

ORGANOMETALLIC CLUSTER CONTAINING SULFUR FOR EUV LITHOGRAPHY

BACKGROUND

[0001] Field

[0002] The disclosed and claimed subject matter relates to Sn6-oxo clusters with carboxylic acids containing a thioether or polysulfide functional group, the synthesis thereof, formulations thereof and use thereof in EUV lithography.

[0003] Related Art

[0004] The semiconductor industry is currently considering the use of metal-containing materials as EUV photoresist material for patterning. Many organometallic complexes especially tin-containing compounds have been evaluated as potential precursors for the formation of photoresist material via either spin coating or chemical vapor deposition.

[0005] Sn compounds/clusters are of interest as photoresists due to their mechanical strength and etch resistivity of the crosslinked material. However, in order to serve as a photoresist, they need to have good photosensitivity and photoresolution.

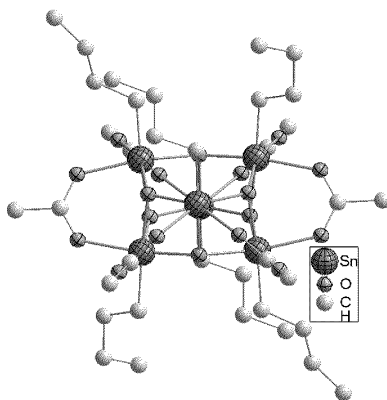
[0006] For example, U.S. Patent No. 10,787,466 discloses compositions of monoalkyltin trialkoxide compounds of formula $\text{RSn}(\text{OR}')_3$ or monoalkyltin triamide compounds of formula $\text{RSn}(\text{NR}'_2)_3$ where (i) R is a hydrocarbyl group with 1-31 carbon atoms, and where R' is a hydrocarbyl group with 1-10 carbon atoms and (ii) the compositions contain no more than 4 mol % of dialkyltin compounds relative to the total amount of tin. Also disclosed is a composition including a monoalkyl triamidotin compound of formula $\text{RSn}(\text{NR}'\text{COR}'')_3$ where R is a hydrocarbyl group with 1-31 carbon atoms, and where R' and R'' are independently a hydrocarbyl group with 1-10 carbon atoms. It is believed that having the dialkyltin compounds (as impurities) in the formulation affects performance.

[0007] WO2019246254 discloses precursor solutions for radiation patternable coatings that are formed with an organic solvent and monoalkyltin trialkoxides in which the water content of the solvent is adjusted to be within 10% of a selected value. Generally, the water content of the solvent is adjusted through the addition of water, although water removal can also be used. For example, in some embodiments, the adjusted water content of the solvent can be from about 250 ppm by wt. to about 10,000 ppm by wt. With the appropriate selection of ligands, the adjusted precursor solutions are asserted to be stable for at least about 42 days, and in some cases at least 8 months.

[0008] U.S. Patent No. 10,732,505 discloses organometallic precursors for the formation of high-resolution lithography patterning coatings based on metal oxide hydroxide chemistry. The precursor compositions generally include ligands that are readily hydrolysable by water vapor or other -OH source under modest conditions. In particular, the organometallic precursors include a radiation sensitive organo ligand to tin that can result in a coating that can be effective for high-resolution patterning at relatively low radiation doses and is particularly useful for EUV patterning.

[0009] Sn₁₂ clusters (*i.e.*, [(RSn)₁₂O₁₄(OH)₆]X₂) have been described as being photosensitive in EUV and eBeam exposures. See Sharps *et al.*, *Chem. Mater.*, 31, 4840-4850 (2019); U.S. Patent No. 9,310,684; Castellanos *et al.*, *Appl. Mat. Int.*, 12, 9881-9889 (2020); and Herman *et al.*, *Appl. Mat. Int.*, 11, 4514-4522 (2019). The changes in the material, coated on a wafer as a photosensitive layer, have been investigated and several hypotheses on how a solubility contrast is induced by exposure to ionizing radiation were discussed. See Castellanos *et al.*, *Appl. Mat. Int.*, 12, 9881-9889 (2020) and Herman *et al.*, *Appl. Mat. Int.*, 11, 4514-4522 (2019).

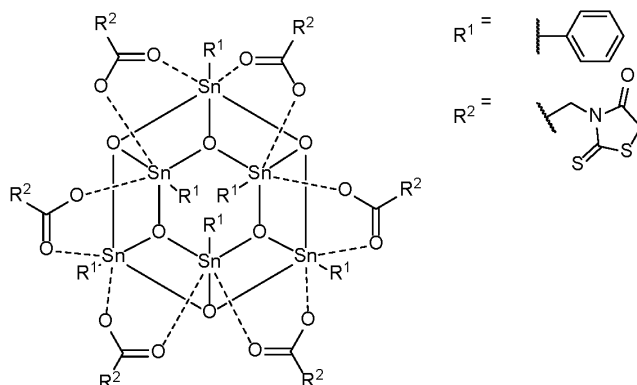
[0010] Sn₆ drum clusters may provide attractive alternatives compared to known Sn-based systems due to their high stability, which is expected to result in a stable formulation as well as a stable photoresist film. Sn₆ drum clusters include a Sn₆O₆ core. This core motif is built up from six (Sn₂O₂) four-membered rings that are fused along their edges into a cyclic structure that resembles a drum. Alternatively, the Sn₆O₆ core can be described as two (Sn₃O₃) rings with Sn-O-Sn linkages. The two rings are aligned so that a drum-like motif is formed and rotated with respect to each other, as an effect of additional Sn-O-bridges between the rings. Each Sn atom is covalently bound to one organic substituent R^{Sn}, typically alkyl or aryl groups. In addition, carboxylate ligands R^{ac}CO²⁻ are present that are bound in a bridging fashion. They form links between two tin atoms from the six-membered rings. This arrangement leads to a specific orientation of the different ligands. The R^{Sn}-groups are all located on the six-membered rings and the carboxylate residues point outwards from the radial part of the cluster core. For example, (*n*BuSn)₆O₆(O₂CCH₃)₆ has the following structure (H atoms not drawn), see Reuter *et al.*, *Acta Cryst.* (2013), E69, m4:



[0011] Various functionalized Sn₆ cluster derivatives have been synthesized and applied for various applications like material science or medicinal chemistry. See Holmes *et al.*, *Inorganic Chemistry*, 24, 13, 1970 (1985); Chandrasekhar *et al.*, *Inorganica Chimica Acta*, 522, 120378 (2021) and Xiao *et al.*, *Journal of Molecular Structure*, 1190, 116 (2019).

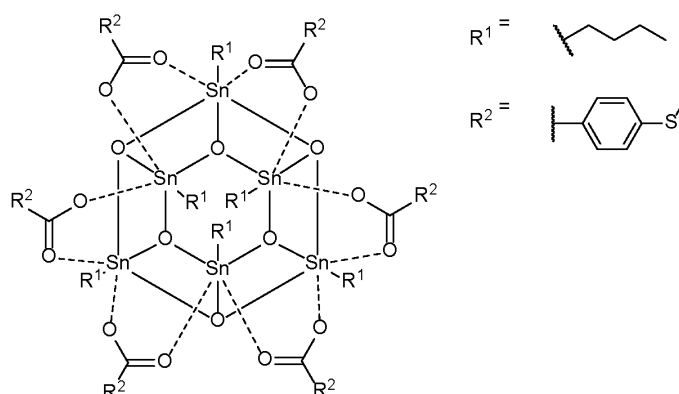
[0012] Despite the huge variety of carboxylate ligands that have been used for the preparation of Sn₆ drum clusters, only a few of these contain sulfur atoms. For example, Zhang *et*

al. have presented rhodanine containing Sn clusters. The sulfur is herein bonded in a dithiocarbamate-moiety:



See Zhang *et al.*, *Journal of Organometallic Chemistry*, 690, 4366 (2005).

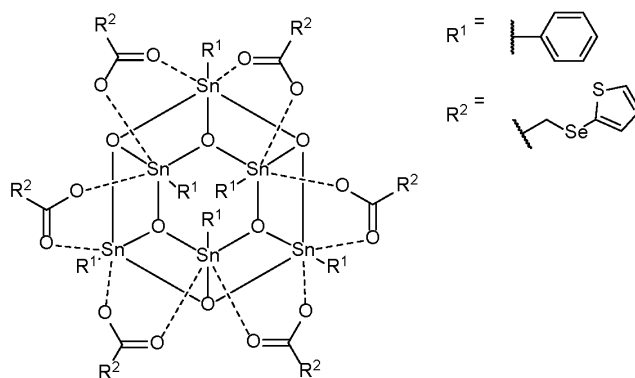
[0013] Chandrasekhar and Narayanan have described a drum cluster with a thiophenole methyl ether moiety:



See V. Chandrasekhar and R.S. Narayanan, *Proc. Nat. Acad. Sci., India, Sect. A*, 86, 627 (2016).

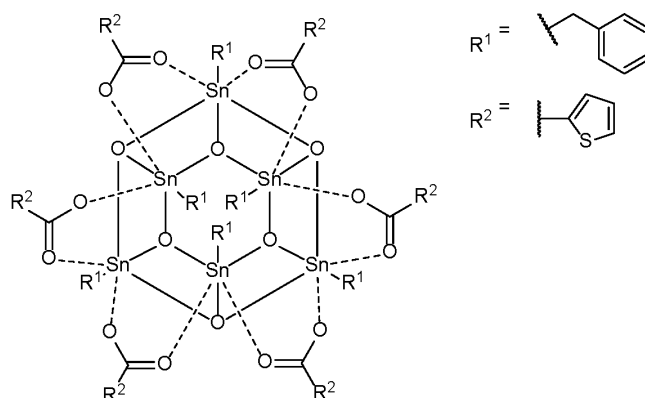
See Comparative Example 1.

[0014] Zhang. *et al.* disclosed a drum cluster with thiophene moiety bound via a seleno-ether group:



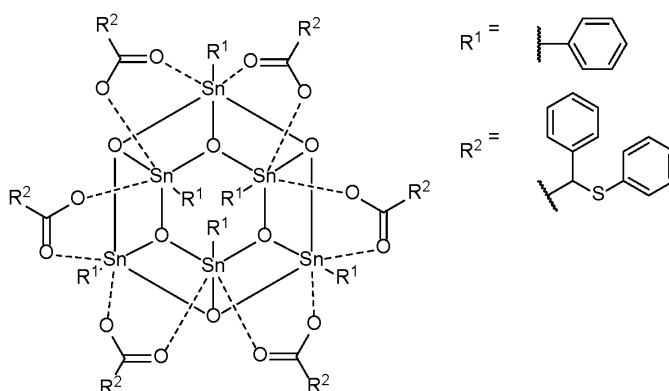
See Zhang *et al.*, *Dalton Trans.*, 45, 8412 (2016).

[0015] Fang *et al.* described a drum cluster containing a thiophene moiety in the backbone:



See Fang *et al.*, *Chem. J. Chin. Univ.*(Chinese Edition), 24, 958 (2003).

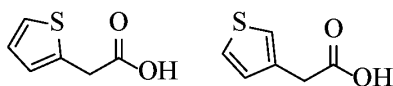
[0016] Zhang *et al.* have presented the synthesis of a drum cluster containing a thiophenole-ether moiety.



See Zhang *et al.*, *Polyhedron*, 29, 881–885 (2010).

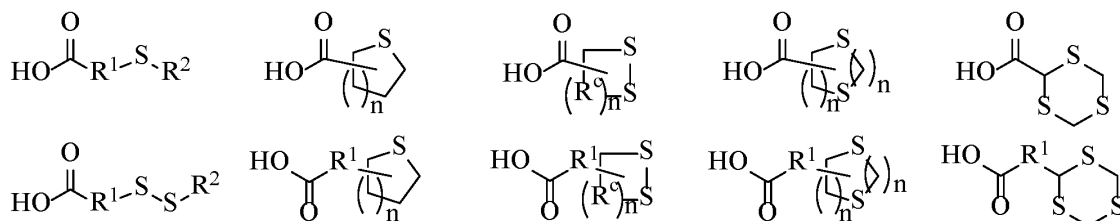
[0017] There has, however, been only very limited research into the use of Sn₆ clusters as EUV resists. For example, Sharps *et al.* mentioned the potential use of Sn₆ drum-cluster type system as EUV resist. In particular, they studied the crystal density and intermolecular distances of non-functionalized drum cluster systems. See Sharps *et al.*, *Cryst. Res. Technol.*, 52, 1700081 (2017). This same group further explored the use of one Sn₆-drum cluster—(*n*BuSn)₆O₆(O₂CCH₃)₆ (“Sn₆-*n*Bu-OAc”)—for the use in e-beam lithography. Here only dose curves have been described and it was stated that this Sn₆-cluster exhibited much lower sensitivity than a comparable Sn₁₂ cluster. See Sharps *et al.*, *Chem. Mater.*, 31, 4840-4850 (2019).

[0018] U.S. Patent Application Publication No. 2021/0087210 discloses a very specific set of Sn₆ clusters for use as photoresists but without supporting application data. The disclosed materials are all *n*BuSn Sn₆ clusters that include different carboxylate groups. Notably, two of the carboxylic acids described contain aromatic heterocyclic groups that contain sulfur (*i.e.*, thiophene):



Thiophene is aromatic, and therefore a very stable system where the sulfur atom is tightly bound and would not participate in any follow-up chemistry that would be triggered by EUV. Put differently, sulfur group(s) in an aromatized system would not be satisfactory for use in an EUV process where the functional groups are required to be available and expected to undergo a chemical reaction. In addition, alkyl chains are more flexible than rigid aromatic units. This increased flexibility enables easier movement of the respective units, for example during baking and curing steps. As these units are expected to take part in the crosslinking processes that are ultimately responsible for the desired solubility contrast in lithography, this increased flexibility is expected to improve the performance of the materials. The compounds disclosed in U.S. Patent Application Publication No. 2021/0087210 were synthesized and tested in electron beam lithography, considered as a good proxy for EUV sensitivity, as comparative examples. Their performance was found to be inferior to the literature reference [(nBuSn)₆O₆(O₂CCH₃)₆]. For this, *see* comparative examples 2 – 4. The analytical data obtained for the prepared materials is in good agreement with what has been published for these compounds.

