

Supporting Information (SI) for the Paper:

A Unified Framework for Understanding the Structure and Modifications of Atomically Precise Monolayer Protected Gold Clusters

Ganapati Natarajan[†], Ammu Mathew[†], Yuichi Negishi[‡], Robert L. Whetten[§], and Thalappil Pradeep^{*,†}

[†]DST Unit of Nanoscience (DST UNS), Department of Chemistry, Indian Institute of Technology Madras, Chennai, 600036, India.

[‡]Department of Applied Chemistry, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku, Tokyo 162-8601, Japan.

[§]Department of Physics and Astronomy, University of Texas at San Antonio, San Antonio, Texas 78249, United States.

*E-mail: pradeep@iitm.ac.in

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Supporting Information 1

Symmetries and Standard Orientation of $\text{Au}_{25}(\text{SR})_{18}$

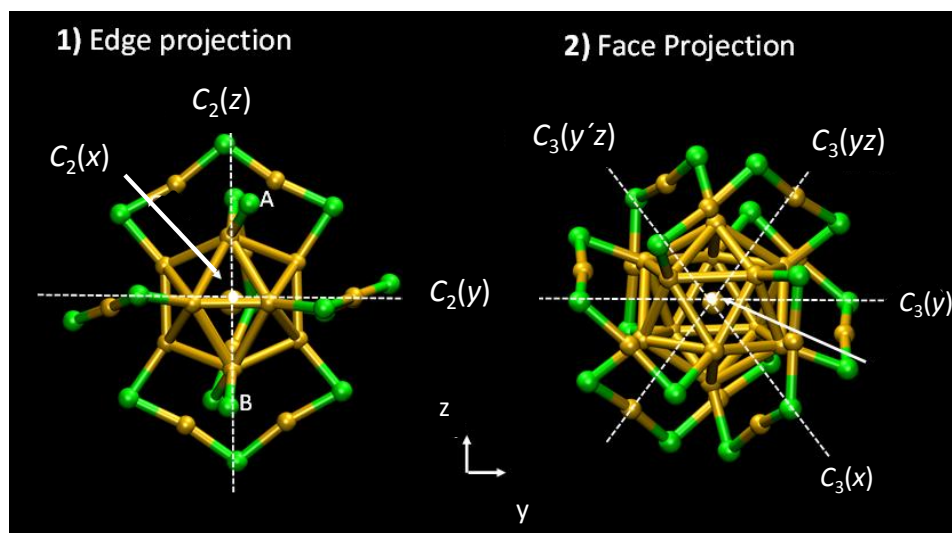


Figure S1: Views of $\text{Au}_{25}(\text{SR})_{18}$ aspicule along different axes of rotational symmetry: 1) C_2 and 2) C_3 axes. In 1) the edge projection of the Au_{12} core is shown with the portion of the front outward pointing staple between sulfur atoms marked A and B deliberately removed to expose the core structure. In 2) the Au_{12} core is seen in the face projection with a C_3 axis pointing outward in the z-direction from the front central triangular face, and the projection of the three other C_3 axes onto the x-y plane are shown and the direction of each of these projected lines of symmetry is indicated in brackets. Gold atoms are shown in gold and the sulfur atoms in green, and the size of the central gold atom has been increased slightly for clarity.

It is appropriate to begin with a review of the molecular symmetry of $\text{Au}_{25}(\text{SR})_{18}$ aspicule which is shown viewed along two different symmetry axes in **Figure S1**.¹ The core icosahedron has 12 vertices (atoms), 20 triangular faces and 30 edges (bonds) and it belongs to the I_h point group. The six dimer staples are arranged in an octahedral manner around the core, so that the central sulfur atom of the staple lies along the directions of the C_2 axes. $\text{Au}_{25}(\text{SR})_{18}$ being a composite entity, consisting of an icosahedral core and an octahedral arrangement of surrounding staples, will have a total symmetry that is reduced from I_h to the octahedral point subgroup of distorted O_h (dO_h).² The dO_h point group lacks C_4 elements, due to the positions of exterior Au atoms in the staples breaking the full octahedral symmetry. There are two types of rotational symmetry axes in $\text{Au}_{25}(\text{SR})_{18}$. Firstly, the four C_3 axes passing through the centre of the icosahedron and through four pairs of opposite triangular faces, one view of which is shown in **Figure S1(2)**. Secondly, the three perpendicular C_2 axes (marked on Figure S1(1) using white dotted lines) which intersect the midpoint of bonds of the icosahedron which lie in the three perpendicular planes that pass through the six pairs of bridging sulfurs which belong to coplanar staples. The

C_2 axes naturally permit a Cartesian axis system to be superimposed on them. Our first objective was to create a labeled diagram of $\text{Au}_{25}(\text{SR})_{18}$ in a standard orientation, as there are visualizations from many different angles in the literature and with the individual Cartesian axes assigned differently with respect to the C_2 axes.

In Figure S1, two views of $\text{Au}_{25}(\text{SR})_{18}$ are shown depending on whether it is viewed along a C_2 or a C_3 axis. We therefore made two conventions: one for the orientation of Cartesian axis and, secondly, for the direction of each of the Cartesian axes with respect to the C_2 axes of $\text{Au}_{25}(\text{SR})_{18}$. We setup Cartesian axes to be fixed in the plane of the paper, as shown in Figure S1, with the y -axis towards the right, the z -axis upwards, and the x -axis coming out of the paper. Secondly, the left hand view, which we term the edge projection, is taken by us to be the standard view used for nomenclature diagrams, unless stated otherwise. The reason for this is that the octahedral arrangement of staples is seen most clearly, while in the face projected view, the staples twist around the core structure.

We defined the standard view of $\text{Au}_{25}(\text{SR})_{18}$ as seen towards the negative z -direction with the rings in each Cartesian plane appearing exactly as shown in Figure S1(1). Viewing the structure along the different Cartesian axes directions will result in a different view of these rings (staples), even though the core always appears in the edge projection.

