sub>'-tetrakis(4-(methoxymethyl)phenyl)biphenyl-4,4'-diamine [segment = N<sub>4</sub>,N<sub>4</sub>,N<sub>4</sub>',N<sub>4</sub>'-tetra-p-tolylbiphenyl-4,4'-diamine; Fg = methoxy ether (-OCH<sub>3</sub>); (1.26 g, 1.9 mmol)], and 6.3 g of 1,4-dioxane and 1.57 g of methyl isobutyl ketone. The mixture was shaken and heated to 60 °C until a homogenous solution resulted, which was then filtered through a 0.45  $\mu\text{m}$  (0.45 micron) PTFE membrane. To the filtered solution was added an acid catalyst delivered as 0.28 g of a 10 wt % solution of p-toluenesulfonic acid in 1,4-dioxane to yield the liquid containing reaction mixture. (Action B) The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 0.25mm (10 mil) gap. (Action C) The metalized MYLAR™ substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 130 °C and left to heat for 4 min. These actions provided an SOF having a thickness ranging from 7-10  $\mu\text{m}$  (7-10 microns) that could be delaminated from the substrate as a single free-standing film. The color of the SOF was green.

### Illustrative EXAMPLE 13: Type 2 SOF

**[0196]** (Action A) The following were combined: the building block 1,6-n-hexanediol [segment = n-hexyl; Fg = hydroxyl (-OH); (0.47 g, 4.0 mmol)] and a second building block N<sub>4</sub>,N<sub>4</sub>,N<sub>4</sub>',N<sub>4</sub>'-tetrakis(4-(methoxymethyl)phenyl)biphenyl-4,4'-diamine [segment = N<sub>4</sub>,N<sub>4</sub>,N<sub>4</sub>',N<sub>4</sub>'-tetra-p-tolylbiphenyl-4,4'-diamine; Fg = methoxy ether (-OCH<sub>3</sub>); (1.31 g, 2.0 mmol)], 6.3 g of 1,4-dioxane, and 1.57 g of n-butyl acetate. The mixture was shaken and heated to 60 °C until a homogenous solution resulted. Upon cooling to room temperature, the solution was filtered through a 0.45  $\mu\text{m}$  (0.45 micron) PTFE membrane. To the filtered solution was added an acid catalyst delivered as 0.22 g of a 10 wt % solution of p-toluenesulfonic acid in 1,4-dioxane to yield the liquid containing reaction mixture. (Action B) The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 0.25 mm (10 mil) gap. (Action C) The metalized MYLAR™ substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 130 °C and left to heat for 40 min. These actions provided an SOF having a thickness ranging from 8-12  $\mu\text{m}$  (8-12 microns) that could be delaminated from the substrate as a single free-standing film. The color of the SOF was green.

### Illustrative EXAMPLE 14: Type 2 SOF

**[0197]** (Action A) Same as illustrative EXAMPLE 10. (Action B) The reaction mixture was applied to a photoconductive layer, containing a pigment and polymeric binder, supported on metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 0.25 mm (10 mil) gap. (Action C) The supported wet layer was rapidly transferred to an actively vented oven preheated to 120 °C and left to heat for 20 min. These actions provided a uniformly coated multilayer device wherein the SOF had a thickness ranging from 9-10  $\mu\text{m}$  10 microns).

### Illustrative EXAMPLE 15: Type 2 SOF

**[0198]** (Action A) The following were combined: the building block 1,6-n-hexanediol [segment = n-hexyl; Fg = hydroxyl



## EP 2 403 657 B1

(-OH); (0.47 g, 4.0 mmol)] and a second building block N<sub>4</sub>,N<sub>4</sub>,N<sub>4</sub>',N<sub>4</sub>'-tetrakis(4-(methoxymethyl)phenyl)biphenyl-4,4'-diamine [segment = N<sub>4</sub>,N<sub>4</sub>,N<sub>4</sub>',N<sub>4</sub>'-tetra-p-tolylbiphenyl-4,4'-diamine; Fg = methoxy ether (-OCH<sub>3</sub>); (1.31 g, 2.0 mmol)], 6.3 g of 1,4-dioxane, and 1.57 g of methyl isobutyl ketone. The mixture was shaken and heated to 60 °C until a homogenous solution resulted. Upon cooling to room temperature, the solution was filtered through a 0.45 μm (0.45 micron) PTFE membrane. To the filtered solution was added an acid catalyst delivered as 0.22 g of a 10 wt % solution of p-toluenesulfonic acid in 1,4-dioxane to yield the liquid containing reaction mixture. (Action B) The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 0.25 mm (10 mil) gap. (Action C) The metalized MYLAR™ substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 130 °C and left to heat for 40 min. These actions provided an SOF having a thickness ranging from 8-12 μm (8-12 microns) that could be delaminated from the substrate as a single free-standing film. The color of the SOF was green.

### Illustrative EXAMPLE 16: Type 2 SOF

**[0199]** (Action A) The following were combined: the building block 4,4'-(cyclohexane-1,1-diyl)diphenol [segment = 4,4'-(cyclohexane-1,1-diyl)diphenyl, Fg = hydroxyl (-OH); (0.8 g)] and a second building block N<sub>4</sub>,N<sub>4</sub>,N<sub>4</sub>',N<sub>4</sub>'-tetrakis(4-(methoxymethyl)phenyl)biphenyl-4,4'-diamine [segment = N<sub>4</sub>,N<sub>4</sub>,N<sub>4</sub>',N<sub>4</sub>'-tetra-p-tolylbiphenyl-4,4'-diamine; Fg = methoxy ether (-OCH<sub>3</sub>); (0.8 g, 1.5 mmol)], 1,4-dioxane, and 1.57 g of n-butyl acetate. The mixture was shaken and heated to 60 °C until a homogenous solution resulted. Upon cooling, the solution was filtered through a 0.45 μm (0.45 micron) PTFE membrane. To the filtered solution was added an acid catalyst delivered as 0.22 g of a 10 wt % solution of p-toluenesulfonic acid in 1,4-dioxane to yield the liquid containing reaction mixture. (Action B) The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 0.25 mm (10 mil) gap. (Action C) The metalized MYLAR™ substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 130 °C and left to heat for 40 min. These actions provided an SOF having a thickness of 12 μm (12 microns) that could be delaminated from the substrate as a single free-standing film. The color of the SOF was green.

### Illustrative EXAMPLE 17: Type 2 SOF

**[0200]** (Action A) Same as illustrative EXAMPLE 13. (Action B) The reaction mixture was applied to a photoconductive layer, containing a pigment and polymeric binder, supported on metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 0.25 mm (10 mil) gap. (Action C) The supported wet layer was rapidly transferred to an actively vented oven preheated to 120 °C and left to heat for 20 min. These actions provided a uniformly coated multilayer device wherein the SOF had a thickness ranging from 9-10 μm (9-10 microns).

### Illustrative EXAMPLE 18: Type 2 SOF

**[0201]** (Action A) The following were combined: the building block 4,4'-(cyclohexane-1,1-diyl)diphenol [segment = 4,4'-(cyclohexane-1,1-diyl)diphenyl; Fg = hydroxyl (-OH); (0.8 g, 3.0 mmol)] and a second building block N<sub>4</sub>,N<sub>4</sub>,N<sub>4</sub>',N<sub>4</sub>'-tetrakis(4-(methoxymethyl)phenyl)biphenyl-4,4'-diamine [segment = N<sub>4</sub>,N<sub>4</sub>,N<sub>4</sub>',N<sub>4</sub>'-tetra-p-tolylbiphenyl-4,4'-diamine; Fg = methoxy ether (-OCH<sub>3</sub>); (0.8 g, 1.5 mmol)], 1,4-dioxane, and 1.57 g of methyl isobutyl ketone. The mixture was shaken and heated to 60 °C until a homogenous solution resulted. Upon cooling to room temperature, the solution was filtered through a 0.45 μm (0.45 micron) PTFE membrane. To the filtered solution was added an acid catalyst delivered as 0.22 g of a 10 wt % solution of p-toluenesulfonic acid in 1,4-dioxane to yield the liquid containing reaction mixture. (Action B) The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 0.25 mm (10 mil) gap. (Action C) The metalized MYLAR™ substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 130 °C and left to heat for 40 min. These actions provide an SOF having a thickness of 12 μm (12 microns) that could be delaminated from the substrate as a single free-standing film. The color of the SOF was green.

### Illustrative EXAMPLE 19: Type 2 SOF

**[0202]** (Action A) Same as illustrative EXAMPLE 7. (Action B) The reaction mixture was applied to a photoconductive layer, containing a pigment and polymeric binder, supported on metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 0.25 mm (10 mil) gap. (Action C) The supported wet layer was allowed to dry at ambient temperature in an actively vented fume hood for 5 min and was then transferred to an actively vented oven preheated to 120 °C and left to heat for 15 min. These actions provided a uniformly coated multilayer device wherein the SOF had a thickness ranging from 9-10 μm (9-10 microns).

Illustrative EXAMPLE 20: Type 2 SOF

5 [0203] (Action A) Same as illustrative EXAMPLE 10. (Action B) The reaction mixture was applied to a photoconductive layer, containing a pigment and polymeric binder, supported on metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 0.25 mm (10 mil) gap. (Action C) The supported wet layer was allowed to dry at ambient temperature in an actively vented fume hood for 5 min and was then transferred to an actively vented oven preheated to 120°C and left to heat for 15 min. These actions provided a uniformly coated multilayer device wherein the SOF had a thickness ranging from 9-10 μm (9-10 microns).

10 Illustrative EXAMPLE 21: Type 2 SOF

15 [0204] (Action A) Same as illustrative EXAMPLE 13. (Action B) The reaction mixture was applied to a photoconductive layer, containing a pigment and polymeric binder, supported on metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 0.25mm (10 mil) gap. (Action C) The supported wet layer was allowed to dry at ambient temperature in an actively vented fume hood for 5 min and was then transferred to an actively vented oven preheated to 120°C and left to heat for 15 min. These actions provided a uniformly coated multilayer device wherein the SOF had a thickness ranging from 9-10μm (9-10 microns) and could not be delaminated

20 Illustrative EXAMPLE 22: Type 2 SOF

25 [0205] (Action A) Same as illustrative EXAMPLE 7. (Action B) The reaction mixture was applied to a layered photo-sensitive member comprising a generator layer and a transport layer containing a diamine type molecule dispersed in a polymeric binder using a constant velocity draw down coater outfitted with a bird bar having a 0.25 mm (10 mil) gap. (Action C) The supported wet layer was allowed to dry at ambient temperature in an actively vented fume hood for 5 min and was then transferred to an actively vented oven preheated to 120°C and left to heat for 15 min. These actions provided a uniformly coated multilayer device wherein the SOF had a thickness ranging from 9-10μm (9-10 microns).

