



(51) International Patent Classification:

B22F 9/24 (2006.01) B82Y 40/00 (2011.01)

C01G 3/00 (2006.01) H01M 4/90 (2006.01)

C01G 5/00 (2006.01) B01J 35/08 (2006.01)

C01G 7/00 (2006.01) B01J 27/057 (2006.01)

TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— of inventorship (Rule 4.17(iv))

(21) International Application Number:

PCT/SG2018/050106

(22) International Filing Date:

07 March 2018 (07.03.2018)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

10201701824P 07 March 2017 (07.03.2017) SG

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,

(54) Title: A METHOD OF PREPARING METAL NANOCLUSTERS

(57) Abstract: The present invention relates to a method of preparing metal nanoclusters. The method comprises a step of mixing a miscible solvent with the aqueous precursors, before mixing with an organic solvent and reducing agent. The present invention also relates to metal nanoclusters and use thereof in electrodes. The nanoclusters contain 1 -80 metal atoms and is protected by 1 -80 ligands. The metal atoms are preferably gold, silver, or copper, and the ligands are preferably selected from hydrophobic ligands benzeneselenolate, 4-tert-butylbenzenethiolate, cyclohexanethiolate, 2- phenylethanethiolate, 4-methylbenzenethiolate, and triphenylphosphine.



## Description

# A Method of Preparing Metal Nanoclusters

### Cross-Reference to Related Application

The present application claims priority to Singapore Provisional Application No. 10201701824P filed on 7 March 2017, the disclosure of which is incorporated by reference in its entirety.

### Technical Field

The present invention generally relates to a method of preparing particles or nanoclusters. The present invention also relates to particles or nanoclusters and use thereof.

### Background Art

Metallic nanostructured materials (MNM) stabilized by a monolayer of organic ligands are of great interest due to their size-dependent properties, as reflected by their impact in diverse fields including catalysis, sensing, photochemistry, optoelectronics, labelling, energy conversion, and medicine. Depending on their size, MNM can be divided into two categories: nanocrystals (greater than 2 nm) and smaller-sized nanoclusters (NCs) (less than 2 nm).

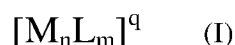
Atomically precise metal nanoclusters are usually defined as  $[M_nL_m]^q$ , where M and L denote the metal and ligand, and n, m, and q denote the number of metal atoms, ligand molecules and net charges, respectively. While various wet-chemical protocols have been developed to control the size, composition and shape of nanocrystals in polar and non-polar solvents, relatively little advances have been made towards tailoring nanoclusters. Despite two decades of synthetic efforts, the synthesis of metal nanoclusters with different size and composition remains a major challenge.

The methods commonly used to synthesize nanoclusters involve the use of charged particles and photons. In this method, sputtered metal atoms were obtained from a target of metal by impinging inert gas ions or pulsed lasers. However, clusters produced by this method tend to be unstable. An alternative method for preparing the nanoclusters involves the use polymer templates. Unfortunately, this approach is not applicable for a wide range of nanoclusters and requires different template to be used to produce different metal nanoclusters. In addition, this strategy does not appear to have the capability to control the size of the nanoclusters produced.

Therefore, the present invention provides an alternative method to synthesize the particles or nanoclusters (NCs) that overcomes, or at least ameliorates, one or more of the disadvantages described above.

### Summary

In one aspect, there is provided a method of preparing particles of formula (I)



wherein:

M represents a metal;

L represents a ligand;

m and n are independently an integer in the range from 1 to 80;

5 q represents a net charge in the range from – 5 to + 5,

said method comprising the steps of:

- a) mixing a metal precursor solution and a ligand precursor solution in the presence of an aqueous solution;
- 10 b) adding a miscible solvent to the mixture obtained in step a);
- c) adding an organic solvent and a reducing agent to the mixture obtained in step b) under basic pH condition to form said particles of formula (I) dispersed therein.

Advantageously, the method described in the present disclosure allows a fast phase separation (typically within several seconds).

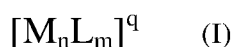
- 15 Further advantageously, the method disclosed in the present disclosure may be undertaken using a device having a straightforward design since there is no additional phase transfer agents, for example tetraoctylammonium bromide (TOAB), needed in said method.

Yet advantageously, the disclosed method forms a two-phase system where the particles can be formed and isolated easily. Hence, the disclosed method does not require any purification treatment as the particles in the form of nanoclusters that form in the organic phase may be spontaneously separated from interfering species, such as sodium hydroxide, reducing agent, and chloride ions in water. This would allow one to carry out a real-time monitoring of the growth of metal nanoclusters within the two-phase and subsequent reduction system by optical absorption spectroscopy and mass spectrometry.

- 25 Another significant advantage of the above method is that it is possible to tune the size of the metal nanoclusters at the atomic level, and investigate the growth mechanisms of metal nanoclusters. Using size-tunable metal nanoclusters as a material, the size effect of nanoclusters on the electrochemical reduction of CO<sub>2</sub> may therefore be examined systematically.

30 Owing to the multiphasic nature of the reaction, the method disclosed herein allows one to not only be able to stop the reduction reaction at the desired time points by removing the aqueous phase, but also to collect and analyse the size or composition of metal nanoclusters samples instantly without post-purification procedures, making investigations of the growth process of the metal nanoclusters possible.

- 35 In another aspect, there is provided particles of formula (I)



wherein:

M represents a metal;

L represents a ligand;

40 m and n are independently an integer in the range from 1 to 80;

q represents a net charge in the range from – 5 to + 5.

In another aspect, there is provided use of particles of formula (I) as electrode materials.

In another aspect, there is provided electrode materials comprising particles of formula (I).

## Definitions

The following words and terms used herein shall have the meaning indicated:

- 5 "Alkyl" as a group or part of a group refers to a straight or branched aliphatic hydrocarbon group, preferably a C<sub>1</sub>-C<sub>50</sub> alkyl, preferably a C<sub>1</sub>-C<sub>12</sub> alkyl, more preferably a C<sub>1</sub>-C<sub>10</sub> alkyl, most preferably C<sub>1</sub>-C<sub>6</sub> unless otherwise noted. Examples of suitable straight and branched C<sub>1</sub>-C<sub>6</sub> alkyl substituents include methyl, ethyl, n-propyl, 2-propyl, n-butyl, sec-butyl, t-butyl, hexyl, and the like. The group may be a terminal group or a bridging group.
- 10 "Aryl" as a group or part of a group denotes (i) an optionally substituted monocyclic, or fused polycyclic, aromatic carbocycle (ring structure having ring atoms that are all carbon) preferably having from 5 to 12 atoms per ring. Examples of aryl groups include phenyl, naphthyl, and the like; (ii) an optionally substituted partially saturated bicyclic aromatic carbocyclic moiety in which a phenyl and a C<sub>5-7</sub> cycloalkyl or C<sub>5-7</sub> cycloalkenyl group are fused together to form a
- 15 cyclic structure, such as tetrahydronaphthyl, indenyl or indanyl. The group may be a terminal group or a bridging group. Typically an aryl group is a C<sub>6</sub>-C<sub>18</sub> aryl group.

"Arylalkyl" means an aryl-alkyl- group in which the aryl and alkyl moieties are as defined herein. Preferred arylalkyl groups contain a C<sub>1-5</sub> alkyl moiety. Exemplary arylalkyl groups include benzyl, phenethyl, 1-naphthalenemethyl and 2-naphthalenemethyl. The group may be a

20 terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the alkyl or aryl group.

"Heteroaryl" either alone or part of a group refers to groups containing an aromatic ring (preferably a 5 or 6 membered aromatic ring) having one or more heteroatoms as ring atoms in the aromatic ring with the remainder of the ring atoms being carbon atoms. Suitable

25 heteroatoms include nitrogen, oxygen and sulphur. Examples of heteroaryl include thiophene, benzothiophene, benzofuran, benzimidazole, benzoxazole, benzothiazole, benzisothiazole, naphtho[2,3-b]thiophene, furan, isoindolizine, xantholene, phenoxazine, pyrrole, imidazole, pyrazole, pyridine, pyrazine, pyrimidine, pyridazine, tetrazole, indole, isoindole, 1H-indazole, purine, quinoline, isoquinoline, phthalazine, naphthyridine, quinoxaline, cinnoline, carbazole,

30 phenanthridine, acridine, phenazine, thiazole, isothiazole, phenothiazine, oxazole, isooxazole, furazane, phenoxazine, 2-, 3- or 4- pyridyl, 2-, 3-, 4-, 5-, or 8- quinolyl, 1-, 3-, 4-, or 5- isoquinolyl, 1-, 2-, or 3- indolyl, and 2-, or 3-thienyl. A heteroaryl group is typically a C<sub>1</sub>-C<sub>18</sub> heteroaryl group. A heteroaryl group may comprise 3 to 8 ring atoms. A heteroaryl group may comprise 1 to 3 heteroatoms independently selected from the group consisting of N, O and S.

35 The group may be a terminal group or a bridging group.

The word "substantially" does not exclude "completely" e.g. a composition which is "substantially free" from Y may be completely free from Y. Where necessary, the word "substantially" may be omitted from the definition of the invention.

Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

As used herein, the term "about", in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more typically +/- 4% of the stated value, more typically +/- 3% of the stated value, more typically, +/- 2% of the stated value, even more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated value.

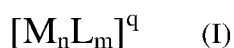
Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

## Detailed Disclosure of Embodiments

Exemplary, non-limiting embodiments of a method for preparing particles of formula (I) will now be disclosed.

In the present disclosure, there is provided a method of preparing particles of formula (I)



wherein:

M represents a metal;

L represents a ligand;

m and n are independently an integer in the range from 1 to 80 such as 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, or 80;

q represents a net charge in the range from - 5 to + 5 such as - 5, - 4, - 3, - 2, - 1, 0, + 1, + 2, + 3, + 4, or + 5,

said method comprising the steps of:

- a) mixing a metal precursor solution and a ligand precursor solution in the presence of an aqueous solution;
- b) adding a miscible solvent to the mixture obtained in step a);

- c) adding an organic solvent and a reducing agent to the mixture obtained in step b) under basic pH condition to form said particles of formula (I) dispersed therein.

The metal M present in particles of formula (I) may be a transition metal. Non-limiting examples of the transition metal include gold (Au), silver (Ag), copper (Cu), platinum (Pt), or palladium (Pd). Preferred transition metals in the present disclosure may be gold (Au), silver (Ag), or copper (Cu).

When metal M in particles of formula (I) is a transition metal, the metal precursor solution above may be referred to as a transition metal precursor solution. Accordingly, it is to be understood that the transition metal used herein may exist in various oxidation states. For example, when copper is used as the transition metal, copper may be present in oxidation state of 0 or +1. The same applies to the other types of transition metals such as gold (being 0 or +1), silver (being 0 or +1), platinum (being 0 or +1), and palladium (being 0 or +1).

The metal precursor described herein is not limited to one type of metal precursor. That is, any other types of metal precursor than those stated in the examples of the present disclosure may also be used provided that they are able to produce identical particles of formula (I). More importantly, the metal precursor used should be substantially soluble in a solvent or a mixture of two or more solvents to form the metal precursor solution. Non-limiting forms of the metal precursors may be found in their acidic, basic, oxide, sulfide, phosphide, or salt form. Salt form may be commonly known metal salts such as metal nitrate, metal sulfate, metal phosphate and metal chloride. For example, the gold precursor used in the present disclosure may be  $\text{HAuCl}_4$ . For copper, the copper precursor may be  $\text{CuSO}_4$ ,  $\text{CuCl}_2$ , and  $\text{Cu}(\text{NO}_3)_2$ . Non-limiting examples of silver precursor may include  $\text{AgNO}_3$  and  $\text{Ag}_2\text{SO}_4$ .

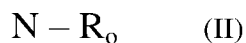
Similar as above, when metal M is a transition metal, the same characteristics of the metal precursor above apply to the transition metal precursor.

The solvent used to dissolve the metal precursor above may be an organic or an aqueous solvent. Non-limiting examples of organic solvent may include acetic acid, acetone, acetonitrile, benzene, 1-butanol, 2-butanol, 2-butanone, t-butyl-alcohol, carbon tetrachloride, chloroform, cyclohexane, 1,2-dichloroethane, dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), ethanol, ethyl acetate, hexane, methanol, methyl t-butyl ether (MTBE), N-methyl-2-pyrrolidinone (NMP), pentane, 1-propanol, 2-propanol, pyridine, tetrahydrofuran (THF), toluene, triethyl amine, o-xylene, m-xylene and p-xylene. The aqueous solvent defined above is essentially water-based solvent or water.

The type of solvent used above may also include protic and aprotic solvents as well as polar and non-polar solvents.

The ligand L as described above may be monodentate, bidentate or polydentate ligand (or chelate). It is to be understood that when said ligand binds to the metal, a coordinate covalent bond may be formed. The term coordinate covalent bond may be used interchangeably with dative bond or coordinate bond. Hence, when the ligand is bonded to the metal, such ligand may be referred as coordinated to the metal thereby forming a ligand coordinated metal or a metal-ligand coordination complex.

The ligand used in the method described herein may be an organic ligand of formula (II)



wherein:

N is a non-metal element selected from Group 15 or Group 16 of the Periodic Table of Elements;

5 R is selected from the group consisting of hydrogen, C<sub>1-20</sub>alkyl, C<sub>3-7</sub>cycloalkyl, C<sub>1-20</sub>alkylaryl, aryl-C<sub>1-20</sub>alkyl, heteroaryl and aryl; and  
o is 1, 2 or 3.

The non-metal element N above may be oxygen (O), sulfur (S), selenium (Se), tellurium (Te), nitrogen (N) or phosphorous (P).

10 The C<sub>1-20</sub>alkyl of the organic ligand of formula (II) as defined above may be a linear or branched alkyl chain having 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 carbon atoms. The C<sub>1-20</sub>alkyl may be a linear or branched alkyl chain having 6 to 10 carbon atoms, or 6 to 8 carbon atoms.

15 The C<sub>3-7</sub>cycloalkyl of the organic ligand of formula (II) above may be a cycloalkyl having 3, 4, 5, 6, or 7 carbon atoms. The cycloalkyl of the ligand L may be a cycloalkyl having 6 carbon atoms.

The aryl of the organic ligand of formula (II) may be phenyl or naphthyl.

20 The C<sub>1-20</sub>alkylaryl of the organic ligand of formula (II) as defined herein may be an alkylaryl having 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 carbon atoms.

The heteroaryl of the organic ligand of formula (II) may be selected from the group consisting of pyridinyl, thiopyranyl, pyrrolyl, imidazolyl, pyrazolyl, furanyl and thiophenyl.

25 When the ligand of formula (II) is bonded to the metal M, it is the non-metal element N that binds to the metal or metal ion via at least one coordinate covalent bond. In this respect, non-metal N may serve as a linker between the metal and the ligand moiety.

The ligand precursor solution as defined herein may therefore comprise the ligand L as defined above, where the ligand L may be an organic ligand of formula (II) as described above dissolved in a solvent or a mixture of two or more solvents as previously described.

The ligand precursor as defined herein may be represented by formula (III)



wherein A is hydrogen or absent; N, R and o are as defined above.

35 Non-limiting examples of the ligand precursor of formula (III) include benzeneselenol, benzenethiol, 4-tert-butylbenzenethiol, cyclohexaneselenol, cyclohexanethiol, benzeneselenol, 2-phenylethanethiol, 4-methylbenzenethiol, and triphenylphosphine. Accordingly, when such ligand precursors of formula (III) are used, the ligands bonded to the metal M in the particle of formula (I) may be referred as benzeneselenolate,

benzenethiolate, 4-tert-butylbenzenethiolate, cyclohexaneselenolate, cyclohexanethiolate, 2-phenylethanethiolate, 4-methylbenzenethiolate, and triphenylphosphine.

Non-limiting examples of the particles of formula (I) are selected from the group consisting of  $\text{Au}_{10}(\text{SeR})_{10}$ ,  $\text{Au}_{15}(\text{SeR})_{12}$ ,  $\text{Au}_{18}(\text{SeR})_{14}$ ,  $\text{Au}_{23}(\text{SeR})_{16}$ ,  $\text{Au}_{25}(\text{SeR})_{18}$ ,  $\text{Au}_{31}(\text{SeR})_{20}$ ,  $\text{Au}_{40}(\text{SeR})_{24}$ ,  $\text{Au}_{61}(\text{SeR})_{31}$ ,  $\text{Au}_{10}(\text{SR})_{10}$ ,  $\text{Au}_{15}(\text{SR})_{13}$ ,  $\text{Au}_{28}(\text{SR})_{20}$ ,  $\text{Au}_{30}(\text{SR})_{22}$ ,  $\text{Au}_{42}(\text{SR})_{26}$ ,  $\text{Au}_{23}(\text{SR})_{16}$ ,  $\text{Au}_{24}(\text{SR})_{20}$ ,  $\text{Au}_{25}(\text{SR})_{18}$ ,  $[\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2]^+$ ,  $\text{Ag}_{44}(\text{SeR})_{30}$ , and  $\text{Cu}_{27}(\text{SeR})_{17}$ , where R is as defined above. Where the particles of formula (I) is  $\text{Au}_{24}(\text{SR})_{20}$ , the particles may be  $\text{Au}_{24}(\text{PET})_{20}$ , where PET denotes 2-phenylethanethiol. Where the particles of formula (I) is  $\text{Au}_{25}(\text{SR})_{18}$ , the particles may be  $\text{Au}_{25}(\text{MBT})_{18}$ , where MBT represents 4-methylbenzenethiol. Where the particles of formula (I) is  $\text{Au}_{23}(\text{SR})_{16}$ , the particles may be  $\text{Au}_{23}(\text{S-c-C}_6\text{H}_{11})_{16}$ , where S-c-C<sub>6</sub>H<sub>11</sub> represents cyclohexanethiol. Where the particles of formula (I) is  $[\text{Au}_{11}(\text{PR})_8]^{3+}$ , the particles may be  $[\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2]^+$ , where Ph is phenyl.

The ligand precursor and the metal precursor may be dissolved in the same or different solvent or mixture of two or more solvents. Specifically, when the ligand precursor and the metal precursor are dissolved separately in two dissimilar solvents, the ligand precursor solution and the metal precursor solution formed may be found in two separate liquid phases when these two solutions are mixed. That is the two dissimilar solvents are immiscible or substantially immiscible to each other. An example of this would be mixing toluene and water or mixing benzene and water. When toluene is mixed with water at any proportions, two separate liquid phases may be formed. Accordingly, if the ligand precursor as defined above is hydrophobic, such ligand precursor may be preferably dissolved in a non-polar solvent such as benzene, carbon tetrachloride, diethyl ether, hexane and methylene chloride or other suitable solvents that are able to substantially dissolve the ligand precursor as defined above. On the other hand, if the metal precursor or the transition metal precursor is hydrophilic, said metal or transition metal precursor may be preferably dissolved in a polar solvent such as water, water-based solvent, acetic acid, ethanol, n-propanol or other suitable solvents that are able to substantially dissolve the metal or transition metal precursor as defined above. In essence, "like dissolves like" principle applies in the examples above.

To prepare the particles of formula (I) above, for example gold selenolate particles, the gold precursor for example  $\text{HAuCl}_4$  may be dissolved in aqueous solution such as water. The ligand precursor such as benzeneselenol may be dissolved in a non-polar solvent such as toluene. Similarly, when gold thiolate particles are desired, the gold precursor for example  $\text{HAuCl}_4$  may be dissolved in aqueous solution such as water and the ligand precursor such as 4-tert butylbenzenethiol may be dissolved in a non-polar solvent such as toluene. Likewise, when gold particles with other ligands than those aforementioned are desired, those ligand precursors such as cyclohexanethiol, 2-phenylethanethiol, 4-methylbenzenethiol and triphenylphosphine may also be dissolved in a non-polar solvent such as toluene.

For completeness, since the method for preparing the particles of formula (I) may also be applied to other metals than gold, for preparing particles of formula (I) with metal M is silver or copper for example, the metal precursor such as  $\text{AgNO}_3$  or  $\text{CuSO}_4$  may be dissolved in aqueous solvent to form corresponding metal precursor solution.

If two separate liquid phases are formed upon mixing the metal precursor solution and the ligand precursor solution, such system may be termed as a two-phase system. As previously stated, in such two-phase system, the two phases are essentially not mixed (i.e. immiscible) and

an interface may therefore be formed. In the present disclosure, the terms organic and aqueous layers and or organic and aqueous phases may also be used interchangeably to describe the two-phase system.

The mixing step above may be undertaken in the presence of an aqueous solution. Such aqueous solution, as the name suggests, may be a water-based solution or water. It is to be noted that when the mixing step is undertaken in the presence of water, the metal precursor that is dissolved in aqueous solution may be substantially mixed with water. However, the ligand precursor that is dissolved in a non-polar solvent may remain as a separate phase. Hence, the two-phase system formed may remain as two-phase system, that is, no additional phase may be formed.

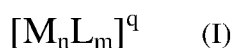
The concentration of the metal precursor and ligand precursor in the solution may be identical or different. Preferably, the concentrations of the precursors are the same or substantially the same. Initial concentration of the precursors (prior to the mixing) may be in the range from about 1 mM to 100 mM, about 1 mM to 5 mM, about 1 mM to 10 mM, about 1 mM to 20 mM, about 1 mM to 30 mM, about 1 mM to 40 mM, about 1 mM to 50 mM, about 1 mM to 60 mM, about 1 mM to 70 mM, about 1 mM to 80 mM, about 1 mM to 90 mM, about 5 mM to 10 mM, about 5 mM to 20 mM, about 5 mM to 30 mM, about 5 mM to 40 mM, about 5 mM to 50 mM, about 5 mM to 60 mM, about 5 mM to 70 mM, about 5 mM to 80 mM, about 5 mM to 90 mM, about 5 mM to 100 mM, about 20 mM to 30 mM, about 20 mM to 40 mM, about 20 mM to 50 mM, about 20 mM to 80 mM, about 20 mM to 100 mM, about 40 mM to 50 mM, about 40 mM to 60 mM, about 40 mM to 80 mM, about 40 mM to 100 mM, about 50 mM to 60 mM, about 50 mM to 80 mM, about 50 mM to 100 mM, or about 80 mM to 100 mM. It is commonly known that mM refers to mmol per liter.

The volume of the metal precursor solution and ligand precursor solution used in the mixing may be in the range of 0.05 mL to 1 mL, such as 0.05 mL, 0.1 mL, 0.2 mL, 0.3 mL, 0.4 mL, 0.5 mL, 0.6 mL or 1 mL. Any other volume that falls within the range may also be used.

The metal precursor solution and ligand precursor solution may be mixed in a suitable ratio. The mole ratio of metal precursor to ligand precursor may be in the range from about 0.1:1 to 10:1, such as about 0.1:1, about 0.2:1, about 0.5:1, about 0.75:1, about 1:1, about 1.5:1, about 2:1, about 2.5:1, about 3:1, about 4:1, about 5:1, about 6:1, about 7:1, about 8:1, about 9:1, or about 10:1. The ratio above may also represent the metal to ligand ratio in the metal complex formed.

In the step of mixing the metal precursor solution and the ligand precursor solution in the presence of the aqueous solution as defined above, the aqueous solution may be substituted by a solvent or a mixture of solvent having similar characteristics as the aqueous solution. Since the aqueous solution is likely to be polar due to the presence of water, said solvent or mixture of solvent should therefore be similarly polar. In an embodiment, where the aqueous solution used is water, water may be substituted by polar solvents such as ethanol or methanol. Hence, the mixing of the metal precursor solution and the ligand precursor solution may be undertaken in the presence of ethanol or methanol.

Therefore, the present disclosure also provides a method of preparing particles of formula (I)



wherein:

M represents a metal;

L represents a ligand;

m and n are independently an integer in the range from 1 to 80 such as 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, or 80;

q represents a net charge in the range from - 5 to + 5 such as - 5, - 4, - 3, - 2, - 1, 0, + 1, + 2, + 3, + 4, or + 5,

said method comprising the steps of:

- a) mixing a metal precursor solution and a ligand precursor solution in the presence of an aqueous solution or a polar solvent;
- b) adding a miscible solvent to the mixture obtained in step a);
- c) adding an organic solvent and a reducing agent to the mixture obtained in step b) under basic pH condition to form said particles of formula (I) dispersed therein.

The polar solvent used in step a) above may include acetic acid, methanol, ethanol, and n-propanol.

The miscible solvent added in step b) of the method as described herein may be selected from the group consisting of DMF, tetrahydrofuran (THF), acetonitrile, ethanol and mixture thereof. The type of the miscible solvent added in step b) is not limited to the miscible solvents provided earlier and therefore may extend to other solvents as long as said miscible solvent is miscible or substantially miscible with both solvents (being the aqueous solvent and the organic solvent), that is, the miscible solvent is miscible or substantially miscible with the metal precursor solution and the ligand precursor solution as defined above.

Said miscible solvent may advantageously facilitate the phase transfer of ligand-coordinated metal (or metal-ligand coordination complex) from water to organic phase. For instance, when DMF is used as miscible solvent in the method of preparing gold selenolate particles of formula (I), DMF may facilitate the interaction between the reducing agent and hydrophobic selenolate-Au(I) complexes at the interface. Specifically, DMF may facilitate the interaction between hydrophilic  $\text{NaBH}_4$  and hydrophobic selenolate-Au(I) complexes at the interface. The importance of miscible solvent in the method described in the present disclosure may be further demonstrated in the Examples provided. It is interesting to note that when the method for preparing particles of formula (I) above is undertaken in the absence of the miscible solvent (step b) above is absent), the particles of formula (I) may not be formed.

In addition to the above, the miscible solvent as defined above may be used to regulate the kinetics of the reducing agent. As a result, a range of particles of formula (I) may be obtained using the above method, by keeping all parameters constant, except the proportion of the miscible solvent added to the mixture in step b) as previously described. Similarly, when the miscible solvent is changed from one to another, for example from DMF to ethanol or acetonitrile or vice versa, and by keeping other parameters identical, different particles of formula (I) may be obtained.

The working principle of the method above may be distinct from that of Brust-Schiffrin synthesis whereby the reduction of Au(I) complexes was supposed to occur in reverse micelles of tetraoctyl ammonium bromide (TOAB) in which hydrophilic  $\text{NaBH}_4$  was encapsulated. In contrast, the method of preparing particles of formula (I) disclosed here may not require the use of phase transfer agent(s) such as tetraoctylammonium bromide (TOAB), hexadecyltrimethyl ammonium bromide (CTAB), or any other phase transfer agents known in the art.

As indicated above, the method described in the present disclosure may be undertaken in the basic pH condition, that is, in the pH range of more than 7 to 14 such as 7.5, 8, 8.5, 9, 9.5, 10, 11, 12, 13, 13.5 or 14. Any other pH values that fall within the range of 7 and 14 may also be used. Suitable basic pH condition for the solution obtained in step b) as defined above may therefore be attained by adding a base. Such base may be a strong base, weak base or mixture thereof. The base added may be in the form of solution and therefore upon addition of the base, such base may be found in either the aqueous (water) or organic phase or in both phases. Typical bases that may be used are  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{LiOH}$ ,  $\text{CsOH}$ ,  $\text{Ba}(\text{OH})_2$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Sr}(\text{OH})_2$  and mixture thereof.

Following the pH adjustment as described above, a reducing agent may then be added. Non-limiting examples of the reducing agent include  $\text{NaBH}_4$ ,  $\text{NaBH}_3\text{CN}$ ,  $\text{KBH}_4$ ,  $\text{LiBH}_4$ ,  $\text{LiAlH}_4$  and mixture thereof. The reducing agent added may reduce the metal complex (or metal coordination complex) to form particles of formula (I). The reduced form of the metal complex (or metal coordination complex) may form clusters.

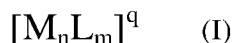
The clusters formed above may have homogeneous size distribution and such clusters may therefore be termed as monodisperse clusters. The clusters produced by the method described in the present disclosure may be in a nanometre range and such clusters may thus be termed as nanoclusters. The nanoclusters or monodisperse nanoclusters here may have particle size less than about 2 nm, such as about 0.4 nm, about 0.5 nm, about 0.6 nm, about 0.7 nm, about 0.8 nm, about 0.9 nm, about 1 nm, about 1.1 nm, about 1.2 nm, about 1.3 nm, about 1.4 nm, about 1.5 nm, about 1.6 nm, about 1.7 nm, about 1.8 nm, or about 1.9 nm.

The nanoclusters or monodisperse clusters above may be formed in the mixture of step c) after about 10 minutes, about 20 minutes, about 30 minutes, about 60 minutes, about 90 minutes, about 120 minutes, about 150 minutes, about 180 minutes, about 210 minutes, about 270 minutes, about 300 minutes, about 360 minutes, or about 600 minutes.

The particles and/ or nanoclusters prepared in accordance with the above method may be characterized using suitable analytical techniques commonly known in the art. Examples of such characterization are shown in the examples of the present disclosure. It is to be noted that the equipment used for particles characterization are not limiting and therefore other characterization techniques not stated here may also be used.

To ensure intimate contact between the reactants and/ or the reagents for preparing the particles of formula (I), in this instant, the metal precursor solution, the ligand precursor solution, miscible solvent, reducing agent and the aqueous solution or the polar solvent, the mixture may be stirred during the preparation process. Such stirring may involve conventional mixing process known in the art and its modification thereof. When the two-phase system is subjected to the stirring process, the stirring may facilitate the contact between the two phases and thereby the reactants found in organic and aqueous layers.

Additionally, the present disclosure also provides a method of preparing nanoclusters of formula (I)



wherein:

5 M represents a metal;

L represents a ligand:

m and n are independently an integer in the range from 1 to 80 such as 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 10 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, or 80;  
q represents a net charge in the range from - 5 to + 5 such as - 5, - 4, - 3, - 2, - 1, 0, + 1, + 2, + 3, + 4, or + 5,

said method comprising the steps of:

- 15 a) mixing a metal precursor solution and a ligand precursor solution in the presence of an aqueous solution or a polar solvent;
- b) adding a miscible solvent to the mixture obtained in step a);
- c) adding an organic solvent and a reducing agent to the mixture obtained in step b) under basic pH condition to form said nanoclusters of formula (I) dispersed therein.

20 As aforementioned, the addition of miscible solvent may be advantageous as it may facilitate the phase transfer of ligand-coordinated metal (or metal-ligand coordination complex) from water to organic phase. For instance, when DMF is used as the miscible solvent in the method of preparing gold selenolate nanoclusters of formula (I), DMF may facilitate the interaction between the reducing agent and hydrophobic selenolate-Au(I) complexes at the interface.  
25 Specifically, DMF may facilitate the interaction between hydrophilic NaBH<sub>4</sub> and hydrophobic selenolate-Au(I) complexes at the interface.

Further, the miscible solvent may also be used to regulate the kinetics of the reducing agent. As a result, a range of nanoclusters of formula (I) may be obtained using the above method, by keeping all parameters constant, except the proportion of the miscible solvent added to the mixture in step b) as previously described. Similarly, when the miscible solvent is changed from one to another, for example from DMF to ethanol or acetonitrile or vice versa, and by keeping other parameters identical, different nanoclusters of formula (I) may be obtained.

For the purpose of illustrating the importance of the miscible solvent in the method of preparing nanoclusters of formula (I), the following exemplary conditions are provided.

### 35 Exemplary conditions 1: Effect of the amount of miscible solvent

Ligand precursor solution: benzeneselenol in toluene; metal precursor solution: aqueous solution of HAuCl<sub>4</sub>; aqueous solution: water; miscible solvent: DMF; organic solvent: toluene; reducing agent: NaBH<sub>4</sub> solution.

Au<sub>10</sub>(SeR)<sub>10</sub> nanoclusters may be prepared as follow:

- a) a toluene solution of benzeneselenol (50 mM, 0.2 mL) and an aqueous solution of HAuCl<sub>4</sub> (50 mM, 0.1 mL) are mixed in 4.5 mL of water with stirring;
- b) 0.5 mL of DMF as the miscible solvent is added to mixture a);
- 5 c) an aqueous NaOH solution (1 M, 0.4 mL) and 4.8 mL of toluene are then introduced to the reaction mixture b), followed by the addition of 0.1 mL of NaBH<sub>4</sub> solution to form Au<sub>10</sub>(SeR)<sub>10</sub> nanoclusters after about 3 hours.

Au<sub>40</sub>(SeR)<sub>24</sub> nanoclusters may be obtained via synthesis as follow:

- 10 a) a toluene solution of benzeneselenol (50 mM, 0.2 mL) and an aqueous solution of HAuCl<sub>4</sub> (50 mM, 0.1 mL) are mixed in 0.5 mL of water with stirring;
- b) 4.5 mL of DMF is added to mixture a) as the miscible solvent;
- c) an aqueous NaOH solution (1 M, 0.4 mL) and 4.8 mL of toluene are then introduced to the reaction mixture b), followed by the addition of 0.1 mL of NaBH<sub>4</sub> solution to form Au<sub>40</sub>(SeR)<sub>24</sub> Nanoclusters after about 3 hours.

## 15 Exemplary conditions 2: Effect of the type of miscible solvent

Ligand precursor solution: benzeneselenol in toluene; metal precursor solution: aqueous solution of HAuCl<sub>4</sub>; aqueous solution: water; miscible solvent: DMF or methanol or acetonitrile; organic solvent: toluene; reducing agent: NaBH<sub>4</sub> solution.

Au<sub>40</sub>(SeR)<sub>24</sub> nanoclusters may be prepared as follow:

- 20 a) a toluene solution of benzeneselenol (50 mM, 0.2 mL) and an aqueous solution of HAuCl<sub>4</sub> (50 mM, 0.1 mL) are mixed in 0.5 mL of water with stirring;
- b) 4.5 mL of DMF is added to mixture a) as the miscible solvent;
- c) an aqueous NaOH solution (1 M, 0.4 mL) and 4.8 mL of toluene are then introduced to the reaction mixture b), followed by the addition of 0.1 mL of NaBH<sub>4</sub> solution to form
- 25 Au<sub>40</sub>(SeR)<sub>24</sub> nanoclusters after about 3 hours.

Au<sub>25</sub>(SeR)<sub>18</sub> nanoclusters may be prepared as follow:

- a) a toluene solution of benzeneselenol (50 mM, 0.2 mL) and an aqueous solution of HAuCl<sub>4</sub> (50 mM, 0.1 mL) are mixed in 0.5 mL of water with stirring;
- b) 0.5 mL of ethanol or acetonitrile as the miscible solvent is added to mixture a);
- 30 c) an aqueous NaOH solution (1 M, 0.4 mL) and 4.8 mL of toluene are then introduced to the reaction mixture b), followed by the addition of 0.1 mL of NaBH<sub>4</sub> solution to form Au<sub>25</sub>(SeR)<sub>18</sub> Nanoclusters after about 3 hours.

At least one or more steps described above may be undertaken at room temperature, which may be in the range from about 20°C to 30°C, such as about 20°C, about 21°C, about 22°C, about 23°C, about 24°C, about 25°C, about 26°C, about 27°C, about 28°C, about 29°C, or about 30°C. Preferably, all steps a), b) and c) described in the present disclosure are undertaken at room temperature.

Based on the above, it can be concluded that the miscible solvent has at least three functions in the present method: (i) it acts as a “go-between” and makes the encounter and reduction between hydrophilic NaBH<sub>4</sub> and hydrophobic selenolate-Au(I) complexes possible, (ii) it

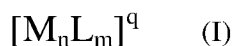
modifies the size of selenolate-Au(I) complexes in the organic phase, and (iii) it controls the reduction kinetics of the selenolate-Au(I) complexes with NaBH<sub>4</sub> by adjusting the number of “go-betweens” (i.e., the proportion of the miscible solvent) to regulate their frequency of encounters.

- 5 Interestingly, when different concentrations of the precursors are used and keeping all other parameters constant, there may be no obvious change to the nanoclusters produced. Similarly, when different metal to ligand ratios are tested and again, keeping all other parameters constant, identical nanoclusters may be produced demonstrating the robustness of the method of the present disclosure. In addition, the method of preparing particles or nanoclusters of formula (I)  
10 here may also be scaled up in a straightforward manner to obtain the desired particles or nanoclusters of formula (I).

Thus, the method described above may therefore be considered as facile, robust, and scalable synthesis.

Exemplary, non-limiting embodiments of particles of formula (I) will now be disclosed.

- 15 The present disclosure provides the particles of formula (I)



wherein:

M represents a metal;

L represents a ligand:

- 20 m and n are independently an integer in the range from 1 to 80 such as 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, or 80;  
q represents a net charge in the range from - 5 to + 5 such as - 5, - 4, - 3, - 2, - 1, 0, + 1, +  
25 2, + 3, + 4, or + 5.

Similar as above, the metal M of particles of formula (I) may be as previously defined and may be a transition metal.

The ligand L may be as defined previously and may be an organic ligand of formula (II)



wherein:

N is a non-metal element selected from the group consisting of elements of Groups 15 and 16 of the Periodic Table;

- R is selected from the group consisting of hydrogen, C<sub>1-20</sub>alkyl, C<sub>3-7</sub>cycloalkyl, C<sub>1-20</sub>alkylaryl, aryl-C<sub>1-20</sub>alkyl, heteroaryl and aryl; and  
35 o is 1, 2 or 3.

In an embodiment, the non-metal element N above may be oxygen (O), sulfur (S), selenium (Se), tellurium (Te), nitrogen (N) or phosphorous (P).

The C<sub>1-20</sub>alkyl of the organic ligand of formula (II) as defined above may be a linear or branched alkyl chain having 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 carbon atoms. The C<sub>4-20</sub>alkyl may be a linear or branched alkyl chain having 4 to 20 carbon atoms, or 6 to 8 carbon atoms.

- 5 The C<sub>3-7</sub>cycloalkyl of the organic ligand of formula (II) above may be a cycloalkyl having 3, 4, 5, 6, or 7 carbon atoms. Preferred cycloalkyl of the ligand L may be a cycloalkyl having 6 carbon atoms.

The aryl of the organic ligand of formula (II) may be phenyl or naphthyl.

- 10 The C<sub>1-20</sub>alkylaryl of the organic ligand of formula (II) as defined herein may be an alkylaryl having 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 carbon atoms.

The heteroaryl of the organic ligand of formula (II) may be selected from the group consisting of pyridinyl, thiopyranyl, pyrrolyl, imidazolyl, pyrazolyl, furanyl and thiophenyl.

- 15 The ligand L of the particles of formula (I) may be as defined above. When bonded to the metal, such ligand may be referred as the first coordination sphere as the ligand is directly attached to the metal. The ligand encapsulating the metal may form at least one layer. When one layer of ligand is formed, such layer is termed as monolayer.

The ligand L of the particles of formula (I) may be hydrophobic ligands having the following characteristics:

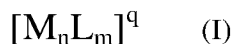
- 20 (i) the ligand L should have a functional group possessing relatively strong binding affinities with metal so that hydrophilic metal species could be stabilized by organic ligands via complexation;  
 (ii) the ligand L should have a hydrophobic entity to ensure their phase transfer ability from water to organic phase.

- 25 Non-limiting examples of the particles of formula (I) are selected from the group consisting of Au<sub>10</sub>(SeR)<sub>10</sub>, Au<sub>15</sub>(SeR)<sub>12</sub>, Au<sub>18</sub>(SeR)<sub>14</sub>, Au<sub>23</sub>(SeR)<sub>16</sub>, Au<sub>25</sub>(SeR)<sub>18</sub>, Au<sub>31</sub>(SeR)<sub>20</sub>, Au<sub>40</sub>(SeR)<sub>24</sub>, Au<sub>61</sub>(SeR)<sub>31</sub>, Au<sub>10</sub>(SR)<sub>10</sub>, Au<sub>15</sub>(SR)<sub>13</sub>, Au<sub>28</sub>(SR)<sub>20</sub>, Au<sub>30</sub>(SR)<sub>22</sub>, Au<sub>42</sub>(SR)<sub>26</sub>, Au<sub>23</sub>(SR)<sub>16</sub>, Au<sub>24</sub>(SR)<sub>20</sub>, Au<sub>25</sub>(SR)<sub>18</sub>, [Au<sub>11</sub>(PPh<sub>3</sub>)<sub>8</sub>Cl<sub>2</sub>]<sup>+</sup>, Ag<sub>44</sub>(SeR)<sub>30</sub>, and Cu<sub>27</sub>(SeR)<sub>17</sub>, where R is as defined above. Where the particles of formula (I) is Au<sub>24</sub>(SR)<sub>20</sub>, the particles may be  
 30 Au<sub>24</sub>(PET)<sub>20</sub>, where PET denotes 2-phenylethanethiol. Where the particles of formula (I) is Au<sub>25</sub>(SR)<sub>18</sub>, the particles may be Au<sub>25</sub>(MBT)<sub>18</sub>, where MBT represents 4-methylbenzenethiol. Where the particles of formula (I) is Au<sub>23</sub>(SR)<sub>16</sub>, the particles may be Au<sub>23</sub>(S-c-C<sub>6</sub>H<sub>11</sub>)<sub>16</sub>, where S-c-C<sub>6</sub>H<sub>11</sub> represents cyclohexanethiol. Where the particles of formula (I) is [Au<sub>11</sub>(PR)<sub>8</sub>]<sup>3+</sup>, the particles may be [Au<sub>11</sub>(PPh<sub>3</sub>)<sub>8</sub>Cl<sub>2</sub>]<sup>+</sup>, where Ph is phenyl.

- 35 The particles of formula (I) may be in the form of clusters. Such clusters may have homogeneous size distribution and may therefore be termed as monodisperse clusters. The clusters described in the present disclosure may be in a nanometre range and such clusters may thus be termed as nanoclusters. The nanoclusters or monodisperse nanoclusters here may have particle size less than about 2 nm, such as about 0.4 nm, about 0.5 nm, about 0.6 nm, about 0.7  
 40 nm, about 0.8 nm, about 0.9 nm, about 1 nm, about 1.1 nm, about 1.2 nm, about 1.3 nm, about 1.4 nm, about 1.5 nm, about 1.6 nm, about 1.7 nm, about 1.8 nm, or about 1.9 nm.

Exemplary, non-limiting embodiments of use of particles of formula (I) will now be disclosed.

The present disclosure also provides the use of particles of formula (I) as defined herein as electrode materials. The particles of formula (I) which may be found in the form of nanoclusters as defined above may be used as electrode materials. The electrode materials may comprise the particles of formula (I)



wherein:

M represents a metal;

L represents a ligand;

m and n are independently an integer in the range from 1 to 80 such as 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, or 80;

q represents a net charge in the range from - 5 to + 5 such as - 5, - 4, - 3, - 2, - 1, 0, + 1, + 2, + 3, + 4, or + 5.

The electrode materials above may be used in an electrolytic process, in particular electrocatalytic process for example for the reduction of carbon dioxide. Such electrocatalytic reduction of carbon dioxide may be considered as a clean and sustainable chemical process for generating useful hydrocarbons (e.g., methane and methanol) or CO.

As the electrode materials, the particles or nanoclusters of formula (I) may be mixed with a support material in the presence of a suitable solvent. Such support material may be carbon. When support material used is carbon, the electrode material may be termed as metal nanoclusters on carbon, which may be deposited on an electrode to form a modified electrode on which the electrocatalytic reduction mentioned above occurs.

In summary, the solvent-directed two-phase synthetic method for the synthesis of monolayer ligand-protected metal nanoclusters with atomic precision may be versatile and efficient: (i) the nanocluster size can be easily tuned by simply varying the proportion and type of the miscible solvent, (ii) monodisperse metal nanoclusters protected by a wide range of ligands such as selenolate, thiolate, and phosphine ligands can be obtained, (iii) the metal core of the nanoclusters can also be changed from gold to silver and copper.

Furthermore, the method above may be considered facile since there is no purification is required, fast ( $\leq 3$  hours), and scalable (to gram-scale easily). The unique features of this method (such as, fast and spontaneous phase separation, no need for purification, and slowed reduction kinetics of the reducing agent) allow one to examine the growth processes of the metal nanoclusters. A sequential  $2x e^-$  jumping mechanism was identified for the size growth of metal nanoclusters within the "NaBH<sub>4</sub> reduction" system.

## Brief Description of Drawings

The accompanying drawings illustrate a disclosed embodiment and serves to explain the principles of the disclosed embodiment. It is to be understood, however, that the drawings

are designed for purposes of illustration only, and not as a definition of the limits of the invention.