Supporting Information 2

Structural Representations of $\text{Au}_{25}(\text{SR})_{18}$

A. Polyhedral Shells

The first approach we tried was based on what we term the polyhedral representation of aspicules. The core and mantle regions of several aspicules such as $\text{Au}_{25}(\text{SR})_{18}$ and $\text{Au}_{102}(\text{p-MBA})_{44}$ ³ have been found to consist of a set of polyhedra, one inside the other, and so this appears to be a generic structural characteristic. The polyhedra may be viewed as a generalization of polyhedra for coordination compounds as their sides do not always represent bonds between the atoms, except in the case of the Au_{12} core, but rather indicate their relative positions in space and symmetries. Polyhedral shells may be defined either by analysis of the bonding network or by classifying atoms according to their element and positional type as shown in the inset of Figure S2(a). The four types of atoms in $\text{Au}_{25}(\text{SR})_{18}$ are: core Au atoms (Au_c), exterior metal atoms in the staples (Au_e), bridging sulfurs (S_μ) which bridge exterior metal atoms and are located at the central position of the staple and lastly the non-bridging sulfur (S_c) atoms which join gold atoms in the core to the exterior gold atoms.

The crystal structure available in the literature for $\text{Au}_{25}(\text{SR})_{18}$ was used.¹ We made extensive use of the molecular building and visualization software Avogadro³ and VMD⁴ for structural manipulation and visualization. We analysed the structure of $\text{Au}_{25}(\text{PET})_{18}$ obtained from its crystal structure by extracting the molecules from the crystalline unit cell, and isolating the gold and sulfur atoms from the model by removing the atoms of the PET ligands, which we refer to as the core and mantle structure. The $\text{Au}_{25}(\text{SR})_{18}$ aspicule is oriented in the edge-projected, octahedral staple configuration shown in Figure S1(1).

For the visualization as concentric shells of polyhedra, the bond radii were chosen such that only the nearest neighbours in each category of atoms would be joined together by a bond. The bond radii between each type of atom in VMD were chosen as 3.2 Å for Au-Au core bonds, 5.5 Å for exterior Au atoms and 5.5 Å for the non-bridging sulfurs and 8.8 Å for the bridging sulfurs. Bonds between the atoms in each category are drawn when the distance between them is less than the bond radii mentioned above. The four polyhedra are shown superimposed on each other in Figure S2(a). Figure S2(a) shows the inner Au icosahedron in gold, the bridging sulfur octahedron in yellow, and the exterior gold icosahedron in blue which protrude out from the green cuboctahedron of non-bridging sulfurs. Figure S2(b) shows only the sulfur polyhedra with the inner sulfur octahedron capping the six square faces of the cuboctahedron. We note that this arrangement of sulfur atoms has already been visualized in the context of ligand exchange.² Thus, by labeling each of the sulfur atoms of the octahedron and the cuboctahedron, we would have a notation for ligand positions.

Generally the positional labels of atoms in a molecule, known as locants, are denoted by numbers or letters in IUPAC nomenclature. Here, we use the Cartesian axis directions, which may also be regarded as Cartesian quadrant bounding directions, to uniquely describe the positions of the atoms in the core and mantle regions⁶. The bridging sulfurs are located at vertices of the yellow octahedron and are labeled by one of the six perpendicular Cartesian

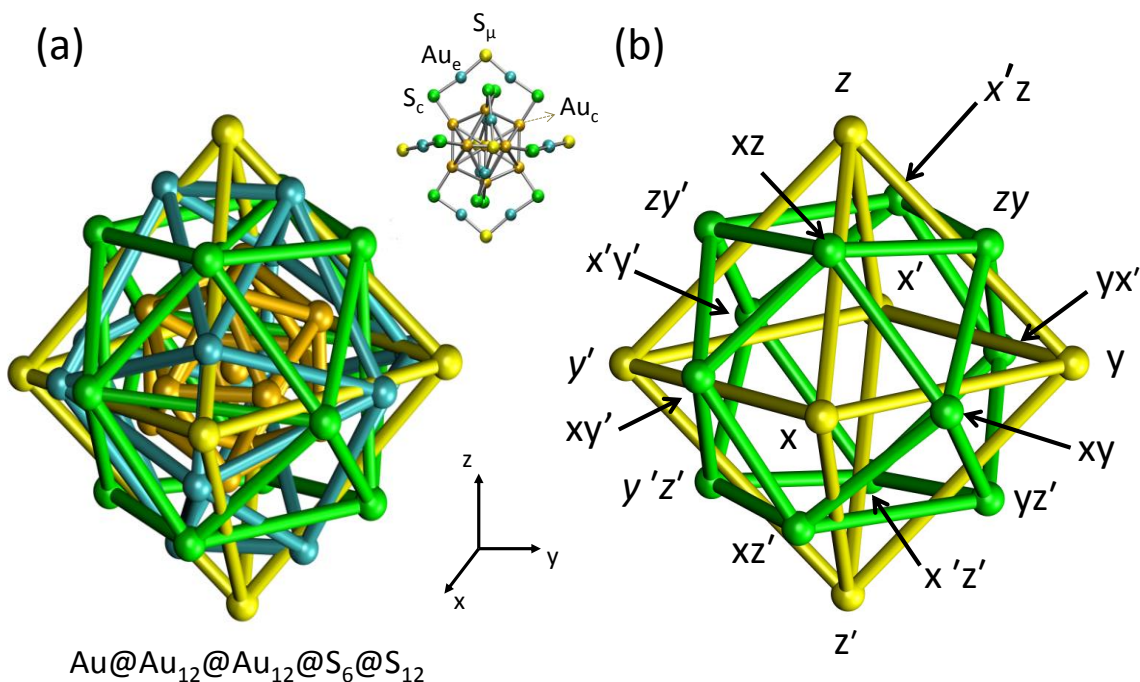


Figure S2. Concentric polyhedral representation of the core and staple atoms of $\text{Au}_{25}(\text{SR})_{18}$ aspicule. Polyhedra formed by connecting atoms of the same category to their nearest neighbors of the same category for (a) both gold and sulfur atoms, and (b) sulfur atoms only with Cartesian atom labels, according to the Cartesian axes shown. The atoms and the lines joining them are colored according to their category as shown in the inset to (a) gold and cyan for the core and exterior gold atoms, while yellow and green represent bridging and non-bridging sulfurs. A shell structure terminology for $\text{Au}_{25}(\text{SR})_{18}$ is given below (a).