[0019] Here, Sn₆ drum clusters with carboxylate ligands that contain at least one aliphatic thioether, polysulfide, or dithioacetal in the backbone are disclosed and claimed. This includes, but does not limit, the choice to carboxylate ligands/moieties derived from carboxylic acids that contain a methylthioether, a dithioacetal moiety as well as those that contain a disulfide group, for example:

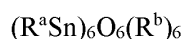


The functional group can be located directly in alpha position to the carboxylate group or connected to it via a bridging carbon chain, ring system, or a combination thereof. The (poly-)sulfide ether can itself be part of a ring system or in a linear chain (n, m = individually 1 – 4).

[0020] Without being bound by theory it is believed that the introduction of these functional groups into the cluster can improve the photospeed of the materials compared to their unfunctionalized derivatives, such as acetate ligands.

SUMMARY

[0021] In one embodiment the disclosed and claimed subject matter relates to Sn₆-oxo clusters with carboxylic acids moieties containing a thioether or polysulfide functional groups of the formula:

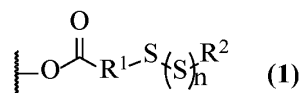


where

(A) R^a is an unsubstituted linear C_1 - C_{10} alkyl group, a linear C_1 - C_6 alkyl group substituted with a halogen, a linear C_1 - C_6 alkyl group substituted with an amino group, a linear C_1 - C_6 alkyl group substituted with a C_5 - C_6 unsubstituted aromatic group, an unsubstituted branched C_3 - C_{10} alkyl group, a branched C_3 - C_{10} alkyl group substituted with a halogen, a C_1 - C_{10} heteroalkylene, a branched C_3 - C_{10} alkyl group substituted with an unsubstituted amine, a substituted amine, $-\text{Si}(\text{CH}_3)_3$, a benzyl group, a C_3 - C_8 unsubstituted cyclic alkyl group, a C_3 - C_8 cyclic alkyl group substituted with a halogen, a C_3 - C_8 cyclic alkyl group substituted with an amino group, a C_4 - C_8 unsubstituted aromatic group, a C_4 - C_8 aromatic group substituted with a halogen, a C_4 - C_8 aromatic group substituted with an amino group, a C_3 - C_{10} heterocyclic group, a C_2 - C_{10} alkenyl group and a C_3 - C_{10} alkynyl group; and

(B) R^b is a carboxylic acid moiety group selected from the group of

(i) formula **(1)**:



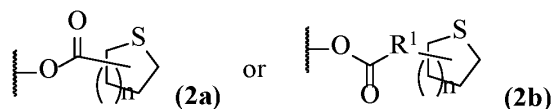
where

$n = 0$ or 1 ;

R^1 is an unsubstituted linear C_1 - C_6 alkylene group, an unsubstituted branched C_3 - C_6 alkylene group, an unsubstituted linear C_2 - C_6 alkenylene group, an unsubstituted branched C_3 - C_6 alkenylene group, an unsubstituted linear C_2 - C_6 alkynylene group, an unsubstituted branched C_4 - C_6 alkynylene group or a C_3 - C_8 unsubstituted cyclic alkylene group; and

R^2 is an unsubstituted linear C_1 - C_6 alkyl group, an unsubstituted branched C_3 - C_6 alkyl group, an unsubstituted linear C_2 - C_6 alkenyl group, an unsubstituted branched C_3 - C_6 alkenyl group, an unsubstituted linear C_2 - C_6 alkynyl group, an unsubstituted branched C_4 - C_6 alkynyl group or a C_3 - C_8 unsubstituted cyclic alkyl group;

(ii) formulae **(2a)** or **(2b)**:

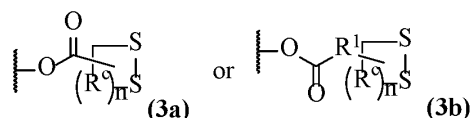


where

$n = 1$ to 4 ; and

R^1 is an unsubstituted linear C_1 - C_6 alkylene group or an unsubstituted branched C_3 - C_6 alkylene group;

(iii) formulae **(3a)** or **(3b)**:



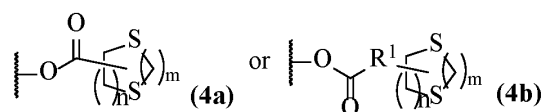
where

$n = 2$ to 5 ;

each R^c is individually an unsubstituted methylene group or a methylene group substituted with one or two C_1 - C_4 alkyl groups; and

R^1 is an unsubstituted linear C_1 - C_6 alkylene group or an unsubstituted branched C_3 - C_6 alkylene group;

(iv) formulae (4a) or (4b):

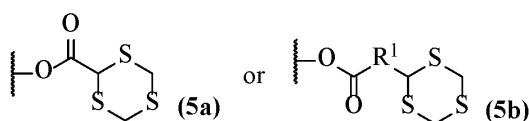


where

n and $m =$ individually 1 to 4 ; and

R^1 is an unsubstituted linear C_1 - C_6 alkylene group or an unsubstituted branched C_3 - C_6 alkylene group; and

(v) formulae (5a) or (5b):



where

R^1 is an unsubstituted linear C_1 - C_6 alkylene group or an unsubstituted branched C_3 - C_6 alkylene group.

[0022] In another aspect, the disclosed and claimed subject matter includes using the Sn6-oxo clusters of the disclosed and claimed subject matter in or to prepare formulations that are useful in EUV processes. Such formulations are or can be used for patterning a radiation sensitive coating in a process that includes (i) forming a coating on a substrate surface with a precursor solution where the precursor solution is prepared from the Sn6-oxo clusters described herein and/or utilized the process for preparing the same, (ii) drying the coating; and (iii) irradiating the dried coating to form a latent image.

[0023] In another aspect, the disclosed and claimed subject matter includes methods for preparing the Sn6-oxo clusters described herein.

[0024] This summary section does not specify every embodiment and/or incrementally novel aspect of the disclosed and claimed subject matter. Instead, this summary only provides a preliminary discussion of different embodiments and corresponding points of novelty over conventional techniques and the known art. For additional details and/or possible perspectives of

the disclosed and claimed subject matter and embodiments, the reader is directed to the Detailed Description section and corresponding figures of the disclosure as further discussed below.

[0025] The order of discussion of the different steps described herein has been presented for clarity's sake. In general, the steps disclosed herein can be performed in any suitable order. Additionally, although each of the different features, techniques, configurations, etc. disclosed herein may be discussed in different places of this disclosure, it is intended that each of the concepts can be executed independently of each other or in combination with each other as appropriate. Accordingly, the disclosed and claimed subject matter can be embodied and viewed in many different ways.

[0026] **BRIEF DESCRIPTION OF THE DRAWINGS**

[0027] The accompanying drawings, which are included to provide a further understanding of the disclosed subject matter and are incorporated in and constitute a part of this specification, illustrate embodiments of the disclosed subject matter and together with the description serve to explain the principles of the disclosed subject matter. In the drawings:

[0028] FIG. 1 illustrates the ^{119}Sn -NMR of $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C-CHS}_2\text{C}_3\text{H}_6)_6]$ prepared in Example 1;

[0029] FIG. 2 illustrates the ^1H -NMR of $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C-CHS}_2\text{C}_3\text{H}_6)_6]$ prepared in Example 1;

[0030] FIG. 3 illustrates the ^{119}Sn -NMR of $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C-CH}_2\text{SCH}_3)_6]$ prepared in Example 2;

[0031] FIG. 4 illustrates the ^1H -NMR of $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C-CH}_2\text{SCH}_3)_6]$ prepared in Example 2;

[0032] FIG. 5 illustrates the ^{119}Sn -NMR of the product from the attempted preparation of $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C-C}_6\text{H}_4\text{SCH}_3)_6]$ prepared in Comparative Example 1;

[0033] FIG. 6 illustrates the ^1H -NMR of the product from the attempted preparation of $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C-C}_6\text{H}_4\text{SCH}_3)_6]$ prepared in Comparative Example 1;

[0034] FIG. 7 illustrates the ^{119}Sn -NMR of $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C-CH}_2\text{-(2-C}_4\text{H}_3\text{S}))_6]$ (top: concentrated reaction solution; bottom: isolated solid) prepared in Comparative Example 2;

[0035] FIG. 8 illustrates the ^1H -NMR of $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C-CH}_2\text{-(2-C}_4\text{H}_3\text{S}))_6]$ (isolated solid) prepared in Comparative Example 2;

[0036] FIG. 9 illustrates the ^{119}Sn -NMR of $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C-CH}_2\text{-(3-C}_4\text{H}_3\text{S}))_6]$ (top: concentrated reaction solution; bottom: isolated solid) prepared in Comparative Example 2; and

[0037] FIG. 10 illustrates the ^1H -NMR of $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C-CH}_2\text{-(3-C}_4\text{H}_3\text{S}))_6]$ (isolated solid) prepared in Comparative Example 2.

[0038] **DEFINITIONS**

[0039] Unless otherwise stated, the following terms used in the specification and claims

shall have the following meanings for this application.

[0040] In this application, the use of the singular includes the plural, and the words “a,” “an” and “the” mean “at least one” unless specifically stated otherwise. Furthermore, the use of the term “including,” as well as other forms such as “includes” and “included,” is not limiting. Also, terms such as “element” or “component” encompass both elements or components including one unit and elements or components that include more than one unit, unless specifically stated otherwise. As used herein, the conjunction “and” is intended to be inclusive and the conjunction “or” is not intended to be exclusive, unless otherwise indicated. For example, the phrase “or, alternatively” is intended to be exclusive. As used herein, the term “and/or” refers to any combination of the foregoing elements including using a single element.

[0041] The term “about” or “approximately,” when used in connection with a measurable numerical variable, refers to the indicated value of the variable and to all values of the variable that are within the experimental error of the indicated value (*e.g.*, within the 95% confidence limit for the mean) or within percentage of the indicated value (*e.g.*, $\pm 10\%$, $\pm 5\%$), whichever is greater.

[0042] As used herein, “C_{x-y}” (where x and y are each integers) designates the number of carbon atoms in a chain. For example, C₁₋₆ alkyl refers to an alkyl chain having a chain of between 1 and 6 carbons (*e.g.*, methyl, ethyl, propyl, butyl, pentyl and hexyl). Unless specifically stated otherwise, the chain can be linear or branched.

[0043] Unless otherwise indicated, “alkyl” refers to hydrocarbon groups which can be linear, branched (*e.g.*, methyl, ethyl, propyl, isopropyl, tert-butyl and the like), cyclic (*e.g.*, cyclohexyl, cyclopropyl, cyclopentyl and the like) or multicyclic (*e.g.*, norbornyl, adamantyl and the like). Suitable acyclic groups can be methyl, ethyl, n- or iso-propyl, n-, iso, or tert-butyl, linear or branched pentyl, hexyl, heptyl, octyl, decyl, dodecyl, tetradecyl and hexadecyl. Unless otherwise stated, alkyl refers to 1-10 carbon atom moieties. The cyclic alkyl groups may be mono-cyclic or polycyclic. Suitable examples of mono-cyclic alkyl groups include substituted cyclopentyl, cyclohexyl, and cycloheptyl groups. As mentioned herein the cyclic alkyl groups may have any of the acyclic alkyl groups as substituent. These alkyl moieties may be substituted or unsubstituted.

[0044] “Halogenated alkyl” refers to a linear, cyclic or branched saturated alkyl group as defined above in which one or more of the hydrogens has been replaced by a halogen (*e.g.*, F, Cl, Br and I). Thus, for example, a fluorinated alkyl (a.k.a. “fluoroalkyl”) refers to a linear, cyclic or branched saturated alkyl group as defined above in which one or more of the hydrogens has been replaced by fluorine (*e.g.*, trifluoromethyl, pentafluoroethyl, 2,2,2-trifluoroethyl, pentafluoroisopropyl, pentafluorocyclohexyl and the like). Such haloalkyl moieties (*e.g.*, fluoroalkyl moieties), if not perhalogenated/multihalogenated, may be unsubstituted or further substituted.

[0045] “Alkoxy” (a.k.a. “alkyloxy”) refers to an alkyl group as defined above which is attached

through an oxy (-O-) moiety (*e.g.*, methoxy, ethoxy, propoxy, butoxy, 1,2-isopropoxy, cyclopentyloxy, cyclohexyloxy and the like). These alkoxy moieties may be substituted or unsubstituted.

[0046] “Alkyl carbonyl” refers to an alkyl group as defined above which is attached through a carbonyl group (-C(=O-)) moiety (*e.g.*, methylcarbonyl, ethylcarbonyl, propylcarbonyl, butylcarbonyl, cyclopentylcarbonyl and the like). These alkyl carbonyl moieties may be substituted or unsubstituted.

[0047] “Halo” or “halide” refers to a halogen (*e.g.*, F, Cl, Br and I).

[0048] “Hydroxy” (a.k.a. “hydroxyl”) refers to an -OH group.

[0049] The term “aryl” denotes an aromatic cyclic functional group having from 4 to 10 carbon atoms, from 5 to 10 carbon atoms, or from 6 to 10 carbon atoms. Exemplary aryl groups include, but are not limited to, phenyl, 1-phenylethyl (Ph(Me)CH-), 1-phenyl-1-methyl-ethyl (Ph(Me)₂C-), benzyl, chlorobenzyl, tolyl, o-xylyl, 1,2,3-triazolyl, pyrrolyl, and furanyl.

[0050] In addition to known and understood representations for the attachment point of a covalent bond, the notation “- $\frac{1}{2}$ -” is intended to also designate the attachment point of a covalent bond.

[0051] “Alkylene” means a linear saturated divalent hydrocarbon radical of one or more carbon atoms or a branched saturated divalent hydrocarbon radical of three to six carbon atoms unless otherwise stated (*e.g.*, methylene, ethylene, propylene, 1-methylpropylene, 2-methylpropylene, butylene, pentylene, and the like). Specific examples of the alkylene linkages include methylene (-CH₂-), ethylene (-CH₂CH₂-), substituted ethylenes, (*e.g.*, -CH(CH₃)CH₂-; -CH(CH₃)CH(CH₃)-; -C(CH₃)₂CH₂-), propylene (-CH₂CH₂CH₂-) and substituted propylenes.

[0052] “Alkenylene” means a linear unsaturated divalent hydrocarbon radical of two or more carbon atoms or a branched divalent hydrocarbon radical of three to six carbon atoms containing at least one double bond between two Carbon atoms unless otherwise stated (*e.g.*, ethenylene, propenylene, 1-methylpropenylene, 2-methylpropenylene, butenylene, pentenylene, and the like). Specific examples of the alkenylene linkages include ethenylene (-CH=CH-), substituted ethenylenes, (*e.g.*, -(CH₃)C=CH-; -(CH₃)C=C(CH₃)-), propenylene (-CH=CHCH₂-) and substituted propenylenes.