### Fig.1

[Fig. 1] is a number of images depicting the UV-vis absorption spectra, Electrospray ionization mass spectrometry (ESI-MS) spectra and digital images of selenolated Au Nanoclusters as prepared according to Example 1. Fig 1(a) depicts the UV-vis absorption spectra of Au<sub>10</sub>(SeR)<sub>10</sub> Nanoclusters (sample #1), Au<sub>15</sub>(SeR)<sub>12</sub> Nanoclusters (sample #2), Au<sub>18</sub>(SeR)<sub>14</sub> Nanoclusters (sample #3), Au<sub>23</sub>(SeR)<sub>16</sub> Nanoclusters (sample #4), Au<sub>25</sub>(SeR)<sub>18</sub> Nanoclusters (sample #5), Au<sub>31</sub>(SeR)<sub>20</sub> Nanoclusters (sample #6), Au<sub>40</sub>(SeR)<sub>24</sub> Nanoclusters (sample #7), and Au<sub>61</sub>(SeR)<sub>31</sub> Nanoclusters (sample #8). The insets show the digital photos of corresponding Au NC solutions. Fig. 1(b) shows the ESI-MS spectra of Nanoclusters prepared according to Example 1. The ESI mass spectra of Au<sub>10</sub>(SeR)<sub>10</sub> and Au<sub>18</sub>(SeR)<sub>14</sub> were acquired in positive mode with the usage of cesium acetate to enhance the ionization of the samples, while the spectra of other samples were acquired in negative mode without the usage of cesium acetate. \* represents fragment species derived from the fragmentation during the ionization process in ESI analysis.

### Fig.2

[Fig. 2] is a number of representative transmission electron microscopy (TEM) images of the as-synthesized selenolated Au nanoclusters synthesized according to Example 1. Figs. 2(a) to 2(h) show the TEM images of Au<sub>10</sub>(SeR)<sub>10</sub>, Au<sub>15</sub>(SeR)<sub>12</sub>, Au<sub>18</sub>(SeR)<sub>14</sub>, Au<sub>23</sub>(SeR)<sub>16</sub>, Au<sub>25</sub>(SeR)<sub>18</sub>, Au<sub>31</sub>(SeR)<sub>20</sub>, Au<sub>40</sub>(SeR)<sub>24</sub>, and Au<sub>61</sub>(SeR)<sub>31</sub> nanoclusters, respectively. The scale bar used in Fig. 2(a) to Fig. 2(h) is 20 nm.

### Fig.3

[Fig. 3] is a number of isotope patterns of ESI mass spectrum for various nanocluster species obtained in Example 1. Figs. 3(a) to 3(h) depict the theoretical and experimental isotope patterns of ESI mass spectrum for the following nanocluster species: [Au<sub>10</sub>(SeR)<sub>10</sub>Cs]<sup>+</sup>, [Au<sub>15</sub>(SeR)<sub>12</sub>]<sup>-</sup>, [Au<sub>18</sub>(SeR)<sub>14</sub>Cs]<sup>+</sup>, [Au<sub>23</sub>(SeR)<sub>16</sub>]<sup>-</sup>, [Au<sub>25</sub>(SeR)<sub>18</sub>]<sup>-</sup>, [Au<sub>31</sub>(SeR)<sub>20</sub>]<sup>-</sup>, [Au<sub>40</sub>(SeR)<sub>24</sub>]<sup>2-</sup>, and [Au<sub>61</sub>(SeR)<sub>31</sub>]<sup>2-</sup>, respectively.

### Fig.4

[Fig. 4] is a number of Au(4f) X-ray photoelectron spectroscopy (XPS) spectra for the as-synthesized selenolated Au nanoclusters prepared according to Example 1. The vertical dotted lines represent the Au(4f<sub>7/2</sub>) binding energies of selenolate-Au(I) complexes and Au(0) film. The selenolate-Au(I) complexes as a reference were prepared by mixing HAuCl<sub>4</sub> with benzeneselenol in a toluene-ethanol solution (molar ratio = 1:1).

### Fig.5

[Fig. 5] is a number of images depicting the UV-vis absorption spectra, ESI-MS spectra and photographs of thiolated Au nanoclusters as prepared according to Example 2. Fig 2(a) depicts the UV-vis absorption spectra of Au<sub>10</sub>(SR)<sub>10</sub> nanoclusters, Au<sub>15</sub>(SR)<sub>13</sub> nanoclusters, Au<sub>28</sub>(SR)<sub>20</sub> nanoclusters, Au<sub>30</sub>(SR)<sub>22</sub> nanoclusters and Au<sub>42</sub>(SR)<sub>26</sub> nanoclusters. The insets

show the digital photos of corresponding Au nanocluster solutions. Fig. 2(b) shows the ESI-MS spectra of nanoclusters prepared according to Example 2. The ESI mass spectra were acquired in the positive mode, and cesium acetate was used to enhance the ionization of Au nanoclusters.

## 5 Fig.6

[Fig. 6] is a number of isotope patterns of ESI mass spectrum for various nanocluster species obtained in Example 2. Figs. 6(a) to 6(e) depict the theoretical and experimental isotope patterns of ESI mass spectrum for the following nanocluster species:  $[\text{Au}_{10}(\text{SR})_{10}\text{Cs}]^+$ ,  $[\text{Au}_{15}(\text{SR})_{13}\text{Cs}]^+$ ,  $[\text{Au}_{28}(\text{SR})_{20}\text{Cs}_2]^{2+}$ ,  $[\text{Au}_{30}(\text{SR})_{22}\text{Cs}_2]^{2+}$ , and  $[\text{Au}_{42}(\text{SR})_{26}\text{Cs}_2]^{2+}$ , respectively.

## 10 Fig.7

[Fig. 7] is a number of graphs depicting the UV-vis absorption and ESI-MS spectrum of the as-synthesized  $\text{Au}_{23}(\text{S-}c\text{-C}_6\text{H}_{11})_{16}$  nanoclusters according to Example 2f. Fig. 7(a) depicts the UV-vis absorption spectrum of the  $\text{Au}_{23}(\text{S-}c\text{-C}_6\text{H}_{11})_{16}$  nanoclusters; Fig. 7(b) shows the ESI mass spectrum of the  $\text{Au}_{23}(\text{S-}c\text{-C}_6\text{H}_{11})_{16}$  nanoclusters. The inset in Fig. 7(a) shows the molecular structure of cyclohexanethiol ( $\text{S-}c\text{-C}_6\text{H}_{11}$ ). The inset in Fig. 7(b) shows the isotope patterns acquired theoretically and experimentally for  $[\text{Au}_{23}(\text{S-}c\text{-C}_6\text{H}_{11})_{16}]^-$ .

## Fig.8

[Fig. 8] is a number of graphs depicting the UV-vis absorption and ESI-MS spectrum of the as-synthesized  $\text{Au}_{24}(\text{PET})_{20}$  nanoclusters according to Example 2g. Fig. 8(a) depicts the UV-vis absorption spectrum of the  $\text{Au}_{24}(\text{PET})_{20}$  nanoclusters; Fig. 8(b) shows the ESI mass spectrum of the  $\text{Au}_{24}(\text{PET})_{20}$  nanoclusters. The inset in Fig. 8(a) shows the molecular structure of 2-phenylethanethiol (PET). The inset in Fig. 8(b) shows the isotope patterns acquired theoretically and experimentally for  $[\text{Au}_{24}(\text{PET})_{20}\text{Cs}]^+$ .

## Fig.9

[Fig. 9] is a number of graphs depicting the UV-vis absorption and ESI-MS spectrum of the as-synthesized  $\text{Au}_{25}(\text{MBT})_{18}$  nanoclusters according to Example 2h. Fig. 9(a) depicts the UV-vis absorption spectrum of the  $\text{Au}_{25}(\text{MBT})_{18}$  nanoclusters; Fig. 9(b) shows the ESI mass spectrum of the  $\text{Au}_{25}(\text{MBT})_{18}$  nanoclusters. The inset in Fig. 9(a) shows the molecular structure of 4-methylbenzenethiol (MBT). The inset in Fig. 9(b) shows the isotope patterns acquired theoretically and experimentally for  $[\text{Au}_{25}(\text{MBT})_{18}]^-$ .

## Fig.10

[Fig. 10] is a number of graphs depicting the UV-vis absorption and ESI-MS spectrum of the  $\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2$  nanoclusters according to Example 3. Fig. 10(a) shows the UV-vis absorption spectrum of the  $\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2$  nanoclusters; Fig. 10(b) shows the ESI mass spectrum of the  $\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2$  nanoclusters. The inset in Fig. 10(a) shows the molecular structure of triphenylphosphine ( $\text{PPh}_3$ ). The inset in Fig. 10(b) shows the isotope patterns acquired theoretically and experimentally for  $[\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2]^+$ .

**Fig.11**

[Fig. 11] is a number of graphs depicting the UV-vis absorption and ESI-MS spectrum of the  $\text{Ag}_{44}(\text{SeR})_{30}$  nanoclusters according to Example 4. Fig. 11(a) shows the UV-vis absorption spectrum of the  $\text{Ag}_{44}(\text{SeR})_{30}$  nanoclusters; Fig. 11(b) shows the ESI mass spectrum of the  $\text{Ag}_{44}(\text{SeR})_{30}$  nanoclusters. The inset in Fig. 11(b) shows the isotope patterns acquired theoretically and experimentally for  $[\text{Ag}_{44}(\text{SeR})_{30}]^{3-}$ .

**Fig.12**

[Fig. 12] is a number of graphs depicting the UV-vis absorption and ESI-MS spectrum of the  $\text{Cu}_{27}(\text{SeR})_{17}$  nanoclusters according to Example 5. Fig. 12(a) shows the UV-vis absorption spectrum of the  $\text{Cu}_{27}(\text{SeR})_{17}$  nanoclusters; Fig. 12(b) shows the ESI mass spectrum of the  $\text{Cu}_{27}(\text{SeR})_{17}$  nanoclusters. The inset in Fig. 12(b) shows the isotope patterns acquired theoretically and experimentally for  $[\text{Cu}_{27}(\text{SeR})_{17}\text{Cs}]^+$ .

**Fig.13**

[Fig. 13] is a number of images depicting the UV-vis absorption spectra, ESI-MS spectra and photograph of  $\text{Au}_{40}(\text{SeR})_{24}$  nanoclusters formed with variable concentrations of selenolate-Au(I) complex precursors as described in Example 6. Fig. 13(a) shows the UV-vis absorption spectra while Fig. 13(b) depicts the ESI mass spectra of  $\text{Au}_{40}(\text{SeR})_{24}$  Nanoclusters synthesized with 1 mM, 2 mM, 3 mM, 4 mM, and 5 mM. The inset in Fig. 13(a) shows the digital photographs of the corresponding Au NC solutions.

**Fig.14**

[Fig. 14] is a number of images depicting the UV-vis absorption spectra, ESI-MS spectra and photograph of  $\text{Au}_{40}(\text{SeR})_{24}$  nanoclusters formed with variable selenolate/Au(III) ratios as described in Example 6. Fig. 14(a) shows the UV-vis absorption spectra while Fig. 14(b) depicts the ESI mass spectra of  $\text{Au}_{40}(\text{SeR})_{24}$  nanoclusters synthesized with selenolate/Au(III) ratios of 1:1, 1.5:1, and 2:1. The inset in Fig. 14(a) shows the digital photographs of the corresponding Au NC solutions.

**Fig.15**

[Fig. 15] is a number of images depicting the UV-vis absorption spectra, ESI-MS spectra and photograph of  $\text{Au}_{40}(\text{SeR})_{24}$  nanoclusters in a 2L-scale as described in Example 6. Fig. 15(a) shows the UV-vis absorption spectra while Fig. 15(b) depicts the ESI mass spectra of  $\text{Au}_{40}(\text{SeR})_{24}$  nanoclusters synthesized a large volume of 2 L. The inset in Fig. 15(a) shows the digital photographs of the corresponding Au NC solutions.

**Fig.16**

[Fig. 16] is a number of images depicting the UV-vis absorption spectra, ESI-MS spectra and photograph of the product derived under the standard synthesis conditions for Au nanoclusters, except that the miscible solvent was not added as described in Example 7a. Fig. 16(a) shows the UV-vis absorption spectra while Fig. 16(b) depicts the ESI mass spectra of the product derived under the standard synthesis conditions for  $\text{Au}_{40}(\text{SeR})_{24}$  nanoclusters, except

that the miscible solvent was not added. The inset in Fig. 16(a) shows the digital photographs of the corresponding product solutions.

### Fig.17

[Fig. 17] is a number of graphs depicting  $^1\text{H}$  Nuclear Magnetic Resonance (NMR) spectra of mixed solvent of  $\text{D}_2\text{O}$  and deuterated DMF (a); mixed solvent of  $\text{D}_2\text{O}$  and deuterated DMF containing NaOH (b); mixed solvent of  $\text{D}_2\text{O}$  and deuterated DMF containing NaOH and  $\text{NaBH}_4$  (c); the aqueous layer of  $\text{D}_2\text{O}$ /deuterated DMF/deuterated toluene mixed with NaOH and  $\text{NaBH}_4$  (d); the organic layer of  $\text{D}_2\text{O}$ /deuterated DMF/deuterated toluene mixed with NaOH and  $\text{NaBH}_4$  (e); the aqueous layer of  $\text{D}_2\text{O}$ /deuterated DMF/deuterated DCM mixed with benzeneselenol (f); the organic layer of  $\text{D}_2\text{O}$ /deuterated DMF/deuterated DCM mixed with benzeneselenol (g); the aqueous layer of  $\text{D}_2\text{O}$ /deuterated DMF/deuterated DCM mixed with selenolate-Au(I) complexes (h); and the organic layer of  $\text{D}_2\text{O}$ /deuterated DMF/deuterated DCM mixed with selenolate-Au(I) complexes (i).

### Fig.18

[Fig. 18] is a number of graphs depicting the ESI-MS spectra (in negative mode) of selenolate-Au(I) complex precursors before the reduction for the synthesis of selenolated Au nanoclusters as prepared according to Example 1. The complexes corresponded to  $\text{Au}_{10}(\text{SeR})_{10}$  as shown in Fig. 18(a),  $\text{Au}_{15}(\text{SeR})_{12}$  as shown in Fig. 18(b), (c)  $\text{Au}_{18}(\text{SeR})_{14}$  as shown in Fig. 18(b),  $\text{Au}_{23}(\text{SeR})_{16}$  as shown in Fig. 18(d),  $\text{Au}_{25}(\text{SeR})_{18}$  as shown in Fig. 18(e),  $\text{Au}_{31}(\text{SeR})_{20}$  as shown in Fig. 18(f),  $\text{Au}_{40}(\text{SeR})_{24}$  as shown in Fig. 18(g), and  $\text{Au}_{61}(\text{SeR})_{31}$  as shown in Fig. 18(h). The species labeled in blue were those newly emerged in the given spectrum; they were labeled in red in subsequent spectra.

### Fig.19

[Fig. 19] is a number of graphs depicting the isotope patterns acquired theoretically and experimentally for species #1–31 identified in Fig. 18.

### Fig.20

[Fig. 20] is a number of graphs depicting  $^1\text{H}$  NMR spectra of the organic phase acquired by mixing (a) 4.5 mL of  $\text{D}_2\text{O}$ , 0.5 mL of deuterated DMF and 5 mL of deuterated toluene, (b) 3.5 mL of  $\text{D}_2\text{O}$ , 1.5 mL of deuterated DMF and 5 mL of deuterated toluene, (c) 2.5 mL of  $\text{D}_2\text{O}$ , 2.5 mL of deuterated DMF and 5 mL of deuterated toluene, (d) 1.5 mL of  $\text{D}_2\text{O}$ , 3.5 mL of deuterated DMF and 5 mL of deuterated toluene, and (e) 0.5 mL of  $\text{D}_2\text{O}$ , 4.5 mL of deuterated DMF and 5 mL of deuterated toluene, as described in Example 7a.

### Fig.21

[Fig. 21] is a number of graphs and images describing the effect of NaOH on the formation of selenolated Au nanoclusters as described in Example 7b. Fig. 21(a) shows the digital photograph of the products synthesized without NaOH and with 100–30% DMF in the aqueous phase. Fig. 21(b) depicts the UV–vis absorption spectra of products #3 (80% DMF) and #4 (70% DMF).

**Fig.22**

[Fig. 22] is a number of graphs and images describing the effect of the organic phase on the formation of selenolated Au nanoclusters as described in Example 7c. Fig. 22(a) shows the digital photograph of the products synthesized without organic phase (e.g., toluene or DCM) and with 100–10% of DMF in the aqueous phase. For the sake of clarity 1 represents 100% DMF and 0% aqueous phase; 2 represents 90% DMF and 10% aqueous phase; 3 represents 80% DMF and 20% aqueous phase; 4 represents 70% DMF and 30% aqueous phase; 5 represents 60% DMF and 40% aqueous phase; 6 represents 50% DMF and 50% aqueous phase; 7 represents 40% DMF and 60% aqueous phase; 8 represents 30% DMF and 70% aqueous phase; 9 represents 20% DMF and 80% aqueous phase; 10 represents 10% DMF and 90% aqueous phase, respectively; Fig. 22(b) depicts the UV–vis absorption spectra of the similar products 1 to 10 as described in Fig. 22(a).

**Fig.23**

[Fig. 23] is a number of graphs describing the time evolution of the reaction solution during the synthesis of  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  to investigate the growth process of Au nanoclusters as described in Example 8. Figs. 23(a) and 23(b) depict the UV–vis absorption spectra. Figs. 23(c) and 23(d) depict the ESI–MS spectra of the reaction solution during the synthesis of  $[\text{Au}_{23}(\text{SeR})_{16}]^-$ ; Fig. 23(e) shows the molecular formulas of the labeled species.

**Fig.24**

[Fig. 24] is a number of graphs depicting the isotope patterns acquired theoretically and experimentally for species #1–22 identified during the growth process of  $\text{Au}_{23}(\text{SeR})_{16}$  nanoclusters shown in Fig. 23.

**Fig.25**

[Fig. 25] is a number of graphs describing the time evolution of the reaction solution during the synthesis of  $[\text{Au}_{25}(\text{SeR})_{18}]^-$  to investigate the growth process of Au Nanoclusters as described in Example 8. Figs. 25(a) and 25(b) depict the UV–vis absorption spectra. Figs. 25(c) and 25(d) depict the ESI–MS spectra of the reaction solution during the synthesis of  $[\text{Au}_{25}(\text{SeR})_{18}]^-$ ; Fig. 25(e) shows the molecular formulas of the labelled species.

**Fig.26**

[Fig. 26] is a number of graphs depicting the isotope patterns acquired theoretically and experimentally for species #1–25 identified during the growth process of  $[\text{Au}_{25}(\text{SeR})_{18}]^-$  nanoclusters shown in Fig. 25.

**Fig.27**

[Fig. 27] is a number of graphs depicting the ESI–MS spectra of NC conversion from  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  nanoclusters to  $[\text{Au}_{25}(\text{SeR})_{18}]^-$  nanoclusters induced by replacing the aqueous phase of the two-phase system as described in Example 8.

**Fig.28**

[Fig. 28] is a number of graphs depicting the ESI-MS spectra of nanocluster conversion from  $[\text{Au}_{25}(\text{SeR})_{18}]^-$  nanoclusters to  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  nanoclusters induced by replacing the aqueous phase of the two-phase system as described in Example 8.

5 **Fig.29**

[Fig. 29] is a number of graphs describing the time evolution of the reaction solution during the synthesis of  $[\text{Au}_{40}(\text{SeR})_{24}]^{2-}$  to investigate the growth process of Au nanoclusters as described in Example 8. Figs. 29(a) and 29(b) depict the UV-vis absorption spectra. Figs. 29(c) and 29(d) depict the ESI-MS spectra of the reaction solution during the synthesis of  $[\text{Au}_{40}(\text{SeR})_{24}]^{2-}$  nanoclusters; Fig. 29(e) shows the molecular formulas of the labelled species.

**Fig.30**

[Fig. 30] is a number of graphs depicting the isotope patterns acquired theoretically and experimentally for species #1–24 identified during the growth process of  $[\text{Au}_{40}(\text{SeR})_{24}]^{2-}$  nanoclusters shown in Fig. 29.

15 **Fig.31**

[Fig. 24] is a number of graphs depicting the ESI-MS spectra of nanocluster conversion from  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  nanoclusters with 8  $e^-$  shell closure to  $[\text{Au}_{40}(\text{SeR})_{24}]^{2-}$  nanoclusters with 18  $e^-$  shell closure as described in Example 8.

**Fig.32**

20 [Fig. 32] is a number of graphs describing the time evolution of the reaction solution during the synthesis of  $[\text{Au}_{61}(\text{SeR})_{31}]^{2-}$  to investigate the growth process of Au nanoclusters as described in Example 8. Figs. 32(a) and 32(b) depict the UV-vis absorption spectra. Figs. 32(c) and 32(d) depict the ESI-MS spectra of the reaction solution during the synthesis of  $[\text{Au}_{61}(\text{SeR})_{31}]^{2-}$  nanoclusters; Fig. 32(e) shows the molecular formulas of the labelled species.

25 **Fig.33**

[Fig. 33] is a number of graphs depicting the isotope patterns acquired theoretically and experimentally for species #1–33 identified during the growth process of  $[\text{Au}_{61}(\text{SeR})_{31}]^{2-}$  nanoclusters shown in Fig. 32.

**Fig.34**

30 [Fig. 34] is a number of TEM images of Au nanoclusters on carbon: Fig. 34(a)  $\text{Au}_{15}(\text{SeR})_{12}/\text{C}$ , Fig. 34(b)  $\text{Au}_{25}(\text{SeR})_{18}/\text{C}$ , Fig. 34(c)  $\text{Au}_{40}(\text{SeR})_{24}/\text{C}$ , and Fig. 34(d)  $\text{Au}_{61}(\text{SeR})_{31}/\text{C}$  as described in Example 9. The scale bar used in Fig. 34(a) to Fig. 34(d) is 5 nm.

**Fig.35**

35 [Fig. 35] is a number of high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of Au nanoclusters on carbon: Fig. 35(a)  $\text{Au}_{15}(\text{SeR})_{12}/\text{C}$ ,

Fig. 35(b)  $\text{Au}_{25}(\text{SeR})_{18}/\text{C}$ , Fig. 35(c)  $\text{Au}_{40}(\text{SeR})_{24}/\text{C}$  and Fig. 35(d)  $\text{Au}_{61}(\text{SeR})_{31}/\text{C}$  as described in Example 9. The scale bar used in Fig. 35(a) to Fig. 35(d) is 20 nm.

### Fig.36

[Fig. 36] is a number of graphs depicting the TEM energy dispersive X-ray (TEM-EDX) analysis of Au nanoclusters supported on carbon: Fig. 36(a)  $\text{Au}_{15}(\text{SeR})_{12}/\text{C}$ , Fig. 36(b)  $\text{Au}_{25}(\text{SeR})_{18}/\text{C}$ , Fig. 36(c)  $\text{Au}_{40}(\text{SeR})_{24}/\text{C}$  and Fig. 36(d)  $\text{Au}_{61}(\text{SeR})_{31}/\text{C}$  as described in Example 9.

### Fig.37

[Fig. 37] is a number of graphs showing the comparison of performance of Au nanoclusters of different sizes for  $\text{CO}_2$  electroreduction (control experiment was using the same electrode devoid of Au nanoclusters) as described in Example 9. Linear sweep voltammograms of  $\text{CO}_2$  electroreduction for Au Nanoclusters on carbon in unstirred 0.1 M  $\text{KHCO}_3$  aqueous solution saturated with  $\text{CO}_2$  (pH = 6.9) at a scan rate of 10 mV/s.

### Fig.38

[Fig. 38] is a number of graphs depicting the potential dependent (a) CO formation rates and (b) FE for CO over Au NC/C in 0.1 M  $\text{KHCO}_3$  saturated with  $\text{CO}_2$  according to Example 9. Solutions were stirred at a constant rate during the one hour electrolysis to prevent the gaseous bubbles produced from building up on the electrode surface.

## Examples

Non-limiting examples of the invention with relevant comparative testing will be further described in greater detail by reference to specific Examples, which should not be construed as in any way limiting the scope of the invention.

## Materials and Instrumentation

Ultrapure Millipore water (18.2 M $\Omega$ ) was used in all experiments. All glassware was washed with *aqua regia* ( $\text{HCl}/\text{HNO}_3$  volume ratio = 3:1), rinsed with ethanol and copious water, and dried in an oven before use. Benzeneselenol, hydrogen tetrachloroaurate (III) hydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ), 4-tert-butylbenzenethiol, cyclohexanethiol, 2-phenylethanethiol (PET), 4-methylbenzenethiol (MBT), triphenylphosphine ( $\text{PPh}_3$ ), copper sulfate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), cesium acetate ( $\text{CH}_3\text{COOCs}$ ), potassium hydrogen carbonate ( $\text{KHCO}_3$ ) and Nafion were purchased from Sigma-Aldrich of St. Louis, Missouri of the United States of America. Sodium borohydride ( $\text{NaBH}_4$ ) and silver nitrate ( $\text{AgNO}_3$ ) were purchased from Merck of Kenilworth, New Jersey of the United States of America. Toluene, ethanol, acetone, acetonitrile, dichloromethane (DCM) and 1,2-dichloroethane (DCE) were purchased from Fisher of Hampton, New Hampshire of the United States of America. *N,N*-dimethylformamide (DMF), methanol and chloroform from J. T. Baker of Phillipsburg, New Jersey of the United States of America. Sodium hydroxide ( $\text{NaOH}$ ) was purchased from Kanto Chemical of Tokyo, Japan. The above chemicals and solvents were used as received.

UV-vis spectra were recorded on an Agilent 8453 UV-visible spectrometer system. The molecular formulas of Au(I) complexes and metal nanoclusters were determined by electrospray

ionization mass spectrometry (ESI-MS) on an Agilent 6210 Time-of-Flight LC/MS system. Samples of 5  $\mu\text{L}$  were directly injected into the chamber. Typical instrument parameters: flow rate of the elution (acetonitrile), 0.3  $\text{mL}\cdot\text{min}^{-1}$ ; capillary voltage, 4 kV; nebulizer, 48 psig; dry gas, 7  $\text{L}\cdot\text{min}^{-1}$  at 350°C;  $m/z$  range, 100–10000. Cesium acetate was used to enhance the ionization of  $\text{Au}_{10}(\text{SeR})_{10}$ ,  $\text{Au}_{18}(\text{SeR})_{14}$ ,  $\text{Cu}_{27}(\text{SeR})_{17}$ , and the 4-tert-butylbenzenethiol-protected Au nanoclusters.  $^1\text{H}$  Nuclear magnetic resonance (NMR) spectra was collected with a Bruker AV-400 (400 MHz) spectrometer at 25°C. The efficiency of phase transfer was analyzed by inductively coupled plasma–mass spectroscopy (ICP-MS) on a Perkin-Elmer Elan DRC II. Transmission electron microscopy (TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were taken on a FEI Tecnai G<sup>2</sup> F20 electron microscope operating at 200 kV. For TEM and HAADF-STEM studies, a drop of the nanoparticle suspension was dispensed onto a 3-mm carbon-coated copper grid. Excess solution was removed by an absorbent paper, and the sample was dried under air at room temperature. X-ray photoelectron spectroscopy (XPS) was conducted on a Kratos AXIS Ultra<sup>DLD</sup> spectrometer. Energy dispersive X-ray (EDX) analysis of the selenolate Au nanoclusters immobilized on the carbon support was performed on the FEI Tecnai G<sup>2</sup> F20 electron microscope equipped with EDX detector.

## Example 1: Preparation of Selenolate-Protected Au Nanoclusters

In Example 1, the detailed preparation of various selenolate-protected Au nanoclusters is described.

### a) Preparation of $\text{Au}_{10}(\text{SeR})_{10}$ Nanoclusters

Aqueous solution of  $\text{HAuCl}_4$  (50 mM) was prepared with ultrapure water while hydrophobic ligands (50 mM) were dissolved in toluene. An aqueous solution of  $\text{NaBH}_4$  was prepared by dissolving 43 mg of  $\text{NaBH}_4$  powder in 10 mL of 0.2 M NaOH solution. In a typical synthesis of  $\text{Au}_{10}(\text{SeR})_{10}$  nanoclusters, a toluene solution of benzeneselenol (50 mM, 0.2 mL) and an aqueous solution of  $\text{HAuCl}_4$  (50 mM, 0.1 mL) were first mixed in 4.5 mL water with stirring, followed by adding 0.5 mL of DMF as the miscible solvent to facilitate the formation of selenolate-Au(I) complexes. An aqueous NaOH solution (1 M, 0.4 mL) and 4.8 mL of toluene were then introduced to the reaction mixture, followed by the addition of 0.1 mL of  $\text{NaBH}_4$  solution. The  $\text{Au}_{10}(\text{SeR})_{10}$  nanoclusters were collected after 3 hours and characterized. It is to be noted that the miscible solvent is not limited to DMF; other suitable miscible solvents including tetrahydrofuran and acetonitrile could also be used for the synthesis of  $\text{Au}_{10}(\text{SeR})_{10}$  nanoclusters. The characterization of  $\text{Au}_{10}(\text{SeR})_{10}$  nanoclusters are shown in Figs. 1, 2(a), 3(a) and 4.

### b) Preparation of $\text{Au}_{15}(\text{SeR})_{12}$ Nanoclusters

In a typical synthesis of  $\text{Au}_{15}(\text{SeR})_{12}$  nanoclusters, a toluene solution of benzeneselenol (50 mM, 0.1 mL) and an aqueous solution of  $\text{HAuCl}_4$  (50 mM, 0.1 mL) were first mixed in 2.5 mL of water with stirring, followed by adding 2.5 mL of DMF as the miscible solvent to facilitate the formation of selenolate-Au(I) complexes. An aqueous NaOH solution (1 M, 0.4 mL) and 4.8 mL of toluene were then introduced to the reaction mixture, followed by the addition of 0.1 mL of  $\text{NaBH}_4$  solution. The  $\text{Au}_{15}(\text{SeR})_{12}$  nanoclusters were collected after 3 hours and characterized accordingly.

Alternatively, the synthesis of  $\text{Au}_{15}(\text{SeR})_{12}$  nanoclusters may also be undertaken by the following procedure: a toluene solution of benzeneselenol (50 mM, 0.2 mL) and an aqueous solution of  $\text{HAuCl}_4$  (50 mM, 0.1 mL) were first mixed in 3 mL of water with stirring, followed by adding 2 mL of DMF as the miscible solvent to facilitate the formation of selenolate-Au(I) complexes. An aqueous NaOH solution (1 M, 0.05 mL) and 4.8 mL of toluene were then introduced to the reaction mixture, followed by the addition of 0.05 mL of  $\text{NaBH}_4$  solution. The  $\text{Au}_{15}(\text{SeR})_{12}$  nanoclusters were collected after 3 hours and characterized. The characterization of  $\text{Au}_{15}(\text{SeR})_{12}$  nanoclusters are shown in Figs. 1, 2(b), 3(b) and 4.

### c) Preparation of $\text{Au}_{18}(\text{SeR})_{14}$ Nanoclusters

In a typical synthesis of  $\text{Au}_{18}(\text{SeR})_{14}$  nanoclusters, a toluene solution of benzeneselenol (50 mM, 0.2 mL) and an aqueous solution of  $\text{HAuCl}_4$  (50 mM, 0.1 mL) were first mixed in 2 mL of water with stirring, followed by adding 3 mL of ethanol as the miscible solvent to facilitate the formation of selenolate-Au(I) complexes. An aqueous NaOH solution (1 M, 0.4 mL) and 4.8 mL of toluene were then introduced to the reaction mixture, followed by the addition of 0.1 mL of  $\text{NaBH}_4$  solution. The  $\text{Au}_{18}(\text{SeR})_{14}$  nanoclusters were collected after 3 hours and characterized.

Alternatively, the synthesis of  $\text{Au}_{18}(\text{SeR})_{14}$  nanoclusters could also be undertaken by the following procedure. A toluene solution of benzeneselenol (50 mM, 0.2 mL) and an aqueous solution of  $\text{HAuCl}_4$  (50 mM, 0.1 mL) were first mixed in 3.5 mL of water with stirring, followed by adding 1.5 mL of DMF as the miscible solvent to facilitate the formation of selenolate-Au(I) complexes. An aqueous NaOH solution (1 M, 0.4 mL) and 4.8 mL of DCE were then introduced to the reaction mixture, followed by the addition of 0.1 mL of  $\text{NaBH}_4$  solution. The  $\text{Au}_{18}(\text{SeR})_{14}$  nanoclusters were collected after 3 hours and characterized. The characterization of  $\text{Au}_{18}(\text{SeR})_{14}$  nanoclusters are shown in Figs. 1, 2(c), 3(c) and 4.

### d) Preparation of $\text{Au}_{23}(\text{SeR})_{16}$ Nanoclusters

In a typical synthesis of  $\text{Au}_{23}(\text{SeR})_{16}$  nanoclusters, a toluene solution of benzeneselenol (50 mM, 0.1 to 0.2 mL) and an aqueous solution of  $\text{HAuCl}_4$  (50 mM, 0.1 mL) were first mixed in 1 mL of water with stirring, followed by adding 4 mL of DMF as the miscible solvent to facilitate the formation of selenolate-Au(I) complexes. An aqueous NaOH solution (1 M, 0.4 mL) and 4.8 mL of toluene were then introduced to the reaction mixture, followed by the addition of 0.1 mL of  $\text{NaBH}_4$  solution. The  $\text{Au}_{23}(\text{SeR})_{16}$  nanoclusters were collected after 3 hours and characterized. The characterization of  $\text{Au}_{23}(\text{SeR})_{16}$  nanoclusters are shown in Figs. 1, 2(d), 3(d) and 4.

### e) Preparation of $\text{Au}_{25}(\text{SeR})_{18}$ Nanoclusters

In a typical synthesis of  $\text{Au}_{25}(\text{SeR})_{18}$  nanoclusters, a toluene solution of benzeneselenol (50 mM, 0.2 mL) and an aqueous solution of  $\text{HAuCl}_4$  (50 mM, 0.1 mL) were first mixed in 0.5 mL of water with stirring, followed by adding 4.5 mL of ethanol or acetonitrile as the miscible solvent to facilitate the formation of selenolate-Au(I) complexes. An aqueous NaOH solution (1 M, 0.4 mL) and 4.8 mL of toluene were then introduced to the reaction mixture, followed by the addition of 0.1 mL of  $\text{NaBH}_4$  solution. The  $\text{Au}_{25}(\text{SeR})_{18}$  nanoclusters were collected after 3 hours and characterized.

Alternatively, the synthesis of  $\text{Au}_{25}(\text{SeR})_{18}$  nanoclusters could also be achieved by changing the organic phase from toluene to DCM or DCE as follows. A toluene solution of benzeneselenol (50 mM, 0.2 mL) and an aqueous solution of  $\text{HAuCl}_4$  (50 mM, 0.1 mL) were first mixed in (i)

2.5 mL of water with stirring, followed by adding 2.5 mL of DMF (i), or (ii) 3 mL of water with stirring, followed by adding 1.5 mL of DMF as the miscible solvent to facilitate the formation of selenolate-Au(I) complexes. An aqueous NaOH solution (1 M, 0.4 mL) and 4.8 mL of (i) DCM or (ii) DCE were then introduced to the reaction mixture, followed by the addition of 0.1 mL of NaBH<sub>4</sub> solution. The Au<sub>25</sub>(SeR)<sub>18</sub> nanoclusters were collected after 3 hours and characterized. The characterization of Au<sub>25</sub>(SeR)<sub>18</sub> nanoclusters are shown in Figs. 1, 2(e), 3(e) and 4.

#### f) Preparation of Au<sub>31</sub>(SeR)<sub>20</sub> Nanoclusters

In a typical synthesis of Au<sub>31</sub>(SeR)<sub>20</sub> nanoclusters, a toluene solution of benzeneselenol (50 mM, 0.2 mL) and an aqueous solution of HAuCl<sub>4</sub> (50 mM, 0.1 mL) were first mixed in 3.5 mL of methanol with stirring, followed by adding 1.5 mL of DMF as the miscible solvent to facilitate the formation of selenolate-Au(I) complexes. An aqueous NaOH solution (1 M, 0.4 mL) and 4.8 mL of toluene were then introduced to the reaction mixture, followed by the addition of 0.1 mL of NaBH<sub>4</sub> solution. The Au<sub>31</sub>(SeR)<sub>20</sub> nanoclusters were collected after 3 hours and characterized accordingly. The characterization of Au<sub>31</sub>(SeR)<sub>20</sub> nanoclusters are shown in Figs. 1, 2(f), 3(f) and 4.

#### g) Preparation of Au<sub>40</sub>(SeR)<sub>24</sub> Nanoclusters

In a typical synthesis of Au<sub>40</sub>(SeR)<sub>24</sub> nanoclusters, a toluene solution of benzeneselenol (50 mM, 0.1 to 0.2 mL) and an aqueous solution of HAuCl<sub>4</sub> (50 mM, 0.1 mL) were first mixed in 0.5 mL of water with stirring, followed by adding 4.5 mL of DMF as the miscible solvent to facilitate the formation of selenolate-Au(I) complexes. An aqueous NaOH solution (1 M, 0.4 mL) and 4.8 mL of toluene were then introduced to the reaction mixture, followed by the addition of 0.1 mL of NaBH<sub>4</sub> solution. The Au<sub>40</sub>(SeR)<sub>24</sub> nanoclusters were collected after 3 hours and characterized accordingly.

As an alternative, the synthesis of Au<sub>40</sub>(SeR)<sub>24</sub> nanoclusters described above could also be undertaken by changing the organic phase from toluene to DCM or DCE, while maintaining all other parameters and conditions. The characterization of Au<sub>40</sub>(SeR)<sub>24</sub> nanoclusters are shown in Figs. 1, 2(g), 3(g) and 4.

#### h) Preparation of Au<sub>61</sub>(SeR)<sub>31</sub> Nanoclusters

In a typical synthesis of Au<sub>61</sub>(SeR)<sub>31</sub> nanoclusters, a toluene solution of benzeneselenol (50 mM, 0.1–0.2 mL) and an aqueous solution of HAuCl<sub>4</sub> (50 mM, 0.1 mL) were first mixed in 5 mL of DMF with stirring to form selenolate-Au(I) complexes. An aqueous NaOH solution (1 M, 0.4 mL) and 4.8 mL of toluene were then introduced to the reaction mixture, followed by the addition of 0.1 mL of NaBH<sub>4</sub> solution. The Au<sub>61</sub>(SeR)<sub>31</sub> nanoclusters were collected after 3 hours and characterized accordingly. The characterization of Au<sub>61</sub>(SeR)<sub>31</sub> nanoclusters are shown in Figs. 1, 2(h), 3(h) and 4.

#### Analysis of nanoclusters obtained in methods a) to h)

As shown in Fig. 1a, the nanoclusters products obtained in methods a) to h) exhibited distinctive absorption features, which was in sharp contrast to those Au nanocrystals with sizes of > 2 nm (surface plasmon resonance band at ~520 nm), ruling out the possibility that the products were large-sized Au nanocrystals. Transmission electron microscopy (TEM) analysis shown in Fig. 2

revealed that the eight Au samples were below 2 nm in size, clearly confirming the formation of Au nanoclusters. In the UV-vis absorption spectra of the samples, a red shift in optical absorption from 345 nm to 823 nm was observed (Fig. 1a, from top to bottom) except for sample Au<sub>25</sub>(SeR)<sub>18</sub> and Au<sub>31</sub>(SeR)<sub>20</sub>, confirming the gradual decrease in energy gaps of the nanoclusters and suggesting the increase in their cluster sizes. While sample Au<sub>25</sub>(SeR)<sub>18</sub> has a typical absorption feature of selenolated Au<sub>25</sub> nanoclusters, the UV-vis absorption of sample Au<sub>61</sub>(SeR)<sub>31</sub> was featureless, which implied that this sample either has the largest cluster size among these eight samples or has a polydispersity in size.

Electrospray ionization mass spectrometry (ESI-MS) was further employed to determine the cluster size of the as-synthesized Au nanoclusters in atomic precision. As shown in Fig. 1b, these selenolated Au nanoclusters generally displayed one set of intense peak in the range of  $m/z$  2500–10000, corroborating the high monodispersity of the as-synthesized Au nanoclusters. Typically, the intense peaks were located at  $m/z$  ~3663 for sample #1 (Au<sub>10</sub>(SeR)<sub>10</sub> nanoclusters), 4827 for sample #2 (Au<sub>15</sub>(SeR)<sub>12</sub> nanoclusters), 5863 for sample #3 (Au<sub>18</sub>(SeR)<sub>14</sub> nanoclusters), 7027 for sample #4 (Au<sub>23</sub>(SeR)<sub>16</sub> nanoclusters), 7733 for sample #5 (Au<sub>25</sub>(SeR)<sub>18</sub> nanoclusters), 9227 for sample #6 (Au<sub>31</sub>(SeR)<sub>20</sub> nanoclusters), 5812 for sample #7 (Au<sub>40</sub>(SeR)<sub>24</sub> nanoclusters), and 8426 for sample #8 (Au<sub>61</sub>(SeR)<sub>31</sub> nanoclusters), which can be assigned to [Au<sub>10</sub>(SeR)<sub>10</sub>Cs]<sup>+</sup>, [Au<sub>15</sub>(SeR)<sub>12</sub>]<sup>-</sup>, [Au<sub>18</sub>(SeR)<sub>14</sub>Cs]<sup>+</sup>, [Au<sub>23</sub>(SeR)<sub>16</sub>]<sup>-</sup>, [Au<sub>25</sub>(SeR)<sub>18</sub>]<sup>-</sup>, [Au<sub>31</sub>(SeR)<sub>20</sub>]<sup>-</sup>, [Au<sub>40</sub>(SeR)<sub>24</sub>]<sup>2-</sup>, and [Au<sub>61</sub>(SeR)<sub>31</sub>]<sup>2-</sup>, respectively. The detailed assignments are presented in Figs. 3a to 3h.

In this example, the size-tuning of selenolated Au nanoclusters in such a broad range (from Au<sub>10</sub> to Au<sub>61</sub>) was unprecedentedly achieved by simply varying the miscible solvent within the two-phase synthesis system. The oxidation state of Au in these eight nanoclusters samples was between Au(0) and Au(I), and displayed a shift towards lower binding energy with increasing cluster size as determined by X-ray photoelectron spectroscopy (XPS) (refer to Fig. 4).

For sample #6 above, the two sets of intense peaks at  $m/z$  ~7027 and ~7733 observed in ESI mass spectrum could be assigned to [Au<sub>23</sub>(SeR)<sub>16</sub>]<sup>-</sup> (Fig. 3d) and [Au<sub>25</sub>(SeR)<sub>18</sub>]<sup>-</sup> (Fig. 3e), respectively. Considering that the optical features of sample #6, including the UV-vis absorption and the solution color (dark green) were different from that of the Au<sub>23</sub>(SeR)<sub>16</sub> (i.e., sample #4, dark brown in solution color) and Au<sub>25</sub>(SeR)<sub>18</sub> (i.e., sample #5, reddish in solution color), it is speculated that sample #6 was Au<sub>31</sub>(SeR)<sub>20</sub> with a relatively poor stability, and the peaks of Au<sub>23</sub>(SeR)<sub>16</sub> and Au<sub>25</sub>(SeR)<sub>18</sub> in the ESI spectrum of sample #6 were derived from fragmentation during the ionization process in ESI analysis. This speculation was further corroborated by X-ray photoelectron spectroscopy (XPS) quantitative elemental analysis. The elemental analysis of sample #6 showed a molar ratio of Au/Se of ~1.53, which was quite close to the molar ratio estimated for Au<sub>31</sub>(SeR)<sub>20</sub> (~1.55), instead of Au<sub>23</sub>(SeR)<sub>16</sub> (~1.44) and Au<sub>25</sub>(SeR)<sub>18</sub> (~1.39).

## Example 2: Preparation of Thiolate-Protected Au Nanoclusters

In addition to selenolated Au nanoclusters described in Example 1, the solvent-directed two-phase synthesis protocol described in the present disclosure is also capable of generating size-tunable thiolated Au nanoclusters. Detailed preparation of thiolate-protected Au nanoclusters is as described below.

**a) Preparation of Au<sub>10</sub>(SR)<sub>10</sub> Nanoclusters**

In a typical synthesis of Au<sub>10</sub>(SR)<sub>10</sub> nanoclusters, a toluene solution of 4-tert-butylbenzenethiol (50 mM, 0.2 mL) and an aqueous solution of HAuCl<sub>4</sub> (50 mM, 0.1 mL) were first mixed in 4.5 mL of water with stirring, followed by the addition of 0.5 mL of DMF as the miscible solvent to facilitate the formation of thiolate-Au(I) complexes. An aqueous NaOH solution (1 M, 0.4 mL) and 4.8 mL of toluene were then introduced to the reaction mixture, followed by the addition of 0.1 mL of NaBH<sub>4</sub> solution. The Au<sub>10</sub>(SR)<sub>10</sub> nanoclusters were collected after 3 hours and characterized accordingly. The characterization of Au<sub>10</sub>(SR)<sub>10</sub> nanoclusters are depicted in Figs. 5 and 6(a).