directions. Shell directions x, y, z, x', y', z' where the primes indicate the negative direction. The primes on the Cartesian axis directions, eg. x' , represents the negative direction of the x -axis. The non-bridging sulfur atoms are associated with the vertices of the cuboctahedron, or equivalently, a pair of the vertices of the octahedron at either end of the edge. Hence they may be labeled by the associated pairs of Cartesian axes. Figure S3, shows the ball and stick visualization of $\text{Au}_{25}(\text{SR})_{18}$ with Cartesian locant labels. Using the ordering of these twelve Cartesian pairs for the non-bridging sulfurs allows us to preserve this information, by placing the direction for the staple on which the core-bonded sulfur resides first. A simple rule is shown at the top left of Figure S3, which is that the pairs are taken anticlockwise when x, y , and z are arranged in a circle. For example, the nonbridging sulfur at the xz position cannot be referred to as zx because the staple this sulfur is located points in the x direction and not in the z direction. The twelve unique ordered pairs specifying the Cartesian quadrants are $xz, xz', x'z, x'z', yx, yx', y'x, y'x'$ and $zy, zy', z'y$ and $z'y'$. It should be noted that the ordering of these pairs are specific to our conventions and about the relative orientation of the Cartesian axes and the $\text{Au}_{25}(\text{SR})_{18}$ aspicule as described in SI 2.

We can also uniquely identify the core gold and exterior gold atoms using the same twelve Cartesian quadrant specifiers as the non-bridging sulfurs since each pair of these gold atoms are the nearest neighbors of the non-bridging sulfurs. Hence, by adding a 'c' or an 'e' to before the direction pair we can indicate the directions of the gold atoms too eg. *c*-xy or *e*-xy indicate the core and exterior gold atoms which are bonded to the non-bridging sulfur located in the xy-direction. The interstitial gold atom is identified by the italicized '*i*'. Some terminologies for ligand and alloy exchanged $\text{Au}_{25}(\text{SR})_{18}$ are given in Table S2.

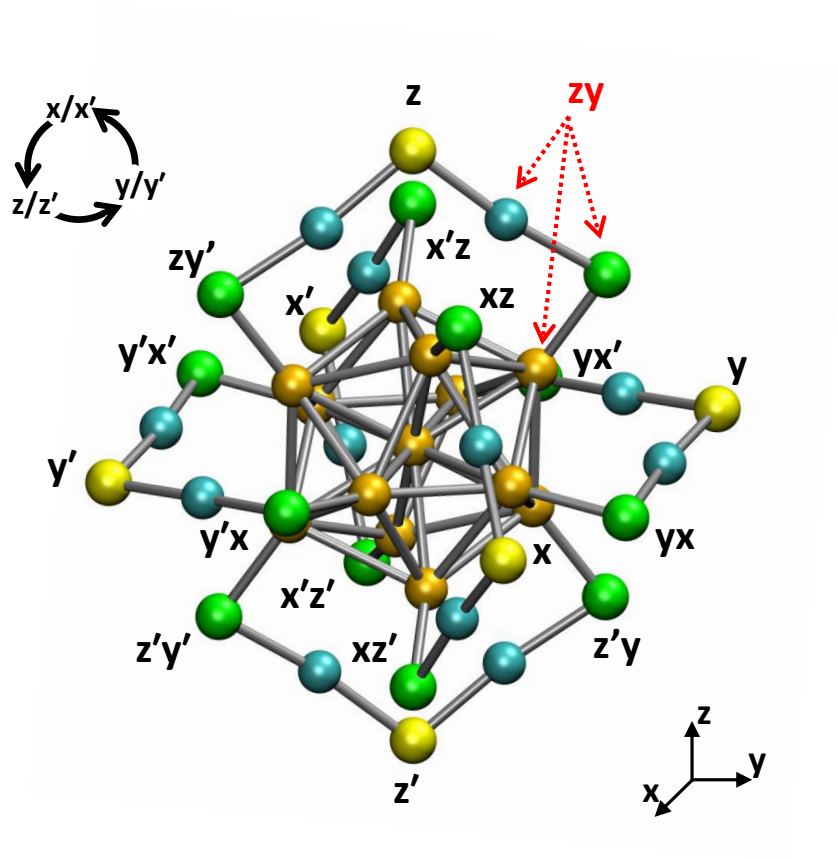


Figure S3. $\text{Au}_{25}(\text{SR})_{18}$ aspicule with Cartesian locant labels for atoms. The core and staple atoms are colored as shown in the inset of Figure S2(a). The same locants are used for core atoms, non-bridging sulfur atoms, and exterior gold atoms which lie in the same Cartesian octant. The red arrows indicate the use of the same zy locant for the green non-bridging sulfur atom which applies to it and its two nearest neighbor atoms consisting of a gold core atom and a light blue exterior gold atom.

B. Molecular graph of $\text{Au}_{25}(\text{SR})_{18}$ aspicule

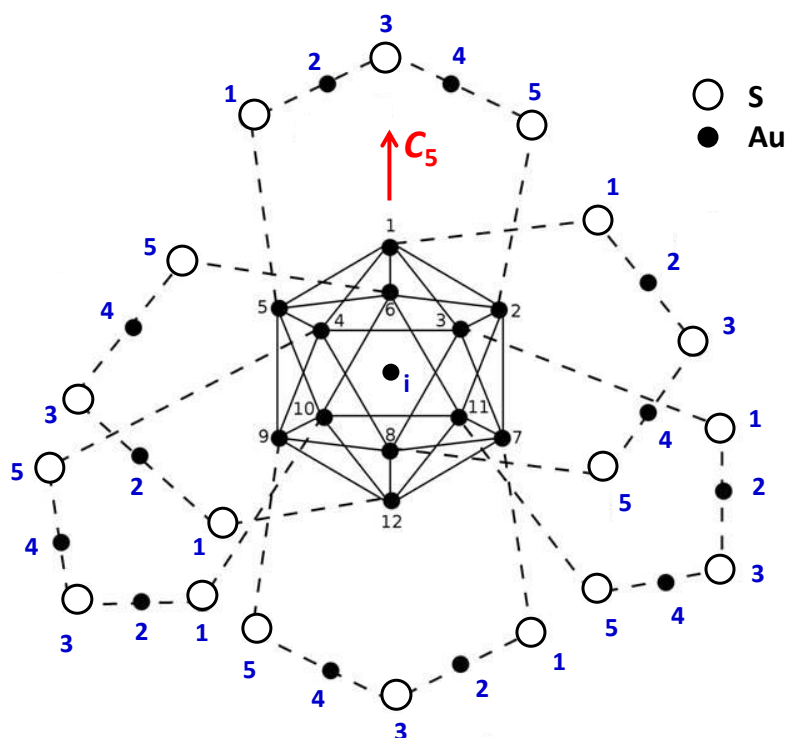


Figure S4. The molecular graph of $\text{Au}_{25}(\text{SR})_{18}$ aspicule. Small black circles show sulfur atoms while large open circles represent sulfur atoms. Au-S bonds are shown by the dashed lines, while Au-Au bonds are shown by the solid lines. The locants of each atom are shown alongside in blue.

