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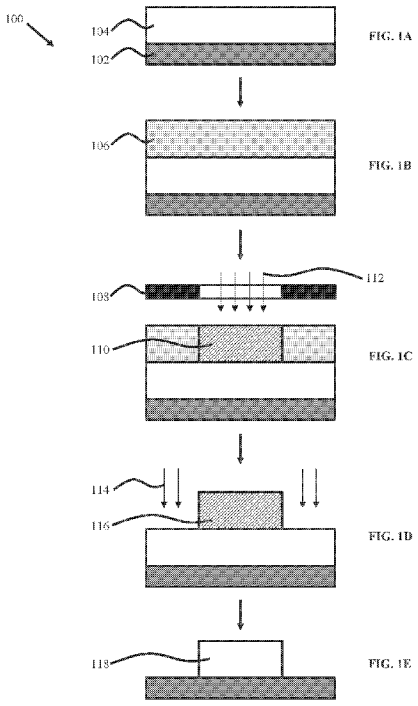
(54) **Title:** UV PATTERNABLE POLYMER BLENDS FOR ORGANIC THIN-FILM TRANSISTORS



(57) **Abstract:** A polymer blend includes at least one organic semiconductor (OSC) polymer, at least one crosslinker, and at least one photoinitiator, such that the at least one OSC polymer is a diketopyrrolopyrrole-fused thiophene polymeric material, the fused thiophene being beta-substituted, and such that the crosslinker includes at least one of: acrylates, epoxides, oxetanes, alkenes, alkynes, azides, thiols, allyloxysilanes, phenols, anhydrides, amines, cyanate esters, isocyanate esters, silyl hydrides, cinnamates, coumarins, fluorosulfates, silyl ethers, or a combination thereof.

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UV PATTERNABLE POLYMER BLENDS FOR ORGANIC THIN-FILM TRANSISTORS

BACKGROUND

[0001] This application claims the benefit of priority under 35 U.S.C. § 119 of Chinese Patent Application Serial No. 201811189790.7, filed on October 12, 2018, the content of which is relied upon and incorporated herein by reference in its entirety.

1. Field

[0002] The disclosure relates to UV patternable organic semiconductor/crosslinker polymer blends as semiconducting layers for organic thin-film transistors (OTFTs).

2. Technical Background

[0003] Organic thin-film transistors (OTFTs) have garnered extensive attention as alternatives to conventional silicon-based technologies, which require high temperature and high vacuum deposition processes, as well as complex photolithographic patterning methods. Semiconducting (i.e., organic semiconductor, OSC) layers are one important component of OTFTs which can effectively influence the performance of devices.

[0004] Traditional technologies in the manufacture of inorganic TFT device arrays often rely on photolithography as the patterning process. However, photolithography usually involves harsh oxygen (O_2) plasma during pattern transfer or photoresist removal and aggressive developing solvents which may severely damage the OSC layer and lead to significant deterioration of device performance.

[0005] This disclosure presents improved UV patternable organic semiconductor/crosslinker polymer blends and use thereof for OSC layers of organic thin-film transistors.

SUMMARY

[0006] In some embodiments, a polymer blend comprises: at least one organic semiconductor (OSC) polymer and at least one crosslinker, wherein the at least one OSC polymer is a diketopyrrolopyrrole-fused thiophene polymeric material, wherein the fused thiophene is beta-substituted, and wherein the crosslinker includes at least one of: acrylates, epoxides, oxetanes, alkenes, alkynes, azides, thiols, allyloxysilanes, phenols, anhydrides, amines, cyanate esters,

isocyanate esters, silyl hydrides, cinnamates, coumarins, fluorosulfates, silyl ethers, or a combination thereof.

[0007] In one aspect, which is combinable with any of the other aspects or embodiments, the at least one OSC polymer is present in a range of 1 wt.% to 99 wt.%; and the at least one crosslinker is present in a range of 1 wt.% to 99 wt.%.

[0008] In one aspect, which is combinable with any of the other aspects or embodiments, the at least one OSC polymer is present in a range of 50 wt.% to 80 wt.%; and the at least one crosslinker is present in a range of 25 wt.% to 55 wt.%.

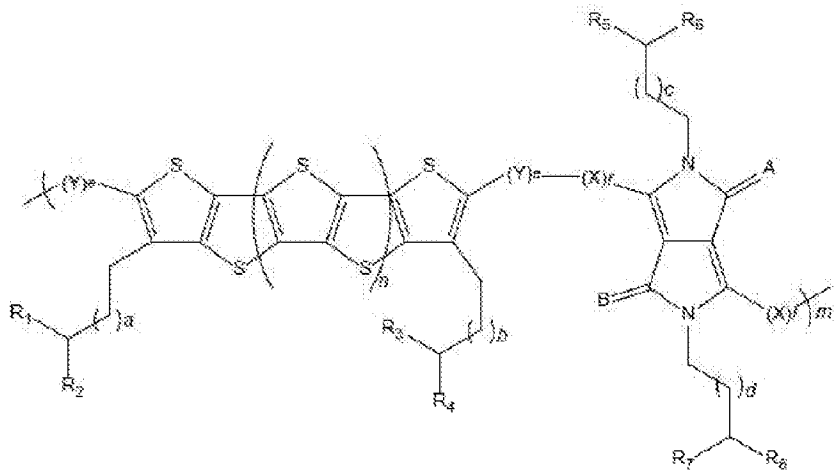
[0009] In one aspect, which is combinable with any of the other aspects or embodiments, the at least one crosslinker comprises a first crosslinker and a second crosslinker, the first crosslinker being present in a range of 30 wt.% to 50 wt.% and the second crosslinker being present in a range of 0.5 wt.% to 25 wt.%.

[00010] In one aspect, which is combinable with any of the other aspects or embodiments, the polymer blend further comprises: at least one photoinitiator, wherein the at least one photoinitiator is present in a range of 0.1 wt.% to 10 wt.%.

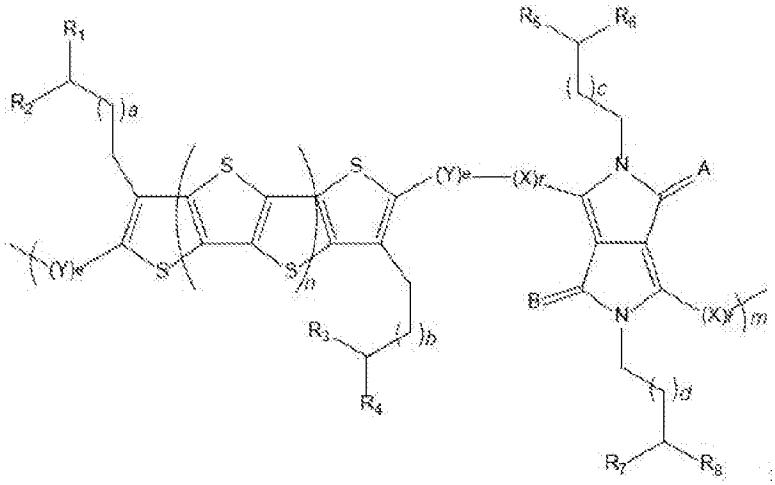
[00011] In one aspect, which is combinable with any of the other aspects or embodiments, the at least one photoinitiator is present in a range of 0.1 wt.% to 5.0 wt.%.

[00012] In one aspect, which is combinable with any of the other aspects or embodiments, the polymer blend further comprises: at least one of antioxidants, lubricants, compatibilizers, leveling agents, or nucleating agents present in a range of 0.05 wt.% to 5 wt.%.

[00013] In one aspect, which is combinable with any of the other aspects or embodiments, the at least one OSC polymer comprises the repeat unit of Formula 1 or Formula 2, or a salt, isomer, or analog thereof:



Formula 1

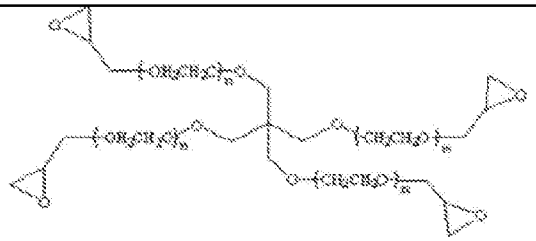


Formula 2

wherein in Formula 1 and Formula 2: m is an integer greater than or equal to one; n is 0, 1, or 2; R_1, R_2, R_3, R_4, R_5, R_6, R_7, and R_8, may be, independently, hydrogen, substituted or unsubstituted C_4 or greater alkyl, substituted or unsubstituted C_4 or greater alkenyl, substituted or unsubstituted C_4 or greater alkynyl, or C_5 or greater cycloalkyl; a, b, c, and d are independently, integers greater than or equal to 3; e and f are integers greater than or equal to zero; X and Y are, independently a covalent bond, an optionally substituted aryl group, an optionally substituted heteroaryl, an optionally substituted fused aryl or fused heteroaryl group, an alkyne or an alkene; and A and B may be, independently, either S or O, with the provisos that: (i) at least one of R_1 or R_2; one of R_3 or R_4; one of R_5 or R_6; and one of R_7 or R_8 is a substituted or unsubstituted alkyl,

substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, or cycloalkyl; (ii) if any of R_1, R_2, R_3, or R_4 is hydrogen, then none of R_5, R_6, R_7, or R_8 are hydrogen; (iii) if any of R_5, R_6, R_7, or R_8 is hydrogen, then none of R_1, R_2, R_3, or R_4 are hydrogen; (iv) e and f cannot both be 0; (v) if either e or f is 0, then c and d, independently, are integers greater than or equal to 5; and (vi) the polymer having a molecular weight, wherein the molecular weight of the polymer is greater than 10,000.

[00014] In one aspect, which is combinable with any of the other aspects or embodiments, the at least one crosslinker comprises at least one of: (A) a polymer selected from:



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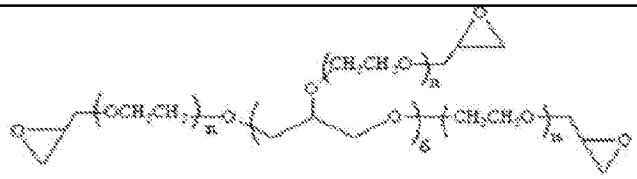

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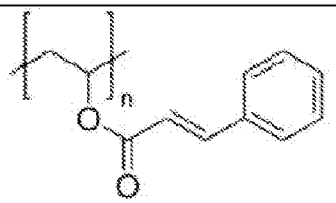
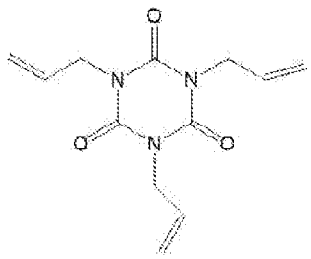


C3

wherein n is an integer greater than or equal to two, or (B) a small-molecule selected from:



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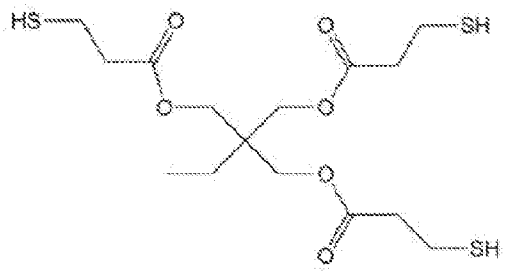

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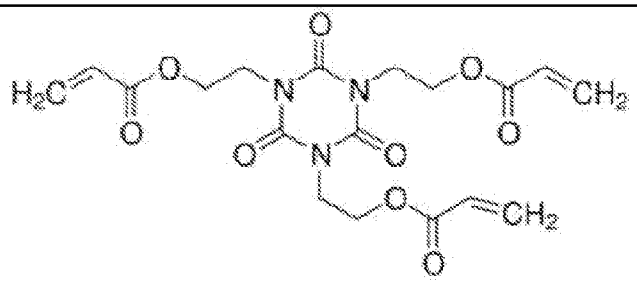
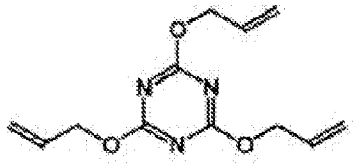
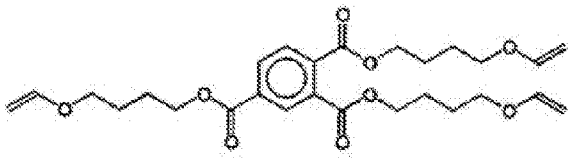
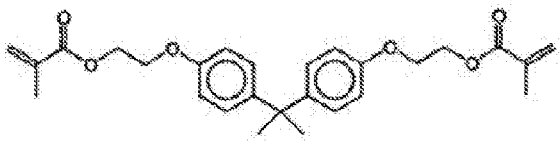
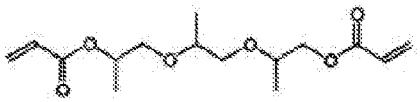
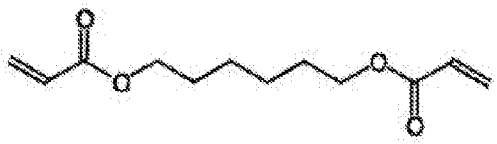
 C6	 C7
 C8	 C9
 C10	 C11
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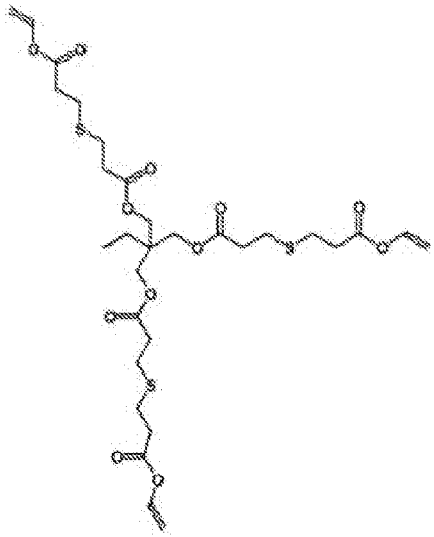
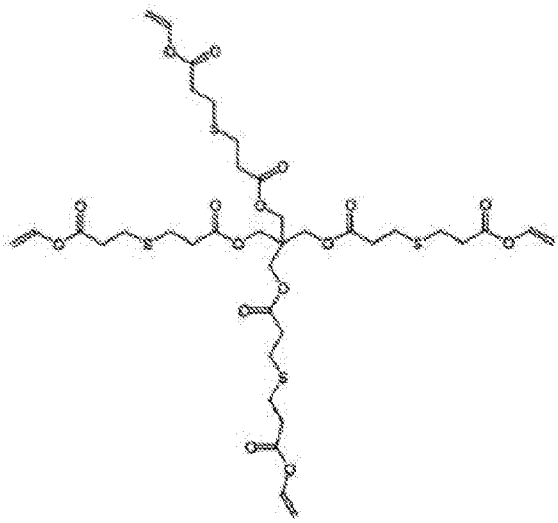
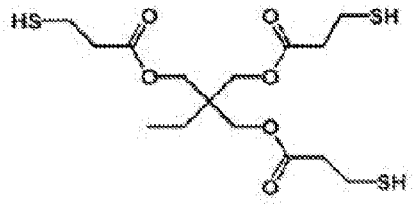
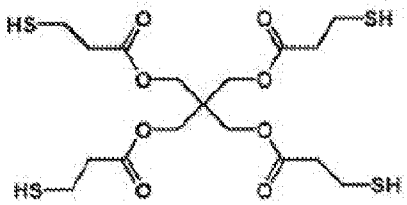
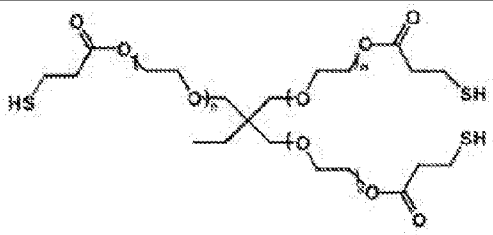
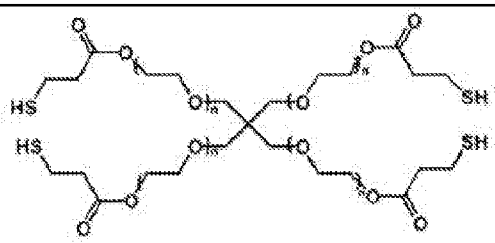
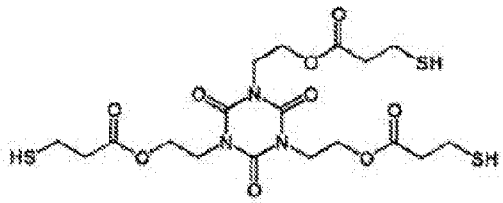
 C13	 C14
 C15	 C16
 C17	 C18



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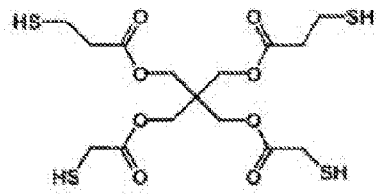

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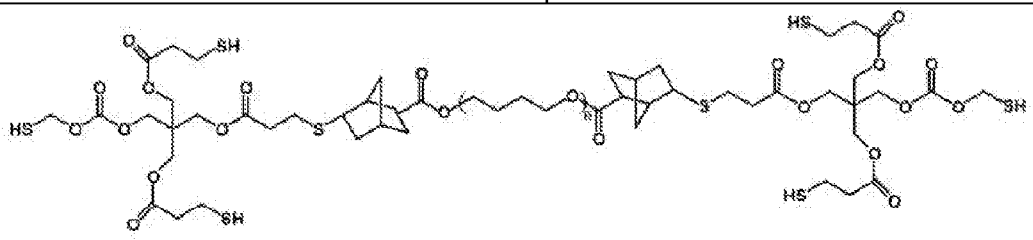

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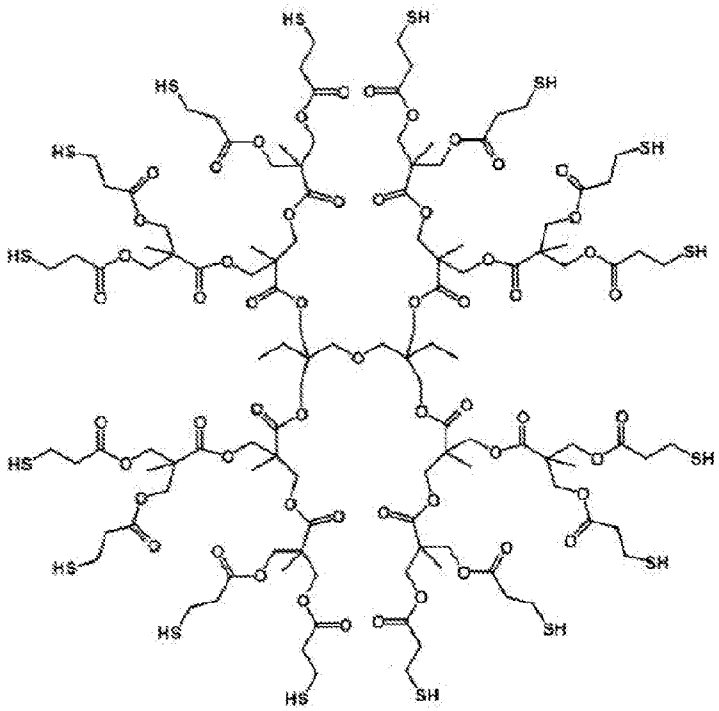

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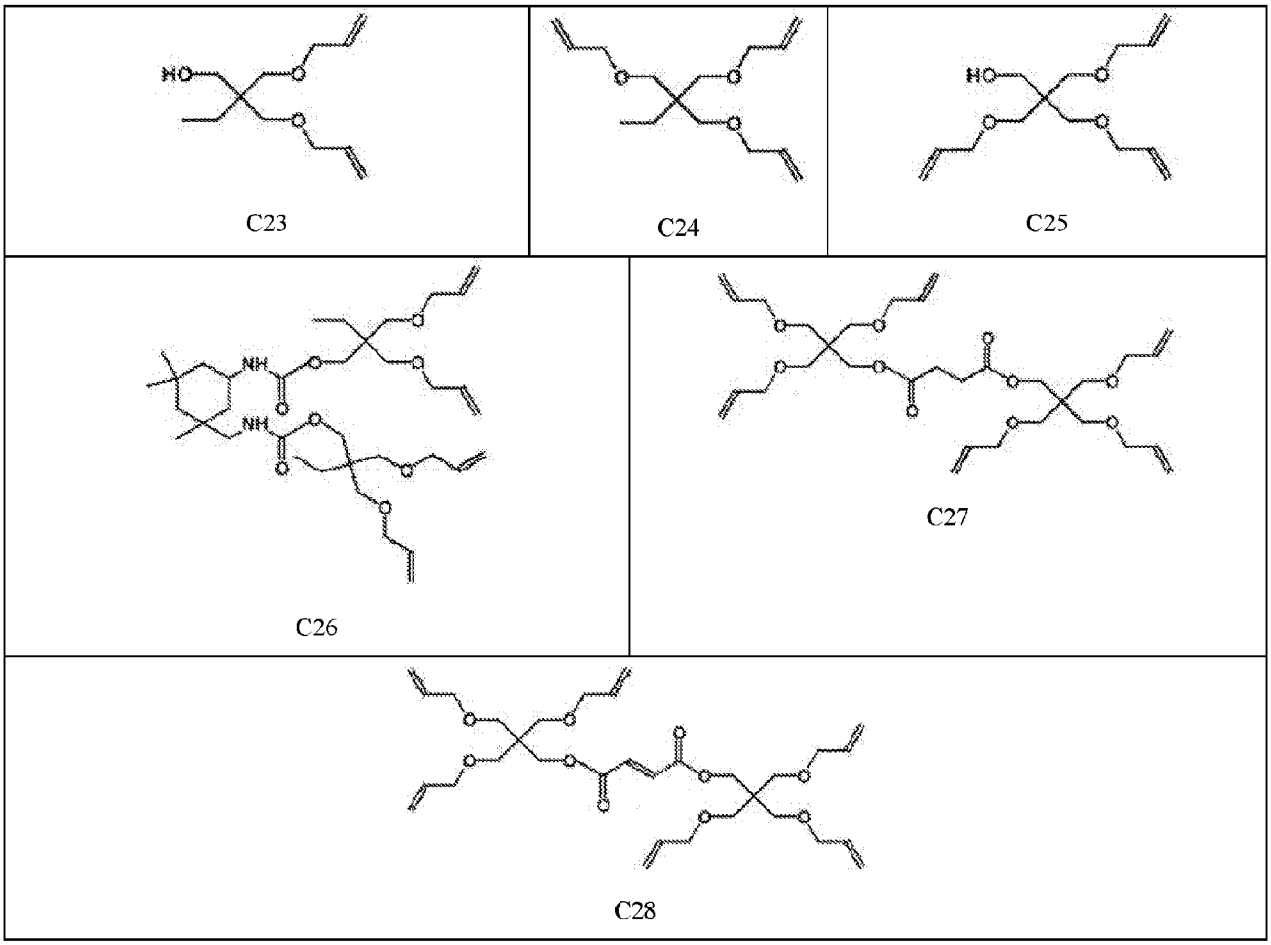
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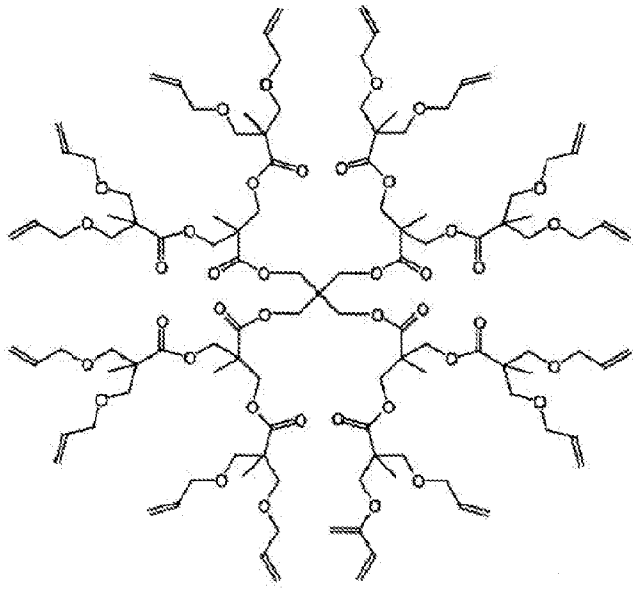

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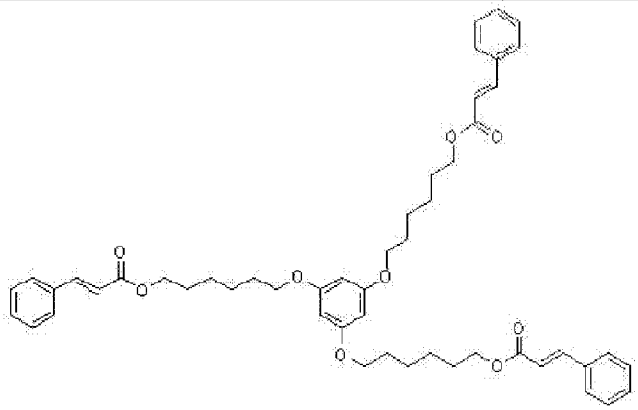

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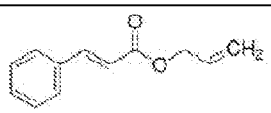

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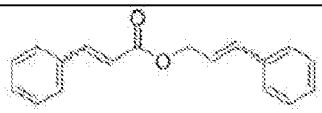

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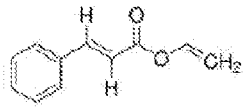
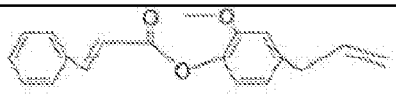
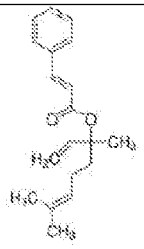
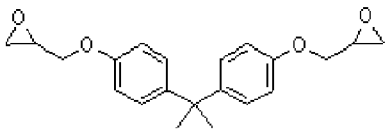
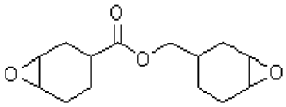
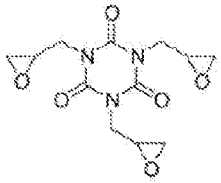
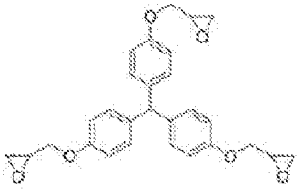
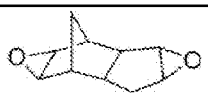
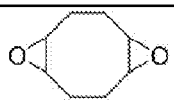
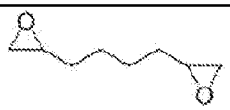
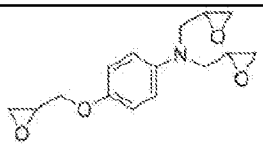
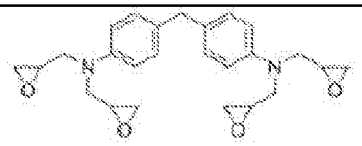
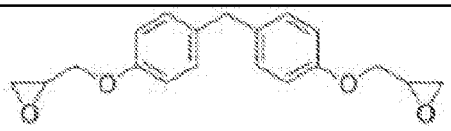
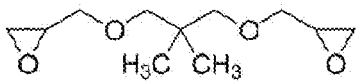
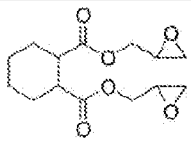
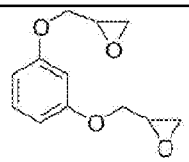
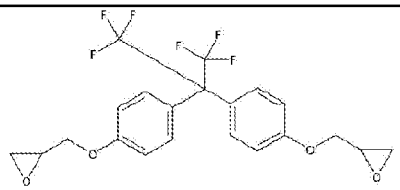
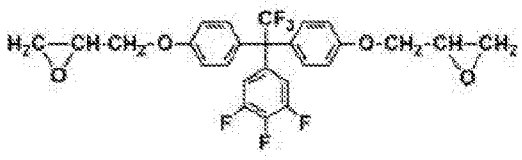
 C33	 C34
 C35	 C36
 C37	 C38
 C39	 C40
 C41	 C42
 C43	 C44

 C45	 C46
 C47	 C48
 C49	 C50
 C51	

or, (C) a combination thereof.

[00015] In one aspect, which is combinable with any of the other aspects or embodiments, the at least one photoinitiator comprises at least one free radical photoinitiator.

[00016] In one aspect, which is combinable with any of the other aspects or embodiments, the at least one photoinitiator comprises at least one cationic photoinitiator.

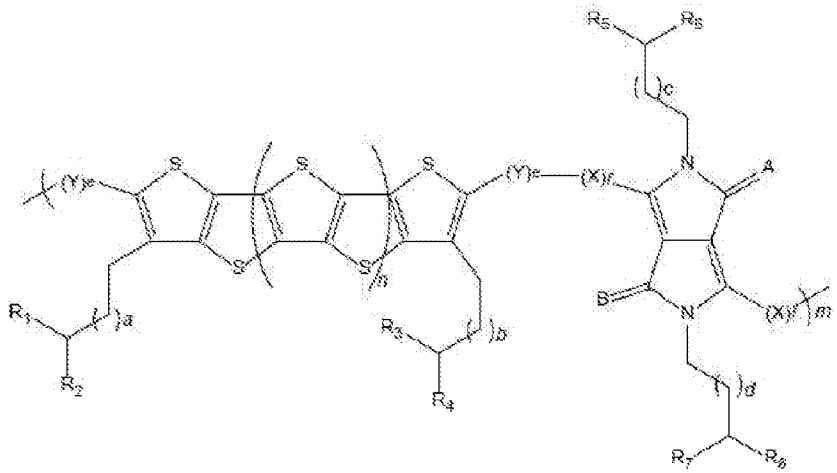
[00017] In one aspect, which is combinable with any of the other aspects or embodiments, the at least one photoinitiator comprises: 1-hydroxy-cyclohexyl-phenyl-ketone (184); 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1 (369); diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO); 2-isopropyl thioxanthone (ITX); 1-[4-(phenylthio) phenyl]-1,2-octanedione 2-(O-benzoyloxime) (HRCURE-OXE01); 2,2-dimethoxy-1,2-

diphenylethan-1-one (BDK); benzoyl peroxide (BPO); hydroxyacetophenone (HAP); 2-hydroxy-2-methylprophenone (1173); 2-methyl-4'-(methylthio)-2-morpholinopropiophenone (907); 2-benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone (IHT-PI 910); Ethyl-4-(dimethylamino)benzoate (EDB); methyl o-benzoyl benzoate (OMBB); bis-(2,6 dimethoxy-benzoyl)-phenyl phosphine oxide (BAPO); 4-benzoyl-4' methyldiphenylsulfide (BMS); benzophenone (BP); 1-chloro-4-propoxy thiozanthone (CPTX); chlorothioxanthone (CTX); 2,2-diethoxyacetophenone (DEAP); diethyl thioxanthone (DETX); 2-dimethyl aminoethyl benzonate (DMB); 2,2-dimethoxy-2-phenyl acetophenone (DMPA); 2-ethyl anthraquinone (2-EA); ethyl-para-N,N-dimethyl-dimethylamino lenzoate (EDAB); 2-ethyl hexyl-dimethylaminolenzoate (EHA); 4,4-bis-(diethylamino)-benzophenone (EMK); methyl benzophenone (MBF); 4-methyl benzophenone (MBP); Michler's ketone (MK); 2-methyl-1-[4(methylthiol)phenyl]-2-morpholino propanone (1) (MMMP); 4-phenylbenzophenone (PBZ); 2,4,6-trimethyl-benzoly-ethoxyl phenyl phosphine oxide (TEPO); bis(4-tert-butylphenyl) iodonium perfluoro-1-butanesulfonate; bis(4-tert-butylphenyl) iodonium p-toluenesulfonate; bis(4-tert-butylphenyl) iodonium triflate; boc-methoxyphenyldiphenylsulfonium triflate; (4-tert-Butylphenyl) diphenylsulfonium triflate; diphenyliodonium hexafluorophosphate; diphenyliodonium nitrate; diphenyliodonium p-toluenesulfonate; diphenyliodonium triflate; (4-fluorophenyl) diphenylsulfonium triflate; N-hydroxynaphthalimide triflate; N-hydroxy-5-norbornene-2,3-dicarboximide perfluoro-1-butanesulfonate; (4-iodophenyl) diphenylsulfonium triflate; (4-methoxyphenyl) diphenylsulfonium triflate; 2-(4-Methoxystyryl)-4,6-bis (trichloromethyl)-1,3,5-triazine; (4-methylthiophenyl) methyl phenyl sulfonium triflate; 1-naphthyl diphenylsulfonium triflate; (4-phenoxyphenyl) diphenylsulfonium triflate; (4-phenylthiophenyl) diphenylsulfonium triflate; triarylsulfonium hexafluoroantimonate salts, mixed 50 wt.% in propylene carbonate; triarylsulfonium hexafluorophosphate salts, mixed 50 wt.% in propylene carbonate; triphenylsulfonium perfluoro-1-butanesufonate; triphenylsulfonium triflate; tris(4-tert-butylphenyl) sulfonium perfluoro-1-butanesulfonate; tris(4-tert-butylphenyl)sulfonium triflate; aryl diazo salts; diaryliodonium salts; triaryl sulfonium salts; aryl ferrocenium salts; or combinations thereof.