**b) Preparation of Au<sub>15</sub>(SR)<sub>13</sub> Nanoclusters**

Au<sub>15</sub>(SR)<sub>13</sub> nanoclusters were prepared according to the following procedure: a toluene solution of 4-tert-butylbenzenethiol (50 mM, 0.2 mL) and an aqueous solution of HAuCl<sub>4</sub> (50 mM, 0.1 mL) were first mixed in 3 mL of water with stirring, followed by the addition of 2 mL of DMF as the miscible solvent to facilitate the formation of thiolate-Au(I) complexes. An aqueous NaOH solution (1 M, 0.4 mL) and 4.8 mL of toluene were then introduced to the reaction mixture, followed by the addition of 0.1 mL of NaBH<sub>4</sub> solution. The Au<sub>15</sub>(SR)<sub>13</sub> nanoclusters were collected after 3 hours and then characterized. The characterization of Au<sub>15</sub>(SR)<sub>13</sub> nanoclusters are depicted in Figs. 5 and 6(b).

**c) Preparation of Au<sub>28</sub>(SR)<sub>20</sub> NCs**

Au<sub>28</sub>(SR)<sub>20</sub> nanoclusters were prepared by mixing a toluene solution of 4-tert-butylbenzenethiol (50 mM, 0.2 mL) and an aqueous solution of HAuCl<sub>4</sub> (50 mM, 0.1 mL) in 3.5 mL of water under stirring condition, followed by the addition of 1.5 mL of DMF as the miscible solvent to facilitate the formation of thiolate-Au(I) complexes. An aqueous NaOH solution (1 M, 0.4 mL) and 4.8 mL of toluene were then introduced to the reaction mixture, followed by the addition of 0.1 mL of NaBH<sub>4</sub> solution. The Au<sub>28</sub>(SR)<sub>20</sub> nanoclusters were collected after 3 hours and characterized accordingly. The characterization of Au<sub>28</sub>(SR)<sub>20</sub> nanoclusters are depicted in Figs. 5 and 6(c).

**d) Preparation of Au<sub>30</sub>(SR)<sub>22</sub> Nanoclusters**

Au<sub>30</sub>(SR)<sub>22</sub> nanoclusters were synthesized by mixing a toluene solution of 4-tert-butylbenzenethiol (50 mM, 0.2 mL) and an aqueous solution of HAuCl<sub>4</sub> (50 mM, 0.1 mL) in 1 mL of water with stirring, followed by the addition of 4 mL of DMF as the miscible solvent to facilitate the formation of thiolate-Au(I) complexes. An aqueous NaOH solution (1 M, 0.4 mL) and 4.8 mL of toluene were then introduced to the reaction mixture, followed by the addition of 0.1 mL of NaBH<sub>4</sub> solution. The Au<sub>30</sub>(SR)<sub>22</sub> nanoclusters were collected after 3 hours and characterized accordingly. The characterization of Au<sub>30</sub>(SR)<sub>22</sub> nanoclusters are depicted in Figs. 5 and 6(d).

**e) Preparation of Au<sub>42</sub>(SR)<sub>26</sub> Nanoclusters**

In a typical synthesis of Au<sub>42</sub>(SR)<sub>26</sub> nanoclusters, a toluene solution of 4-tert-butylbenzenethiol (50 mM, 0.2 mL) and an aqueous solution of HAuCl<sub>4</sub> (50 mM, 0.1 mL) were first mixed in 0.5 mL of water with stirring, followed by the addition of 4.5 mL of DMF as the miscible solvent to facilitate the formation of thiolate-Au(I) complexes. An

aqueous NaOH solution (1 M, 0.4 mL) and 4.8 mL of toluene were then introduced to the reaction mixture, followed by the addition of 0.1 mL of NaBH<sub>4</sub> solution. The Au<sub>42</sub>(SR)<sub>26</sub> nanoclusters were collected after 3 hours and characterized. The characterization of Au<sub>42</sub>(SR)<sub>26</sub> nanoclusters are depicted in Figs. 5 and 6(e).

#### 5 f) Preparation of Au<sub>23</sub>(S-*c*-C<sub>6</sub>H<sub>11</sub>)<sub>16</sub> Nanoclusters

Au<sub>23</sub>(S-*c*-C<sub>6</sub>H<sub>11</sub>)<sub>16</sub> nanoclusters were prepared by mixing a toluene solution of cyclohexanethiol (50 mM, 0.1 mL) and aqueous solution of HAuCl<sub>4</sub> (50 mM, 0.1 mL) in 1 mL of water with stirring, followed by the addition of 4 mL of DMF as the miscible solvent to facilitate the formation of thiolate-Au(I) complexes. An aqueous NaOH solution (1 M, 0.05 mL) and 4.8 mL of toluene were then introduced to the reaction mixture, followed by the addition of 0.1 mL of NaBH<sub>4</sub> solution. The Au<sub>23</sub>(S-*c*-C<sub>6</sub>H<sub>11</sub>)<sub>16</sub> nanoclusters were collected after 3 hours and characterized accordingly.

Alternatively, the synthesis of Au<sub>23</sub>(S-*c*-C<sub>6</sub>H<sub>11</sub>)<sub>16</sub> nanoclusters can also be undertaken by the following procedure. A toluene solution of cyclohexanethiol (50 mM, 0.2 mL) and an aqueous solution of HAuCl<sub>4</sub> (50 mM, 0.1 mL) were first mixed in 5 mL of DMF with stirring to form thiolate-Au(I) complexes. An aqueous NaOH solution (1 M, 0.4 mL) and 4.8 mL of toluene were then introduced to the reaction mixture, followed by the addition of 0.1 mL of NaBH<sub>4</sub> solution. The Au<sub>23</sub>(S-*c*-C<sub>6</sub>H<sub>11</sub>)<sub>16</sub> nanoclusters were collected after 3 hours and characterized. The characterization of Au<sub>23</sub>(S-*c*-C<sub>6</sub>H<sub>11</sub>)<sub>16</sub> nanoclusters are depicted in Fig. 7.

#### 20 g) Preparation of Au<sub>24</sub>(PET)<sub>20</sub> Nanoclusters

In a typical synthesis of Au<sub>24</sub>(PET)<sub>20</sub> nanoclusters, a toluene solution of 2-phenylethanethiol (PET, 50 mM, 0.2 mL) and an aqueous solution of HAuCl<sub>4</sub> (50 mM, 0.1 mL) were first mixed in 1.5 mL of water with stirring, followed by the addition of 3.5 mL of DMF as the miscible solvent to facilitate the formation of thiolate-Au(I) complexes. An aqueous NaOH solution (1 M, 0.05 mL) and 4.8 mL of toluene were then introduced to the reaction mixture, followed by the addition of 0.1 mL of NaBH<sub>4</sub> solution. The Au<sub>24</sub>(PET)<sub>20</sub> nanoclusters were collected after 3 hours and characterized. The characterization of Au<sub>24</sub>(PET)<sub>20</sub> nanoclusters are shown in Fig. 8.

#### h) Preparation of Au<sub>25</sub>(MBT)<sub>18</sub> Nanoclusters

Au<sub>25</sub>(MBT)<sub>18</sub> nanoclusters were synthesized by mixing a toluene solution of 4-methylbenzenethiol (MBT, 50 mM, 0.2 mL) and an aqueous solution of HAuCl<sub>4</sub> (50 mM, 0.1 mL) in 0.5 mL of water with stirring, followed by the addition of 4.5 mL of DMF as the miscible solvent to facilitate the formation of thiolate-Au(I) complexes. An aqueous NaOH solution (1 M, 0.4 mL) and 4.8 mL of toluene were then introduced to the reaction mixture, followed by the addition of 0.1 mL of NaBH<sub>4</sub> solution. The Au<sub>25</sub>(MBT)<sub>18</sub> nanoclusters were collected after 3 hours and characterized accordingly. The characterization of Au<sub>25</sub>(MBT)<sub>18</sub> nanoclusters are shown in Fig. 9.

### Example 3: Preparation of Phosphine-Protected Au Nanoclusters: Au<sub>11</sub>(PPh<sub>3</sub>)<sub>8</sub>Cl<sub>2</sub> Nanoclusters

Au<sub>11</sub>(PPh<sub>3</sub>)<sub>8</sub>Cl<sub>2</sub> nanoclusters were prepared by mixing a toluene solution of triphenylphosphine (PPh<sub>3</sub>, 50 mM, 0.2 mL) and an aqueous solution of HAuCl<sub>4</sub> (50 mM, 0.1 mL) in 1 mL of water with stirring, followed by the addition of 4 mL of DMF as the miscible solvent to facilitate the

formation of  $\text{PPh}_3\text{-Au(I)}$  complexes. An aqueous NaOH solution (1 M, 0.4 mL) and 4.8 mL of toluene were then introduced to the reaction mixture, followed by the addition of 0.02 mL of  $\text{NaBH}_4$  solution. The  $\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2$  nanoclusters were collected after 3 hours and characterized accordingly. The characterization of  $\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2$  nanoclusters are shown in Fig. 10.

- 5 As can be seen from Examples 2 and 3, by using 4-tert-butylbenzenethiol (HSR) as a model ligand, five Au NC species:  $\text{Au}_{10}(\text{SR})_{10}$ ,  $\text{Au}_{15}(\text{SR})_{13}$ ,  $\text{Au}_{28}(\text{SR})_{20}$ ,  $\text{Au}_{30}(\text{SR})_{22}$  and  $\text{Au}_{42}(\text{SR})_{26}$ , can be synthesized by simply tuning the proportion of the miscible solvent (e.g., DMF) in aqueous phase (refer to Example 2, parts (a) to (e) and Figs. 5 and 6). It should be noted that the method described herein is very versatile and has significant flexibility in ligand selection (e.g., other
- 10 hydrophobic thiolate and phosphine ligands). For instance, by using cyclohexanethiol ( $\text{HS-}c\text{-C}_6\text{H}_{11}$ ), 2-phenylethanethiol (PET), 4-methylbenzenethiol (MBT), and triphenylphosphine ( $\text{PPh}_3$ ) as protecting *cum* phase transfer ligands,  $\text{Au}_{23}(\text{S-}c\text{-C}_6\text{H}_{11})_{16}$ ,  $\text{Au}_{24}(\text{PET})_{20}$ ,  $\text{Au}_{25}(\text{MBT})_{18}$ ,  $\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2$  nanoclusters could be synthesized, respectively (refer to Figs. 7 to 10). In addition to engineering the outside monolayer of Au nanoclusters from selenolate, thiolate to
- 15 phosphine, the inner metal core of nanoclusters can also be replaced from gold to silver and copper within the synthetic system described herein. For example, monodisperse  $\text{Ag}_{44}(\text{SeR})_{30}$  and  $\text{Cu}_{27}(\text{SeR})_{17}$  nanoclusters could be derived by this method as described in Examples 4 and 5.

#### Example 4: Preparation of Selenolate-Protected Ag Nanoclusters

- $\text{Ag}_{44}(\text{SeR})_{30}$  nanoclusters were prepared by mixing a toluene solution of benzeneselenol (50 mM, 0.2 mL) and an aqueous solution of  $\text{AgNO}_3$  (50 mM, 0.1 mL) in 0.5 mL of water with stirring, followed by the addition of 4.5 mL of DMF as the miscible solvent to facilitate the formation of selenolate-Ag(I) complexes. 4.8 mL of DCM and an aqueous NaOH solution (1 M, 0.05 mL) were then introduced to the reaction mixture, followed by the addition of 0.1 mL of  $\text{NaBH}_4$  solution. The  $\text{Ag}_{44}(\text{SeR})_{30}$  nanoclusters were collected after 3 hours and
- 20 characterized. The characterization of  $\text{Ag}_{44}(\text{SeR})_{30}$  nanoclusters are shown in Fig. 11.
- 25

#### Example 5: Preparation of Selenolate-Protected Cu Nanoclusters

- In a typical synthesis of  $\text{Cu}_{27}(\text{SeR})_{17}$  nanoclusters, a toluene solution of benzeneselenol (50 mM, 0.2 mL) and an aqueous solution of  $\text{CuSO}_4$  (50 mM, 0.1 mL) were first mixed in 2 mL of water with stirring, followed by the addition of 3 mL of DMF as the miscible solvent to
- 30 facilitate the formation of selenolate-Cu(I) complexes. An aqueous NaOH solution (1 M, 0.05 mL) and 4.8 mL of toluene were then introduced to the reaction mixture, followed by the addition of 0.075 mL of  $\text{NaBH}_4$  solution. The  $\text{Cu}_{27}(\text{SeR})_{17}$  nanoclusters were collected after 3 hours and characterized accordingly. The characterization of  $\text{Cu}_{27}(\text{SeR})_{17}$  nanoclusters are shown in Fig. 12.

#### 35 Example 6: Robustness and Scalability of the Synthetic Method

- To investigate the robustness and scalability of the synthetic method described above, concentrations of selenolate-Au(I) complexes and ligand/Au ratios used in the synthesis of  $\text{Au}_{40}(\text{SeR})_{24}$  nanoclusters were varied as described below. It is to be understood that when the concentrations of selenolate-Au(I) complexes and/ or the ligand/Au ratios were varied, all other
- 40 parameters remained unchanged. In addition, the preparation of the  $\text{Au}_{40}(\text{SeR})_{24}$  nanoclusters was scaled up to 2 L as compared to the typical synthesis scale as described in the previous examples. During the scaling up, it is to be understood that all parameters were adjusted

accordingly. Therefore, when desired, it may be possible to prepare the metal nanoclusters as defined herein at a higher scale such as in a 200-L reactor or 2,000-L reactor scale.

As shown in Figs. 13(a) and 14(a), the absorption spectra of  $\text{Au}_{40}(\text{SeR})_{24}$  nanoclusters synthesized using different concentrations of selenolate-Au(I) complexes (from 1 to 5 mM) and different ligand/Au ratios (from 1:1 to 2:1) were nearly identical. ESI mass spectra results further confirmed that the quality of  $\text{Au}_{40}(\text{SeR})_{24}$  nanoclusters were unaffected by the different selenolate-Au(I) complex concentrations and ligand/Au ratios (refer to Figs. 13(b) and 14(b), confirming the high-quality of  $\text{Au}_{40}(\text{SeR})_{24}$  nanoclusters synthesized under such reaction conditions and the robustness of the synthetic method.

Similarly, when the synthesis of the  $\text{Au}_{40}(\text{SeR})_{24}$  nanoclusters described in Example 1(g) was scaled up to 2L, the UV-vis and ESI analysis of the obtained  $\text{Au}_{40}(\text{SeR})_{24}$  nanoclusters revealed that the corresponding spectra were nearly identical to those obtained in Example 1(g) suggesting that the quality of  $\text{Au}_{40}(\text{SeR})_{24}$  nanoclusters remained unchanged (refer to Fig. 15).

## Example 7: Effect of the Solvent on the Synthetic Method

### a) Effect of Miscible Solvent

The role of the miscible solvent was investigated. Without the addition of the miscible solvent to the reaction mixture, no Au nanoclusters was obtained after 3 hours of reaction (refer to Fig. 16). This indicated that the miscible solvent played a vital role in the reduction of hydrophobic selenolate-Au(I) complexes to selenolated Au nanoclusters by hydrophilic  $\text{NaBH}_4$ . The ESI mass spectrum in Fig. 16(b) showed that no  $\text{Au}_{40}(\text{SeR})_{24}$  nanoclusters were formed, and only selenolate-Au(I) complexes smaller than  $\text{Au}_8(\text{SeR})_9$  were obtained in this experiment. This illustrated the critical role of the miscible solvent in this two-phase synthesis method.

$^1\text{H}$  nuclear magnetic resonance (NMR) technique was employed to detect the location of the reactants in the two-phase system. As shown in Fig. 17, hydrophilic  $\text{NaBH}_4$  (peak at around 0 ppm) was not detected in the organic phase even after adding the miscible solvent in the two-phase system (refer to Fig. 17(e)). This clearly indicated that the miscible solvent was not able to carry the reducing agent  $\text{NaBH}_4$  into the organic phase. On the other hand, the selenolate-Au(I) complexes (peak at 7.2 ppm) could only be detected in the organic phase based on  $^1\text{H}$  NMR analysis (refer to Fig. 17(i)), which was further corroborated by inductively coupled plasma mass spectrometry (ICP-MS) results (97.6% of phase transfer efficiency of the Au species by the selenolate ligand). Therefore, it can be concluded that the reduction reaction occurred at the interface between the aqueous phase and the organic phase, and the miscible solvent served as a “go-between” and facilitated the interaction between hydrophilic  $\text{NaBH}_4$  and hydrophobic selenolate-Au(I) complexes at the interface. The working principle of the method described herein is substantially different from that of Brust-Schiffrin synthesis where the reduction of Au(I) complexes was supposed to occur in reverse micelles of TOAB in which hydrophilic  $\text{NaBH}_4$  was encapsulated.

It was found that the variation of the miscible solvent could influence the size distributions of selenolate-Au(I) complexes. To further investigate this, the selenolate-Au(I) complexes of those 8 selenolated-Au NC samples (of Examples 1(a) to 1(h)) before  $\text{NaBH}_4$  reduction by using ESI mass spectrometry. All species of selenolate-Au(I) complexes presented in each spectrum were

labelled and identified (refer to Figs. 18 and 19), and the size distributions of these selenolate-Au(I) complexes were summarized in Table 1 below.

**Table 1.** Summary of size distributions of selenolate-Au(I) complex precursors for 8 monodisperse selenolated Au nanoclusters.

| Size Distributions |                                                    | Complexes of     |                  |                  |                  |                  |                  |                  |                  |
|--------------------|----------------------------------------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
|                    |                                                    | Au <sub>10</sub> | Au <sub>15</sub> | Au <sub>18</sub> | Au <sub>23</sub> | Au <sub>25</sub> | Au <sub>31</sub> | Au <sub>40</sub> | Au <sub>61</sub> |
| Small              | Au <sub>1</sub> (SeR) <sub>1</sub>                 |                  | ✓                | ✓                | ✓                | ✓                | ✓                | ✓                | ✓                |
|                    | Au <sub>1</sub> (SeR) <sub>2</sub>                 | ✓                | ✓                | ✓                | ✓                | ✓                | ✓                | ✓                | ✓                |
|                    | Au <sub>2</sub> (SeR) <sub>1</sub> Cl <sub>2</sub> |                  |                  |                  |                  |                  |                  | ✓                |                  |
|                    | Au <sub>2</sub> (SeR) <sub>2</sub>                 |                  |                  |                  |                  |                  |                  |                  | ✓                |
|                    | Au <sub>2</sub> (SeR) <sub>3</sub>                 | ✓                | ✓                |                  | ✓                | ✓                | ✓                | ✓                | ✓                |
|                    | Au <sub>3</sub> (SeR) <sub>2</sub> Cl <sub>2</sub> |                  |                  |                  |                  |                  |                  | ✓                |                  |
|                    | Au <sub>3</sub> (SeR) <sub>3</sub> Cl              |                  |                  |                  |                  |                  |                  | ✓                |                  |
|                    | Au <sub>3</sub> (SeR) <sub>4</sub>                 |                  | ✓                |                  | ✓                | ✓                | ✓                | ✓                |                  |
|                    | Au <sub>3</sub> (SeR) <sub>5</sub>                 |                  | ✓                | ✓                | ✓                | ✓                | ✓                | ✓                | ✓                |
|                    | Au <sub>4</sub> (SeR) <sub>4</sub>                 |                  |                  |                  | ✓                |                  |                  |                  | ✓                |
|                    | Au <sub>4</sub> (SeR) <sub>5</sub> Cl              |                  |                  |                  | ✓                | ✓                | ✓                |                  |                  |
|                    | Au <sub>5</sub> (SeR) <sub>5</sub>                 |                  |                  |                  |                  | ✓                | ✓                |                  | ✓                |
|                    | Au <sub>5</sub> (SeR) <sub>7</sub>                 |                  |                  |                  |                  |                  |                  |                  | ✓                |
|                    | Au <sub>6</sub> (SeR) <sub>4</sub> Cl              |                  |                  |                  | ✓                |                  |                  |                  |                  |
|                    | Au <sub>6</sub> (SeR) <sub>7</sub>                 |                  |                  |                  |                  | ✓                |                  |                  | ✓                |
|                    | Au <sub>6</sub> (SeR) <sub>8</sub>                 |                  |                  |                  |                  |                  |                  |                  | ✓                |
|                    | Au <sub>7</sub> (SeR) <sub>8</sub>                 |                  |                  |                  |                  |                  |                  |                  |                  |
|                    | Au <sub>7</sub> (SeR) <sub>9</sub>                 |                  |                  |                  |                  |                  |                  |                  | ✓                |
|                    | Au <sub>8</sub> (SeR) <sub>5</sub> Cl              |                  |                  |                  |                  | ✓                |                  | ✓                |                  |
|                    | Au <sub>8</sub> (SeR) <sub>9</sub>                 |                  |                  |                  | ✓                | ✓                | ✓                |                  | ✓                |
|                    | Au <sub>9</sub> (SeR) <sub>9</sub> Cl              |                  |                  |                  |                  |                  |                  | ✓                |                  |
|                    | Au <sub>9</sub> (SeR) <sub>10</sub>                |                  |                  |                  | ✓                | ✓                | ✓                | ✓                | ✓                |
|                    | Au <sub>10</sub> (SeR) <sub>10</sub> Cl            |                  |                  |                  |                  | ✓                |                  | ✓                |                  |
|                    | Au <sub>10</sub> (SeR) <sub>11</sub>               |                  |                  |                  |                  | ✓                | ✓                |                  | ✓                |
|                    | Au <sub>11</sub> (SeR) <sub>11</sub> Cl            |                  |                  |                  |                  |                  |                  | ✓                |                  |
|                    | Au <sub>11</sub> (SeR) <sub>12</sub>               |                  |                  |                  |                  | ✓                |                  |                  | ✓                |
| Large              |                                                    |                  |                  |                  |                  |                  |                  |                  |                  |

For Au<sub>10</sub>, Au<sub>15</sub>, and Au<sub>18</sub> samples, the selenolate-Au(I) complex precursors were smaller than Au<sub>4</sub>(SeR)<sub>6</sub>, while those for the other 5 samples (i.e., Au<sub>23</sub>, Au<sub>25</sub>, Au<sub>31</sub>, Au<sub>40</sub>, and Au<sub>61</sub>) have broad size distributions ranging from Au<sub>1</sub>(SeR)<sub>1</sub> to Au<sub>11</sub>(SeR)<sub>12</sub>. The difference in size distributions could be attributed to the variation of miscible solvent in the reaction system. Fig. 20 shows that the shifts of the H<sub>2</sub>O peak (from (a) ~ 0.82 ppm to (e) ~ 4 ppm) and the DMF peak (from (c) ~ 7.6 ppm to (e) ~ 7.86 ppm), along with the gradual increase in the H<sub>2</sub>O peak and DMF peak intensities (from (a) to (e)). This illustrated the proportional increase of DMF and water in the organic phase with the increasing introduction of DMF to the two-phase reaction system. The proportional increase of DMF and water in the organic phase could vary the solvent polarities of the organic phase, which could further affect the size distributions of the selenolate-Au(I) complexes in the organic phase.

From NMR quantitative analysis shown in Fig. 20, it can be deduced that introduction of more miscible solvent to the two-phase system resulted in a slight increase of the miscible solvent and water in the organic phase, and the corresponding variation in solvent polarity of the organic phase could be the main reason for the changes in size distributions for the selenolate-Au(I) complexes.

In addition, it was found that the miscible solvent could control the reduction kinetics of the reaction. It was observed that the reduction of selenolate-Au(I) complexes proceeded faster if more miscible solvent was added to the reaction system, as evidenced by the quick color change of the interface from colorless to brown. This fact was not unexpected considering that the chance of encounter between hydrophilic  $\text{NaBH}_4$  and hydrophobic selenolate-Au(I) complexes was significantly enhanced with an increase in the miscible solvent. Furthermore, this experiment showed that more miscible solvent resulted in larger Au nanoclusters. For example, if 5 mL of DMF was added to the reaction system,  $\text{Au}_{61}(\text{SeR})_{31}$  nanoclusters could be obtained, while only  $\text{Au}_{10}(\text{SeR})_{10}$  nanoclusters were derived if 0.5 mL of DMF was introduced. This phenomenon could be explained as follows. Introduction of more miscible solvent to the system facilitated the reduction due to the solvent-driven contact between hydrophobic selenolate-Au(I) complexes and hydrophilic  $\text{NaBH}_4$  at the interface, which led to the formation of larger Au nanoclusters. In contrast, introduction of less miscible solvent rendered the reduction reaction relatively difficult. On the other hand, free selenolate ligands in organic phase could simultaneously and sufficiently digest the Au nanoclusters. Such an unequilibrated reduction-digestion process led to Au nanoclusters that were smaller in size.

Based on the above, the miscible solvent has three functions in the method disclosed herein:

- (i) it acts as a “go-between” and makes the encounter and reduction between hydrophilic  $\text{NaBH}_4$  and hydrophobic selenolate-Au(I) complexes possible,
- (ii) it modifies the size of selenolate-Au(I) complexes in the organic phase, and
- (iii) it controls the reduction kinetics of the selenolate-Au(I) complexes with  $\text{NaBH}_4$  by adjusting the number of “go-betweens” (i.e., the proportion of the miscible solvent) to regulate their frequency of encounters.

## **b) Effect of NaOH on the Formation of Selenolated Au Nanoclusters**

The functions of NaOH, aqueous phase were also identified. In this protocol, the role of NaOH was also significant for the formation of monodisperse Au nanoclusters. Like  $\text{NaBH}_4$ , NaOH was only present in aqueous phase due to its hydrophilicity. It could efficiently weaken the reducing power of  $\text{NaBH}_4$ , but prolonged its effectiveness through retarding the self-hydrolysis of  $\text{NaBH}_4$ .

In the previous examples, it has been demonstrated that high-quality selenolated Au nanoclusters with sizes of  $\text{Au}_{61}$  to  $\text{Au}_{15}$  could be synthesized under the same synthetic conditions if an appropriate amount of NaOH was introduced to the reaction system. In contrast, without NaOH in the system, the reduction reaction proceeded too fast and in an uncontrollable manner (e.g., could be finished in several seconds); monodisperse Au nanoclusters were not obtained in this case as shown in Fig. 21. Product #3 showed a typical surface plasmon resonance peak at 520 nm, indicating the formation of Au nanoparticles instead of nanoclusters. The solution color of the other samples also confirmed that Au nanoclusters were not formed in the organic phase (refer to Fig. 21(a)).

In view of the above, it can therefore be deduced that the aqueous phase containing  $\text{NaBH}_4$  and NaOH served as a reservoir for the reducing agents in the two-phase synthesis system described in the present disclosure.

### c) Effect of the Organic Phase on the Formation of Selenolated Au Nanoclusters

The function of organic phase in the method described above was revealed by a control experiment that did not involve the addition of organic phase. Fig. 22 shows that no high-quality nanoclusters were formed in the absence of organic phase, indicating the important role of organic phase in this two-phase synthetic method. It can therefore be deduced that the functions of the organic phase (e.g., toluene) are as follows:

- (i) storage of the selenolate-Au(I) complexes and the reduced Au nanoclusters,
- (ii) providing a benign environment for NC growth/digestion, and
- (iii) effective separation of Au species from the hydrophilic  $\text{NaBH}_4$  to prevent possible undue reactions.

An added advantage of this method was the spontaneous yet fast separation (i.e., within several seconds) of the Au NC species from hydrophilic interfering species (i.e.,  $\text{NaOH}$ ,  $\text{NaBH}_4$ , and  $\text{Cl}^-$ ), which allowed one to be able to not only stop the reduction reaction at the desired time points by removing the aqueous phase, but also collect and analyse the size or composition of Au NC samples instantly without post-purification procedures making investigations of the growth process of the Au nanoclusters possible.

### Example 8: Growth Process of Au Nanoclusters

In the method described herein, the growth processes of four larger Au NC species with good stabilities (selenolated  $\text{Au}_{23}$ ,  $\text{Au}_{25}$ ,  $\text{Au}_{40}$  and  $\text{Au}_{61}$ ) were monitored by UV-vis absorption spectroscopy and ESI-MS.

#### Growth Process of $[\text{Au}_{23}(\text{SeR})_{16}]^-$ Nanoclusters

The growth process of  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  nanoclusters was firstly studied. The UV-vis absorption spectra of the reaction solution showed a gradual rise in absorbance at  $\sim 600$  and  $\sim 800$  nm in the first 10 min (refer to Fig. 23(a)), indicating the formation and growth of selenolated Au nanoclusters. Between 10 min and 90 min, the UV-vis absorption spectra (Fig. 23(b)) primarily displayed the growth of distinct peaks of  $\text{Au}_{23}(\text{SeR})_{16}$  nanoclusters, and these peaks became progressively better defined between 90 min and 3 hours (Fig. 23(b)).

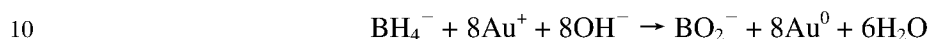
ESI-MS spectra of the reaction solution (Fig. 23(c) and 23(d)) were acquired with isotope resolution. In total, 22 species were identified (refer to Fig. 24 for assignment), and could be represented by the formula  $[\text{Au}_n(\text{SeR})_m]^q$  with valence electron count of  $N^* = n - m - q$ . As shown in Fig. 23(e), all Au precursor species (#1–18) are selenolate-Au(I) complexes with 0 valence electron (i.e., no Au(0) core), confirming that selenolate was capable of reducing Au(III) to Au(I) but incapable of reducing Au(I) to Au(0).

As shown in Figs. 23(c) and 23(d), the selenolate-Au(I) complexes ranged from  $\text{Au}_1(\text{SeR})_1$  to  $[\text{Au}_{11}(\text{SeR})_{12}]^-$  (i.e., species #1–18, black curves). However, those species larger than  $\text{Au}_3(\text{SeR})_4$  (species #9) disappeared once the  $\text{NaBH}_4$  was added (0 min), which revealed the strong reducing power of  $\text{NaBH}_4$ . In one minute after  $\text{NaBH}_4$  addition,  $[\text{Au}_{15}(\text{SeR})_{11}\text{Cl}_2]^0$  with  $2 e^-$  (species #19) and  $[\text{Au}_{15}(\text{SeR})_{12}]^-$  with  $4 e^-$  (species #20) were formed. Surprisingly,  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  species with an  $8 e^-$  shell closure began to emerge at 2.5 minutes after  $\text{NaBH}_4$  addition. Within 10 minutes after  $\text{NaBH}_4$  addition, the  $[\text{Au}_{15}(\text{SeR})_{11}\text{Cl}_2]^0$  and  $[\text{Au}_{15}(\text{SeR})_{12}]^-$

species grew to form  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  nanoclusters, which illustrated the rapid formation of  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  in the system. With further reaction, the peak of  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  increased, while the peaks of selenolate-Au(I) complexes gradually disappeared in the ESI-MS spectra, validating the improved yield and purity of  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  nanoclusters. Pure  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  nanoclusters could be obtained 3 hours after  $\text{NaBH}_4$  addition.

### 2x $e^-$ Jumping Mechanism

The unique 2x  $e^-$  jumping mechanism identified in the growth of  $[\text{Au}_n(\text{SeR})_m]^q$  nanoclusters within the  $\text{NaBH}_4$  reduction system could be ascribed to the feature of the  $\text{NaBH}_4$  in donating electrons. The reduction reaction of  $\text{NaBH}_4$  with Au(I) ions can be expressed as follows:



One  $\text{BH}_4^-$  anion can donate 8 electrons. In other words, one hydrogen species in  $\text{NaBH}_4$  can donate 2 electrons, which would be the minimum reaction unit. Hence, donation of electrons in  $\text{NaBH}_4$  always involves bi-electrons (i.e., 2  $e^-$ ). Moreover, unlike gaseous CO, which is a mild reducing agent (two electrons can be generated by one CO molecule), and the 2  $e^-$  jumping mechanism identified in the CO-mediated synthesis of Au nanoclusters,  $\text{NaBH}_4$  has strong reducing power. Therefore, more than one hydrogen species in  $\text{NaBH}_4$  could simultaneously donate electrons during the reduction reaction, and this resulted in the growth of  $[\text{Au}_n(\text{SeR})_m]^q$  nanoclusters with a sequential 2x  $e^-$  jumping mechanism (where  $x$  = number of reacting hydrogen species of  $\text{NaBH}_4$  molecules;  $x = 1, 2, 3, \dots$ ) within the  $\text{NaBH}_4$  reduction system.

It should be noted that this is the first disclosure on the 2x  $e^-$  jumping mechanism of Au NC growth in  $\text{NaBH}_4$  reduction system. In addition, the 2x  $e^-$  jumping mechanism of metal NC growth also elucidated the significant role of NaOH in the synthesis of monodisperse metal nanoclusters in  $\text{NaBH}_4$  reduction system. NaOH could weaken the reducing power of  $\text{NaBH}_4$ , and it enabled electron donation by the hydrogen species of  $\text{NaBH}_4$  to proceed in a mild fashion, which allowed the growth of metal nanoclusters via controllable 2x  $e^-$  jumping. Therefore, monodisperse metal nanoclusters could be easily obtained upon etching treatment. In contrast, without NaOH in the  $\text{NaBH}_4$  reduction system, abundant electrons could be simultaneously donated by  $\text{NaBH}_4$ ; metal nanoclusters would grow in size in an uncontrollable manner, leading to the formation of metal nanoclusters with a broad size distribution that could not be narrowed even after etching treatment.

As discussed above, the growth of  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  was driven by increasing the valence electron count of Au nanoclusters in sequential 2x  $e^-$  jumping ( $x = 0, 1$ , and 2; i.e.,  $0 e^- \rightarrow 2 e^- / 4 e^- \rightarrow 8 e^-$ ), which was different from the previously reported growth mechanism of Au nanoclusters within the CO-mediated reduction system whereby only sequential 2  $e^-$  jumping was observed. The 2x  $e^-$  jumping mechanism identified in the present system probably originated from the feature of the reducing agent  $\text{NaBH}_4$  in donating electrons. Interestingly, at 60 minutes, peak #22 (corresponding to  $\text{Au}_{25}(\text{SeR})_{18}$ ) emerged, but subsequently diminished at 90 minutes and vanished at 3 hours. Given that no  $\text{Au}_{15}(\text{SeR})_{11}\text{Cl}_2$  and  $\text{Au}_{15}(\text{SeR})_{12}$  intermediate (species #19 and #20) remained and only  $\text{Au}_{23}(\text{SeR})_{16}$  existed during this period (i.e., from 60 minutes to 3 hours), it is plausible that the  $[\text{Au}_{25}(\text{SeR})_{18}]^-$  species (8  $e^-$ ) was most likely converted from  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  nanoclusters (8  $e^-$ ).

The above observation suggested a reversible conversion process between  $[\text{Au}_{25}(\text{SeR})_{18}]^-$  nanoclusters and  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  nanoclusters under the 8  $e^-$  shell closure during this period.

Such phenomenon is discussed in more detail below. Nevertheless, the growth of  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  nanoclusters could be regarded as a size-focusing process (a typical principle in the synthesis of monodisperse metal nanoclusters) due to the combination of both the conversion of larger  $[\text{Au}_{25}(\text{SeR})_{18}]^-$  nanoclusters to  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  nanoclusters and the growth of smaller  $[\text{Au}_{15}(\text{SeR})_{12}]^-$  nanoclusters to  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  nanoclusters.

The growth processes of  $[\text{Au}_{25}(\text{SeR})_{18}]^-$  ( $8 e^-$ ),  $[\text{Au}_{40}(\text{SeR})_{24}]^{2-}$  ( $18 e^-$ ), and  $[\text{Au}_{61}(\text{SeR})_{31}]^{2-}$  nanoclusters ( $32 e^-$ ) were also monitored (refer to Figs. 25 and 26 for the growth process of  $[\text{Au}_{25}(\text{SeR})_{18}]^-$  ( $8 e^-$ ) nanoclusters, Figs. 29 and 30 for the growth process of  $[\text{Au}_{40}(\text{SeR})_{24}]^{2-}$  ( $18 e^-$ ) nanoclusters, and Figs. 32 and 33 for the growth process of  $[\text{Au}_{61}(\text{SeR})_{31}]^{2-}$  nanoclusters). Their growth also involved a sequential  $2x e^-$  jumping mechanism ( $x = 0-5$ ), which indicated that the sequential  $2x e^-$  jumping mechanism could be universal in synthesizing metal Nanoclusters using the “ $\text{NaBH}_4$  reduction” system. Detailed discussions can be found in the section below.

### Conversion Between $[\text{Au}_{25}(\text{SeR})_{18}]^-$ Nanoclusters and $[\text{Au}_{23}(\text{SeR})_{16}]^-$ Nanoclusters

Similar to the phenomenon that a reversible conversion between  $[\text{Au}_{25}(\text{SeR})_{18}]^-$  and  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  could occur during the growth process of  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  nanoclusters, in the growth process of  $[\text{Au}_{25}(\text{SeR})_{18}]^-$  nanoclusters (Fig. 25), the conversion of  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  (species #25) to  $[\text{Au}_{25}(\text{SeR})_{18}]^-$  (species #24) was observed. This observation revealed that the reversible conversion between  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  and  $[\text{Au}_{25}(\text{SeR})_{18}]^-$  could occur under the same shell closure ( $8 e^-$ ).

The structure of  $[\text{Au}_{23}(\text{SR})_{16}]^-$  nanoclusters has been proposed to be comprised of a bipyramidal  $\text{Au}_{15}$  kernel (with a FCC packing mode (FCC = face centered cubic)) protected by two staple-like trimeric  $\text{Au}_3(\text{SR})_4$  motifs, two monomeric  $\text{Au}(\text{SR})_2$  and four plain bridging SR ligands, while  $[\text{Au}_{25}(\text{SR})_{18}]^-$  nanoclusters consisted of an icosahedral  $\text{Au}_{13}$  core (with a non-fcc packing mode) and six  $\text{Au}_2(\text{SR})_3$  oligomer motifs. Although  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  and  $[\text{Au}_{25}(\text{SeR})_{18}]^-$  NC species have significantly different structures, the reversible conversion between them with the simultaneous attachment/detachment of  $\text{Au}_2(\text{SeR})_2$  was experimentally observed for the first time based on monitoring the growth processes of  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  and  $[\text{Au}_{25}(\text{SeR})_{18}]^-$ . This result was significant towards understanding the structural variation of  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  and  $[\text{Au}_{25}(\text{SeR})_{18}]^-$ . Given that both the Au-SR motifs and the packing modes were different between  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  and  $[\text{Au}_{25}(\text{SeR})_{18}]^-$ , it is likely that a structural reorganization might have occurred during the conversion process, and the same electron shell closure ( $8 e^-$ ) made the conversion possible. More insights could be gained from theoretical simulations and X-ray crystallography.

The conversion between  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  and  $[\text{Au}_{25}(\text{SeR})_{18}]^-$  may occur possibly due to the synthetic environment (e.g., the miscible solvent), which favoured the conversion between these two nanoclusters with the same electron shell closure ( $8 e^-$ ). To verify this, two experiments to examine the effect of solvent on the conversion between  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  and  $[\text{Au}_{25}(\text{SeR})_{18}]^-$  were carried out.

In the first experiment, an aqueous solution of 0.5 mL of ultrapure water + 4.5 mL of acetonitrile + 0.4 mL of  $\text{NaOH}$  + 0.1 mL of  $\text{NaBH}_4$  was prepared (note: this solution has the same composition as the aqueous phase in the two-phase synthetic system for  $\text{Au}_{25}(\text{SeR})_{18}$  nanoclusters). The solvent composition in the two-phase synthetic system for  $\text{Au}_{25}(\text{SeR})_{18}$

nanoclusters was used to replace the aqueous phase (1 mL of ultrapure water + 4 mL of DMF + 0.4 mL of NaOH + 0.1 mL of NaBH<sub>4</sub>) of the two-phase synthetic system for [Au<sub>23</sub>(SeR)<sub>16</sub>]<sup>−</sup> nanoclusters. It is expected that the replacement of the aqueous phase of the two-phase synthetic system could induce the conversion of [Au<sub>23</sub>(SeR)<sub>16</sub>]<sup>−</sup> nanoclusters to [Au<sub>25</sub>(SeR)<sub>18</sub>]<sup>−</sup> nanoclusters. After stirring of 2 hours, the [Au<sub>23</sub>(SeR)<sub>16</sub>]<sup>−</sup> nanoclusters were indeed converted to [Au<sub>25</sub>(SeR)<sub>18</sub>]<sup>−</sup> nanoclusters (see Fig. 27), indicating that the solvent could induce the nanoclusters conversion.

In the second experiment, the aqueous phase of the two-phase synthetic system for [Au<sub>25</sub>(SeR)<sub>18</sub>]<sup>−</sup> nanoclusters was replaced with an aqueous solution of 1 mL of ultrapure water + 4 mL of DMF + 0.4 mL of NaOH + 0.1 mL of NaBH<sub>4</sub> (note: this solution has the same composition as the aqueous phase of the two-phase synthetic system for Au<sub>23</sub>(SeR)<sub>16</sub> nanoclusters), which successfully converted [Au<sub>25</sub>(SeR)<sub>18</sub>]<sup>−</sup> nanoclusters to [Au<sub>23</sub>(SeR)<sub>16</sub>]<sup>−</sup> nanoclusters (see Fig. 28). These two experiments corroborated the postulate that the synthetic environment (e.g., the miscible solvent) could induce the conversion between two nanoclusters with the same electron shell closure (8 e<sup>−</sup>).

### Growth Processes of [Au<sub>25</sub>(SeR)<sub>18</sub>]<sup>−</sup>, [Au<sub>40</sub>(SeR)<sub>24</sub>]<sup>2−</sup>, and [Au<sub>61</sub>(SeR)<sub>31</sub>]<sup>2−</sup> Nanoclusters

The growth mechanism of metal nanoclusters synthesized via NaBH<sub>4</sub> reduction routes has major significance towards the understanding of NC formation. However, it has remained elusive due to the fast reduction rate of NaBH<sub>4</sub>, difficulty in terminating the reduction reaction at specific time points, and the complicated and time-consuming sample purification procedures prior to size characterization.

For the growth process of [Au<sub>25</sub>(SeR)<sub>18</sub>]<sup>−</sup> nanoclusters (with 8 e<sup>−</sup> shell closure), 25 species were identified and listed in Fig. 25(e). As shown in Fig. 25(a), in the first 5 minutes, there was a bump at around 630 nm in UV–vis absorption spectra, which was similar to the optical feature of Au<sub>18</sub>(SeR)<sub>14</sub>. ESI mass spectra (Figs. 25(c), 25(d), 25(e) and Fig. 26) corroborated the formation of [Au<sub>17</sub>(SeR)<sub>14</sub>]<sup>−</sup> (4 e<sup>−</sup>, species #22) and [Au<sub>18</sub>(SeR)<sub>15</sub>]<sup>−</sup> (4 e<sup>−</sup>, species #23) in the first 5 minutes (refer to Fig. 25(d)). Between 5 and 30 minutes, UV–vis absorption peaks at 500 nm, 600 nm, and 720 nm gradually increased (Fig. 25(a)), indicating the formation of more Au<sub>25</sub>(SeR)<sub>18</sub> nanoclusters. This finding was further confirmed by ESI mass spectra; the peak of [Au<sub>25</sub>(SeR)<sub>18</sub>]<sup>−</sup> nanoclusters (8 e<sup>−</sup>, species #24) increased in intensity. In the same duration, peaks of [Au<sub>17</sub>(SeR)<sub>14</sub>]<sup>−</sup> and [Au<sub>18</sub>(SeR)<sub>15</sub>]<sup>−</sup> species gradually disappeared, while the peak of [Au<sub>25</sub>(SeR)<sub>18</sub>]<sup>−</sup> increased. This result suggested that the Au<sub>25</sub>(SeR)<sub>18</sub> nanoclusters were formed from growing [Au<sub>17</sub>(SeR)<sub>14</sub>]<sup>−</sup> and [Au<sub>18</sub>(SeR)<sub>15</sub>]<sup>−</sup> nanoclusters with a 2x e<sup>−</sup> jumping mechanism (x = 2, i.e., 4 e<sup>−</sup> → 8 e<sup>−</sup>).

As the reaction progressed to 180 minutes (Fig. 25(b)), the UV–vis absorption peaks at 500 nm and 720 nm increased further, while the peak at 600 nm disappeared. The well-defined absorption feature illustrated the formation of pure Au<sub>25</sub>(SeR)<sub>18</sub> nanoclusters at 180 minutes. ESI mass spectra showed that the peak intensity of [Au<sub>25</sub>(SeR)<sub>18</sub>]<sup>−</sup> (i.e., species #24) experienced an increase at 30 minutes, a decrease at 60–90 minutes, followed by an increase at 180 minutes, which was associated with the changes of selenolate-Au(I) complexes during this period. This suggested that the formation of [Au<sub>25</sub>(SeR)<sub>18</sub>]<sup>−</sup> nanoclusters involved a reversible cluster growth-digestion-growth process.

