

**ORGANOMETALLIC TIN OXO CARBOXYLATE CLUSTERS WITH MIXED
ORGANIC LIGANDS FOR EUV LITHOGRAPHY**

[0001] BACKGROUND

[0002] Field

[0003] The disclosed and claimed subject matter relates to Sn₆-oxo clusters with mixed organic ligands, the synthesis thereof, formulations thereof and use thereof in EUV lithography.

[0004] Related Art

[0005] Moore's law continues to apply to the microelectronics industry. The trend in optical lithography that smaller is considered better has led to the use of shorter-wavelength light sources to produce high-density and high-performance semiconductor devices. For instance, EUV (extreme ultraviolet) lithography uses wavelength as small as 13.5 nm. However, the low power of EUV light sources requires the use of highly sensitive EUV resist materials and hence, traditional, chemically amplified photoresist systems that have been used in traditional lithography, reached their limits due to their poor photon absorption in thin-films, moderate etch selectivity and limited grains in resolution.

[0006] 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. Some of these inorganic photoresists show higher sensitivity, can form thin layers, have higher etching resistance, and potentially yield both lower line-edge roughness and higher resolution.

[0007] Sn compounds/clusters are of interest as photoresists due to their mechanical strength and etch resistivity of the crosslinked material. However, to serve as a photoresist, they need to have good photosensitivity and photoresolution.

[0008] 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.

[0009] 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.

[0010] 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.

[0011] US 2021/0087210 describes the synthesis of Sn₆ drum clusters with only nBu substituents with a single, narrowly defined type of carboxylate ligands, where all carboxylate ligands in one compound are the same, and their potential use as photoresists in EUV lithography processes. Due to the nature of the ligands used, the solubility of the compounds is expected to be relatively poor and to necessitate the use of aromatic solvents such as toluene or xylene. These solvents are not suitable for industrial applications in IC manufacturing, as they pose serious health hazards.

[0012] US 2022/0365428 describes bisalkyl Sn clusters bearing two or more different types of carboxylate ligands and their use as photoresist materials in EUV lithography. The disclosure does not cover compounds in which the individual Sn atoms carry different alkyl ligands. In general, bisalkyl Sn compounds are more toxic than the respective monoalkyl compounds. Therefore, the monoalkyl compounds are the preferred choice when organotin compounds are needed.

[0013] Sn₁₂ clusters (*i.e.*, (RSn)₁₂O₁₄(OH)₆]X₂) have been described as 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).

[0014] The disclosed and claimed subject matter is based on functionalized Sn-6 drum clusters. 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 an 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^a”), typically alkyl or aryl groups. In addition, carboxylate ligands (“O₂C-R^b”) 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^a-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, (nBuSn)₆O₆(O₂CCH₃)₆ has the structure shown in FIG. 14 (H atoms not drawn).

[0015] This type of cluster has been described for the first times by Chandrasekhar *et al.* See Chandrasekhar *et al.*, *Inorg. Chem.*, 24, 1970-1971 (1985). Over the last decades various functionalized derivatives have been synthesized and applied for various applications like material science or medicinal chemistry. In all cases, one alkyl-Sn source is used as a starting material, typically n-butyl stannic acid, and various kinds of carboxylic acids are employed. All experiments yield clusters with a single type of alkyl group bound to the tin atoms and in all cases only one carboxylic acid was used in the syntheses, never a mixture. 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).

[0016] However, Sn6 clusters suffer from low solubility in common organic solvents. This is even more relevant when alkyl groups with a low number of carbon atoms are applied as substituent on the tin. For example, the cluster (MeSn)₆O₆(O₂CCH₃)₆ is described to have a very low solubility, which allowed no recording of NMR spectra in solution. See Holmes *et al.*, *Inorganic Chemistry*, Vol. 27, No. 16, 1988, 2887-2893. Therefore, Sn6 clusters with non-bulky alkyl groups as a substituent on the tin are hardly described in literature. Notwithstanding the above, less bulky substituents are considered as advantageous for achieving a higher packing density in the solid state. It was shown that the solubility of a Sn6 cluster containing less bulky substituents on the tin can be increased in

industrially accepted solvents by applying mixed ligands. With this approach, clusters containing small alkyl groups as well as formate and acetate ligands can be solubilized to an extent, at which they can be used for photoresist applications. This is demonstrated in Comparative Study 1.

[0017] There has only been 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. They studied the crystal density and intermolecular distances of non-functionalized drum cluster systems. Small alkyl groups bound to the Sn atoms increase the cluster packing density due to a reduced steric demand per cluster. As a result, the intermolecular distances are reduced, which is considered to be advantageous for the use as an EUV resist. See Sharps *et al.*, *Cryst. Res. Technol.*, 52, 1700081 (2017). The same group further explored the use of one Sn₆-drum cluster (nBuSn)₆O₆(O₂CCH₃)₆ for the use in e-beam lithography. Here 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). However, in the publication the (nBuSn)₆O₆(O₂CCH₃)₆ material was coated from toluene. This is a solvent that cannot be used in an industrial IC fabrication process due to its health and safety hazards.

[0018] The literature states that the sensitivity of the [(nBuSn)₆O₆(O₂CCH₃)₆] compound is inferior to the Sn₁₂ cluster material in e-beam experiments. This was confirmed in internal experiments. Further interference lithography experiments using EUV radiation (13.5 nm) were conducted using a range of Sn₆ cluster materials. It was shown that the Sn₆ materials sensitivity can be drastically increased by introducing the proper mixture of ligands. This is demonstrated in Comparative Studies 2 and 3.

[0019] Notwithstanding the above, there has notably been no report of mixed R^a groups within one cluster molecule, as all syntheses rely on the use of one alkyl-Sn starting material, never a mixture.

[0020] It has been shown that a Sn₆ drum cluster [(nBuSn)₆O₆(O₂CCH₃)₆] can be prepared from a larger Sn cluster via addition of acetic acid. See, e.g., Colton *et al.*, *J. Organomet. Chem.*, 476, 33-40 (1994) and Ribot *et al.*, *New J. Chem.*, 19, 1145-1153 (1995). However, only the n-Bu derivative is used, and only acetic acid has been used for the transformation. When one equivalent of carboxylic acid per Sn atom is added, pure Sn₆ drum cluster is formed.

[0021] Here, Sn₆ drum clusters with mixed organic ligands and/or mixed carboxylate ligands are disclosed and claimed. Without being bound by theory it is believed that the introduction of mixed organic ligands and/or mixed carboxylic ligands into the cluster can increase

their solubility in many organic solvents, especially those which are relevant for an industrial application. A benefit from this is an improved coating quality on substrates via spin coating. This improved coating can be observed in that film thickness can be adjusted better, crystallization of the material is suppressed to yield amorphous films, and a smooth surface is generated. Another benefit from this is a greater degree of adjustability of the properties of the Sn clusters.

SUMMARY

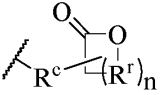
[0022] In one embodiment, the disclosed and claimed subject matter relates to an Sn₆-oxo drum cluster that includes mixed organic ligands and/or mixed carboxylate ligands of the formula: $[(R^{a1}Sn)(R^{a2}Sn)(R^{a3}Sn)(R^{a4}Sn)(R^{a5}Sn)(R^{a6}Sn)]O_6[(O_2C-R^{b1})(O_2C-R^{b2})(O_2C-R^{b3})(O_2C-R^{b4})(O_2C-R^{b5})(O_2C-R^{b6})]$

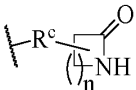
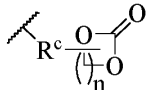
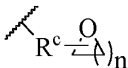
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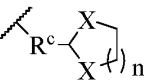
(A) each of R^{a1} , R^{a2} , R^{a3} , R^{a4} , R^{a5} and R^{a6} is individually selected from the group consisting of an unsubstituted linear C₁-C₁₀ alkyl group, a linear C₁-C₆ alkyl group substituted with a halogen, a linear C₁-C₆ alkyl group substituted with an amino group, a linear C₁-C₆ alkyl group substituted with a C₅-C₆ unsubstituted aromatic group, an unsubstituted branched C₃-C₁₀ alkyl group, a branched C₃-C₁₀ alkyl group substituted with a halogen, a C₁-C₁₀ heteroalkyl, a branched C₃-C₁₀ alkyl group substituted with an amino group, an unsubstituted amine, a substituted amine, -Si(CH₃)₃, a benzyl group, a C₃-C₈ unsubstituted cyclic alkyl group, a C₃-C₈ cyclic alkyl group substituted with a halogen, a C₃-C₈ cyclic alkyl group substituted with an amino group, a C₄-C₈ unsubstituted aromatic group, a C₄-C₈ aromatic group substituted with a halogen, a C₄-C₈ aromatic group substituted with an amino group, a C₃-C₁₀ heterocyclic group, an unsubstituted linear C₂-C₁₀ alkenyl group, an unsubstituted branched C₃-C₁₀ alkenyl group, an unsubstituted linear C₂-C₁₀ alkynyl group and an unsubstituted branched C₄-C₁₀ alkynyl group;

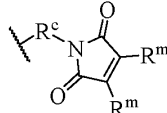
(B) each of R^{b1} , R^{b2} , R^{b3} , R^{b4} , R^{b5} and R^{b6} is individually selected from the group consisting of H; an unsubstituted linear C₁-C₁₀ alkyl group; a substituted linear C₁-C₁₀ alkyl group substituted with one or more of a -CN group, an -OH group, an -OR' group, an -SR' or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl group, an -NO₂ group, a halogen or a -C(=O)H group; an unsubstituted branched C₃-C₁₀ alkyl group; a substituted branched C₃-C₁₀ alkyl group substituted with one or more of a -CN group, an -OH group, a -OR' group, an -SR' or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl unit,

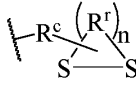
a -NO₂ group, a halogen or a -C(=O)H group; a C₃-C₈ unsubstituted cyclic alkyl group; a linear C₂-C₁₀ alkenyl group; a branched C₃-C₁₀ alkenyl group, a 5-membered heterocyclic ring; and a 6-

membered heterocyclic ring; a  group where (i) n = 1-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl

groups; a  group where n = 1-4, a  group where n = 1-4; a  group where n = 1-4; a

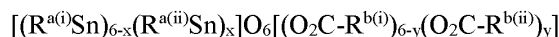
group where n = 1-6; a  group where each X is individually selected from O and S and

n = 1-4; a  group where each R^m group is independently selected from H, a linear

C₁-C₄ chain or a branched C₃-C₄ chain; a  group where (i) n = 3-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups; where R^c in each of the foregoing groups is (i) a direct covalent bond or (ii) an unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group; and

(C) (i) at least one of R^{a1}, R^{a2}, R^{a3}, R^{a4}, R^{a5} and R^{a6} is different from the remainder of R^{a1}, R^{a2}, R^{a3}, R^{a4}, R^{a5} and R^{a6} and/or (ii) at least one of R^{b1}, R^{b2}, R^{b3}, R^{b4}, R^{b5} and R^{b6} is different from the remainder of R^{b1}, R^{b2}, R^{b3}, R^{b4}, R^{b5} and R^{b6}.

[0023] In another embodiment, the disclosed and claimed subject matter relates to an Sn₆-oxo drum cluster that includes mixed organic ligands and/or mixed carboxylate ligands of the macroscopic formula, also describing mixtures of compounds:

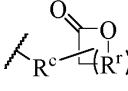


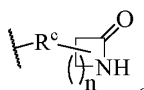
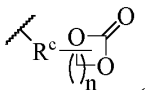
where

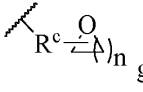
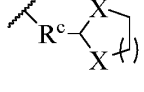
(A) (i) R^{a(i)} ≠ R^{a(ii)} and (ii) R^{a(i)} and R^{a(ii)} are each individually selected from the group consisting of an unsubstituted linear C₁-C₁₀ alkyl group, a linear C₁-C₆ alkyl group substituted with a halogen, a linear C₁-C₆ alkyl group substituted with an amino group, a linear C₁-C₆ alkyl group substituted with a C₅-C₆ unsubstituted aromatic group, an unsubstituted branched C₃-C₁₀ alkyl

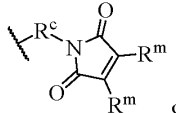
group, a branched C₃-C₁₀ alkyl group substituted with a halogen, a C₁-C₁₀ heteroalkyl group, a branched C₃-C₁₀ alkyl group substituted with an amino group, an unsubstituted amine, a substituted amine, -Si(CH₃)₃, a benzyl group, a C₃-C₈ unsubstituted cyclic alkyl group, a C₃-C₈ cyclic alkyl group substituted with a halogen, a C₃-C₈ cyclic alkyl group substituted with an amino group, a C₄-C₈ unsubstituted aromatic group, a C₄-C₈ aromatic group substituted with a halogen, a C₄-C₈ aromatic group substituted with an amino group, a C₃-C₁₀ heterocyclic group, an unsubstituted linear C₂-C₁₀ alkenyl group, an unsubstituted branched C₃-C₁₀ alkenyl group, an unsubstituted linear C₂-C₁₀ alkynyl group and an unsubstituted branched C₄-C₁₀ alkynyl group;

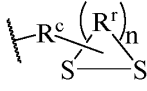
(B) (i) R^{b(i)} ≠ R^{b(ii)} and (ii) R^{b(i)} and R^{b(ii)} are each individually selected from the group consisting of H; an unsubstituted linear C₁-C₁₀ alkyl group; a substituted linear C₁-C₁₀ alkyl group substituted with one or more of a -CN group, an -OH group, an -OR' group, an -SR' or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl group, an -NO₂ group, a halogen or a -C(=O)H group; an unsubstituted branched C₃-C₁₀ alkyl group; a substituted branched C₃-C₁₀ alkyl group substituted with one or more of a -CN group, an -OH group, a -OR' group, an -SR' or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl unit, a -NO₂ group, a halogen or a -C(=O)H group; a C₃-C₈ unsubstituted cyclic alkyl group; a linear C₂-C₁₀ alkenyl group; a branched C₃-C₁₀ alkenyl group, a 5-membered heterocyclic

ring; and a 6-membered heterocyclic ring; a  group where (i) n = 1-5 and (ii) each R' is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-

C₄ alkyl groups; a  group where n = 1-4, a  group where n = 1-4; a

 group where n = 1-6; a  group where each X is individually selected from

O and S and n = 1-4; a  group where each R^m group is independently selected from

H, or a linear C₁-C₄ chain, or a branched C₃-C₄ chain; a  group where (i) n = 3-5 and (ii) each R^f is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups; where R^e in each of the foregoing groups is (i) a direct covalent bond or (ii) an unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group.

[0024] In another aspect, the disclosed and claimed subject matter includes mixtures of one or more of the above Sn6-oxo drum clusters. As those skilled in the art will understand, that the **average** value of x and y may differ from that of the individual clusters making up the mixture. Thus, in such mixtures, (i) x and y each independently equal a whole number or fractional number of 0 < x and/or y < 6 or (ii) one of x or y = 0 and the other of x or y = a whole or fractional number of 0 < x and/or y < 6.

[0025] 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 cluster solution where the cluster solution (a) is prepared from the Sn6-oxo clusters described herein and/or utilized the process for preparing the same, (b) has a uniform composition resulting from adjusting the water content of the solvent used to form the adjusted starting material solution within about ± 15% of a target value and (c) has a selected water content is from about 300 ppm by weight to about 10,000 ppm by weight; (ii) drying the coating; and (iii) irradiating the dried coating to form a latent image.

[0026] In another aspect, the disclosed and claimed subject matter includes methods for preparing the Sn6-oxo clusters described herein.

[0027] 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.

[0028] 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.

[0029] BRIEF DESCRIPTION OF THE DRAWINGS

[0030] 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:

[0031] FIG. 1 illustrates the ^{119}Sn NMR of the Sn6 clusters of Example 1;

[0032] FIG. 2 illustrates the ^{119}Sn NMR of the Sn6 clusters of Example 2;

[0033] FIG. 3 illustrates the ^{119}Sn NMR of the Sn6 clusters of Example 3;

[0034] FIG. 4 illustrates the ^{119}Sn NMR of the Sn6 clusters of Example 4;

[0035] FIG. 5 illustrates the ^{119}Sn NMR of a solution sample vs. redissolved material of the Sn6 clusters of Example 5;

[0036] FIG. 6 illustrates the line-space pattern of $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{CCH}_3)_6]$ at 80 nm pitch;

[0037] FIG. 7 illustrates the line-space pattern of $[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{CH})_6]$ at 80 nm pitch;

[0038] FIG. 8 illustrates the line-space pattern of $[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{CH})_3(\text{O}_2\text{CC}_4\text{H}_9\text{O}_2)_3]$ at 70 nm pitch;

[0039] FIG. 9 illustrates the line-space pattern of $[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{CH})_3(\text{O}_2\text{C}(\text{CH}_2\text{S}_2\text{C}_3\text{H}_6))_3]$ at 80 nm pitch;

[0040] FIG. 10 illustrates the ^{119}Sn - ^{119}Sn -INADEQUATE NMR spectrum of the Sn6 clusters of Example 9;

[0041] FIG. 11 illustrates the mass spectrum of the Sn6 clusters of Example 9;

[0042] FIG. 12 illustrates the mass spectrum of the Sn6 clusters of Example 11;

[0043] FIG. 13 illustrates the mass spectrum of the Sn6 clusters of Example 16; and

[0044] FIG. 14 illustrates the crystal structure of $(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{CCH}_3)_6$.

[0045] DEFINITIONS

[0046] Unless otherwise stated, the following terms used in the specification and claims shall have the following meanings for this application.

[0047] 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.

[0048] As used herein, “about” or “approximately” are intended to correspond to within $\pm$ 5% of the stated value.

[0049] As used herein, “C_{x-y}” (where x and y are each integers (also referred to as “whole numbers”)) 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. The term “chain”, unless specifically stated otherwise, refers to any linear or branched hydrocarbon group, including alkyl, alkenyl and alkynyl, preferably alkyl.

[0050] 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.

[0051] “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, perfluoroethyl, 2,2,2-trifluoroethyl, perfluoroisopropyl, perfluorocyclohexyl and the like). Such haloalkyl moieties (*e.g.*, fluoroalkyl moieties), if not perhalogenated/multihalogenated, may be unsubstituted or further substituted.

[0052] “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.

[0053] “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.

[0054] “Halo” or “halide” refers to a halogen (*e.g.*, F, Cl, Br and I).

[0055] “Hydroxy” (a.k.a. “hydroxyl”) refers to an -OH group.

[0056] 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.

[0057] The alkoxy ligand O-t-amyl represents O-CCH₃CH₃CH₂CH₃.

[0058] In addition to known and understood representations for the attachment point of a covalent bond, the notation “ $\text{---}\frac{\text{X}}{\text{Y}}\text{---}$ ” is intended to also designate the attachment point of a covalent bond.

[0059] “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) serving as a linkage between R¹ and R² in the disclosed and claimed compounds such as an ethylene bridge. 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.

[0060] “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.

[0061] “Heteroalkyl” means an alkyl group as defined above where one, two or three carbons in the alkyl 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.

[0062] 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.

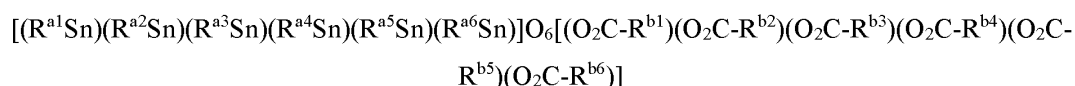
[0063] The section headings used herein are for organizational purposes and are not to be construed as limiting the subject matter described. All documents, or portions of documents, cited in this application, including, but not limited to, patents, patent applications, articles, books, and treatises, 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

[0064] 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.

[0065] Sn6-Oxo Clusters and Mixtures Thereof

[0066] In one embodiment, the disclosed and claimed subject matter relates to an Sn6-oxo drum cluster that includes mixed organic ligands and/or mixed carboxylate ligands of the formula:

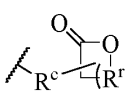


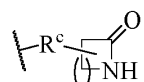
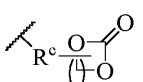
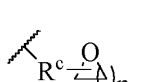
where

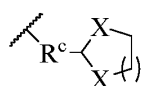
(A) each of R^{a1} , R^{a2} , R^{a3} , R^{a4} , R^{a5} and R^{a6} is individually selected from the group consisting of an unsubstituted linear C_1 - C_{10} alkyl group, a linear C_1 - C_6 alkyl group substituted with a halogen, a linear C_1 - C_6 alkyl group substituted with an amino group, a linear 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} heteroalkyl group, a branched C_3 - C_{10} alkyl group substituted with an amino group, 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 -

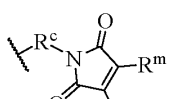
C₈ unsubstituted aromatic group, a C₄-C₈ aromatic group substituted with a halogen, a C₄-C₈ aromatic group substituted with an amino group, a C₃-C₁₀ heterocyclic group, an unsubstituted linear C₂-C₁₀ alkenyl group, an unsubstituted branched C₃-C₁₀ alkenyl group, an unsubstituted linear C₂-C₁₀ alkynyl group and an unsubstituted branched C₄-C₁₀ alkynyl group;

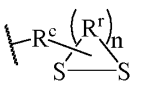
(B) each of R^{b1}, R^{b2}, R^{b3}, R^{b4}, R^{b5} and R^{b6} is individually selected from the group consisting of H; an unsubstituted linear C₁-C₁₀ alkyl group; a substituted linear C₁-C₁₀ alkyl group substituted with one or more of a -CN group, an -OH group, an -OR' group, an -SR' or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl group, an -NO₂ group, a halogen or a -C(=O)H group; an unsubstituted branched C₃-C₁₀ alkyl group; a substituted branched C₃-C₁₀ alkyl group substituted with one or more of a -CN group, an -OH group, a -OR' group, an -SR' or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl unit, a -NO₂ group, a halogen or a -C(=O)H group; a C₃-C₈ unsubstituted cyclic alkyl group; a linear C₂-C₁₀ alkenyl group; a branched C₃-C₁₀ alkenyl group, a 5-membered heterocyclic ring; and a 6-

membered heterocyclic ring; a  group where (i) n = 1-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl

groups; a  group where n = 1-4, a  group where n = 1-4; a  group

where n = 1-6; a  group where each X is individually selected from O and S and n =

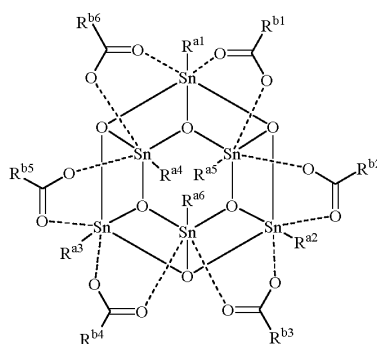
1-4; a  group where each R^m group is independently selected from H, a linear C₁-C₄

chain or a branched C₃-C₄ chain; a  group where (i) n = 3-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups; where R^c in each of the foregoing groups is (i) a direct covalent bond or (ii) an unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group; and

(C) (i) at least one of R^{a1}, R^{a2}, R^{a3}, R^{a4}, R^{a5} and R^{a6} is different from the remainder

of R^{a1} , R^{a2} , R^{a3} , R^{a4} , R^{a5} and R^{a6} and/or (ii) at least one of R^{b1} , R^{b2} , R^{b3} , R^{b4} , R^{b5} and R^{b6} is different from the remainder of R^{b1} , R^{b2} , R^{b3} , R^{b4} , R^{b5} and R^{b6} .