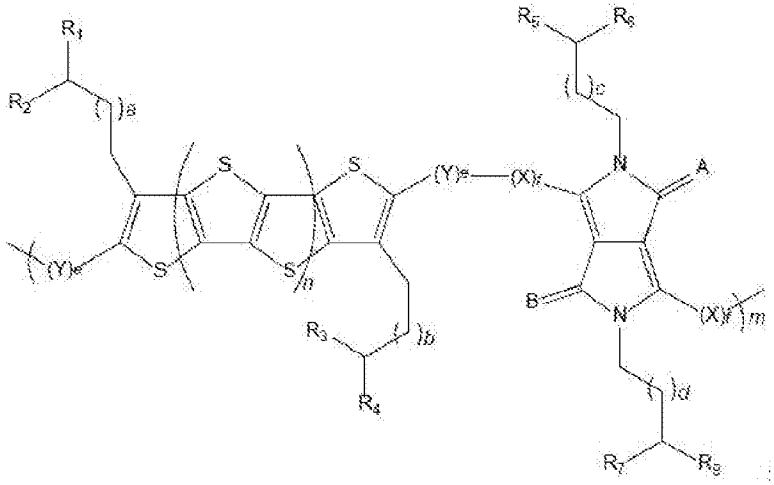
[00018] In one aspect, which is combinable with any of the other aspects or embodiments, the at least one crosslinker comprises C=C bonds, thiols, oxetanes, halides, azides, or combinations thereof.

[00019] In some embodiments, a polymer blend, consists of: at least one organic semiconductor (OSC) polymer and at least one crosslinker, wherein the at least one OSC polymer is a diketopyrrolopyrrole-fused thiophene polymeric material, wherein the fused thiophene is beta-substituted, wherein the crosslinker includes at least one of: acrylates, epoxides, oxetanes, alkenes, alkynes, azides, thiols, allyloxysilanes, phenols, anhydrides, amines, cyanate esters, isocyanate esters, silyl hydrides, cinnamates, coumarins, fluorosulfates, silyl ethers, or a combination thereof.

[00020] In one aspect, which is combinable with any of the other aspects or embodiments, the at least one OSC polymer comprises the repeat unit of Formula 1 or Formula 2, or a salt, isomer, or analog thereof:



Formula 1



Formula 2

wherein in Formula 1 and Formula 2: m is an integer greater than or equal to one; n is 0, 1, or 2; R_1, R_2, R_3, R_4, R_5, R_6, R_7, and R_8, may be, independently, hydrogen, substituted or unsubstituted C_4 or greater alkyl, substituted or unsubstituted C_4 or greater alkenyl, substituted or unsubstituted C_4 or greater alkynyl, or C_5 or greater cycloalkyl; a, b, c, and d are independently, integers greater than or equal to 3; e and f are integers greater than or equal to zero; X and Y are, independently a covalent bond, an optionally substituted aryl group, an optionally substituted heteroaryl, an optionally substituted fused aryl or fused heteroaryl group, an alkyne or an alkene; and A and B may be, independently, either S or O, with the provisos that: (i) at least one of R_1 or R_2; one of R_3 or R_4; one of R_5 or R_6; and one of R_7 or R_8 is a substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, or cycloalkyl; (ii) if any of R_1, R_2, R_3, or R_4 is hydrogen, then none of R_5, R_6, R_7, or R_8 are hydrogen; (iii) if any of R_5, R_6, R_7, or R_8 is hydrogen, then none of R_1, R_2, R_3, or R_4 are hydrogen; (iv) e and f cannot both be 0; (v) if either e or f is 0, then c and d, independently, are integers greater than or equal to 5; and (vi) the polymer having a molecular weight, wherein the molecular weight of the polymer is greater than 10,000.

[00021] In one aspect, which is combinable with any of the other aspects or embodiments, the at least one crosslinker comprises at least one of: (A) a polymer selected from:

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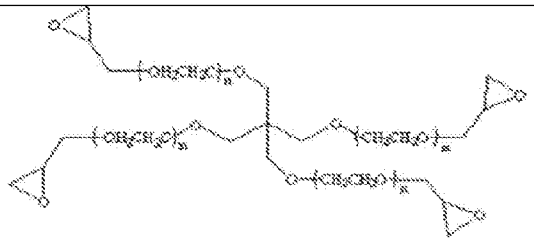
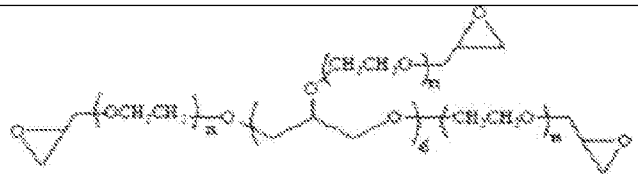
<tr><td> 
C1</td><td> 
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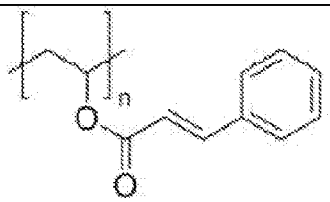
<tr><td> 
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wherein n is an integer greater than or equal to two, or (B) a small-molecule selected from:

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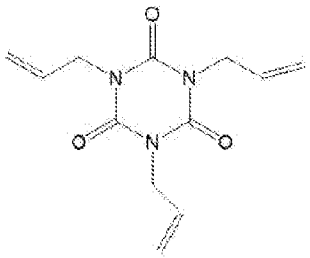
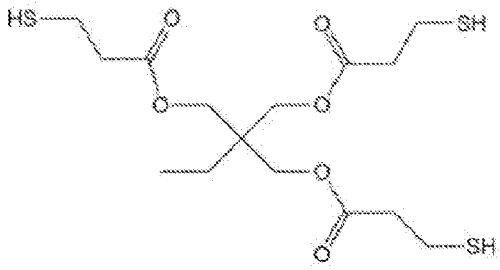
<tr><td> 
C4</td><td> 
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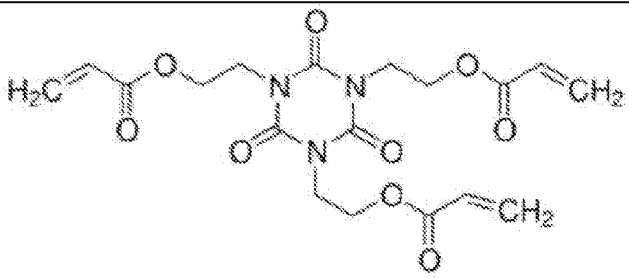
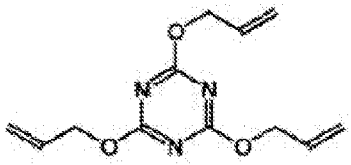
<tr><td> 
C6</td><td> 
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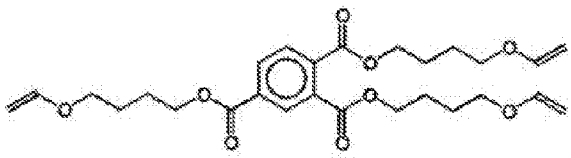
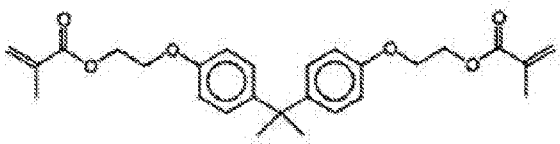
<tr><td> 
C8</td><td> 
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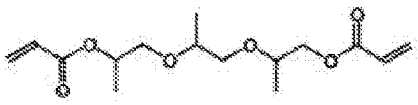
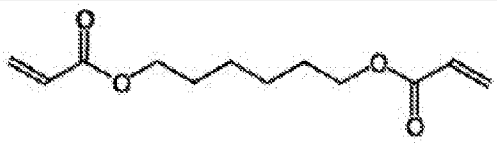
<tr><td> 
C10</td><td> 
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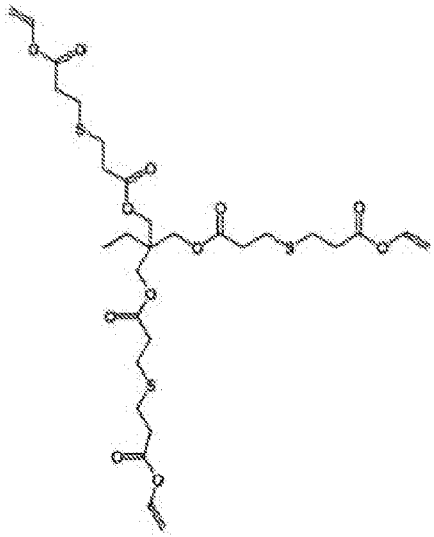
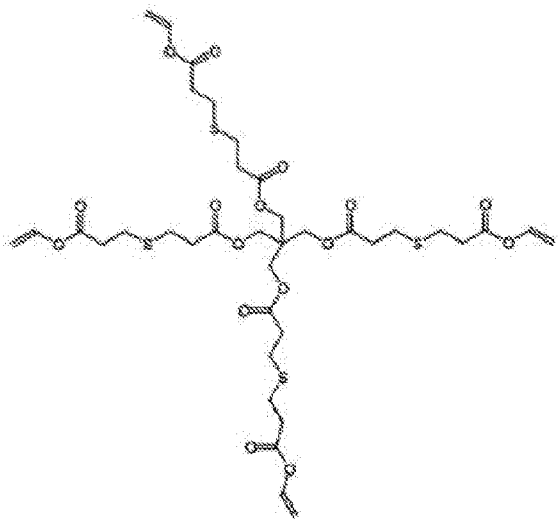
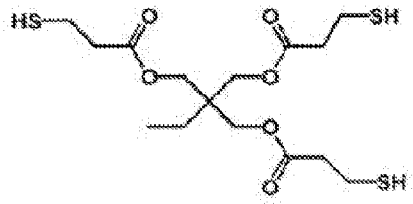
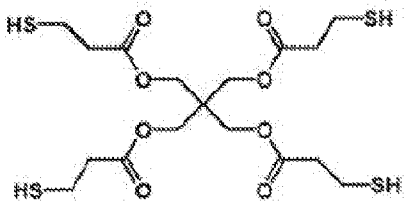
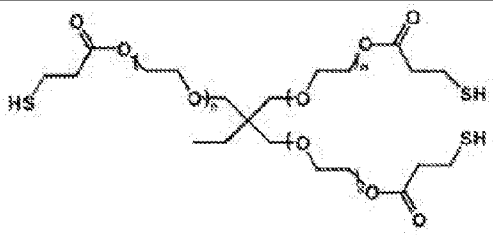
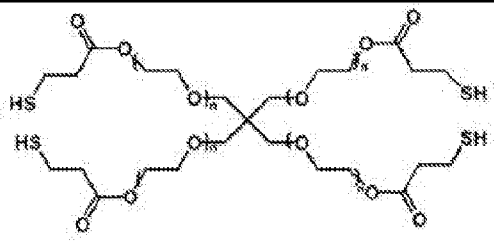
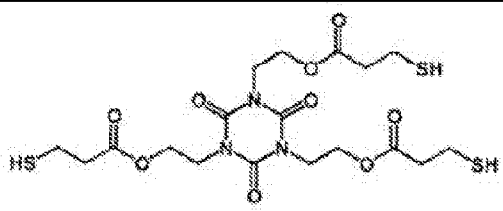
 C13	 C14
 C15	 C16
 C17	 C18



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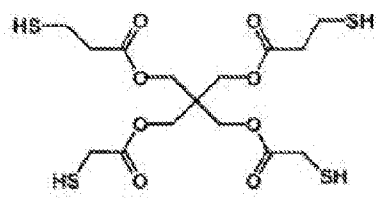

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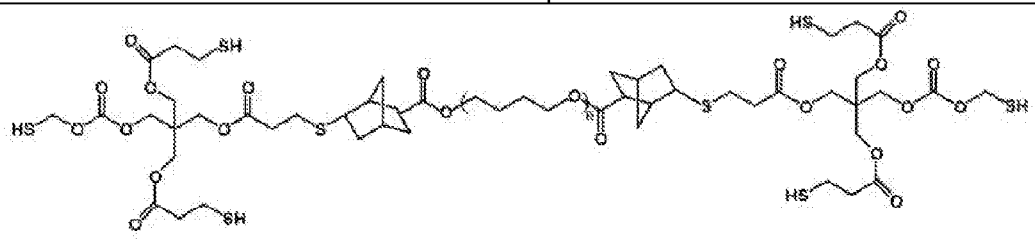

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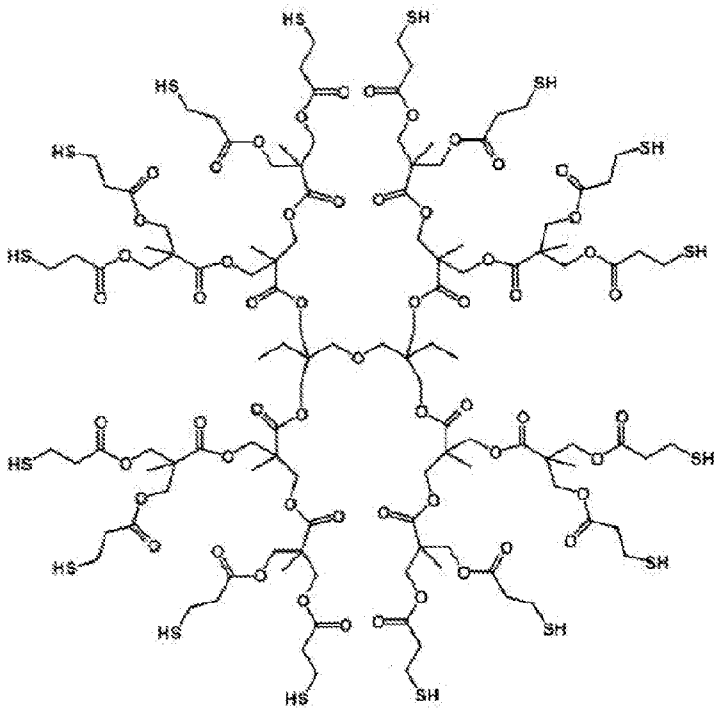

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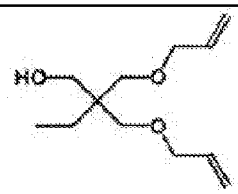

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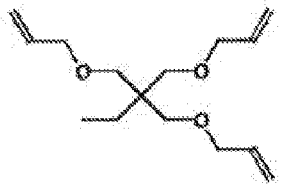

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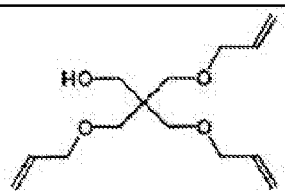

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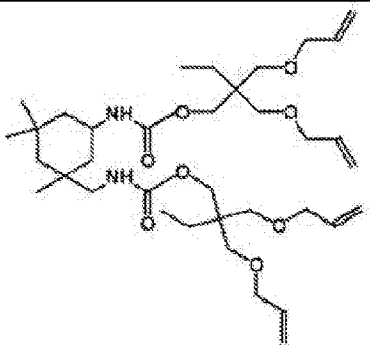

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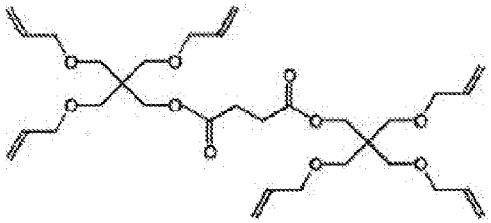

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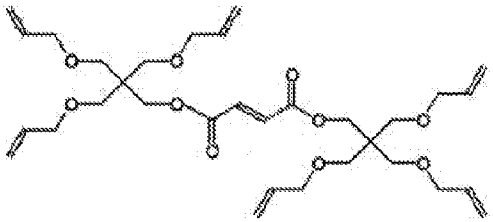

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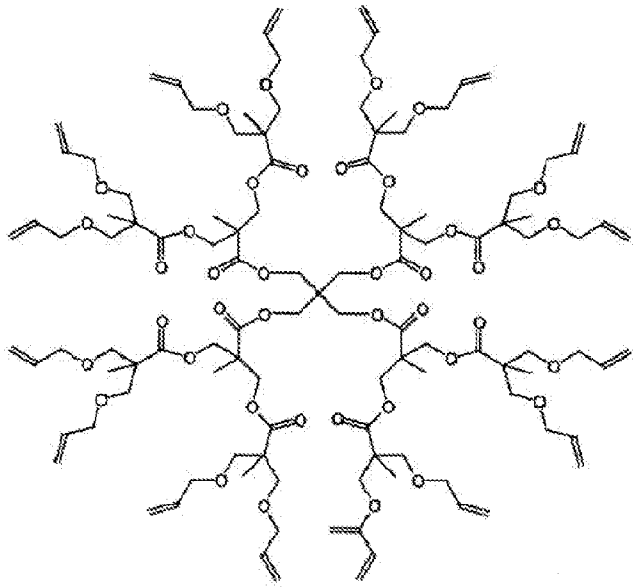

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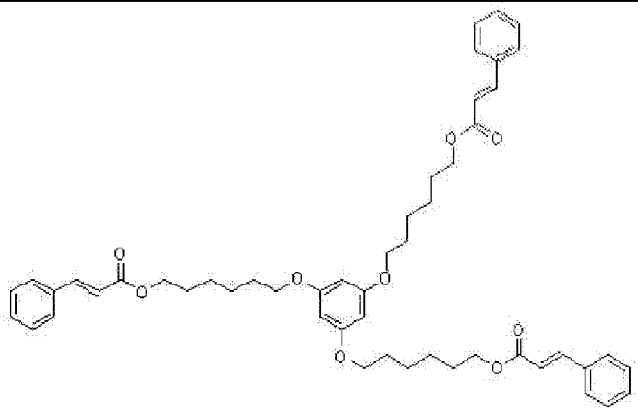

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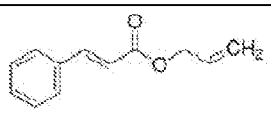

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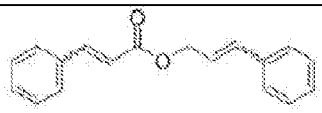

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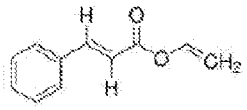
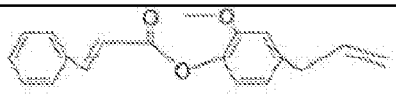
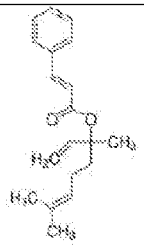
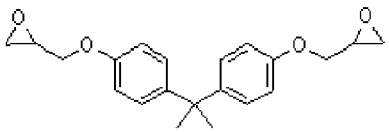
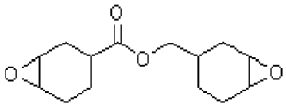
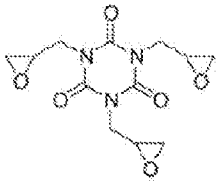
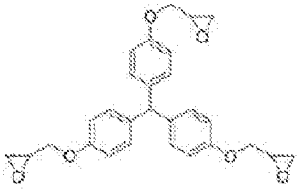
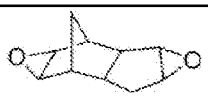
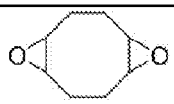
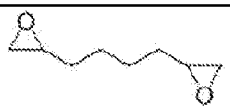
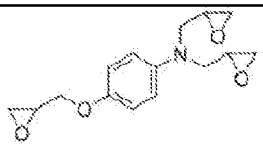
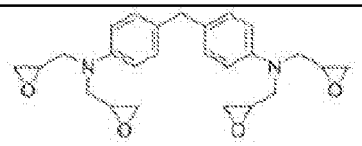
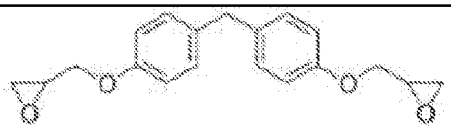
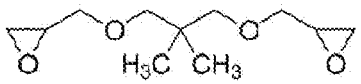
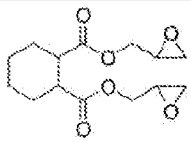
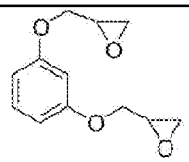
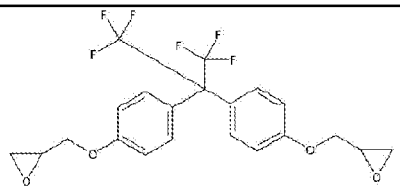
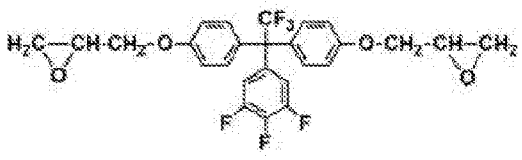
 C33	 C34
 C35	 C36
 C37	 C38
 C39	 C40
 C41	 C42
 C43	 C44

 C45	 C46
 C47	 C48
 C49	 C50
 C51	

or, (C) a combination thereof.

[00022] In one aspect, which is combinable with any of the other aspects or embodiments, the polymer blend further comprises: at least one photoinitiator.

[00023] In one aspect, which is combinable with any of the other aspects or embodiments, the at least one photoinitiator comprises: 1-hydroxy-cyclohexyl-phenyl-ketone (184); 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1 (369); diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO); 2-isopropyl thioxanthone (ITX); 1-[4-(phenylthio) phenyl]-1,2-octanedione 2-(O-benzoyloxime) (HRCURE-OXE01); 2,2-dimethoxy-1,2-diphenylethan-1-one (BDK); benzoyl peroxide (BPO); hydroxyacetophenone (HAP); 2-hydroxy-2-methylprophenone (1173); 2-methyl-4'-(methylthio)-2-morpholinopropiophenone (907); 2-

benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone (IHT-PI 910); Ethyl-4-(dimethylamino)benzoate (EDB); methyl o-benzoyl benzoate (OMBB); bis-(2,6 dimethoxy-benzoyl)-phenyl phosphine oxide (BAPO); 4-benzoyl-4' methyldiphenylsulfide (BMS); benzophenone (BP); 1-chloro-4-propoxy thiozanthone (CPTX); chlorothioxanthone (CTX); 2,2-diethoxyacetophenone (DEAP); diethyl thioxanthone (DETX); 2-dimethyl aminoethyl benzonate (DMB); 2,2-dimethoxy-2-phenyl acetophenone (DMPA); 2-ethyl anthraquinone (2-EA); ethyl-para-N,N-dimethyl-dimethylamino lenzoate (EDAB); 2-ethyl hexyl-dimethylaminolenzoate (EHA); 4,4-bis-(diethylamino)-benzophenone (EMK); methyl benzophenone (MBF); 4-methyl benzophenone (MBP); Michler's ketone (MK); 2-methyl-1-[4(methylthiol)phenyl]-2-morpholino propanone (1) (MMMP); 4-phenylbenzophenone (PBZ); 2,4,6-trimethyl-benzoly-ethoxyl phenyl phosphine oxide (TEPO); bis(4-tert-butylphenyl) iodonium perfluoro-1-butanesulfonate; bis(4-tert-butylphenyl) iodonium p-toluenesulfonate; bis(4-tert-butylphenyl) iodonium triflate; boc-methoxyphenyldiphenylsulfonium triflate; (4-tert-Butylphenyl) diphenylsulfonium triflate; diphenyliodonium hexafluorophosphate; diphenyliodonium nitrate; diphenyliodonium p-toluenesulfonate; diphenyliodonium triflate; (4-fluorophenyl) diphenylsulfonium triflate; N-hydroxynaphthalimide triflate; N-hydroxy-5-norbornene-2,3-dicarboximide perfluoro-1-butanesulfonate; (4-iodophenyl) diphenylsulfonium triflate; (4-methoxyphenyl) diphenylsulfonium triflate; 2-(4-Methoxystyryl)-4,6-bis (trichloromethyl)-1,3,5-triazine; (4-methylthiophenyl) methyl phenyl sulfonium triflate; 1-naphthyl diphenylsulfonium triflate; (4-phenoxyphenyl) diphenylsulfonium triflate; (4-phenylthiophenyl) diphenylsulfonium triflate; triarylsulfonium hexafluoroantimonate salts, mixed 50 wt.% in propylene carbonate; triarylsulfonium hexafluorophosphate salts, mixed 50 wt.% in propylene carbonate; triphenylsulfonium perfluoro-1-butanesufonate; triphenylsulfonium triflate; tris(4-tert-butylphenyl) sulfonium perfluoro-1-butanesulfonate; tris(4-tert-butylphenyl)sulfonium triflate; aryl diazo salts; diaryliodonium salts; triaryl sulfonium salts; aryl ferrocenium salts; or combinations thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

[00024] The disclosure will become more fully understood from the following detailed description, taken in conjunction with the accompanying figures, in which:

[00025] FIGS. 1A to 1E illustrate traditional patterning techniques of organic semiconductor blends utilizing photoresists.

[00026] FIGS. 2A to 2C illustrate patterning techniques of organic semiconductor blends, according to some embodiments.

[00027] FIG. 3 illustrates an exemplary OTFT device, according to some embodiments.

[00028] FIG. 4 illustrates an exemplary OTFT device, according to some embodiments.

[00029] FIGS. 5 to 10D illustrate I_d-V_g curves of test OFET devices prepared according to some embodiments.

[00030] FIG. 11A to 11D illustrate confocal laser scanning microscope (CLSM) images of OSC polymer blends (FIGS. 11A and 11B) and OSC polymer/crosslinker blends (FIGS. 11C and 11D), according to some embodiments.

DETAILED DESCRIPTION

[00031] Reference will now be made in detail to exemplary embodiments which are illustrated in the accompanying drawings. Whenever possible, the same reference numerals will be used throughout the drawings to refer to the same or like parts. The components in the drawings are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the exemplary embodiments. It should be understood that the present application is not limited to the details or methodology set forth in the description or illustrated in the figures. It should also be understood that the terminology is for the purpose of description only and should not be regarded as limiting.

[00032] Additionally, any examples set forth in this specification are illustrative, but not limiting, and merely set forth some of the many possible embodiments of the claimed invention. Other suitable modifications and adaptations of the variety of conditions and parameters normally encountered in the field, and which would be apparent to those skilled in the art, are within the spirit and scope of the disclosure.

[00033] Definitions

[00034] The term "alkyl group" refers to a monoradical branched or unbranched saturated hydrocarbon chain having 1 to 40 carbon atoms. This term is exemplified by groups such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl, pentyl, n-hexyl, n-heptyl, n-octyl, n-decyl, or tetradecyl, and the like. The alkyl group can be substituted or unsubstituted.

[00035] The term "substituted alkyl group" refers to: (1) an alkyl group as defined above, having 1, 2, 3, 4 or 5 substituents, typically 1 to 3 substituents, selected from the group consisting of alkenyl, alkynyl, alkoxy, aralkyl, aldehyde, cycloalkyl, cycloalkenyl, acyl, acylamino, acyl halide, acyloxy, amino, aminocarbonyl, alkoxycarbonylamino, azido, cyano, halogen, hydroxy, keto, thiocarbonyl, carboxy, carboxyalkyl, arylthiol, ester, heteroarylthio, heterocyclylthio, hydroxyl, thiol, alkylthio, aryl, aryloxy, heteroaryl, aminosulfonyl, aminocarbonylamino, heteroaryloxy, heterocyclyl, heterocyclooxy, hydroxyamino, alkoxyamino, nitro, -SO–alkyl, -SO–aryl, -SO–heteroaryl, $-SO_2$–alkyl, $-SO_2$–aryl and $-SO_2$–heteroaryl, thioalkyl, vinyl ether. Unless otherwise constrained by the definition, all substituents may optionally be further substituted by 1, 2, or 3 substituents chosen from alkyl, carboxy, carboxyalkyl, aminocarbonyl, hydroxy, alkoxy, halogen, CF_3, amino, substituted amino, cyano, and $-S(O)_nR_{SO}$, where R_{SO} is alkyl, aryl, or heteroaryl and n is 0, 1 or 2; or (2) an alkyl group as defined above that is interrupted by 1-10 atoms independently chosen from oxygen, sulfur and NR_a, where R_a is chosen from hydrogen, alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, aryl, heteroaryl and heterocyclyl. All substituents may be optionally further substituted by alkyl, alkoxy, halogen, CF_3, amino, substituted amino, cyano, or $-S(O)_nR_{SO}$, in which R_{SO} is alkyl, aryl, or heteroaryl and n is 0, 1 or 2; or (3) an alkyl group as defined above that has both 1, 2, 3, 4 or 5 substituents as defined above and is also interrupted by 1-10 atoms as defined above. For example, the alkyl groups can be an alkyl hydroxy group, where any of the hydrogen atoms of the alkyl group are substituted with a hydroxyl group.

[00036] The term "alkyl group" as defined herein also includes cycloalkyl groups. The term "cycloalkyl group" as used herein is a non-aromatic carbon-based ring (i.e., carbocyclic) composed of at least three carbon atoms, and in some embodiments from three to 20 carbon atoms, having a single cyclic ring or multiple condensed rings. Examples of single ring cycloalkyl groups include, but are not limited to, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclooctyl, and the like. Examples of multiple ring cycloalkyl groups include, but are not limited to, adamantanyl, bicyclo[2.2.1]heptane, 1,3,3-trimethylbicyclo[2.2.1]hept-2-yl, (2,3,3-trimethylbicyclo[2.2.1]hept-2-yl), or carbocyclic groups to which is fused an aryl group, for example indane, and the like. The term cycloalkyl group also includes a heterocycloalkyl group, where at least one of the carbon atoms of the ring is substituted with a heteroatom such as, but not limited to, nitrogen, oxygen, sulfur, or phosphorus.

[00037] The term "unsubstituted alkyl group" is defined herein as an alkyl group composed of just carbon and hydrogen.

[00038] The term "acyl" denotes a group $-C(O)R_{CO}$, in which R_{CO} is hydrogen, optionally substituted alkyl, optionally substituted cycloalkyl, optionally substituted heterocyclyl, optionally substituted aryl, and optionally substituted heteroaryl.

[00039] The term "aryl group" as used herein is any carbon-based aromatic group (i.e., aromatic carbocyclic) such as having a single ring (e.g., phenyl) or multiple rings (e.g., biphenyl), or multiple condensed (fused) rings (e.g., naphthyl or anthryl). These may include, but are not limited to, benzene, naphthalene, phenyl, etc.

[00040] The term "aryl group" also includes "heteroaryl group," meaning a radical derived from an aromatic cyclic group (i.e., fully unsaturated) having 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, or 15 carbon atoms and 1, 2, 3 or 4 heteroatoms selected from oxygen, nitrogen, sulfur, and phosphorus within at least one ring. In other words, heteroaryl groups are aromatic rings composed of at least three carbon atoms that has at least one heteroatom incorporated within the ring of the aromatic group. Such heteroaryl groups can have a single ring (e.g., pyridyl or furyl) or multiple condensed rings (e.g., indolizinyl, benzothiazolyl, or benzothienyl). Examples of heteroaryls include, but are not limited to, [1,2,4]oxadiazole, [1,3,4]oxadiazole, [1,2,4]thiadiazole, [1,3,4]thiadiazole, pyrrole, imidazole, pyrazole, pyridine, pyrazine, pyrimidine, pyridazine, indolizine, isoindole, indole, indazole, purine, quinolizine, isoquinoline, quinoline, phthalazine, naphthylpyridine, quinoxaline, quinazoline, cinnoline, pteridine, carbazole, carboline, phenanthridine, acridine, phenanthroline, isothiazole, phenazine, isoxazole, phenoxazine, phenothiazine, imidazolidine, imidazoline, triazole, oxazole, thiazole, naphthyridine, and the like as well as N-oxide and N-alkoxy derivatives of nitrogen containing heteroaryl compounds, for example pyridine-N-oxide derivatives.

[00041] Unless otherwise constrained by the definition for the heteroaryl substituent, such heteroaryl groups can be optionally substituted with 1 to 5 substituents, typically 1 to 3 substituents selected from the group consisting of alkyl, alkenyl, alkynyl, alkoxy, cycloalkyl, cycloalkenyl, acyl, acylamino, acyloxy, amino, aminocarbonyl, alkoxycarbonylamino, azido, cyano, halogen, hydroxy, keto, thiocarbonyl, carboxy, carboxyalkyl, arylthio, heteroarylthio, heterocyclylthio, thiol, alkylthio, aryl, aryloxy, heteroaryl, aminosulfonyl, aminocarbonylamino, heteroaryloxy, heterocyclyl, heterocyclooxy, hydroxyamino, alkoxyamino, nitro, –SO–alkyl, –

SO–aryl, –SO–heteroaryl, –SO_2–alkyl, SO_2–aryl and –SO_2–heteroaryl. Unless otherwise constrained by the definition, all substituents may optionally be further substituted by 1-3 substituents chosen from alkyl, carboxy, carboxyalkyl, aminocarbonyl, hydroxy, alkoxy, halogen, CF_3, amino, substituted amino, cyano, and –$S(O)_nR_{SO}$, where R_{SO} is alkyl, aryl, or heteroaryl and n is 0, 1 or 2.