[0053] “Alkynylene” means a linear unsaturated divalent hydrocarbon radical of two or more carbon atoms or a branched unsaturated divalent hydrocarbon radical of four to six carbon atoms containing at least one triple bond between two Carbon atoms unless otherwise stated (*e.g.*, ethynylene, propynylene, 3-methylpropynylene, butynylene, pentynylene, and the like). Specific examples of the alkynylene linkages include ethynylene (-C≡C-), propynylene (-C≡CCH₂-) and substituted propynylenes.

[0054] “Heteroalkylene” means an -(alkylene)- radical as defined above where one, two or three carbons in the alkylene chain is replaced by -O-, N(H, alkyl, or substituted alkyl), S, SO, SO₂,

or CO. In some preferred embodiments, the carbons are replaced by O or N.

[0055] Unless otherwise indicated, the term “substituted” when referring to an alkyl, alkoxy, fluorinated alkyl and the like refers to one of these moieties which also contains one or more substituents including, but not limited, to the following substituents: alkyl, substituted alkyl, unsubstituted aryl, substituted aryl, alkyloxy, alkylaryl, haloalkyl, halide, hydroxy, amino and amino alkyl. Similarly, the term “unsubstituted” refers to these same moieties where no substituents apart from hydrogen are present.

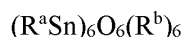
[0056] The section headings used herein are for organizational purposes and are not to be construed as limiting the subject matter described. All documents, or portions of documents, cited in this application, including, but not limited to, patents, patent applications, articles, books, and treatises, are hereby expressly incorporated herein by reference in their entirety for any purpose. In the event that any of the incorporated literature and similar materials defines a term in a manner that contradicts the definition of that term in this application, this application controls.

DETAILED DESCRIPTION

[0057] It is to be understood that both the foregoing general description and the following detailed description are illustrative and explanatory, and are not restrictive of the subject matter, as claimed. The objects, features, advantages and ideas of the disclosed subject matter will be apparent to those skilled in the art from the description provided in the specification, and the disclosed subject matter will be readily practicable by those skilled in the art on the basis of the description appearing herein. The description of any “preferred embodiments” and/or the examples which show preferred modes for practicing the disclosed subject matter are included for the purpose of explanation and are not intended to limit the scope of the claims.

[0058] Sn6-Oxo Clusters

[0059] As set forth above, the disclosed subject matter relates to Sn6-oxo clusters with carboxylic acids moieties containing a thioether or polysulfide functional groups of the formula:



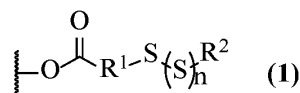
where

(A) R^a is an unsubstituted linear C_1 - C_{10} alkyl group, a linear C_1 - C_6 alkyl group substituted with a halogen, a linear C_1 - C_6 alkyl group substituted with an amino group, a linear C_1 - C_6 alkyl group substituted with a C_5 - C_6 unsubstituted aromatic group, an unsubstituted branched C_3 - C_{10} alkyl group, a branched C_3 - C_{10} alkyl group substituted with a halogen, a C_1 - C_{10} heteroalkylene, a branched C_3 - C_{10} alkyl group substituted with an unsubstituted amine, a substituted amine, $-Si(CH_3)_3$, a benzyl group, a C_3 - C_8 unsubstituted cyclic alkyl group, a C_3 - C_8 cyclic alkyl group substituted with a halogen, a C_3 - C_8 cyclic alkyl group substituted with an amino group, a C_4 - C_8 unsubstituted aromatic group, a C_4 - C_8 aromatic group substituted with a halogen, a C_4 - C_8 aromatic group substituted with an

amino group, a C₃-C₁₀ heterocyclic group, a C₂-C₁₀ alkenyl group and a C₃-C₁₀ alkynyl group; and

(B) R^b is a carboxylic acid moiety group selected from the group of

(i) formula (1):



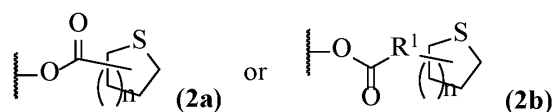
where

n = 0 or 1;

R¹ is an unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group, an unsubstituted linear C₂-C₆ alkenylene group, an unsubstituted branched C₃-C₆ alkenylene group, an unsubstituted linear C₂-C₆ alkynylene group, an unsubstituted branched C₄-C₆ alkynylene group or a C₃-C₈ unsubstituted cyclic alkylene group; and

R² is an unsubstituted linear C₁-C₆ alkyl group, an unsubstituted branched C₃-C₆ alkyl group, an unsubstituted linear C₂-C₆ alkenyl group, an unsubstituted branched C₃-C₆ alkenyl group, an unsubstituted linear C₂-C₆ alkynyl group, an unsubstituted branched C₄-C₆ alkynyl group or a C₃-C₈ unsubstituted cyclic alkyl group;

(ii) formulae (2a) or (2b):

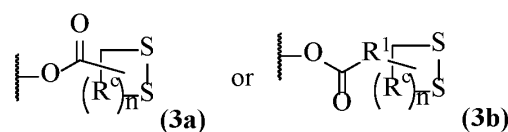


where

n = 1 to 4; and

R¹ is an unsubstituted linear C₁-C₆ alkylene group or an unsubstituted branched C₃-C₆ alkyl group;

(iii) formulae (3a) or (3b):



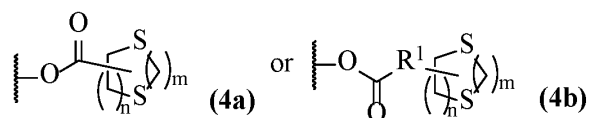
where

n = 2 to 5; and

each R^c is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups;

R¹ is an unsubstituted linear C₁-C₆ alkylene group or an unsubstituted branched C₃-C₆ alkylene group;

(iv) formulae (4a) or (4b):

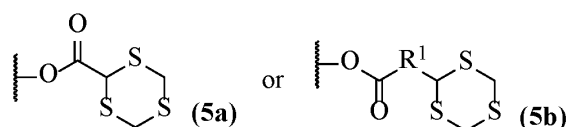


where

n and m = individually 1 to 4; and

R¹ is an unsubstituted linear C₁-C₆ alkylene group or an unsubstituted branched C₃-C₆ alkylene group; and

(v) formulae (5a) or (5b):



where

R¹ is an unsubstituted linear C₁-C₆ alkylene group or an unsubstituted branched C₃-C₆ alkylene group.

[0060] R^a Groups

[0061] In one embodiment, R^a is an unsubstituted linear C₁-C₄ alkyl group, an unsubstituted branched C₃-C₄ alkyl group, a C₂-C₆ alkenyl group and a C₄-C₆ unsubstituted aromatic group.

[0062] In a further aspect of this embodiment, R^a is selected from the group consisting of a -CH₃ group, a -CH(CH₃)₂ group, a -C(CH₃)₃ group, a -CH=CH₂ group, a -CH₂CH=CH₂ group, a -CH₂CH₂CH=CH₂ group, a -CH₂CH₂CH₂CH₃ group, a -C₆H₅ group and a -CH₂-C₆H₅ group.

[0063] In a further aspect of this embodiment, R^a is selected from the group consisting of a -CH₃ group, a -CH(CH₃)₂ group, a -C(CH₃)₃ group, a -CH=CH₂ group, a -CH₂CH=CH₂ group, a -CH₂CH₂CH=CH₂ group and a -CH₂CH₂CH₂CH₃ group.

[0064] In a further aspect of this embodiment, R^a is selected from the group consisting of a -CH₃ group, a -CH(CH₃)₂ group, a -C(CH₃)₃ group and a -CH₂CH₂CH₂CH₃ group.

[0065] In a further aspect of this embodiment, R^a is selected from the group consisting of a -CH₃ group, a -CH(CH₃)₂ group and a -CH₂CH₂CH₂CH₃ group.

[0066] In one aspect of this embodiment, R^a is a methyl group. In one aspect of this embodiment, R^a is an isopropyl group. In one aspect of this embodiment, R^a is a n-butyl group. In one aspect of this embodiment, R^a is a t-butyl group.

[0067] R^b Groups

[0068] In one embodiment, R^b is a carboxylic acid moiety of formula (1). In one aspect of this embodiment, n = 0. In one aspect of this embodiment, n = 1. In one aspect of this embodiment, one R¹ and R² are the same group. As those skilled in the art will understand, R¹ is considered to be the “same” as R² when R¹ is the corresponding hydrocarbon radical of the R² group. Thus, for

example, if R^2 is a methyl group and R^1 is the “same” then R^1 is a methylene group (*i.e.*, the corresponding hydrocarbon radical group of a methyl group). In one aspect of this embodiment, one R^1 and R^2 are each a different group.

[0069] In one aspect of this embodiment, one or both of R^1 is an unsubstituted linear C_1 - C_6 alkylene group and R^2 is an unsubstituted linear C_1 - C_6 alkyl group. In one aspect of this embodiment, one or both of R^1 R^1 is an unsubstituted branched C_3 - C_6 alkylene group and R^2 is an unsubstituted branched C_3 - C_6 alkyl group. In one aspect of this embodiment, one or both of R^1 is an unsubstituted linear C_2 - C_6 alkenylene group and R^2 is an unsubstituted linear C_2 - C_6 alkenyl group. In one aspect of this embodiment, one or both of R^1 is an unsubstituted branched C_3 - C_6 alkenylene group and R^2 is an unsubstituted branched C_3 - C_6 alkenyl group. In one aspect of this embodiment, one or both of R^1 is an unsubstituted linear C_2 - C_6 alkynylene group and R^2 is an unsubstituted linear C_2 - C_6 alkynyl group. In one aspect of this embodiment, one or both of R^1 is an unsubstituted branched C_4 - C_6 alkynylene group and R^2 is an unsubstituted branched C_4 - C_6 alkynyl group. In one aspect of this embodiment, one or both of R^1 is a C_3 - C_8 unsubstituted cyclic alkylene group and R^2 is a C_3 - C_8 unsubstituted cyclic alkyl group.

[0070] In one aspect of this embodiment, R^1 is a methylene group. In one aspect of this embodiment, R^1 is an ethylene group. In one aspect of this embodiment, R^1 is a n-propylene group. In one aspect of this embodiment, R^1 is an isopropylene group. In one aspect of this embodiment, R^1 is a s-butylene group. In one aspect of this embodiment, R^1 is a n-butylene group. In one aspect of this embodiment, R^1 is an isobutylene group. In one aspect of this embodiment, R^1 is a t-butylene group.

[0071] In one aspect of this embodiment, R^2 is an unsubstituted linear C_1 - C_6 alkyl group. In one aspect of this embodiment, R^2 is an unsubstituted branched C_3 - C_6 alkyl group. In one aspect of this embodiment, R^2 is a C_5 - C_8 unsubstituted cyclic alkyl group. In one aspect of this embodiment, R^2 is a C_3 - C_8 unsubstituted aromatic group.

[0072] In one aspect of this embodiment, R^2 is a methyl group. In one aspect of this embodiment, R^2 is an ethyl group. In one aspect of this embodiment, R^2 is a n-propyl group. In one aspect of this embodiment, R^2 is an isopropyl group. In one aspect of this embodiment, R^2 is a s-butyl group. In one aspect of this embodiment, R^2 is a n-butyl group. In one aspect of this embodiment, R^2 is an isobutyl group. In one aspect of this embodiment, R^2 is a t-butyl group. In one aspect of this embodiment, R^2 is an allyl group.

[0073] In one embodiment, R^b is a carboxylic acid moiety of formula (2a). In one aspect of this embodiment, $n = 1$. In one aspect of this embodiment, $n = 2$. In one aspect of this embodiment, $n = 3$. In one aspect of this embodiment, $n = 4$.

[0074] In one embodiment, R^b is a carboxylic acid moiety of formula (2b). In one aspect of this embodiment, $n = 1$. In one aspect of this embodiment, $n = 2$. In one aspect of this embodiment, $n = 3$. In one aspect of this embodiment, $n = 4$. In one aspect of this embodiment,

R¹ is an unsubstituted linear C₁-C₆ alkylene group. In one aspect of this embodiment, R¹ is an unsubstituted branched C₃-C₆ alkylene group. In one aspect of this embodiment, R¹ is a methylene group. In one aspect of this embodiment, R¹ is an ethylene group. In one aspect of this embodiment, R¹ is a n-propylene group. In one aspect of this embodiment, R¹ is an isopropylene group. In one aspect of this embodiment, R¹ is a s-butylene group. In one aspect of this embodiment, R¹ is a n-butylene group. In one aspect of this embodiment, R¹ is an isobutylene group. In one aspect of this embodiment, R¹ is a t-butylene group.

[0075] In one embodiment, R^b is a carboxylic acid moiety of formula (3a). In one aspect of this embodiment, n = 2. In one aspect of this embodiment, n = 3. In one aspect of this embodiment, n = 4. In one aspect of this embodiment, n = 5. In one aspect of this embodiment each R^c is a methylene group. In one aspect of this embodiment at least one R^c is a methylene group. In one aspect of this embodiment at least one R^c is a methylene group substituted with one C₁-C₄ alkyl group. In one aspect of this embodiment at least one R^c is a methylene group substituted with one methyl group. In one aspect of this embodiment at least one R^c is a methylene group substituted with two C₁-C₄ alkyl groups.

[0076] In one embodiment, R^b is a carboxylic acid moiety of formula (3b). In one aspect of this embodiment, n = 2. In one aspect of this embodiment, n = 3. In one aspect of this embodiment, n = 4. In one aspect of this embodiment, n = 5. In one aspect of this embodiment, R¹ is an unsubstituted linear C₁-C₆ alkylene group. In one aspect of this embodiment, R¹ is an unsubstituted branched C₃-C₆ alkylene group. In one aspect of this embodiment, R¹ is a methylene group. In one aspect of this embodiment, R¹ is an ethylene group. In one aspect of this embodiment, R¹ is a n-propylene group. In one aspect of this embodiment, R¹ is an isopropylene group. In one aspect of this embodiment, R¹ is a s-butylene group. In one aspect of this embodiment, R¹ is a n-butylene group. In one aspect of this embodiment, R¹ is an isobutylene group. In one aspect of this embodiment, R¹ is a t-butylene group. In one aspect of this embodiment each R^c is a methylene group. In one aspect of this embodiment at least one R^c is a methylene group. In one aspect of this embodiment at least one R^c is a methylene group substituted with one C₁-C₄ alkyl group. In one aspect of this embodiment at least one R^c is a methylene group substituted with one methyl group. In one aspect of this embodiment at least one R^c is a methylene group substituted with two C₁-C₄ alkyl groups.