[0067] As those skilled in the art will understand, the Sn₆-oxo drum clusters of the disclosed and claimed subject matter have the following general structure:



[0068] In one aspect of this embodiment, each of R^{a1} , R^{a2} , R^{a3} , R^{a4} , R^{a5} and R^{a6} is the same. In one aspect of this embodiment, at least one of R^{a1} , R^{a2} , R^{a3} , R^{a4} , R^{a5} and R^{a6} is different from the other of R^{a1} , R^{a2} , R^{a3} , R^{a4} , R^{a5} and R^{a6} . In one aspect of this embodiment, each of R^{b1} , R^{b2} , R^{b3} , R^{b4} , R^{b5} and R^{b6} is the same. In one aspect of this embodiment, at least one of R^{b1} , R^{b2} , R^{b3} , R^{b4} , R^{b5} and R^{b6} is different from the other of R^{b1} , R^{b2} , R^{b3} , R^{b4} , R^{b5} and R^{b6} . In one aspect of this embodiment, at least one of R^{a1} , R^{a2} , R^{a3} , R^{a4} , R^{a5} and R^{a6} is different from the other of R^{a1} , R^{a2} , R^{a3} , R^{a4} , R^{a5} and R^{a6} and at least one of R^{b1} , R^{b2} , R^{b3} , R^{b4} , R^{b5} and R^{b6} is different from the other of R^{b1} , R^{b2} , R^{b3} , R^{b4} , R^{b5} and R^{b6} .

[0069] In a further aspect of this embodiment, (A) each of R^{a1} , R^{a2} , R^{a3} , R^{a4} , R^{a5} and R^{a6} is individually selected from the group consisting of an unsubstituted linear C₁-C₄ alkyl group, an unsubstituted branched C₃-C₄ alkyl group, an unsubstituted linear C₂-C₆ alkenyl group, an unsubstituted branched C₃-C₆ alkenyl group and a C₄-C₆ unsubstituted aromatic group.

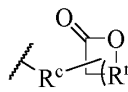
[0070] In a further aspect of this embodiment, (A) each of R^{a1} , R^{a2} , R^{a3} , R^{a4} , R^{a5} and R^{a6} is individually selected from the group consisting of a -CH₃ group, a -CH(CH₃)₂ group, a -C(CH₃)₃ group, a -CH=CH₂ group, a -CH₂CH=CH₂ group, a -CH₂CH₂CH=CH₂ group, a -CH₂CH₂CH₂CH₃ group, a -C₆H₅ group and a -CH₂-C₆H₅ group.

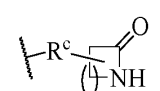
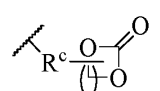
[0071] In a further aspect of this embodiment, (A) each of R^{a1} , R^{a2} , R^{a3} , R^{a4} , R^{a5} and R^{a6} is individually selected from the group consisting of a -CH₃ group, a -CH(CH₃)₂ group, a -C(CH₃)₃ group, a -CH=CH₂ group, a -CH₂CH=CH₂ group, a -CH₂CH₂CH=CH₂ group and a -CH₂CH₂CH₂CH₃ group.

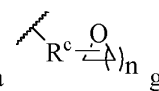
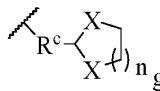
[0072] In a further aspect of this embodiment, (A) each of R^{a1} , R^{a2} , R^{a3} , R^{a4} , R^{a5} and R^{a6} is individually selected from the group consisting of a $-CH_3$ group, a $-CH(CH_3)_2$ group, a $-C(CH_3)_3$ group, a $-CH=CH_2$ group, a $-CH_2CH=CH_2$ group, and a $-CH_2CH_2CH_2CH_3$ group.

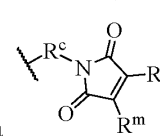
[0073] In a further aspect of this embodiment, (A) each of R^{a1} , R^{a2} , R^{a3} , R^{a4} , R^{a5} and R^{a6} is individually selected from the group consisting of a $-CH_3$ group, a $-CH(CH_3)_2$ group, a $-CH=CH_2$ group, and a $-CH_2CH_2CH_2CH_3$ group.

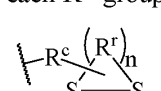
[0074] In a further aspect of this embodiment, (B) each of R^{b1} , R^{b2} , R^{b3} , R^{b4} , R^{b5} and R^{b6} is individually selected from the group consisting of $-H$; an unsubstituted linear C_1 - C_6 alkyl group; a substituted linear C_1 - C_6 alkyl group substituted with one or more of a $-CN$ group, an $-OH$ group, an $-OR'$ group, an $-SR'$, or an $-S-S-R'$ group where R' is a linear or branched C_1 - C_4 alkyl group, a $-C(=O)OR''$ group where R'' is a linear or branched C_1 - C_4 alkyl group, an $-NO_2$ group, a halogen, or a $-C(=O)H$ group; an unsubstituted branched C_3 - C_6 alkyl group; a substituted branched C_3 - C_6 alkyl group substituted with one or more of a $-CN$ group, an $-OH$ group, a $-OR'$ group, an $-SR'$, or an $-S-S-R'$ group where R' is a linear or branched C_1 - C_4 alkyl group, a $-C(=O)OR''$ group where R'' is a linear or branched C_1 - C_4 alkyl unit, a $-NO_2$ group, a halogen, or a $-C(=O)H$ group; a C_3 - C_6 unsubstituted cyclic alkyl group; a linear C_2 - C_6 alkenyl group; a branched C_3 - C_6 alkenyl group, a 5-membered

heterocyclic ring; and a 6-membered heterocyclic ring; a  group where (i) $n = 1-5$ and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with

one or two C_1 - C_4 alkyl groups; a  group where $n = 1-4$, a  group where $n =$

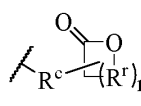
1-4; a  group where $n = 1-6$; a  group where each X is individually selected

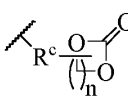
from O and S and $n = 1-4$; a  group where each R^m group is independently selected

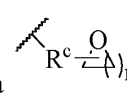
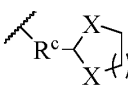
from H, or a linear C_1 - C_4 chain, or a branched C_3 - C_4 chain; a  group where (i) $n = 3-5$ and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C_1 - C_4 alkyl groups; where R^c in each of the foregoing groups is (i) a direct covalent bond or

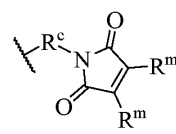
(ii) an unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group.

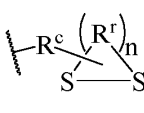
[0075] In a further aspect of this embodiment, **(B)** each of R^{b1}, R^{b2}, R^{b3}, R^{b4}, R^{b5} and R^{b6} is individually selected from the group consisting of -H; an unsubstituted linear C₁-C₆ alkyl group; a substituted linear C₁-C₆ alkyl group substituted with one or more of a -CN group, an -OR' group, an -SR', or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl group, an -NO₂ group, or a -C(=O)H group; an unsubstituted branched C₃-C₆ alkyl group; a substituted branched C₃-C₆ alkyl group substituted with one or more of a -CN group, a -OR' group, an -SR', or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl unit, a -NO₂ group, or a -C(=O)H group; a linear C₂-C₆ alkenyl group; a branched C₃-C₆ alkenyl group, a

 group where (i) n = 1-5 and (ii) each R^r is individually an unsubstituted methylene group

or a methylene group substituted with one or two C₁-C₄ alkyl groups; a  group where n =

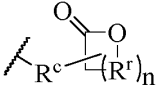
1-4; a  group where n = 1-6; a  group where each X is individually selected

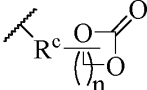
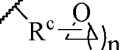
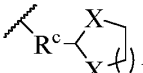
from O and S and n = 1-4; a  group where each R^m group is independently selected

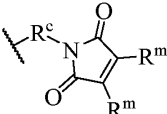
from H, or a linear C₁-C₄ chain, or a branched C₃-C₄ chain; a  group where (i) n = 3-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups; where R^c in each of the forgoing groups is (i) a direct covalent bond or (ii) an unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group.

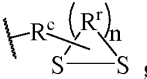
[0076] In a further aspect of this embodiment, **(B)** each of R^{b1}, R^{b2}, R^{b3}, R^{b4}, R^{b5} and R^{b6} is individually selected from the group consisting of -H; an unsubstituted linear C₁-C₆ alkyl group; a substituted linear C₁-C₆ alkyl group substituted with one or more of a -CN group, an -OR' group where R' is a linear or branched C₁-C₄ alkyl group, or a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl group; an unsubstituted branched C₃-C₆ alkyl group; a substituted branched

C₃-C₆ alkyl group substituted with one or more of a -CN group, a -OR' group where R' is a linear or branched C₁-C₄ alkyl group, or a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl

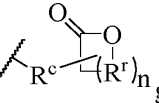
unit; a  group where (i) n = 1-5 and (ii) each R^f is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups; a

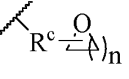
 group where n = 1-4; a  group where n = 1-6; a  group

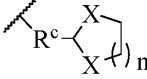
where each X is individually selected from O and S and n = 1-4; a  group where each R^m group is independently selected from H, or a linear C₁-C₄ chain, or a branched C₃-C₄ chain; a

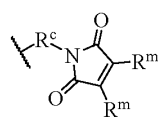
 group where (i) n = 3-5 and (ii) each R^f is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups; where R^c in each of the foregoing groups is (i) a direct covalent bond or (ii) an unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group.

[0077] In a further aspect of this embodiment, (B) each of R^{b1}, R^{b2}, R^{b3}, R^{b4}, R^{b5} and R^{b6} is individually selected from the group consisting of -H; an unsubstituted linear C₁-C₆ alkyl group; a substituted linear C₁-C₆ alkyl group substituted with one or more of a -CN group, or an -OR' group where R' is a linear or branched C₁-C₄ alkyl group; an unsubstituted branched C₃-C₆ alkyl group; a substituted branched C₃-C₆ alkyl group substituted with one or more of a -CN group, or

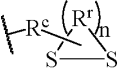
a -OR' group where R' is a linear or branched C₁-C₄ alkyl group; a  group where (i) n = 1-5 and (ii) each R^f is individually an unsubstituted methylene group or a methylene group

substituted with one or two C₁-C₄ alkyl groups; a  group where n = 1-6; a

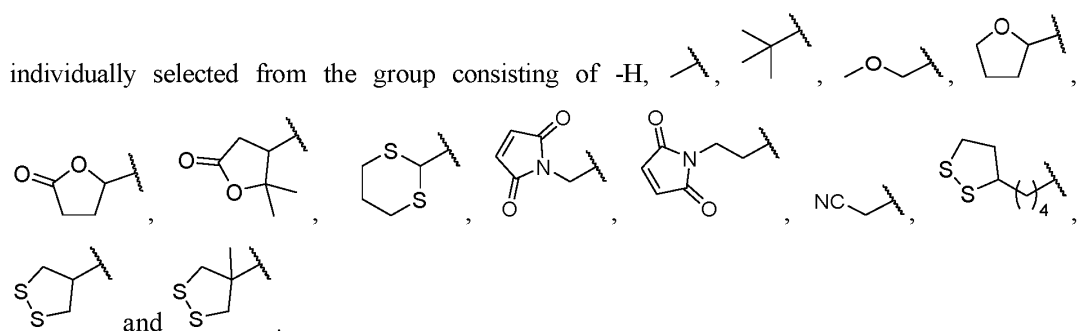
 group where each X is individually selected from O and S and n = 1-4; a



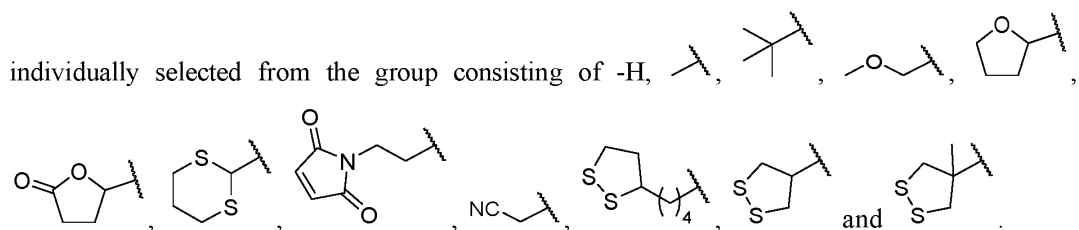
group where each R^m group is independently selected from H, or a linear C_1 - C_4

chain, or a branched C_3 - C_4 chain; a  group where (i) $n = 3-5$ and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C_1 - C_4 alkyl groups; where R^c in each of the foregoing groups is (i) a direct covalent bond or (ii) an unsubstituted linear C_1 - C_6 alkylene group, an unsubstituted branched C_3 - C_6 alkylene group.

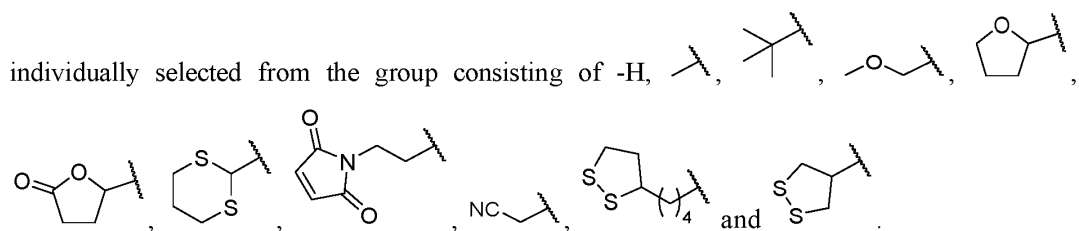
[0078] In a further aspect of this embodiment, **(B)** each of R^{b1} , R^{b2} , R^{b3} , R^{b4} , R^{b5} and R^{b6} is



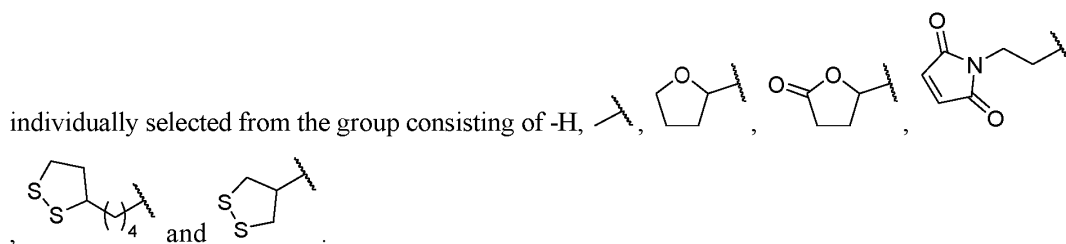
[0079] In a further aspect of this embodiment, **(B)** each of R^{b1} , R^{b2} , R^{b3} , R^{b4} , R^{b5} and R^{b6} is



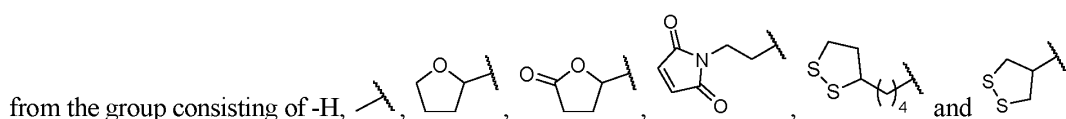
[0080] In a further aspect of this embodiment, **(B)** each of R^{b1} , R^{b2} , R^{b3} , R^{b4} , R^{b5} and R^{b6} is



[0081] In a further aspect of this embodiment, **(B)** each of R^{b1} , R^{b2} , R^{b3} , R^{b4} , R^{b5} and R^{b6} is



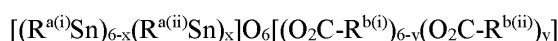
[0082] In a further aspect of this embodiment, (A) each of R^{a1} , R^{a2} , R^{a3} , R^{a4} , R^{a5} and R^{a6} is individually selected from the group consisting of -CH₃ group, a -CH(CH₃)₂ group, a -CH=CH₂ group, and a -CH₂CH₂CH₂CH₃ group and (B) each of R^{b1} , R^{b2} , R^{b3} , R^{b4} , R^{b5} and R^{b6} is individually selected



[0083] In another aspect, the disclosed and claimed subject matter includes mixtures of one or more of the above Sn6-oxo drum clusters.

[0084] Exemplified Sn6-Oxo Cluster Compounds

[0085] In one embodiment of the above, the disclosed Sn6-oxo drum clusters include (i) a proportion (*e.g.*, half, etc.) of R^{a1} , R^{a2} , R^{a3} , R^{a4} , R^{a5} and R^{a6} are a same first group (" $R^{a(i)}$ ") and the remainder of R^{a1} , R^{a2} , R^{a3} , R^{a4} , R^{a5} and R^{a6} are a same second group (" $R^{a(ii)}$ ") that is different than the first group (" $R^{a(i)}$ ") and/or (ii) a proportion (*e.g.*, half, etc.) of R^{b1} , R^{b2} , R^{b3} , R^{b4} , R^{b5} and R^{b6} are a same first group (" $R^{b(i)}$ ") and the remainder of R^{b1} , R^{b2} , R^{b3} , R^{b4} , R^{b5} and R^{b6} are a same second group (" $R^{b(ii)}$ ") that is different than the first group (" $R^{b(i)}$ "). Thus, the disclosed and claimed Sn6-oxo drum cluster includes mixed organic ligands and/or mixed carboxylate ligands of the formula:

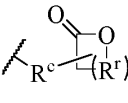


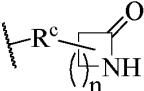
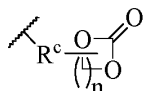
where

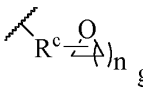
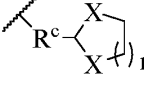
(A) (i) $R^{a(i)} \neq R^{a(ii)}$ and (ii) $R^{a(i)}$ and $R^{a(ii)}$ are each individually selected from the group consisting of an unsubstituted linear C₁-C₁₀ alkyl group, a linear C₁-C₆ alkyl group substituted with a halogen, a linear C₁-C₆ alkyl group substituted with an amino group, a linear C₁-C₆ alkyl group substituted with a C₅-C₆ unsubstituted aromatic group, an unsubstituted branched C₃-C₁₀ alkyl group, a branched C₃-C₁₀ alkyl group substituted with a halogen, a C₁-C₁₀ heteroalkyl group, a branched C₃-C₁₀ alkyl group substituted with an amino group, an unsubstituted amine, a substituted amine, -Si(CH₃)₃, a benzyl group, a C₃-C₈ unsubstituted cyclic alkyl group, a C₃-C₈ cyclic alkyl

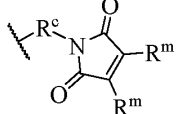
group substituted with a halogen, a C₃-C₈ cyclic alkyl group substituted with an amino group, a C₄-C₈ unsubstituted aromatic group, a C₄-C₈ aromatic group substituted with a halogen, a C₄-C₈ aromatic group substituted with an amino group, a C₃-C₁₀ heterocyclic group, an unsubstituted linear C₂-C₁₀ alkenyl group, an unsubstituted branched C₃-C₁₀ alkenyl group, an unsubstituted linear C₂-C₁₀ alkynyl group and an unsubstituted branched C₄-C₁₀ alkynyl group;

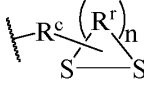
(B) (i) R^{b(i)} ≠ R^{b(ii)} and (ii) R^{b(i)} and R^{b(ii)} are each individually selected from the group consisting of H; an unsubstituted linear C₁-C₁₀ alkyl group; a substituted linear C₁-C₁₀ alkyl group substituted with one or more of a -CN group, an -OH group, an -OR' group, an -SR' or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl group, an -NO₂ group, a halogen or a -C(=O)H group; an unsubstituted branched C₃-C₁₀ alkyl group; a substituted branched C₃-C₁₀ alkyl group substituted with one or more of a -CN group, an -OH group, a -OR' group, an -SR' or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl unit, a -NO₂ group, a halogen or a -C(=O)H group; a C₃-C₈ unsubstituted cyclic alkyl group; a linear C₂-C₁₀ alkenyl group; a branched C₃-C₁₀ alkenyl group, a 5-membered heterocyclic

ring; and a 6-membered heterocyclic ring; a  group where (i) n = 1-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-

C₄ alkyl groups; a  group where n = 1-4, a  group where n = 1-4; a

 group where n = 1-6; a  group where each X is individually selected from

O and S and n = 1-4; a  group where each R^m group is independently selected from H,

or a linear C₁-C₄ chain, or a branched C₃-C₄ chain; a  group where (i) n = 3-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups; where R^c in each of the forgoing groups is (i) a direct covalent bond or (ii) an

unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group; and

(C) (i) x and y each independently equal a whole number of 1 to 5 or (ii) one of x or y = 0 and the other of x or y = a whole number of 1 to 5.

[0086] In a further aspect of this embodiment, (A) each of R^{a(i)} and R^{a(ii)} is individually selected from the group consisting of an unsubstituted linear C₁-C₄ alkyl group, an unsubstituted branched C₃-C₄ alkyl group, an unsubstituted linear C₂-C₆ alkenyl group, an unsubstituted branched C₃-C₆ alkenyl group and a C₄-C₆ unsubstituted aromatic group.