Unlike the growth of  $[\text{Au}_{23}(\text{SeR})_{18}]^-$  nanoclusters where a size-focusing principle was followed, no NC species larger than  $\text{Au}_{25}$  was detected in the entire growth process of  $[\text{Au}_{25}(\text{SeR})_{18}]^-$  nanoclusters. This showed that the formation of  $[\text{Au}_{25}(\text{SeR})_{18}]^-$  nanoclusters in the present reaction system followed a strict bottom-up growth principle with sequential  $2x e^-$  jumping ( $x = 0-2$ , i.e.,  $0 e^- \rightarrow 2 e^- \rightarrow 4 e^- \rightarrow 8 e^-$ ).

In the growth process of  $[\text{Au}_{40}(\text{SeR})_{24}]^{2-}$  nanoclusters (with  $18 e^-$  shell closure),  $[\text{Au}_{15}(\text{SeR})_{12}]^-$  nanoclusters ( $4 e^-$ ),  $[\text{Au}_{19}(\text{SeR})_{14}]^-$  nanoclusters ( $6 e^-$ ),  $[\text{Au}_{20}(\text{SeR})_{15}]^-$  nanoclusters ( $6 e^-$ ),  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  nanoclusters ( $8 e^-$ ) and  $[\text{Au}_{25}(\text{SeR})_{18}]^-$  nanoclusters ( $8 e^-$ ) were formed initially (species #19–23, Fig. 29). These NC species gradually converged to  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  in 10 minutes ( $8 e^-$ , species #22). For instance, only a small amount of  $[\text{Au}_{15}(\text{SeR})_{12}]^-$  nanoclusters ( $4 e^-$ , species #19) was observed in the ESI spectrum at 7.5 minutes, and this species completely disappeared 10 minutes after  $\text{NaBH}_4$  addition.

On the other hand,  $[\text{Au}_{40}(\text{SeR})_{24}]^{2-}$  nanoclusters ( $18 e^-$ , species #24) started to form at 10 minutes. Between 10 and 180 min,  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  nanoclusters were gradually converted to  $[\text{Au}_{40}(\text{SeR})_{24}]^{2-}$  nanoclusters ( $8 e^- \rightarrow 18 e^-$ ). While the crystal structure of  $[\text{Au}_{40}(\text{SeR})_{24}]^{2-}$  nanoclusters was unclear, this species could be derived from the combination of two  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  nanoclusters with the detachment of two trimeric  $\text{Au}_3(\text{SeR})_4$  motifs. To verify this, an experiment using  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  nanoclusters as seeds for the formation of  $[\text{Au}_{40}(\text{SeR})_{24}]^{2-}$  nanoclusters was carried out. 5 mL of toluene solution containing  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  nanoclusters was mixed with 0.5 mL of ultrapure water, 4.5 mL of DMF, 0.4 mL of  $\text{NaOH}$  (1 M), and 0.1 mL of  $\text{NaBH}_4$  (~112 mM), and stirred for one hour. It was found that  $[\text{Au}_{40}(\text{SeR})_{24}]^{2-}$  nanoclusters could be obtained at the expense of  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  nanoclusters (Fig. 31), which further corroborated that two  $[\text{Au}_{23}(\text{SeR})_{16}]^-$  nanoclusters could be combined to form one  $[\text{Au}_{40}(\text{SeR})_{24}]^{2-}$  NC with detaching two trimeric  $\text{Au}_3(\text{SeR})_4$  motifs. This could be further examined with theoretical simulations or X-ray crystallography analysis. The growth of  $[\text{Au}_{40}(\text{SeR})_{24}]^{2-}$  nanoclusters also followed the sequential  $2x e^-$  jumping mechanism ( $x = 0-5$ , i.e.,  $0 e^- \rightarrow 4 e^- \rightarrow 6 e^- \rightarrow 8 e^- \rightarrow 18 e^-$ ).

In the growth process of  $[\text{Au}_{61}(\text{SeR})_{31}]^{2-}$  nanoclusters (with  $32 e^-$  shell closure),  $[\text{Au}_{25}(\text{SeR})_{18}]^-$  NC species ( $8 e^-$ , species #30) was formed initially, and then grew to  $[\text{Au}_{40}(\text{SeR})_{24}]^{2-}$  NC species ( $18 e^-$ , species #31) within 10 minutes (Fig. 32). Between 10 and 60 minutes, the yield of  $[\text{Au}_{40}(\text{SeR})_{24}]^{2-}$  nanoclusters became higher. At 90 minutes, the peak of  $[\text{Au}_{40}(\text{SeR})_{24}]^{2-}$  nanoclusters disappeared, while the peaks of  $[\text{Au}_{43}(\text{SeR})_{23}]^{2-}$  ( $22 e^-$ , species #32) and  $[\text{Au}_{61}(\text{SeR})_{31}]^{2-}$  nanoclusters ( $32 e^-$ , species #33) were observed, indicating that  $[\text{Au}_{40}(\text{SeR})_{24}]^{2-}$  nanoclusters have further transformed to  $[\text{Au}_{43}(\text{SeR})_{23}]^{2-}$  nanoclusters.

$[\text{Au}_{43}(\text{SeR})_{23}]^{2-}$  nanoclusters were fully converted to  $[\text{Au}_{61}(\text{SeR})_{31}]^{2-}$  nanoclusters at 180 min. Therefore,  $[\text{Au}_{61}(\text{SeR})_{31}]^{2-}$  nanoclusters with a  $32 e^-$  shell closure are obtained via the evolution of  $[\text{Au}_{25}(\text{SeR})_{18}]^-$ ,  $[\text{Au}_{40}(\text{SeR})_{24}]^{2-}$  and  $[\text{Au}_{43}(\text{SeR})_{23}]^{2-}$  nanoclusters with a sequential  $2x e^-$  jumping mechanism ( $x = 0-5$ , i.e.,  $0 e^-$ ,  $2 e^- \rightarrow 8 e^- \rightarrow 18 e^- \rightarrow 22 e^- \rightarrow 32 e^-$ ). Fig. 33 shows the detailed assignment of the identified species.

## Example 9: Size Effect of Au Nanoclusters on the Electrochemical Reduction of $\text{CO}_2$

Electrocatalytic reduction of  $\text{CO}_2$  is a clean and sustainable chemical process that generates useful hydrocarbons (e.g. methane, methanol) or CO. It can help to address the increasing

need to treat CO<sub>2</sub> emissions from fossil fuel combustion. A number of catalytic systems based on noble metals have been reported for the electrochemical CO<sub>2</sub> reduction to CO, and some recent studies have shown that Au-based nanocrystals or nanoclusters have enhanced electrocatalytic activities compared to polycrystalline Au electrode. With selenolated Au nanoclusters that could be tuned in size with atomic precision, the effect of cluster size on the electrochemical CO<sub>2</sub> reduction to CO can be thus examined.

### Immobilization of the Selenolated Au Nanoclusters on Carbon

A solution of the selenolated Au nanoclusters in dichloromethane (0.8 mg of Au dissolved in 12 mL of DCM) was added dropwise to a suspension of Vulcan XC-72 carbon (0.02 g) in DCM (8 mL) with vigorous stirring. The resulting suspension was stirred at room temperature under air for 5 hours. The solids were collected *via* centrifugation, washed twice with DCM (4 mL), and dried at room temperature under vacuum overnight. The Au nanoclusters on carbon were characterized by TEM, TEM-EDX, HAADF-STEM, and ICP-MS.

Four selenolated Au nanoclusters (Au<sub>15</sub>(SeR)<sub>12</sub>, Au<sub>25</sub>(SeR)<sub>18</sub>, Au<sub>40</sub>(SeR)<sub>24</sub> and Au<sub>61</sub>(SeR)<sub>31</sub>) were successfully immobilized on a Vulcan XC-72 carbon support, as confirmed by TEM, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and TEM energy dispersive X-ray (TEM-EDX). Refer to Figs. 34 to 36.

### Electrochemical Test

Electrochemical experiments were performed in a one-compartment, three-electrode electrochemical cell using CH Instruments CHI760C bipotentiostat. 0.1 M KHCO<sub>3</sub> solutions were prepared using ultrapure water and purged with CO<sub>2</sub> (pH 6.9) for 30 minutes. A platinum wire was used as the counter electrode (CE), and a Ag/AgCl electrode was used as the reference electrode (1.0 M KCl). The measured potentials (vs. Ag/AgCl) were converted to the reversible hydrogen electrode (RHE) scale using the equation:  $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{ pH} + E^{\circ}_{\text{Ag/AgCl}}$  V (where  $E^{\circ}_{\text{Ag/AgCl}}$  (1.0 M KCl) = 0.235 V).

Selenolated Au nanoclusters on carbon deposited on glassy carbon electrode (3 mm diameter) was used as the working electrode (WE). The Au nanoclusters on carbon (2 mg) were sonicated in a mixture of ultrapure water (1.16 mL), ethanol (0.8 mL) and Nafion (40 μL of 5% solution) for 20 minutes. The glassy carbon electrode was polished with 0.05-μm de-agglomerated alumina slurry, sonicated and rinsed with deionized water and dried in air. 2 μL of the catalyst dispersion was deposited onto the glassy carbon electrode, and allowed to dry at room temperature under air. The electrochemical surface area (ECSA) of the Au catalyst was determined from the cathodic peak of the oxidized Au in N<sub>2</sub>-purged 0.1 M KHCO<sub>3</sub>. Linear sweep voltammetry currents were normalized to the catalyst ECSA.

Electrolysis of CO<sub>2</sub> was performed in a gas-tight three-compartment electrochemical cell; the working, counter and reference electrodes were housed in different compartments. During the CO<sub>2</sub> electrolysis, various voltages (-0.6, -0.8, -1.0 or -1.2 V vs. RHE) were applied for one hour and the solution was stirred at a constant rate to prevent the build-up of gaseous product on the electrode surface. After one hour of electrolysis, the gaseous product was analyzed using a Shimadzu GC-2014 gas chromatograph equipped with a thermal conductivity detector. CO

formation rates were normalized to the catalyst ECSA. The Faradaic efficiency for CO was calculated using the following equation:

$$\text{Faradaic efficiency (\%)} = \frac{n_{\text{CO}} \times F \times n_e}{C} \times 100\%$$

where  $n_{\text{CO}}$  represents the number of moles of CO produced,  $F$  is the Faraday's constant (96485.34 C/mol),  $n_e$  is the theoretical number of electrons required to reduce CO<sub>2</sub> to CO, and  $C$  represents the total quantity of measured input charge.

Although the Au<sub>15</sub>(SeR)<sub>12</sub> and Au<sub>25</sub>(SeR)<sub>18</sub> nanoclusters could not be distinctly discerned from their TEM images (Figs. 34(a) and 34(b)), the presence of the Au<sub>40</sub>(SeR)<sub>24</sub> and Au<sub>61</sub>(SeR)<sub>31</sub> nanoclusters on the carbon support could be clearly observed by TEM (Figs. 34(c) and 34(d)). In addition, all four selenolated Au NC samples supported on carbon could be easily distinguished from their high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images (Fig. 35).

TEM energy dispersive X-ray (TEM-EDX) analysis as shown in Fig. 36 confirmed the presence of Au and Se in these nanomaterials, indicating the successful immobilization of Au nanoclusters on Vulcan XC-72 carbon support.

The electrocatalytic reduction of CO<sub>2</sub> on the four carbon-supported selenolated Au nanoclusters (Au<sub>15</sub>(SeR)<sub>12</sub>/C, Au<sub>25</sub>(SeR)<sub>18</sub>/C, Au<sub>40</sub>(SeR)<sub>24</sub>/C and Au<sub>61</sub>(SeR)<sub>31</sub>/C) were investigated (Fig. 37). Decreasing the NC size resulted in a corresponding increase in the electrocatalytic activity over the potential range from -0.4 to -1.2 V vs. RHE. The electrocatalytic activity of Au<sub>15</sub>(SeR)<sub>12</sub>/C was ~5 times greater than that of Au<sub>61</sub>(SeR)<sub>31</sub>/C. Control experiment by using Vulcan XC-72 carbon support as the electrocatalyst showed that no significant electrocatalytic activity was observed in the absence of the Au nanoclusters.

Fig. 38 summarized the potential-dependent CO formation rates and Faradaic efficiencies (FE) for CO for the four Au nanoclusters. The CO formation rates increased as the applied potential decreased for all the four Au NC electrocatalysts (refer to Fig. 38(a)). On the other hand, the FE for CO decreased as the applied potential became more negative (refer to Fig. 38(b)). This was due to the increased formation of H<sub>2</sub>, which was the only other gaseous product formed at the more negative applied potentials. At the same applied potential, CO formation rates increased with a decrease in the Au NC size (refer to Fig. 38(a)). However, similar FEs for CO were attained for all four carbon-supported selenolated Au nanoclusters regardless of their NC size at the same applied potential (refer to Fig. 38(b)).

## Industrial Applicability

Owing to their attractive electronic, optical, and chemical properties compared to their larger counterparts, metal nanoclusters offer a range of potential applications for example in catalysis, energy conversion and photochemistry.

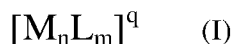
As stated above, nanoclusters of the present invention may be used for energy conversion applications such as light absorbing material for harvesting solar energy. The excited state properties of metal nanoclusters may be correlated with the photovoltaic performance of metal cluster sensitized solar cell. Further, the unique reactivity properties and the ability to control the size and number of atoms in nanoclusters may be valuable for developing a

method for increasing activity and tuning the selectivity in a catalytic process and catalytic applications relevant to industrial chemical processing.

5 It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

## Claims

1. A method of preparing particles of formula (I)



wherein:

- 5 M represents a metal;  
L represents a ligand;  
m and n are independently an integer in the range from 1 to 80;  
q represents a net charge in the range from - 5 to + 5,
- 10 said method comprising the steps of:
- a) mixing a metal precursor solution and a ligand precursor solution in the presence of an aqueous solution;
  - b) adding a miscible solvent to the mixture obtained in step a);
  - 15 c) adding an organic solvent and a reducing agent to the mixture obtained in step b) under basic pH condition to form said particles of formula (I) dispersed therein.

2. The method of claim 1, wherein the metal M is a transition metal.

3. The method of claim 1 or 2, wherein the ligand L is an organic ligand of formula (II)



wherein:

- N is a non-metal element selected from Group 15 or Group 16 of the Periodic Table of Elements;
- R is selected from the group consisting of hydrogen, C<sub>1-20</sub>alkyl, C<sub>3-7</sub>cycloalkyl, C<sub>1-20</sub>alkylaryl, aryl-C<sub>1-20</sub>alkyl, heteroaryl and aryl; and
- 25 o is 1, 2 or 3.

4. The method of any one of claims 1 to 3, wherein the ligand L is selected from the group consisting of benzeneselenolate, 4-tert-butylbenzenethiolate, cyclohexanethiolate, 2-phenylethanethiolate, 4-methylbenzenethiolate, and triphenylphosphine.

- 30 5. The method of any one of claims 1 to 4, wherein the particles of formula (I) are selected from the group consisting of Au<sub>10</sub>(SeR)<sub>10</sub>, Au<sub>15</sub>(SeR)<sub>12</sub>, Au<sub>18</sub>(SeR)<sub>14</sub>, Au<sub>23</sub>(SeR)<sub>16</sub>, Au<sub>25</sub>(SeR)<sub>18</sub>, Au<sub>31</sub>(SeR)<sub>20</sub>, Au<sub>40</sub>(SeR)<sub>24</sub>, Au<sub>61</sub>(SeR)<sub>31</sub>, Au<sub>10</sub>(SR)<sub>10</sub>, Au<sub>15</sub>(SR)<sub>13</sub>, Au<sub>28</sub>(SR)<sub>20</sub>, Au<sub>30</sub>(SR)<sub>22</sub>, Au<sub>42</sub>(SR)<sub>26</sub>, Au<sub>23</sub>(SR)<sub>16</sub>, Au<sub>24</sub>(SR)<sub>20</sub>, Au<sub>25</sub>(SR)<sub>18</sub>, [Au<sub>11</sub>(PR)<sub>8</sub>]<sup>3+</sup>, Ag<sub>44</sub>(SeR)<sub>30</sub>, and Cu<sub>27</sub>(SeR)<sub>17</sub>,

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wherein R is as defined in claim 3.

6. The method of any one of claims 1 to 5, wherein the metal precursor is in its acidic, basic, oxide, sulfide, phosphide, or salt form.

7. The method of any one of claims 1 to 6, wherein the ligand precursor is represented by formula (III)



wherein A is hydrogen or absent; N, R and o are as defined in claim 3.

8. The method of claim 7, wherein the ligand precursor is selected from the group consisting of benzeneselenol, benzenethiol, 4-tert-butylbenzenethiol, cyclohexaneselenol, cyclohexanethiol, benzeneethaneselenol, 2-phenylethanethiol, 4-methylbenzenethiol, and triphenylphosphine.

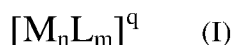
9. The method of any one of claims 1 to 8, wherein the miscible solvent is selected from the group consisting of DMF, tetrahydrofuran (THF), acetonitrile, ethanol and mixture thereof.

10. The method of any one of claims 1 to 9, wherein the reducing agent is selected from the group consisting of  $NaBH_4$ ,  $NaBH_3CN$ ,  $KBH_4$ ,  $LiBH_4$ ,  $LiAlH_4$  and mixture thereof.

11. The method of any one of claims 1 to 10, wherein the basic pH condition is in the pH range of more than 7 to 14.

12. The method of any one of claims 1 to 11, wherein the base is a strong base, a weak base or mixture thereof.

13. Particles of formula (I)



wherein:

M represents a metal;

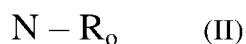
L represents a ligand;

m and n are independently an integer in the range from 1 to 80; and

q represents a net charge in the range from - 5 to + 5.

14. The particles of claim 13, wherein the metal M is a transition metal.

15. The particles of claim 13 or 14, wherein the ligand L is an organic ligand of formula (II)



wherein:

N is a non-metal element selected from the group consisting of elements of Group 15 or Group 16 of the Periodic Table;

R is selected from the group consisting of hydrogen,  $C_{1-20}$ alkyl,  $C_{3-7}$ cycloalkyl,  $C_{1-20}$ alkylaryl, aryl- $C_{1-20}$ alkyl, heteroaryl and aryl; and

o is 1, 2 or 3.

16. The particles of any one of claims 13 to 15, wherein the ligand L is selected from the group consisting of benzeneselenolate, 4-tert-butylbenzenethiolate, cyclohexanethiolate, 2-phenylethanethiolate, 4-methylbenzenethiolate, and triphenylphosphine.

17. The particles of any one of claims 13 to 16, wherein the particles of formula (I) are selected from the group consisting of  $\text{Au}_{10}(\text{SeR})_{10}$ ,  $\text{Au}_{15}(\text{SeR})_{12}$ ,  $\text{Au}_{18}(\text{SeR})_{14}$ ,  $\text{Au}_{23}(\text{SeR})_{16}$ ,  $\text{Au}_{25}(\text{SeR})_{18}$ ,  $\text{Au}_{31}(\text{SeR})_{20}$ ,  $\text{Au}_{40}(\text{SeR})_{24}$ ,  $\text{Au}_{61}(\text{SeR})_{31}$ ,  $\text{Au}_{10}(\text{SR})_{10}$ ,  $\text{Au}_{15}(\text{SR})_{13}$ ,  $\text{Au}_{28}(\text{SR})_{20}$ ,  $\text{Au}_{30}(\text{SR})_{22}$ ,  $\text{Au}_{42}(\text{SR})_{26}$ ,  $\text{Au}_{23}(\text{SR})_{16}$ ,  $\text{Au}_{24}(\text{SR})_{20}$ ,  $\text{Au}_{25}(\text{SR})_{18}$ ,  $[\text{Au}_{11}(\text{PR})_8]^{3+}$ ,  $\text{Ag}_{44}(\text{SeR})_{30}$ , and  $\text{Cu}_{27}(\text{SeR})_{17}$ ,

wherein R is as defined in claim 15.

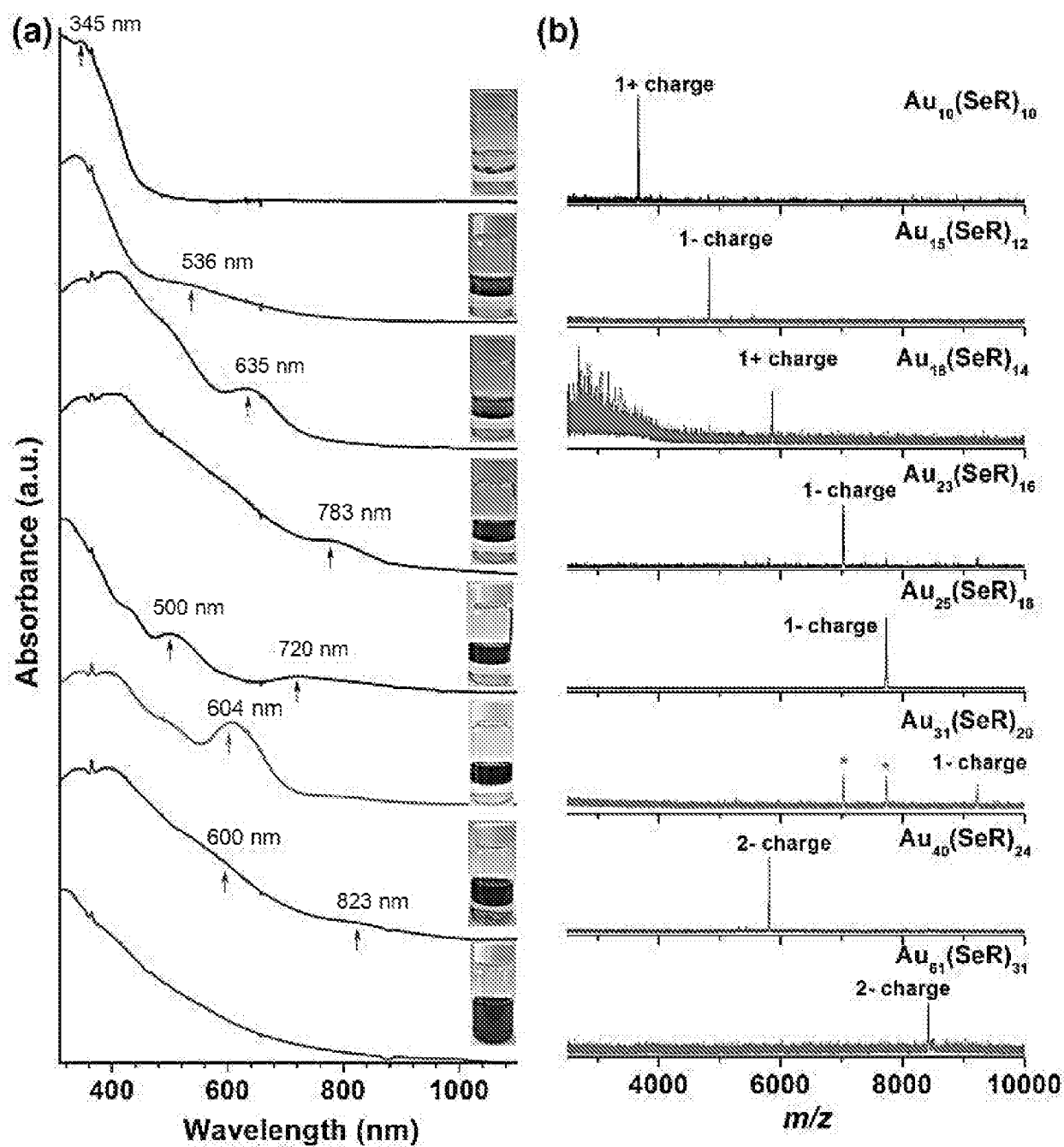
18. The particles of any one of claims 13 to 17, wherein the particles have a uniform particle size distribution.

19. The particles of any one of claims 13 to 18, wherein the average particle size of the particles of formula (I) is less than 2 nm.

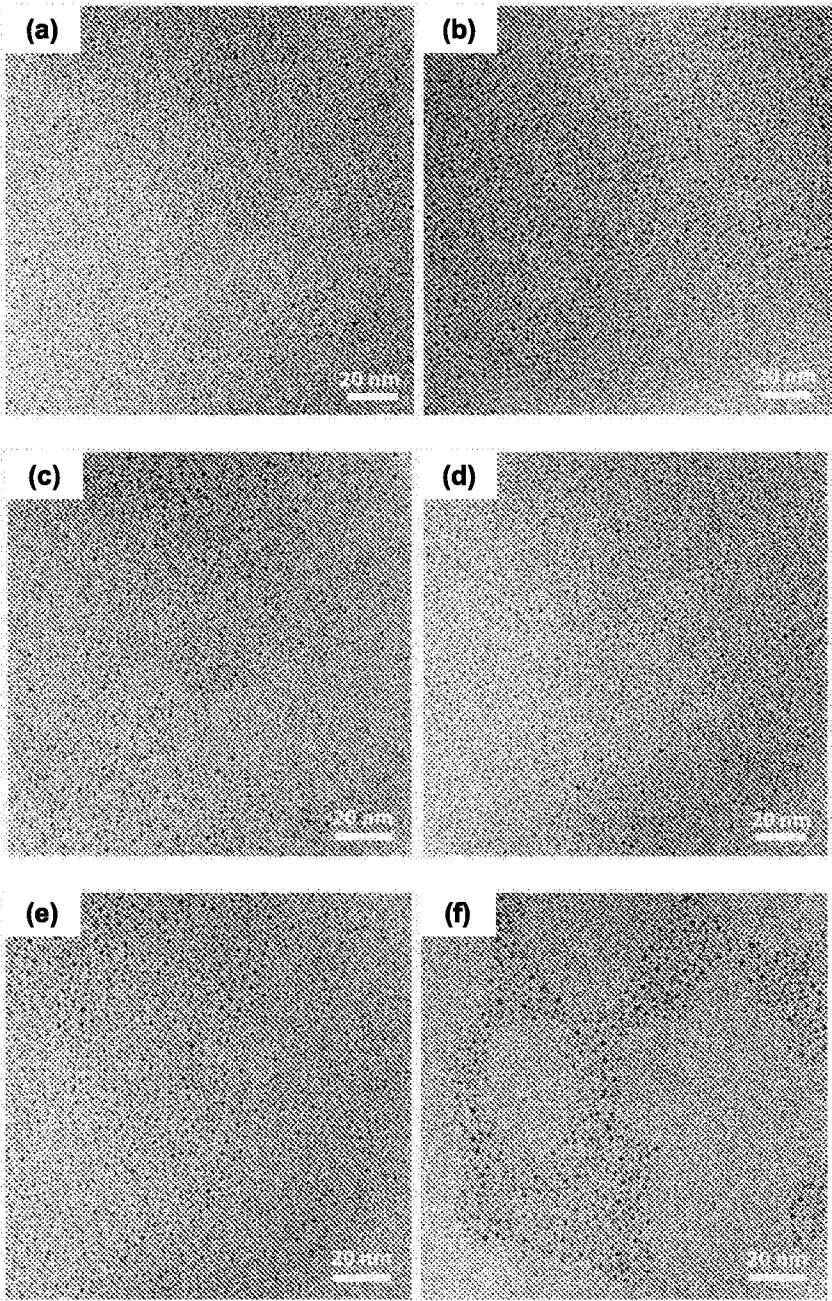
20. Use of particles of any one of claims 13 to 19 as electrode materials.

21. Electrode materials comprising particles of any one of claims 13 to 19.

[Fig. 1]

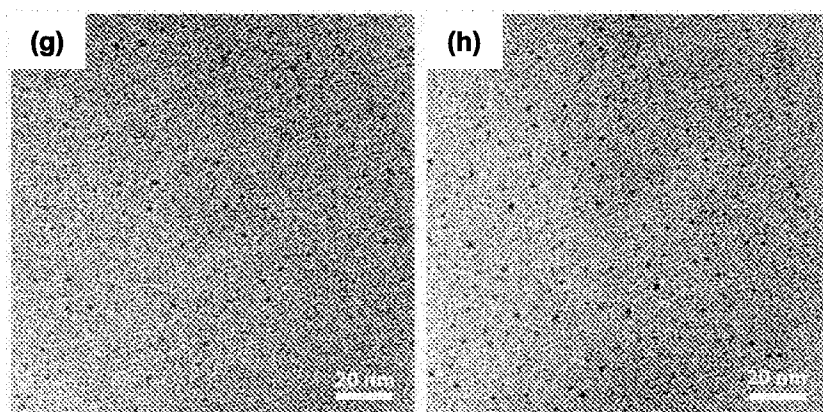


[Fig. 2]



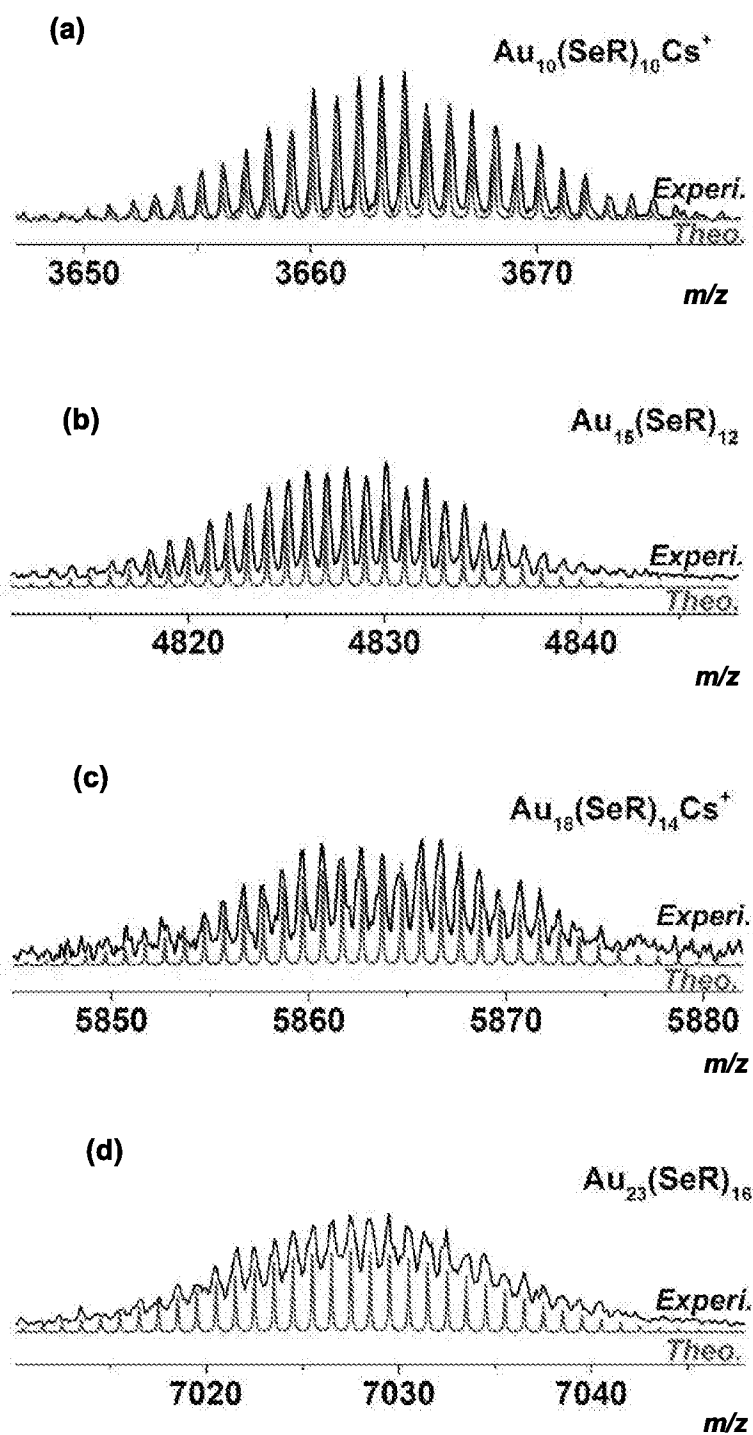
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[Fig. 2]



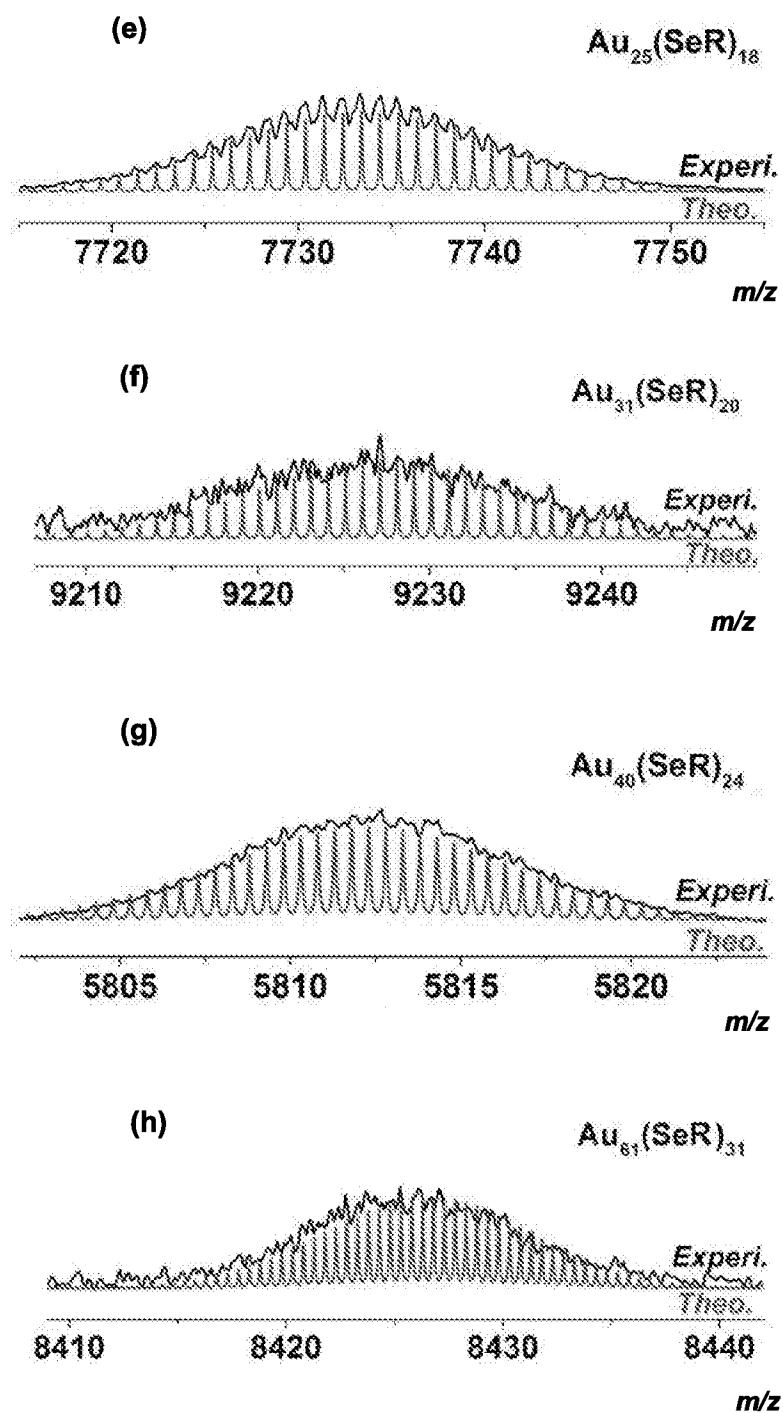
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[Fig. 3]

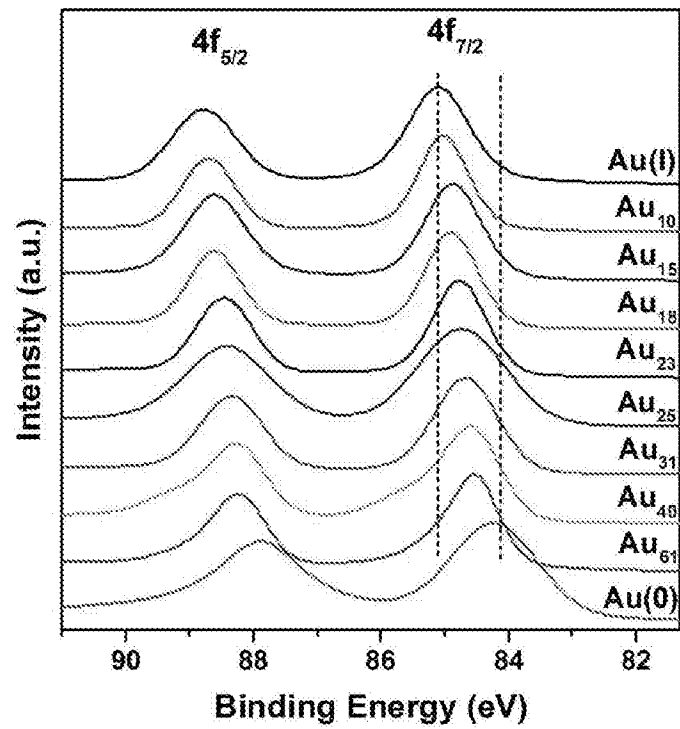


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[Fig. 3]

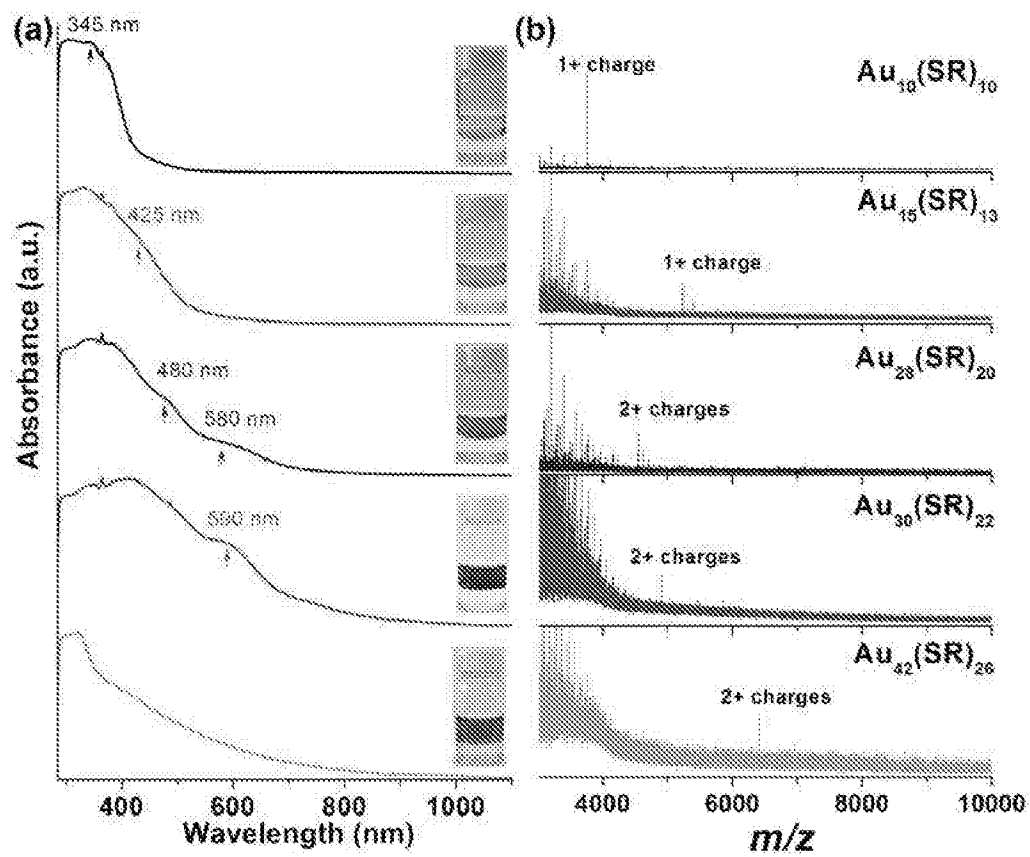


[Fig. 4]



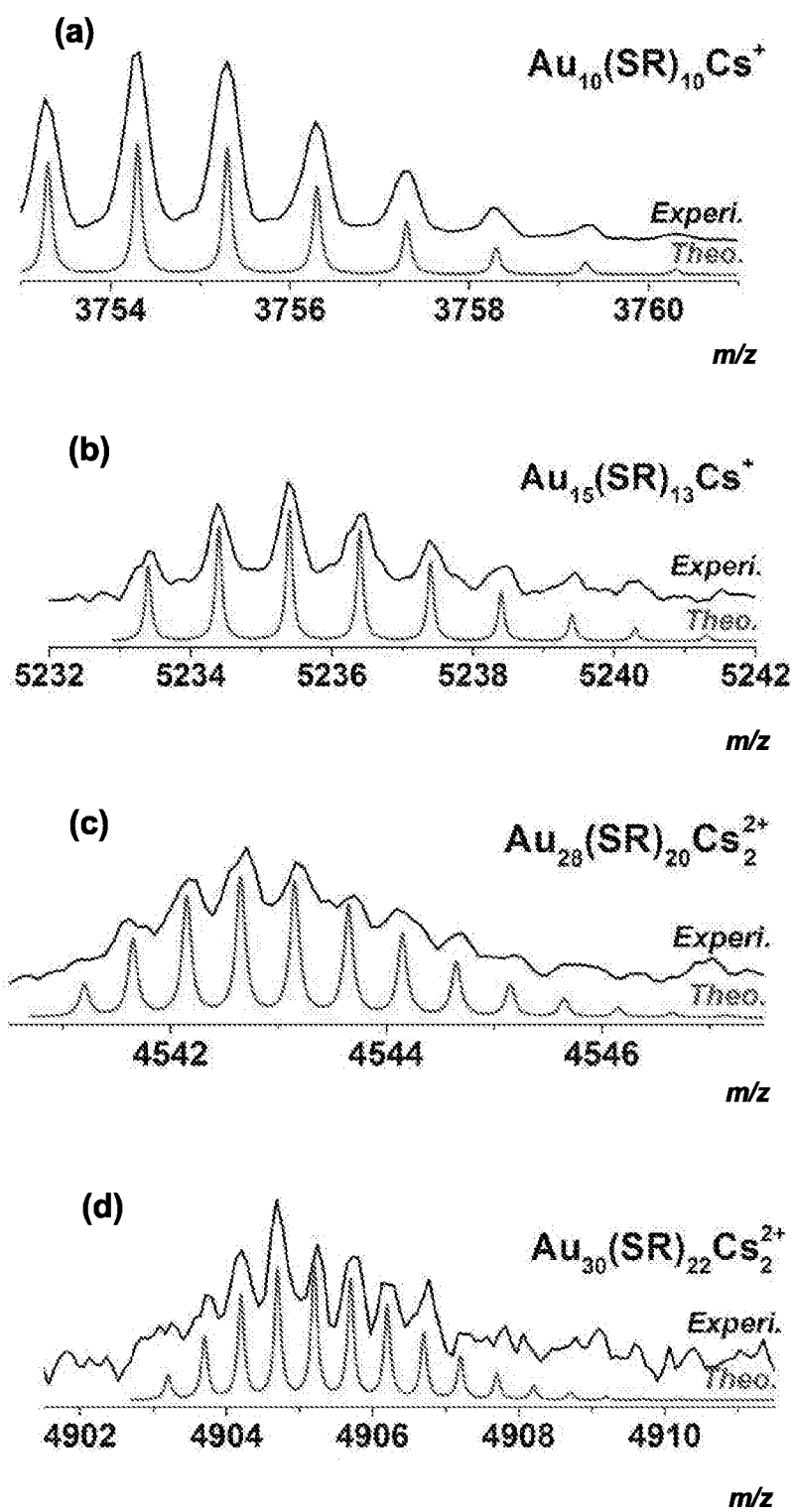
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[Fig. 5]



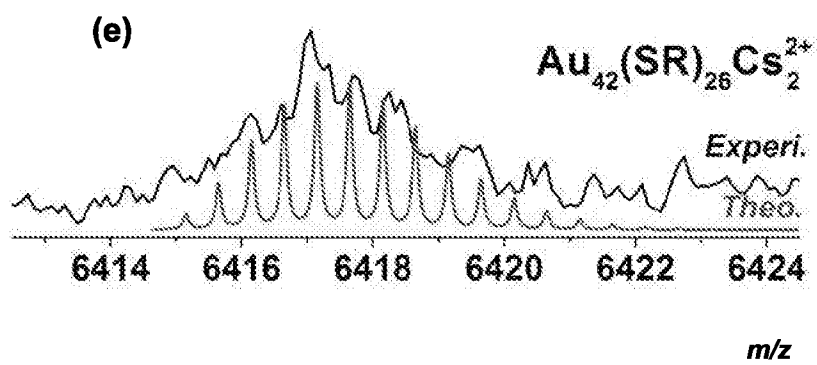
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[Fig. 6]