[0077] In one embodiment, R^b is a carboxylic acid moiety of formula (4a). In one aspect of this embodiment, n = 1. In one aspect of this embodiment, n = 2. In one aspect of this embodiment, n = 3. In one aspect of this embodiment, n = 4. In one aspect of this embodiment, m = 1. In one aspect of this embodiment, m = 2. In one aspect of this embodiment, m = 3. In one aspect of this embodiment, m = 4.

[0078] In one embodiment, R^b is a carboxylic acid moiety of formula (4b). In one aspect of this embodiment, n = 1. In one aspect of this embodiment, n = 2. In one aspect of this embodiment,

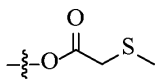
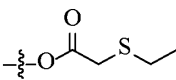
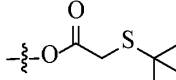
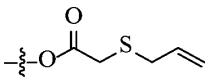
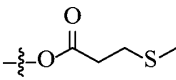
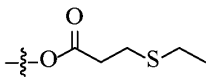
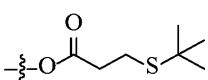
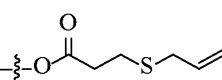
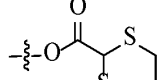
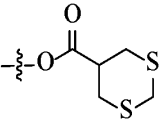
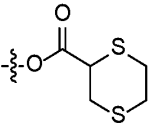
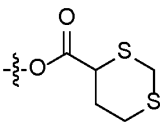
$n = 3$. In one aspect of this embodiment, $n = 4$. In one aspect of this embodiment, $m = 1$. In one aspect of this embodiment, $m = 2$. In one aspect of this embodiment, $m = 3$. In one aspect of this embodiment, $m = 4$. In one aspect of this embodiment, R^1 is an unsubstituted linear C_1 - C_6 alkylene group. In one aspect of this embodiment, R^1 is an unsubstituted branched C_3 - C_6 alkylene group. In one aspect of this embodiment, R^1 is a methylene group. In one aspect of this embodiment, R^1 is an ethylene group. In one aspect of this embodiment, R^1 is a n -propylene group. In one aspect of this embodiment, R^1 is an isopropylene group. In one aspect of this embodiment, R^1 is a s -butylene group. In one aspect of this embodiment, R^1 is a n -butylene group. In one aspect of this embodiment, R^1 is an isobutylene group. In one aspect of this embodiment, R^1 is a t -butylene group.

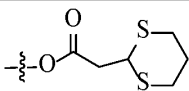
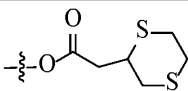
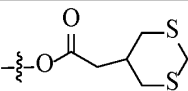
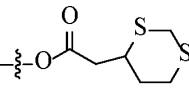
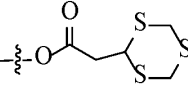
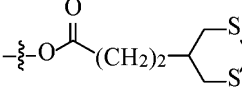
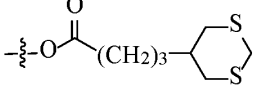
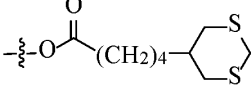
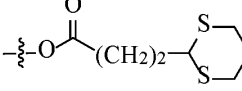
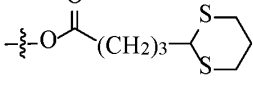
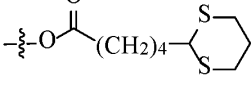
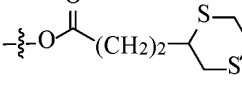
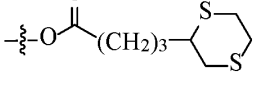
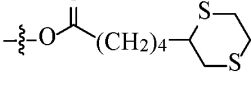
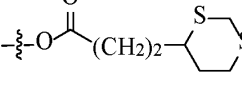
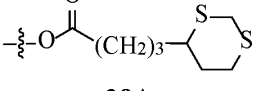
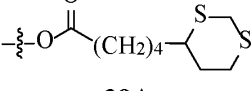
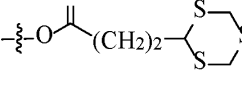
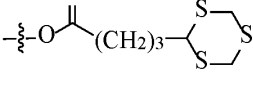
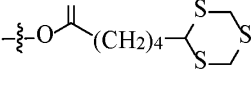
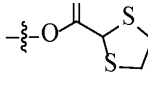
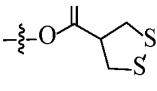
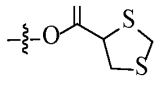
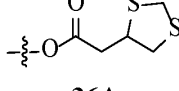
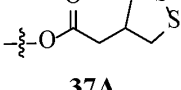
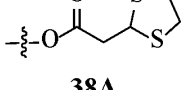
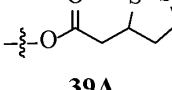
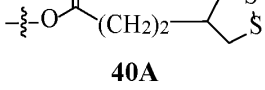
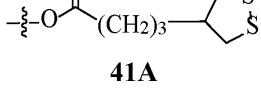
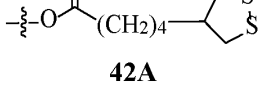
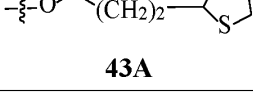
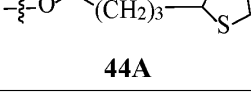
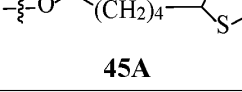
[0079] In one embodiment, R^b is a carboxylic acid moiety of formula (5a).

[0080] In one embodiment, R^b is a carboxylic acid moiety of formula (5b). In one aspect of this embodiment, R^1 is an unsubstituted linear C_1 - C_6 alkylene group. In one aspect of this embodiment, R^1 is an unsubstituted branched C_3 - C_6 alkylene group. In one aspect of this embodiment, R^1 is a methylene group. In one aspect of this embodiment, R^1 is an ethylene group. In one aspect of this embodiment, R^1 is a n -propylene group. In one aspect of this embodiment, R^1 is an isopropylene group. In one aspect of this embodiment, R^1 is a s -butylene group. In one aspect of this embodiment, R^1 is a n -butylene group. In one aspect of this embodiment, R^1 is an isobutylene group. In one aspect of this embodiment, R^1 is a t -butylene group.

[0081] Specific R^b Carboxylic Acid Moiety Groups

[0082] In one aspect of this embodiment, R^b is a carboxylic acid moiety group as illustrated in Table 1:

		
1A	2A	3A
		
4A	5A	6A
		
7A	8A	9A
		
10A	11A	12A

 13A	 14A	 15A
 16A	 17A	 18A
 19A	 20A	 21A
 22A	 23A	 24A
 25A	 26A	 27A
 28A	 29A	 30A
 31A	 32A	 33A
 34A	 35A	 36A
 37A	 38A	 39A
 40A	 41A	 42A
 43A	 44A	 45A

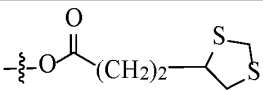
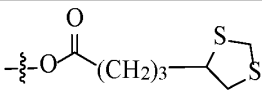
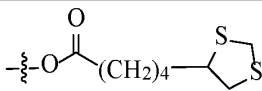
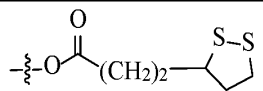
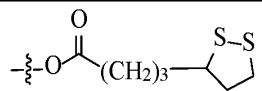
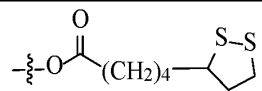
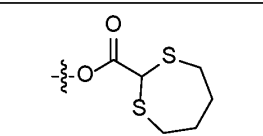
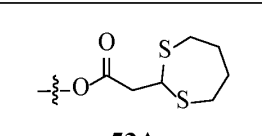
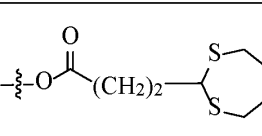
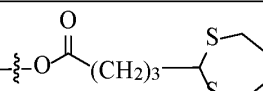
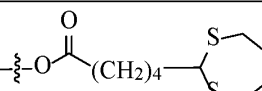
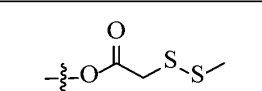
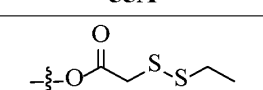
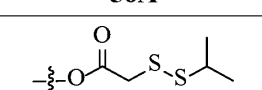
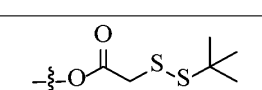
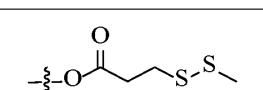
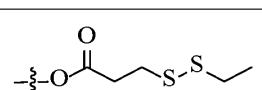
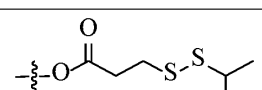
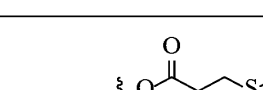
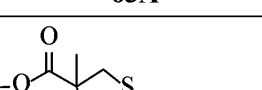
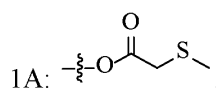
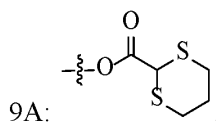
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 64A	 65A	

Table 1

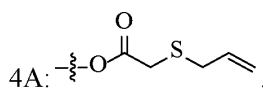
[0083] In one aspect of this embodiment, R^b is a carboxylic acid moiety group of structure



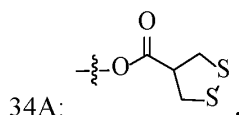
[0084] In one aspect of this embodiment, R^b is a carboxylic acid moiety group of structure



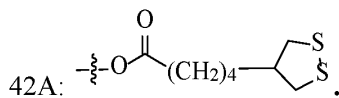
[0085] In one aspect of this embodiment, R^b is a carboxylic acid moiety group of structure



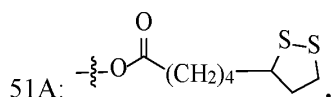
[0086] In one aspect of this embodiment, R^b is a carboxylic acid moiety group of structure



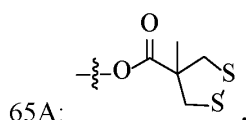
[0087] In one aspect of this embodiment, R^b is a carboxylic acid moiety group of structure



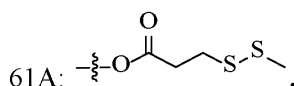
[0088] In one aspect of this embodiment, R^b is a carboxylic acid moiety group of structure



[0089] In one aspect of this embodiment, R^b is a carboxylic acid moiety group of structure



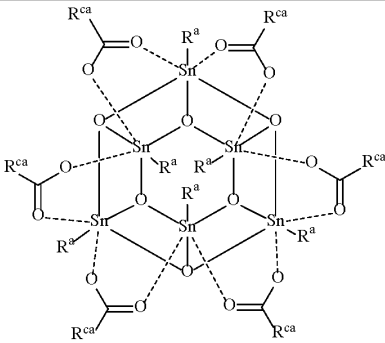
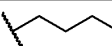
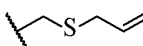
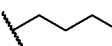
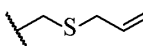
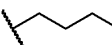
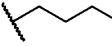
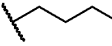
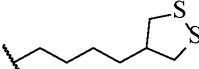
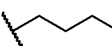
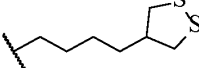
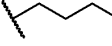
[0090] In one aspect of this embodiment, R^b is a carboxylic acid moiety group of structure



[0091] In one embodiment, each of R^a and R¹ are the same group. In one embodiment, each of R^a and R^c are the same group. In some embodiments, each of R^a, R¹ and R² are the same group. In another embodiment, each of R^a, R¹ and R^c are the same group. In another embodiment, two of R^a, R¹ and R² are the same group. In another embodiment, two of R^a, R¹ and R^c are the same group. In another embodiment, each of R^a and R² are the same group. In another embodiment, R¹ and R^c (when present) are the same group. In another embodiment, R¹ and R² are the same group. In another embodiment, R² and R^c are the same group. As those skilled in the art will understand, when R¹ is considered to be the “same” as one or both of R^a and/or R² when R¹ is the corresponding hydrocarbon radical of the R^a and/or R² group. Thus, for example, if R^a and/or R² is a methyl group and R¹ is the “same” then R¹ is a methylene group (*i.e.*, the corresponding hydrocarbon radical group of a methyl group). In other embodiments, when present R^a, R¹, R² and R^c can be different from one another.

[0092] Exemplary Sn6-Oxo Clusters

[0093] In one aspect, the Sn6-oxo clusters with carboxylic acids moieties containing a (poly)thioether or polysulfide functional groups have one or more of the following structures as illustrated in Table 2:

Formula	 Cluster Structure	
	R ^a	R ^{ca}
$[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_2\text{SCH}_3)_6]$		
$[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_2\text{SCH}_3)_6]$		
$[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_2\text{SCH}_2\text{CH}=\text{CH}_2)_6]$		
$[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_2\text{SCH}_2\text{CH}=\text{CH}_2)_6]$		
$[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CHS}_2\text{C}_3\text{H}_6)_6]$		
$[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CHS}_2\text{C}_3\text{H}_6)_6]$		
$[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CHS}_3\text{C}_2\text{H}_4)_6]$		
$[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CHS}_3\text{C}_2\text{H}_4)_6]$		
$[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CHC}_2\text{H}_4\text{S}_2)_6]$		
$[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CHC}_2\text{H}_4\text{S}_2)_6]$		
$[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{C}-(\text{CH}_2)_4\text{CHS}_2\text{C}_2\text{H}_4)_6]$		
$[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-(\text{CH}_2)_4\text{CHS}_2\text{C}_2\text{H}_4)_6]$		
$[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{C}-\text{C}(\text{CH}_3)\text{C}_2\text{H}_4\text{S}_2)_6]$		
$[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{C}(\text{CH}_3)\text{C}_2\text{H}_4\text{S}_2)_6]$		

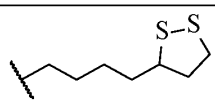
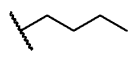
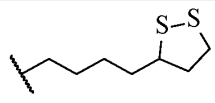
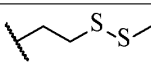
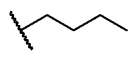
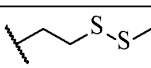
$[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{C}-(\text{CH}_2)_4\text{CHC}_2\text{H}_4\text{S}_2)_6]$		
$[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-(\text{CH}_2)_4\text{CHC}_2\text{H}_4\text{S}_2)_6]$		
$[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{C}-\text{C}_2\text{H}_4\text{S}_2\text{CH}_3)_6]$		
$[((n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{C}_2\text{H}_4\text{S}_2\text{CH}_3)_6)]$		

Table 2

[0094] Processes for Preparing Sn6-Oxo Clusters

[0095] As set forth above, the disclosed subject matter relates further includes processes for synthesizing the disclosed and claimed Sn6-oxo clusters.