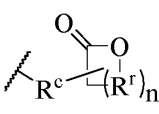
[0087] In a further aspect of this embodiment, (A) each of R^{a(i)} and R^{a(ii)} is individually selected from the group consisting of a -CH₃ group, a -CH(CH₃)₂ group, a -C(CH₃)₃ group, a -CH=CH₂ group, a -CH₂CH=CH₂ group, a -CH₂CH₂CH=CH₂ group, a -CH₂CH₂CH₂CH₃ group, a -C₆H₅ group and a -CH₂-C₆H₅ group.

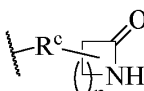
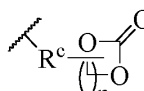
[0088] In a further aspect of this embodiment, (A) each of R^{a(i)} and R^{a(ii)} is individually selected from the group consisting of a -CH₃ group, a -CH(CH₃)₂ group, a -C(CH₃)₃ group, a -CH=CH₂ group, a -CH₂CH=CH₂ group, a -CH₂CH₂CH=CH₂ group and a -CH₂CH₂CH₂CH₃ group.

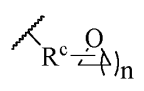
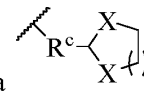
[0089] In a further aspect of this embodiment, (A) each of R^{a(i)} and R^{a(ii)} is individually selected from the group consisting of a -CH₃ group, a -CH(CH₃)₂ group, a -C(CH₃)₃ group, a -CH=CH₂ group, a -CH₂CH=CH₂ group, and a -CH₂CH₂CH₂CH₃ group.

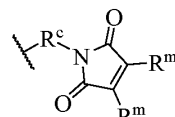
[0090] In a further aspect of this embodiment, (A) each of R^{a(i)} and R^{a(ii)} is individually selected from the group consisting of a -CH₃ group, a -CH(CH₃)₂ group, a -CH=CH₂ group, and a -CH₂CH₂CH₂CH₃ group.

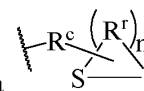
[0091] In a further aspect of this embodiment, (B) each of R^{b(i)} and R^{b(ii)} is individually selected from the group consisting of -H; an unsubstituted linear C₁-C₆ alkyl group; a substituted linear C₁-C₆ alkyl group substituted with one or more of a -CN group, an -OH group, an -OR' group, an -SR', or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl group, an -NO₂ group, a halogen, or a -C(=O)H group; an unsubstituted branched C₃-C₆ alkyl group; a substituted branched C₃-C₆ alkyl group substituted with one or more of a -CN group, an -OH group, a -OR' group, an -SR', or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl unit, a -NO₂ group, a halogen, or a -C(=O)H group; a C₃-C₆ unsubstituted cyclic alkyl group; a linear C₂-C₆ alkenyl group; a branched C₃-C₆ alkenyl group, a 5-membered heterocyclic ring;

and a 6-membered heterocyclic ring; a  group where (i) n = 1-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-

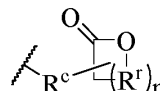
C₄ alkyl groups; a  group where n = 1-4, a  group where n = 1-4; a

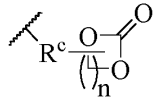
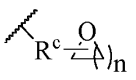
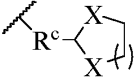
 group where n = 1-6; a  group where each X is individually selected from

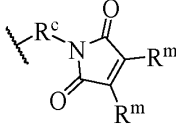
O and S and n = 1-4; a  group where each R^m group is independently selected from

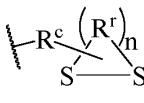
H, or a linear C₁-C₄ chain, or a branched C₃-C₄ chain; a  group where (i) n = 3-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups; where R^c in each of the foregoing groups is (i) a direct covalent bond or (ii) an unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group.

[0092] In a further aspect of this embodiment, **(B)** each of R^{b(i)} and R^{b(ii)} is individually selected from the group consisting of -H; an unsubstituted linear C₁-C₆ alkyl group; a substituted linear C₁-C₆ alkyl group substituted with one or more of a -CN group, an -OR' group, an -SR', or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl group, an -NO₂ group, or a -C(=O)H group; an unsubstituted branched C₃-C₆ alkyl group; a substituted branched C₃-C₆ alkyl group substituted with one or more of a -CN group, a -OR' group, an -SR', or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl unit, a -NO₂ group,

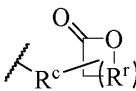
or a -C(=O)H group; a linear C₂-C₆ alkenyl group; a branched C₃-C₆ alkenyl group, a  group where (i) n = 1-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene

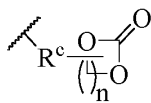
group substituted with one or two C₁-C₄ alkyl groups; a  group where n = 1-4; a  group where n = 1-6; a  group where each X is individually selected from

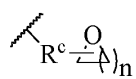
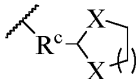
O and S and n = 1-4; a  group where each R^m group is independently selected from H,

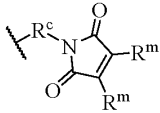
or a linear C₁-C₄ chain, or a branched C₃-C₄ chain; a  group where (i) n = 3-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups; where R^c in each of the forgoing groups is (i) a direct covalent bond or (ii) an unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group.

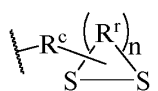
[0093] In a further aspect of this embodiment, **(B)** each of R^{b(i)} and R^{b(ii)} is individually selected from the group consisting of -H; an unsubstituted linear C₁-C₆ alkyl group; a substituted linear C₁-C₆ alkyl group substituted with one or more of a -CN group, an -OR' group where R' is a linear or branched C₁-C₄ alkyl group, or a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl group; an unsubstituted branched C₃-C₆ alkyl group; a substituted branched C₃-C₆ alkyl group substituted with one or more of a -CN group, a -OR' group where R' is a linear or branched C₁-C₄ alkyl group, or a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl unit; a

 group where (i) n = 1-5 and (ii) each R^r is individually an unsubstituted methylene

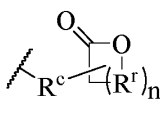
group or a methylene group substituted with one or two C₁-C₄ alkyl groups; a  group

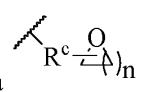
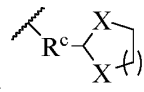
where n = 1-4; a  group where n = 1-6; a  group where each X is

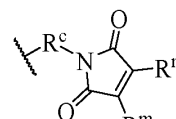
individually selected from O and S and n = 1-4; a  group where each R^m group is

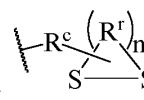
independently selected from H, or a linear C₁-C₄ chain, or a branched C₃-C₄ chain; a  group where (i) n = 3-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups; where R^c in each of the foregoing groups is (i) a direct covalent bond or (ii) an unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group.

[0094] In a further aspect of this embodiment, **(B)** each of R^{b(i)} and R^{b(ii)} is individually selected from the group consisting of -H; an unsubstituted linear C₁-C₆ alkyl group; a substituted linear C₁-C₆ alkyl group substituted with one or more of a -CN group, or an -OR' group where R' is a linear or branched C₁-C₄ alkyl group; an unsubstituted branched C₃-C₆ alkyl group; a substituted branched C₃-C₆ alkyl group substituted with one or more of a -CN group, or a -OR' group where R' is a linear or

branched C₁-C₄ alkyl group; a  group where (i) n = 1-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups;

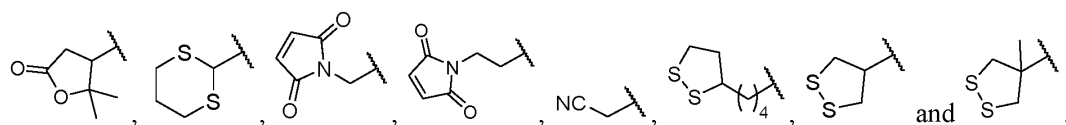
a  group where n = 1-6; a  group where each X is individually selected from

O and S and n = 1-4; a  group where each R^m group is independently selected from H,

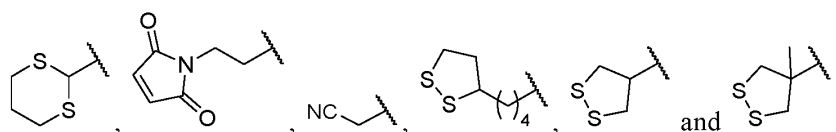
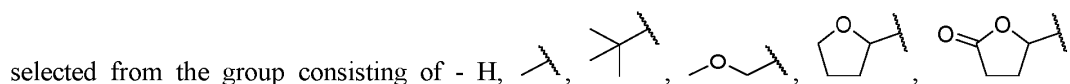
or a linear C₁-C₄ chain, or a branched C₃-C₄ chain; a  group where (i) n = 3-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups; where R^c in each of the foregoing groups is (i) a direct covalent bond or (ii) an unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group.

[0095] In a further aspect of this embodiment, **(B)** each of R^{b(i)} and R^{b(ii)} is individually

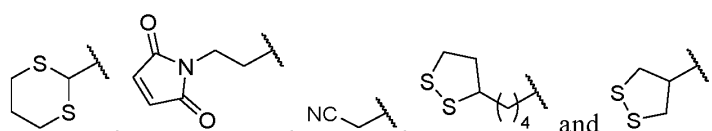
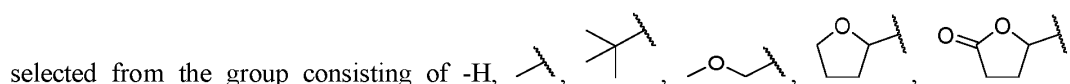
selected from the group consisting of -H, , , , , , ,



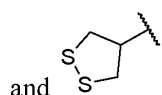
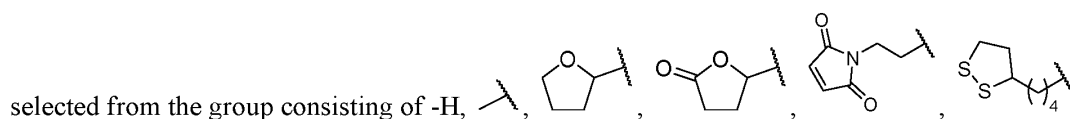
[0096] In a further aspect of this embodiment, **(B)** each of $R^{b(i)}$ and $R^{b(ii)}$ is individually



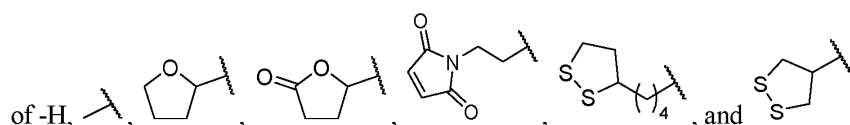
[0097] In a further aspect of this embodiment, **(B)** each of $R^{b(i)}$ and $R^{b(ii)}$ is individually



[0098] In a further aspect of this embodiment, **(B)** each of $R^{b(i)}$ and $R^{b(ii)}$ is individually



[0099] In a further aspect of this embodiment, **(A)** each of $R^{a(i)}$ and $R^{a(ii)}$ is individually selected from the group consisting of $-CH_3$ group, a $-CH(CH_3)_2$ group, a $-CH=CH_2$ group, and a $-CH_2CH_2CH_2CH_3$ group and **(B)** each of $R^{b(i)}$ and $R^{b(ii)}$ is individually selected from the group consisting



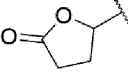
[0100] In one aspect of this embodiment, the disclosed and claimed subject matter includes Sn6-oxo drum clusters in which (i) a proportion (*e.g.*, half, etc.) of R^{a1} , R^{a2} , R^{a3} , R^{a4} , R^{a5} and R^{a6} are a same first group (" $R^{a(i)}$ ") and the remainder of R^{a1} , R^{a2} , R^{a3} , R^{a4} , R^{a5} and R^{a6} are a same second group (" $R^{a(ii)}$ ") that is different than the first group (" $R^{a(i)}$ ") and (ii) each of R^{b1} , R^{b2} , R^{b3} ,

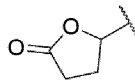
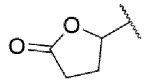
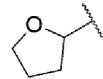
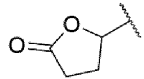
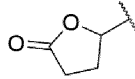
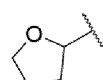
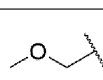
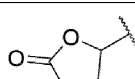
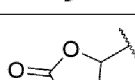
R^{b4} , R^{b5} and R^{b6} are a same group (*i.e.*, $R^{b1}=R^{b2}=R^{b3}=R^{b4}=R^{b5}=R^{b6}$, “ R^b ”). As those skilled in the art will understand, the proportion of $R^{a(i)}$ to $R^{a(ii)}$ can be defined as a ratio: $R^{a(i)}:R^{a(ii)} = (5-u):(1+u)$ where u = a whole number from 0 to 4. Thus, mixed ligand clusters of this type have the formula: $[(R^{a(i)}Sn)_{6-x}(R^{a(ii)}Sn)_x]O_6(O_2C-R^b)_6$ where x = a whole number of 1 to 5.

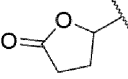
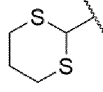
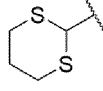
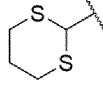
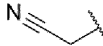
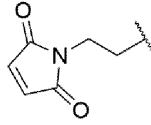
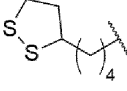
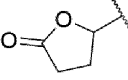
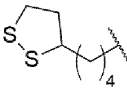
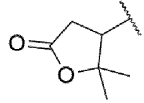
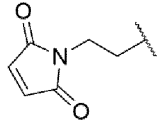
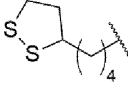
[0101] In another aspect of this embodiment, the disclosed and claimed subject matter includes Sn6-oxo drum clusters where (i) each of R^{a1} , R^{a2} , R^{a3} , R^{a4} , R^{a5} and R^{a6} are a same group (*i.e.*, $R^{a1}=R^{a2}=R^{a3}=R^{a4}=R^{a5}=R^{a6}$, “ R^a ”) and (ii) a proportion (*e.g.*, half, etc.) of R^{b1} , R^{b2} , R^{b3} , R^{b4} , R^{b5} and R^{b6} are a same first group (“ $R^{b(i)}$ ”) and the remainder of R^{b1} , R^{b2} , R^{b3} , R^{b4} , R^{b5} and R^{b6} are a same second group (“ $R^{b(ii)}$ ”) that is different than the first group (“ $R^{b(i)}$ ”). As those skilled in the art will understand, the proportion of $R^{b(i)}$ to $R^{b(ii)}$ can be defined as a ratio: $R^{b(i)}:R^{b(ii)} = (5-p):(1+p)$ where p = a whole number from 0 to 4. Thus, mixed ligand clusters of this type have the formula: $(R^aSn)_6O_6[(O_2C-R^{b(i)})_{6-y}(O_2C-R^{b(ii)})_y]$ where y = a whole number of 1 to 5.

[0102] In a further aspect of this embodiment, the disclosed and claimed subject matter includes Sn6-oxo drum clusters where (i) a proportion (*e.g.*, half, etc.) of R^{a1} , R^{a2} , R^{a3} , R^{a4} , R^{a5} and R^{a6} are a same first group (“ $R^{a(i)}$ ”) and the remainder of R^{a1} , R^{a2} , R^{a3} , R^{a4} , R^{a5} and R^{a6} are a same second group (“ $R^{a(ii)}$ ”) that is different than the first group (“ $R^{a(i)}$ ”) and (ii) a proportion (*e.g.*, half, etc.) of R^{b1} , R^{b2} , R^{b3} , R^{b4} , R^{b5} and R^{b6} are a same first group (“ $R^{b(i)}$ ”) and the remainder of R^{b1} , R^{b2} , R^{b3} , R^{b4} , R^{b5} and R^{b6} are a same second group (“ $R^{b(ii)}$ ”) that is different than the first group (“ $R^{b(i)}$ ”). As those skilled in the art will understand, the proportion of $R^{a(i)}$ to $R^{a(ii)}$ can be defined as a ratio: $R^{a(i)}:R^{a(ii)} = (5-u):(1+u)$ where u = a whole number from 0 to 4 and the proportion of $R^{b(i)}$ to $R^{b(ii)}$ can be defined as a ratio: $R^{b(i)}:R^{b(ii)} = (5-p):(1+p)$ where p = a whole number from 0 to 4. Thus, mixed ligand clusters of this type have the formula: $[(R^{a(i)}Sn)_{6-x}(R^{a(ii)}Sn)_x]O_6[(O_2C-R^{b(i)})_{6-y}(O_2C-R^{b(ii)})_y]$ where x and y each independently = a whole number of 1 to 5.

[0103] As those skilled in the art will further understand, because x and/or y can be a fractional number in mixtures of different Sn6-oxo drum clusters (described below), the respective ratios of $R^{a(i)}:R^{a(ii)}$ and/or $R^{b(i)}:R^{b(ii)}$ can be expressed as non-whole numbers/fractional (*e.g.*, $R^{a(i)}:R^{a(ii)}$ can be 1.5:4.5 when $x = 4.5$). On the other hand, when x and/or y are a whole number, the respective ratios of $R^{a(i)}:R^{a(ii)}$ and/or $R^{b(i)}:R^{b(ii)}$ will also be expressed as a whole number (*e.g.*, $R^{b(i)}:R^{b(ii)}$ can be 3:3 when $y = 3$). Examples of whole number ratio Sn6-oxo drum clusters included in the disclosed and claimed subject matter are set forth in Table 1 below:

Macroscopic Formula: $[(R^{a(i)}Sn)_{6-x}(R^{a(ii)}Sn)_x]O_6[(O_2C-R^{b(i)})_{6-y}(O_2C-R^{b(ii)})_y]$						
Ex.	$R^{a(i)}: R^{a(ii)}$ Distribution (x values)	R^a Group(s)		$R^{a(i)}: R^{a(ii)}$ Distribution (y values)	R^b Group(s)	
		$R^{a(i)}$	$R^{a(ii)}$		$R^{b(i)}$	$R^{b(ii)}$
1	1:5	Me	n-Bu	All same (y = 0)		--
2	1:5	Me	n-Bu	All same (y = 0)		--
3	1:5	iPr	n-Bu	All same (y = 0)		--
4	2:4	Me	n-Bu	All same (y = 0)		--
5	2:4	Me	n-Bu	All same (y = 0)		--
6	2:4	iPr	n-Bu	All same (y = 0)		--
7	3:3	Me	n-Bu	All same (y = 0)		--
8	3:3	Me	n-Bu	All same (y = 0)		--
9	3:3	Me	n-Bu	All same (y = 0)		--
10	3:3	iPr	n-Bu	All same (y = 0)		--
11	4:2	Me	n-Bu	All same (y = 0)		--
12	4:2	Me	n-Bu	All same (y = 0)		--
13	5:1	Me	n-Bu	All same (y = 0)		--
14	5:1	Me	n-Bu	All same (y = 0)		--

15	5:1	Me	iPr	1:1		
16	All same (x = 0)	n-Bu	--	1:5		
17	All same (x = 0)	n-Bu	--	1:5		
18	All same (x = 0)	n-Bu	--	1:5		
19	All same (x = 0)	Me	--	1:5		
20	All same (x = 0)	Me	--	1:5		
21	All same (x = 0)	Me	--	1:5		
22	All same (x = 0)	Me	--	2:4		
23	All same (x = 0)	Me	--	2:4		
24	All same (x = 0)	Me	--	2:4		
25	All same (x = 0)	n-Bu	--	3:3		
26	All same (x = 0)	n-Bu	--	3:3		
27	All same (x = 0)	n-Bu	--	3:3		
28	All same (x = 0)	Me	--	3:3		
29	All same (x = 0)	Me	--	3:3		

30	All same (x = 0)	Me	--	3:3		
31	All same (x = 0)	Me	--	3:3		
32	All same (x = 0)	Me	--	3:3		
33	All same (x = 0)	Me	--	3:3		
34	All same (x = 0)	Me	--	3:3		
35	All same (x = 0)	n-Bu	--	3:3		
36	All same (x = 0)	Me	--	3:3		
37	All same (x = 0)	n-Bu	--	3:3		
38	All same (x = 0)	n-Bu	--	4:1		
39	All same (x = 0)	Me	--	4:1		
40	All same (x = 0)	Me	--	4:2		
41	All same (x = 0)	Me	--	3:3		
42	3:3	Me	n-Bu	3:3		

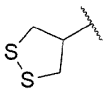
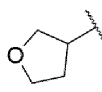
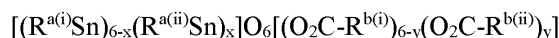
43	All same (x = 0)	n-Bu	-	1:1		
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Table 1

[0104] As those skilled in the art will recognize, the proportion of R^{a1} , R^{a2} , R^{a3} , R^{a4} , R^{a5} and R^{a6} and/or of R^{b1} , R^{b2} , R^{b3} , R^{b4} , R^{b5} and R^{b6} respectively can be controlled stoichiometrically during the synthesis of the Sn6-oxo clusters. In addition, the disclosed and claimed subject matter includes mixtures and formulations including the compounds described above, including in particular those identified in Table 1.