Illustrative EXAMPLE 23: Type 2 SOF

30 [0206] (Action A) Same as illustrative EXAMPLE 10. (Action B) The reaction mixture was applied to layered photo-sensitive member comprising a generator layer and a transport layer containing a diamine type molecule dispersed in a polymeric binder using a constant velocity draw down coater outfitted with a bird bar having a 0.25 mm (10 mil) gap. (Action C) The supported wet layer was allowed to dry at ambient temperature in an actively vented fume hood for 5 min and was then transferred to an actively vented oven preheated to 120°C and left to heat for 15 min. These actions provided a uniformly coated multilayer device wherein the SOF had a thickness ranging from 9-10 μm (9-10 microns).

Illustrative EXAMPLE 24: Type 2 SOF

40 [0207] (Action A) Same as illustrative EXAMPLE 13. (Action B) The reaction mixture was applied to layered photo-sensitive member comprising a generator layer and a transport layer containing a diamine type molecule dispersed in a polymeric binder using a constant velocity draw down coater outfitted with a bird bar having a 0.25 mm (10 mil) gap. (Action C) The supported wet layer was allowed to dry at ambient temperature in an actively vented fume hood for 5 min and was then transferred to an actively vented oven preheated to 120 °C and left to heat for 15 min. These actions provided a uniformly coated multilayer device wherein the SOF had a thickness ranging from 9-10μm (9-10 microns).

45 Illustrative EXAMPLE 25: Type 1 SOF

50 [0208] (Action A) The following were combined: the building block (4,4',4",4'''-(biphenyl-4,4'-diylbis(azanetriyl))tetrakis(benzene-4,1-diyl))tetramethanol [segment = (4,4',4",4'''-(biphenyl-4,4'-diylbis(azanetriyl))tetrakis(benzene-4,1-diyl))tetramethyl, Fg = hydroxyl (-OH); (1.48 g, 2.4 mmol)], and 8.3 g of 1,4-dioxane. The mixture was shaken and heated to 60°C until a homogenous solution resulted. Upon cooling to room temperature, the solution was filtered through a 0.45 μm (0.45 micron) PTFE membrane. To the filtered solution was added an acid catalyst delivered as 0.15 g of a 10 wt % solution of p-toluenesulfonic acid in 1,4-dioxane to yield the liquid containing reaction mixture. (Action B) The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 0.64 mm (25 mil) gap. (Action C) The metalized MYLAR™ substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 130°C and left to heat for 40 min. These actions provided an SOF having a thickness ranging from 8-24 μm (8-24 microns). The color of the SOF was green.

## Illustrative EXAMPLE 26: Type 1 SOF

5 [0209] (Action A) The following were combined: the building 4,4',4"-nitrotris(benzene-4,1-diyl)trimethanol [segment = (4,4',4"-nitrotris(benzene-4,1-diyl)tamethyl); Fg = hydroxyl (-OH); (1.48 g, 4.4 mmol)], and 8.3 g of 1,4-dioxane. The mixture was shaken and heated to 60°C until a homogenous solution resulted. Upon cooling to room temperature, the solution was filtered through a 0.45 μm (0.45 micron) PTFE membrane. To the filtered solution was added an acid catalyst delivered as 0.15 g of a 10 wt % solution of p-toluenesulfonic acid in 1,4-dioxane to yield the liquid containing reaction mixture. (Action B) The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 0.38 mm (15 mil) gap. (Action C) The metalized MYLAR™ substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 130 °C and left to heat for 40 min. These actions provided an SOF having a thickness ranging from 6-15 μm (6-15 microns) that could be delaminated from the substrate as a single free-standing film. The color of the SOF was green. The Fourier-transform infrared spectrum of this film is provided in FIG. 9. Two-dimensional X-ray scattering data is provided in FIG. 15. As seen in FIG. 15, no signal above the background is present, indicating the absence of molecular order having any detectable periodicity.

## Illustrative EXAMPLE 27: Type 2 SOF

20 [0210] (Action A) The following were combined: the building block N4,N4,N4',N4'-tetrakis(4-(methoxymethyl)phenyl)bi-phenyl-4,4'-diamine [segment = N4,N4,N4',N4'-tetra-p-tolylbiphenyl-4,4'-diamine; Fg = methoxy ether (-OCH<sub>3</sub>); (0.26 g, 0.40 mmol)] and a second building block 3,3'-(4,4'-(biphenyl-4-ylazanediyl)bis(4.1-phenylene))dipropan-1-ol [segment = 3,3'-(4,4'-(biphenyl-4-ylazanediyl)bis(4.1-phenylene))dipropyl; Fg = hydroxyl (-OH): OH): (0.34 g, 0.78 mmol)], and 1.29 mL of 1-methoxy-2-propanol. The mixture was shaken and heated to 60°C until a homogenous solution resulted. Upon cooling to room temperature, the solution was filtered through a 0.45 μm (0.45 micron) PTFE membrane. To the filtered solution was added an acid catalyst delivered as 0.2 g of a 10 wt % solution of p-toluenesulfonic acid in 1-methoxy-2-propanol to yield the liquid containing reaction mixture. (Action B) The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 0.2 mm (8 mil) gap. (Action C) The metalized MYLAR™ substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 150°C and left to heat for 40 min. These actions provided an SOF having a thickness ranging from 15-20 μm (15-20 microns) that could be delaminated from the substrate as a single free-standing film. The color of the SOF was green.

## illustrative EXAMPLE 28: Type 2 SOF

35 [0211] (Action A) Same as illustrative EXAMPLE 24. (Action B) The reaction mixture was applied to a layered photo-sensitive member comprising a generator layer and a transport layer containing a diamine type molecule dispersed in a polymeric binder using a constant velocity draw down coater outfitted with a bird bar having a 0.13 mm (5 mil) gap. (Action C) The supported wet layer was rapidly transferred to an actively vented oven preheated to 130°C and left to heat for 40 min. These actions provided a uniformly coated multilayer device wherein the SOF had a thickness of 5 μm (5 microns).

## Illustrative EXAMPLE 29: Type 2 SOF

45 [0212] (Action A) Same as illustrative EXAMPLE 24. (Action B) The reaction mixture was applied to layered photo-sensitive member comprising a generator layer and a transport layer containing a diamine type molecule dispersed in a polymeric binder affixed to a spin coating device rotating at 750 rpm. The liquid reaction mixture was dropped at the centre rotating substrate to deposit the wet layer. (Action C) The supported wet layer was rapidly transferred to an actively vented oven preheated to 140°C and left to heat for 40 min. These actions provided a uniformly coated multilayer device wherein the SOF had a thickness of 0.2 μm (0.2 microns).

## Illustrative EXAMPLE 30: Type 2 SOF

55 [0213] (Action A) The following were combined: the building block terephthalaldehyde [segment = benzene; Fg = aldehyde (-CHO); (0.18 g, 1.3 mmol)] and a second building block tris(4-aminophenyl)amine [segment = triphenylamine; Fg = amine (-NH<sub>2</sub>); (0.26 g, 0.89 mmol)], and 2.5 g of tetrahydrofuran. The mixture was shaken until a homogenous solution resulted. Upon cooling to room temperature, the solution was filtered through a 0.45 μm (0.45 micron) PTFE membrane. To the filtered solution was added an acid catalyst delivered as 0.045 g of a 10 wt % solution of p-toluenesulfonic acid in 1-tetrahydrofuran to yield the liquid containing reaction mixture. (Action B) The reaction mixture was

## EP 2 403 657 B1

applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 0.13 mm (5 mil) gap. (Action C) The metalized MYLAR™ substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 120 °C and left to heat for 40 min. These actions provided an SOF having a thickness of 6 μm (6 microns) that could be delaminated from the substrate as a single free-standing film. The color of the SOF was red-orange. The Fourier-transform infrared spectrum of this film is provided in FIG 10.

Illustrative EXAMPLE 31: Type 1 SOF

**[0214]** (Action A) The following were combined: the building block 4,4',4"-nitritotribenzaldehyde [segment = triphenylamine; Fg = aldehyde (-CHO); (0.16 g, 0.4 mmol)] and a second building block tris(4-aminophenyl)amine [segment = triphenylamine; Fg = amine (-NH<sub>2</sub>); (0.14 g, 0.4 mmol)], and 1.9 g of tetrahydrofuran. The mixture was stirred until a homogenous solution resulted. Upon cooling to room temperature, the solution was filtered through a 0.45 μm (0.45 micron) PTFE membrane. (Action B) The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 1.3 mm (5 mil) gap. (Action C) The metalized MYLAR™ substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 120°C and left to heat for 40 min. These actions provided an SOF having a thickness of 6 μm (6 microns) that could be delaminated from the substrate as a single free-standing film. The color of the SOF was red. The Fourier-transform infrared spectrum of this film is provided in FIG 11.

Illustrative EXAMPLE 32: Type 2 SOF

**[0215]** (Action A) The following were combined: the building block glyoxal [segment = single covalent bond; Fg = aldehyde (-CHO); (0.31 g, 5.8 mmol - added as 40 wt % solution in water i.e. 0.77 g aqueous glyoxal)] and a second building block tris(4-aminophenyl)amine [segment = triphenylamine; Fg = amine (-NH<sub>2</sub>); (1.14 g, (3.9 mmol)], and 8.27 g of tetrahydrofuran. The mixture was shaken until a homogenous solution resulted. Upon cooling to room temperature, the solution was filtered through a 0.45 μm (0.45 micron) PTFE membrane. (Action B) The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 0.25mm (10 mil) gap. (Action C) The metalized MYLAR™ substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 120°C and left to heat for 40 min. These actions provided an SOF having a thickness ranging from 6-12 μm (6-12 microns) that could be delaminated from the substrate as a single free-standing film. The color of the SOF was red.