[0096] In a typical synthesis, a tin-containing acid (*e.g.*, butyl stannic acid; 0.5 – 50 eq.), is weighed into a round bottom flask of appropriate size, optionally equipped with stirring device. A suitable solvent (*e.g.*, toluene; 5 – 10000 eq.) is added as a solvent and a sulfur-containing carboxylic acid (1 eq.) is added. The order of addition can be altered. The solution is heated with optional stirring to remove water from the reaction mixture (which can be collected in a Dean-Stark apparatus). The reaction mixture is heated at least until no more water is removed (*e.g.*, 1 hour to 72 hours). Afterwards, the solution is cooled to room temperature and filtered to remove any particles, affording a clear solution. Volatiles can be optionally removed under reduced pressure and/or increased temperature (*e.g.*, 25 °C – 130 °C) to yield the desired Sn6 drum cluster product (typically as an amorphous to crystalline material).

[0097] In another synthesis, a solution of a monoorgano Sn starting material with a desired ligand(s), typically alkoxy, is prepared in an organic solvent or a mixture of solvent(s). Under stirring, water is added to (neat or as solution in an organic solvent or mixture of organic solvents). Stirring is continued and a carboxylic acid (1 eq. with respect to Sn) is either added as neat substance or as solution in an organic solvent or a solvent mixture to the reaction solution. The reaction solution is continued to stir, typically for several hours or overnight. The Sn6-oxo cluster can be isolated via removal of the solvent by filtration or evaporation, optionally at reduced pressure and/or elevated temperature. The reaction can be performed in a way that the resulting solution has an adjusted concentration so that it can directly be used for application purposes.

[0098] In one aspect, the solvent is selected from toluene, THF, PGME, cyclohexanone, 2-heptanone, CPME, anisole and a mixture thereof. In one aspect, each addition step is performed at room temperature but can alternatively be performed at reduced or elevated temperatures in the range between the freezing and boiling points of the solvent(s). For instance, the addition of water may be

performed at room temperature and the addition of the carboxylic acid may be performed at elevated temperatures or vice versa. The addition steps may also be performed at the same temperature. Thus, in one aspect, some or all of the steps of the process are conducted at a temperature of between about 0 °C to a temperature which is at or below the boiling point of the solvent(s) employed. In another aspect, some or all of the steps of the process are conducted at a temperature of between about 10 °C to about 60 °C. In another aspect, some or all of the steps of the process are conducted at a temperature of between about 15 °C to about 30 °C. In another aspect, some or all of the steps of the process are conducted at a temperature of between about 18 °C to about room temperature. In another aspect, all of the steps are performed at a temperature of between about room temperature and a temperature which is at or below the boiling point of the solvent(s) employed. In another aspect, all of the steps of the process are performed at room temperature.

[0099] In one aspect, the yield of the Sn6-oxo clusters from the process is about or above 80%. In another aspect, the yield of the Sn6-oxo clusters from the process is about or above 85%. In another aspect, the yield of the Sn6-oxo clusters from the process is about or above 90%. In another aspect, the yield of the Sn6-oxo clusters from the process is about or above 95%.

[0100] Sn6-Oxo Cluster Formulations and Uses Thereof

[0101] In another aspect, the disclosed and claimed subject matter includes formulations that include (i) one or more of the disclosed and claimed Sn6-oxo clusters and (ii) one or more solvents suitable for use in a spin-coating process. In one embodiment, the formulation includes (i) two or more of the disclosed and claimed Sn6-oxo clusters and (ii) one or more solvents suitable for use in a spin-coating process.

[0102] In another aspect, the disclosed and claimed subject matter includes preparing the target compounds in a spin-coating solvent (mixture) at the desired concentration, circumventing the isolation of the material and direct formation of the spin-coatable formulation. In one aspect, such formulations are free of toluene.

[0103] In one embodiment, the one or more solvents suitable for use in a spin-coating process includes one or more of an alcohol, an ester, a ketone, a lactone, a diketone, a solvent with aromatic moieties, a solvent with a carboxylic acid, an amide and mixtures thereof.

[0104] In another embodiment, the one or more solvents suitable for use in a spin-coating process includes one or more of 1-methoxy-2-propanyl acetate (PGMEA), 1-methoxy-2-propanol (PGME), butyl acetate, amyl acetate, cyclohexyl acetate, 3-methoxybutyl acetate, methyl ethyl ketone, methyl amyl ketone, cyclohexanone, cyclopentanone, ethyl-3-ethoxy propanoate, methyl-3-ethoxy propanoate, methyl-3-methoxy propanoate, methyl acetoacetate, ethyl acetoacetate, diacetone alcohol, methyl pivalate, ethyl pivalate, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol monomethyl ether propanoate, propylene glycol

monoethyl ether propanoate, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, 3-methyl-3-methoxybutanol, N-methylpyrrolidone, dimethyl sulfoxide, gamma-butyrolactone, gamma valerolactone, cyclopentyl methyl ether, propylene glycol methyl ether acetate, propylene glycol ethyl ether acetate, propylene glycol propyl ether acetate, methyl lactate, ethyl lactate, propyl lactate, tetramethylene sulfone, propylene glycol dimethyl ether, dipropylene glycol dimethyl ether, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, toluene, 2-heptanone, 1-hexanol, 4-methyl-2-pentanol and anisole. In a further aspect of this embodiment, the one or more solvents for use in a spin-coating process includes one or more of toluene, THF, cyclohexanone, PGME, PGMEA, anisole, 2-heptanone and 4-methyl-2-pentanol. In a further aspect of this embodiment, the one or more solvents for use in a spin-coating process includes one or more of THF, cyclohexanone, PGME, PGMEA, anisole, 2-heptanone and 4-methyl-2-pentanol. In one aspect, such formulations are free of toluene.

[0105] In another embodiment, the Sn6-oxo cluster formulations have a concentration of Sn clusters of about 1 mg/mL to about 1000 mg/mL. In another embodiment, the Sn6-oxo clusters can be formulated into solutions having a concentration of Sn clusters of about 1 mg/mL to about 100 mg/mL. In another embodiment, the Sn6-oxo clusters can be formulated into solutions having a concentration of Sn clusters of about 1 mg/mL to about 50 mg/mL. In another embodiment, the Sn6-oxo clusters can be formulated into solutions having a concentration of Sn clusters of about 10 mg/mL to about 50 mg/mL. In another embodiment, the Sn6-oxo cluster formulations have a concentration of Sn clusters of about 25 mg/mL to about 50 mg/mL. In another embodiment, the Sn6-oxo cluster formulations have a concentration of Sn clusters of about 50 mg/mL to about 100 mg/mL.

[0106] The disclosed and claimed subject matter further includes using the disclosed and claimed Sn6-oxo cluster formulations in EUV and ebeam processes. Such formulations are or can be used for patterning a radiation sensitive coating in a process that includes the steps of (i) forming a coating on a substrate surface with one or more of the disclosed and claimed Sn6-oxo cluster formulations, (ii) drying the coating to produce a dried layer; and (iii) irradiating at least a portion of the dried layer to form a latent image.

[0107] In one embodiment, the substrate of step (i) includes silicon. In one embodiment, the substrate of step (i) includes silicon and at least one additional material layer (*i.e.*, a stack of materials) on top of which the material is deposited.

[0108] In one embodiment, the dried layer of step (ii) has a thickness of about 1 nm to about 500 nm. In one embodiment, the dried layer of step (ii) has a thickness of about 10 nm to about 100 nm. In one embodiment, the dried layer of step (ii) has a thickness of about 15 nm to about 50 nm.

[0109] In one embodiment, the irradiating of step (iii) includes exposing at least a portion of

the dried layer to ionizing radiation. In one aspect of this embodiment, the ionizing radiation has a wavelength range of about 10 nm to about 365 nm. In one aspect of this embodiment, the ionizing radiation is generated via electron beams.

[0110] Method of photopatterning the materials: spincoating on a substrate at 500rpm/5s then 800-5000 rpm for 15-120 s, a soft bake of 15-300s at 40-200°C, exposing with e-beam at 2-100 keV for 1-10000 μ C or EUV (13.5 nm) through a mask, baking the exposed wafer for 0.5-20 minutes at 100-200 °C, developing for 15-300 sec in organic solvent (mixtures). Solvents and mixtures thereof include, but are not limited to, 2-hetptanone, cyclohexanone, PGMEA, PGME, a mixture of anisole and PGMEA, a mixture of anisole and cyclohexanone and a mixture of anisole and 2-heptanone.

[0111] It will also be apparent to those skilled in the art that various modifications may be made in how the disclosed subject matter is practiced based on described aspects in the specification without departing from the spirit and scope of the disclosed subject matter disclosed herein.

[0112] EXAMPLES

[0113] Reference will now be made to more specific embodiments of the present disclosure and experimental results that provide support for such embodiments. The examples are given below to more fully illustrate the disclosed subject matter and should not be construed as limiting the disclosed subject matter in any way.

[0114] It will be apparent to those skilled in the art that various modifications and variations can be made in the disclosed subject matter and specific examples provided herein without departing from the spirit or scope of the disclosed subject matter. Thus, it is intended that the disclosed subject matter, including the descriptions provided by the following examples, covers the modifications and variations of the disclosed subject matter that come within the scope of any claims and their equivalents.

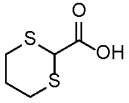
[0115] Materials and Methods:

[0116] The disclosed and claimed processes utilizes commercially available materials (*e.g.*, THF, PGME, cyclohexanone, toluene, acetic acid, 1,3-dithiane-2-carboxylic acid (CAS 20461-89-6), (methylthio)acetic acid (CAS 2444-37-3), 2-(prop-2-en-1-ylsulfanyl)acetic acid, (CAS 20600-63-9), 1,2-dithiolane carboxylic acid (CAS 2224-02-4), 5-(1,2-dithiolan-4-yl)pentanoic acid (CAS 5694-54-2), CDCl_3 , C_6D_6 . 4-Methyl-1,2-dithiolane-4-carboxylic acid (CAS 208243-72-5) and 3-(Methyldithio)propanoic acid (CAS 138148-59-1) were prepared according to modified literature procedures. *See* P. Rivera-Fuentes *et al.*, *Syn. Lett.*, 29, 1289-1292 (2018) and R. Chari *et al.*, *J. Med. Chem.*, 49, 4392-4408 (2006). $\text{RSn}(\text{OR}')_3$ compounds were prepared according to (modified) literature procedures. *See* F. Banse *et al.*, *Inorg. Chem*, 34, 6371 (1995). $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_3)_6]$ was prepared according to modified literature procedures. *See* Chandrasekhar *et al.*, *Inorg. Chem.*, 26, 1050 (1987).

[0117] Example 1: Synthesis of $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CHS}_2\text{C}_3\text{H}_6)_6]$

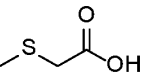
[0118] A 250 mL 4-neck round bottom flask was equipped with a Dean-Stark condenser,

a thermometer and a magnetic stir bar. It was charged with n-butyl tin hydroxide oxide hydrate (1.89 g, 0.01 mol, 1 eq., nBuSnOOH*H₂O, CAS 304671-74-7) and 100 mL of toluene. 1,3-

Dithiane-2-carboxylic acid  (1.2 g, 0.01 mol, 0.9 eq., CAS 20461-89-6) was added. The flask was closed with stoppers and the atmosphere was purged with nitrogen via an overpressure release valve. The solution was heated to reflux for 18 hours, and the water was collected in the Dean-Stark trap. The slightly milky solution that was obtained was allowed to cool to room temperature. Thereafter, all solids were removed via filtration to afford a clear solution. All volatiles were then removed on a rotary evaporator at 30 °C and full vacuum to afford 2.7 g of a white powder (quantitative yield). The substance was identified as (nBuSn)₆O₆(O₂C-CHS₂C₃H₆)₆ via ¹H and ¹¹⁹Sn-NMR (CDCl₃; compound shows a signal at -478 ppm in the ¹¹⁹Sn-NMR). See FIG. 1 and FIG 2.

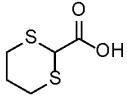
[0119] Example 2: Synthesis of [(nBuSn)₆O₆(O₂C-CH₂SCH₃)₆]

[0120] A 100 mL 4-neck round bottom flask was equipped with a Dean-Stark condenser, a thermometer and a magnetic stir bar. It was charged with n-butyl tin hydroxide oxide hydrate (1.5 g, 0.01 mol, 1 eq., nBuSnOOH*H₂O, CAS 304671-74-7) and 75 mL of toluene (CAS 108-

88-3). (Methylthio)acetic acid  (0.681 g, 0.01 mol, 1 eq., CAS 2444-37-3) was added. The flask was closed with stoppers and the atmosphere was purged with nitrogen via an overpressure release valve. The solution was heated to reflux for 18 hours, and the water was collected in the Dean-Stark trap. The slightly milky solution that was obtained was allowed to cool to room temperature. Thereafter, all solids were removed via filtration to afford a clear solution. All volatiles were then removed on a rotary evaporator at 30 °C and full vacuum to afford 2 g of a white powder (99% yield). The substance was identified as (nBuSn)₆O₆(O₂C-CH₂SCH₃)₆ via ¹H and ¹¹⁹Sn-NMR (CDCl₃; compound shows a signal at -481 ppm in the ¹¹⁹Sn-NMR). See FIG. 3 and FIG 4.

[0121] Example 3: Synthesis of (MeSn)₆O₆(O₂C-CHS₂C₃H₆)₆

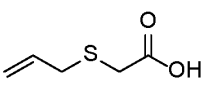
[0122] The Sn starting material MeSn(OtAmyl)₃ (2.7 mmol, 1 eq) is weighed into a crimp vial (reaction vial), equipped with a stir bar, inside a glovebox. 20 mL of THF are added and the vial is closed. It is transferred to a fume hood, where water (8.1 mmol, 3 eq.) is added with a syringe while

stirring, resulting in milky solution. In a separate vial, Dithiane-2-carboxylic acid  (CAS 20461-89-6) (2.7 mmol, 1 eq) is dissolved in 5 mL THF and the resulting solution is slowly added dropwise to the reaction vial with a syringe. The precipitate dissolves within one hour and the solution is stirred overnight. The next day, all volatiles are removed in vacuo, affording the product as a white powder (768 mg, 94%). The substance was identified as (MeSn)₆O₆(O₂C-CHS₂C₃H₆)₆ via ¹H and

^{119}Sn -NMR (CDCl_3 ; compound shows a signal at -457 ppm in the ^{119}Sn -NMR).