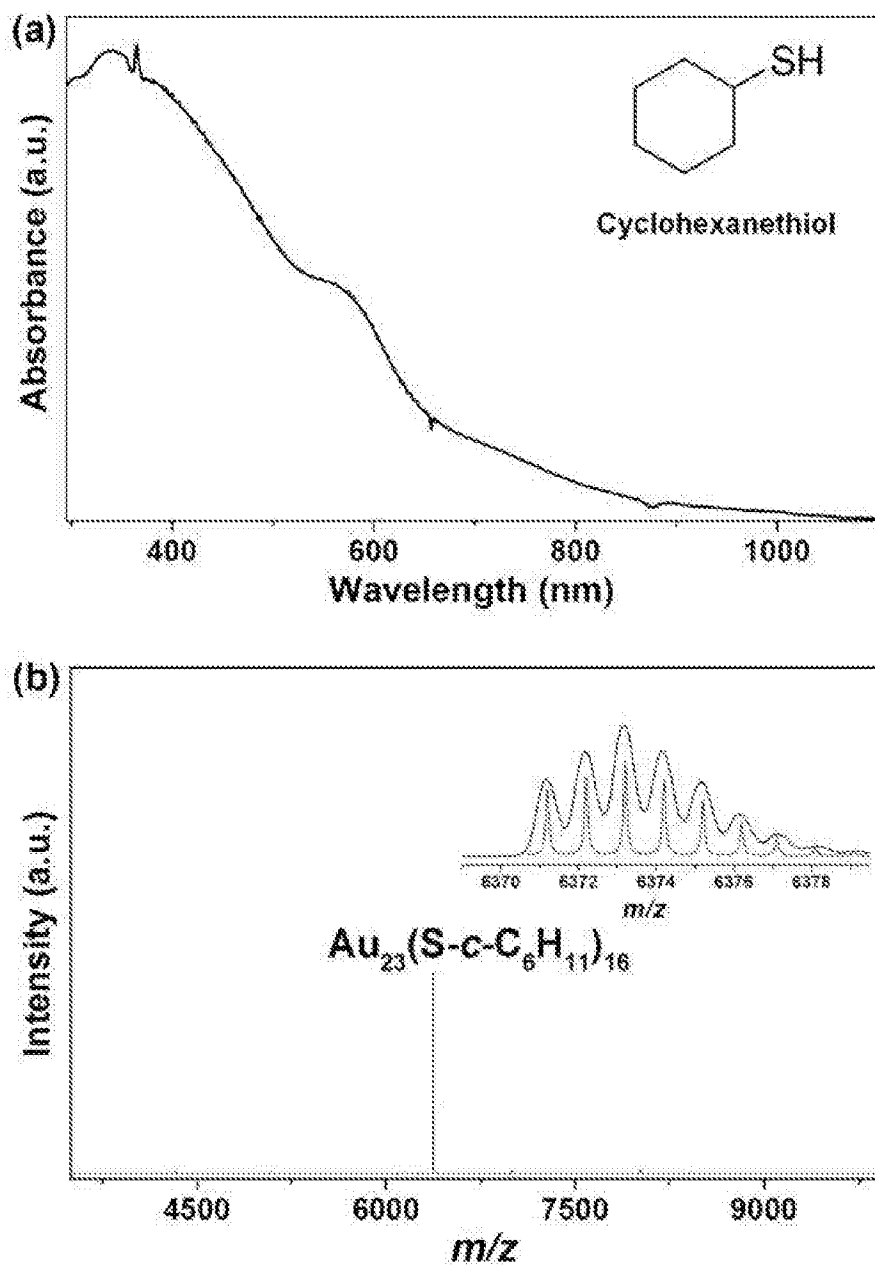
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[Fig. 6]



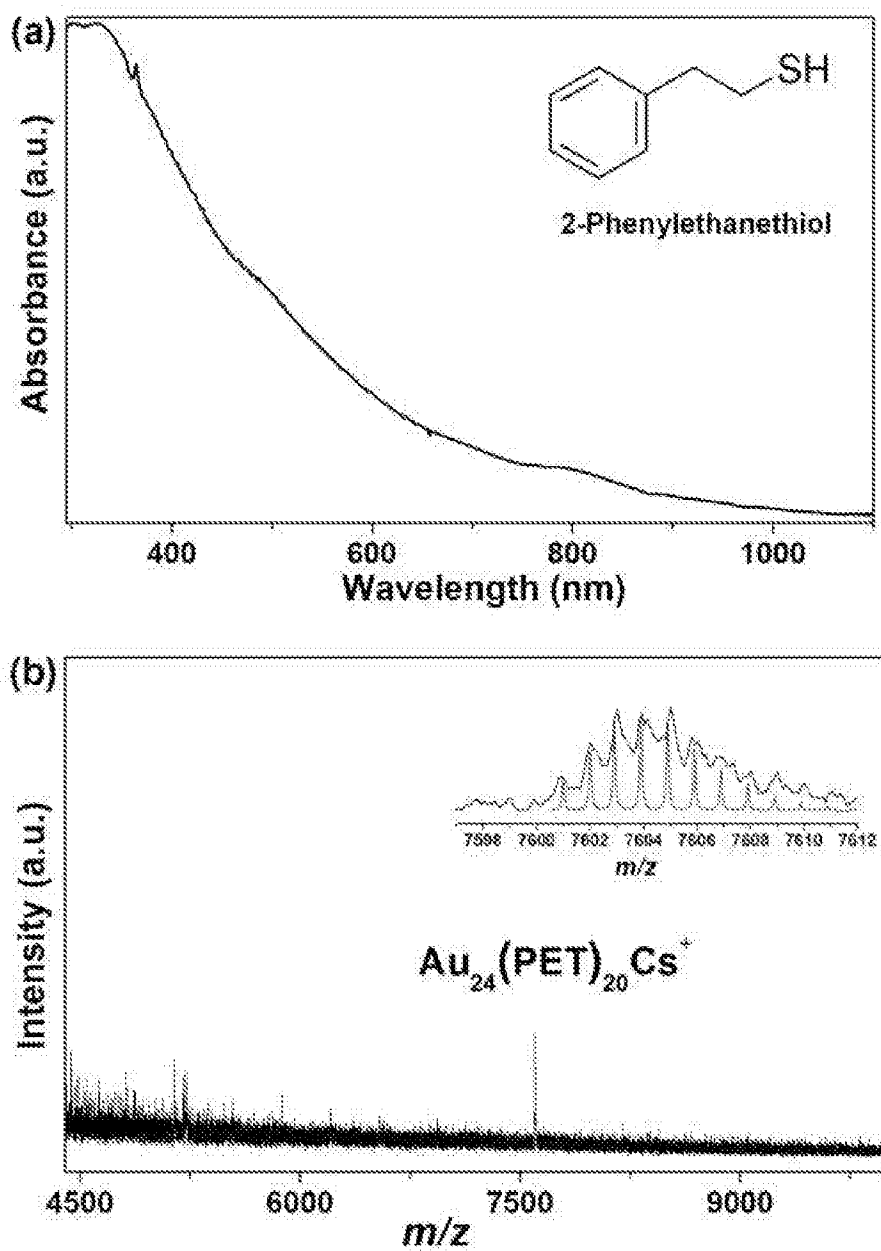
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[Fig. 7]



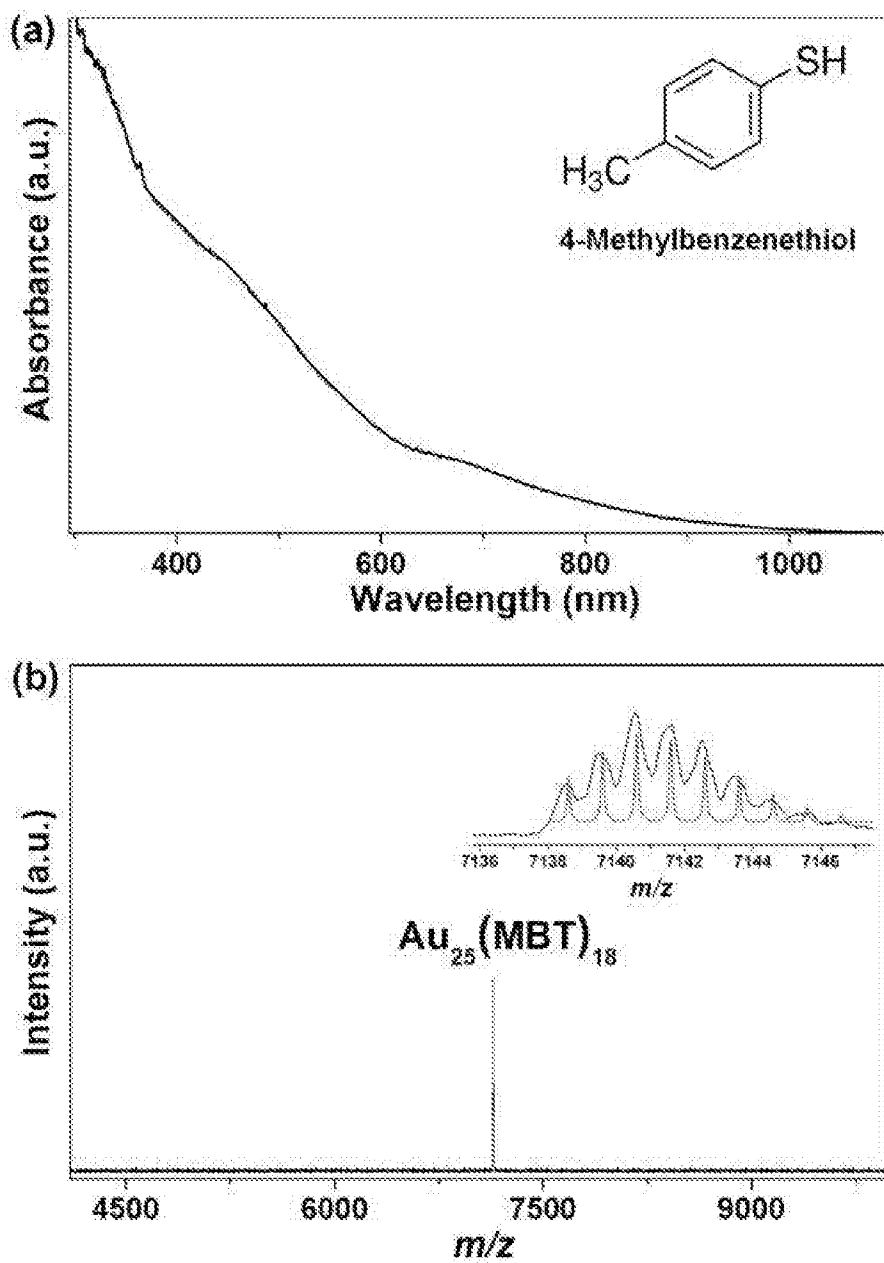
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[Fig. 8]



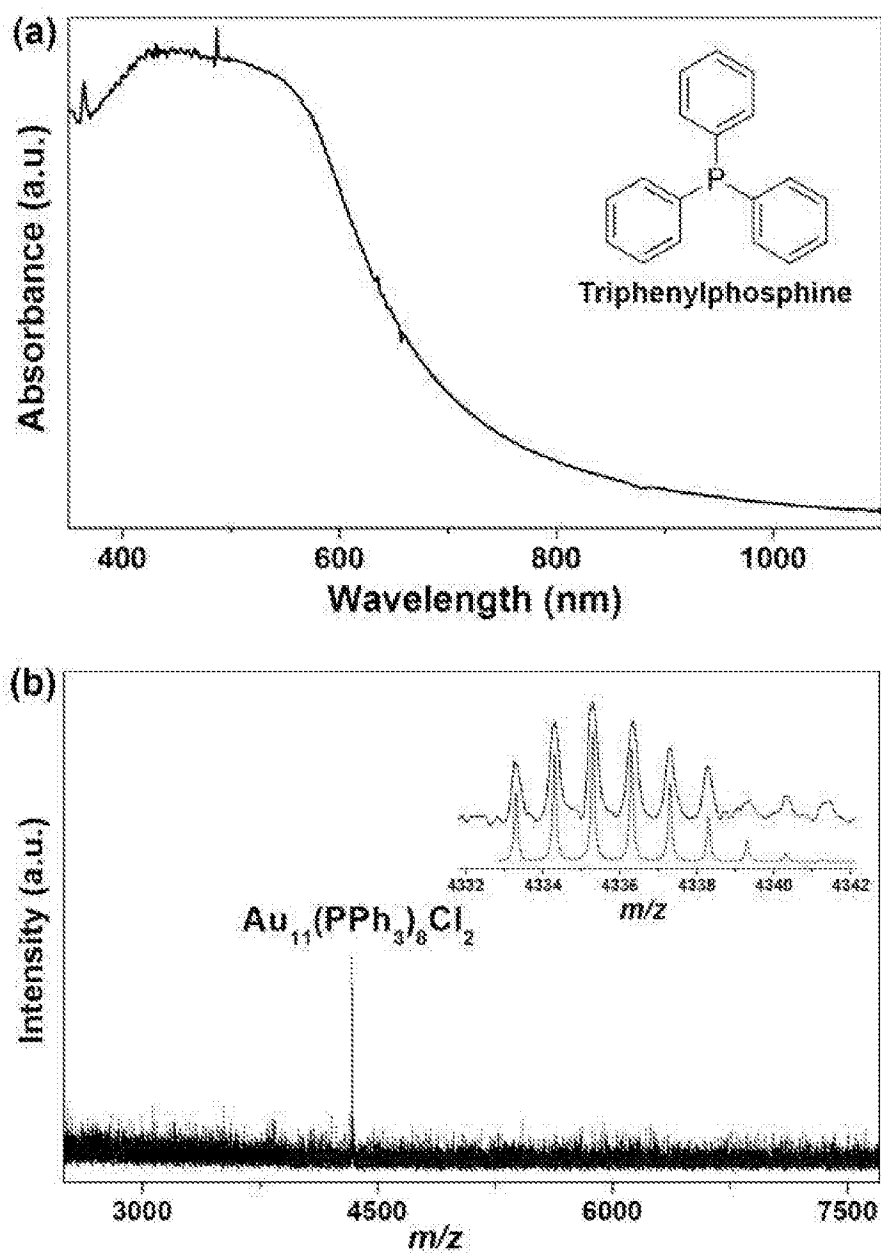
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[Fig. 9]



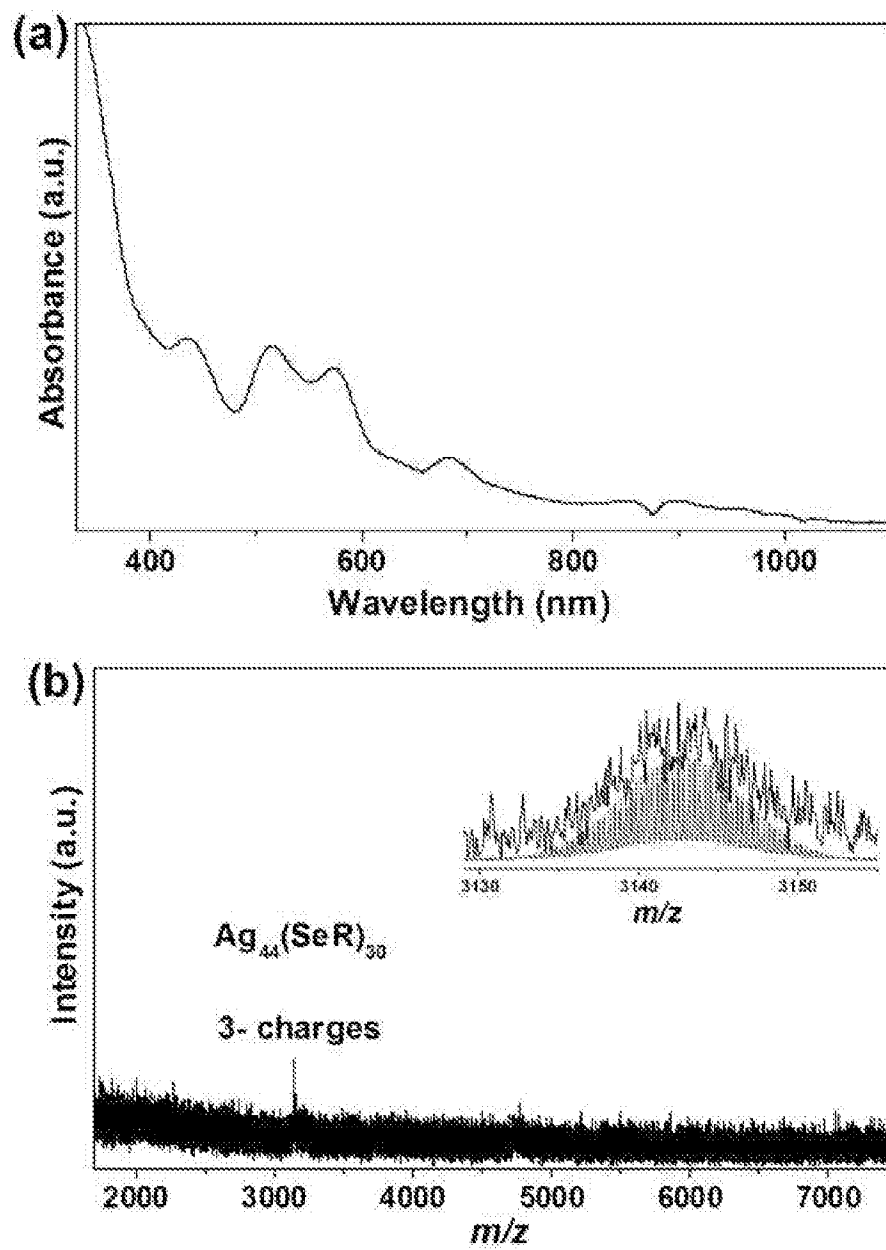
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[Fig. 10]



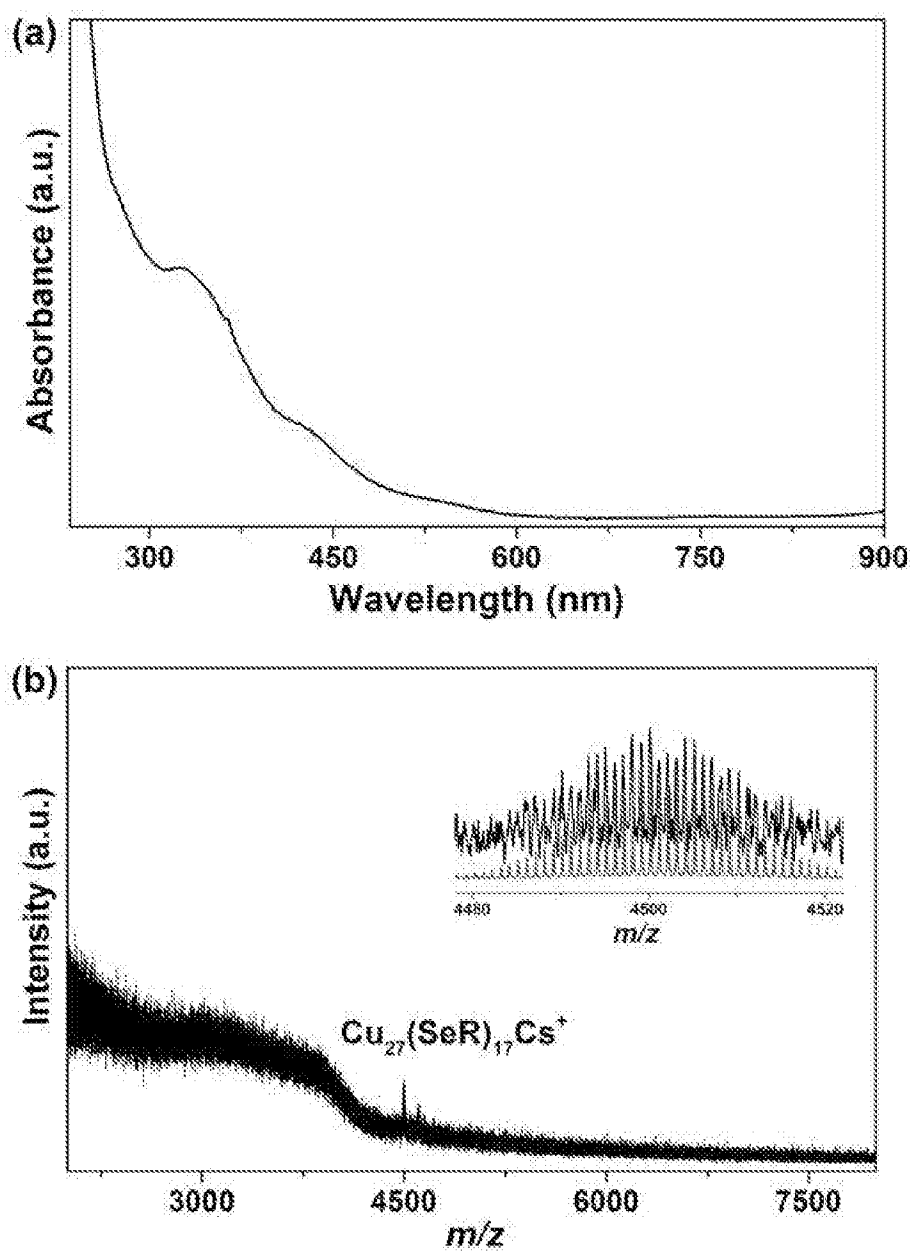
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[Fig. 11]

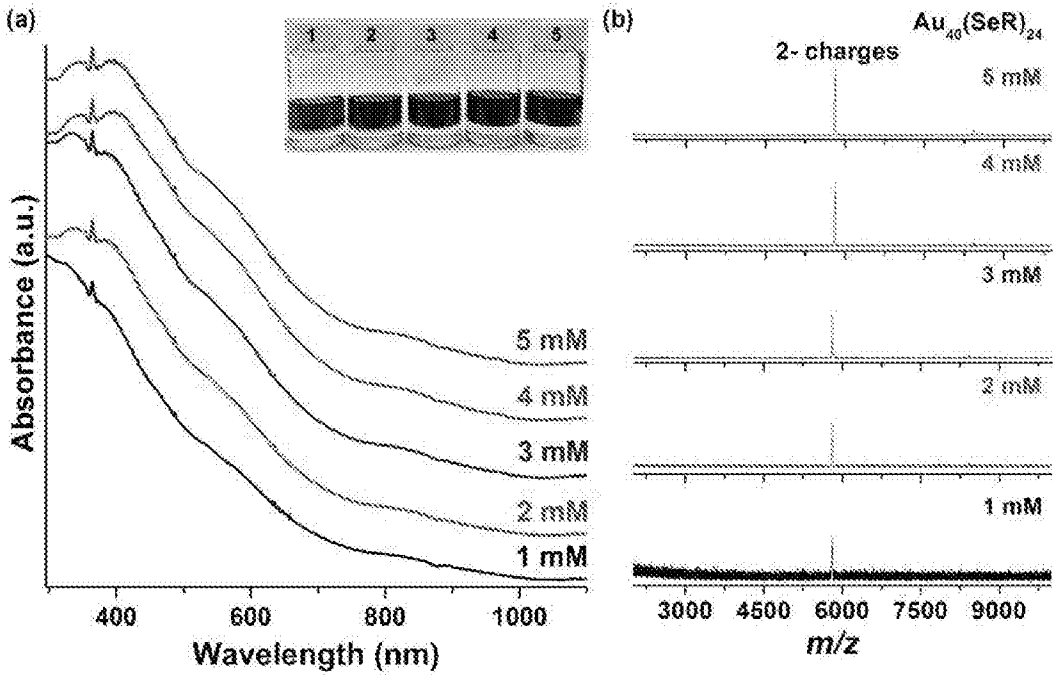


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[Fig. 12]

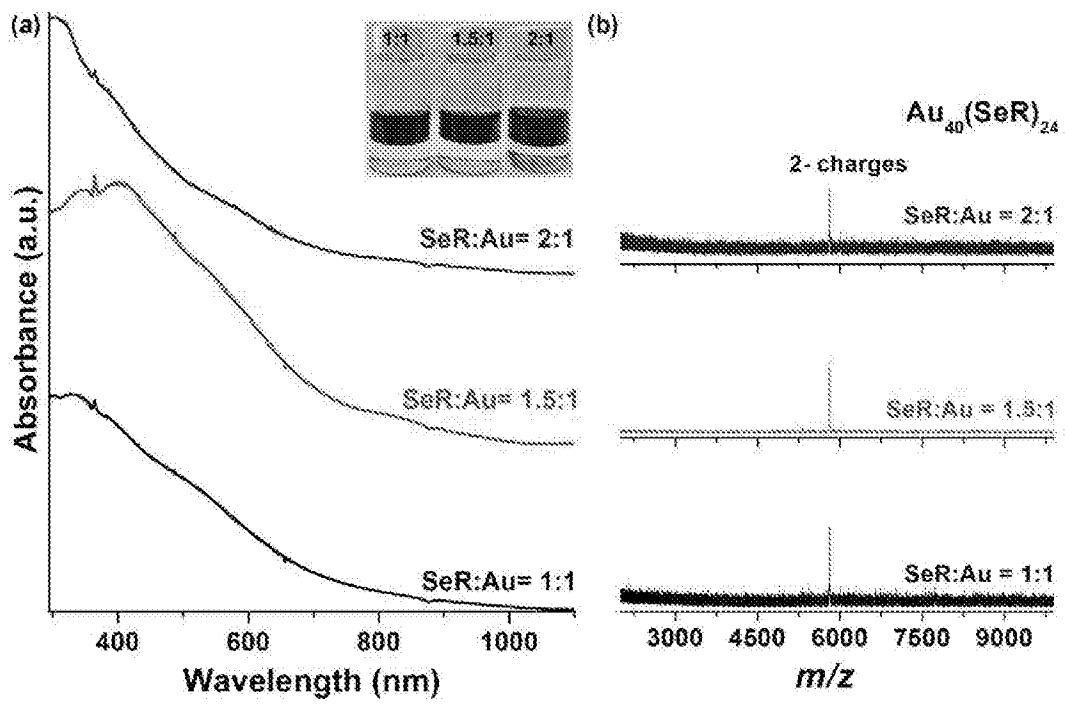


[Fig. 13]



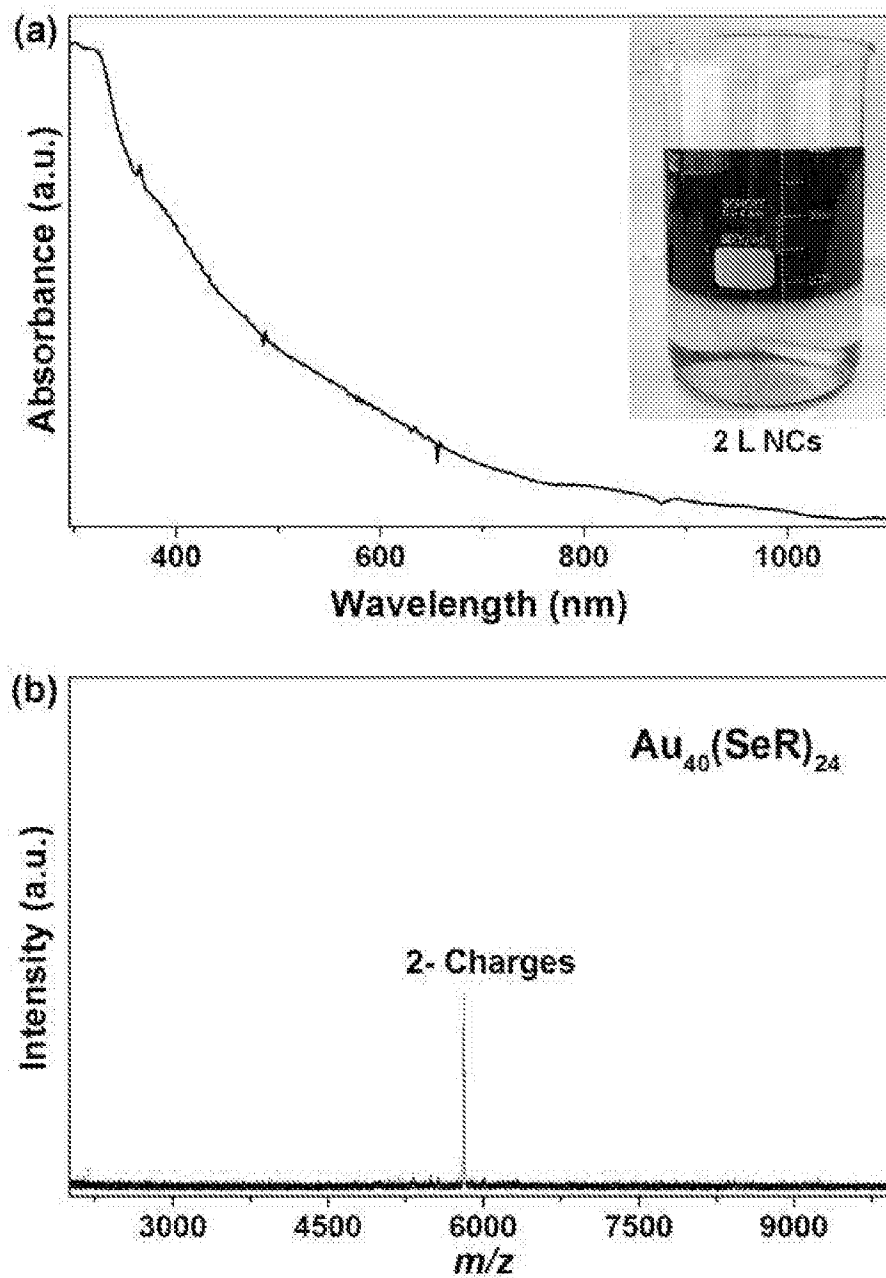
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[Fig. 14]



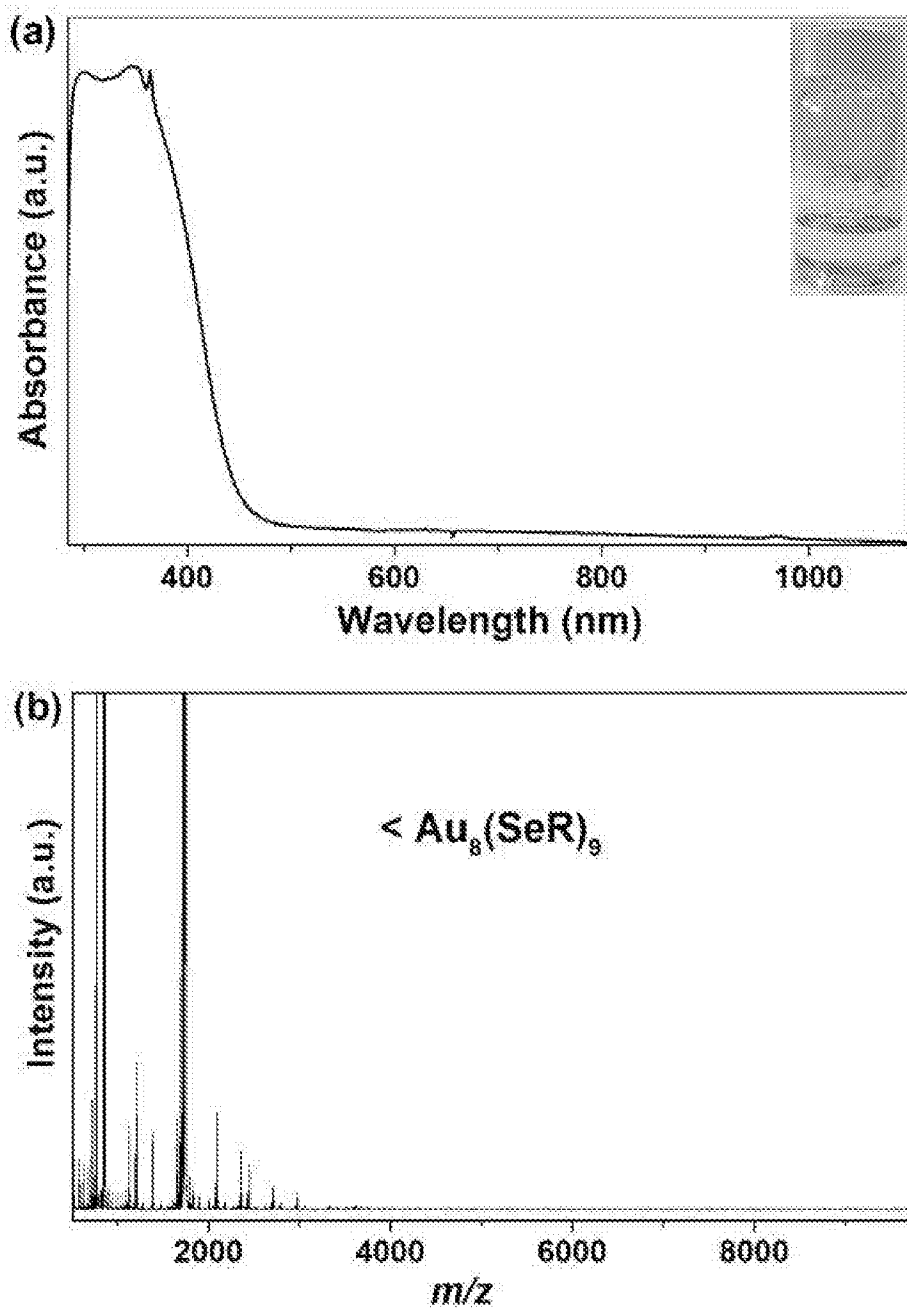
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[Fig. 15]



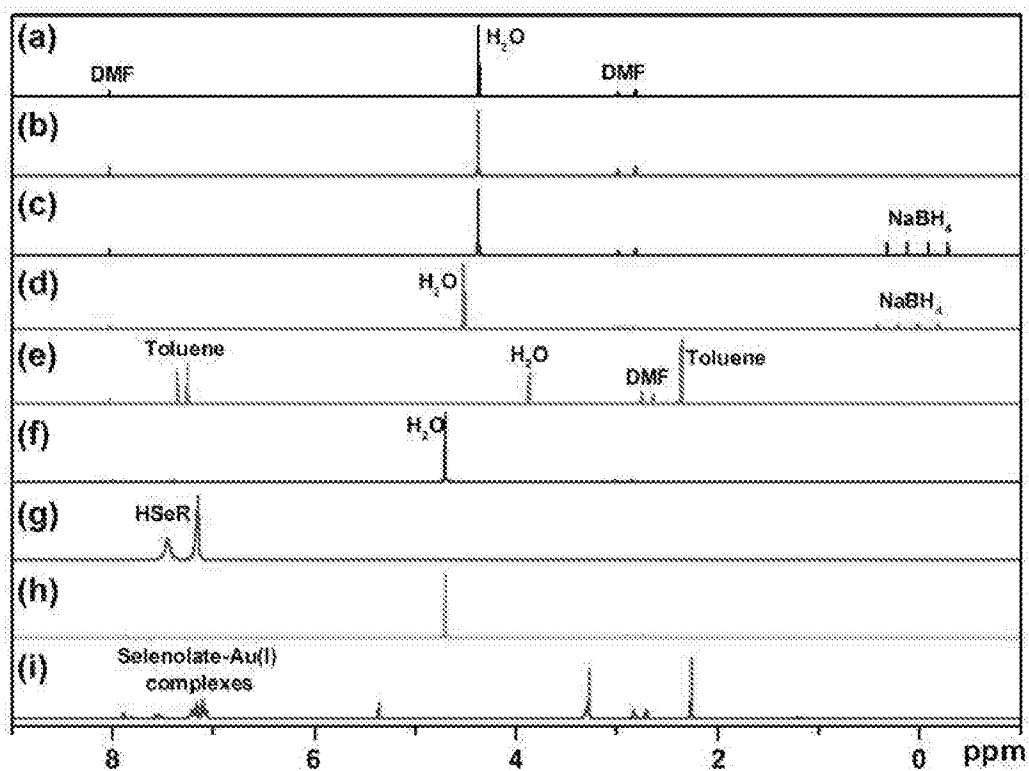
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[Fig. 16]

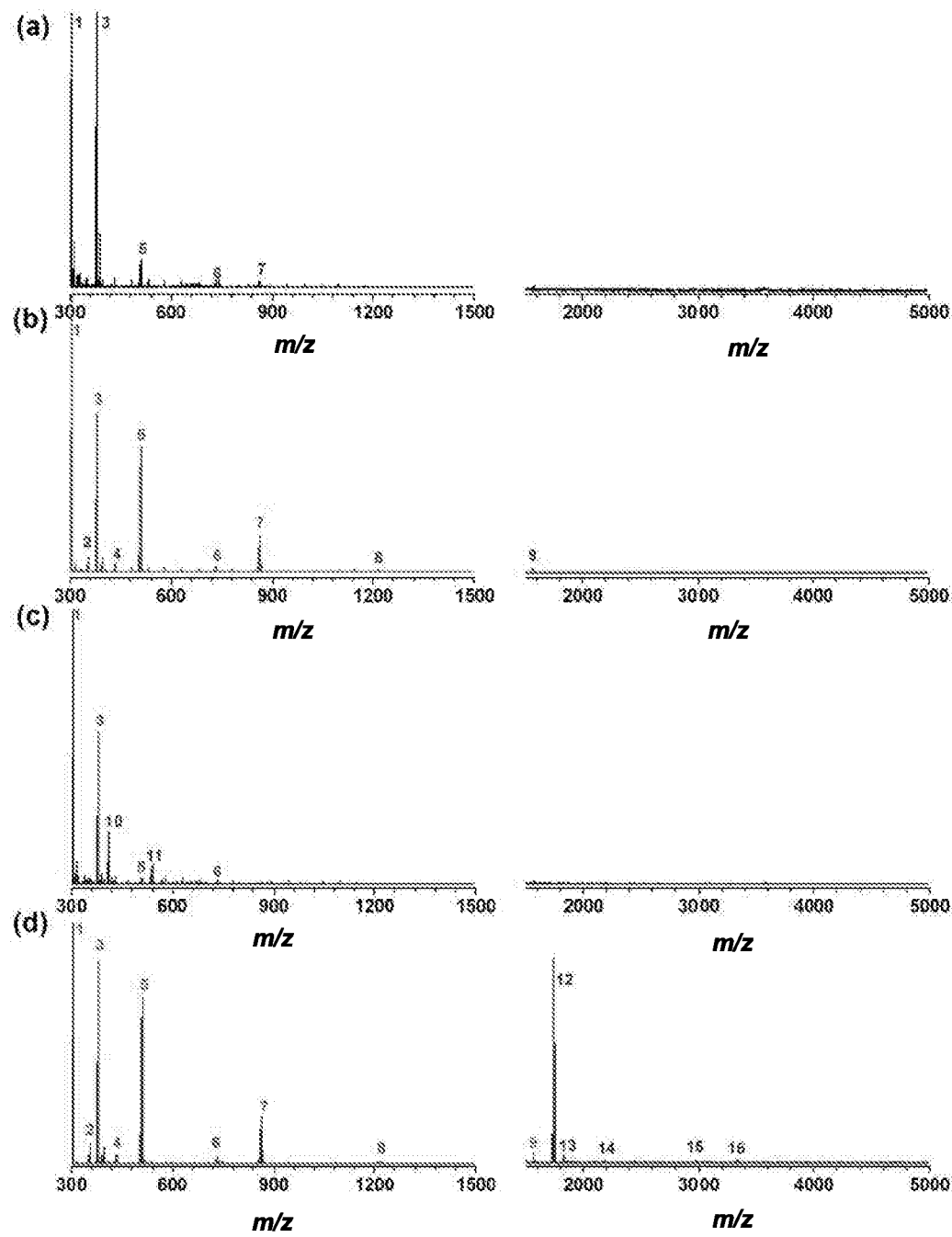


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[Fig. 17]

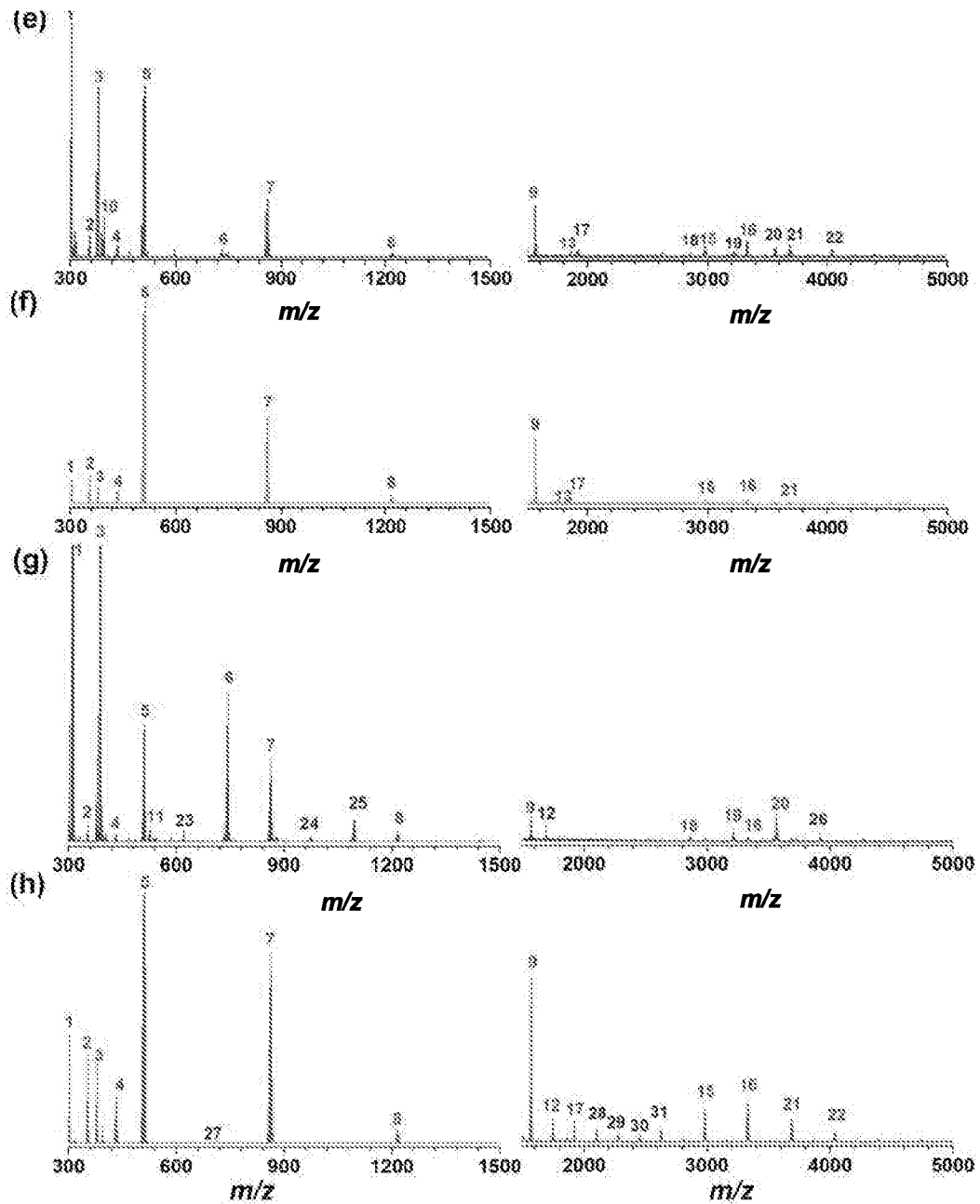


[Fig. 18]



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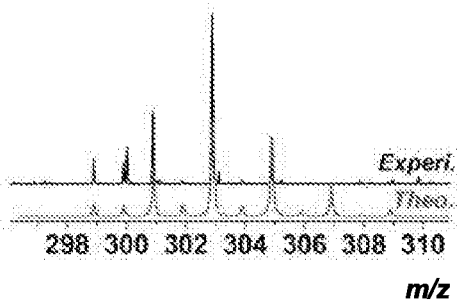
[Fig. 18]



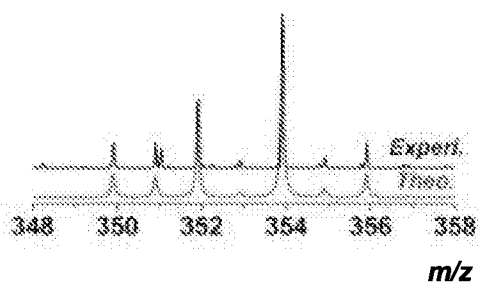
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[Fig. 19]

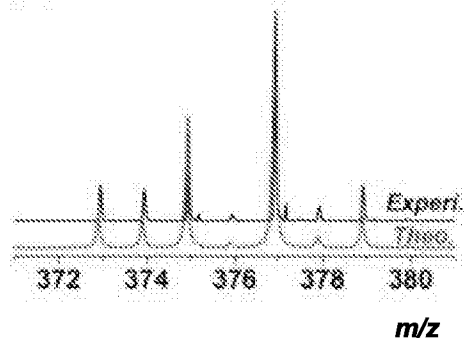
(1)  $(\text{HSeR})\text{Cl}_3\text{NaOH}$