Illustrative EXAMPLE 33: Type 2 SOF

**[0216]** (Action A) The following were combined: the building block terephthalaldehyde [segment = benzene; Fg = aldehyde (-CHO); (0.18 g, 1.3 mmol)] and a second building block tris(4-aminophenyl)amine [segment = triphenylamine; Fg = amine (-NH<sub>2</sub>); (0.26 g, 0.89 mmol)], 2.5 g of tetrahydrofuran, and 0.4 g water. The mixture was shaken until a homogenous solution resulted. Upon cooling to room temperature, the solution was filtered through a 0.45 μm (0.45 micron) PTFE membrane. (Action B) The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 1.3 mm (5 mil) gap. (Action C) The metalized MYLAR™ substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 120°C and left to heat for 40 min. These actions provided an SOF having a thickness ranging 6 μm (6 microns) that could be delaminated from the substrate as a single free-standing film. The color of the SOF was red-orange.

Illustrative EXAMPLE 34: Type 1 SOF

**[0217]** (Action A) The following were combined: the building block 4,4',4"-nitritotribenzaldehyde [segment = triphenylamine; Fg = aldehyde (-CHO); (0.16 g, 0.4 mmol)] and a second building block tris(4-aminophenyl)amine [segment = triphenylamine; Fg = amine (-NH<sub>2</sub>); (0.14 g, 0.4 mmol)], 1.9 g of tetrahydrofuran, and 0.4 g water. The mixture was stirred until a homogenous solution resulted. Upon cooling to room temperature, the solution was filtered through a 0.45 μm (0.45 micron) PTFE membrane. (Action B) The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 1.3 mm (5 mil) gap. (Action C) The metalized MYLAR™ substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 120°C and left to heat for 40 min. These actions provided an SOF having a thickness of 6 μm (6 microns) that could be delaminated from the substrate as a single free-standing film. The color of the SOF was red-orange.

## EP 2 403 657 B1

### Illustrative EXAMPLE 35: Type 2 SOF

**[0218]** (Action A) Same as illustrative EXAMPLE 28. (Action B) The reaction mixture was dropped from a glass pipette onto a glass slide. (Action C) The glass slide was heated to 80 °C on a heating stage yielding a deep red SOF having a thickness of 200 μm (200 microns) which could be delaminated from the glass slide.

### Illustrative EXAMPLE 36: Type 1 SOF

**[0219]** (Action A) The following were combined: the building block tris-[(4-hydroxymethyl)-phenyl]-amine [segment = tri-(*p*-tolyl)-amine; Fg = hydroxyl (-OH); 5.12 g]; the additives Cymel303 (55 mg) and Silclean 3700 (210 mg), and the catalyst Nacure XP-357 (267 mg) and 1-methoxy-2-propanol (13.27 g). The mixture was mixed on a rolling wave rotator for 10 min and then heated at 55 °C for 65 min until a homogenous solution resulted. The mixture was placed on the rotator and cooled to room temperature. The solution was filtered through a 1 μm (1 micron) PTFE membrane. (Action B) The reaction mixture was applied to a commercially available, 30 mm drum photoreceptor using a cup coater (Tsukiage coating) at a pull-rate of 240 mm/min. (Action C) The photoreceptor drum supporting the wet layer was rapidly transferred to an actively vented oven preheated to 140 °C and left to heat for 40 min. These actions provided an SOF having a thickness of 6.9 μm (6.9 microns). FIG. 12 is a photo-induced discharge curve (PIDC) illustrating the photoconductivity of this SOF overcoat layer (voltage at 75 ms (expose-to-measure) 1N/m corresponds to 1000 ergs/cm<sup>2</sup>).

### Illustrative EXAMPLE 37: Type 1 SOF with additives

**[0220]** (Action A) The following were combined: the building block tris-[(4-hydroxymethyl)-phenyl]-amine [segment = tri-(*p*-tolyl)-amine; Fg = hydroxyl (-OH); 4.65 g]; the additives Cymel303 (49 mg) and Silclean 3700 (205 mg), and the catalyst Nacure XP-357 (254 mg) and 1-methoxy-2-propanol (12.25 g). The mixture was mixed on a rolling wave rotator for 10 min and then heated at 55 °C for 65 min until a homogenous solution resulted. The mixture was placed on the rotator and cooled to room temperature. The solution was filtered through a 1 μm (1 micron) PTFE membrane. A polyethylene wax dispersion (average particle size = 5.5 μm (5.5 microns), 40% solids in *i*-propyl alcohol, 613 mg) was added to the reaction mixture which was sonicated for 10 min and mixed on the rotator for 30 min. (Action B) The reaction mixture was applied to a commercially available, 30 mm drum photoreceptor using a cup coater (Tsukiage coating) at a pull-rate of 240 mm/min. (Action C) The photoreceptor drum supporting the wet layer was rapidly transferred to an actively vented oven preheated to 140 °C and left to heat for 40 min. These actions provided a film having a thickness of 6.9 μm (6.9 microns) with even incorporation of the wax particles in the SOF. FIG 13 is a photo-induced discharge curve (PIDC) illustrating the photoconductivity of this SOF overcoat layer (voltage at 75 ms (expose-to-measure) 1N/m corresponds to 1000 ergs/cm<sup>2</sup>).

### Illustrative EXAMPLE 38: Type 2 SOF

**[0221]** (Action A) The following were combined: the building block *N,N,N',N'*-tetrakis-[(4-hydroxymethyl)phenyl]-biphenyl-4,4'-diamine [segment = *N,N,N',N'*-tetra-(*p*-tolyl)biphenyl-4,4'-diamine; Fg = hydroxyl (-OH); 3.36 g] and the building block *N,N'*-diphenyl-*N,N'*-bis-(3-hydroxyphenyl)-biphenyl-4,4'-diamine [segment = *N,N,N',N'*-tetraphenyl-biphenyl-4,4'-diamine; Fg = hydroxyl (-OH); 5.56 g]; the additives Cymel303 (480 mg) and Silclean 3700 (383 mg), and the catalyst Nacure XP-357 (480 mg) and 1-methoxy-2-propanol (33.24g). The mixture was mixed on a rolling wave rotator for 10 min and then heated at 55 °C for 65 min until a homogenous solution resulted. The mixture was placed on the rotator and cooled to room temperature. The solution was filtered through a 1 μm (1 micron) PTFE membrane. (Action B) The reaction mixture was applied to a commercially available, 30 mm drum photoreceptor using a cup coater (Tsukiage coating) at a pull-rate of 485 mm/min. (Action C) The photoreceptor drum supporting the wet layer was rapidly transferred to an actively vented oven preheated to 140°C and left to heat for 40 min. These actions provided a film having a thickness ranging from 6.0 to 6.2 μm (6.0 to 6.2 microns). FIG. 14 is a photo-induced discharge curve (PIDC) illustrating the photoconductivity of this SOF overcoat layer (voltage at 75 ms (expose-to-measure) 1N/m corresponds to 1000 ergs/cm<sup>2</sup>).

### EXAMPLE 39: Illustrative Type 2 SOF

**[0222]** (Action A) The following were combined: the building block dipropylcarbonate [segment = carbonyl [-C(=O)-]; Fg = propoxy (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>O-); 4.38 g, 30 mmol] and the building block 1,3,5-trihydroxycyclohexane [segment = cyclohexane; Fg = hydroxyl (-OH); 3.24 g, 20 mmol] and catalyst sodium methoxide (38 mg) and *N*-methyl-2-pyrrolidinone (25.5 g). The mixture was mixed on a rolling wave rotator for 10 min and filtered through a 1 μm (1 micron) PTFE membrane. (Action B) The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 1.3 mm (5 mil) gap. (Action C) The substrate

## EP 2 403 657 B1

supporting the wet layer was rapidly transferred to an actively vented oven preheated to 200 °C and heated for 40 min.

### Illustrative EXAMPLE 40: Type 2 SOF

- 5 **[0223]** (Action A) The following were combined: the building block dipropylcarbonate [segment = carbonyl [-C(=O)-]; Fg = propoxy (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>O-); 4.38 g, 30 mmol] and the building block 1,3,5-trihydroxycyclohexane [segment = cyclohexane; Fg = hydroxyl (-OH); 3.24 g, 20 mmol]; phosphoric acid (2 M aq, 100 mg); and N-methyl-2-pyrrolidinone (25.5 g). The mixture was mixed on a rolling wave rotator for 10 min and filtered through a 1 μm (1 micron) PTFE membrane. (Action B) The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 1.3 mm (5 mil) gap. (Action C) The substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 200°C and left to heat for 40 min.

### Illustrative EXAMPLE 41: Type 2 SOF

- 15 **[0224]** (Action A) The following were combined: the building block 1,1'-carbonyldiimidazole [segment = carbonyl [-C(=O)-]; Fg = imidazole; 4.86 g, 30 mmol] and the building block 1,3,5-trihydroxycyclohexane [segment = cyclohexane; Fg = hydroxyl (-OH); 3.24 g, 20 mmol] and catalyst sodium methoxide (38 mg) and N-methyl-2-pyrrolidinone (25.5 g). The mixture was mixed on a rolling wave rotator for 10 min and filtered through a 1 μm (1 micron) PTFE membrane. (Action B) The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 1.3 mm (5 mil) gap. (Action C) The substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 200 °C and left to heat for 40 min.

### Illustrative EXAMPLE 42: Type 2 SOF

- 25 **[0225]** (Action A) The following were combined: the building block carbonyldiimidazole [segment = carbonyl [-C(=O)-]; Fg = imidazole; 4.86 g, 30 mmol] and the building block 1,3,5-trihydroxycyclohexane [segment = cyclohexane; Fg = hydroxyl (-OH); 3.24 g, 20 mmol]; phosphoric acid (2 M aq, 100 mg); and N-methyl-2-pyrrolidinone (25.5 g). The mixture was mixed on a rolling wave rotator for 10 min and filtered through a 1 μm (1 micron) PTFE membrane. (Action B) The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 1.3 mm (5 mil) gap. (Action C) The substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 200°C and left to heat for 40 min.