[00042] The aryl group can be substituted or unsubstituted. Unless otherwise constrained by the definition for the aryl substituent, such aryl groups can optionally be substituted with from 1 to 5 substituents, typically 1 to 3 substituents, selected from the group consisting of alkyl, alkenyl, alkynyl, alkoxy, aldehyde, cycloalkyl, cycloalkenyl, acyl, acylamino, acyloxy, amino, aminocarbonyl, alkoxycarbonylamino, azido, cyano, ester, halogen, hydroxy, keto, thiocarbonyl, carboxy, carboxyalkyl, arylthio, heteroarylthio, heterocyclylthio, thiol, alkylthio, aryl, aryloxy, heteroaryl, aminosulfonyl, aminocarbonylamino, heteroaryloxy, heterocyclyl, heterocyclooxy, hydroxyamino, alkoxyamino, nitro, –SO-alkyl, –SO-aryl, –SO-heteroaryl, –SO_2-alkyl, SO_2-aryl and –SO_2-heteroaryl. Unless otherwise constrained by the definition, all substituents may optionally be further substituted by 1-3 substituents chosen from alkyl, carboxy, carboxyalkyl, aminocarbonyl, hydroxy, alkoxy, halogen, CF_3, amino, substituted amino, cyano, and –$S(O)_nR_{SO}$, where R_{SO} is alkyl, aryl, or heteroaryl and n is 0, 1 or 2. In some embodiments, the term "aryl group" is limited to substituted or unsubstituted aryl and heteroaryl rings having from three to 30 carbon atoms.

[00043] The term "aralkyl group" as used herein is an aryl group having an alkyl group or an alkylene group as defined herein covalently attached to the aryl group. An example of an aralkyl group is a benzyl group. "Optionally substituted aralkyl" refers to an optionally substituted aryl group covalently linked to an optionally substituted alkyl group or alkylene group. Such aralkyl groups are exemplified by benzyl, phenylethyl, 3-(4-methoxyphenyl)propyl, and the like.

[00044] The term "heteroaralkyl" refers to a heteroaryl group covalently linked to an alkylene group, where heteroaryl and alkylene are defined herein. "Optionally substituted heteroaralkyl" refers to an optionally substituted heteroaryl group covalently linked to an optionally substituted alkylene group. Such heteroaralkyl groups are exemplified by 3-pyridylmethyl, quinolin-8-ylethyl, 4-methoxythiazol-2-ylpropyl, and the like.

[00045] The term "alkenyl group" refers to a monoradical of a branched or unbranched unsaturated hydrocarbon group typically having from 2 to 40 carbon atoms, more typically 2 to

10 carbon atoms and even more typically 2 to 6 carbon atoms and having 1-6, typically 1, double bond (vinyl). Typical alkenyl groups include ethenyl or vinyl (–CH=CH_2), 1-propylene or allyl (–CH_2CH=CH_2), isopropylene (–C(CH_3)=CH_2), bicyclo[2.2.1]heptene, and the like. When alkenyl is attached to nitrogen, the double bond cannot be alpha to the nitrogen.

[00046] The term "substituted alkenyl group" refers to an alkenyl group as defined above having 1, 2, 3, 4 or 5 substituents, and typically 1, 2, or 3 substituents, selected from the group consisting of alkyl, alkenyl, alkynyl, alkoxy, cycloalkyl, cycloalkenyl, acyl, acylamino, acyloxy, amino, aminocarbonyl, alkoxycarbonylamino, azido, cyano, halogen, hydroxy, keto, thiocarbonyl, carboxy, carboxyalkyl, arylthio, heteroarylthio, heterocyclylthio, thiol, alkylthio, aryl, aryloxy, heteroaryl, aminosulfonyl, aminocarbonylamino, heteroaryloxy, heterocyclyl, heterocyclooxy, hydroxyamino, alkoxyamino, nitro, –SO–alkyl, –SO–aryl, –SO–heteroaryl, –SO_2–alkyl, SO_2–aryl and –SO_2–heteroaryl. Unless otherwise constrained by the definition, all substituents may optionally be further substituted by 1, 2, or 3 substituents chosen from alkyl, carboxy, carboxyalkyl, aminocarbonyl, hydroxy, alkoxy, halogen, CF_3, amino, substituted amino, cyano, and –$S(O)_nR_{SO}$, where R_{SO} is alkyl, aryl, or heteroaryl and n is 0, 1 or 2.

[00047] The term "cycloalkenyl group" refers to carbocyclic groups of from 3 to 20 carbon atoms having a single cyclic ring or multiple condensed rings with at least one double bond in the ring structure.

[00048] The term "alkynyl group" refers to a monoradical of an unsaturated hydrocarbon, typically having from 2 to 40 carbon atoms, more typically 2 to 10 carbon atoms and even more typically 2 to 6 carbon atoms and having at least 1 and typically from 1-6 sites of acetylene (triple bond) unsaturation. Typical alkynyl groups include ethynyl, (–C≡CH), propargyl (or prop-1-yn-3-yl, –CH_2C≡CH), and the like. When alkynyl is attached to nitrogen, the triple bond cannot be alpha to the nitrogen.

[00049] The term "substituted alkynyl group" refers to an alkynyl group as defined above having 1, 2, 3, 4 or 5 substituents, and typically 1, 2, or 3 substituents, selected from the group consisting of alkyl, alkenyl, alkynyl, alkoxy, cycloalkyl, cycloalkenyl, acyl, acylamino, acyloxy, amino, aminocarbonyl, alkoxycarbonylamino, azido, cyano, halogen, hydroxy, keto, thiocarbonyl, carboxy, carboxyalkyl, arylthio, heteroarylthio, heterocyclylthio, thiol, alkylthio, aryl, aryloxy, heteroaryl, aminosulfonyl, aminocarbonylamino, heteroaryloxy, heterocyclyl, heterocyclooxy, hydroxyamino, alkoxyamino, nitro, –SO-alkyl, –SO-aryl, –SO-heteroaryl, –SO_2-

alkyl, SO_2-aryl and $-SO_2$-heteroaryl. Unless otherwise constrained by the definition, all substituents may optionally be further substituted by 1, 2, or 3 substituents chosen from alkyl, carboxy, carboxyalkyl, aminocarbonyl, hydroxy, alkoxy, halogen, CF_3, amino, substituted amino, cyano, and $-S(O)_nR_{SO}$, where R_{SO} is alkyl, aryl, or heteroaryl and n is 0, 1 or 2.

[00050] The term "alkylene group" is defined as a diradical of a branched or unbranched saturated hydrocarbon chain, having 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 carbon atoms, typically 1-10 carbon atoms, more typically 1, 2, 3, 4, 5 or 6 carbon atoms. This term is exemplified by groups such as methylene ($-CH_2-$), ethylene ($-CH_2CH_2-$), the propylene isomers (e.g., $-CH_2CH_2CH_2-$ and $-CH(CH_3)CH_2-$) and the like.

[00051] The term "substituted alkylene group" refers to: (1) an alkylene group as defined above having 1, 2, 3, 4, or 5 substituents selected from the group consisting of alkyl, alkenyl, alkynyl, alkoxy, cycloalkyl, cycloalkenyl, acyl, acylamino, acyloxy, amino, aminocarbonyl, alkoxycarbonylamino, azido, cyano, halogen, hydroxy, keto, thiocarbonyl, carboxy, carboxyalkyl, arylthio, heteroarylthio, heterocyclylthio, thiol, alkylthio, aryl, aryloxy, heteroaryl, aminosulfonyl, aminocarbonylamino, heteroaryloxy, heterocyclyl, heterocyclooxy, hydroxyamino, alkoxyamino, nitro, –SO-alkyl, –SO-aryl, –SO-heteroaryl, $-SO_2$-alkyl, $-SO_2$-aryl and $-SO_2$-heteroaryl. Unless otherwise constrained by the definition, all substituents may optionally be further substituted by 1, 2, or 3 substituents chosen from alkyl, carboxy, carboxyalkyl, aminocarbonyl, hydroxy, alkoxy, halogen, CF_3, amino, substituted amino, cyano, and $-S(O)_nR_{SO}$, where R_{SO} is alkyl, aryl, or heteroaryl and n is 0, 1 or 2; or (2) an alkylene group as defined above that is interrupted by 1-20 atoms independently chosen from oxygen, sulfur and NR_a-, where R_a is chosen from hydrogen, optionally substituted alkyl, cycloalkyl, cycloalkenyl, aryl, heteroaryl and heterocyclyl, or groups selected from carbonyl, carboxyester, carboxyamide and sulfonyl; or (3) an alkylene group as defined above that has both 1, 2, 3, 4 or 5 substituents as defined above and is also interrupted by 1-20 atoms as defined above. Examples of substituted alkylenes are chloromethylene ($-CH(Cl)-$), aminoethylene ($-CH(NH_2)CH_2-$), methylaminoethylene ($-CH(NHMe)CH_2-$), 2-carboxypropylene isomers ($-CH_2CH(CO_2H)CH_2-$), ethoxyethyl ($-CH_2CH_2O-CH_2CH_2-$), ethylmethylaminoethyl ($-CH_2CH_2N(CH_3)CH_2CH_2-$), and the like.

[00052] The term "alkoxy group" refers to the group R–O–, where R is an optionally substituted alkyl or optionally substituted cycloalkyl, or R is a group –Y–Z, in which Y is optionally

substituted alkylene and Z is optionally substituted alkenyl, optionally substituted alkynyl; or optionally substituted cycloalkenyl, where alkyl, alkenyl, alkynyl, cycloalkyl and cycloalkenyl are as defined herein. Typical alkoxy groups are optionally substituted alkyl–O– and include, by way of example, methoxy, ethoxy, n-propoxy, iso-propoxy, n-butoxy, tert-butoxy, sec-butoxy, n-pentoxy, n-hexoxy, 1,2-dimethylbutoxy, trifluoromethoxy, and the like.

[00053] The term "alkylthio group" refers to the group R_S–S–, where R_S is as defined for alkoxy.

[00054] The term "aminocarbonyl" refers to the group –C(O)NR_NR_N where each R_N is independently hydrogen, alkyl, aryl, heteroaryl, heterocyclyl or where both R_N groups are joined to form a heterocyclic group (e.g., morpholino). Unless otherwise constrained by the definition, all substituents may optionally be further substituted by 1-3 substituents chosen from alkyl, carboxy, carboxyalkyl, aminocarbonyl, hydroxy, alkoxy, halogen, CF_3, amino, substituted amino, cyano, and –$S(O)_nR_{SO}$, where R_{SO} is alkyl, aryl, or heteroaryl and n is 0, 1 or 2.

[00055] The term "acylamino" refers to the group –NR_{NCO}C(O)R where each R_{NCO} is independently hydrogen, alkyl, aryl, heteroaryl, or heterocyclyl. Unless otherwise constrained by the definition, all substituents may optionally be further substituted by 1-3 substituents chosen from alkyl, carboxy, carboxyalkyl, aminocarbonyl, hydroxy, alkoxy, halogen, CF_3, amino, substituted amino, cyano, and –$S(O)_nR_{SO}$, where R_{SO} is alkyl, aryl, or heteroaryl and n is 0, 1 or 2.

[00056] The term "acyloxy" refers to the groups –O(O)C-alkyl, –O(O)C-cycloalkyl, –O(O)C-aryl, –O(O)C-heteroaryl, and –O(O)C-heterocyclyl. Unless otherwise constrained by the definition, all substituents may be optionally further substituted by alkyl, carboxy, carboxyalkyl, aminocarbonyl, hydroxy, alkoxy, halogen, CF_3, amino, substituted amino, cyano, and –$S(O)_nR_{SO}$, where R_{SO} is alkyl, aryl, or heteroaryl and n is 0, 1 or 2.

[00057] The term "aryloxy group" refers to the group aryl–O– wherein the aryl group is as defined above, and includes optionally substituted aryl groups as also defined above.

[00058] The term "heteroaryloxy" refers to the group heteroaryl–O–.

[00059] The term "amino" refers to the group –NH_2.

[00060] The term "substituted amino" refers to the group –NR_wR_w where each R_w is independently selected from the group consisting of hydrogen, alkyl, cycloalkyl, carboxyalkyl (for example, benzyloxycarbonyl), aryl, heteroaryl and heterocyclyl provided that both R_w

groups are not hydrogen, or a group –Y–Z, in which Y is optionally substituted alkylene and Z is alkenyl, cycloalkenyl, or alkynyl. Unless otherwise constrained by the definition, all substituents may optionally be further substituted by 1-3 substituents chosen from alkyl, carboxy, carboxyalkyl, aminocarbonyl, hydroxy, alkoxy, halogen, CF_3, amino, substituted amino, cyano, and $–S(O)_nR_{SO}$, where R_{SO} is alkyl, aryl, or heteroaryl and n is 0, 1 or 2.

[00061] The term "carboxy" refers to a group –C(O)OH. The term "carboxyalkyl group" refers to the groups –C(O)O–alkyl or –C(O)O–cycloalkyl, where alkyl and cycloalkyl, are as defined herein, and may be optionally further substituted by alkyl, alkenyl, alkynyl, alkoxy, halogen, CF_3, amino, substituted amino, cyano, and $–S(O)_nR_{SO}$, in which R_{SO} is alkyl, aryl, or heteroaryl and n is 0, 1 or 2.

[00062] The terms "substituted cycloalkyl group" or "substituted cycloalkenyl group" refer to cycloalkyl or cycloalkenyl groups having 1, 2, 3, 4 or 5 substituents, and typically 1, 2, or 3 substituents, selected from the group consisting of alkyl, alkenyl, alkynyl, alkoxy, cycloalkyl, cycloalkenyl, acyl, acylamino, acyloxy, amino, aminocarbonyl, alkoxycarbonylamino, azido, cyano, halogen, hydroxy, keto, thiocarbonyl, carboxy, carboxyalkyl, arylthio, heteroarylthio, heterocyclylthio, thiol, alkylthio, aryl, aryloxy, heteroaryl, aminosulfonyl, aminocarbonylamino, heteroaryloxy, heterocyclyl, heterocyclooxy, hydroxyamino, alkoxyamino, nitro, –SO-alkyl, –SO–aryl, –SO–heteroaryl, $–SO_2–$alkyl, $SO_2–$aryl and $–SO_2–$heteroaryl. Unless otherwise constrained by the definition, all substituents may optionally be further substituted by 1, 2, or 3 substituents chosen from alkyl, carboxy, carboxyalkyl, aminocarbonyl, hydroxy, alkoxy, halogen, CF_3, amino, substituted amino, cyano, and $–S(O)_nR_{SO}$, where R_{SO} is alkyl, aryl, or heteroaryl and n is 0, 1 or 2.

[00063] The term "conjugated group" is defined as a linear, branched or cyclic group, or combination thereof, in which p-orbitals of the atoms within the group are connected via delocalization of electrons and wherein the structure can be described as containing alternating single and double or triple bonds and may further contain lone pairs, radicals, or carbenium ions. Conjugated cyclic groups may comprise both aromatic and non-aromatic groups, and may comprise polycyclic or heterocyclic groups, such as diketopyrrolopyrrole. Ideally, conjugated groups are bound in such a way as to continue the conjugation between the thiophene moieties they connect. In some embodiments, "conjugated groups" is limited to conjugated groups having three to 30 carbon atoms.

[00064] The term "halogen," "halo," or "halide" may be referred to interchangeably and refer to fluoro, bromo, chloro, and iodo.

[00065] The term "heterocyclyl" refers to a monoradical saturated or partially unsaturated group having a single ring or multiple condensed rings, having from 1 to 40 carbon atoms and from 1 to 10 hetero atoms, typically 1, 2, 3 or 4 heteroatoms, selected from nitrogen, sulfur, phosphorus, and/or oxygen within the ring. Heterocyclic groups can have a single ring or multiple condensed rings, and include tetrahydrofuranyl, morpholino, piperidinyl, piperazino, dihydropyridino, and the like.

[00066] Unless otherwise constrained by the definition for the heterocyclyl substituent, such heterocyclyl groups can be optionally substituted with 1, 2, 3, 4 or 5, and typically 1, 2 or 3 substituents, selected from the group consisting of alkyl, alkenyl, alkynyl, alkoxy, cycloalkyl, cycloalkenyl, acyl, acylamino, acyloxy, amino, aminocarbonyl, alkoxycarbonylamino, azido, cyano, halogen, hydroxy, keto, thiocarbonyl, carboxy, carboxyalkyl, arylthio, heteroarylthio, heterocyclylthio, thiol, alkylthio, aryl, aryloxy, heteroaryl, aminosulfonyl, aminocarbonylamino, heteroaryloxy, heterocyclyl, heterocyclooxy, hydroxyamino, alkoxyamino, nitro, –SO–alkyl, –SO–aryl, –SO–heteroaryl, $–SO_2–$alkyl, $–SO_2–$aryl and $–SO_2–$heteroaryl. Unless otherwise constrained by the definition, all substituents may optionally be further substituted by 1-3 substituents chosen from alkyl, carboxy, carboxyalkyl, aminocarbonyl, hydroxy, alkoxy, halogen, CF_3, amino, substituted amino, cyano, and $–S(O)_nR_{SO}$, where R_{SO} is alkyl, aryl, or heteroaryl and n is 0, 1 or 2.

[00067] The term "thiol" refers to the group –SH. The term "substituted alkylthio" refers to the group –S–substituted alkyl. The term "arylthiol group" refers to the group aryl–S–, where aryl is as defined as above. The term "heteroarylthiol" refers to the group –S–heteroaryl wherein the heteroaryl group is as defined above including optionally substituted heteroaryl groups as also defined above.

[00068] The term "sulfoxide" refers to a group $–S(O)R_{SO}$, in which R_{SO} is alkyl, aryl, or heteroaryl. The term "substituted sulfoxide" refers to a group $–S(O)R_{SO}$, in which R_{SO} is substituted alkyl, substituted aryl, or substituted heteroaryl, as defined herein. The term "sulfone" refers to a group $–S(O)_2R_{SO}$, in which R_{SO} is alkyl, aryl, or heteroaryl. The term "substituted sulfone" refers to a group $– S(O)_2R_{SO}$, in which R_{SO} is substituted alkyl, substituted aryl, or substituted heteroaryl, as defined herein.

[00069] The term "keto" refers to a group –C(O)–. The term "thiocarbonyl" refers to a group –C(S)–.

[00070] As used herein, the term "room temperature" is 20°C to 25°C.

[00071] Disclosed are compounds, compositions, and components that can be used for, can be used in conjunction with, can be used in preparation of, or are products of the disclosed methods and compositions. These and other materials are disclosed herein, and it is understood that when combinations, subsets, interactions, groups, etc. of these materials are disclosed that while specific reference of each various individual and collective combinations and permutation of these compounds may not be explicitly disclosed, each is specifically contemplated and described herein. Thus, if a class of molecules A, B, and C are disclosed as well as a class of molecules D, E, and F and an example of a combination molecule, A-D is disclosed, then even if each is not individually recited, each is individually and collectively contemplated. Thus, in this example, each of the combinations A-E, A-F, B-D, B-E, B-F, C-D, C-E, and C-F are specifically contemplated and should be considered disclosed from disclosure of A, B, and C; D, E, and F; and the example combination A-D. Likewise, any subset or combination of these is also specifically contemplated and disclosed. Thus, for example, the sub-group of A-E, B-F, and C-E are specifically contemplated and should be considered disclosed from disclosure of A, B, and C; D, E, and F; and the example combination A-D. This concept applies to all aspects of this disclosure including, but not limited to, steps in methods of making and using the disclosed compositions. Thus, if there are a variety of additional steps that can be performed it is understood that each of these additional steps can be performed with any specific embodiment or combination of embodiments of the disclosed methods, and that each such combination is specifically contemplated and should be considered disclosed.

[00072] A weight percent of a component, unless specifically stated to the contrary, is based on the total weight of the formulation or composition in which the component is included.

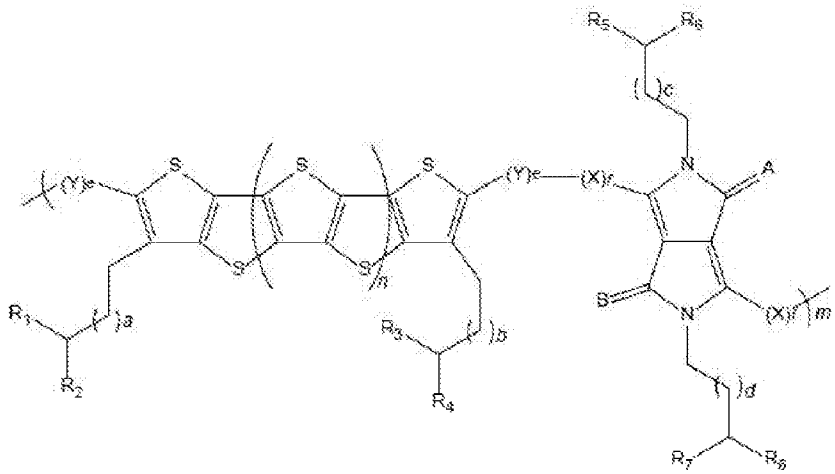
[00073] Organic semiconductors as functional materials may be used in a variety of applications including, for example, printed electronics, organic transistors, including organic thin-film transistors (OTFTs) and organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), organic integrated circuits, organic solar cells, and disposable sensors. Organic transistors may be used in many applications, including smart cards, security tags, and the backplanes of flat panel displays. Organic semiconductors may substantially reduce cost

compared to inorganic counterparts, such as silicon. Depositing OSCs from solution may enable fast, large-area fabrication routes such as various printing methods and roll-to-roll processes.

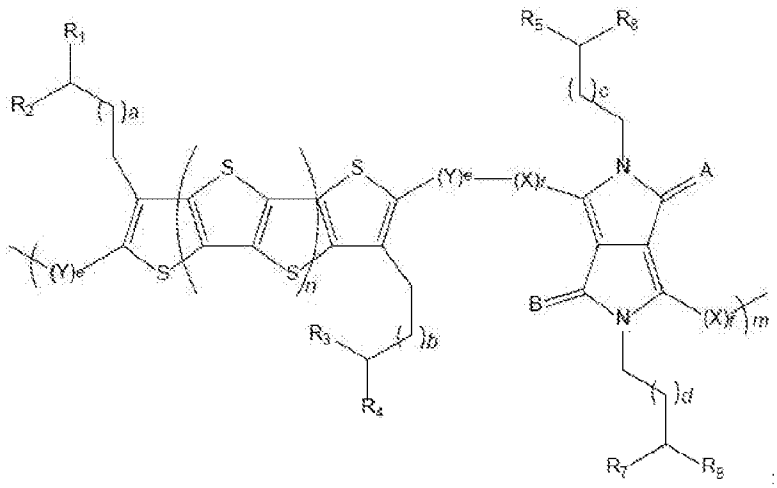
[00074] Organic thin-film transistors are particularly interesting because their fabrication processes are less complex as compared with conventional silicon-based technologies. For example, OTFTs generally rely on low temperature deposition and solution processing, which, when used with semiconducting conjugated polymers, can achieve valuable technological attributes, such as compatibility with simple-write printing techniques, general low-cost manufacturing approaches, and flexible plastic substrates. Other potential applications for OTFTs include flexible electronic papers, sensors, memory devices (e.g., radio frequency identification cards (RFIDs)), remote controllable smart tags for supply chain management, large-area flexible displays, and smart cards.

[00075] Organic Semiconductor (OSC) Polymer

[00076] An OSC polymer may be used to produce organic semiconductor devices. In some examples, a polymer blend comprises an organic semiconductor polymer. In some examples, the OSC polymer has a main backbone that is fully conjugated. In some examples, the OSC is a diketopyrrolopyrrole (DPP) fused thiophene polymeric material. In some examples, the fused thiophene is beta-substituted. This OSC may contain both fused thiophene and diketopyrrolopyrrole units. In some examples, the OSC is used in OTFT applications. For example, the OSC polymer may comprise the repeat unit of Formula 1 or Formula 2, or a salt, isomer, or analog thereof:



Formula 1

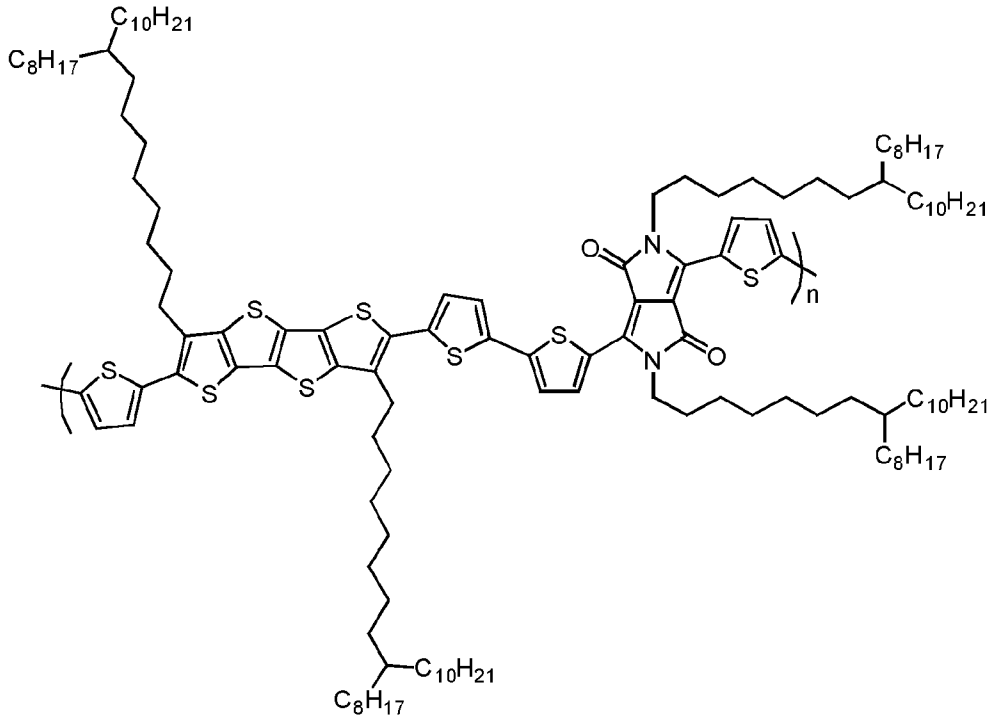


Formula 2

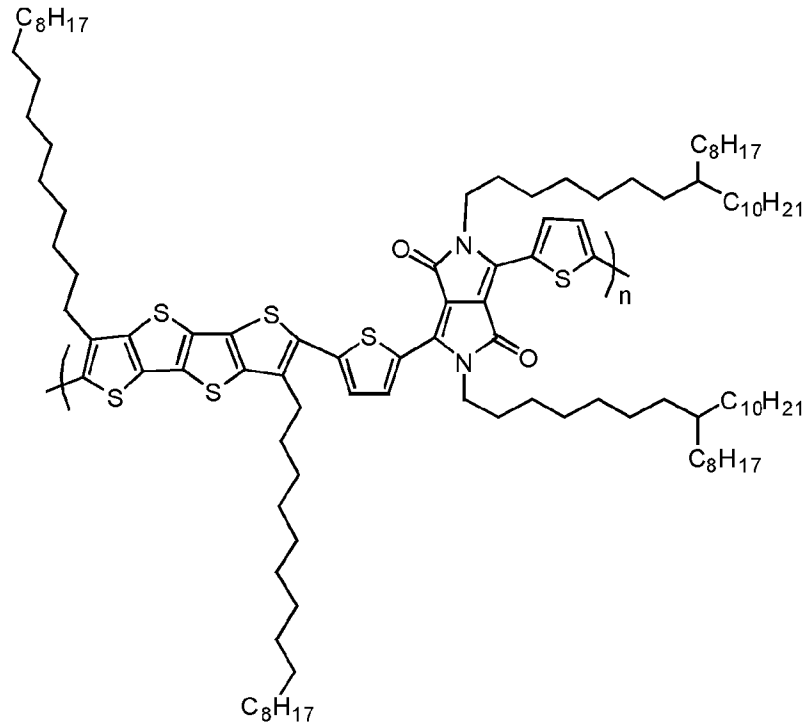
[00077] wherein in Formula 1 and Formula 2: m is an integer greater than or equal to one; n is 0, 1, or 2; R_1, R_2, R_3, R_4, R_5, R_6, R_7, and R_8, may be, independently, hydrogen, substituted or unsubstituted C_4 or greater alkyl, substituted or unsubstituted C_4 or greater alkenyl, substituted or unsubstituted C_4 or greater alkynyl, or C_5 or greater cycloalkyl; a, b, c, and d are independently, integers greater than or equal to 3; e and f are integers greater than or equal to zero; X and Y are, independently a covalent bond, an optionally substituted aryl group, an optionally substituted heteroaryl, an optionally substituted fused aryl or fused heteroaryl group, an alkyne or an alkene; and A and B may be, independently, either S or O, with the provisos that: (i) at least one of R_1 or R_2; one of R_3 or R_4; one of R_5 or R_6; and one of R_7 or R_8 is a substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, or cycloalkyl; (ii) if any of R_1, R_2, R_3, or R_4 is hydrogen, then none of R_5, R_6, R_7, or R_8 are hydrogen; (iii) if any of R_5, R_6, R_7, or R_8 is hydrogen, then none of R_1, R_2, R_3, or R_4 are hydrogen; (iv) e and f cannot both be 0; (v) if either e or f is 0, then c and d, independently, are integers greater than or equal to 5; and (iv) the polymer having a molecular weight, wherein the molecular weight of the polymer is greater than 10,000.

[00078] In some embodiments, the OSC polymers defined in Formula 1 or Formula 2 enable simple transistor fabrication at relatively low temperatures, which is particularly important for the realization of large-area, mechanically flexible electronics. A beta-substituted OSC polymer can also help to improve solubility.

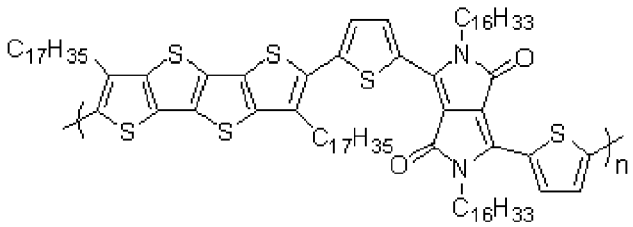
[00079] In some examples, the OSC polymer may comprise the repeat unit of Formula 3, Formula 4, Formula 5, or a salt, isomer, or analog thereof:



Formula 3



Formula 4



Formula 5

[00080] In some examples, the OSC has a solubility of 0.5 mg/mL, 1 mg/mL, 2 mg/mL, 3 mg/mL, 4 mg/mL, 5 mg/mL, or any range defined by any two of those endpoints. In some examples, the OSC has a solubility of 1 mg/mL or more at room temperature.

[00081] In some examples, the OSC has hole mobilities of 1 $cm^2V^{-1}s^{-1}$, 2 $cm^2V^{-1}s^{-1}$, 3 $cm^2V^{-1}s^{-1}$, 4 $cm^2V^{-1}s^{-1}$, 5 $cm^2V^{-1}s^{-1}$, 10 $cm^2V^{-1}s^{-1}$, or any range defined by any two of those endpoints. The hole mobilities may be equal to or greater than any of these values. In some examples, the OSC has hole mobilities of 1 to 4 $cm^2V^{-1}s^{-1}$. In some examples, the OSC has hole mobilities of 2 $cm^2V^{-1}s^{-1}$. In some examples, the OSC has hole mobilities of 2 $cm^2V^{-1}s^{-1}$ or more.

[00082] In some examples, the OSC polymers have On/Off ratios of greater than 10^5. In some examples, the OSC polymers have On/Off ratios of greater than 10^6.

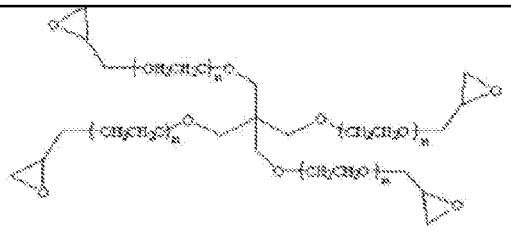
[00083] In some examples, the OSC polymers have a threshold voltage in thin film transistor devices of 1 V, 2 V, 3V, 4 V, 5 V, 10 V, or any range defined by any two of those endpoints. In some examples, the OSC polymers have a threshold voltage in a range of 1 V to 3 V in thin film transistor devices. In some examples, the OSC polymers have a threshold voltage of 2 V in thin film transistor devices.