[0105] **Sn6-Oxo Cluster Mixtures**

[0106] In another aspect, the disclosed and claimed subject matter includes mixtures of one or more of the above Sn6-oxo drum clusters. As those skilled in the art will understand, that the **average** value of x and y may differ from that of the individual clusters making up the mixture. Thus, in such mixtures, (i) x and y each independently equal a whole number or fractional number of $0 < x$ and/or $y < 6$ or (ii) one of x or y = 0 and the other of x or y = a whole or fractional number of $0 < x$ and/or $y < 6$ due. Accordingly, the disclosed and claimed subject includes mixtures of the above-described Sn6-oxo drum clusters in which the mixture of Sn6-oxo drum clusters has the formula:

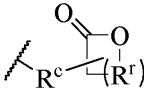


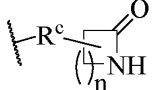
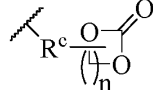
where

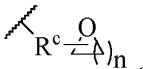
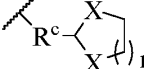
(A) (i) $R^{a(i)} \neq R^{a(ii)}$ and (ii) $R^{a(i)}$ and $R^{a(ii)}$ are each individually selected from the group consisting of an unsubstituted linear C_1 - C_{10} alkyl group, a linear C_1 - C_6 alkyl group substituted with a halogen, a linear C_1 - C_6 alkyl group substituted with an amino group, 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} heteroalkyl group, a branched C_3 - C_{10} alkyl group substituted with an amino group, 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, an unsubstituted linear C_2 - C_{10} alkenyl group, an unsubstituted branched C_3 - C_{10} alkenyl group, an unsubstituted linear C_2 - C_{10} alkynyl group and an unsubstituted branched C_4 - C_{10} alkynyl group;

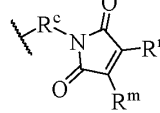
(B) (i) $R^{b(i)} \neq R^{b(ii)}$ and (ii) $R^{b(i)}$ and $R^{b(ii)}$ are each individually selected from the

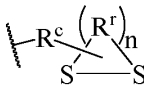
group consisting of H; an unsubstituted linear C₁-C₁₀ alkyl group; a substituted linear C₁-C₁₀ alkyl group substituted with one or more of a -CN group, an -OH group, an -OR' group, an -SR' or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl group, an -NO₂ group, a halogen or a -C(=O)H group; an unsubstituted branched C₃-C₁₀ alkyl group; a substituted branched C₃-C₁₀ alkyl group substituted with one or more of a -CN group, an -OH group, a -OR' group, an -SR' or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl unit, a -NO₂ group, a halogen or a -C(=O)H group; a C₃-C₈ unsubstituted cyclic alkyl group; a linear C₂-C₁₀ alkenyl group; a branched C₃-C₁₀ alkenyl group, a 5-membered heterocyclic

ring; and a 6-membered heterocyclic ring; a  group where (i) n = 1-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-

C₄ alkyl groups; a  group where n = 1-4, a  group where n = 1-4; a

 group where n = 1-6; a  group where each X is individually selected from

O and S and n = 1-4; a  group where each R^m group is independently selected from H,

or a linear C₁-C₄ chain, or a branched C₃-C₄ chain; a  group where (i) n = 3-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups; where R^c in each of the foregoing groups is (i) a direct covalent bond or (ii) an unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group; and

(C) (i) x and y each independently equal a whole or fractional number of 0 < x and/or y < 6 or (ii) one of x or y = 0 and the other of x or y = a whole or fractional number of 0 < x and/or y < 6.

[0107] In a further aspect of this embodiment, (A) each of R^{a(i)} and R^{a(ii)} is individually selected from the group consisting of an unsubstituted linear C₁-C₄ alkyl group, an unsubstituted

branched C₃-C₄ alkyl group, an unsubstituted linear C₂-C₆ alkenyl group, an unsubstituted branched C₃-C₆ alkenyl group and a C₄-C₆ unsubstituted aromatic group.

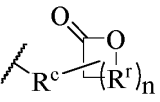
[0108] In a further aspect of this embodiment, **(A)** each of R^{a(i)} and R^{a(ii)} is individually selected from the group consisting of a -CH₃ group, a -CH(CH₃)₂ group, a -C(CH₃)₃ group, a -CH=CH₂ group, a -CH₂CH=CH₂ group, a -CH₂CH₂CH=CH₂ group, a -CH₂CH₂CH₂CH₃ group, a -C₆H₅ group and a -CH₂-C₆H₅ group.

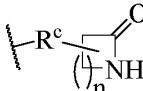
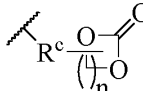
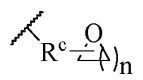
[0109] In a further aspect of this embodiment, **(A)** each of R^{a(i)} and R^{a(ii)} is individually selected from the group consisting of a -CH₃ group, a -CH(CH₃)₂ group, a -C(CH₃)₃ group, a -CH=CH₂ group, a -CH₂CH=CH₂ group, a -CH₂CH₂CH=CH₂ group and a -CH₂CH₂CH₂CH₃ group.

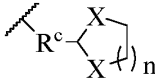
[0110] In a further aspect of this embodiment, **(A)** each of R^{a(i)} and R^{a(ii)} is individually selected from the group consisting of a -CH₃ group, a -CH(CH₃)₂ group, a -C(CH₃)₃ group, a -CH=CH₂ group, a -CH₂CH=CH₂ group, and a -CH₂CH₂CH₂CH₃ group.

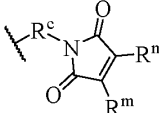
[0111] In a further aspect of this embodiment, **(A)** each of R^{a(i)} and R^{a(ii)} is individually selected from the group consisting of a -CH₃ group, a -CH(CH₃)₂ group, a -CH=CH₂ group, and a -CH₂CH₂CH₂CH₃ group.

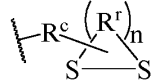
[0112] In a further aspect of this embodiment, **(B)** each of R^{b(i)} and R^{b(ii)} is individually selected from the group consisting of -H; an unsubstituted linear C₁-C₆ alkyl group; a substituted linear C₁-C₆ alkyl group substituted with one or more of a -CN group, an -OH group, an -OR' group, an -SR', or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl group, an -NO₂ group, a halogen, or a -C(=O)H group; an unsubstituted branched C₃-C₆ alkyl group; a substituted branched C₃-C₆ alkyl group substituted with one or more of a -CN group, an -OH group, a -OR' group, an -SR', or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl unit, a -NO₂ group, a halogen, or a -C(=O)H group; a C₃-C₆ unsubstituted cyclic alkyl group; a linear C₂-C₆ alkenyl group; a branched C₃-C₆ alkenyl group, a 5-membered heterocyclic ring; and a 6-

membered heterocyclic ring; a  group where (i) n = 1-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups;

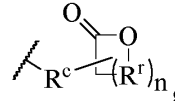
a  group where n = 1-4, a  group where n = 1-4; a  group where

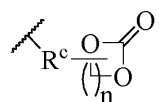
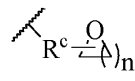
$n = 1-6$; a  group where each X is individually selected from O and S and $n = 1-4$; a

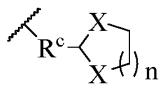
 group where each R^m group is independently selected from H, or a linear C_1-C_4 chain,

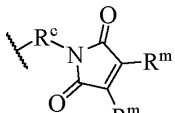
or a branched C_3-C_4 chain; a  group where (i) $n = 3-5$ and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C_1-C_4 alkyl groups; where R^c in each of the foregoing groups is (i) a direct covalent bond or (ii) an unsubstituted linear C_1-C_6 alkylene group, an unsubstituted branched C_3-C_6 alkylene group.

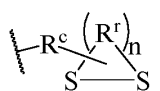
[0113] In a further aspect of this embodiment, **(B)** each of $R^{b(i)}$ and $R^{b(ii)}$ is individually selected from the group consisting of -H; an unsubstituted linear C_1-C_6 alkyl group; a substituted linear C_1-C_6 alkyl group substituted with one or more of a -CN group, an -OR' group, an -SR', or an -S-S-R' group where R' is a linear or branched C_1-C_4 alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C_1-C_4 alkyl group, an -NO₂ group, or a -C(=O)H group; an unsubstituted branched C_3-C_6 alkyl group; a substituted branched C_3-C_6 alkyl group substituted with one or more of a -CN group, a -OR' group, an -SR', or an -S-S-R' group where R' is a linear or branched C_1-C_4 alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C_1-C_4 alkyl unit, a -NO₂ group, or a -C(=O)H

group; a linear C_2-C_6 alkenyl group; a branched C_3-C_6 alkenyl group, a  group where (i) $n = 1-5$ and (ii) each R^r is individually an unsubstituted methylene group or a methylene group

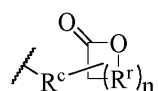
substituted with one or two C_1-C_4 alkyl groups; a  group where $n = 1-4$; a 

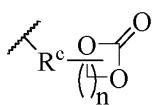
group where $n = 1-6$; a  group where each X is individually selected from O and S and

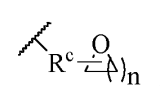
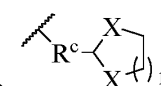
$n = 1-4$; a  group where each R^m group is independently selected from H, or a linear

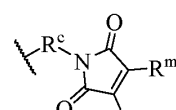
C₁-C₄ chain, or a branched C₃-C₄ chain; a  group where (i) n = 3-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups; where R^e in each of the foregoing groups is (i) a direct covalent bond or (ii) an unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group.

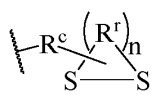
[0114] In a further aspect of this embodiment, **(B)** each of R^{b(i)} and R^{b(ii)} is individually selected from the group consisting of -H; an unsubstituted linear C₁-C₆ alkyl group; a substituted linear C₁-C₆ alkyl group substituted with one or more of a -CN group, an -OR' group where R' is a linear or branched C₁-C₄ alkyl group, or a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl group; an unsubstituted branched C₃-C₆ alkyl group; a substituted branched C₃-C₆ alkyl group substituted with one or more of a -CN group, a -OR' group where R' is a linear or branched C₁-C₄ alkyl group, or a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl unit; a

 group where (i) n = 1-5 and (ii) each R^r is individually an unsubstituted methylene

group or a methylene group substituted with one or two C₁-C₄ alkyl groups; a  group

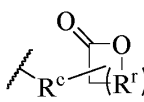
where n = 1-4; a  group where n = 1-6; a  group where each X is

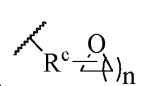
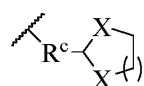
individually selected from O and S and n = 1-4; a  group where each R^m group is

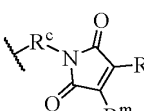
independently selected from H, or a linear C₁-C₄ chain, or a branched C₃-C₄ chain; a  group where (i) n = 3-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups; where R^e in each of the foregoing groups is (i) a direct covalent bond or (ii) an unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group.

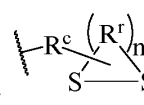
[0115] In a further aspect of this embodiment, **(B)** each of R^{b(i)} and R^{b(ii)} is individually selected from the group consisting of -H; an unsubstituted linear C₁-C₆ alkyl group; a substituted linear C₁-C₆

alkyl group substituted with one or more of a -CN group, or an -OR' group where R' is a linear or branched C₁-C₄ alkyl group; an unsubstituted branched C₃-C₆ alkyl group; a substituted branched C₃-C₆ alkyl group substituted with one or more of a -CN group, or a -OR' group where R' is a linear or

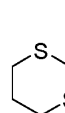
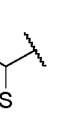
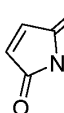
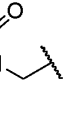
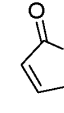
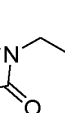
branched C₁-C₄ alkyl group; a  group where (i) n = 1-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups;

a  group where n = 1-6; a  group where each X is individually selected from

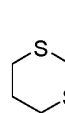
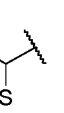
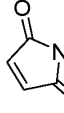
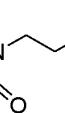
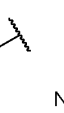
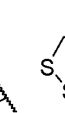
O and S and n = 1-4; a  group where each R^m group is independently selected from H,

or a linear C₁-C₄ chain, or a branched C₃-C₄ chain; a  group where (i) n = 3-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups; where R^c in each of the forgoing groups is (i) a direct covalent bond or (ii) an unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group.

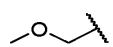
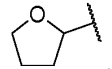
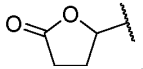
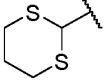
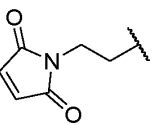
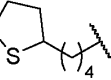
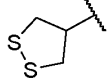
[0116] In a further aspect of this embodiment, (B) each of R^{b(i)} and R^{b(ii)} is individually selected

from the group consisting of -H, , , , , , , , , , , , , and .

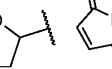
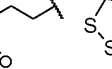
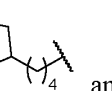
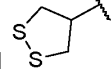
[0117] In a further aspect of this embodiment, (B) each of R^{b(i)} and R^{b(ii)} is individually

selected from the group consisting of -H, , , , , , , , , , , , and .

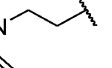
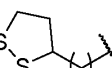
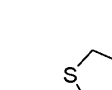
[0118] In a further aspect of this embodiment, (B) each of R^{b(i)} and R^{b(ii)} is individually

selected from the group consisting of -H, , , , , , , , , , and .

[0119] In a further aspect of this embodiment, **(B)** each of $R^{b(i)}$ and $R^{b(ii)}$ is individually selected

from the group consisting of -H, , , , , , and .

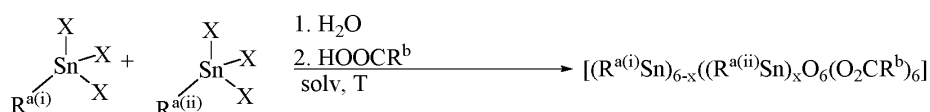
[0120] In a further aspect of this embodiment, **(A)** each of $R^{a(i)}$ and $R^{a(ii)}$ is individually selected from the group consisting of -CH₃ group, a -CH(CH₃)₂ group, a -CH=CH₂ group, and a -CH₂CH₂CH₂CH₃ group and **(B)** each of $R^{b(i)}$ and $R^{b(ii)}$ is individually selected from the group

consisting of -H, , , , , , and .

[0121] **Processes for Preparing Sn6-Oxo Clusters**

[0122] As set forth above, the disclosed subject matter relates further includes a process for synthesizing the disclosed and claimed Sn6-oxo clusters.

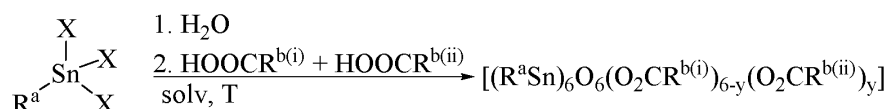
[0123] In another aspect, the disclosed and claimed subject matter relates to a process for preparing Sn6-oxo drum clusters having mixed organic ligands (*i.e.*, the R^a ligands). A mixture of at least two monoorgano Sn starting materials with different organic groups bound to the Sn atoms and with ligands X, typically alkoxy, is prepared, optionally in an organic solvent or a mixture of solvents. Under stirring, water is added thereto (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 total 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.



[0124] 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.

[0125] 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%.

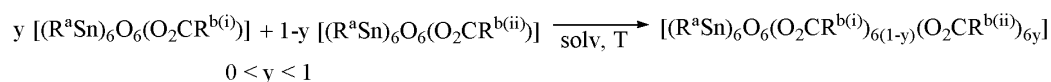
[0126] In another aspect, the disclosed and claimed subject matter relates to a process for preparing Sn6-oxo drum clusters having mixed carboxylate ligands (*i.e.*, the R^b ligands). In a typical synthesis, a monoorgano (*i.e.*, all R^a are the same) Sn starting material with ligands X, typically alkoxy, optionally in an organic solvent or a mixture of solvents, (*e.g.*, THF), is reacted with water. Stirring is continued and a mixture of acids (total carboxylate amount = 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. Stirring is further continued, 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.



[0127] 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.

[0128] 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%.

[0129] In an aspect, the disclosed and claimed subject matter relates to a process for preparing Sn₆-oxo drum clusters having mixed carboxylate ligands (*i.e.*, the R^b ligands). Two (or more) “pure” Sn₆-oxo-drum clusters with different carboxylate ligands are mixed in solution to afford Sn₆-oxo-drum clusters with mixed carboxylate ligands. This process is shown schematically for the mixing of two different cluster materials.



[0130] In another aspect, the process relates to a process for preparing Sn₆-oxo drum clusters having mixed organic ligands (*i.e.*, the R^a ligands) and mixed carboxylate ligands (*i.e.*, the R^b ligands). A mixture of at least two monoorgano Sn starting materials with different organic groups bound to the Sn atoms and with ligands X, typically alkoxy, is prepared, optionally in an organic solvent. Under stirring, water is added thereto (neat or as solution in an organic solvent or mixture of organic solvents). Stirring is continued and a mixture of acids (total carboxylate amount = 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. Stirring is further continued, 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.



[0131] 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.

[0132] 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%.

[0133] Monitoring of mixed cluster formations: Sn6 drum clusters without mixed ligands are known in the literature and have been shown to yield sharp NMR signals in the range of approximately -440 ppm to -520 ppm for R^{a} = Me, nBu, and iPr. See Example 3, FIG. 6. The exact chemical shift of the respective signals is dependent on the coordination environment, hence a function of the coordination number, the carboxylate ligands as well as the alkyl substituents (R^{a}). Upon formation of mixed cluster species these signals broaden, due to the presence of multiple Sn atoms with slightly altered chemical environments within the clusters. This broadening is indicative for mixed clusters, and representative spectra are shown in the experimental examples. If the clusters contain Sn atoms with different R^{a} groups, e.g., Me and nBu, a broadened signal for each type of Sn atoms can arise.

[0134] In general, cluster formation can be monitored directly in solution via ^{119}Sn -NMR, given a high enough concentration of the material. Via partial removal of the solvent(s), a higher concentration can be achieved. For these experiments, a capillary insert containing a deuterated solvent is typically used. This way, the reaction solution is not altered by addition of a further solvent. Another approach is the isolation of the compounds by complete removal of the solvent and subsequent redissolution in a deuterated solvent. In Example 5, (See FIG. 12) the ^{119}Sn -NMR spectra of a mixed compound in the reaction solution as well as of a redissolved solid sample are compared and found to be identical. Both procedures for monitoring of compound formation can

be used interchangeably and both are used in the experimental examples.

[0135] Sn6-Oxo Cluster Formulations and Uses Thereof

[0136] 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.

[0137] 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.

[0138] 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.

[0139] 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. In another aspect, the formulation comprises one of 2-heptanone, cyclohexanone, PGMEA, PGME, a mixture of anisole and PGMEA, a mixture of anisole and cyclohexanone and a mixture of anisole and 2-heptanone.

[0140] 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.

[0141] 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.

[0142] 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.

[0143] 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.

[0144] 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.

[0145] Method of photopatterning the materials: spincoating on a substrate at 500rpm/5s then 800-5000 rpm for 15-120 s, 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-heptanone, cyclohexanone, PGMEA, PGME, a mixture of anisole and PGMEA, a mixture of anisole and cyclohexanone and a mixture of anisole and 2-heptanone.

[0146] 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.

[0147] **Use As Metal Hardmask**

[0148] Application of material through spincoating, followed by a bake to convert the metal precursor film to MO_x film. The film will now act as a metal hardmask, which can be used with other photopatternable resists such as CAR. Optionally, a lithographic exposure step can be used to pattern the hardmask material. In that case, the metal oxide material is applied through spincoating, followed by a softbaking step and subsequently exposed through a mask with electromagnetic radiation. This is followed by a baking step. Optionally, the film is then developed with a solvent whereby either the exposed or the non-exposed parts are washed off. Alternatively, an etch is directly applied to the film, for example using HBr etch gas.

[0149] **EXAMPLES**

[0150] 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.

[0151] 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.

[0152] **Materials and Methods:**

[0153] The disclosed and claimed processes utilizes commercially available materials (*e.g.*, THF, PGME, cyclohexanone, toluene, methoxyacetic acid, formic acid, acetic acid, pivalic acid, tetrahydrofuran-2-carboxylic acid (CAS 16874-33-2, 1,3-dithiane-2-carboxylic acid (CAS 20461-89-6), 5-Oxo-2-tetrahydrofurancarboxylic acid (CAS 4344-84-7), CDCl₃, C₆D₆.)

$\text{RSn}(\text{OR}')_3$ ($\text{R} = \text{Me}, \text{nBu}$; $\text{R}' = \text{tBu}, \text{tAmyl}$) compounds were prepared according to (modified) literature procedures. See F. Banse *et al.*, *Inorg. Chem.*, 34, 6371 (1995).

[0154] **Example 1: Preparation of a Series of Sn_6 drum clusters with methoxyacetate ligands with Varying Ratios of Me and nBu Ligands Bound to the Sn Atoms**

[0155] General formula of the targeted compounds: $[(\text{MeSn})_x(\text{nBuSn})_{6-x}\text{O}_6(\text{O}_2\text{CCH}_2\text{OMe})_6]$.

[0156] A mixture of two Sn starting materials $\text{RSn}(\text{OtAmyl})_3$ (total 1 mmol, 1 eq, $\text{R} = \text{Me}$ and nBu) with different ratios of Me:Bu (1:5, 1:2, 1:1, 2:1, 5:1) is weighed into a crimp vial (reaction vial), equipped with a stir bar, inside a glovebox. 4 mL of tetrahydrofuran are added, and the vial is closed. After transfer into a hood water (0.98 mmol, 3 eq.) is added with a syringe while stirring. In a separate vial, methoxyacetic acid  (1 mmol, 1 eq.) is dissolved in 5 mL of tetrahydrofuran and the solution is slowly added dropwise to the reaction vial with a syringe. The solution is stirred overnight, and a clear solution results the next day. All volatiles are removed in vacuo on a rotary evaporator (30 °C, 1 mbar), affording the products as transparent to white solids. Yield values are as follows:

Ratio nBu:Me	Yield (%)
5:1	Quantitative
2:1	Quantitative
1:1	Quantitative
1:2	Quantitative
1:5	90

Table 2

A sample of the isolated material from each reaction is individually dissolved in CDCl_3 and NMR measurements are performed. See FIG. 1.

[0157] **Example 2: Preparation of Series of Sn_6 drum clusters with formate ligands with varying ratios of Me and nBu Ligands Bound to Sn Atoms**

[0158] General formula of the targeted compounds: $[(\text{MeSn})_x(\text{nBuSn})_{6-x}\text{O}_6(\text{O}_2\text{CH})_6]$.

[0159] A mixture of two Sn starting materials $\text{RSn}(\text{OtAmyl})_3$ (total 0.326 mmol, 1 eq, $\text{R} = \text{Me}$ and nBu) with different ratios of Me:Bu (1:5, 1:2, 1:1, 2:1, 5:1) is weighed into a crimp vial (reaction vial), equipped with a stir bar, inside a glovebox. 4 mL of tetrahydrofuran are added, and the vial is closed. After transfer into a hood water (0.98 mmol, 3 eq.) is added with a syringe while

stirring. In a separate vial, formic acid  (0.33 mmol, 1 eq.) is dissolved in 5 mL of

tetrahydrofuran and the solution is slowly added dropwise to the reaction vial with a syringe. The solution is stirred overnight. All volatiles are removed in vacuo on a rotary evaporator (30 °C, 1 mbar), affording the products as white solids. Yield values are as follows:

Ratio nBu:Me	Yield (%)
5:1	Quantitative
2:1	94%
1:1	16%
1:2	Quantitative
1:5	Quantitative

Table 3

A sample of the isolated material from each reaction is individually dissolved in CDCl₃ and NMR measurements are performed. *See* FIG. 2.