### Illustrative EXAMPLE 43: Type 2 SOF

- 35 **[0226]** (Action A) The following can be combined: the building block trimesic acid [segment = 1,3,5-benzenetricarboxylate; Fg = H; 4.20 g, 20 mmol] and the building block 1,6-hexanediol [segment = hexane; Fg = hydroxyl (-OH); 3.55 g, 30 mmol]; phosphoric acid (2 M aq, 100 mg); and N-methyl-2-pyrrolidinone (25.5 g). The mixture was mixed on a rolling wave rotator for 10 min and filtered through a 1 μm (1 micron) PTFE membrane. (Action B) The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 1.3 mm (5 mil) gap. (Action C) The substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 200°C and left to heat for 40 min.

### Illustrative EXAMPLE 44: Type 2 SOF

- 45 **[0227]** (Action A) The following were combined: the building block trimesic acid [segment = 1,3,5-benzenetricarboxylate; Fg = H; 4.20 g, 20 mmol] and the building block 1,6-hexanediol [segment = hexane; Fg = hydroxyl (-OH); 3.55 g, 30 mmol]; N,N-dimethyl-4-aminopyridine (50 mg); and N-methyl-2-pyrrolidinone (25.5 g). The mixture was mixed on a rolling wave rotator for 10 min and filtered through a 1 μm (1 micron) PTFE membrane. (Action B) The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 1.3 mm (5 mil) gap. (Action C) The substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 200°C and left to heat for 40 min.

### Illustrative EXAMPLE 45: Type 2 SOF

- 55 **[0228]** (Action A) The following were combined: the building block trimesic acid [segment = 1,3,5-benzenetricarboxylate; Fg = H; 4.20 g, 20 mmol] and the building block hexamethylenediamine [segment = hexane; Fg = amine (-NH<sub>2</sub>); 3.49 g, 30 mmol]; phosphoric acid (2 M aq, 100 mg); and N-methyl-2-pyrrolidinone (25.5 g). The mixture was mixed on a rolling wave rotator for 10 min and filtered through a 1 μm (1 micron) PTFE membrane. (Action B) The reaction mixture

## EP 2 403 657 B1

was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 1.3 mm (5 mil) gap. (Action C) The substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 200°C and left to heat for 40 min.

### 5 Illustrative EXAMPLE 46: Type 2 SOF

**[0229]** (Action A) The following were combined: the building block trimesic acid [segment = 1,3,5-benzenetricarboxylate; Fg = H; 4.20 g, 20 mmol] and the building block hexamethylenediamine [segment = hexane; Fg = amine (-NH<sub>2</sub>); 3.49 g, 30 mmol]; N,N-dimethyl-4-aminopyridine (50 mg); and N-methyl-2-pyrrolidinone (25.5 g). The mixture was mixed  
10 on a rolling wave rotator for 10 min and filtered through a 1 μm (1 micron) PTFE membrane. (Action B) The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 1.3 mm (5 mil) gap. (Action C) The substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 200°C and left to heat for 40 min.

### 15 Illustrative EXAMPLE 47: Type 2 SOF

**[0230]** (Action A) Preparation of liquid containing reaction mixture. The following were combined: the building block 1,4-diisocyanatobenzene [segment = phenyl; Fg = isocyanate (-N=C=O); (0.5 g, 3.1 mmol)] and a second building block 4,4',4''-nitriлотris(benzene-4,1-diyl)trimethanol [segment = (4,4',4''-nitriлотris(benzene-4,1-diyl)trmethyl); Fg = hydroxyl (-OH) (0.69, 2.1 mmol)] 10.1 g of dimethylformamide, and 1.0 g of triethylamine. The mixture was stirred until a homogenous solution was obtained. Upon cooling to room temperature, the solution was filtered through a 0.45 μm (0.45 micron) PTFE membrane. (Action B) The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 0.2 mm (8 mil) gap. (Action C) The metalized MYLAR™ substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated  
20 to 130 °C and left to heat for 120 min.

### 25 Illustrative EXAMPLE 48: Type 2 SOF

**[0231]** (Action A) Preparation of liquid containing reaction mixture. The following were combined: the building block 1,4-diisocyanatohexane [segment = hexyl; Fg = isocyanate (-N=C=O); (0.38 g, 3.6 mmol)] and a second building block triethanolamine [segment = triethylamine; Fg = hydroxyl (-OH) (0.81, 5.6 mmol)] 10.1 g of dimethylformamide, and 1.0 g of triethylamine. The mixture was stirred until a homogenous solution was obtained. Upon cooling to room temperature, the solution was filtered through a 0.45 μm (0.45 micron) PTFE membrane. (Action B) The reaction mixture was applied  
30 to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 0.2 mm (8 mil) gap. (Action C) The metalized MYLAR™ substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 130 °C and left to heat for 120 min.

### 35 Illustrative EXAMPLE 49: Type 2 SOF

**[0232]** (Action A) The following were combined: the building block N,N,N',N'-tetrakis-[(4-hydroxymethyl)phenyl]-biphenyl-4,4'-diamine [segment = N,N,N',N'-tetra-(p-tolyl)biphenyl-4,4'-diamine; Fg = hydroxyl (-OH); 4.24 g] and the building block N,N'-diphenyl-N,N'-bis-(3-hydroxyphenyl)-terphenyl-4,4'-diamine [segment = N,N,N',N'-tetraphenyl-terphenyl-4,4'-diamine; Fg = hydroxyl (-OH); 5.62 g]; the additives Cymel303 (530 mg) and Silclean 3700 (420 mg), and the catalyst Nacure XP-357 (530 mg) and 1-methoxy-2-propanol (41.62 g). The mixture was mixed on a rolling wave rotator for 10  
40 min and then heated at 55°C for 65 min until a homogenous solution resulted. The mixture was placed on the rotator and cooled to room temperature. The solution was filtered through a 1 μm (1 micron) PTFE membrane. (Action B) The reaction mixture was applied to a commercially available, 30 mm drum photoreceptor using a cup coater (Tsukiage coating) at a pull-rate of 485 mm/min. (Action C) The photoreceptor drum supporting the wet layer was rapidly transferred to an actively vented oven preheated to 140 °C and left to heat for 40 min. These actions provided an SOF having a thickness of 6.2 μm (6.2 microns).

### 45 Illustrative EXAMPLE 50: (Type 1 SOF attempt)

**[0233]** (Action A) Attempted preparation of the liquid containing reaction mixture. The following were combined: the building block tris-[(4-hydroxymethyl)-phenyl]-amine [segment = tri-(p-tolyl)-amine; Fg = hydroxyl (-OH); 5.12 g]; the additives Cymel303 (55 mg), Silclean 3700 (210 mg), and 1-methoxy-2-propanol (13.27 g). The mixture was heated to 55°C for 65 min in an attempt to fully dissolve the molecular building block. However it did not fully dissolve. A catalyst Nacure XP-357 (267 mg) was added and the heterogeneous mixture was further mixed on a rolling wave rotator for 10  
50

## EP 2 403 657 B1

min. In this Example, the catalyst was added after the heating step. The solution was not filtered prior to coating due to the amount of undissolved molecular building block. (Action B) Deposition of reaction mixture as a wet film. The reaction mixture was applied to a commercially available, 30 mm drum photoreceptor using a cup coater (Tsukiage coating) at a pull-rate of 240 mm/min. (Action C) Promotion of the change of the wet film to a dry film. The photoreceptor drum supporting the wet layer was rapidly transferred to an actively vented oven preheated to 140°C and left to heat for 40 min. These actions did not provide a uniform film. There were some regions where a non-uniform film formed that contained particles and other regions where no film was formed at all.

### Illustrative EXAMPLE 51: Type 1 SOF

**[0234]** (Action A) The following were combined: the building block tris-[(4-hydroxymethyl)-phenyl]-amine [segment = tri-(p-tolyl)-amine; Fg = hydroxyl (-OH); 5.12 g]; the additives Cymel303 (55 mg) and Silclean 3700 (210 mg), and the catalyst Nacure XP-357 (267 mg) and 1-methoxy-2-propanol (13.27 g). The mixture was mixed on a rolling wave rotator for 10 min and then heated at 55°C for 65 min until a homogenous solution resulted. The mixture was placed on the rotator and cooled to room temperature. The solution was filtered through a 1 µm (1 micron) PTFE membrane. It was noted that the viscosity of the reaction mixture increased after the heating step (although the viscosity of the solution before and after heating was not measured). (Action B) The reaction mixture was applied to a commercially available, 30 mm drum photoreceptor using a cup coater (Tsukiage coating) at a pull-rate of 240 mm/min. (Action C) The photoreceptor drum supporting the wet layer was rapidly transferred to an actively vented oven preheated to 140°C and left to heat for 40 min. These actions provided an SOF having a thickness of 6.3 µm microns).

### Illustrative EXAMPLE 52 : Type 2 SOF

**[0235]** (Action A) The following were combined: the building block N,N,N',N'-tetrakis-((4-hydroxymethyl)phenyl)-biphenyl-4,4'-diamine [segment = N,N,N',N'-tetra-(p-tolyl)biphenyl-4,4'-diamine; Fg = hydroxyl (-OH); 1.84 g] and the building block 3,3'-(4,4'-(biphenyl-4-ylazanediyl)bis(4,1-phenylene))dipropan-1-ol [segment = 3,3'-(4,4'-(biphenyl-4-ylazanediyl)bis(4,1-phenylene))dipropyl; Fg = hydroxyl (-OH); (2.41 g) and a catalyst p-toluenesulphonic acid (10 wt% solution in dowanol, 460 mg) and 1-methoxy-2-propanol (16.9 g - containing 50 ppm DC510). The mixture was mixed on a rolling wave rotator for 5 min and then heated at 70°C for 30 min until a homogenous solution resulted. The mixture was placed on the rotator and cooled to room temperature. The solution was filtered through a 1 µm (1 micron) PTFE membrane. (Action B) The reaction mixture was applied to a production-coated web photoreceptor with a Hirano web coater. Syringe pump speed: 4.5 mL/min. (Action C) The photoreceptor supporting the wet layer was fed at a rate of 1,5 m/min into an actively vented oven preheated to 130 °C for 2 min. These actions provided an SOF overcoat layer having a thickness of 2.1 µm (2.1 microns) on a photoreceptor

### Illustrative EXAMPLE 53: Type 2 SOF

**[0236]** (Action A) The following were combined: the building block N,N,N',N'-tetrakis-[(4-hydroxymethyl)phenyl]-biphenyl-4,4'-diamine [segment = N,N,N',N'-tetra-(p-tolyl)biphenyl-4,4'-diamine; Fg = hydroxyl (-OH); 5.0 g] and the building block benzenedimethanol [segment = p-xylyl; Fg = hydroxyl (-OH); 2.32 g] and a catalyst p-toluenesulphonic acid (10 wt% solution in dowanol, 720 mg) and 1-methoxy-2-propanol (22.5 g - containing 50 ppm DC510). The mixture was mixed on a rolling wave rotator for 5 min and then heated at 40°C for 5 min until a homogenous solution resulted. The mixture was placed on the rotator and cooled to room temperature. The solution was filtered through a 1 µm (1 micron) PTFE membrane. (Action B) The reaction mixture was applied to a production-coated, production web photoreceptor a Hirano web coater. Syringe pump speed: 5 mL/min. (Action C) The photoreceptor supporting the wet layer was fed at a rate of 1.5 m/min into an actively vented oven preheated to 130 °C for 2 min. These actions provided an SOF overcoat layer having a thickness of 2.2 µm (2.2 microns) on a photoreceptor.