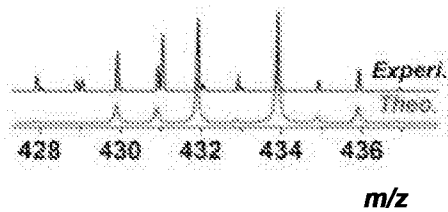
(2)  $\text{Au}(\text{SeR})$



(3)  $\text{Au}(\text{SeR})\text{Na}$

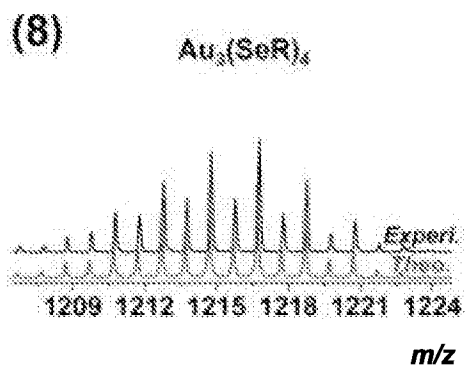
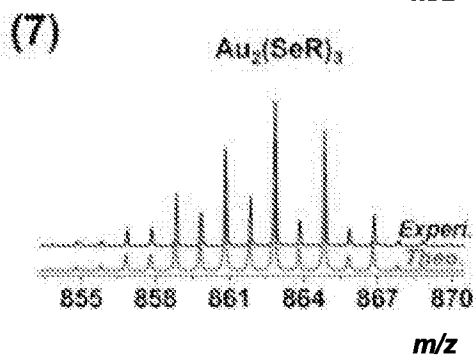
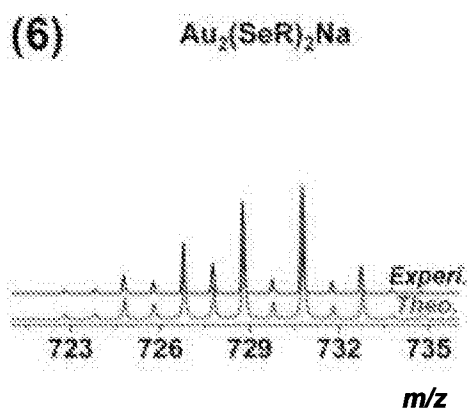
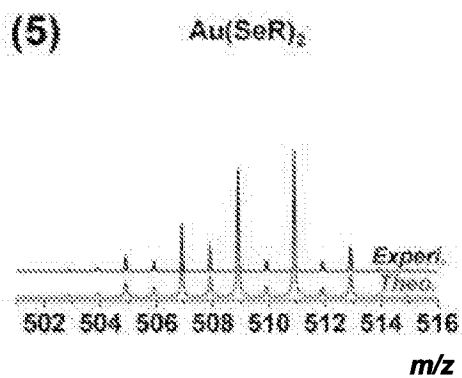


(4)  $\text{Au}(\text{SeR})(\text{NaOH})_2$



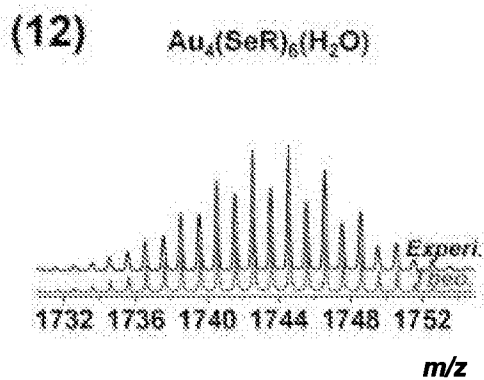
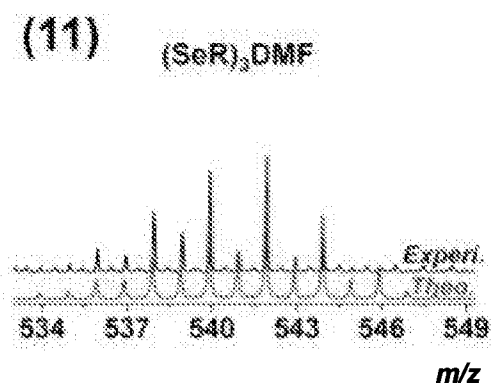
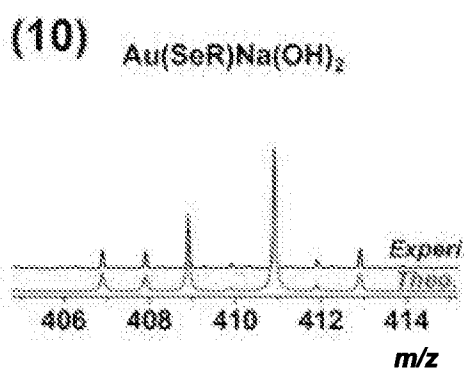
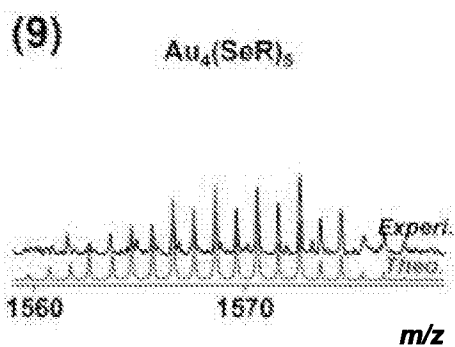
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[Fig. 19]



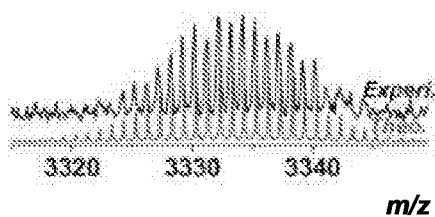
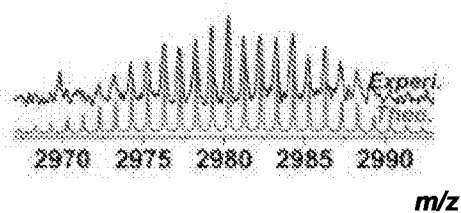
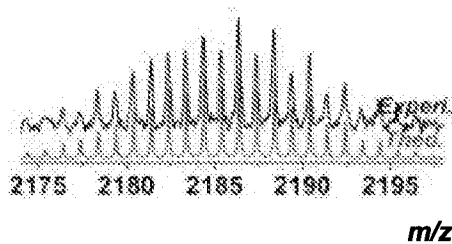
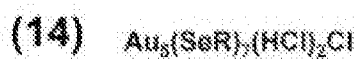
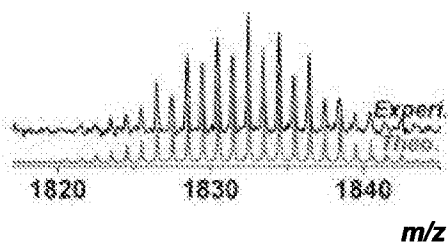
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[Fig. 19]



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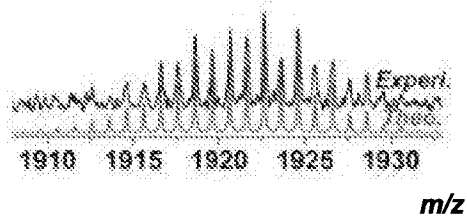
[Fig. 19]



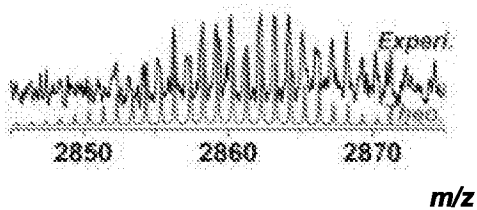
27/78

[Fig. 19]

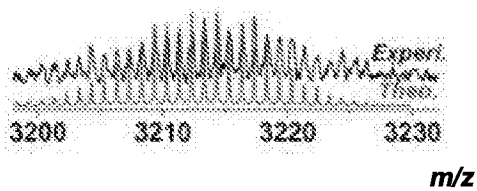
(17)  $\text{Au}_5(\text{SeR})_8$



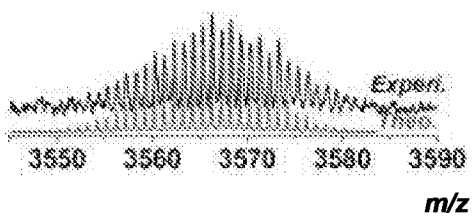
(18)  $\text{Au}_6(\text{SeR})_8\text{Cl}$



(19)  $\text{Au}_9(\text{SeR})_8\text{Cl}$



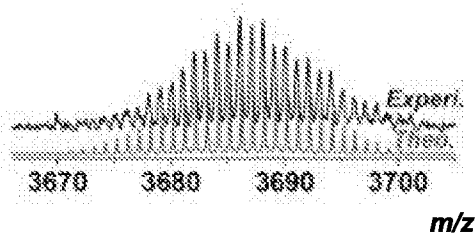
(20)  $\text{Au}_{10}(\text{SeR})_{10}\text{Cl}$



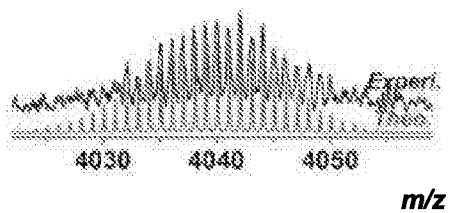
28/78

[Fig. 19]

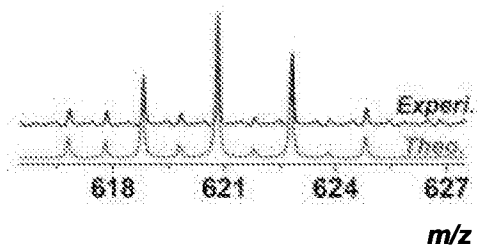
(21)  $\text{Au}_{10}(\text{SeR})_{11}$



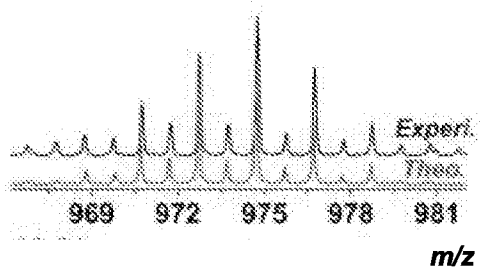
(22)  $\text{Au}_{11}(\text{SeR})_{12}$



(23)  $\text{Au}_2(\text{SeR})\text{Cl}_2$



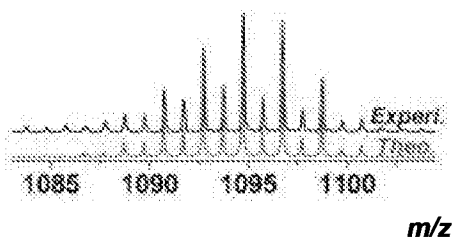
(24)  $\text{Au}_3(\text{SeR})_2\text{Cl}_2$



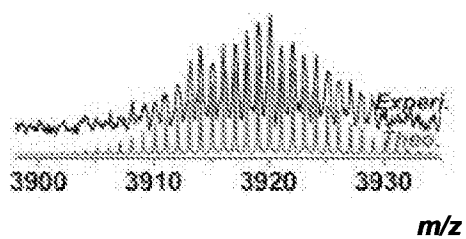
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[Fig. 19]

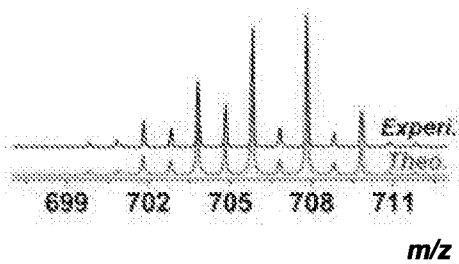
(25)  $\text{Au}_5(\text{SeR})_5\text{Cl}$



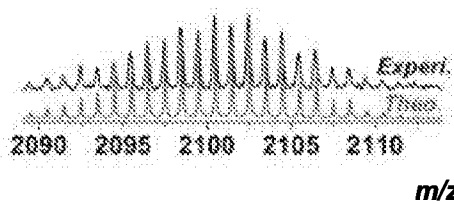
(26)  $\text{Au}_{11}(\text{SeR})_{11}\text{Cl}$



(27)  $\text{Au}_2(\text{SeR})_2$



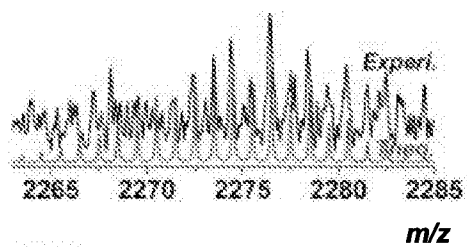
(28)  $\text{Au}_5(\text{SeR})_5\text{Na}$



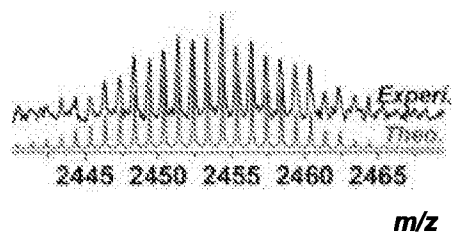
30/78

[Fig. 19]

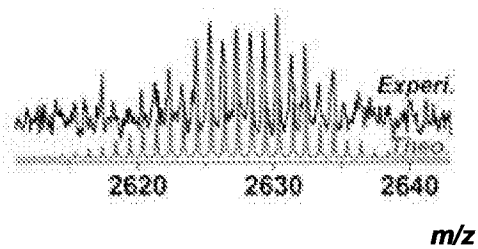
(29)  $\text{Au}_5(\text{SeR})_7$



(30)  $\text{Au}_6(\text{SeR})_8\text{Na}$

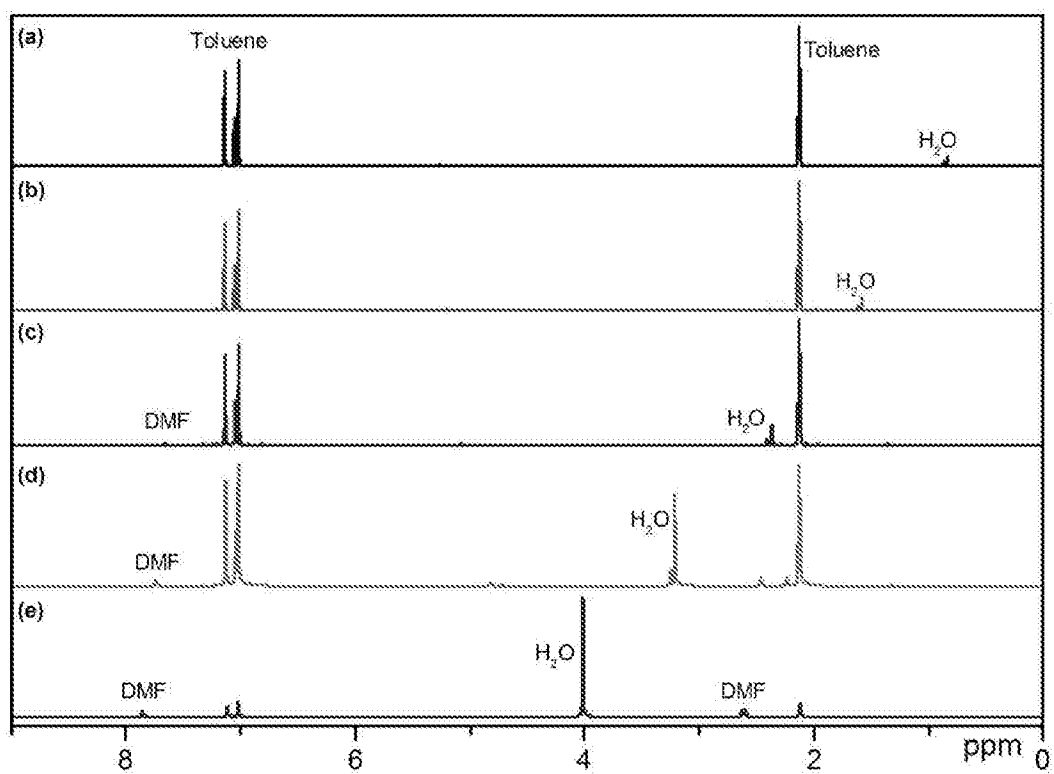


(31)  $\text{Au}_7(\text{SeR})_8$



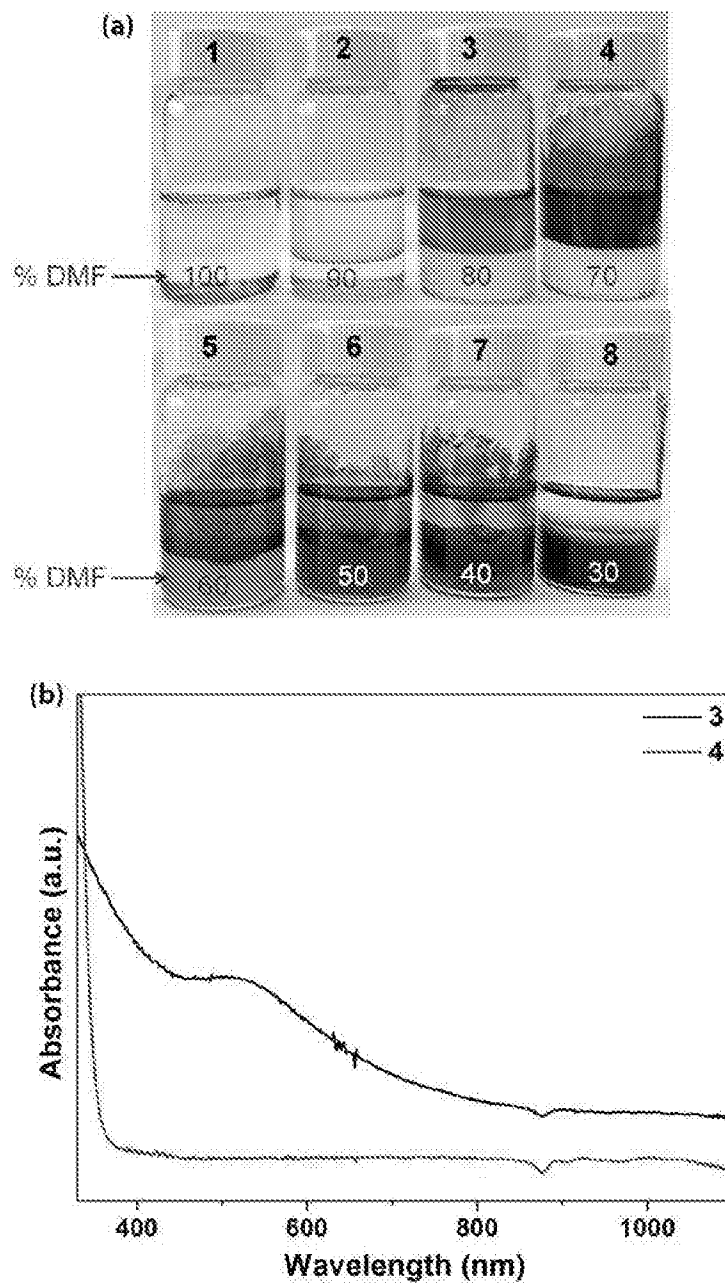
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[Fig. 20]



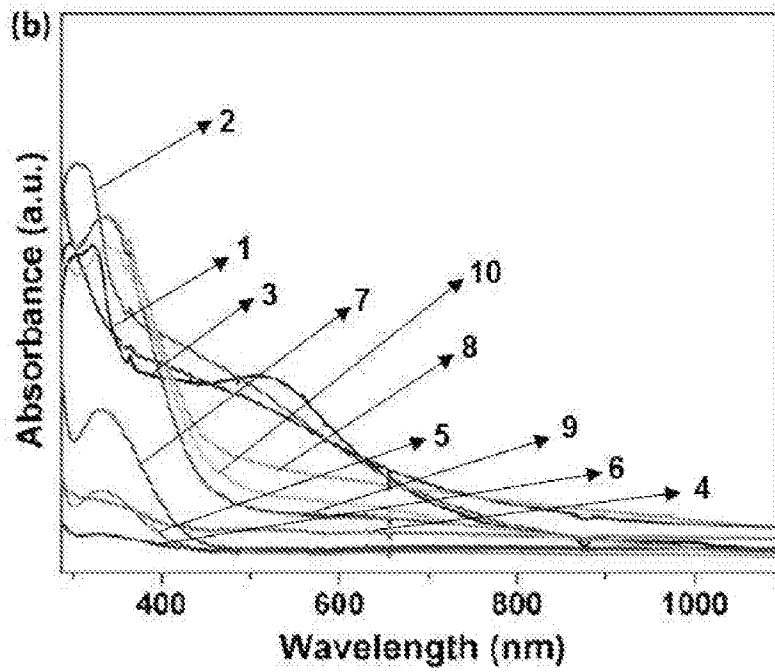
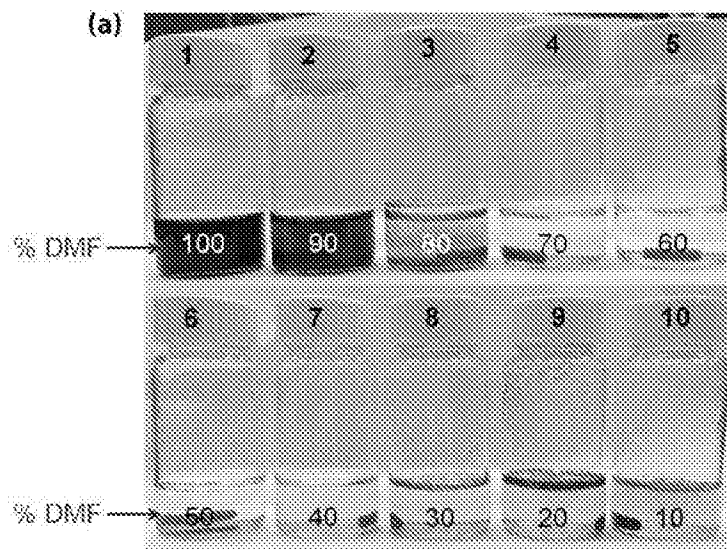
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[Fig. 21]

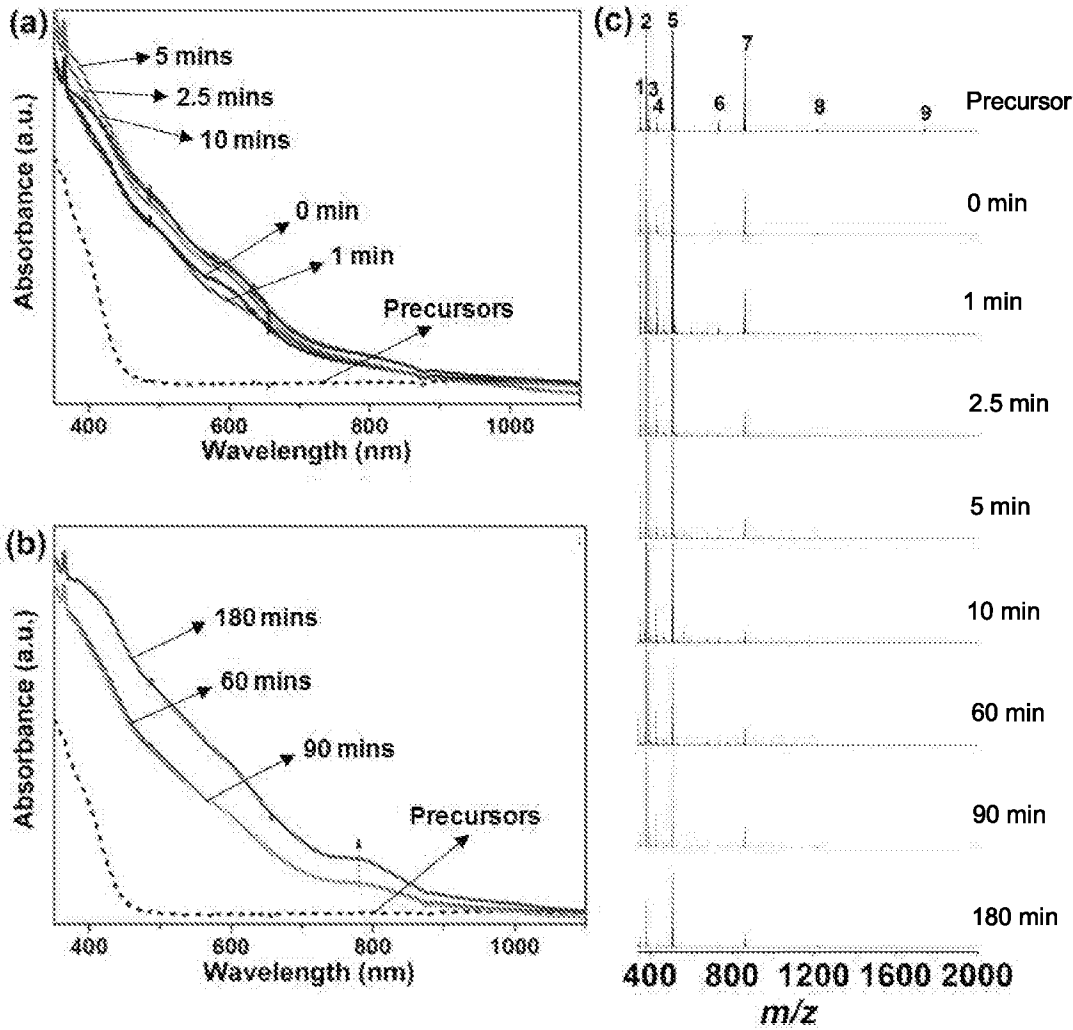


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[Fig. 22]

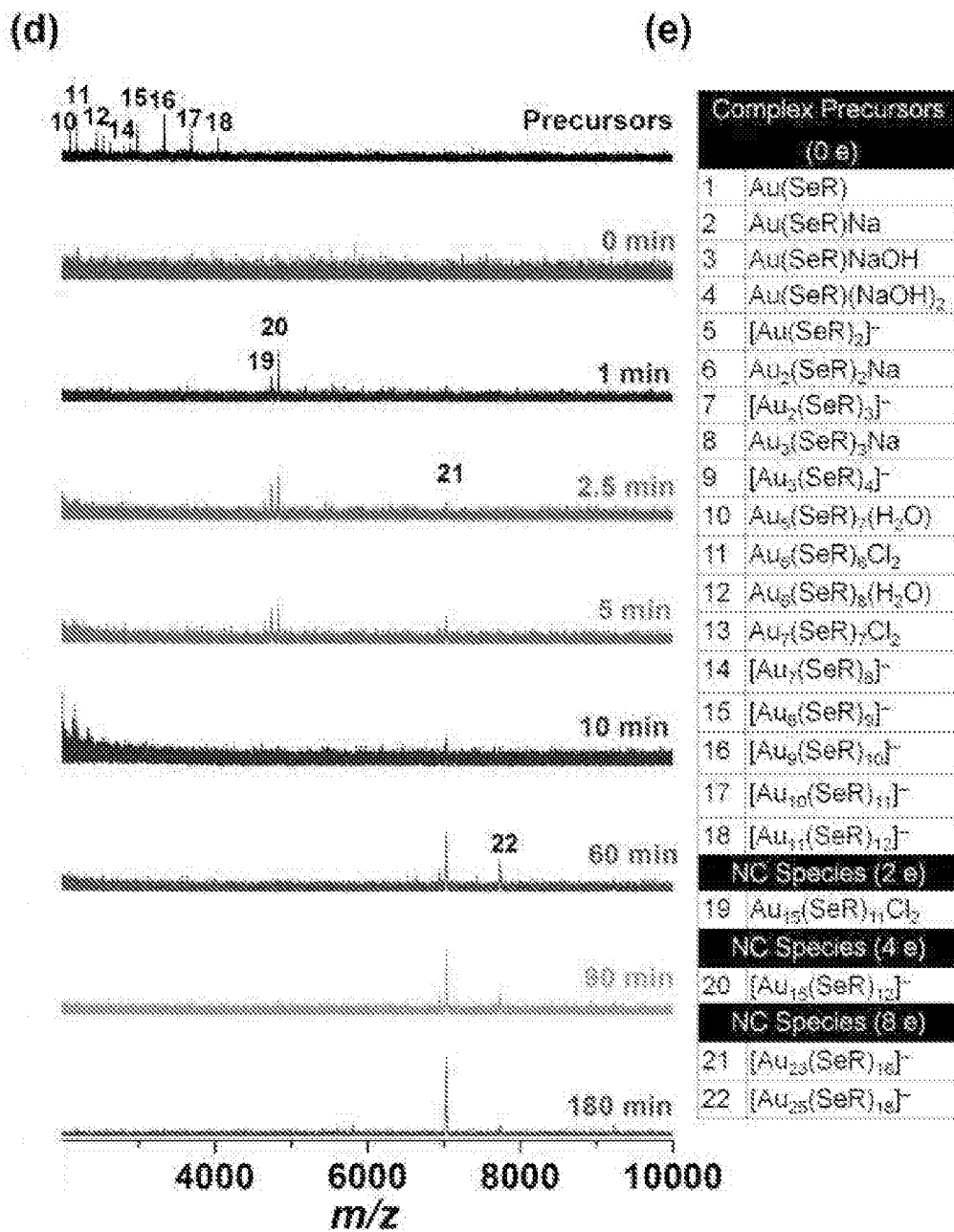


[Fig. 23]



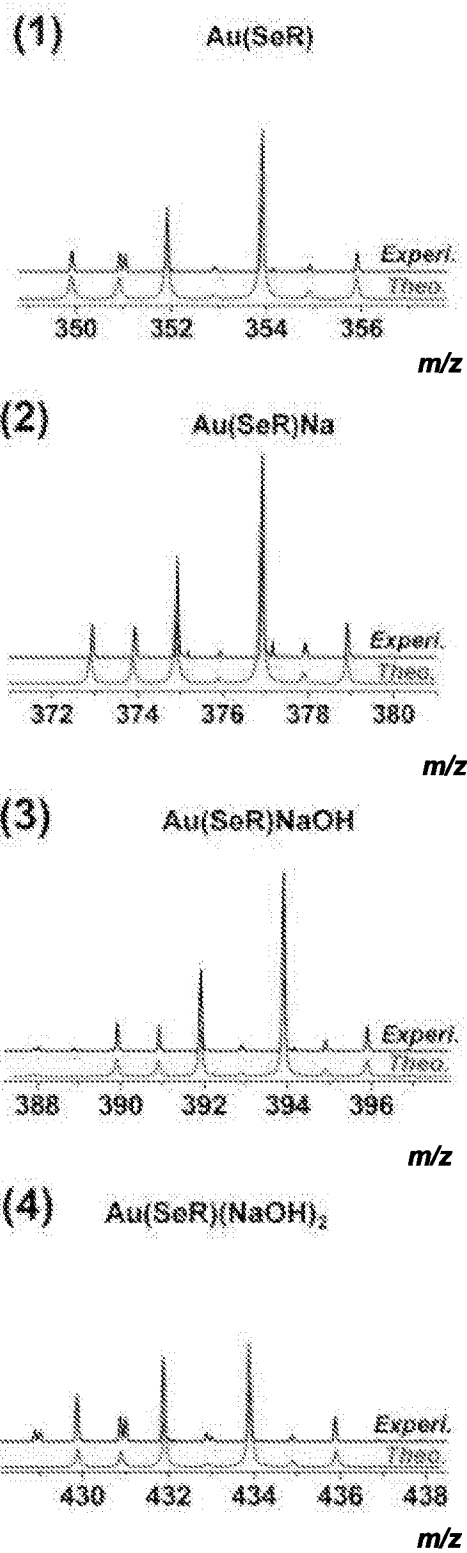
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[Fig. 23]



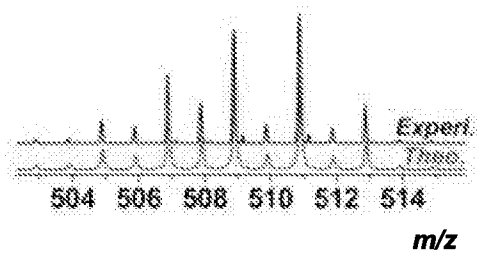
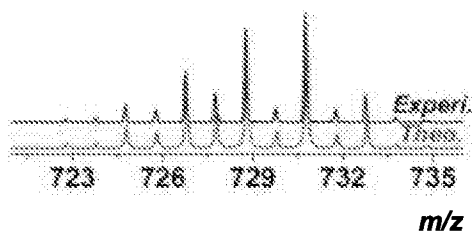
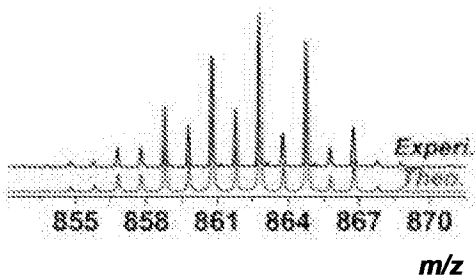
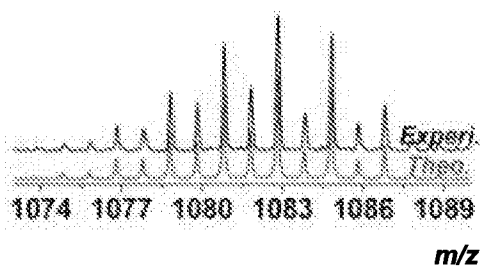
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[Fig. 24]



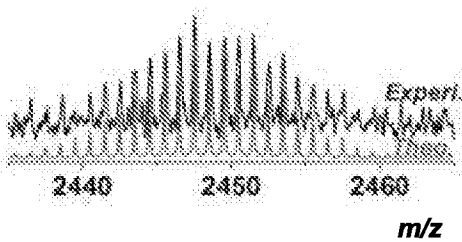
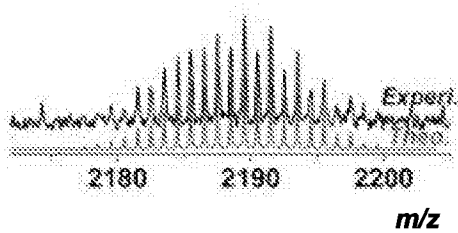
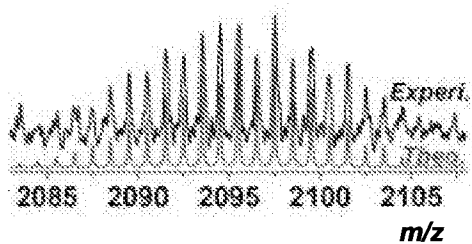
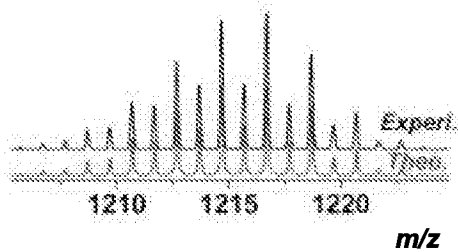
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[Fig. 24]

(5)  $[\text{Au}(\text{SeR})_2]^-$ (6)  $\text{Au}_2(\text{SeR})_2\text{Na}$ (7)  $[\text{Au}_2(\text{SeR})_3]^-$ (8)  $\text{Au}_3(\text{SeR})_3\text{Na}$ 

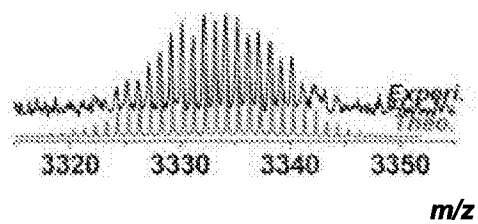
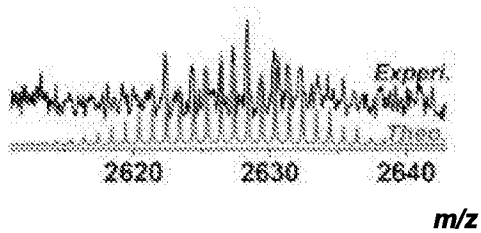
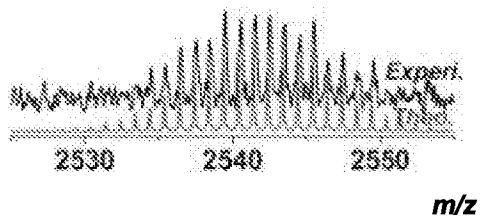
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[Fig. 24]



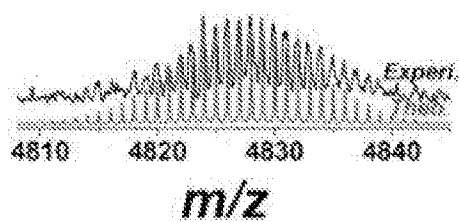
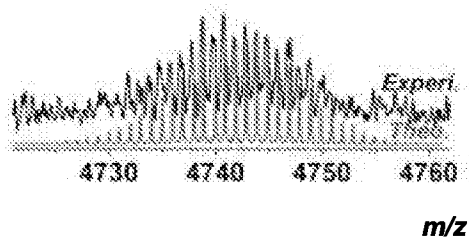
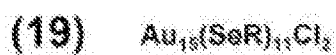
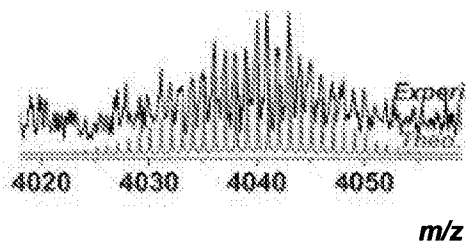
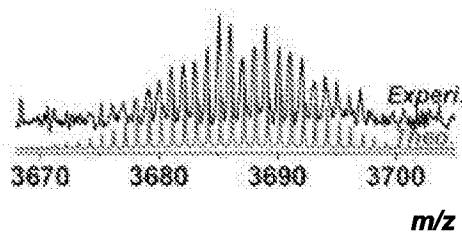
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[Fig. 24]



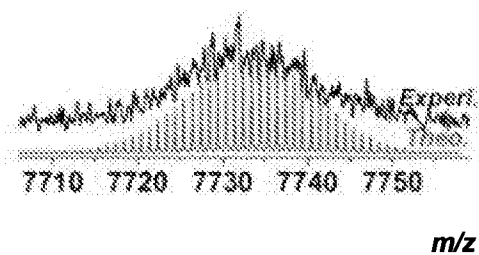
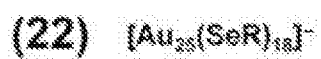
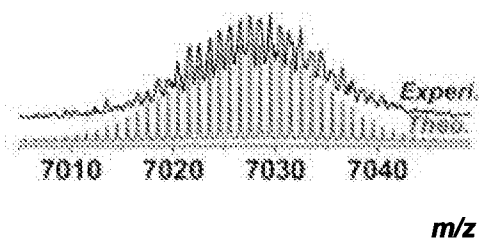
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[Fig. 24]

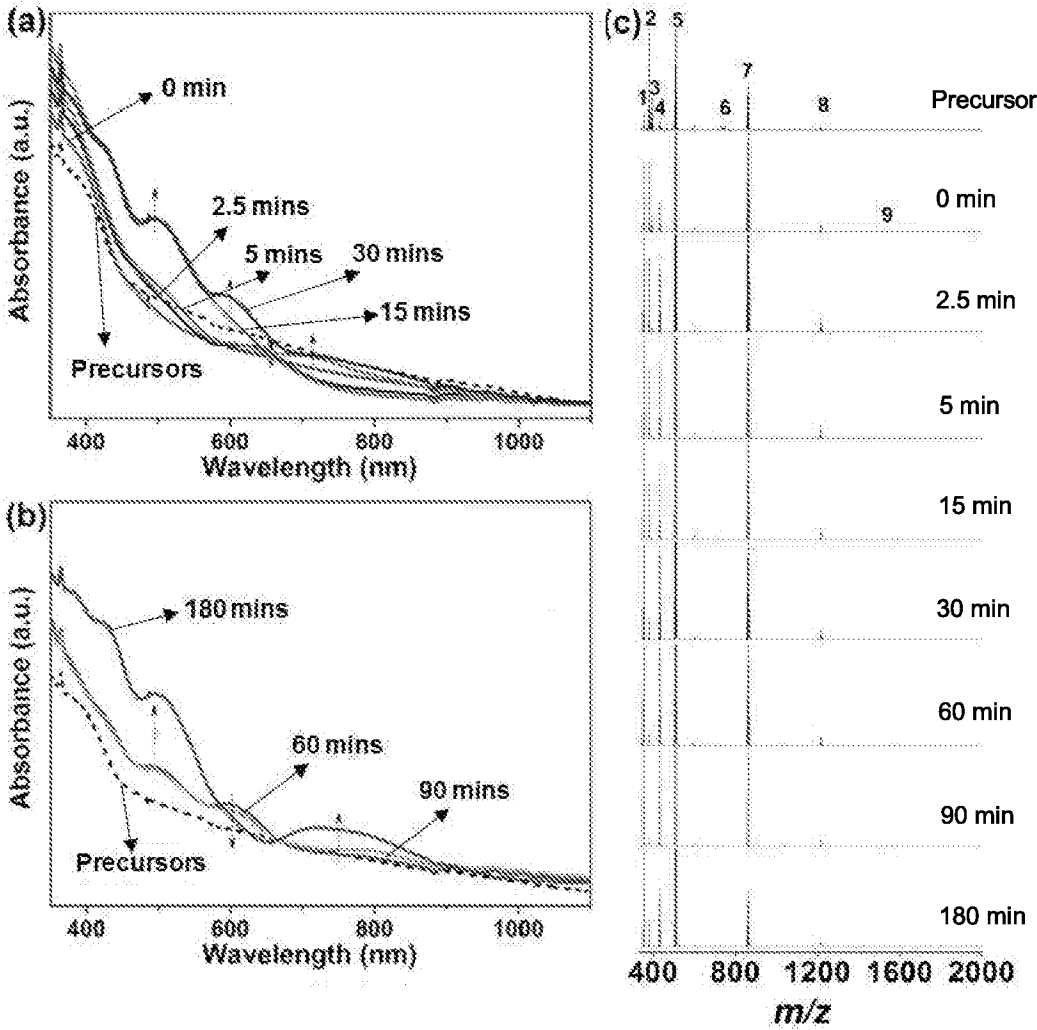


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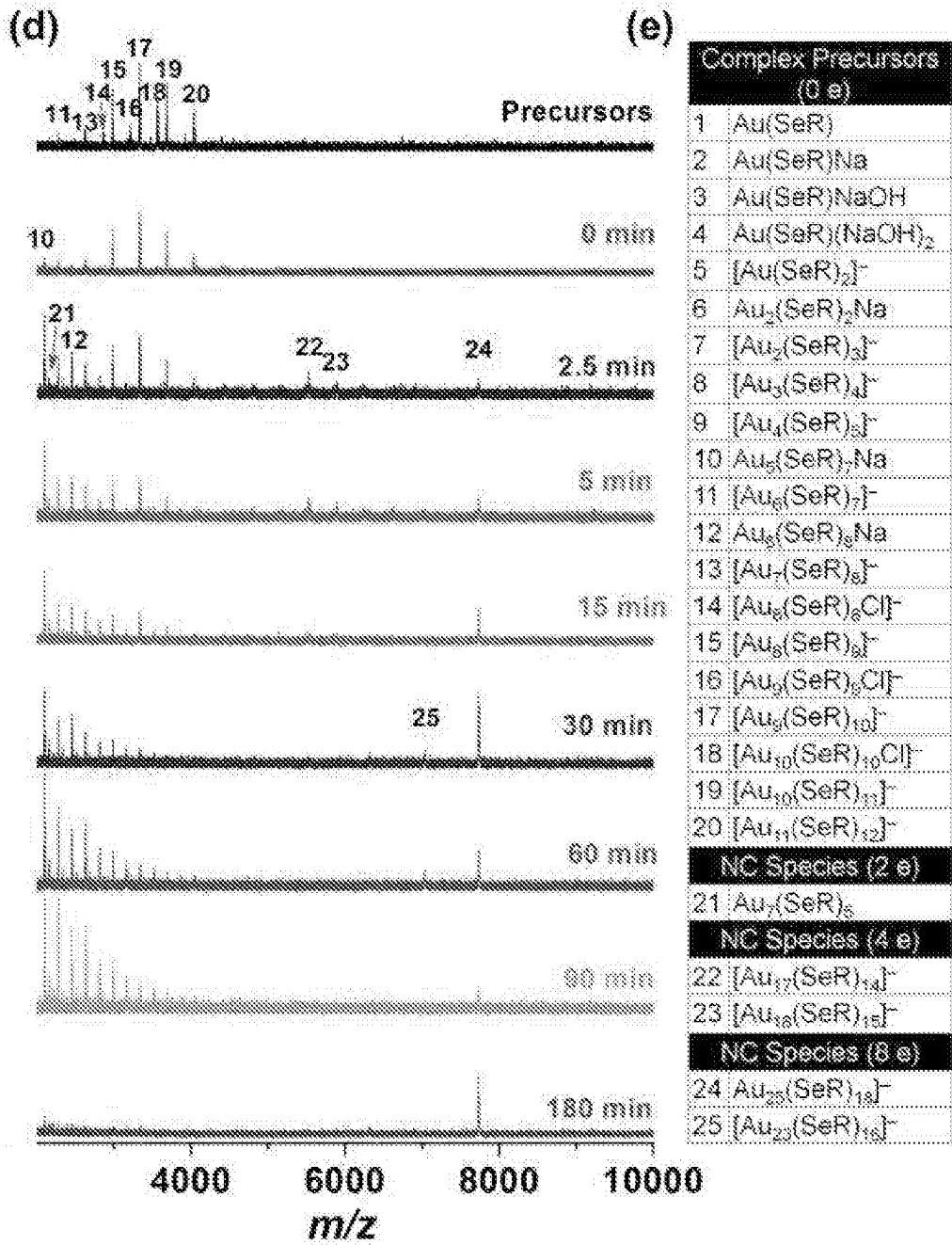
[Fig. 24]