The visualizations of $\text{Au}_{25}(\text{SR})_{18}$ in Figures S1, S2 and S3 being in three dimensions are less convenient for developing nomenclature which is generally based on diagrams involving lines and element symbols to represent the bonds and the atoms of the 3D structure on the 2D plane. The molecular graph of $\text{Au}_{25}(\text{SR})_{18}$, shown in Figure S4, is just such a 2D representation showing all Au/S atoms as dots/circles and the bonds as lines joining them. The icosahedron is shown in face projection and the bonds from the aurophilic interactions between the core and exterior Au atoms and those between the interstitial Au atom and the other core atoms have been omitted. The highest symmetry C_5 axis of the icosahedral core is oriented vertically the atoms are numbered on planes perpendicular to this axis, as shown in Figure S4. Numbering of the atoms within a plane is done in a clockwise fashion with the lowest number being to the far right of the C_5 axis. The staple atoms are numbered from 1 to 5, starting at the leftmost atom of the staple and counting clockwise around it. Each staple may be identified by the start and end atoms of the core atoms to which it is bonded. Nevertheless, this diagram is quite difficult to remember and draw by hand due to the use of the face projection so we searched for a simpler representation based on the edge-projected structure of $\text{Au}_{25}(\text{SR})_{18}$ based on its three ring structure.

Supporting Information 3

$\text{Au}_{25}(\text{SR})_{18}$ Tomographic Diagram with a C_3 Principal Axis

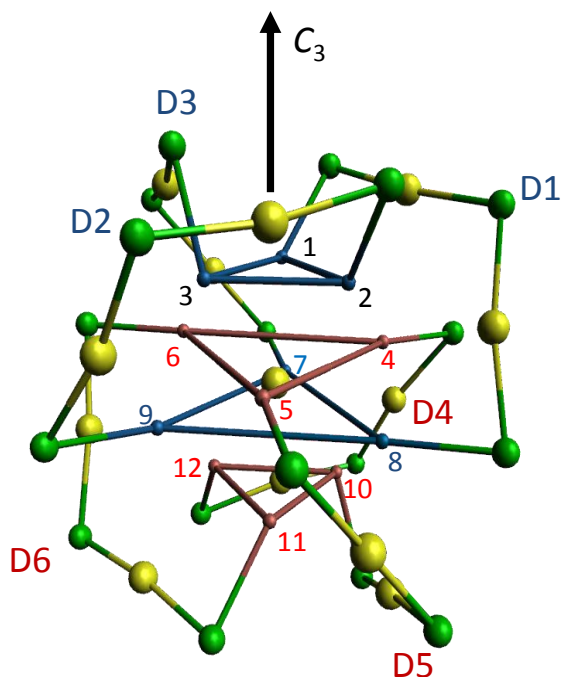


Figure S5. $\text{Au}_{25}(\text{SR})_{18}$ aspicule with locants with the C_3 axis as the principal axis. Only the core and staple structure is shown with the ligands. The connectivity of core atoms in the same plane are indicated by bonds. Both the bonds and core atoms which are shown as small spheres, are colored blue in the case that the core atoms are bonded to the upper group of three dimer staples (D1-D3) and red in the case that they are bonded to the lower group of three dimer staples (D4-D6). The interstitial Au atom as larger yellow sphere, staple Au atoms are shown in yellow and the sulfur atoms in green. The locants of the core atoms are colored by the same scheme as the triangle they lie on. The six dimer staples, D1 to D6, are labeled in red. Staple atom numbers are not shown, but may be added according to the rules given in the Manuscript.

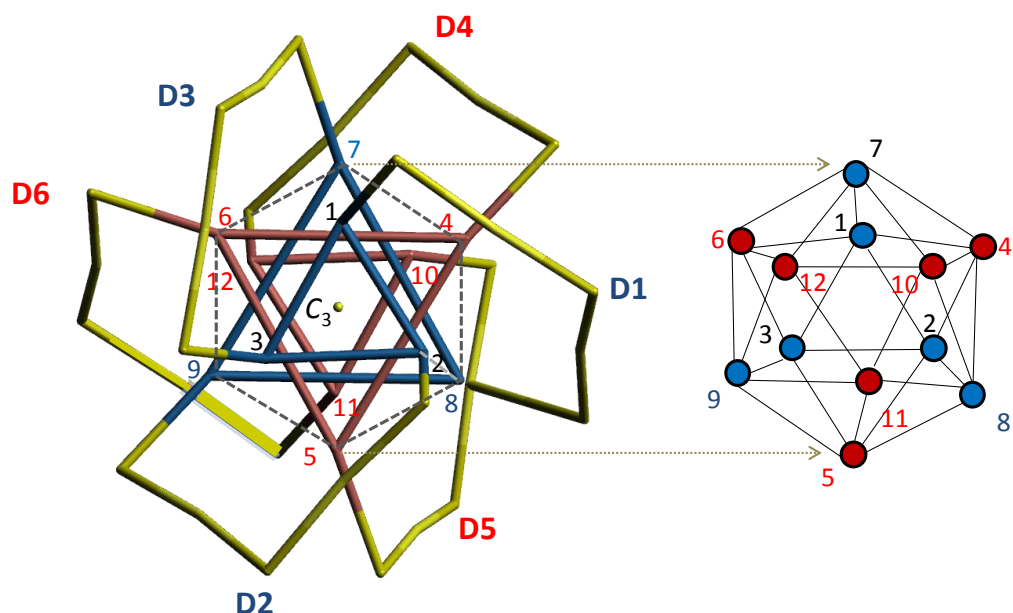


Figure S6. A “Star of David” projection of $\text{Au}_{25}(\text{SR})_{18}$ aspicule in planes perpendicular to the C_3 axis coming out of the plane of the paper with the twelve core atoms of the icosahedron sectioned into four parallel triangles each containing three atoms. The triangles are colored alternately blue and red, with the smaller blue and red triangles being at the front and back, respectively and the larger triangles in the middle. The stick bond representation has been used and the staples are shown in yellow and gold for the sulfur and gold stick bonds respectively. Right: A schematic of the core icosahedron in face-projection with the Au-Au bonds shown as lines and atoms represented by filled circles colored according to the color of the triangle they lie in.