[00084] **Crosslinker**

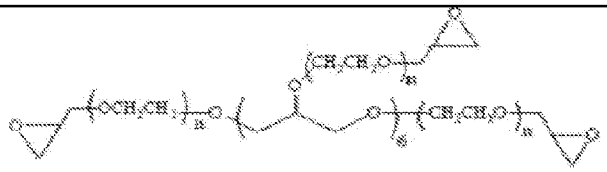
[00085] In some examples, a polymer blend comprises at least one organic semiconductor (OSC) polymer and at least one crosslinker, such that the crosslinker includes at least one of: acrylates, epoxides, oxetanes, alkenes, alkynes, azides, thiols, allyloxysilanes, phenols, anhydrides, amines, cyanate esters, isocyanate esters, silyl hydrides, cinnamates, coumarins, fluorosulfates, silyl ethers, or a combination thereof. In some examples, the at least one crosslinker comprises C=C bonds, thiols, oxetanes, halides, azides, or combinations thereof.

[00086] In some examples, the crosslinker may be a small molecule or a polymer that reacts with the OSC polymer by one or a combination of reaction mechanisms, depending on functional moieties present in the crosslinker molecule. For example, crosslinkers comprising thiol groups may react with double bonds in the OSC polymer via thiol-ene click chemistry. In some examples, crosslinkers comprising vinyl groups may react with double bonds in the OSC polymer via addition reaction. In some examples, crosslinkers (comprising thiols, vinyl groups, etc., or combinations thereof) may react with crosslinkable functionalities incorporated in the side chains of OSC polymers. These include, for example, acrylates, epoxides, oxetanes, alkenes, alkynes, azides, thiols, allyloxysilanes, phenols, anhydrides, amines, cyanate esters, isocyanate esters, silyl hydrides, cinnamates, coumarins, fluorosulfates, silyl ethers, or combinations thereof.

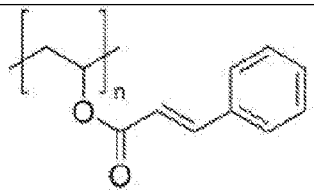
[00087] In one aspect, which is combinable with any of the other aspects or embodiments, the at least one crosslinker comprises at least one of: (A) a polymer selected from:



C1

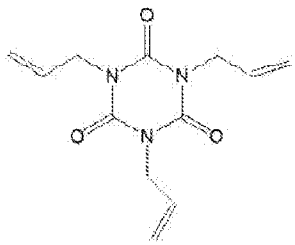


C2



C3

wherein n is an integer greater than or equal to two, or (B) a small-molecule selected from:



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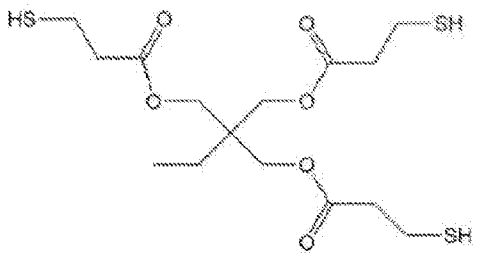

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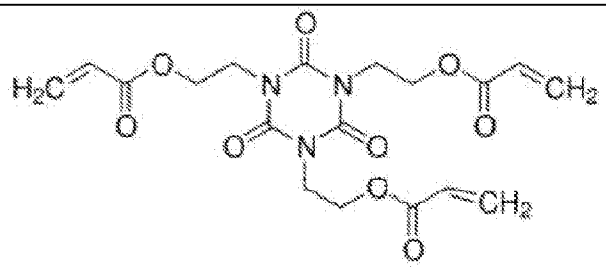
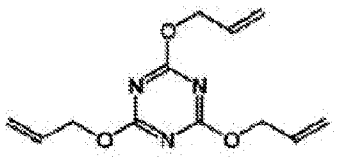
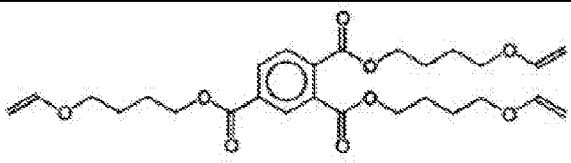


C6



C7



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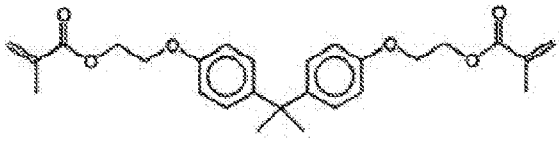

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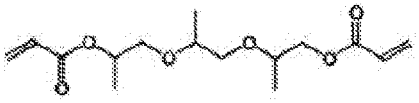
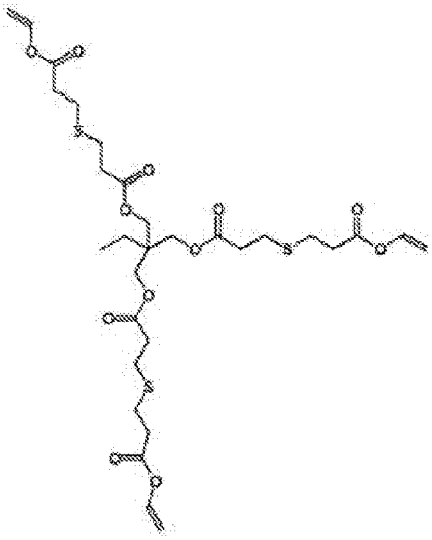


C10

C11

C12



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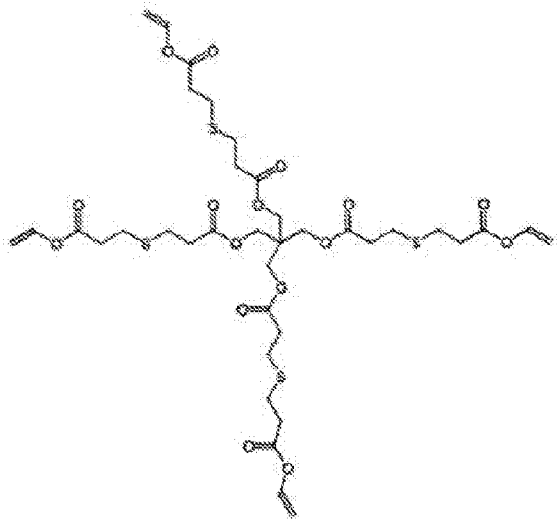

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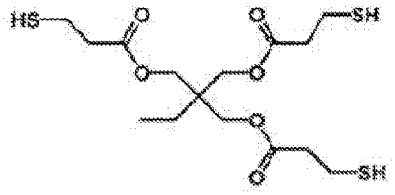

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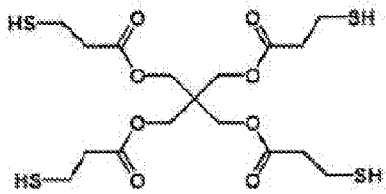
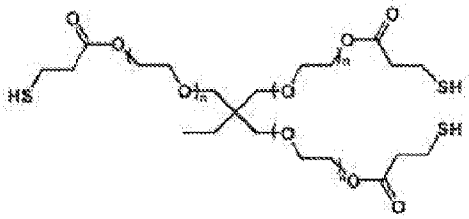


C16



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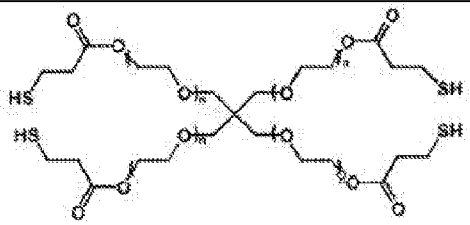
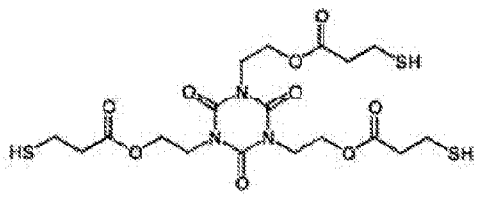


C18



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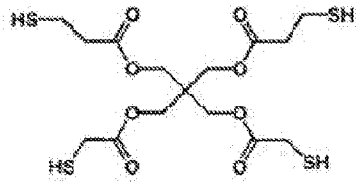

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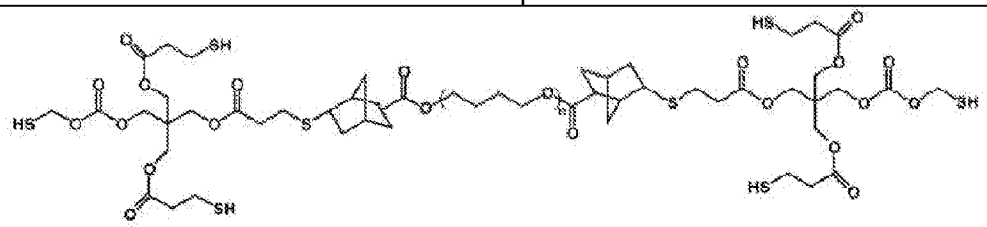

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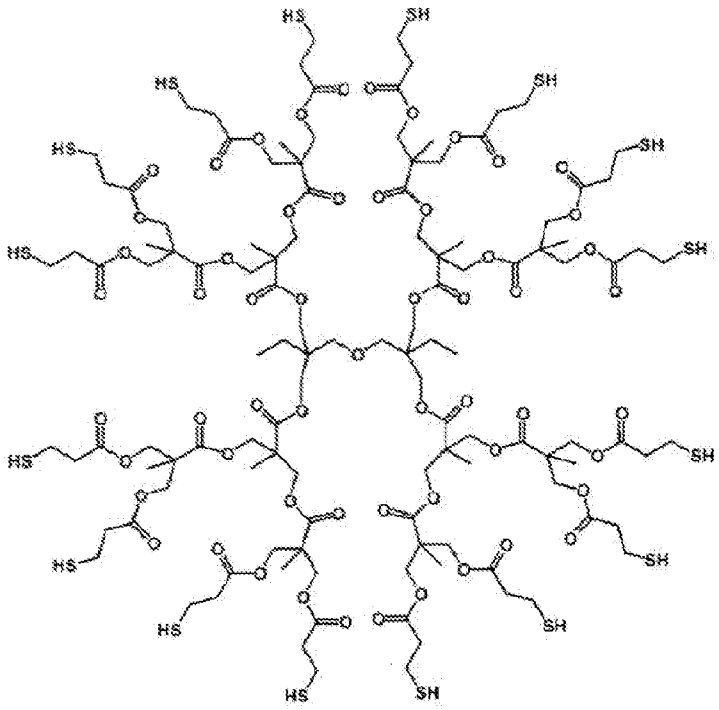

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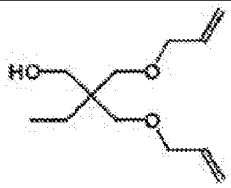

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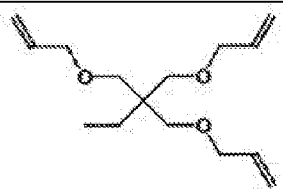

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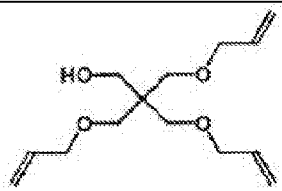

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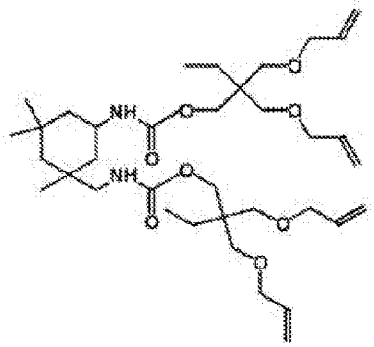

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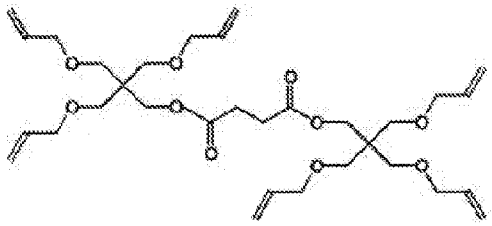

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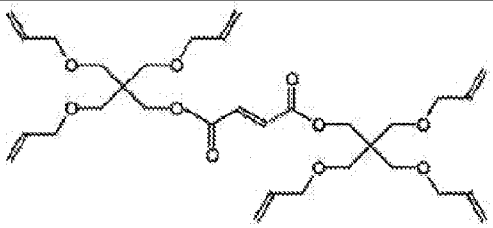

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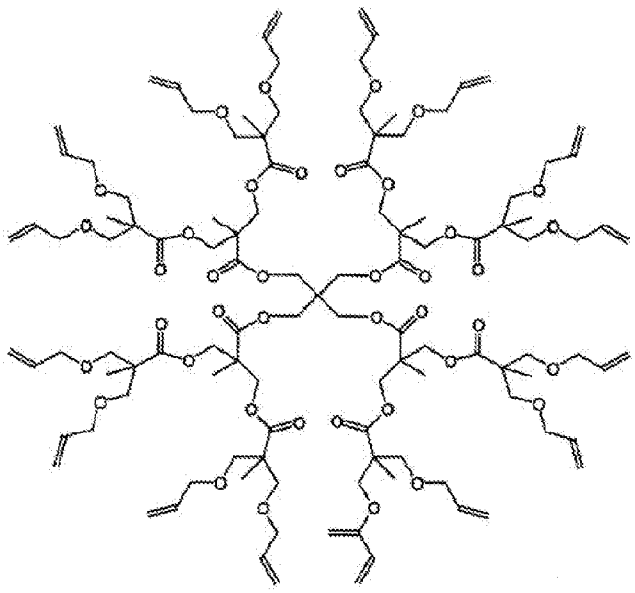

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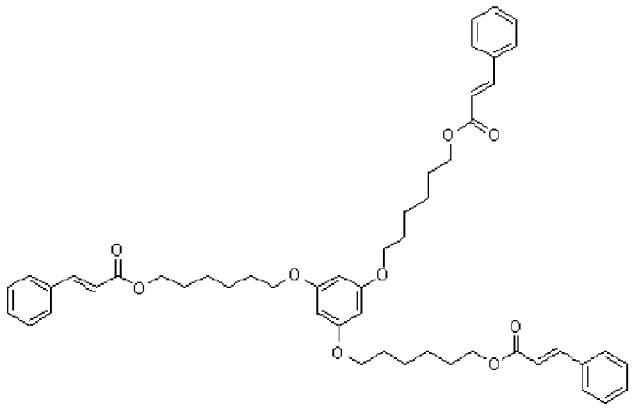
<tr><td colspan="2"> 
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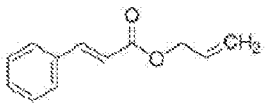
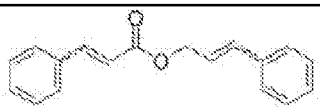
<tr><td> 
C31</td><td> 
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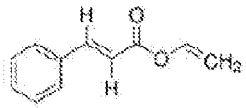
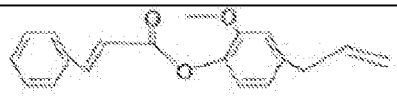
<tr><td> 
C33</td><td> 
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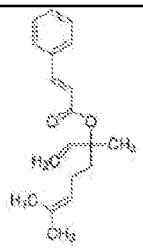
<tr><td> 
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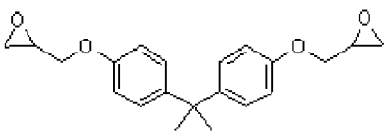
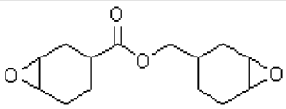
<tr><td> 
C37</td><td> 
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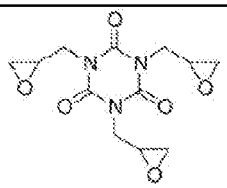
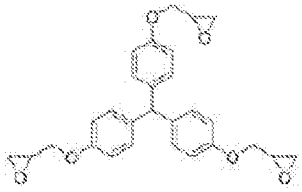
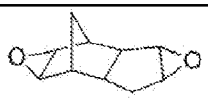
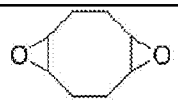
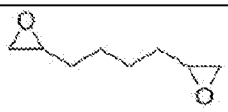
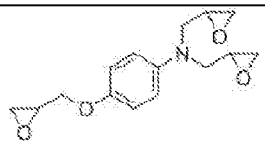
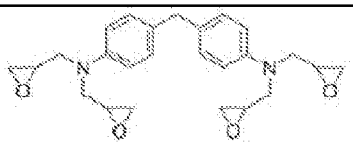
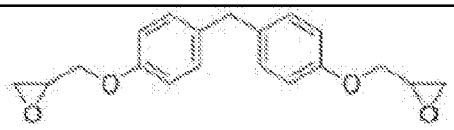
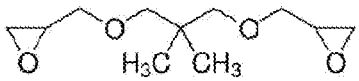
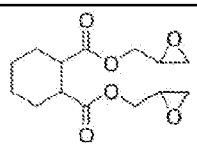
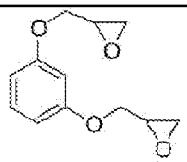
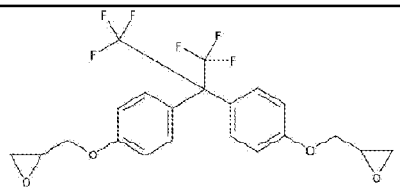
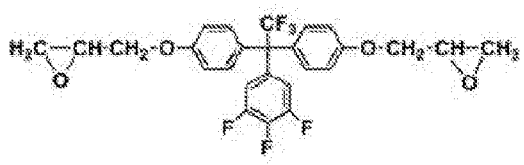
 C39	 C40
 C41	 C42
 C43	 C44
 C45	 C46
 C47	 C48
 C49	 C50



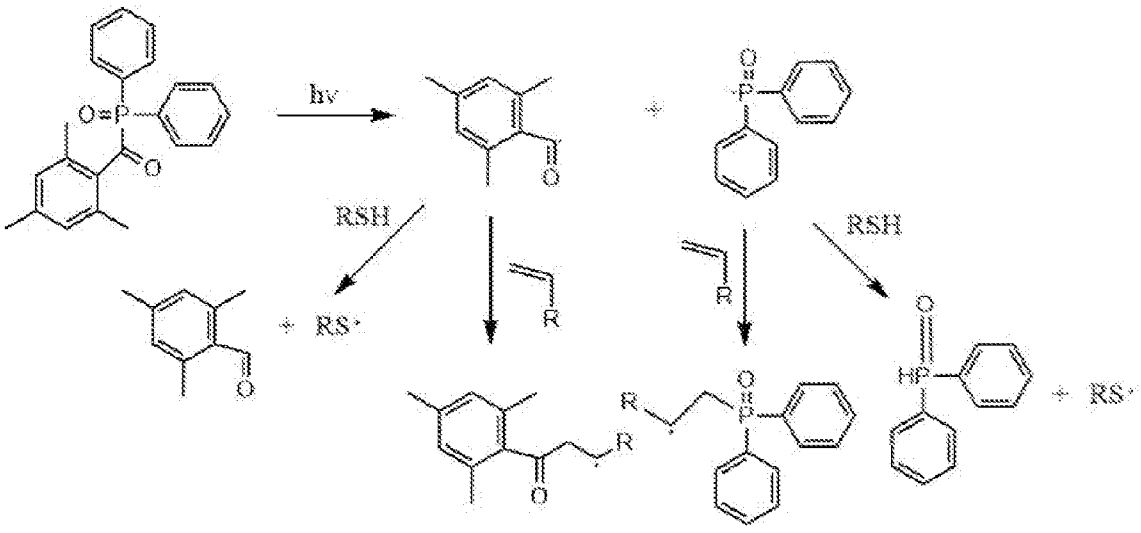
C51

or, (C) a combination thereof.

[00088] Photoinitiator

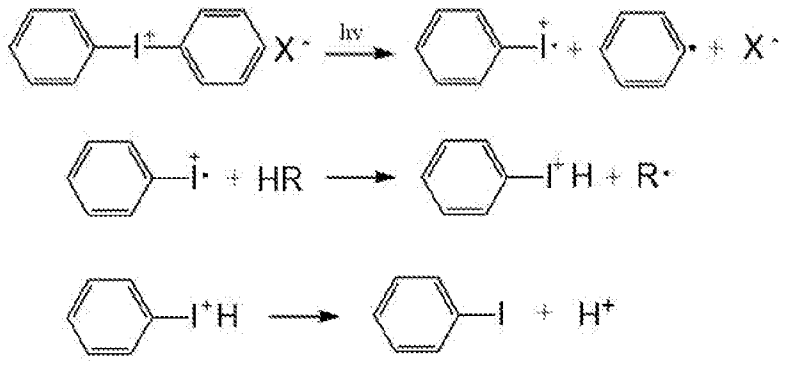
[00089] In some examples, a polymer blend comprises at least one OSC polymer, at least one crosslinker, and at least one photoinitiator.

[00090] The photoinitiator is a key component of photocuring products. In some examples, the photoinitiator comprises at least one free radical photoinitiator. Free-radical based photoinitiators include reactive free radicals that initiate photo-polymerization when exposed to UV light. In one example, the mechanism by which photoinitiator TPO initiates thiol-ene free-radical polymerization is shown below.



[00091] In some examples, the photoinitiator comprises at least one cationic photoinitiator. Cationic photoinitiators are also called photo-acid generators (PAGs). Once a cationic photoinitiator absorbs UV light, the initiator molecule is converted into a strong acid species, either a Lewis or Brönsted acid, that initiates polymerization. Typical photoacids/photoacid

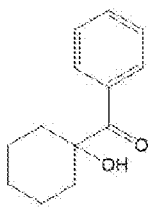
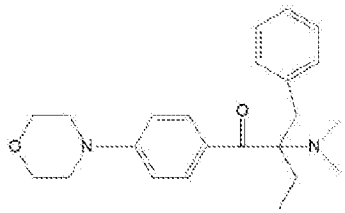
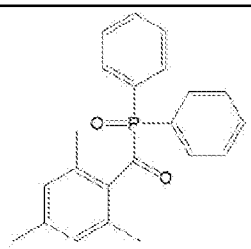
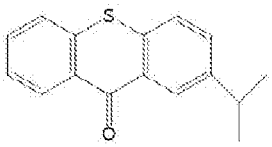
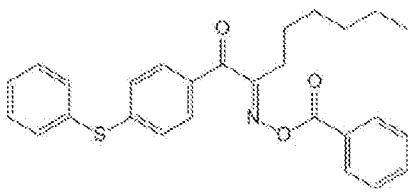
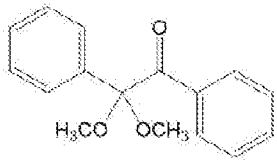
generators include aryl diazo salts, diaryliodonium salts, triaryl sulfonium salts, and aryl ferrocenium salts. In one example, the mechanism by which polymerization proceeds in using PAGs is shown below.



[00092] In some examples, the at least one photoinitiator includes: 1-hydroxy-cyclohexyl-phenyl-ketone (184); 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1 (369); diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO); 2-isopropyl thioxanthone (ITX); 1-[4-(phenylthio) phenyl]-1,2-octanedione 2-(O-benzoyloxime) (HRCURE-OXE01); 2,2-dimethoxy-1,2-diphenylethan-1-one (BDK); benzoyl peroxide (BPO); hydroxyacetophenone (HAP); 2-hydroxy-2-methylprophenone (1173); 2-methyl-4'-(methylthio)-2-morpholinopropiophenone (907); 2-benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone (IHT-PI 910); Ethyl-4-(dimethylamino)benzoate (EDB); methyl o-benzoyl benzoate (OMBB); bis-(2,6 dimethoxy-benzoyl)-phenyl phosphine oxide (BAPO); 4-benzoyl-4' methyldiphenylsulfide (BMS); benzophenone (BP); 1-chloro-4-propoxy thiozanthone (CPTX); chlorothioxanthone (CTX); 2,2-diethoxyacetophenone (DEAP); diethyl thioxanthone (DETX); 2-dimethyl aminoethyl benzonate (DMB); 2,2-dimethoxy-2-phenyl acetophenone (DMPA); 2-ethyl anthraquinone (2-EA); ethyl-para-N,N-dimethyl-dimethylamino lenzoate (EDAB); 2-ethyl hexyl-dimethylaminolenzoate (EHA); 4,4-bis-(diethylamino)-benzophenone (EMK); methyl benzophenone (MBF); 4-methyl benzophenone (MBP); Michler's ketone (MK); 2-methyl-1-[4(methylthiol)phenyl]-2-morpholino propanone (1) (MMMP); 4-phenylbenzophenone (PBZ); 2,4,6-trimethyl-benzoly-ethoxyl phenyl phosphine oxide (TEPO); bis(4-tert-butylphenyl) iodonium perfluoro-1-butanesulfonate; bis(4-tert-butylphenyl) iodonium p-toluenesulfonate; bis(4-tert-butylphenyl) iodonium triflate; boc-

methoxyphenyldiphenylsulfonium triflate; (4-tert-Butylphenyl) diphenylsulfonium triflate; diphenyliodonium hexafluorophosphate; diphenyliodonium nitrate; diphenyliodonium p-toluenesulfonate; diphenyliodonium triflate; (4-fluorophenyl) diphenylsulfonium triflate; N-hydroxynaphthalimide triflate; N-hydroxy-5-norbornene-2,3-dicarboximide perfluoro-1-butanesulfonate; (4-iodophenyl) diphenylsulfonium triflate; (4-methoxyphenyl) diphenylsulfonium triflate; 2-(4-Methoxystyryl)-4,6-bis (trichloromethyl)-1,3,5-triazine; (4-methylthiophenyl) methyl phenyl sulfonium triflate; 1-naphthyl diphenylsulfonium triflate; (4-phenoxyphenyl) diphenylsulfonium triflate; (4-phenylthiophenyl) diphenylsulfonium triflate; triarylsulfonium hexafluoroantimonate salts, mixed 50 wt.% in propylene carbonate; triarylsulfonium hexafluorophosphate salts, mixed 50 wt.% in propylene carbonate; triphenylsulfonium perfluoro-1-butanesufonate; triphenylsulfonium triflate; tris(4-tert-butylphenyl) sulfonium perfluoro-1-butanesulfonate; tris(4-tert-butylphenyl)sulfonium triflate; aryl diazo salts; diaryliodonium salts; triaryl sulfonium salts; aryl ferrocenium salts; or combinations thereof.

[00093] Structures for representative photoinitiators are shown in Table 1 below.

 P1	 P2	 P3
 P4	 P5	 P6

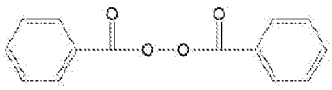
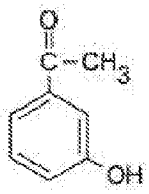
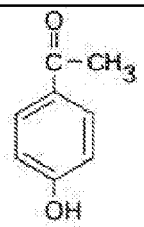
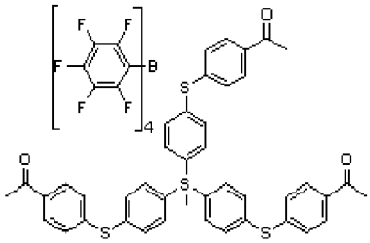
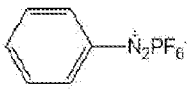
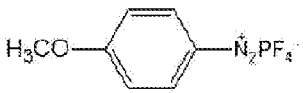
 P7	 P8	 P9
 P10		

Table 1

[00094] Structures for representative aryl diazo salt, diaryliodonium salt, triaryl sulfonium salt, and aryl ferrocenium salt photoinitiators are shown in Table 2 below.

Aryl diazo salts	
 P11	 P12
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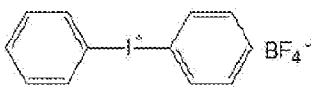
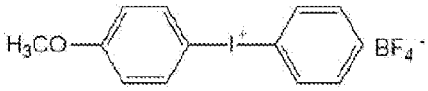
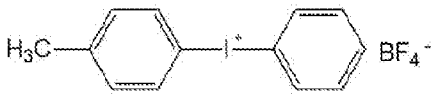
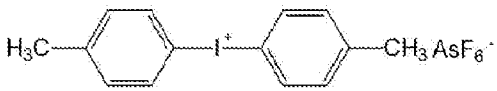
 P13	 P14
	

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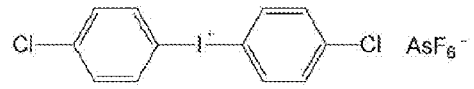
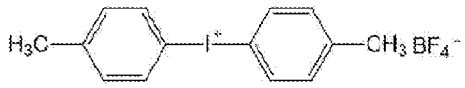
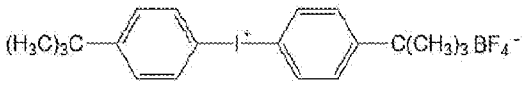
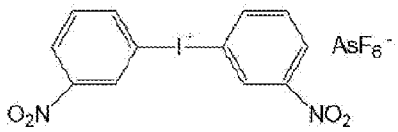
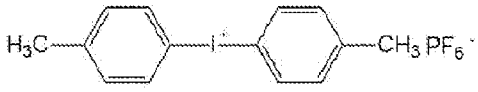
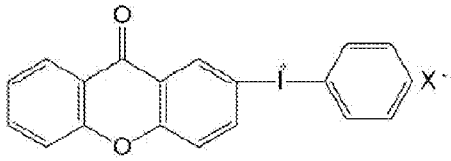
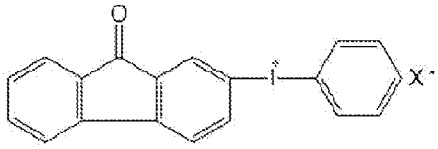
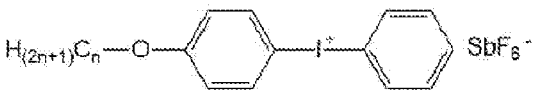
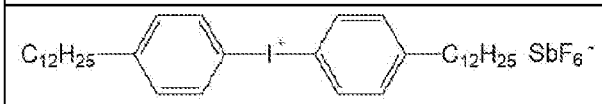
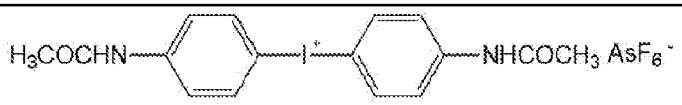
 P17	 P18
 P19	 P20
 P21	 P22
 P23	 P24
 P25	 P26
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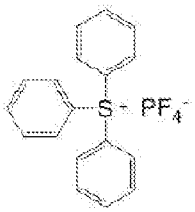
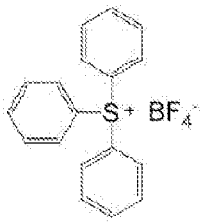
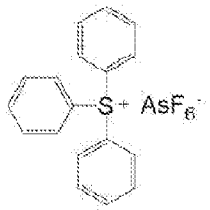
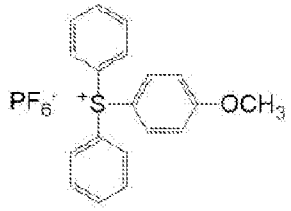
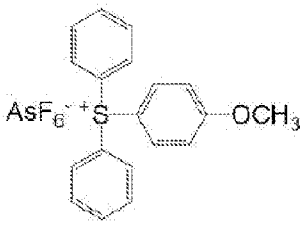
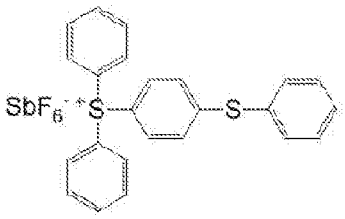
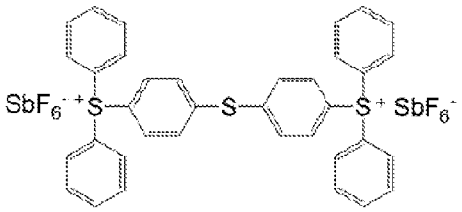
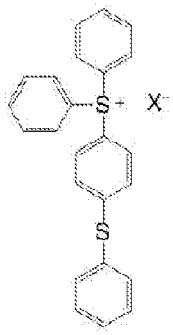
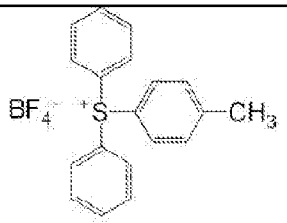
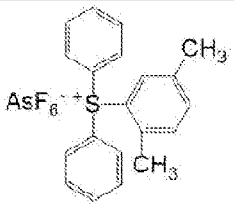
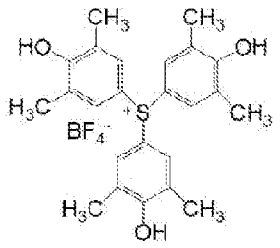
 P27	 P28

 P29	 P30
 P31	 P32
 P33	 P34
 P35	 P36

 P37	
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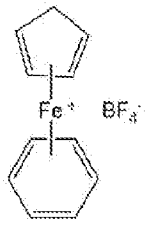
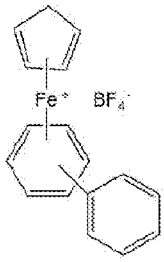
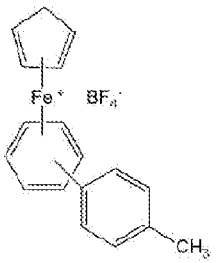
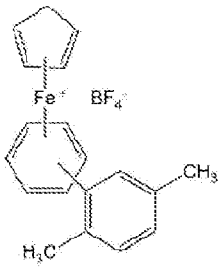
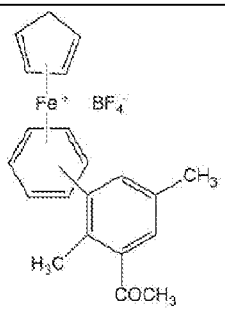
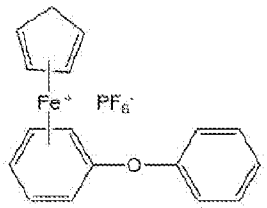
 P38	 P39
 P40	 P41
 P42	 P43

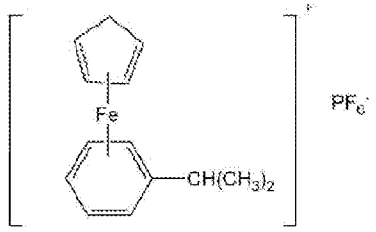
 P44	

Table 2

[00095] Additives

[00096] In some examples, a polymer blend comprises at least one OSC polymer, at least one crosslinker, at least one photoinitiator, and at least one additive, such as antioxidants (i.e., oxygen inhibitors), lubricants, compatibilizers, leveling agents, nucleating agents, or combinations thereof. In some examples, oxygen inhibitors include phenols, thiols, amines, ethers, phosphites, organic phosphines, hydroxylamines, or combinations thereof.