[0160] Example 3: Preparation of Mixed nBu-Sn₆ drum cluster with pivalate and acetate ligands from pure nBu Sn₆ pivalate and acetate drum cluster compounds

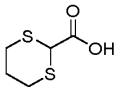
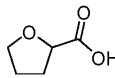
[0161] General formula of the targeted compounds: [(nBuSn)₆O₆(O₂CCH₃)₃(O₂CC(CH₃)₃)₃].

[0162] The starting materials were synthesized according to known literature procedures. [(nBuSn)₆O₆(O₂CCH₃)₆] (200 mg, 132 μmol) is placed in a vial, dissolved in 3 mL of toluene-d₈ and stirred for 30 minutes. The resulting solution is filtered through a 0.2 μm syringe filter into a second vial containing [(nBuSn)₆O₆(O₂CC(CH₃)₃)₆] (230 mg, 131 μmol). The solution is stirred for 5 minutes, before a sample (0.6 mL) is taken for NMR measurements. Stirring is continued overnight and a second sample is taken for NMR measurements. NMR spectra are recorded directly from the reaction solution. Characteristic signals and a broadening of the signals over time are detected at -485 ppm and -486 ppm in the ¹¹⁹Sn NMR spectrum. *See* FIG. 3.

[0163] Example 4: Preparation of Me-Sn₆ drum clusters with a mixture of Tetrahydrofuran-2-carboxylate and 1,3-Dithiane-2-carboxylate ligands

[0164] Formula of the targeted compound: [(MeSn)₆O₆(O₂C(C₄H₇O))₃(O₂C(C₄H₇S₂))₃].

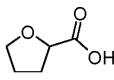
[0165] The Sn starting material MeSn(OtAmyl)₃ (4.11 mmol, 1 eq) is weighed into a crimp vial (reaction vial), equipped with a stir bar, inside a glovebox. 28 mL of 1-methoxypropan-2-ol and 4.9 mL Cyclohexanone are added, and the vial is closed. After transfer into a hood water (12.3 mmol, 3 eq.) is added with a syringe while stirring. A cloudy mixture is formed. In a separate vial, the

desired acids  and  (each 2.05 mmol, 0.5 eq) are 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. NMR spectra are recorded on solids isolated by removal of the solvents and redissolution in THF-d8. Characteristic signals and a broadening of the signals are detected at -457 ppm and -458 – -459 ppm in the ^{119}Sn NMR spectrum. *See* FIG. 4.

[0166] Example 5: Preparation of Me-Sn6 drum clusters with a mixture of Tetrahydrofuran-2-carboxylate and pivalate ligands

[0167] Formula of the targeted compound: $[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{C}(\text{C}_4\text{H}_7\text{O}))_3(\text{O}_2\text{CC}(\text{CH}_3)_3)_3]$.

[0168] The Sn starting material $\text{MeSn}(\text{OtAmyl})_3$ (0.77 mmol, 1 eq) is weighed into a crimp vial (reaction vial), equipped with a stir bar, inside a glovebox. 8 mL of toluene are added, and the vial is closed. After transfer into a hood water (2.31 mmol, 3 eq.) is added with a syringe while

stirring. A cloudy mixture is formed. In a separate vial, the desired acids  and  (each 0.39 mmol, 0.5 eq) are dissolved in 2 mL of toluene and the resulting solution is slowly added dropwise to the reaction vial with a syringe. Afterwards a clear to slightly cloudy solution is formed. The solution is stirred overnight, and a cloudy solution results the next day. 1.5 mL of the homogenized solution placed in a round-bottom flask and all solvent is removed on a rotary evaporator. The isolated white solid is redissolved in 0.7 CDCl_3 and submitted for NMR measurements. *See* FIG 5 for a comparison of ^{119}Sn NMR spectra of a higher concentrated solution vs. redissolved isolated material. Characteristic signals are detected at -463 ppm and -465 ppm in the ^{119}Sn NMR spectrum. A sample of the solution is diluted in THF and a mass spectrum is recorded. The detected mixed ligand cluster species are listed in Table 4.

Cluster Formula	Ligand ratio	
	Ligand 1: pivalate	Ligand 2: 2THF
$[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{C}_5\text{H}_9)_2(\text{O}_3\text{C}_5\text{H}_7)_4]$	2	4
$[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{C}_5\text{H}_9)_3(\text{O}_3\text{C}_5\text{H}_7)_3]$	3	3
$[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{C}_5\text{H}_9)_4(\text{O}_3\text{C}_5\text{H}_7)_2]$	4	2
$[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{C}_5\text{H}_9)_5(\text{O}_3\text{C}_5\text{H}_7)_1]$	5	1
$[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{C}_5\text{H}_9)_5]$	5	0
$[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{C}_5\text{H}_9)_4(\text{O}_3\text{C}_5\text{H}_7)_1]$	4	1

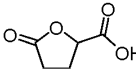
$[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{C}_5\text{H}_9)_3(\text{O}_3\text{C}_5\text{H}_7)_2]$	3	2
$[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{C}_5\text{H}_9)_2(\text{O}_3\text{C}_5\text{H}_7)_3]$	2	3

Table 4

[0169] **Example 6: Preparation of Me-Sn6 drum clusters with a mixture of 5-Oxo-2-tetrahydrofurancarboxylate and formate ligands**

[0170] Formula of the targeted compound: $[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{CH})_3(\text{O}_2\text{C}(\text{C}_4\text{H}_5\text{O}_2))_3]$.

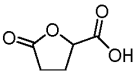
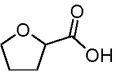
[0171] The Sn starting material $\text{MeSn}(\text{OtAmyl})_3$ (3.34 mmol, 1 eq) is weighed into a crimp vial (reaction vial), equipped with a stir bar, and the vial is closed inside a glovebox. After transfer into a hood 9 mL of 1-methoxypropan-2-ol and 9 mL cyclohexanone are added to afford a clear solution. In the next step water (10 mmol, 3 eq.) is added with a syringe while stirring. A cloudy

solution is formed. In separate vials, the desired acids  and  (each 1.67 mmol, 0.5 eq) are dissolved in 1 mL of the solvent mixture 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 -458 ppm in the ^{119}Sn NMR spectrum.

[0172] **Example 7: Preparation of Me-Sn6 drum clusters with a mixture of 5-Oxo-2-tetrahydrofurancarboxylate and Tetrahydrofuran-2-carboxylate ligands**

[0173] Formula of the targeted compound: $[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{CH})_3(\text{O}_2\text{C}(\text{C}_4\text{H}_5\text{O}_2))_3(\text{O}_2\text{C}(\text{C}_4\text{H}_7\text{O}))_3]$.

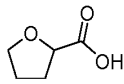
[0174] The Sn starting material $\text{MeSn}(\text{OtAmyl})_3$ (4.41 mmol, 1 eq) is weighed into a crimp vial (reaction vial), equipped with a stir bar, and the vial is closed inside a glovebox. After transfer into a hood 24 mL of 1-methoxypropan-2-ol and 24 mL cyclohexanone are added to afford a clear solution. In the next step water (13.22 mmol, 3 eq.) is added with a syringe while stirring. In separate

vials, the desired acids  and  (each 2.2 mmol, 0.5 eq) are dissolved in 2 mL of the solvent mixture and slowly added dropwise to the reaction vial with a syringe. The solution is stirred overnight. A sample is taken for ^{119}Sn -NMR measurement with a capillary insert containing C_6D_6 for locking. Characteristic signals are detected at -459 and -462 ppm in the ^{119}Sn NMR spectrum.

[0175] **Example 8: Preparation of Sn6 drum clusters Me and iPr Ligands Bound to the Sn Atoms and a mixture of Tetrahydrofuran-2-carboxylate and formate ligands**

[0176] Formula of the targeted compound: $[(\text{MeSn})_5(\text{iPrSn})_1\text{O}_6(\text{O}_2\text{CH})_3(\text{O}_2\text{C}(\text{C}_4\text{H}_7\text{O}))_3]$.

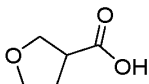
[0177] The Sn starting materials $\text{MeSn}(\text{OtAmyl})_3$ (1.42 mmol, 5 eq) and $\text{iPrSn}(\text{OtAmyl})_3$ (0.28 mmol, 1 eq) are weighed into a crimp vial (reaction vial), equipped with a stir bar, and the vial is closed inside a glovebox. After transfer into a hood 9 mL of 1-methoxypropan-2-ol and 9 mL cyclohexanone are added to afford a clear solution. In the next step water (5.12 mmol, 18 eq.)

is added with a syringe while stirring. In separate vials, the desired acids  and HCOOH (each 0.85 mmol, 3 eq) are dissolved in 1 mL of the solvent mixture and slowly added dropwise to the reaction vial with a syringe. The clear solution is stirred overnight. A 4 mL sample concentrated to approximately 1 mL and then used for ^{119}Sn -NMR measurement with a capillary insert containing C_6D_6 for locking. Characteristic signals are detected at -460 ppm (Me-Sn) and -502 ppm (iPr-Sn) in the ^{119}Sn NMR spectrum.

[0178] **Example 9: Preparation of Sn₆ drum cluster with Tetrahydrofuran-3-carboxylate ligands with Me and nBu Ligands Bound to Sn Atoms in the same cluster**

[0179] General formula of the targeted compounds: $[(\text{MeSn})_3(\text{nBuSn})_3\text{O}_6(\text{O}_3\text{C}_5\text{H}_7)_6]$.

[0180] A mixture of two Sn starting materials $\text{MeSn}(\text{OtBu})_3$ (0.69 mmol, 244 mg) and $\text{nBuSn}(\text{OtAmyl})_3$ (0.69 mmol, 302 mg) is weighed into a crimp vial equipped with a stir bar inside a glovebox and the vial is closed. After transfer into a hood, 9 mL of cyclohexanone are added. While stirring, water (4.15 mmol, 3 eq.) is added with a syringe. In a separate vial tetrahydrofuran-3-

carboxylic acid  (1.38 mmol, 1 eq.) is dissolved in 1 mL of cyclohexanone and the solution is 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 1D and 2D ^{119}Sn -NMR measurements with a capillary insert containing C_6D_6 for locking. A mass spectrometry sample is prepared by dilution of the reaction mixture in THF. FIG. 10 illustrates the ^{119}Sn - ^{119}Sn -INADEQUATE NMR spectrum. This technique detects coupling between individual Sn atoms. The observed coupling proves the presence of MeSn and nBuSn fragments within the same molecule. The Me-Sn signals are detected at -463 ppm and the nBu-Sn signals at -484 ppm.

[0181] FIG. 11 provides an overview of the recorded mass spectrum and a comparison with the simulated isotopic patterns for the cluster species listed in Table 5. The following cluster species were detected by mass spectrometry:

Cluster Formula	Ligand Ratio
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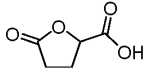
$[(\text{MeSn})_x(\text{nBuSn})_{6-x}\text{O}_6(\text{O}_2\text{C}(\text{C}_4\text{H}_7\text{O}))_6]$	Ligand 1: Me	Ligand 2: nBu
$[(\text{MeSn})_5(\text{nBuSn})_1\text{O}_6(\text{O}_2\text{C}(\text{C}_4\text{H}_7\text{O}))_6]$	5	1
$[(\text{MeSn})_4(\text{nBuSn})_2\text{O}_6(\text{O}_2\text{C}(\text{C}_4\text{H}_7\text{O}))_6]$	4	2
$[(\text{MeSn})_3(\text{nBuSn})_3\text{O}_6(\text{O}_2\text{C}(\text{C}_4\text{H}_7\text{O}))_6]$	3	3
$[(\text{MeSn})_2(\text{nBuSn})_4\text{O}_6(\text{O}_2\text{C}(\text{C}_4\text{H}_7\text{O}))_6]$	2	4
$[(\text{MeSn})_1(\text{nBuSn})_5\text{O}_6(\text{O}_2\text{C}(\text{C}_4\text{H}_7\text{O}))_6]$	1	5

Table 5

[0182] **Example 10: Preparation of Me-Sn6 drum clusters with a mixture of 5-Oxo-2-tetrahydrofurancarboxylate and formate ligands**

[0183] Formula of the targeted compound: $[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{CH})_2(\text{O}_2\text{C}(\text{C}_4\text{H}_5\text{O}_2))_4]$.

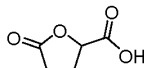
[0184] The Sn starting material $\text{MeSn}(\text{OtBu})_3$ (3.98 mmol, 1 eq) is weighed into a 100 mL round-bottom nitrogen flask (reaction flask), equipped with a stir bar, 44 mL THF are added to afford a clear solution. The flask is closed, transfer into a hood and connected to an inert gas line.

The acids  (2.65 mmol, 0.67 eq) and $\text{H}-\text{C}(=\text{O})-\text{OH}$ (1.31 mmol, 0.33 eq) are dissolved in 6 mL of THF and slowly added dropwise to the reaction flask with a syringe. The cloudy solution is stirred overnight, and a clear solution results the next day. All volatiles are removed in vacuum to afford the product as a white powder. A sample is dissolved in dry cyclohexanone and used for ^{119}Sn -NMR measurement with a capillary insert containing C_6D_6 for locking. A characteristic signal is detected at -456 ppm in the ^{119}Sn NMR spectrum.

[0185] **Example 11: Preparation of Me-Sn6 drum clusters with a mixture of 5-Oxo-2-tetrahydrofurancarboxylate and formate ligands**

[0186] Formula of the targeted compound: $[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{CH})_3(\text{O}_2\text{C}(\text{C}_4\text{H}_5\text{O}_2))_3]$.

[0187] The Sn starting material $\text{MeSn}(\text{OtBu})_3$ (8.4 mmol, 1 eq) is weighed into a 100 mL round-bottom nitrogen flask (reaction flask), equipped with a stir bar, 96 mL of cyclohexanone are added to afford a clear solution. The flask is closed, transfer into a hood and connected to an inert gas

line. The acids  (4.2 mmol, 0.5 eq) and $\text{H}-\text{C}(=\text{O})-\text{OH}$ (4.2 mmol, 0.5 eq) are dissolved in 4 mL of cyclohexanone and slowly added dropwise to the reaction flask with a syringe. The cloudy solution is stirred overnight, and a clear solution results the next day. A sample is taken for NMR measurements with a capillary insert containing C_6D_6 for locking. A characteristic signal is detected at -459 ppm in the ^{119}Sn NMR spectrum. The final reaction solution was characterized via mass

spectrometry to confirm the presence of ligand mixtures within the cluster. FIG. 12 provides an overview of the recorded mass spectrum and a comparison with the simulated isotopic patterns for the mixed ligand cluster species listed in Table 6.

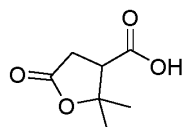
Cluster Formula	Ligand Ratio	
	Ligand 1: Formyl	Ligand 2: Lactone
$[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{CH})_3(\text{O}_2\text{C}(\text{C}_4\text{H}_5\text{O}_2))_3]$	3	3
$[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{CH})_2(\text{O}_2\text{C}(\text{C}_4\text{H}_5\text{O}_2))_4]$	2	4
$[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{CH})_4(\text{O}_2\text{C}(\text{C}_4\text{H}_5\text{O}_2))_2]$	4	2
$[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{CH})_4(\text{O}_2\text{C}(\text{C}_4\text{H}_5\text{O}_2))_1]$	5	1
$[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{CH})_5]$	5	0
$[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{CH})_4(\text{O}_2\text{C}(\text{C}_4\text{H}_5\text{O}_2))_1]$	4	1
$[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{CH})_3(\text{O}_2\text{C}(\text{C}_4\text{H}_5\text{O}_2))_2]$	3	2
$[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{CH})_2(\text{O}_2\text{C}(\text{C}_4\text{H}_5\text{O}_2))_3]$	2	3

Table 6

[0188] **Example 12: Preparation of Me-Sn₆ drum clusters with a mixture of 2,2-Dimethyl-5-oxo-2-tetrahydrofurancarboxylate and formate ligands**

[0189] Formula of the targeted compound: $[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{CH})_2(\text{O}_2\text{C}(\text{C}_6\text{H}_9\text{O}_2))_4]$.

[0190] The Sn starting material $\text{MeSn}(\text{OtAmyl})_3$ (2.2 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 25 mL of cyclohexanone are added to afford a clear solution. In the next step water (26.7 mmol, 3 eq.) is added with a syringe while stirring. A cloudy solution is formed. In a separate vial,



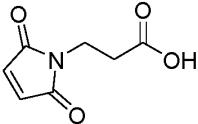
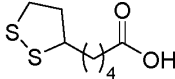
the desired acids (1.5 mmol, 0.67 eq) and $\text{H}-\text{C}(=\text{O})-\text{OH}$ (0.7 mmol, 0.33 eq) are dissolved in 5 mL of cyclohexanone and slowly added dropwise to the reaction vial with a syringe. The cloudy solution is stirred overnight, and a clear solution results the next day. A sample is taken for ^{119}Sn -NMR measurement with a capillary insert containing C_6D_6 for locking. A characteristic signal is detected at -459 ppm in the ^{119}Sn NMR spectrum.

[0191] **Example 13: Preparation of nBu-Sn₆ drum clusters with a mixture of lipoate and 3-Maleimide propionate ligands**

[0192] Formula of the targeted compound:

$[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{C}(\text{CH}_2)_2(\text{NC}_4\text{O}_2\text{H}_2))_3(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_3]$.

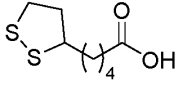
[0193] The Sn starting material $\text{nBuSn}(\text{OtAmyl})_3$ (2.1 mmol, 1 eq) is weighed into a crimp vial (reaction vial), equipped with a stir bar, and the vial is closed inside a glovebox. After transfer into a hood 36 mL cyclohexanone are added to afford a clear solution. In the next step water (6.3 mmol, 3 eq.) is added with a syringe while stirring. A clear solution is formed. In a separate vial, the

desired acids  (1.1 mmol, 0.5 eq) and  (1.1 mmol, 0.5 eq) are dissolved in 4 mL of the solvent and slowly added dropwise to the reaction vial with a syringe. The clear 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. Characteristic signals are detected at -484 ppm and -485 ppm in the ^{119}Sn NMR spectrum.

[0194] Example 14: Preparation of nBu-Sn_6 drum clusters with a mixture of acetate and lipoate ligands

[0195] Formula of the targeted compound: $[(\text{nBuSn})_6\text{O}_6(\text{O}_2\text{CCH}_3)_{4.8}(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_{1.2}]$.

[0196] The Sn starting material $\text{nBuSn}(\text{OtAmyl})_3$ (2.9 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. In the next step water (8.5 mmol, 3 eq.) is added with a syringe while stirring. A clear solution is formed. In a separate vial,

the desired acids  (2.3 mmol, 0.8 eq) and  (0.6 mmol, 0.2 eq) are dissolved in 4 mL of the solvent and slowly added dropwise to the reaction vial with a syringe. The clear 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. Characteristic signals are detected at -486.0 ppm and -486.8 ppm in the ^{119}Sn NMR spectrum. The mixed ligand cluster species detected by mass spectrometry are listed in Table 7:

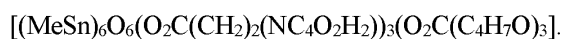
Cluster Formula	Ligand Ratio	
	Ligand 1: OAc	Ligand 2: Lip
$[(\text{nBuSn})_6\text{O}_6(\text{O}_2\text{CCH}_3)_{6-x}(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_x]$		
$[(\text{nBuSn})_6\text{O}_6(\text{O}_2\text{CCH}_3)_2(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_4]$	2	4
$[(\text{nBuSn})_6\text{O}_6(\text{O}_2\text{CCH}_3)_3(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_3]$	3	3

$[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{CCH}_3)_4(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_2]$	4	2
$[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{CCH}_3)_5(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_1]$	5	1
$[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{CCH}_3)_5]$	5	0
$[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{CCH}_3)_4(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_1]$	4	1
$[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{CCH}_3)_3(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_2]$	3	2
$[(n\text{BuSn})_6\text{O}_6(\text{O}_2\text{CCH}_3)_2(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_3]$	2	3

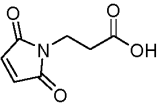
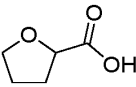
Table 7

[0197] **Example 15: Preparation of nBu-Sn6 drum clusters with a mixture of 3-Maleimide propionate and 2THF-carboxylate ligands**

[0198] Formula of the targeted compound:



[0199] The Sn starting material $\text{MeSn}(\text{OtBu})_3$ (2.1 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 cyclohexanone are added to afford a clear solution. In the next step water (6.2 mmol, 3 eq.) is added with a syringe while stirring. A cloudy solution is formed. In a separate vial, the desired

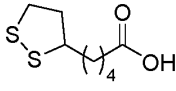
acids  (1.0 mmol, 0.5 eq) and  (1.0 mmol, 0.5 eq) are dissolved in 2 mL of the solvent and slowly added dropwise to the reaction vial with a syringe. The cloudy solution is stirred overnight, and a clear solution results the next day. A sample is taken for ^{119}Sn -NMR measurement with a capillary insert containing C_6D_6 for locking. Characteristic signals are detected at -462 and -464 ppm in the ^{119}Sn NMR spectrum.