Supporting Information 4

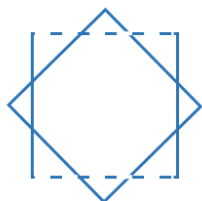
Drawing the Borromean-Rings Diagram of $\text{Au}_{25}(\text{SR})_{18}$

Scheme S1: Visual instructions are shown below for drawing the Borromean-Rings diagram of $\text{Au}_{25}(\text{SR})_{18}$ in nine steps.

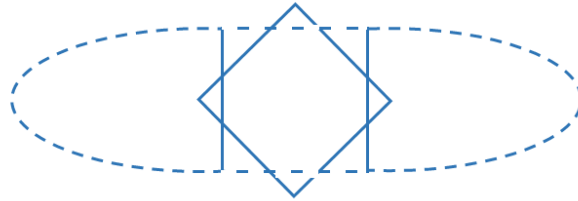
- 1. Draw a square with its horizontal edges as dashed lines and its vertical edges as solid lines**



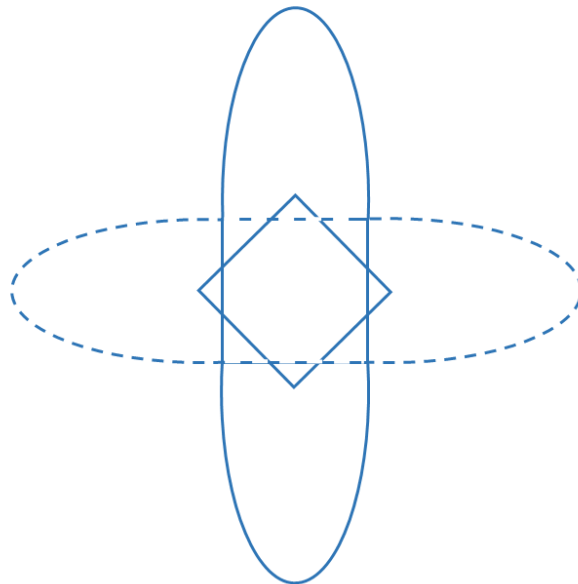
- 2. Draw a second square over the first rotated by 45 degrees**



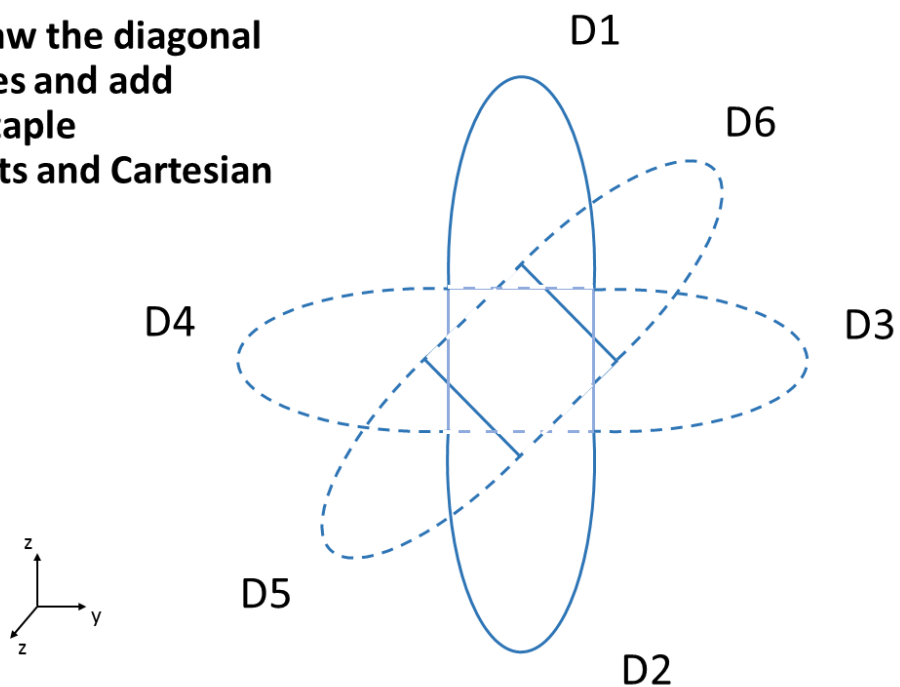
3. Draw the horizontal staples using dashed lines



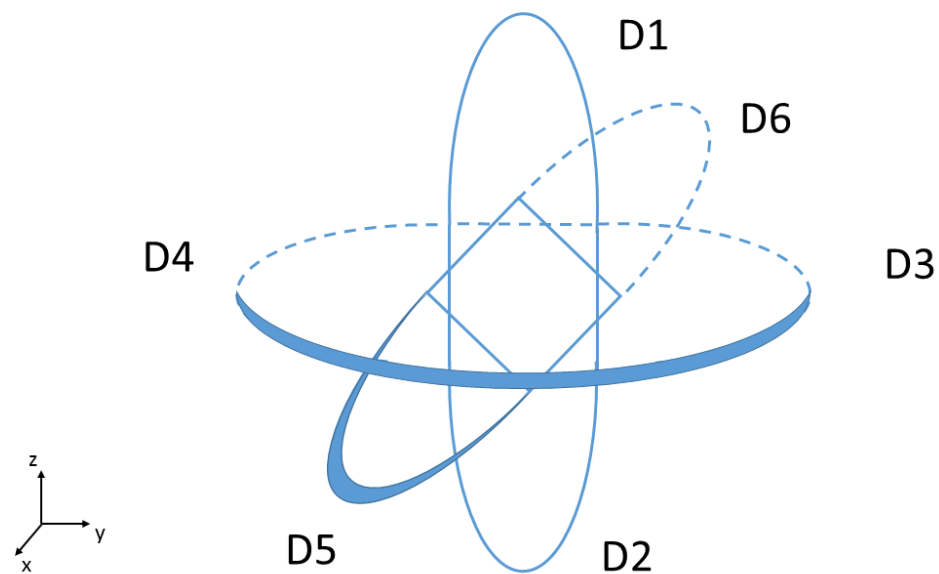
4. Draw the vertical staples using solid lines