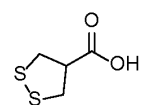
[0123] Example 4: Synthesis of $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_2\text{SCH}_2\text{CH}=\text{CH}_2)_6]$

[0124] A 250 mL 4-neck round bottom flask was equipped with a Dean-Stark condenser, a thermometer and a magnetic stir bar. It was charged with n-butyl tin hydroxide oxide hydrate (3 g, 0.01 mol, 1 eq., $n\text{BuSnOOH}\cdot\text{H}_2\text{O}$, CAS 304671-74-7) and 150 mL of toluene (CAS 108-88-3).

2-(prop-2-en-1-ylsulfanyl)acetic acid  (1.6 g, 0.01 mol, 1 eq., CAS 20600-63-9) was added. The flask was closed with stoppers and the atmosphere was purged with nitrogen via an overpressure release valve. The solution was heated to reflux for 18 hours, and the water was collected in the Dean-Stark trap. The slightly milky and yellowish solution that was obtained was allowed to cool to room temperature. Thereafter, all solids were removed via filtration to afford a clear solution. All volatiles were then removed on a rotary evaporator at 30 °C and full vacuum to afford the product as a yellowish oil that becomes wax-like after some time (4.1 g, 98% yield). The substance was identified as $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_2\text{SCH}_2\text{CH}=\text{CH}_2)_6]$ via ^1H and ^{119}Sn -NMR (CDCl_3 ; compound shows a signal at -481 ppm).

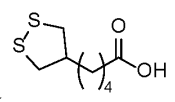
[0125] Example 5: Synthesis of $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CHC}_2\text{H}_4\text{S}_2)_6]$

[0126] A 50 mL round bottom flask was charged with n-butyl tin hydroxide oxide hydrate (0.39 g, 1.7 mmol, 1 eq., $n\text{BuSnOOH}\cdot\text{H}_2\text{O}$, CAS 304671-74-7), 1,2-dithiolane carboxylic acid

 (0.251 g, 1.7 mmol, 1 eq., CAS 2224-02-4), 0.4 g of pre-activated molecular sieves and 20 mL of toluene (CAS 108-88-3). The flask was closed with a stopper and the solution stirred overnight at 50 °C. A milky, orange solution resulted that was allowed to cool to room temperature. Thereafter, all solids were removed via filtration to afford a clear solution. All volatiles were then removed on a rotary evaporator at 30 °C and full vacuum to afford the product as a yellowish solid (0.41 g, 70% yield). The substance was identified as $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CHC}_2\text{H}_4\text{S}_2)_6]$ via ^1H and ^{119}Sn -NMR (CDCl_3 ; compound shows a signal at -481 ppm in the ^{119}Sn -NMR).

[0127] Example 6: Synthesis of $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-(\text{CH}_2)_4\text{CHS}_2\text{C}_2\text{H}_4)_6]$

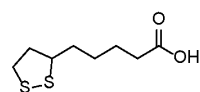
[0128] A 50 mL round bottom flask was charged with n-butyl tin hydroxide oxide hydrate (0.25 g, 1.1 mmol, 1 eq., $n\text{BuSnOOH}\cdot\text{H}_2\text{O}$, CAS 304671-74-7), 5-(1,2-dithiolan-4-yl)pentanoic

acid  (0.251 g, 1.1 mmol, 1 eq., CAS 5694-54-2), and 13 mL of toluene (CAS 108-88-3). The mixture was stirred for one hour until most materials were dissolved before 0.25 g of pre-activated molecular sieves were added. The flask was closed with a stopper and the solution was stirred overnight at 50 °C. A milky, yellowish solution resulted that was allowed to cool to room

temperature. Thereafter, all solids were removed via filtration to afford a clear solution. All volatiles were then removed on a rotary evaporator at 30 °C and full vacuum to afford the product as a yellowish oil (0.2 g, 49% yield). The substance was identified as $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-(\text{CH}_2)_4\text{CHS}_2\text{C}_2\text{H}_4)_6]$ via ^1H and ^{119}Sn -NMR (CDCl_3 ; compound shows a signal at -484 ppm in the ^{119}Sn -NMR).

[0129] Example 7: Synthesis of $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-(\text{CH}_2)_4\text{CHC}_2\text{H}_4\text{S}_2)_6]$

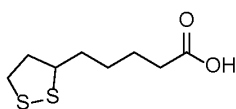
[0130] The Sn starting material $n\text{BuSn}(\text{OtAmyl})_3$ (1.95 mmol, 1 eq) is weighed into a crimp vial (reaction vial), equipped with a stir bar, and the vial is closed inside a glovebox. After transfer into a hood 38 mL of cyclohexanone are added to afford a clear solution. Water (5.86 mmol, 3 eq.) is then added with a syringe while stirring. A cloudy solution is formed. In a separate vial, the desired acid



(1.95 mmol, 1 eq) is dissolved in 2 mL of cyclohexanone and slowly added dropwise to the reaction vial with a syringe. The cloudy solution is stirred overnight, and a clear solution results the next day. A sample is taken for ^{119}Sn -NMR measurement with a capillary insert containing C_6D_6 for locking. A characteristic cluster signal is detected at -485 ppm in the ^{119}Sn NMR spectrum. The identity of the compound is confirmed via mass spectrometry. The solution is filtered and used as resist formulation afterwards.

[0131] Example 8: Synthesis of $[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{C}-(\text{CH}_2)_4\text{CHC}_2\text{H}_4\text{S}_2)_6]$

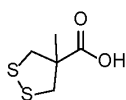
[0132] The Sn starting material $\text{MeSn}(\text{OtBu})_3$ (2.25 mmol, 1 eq) is weighed into a crimp vial (reaction vial), equipped with a stir bar, and the vial is closed inside a glovebox. After transfer into a hood 36 mL of cyclohexanone are added to afford a clear solution. In the next step water (6.75 mmol, 3 eq.) is added with a syringe while stirring. A cloudy solution is formed. In a separate vial, the



desired acid (2.25 mmol, 1 eq) is dissolved in 4 mL of cyclohexanone and slowly added dropwise to the reaction vial with a syringe. The cloudy solution is stirred overnight, and a clear solution results the next day. A sample is taken for ^{119}Sn -NMR measurement with a capillary insert containing C_6D_6 for locking. A characteristic cluster signal is detected at -465 ppm in the ^{119}Sn NMR spectrum. The identity of the compound is confirmed via mass spectrometry.

[0133] Example 9: Synthesis of $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-(\text{CH}_2)_4\text{CHS}_2\text{C}_2\text{H}_4)_6]$

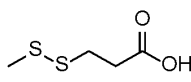
[0134] The Sn starting material $n\text{BuSn}(\text{OtAmyl})_3$ (1.69 mmol, 1 eq) is weighed into a crimp vial (reaction vial), equipped with a stir bar, and the vial is closed inside a glovebox. After transfer into a hood 28 mL of cyclohexanone are added to afford a clear solution. In the next step water (5.06 mmol, 3 eq.) is added with a syringe while stirring. A clear solution is formed. In a separate vial, the



desired acid (1.69 mmol, 1 eq) is dissolved in 2 mL of cyclohexanone and slowly added dropwise to the reaction vial with a syringe. The solution is stirred overnight, and a clear solution results the next day. A sample is taken for ^{119}Sn -NMR measurement with a capillary insert containing C_6D_6 for locking. A characteristic cluster signal is detected at -480 ppm in the ^{119}Sn NMR spectrum. The identity of the compound is confirmed via mass spectrometry.

[0135] Example 10: Synthesis of $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{C}_2\text{H}_4\text{S}_2\text{CH}_3)_6]$

[0136] The Sn starting material $n\text{BuSn}(\text{OtAmyl})_3$ (1.57 mmol, 1 eq) is weighed into a crimp vial (reaction vial), equipped with a stir bar, and the vial is closed inside a glovebox. After transfer into a hood 22 mL of cyclohexanone are added to afford a clear solution. In the next step water (4.71 mmol, 3 eq.) is added with a syringe while stirring. A clear solution is formed. In a separate vial, the



desired acid (1.57 mmol, 1 eq) is dissolved in 5 mL of cyclohexanone and slowly added dropwise to the reaction vial with a syringe. The solution is stirred overnight, and a clear solution results the next day. A sample is taken for ^{119}Sn -NMR measurement with a capillary insert containing C_6D_6 for locking. A characteristic cluster signal is detected at -484 ppm in the ^{119}Sn NMR spectrum. The identity of the compound is confirmed via mass spectrometry.

[0137] Example 11: $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CHS}_2\text{C}_3\text{H}_6)_6]$ Solution

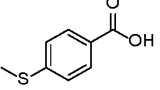
[0138] A sample of the $(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CHS}_2\text{C}_3\text{H}_6)_6$ produced in Example 1 was combined with toluene to produce solution with a concentration of 10 mg/mL. Thereafter, the solution was filtered through a 0.2 μm PTFE syringe filter before use in wafer coating.

[0139] Example 12: Electron Beam Lithography Process for $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CHS}_2\text{C}_3\text{H}_6)_6]$

[0140] Wafer coating of a 2-inch wafer was performed using 1 mL of the solution prepared in Example 11. The solution was applied first at 500 rpm/10s and then at 3500 rpm/30s followed by a soft bake at 80 °C for 120 seconds. Thereafter, an E-beam exposure was conducted at 30 KeV, working distance 4, BI 10 and beam current 240 pA with a dose range of 10-5000 $\mu\text{C}/\text{cm}^2$. A post exposure bake was then conducted at 120 °C for 120 seconds. A development was performed in 2-heptanone for 15 seconds followed by rinsing with 2-heptanone and then drying with a nitrogen gun. The process resulted in the deposition of a 40 nm film as determined via a Bruker profilometer. FIG. 11 shows the Dose curve for the $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CHS}_2\text{C}_3\text{H}_6)_6]$ formulation as used in the above process in comparison to a dose curve of $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{CCH}_3)_6]$ (with acetic acid as additive for coating).

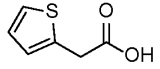
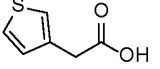
[0141] Comparative Example 1: Attempted Preparation of $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{C}_6\text{H}_4\text{SMe})_6]$

[0142] The Sn starting material $n\text{BuSn}(\text{OtAmyl})_3$ (2.2 mmol, 1 eq) is weighed into a crimp vial (reaction vial), equipped with a stir bar, inside a glovebox and closed. The vial is transferred to a fume hood, where 35 mL of THF are added. Water (12.3 mmol, 3 eq.) is added with a syringe while

stirring, resulting in a clear solution. In a separate vial,  (CAS 13205-48-6) (2.2 mmol, 1 eq) is dissolved in 5 mL THF and the resulting solution is slowly added dropwise to the reaction vial with a syringe. The solution is stirred overnight. The next day a milky solution is obtained. It is filtered but approx. 3 h after filtration a white precipitate begins to form again. The solution is used for wafer coating but is again filtered right before coating. NMR spectra are recorded on concentrated reaction solutions (5 mL to approx. 1 mL) and on solids isolated by removal of the solvents (5 mL solution) and redissolution in CDCl_3 . ^1H and ^{119}Sn NMR spectra of the resulting product are shown in FIG. 5 and FIG. 6. The absence of a sharp signal at ~ 480 ppm in the ^{119}Sn NMR indicates that the Sn_6 drum cluster formation has not been successful. The acid is not soluble in a 1:1 PGME:Cyclohexanone mixture and the preparation was therefore performed in THF.

[0143] **Comparative example 2: Preparation of $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_2-(2-\text{C}_4\text{H}_3\text{S}))_6]$ and $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_2-(3-\text{C}_4\text{H}_3\text{S}))_6]$**

[0144] The Sn starting material $n\text{BuSn}(\text{OtAmyl})_3$ (2.4 mmol, 1 eq) is weighed into a crimp vial (reaction vial), equipped with a stir bar, inside a glovebox and closed. The vial is transferred to a fume hood, where 19 mL of a 1:1 v/v mixture of 1-methoxypropan-2-ol and cyclohexanone are added. Water (12.3 mmol, 3 eq.) is added with a syringe while stirring, resulting in a clear solution. In a separate vial,

the desired acid  (CAS 1918-77-0), or  (CAS 6964-21-2) (2.4 mmol, 1 eq) respectively, is dissolved in 2 mL of the solvent mixture and the resulting solution is slowly added dropwise to the reaction vial with a syringe. The solution is stirred overnight and is still clear the next day. It is filtered and used for wafer coating as is. NMR spectra are recorded on concentrated reaction solutions (5 mL to approx. 1 mL) and on solids isolated by removal of the solvents (5 mL solution) and redissolution in CDCl_3 . The materials were identified as the desired products via ^1H and ^{119}Sn NMR spectroscopy. For ^{119}Sn NMR Spectroscopy, a concentrated reaction was used in addition to the isolated material obtained from removal of solvent in vacuo and redissolution in CDCl_3 . See FIG. 7 (top: concentrated solution; bottom: redissolved solids) and FIG. 8 for the ^{119}Sn and ^1H spectra of $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_2-(2-\text{C}_4\text{H}_3\text{S}))_6]$. See FIG. 9 (top: concentrated solution; bottom: redissolved solids) and FIG. 10 for the ^{119}Sn and ^1H spectra of $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_2-(3-\text{C}_4\text{H}_3\text{S}))_6]$. The analytical data obtained for the prepared materials is in good agreement with what has been published for these compounds in U.S. Patent Application Publication No. 2021/0087210.