### Illustrative EXAMPLE 54: Type 2 SOF

**[0237]** (Action A) The following were combined: the building block N,N,N',N'-tetrakis-[(4-hydroxymethyl)phenyl]-biphenyl-4,4'-diamine [segment = N,N,N',N'-tetra-(p-tolyl)biphenyl-4,4'-diamine; Fg = hydroxyl (-OH); 5.0 g] and the building block benzenedimethanol [segment = p-xylyl; Fg = hydroxyl (-OH); 2.32 g] and a catalyst p-toluenesulphonic acid (10 wt% solution in dowanol, 720 mg) and 1-methoxy-2-propanol (22.5 g - containing 50 ppm DC510). The mixture was mixed on a rolling wave rotator for 5 min and then heated at 40 °C for 5 min until a homogenous solution resulted. The mixture was placed on the rotator and cooled to room temperature. The solution was filtered through a 1 µm (1 micron) PTFE membrane. (Action B) The reaction mixture was applied to a production-coated, production web photoreceptor with a Hirano web coater. Syringe pump speed: 10 mL/min. (Action C) The photoreceptor supporting the wet layer was



## EP 2 403 657 B1

fed at a rate of 1.5 m/min into an actively vented oven preheated to 130°C for 2 min. These actions provided an SOF overcoat layer having a thickness of 4.3 μm (4.3 microns) on a photoreceptor.

### Illustrative EXAMPLE 55: Type 1 SOF

**[0238]** (Action A) The following were combined: the building block 4,4',4''-nitrotris(benzene-4,1-diyl)trimethanol [segment = (4,4',4''-nitrotris(benzene-4,1-diyl)trimethyl); Fg = hydroxyl (-OH); (1.48 g, 4.4 mmol)], 0.5 g water and 7.8 g of 1,4-dioxane. The mixture was shaken and heated to 60°C until a homogenous solution resulted. Upon cooling to room temperature, the solution was filtered through 0.45 μm (0.45 micron) PTFE membrane. To the filtered solution was added an acid catalyst delivered as 0.15 g of a 10 wt% solution of p-toluenesulfonic acid in 1,4-dioxane to yield the liquid containing reaction mixture. (Action B) The reaction mixture was applied to the reflective side of a metalized (TiZr) MYLAR™ substrate using a constant velocity draw down coater outfitted with a bird bar having a 0.38 mm (15 mil) gap. (Action C) The metalized MYLAR™ substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 130°C and left to heat for 40 min. These actions provided an SOF having a thickness ranging from 4-10 μm (4-10 microns) that could be delaminated from the substrate as a single free-standing film. The color of the SOF was green. Two-dimensional X-ray scattering data is provided in FIG. 15. As seen in FIG. 15, 2θ is 17.8 and d is 0.497 nm (4.97 angstroms), indicating that the SOF possesses molecular order having a periodicity of 0.5 nm.

### Illustrative EXAMPLE 56: Type 2 SOF

**[0239]** (Action A) The following were combined: the building block 4-hydroxybenzyl alcohol [segment = toluene; Fg = hydroxyl (-OH); (0.0272 g, 0.22 mmol)] and a second building block N4,N4,N4',N4'-tetrakis(4-(methoxymethyl)phenyl)biphenyl-4,4'-diamine [segment = N4,N4,N4',N4'-tetra-p-tolylbiphenyl-4,4'-diamine; Fg = methoxy ether (-OCH3); (0.0728 g, 0.11 mmol)], and 0.88 g of 1-methoxy-2-propanol and 0.01 g of a 10 wt % solution of silclean in 1-methoxy-2-propanol. The mixture was shaken and heated to 55°C until a homogenous solution was obtained. Upon cooling to rt, the solution was filtered through a 0.45 μm (0.45 micron) PTFE membrane. To the filtered solution was added an acid catalyst delivered as 0.01 g of a 10 wt % solution of p-toluenesulfonic acid in 1-methoxy-2-propanol to yield the liquid containing reaction mixture. (Action B) The reaction mixture was applied to the aluminum substrate using a constant velocity draw down coater outfitted with a bird bar having a 1.3 mm (5 mil) gap. (Action C) The aluminum substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 140 °C and left to heat for 40 min.

### Illustrative EXAMPLE 57: Type 2 SOF

**[0240]** (Action A) The following were combined: the building block 4-(hydroxymethyl)benzoic acid [segment = 4-methylbenzaldehyde; Fg = hydroxyl (-OH); (0.0314 g, 0.206 mmol)] and a second building block N4,N4,N4',N4'-tetrakis(4-(methoxymethyl)phenyl)biphenyl-4,4'-diamine [segment = N4,N4,N4',N4'-tetra-p-tolylbiphenyl-4,4'-diamine; Fg = methoxy ether (-OCH3); (0.0686 g, 0.103 mmol)], and 0.88 g of 1-methoxy-2-propanol and 0.01 g of a 10 wt % solution of silclean in 1-methoxy-2-propanol. The mixture was shaken and heated to 55 °C until a homogenous solution was obtained. Upon cooling to rt, the solution was filtered through a 0.45 μm (0.45 micron) PTFE membrane. To the filtered solution was added an acid catalyst delivered as 0.01 g of a 10 wt % solution of p-toluenesulfonic acid in 1-methoxy-2-propanol to yield the liquid containing reaction mixture. (Action B) The reaction mixture was applied to the aluminum substrate using a constant velocity draw down coater outfitted with a bird bar having a 1.3 mm (5 mil) gap. (Action C) The aluminum substrate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 140°C and left to heat for 40 min.

### Illustrative EXAMPLE 58: Type 1 SOF

**[0241]** (Action A) The following were combined: the building block 1,4 diaminobenzene [segment = benzene; Fg = amine (-NH<sub>2</sub>); (0.14 g, 1.3 mmol)] and a second building block 1,3,5-triformylbenzene [segment = benzene; Fg = aldehyde (-CHO); (0.144 g, 0.89 mmol)], and 2.8 g of NMP. The mixture was shaken until a homogenous solution resulted. Upon cooling to room temperature, the solution was filtered through a 0.45 μm (0.45 micron) PTFE membrane. To the filtered solution was added an acid catalyst delivered as 0.02 g of a 2.5 wt % solution of p-toluenesulfonic acid in NMP to yield the liquid containing reaction mixture. (Action B) The reaction mixture was applied quartz plate affixed to the rotating unit of a variable velocity spin coater rotating at 1000 RPM for 30 seconds. (Action C) The quartz plate supporting the wet layer was rapidly transferred to an actively vented oven preheated to 180°C and left to heat for 120 min. These actions provided a yellow film having a thickness of 400 nm that could be delaminated from the substrate upon immersion in water.

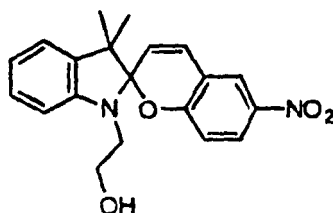
## Illustrative EXAMPLE5 59: Composite SOFs

**[0242]** Composite SOFs were prepared involving the process and building blocks described in illustrative EXAMPLE. In these cases the solvent used was dioxane. All SOFs were prepared on metalized Mylar substrates, by depositing a wet layer with a 0.5 mm (20 mil) bird bar and promoting a change of the wet layer at 130 °C for 40 min at total 30 % solids loading in the reaction mixture with 10 % of the solids loading being from the secondary component. Secondary components were introduced by including them in the reaction mixture before promoting the change of the wet layer to form the SOF. Six different composite SOFs were produced, each containing a different secondary component: composite SOF 1 including a hole transport molecule (N4,N4'-diphenyl-N4,N4'-di-m-tolyl-[1,1'-biphenyl]-4,4'-diamine), composite SOF 2 including a polymer (polystyrene), composite SOF 3 including nanoparticles (C60 Buckminster fullerene), composite SOF 4 including small organic molecules (biphenyl), composite SOF 5 including metal particles (copper micropowder), and composite SOF 6 including electron acceptors (quinone). Some secondary components were soluble in the reaction mixture; some were dispersed (not soluble) in the reaction mixture. The six composite SOFs produced were substantially defect free SOFs that included the composite materials incorporated into the SOFs. In some cases (e.g. copper micropowder composite SOF) the dispersion of the secondary component (dopant) was visually evident. The thicknesses of these SOFs ranged from 15 to 25  $\mu\text{m}$  (15-25 microns).