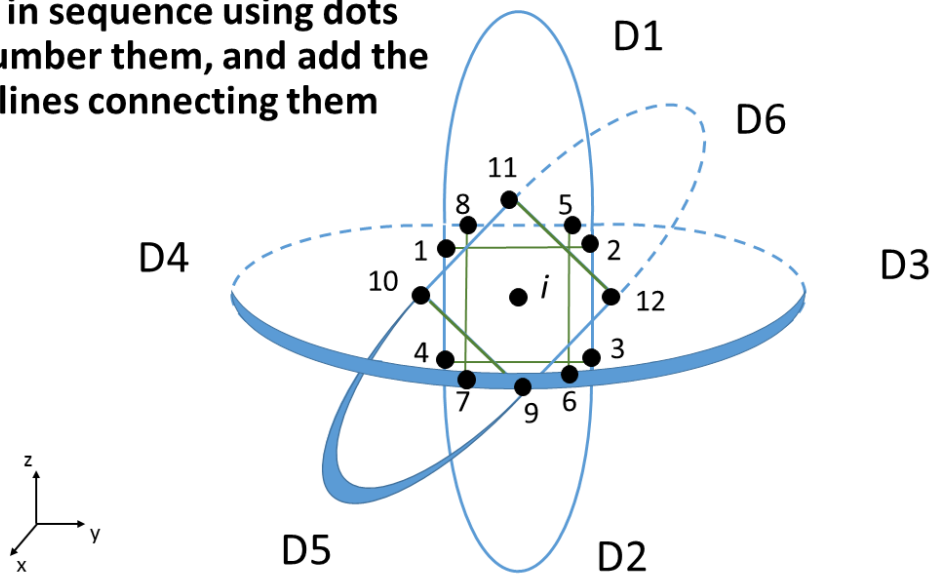
5. Draw the diagonal staples and add the staple locants and Cartesian axes



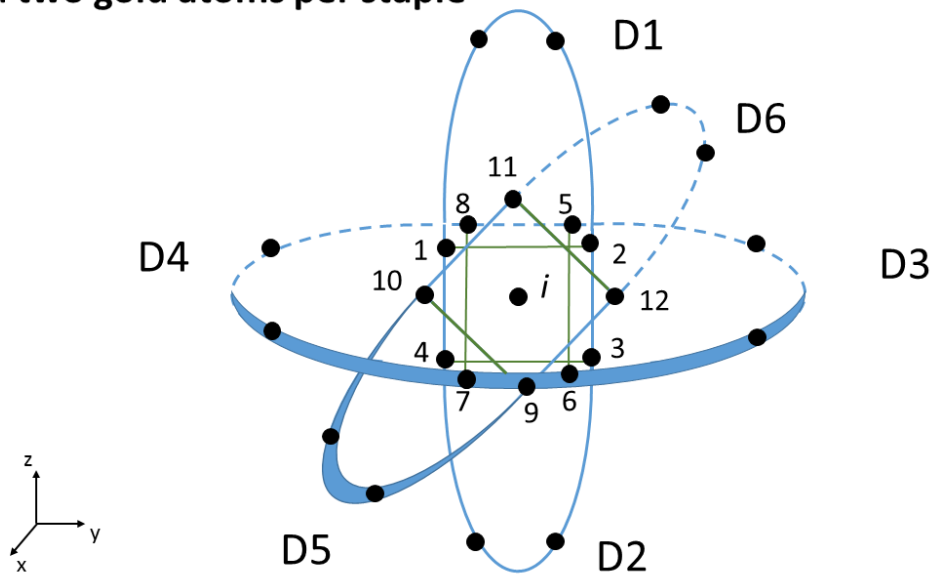
6. Add thick tapering lines as shown to get the 3D-effect



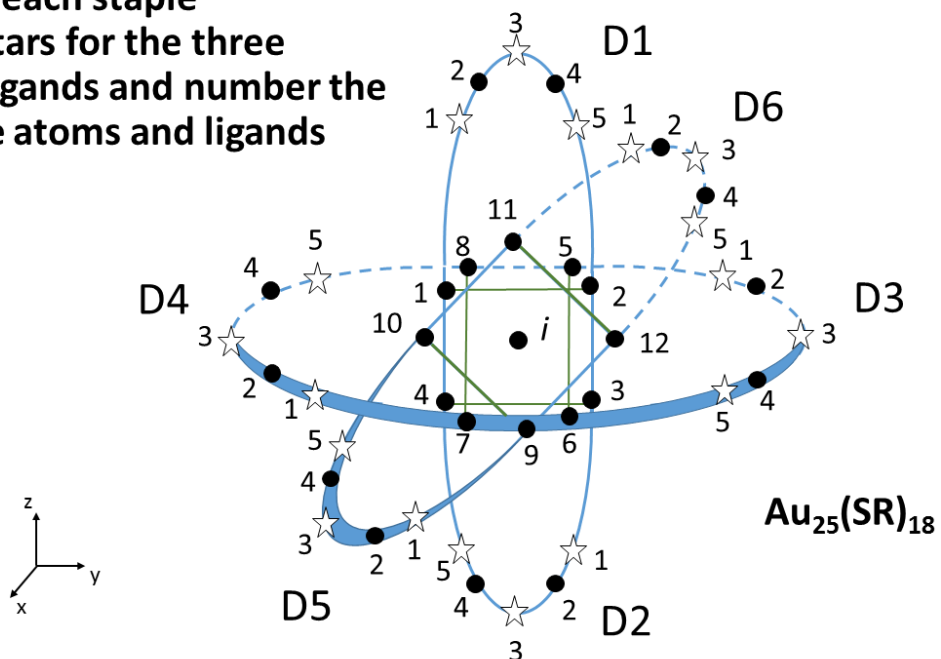
7. Mark the central core gold atoms in sequence using dots and number them, and add the green lines connecting them