[Fig. 25]

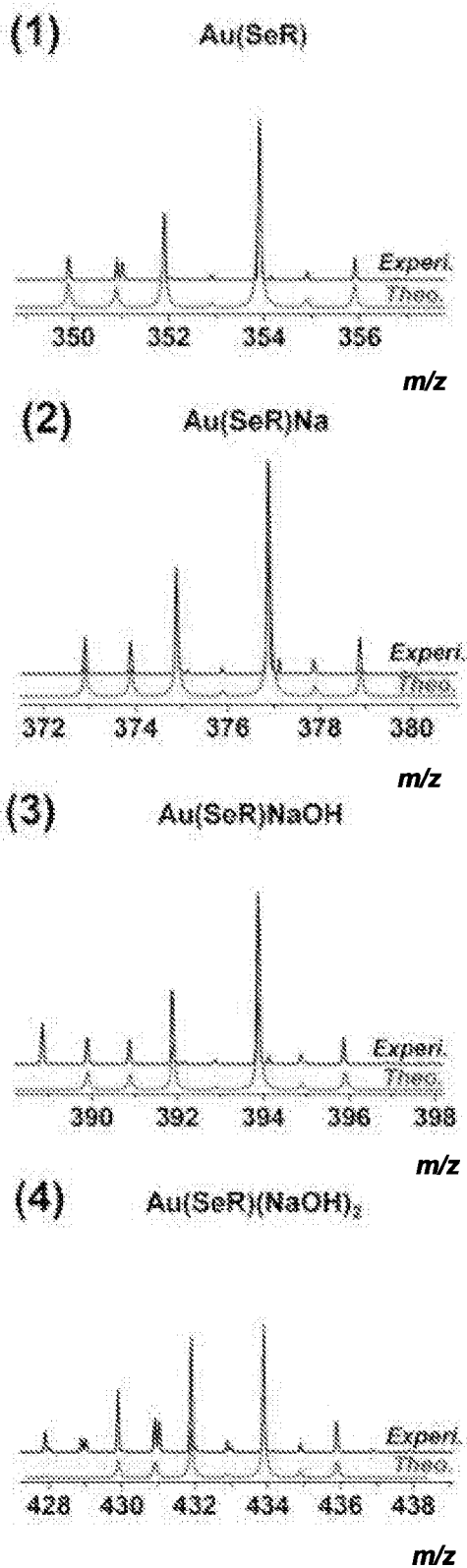


[Fig. 25]



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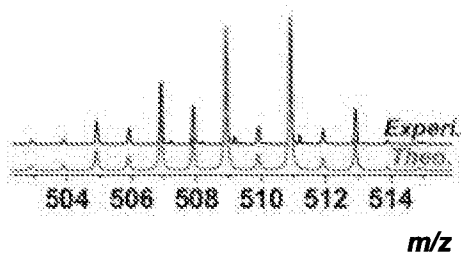
[Fig. 26]



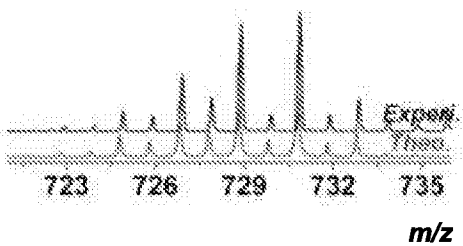
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[Fig. 26]

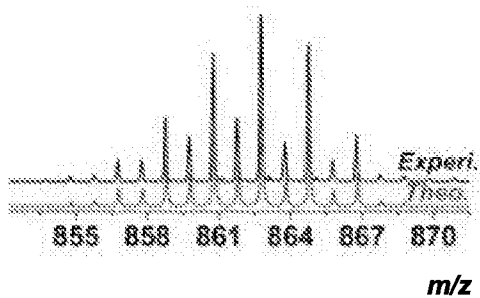
(5)  $[\text{Au}(\text{SeR})_2]^-$



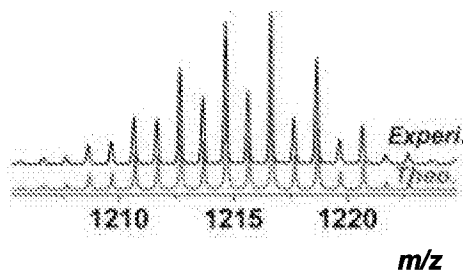
(6)  $\text{Au}_2(\text{SeR})_2\text{Na}$



(7)  $[\text{Au}_2(\text{SeR})_3]^-$

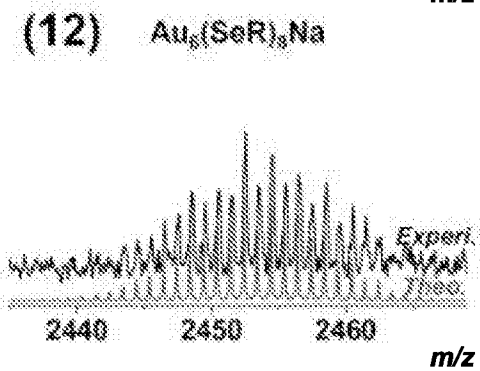
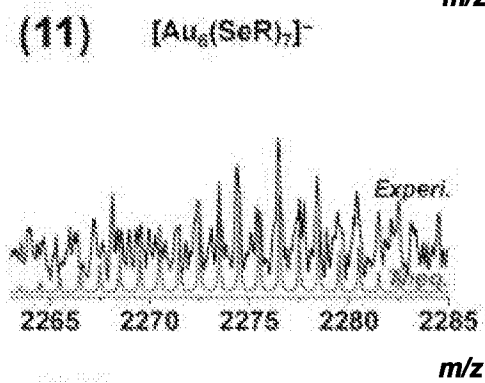
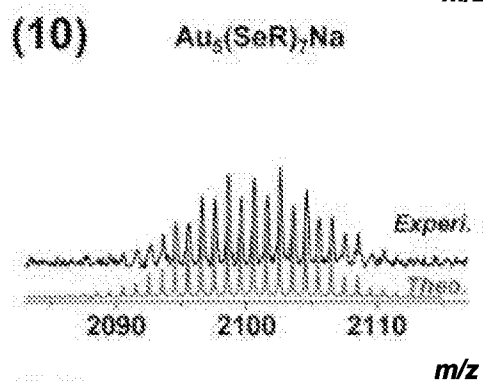
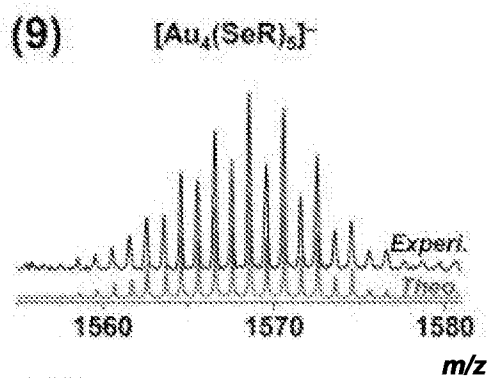


(8)  $[\text{Au}_3(\text{SeR})_4]^-$



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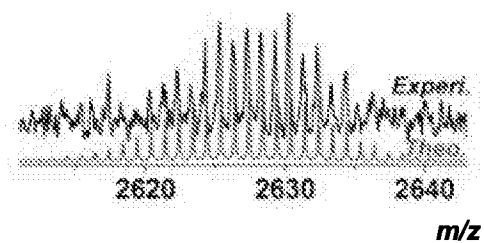
[Fig. 26]



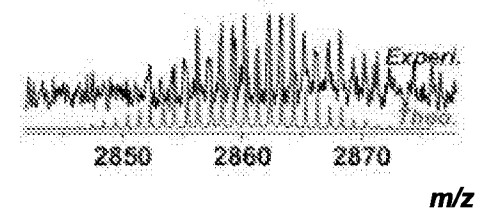
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[Fig. 26]

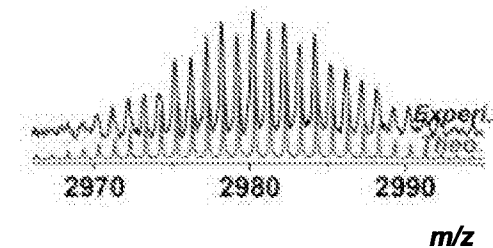
(13)  $[\text{Au}_7(\text{SeR})_8]^-$



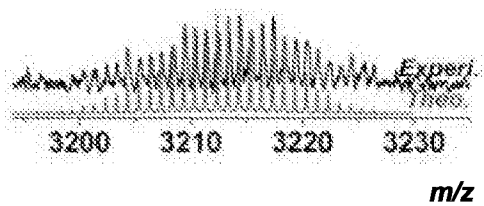
(14)  $[\text{Au}_8(\text{SeR})_8\text{Cl}]^-$



(15)  $[\text{Au}_9(\text{SeR})_9]^-$

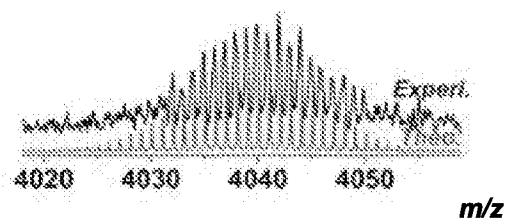
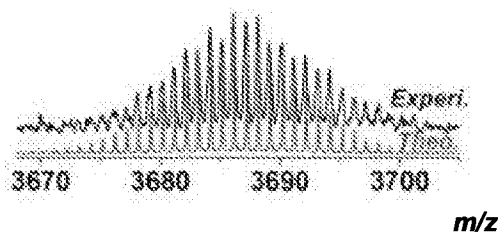
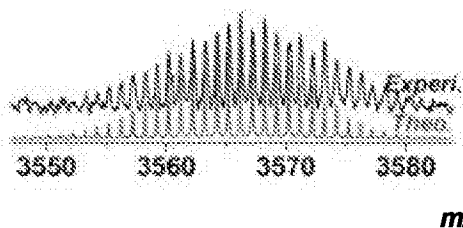
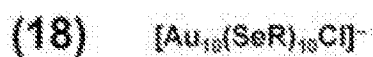
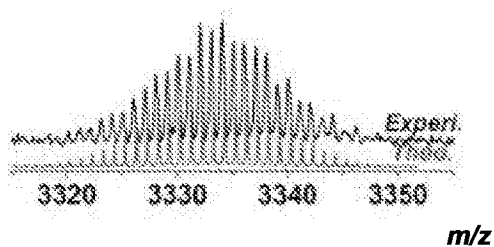


(16)  $[\text{Au}_9(\text{SeR})_9\text{Cl}]^-$



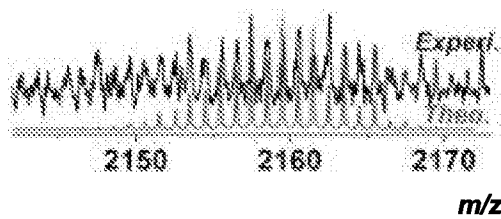
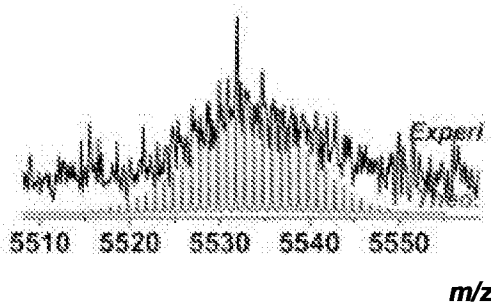
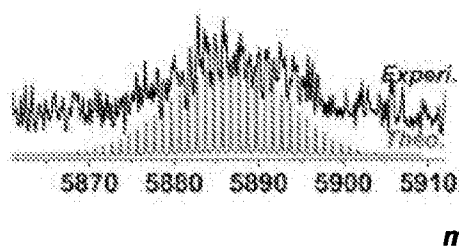
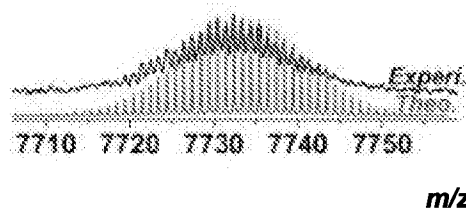
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[Fig. 26]



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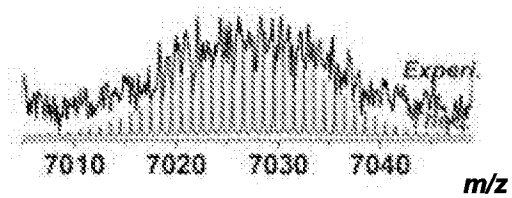
[Fig. 26]

(21)  $\text{Au}_7(\text{SeR})_5$ (22)  $[\text{Au}_{17}(\text{SeR})_{13}]^-$ (23)  $[\text{Au}_{18}(\text{SeR})_{13}]^-$ (24)  $[\text{Au}_{25}(\text{SeR})_{13}]^-$ 

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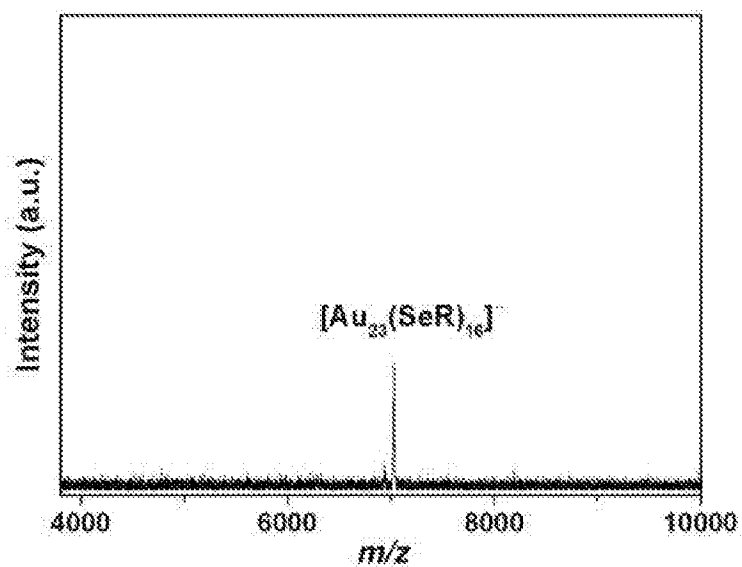
[Fig. 26]

(25)  $[\text{Au}_{23}(\text{SeR})_{13}]^-$

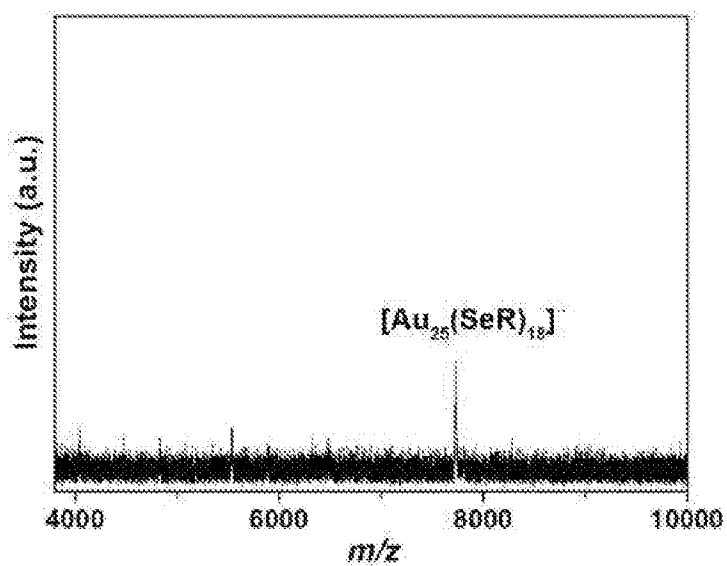


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[Fig. 27]

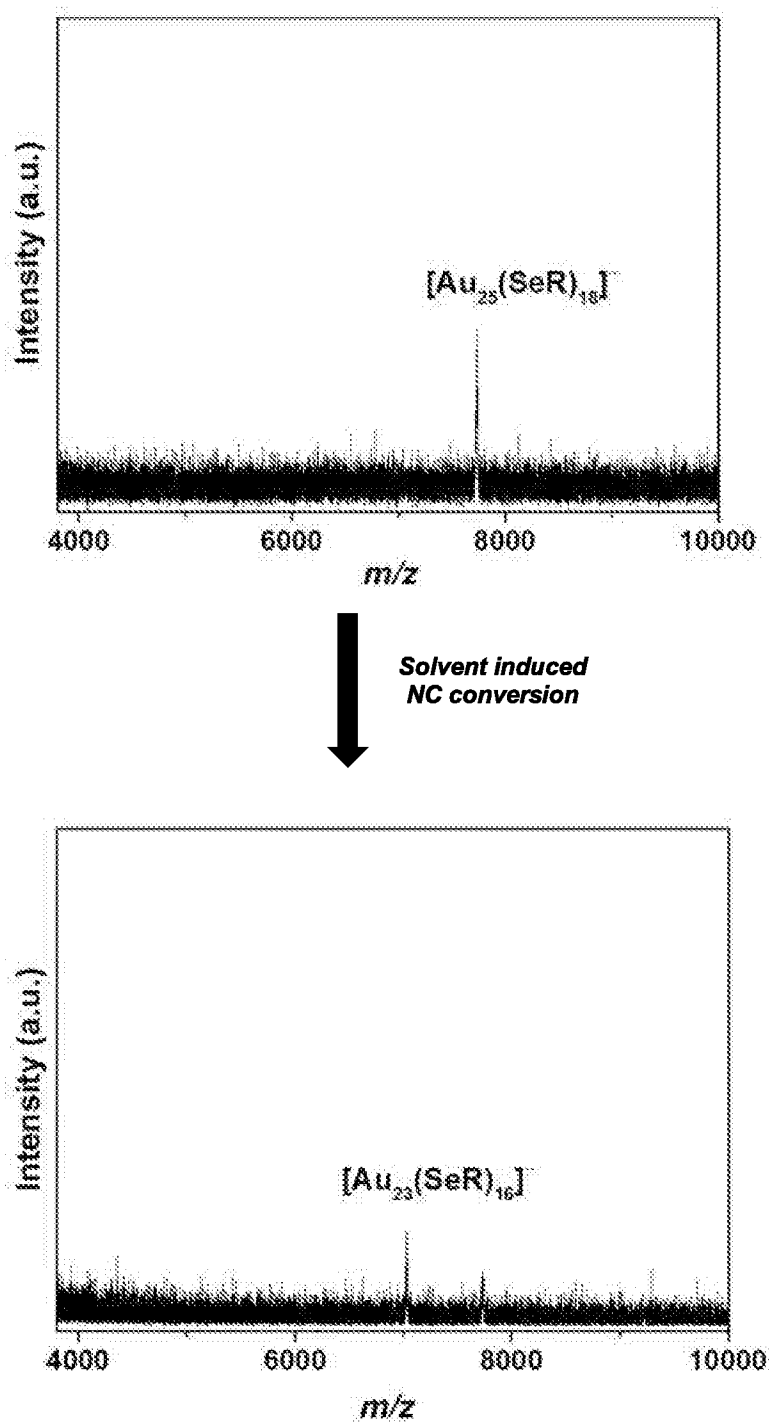


*Solvent induced  
NC conversion*

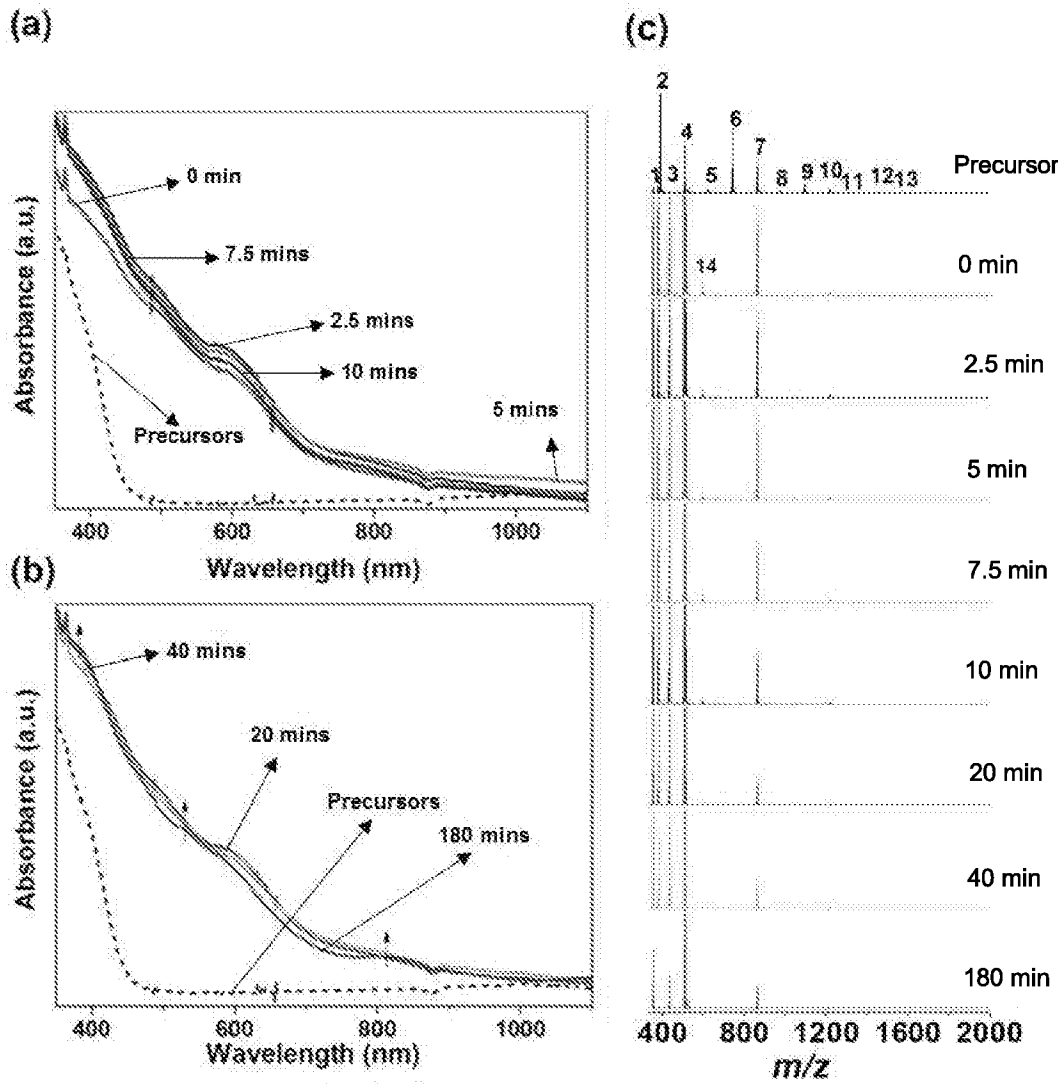


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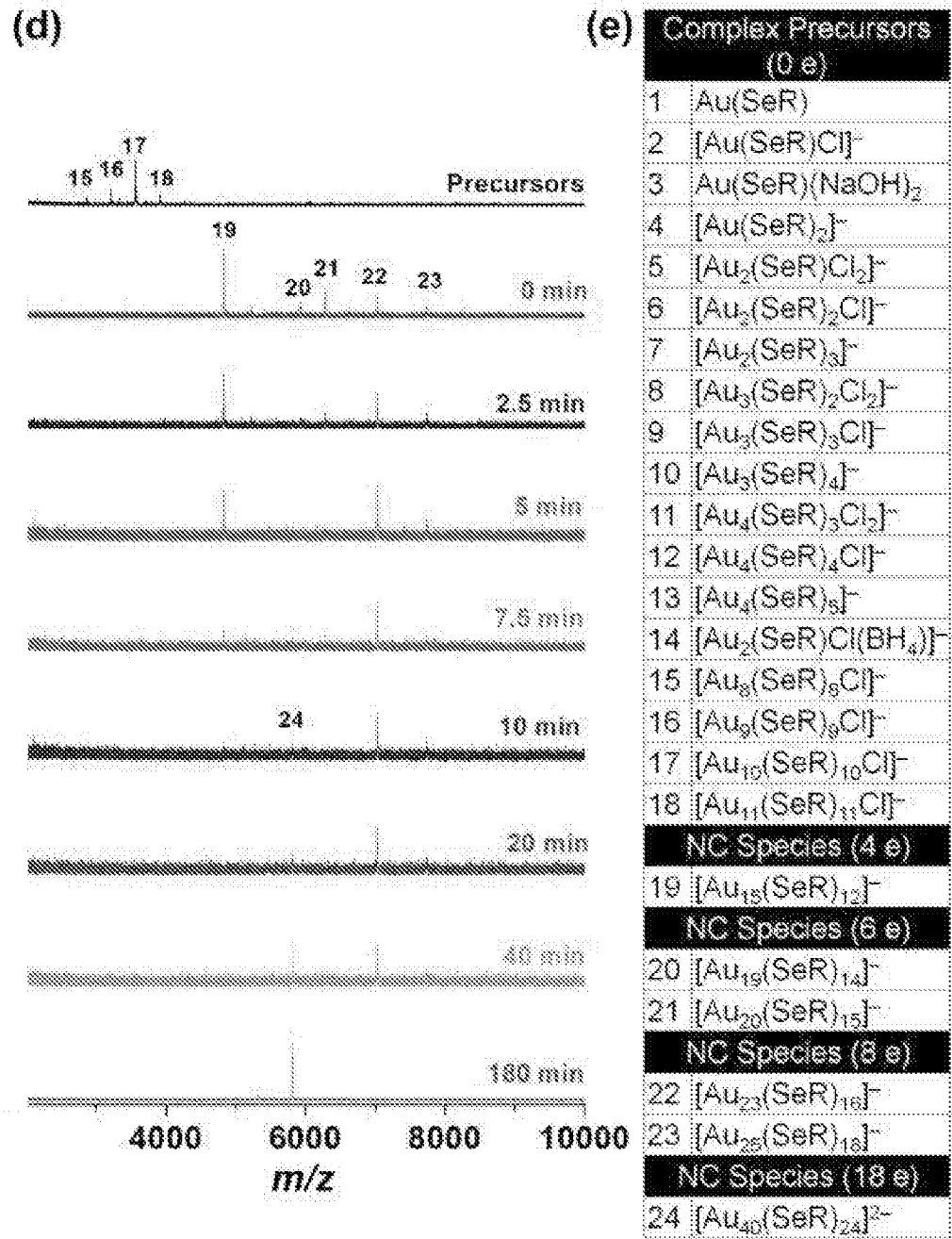
[Fig. 28]



[Fig. 29]

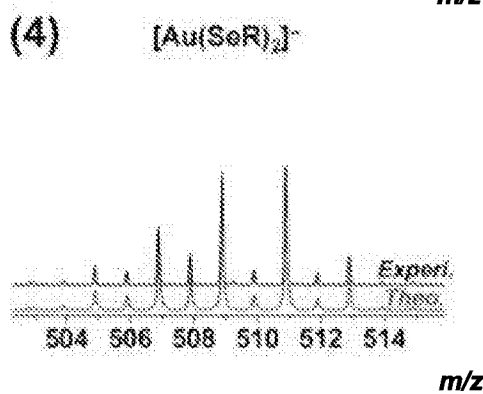
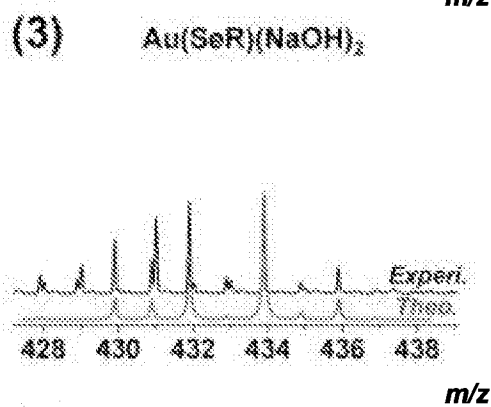
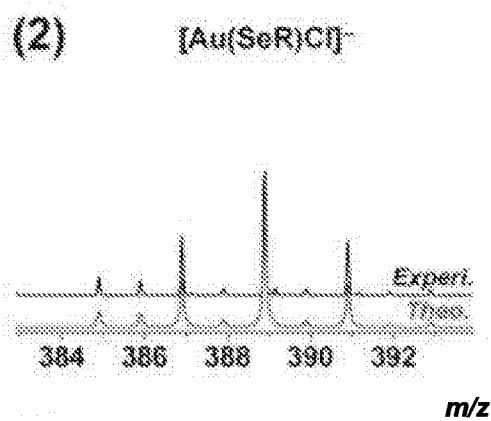
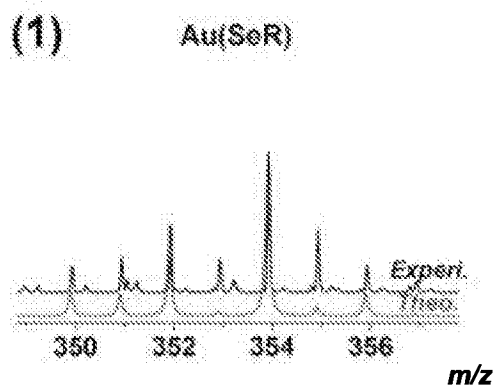


[Fig. 29]



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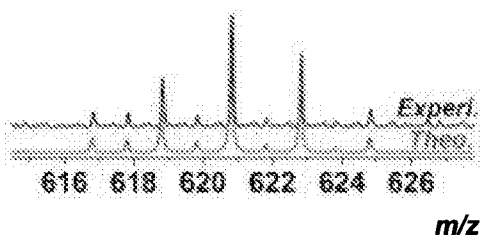
[Fig. 30]



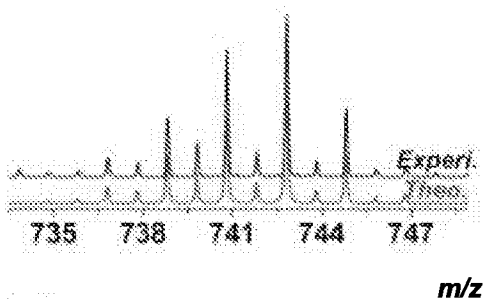
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[Fig. 30]

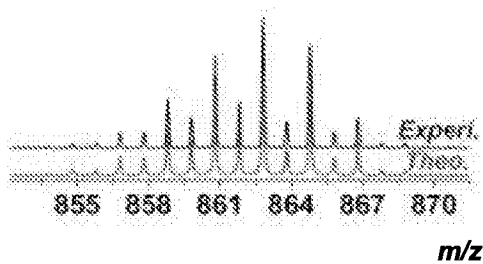
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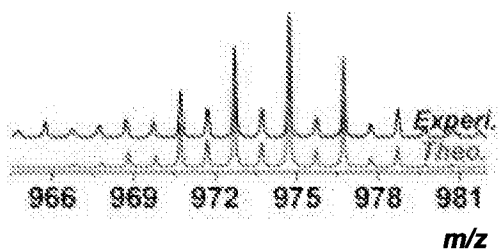
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(7)  $[\text{Au}_2(\text{SeR})_3]^-$

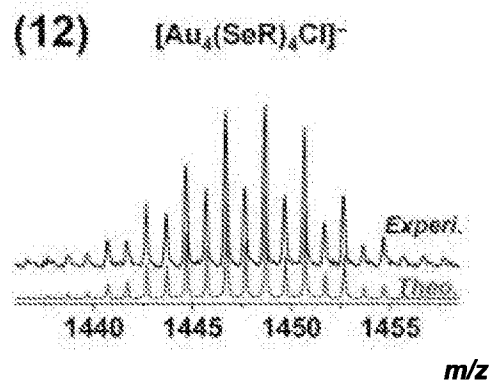
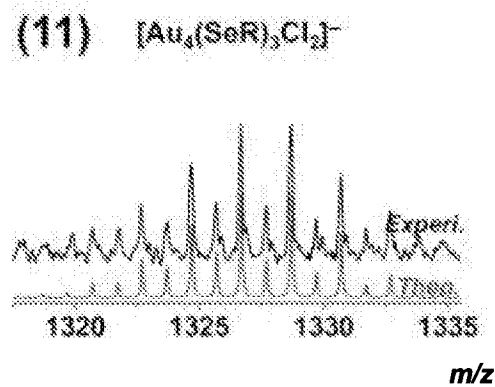
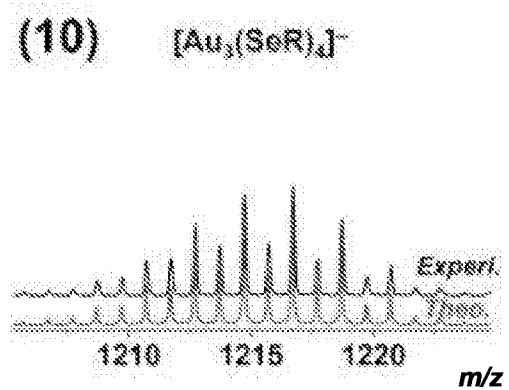
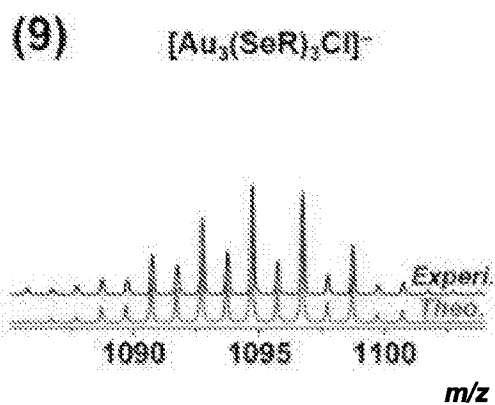


(8)  $[\text{Au}_3(\text{SeR})_2\text{Cl}_2]^-$



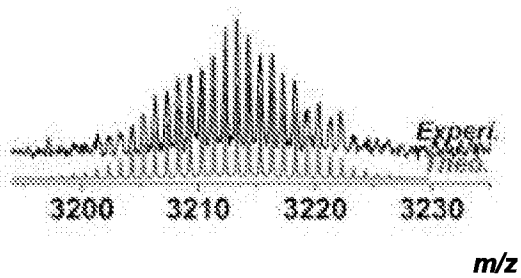
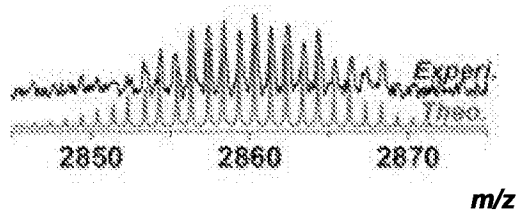
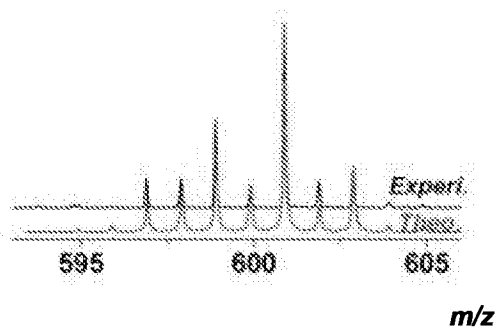
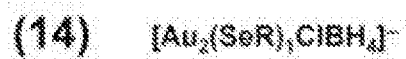
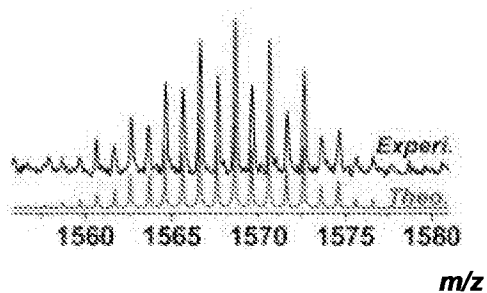
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[Fig. 30]



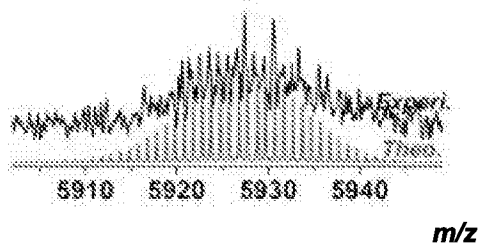
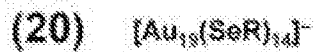
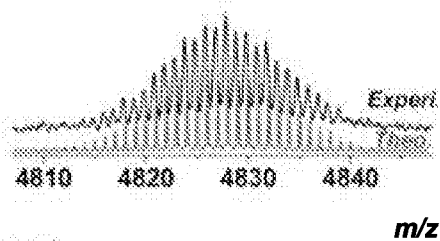
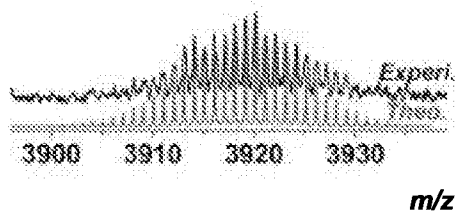
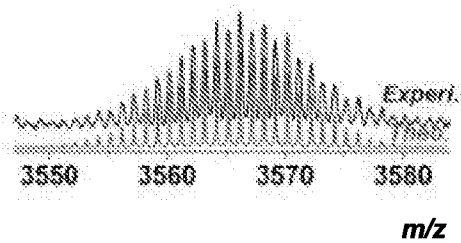
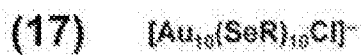
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[Fig. 30]



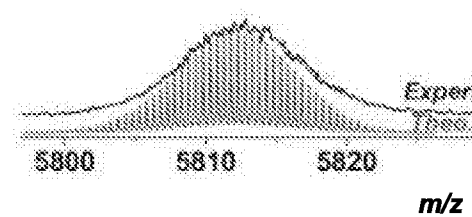
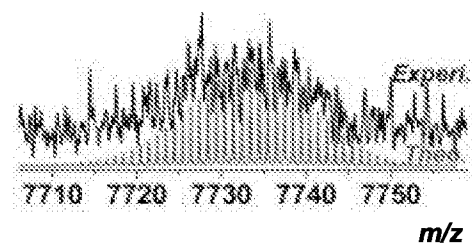
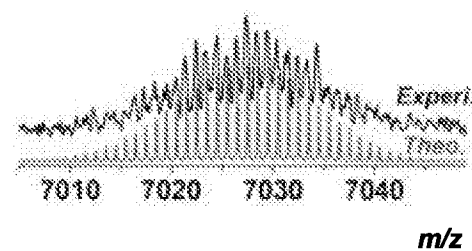
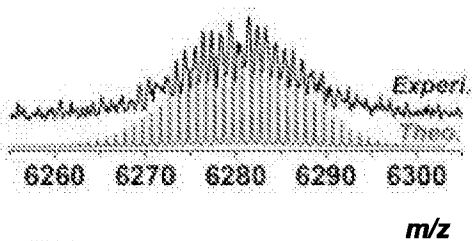
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[Fig. 30]



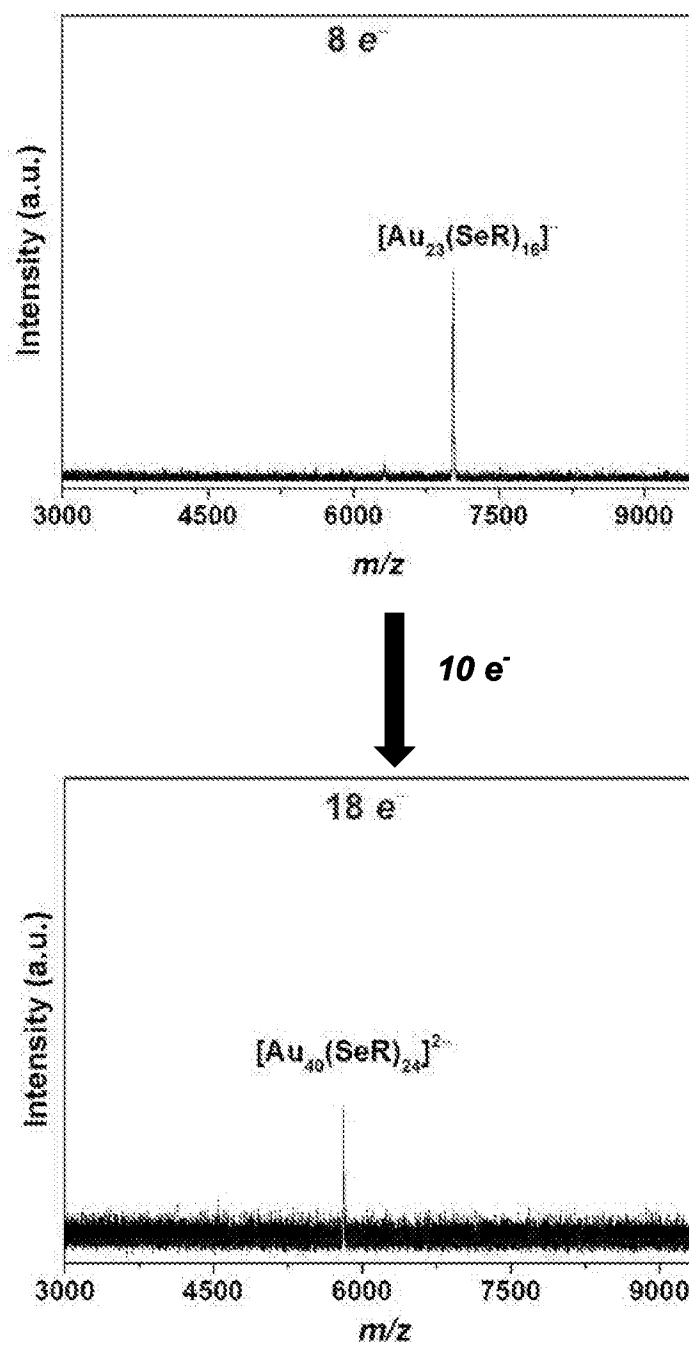
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[Fig. 30]