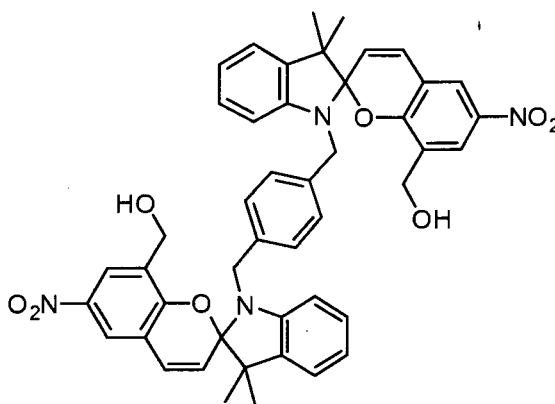
## Illustrative Example 60: Photochromic SOFs

**[0243]** (Action A) The following were combined: the SOF building block tris-(4-hydroxymethyl)triphenylamine [segment = triphenylamine; Fg = hydroxyl (-OH); 0.200 g]; the photochromic molecules 1-5 (see below) (0.02 g), and the catalyst p-toluene sulfonic acid (0.01 g); and, 1-methoxy-2-propanol (0.760 g). The mixture was mixed on a rolling wave rotator for 10 min and then heated at 55 °C for 5 min until a homogenous solution resulted. The solution was filtered through a 1  $\mu\text{m}$  (1 micron) PTFE membrane. (Action B) The reaction mixture was applied to a 0.08 mm (3 mil) Mylar substrate using a constant velocity draw down coater outfitted with a 1.3 mm (5 mil) gap bird bar. (Action C). The Mylar sheet supporting the wet layer was rapidly transferred to an actively vented oven preheated to 120°C and left to heat for 5 min. These actions provided a film having a thickness of 3 to 5  $\mu\text{m}$  (3-5 microns). The following photochromic molecules were incorporated in SOFs:

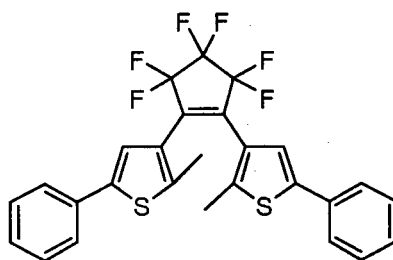
- (1) Spiropyran 1-OH (functional SOF capping building block)



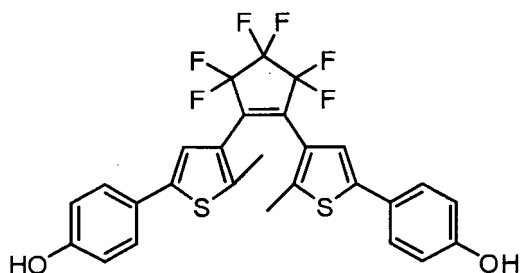
- (2) Bisspiropyran 2-OH (functional SOF building block)



- (3) Spirooxazine (composite SOF)  
 (4) DTE (composite SOF)



(5) DTE 2-OH (functional SOF building block)



[0244] All formulations formed substantially defect free films, however photochromic molecules (4) and (5) performed the best.

25

Photochromic Molecule	Color as synthesized	Color After Write at 365 nm for 6 s.	Erase?
SOF only	Light yellow	n/a	n/a
(4) DTE (composite SOF)	Light yellow	Dark purple	YES
(5) DTE 2-OH (functional SOF building block)	Light green	Dark purple	YES

30

[0245] UV-Visible spectra of photochromic SOFs with molecules (4) and (5) clearly demonstrated the coloration (presence of broad absorbance centered ~600 nm after UVA write) and erasure capability (loss of ~600 nm absorbance following visible light erase) of the photochromic SOFs. The photochromic responses were comparable to polymer matrix systems in terms of writing/erasing speed and contrast of image. This indicated the SOF did not affect the performance of these DTE type photochromic materials.

35

[0246] To test chemical/environmental/mechanical stability, the photochromic SOFs were placed in acetone for 15 minutes. Experimental observations are detailed in the table below. The photochromic SOF with molecule (5) fully preserved film integrity and photochromic behavior. The photochromic SOF with molecule (4) leached out the photochromic component and as a result lost photochromic activity.

40

Sample	Optical Density Before Acetone Stress Test	Optical Density After Acetone Stress Test	Performance After Acetone Stress Test
(4) DTE (composite SOF)	0.69	0.14	SOF largely maintains integrity (some swelling and softening was observed) Photochromic molecule leaches into acetone  SOF is no longer writable

45

50

55

(continued)

Sample	Optical Density Before Acetone Stress Test	Optical Density After Acetone Stress Test	Performance After Acetone Stress Test
(5) DTE 2-OH (functional SOF building block)	0.83	0.91	SOF maintains integrity No observed leaching of photochromic molecule  SOF has excellent writing properties

**[0247]** The photochromic SOF with molecule (5) was placed in acetone and sonicated for 5 minutes. This was an extreme test that polymer-based photochromic systems would not survive. After removal from the solvent, the photochromic SOF with molecule (5) essentially maintained the SOF integrity and wrote at about the same level when exposed to a UV LED device, i.e. photochromic activity was preserved. The photochromic SOF derived from the photochromic molecule (5), which chemically bonds to the SOF structure, did not leach from the SOF and could withstand harsh chemical (acetone solvent) and mechanical (ultrasonication) stresses.

## Claims

1. A process for preparing a structured organic film (SOF) comprising a plurality of segments which are linked together by a plurality of linkers forming a covalent organic framework (COF), said process comprising:
  - (a) preparing a liquid-containing reaction mixture comprising:
    - a plurality of molecular building blocks each comprising a segment and a number of functional groups;
    - (b) forming a pre-SOF in the reaction mixture by partially reacting the molecular building blocks and/or activating the functional groups;
    - (c) depositing the reaction mixture as a wet film; and
    - (d) promoting a change of the wet film to form a dry film comprising said SOF **characterized in that** the plurality of linkers comprises at least a first and a second linker that are different in structure, and the plurality of segments either comprises at least a first and a second segment that are different in structure, wherein the first segment, when not at an edge of the SOF, is connected by linkers to at least three other segments, wherein at least one connection is via the first linker and at least one connection is via the second linker, or consists of segments having an identical structure, wherein the segments that are not at edges of the SOF are connected by linkers to at least three other segments, wherein at least one connection is via the first linker and at least one connection is via the second linker.
2. The process of claim 1, wherein the reaction mixture further comprises a catalyst.
3. The process of claim 2, wherein the catalyst is selected from the group consisting of Brønsted acids, Lewis acids, Brønsted bases, Lewis bases, free radical initiators, and transition metal complexes.
4. The process of claim 2, wherein the weight of the catalyst divided by the total weight of the molecular building blocks is from 0.0001 to 0.25.
5. The process of claim 2, wherein the catalyst is not present in the SOF.
6. The process of claim 2, wherein the catalyst is present in the SOF.
7. The process claim 1, wherein forming the pre-SOF comprises heating the reaction mixture at a temperature that is lower than the boiling point of the reaction mixture.
8. The process of claim 1, wherein forming the pre-SOF comprises exposing the reaction mixture to UV irradiation.
9. The process of claim 1, wherein the forming the pre-SOF lasts 10 seconds to 48 hours.

10. The process of claim 1, wherein the SOF is a substantially defect-free film.
11. The process of claim 1, wherein the liquid-containing reaction mixture further comprises a secondary component, and the SOF incorporates the secondary component.
12. The process of claim 1, wherein the liquid-containing reaction mixture further comprises a first solvent and a second solvent.
13. The process of claim 1, wherein the SOF includes an added functionality, said process comprising preparing the liquid-containing reaction mixture comprising the plurality of molecular building blocks each comprising a segment and a number of functional groups, wherein the molecular building blocks are selected to provide the added functionality in the SOF, and promoting the change of the wet film to form the dry film comprising said SOF, wherein said SOF possesses said added functionality.
14. The process of claims 1, 11, 12, or 13, wherein forming the pre-SOF comprises heating the reaction mixture in the presence of a catalyst.
15. The process of claims 11, 12, or 13, wherein the SOF is a substantially defect-free film.

### Patentansprüche

1. Verfahren zum Herstellen eines strukturierten organischen Films (SOF) umfassend eine Mehrzahl von Segmenten, welche durch eine Mehrzahl von Linkern miteinander verbunden sind unter Bildung eines kovalenten organischen Gerüsts (covalent organic framework, COF), wobei das Verfahren umfasst:
- (a) das Herstellen einer Flüssigkeit enthaltenden Reaktionsmischung umfassend:
- eine Mehrzahl von molekularen Bausteinen, die jeweils ein Segment und eine Anzahl von funktionellen Gruppen umfassen;
- (b) das Bilden eines Prä-SOF in der Reaktionsmischung durch teilweises Umsetzen der molekularen Bausteine und/oder Aktivieren der funktionellen Gruppen;
- (c) das Abscheiden der Reaktionsmischung als ein Nassfilm; und
- (d) das Fördern einer Umwandlung des Nassfilms, um einen Trockenfilm zu bilden, der den SOF umfasst, **dadurch gekennzeichnet, dass** die Mehrzahl von Linkern wenigstens einen ersten und einen zweiten Linker umfasst, welche eine unterschiedliche Struktur aufweisen, und die Mehrzahl von Segmenten entweder wenigstens ein erstes und ein zweites Segment umfasst, welche eine unterschiedliche Struktur aufweisen, wobei das erste Segment, wenn es sich nicht an einem Rand des SOF befindet, durch Linker mit wenigstens drei anderen Segmenten verbunden ist, wobei wenigstens eine Verbindung mittels des ersten Linkers erfolgt und wenigstens eine Verbindung mittels des zweiten Linkers erfolgt, oder aus Segmenten mit einer identischen Struktur besteht, wobei die Segmente, welche sich nicht an Rändern des SOF befinden, durch Linker mit wenigstens drei anderen Segmenten verbunden sind, wobei wenigstens eine Verbindung mittels des ersten Linkers erfolgt und wenigstens eine Verbindung mittels des zweiten Linkers erfolgt.
2. Verfahren nach Anspruch 1, wobei die Reaktionsmischung außerdem einen Katalysator umfasst.
3. Verfahren nach Anspruch 2, wobei der Katalysator ausgewählt ist aus der Gruppe bestehend aus Brönsted-Säuren, Lewis-Säuren, Brönsted-Basen, Lewis-Basen, Radikalstartern und Übergangsmetall-Komplexen.
4. Verfahren nach Anspruch 2, wobei das Gewicht des Katalysators dividiert durch das Gesamtgewicht der molekularen Bausteine 0,0001 bis 0,25 beträgt.
5. Verfahren nach Anspruch 2, wobei der Katalysator in dem SOF nicht vorhanden ist.
6. Verfahren nach Anspruch 2, wobei der Katalysator in dem SOF vorhanden ist.
7. Verfahren nach Anspruch 1, wobei das Bilden des Prä-SOFs das Erwärmen der Reaktionsmischung auf eine Tem-

peratur umfasst, welche niedriger ist als der Siedepunkt der Reaktionsmischung.