8. Add two gold atoms per staple



9. On each staple
add stars for the three
(SR) ligands and number the
staple atoms and ligands



Supporting Information 5

Structural Nomenclature of Aspicules

This section can be appreciated better after going through Figure 1 of the Manuscript. In this section we present names, which can describe the structure of the parent aspicule in detail and also the type and nature of substituents, either metal atoms or ligands. We assume the locant assignment scheme for $\text{Au}_{25}(\text{SR})_{18}$ aspicule shown in Figure 1 in the Manuscript and provide examples for modifications in this structural nomenclature in Table S7.

The general structure of the name would be:

Staple-core locants-(Ligand-Staple name)-(Core name) (Suffix)

where the brackets have been used for clarity but are not included in the actual name.

A name which describes the full structure of $\text{Au}_{25}(\text{SMe})_{18}$, would then be:

D1(1,2):D2(3,4):D3(5,6):D4(7,8):D5(9,10):D6(11,12)-hexa(1,3,5-methylthiolato-2,4-Au)-auro-25 aspicule(1-) (*i@I,3C₂*)

A slightly shorter name using the (SR) terminology for the ligand, as described in the Manuscript) would be:

D1(1,2):D2(3,4):D3(5,6):D4(7,8):D5(9,10):D6(11,12)-(1,3,5-SMe-2,4-Au)₆-auro-25 aspicule(1-) (*i@I,3C₂*)

The above structural name is interpreted as follows: This is an aspicule which has six dimer staples, with locants D1 to D6, and these six staples are attached to the core atoms with numbers 1 and 2, 3 and 4, 5 and 6 and so on. It has SMe ligands at the 1, 3 and 5 positions along each of the staples, counting from the left hand end of the staple. The whole structure has a total of 25 gold atoms and there is a single negative charge on the molecule. Lastly, the core polyhedron is an icosahedron with an additional central atom and the principal symmetry axes used for locant assignment are the three perpendicular C_2 axes (denoted by $3C_2$ which coincide with the Cartesian x, y, z axes oriented in the standard way).

A. Ligand and Staple name

The various parts of the structural name are now described in detail. We regard the staple and its ligands as a branched chain molecule, with the staple being the chain and the ligands the branches. The ligand and staple name is a combined name of the form (in its shorter version): (1,3,5-SMe-2,4-Au).

The name of the ligand (SMe) is prefixed by 1,3,5 followed by a hyphen which are the sulfur positions on the dimer staple, and this is followed by a hyphen and the positions of the Au atoms on the chain. We use square brackets to enclose the ligand name and staple name, and we place

the number of staple/ligand combinations of that kind in the subscript outside the brackets. Hence, when presented with the structure of a modified $\text{Au}_{25}(\text{SR})_{18}$ aspicule, we first identify the different combinations of staple metal atoms and their attached ligands eg. (3-PET,1,5-SMe-2-Pd,4-Au), and we use as many ligand and staple names as are needed to name each of the distinct combinations present. In the case of unmodified $\text{Au}_{25}(\text{SR})_{18}$, we have the same ligand and staple configuration repeated, and so we put its multiplicity in the subscript eg. (1,3,5-SMe-2,4-Au)₆.

Whenever there is more than one ligand-staple name they are separated by a comma. The ligand-staples name and their prefixed staple locants are placed in increasing order of prevalence. Each ligand-staple name is prefixed by the locants of all the staples that are described by it. The description of the staples consists of a staple locant and the staple-core locant described below.

B. Staple locants

1. The locants of the staples have two parts, a letter which corresponds to the type of staple and the number of the staple. The following letters are used: M for a monomer staple, D for a dimer staple and Tr for trimer, etc. Further details on the method of assignment of the staple locants are given in the Manuscript. Examples of staple locants are M1, D1, etc.

2. A consecutive sequence of staples the first and last staple separated by a hyphen, also all enclosed in square brackets eg. [D1-D6].

3. A staple-core locant consist of the pair of comma-separated numbers of the core atoms on which the staples begin and end (eg. 1,2) with each pair being enclosed in brackets and prefixed by the staple locant eg. D1(1,2) is an example of a staple-core locant which signifies that the dimer staple one is bonded to core atoms 1 and 2. Staple-core locants are separated by a colon with spaces either side of it, and there are no spaces after the commas. In $\text{Au}_{25}(\text{SR})_{18}$, from the locants of Manuscript Figure 1, we obtain the six staple-core locants as D1(1,2):D2(3,4):D3(5,6):D4(7,8):D5(9,10):D6(11,12).

We note that if the locants of the molecular graph of Figure S4 are used, a more difficult to remember sequence of staple-core locants results which is D1(1,8):D2(6,12):D3(7,9):D4(3,11):D5(4,10), hence we will employ those of Manuscript Figure 1 for reasons of simplicity.

5. We may also use a contracted staple locant sequence, if all the the locant numbers are in consecutive order by placing an ellipsis between the colons to indicate the missing locants in the sequence: D1(1,2); ... ;D6(11,12)-(1,3,5-SMe-2,4-Au)₆.

There are spaces after the commas when they surround an ellipsis.

C. Core Metal Name

(i) The core metal name contains the description of the metal atoms of the core and staples and their substituents. Metal names of the form auro, pallado and argento, which correspond to the elements Au, Pd and Ag, are assigned using IUPAC inorganic nomenclature. The presence of more than one type of metal element present is indicated by forming compound names, and the

additional metal element is treated as a substituent and hence carries a prefix to indicate the positions of substitution. The following rules are applied:

(i) The minority (substituent) metal element names being placed in front of the majority metal element names such as palladoauro and argentoauro.

(ii) The number of metal atom substituents of a particular element is indicated by adding the Latin prefixes mono, di, tri, tetra, penta, hexa, hepta, octa, nona, deca, etc., to the substituent metal element name. Optionally, and if there are larger number of metal atom substituents, the number of them can be prefixed to the substituent name eg. (23)-palladoauro-25.