[0200] **Example 16: Preparation of Sn6 drum clusters with mixtures Me- and nBu-Sn units and a mixture of lipoate and acetate ligands**

[0201] Formula of the targeted compound:



[0202] The Sn starting materials $\text{MeSn}(\text{OtBu})_3$ (0.7 mmol, 1 eq) and $\text{nBuSn}(\text{OtAmyl})_3$ (0.7 mmol, 1 eq) are 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 16 mL cyclohexanone are added to afford a clear solution. In the next step water (4.4 mmol, 6 eq.) is added with a syringe while stirring. A cloudy

solution is formed. In a separate vial, the desired acids  (0.7 mmol, 1 eq) and  (0.7 mmol, 1 eq) are separately dissolved in 2 mL of the solvent 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. Characteristic signals are detected at -465 and -487 ppm in the ^{119}Sn NMR spectrum. FIG. 13 provides an overview of the recorded mass spectrum and a comparison with the simulated isotopic patterns for the mixed ligand cluster species listed in Table 8:

Cluster Formula [(MeSn) _{6-x} (nBuSn) _x O ₆ (O ₂ CCH ₃) _{6-y} (O ₂ C(CH ₂) ₄ (C ₃ H ₅ S ₂)) _y]	Ligand Ratios			
	R ^{Sn} : Me	R ^{Sn} : nBu	Ligand 1: OAc	Ligand 2: Lip
[(MeSn) ₆ O ₆ (O ₂ CCH ₃) ₅ (O ₂ C(CH ₂) ₄ (C ₃ H ₅ S ₂)) ₁]	6	0	5	1
[(MeSn) ₆ O ₆ (O ₂ CCH ₃) ₄ (O ₂ C(CH ₂) ₄ (C ₃ H ₅ S ₂)) ₂]	--	--	4	2
[(MeSn) ₆ O ₆ (O ₂ CCH ₃) ₃ (O ₂ C(CH ₂) ₄ (C ₃ H ₅ S ₂)) ₃]	--	--	3	3
[(MeSn) ₆ O ₆ (O ₂ CCH ₃) ₂ (O ₂ C(CH ₂) ₄ (C ₃ H ₅ S ₂)) ₄]	--	--	2	4
[(MeSn) ₅ (nBuSn) ₁ O ₆ (O ₂ CCH ₃) ₆]	5	1	6	0
[(MeSn) ₅ (nBuSn) ₁ O ₆ (O ₂ CCH ₃) ₅ (O ₂ C(CH ₂) ₄ (C ₃ H ₅ S ₂)) ₁]	--	--	5	1
[(MeSn) ₅ (nBuSn) ₁ O ₆ (O ₂ CCH ₃) ₄ (O ₂ C(CH ₂) ₄ (C ₃ H ₅ S ₂)) ₂]	--	--	4	2
[(MeSn) ₅ (nBuSn) ₁ O ₆ (O ₂ CCH ₃) ₃ (O ₂ C(CH ₂) ₄ (C ₃ H ₅ S ₂)) ₃]	--	--	3	3
[(MeSn) ₅ (nBuSn) ₁ O ₆ (O ₂ CCH ₃) ₂ (O ₂ C(CH ₂) ₄ (C ₃ H ₅ S ₂)) ₄]	--	--	2	4
[(MeSn) ₅ (nBuSn) ₁ O ₆ (O ₂ CCH ₃) ₁ (O ₂ C(CH ₂) ₄ (C ₃ H ₅ S ₂)) ₅]	--	--	1	5
[(MeSn) ₄ (nBuSn) ₂ O ₆ (O ₂ CCH ₃) ₆]	4	2	6	0
[(MeSn) ₄ (nBuSn) ₂ O ₆ (O ₂ CCH ₃) ₅ (O ₂ C(CH ₂) ₄ (C ₃ H ₅ S ₂)) ₁]	--	--	5	1
[(MeSn) ₄ (nBuSn) ₂ O ₆ (O ₂ CCH ₃) ₄ (O ₂ C(CH ₂) ₄ (C ₃ H ₅ S ₂)) ₂]	--	--	4	2
[(MeSn) ₄ (nBuSn) ₂ O ₆ (O ₂ CCH ₃) ₃ (O ₂ C(CH ₂) ₄ (C ₃ H ₅ S ₂)) ₃]	--	--	3	3
[(MeSn) ₄ (nBuSn) ₂ O ₆ (O ₂ CCH ₃) ₂ (O ₂ C(CH ₂) ₄ (C ₃ H ₅ S ₂)) ₄]	--	--	2	4
[(MeSn) ₄ (nBuSn) ₂ O ₆ (O ₂ CCH ₃) ₁ (O ₂ C(CH ₂) ₄ (C ₃ H ₅ S ₂)) ₅]	--	--	1	5
[(MeSn) ₄ (nBuSn) ₂ O ₆ (O ₂ C(CH ₂) ₄ (C ₃ H ₅ S ₂)) ₆]	--	--	0	6
[(MeSn) ₃ (nBuSn) ₃ O ₆ (O ₂ CCH ₃) ₆]	3	3	6	0
[(MeSn) ₃ (nBuSn) ₃ O ₆ (O ₂ CCH ₃) ₅ (O ₂ C(CH ₂) ₄ (C ₃ H ₅ S ₂)) ₁]	--	--	5	1

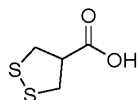
$[(\text{MeSn})_3(\text{nBuSn})_3\text{O}_6(\text{O}_2\text{CCH}_3)_4(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_2]$	--	--	4	2
$[(\text{MeSn})_3(\text{nBuSn})_3\text{O}_6(\text{O}_2\text{CCH}_3)_3(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_3]$	--	--	3	3
$[(\text{MeSn})_3(\text{nBuSn})_3\text{O}_6(\text{O}_2\text{CCH}_3)_2(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_4]$	--	--	2	4
$[(\text{MeSn})_3(\text{nBuSn})_3\text{O}_6(\text{O}_2\text{CCH}_3)_1(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_5]$	--	--	1	5
$[(\text{MeSn})_3(\text{nBuSn})_3\text{O}_6(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_6]$	--	--	0	6
$[(\text{MeSn})_2(\text{nBuSn})_4\text{O}_6(\text{O}_2\text{CCH}_3)_5(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_1]$	2	4	5	1
$[(\text{MeSn})_2(\text{nBuSn})_4\text{O}_6(\text{O}_2\text{CCH}_3)_4(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_2]$	--	--	4	2
$[(\text{MeSn})_2(\text{nBuSn})_4\text{O}_6(\text{O}_2\text{CCH}_3)_3(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_3]$	--	--	3	3
$[(\text{MeSn})_2(\text{nBuSn})_4\text{O}_6(\text{O}_2\text{CCH}_3)_2(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_4]$	--	--	2	4
$[(\text{MeSn})_2(\text{nBuSn})_4\text{O}_6(\text{O}_2\text{CCH}_3)_1(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_5]$	--	--	1	5
$[(\text{MeSn})_2(\text{nBuSn})_4\text{O}_6(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_6]$	--	--	0	6
$[(\text{MeSn})_1(\text{nBuSn})_5\text{O}_6(\text{O}_2\text{CCH}_3)_5(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_1]$	1	5	5	1
$[(\text{MeSn})_1(\text{nBuSn})_5\text{O}_6(\text{O}_2\text{CCH}_3)_4(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_2]$	--	--	4	2
$[(\text{MeSn})_1(\text{nBuSn})_5\text{O}_6(\text{O}_2\text{CCH}_3)_3(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_3]$	--	--	3	3
$[(\text{MeSn})_1(\text{nBuSn})_5\text{O}_6(\text{O}_2\text{CCH}_3)_2(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_4]$	--	--	2	4
$[(\text{MeSn})_1(\text{nBuSn})_5\text{O}_6(\text{O}_2\text{CCH}_3)_1(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_5]$	--	--	1	5
$[(\text{nBuSn})_6\text{O}_6(\text{O}_2\text{CCH}_3)_4(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_2]$	0	6	4	2
$[(\text{nBuSn})_6\text{O}_6(\text{O}_2\text{CCH}_3)_3(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_3]$	--	--	3	3
$[(\text{nBuSn})_6\text{O}_6(\text{O}_2\text{CCH}_3)_2(\text{O}_2\text{C}(\text{CH}_2)_4(\text{C}_3\text{H}_5\text{S}_2))_4]$	--	--	2	4

Table 8

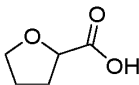
[0203] **Example 17: Preparation of nBu-Sn6 drum clusters with a mixture of 1,2-Dithiolane-4-carboxylate ligands and 3THF-carboxylate ligands**

[0204] Formula of the targeted compound: $[(\text{nBuSn})_6\text{O}_6(\text{O}_2\text{C}(\text{C}_3\text{H}_5\text{S}_2))_3(\text{O}_2\text{C}(\text{C}_4\text{H}_7\text{O}))_3]$.

[0205] The Sn starting material $\text{nBuSn}(\text{OtAmyl})_3$ (0.55 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 5 mL cyclohexanone are added to afford a clear solution. In the next step water (1.66 mmol, 3 eq.) is added with a syringe while stirring. A clear solution is formed. In one vial



(0.28 mmol, 0.5 eq) in 1.7 mL of toluene is diluted with 0.8 mL of cyclohexanone. In

a separate vial  (0.28 mmol, 0.5 eq) is dissolved in 2 mL of cyclohexanone. Both carboxylic acid solutions are 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. Characteristic signals are detected at -465 and -487 ppm in the ^{119}Sn NMR spectrum.

[0206] Comparative Study 1: Solubility Studies

[0207] Pure and mixed Sn6 clusters have been prepared according to example 6 in a solvent mixture of cyclohexanone/1-methoxy-2-propanol (1/1) with different target concentrations. Cyclohexanone and 1-methoxy-2-propanol are commonly accepted industrial solvents. The solubility of the respective cluster has been determined by visual observation of the mixture. The formation of a precipitate indicates that the solubility product of a species present in solution was exceeded. These results show that the pure Sn6 drum cluster materials with $\text{R}^{\text{a}} = \text{Me}$ and formate or acetate ligands are insoluble in the solvent mixture at any of the given concentrations, while the sample with $\text{R}^{\text{a}} = \text{nBu}$ and acetate ligands fails the solubility at 20 g/L. Introduction of mixed ligands, either for R^{a} or R^{b} drastically increases the solubility of the compounds and enables the use of the resulting solutions for coating purposes.

		Compound				Concentration (g/L)		
		$\text{R}^{\text{a}(\text{i})}$	$\text{R}^{\text{a}(\text{ii})}$	$\text{R}^{\text{b}(\text{i})}$	$\text{R}^{\text{b}(\text{ii})}$	20	10	5
1	C	[(MeSn) $_6$ O $_6$ (O $_2$ CCH $_3$) $_6$]				X	X	X
		Me	-		-			
2	C	[(MeSn) $_6$ O $_6$ (O $_2$ CH) $_6$]				X	X	X
		Me	-	H 	-			
3	C	[(nBuSn) $_6$ O $_6$ (O $_2$ CCH $_3$) $_6$]				X	O	O
		nBu	-		-			
4	M	[(MeSn) $_3$ (nBuSn) $_3$ O $_6$ (O $_2$ CH) $_6$]				O	O	O
		Me	nBu	H 	-			
5	M	[(MeSn) $_3$ (nBuSn) $_3$ O $_6$ (O $_2$ CCH $_3$) $_6$]				O	O	O
		Me	nBu		-			

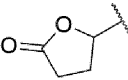
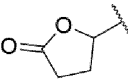
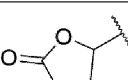
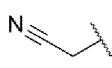
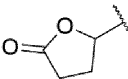
6	M	[(MeSn) ₆ O ₆ (O ₂ CH) ₃ (O ₂ CC ₄ H ₇ O) ₃]						
		Me	-			O	O	O
	M	[(MeSn) ₆ O ₆ (O ₂ CH) ₃ (O ₂ CC ₄ H ₅ O ₂) ₃]						
		Me	-			O	O	O
	M	[(MeSn) ₆ O ₆ (O ₂ CCH ₃) ₃ (O ₂ CC ₄ H ₅ O ₂) ₃]						
		Me	-			O	O	O
	M	[(MeSn) ₆ O ₆ (O ₂ CC ₄ H ₇ O) ₃ (O ₂ CC ₄ H ₅ O ₂) ₃]						
		Me	-			O	O	O
	M	[(MeSn) ₆ O ₆ (O ₂ CH) ₃ (O ₂ C(CH ₂ S ₂ C ₃ H ₆)) ₃]						
		Me	-			O	O	O
	M	[(MeSn) ₆ O ₆ (O ₂ CCH ₂ CN) ₃ (O ₂ C(CH ₂ S ₂ C ₃ H ₆)) ₃]						
		Me	-			O	O	O
	M	[(MeSn) ₅ (iPrSn) ₁ O ₆ (O ₂ CH) ₃ (O ₂ CC ₄ H ₅ O ₂) ₃]						
		Me	iPr			O	O	O
C: Comparative example pure cluster M: Mixed Cluster X = Formation of precipitate O = Visually clear solution								

Table 9

[0208] **Comparative Study 2: eBeam sensitivity of formate and acetate ligand containing Sn₆ drum clusters for pure and mixed ligand clusters**

[0209] [(nBuSn)₆O₆(O₂CCH₃)₆] formulations were prepared by dissolution of the solid material, synthesized via literature known procedures, in toluene. See Chandrasekhar *et al.*, *Inorg. Chem.*, 26, 1050 (1987). [(nBuSn)₆O₆(O₂CH)₆] was prepared according to example 5 using

cyclohexanone as solvent instead of toluene. All formulations of mixed ligand Sn6 drum compounds were prepared according to the procedures described above (*see* examples 4, 6-8), albeit at different scales with a target concentration of 20 g/L of cluster compound.

[0210] Wafer preparation and eBeam exposure procedure

[0211] A silicon wafer was cleaned by oxygen plasma for 10 mins. The respective solution was then spin coated onto the wafer with a cycle of 500 rpm/5 sec then 800-4000 rpm for 30 sec. A soft bake of 100 °C was then applied for 120 sec to obtain a film 25-35 nm in thickness determined by ellipsometry. The wafer was then broken into 1x1 cm pieces and exposed to E-beam radiation with dose range for 1-5000 $\mu\text{C}/\text{cm}^2$, accelerating voltage 30 keV and working distance 4 mm. The resist was then developed in 2-heptanone at room temperature for 120 sec and dried with nitrogen for 60 sec. The structures were then determined via profilometry and peak height to dose are translated into fitted dose level curves. The D_{50} value is defined as the exposure dose at which 50% of the film thickness of the fully cured material is retained after development. This value is used as a performance indicator for the sensitivity of a given material.

[0212] Comparison of sensitivity of acetate ligand containing Sn6 drum clusters in e-Beam exposure experiments

[0213] The D_{50} values for the $[(\text{nBuSn})_6\text{O}_6(\text{O}_2\text{CCH}_3)_6]$, $[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{CCH}_3)_3(\text{O}_2\text{CC}_4\text{H}_5\text{O}_2)_3]$ and $[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{CCH}_3)_3(\text{O}_2\text{CC}_4\text{H}_7\text{O})_3]$ are 251, 178 and 156 $\mu\text{C}/\text{cm}^2$ respectively. There is a clear increase in E-beam sensitivity for the acetate containing mixed clusters compared to the reference compound $[(\text{nBuSn})_6\text{O}_6(\text{O}_2\text{CCH}_3)_6]$ without mixed ligands.

[0214] Comparison of sensitivity of formate ligand containing Sn6 drum clusters in eBeam exposure experiments

[0215] The D_{50} values for the $[(\text{nBuSn})_6\text{O}_6(\text{O}_2\text{CH})_6]$, $[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{CH})_3(\text{O}_2\text{CCH}_2\text{OCH}_3)_3]$, $[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{CH})_3(\text{O}_2\text{CC}_4\text{H}_5\text{O}_2)_3]$ and $[(\text{MeSn})_6\text{O}_6(\text{O}_2\text{CH})_3(\text{O}_2\text{C}(\text{CH}_2\text{S}_2\text{C}_3\text{H}_6))_3]$ are 178, 50, 73, and 57 $\mu\text{C}/\text{cm}^2$ respectively. There is a clear increase in e-beam sensitivity for the formyl containing mixed clusters compared to the $[(\text{nBuSn})_6\text{O}_6(\text{O}_2\text{CH})_6]$ cluster.

[0216] Comparative Study 3: EUV sensitivity and patterning of Sn6 drum cluster

[0217] $[(\text{nBuSn})_6\text{O}_6(\text{O}_2\text{CCH}_3)_6]$ formulations were prepared by dissolution of the solid material, synthesized via literature known procedures in toluene. *See* Chandrasekhar *et al.*, *Inorg. Chem.*, 26, 1050 (1987). $[(\text{nBuSn})_6\text{O}_6(\text{O}_2\text{CH})_6]$ was prepared according to example 5 using cyclohexanone as solvent instead of toluene. All formulations of mixed ligand Sn6 drum

compounds were prepared according to the procedures described above (*see* Examples 4, 6–8), albeit at different scales with a target concentration of 20 g/L of cluster compound.

[0218] Coating and EUV exposure experiments were carried out at the Paul-Scherrer-Institute in Switzerland. Formulations were deposited on 4” silicon wafers via spin-coating with a final spin speed in the range 800-4000rpm. A post application bake of 100 °C for 120 sec was applied. The resulting films were exposed to EUV (13.5 nm) radiation through an interference mask and developed in 2-heptanone for 120 sec. Critical dimension (CD) and line width roughness (LWR) were determined from image analysis from open-source software SMILE. The dose-to-gel structures were then determined via profilometry and peak height to dose are translated into fitted dose level curves.

Resist Material			Dose-to-gel (mJ/cm ²)	Pitch (nm)	Dose-to-size (mJ/cm ²)	LWR unbias (nm)
1	C	[(nBuSn) ₆ O ₆ (O ₂ CCH ₃) ₆]	39.9	80	139	3.43
2	C	[(nBuSn) ₆ O ₆ (O ₂ CH) ₆]	37.9	80	102	4.32
3	M	[(MeSn) ₆ O ₆ (O ₂ CH) ₃ (O ₂ CC ₄ H ₅ O ₂) ₃]	14.57	70	92	2.76
4	M	[(MeSn) ₆ O ₆ (O ₂ CH) ₃ (O ₂ C(CH ₂ SC ₃ H ₆) ₃)]	-	80	43	4.85

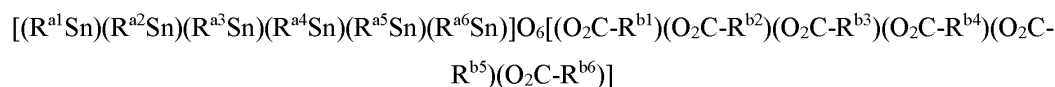
Table 10

[0219] The mixed cluster ligand Sn6 drum compounds showed improvements in dose-to-size compared to [(nBuSn)₆O₆(O₂CCH₃)₆] and [(nBuSn)₆O₆(O₂CH)₆] without mixed ligands. The [(MeSn)₆O₆(O₂CH)₃(O₂CC₄H₅O₂)₃] showed improve dose-to-gel and LWR compared to [(nBuSn)₆O₆(O₂CCH₃)₆] and [(nBuSn)₆O₆(O₂CH)₆]. Line-Space patterns were obtained for all materials. SEM images of the patterns are depicted in FIGs. 6-9.

[0220] 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:

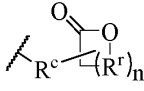
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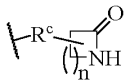
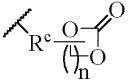
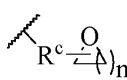


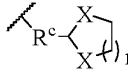
wherein

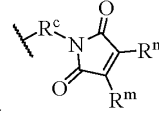
(A) each of R^{a1} , R^{a2} , R^{a3} , R^{a4} , R^{a5} and R^{a6} is individually selected from the group consisting of an unsubstituted linear C_1 - C_{10} alkyl group, a linear C_1 - C_6 alkyl group substituted with a halogen, a linear C_1 - C_6 alkyl group substituted with an amino group, a linear 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} heteroalkyl group, a branched C_3 - C_{10} alkyl group substituted with an amino group, 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, an unsubstituted linear C_2 - C_{10} alkenyl group, an unsubstituted branched C_3 - C_{10} alkenyl group, an unsubstituted linear C_2 - C_{10} alkynyl group and an unsubstituted branched C_4 - C_{10} alkynyl group;

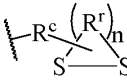
(B) each of R^{b1} , R^{b2} , R^{b3} , R^{b4} , R^{b5} and R^{b6} is individually selected from the group consisting of H; an unsubstituted linear C_1 - C_{10} alkyl group; a substituted linear C_1 - C_{10} alkyl group substituted with one or more of a $-CN$ group, an $-OH$ group, an $-OR'$ group, an $-SR'$ or an $-S-S-R'$ group where R' is a linear or branched C_1 - C_4 alkyl group, a $-C(=O)OR''$ group where R'' is a linear or branched C_1 - C_4 alkyl group, an $-NO_2$ group, a halogen or a $-C(=O)H$ group; an unsubstituted branched C_3 - C_{10} alkyl group; a substituted branched C_3 - C_{10} alkyl group substituted with one or more of a $-CN$ group, an $-OH$ group, a $-OR'$ group, an $-SR'$ or an $-S-S-R'$ group where R' is a linear or branched C_1 - C_4 alkyl group, a $-C(=O)OR''$ group where R'' is a linear or branched C_1 - C_4 alkyl unit, a $-NO_2$ group, a halogen or a $-C(=O)H$ group; a C_3 - C_8 unsubstituted cyclic alkyl group; a linear C_2 - C_{10} alkenyl group; a branched C_3 - C_{10} alkenyl group, a 5-membered heterocyclic ring; and a 6-

membered heterocyclic ring; a  group where (i) $n = 1-5$ and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C_1 - C_4 alkyl

groups; a  group where n = 1-4; a  group where n = 1-4; a  group

where n = 1-6; a  group where each X is individually selected from O and S and n = 1-

4; a  group where each R^m group is independently selected from H, a linear C₁-C₄

chain or a branched C₃-C₄ chain; a  group where (i) n = 3-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups; where R^c in each of the forgoing groups is (i) a direct covalent bond or (ii) an unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group; and

(C) (i) at least one of R^{a1}, R^{a2}, R^{a3}, R^{a4}, R^{a5} and R^{a6} is different from the remainder of R^{a1}, R^{a2}, R^{a3}, R^{a4}, R^{a5} and R^{a6} and/or (ii) at least one of R^{b1}, R^{b2}, R^{b3}, R^{b4}, R^{b5} and R^{b6} is different from the remainder of R^{b1}, R^{b2}, R^{b3}, R^{b4}, R^{b5} and R^{b6}.

2. The tin cluster of claim 1, wherein at least one of R^{a1}, R^{a2}, R^{a3}, R^{a4}, R^{a5} and R^{a6} is different from the other of R^{a1}, R^{a2}, R^{a3}, R^{a4}, R^{a5} and R^{a6}.

3. The tin cluster of claim 1, wherein at least one of R^{b1}, R^{b2}, R^{b3}, R^{b4}, R^{b5} and R^{b6} is different from the other of R^{b1}, R^{b2}, R^{b3}, R^{b4}, R^{b5} and R^{b6}.