8. Verfahren nach Anspruch 1, wobei das Bilden des Prä-SOFs das Aussetzen der Reaktionsmischung einer UV-Strahlung umfasst.

9. Verfahren nach Anspruch 1, wobei das Bilden des Prä-SOFs 10 Sekunden bis 48 Stunden dauert.

10. Verfahren nach Anspruch 1, wobei der SOF ein im Wesentlichen defektfreier Film ist.

11. Verfahren nach Anspruch 1, wobei die Flüssigkeit enthaltende Reaktionsmischung außerdem eine sekundäre Komponente umfasst und der SOF die sekundäre Komponente inkorporiert.

12. Verfahren nach Anspruch 1, wobei die Flüssigkeit enthaltende Reaktionsmischung außerdem ein erstes Lösungsmittel und ein zweites Lösungsmittel umfasst.

13. Verfahren nach Anspruch 1, wobei der SOF eine zusätzliche Funktionalität einschließt, wobei das Verfahren das Herstellen der Flüssigkeit enthaltenden Reaktionsmischung, die die Mehrzahl von molekularen Bausteinen umfasst, die jeweils ein Segment und eine Anzahl von funktionellen Gruppen umfassen, wobei die molekularen Bausteine ausgewählt sind, um die zusätzliche Funktionalität in dem SOF bereitzustellen, und das Fördern der Umwandlung des Nassfilms umfasst, um den Trockenfilm, der den SOF umfasst, zu bilden, wobei der SOF die zusätzliche Funktionalität besitzt.

14. Verfahren nach den Ansprüchen 1, 11, 12 oder 13, wobei das Bilden des Prä-SOFs das Erwärmen der Reaktionsmischung in Gegenwart eines Katalysators umfasst.

15. Verfahren nach den Ansprüchen 11, 12 oder 13, wobei der SOF ein im Wesentlichen defektfreier Film ist.

## Revendications

1. Procédé de préparation d'un film organique structuré (SOF) comprenant une pluralité de segments qui sont liés ensemble par une pluralité de lieux formant une charpente organique covalente (COF), ledit procédé comprenant :

(a) la préparation d'un mélange réactionnel contenant un liquide comprenant :

une pluralité d'éléments structuraux moléculaires comprenant chacun un segment et un certain nombre de groupes fonctionnels ;

(b) la formation d'un pré-SOF dans le mélange réactionnel par réaction partielle des éléments structuraux moléculaires et/ou activation des groupes fonctionnels ;

(c) le dépôt du mélange réactionnel sous la forme d'un film humide ; et

(d) l'induction d'un changement dans le film humide pour former un film sec comprenant ledit SOF,

**caractérisé en ce que** la pluralité de lieux comprend au moins des premier et second lieux qui ont des structures différentes, et **en ce que** la pluralité de segments soit comprend des premier et second segments qui ont des structures différentes, dans laquelle le premier segment, quand il n'est pas à un bord du SOF, est lié par des lieux à au moins trois autres segments, dans laquelle au moins une liaison s'opère par l'intermédiaire du premier lieu et au moins une liaison s'opère par l'intermédiaire du second lieu, soit est constituée de segments ayant une structure identique, dans laquelle les segments qui ne sont pas aux bords du SOF, sont liés par des lieux à au moins trois autres segments, dans laquelle au moins une liaison s'opère par l'intermédiaire du premier lieu et au moins une liaison s'opère par l'intermédiaire du second lieu.

2. Procédé selon la revendication 1, dans lequel le mélange réactionnel comprend en outre un catalyseur.

3. Procédé selon la revendication 2, dans lequel le catalyseur est choisi dans le groupe constitué par les acides de Brønsted, les acides de Lewis, les bases de Brønsted, les bases de Lewis, les initiateurs de radicaux libres et les complexes de métaux de transition.

## EP 2 403 657 B1

4. Procédé selon la revendication 2, dans lequel le poids du catalyseur divisé par le poids total des éléments structuraux moléculaires est de 0,0001 à 0,25.
- 5
5. Procédé selon la revendication 2, dans lequel le catalyseur n'est pas présent dans le SOF.
6. Procédé selon la revendication 2, dans lequel le catalyseur est présent dans le SOF.
7. Procédé selon la revendication 1, dans lequel la formation du pré-SOF comprend le chauffage du mélange réactionnel à une température qui est inférieure au point d'ébullition du mélange réactionnel.
- 10
8. Procédé selon la revendication 1, dans lequel la formation du pré-SOF comprend l'exposition du mélange réactionnel à un rayonnement UV.
9. Procédé selon la revendication 1, dans lequel la formation du pré-SOF dure de 10 secondes à 48 heures.
- 15
10. Procédé selon la revendication 1, dans lequel le SOF est un film sensiblement exempt de défauts.
11. Procédé selon la revendication 1, dans lequel le mélange réactionnel contenant un liquide comprend en outre un composant secondaire, et le SOF contient le composant secondaire.
- 20
12. Procédé selon la revendication 1, dans lequel le mélange réactionnel contenant un liquide comprend en outre un premier solvant et un second solvant.
13. Procédé selon la revendication 1, dans lequel le SOF contient une fonctionnalité ajoutée, ledit procédé comprenant la préparation du mélange réactionnel contenant un liquide comprenant la pluralité d'éléments structuraux moléculaires chacun comprenant un segment et un certain nombre de groupes fonctionnels, dans lequel les éléments structuraux moléculaires sont choisis pour introduire la fonctionnalité ajoutée dans le SOF, et l'induction du changement dans le film humide pour former le film sec comprenant ledit SOF, dans lequel ledit SOF possède ladite fonctionnalité ajoutée.
- 25
- 30
14. Procédé selon les revendications 1, 11, 12, ou 13, dans lequel la formation du pré-SOF comprend le chauffage du mélange réactionnel en présence d'un catalyseur.
- 35
15. Procédé selon les revendications 11, 12, ou 13, dans lequel le SOF est un film sensiblement exempt de défauts.
- 40
- 45
- 50
- 55