[00097] Polymer Blend

[00098] In some examples, the performance of a device comprising the OSC polymer may be improved by blending the OSC polymer with a crosslinker. In some examples, the OSC polymer is blended with a crosslinker in a solvent. In some examples, the solvent is chloroform, methylethylketone, toluene, xylenes, chlorobenzene, 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, tetralin, naphthalene, chloronaphthalene, or combinations thereof. In some examples, a mixture of more than one solvent may be used.

[00099] In some examples, the at least one OSC polymer is present in a range of 1 wt.% to 99 wt.%, or in a range of 5 wt.% to 95 wt.%, or in a range of 10 wt.% to 90 wt.%, or in a range of 25 wt.% to 85 wt.%, or in a range of 50 wt.% to 80 wt.%. In some examples, the at least one OSC polymer is present at 1 wt.%, or 2 wt.%, or 3 wt.%, or 5 wt.%, or 10 wt.%, or 15 wt.%, or 20 wt.%, or 25 wt.%, or 30 wt.%, or 35 wt.%, or 40 wt.%, or 50 wt.%, or 60 wt.%, or 70 wt.%, or 80 wt.%, or 90 wt.%, or 95 wt.%, or 99 wt.%, or any range defined by any two of those endpoints.

[000100] In some examples, the at least one crosslinker is present in a range of 1 wt.% to 99 wt.%, or in a range of 5 wt.% to 95 wt.%, or in a range of 10 wt.% to 90 wt.%, or in a range of

15 wt.% to 85 wt.%, or in a range of 20 wt.% to 80 wt.%, or in a range of 25 wt.% to 75 wt.%, or in a range of 25 wt.% to 65 wt.%, or in a range of 25 wt.% to 55 wt.%. In some examples, the at least one crosslinker is present at 0.1 wt.%, or 0.2 wt.%, or 0.3 wt.%, or 0.5 wt.%, or 0.8 wt.%, or 1 wt.%, or 2 wt.%, or 3 wt.%, or 5 wt.%, or 10 wt.%, or 15 wt.%, or 20 wt.%, or 25 wt.%, or 30 wt.%, or 35 wt.%, or 40 wt.%, or 45 wt.%, or 50 wt.%, or 55 wt.%, or 60 wt.%, or 65 wt.%, or 70 wt.%, or 75 wt.%, or 80 wt.%, or 85 wt.%, or 90 wt.%, or 95 wt.%, or 99 wt.%, or any range defined by any two of those endpoints. In some examples, the at least one crosslinker comprises a first crosslinker and a second crosslinker, the first crosslinker being present in a range of 30 wt.% to 50 wt.% and the second crosslinker being present in a range of 0.5 wt.% to 25 wt.%.

[000101] In some examples, the at least one photoinitiator is present in a range of 0.1 wt.% to 10 wt.%; or in a range of 0.2 wt.% to 8 wt.%, or in a range of 0.3 wt.% to 6 wt.%, or in a range of 0.4 wt.% to 5 wt.%, or in a range of 0.5 wt.% to 4.5 wt.%, or in a range of 0.5 wt.% to 4 wt.%, or in a range of 0.6 wt.% to 3.5 wt.%, or in a range of 0.7 wt.% to 3 wt.%. In some examples, the at least one photoinitiator is present at 0.1 wt.%, or 0.2 wt.%, or 0.3 wt.%, or 0.4 wt.%, or 0.5 wt.%, or 0.6 wt.%, or 0.7 wt.%, or 0.8 wt.%, or 0.9 wt.%, or 1 wt.%, or 1.5 wt.%, or 2 wt.%, or 2.5 wt.%, or 3 wt.%, or 3.5 wt.%, or 4 wt.%, or 4.5 wt.%, or 5 wt.%, or 6 wt.%, or 7 wt.%, or 8 wt.%, or 9 wt.%, or 10 wt.%, or any range defined by any two of those endpoints.

[000102] In some examples, the at least one OSC polymer is present in a range of 1 wt.% to 99 wt.%; the at least one crosslinker is present in a range of 1 wt.% to 99 wt.%; and the at least one photoinitiator is present in a range of 0.1 wt.% to 10 wt.%. In some examples, the at least one OSC polymer is present in a range of 50 wt.% to 80 wt.%; and the at least one crosslinker is present in a range of 25 wt.% to 55 wt.%.

[000103] In some examples, the at least one antioxidant, lubricant, compatibilizer, leveling agent, or nucleating agent may each be present, independently, in a range of 0.05 wt.% to 5 wt.%, or in a range of 0.1 wt.% to 4.5 wt.%, or in a range of 0.2 wt.% to 4 wt.%, or in a range of 0.3 wt.% to 3.5 wt.%, or in a range of 0.4 wt.% to 3 wt.%, or in a range of 0.5 wt.% to 2.5 wt.%. In some examples, the at least one antioxidant, lubricant, compatibilizer, leveling agent, or nucleating agent may each be present, independently, at 0.05 wt.%, or 0.1 wt.%, or 0.2 wt.%, or 0.3 wt.%, or 0.4 wt.%, or 0.5 wt.%, or 0.6 wt.%, or 0.7 wt.%, or 0.8 wt.%, or 0.9 wt.%, or 1 wt.%, or 1.5

wt.%, or 2 wt.%, or 2.5 wt.%, or 3 wt.%, or 3.5 wt.%, or 4 wt.%, or 4.5 wt.%, or 5 wt.%, or any range defined by any two of those endpoints.

[000104] In some examples, the blend comprises at least two of: OSC polymers, crosslinkers, photoinitiators, and additives as described herein. In some examples, the blend comprises at least three of: OSC polymers, crosslinkers, photoinitiators, and additives as described herein. In some examples, the blend comprises at least four of: OSC polymers, crosslinkers, photoinitiators, and additives as described herein.

[000105] OTFT Device Fabrication

[000106] Applications using OTFT devices require patterning of organic semiconducting materials to prevent undesired high off-currents and crosstalk between adjacent devices. As explained above, photolithography is a common patterning technique in semiconductor device fabrication. However, photolithography usually involves harsh O_2 plasma during pattern transfer or photoresist removal and aggressive developing solvents which may severely damage the OSC layer and lead to significant deterioration of OTFT device performance. In other words, conjugated organic materials tend to degrade when exposed to light and the chemicals used in photolithography may have an adverse effect on organic thin film transistors. Therefore, patterning of organic semiconducting materials using photolithography is not practical. Moreover, currently available patternable semiconducting polymers with photosensitive side groups require time-consuming molecule design and synthesis. These crosslinked polymers may also have adverse effect on OTFT devices, due to reduction of the effective conjugation of the polymer's crosslinked backbone.

[000107] FIGS. 1A to 1E illustrate traditional patterning techniques 100 of organic semiconductor blends utilizing photoresists. In a first step (FIG. 1A), a thin film 104 of the blended OSC polymer is deposited over a substrate 102 followed by deposition of a photoresist layer 106 thereon in FIG. 1B. Optionally, the thin film 104 may be thermally annealed. The photoresist deposition may be conducted using processes known in the art such as spin coating. For example, the photoresist, rendered into a liquid form by dissolving the solid components in a solvent, is poured onto the substrate, which is then spun on a turntable at a high speed producing the desired film. Thereafter, the resulting resist film may experience a post-apply bake process (i.e., soft-bake or prebake) to dry the photoresist in removing excess solvent.

[000108] In the step of FIG. 1C, the photoresist layer 106 is exposed to UV light 112 through a master pattern called a photomask 108 positioned some distance away from the photoresist layer 106 to form a higher crosslinked portion 110 of the photoresist layer 106. The exposure to UV light operates to change the solubility of the photoresist in a subsequent developer solvent solution for pattern formation atop the substrate. Prior to the developer, the resist layer may experience a post exposure bake. In the step of FIG. 1D, the pattern 116 of the photoresist layer is transferred into the thin film 104 via subtractive etching 114 (i.e., O_2 plasma dry etching). The patterned photoresist layer 116 "resists" the etching and protects the material covered by the photoresist. When the etching is complete, the photoresist is stripped (e.g., using organic or inorganic solutions, and dry (plasma) stripping) leaving the desired pattern 118 etched into the thin film layer.

[000109] However, as explained above, aspects of traditional photolithography processes such as harsh O_2 plasma during pattern transfer and aggressive photoresist developer solvents and/or stripping solvents may severely damage the OSC layer and lead to significant deterioration of device performance.

[000110] FIGS. 2A to 2C illustrate patterning techniques 200 of organic semiconductor blends, according to some embodiments. In a first step (FIG. 2A), a thin film 204 of the blended OSC polymer is deposited over a substrate 202. Optionally, the thin film 204 may be thermally annealed. In some examples, depositing comprises at least one of spin coating; dip coating; spray coating; electrodeposition; meniscus coating; plasma deposition; and roller, curtain and extrusion coating.

[000111] The thin film 204 was prepared as a polymer blend described above comprising at least one organic semiconductor (OSC) polymer, at least one crosslinker, at least one photoinitiator, and optionally, at least one additive, wherein the at least one OSC polymer is a diketopyrrolopyrrole-fused thiophene polymeric material, wherein the fused thiophene is beta-substituted, and wherein the crosslinker includes at least one of: acrylates, epoxides, oxetanes, alkenes, alkynes, azides, thiols, allyloxysilanes, phenols, anhydrides, amines, cyanate esters, isocyanate esters, silyl hydrides, cinnamates, coumarins, fluorosulfates, silyl ethers, or a combination thereof.

[000112] In some examples, the blending includes dissolving the at least one OSC polymer in a first organic solvent to form a first solution, dissolving the at least one crosslinker in a second

organic solvent to form a second solution, and dissolving at least one photoinitiator in a third organic solvent to form a third solution; and combining the first, second, and third solutions in any suitable order to create the polymer blend. In some examples, the first, second, and third solutions may be combined simultaneously. In some examples, the at least one OSC polymer, at least one crosslinker, and at least one photoinitiator may be prepared together in a single organic solvent. The weight compositions of each component of the polymer blend is as provided above.

[000113] In some examples, after the thin film of the blended OSC polymer is deposited over the substrate and before exposing the thin film to UV light, the thin film may be heated at a temperature in a range of 50°C to 200°C for a time in a range of 10 sec to 10 min to remove excess solvent.

[000114] In a second step (FIG. 2B), the thin film 204 was exposed to UV light 208 through a photomask 206 to form a higher crosslinked portion 210 of the thin film 204. In some examples, the exposing comprises exposing the thin film to UV light having an energy in a range of 10 mJ/cm^2 to 600 mJ/cm^2 (e.g., 400 mJ/cm^2) for a time in a range of 1 sec to 60 sec (e.g., 10 sec). In some examples, the UV light may have an energy in a range of 300 mJ/cm^2 to 500 mJ/cm^2 and be operable for a time in a range of 5 sec to 20 sec. Similar to photoresist functionality described in FIGS. 1A to 1E, the exposure to UV light operates to change the solubility of the thin film in a subsequent developer solvent solution for pattern formation atop the substrate.

[000115] In the step of FIG. 2C, when light exposure is complete, the portion of the thin film 204 not exposed to UV light 208 was stripped using a predetermined solvent 212, thereby leaving the desired pattern 214 into the thin film layer. In other words, the higher crosslinked portion 210 was developed in a solvent to remove an un-patterned region of the thin film 204. In some examples, the developing comprises exposing the un-patterned region of the thin film to a solvent comprising chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,2,4-trichlorobenzene, dioxane, p-xylene, m-xylene, toluene, cyclopentanone, cyclohexanone, methyl lactate, 2-butanone, 2-pentanone, 3-pentanone, 2-heptanone, 3-heptanone, anisole, mesitylene, decalin, butylbenzene, cyclooctane, tetralin, chloroform, or combinations thereof, for a time in a range of 10 sec to 10 min. In some examples, the developer solution comprises chlorobenzene, p-xylene, dioxane, or combinations thereof.

[000116] In some examples, after developing the patterned thin film in a solvent to remove the un-patterned region of the thin film, the thin film may be heated at a temperature in a range of 50°C to 200°C for a time in a range of 10 sec to 30 min.

[000117] Thereafter, the OTFT devices may be completed by forming a gate electrode over the substrate; forming a gate dielectric layer over the substrate; forming patterned source and drain electrodes over the gate dielectric layer; forming an organic semiconductor active layer over the and gate dielectric layer, and forming an insulator layer over the patterned organic semiconductor active layer. (FIGS. 3 and 4).

EXAMPLES

[000118] The embodiments described herein will be further clarified by the following examples.

[000119] **Example 1**

[000120] Example 1 is based on the OFET structure as shown in FIG. 3. FIGS. 5-6D illustrate I_d-V_g curves of test OFET devices prepared with formulations shown in Table 3 below. The on/off ratio is approximately 10^4, with turn-on voltages ranging from 0V and 10V. FIG. 5 and corresponding data demonstrate high UV patterning efficiency of the fundamental formulation, as well as satisfactory device performance based thereon. FIGS 6A and 6B demonstrate an importance of crosslinker C5; higher ratios of C5 in the formulation improved 'On' current. FIGS 6C and 6D demonstrate an importance of the photoinitiator; higher ratios of photoinitiator in the formulation improved 'On' current.

FIG.	OSC Polymer (wt.%)	Crosslinker 1 (wt.%)	Crosslinker 2 (wt.%)	Photoinitiator (wt.%)	'On' Current (nA) (Vg = -15V)
5	Formula 5 (14.73) Formula 4 (34.38)	Vinyl-terminating (49.12)	C5 (0.98)	P5 (0.79)	353 – 945
6A	Formula 5 (14.73) Formula 4 (34.38)	Vinyl-terminating (49.12)	C5 (0.98)	P5 (0.79)	154 – 188
6B	Formula 5 (14.59) Formula 4 (34.04)	Vinyl-terminating (48.64)	C5 (1.95)	P5 (0.78)	147 – 300
6C	Formula 5 (14.56) Formula 4 (33.98)	Vinyl-terminating (48.55)	C5 (0.97)	P3 (1.94)	42 – 165

6D	Formula 5 (14.42) Formula 4 (33.65)	Vinyl-terminating (48.08)	C5 (0.96)	P3 (2.89)	113 – 245

Table 3

[000121] Example 2

[000122] Example 2 is based on the OFET structure as shown in FIG. 3. FIGS. 7A-8 illustrate I_d-V_g curves of test OFET devices prepared with formulations shown in Table 4 below. The on/off ratio is approximately 10^4, with turn-on voltages ranging from 0V and 5V. Moreover, the 'on' current (V_g = -15V) are between 400 nA and 500 nA. The difference between the formulation in FIG. 7B and the formulation in FIG. 7D is dissolution solvent, with FIG. 7B solvent being double the concentration of chlorobenzene (20 mg/ml) than the FIG. 7D solvent (10 mg/ml). FIGS. 7A and 7B and corresponding data demonstrate robustness of the UV patterning formulation with respect to the purity of the vinyl-terminating Crosslinker 1 (from Table 4). FIGS. 7A and 7D and corresponding data demonstrate the importance of solution concentrations. Device performance, especially 'On' current, is very sensitive to the concentration of spin-coating solutions. FIGS. 7A, 7C and 8 and corresponding data demonstrate the high efficiency of the UV patterning formulation. With decreased amount of vinyl-terminating Crosslinker 1, 'On' current remains high.

FIG.	OSC Polymer (wt.%)	Crosslinker 1 (wt.%)	Crosslinker 2 (wt.%)	Photoinitiator (wt.%)
7A	Formula 5 (14.42) Formula 4 (33.65)	Vinyl-terminating (48.08) (80% purity)	C5 (0.96)	P3 (2.89)
7B		Vinyl-terminating (48.08) (95% purity)		
7C	Formula 5 (17.31) Formula 4 (40.38)	Vinyl-terminating (38.46) (95% purity)		
7D	Formula 5 (14.42) Formula 4 (33.65)	Vinyl-terminating (48.08) (95% purity)		

8	Formula 5 (20.19) Formula 4 (47.11)	Vinyl-terminating (28.85) (95% purity)		

Table 4

[000123] Example 3

[000124] Example 3 is based on the OFET structure as shown in FIG. 4. FIGS. 9A-9C illustrate I_d-V_g curves of test OFET devices prepared with formulations shown in Table 5 below. The on/off ratio is approximately 10^3, with turn-on voltages ranging from 6V and 16V. Moreover, the 'on' current (V_g = -15V) are between 800 nA and 850 nA. FIGS. 9A and 9B and corresponding data demonstrate functional OFET device based on cationic-based UV patternable OSC blends. FIG. 9C demonstrates that photoinitiators are not compulsory components in UV patterning formulations.

FIG.	OSC Polymer (wt.%)	Crosslinker 1 (wt.%)	Crosslinker 2 (wt.%)	Photoinitiator (wt.%)
9A	Formula 4 (48)	C37 (49)	N/A	P10 (3)
9B		C38 (49)		
9C	Formula 4 (50)	C30 (50)		N/A

Table 5

[000125] Example 4

[000126] Example 4 is based on the OFET structure as shown in FIG. 4. FIGS. 10A-10D illustrate I_d-V_g curves of test OFET devices prepared with formulations shown in Table 6 below. The on/off ratio is approximately 10^2, with turn-on voltages ranging from 14V and 17V. Moreover, the 'on' current (V_g = -15V) are between 2.37 μA and 3.33 μA. As stated earlier, FIGS. 10A to 10D and corresponding data demonstrate that methods disclosed herein are also applicable to OFET devices based on the structure shown in FIG. 4.

FIG.	OSC Polymer (wt.%)	Crosslinker 1 (wt.%)	Crosslinker 2 (wt.%)	Photoinitiator (wt.%)
10A	Formula 4 (50)	Vinyl-terminating (48.2)	C5 (1)	P5 (0.8)

10B	Formula 4 (60)	Vinyl-terminating (38.2)		
10C	Formula 4 (70)	Vinyl-terminating (28.2)		
10D	Formula 4 (80)	Vinyl-terminating (18.2)		

Table 6

[000127] Example 5

[000128] General manufacturing procedure for OTFT device

[000129] In some examples, a bottom gate, bottom contact OTFT device can be formed as following: patterning a gold (Au) or silver (Ag) gate electrode onto a substrate, followed by spin-coating a dielectric onto the substrate and treating to obtain a gate dielectric layer. After patterning Au or Ag source and drain electrodes, an OSC layer may be formed by the materials and methods of patterning as described herein to a thickness in a range of 10 nm to 200 nm. Finally, an insulator layer was positioned. One example of the formed OTFT device is shown in FIG. 3.

[000130] Example 6

[000131] FIG. 11A to 11D illustrate confocal laser scanning microscope (CLSM) images of OSC polymer blends (FIGS. 11A and 11B) and OSC polymer/crosslinker blends (FIGS. 11C and 11D). Specifically, FIGS. 11A and 11B show OSC polymer blend layers before and after developing, respectively, while FIGS. 11C and 11D show OSC polymer/crosslinker blend layers before and after developing, respectively.

[000132] Compared with UV-curable OSC polymeric blends with polymers as doping partners, OSC polymer/crosslinker blends, as disclosed herein, possess a much smoother film surface, as well as significantly improved phase separation, leading to better and more stable patterning effects and OFET performance.

[000133] Thus, as presented herein, improved UV patternable organic semiconductor/crosslinker polymer blends and use thereof for OSC layers of organic thin-film transistors are disclosed.

[000134] Advantages of the UV patternable organic semiconductor/crosslinker polymer blends include: (1) compared with UV-curable OSC polymeric blends with polymers as doping partners (FIGS. 11A and 11B), OSC polymer/crosslinker blends (FIGS. 11C and 11D), as disclosed

herein, possess a much smoother film surface, as well as significantly improved phase separation, leading to better and more stable patterning effects and OFET performance; (2) comparing with traditional photolithography (FIGS. 1A-1E), the disclosed patterning method (FIGS. 2A-2C) is less complex and does not require photoresists or aggressive developing solvents, thereby leading to less damage to OSC materials and better OFET device performance; (3) compared with conventional inkjet printing techniques, the disclosed patterning method provides better resolutions (up to several microns) with higher accuracy and efficiency; (4) compared with UV-curable OSC polymeric blends, which require challenging synthesis techniques to incorporate the UV-curable functionality into the OSC polymer, the disclosed OSC polymer/crosslinker blends avoid time-consuming synthetic development; and (5) the disclosed UV patterning method, either based on radical photoinitiators or cationic photoinitiators, can be carried out in air, which allows for low cost OFET devices based on patterned OSC films.

[000135] As utilized herein, the terms "approximately," "about," "substantially", and similar terms are intended to have a broad meaning in harmony with the common and accepted usage by those of ordinary skill in the art to which the subject matter of this disclosure pertains. It should be understood by those of skill in the art who review this disclosure that these terms are intended to allow a description of certain features described and claimed without restricting the scope of these features to the precise numerical ranges provided. Accordingly, these terms should be interpreted as indicating that insubstantial or inconsequential modifications or alterations of the subject matter described and claimed are considered to be within the scope of the invention as recited in the appended claims.

[000136] As utilized herein, "optional," "optionally," or the like are intended to mean that the subsequently described event or circumstance can or cannot occur, and that the description includes instances where the event or circumstance occurs and instances where it does not occur. The indefinite article "a" or "an" and its corresponding definite article "the" as used herein means at least one, or one or more, unless specified otherwise.

[000137] References herein to the positions of elements (e.g., "top," "bottom," "above," "below," etc.) are merely used to describe the orientation of various elements in the FIGURES. It should be noted that the orientation of various elements may differ according to other exemplary embodiments, and that such variations are intended to be encompassed by the present disclosure.

[000138] With respect to the use of substantially any plural and/or singular terms herein, those having skill in the art can translate from the plural to the singular and/or from the singular to the plural as is appropriate to the context and/or application. The various singular/plural permutations may be expressly set forth herein for the sake of clarity.

[000139] It will be apparent to those skilled in the art that various modifications and variations can be made without departing from the spirit or scope of the claimed subject matter. Accordingly, the claimed subject matter is not to be restricted except in light of the attached claims and their equivalents.

WHAT IS CLAIMED IS:

1. A polymer blend, comprising:

at least one organic semiconductor (OSC) polymer and at least one crosslinker,

wherein the at least one OSC polymer is a diketopyrrolopyrrole-fused thiophene polymeric material, wherein the fused thiophene is beta-substituted, and

wherein the crosslinker includes at least one of: acrylates, epoxides, oxetanes, alkenes, alkynes, azides, thiols, allyloxysilanes, phenols, anhydrides, amines, cyanate esters, isocyanate esters, silyl hydrides, cinnamates, coumarins, fluorosulfates, silyl ethers, or a combination thereof.

2. The polymer blend of claim 1, wherein:

the at least one OSC polymer is present in a range of 1 wt.% to 99 wt.%; and

the at least one crosslinker is present in a range of 1 wt.% to 99 wt.%.

3. The polymer blend of claim 1 or claim 2, wherein:

the at least one OSC polymer is present in a range of 50 wt.% to 80 wt.%; and

the at least one crosslinker is present in a range of 25 wt.% to 55 wt.%.

4. The polymer blend of any one of claims 1-3, wherein the at least one crosslinker comprises a first crosslinker and a second crosslinker, the first crosslinker being present in a range of 30 wt.% to 50 wt.% and the second crosslinker being present in a range of 0.5 wt.% to 25 wt.%.

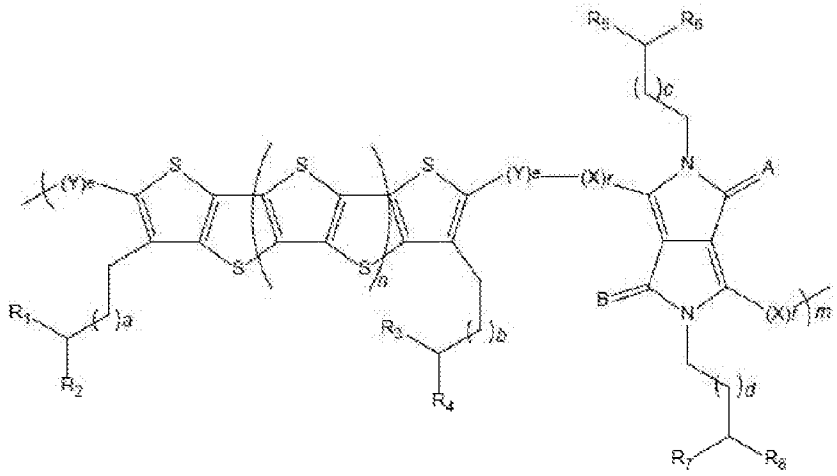
5. The polymer blend of any one of claims 1-4, further comprising: at least one photoinitiator, wherein the at least one photoinitiator is present in a range of 0.1 wt.% to 10 wt.%.

6. The polymer blend of claim 5, wherein the at least one photoinitiator is present in a range of 0.1 wt.% to 5.0 wt.%.

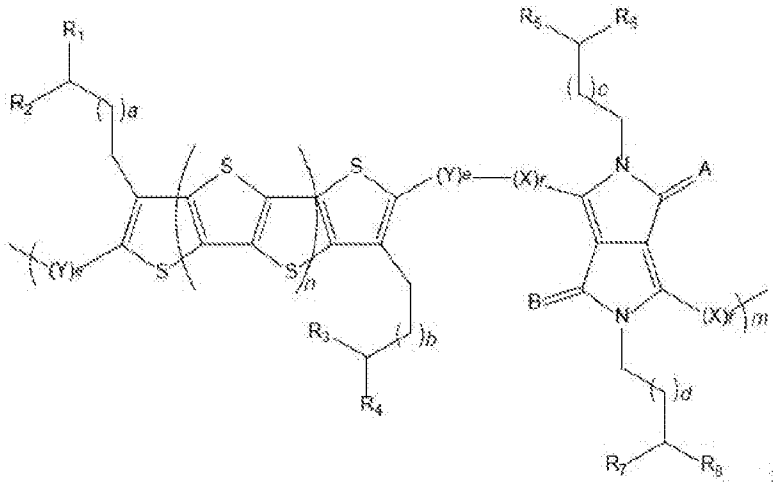
7. The polymer blend of any one of claims 1-6, further comprising:

at least one of antioxidants, lubricants, compatibilizers, leveling agents, or nucleating agents present in a range of 0.05 wt.% to 5 wt.%.

8. The polymer blend of any one of claims 1-7, wherein the at least one OSC polymer comprises the repeat unit of Formula 1 or Formula 2, or a salt, isomer, or analog thereof:



Formula 1



Formula 2

wherein in Formula 1 and Formula 2:

m is an integer greater than or equal to one;

n is 0, 1, or 2;

R_1, R_2, R_3, R_4, R_5, R_6, R_7, and R_8, may be, independently, hydrogen, substituted or unsubstituted C_4 or greater alkyl, substituted or unsubstituted C_4 or greater alkenyl, substituted or unsubstituted C_4 or greater alkynyl, or C_5 or greater cycloalkyl;

a, b, c, and d are independently, integers greater than or equal to 3;

e and f are integers greater than or equal to zero;

X and Y are, independently a covalent bond, an optionally substituted aryl group, an optionally substituted heteroaryl, an optionally substituted fused aryl or fused heteroaryl group, an alkyne or an alkene; and

A and B may be, independently, either S or O, with the provisos that:

i. at least one of R_1 or R_2; one of R_3 or R_4; one of R_5 or R_6; and one of R_7 or R_8 is a substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, or cycloalkyl;

ii. if any of R_1, R_2, R_3, or R_4 is hydrogen, then none of R_5, R_6, R_7, or R_8 are hydrogen;

iii. if any of R_5, R_6, R_7, or R_8 is hydrogen, then none of R_1, R_2, R_3, or R_4 are hydrogen;

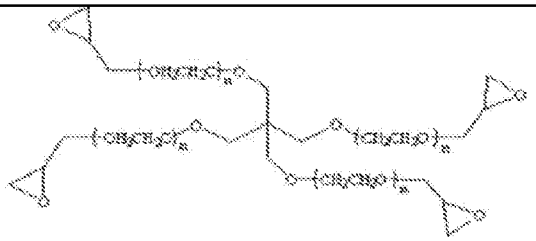
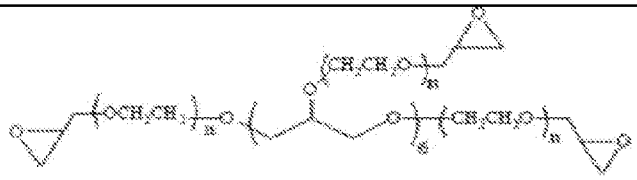
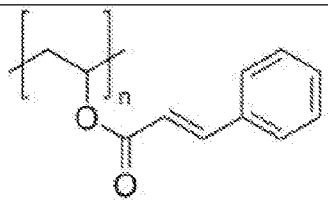
iv. e and f cannot both be 0;

v. if either e or f is 0, then c and d, independently, are integers greater than or equal to 5; and

vi. the polymer having a molecular weight, wherein the molecular weight of the polymer is greater than 10,000.