4. The tin cluster of claim 1, wherein at least one of R^{a1}, R^{a2}, R^{a3}, R^{a4}, R^{a5} and R^{a6} is different from the other of R^{a1}, R^{a2}, R^{a3}, R^{a4}, R^{a5} and R^{a6} and at least one of R^{b1}, R^{b2}, R^{b3}, R^{b4}, R^{b5} and R^{b6} is different from the other of R^{b1}, R^{b2}, R^{b3}, R^{b4}, R^{b5} and R^{b6}.

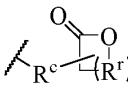
5. The tin cluster of claim 1, wherein (A) each of R^{a1}, R^{a2}, R^{a3}, R^{a4}, R^{a5} and R^{a6} is individually selected from the group consisting of an unsubstituted linear C₁-C₄ alkyl group, an unsubstituted branched C₃-C₄ alkyl group, a C₂-C₆ alkenyl group and a C₄-C₆ unsubstituted aromatic group.

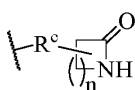
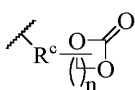
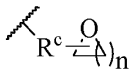
6. The tin cluster of claim 1, wherein (A) each of R^{a1}, R^{a2}, R^{a3}, R^{a4}, R^{a5} and R^{a6} is individually selected from the group consisting of a -CH₃ group, a -CH(CH₃)₂ group, a -C(CH₃)₃ group, a -CH=CH₂ group, a -CH₂CH=CH₂ group, a -CH₂CH₂CH=CH₂ group, a -CH₂CH₂CH₂CH₃ group, a -C₆H₅ group and a -CH₂-C₆H₅ group.

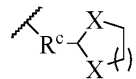
7. The tin cluster of claim 1, wherein (A) each of R^{a1}, R^{a2}, R^{a3}, R^{a4}, R^{a5} and R^{a6} is individually selected from the group consisting of a -CH₃ group, a -CH(CH₃)₂ group, a -CH=CH₂ group, and a -

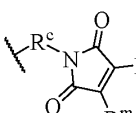
CH₂CH₂CH₂CH₃ group.

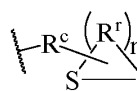
8. The tin cluster of claim 1, wherein (B) each of R^{b1}, R^{b2}, R^{b3}, R^{b4}, R^{b5} and R^{b6} is individually Selected from the group consisting of -H; an unsubstituted linear C₁-C₆ alkyl group; a substituted linear C₁-C₆ alkyl group substituted with one or more of a -CN group, an -OH group, an -OR' group, an -SR', or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl group, an -NO₂ group, a halogen, or a -C(=O)H group; an unsubstituted branched C₃-C₆ alkyl group; a substituted branched C₃-C₆ alkyl group substituted with one or more of a -CN group, an -OH group, a -OR' group, an -SR', or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl unit, a -NO₂ group, a halogen, or a -C(=O)H group; a C₃-C₆ unsubstituted cyclic alkyl group; a linear C₂-C₆ alkenyl group; a branched C₃-C₆ alkenyl group, a 5-membered heterocyclic ring; and a 6-

membered heterocyclic ring; a  group where (i) n = 1-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups;

a  group where n = 1-4, a  group where n = 1-4; a  group where

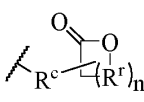
n = 1-6; a  group where each X is individually selected from O and S and n = 1-4; a

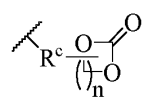
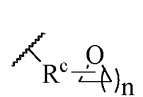
 group where each R^m group is independently selected from H, or a linear C₁-C₄ chain,

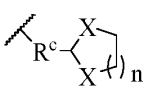
or a branched C₃-C₄ chain; a  group where (i) n = 3-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups; where R^c in each of the forgoing groups is (i) a direct covalent bond or (ii) an unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group.

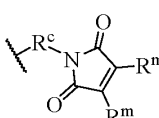
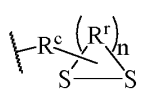
9. The tin cluster of claim 1, wherein (B) each of R^{b1}, R^{b2}, R^{b3}, R^{b4}, R^{b5} and R^{b6} is individually selected from the group consisting of -H; an unsubstituted linear C₁-C₆ alkyl group; a substituted linear C₁-C₆ alkyl group substituted with one or more of a -CN group, an -OR' group, an -SR', or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear

or branched C₁-C₄ alkyl group, an -NO₂ group, or a -C(=O)H group; an unsubstituted branched C₃-C₆ alkyl group; a substituted branched C₃-C₆ alkyl group substituted with one or more of a -CN group, a -OR' group, an -SR', or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl unit, a -NO₂ group, or a -C(=O)H

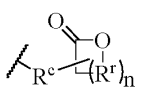
group; a linear C₂-C₆ alkenyl group; a branched C₃-C₆ alkenyl group, a  group where (i) n = 1-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group

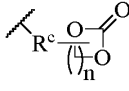
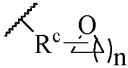
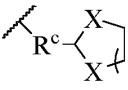
substituted with one or two C₁-C₄ alkyl groups; a  group where n = 1-4; a  group where n = 1-4; a

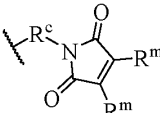
group where n = 1-6; a  group where each X is individually selected from O and S and n = 1-4; a

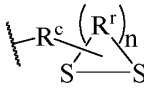
 group where each R^m group is independently selected from H, or a linear C₁-C₄ chain, or a branched C₃-C₄ chain; a  group where (i) n = 3-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups; where R^c in each of the foregoing groups is (i) a direct covalent bond or (ii) an unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group.

10. The tin cluster of claim 1, wherein **(B)** each of R^{b1}, R^{b2}, R^{b3}, R^{b4}, R^{b5} and R^{b6} is individually selected from the group consisting of -H; an unsubstituted linear C₁-C₆ alkyl group; a substituted linear C₁-C₆ alkyl group substituted with one or more of a -CN group, an -OR' group where R' is a linear or branched C₁-C₄ alkyl group, or a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl group; an unsubstituted branched C₃-C₆ alkyl group; a substituted branched C₃-C₆ alkyl group substituted with one or more of a -CN group, a -OR' group where R' is a linear or branched C₁-C₄

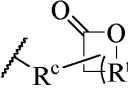
alkyl group, or a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl unit; a  group where (i) n = 1-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene

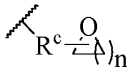
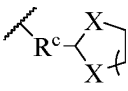
group substituted with one or two C₁-C₄ alkyl groups; a  group where n = 1-4; a  group where n = 1-6; a  group where each X is individually selected from

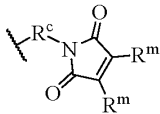
O and S and n = 1-4; a  group where each R^m group is independently selected from H,

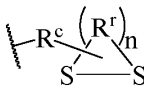
or a linear C₁-C₄ chain, or a branched C₃-C₄ chain; a  group where (i) n = 3-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups; where R^c in each of the forgoing groups is (i) a direct covalent bond or (ii) an unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group.

11. The tin cluster of claim 1, wherein (B) each of R^{b1}, R^{b2}, R^{b3}, R^{b4}, R^{b5} and R^{b6} is individually selected from the group consisting of -H; an unsubstituted linear C₁-C₆ alkyl group; a substituted linear C₁-C₆ alkyl group substituted with one or more of a -CN group, or an -OR' group where R' is a linear or branched C₁-C₄ alkyl group; an unsubstituted branched C₃-C₆ alkyl group; a substituted branched C₃-C₆ alkyl group substituted with one or more of a -CN group, or a -OR' group where R' is a linear

or branched C₁-C₄ alkyl group; a  group where (i) n = 1-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups;

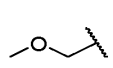
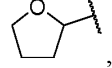
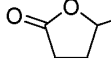
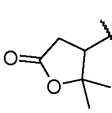
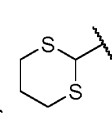
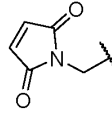
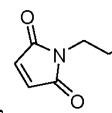
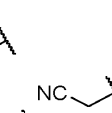
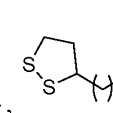
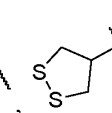
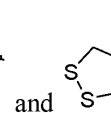
a  group where n = 1-6; a  group where each X is individually selected from

O and S and n = 1-4; a  group where each R^m group is independently selected from H,

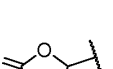
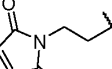
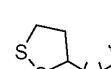
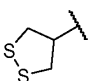
or a linear C₁-C₄ chain, or a branched C₃-C₄ chain; a  group where (i) n = 3-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups; where R^c in each of the forgoing groups is (i) a direct covalent bond or (ii) an

unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group.

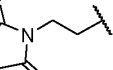
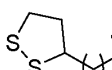
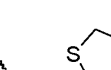
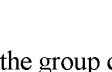
12. The tin cluster of claim 1, wherein (B) each of R^{b1}, R^{b2}, R^{b3}, R^{b4}, R^{b5} and R^{b6} is individually

selected from the group consisting of -H, , , , , , , , , , , , , and .

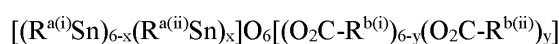
13. The tin cluster of claim 1, wherein (B) each of R^{b1}, R^{b2}, R^{b3}, R^{b4}, R^{b5} and R^{b6} is individually

selected from the group consisting of -H, , , , , , , and .

14. The tin cluster of claim 1, wherein (A) each of R^{a1}, R^{a2}, R^{a3}, R^{a4}, R^{a5} and R^{a6} is individually selected from the group consisting of -CH₃ group, a -CH(CH₃)₂ group, a -CH=CH₂ group, and a -CH₂CH₂CH₂CH₃ group and (B) each of R^{b1}, R^{b2}, R^{b3}, R^{b4}, R^{b5} and R^{b6} is individually selected from

the group consisting of -H, , , , , , , and .

15. A tin cluster of the formula:

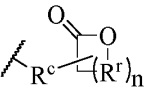


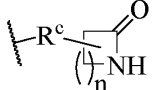
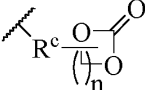
wherein

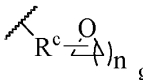
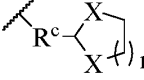
(A) (i) R^{a(i)} ≠ R^{a(ii)} and (ii) R^{a(i)} and R^{a(ii)} are each individually selected from the group consisting of an unsubstituted linear C₁-C₁₀ alkyl group, a linear C₁-C₆ alkyl group substituted with a halogen, a linear C₁-C₆ alkyl group substituted with an amino group, a linear C₁-C₆ alkyl group substituted with a C₅-C₆ unsubstituted aromatic group, an unsubstituted branched C₃-C₁₀ alkyl group, a branched C₃-C₁₀ alkyl group substituted with a halogen, a C₁-C₁₀ heteroalkyl group, a branched C₃-C₁₀ alkyl group substituted with an amino group, an unsubstituted amine, a substituted amine, -Si(CH₃)₃, a benzyl group, a C₃-C₈ unsubstituted cyclic alkyl group, a C₃-C₈ cyclic alkyl group substituted with a halogen, a C₃-C₈ cyclic alkyl group substituted with an amino group, a C₄-C₈ unsubstituted aromatic group, a C₄-C₈ aromatic group substituted with a halogen, a C₄-C₈

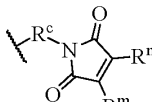
aromatic group substituted with an amino group, a C₃-C₁₀ heterocyclic group, an unsubstituted linear C₂-C₁₀ alkenyl group, an unsubstituted branched C₃-C₁₀ alkenyl group, an unsubstituted linear C₂-C₁₀ alkynyl group and an unsubstituted branched C₄-C₁₀ alkynyl group;

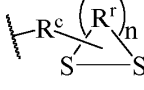
(B) (i) $R^{b(i)} \neq R^{b(ii)}$ and (ii) $R^{b(i)}$ and $R^{b(ii)}$ are each individually selected from the group consisting of H; an unsubstituted linear C₁-C₁₀ alkyl group; a substituted linear C₁-C₁₀ alkyl group substituted with one or more of a -CN group, an -OH group, an -OR' group, an -SR' or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl group, an -NO₂ group, a halogen or a -C(=O)H group; an unsubstituted branched C₃-C₁₀ alkyl group; a substituted branched C₃-C₁₀ alkyl group substituted with one or more of a -CN group, an -OH group, a -OR' group, an -SR' or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl unit, a -NO₂ group, a halogen or a -C(=O)H group; a C₃-C₈ unsubstituted cyclic alkyl group; a linear C₂-C₁₀ alkenyl group; a branched C₃-C₁₀ alkenyl group, a 5-membered heterocyclic

ring; and a 6-membered heterocyclic ring; a  group where (i) n = 1-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-

C₄ alkyl groups; a  group where n = 1-4, a  group where n = 1-4; a

 group where n = 1-6; a  group where each X is individually selected from

O and S and n = 1-4; a  group where each R^m group is independently selected from H,

or a linear C₁-C₄ chain, or a branched C₃-C₄ chain; a  group where (i) n = 3-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups; where R^c in each of the forgoing groups is (i) a direct covalent bond or (ii) an unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group; and

(C) (i) x and y each independently equal a whole number of 1 to 5 or (ii) one of

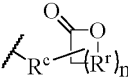
x or y = 0 and the other of x or y = a whole number of 1 to 5.

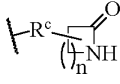
16. The tin cluster of claim 15, wherein (A) each of $R^{a(i)}$ and $R^{a(ii)}$ is individually selected from the group consisting of an unsubstituted linear C₁-C₄ alkyl group, an unsubstituted branched C₃-C₄ alkyl group, an unsubstituted linear C₂-C₆ alkenyl group, an unsubstituted branched C₃-C₆ alkenyl group and a C₄-C₆ unsubstituted aromatic group.

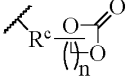
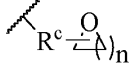
17. The tin cluster of claim 15, wherein (A) each of $R^{a(i)}$ and $R^{a(ii)}$ is individually selected from the group consisting of a -CH₃ group, a -CH(CH₃)₂ group, a -C(CH₃)₃ group, a -CH=CH₂ group, a -CH₂CH=CH₂ group, a -CH₂CH₂CH=CH₂ group, a -CH₂CH₂CH₂CH₃ group, a -C₆H₅ group and a -CH₂-C₆H₅ group.

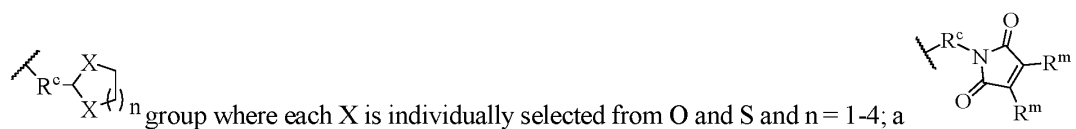
18. The tin cluster of claim 15, wherein (A) each of $R^{a(i)}$ and $R^{a(ii)}$ is individually selected from the group consisting of a -CH₃ group, a -CH(CH₃)₂ group, a -CH=CH₂ group, and a -CH₂CH₂CH₂CH₃ group.

19. The tin cluster of claim 15, wherein (B) each of $R^{b(i)}$ and $R^{b(ii)}$ is individually selected from the group consisting of -H; an unsubstituted linear C₁-C₆ alkyl group; a substituted linear C₁-C₆ alkyl group substituted with one or more of a -CN group, an -OH group, an -OR' group, an -SR', or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl group, an -NO₂ group, a halogen, or a -C(=O)H group; an unsubstituted branched C₃-C₆ alkyl group; a substituted branched C₃-C₆ alkyl group substituted with one or more of a -CN group, an -OH group, a -OR' group, an -SR', or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl unit, a -NO₂ group, a halogen, or a -C(=O)H group; a C₃-C₆ unsubstituted cyclic alkyl group; a linear C₂-C₆ alkenyl group; a branched C₃-C₆ alkenyl group, a 5-membered heterocyclic ring; and a 6-membered

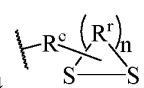
heterocyclic ring; a  group where (i) n = 1-5 and (ii) each R^r is individually an unsubstituted

methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups; a 

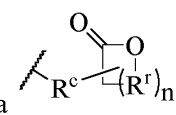
group where n = 1-4, a  group where n = 1-4; a  group where n = 1-6; a

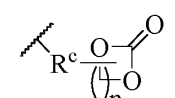
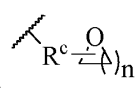


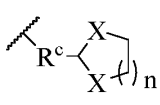
group where each R^m group is independently selected from H, or a linear C_1 - C_4 chain, or a branched

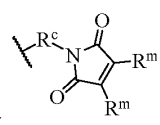
C_3 - C_4 chain; a  group where (i) $n = 3-5$ and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C_1 - C_4 alkyl groups; where R^c in each of the forgoing groups is (i) a direct covalent bond or (ii) an unsubstituted linear C_1 - C_6 alkylene group, an unsubstituted branched C_3 - C_6 alkylene group.

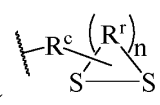
20. The tin cluster of claim 15, wherein **(B)** each of $\text{R}^{b(i)}$ and $\text{R}^{b(ii)}$ is individually selected from the group consisting of -H; an unsubstituted linear C_1 - C_6 alkyl group; a substituted linear C_1 - C_6 alkyl group substituted with one or more of a -CN group, an -OR' group, an -SR', or an -S-S-R' group where R' is a linear or branched C_1 - C_4 alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C_1 - C_4 alkyl group, an -NO₂ group, or a -C(=O)H group; an unsubstituted branched C_3 - C_6 alkyl group; a substituted branched C_3 - C_6 alkyl group substituted with one or more of a -CN group, a -OR' group, an -SR', or an -S-S-R' group where R' is a linear or branched C_1 - C_4 alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C_1 - C_4 alkyl unit, a -NO₂ group, or a -C(=O)H

group; a linear C_2 - C_6 alkenyl group; a branched C_3 - C_6 alkenyl group, a  group where (i) $n = 1-5$ and (ii) each R^r is individually an unsubstituted methylene group or a methylene group

substituted with one or two C_1 - C_4 alkyl groups; a  group where $n = 1-4$; a 

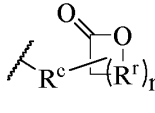
group where $n = 1-6$; a  group where each X is individually selected from O and S and

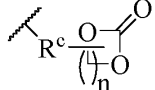
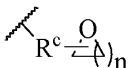
$n = 1-4$; a  group where each R^m group is independently selected from H, or a linear

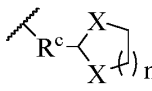
C_1 - C_4 chain, or a branched C_3 - C_4 chain; a  group where (i) $n = 3-5$ and (ii) each R^r is

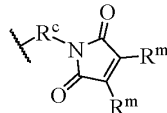
individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups; where R^c in each of the forgoing groups is (i) a direct covalent bond or (ii) an unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group.

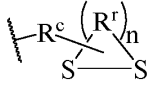
21. The tin cluster of claim 15, wherein **(B)** each of R^{b(i)} and R^{b(ii)} is individually selected from the group consisting of -H; an unsubstituted linear C₁-C₆ alkyl group; a substituted linear C₁-C₆ alkyl group substituted with one or more of a -CN group, an -OR' group where R' is a linear or branched C₁-C₄ alkyl group, or a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl group; an unsubstituted branched C₃-C₆ alkyl group; a substituted branched C₃-C₆ alkyl group substituted with one or more of a -CN group, a -OR' group where R' is a linear or branched C₁-C₄ alkyl group, or a

-C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl unit; a  group where (i) n = 1-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group

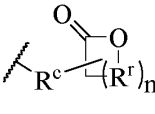
substituted with one or two C₁-C₄ alkyl groups; a  group where n = 1-4; a  group where n = 1-4; a

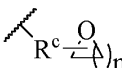
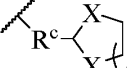
group where n = 1-6; a  group where each X is individually selected from O and S and

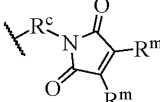
n = 1-4; a  group where each R^m group is independently selected from H, or a linear

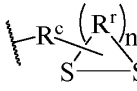
C₁-C₄ chain, or a branched C₃-C₄ chain; a  group where (i) n = 3-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups; where R^c in each of the forgoing groups is (i) a direct covalent bond or (ii) an unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group.

22. The tin cluster of claim 15, wherein **(B)** each of R^{b(i)} and R^{b(ii)} is individually selected from the group consisting of -H; an unsubstituted linear C₁-C₆ alkyl group; a substituted linear C₁-C₆ alkyl group substituted with one or more of a -CN group, or an -OR' group where R' is a linear or branched C₁-C₄ alkyl group; an unsubstituted branched C₃-C₆ alkyl group; a substituted branched C₃-C₆ alkyl group substituted with one or more of a -CN group, or a -OR' group where R' is a linear or branched

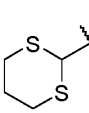
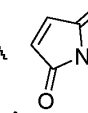
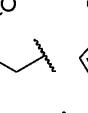
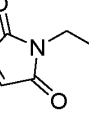
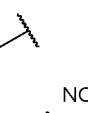
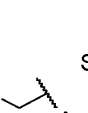
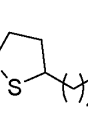
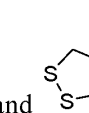
C₁-C₄ alkyl group; a  group where (i) n = 1-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups;

a  group where n = 1-6; a  group where each X is individually selected

from O and S and n = 1-4; a  group where each R^m group is independently selected

from H, or a linear C₁-C₄ chain, or a branched C₃-C₄ chain; a  group where (i) n = 3-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups; where R^c in each of the foregoing groups is (i) a direct covalent bond or (ii) an unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group.

23. The tin cluster of claim 15, wherein **(B)** each of R^{b(i)} and R^{b(ii)} is individually selected from

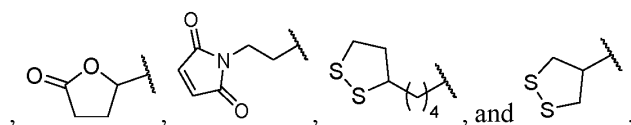
the group consisting of -H, , , , , , , , , , , , , , , and .

24. The tin cluster of claim 15, wherein **(B)** each of R^{b(i)} and R^{b(ii)} is individually selected from

the group consisting of -H, , , , , , and .