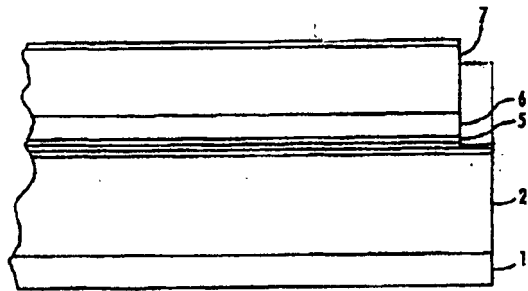


FIG. 1

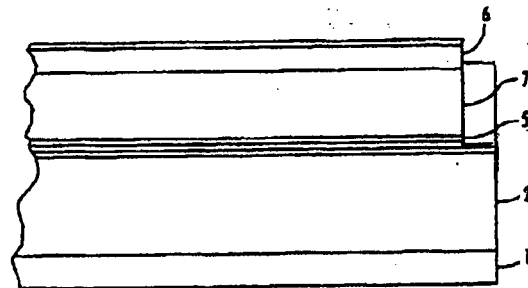


FIG. 2



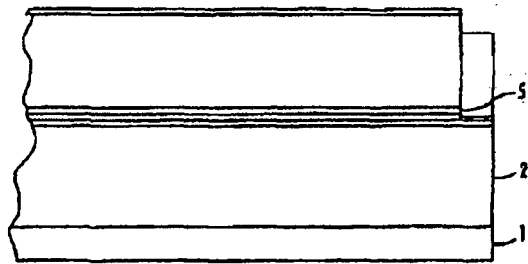


FIG. 3

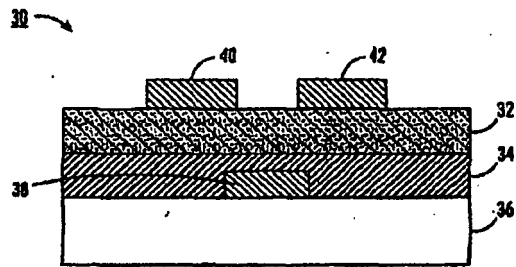


FIG. 4

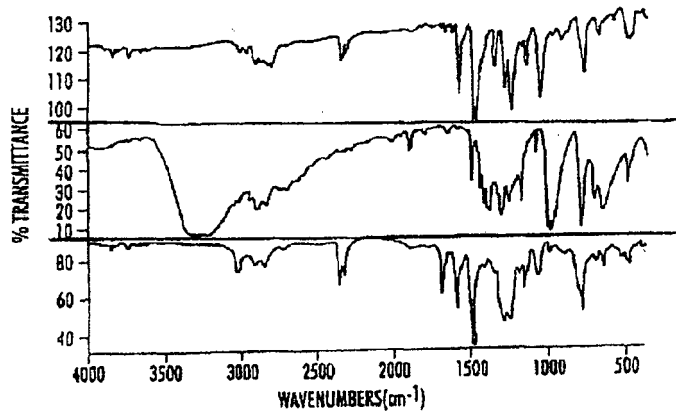


FIG. 5

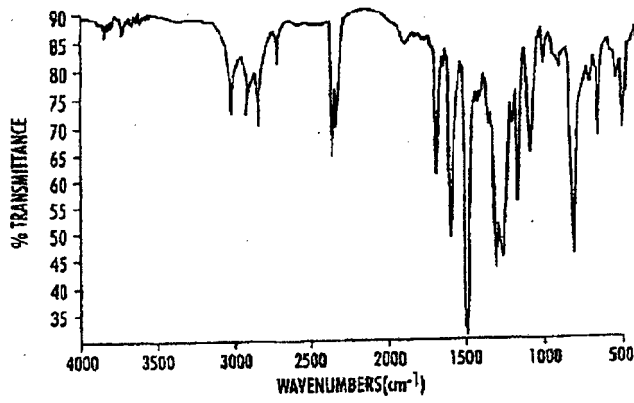


FIG. 6

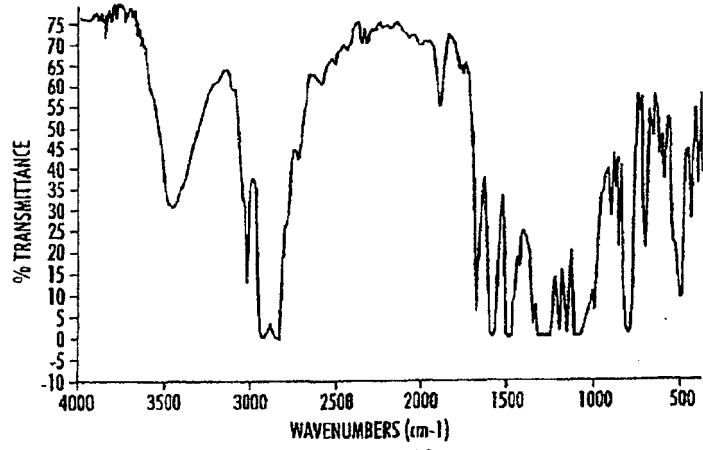


FIG. 7

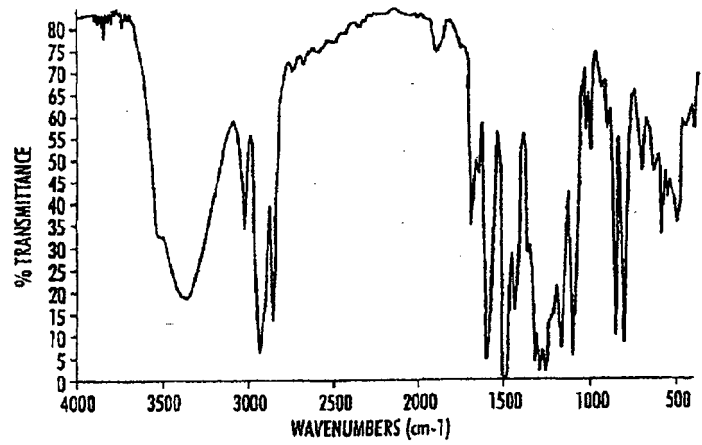
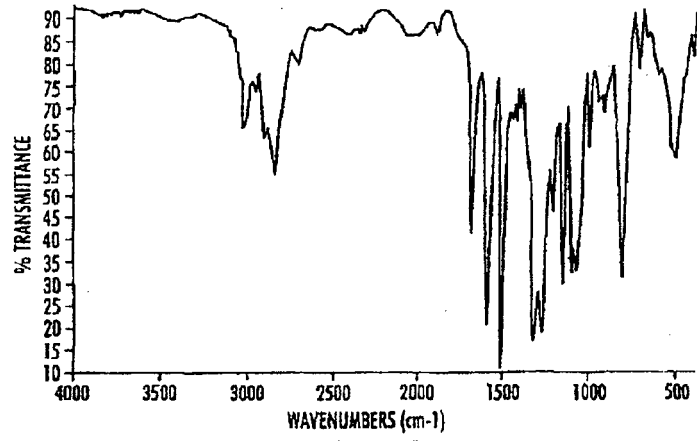
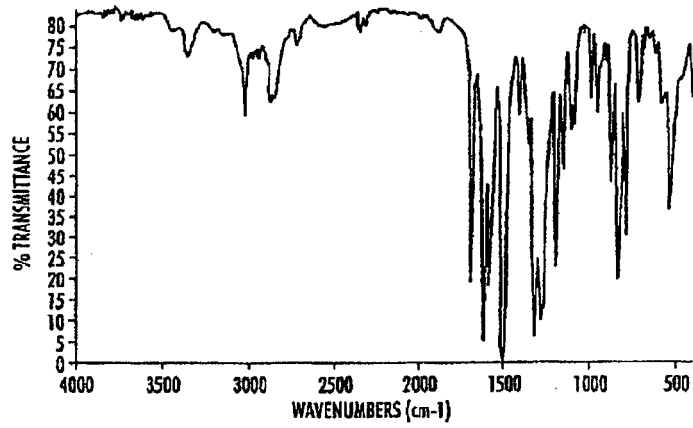


FIG. 8



**FIG. 9**



**FIG. 10**

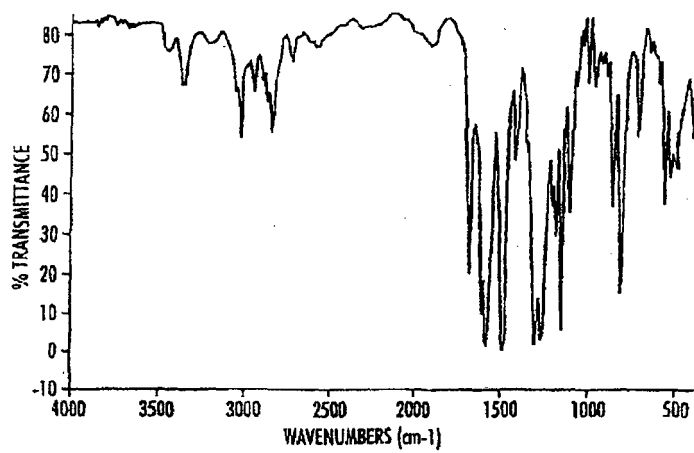


FIG. 11

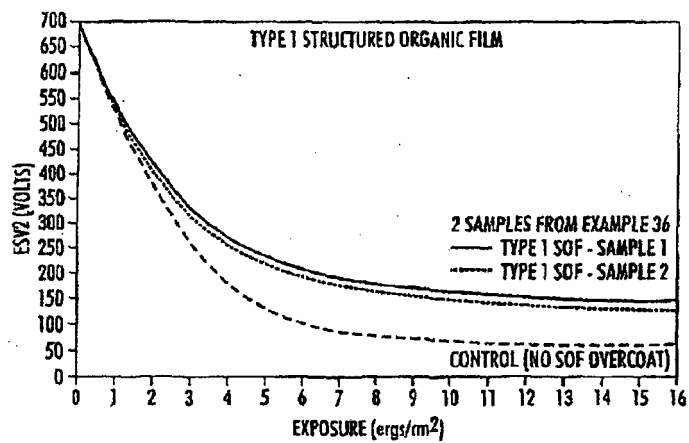


FIG. 12

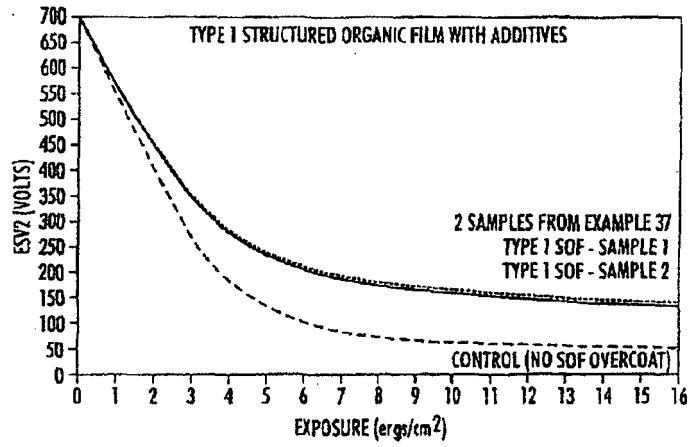


FIG. 13

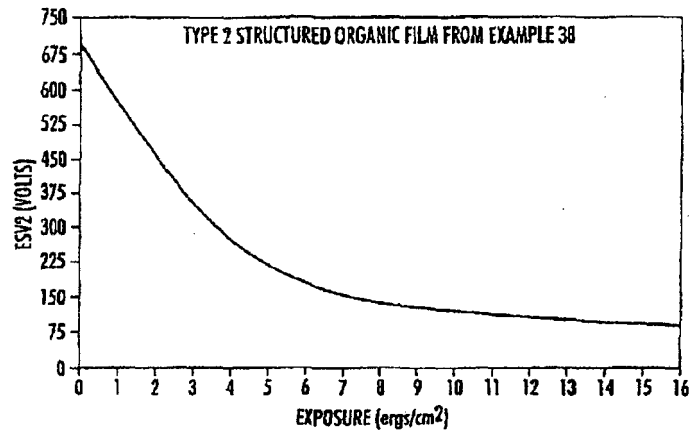


FIG. 14

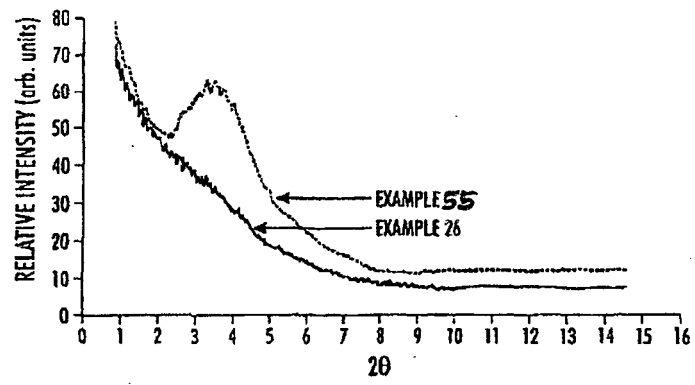


FIG. 15

**REFERENCES CITED IN THE DESCRIPTION**

*This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.*

**Patent documents cited in the description**

- US 7582798 B [0005]
- WO 2007098263 A [0006]
- US 2006097393 A1 [0007]
- US 5231162 A [0008]
- US 7202002 B2, Tokarski [0084]
- US 7416824 B2, Kondoh [0084]
- US 5165909 A [0127]
- US 5456897 A [0127]
- US 5707916 A [0127]
- US 5877110 A [0127]
- US 5110693 A [0127]
- US 5500200 A [0127]
- US 5569635 A [0127]
- US 4921769 A [0131]
- US 4265990 A [0131]
- US 4306008 A [0131]
- US 4304829 A [0131]
- US 4233384 A [0131]
- US 4115116 A [0131]
- US 4299897 A [0131]
- US 4081274 A [0131]
- US 5139910 A [0131]
- US 4921773 A [0131]
- US 4464450 A [0131]
- US 5455136 A [0149]

**Non-patent literature cited in the description**

- **R.J. JENG et al.** how Cross Second-Order Moulinear Optical Polymers Based on All Organic Sol-Gel Materials. *Journal of Applied Polymer Science*, 10 January 1995, vol. 55 (2), 209-214 [0009]