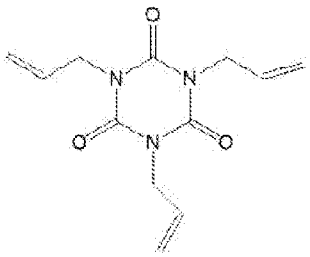
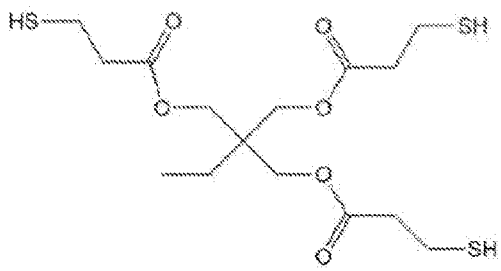
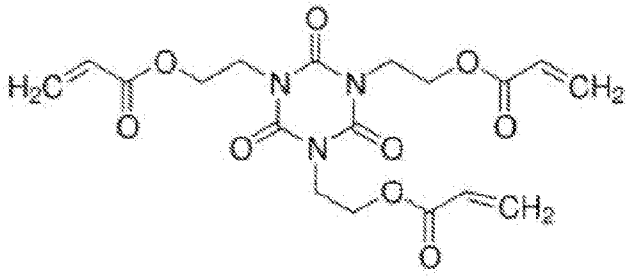
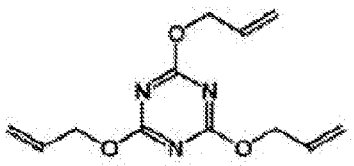
9. The polymer blend of any one of claims 1-8, wherein the at least one crosslinker comprises at least one of:

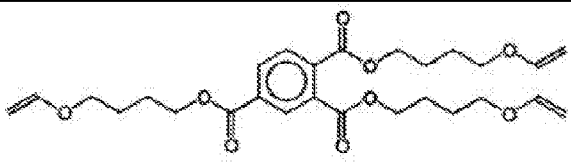
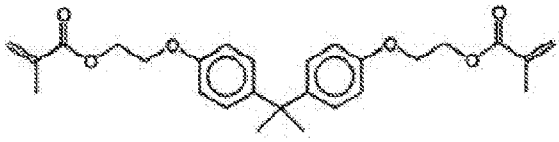
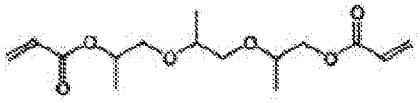
(A) a polymer selected from:

 C1	 C2
 C3	

wherein n is an integer greater than or equal to two, or

(B) a small-molecule selected from:

 C4	 C5
 C6	 C7

 C8	 C9
 C10	 C11
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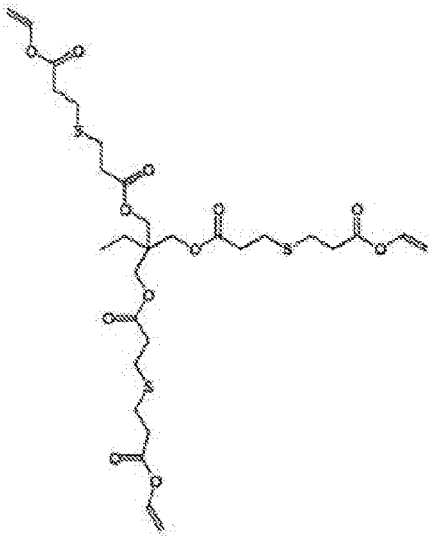
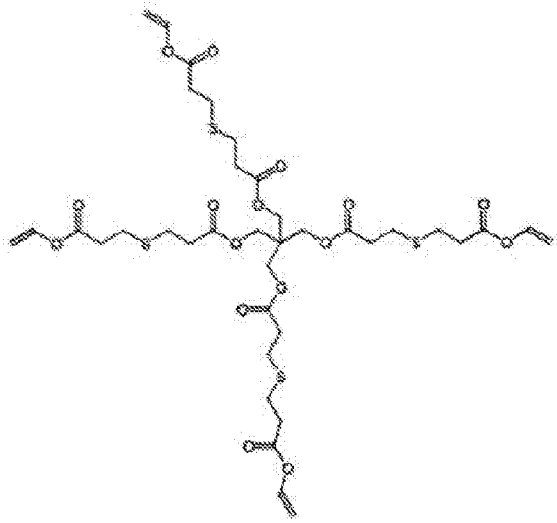
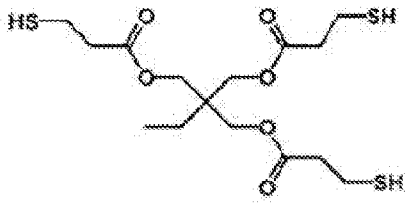
 C13	 C14



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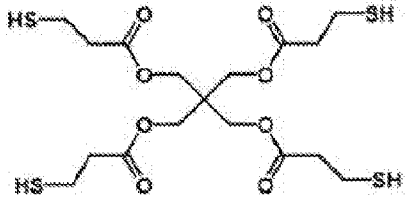

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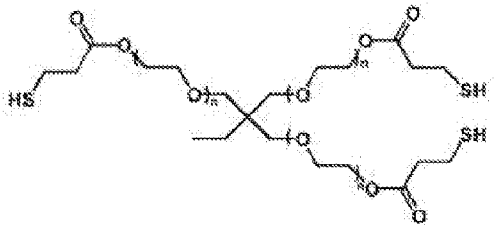

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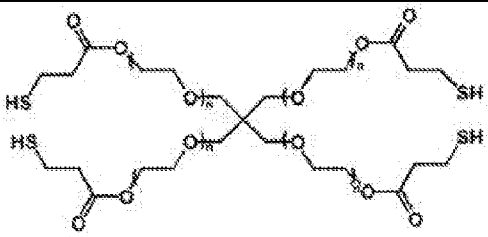

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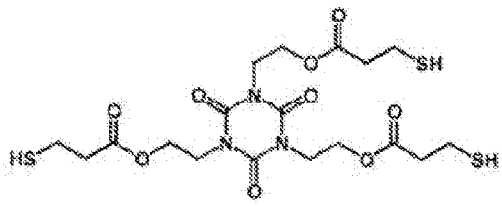

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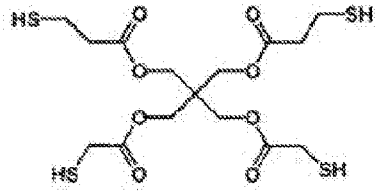

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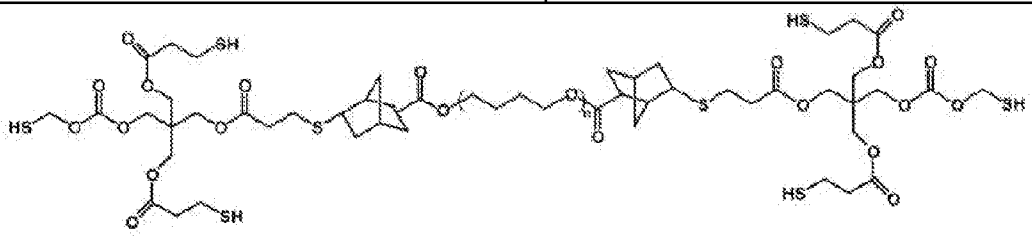

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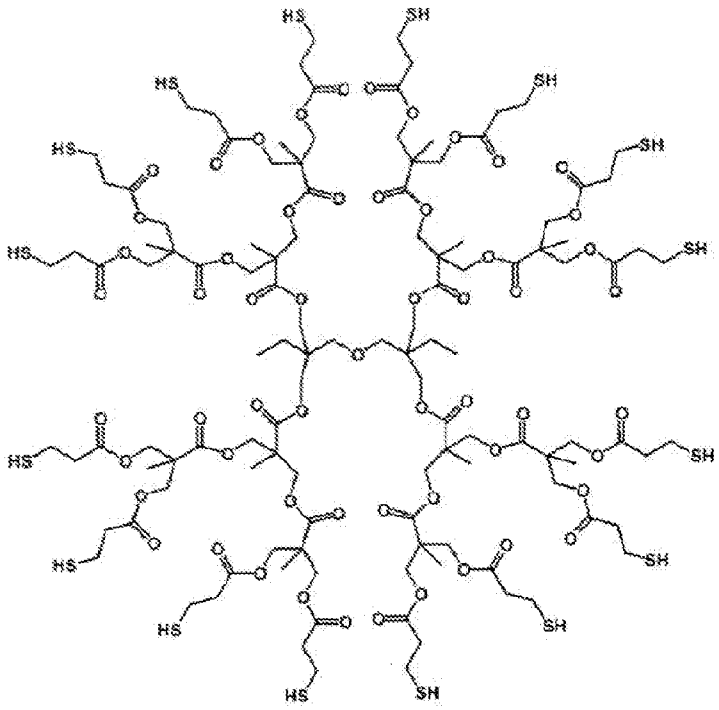

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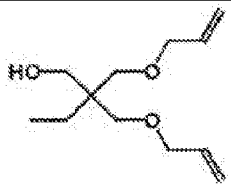

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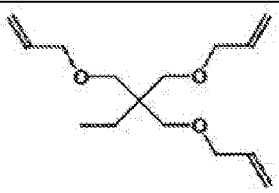

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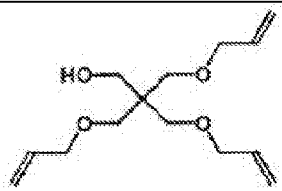

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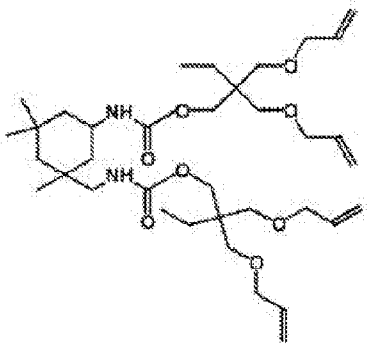

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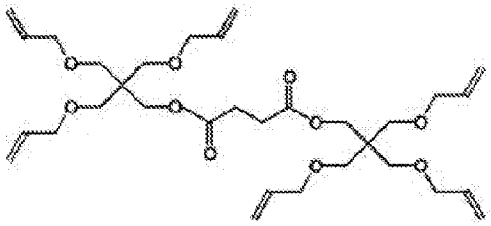

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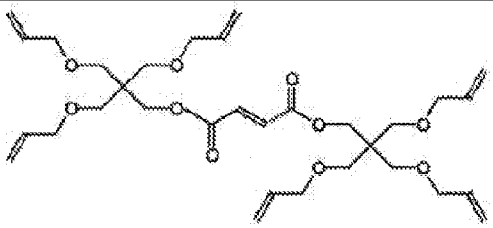

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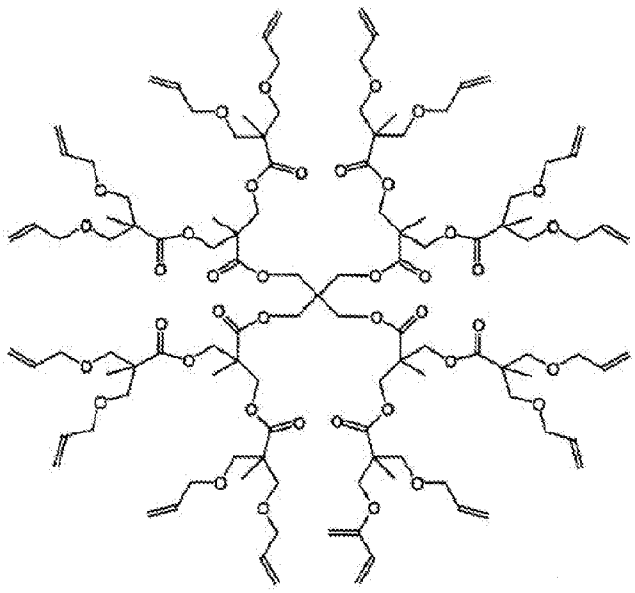

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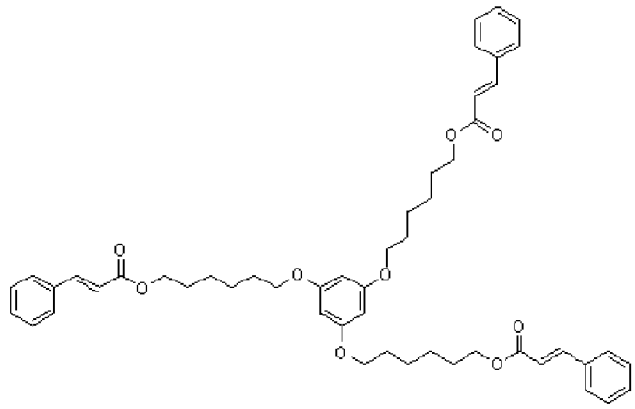

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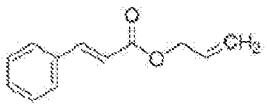

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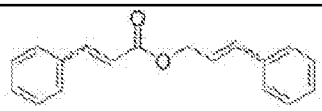

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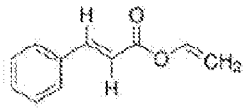

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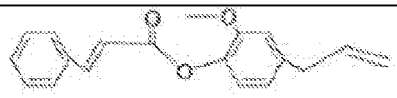

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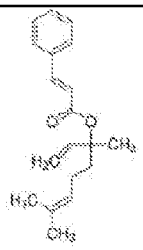
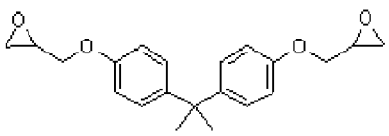


C35

C36



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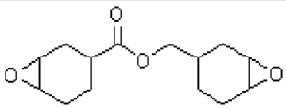

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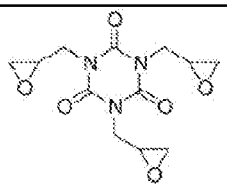
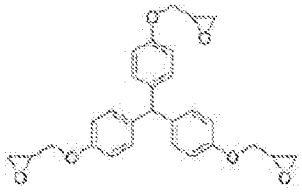
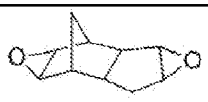
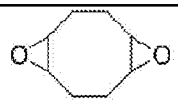
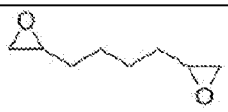
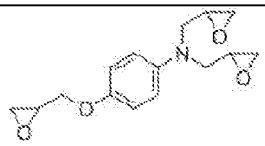
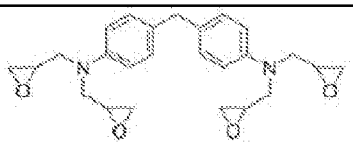
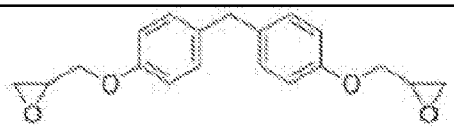
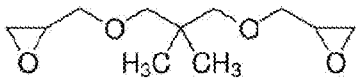
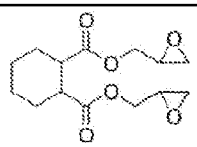
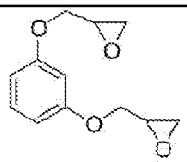
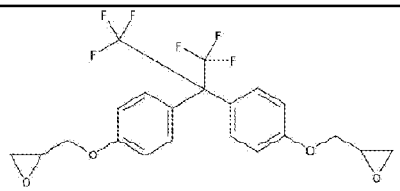
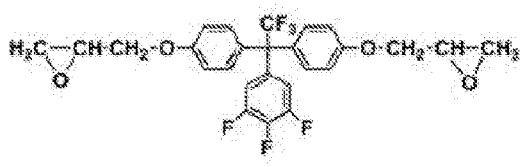
 C39	 C40
 C41	 C42
 C43	 C44
 C45	 C46
 C47	 C48
 C49	 C50



C51

or,

(C) a combination thereof.

10. The polymer blend of claim 5, wherein the at least one photoinitiator comprises at least one free radical photoinitiator.

11. The polymer blend of claim 5, wherein the at least one photoinitiator comprises at least one cationic photoinitiator.

12. The polymer blend of claim 5, wherein the at least one photoinitiator comprises: 1-hydroxy-cyclohexyl-phenyl-ketone (184); 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1 (369); diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO); 2-isopropyl thioxanthone (ITX); 1-[4-(phenylthio) phenyl]-1,2-octanedione 2-(O-benzoyloxime) (HRCURE-OXE01); 2,2-dimethoxy-1,2-diphenylethan-1-one (BDK); benzoyl peroxide (BPO); hydroxyacetophenone (HAP); 2-hydroxy-2-methylprophenone (1173); 2-methyl-4'-(methylthio)-2-morpholinopropiophenone (907); 2-benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone (IHT-PI 910); Ethyl-4-(dimethylamino)benzoate (EDB); methyl o-benzoyl benzoate (OMBB); bis-(2,6 dimethoxy-benzoyl)-phenyl phosphine oxide (BAPO); 4-benzoyl-4' methyldiphenylsulfide (BMS); benzophenone (BP); 1-chloro-4-propoxy thiozanthone (CPTX); chlorothioxanthone (CTX); 2,2-diethoxyacetophenone (DEAP); diethyl thioxanthone (DETX); 2-dimethyl aminoethyl benzonate (DMB); 2,2-dimethoxy-2-phenyl acetophenone (DMPA); 2-ethyl anthraquinone (2-EA); ethyl-para-N,N-dimethyl-dimethylamino lenzoate (EDAB); 2-ethyl hexyl-dimethylaminolenzoate (EHA); 4,4-bis-(diethylamino)-benzophenone (EMK); methyl benzophenone (MBF); 4-methyl benzophenone (MBP); Michler's ketone (MK); 2-methyl-1-[4(methylthiol)phenyl]-2-morpholino propanone (1) (MMMP); 4-phenylbenzophenone (PBZ);

2,4,6-trimethyl-benzoly-ethoxyl phenyl phosphine oxide (TEPO); bis(4-tert-butylphenyl) iodonium perfluoro-1-butanesulfonate; bis(4-tert-butylphenyl) iodonium p-toluenesulfonate; bis(4-tert-butylphenyl) iodonium triflate; boc-methoxyphenyldiphenylsulfonium triflate; (4-tert-Butylphenyl) diphenylsulfonium triflate; diphenyliodonium hexafluorophosphate; diphenyliodonium nitrate; diphenyliodonium p-toluenesulfonate; diphenyliodonium triflate; (4-fluorophenyl) diphenylsulfonium triflate; N-hydroxynaphthalimide triflate; N-hydroxy-5-norbornene-2,3-dicarboximide perfluoro-1-butanesulfonate; (4-iodophenyl) diphenylsulfonium triflate; (4-methoxyphenyl) diphenylsulfonium triflate; 2-(4-Methoxystyryl)-4,6-bis (trichloromethyl)-1,3,5-triazine; (4-methylthiophenyl) methyl phenyl sulfonium triflate; 1-naphthyl diphenylsulfonium triflate; (4-phenoxyphenyl) diphenylsulfonium triflate; (4-phenylthiophenyl) diphenylsulfonium triflate; triarylsulfonium hexafluoroantimonate salts, mixed 50 wt.% in propylene carbonate; triarylsulfonium hexafluorophosphate salts, mixed 50 wt.% in propylene carbonate; triphenylsulfonium perfluoro-1-butanesufonate; triphenylsulfonium triflate; tris(4-tert-butylphenyl) sulfonium perfluoro-1-butanesulfonate; tris(4-tert-butylphenyl)sulfonium triflate; aryl diazo salts; diaryliodonium salts; triaryl sulfonium salts; aryl ferrocenium salts; or combinations thereof.

13. The polymer blend of any one of claims 1-12, wherein the at least one crosslinker comprises C=C bonds, thiols, oxetanes, halides, azides, or combinations thereof.

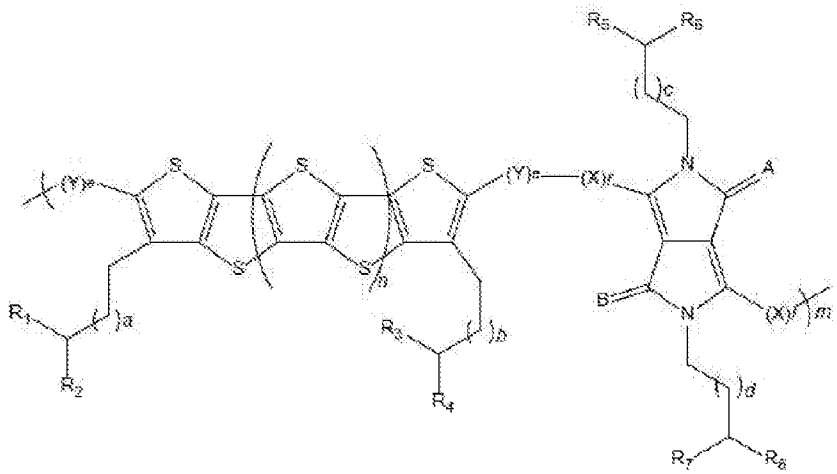
14. A polymer blend, consisting of:

at least one organic semiconductor (OSC) polymer and at least one crosslinker,

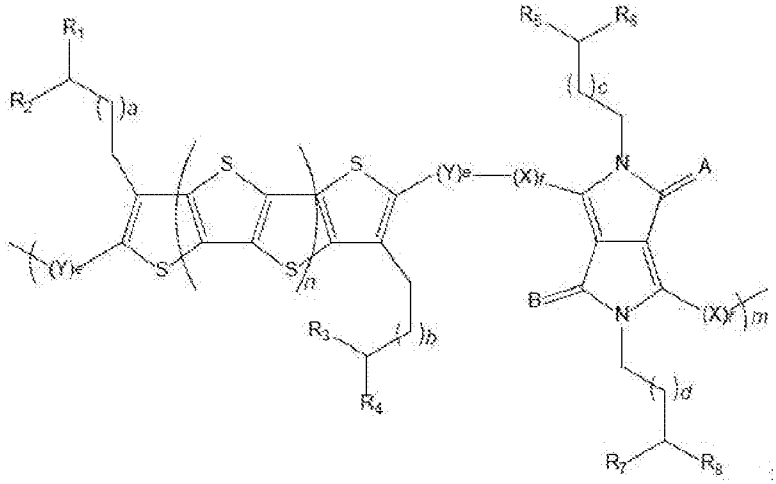
wherein the at least one OSC polymer is a diketopyrrolopyrrole-fused thiophene polymeric material, wherein the fused thiophene is beta-substituted,

wherein the crosslinker includes at least one of: acrylates, epoxides, oxetanes, alkenes, alkynes, azides, thiols, allyloxysilanes, phenols, anhydrides, amines, cyanate esters, isocyanate esters, silyl hydrides, cinnamates, coumarins, fluorosulfates, silyl ethers, or a combination thereof.

15. The polymer blend of claim 14, wherein the at least one OSC polymer comprises the repeat unit of Formula 1 or Formula 2, or a salt, isomer, or analog thereof:



Formula 1



Formula 2

wherein in Formula 1 and Formula 2:

m is an integer greater than or equal to one;

n is 0, 1, or 2;

R_1, R_2, R_3, R_4, R_5, R_6, R_7, and R_8, may be, independently, hydrogen, substituted or unsubstituted C_4 or greater alkyl, substituted or unsubstituted C_4 or greater alkenyl, substituted or unsubstituted C_4 or greater alkynyl, or C_5 or greater cycloalkyl;

a, b, c, and d are independently, integers greater than or equal to 3;

e and f are integers greater than or equal to zero;

X and Y are, independently a covalent bond, an optionally substituted aryl group, an optionally substituted heteroaryl, an optionally substituted fused aryl or fused heteroaryl group, an alkyne or an alkene; and

A and B may be, independently, either S or O, with the provisos that:

i. at least one of R_1 or R_2; one of R_3 or R_4; one of R_5 or R_6; and one of R_7 or R_8 is a substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, or cycloalkyl;

ii. if any of R_1, R_2, R_3, or R_4 is hydrogen, then none of R_5, R_6, R_7, or R_8 are hydrogen;

iii. if any of R_5, R_6, R_7, or R_8 is hydrogen, then none of R_1, R_2, R_3, or R_4 are hydrogen;

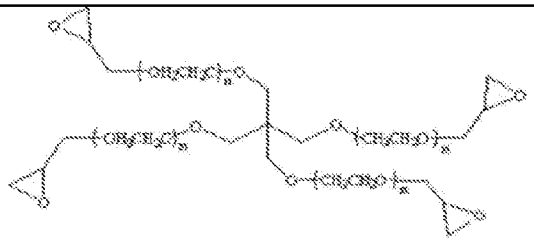
iv. e and f cannot both be 0;

v. if either e or f is 0, then c and d, independently, are integers greater than or equal to 5; and

vi. the polymer having a molecular weight, wherein the molecular weight of the polymer is greater than 10,000.

16. The polymer blend of claim 14 or claim 15, wherein the at least one crosslinker comprises at least one of:

(A) a polymer selected from:



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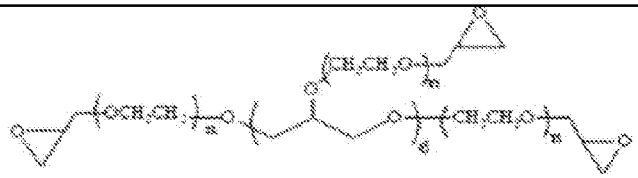

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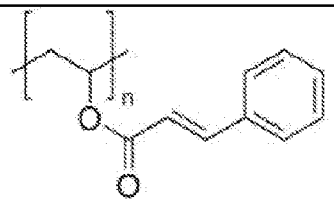
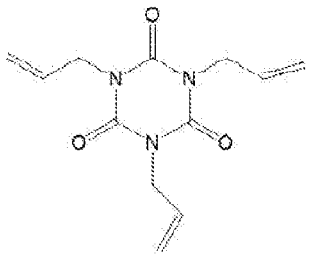
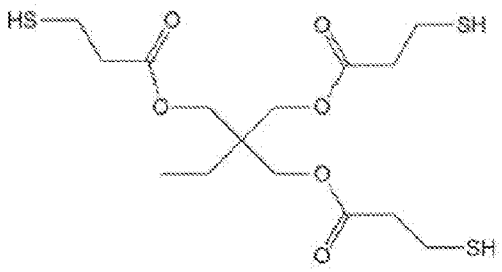
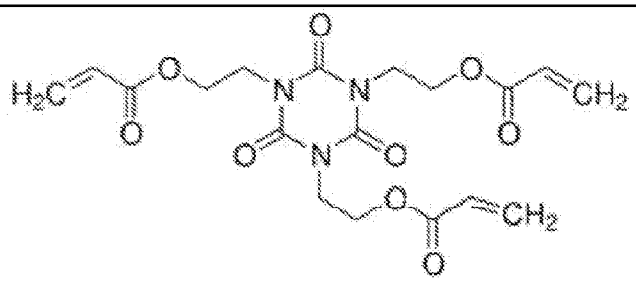
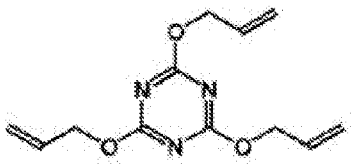
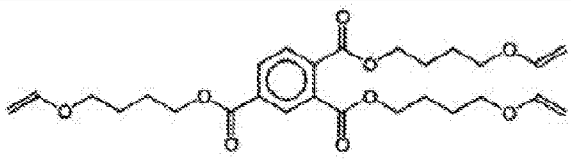
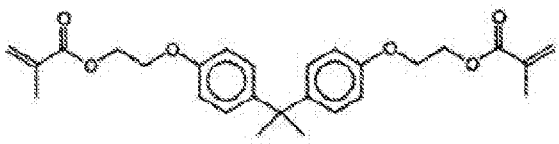
 C3	

wherein n is an integer greater than or equal to two, or

(B) a small-molecule selected from:

 C4	 C5
 C6	 C7
 C8	 C9

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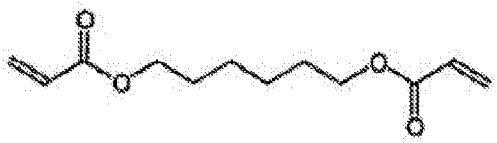

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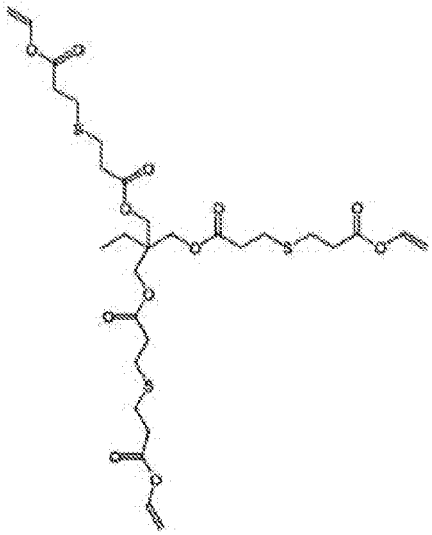

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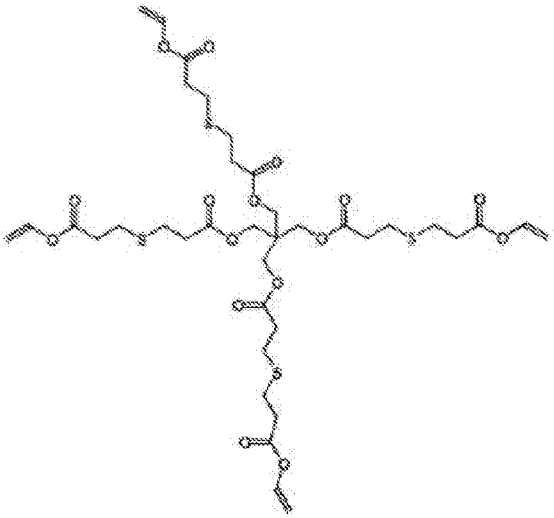

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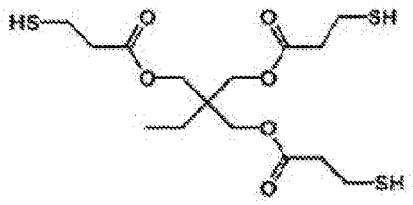

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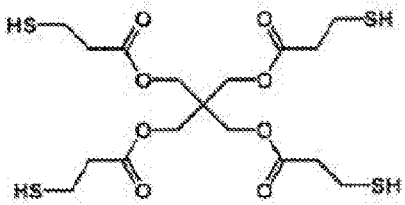

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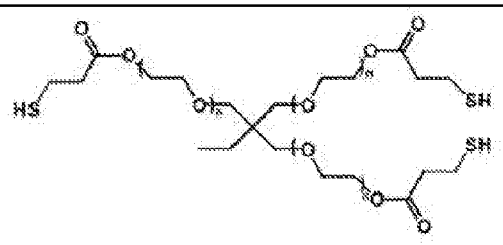

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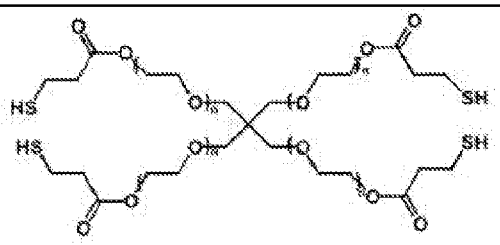

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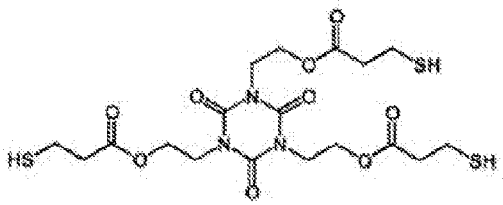

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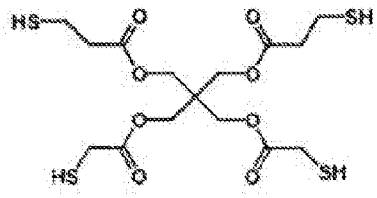

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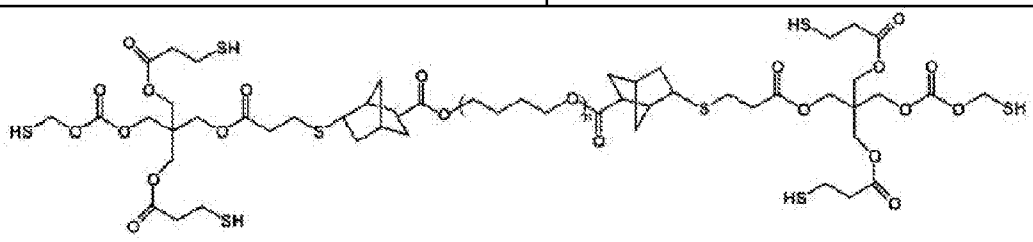

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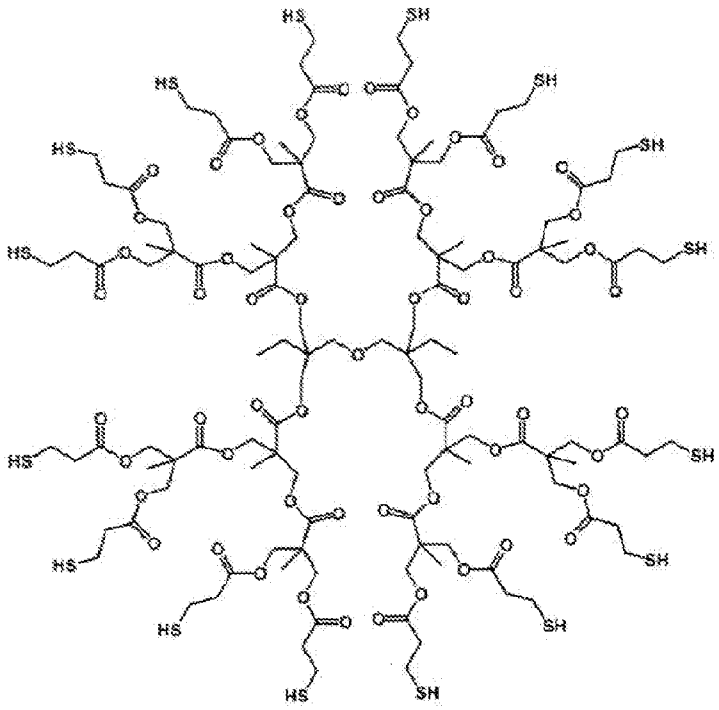

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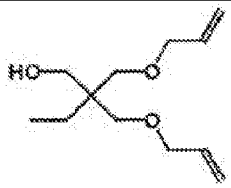

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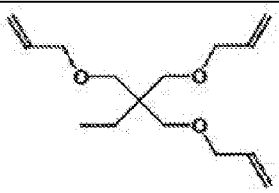