25. The tin cluster of claim 15, wherein **(A)** each of R^{a(i)} and R^{a(ii)} is individually selected from the group consisting of -CH₃ group, a -CH(CH₃)₂ group, a -CH=CH₂ group, and a -CH₂CH₂CH₂CH₃ group

and **(B)** each of R^{b(i)} and R^{b(ii)} is individually selected from the group consisting of -H, , , and .



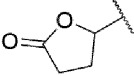
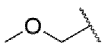
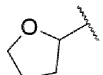
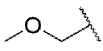
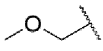
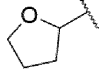
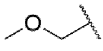
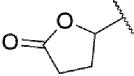
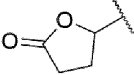
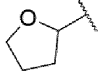
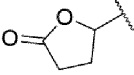
26. The tin cluster of claim 15 having the formula: $[(R^{a(i)}Sn)_{6-x}(R^{a(ii)}Sn)_x]O_6(O_2C-R^{b(i)})_y$ wherein $x =$ a whole number of 1 to 5, $y = 6$ and the proportion of $R^{a(i)}$ to $R^{a(ii)}$ has a ratio: $R^{a(i)}:R^{a(ii)} = (5-u):(1+u)$ where $u =$ a whole number from 0 to 4.

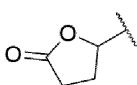
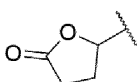
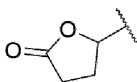
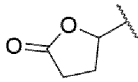
27. The tin cluster of claim 15 having the formula: $(R^{a(i)}Sn)_xO_6[(O_2C-R^{b(i)})_{6-y}(O_2C-R^{b(ii)})_y]$ wherein $x = 6$, $y =$ a whole number of 1 to 5 and the proportion of $R^{b(i)}$ to $R^{b(ii)}$ has a ratio: $R^{b(i)}:R^{b(ii)} = (5-p):(1+p)$ where $p =$ a whole number from 0 to 4.

28. The tin cluster of claim 15 having the formula: $[(R^{a(i)}Sn)_{6-x}(R^{a(ii)}Sn)_x]O_6[(O_2C-R^{b(i)})_{6-y}(O_2C-R^{b(ii)})_y]$ wherein $x = 6$ or is it a whole number of 1 to 5, $y =$ a whole number of 1 to 5, the proportion of $R^{a(i)}$ to $R^{a(ii)}$ has a ratio: $R^{a(i)}:R^{a(ii)} = (5-u):(1+u)$ where $u =$ a whole number from 0 to 4 and the proportion of $R^{b(i)}$ to $R^{b(ii)}$ has a ratio: $R^{b(i)}:R^{b(ii)} = (5-p):(1+p)$ where $p =$ a whole number from 0 to 4.

29. The tin cluster of claim 15, wherein the tin cluster comprises a tin cluster of Table 1:

Macroscopic Formula: $[(R^{a(i)}Sn)_{6-x}(R^{a(ii)}Sn)_x]O_6[(O_2C-R^{b(i)})_{6-y}(O_2C-R^{b(ii)})_y]$						
Ex.	$R^{a(i)}: R^{a(ii)}$ Distribution (x values)	R^a Group(s)		$R^{a(i)}: R^{a(ii)}$ Distribution (y values)	R^b Group(s)	
		$R^{a(i)}$	$R^{a(ii)}$		$R^{b(i)}$	$R^{b(ii)}$
1	1:5	Me	n-Bu	All same (y = 0)		--
2	1:5	Me	n-Bu	All same (y = 0)		--
3	1:5	iPr	n-Bu	All same (y = 0)		--
4	2:4	Me	n-Bu	All same (y = 0)		--
5	2:4	Me	n-Bu	All same (y = 0)		--
6	2:4	iPr	n-Bu	All same (y = 0)		--

7	3:3	Me	n-Bu	All same (y = 0)		--
8	3:3	Me	n-Bu	All same (y = 0)		--
9	3:3	Me	n-Bu	All same (y = 0)		--
10	3:3	iPr	n-Bu	All same (y = 0)		--
11	4:2	Me	n-Bu	All same (y = 0)		--
12	4:2	Me	n-Bu	All same (y = 0)		--
13	5:1	Me	n-Bu	All same (y = 0)		--
14	5:1	Me	n-Bu	All same (y = 0)		--
15	5:1	Me	iPr	1:1		
16	All same (x = 0)	n-Bu	--	1:5		
17	All same (x = 0)	n-Bu	--	1:5		
18	All same (x = 0)	n-Bu	--	1:5		
19	All same (x = 0)	Me	--	1:5		
20	All same (x = 0)	Me	--	1:5		
21	All same (x = 0)	Me	--	1:5		
22	All same (x = 0)	Me	--	2:4		

23	All same (x = 0)	Me	--	2:4		
24	All same (x = 0)	Me	--	2:4		
25	All same (x = 0)	n-Bu	--	3:3		
26	All same (x = 0)	n-Bu	--	3:3		
27	All same (x = 0)	n-Bu	--	3:3		
28	All same (x = 0)	Me	--	3:3		
29	All same (x = 0)	Me	--	3:3		
30	All same (x = 0)	Me	--	3:3		
31	All same (x = 0)	Me	--	3:3		
32	All same (x = 0)	Me	--	3:3		
33	All same (x = 0)	Me	--	3:3		
34	All same (x = 0)	Me	--	3:3		
35	All same (x = 0)	n-Bu	--	3:3		
36	All same (x = 0)	Me	--	3:3		

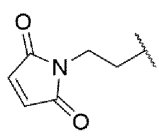
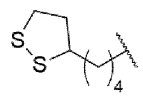
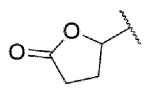
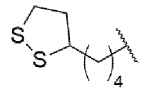
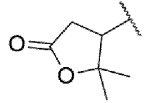
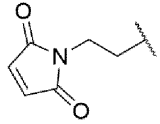
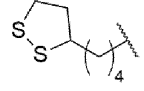
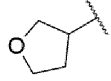
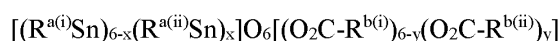
37	All same (x = 0)	n-Bu	--	3:3		
38	All same (x = 0)	n-Bu	--	4:1		
39	All same (x = 0)	Me	--	4:1		
40	All same (x = 0)	Me	--	4:2		
41	All same (x = 0)	Me	--	3:3		
42	3:3	Me	n-Bu	3:3		
43	All same (x = 0)	n-Bu	-	1:1		

Table 1

30. A mixture of tin clusters comprising more than one tin cluster of any of claims 1-29.
31. A mixture of tin clusters comprising more than one tin cluster of Table 1 according to claim 29.
32. A mixture of tin clusters comprising more than one tin cluster of the formula:

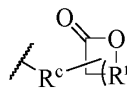


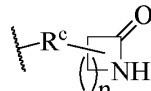
wherein

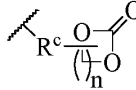
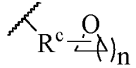
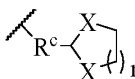
(A) (i) $R^{a(i)} \neq R^{a(ii)}$ and (ii) $R^{a(i)}$ and $R^{a(ii)}$ are each individually selected from the group consisting of an unsubstituted linear C₁-C₁₀ alkyl group, a linear C₁-C₆ alkyl group substituted with a halogen, a linear C₁-C₆ alkyl group substituted with an amino group, a linear C₁-C₆ alkyl group substituted with a C₅-C₆ unsubstituted aromatic group, an unsubstituted branched C₃-C₁₀ alkyl group, a branched C₃-C₁₀ alkyl group substituted with a halogen, a C₁-C₁₀ heteroalkyl group, a branched C₃-C₁₀ alkyl group substituted with an amino group, an unsubstituted amine, a substituted

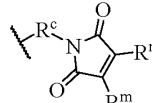
amine, $-\text{Si}(\text{CH}_3)_3$, a benzyl group, a $\text{C}_3\text{-C}_8$ unsubstituted cyclic alkyl group, a $\text{C}_3\text{-C}_8$ cyclic alkyl group substituted with a halogen, a $\text{C}_3\text{-C}_8$ cyclic alkyl group substituted with an amino group, a $\text{C}_4\text{-C}_8$ unsubstituted aromatic group, a $\text{C}_4\text{-C}_8$ aromatic group substituted with a halogen, a $\text{C}_4\text{-C}_8$ aromatic group substituted with an amino group, a $\text{C}_3\text{-C}_{10}$ heterocyclic group, an unsubstituted linear $\text{C}_2\text{-C}_{10}$ alkenyl group, an unsubstituted branched $\text{C}_3\text{-C}_{10}$ alkenyl group, an unsubstituted linear $\text{C}_2\text{-C}_{10}$ alkynyl group and an unsubstituted branched $\text{C}_4\text{-C}_{10}$ alkynyl group;

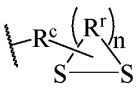
(B) (i) $\text{R}^{b(i)} \neq \text{R}^{b(ii)}$ and (ii) $\text{R}^{b(i)}$ and $\text{R}^{b(ii)}$ are each individually selected from the group consisting of H; an unsubstituted linear $\text{C}_1\text{-C}_{10}$ alkyl group; a substituted linear $\text{C}_1\text{-C}_{10}$ alkyl group substituted with one or more of a $-\text{CN}$ group, an $-\text{OH}$ group, an $-\text{OR}'$ group, an $-\text{SR}'$ or an $-\text{S-S-R}'$ group where R' is a linear or branched $\text{C}_1\text{-C}_4$ alkyl group, a $-\text{C}(=\text{O})\text{OR}''$ group where R'' is a linear or branched $\text{C}_1\text{-C}_4$ alkyl group, an $-\text{NO}_2$ group, a halogen or a $-\text{C}(=\text{O})\text{H}$ group; an unsubstituted branched $\text{C}_3\text{-C}_{10}$ alkyl group; a substituted branched $\text{C}_3\text{-C}_{10}$ alkyl group substituted with one or more of a $-\text{CN}$ group, an $-\text{OH}$ group, a $-\text{OR}'$ group, an $-\text{SR}'$ or an $-\text{S-S-R}'$ group where R' is a linear or branched $\text{C}_1\text{-C}_4$ alkyl group, a $-\text{C}(=\text{O})\text{OR}''$ group where R'' is a linear or branched $\text{C}_1\text{-C}_4$ alkyl unit, a $-\text{NO}_2$ group, a halogen or a $-\text{C}(=\text{O})\text{H}$ group; a $\text{C}_3\text{-C}_8$ unsubstituted cyclic alkyl group; a linear $\text{C}_2\text{-C}_{10}$ alkenyl group; a branched $\text{C}_3\text{-C}_{10}$ alkenyl group, a 5-membered heterocyclic ring; and a 6-membered heterocyclic ring;

a  group where (i) $n = 1\text{-}5$ and (ii) each R^r is individually an unsubstituted methylene

group or a methylene group substituted with one or two $\text{C}_1\text{-C}_4$ alkyl groups; a  group

where $n = 1\text{-}4$, a  group where $n = 1\text{-}4$; a  group where $n = 1\text{-}6$; a  group

group where each X is individually selected from O and S and $n = 1\text{-}4$; a  group where each R^m group is independently selected from H, or a linear $\text{C}_1\text{-C}_4$ chain, or a branched $\text{C}_3\text{-C}_4$ chain; a

 group where (i) $n = 3\text{-}5$ and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two $\text{C}_1\text{-C}_4$ alkyl groups; where R^e in each of the foregoing

groups is (i) a direct covalent bond or (ii) an unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group; and

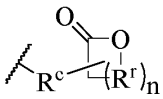
(C) (i) x and y each independently equal a whole or fractional number of $0 < x$ and/or $y < 6$ or (ii) one of x or y = 0 and the other of x or y = a whole or fractional number of $0 < x$ and/or $y < 6$.

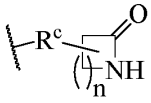
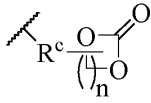
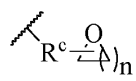
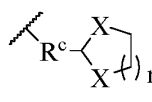
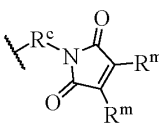
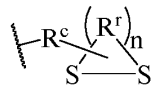
33. The tin cluster of claim 32, wherein (A) each of R^{a(i)} and R^{a(ii)} is individually selected from the group consisting of an unsubstituted linear C₁-C₄ alkyl group, an unsubstituted branched C₃-C₄ alkyl group, an unsubstituted linear C₂-C₆ alkenyl group, an unsubstituted branched C₃-C₆ alkenyl group and a C₄-C₆ unsubstituted aromatic group.

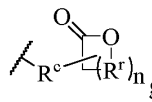
34. The tin cluster of claim 32, wherein (A) each of R^{a(i)} and R^{a(ii)} is individually selected from the group consisting of a -CH₃ group, a -CH(CH₃)₂ group, a -C(CH₃)₃ group, a -CH=CH₂ group, a -CH₂CH=CH₂ group, a -CH₂CH₂CH=CH₂ group, a -CH₂CH₂CH₂CH₃ group, a -C₆H₅ group and a -CH₂-C₆H₅ group.

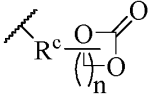
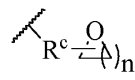
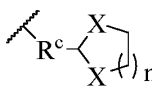
35. The tin cluster of claim 32, wherein (A) each of R^{a(i)} and R^{a(ii)} is individually selected from the group consisting of a -CH₃ group, a -CH(CH₃)₂ group, a -CH=CH₂ group, and a -CH₂CH₂CH₂CH₃ group.

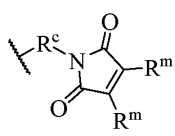
36. The tin cluster of claim 32, wherein (B) each of R^{b(i)} and R^{b(ii)} is individually selected from the group consisting of -H; an unsubstituted linear C₁-C₆ alkyl group; a substituted linear C₁-C₆ alkyl group substituted with one or more of a -CN group, an -OH group, an -OR' group, an -SR', or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl group, an -NO₂ group, a halogen, or a -C(=O)H group; an unsubstituted branched C₃-C₆ alkyl group; a substituted branched C₃-C₆ alkyl group substituted with one or more of a -CN group, an -OH group, a -OR' group, an -SR', or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl unit, a -NO₂ group, a halogen, or a -C(=O)H group; a C₃-C₆ unsubstituted cyclic alkyl group; a linear C₂-C₆ alkenyl group; a branched C₃-C₆ alkenyl group, a 5-membered heterocyclic ring; and a 6-membered

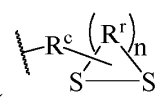
heterocyclic ring; a  group where (i) n = 1-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups;

a  group where n = 1-4; a  group where n = 1-4; a  group where n = 1-6; a  group where each X is individually selected from O and S and n = 1-4; a  group where each R^m group is independently selected from H, or a linear C₁-C₄ chain, or a branched C₃-C₄ chain; a  group where (i) n = 3-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups; where R^c in each of the foregoing groups is (i) a direct covalent bond or (ii) an unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group.

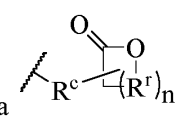
37. The tin cluster of claim 32, wherein (B) each of R^{b(i)} and R^{b(ii)} is individually selected from the group consisting of -H; an unsubstituted linear C₁-C₆ alkyl group; a substituted linear C₁-C₆ alkyl group substituted with one or more of a -CN group, an -OR' group, an -SR', or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl group, an -NO₂ group, or a -C(=O)H group; an unsubstituted branched C₃-C₆ alkyl group; a substituted branched C₃-C₆ alkyl group substituted with one or more of a -CN group, a -OR' group, an -SR', or an -S-S-R' group where R' is a linear or branched C₁-C₄ alkyl group, a -C(=O)OR'' group where R'' is a linear or branched C₁-C₄ alkyl unit, a -NO₂ group, or a -C(=O)H group; a linear C₂-C₆ alkenyl group; a branched C₃-C₆ alkenyl group, a  group where (i) n = 1-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group

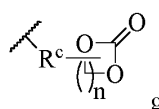
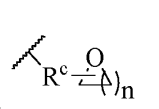
substituted with one or two C₁-C₄ alkyl groups; a  group where n = 1-4; a  group where n = 1-6; a  group where each X is individually selected from O and S and

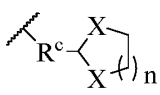
 $n = 1-4$; a group where each R^m group is independently selected from H, or a linear

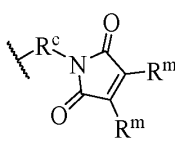
C_1-C_4 chain, or a branched C_3-C_4 chain; a  group where (i) $n = 3-5$ and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C_1-C_4 alkyl groups; where R^c in each of the foregoing groups is (i) a direct covalent bond or (ii) an unsubstituted linear C_1-C_6 alkylene group, an unsubstituted branched C_3-C_6 alkylene group.

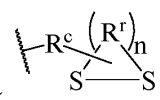
38. The tin cluster of claim 32, wherein **(B)** each of $R^{b(i)}$ and $R^{b(ii)}$ is individually selected from the group consisting of -H; an unsubstituted linear C_1-C_6 alkyl group; a substituted linear C_1-C_6 alkyl group substituted with one or more of a -CN group, an -OR' group where R' is a linear or branched C_1-C_4 alkyl group, or a -C(=O)OR'' group where R'' is a linear or branched C_1-C_4 alkyl group; an unsubstituted branched C_3-C_6 alkyl group; a substituted branched C_3-C_6 alkyl group substituted with one or more of a -CN group, a -OR' group where R' is a linear or branched C_1-C_4 alkyl group, or a

-C(=O)OR'' group where R'' is a linear or branched C_1-C_4 alkyl unit; a  group where (i) $n = 1-5$ and (ii) each R^r is individually an unsubstituted methylene group or a methylene group

substituted with one or two C_1-C_4 alkyl groups; a  group where $n = 1-4$; a 

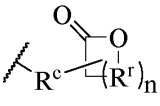
group where $n = 1-6$; a  group where each X is individually selected from O and S and

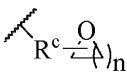
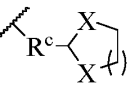
 $n = 1-4$; a group where each R^m group is independently selected from H, or a linear

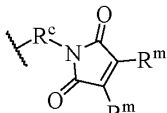
C_1-C_4 chain, or a branched C_3-C_4 chain; a  group where (i) $n = 3-5$ and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C_1-C_4 alkyl groups; where R^c in each of the foregoing groups is (i) a direct covalent bond or (ii) an

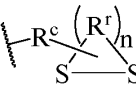
unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group.

39. The tin cluster of claim 32, wherein **(B)** each of R^{b(i)} and R^{b(ii)} is individually selected from the group consisting of -H; an unsubstituted linear C₁-C₆ alkyl group; a substituted linear C₁-C₆ alkyl group substituted with one or more of a -CN group, or an -OR' group where R' is a linear or branched C₁-C₄ alkyl group; an unsubstituted branched C₃-C₆ alkyl group; a substituted branched C₃-C₆ alkyl group substituted with one or more of a -CN group, or a -OR' group where R' is a linear or branched

C₁-C₄ alkyl group; a  group where (i) n = 1-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups;

a  group where n = 1-6; a  group where each X is individually selected

from O and S and n = 1-4; a  group where each R^m group is independently selected

from H, or a linear C₁-C₄ chain, or a branched C₃-C₄ chain; a  group where (i) n = 3-5 and (ii) each R^r is individually an unsubstituted methylene group or a methylene group substituted with one or two C₁-C₄ alkyl groups; where R^c in each of the foregoing groups is (i) a direct covalent bond or (ii) an unsubstituted linear C₁-C₆ alkylene group, an unsubstituted branched C₃-C₆ alkylene group.

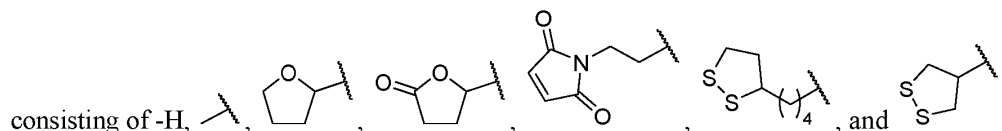
40. The tin cluster of claim 32, wherein **(B)** each of R^{b(i)} and R^{b(ii)} is individually selected from

the group consisting of -H, , , , , , , , , , , , , , , , and .

41. The tin cluster of claim 32, wherein **(B)** each of R^{b(i)} and R^{b(ii)} is individually selected from

the group consisting of -H, , , , , , , and .

42. The tin cluster of claim 32, wherein (A) each of $R^{a(i)}$ and $R^{a(ii)}$ is individually selected from the group consisting of $-CH_3$ group, a $-CH(CH_3)_2$ group, a $-CH=CH_2$ group, and a $-CH_2CH_2CH_2CH_3$ group and (B) each of $R^{b(i)}$ and $R^{b(ii)}$ is individually selected from the group



43. A spin-coatable formulation comprising:

- (i) one or more of the Sn6-oxo clusters of any of claims 1-42; and
- (ii) one or more solvents suitable for use in a spin-coating process.

44. The spin-coatable formulation of claim 43, wherein the one or more solvents suitable 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.

45. The spin-coatable formulation of claim 43, 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.

46. The spin-coatable formulation of claim 43, 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.

47. The spin-coatable formulation of claim 43, 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.

- 48. The spin-coatable formulation of claim 43, wherein the formulation is free of toluene.
- 49. The spin-coatable formulation of claim 43, wherein the formulation comprises one of 2-heptanone, cyclohexanone, PGMEA, PGME, a mixture of anisole and PGMEA, a mixture of anisole and cyclohexanone and a mixture of anisole and 2-heptanone.
- 50. The spin-coatable formulation of claim 43, wherein the formulation has a concentration of Sn cluster of about 1 mg/mL to about 1000 mg/mL.
- 51. The spin-coatable formulation of claim 43, wherein the formulation has a concentration of Sn cluster of about 1 mg/mL to about 100 mg/mL.
- 52. The spin-coatable formulation of claim 43, wherein the formulation has a concentration of Sn cluster of about 1 mg/mL to about 50 mg/mL.
- 53. The spin-coatable formulation of claim 43, wherein the formulation has a concentration of Sn cluster of about 10 mg/mL to about 50 mg/mL.
- 54. The spin-coatable formulation of claim 43, wherein the formulation has a concentration of Sn cluster of about 25 mg/mL to about 50 mg/mL.
- 55. The spin-coatable formulation of claim 43, wherein the formulation has a concentration of Sn cluster of about 50 mg/mL to about 100 mg/mL.
- 56. The use of the tin cluster according to any one of claims 1 to 42 or the spin-coatable formulation according to any one of claims 43 to 55 in EUV processes.