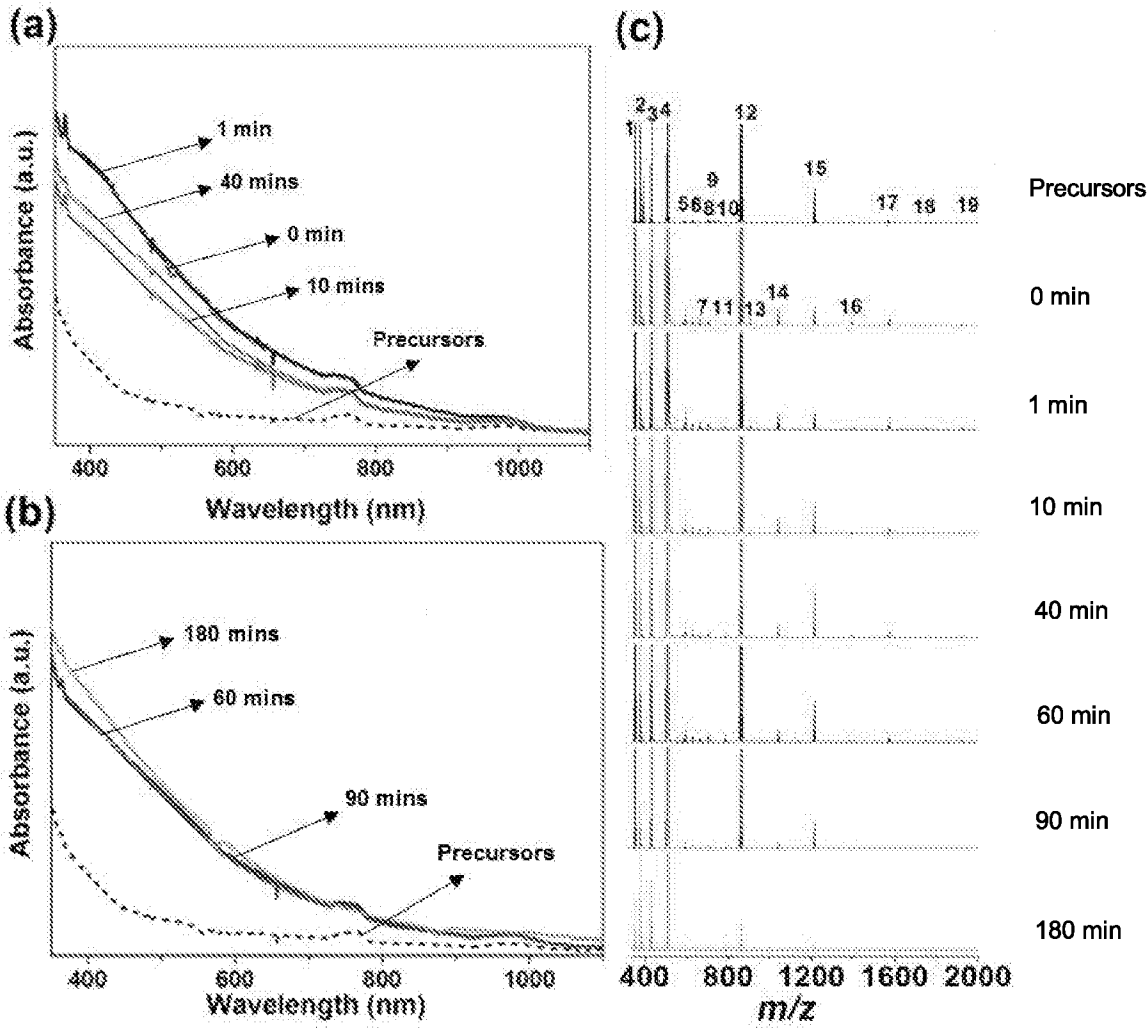


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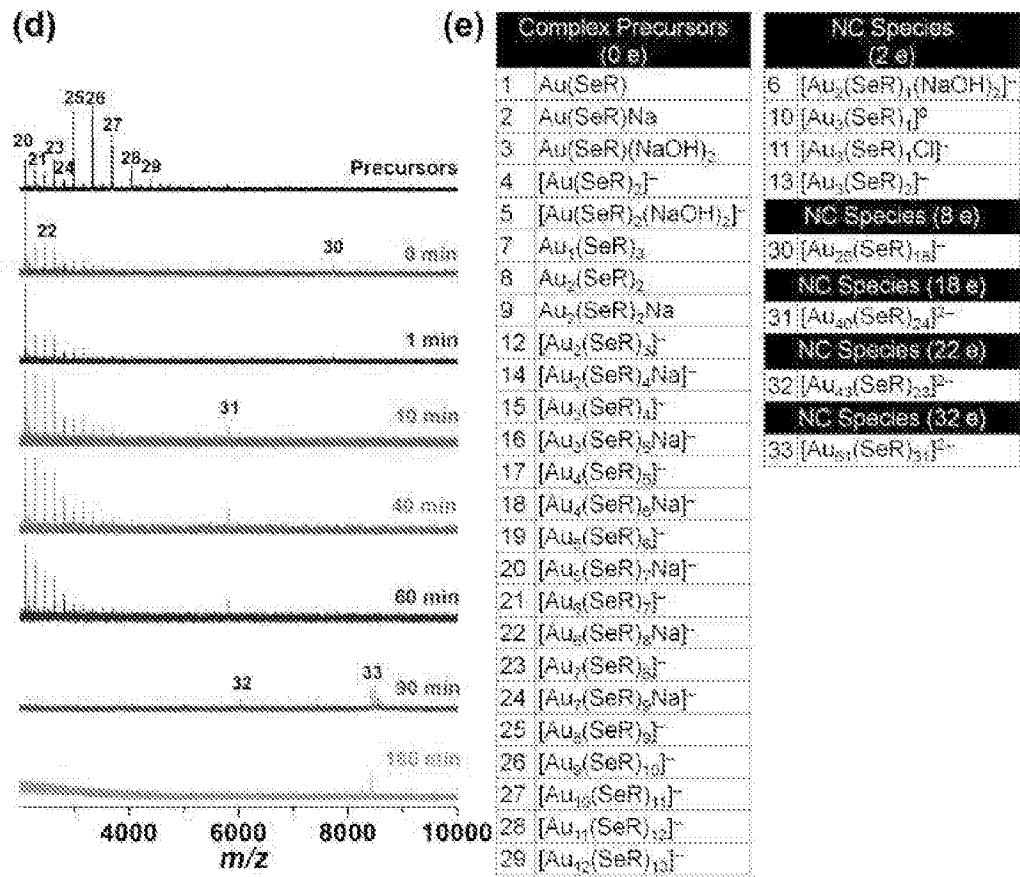
[Fig. 31]



[Fig. 32]

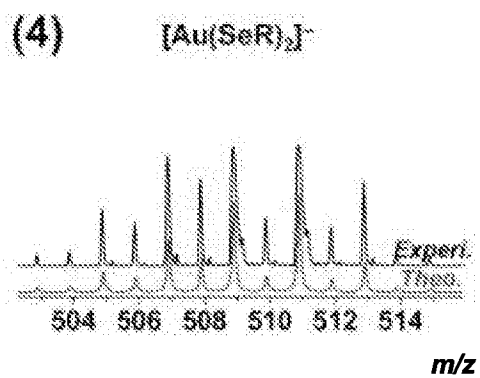
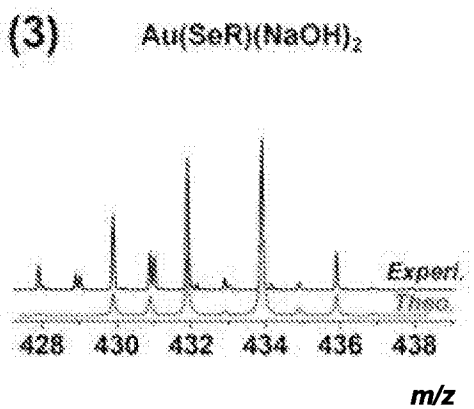
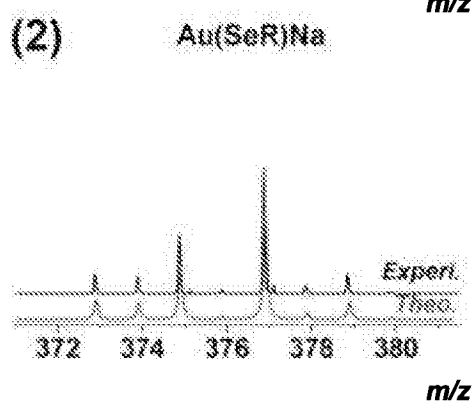
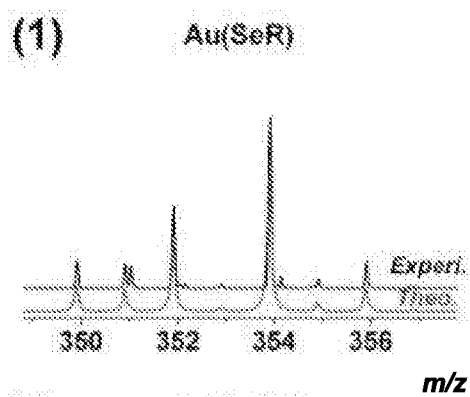


[Fig. 32]



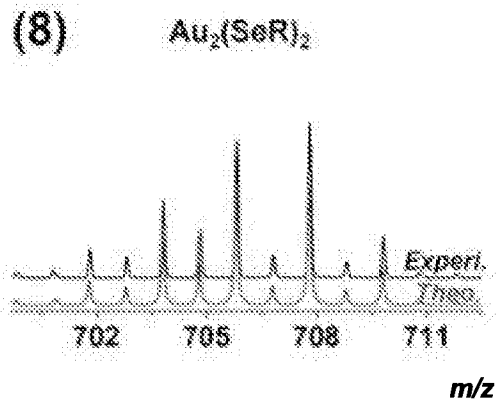
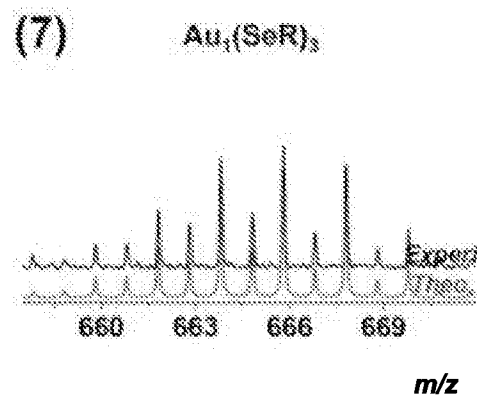
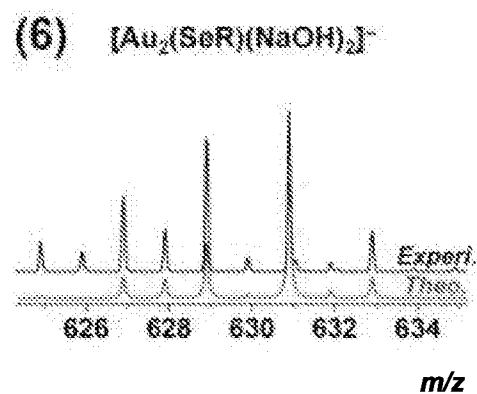
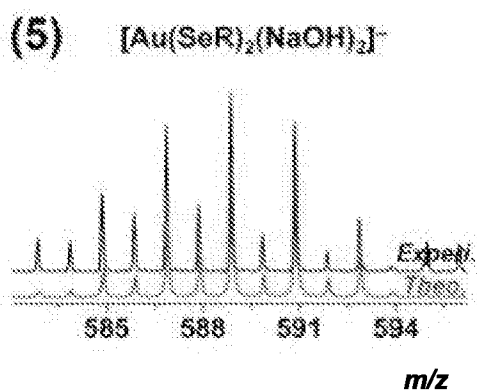
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[Fig. 33]



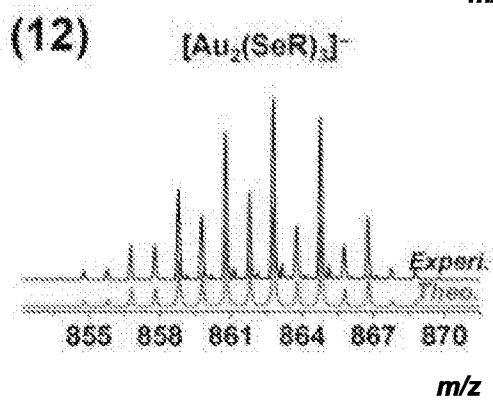
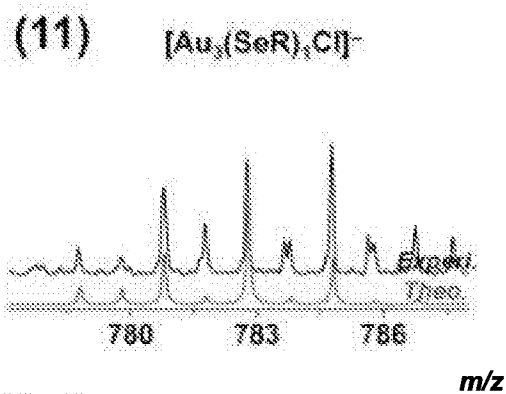
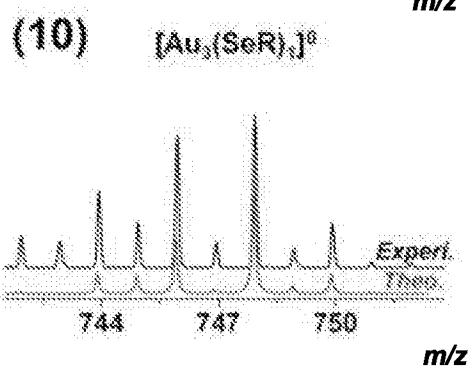
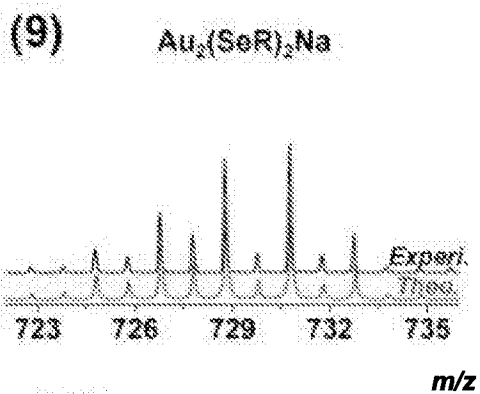
65/78

[Fig. 33]



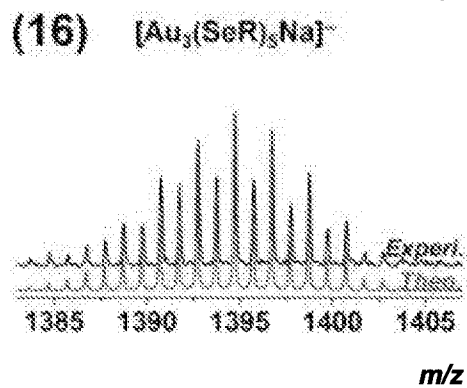
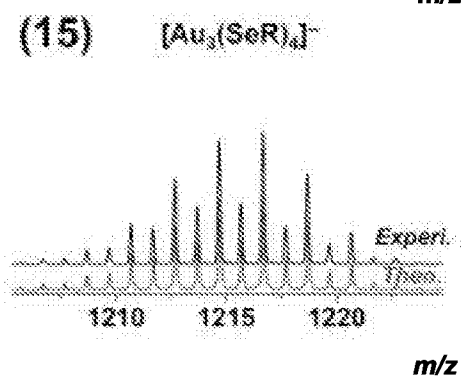
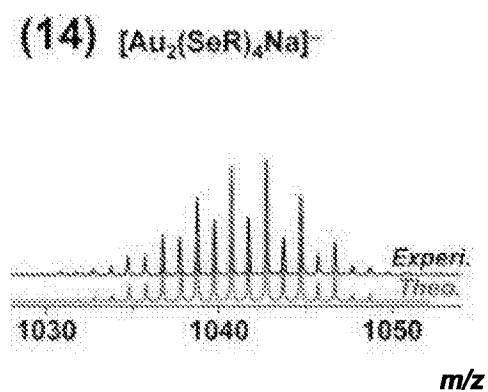
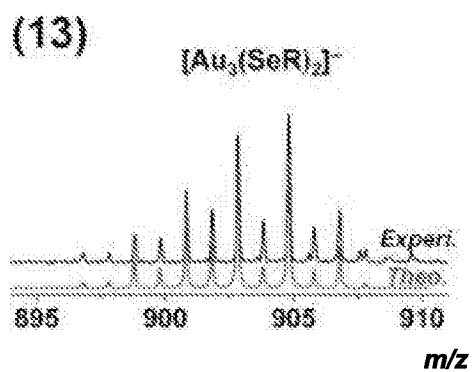
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[Fig. 33]



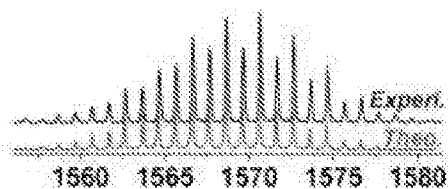
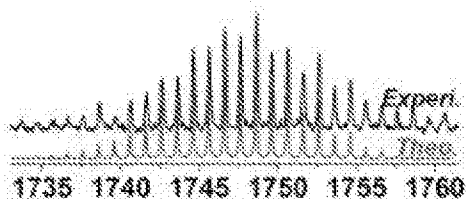
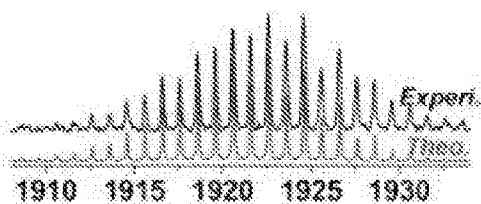
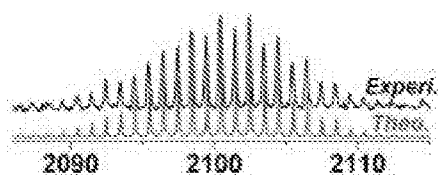
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[Fig. 33]



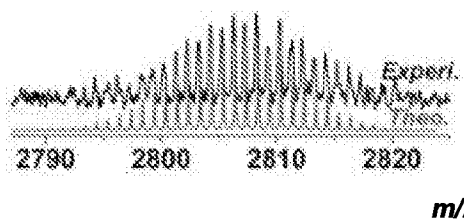
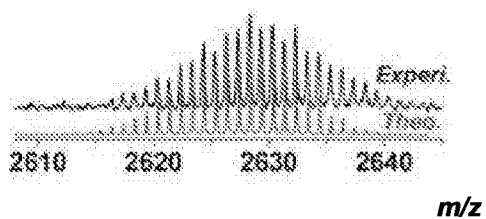
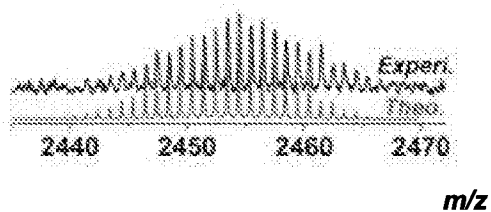
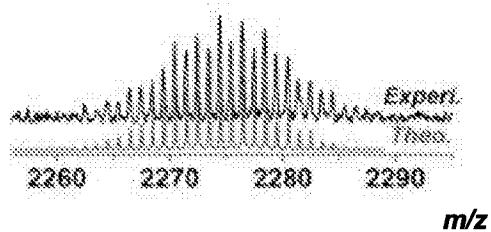
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[Fig. 33]

 $m/z$  $m/z$  $m/z$  $m/z$

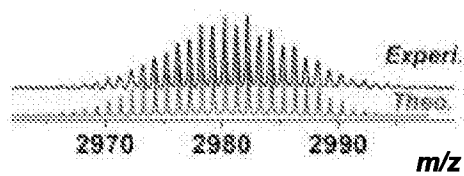
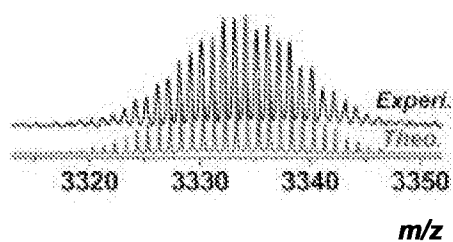
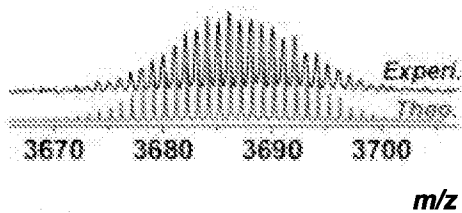
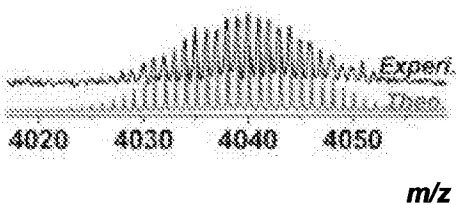
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[Fig. 33]



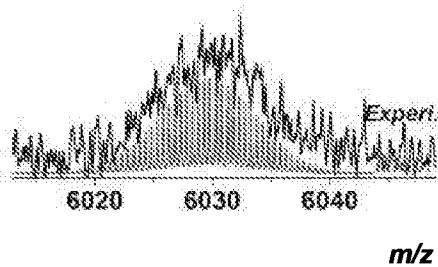
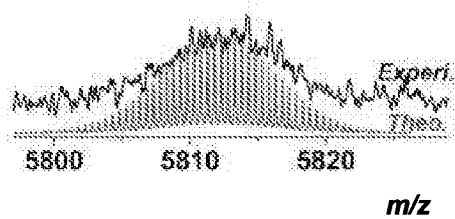
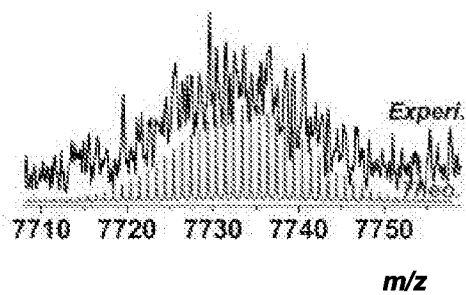
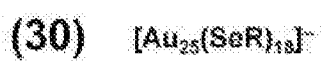
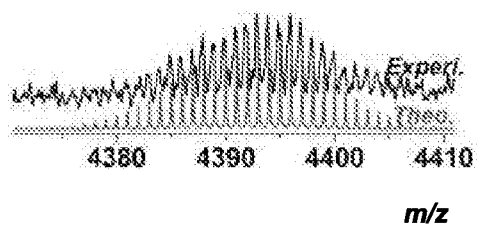
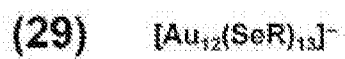
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[Fig. 33]

(25)  $[\text{Au}_9(\text{SeR})_9]^-$ (26)  $[\text{Au}_9(\text{SeR})_{10}]^-$ (27)  $[\text{Au}_{10}(\text{SeR})_{11}]^-$ (28)  $[\text{Au}_{11}(\text{SeR})_{12}]^-$ 

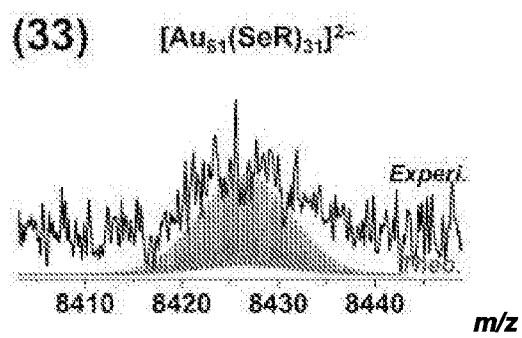
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[Fig. 33]



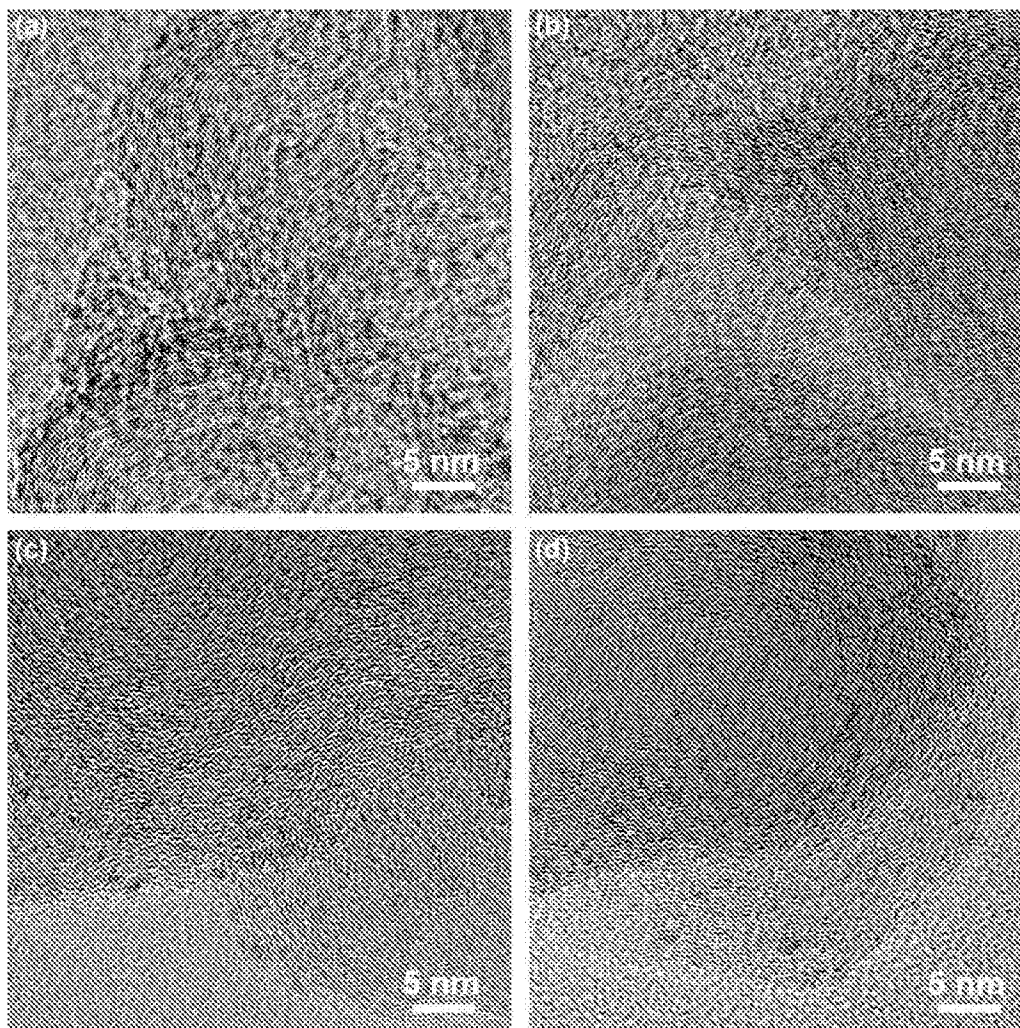
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[Fig. 33]



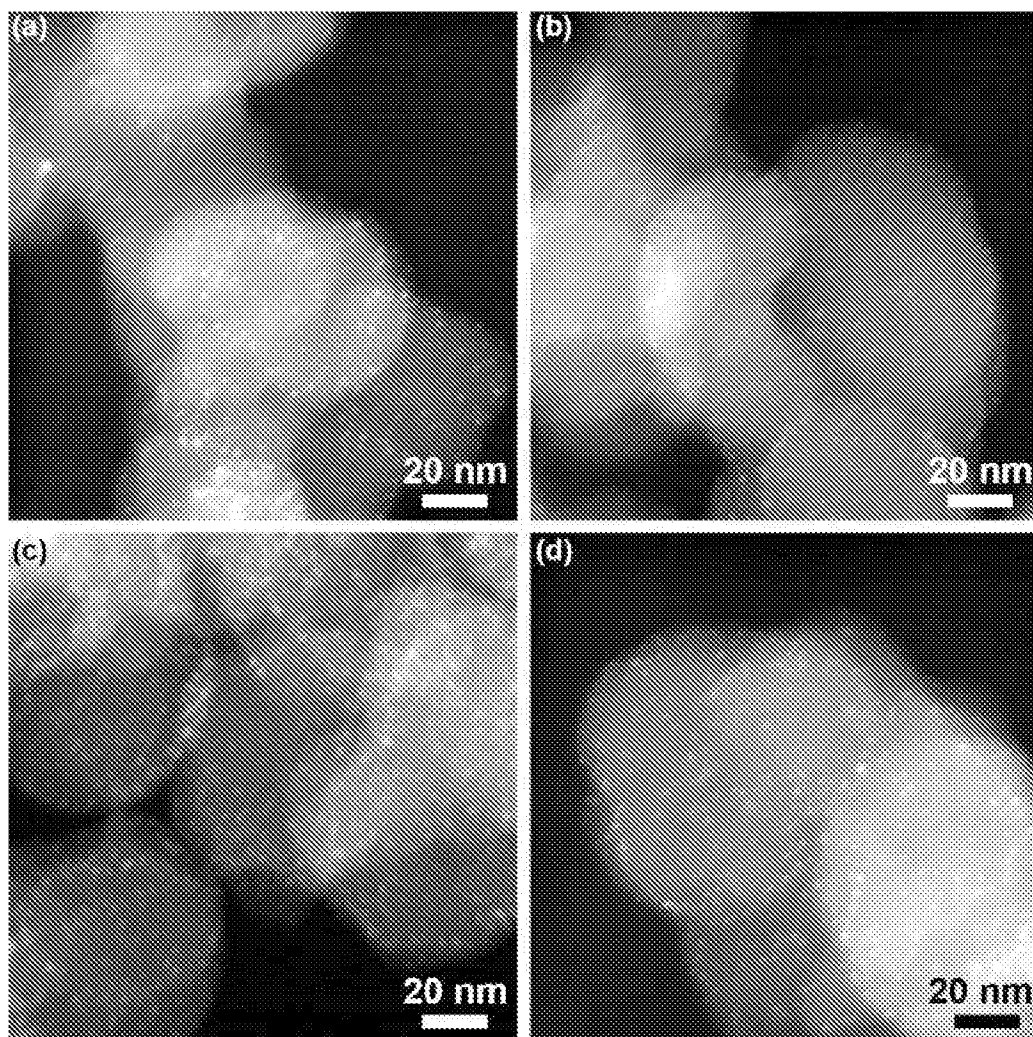
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[Fig. 34]

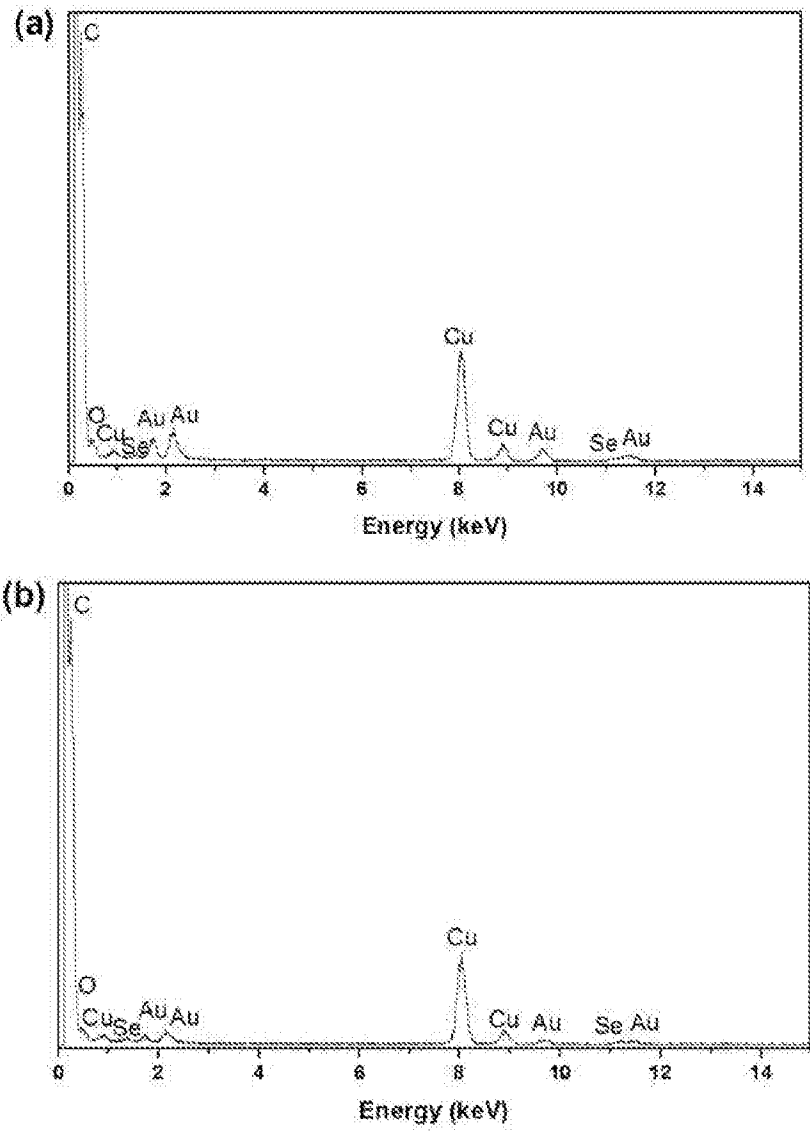


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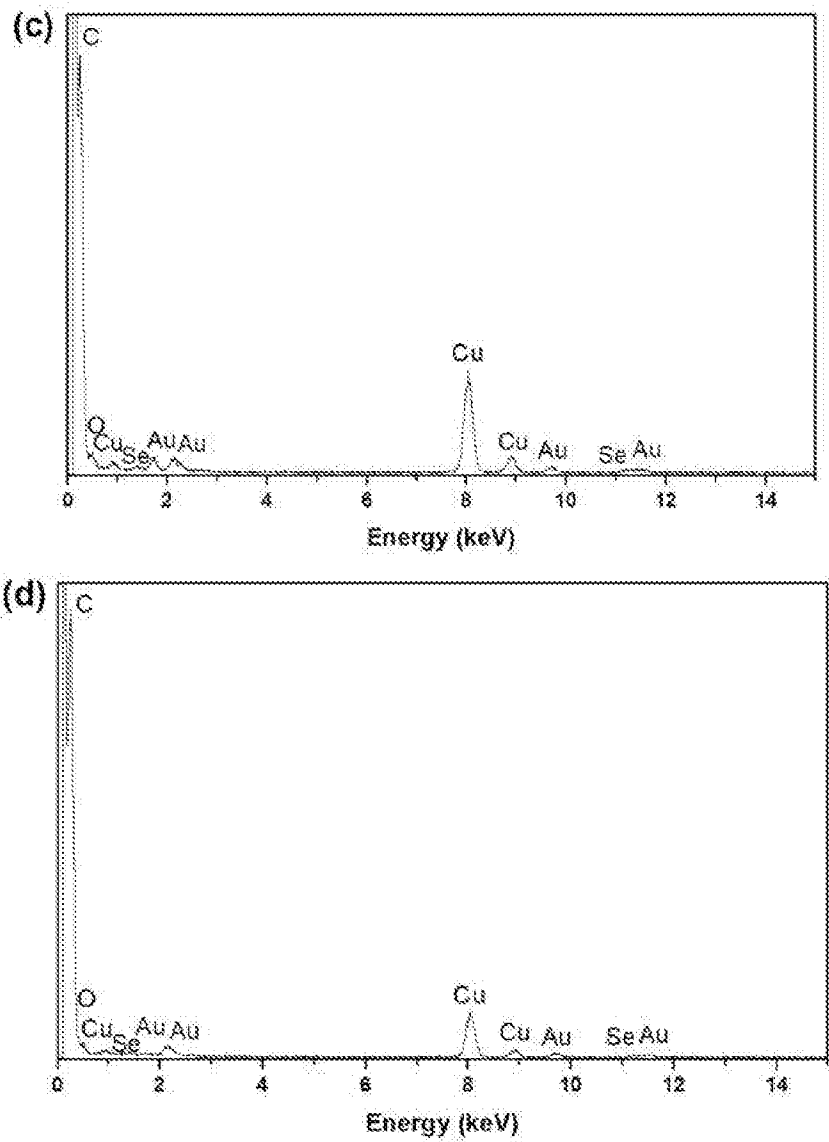
[Fig. 35]



[Fig. 36]

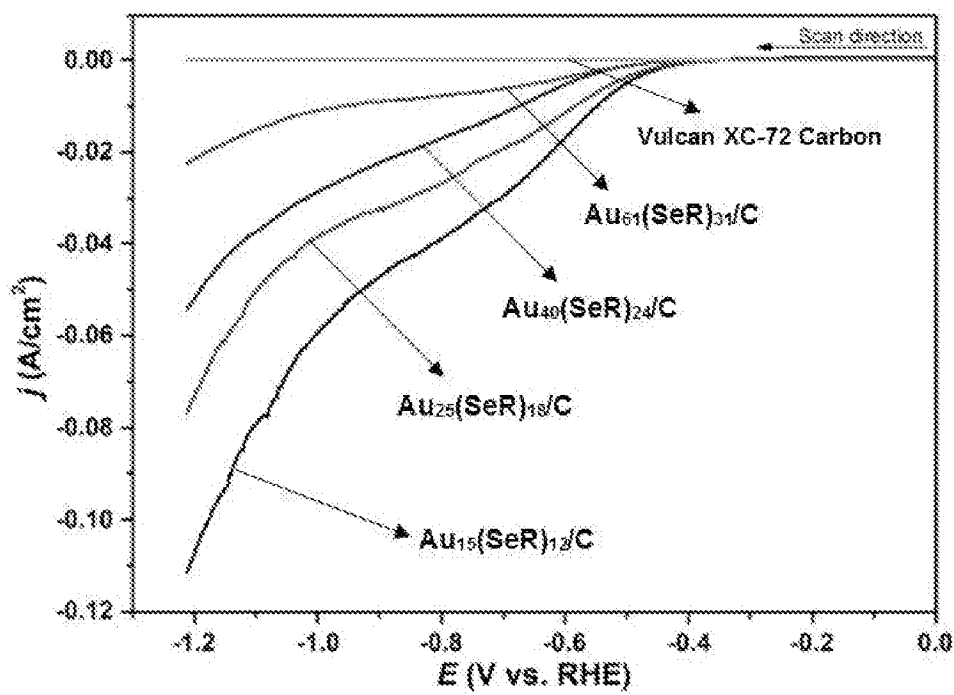


[Fig. 36]

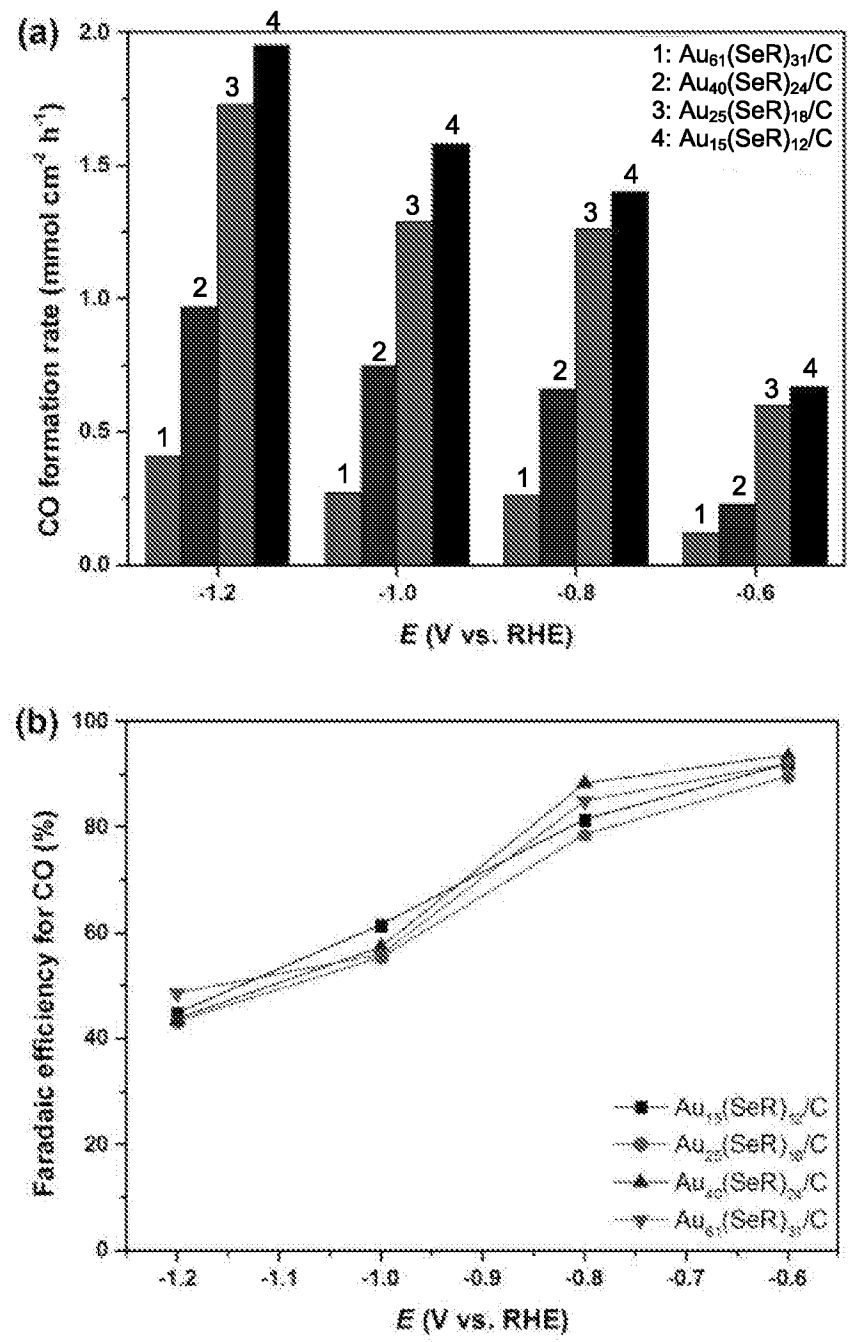


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[Fig. 37]



[Fig. 38]



# INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2018/050106

## A. CLASSIFICATION OF SUBJECT MATTER

See Supplemental Box

According to International Patent Classification (IPC)

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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

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

CAS Registry and CAplus: nanoclusters, gold, silver, copper, miscible, ethanol, aqueous, organic, ligands, selenol, and like terms

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                          | Relevant to claim No. |
|-----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X         | YUAN X., ET AL., Fast Synthesis of Thiolated Au <sub>25</sub> Nanoclusters via Protection-Deprotection Method. <i>The Journal of Physical Chemistry Letters</i> , 8 August 2012, Vol. 3, No. 17, pages 2310-2314<br>[Retrieved on 2018-05-09] <DOI: 10.1021/JZ300960B><br>Page 2311; Figs. 1, 3             | 1-19                  |
| X         | GHOSH A., ET AL., Synthesis of Atomically Precise Silver Clusters by Using the Miscibility Principle. <i>European Journal of Inorganic Chemistry</i> , 28 July 2014, Vol. 2014, No. 31, pages 5271-5275<br>[Retrieved on 2018-05-09] <DOI: 10.1002/EJIC.201402587><br>Figs. 1 and 3; page 5273 right column | 1-19                  |
| X         | GARCÍA-RAYA D., ET AL., Electrochemistry of Molecule-like Au <sub>25</sub> Nanoclusters Protected by Hexanethiolate. <i>The Journal of Physical Chemistry C</i> , 22 April 2009, Vol. 113, No. 20, pages 8756-8761<br>[Retrieved on 2018-05-09] <DOI: 10.1021/JP901118T><br>Para 1; Figs. 2-6               | 13-21                 |

☒ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

\*Special categories of cited documents:

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

09/05/2018 (day/month/year)

Date of mailing of the international search report

16/05/2018 (day/month/year)

Name and mailing address of the ISA/SG

**IPPOS** Intellectual Property Office of Singapore  
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#01-01 Manulife Centre  
Singapore 189554

Email: pct@ippos.gov.sg

Authorized officer

Cao Ye (Dr)

IPOS Customer Service Tel. No.: (+65) 6339 8616

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2018/050106

| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                       |
|-------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| Category*                                             | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                                                                                                                                                                              | Relevant to claim No. |
| X                                                     | JESEENTHARANI V., ET AL., Atomically Precise Noble Metal Clusters Harvest Visible Light to Produce Energy. <i>Chemistry Select</i> , 3 February 2017, Vol. 2, No. 4, pages 1454-1463<br>[Retrieved on 2018-05-09] <DOI: 10.1002/SLCT.201601730><br>Supporting Information pages 1-2 and 4                                                                                                                                                                                       | 13-21                 |
| X                                                     | YUAN X., ET AL., Balancing the Rate of Cluster Growth and Etching for Gram-Scale Synthesis of Thiolate-Protected Au(25) Nanoclusters with Atomic Precision. <i>Angewandte Chemie International Edition</i> , 24 March 2014, Vol. 53, No. 18, pages 4623-4627<br>[Retrieved on 2018-05-09] <DOI: 10.1002/ANIE.201311177><br>Supporting Information Section I.c., I.d                                                                                                             | 13-19                 |
| X                                                     | ZHONG J., ET AL., Density Functional Theory Studies on Structure, Ligand Exchange, and Optical Properties of Ligand-Protected Gold Nanoclusters: Thiolate versus Selenolate. <i>The Journal of Physical Chemistry C</i> , 6 April 2015, Vol. 119, No. 17, pages 9205-9214<br>[Retrieved on 2018-05-09] <DOI: 10.1021/JP511615R><br>Introduction para 1-2, Tables 1-4, Fig. 5                                                                                                    | 13-19                 |
| X                                                     | LI M.-B., ET AL., Peeling the Core-Shell Au <sub>25</sub> Nanocluster by Reverse Ligand-Exchange. <i>Chemistry of Materials</i> , 1 February 2016, Vol. 28, No. 4, pages 1022-1025<br>[Retrieved on 2018-05-09] <DOI: 10.1021/ACS.CHEMMATER.5B04907><br>Figs. 3-4                                                                                                                                                                                                               | 13-19                 |
| X                                                     | CHAKRABORTY I., ET AL., Ag <sub>44</sub> (SeR) <sub>30</sub> : A Hollow Cage Silver Cluster with Selenolate Protection. <i>The Journal of Physical Chemistry Letters</i> , 20 September 2013, Vol. 4, No. 19, pages 3351-3355<br>[Retrieved on 2018-05-09] <DOI: 10.1021/JZ401879C><br>Fig. 1-2, 4                                                                                                                                                                              | 13-19                 |
| X                                                     | GAO X., ET AL., Sub-nanometer sized Cu <sub>6</sub> (GSH) <sub>3</sub> clusters: one-step synthesis and electrochemical detection of glucose. <i>Journal of Materials Chemistry C</i> , 9 March 2015, Vol. 3, No. 16, pages 4050-4056<br>[Retrieved on 2018-05-09] <DOI: 10.1039/C5TC00246J><br>Abstract                                                                                                                                                                        | 13-19                 |
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# INTERNATIONAL SEARCH REPORT

International application No.

**PCT/SG2018/050106**

## Supplemental Box

(Classification of Subject Matter)

Int. Cl.

**B22F 9/24 (2006.01)**

**C01G 3/00 (2006.01)**

**C01G 5/00 (2006.01)**

**C01G 7/00 (2006.01)**

**B82Y 40/00 (2011.01)**

**H01M 4/90 (2006.01)**

**B01J 35/08 (2006.01)**

**B01J 27/057 (2006.01)**