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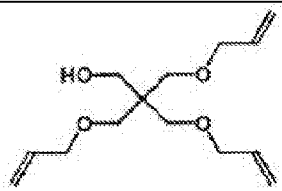

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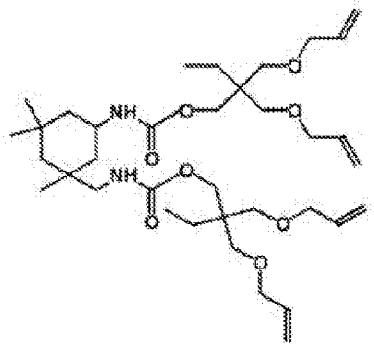

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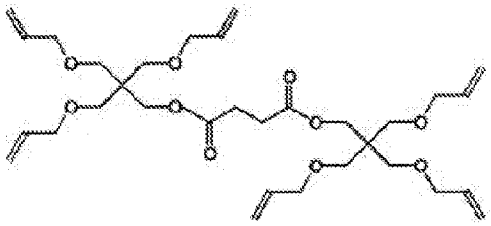

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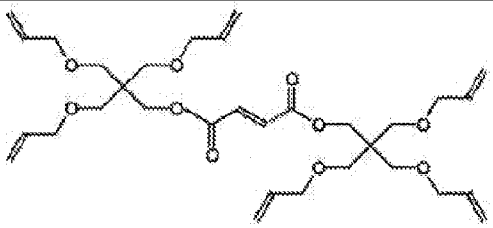

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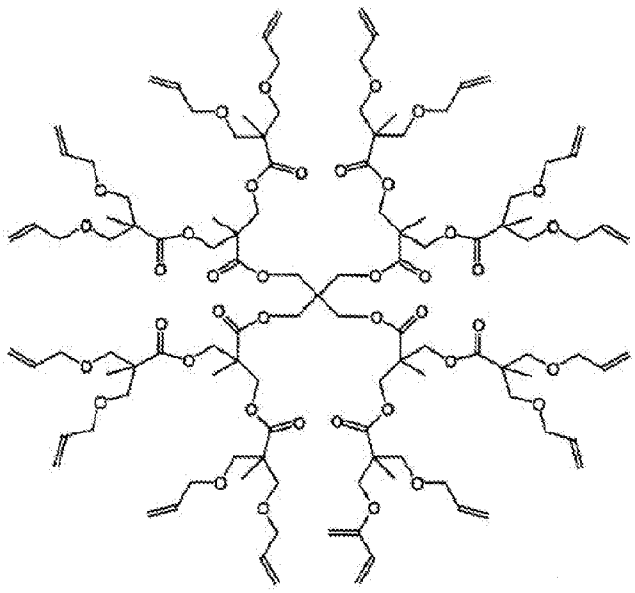

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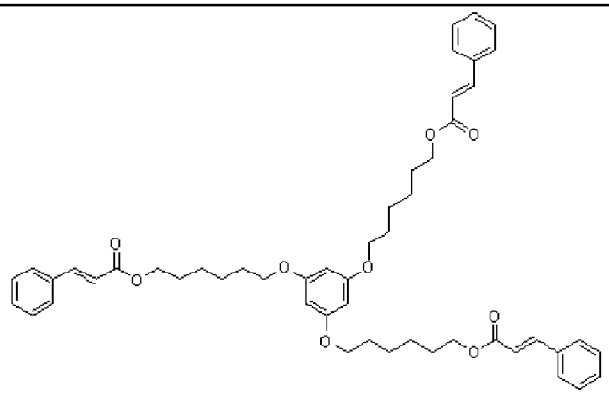
<tr><td colspan="2"> 
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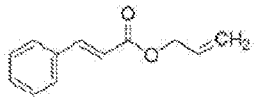
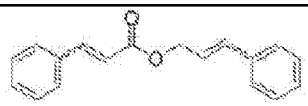
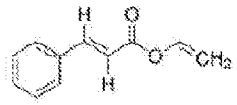
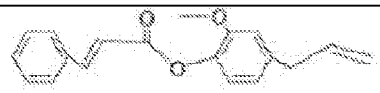
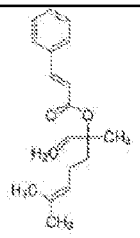
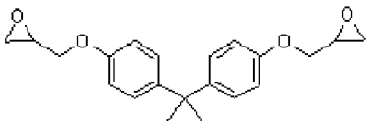
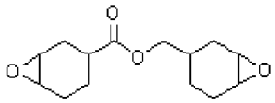
<tr><td> 
C31</td><td> 
C32</td></tr>
<tr><td> 
C33</td><td> 
C34</td></tr>
<tr><td> 
C35</td><td> 
C36</td></tr>
<tr><td> 
C37</td><td> 
C38</td></tr>
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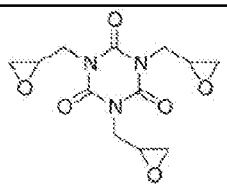
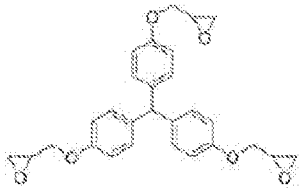
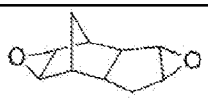
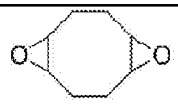
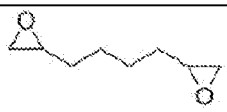
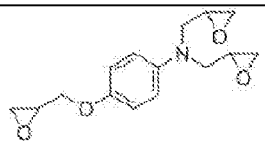
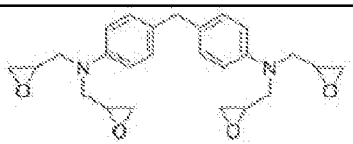
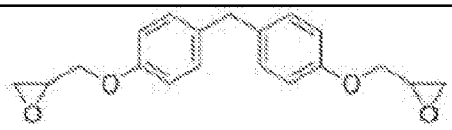
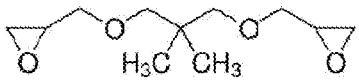
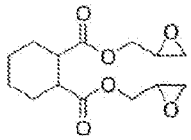
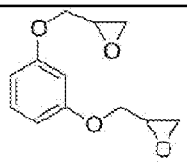
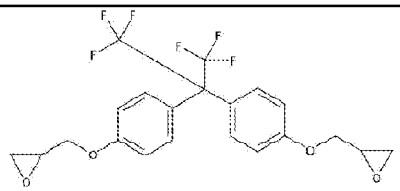
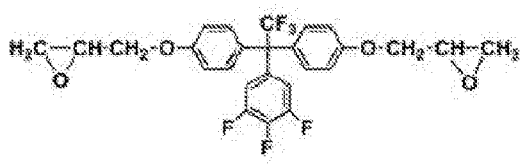
 C39	 C40
 C41	 C42
 C43	 C44
 C45	 C46
 C47	 C48
 C49	 C50



C51

or,

(C) a combination thereof.

17. The polymer blend of any one of claims 14-16, further comprising at least one photoinitiator.

18. The polymer blend of claim 17, wherein the at least one photoinitiator comprises: 1-hydroxy-cyclohexyl-phenyl-ketone (184); 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1 (369); diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO); 2-isopropyl thioxanthone (ITX); 1-[4-(phenylthio) phenyl]-1,2-octanedione 2-(O-benzoyloxime) (HRCURE-OXE01); 2,2-dimethoxy-1,2-diphenylethan-1-one (BDK); benzoyl peroxide (BPO); hydroxyacetophenone (HAP); 2-hydroxy-2-methylprophenone (1173); 2-methyl-4'-(methylthio)-2-morpholinopropiophenone (907); 2-benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone (IHT-PI 910); Ethyl-4-(dimethylamino)benzoate (EDB); methyl o-benzoyl benzoate (OMBB); bis-(2,6 dimethoxy-benzoyl)-phenyl phosphine oxide (BAPO); 4-benzoyl-4' methyldiphenylsulfide (BMS); benzophenone (BP); 1-chloro-4-propoxy thiozanthone (CPTX); chlorothioxanthone (CTX); 2,2-diethoxyacetophenone (DEAP); diethyl thioxanthone (DETX); 2-dimethyl aminoethyl benzonate (DMB); 2,2-dimethoxy-2-phenyl acetophenone (DMPA); 2-ethyl anthraquinone (2-EA); ethyl-para-N,N-dimethyl-dimethylamino lenzoate (EDAB); 2-ethyl hexyl-dimethylaminolenzoate (EHA); 4,4-bis-(diethylamino)-benzophenone (EMK); methyl benzophenone (MBF); 4-methyl benzophenone (MBP); Michler's ketone (MK); 2-methyl-1-[4(methylthiol)phenyl]-2-morpholino propanone (1) (MMMP); 4-phenylbenzophenone (PBZ); 2,4,6-trimethyl-benzoly-ethoxyl phenyl phosphine oxide (TEPO); bis(4-tert-butylphenyl) iodonium perfluoro-1-butanesulfonate; bis(4-tert-butylphenyl) iodonium p-toluenesulfonate; bis(4-tert-butylphenyl) iodonium triflate; boc-methoxyphenyldiphenylsulfonium triflate; (4-tert-

Butylphenyl) diphenylsulfonium triflate; diphenyliodonium hexafluorophosphate; diphenyliodonium nitrate; diphenyliodonium p-toluenesulfonate; diphenyliodonium triflate; (4-fluorophenyl) diphenylsulfonium triflate; N-hydroxynaphthalimide triflate; N-hydroxy-5-norbornene-2,3-dicarboximide perfluoro-1-butanesulfonate; (4-iodophenyl) diphenylsulfonium triflate; (4-methoxyphenyl) diphenylsulfonium triflate; 2-(4-Methoxystyryl)-4,6-bis (trichloromethyl)-1,3,5-triazine; (4-methylthiophenyl) methyl phenyl sulfonium triflate; 1-naphthyl diphenylsulfonium triflate; (4-phenoxyphenyl) diphenylsulfonium triflate; (4-phenylthiophenyl) diphenylsulfonium triflate; triarylsulfonium hexafluoroantimonate salts, mixed 50 wt.% in propylene carbonate; triarylsulfonium hexafluorophosphate salts, mixed 50 wt.% in propylene carbonate; triphenylsulfonium perfluoro-1-butanesufonate; triphenylsulfonium triflate; tris(4-tert-butylphenyl) sulfonium perfluoro-1-butanesulfonate; tris(4-tert-butylphenyl)sulfonium triflate; aryl diazo salts; diaryliodonium salts; triaryl sulfonium salts; aryl ferrocenium salts; or combinations thereof.

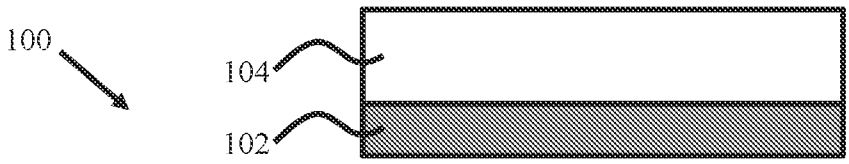


FIG. 1A

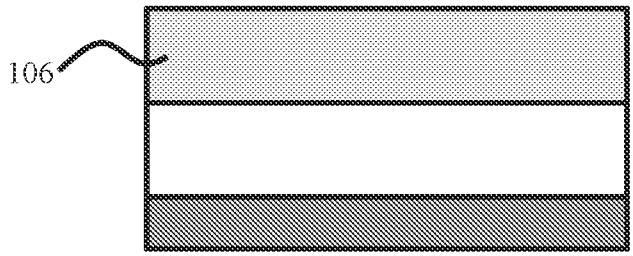
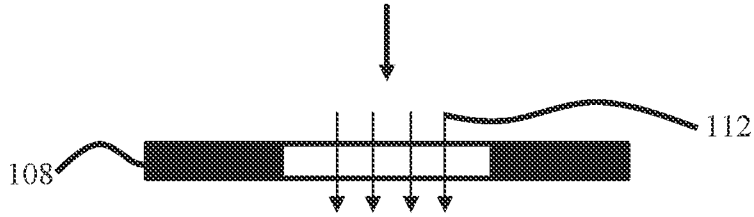


FIG. 1B



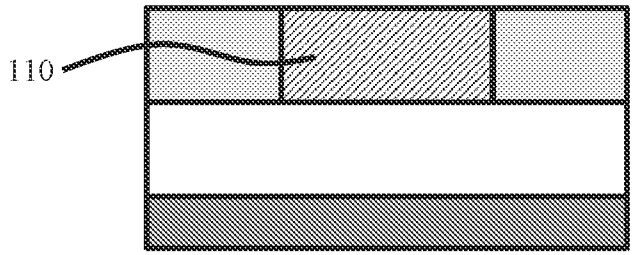


FIG. 1C

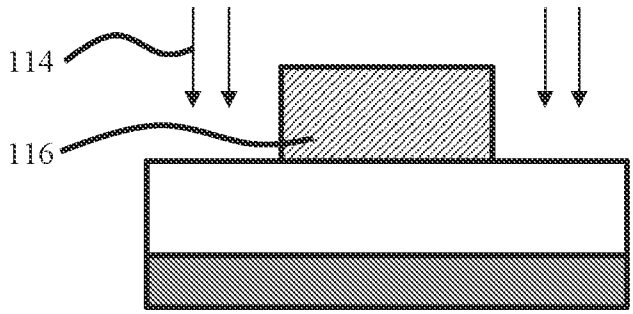


FIG. 1D

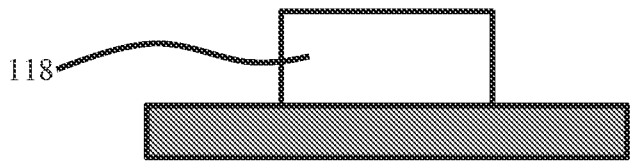


FIG. 1E

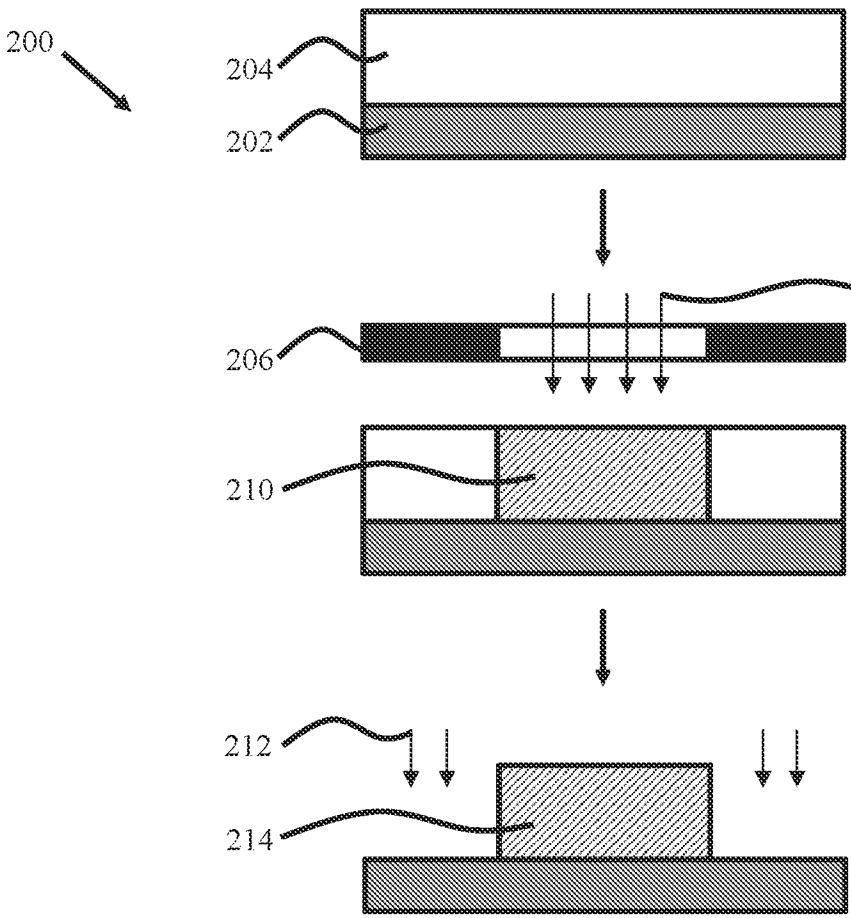


FIG. 2A

FIG. 2B

FIG. 2C

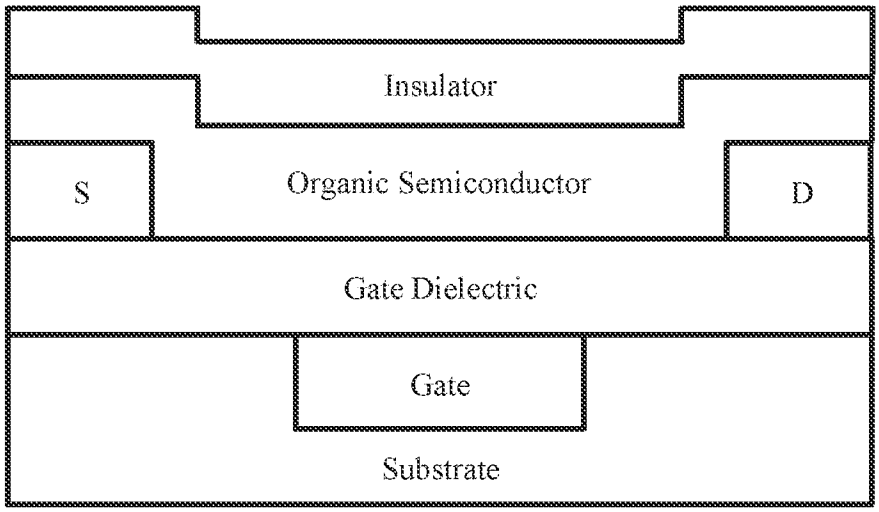

Insulator
S
Organic Semiconductor
D
Gate Dielectric
Gate
Substrate

FIG. 3

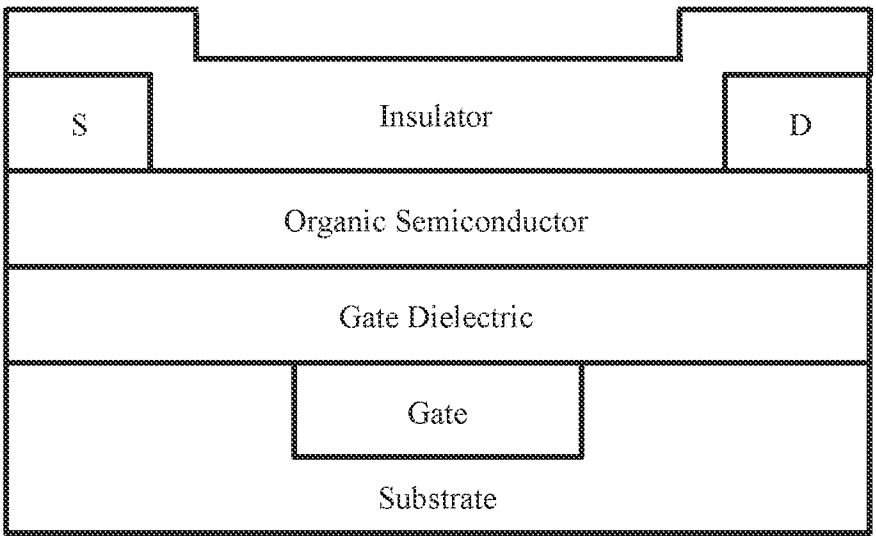

S
Insulator
D
Organic Semiconductor
Gate Dielectric
Gate
Substrate

FIG. 4

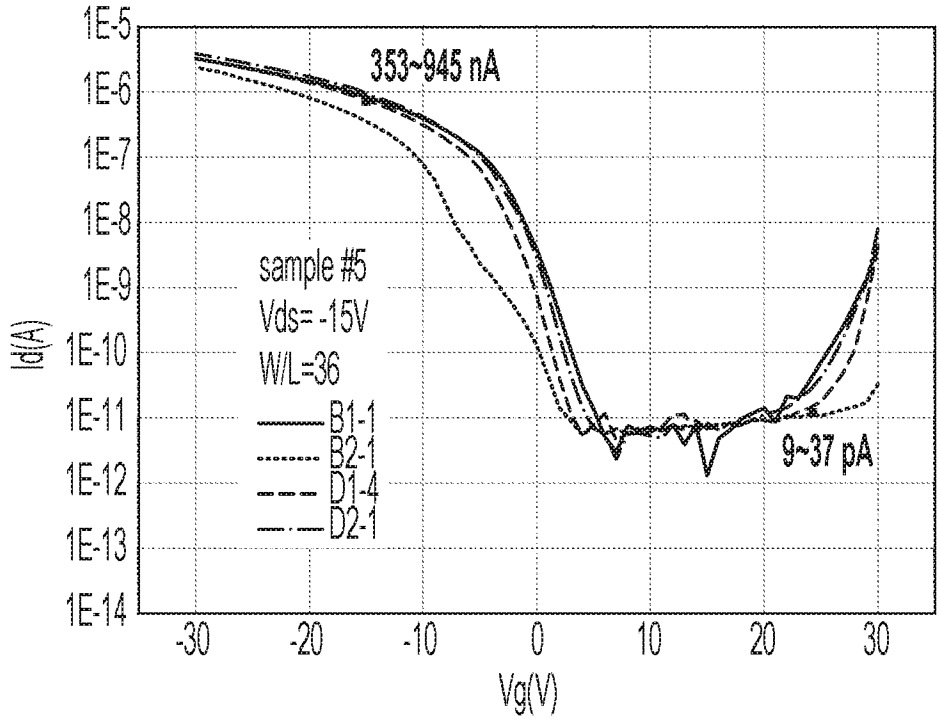

1E-5
1E-6
1E-7
1E-8
1E-9
1E-10
1E-11
1E-12
1E-13
1E-14
Id(A)
353~945 nA
sample #5
Vds= -15V
W/L=36
B1-1
B2-1
D1-4
D2-1
9~37 pA
-30
-20
-10
0
10
20
30
Vg(V)

FIG. 5

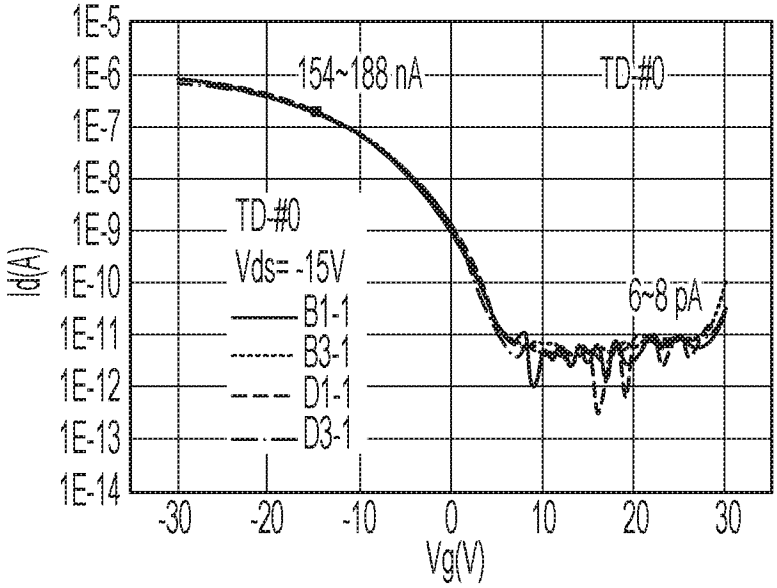


FIG. 6A

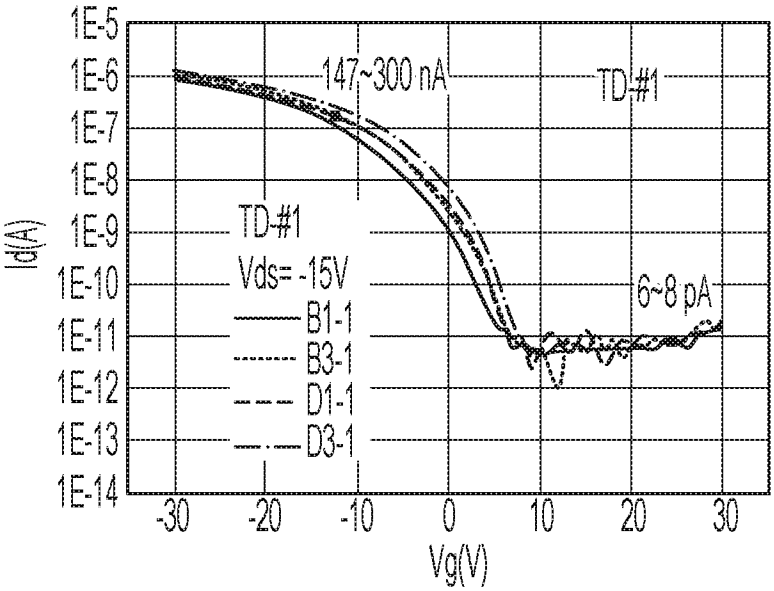


FIG. 6B

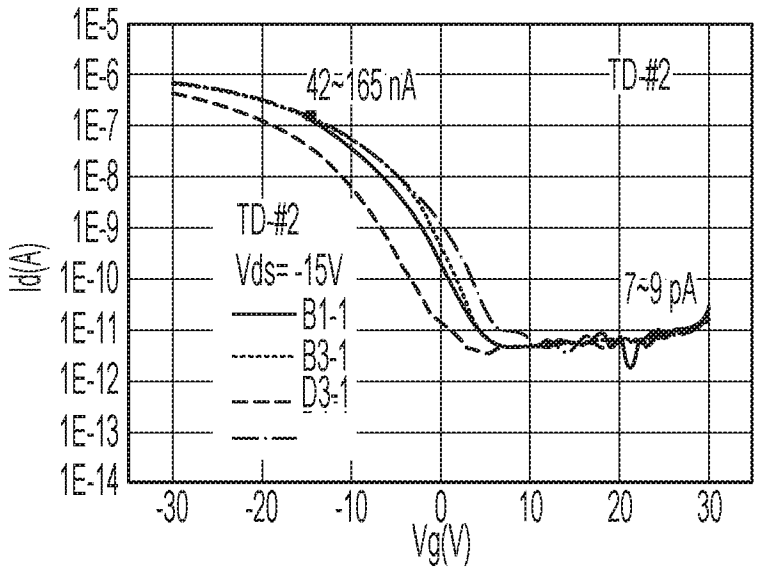


FIG. 6C

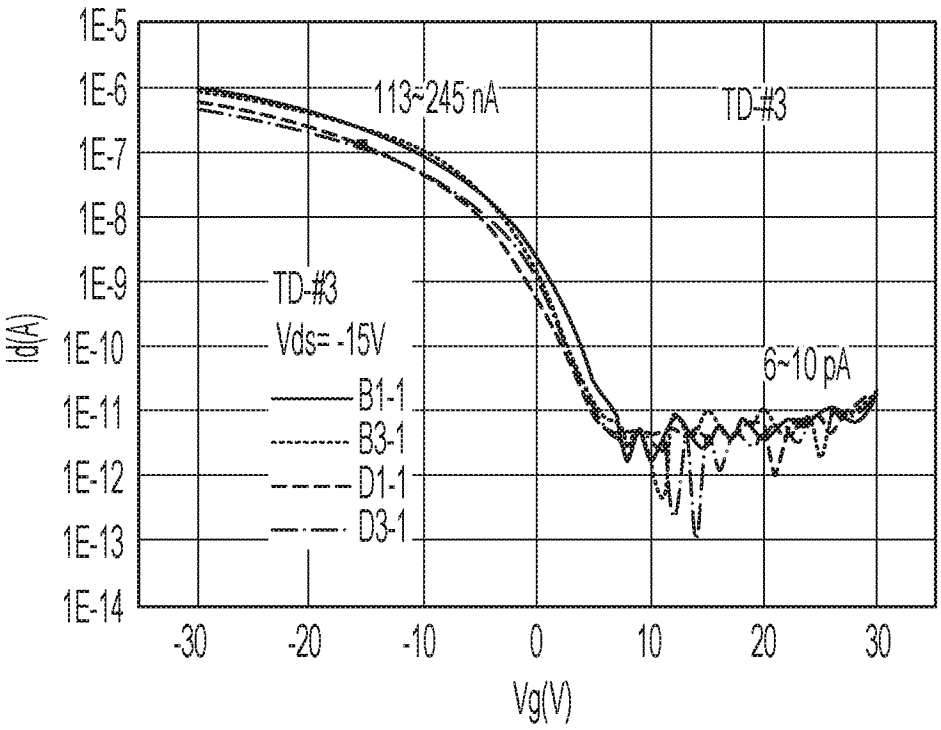

1E-5
1E-6
1E-7
1E-8
1E-9
1E-10
1E-11
1E-12
1E-13
1E-14
Id(A)
113~245 nA
TD=#3
TD-#3
Vds= -15V
B1-1
B3-1
D1-1
D3-1
6~10 pA
-30
-20
-10
0
10
20
30
Vg(V)

FIG. 6D

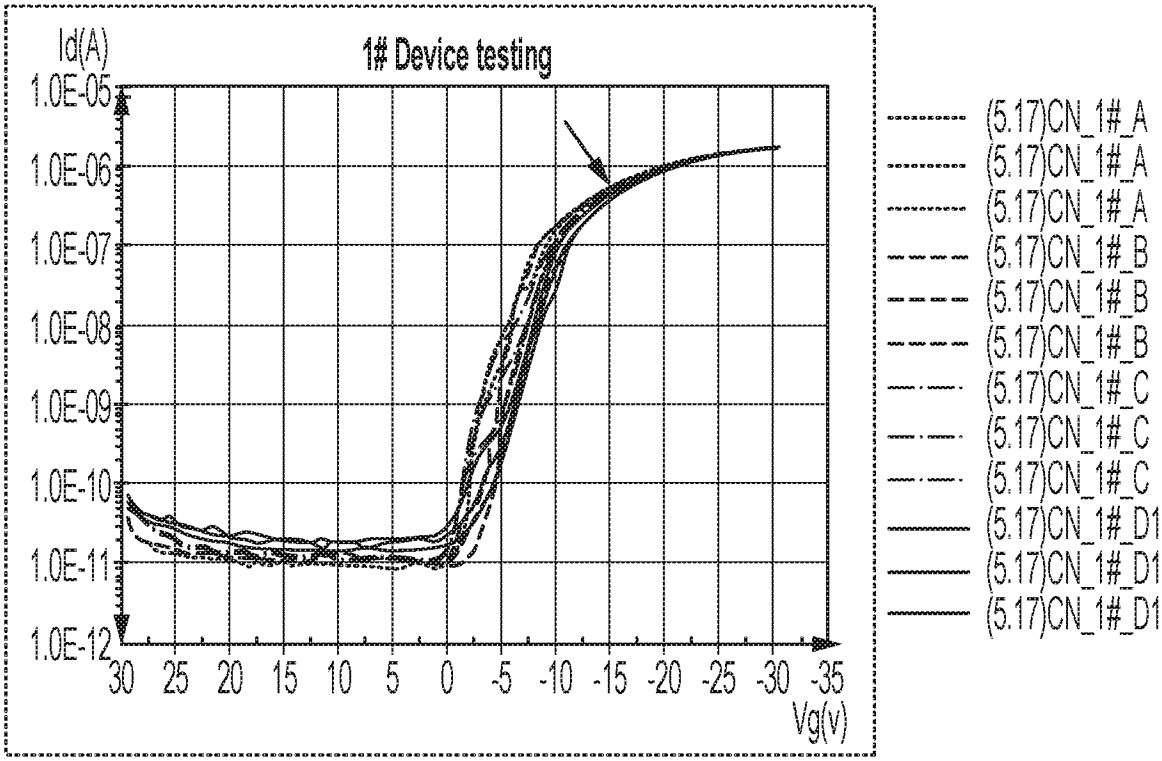

Id(A)
1# Device testing
1.0E-05
1.0E-06
1.0E-07
1.0E-08
1.0E-09
1.0E-10
1.0E-11
1.0E-12
30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35
Vg(v)
(5.17)CN_1#_A
(5.17)CN_1#_A
(5.17)CN_1#_A
(5.17)CN_1#_B
(5.17)CN_1#_B
(5.17)CN_1#_B
(5.17)CN_1#_C
(5.17)CN_1#_C
(5.17)CN_1#_C
(5.17)CN_1#_D1
(5.17)CN_1#_D1
(5.17)CN_1#_D1