[0145] **Comparative example 3: Wafer coating of reference materials**

$[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{C}_6\text{H}_4\text{SMe})_6]$, $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_2-(2-\text{C}_4\text{H}_3\text{S}))_6]$, and $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_2-(3-\text{C}_4\text{H}_3\text{S}))_6]$

[0146] The solutions from comparative examples 1 and 2 were used for wafer coating for subsequent EBL testing. Formulations with the $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{C}_6\text{H}_4\text{SMe})_6]$, $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_2-(2-\text{C}_4\text{H}_3\text{S}))_6]$, and $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_2-(3-\text{C}_4\text{H}_3\text{S}))_6]$ cluster materials were spin coated on a 2 inch Si wafer with a spin speed depending on the viscosity of the formulation with target film thickness of 30 nm after soft bake at 100 °C for 2 minutes. Then the dried layer is exposed by electron beam with 30 kV acceleration voltage with dose levels from 1 to 500 or 10 to 5000 $\mu\text{C}/\text{cm}^2$ in 18 steps. After post exposure bake at 120 °C for 2 minutes the film is developed in 2-heptanone for 2 minutes. The coating of $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{C}_6\text{H}_4\text{SMe})_6]$ resulted in a very rough surface preventing further use in the testing process.

[0147] **Comparative example 4: Electron-beam Lithography of $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_2-(2-\text{C}_4\text{H}_3\text{S}))_6]$, and $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_2-(3-\text{C}_4\text{H}_3\text{S}))_6]$**

[0148] The dried layer on the wafer is exposed by electron beam with 30 kV acceleration voltage with dose levels from 1 to 500 or 10 to 5000 $\mu\text{C}/\text{cm}^2$ in 18 steps. After post exposure bake at 120 °C for 2 minutes the film is developed in 2-heptanone for 2 minutes and rinsed with 2-heptanone for 15 seconds. For both materials $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_2-(2-\text{C}_4\text{H}_3\text{S}))_6]$ and $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_2-(3-\text{C}_4\text{H}_3\text{S}))_6]$ a pattern formation could be observed, but the residual pattern thickness of $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_2-(2-\text{C}_4\text{H}_3\text{S}))_6]$ was so thin, that further data processing was unreasonable. The low residual film thickness indicates a very low photospeed for the material. For $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_2-(3-\text{C}_4\text{H}_3\text{S}))_6]$ a dose curve was obtained, but the photospeed of this material was very low with D50 of 530 $\mu\text{C}/\text{cm}^2$ (dose level at 50% film thickness). In comparison to other materials, e.g., the literature reference $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_3)_6]$ and the compound $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_2\text{C}_3\text{H}_6)_6]$ disclosed herein, this is a very slow photospeed.

[0149] A summary list of D50, dose level at 50% film thickness for materials $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_3)_6]$, $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_2-(3-\text{C}_4\text{H}_3\text{S}))_6]$ and $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_2\text{C}_3\text{H}_6)_6]$.

Formula	D50 E-beam ($\mu\text{C}/\text{cm}^2$)
$[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_3)_6]$	250
$[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_2-(3-\text{C}_4\text{H}_3\text{S}))_6]$	530
$[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_2\text{C}_3\text{H}_6)_6]$	180

[0150] **EUV application at PSI for $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_2\text{C}_3\text{H}_6)_6]$**

[0151] Wafers were processed the same way for spin coating and soft bake as for EBL. Exposure was done on a synchrotron beam line at PSI (Paul Scherrer Institute, Switzerland). Post exposure bake and development were the same as for EBL again. For $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{C}-\text{CH}_3)_6]$ in

the dose curve a D50 value of 40 mJ/cm² was measured, for [(*n*BuSn)₆O₆(O₂C-CHS₂C₃H₆)₆] a D50 value of 34 mJ/cm².

[0152] Although the invention has been described and illustrated with a certain degree of particularity, it is understood that the disclosure has been made only by way of example, and that numerous changes in the conditions and order of steps can be resorted to by those skilled in the art without departing from the spirit and scope of the invention.

What is claimed is:

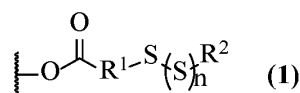
1. A tin compound of the formula $(R^aSn)_6O_6(R^b)_6$,

wherein

(A) R^a is an unsubstituted linear C_1 - C_{10} alkyl group, a linear C_1 - C_6 alkyl group substituted with a halogen, a linear C_1 - C_6 alkyl group substituted with an amino group, a linear C_1 - C_6 alkyl group substituted with a C_5 - C_6 unsubstituted aromatic group, an unsubstituted branched C_3 - C_{10} alkyl group, a branched C_3 - C_{10} alkyl group substituted with a halogen, a C_1 - C_{10} heteroalkylene, a branched C_3 - C_{10} alkyl group substituted with an unsubstituted amine, a substituted amine, $-Si(CH_3)_3$, a benzyl group, a C_3 - C_8 unsubstituted cyclic alkyl group, a C_3 - C_8 cyclic alkyl group substituted with a halogen, a C_3 - C_8 cyclic alkyl group substituted with an amino group, a C_4 - C_8 unsubstituted aromatic group, a C_4 - C_8 aromatic group substituted with a halogen, a C_4 - C_8 aromatic group substituted with an amino group, a C_3 - C_{10} heterocyclic group, a C_2 - C_{10} alkenyl group and a C_3 - C_{10} alkynyl group; and

(B) R^b is a carboxylic acid moiety group selected from the group of

(i) formula (1):



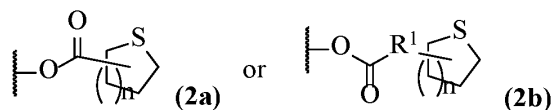
wherein

$n = 0$ or 1 ;

R^1 is an unsubstituted linear C_1 - C_6 alkylene group, an unsubstituted branched C_3 - C_6 alkylene group, an unsubstituted linear C_2 - C_6 alkenylene group, an unsubstituted branched C_3 - C_6 alkenylene group, an unsubstituted linear C_2 - C_6 alkynylene group, an unsubstituted branched C_4 - C_6 alkynylene group or a C_3 - C_8 unsubstituted cyclic alkylene group; and

R^2 is an unsubstituted linear C_1 - C_6 alkyl group, an unsubstituted branched C_3 - C_6 alkyl group, an unsubstituted linear C_2 - C_6 alkenyl group, an unsubstituted branched C_3 - C_6 alkenyl group, an unsubstituted linear C_2 - C_6 alkynyl group, an unsubstituted branched C_4 - C_6 alkynyl group or a C_3 - C_8 unsubstituted cyclic alkyl group;

(ii) formulae (2a) or (2b):

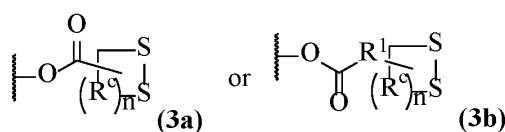


wherein

$n = 1$ to 4 ; and

R^1 is an unsubstituted linear C_1 - C_6 alkylene group or an unsubstituted branched C_3 - C_6 alkyl group;

(iii) formulae (3a) or (3b):



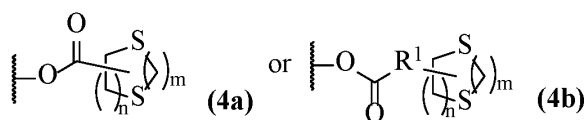
wherein

$n = 2$ to 5 ;

each R^c is individually an unsubstituted methylene group or a methylene group substituted with one or two C_1 - C_4 alkyl groups; and

R^1 is an unsubstituted linear C_1 - C_6 alkylene group or an unsubstituted branched C_3 - C_6 alkylene group;

(iv) formulae (4a) or (4b):

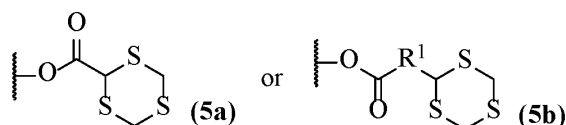


wherein

n and $m =$ individually 1 to 4 ; and

R^1 is an unsubstituted linear C_1 - C_6 alkylene group or an unsubstituted branched C_3 - C_6 alkylene group; and

(v) formulae (5a) or (5b):



wherein

R^1 is an unsubstituted linear C_1 - C_6 alkylene group or an unsubstituted branched C_3 - C_6 alkylene group.

2. The compound of claim 1, wherein R^a is selected from the group consisting of an unsubstituted linear C_1 - C_4 alkyl group, an unsubstituted branched C_3 - C_4 alkyl group, a C_2 - C_6 alkenyl group and a C_4 - C_6 unsubstituted aromatic group.

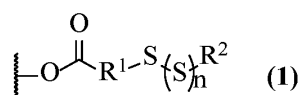
3. The compound of claim 1, wherein R^a is selected from the group consisting of a $-CH_3$ group, a $-CH(CH_3)_2$ group, a $-C(CH_3)_3$ group, a $-CH=CH_2$ group, a $-CH_2CH=CH_2$ group, a $-CH_2CH_2CH=CH_2$ group, a $-CH_2CH_2CH_2CH_3$ group, a $-C_6H_5$ group and a $-CH_2-C_6H_5$ group.

4. The compound of claim 1, wherein R^a is selected from the group consisting of a $-CH_3$ group, a $-CH(CH_3)_2$ group, a $-C(CH_3)_3$ group, a $-CH=CH_2$ group, a $-CH_2CH=CH_2$ group, a $-CH_2CH_2CH=CH_2$ group and a $-CH_2CH_2CH_2CH_3$ group.

5. The compound of claim 1, wherein R^a is selected from the group consisting of a $-CH_3$

group, a $-\text{CH}(\text{CH}_3)_2$ group, a $-\text{C}(\text{CH}_3)_3$ group and a $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ group.

6. The compound of claim 1, wherein R^a is selected from the group consisting of a $-\text{CH}_3$ group, a $-\text{CH}(\text{CH}_3)_2$ group and a $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ group.
7. The compound of claim 1, wherein R^a is a methyl group.
8. The compound of claim 1, wherein R^a is an isopropyl group.
9. The compound of claim 1, wherein R^a is a n-butyl group.
10. The compound of claim 1, wherein R^a is a t-butyl group.
11. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1):



12. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein $n = 0$.
13. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein $n = 1$.
14. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R^1 and R^2 are the same group.
15. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R^1 and R^2 are each a different group.
16. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R^1 is an unsubstituted linear $\text{C}_1\text{-C}_6$ alkylene group and R^2 is an unsubstituted linear $\text{C}_1\text{-C}_6$ alkyl group.
17. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R^1 is an unsubstituted branched $\text{C}_3\text{-C}_6$ alkylene group and R^2 is an unsubstituted branched $\text{C}_3\text{-C}_6$ alkyl group.
18. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R^1 is an unsubstituted linear $\text{C}_2\text{-C}_6$ alkenylene group and R^2 is an unsubstituted linear $\text{C}_2\text{-C}_6$ alkenyl group.
19. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R^1 is an unsubstituted branched $\text{C}_3\text{-C}_6$ alkenylene group and R^2 is an unsubstituted branched $\text{C}_3\text{-C}_6$ alkenyl group.
20. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R^1 is an unsubstituted linear $\text{C}_2\text{-C}_6$ alkynylene group and R^2 is an unsubstituted linear $\text{C}_2\text{-C}_6$ alkynyl group.
21. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R^1 is an unsubstituted branched $\text{C}_4\text{-C}_6$ alkynylene group and R^2 is an unsubstituted branched $\text{C}_4\text{-C}_6$ alkynyl group.
22. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R^1 is a $\text{C}_3\text{-C}_8$ unsubstituted cyclic alkylene group and R^2 is a $\text{C}_3\text{-C}_8$ unsubstituted cyclic alkyl group.
23. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R^1 is a methylene group.

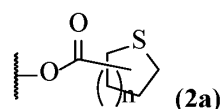
24. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R¹ is an ethylene group.
25. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R¹ is a n-propylene group.
26. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R¹ is an isopropylene group.
27. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R¹ is a s-butylene group.
28. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R¹ is a n-butylene group.
29. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R¹ is an isobutylene group.
30. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R¹ is a t-butylene group.
31. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R² is an unsubstituted linear C₁-C₆ alkyl group.
32. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R² is an unsubstituted branched C₃-C₆ alkyl group.
33. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R² is a C₃-C₈ unsubstituted cyclic alkyl group.
34. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R² is a C₅-C₈ unsubstituted aromatic group.
35. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R² is a methyl group.
36. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R² is an ethyl group.
37. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R² is a n-propyl group.
38. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R² is an isopropyl group.
39. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R² is a s-butyl group.
40. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R² is a n-butyl group.
41. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein

R² is an isobutyl group.

42. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R² is a t-butyl group.

43. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (1) wherein R² is an allyl group.

44. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (2a):



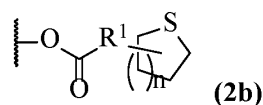
45. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (2a) wherein n = 1.

46. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (2a) wherein n = 2.

47. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (2a) wherein n = 3.

48. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (2a) wherein n = 4.

49. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (2b):



50. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (2b) wherein n = 1.

51. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (2b) wherein n = 2.

52. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (2b) wherein n = 3.

53. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (2b) wherein n = 4.

54. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (2b) wherein R¹ is an unsubstituted linear C₁-C₆ alkylene group.

55. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (2b) wherein R¹ is an unsubstituted branched C₃-C₆ alkylene group.

56. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (2b) wherein R¹ is a methylene group.

57. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (2b) wherein

R¹ is an ethylene group.

58. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (2b) wherein R¹ is a n-propylene group.

59. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (2b) wherein R¹ is an isopropylene group.

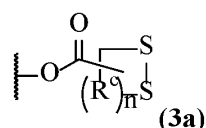
60. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (2b) wherein R¹ is a s-butylene group.

61. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (2b) wherein R¹ is a n-butylene group.

62. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (2b) wherein R¹ is an isobutylene group.

63. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (2b) wherein R¹ is a t-butylene group.

64. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3a):



65. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3a) wherein n = 2.

66. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3a) wherein n = 3.

67. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3a) wherein n = 4.

68. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3a) wherein n = 5.

69. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3a) wherein each R^c is a methylene group.

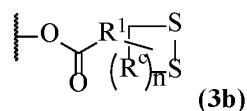
70. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3a) wherein at least one R^c is a methylene group.

71. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3a) wherein at least one R^c is a methylene group substituted with one C₁-C₄ alkyl group.

72. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3a) wherein at least one R^c is a methylene group substituted with one methyl group.

73. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3a) wherein at least one R^c is a methylene group substituted with two C₁-C₄ alkyl groups.

74. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3b):



75. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3b) wherein $n = 2$.

76. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3b) wherein $n = 3$.

77. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3b) wherein $n = 4$.

78. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3b) wherein $n = 5$.

79. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3b) wherein R^1 is an unsubstituted linear C_1 - C_6 alkylene group.

80. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3b) wherein R^1 is an unsubstituted branched C_3 - C_6 alkylene group.

81. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3b) wherein R^1 is a methylene group.

82. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3b) wherein R^1 is an ethylene group.

83. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3b) wherein R^1 is a n-propylene group.

84. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3b) wherein R^1 is an isopropylene group.

85. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3b) wherein R^1 is a s-butylene group.

86. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3b) wherein R^1 is a n-butylene group.

87. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3b) wherein R^1 is an isobutylene group.

88. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3b) wherein R^1 is a t-butylene group.

89. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3b) wherein each R^c is a methylene group.

90. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3b) wherein

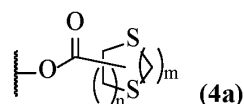
at least one R^c is a methylene group.

91. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3b) wherein at least one R^c is a methylene group substituted with one C₁-C₄ alkyl group.

92. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3b) wherein at least one R^c is a methylene group substituted with one methyl group.

93. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (3b) wherein at least one R^c is a methylene group substituted with two C₁-C₄ alkyl groups.

94. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (4a):



95. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (4a) wherein n = 1.

96. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (4a) wherein n = 2.

97. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (4a) wherein n = 3.

98. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (4a) wherein n = 4.

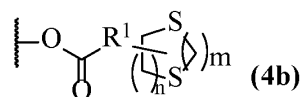
99. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (4a) wherein m = 1.

100. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (4a) wherein m = 2.

101. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (4a) wherein m = 3.

102. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (4a) wherein m = 4.

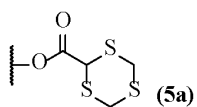
103. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (4b):



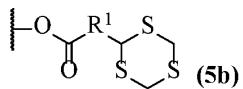
104. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (4b) wherein n = 1.

105. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (4b) wherein n = 2.

- 106.** The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (4b) wherein $n = 3$.
- 107.** The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (4b) wherein $n = 4$.
- 108.** The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (4b) wherein $m = 1$.
- 109.** The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (4b) wherein $m = 2$.
- 110.** The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (4b) wherein $m = 3$.
- 111.** The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (4b) wherein $m = 4$.
- 112.** The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (4b) wherein R^1 is an unsubstituted linear C_1 - C_6 alkylene group.
- 113.** The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (4b) wherein R^1 is an unsubstituted branched C_3 - C_6 alkylene group.
- 114.** The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (4b) wherein R^1 is a methylene group.
- 115.** The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (4b) wherein R^1 is an ethylene group.
- 116.** The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (4b) wherein R^1 is a n-propylene group.
- 117.** The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (4b) wherein R^1 is an isopropylene group.
- 118.** The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (4b) wherein R^1 is a s-butylene group.
- 119.** The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (4b) wherein R^1 is a n-butylene group.
- 120.** The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (4b) wherein R^1 is an isobutylene group.
- 121.** The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (4b) wherein R^1 is a t-butylene group.
- 122.** The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (5a):



123. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (5b):



124. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (5b) wherein R¹ is an unsubstituted linear C₁-C₆ alkylene group.

125. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (5b) wherein R¹ is an unsubstituted branched C₃-C₆ alkylene group.

126. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (5b) wherein R¹ is a methylene group.

127. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (5b) wherein R¹ is an ethylene group.

128. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (5b) wherein R¹ is a n-propylene group.

129. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (5b) wherein R¹ is an isopropylene group.

130. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (5b) wherein R¹ is a s-butylene group.

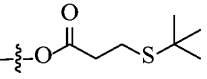
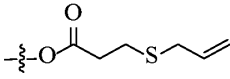
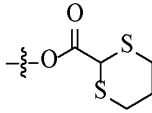
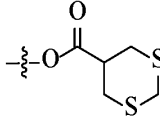
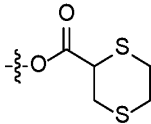
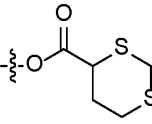
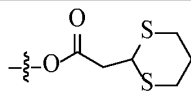
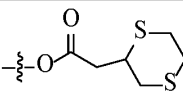
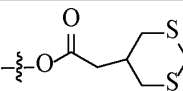
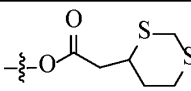
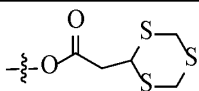
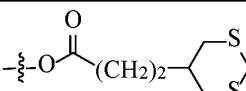
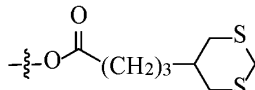
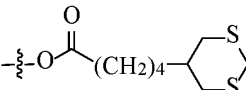
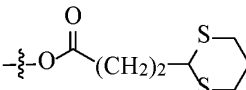
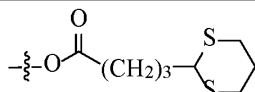
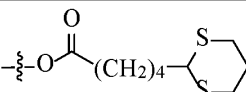
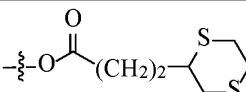
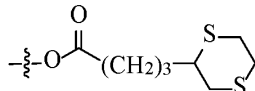
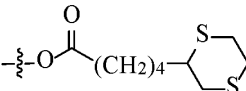
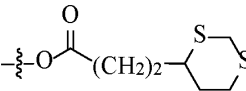
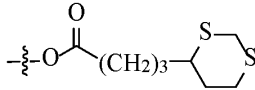
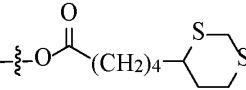
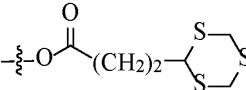
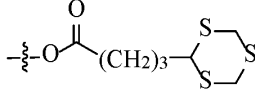
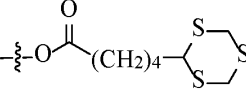
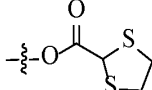
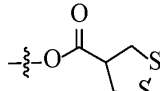
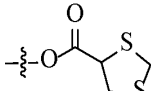
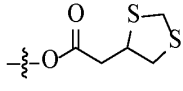
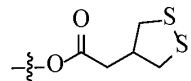
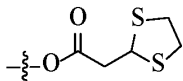
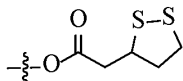
131. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (5b) wherein R¹ is a n-butylene group.

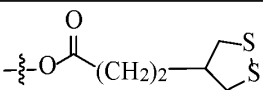
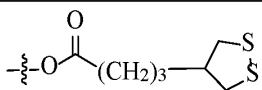
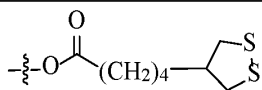
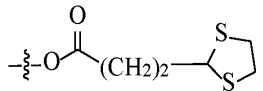
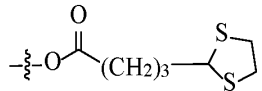
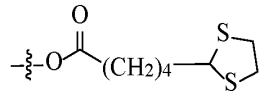
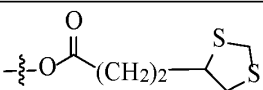
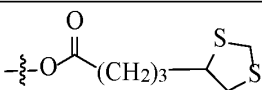
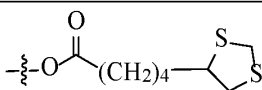
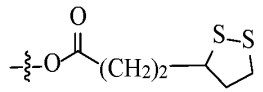
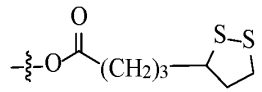
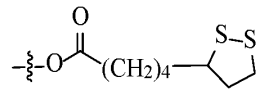
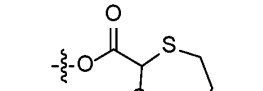
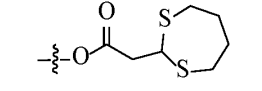
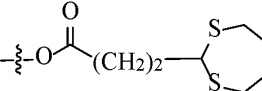
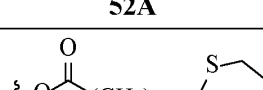
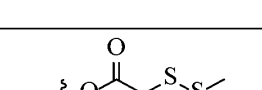
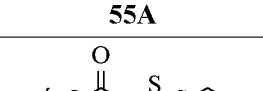
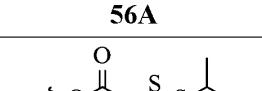
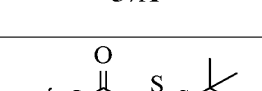
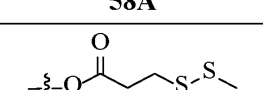
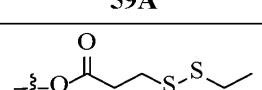
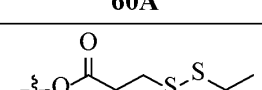
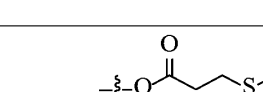
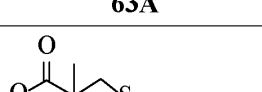
132. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (5b) wherein R¹ is an isobutylene group.

133. The compound of claim 1, wherein R^b is a carboxylic acid moiety of formula (5b) wherein R¹ is a t-butylene group.

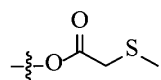
134. The compound of claim 1, wherein R^b is selected from the group of:

1A	2A	3A
4A	5A	6A

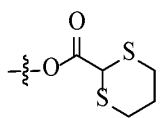
 7A	 8A	 9A
 10A	 11A	 12A
 13A	 14A	 15A
 16A	 17A	 18A
 19A	 20A	 21A
 22A	 23A	 24A
 25A	 26A	 27A
 28A	 29A	 30A
 31A	 32A	 33A
 34A	 35A	 36A
 37A	 38A	 39A

37A  40A	38A  41A	39A  42A
 43A	 44A	 45A
 46A	 47A	 48A
 49A	 50A	 51A
 52A	 53A	 54A
 55A	 56A	 57A
 58A	 59A	 60A
 61A	 62A	 63A
 64A	 65A	

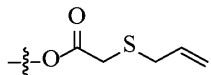
135. The compound of claim 1, wherein R^b is a carboxylic acid moiety group of structure 1A:



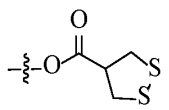
136. The compound of claim 1, wherein R^b is a carboxylic acid moiety group of structure 9A:



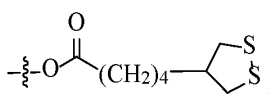
137. The compound of claim 1, wherein R^b is a carboxylic acid moiety group of structure 4A:



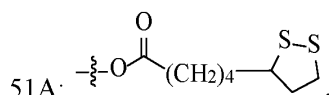
138. The compound of claim 1, wherein R^b is a carboxylic acid moiety group of structure 34A:



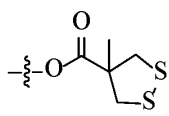
139. The compound of claim 1, wherein R^b is a carboxylic acid moiety group of structure 42A:



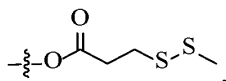
140. The compound of claim 1, wherein R^b is a carboxylic acid moiety group of structure



141. The compound of claim 1, wherein R^b is a carboxylic acid moiety group of structure 65A:



142. The compound of claim 1, wherein R^b is a carboxylic acid moiety group of structure 61A:



143. A formulation comprising (i) a compound of any of claims 1-142 and (ii) one or more solvents suitable for use in a spin-coating process.

144. The formulation of claim 143, wherein the one or more solvents suitable for use in a spin-coating process comprises one or more of an alcohol, an ester, a ketone, a lactone, a diketone, a solvent with aromatic moieties, a solvent with a carboxylic acid, an amide and mixtures thereof.

145. The formulation of claim 143, wherein the one or more solvents suitable for use in a spin-coating process comprises one or more of 1-methoxy-2-propanyl acetate (PGMEA), 1-methoxy-2-propanol (PGME), butyl acetate, amyl acetate, cyclohexyl acetate, 3-methoxybutyl acetate, methyl ethyl ketone, methyl amyl ketone, cyclohexanone, cyclopentanone, ethyl-3-ethoxy propanoate, methyl-3-ethoxy propanoate, methyl-3-methoxy propanoate, methyl acetoacetate, ethyl acetoacetate, diacetone alcohol, methyl pivalate, ethyl pivalate, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol monomethyl ether propanoate, propylene glycol monoethyl

ether propanoate, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, 3-methyl-3-methoxybutanol, N-methylpyrrolidone, dimethyl sulfoxide, gamma-butyrolactone, gamma valerolactone, cyclopentyl methyl ether, propylene glycol methyl ether acetate, propylene glycol ethyl ether acetate, propylene glycol propyl ether acetate, methyl lactate, ethyl lactate, propyl lactate, tetramethylene sulfone, propylene glycol dimethyl ether, dipropylene glycol dimethyl ether, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, toluene, 2-heptanone, 1-hexanol, 4-methyl-2-pentanol and anisole.

146. The formulation of claim 143, wherein the one or more solvents suitable for use in a spin-coating process comprises one or more of toluene, THF, cyclohexanone, PGME, PGMEA, anisole, 2-heptanone and 4-methyl-2-pentanol.

147. The formulation of claim 143, wherein the one or more solvents suitable for use in a spin-coating process comprises one or more of THF, cyclohexanone, PGME, PGMEA, anisole, 2-heptanone and 4-methyl-2-pentanol.

148. The formulation of claim 143, wherein the formulation is free of toluene.

149. The formulation of claim 143, wherein the formulation has a concentration of Sn clusters of about 1 mg/mL to about 1000 mg/mL.

150. A process for patterning a radiation sensitive coating comprising:

- (i) forming a coating on a substrate surface with a formulation comprising one or more compounds of any of claims 1-142;
- (ii) drying the coating to produce a dried layer; and
- (iii) irradiating at least a portion of the dried layer to form a latent image.

151. The process of claim 150, wherein the substrate of step (i) includes silicon.

152. The process of claim 150, wherein the dried coating of step (ii) has a thickness of about 1 nm to about 500 nm.

153. The process of claim 150, wherein the dried coating of step (ii) has a thickness of about 10 nm to about 100 nm.

154. The process of claim 150, wherein the dried coating of step (ii) has a thickness of about 15 nm to about 50 nm.

155. The process of claim 150, wherein the irradiating of step (iii) includes exposing at least a portion of the dried coating to ionizing radiation.

156. The process of claim 150, wherein the irradiating of step (iii) includes exposing at least a portion of the dried coating to ionizing radiation having a wavelength range of about 10 nm to about 365 nm.

157. The process of claim 150, wherein the ionizing radiation is generated via electron beams.

158. Use of one or more compounds of any of claims 1-142 in a process for patterning a radiation sensitive coating.