FIG. 7A

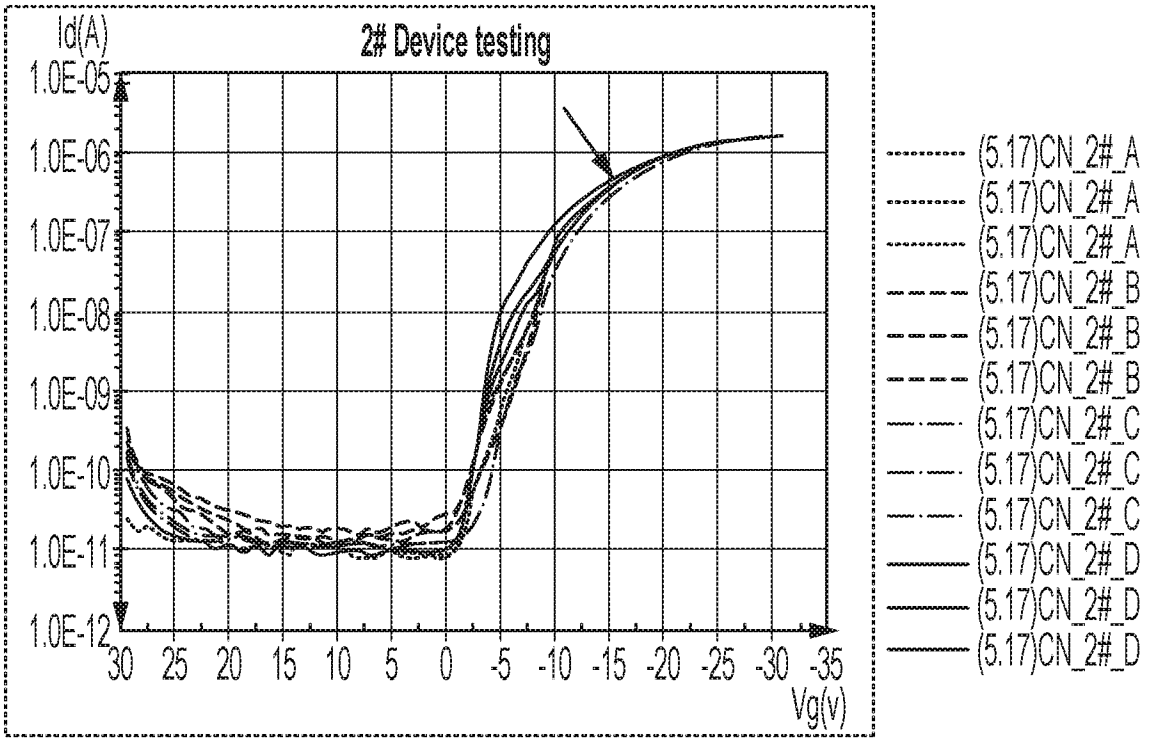

Id(A)
2# Device testing
1.0E-05
1.0E-06
1.0E-07
1.0E-08
1.0E-09
1.0E-10
1.0E-11
1.0E-12
30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35
Vg(v)
(5.17)CN_2#_A
(5.17)CN_2#_A
(5.17)CN_2#_A
(5.17)CN_2#_B
(5.17)CN_2#_B
(5.17)CN_2#_B
(5.17)CN_2#_C
(5.17)CN_2#_C
(5.17)CN_2#_C
(5.17)CN_2#_D
(5.17)CN_2#_D
(5.17)CN_2#_D

FIG. 7B

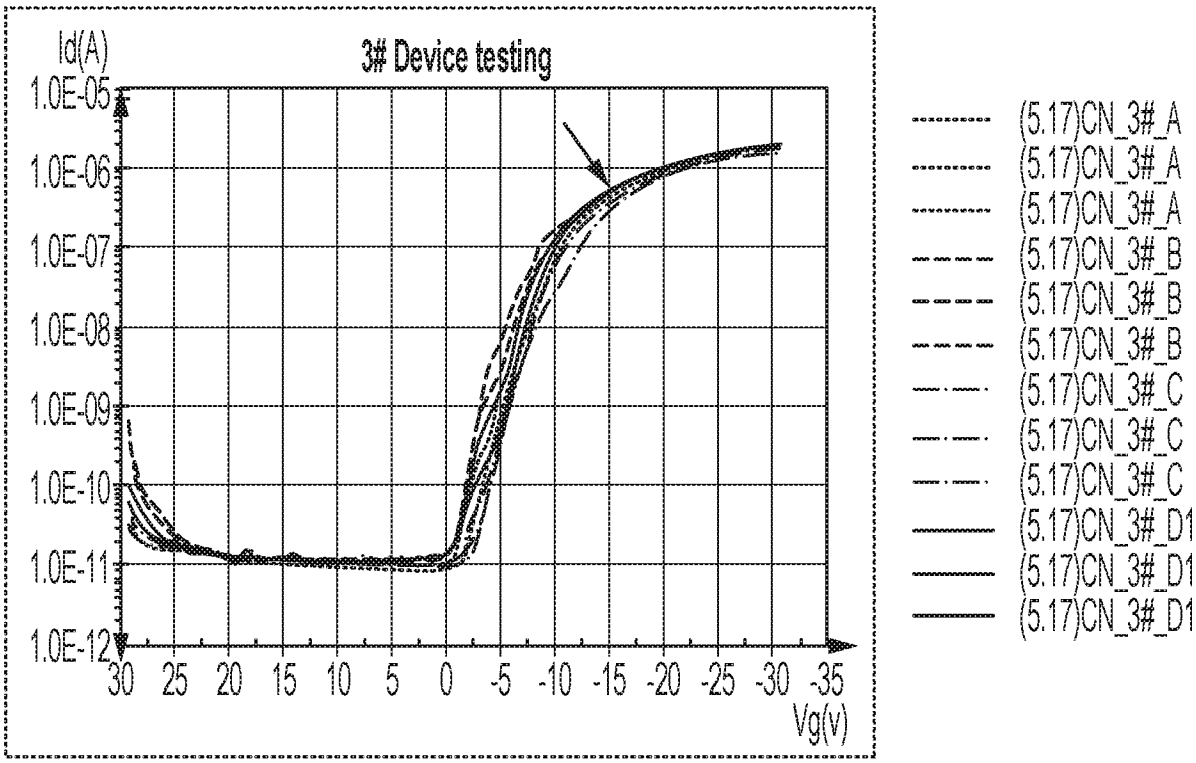

Id(A)
3# Device testing
1.0E-05
1.0E-06
1.0E-07
1.0E-08
1.0E-09
1.0E-10
1.0E-11
1.0E-12
30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35
Vg(v)
(5.17)CN_3#_A
(5.17)CN_3#_A
(5.17)CN_3#_A
(5.17)CN_3#_B
(5.17)CN_3#_B
(5.17)CN_3#_B
(5.17)CN_3#_C
(5.17)CN_3#_C
(5.17)CN_3#_C
(5.17)CN_3#_D1
(5.17)CN_3#_D1
(5.17)CN_3#_D1

FIG. 7C

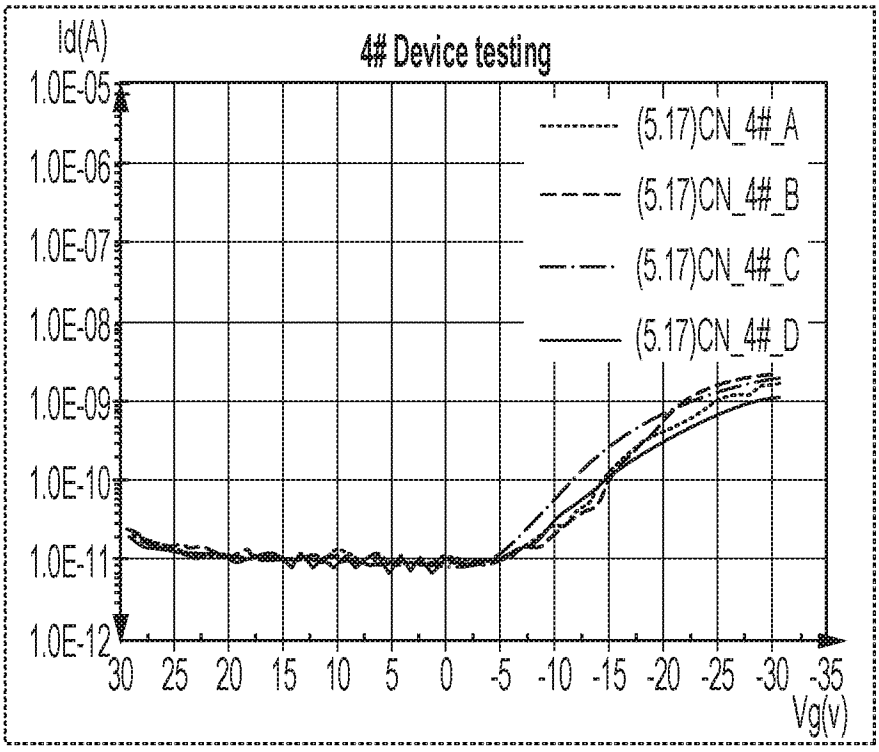

Id(A)
4# Device testing
1.0E-05
1.0E-06
1.0E-07
1.0E-08
1.0E-09
1.0E-10
1.0E-11
1.0E-12
30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35
Vg(v)
(5.17)CN_4#_A
(5.17)CN_4#_B
(5.17)CN_4#_C
(5.17)CN_4#_D

FIG. 7D

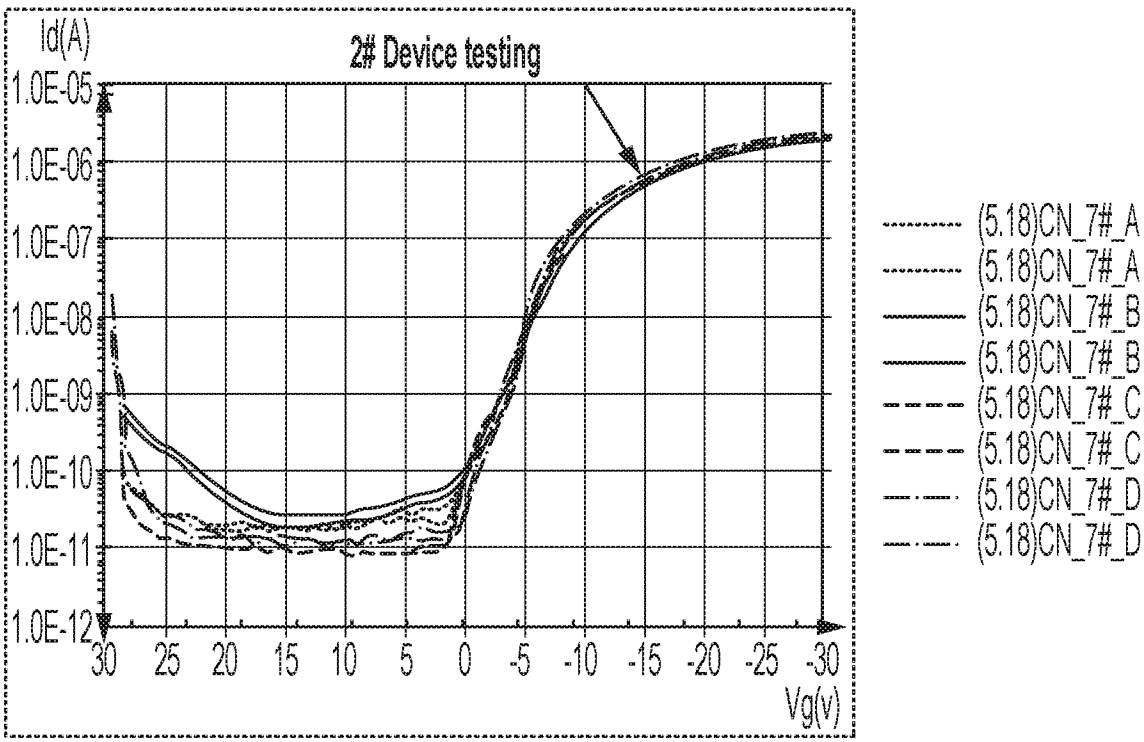

Id(A)
2# Device testing
1.0E-05
1.0E-06
1.0E-07
1.0E-08
1.0E-09
1.0E-10
1.0E-11
1.0E-12
30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30
Vg(v)
(5.18)CN_7#_A
(5.18)CN_7#_A
(5.18)CN_7#_B
(5.18)CN_7#_B
(5.18)CN_7#_C
(5.18)CN_7#_C
(5.18)CN_7#_D
(5.18)CN_7#_D

FIG. 8

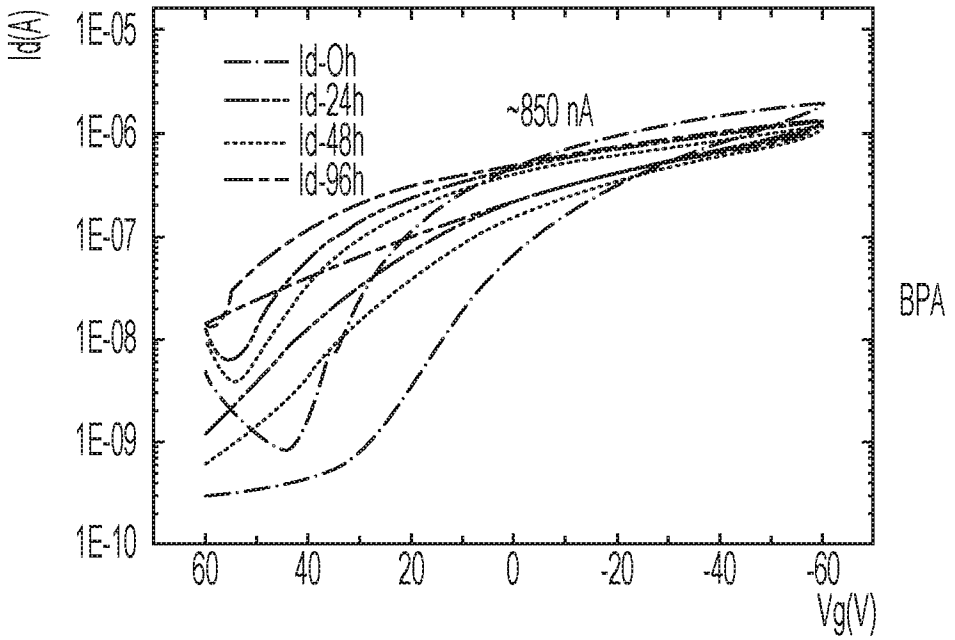

Id(A)
1E-05
1E-06
1E-07
1E-08
1E-09
1E-10
Id-0h
Id-24h
Id-48h
Id-96h
~850 nA
60
40
20
0
-20
-40
-60
Vg(V)
BPA

FIG. 9A

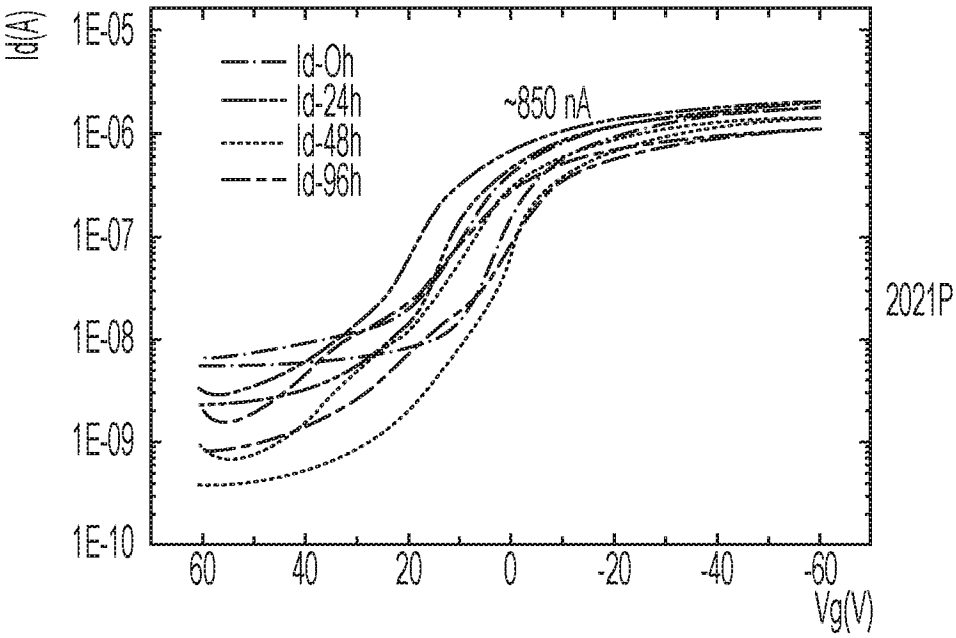

Id(A)
1E-05
1E-06
1E-07
1E-08
1E-09
1E-10
Id-0h
Id-24h
Id-48h
Id-96h
~850 nA
60
40
20
0
-20
-40
-60
Vg(V)
2021P

FIG. 9B

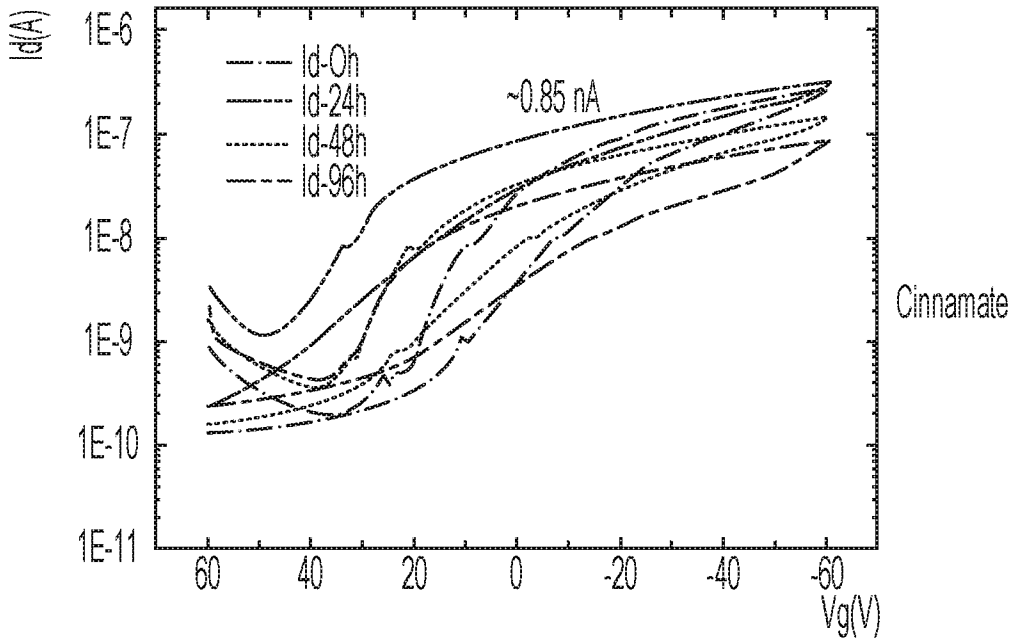

Id(A)
1E-6
1E-7
1E-8
1E-9
1E-10
1E-11
Id-0h
Id-24h
Id-48h
Id-96h
~0.85 nA
Cinnamate
60
40
20
0
-20
-40
-60
Vg(V)

FIG. 9C

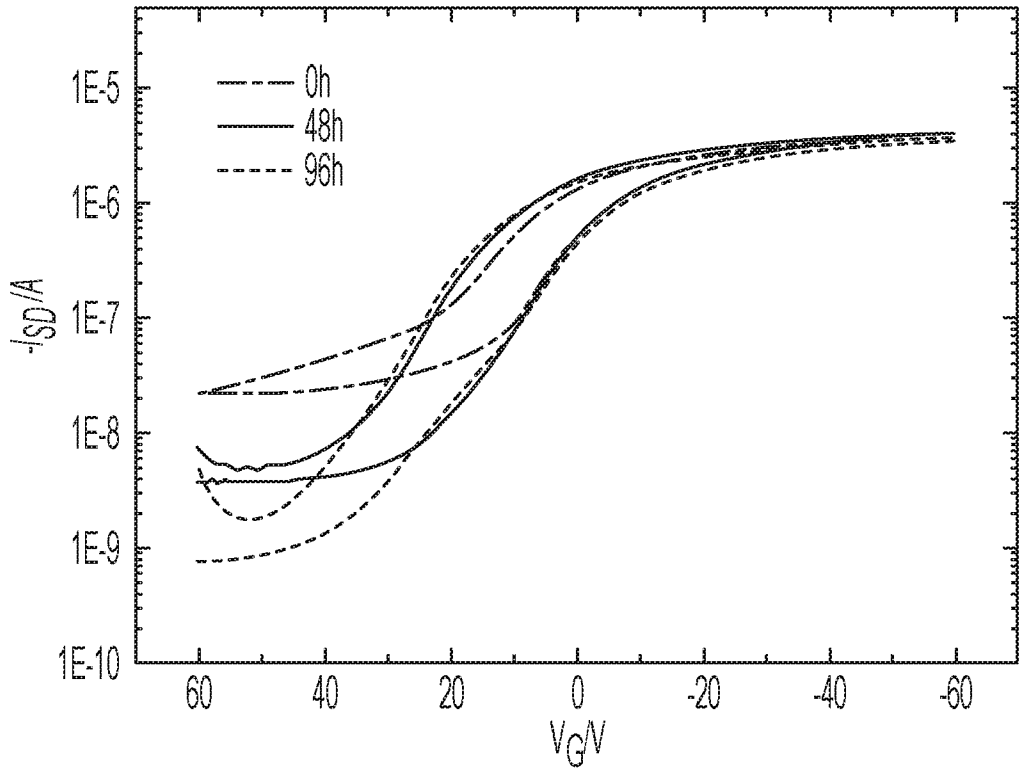


FIG. 10A

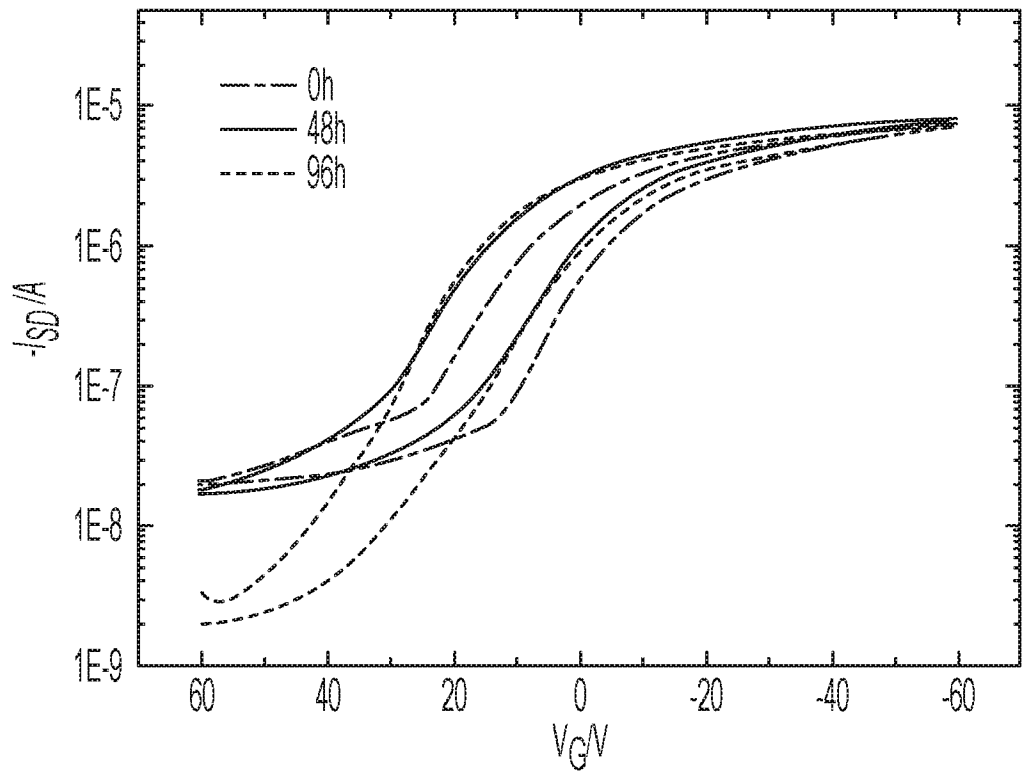


FIG. 10B

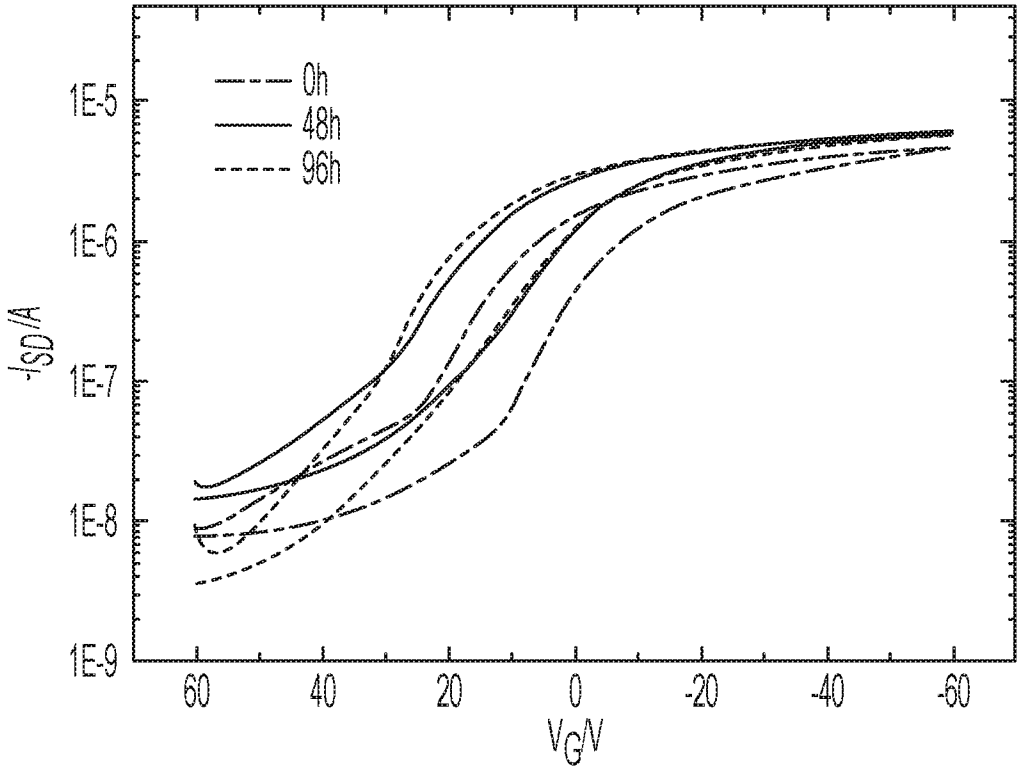


FIG. 10C

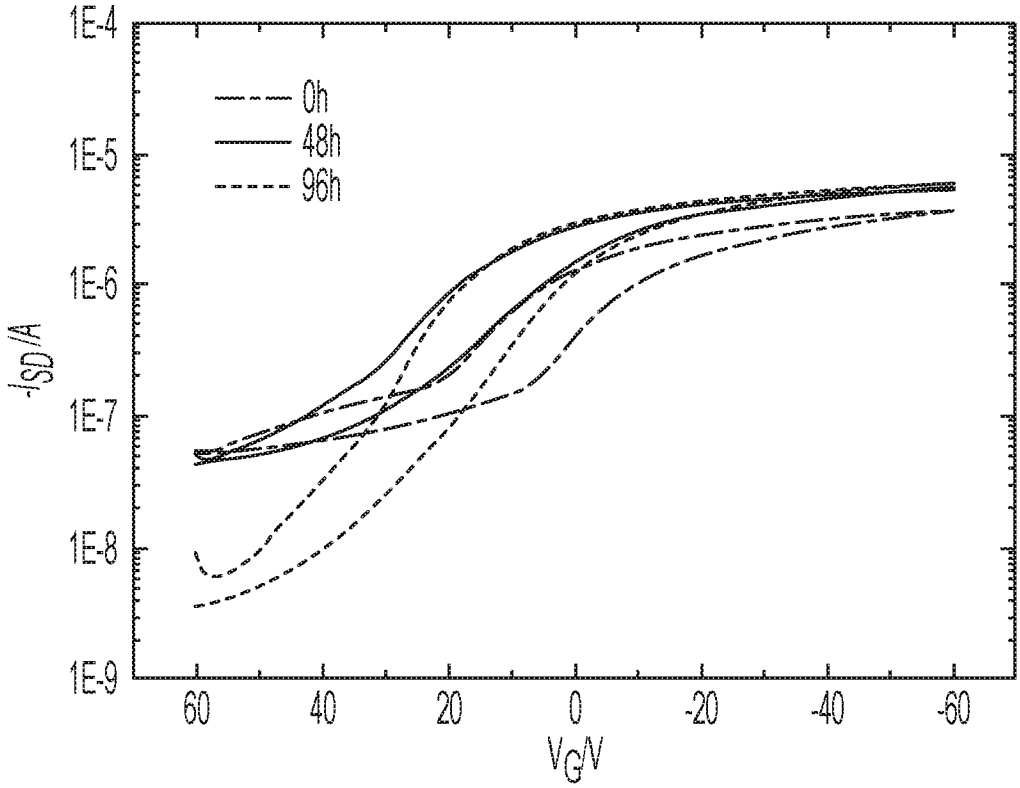


FIG. 10D

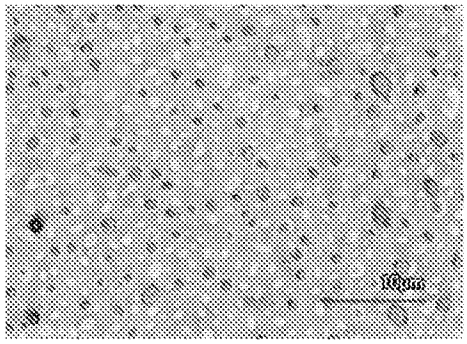


FIG. 11A

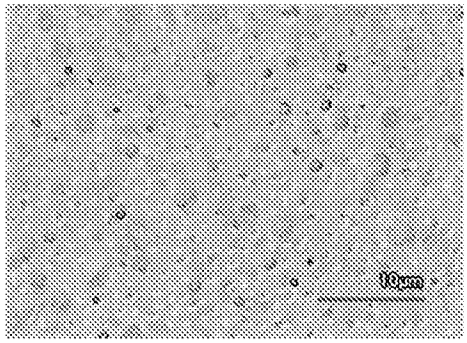


FIG. 11B

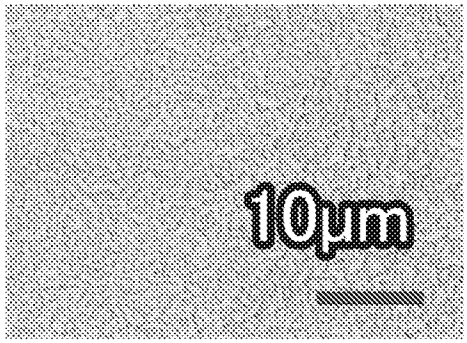


FIG. 11C

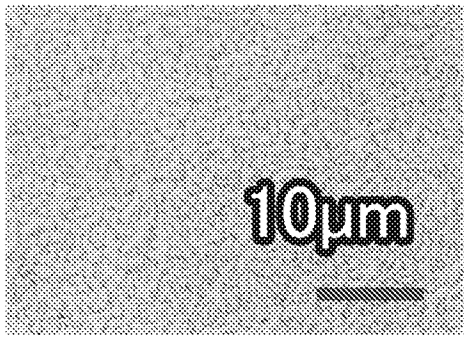


FIG. 11D

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/055285

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G61/12 H01L51/00 H01L51/05
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08G C09J H01L

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JAMES R. MATTHEWS ET AL: "Scalable Synthesis of Fused Thiophene-Diketopyrrolopyrrole Semiconducting Polymers Processed from Nonchlorinated Solvents into High Performance Thin Film Transistors", CHEMISTRY OF MATERIALS, vol. 25, no. 5, 12 March 2013 (2013-03-12) , pages 782-789, XP055205802, ISSN: 0897-4756, DOI: 10.1021/cm303953e	1-7,13, 14,17
A	abstract Scheme 3 "Device Characterization"; page 785; table 2	8-12,15, 16,18

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[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 January 2020	10/02/2020

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Meiser, Wibke

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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JOSEPH W. RUMER ET AL: "Organic photovoltaics: Crosslinking for optimal morphology and stability", MATERIALS TODAY, vol. 18, no. 8, 1 October 2015 (2015-10-01), pages 425-435, XP055658371, AMSTERDAM, NL ISSN: 1369-7021, DOI: 10.1016/j.mattod.2015.04.001	1-7,13, 14,17
A	figure 3 "Crosslinkable polymers to control bulk heterojunction morphology"; page 428 - page 429; table 1	8-12,15, 16,18

T	WEIJUN NIU ET AL: "Synthesis and Properties of Soluble Fused Thiophene Diketopyrrolopyrrole-Based Polymers with Tunable Molecular Weight", MACROMOLECULES, vol. 51, no. 23, 15 November 2018 (2018-11-15), pages 9422-9429, XP055657322, WASHINGTON, DC, UNITED STATES ISSN: 0024-9297, DOI: 10.1021/acs.macromol.8b01760 abstract Scheme 1	