(iii) The sets of locants for the positions of the minority metal atoms, separated by commas and in parentheses, are prefixed to their respective minority metal names. Eg. (1,2)-dipalladoauro. For example, a case where there are two types of minority metal element, with Pd in positions 1 and 2 and Ag in positions 3 and 4, might be called (1,2)-dipallado-(3,4)-diargentoauro-25 aspicule(1-). A hyphen is used after the first metal minority atom name to separate it from the locant prefix of second (more numerous) metal element name.

(iv) The number of metal atoms which is characteristic of the structure; eg. auro-25, where a hyphen separates it from the metal name.

D. Suffix of the name

Following the core name we attach a suffix of the form: **aspicule(charge) (structural descriptor)**.

The word aspicule indicates the family of molecules in an analogous way to the suffix fullerene in fullerene nomenclature. The charge is written in brackets as the final suffix eg. (1-), (1+), or (0).

After the charge a space is left and a final suffix consisting of a structural descriptor of the form: **(core polyhedral descriptor, principal symmetry axis)**. The rules below govern the formation of the structural descriptor.

(i) The geometrical shape of each polyhedral cluster comprising the core is designated by a core polyhedral descriptor which is its first letter which is italicized and in capitals, eg. tetrahedro (*T*), octahedro (*O*), dodecahedro (*D*), icosahedro (*I*), or, by forming an acronym out of several of its letters by splitting the name into its distinctive parts eg. rhomboicosidodecahedron (*R-I-D*) to form *RID*. If the polyhedron name consists of more than one word for example a Marks decahedron, we use the first letter of each word (*MD*).

(ii) If there is a core atom polyhedron inside the other, we may use, for example, the notation *I@D* for a central icosahedral (*I*) cage within a dodecahedral (*D*) cage.

(iii) If there is a single central atom within the polyhedral core it is designated by adding the symbol 'i', which stands for interstitial, and if there is more than one central atom each of their

locants may be designated as i_1, i_2, i_3, i_4 , etc., and if these central atoms form a polyhedron we place this polyhedron's acronym first in the core polyhedral descriptor. For example, $\text{Au}_{38}(\text{SR})_{24}$ consists of an interstitial trigonal-bipyramidal (*TBP*) structure capped on its top and bottom by nine-atom caps designated as BIC_{18} , an 18-atom fragment of the bi-icosahedron (*BIC*) and the complete core structure of $\text{Au}_{38}(\text{SR})_{24}$ aspicule would be described as $\text{TBP} @ (\text{BIC}_{18})$ which is an alternative way of viewing the structure to a bi-icosahedral core consisting of a face-fused pair of icosahedra. For $\text{Au}_{102}(\text{SR})_{44}$ we find a central pentagonal bipyramid (*PBP*) within a 42-atom Marks decahedral shell (MD_{42}) which may be written as $\text{PBP} @ \text{MD}_{42}$, and this comprises the 49-atom Marks decahedron.

E. Stereodescriptor prefixes

A prefix to the front of the name indicating chiral and geometric isomerism may be added as described in the Manuscript, and S-C bond directions may also be included. (See SI 6).

F. Compact structural name

A more compact structural name can be obtained by omitting the connectivity information of the staples to the core atoms and substituting these by the labels of the staples and placing these as a prefix to the ligand-staple name they apply to.

Staple locants-(Ligand-Staple name)-(Core name) (Suffix)

A compact structural name for $\text{Au}_{25}(\text{SR})_{18}$ would be $[\text{D1-D6}]-(1,3,5\text{-SMe-2,4-Au})_6\text{-auro-25 aspicule}(1-) (i @ I, 3C_2)$.

Examples of aspicule structural names are given in Table S8 for modifications of $\text{Au}_{25}(\text{SR})_{18}$, $\text{Au}_{38}(\text{SR})_{24}$ and $\text{Au}_{102}(\text{SR})_{44}$ and modifications in both compact and standard aspicule structural nomenclature are given in Tables S9 and S10.

Supporting Information 6

Terminologies of $\text{Au}_{25}(\text{SR})_{18}$ with Substituent Positions for Modifications

Table S1: Aspicule terminologies for ligand-exchanged and alloy modifications of $\text{Au}_{25}(\text{SR})_{18}$ aspicules. Only one of the names of the isomers of a given formula name of a modification is presented.

Formula name	Aspicule Formula name
$\text{Au}_{25}(\text{SMe})_{18}$	$\text{Au}_{25}(\text{SMe})_{18}$
$\text{Au}_{25}(\text{SMe})_{17}(\text{PET})_1$	$\text{Au}_{25}(\text{SMe})_{17}((\text{D1-3})\text{-PET})_1$
$\text{Au}_{25}(\text{SMe})_{16}(\text{PET})_2$	$\text{Au}_{25}(\text{SMe})_{16}((\text{D1-3}, \text{D2-3})\text{-PET})_2$
$\text{Au}_{25}(\text{SMe})_{12}(\text{PET})_6$	$\text{Au}_{25}(\text{SMe})_{12}(((\text{D1-D6})\text{-3})\text{-PET})_6$
$\text{Au}_{25}(\text{SMe})_{11}(\text{PET})_7$	$\text{Au}_{25}(\text{SMe})_{11}(((\text{D1-D6})\text{-3}, \text{D3-5})\text{-PET})_7$
$\text{Au}_{24}\text{Pd}(\text{SMe})_{18}$	$\text{Au}_{24}((i)\text{-Pd})(\text{SMe})_{18}$
$\text{Au}_{22}\text{Pd}_3(\text{SMe})_{18}$	$\text{Au}_{22}((i, \text{D1-2}, \text{D1-4})\text{-Pd})_3(\text{SMe})_{18}$
$\text{Au}_{21}\text{Pd}_4(\text{SMe})_{18}$	$\text{Au}_{21}((i, 2, \text{D1-2}, \text{D1-4})\text{-Pd})_4(\text{SMe})_{18}$

Table S2: Precise terminologies for ligand-exchanged and alloy modifications of $\text{Au}_{25}(\text{SR})_{18}$ using formula names and polyhedral shell names. Only one of the names of the isomers of a given formula name of a modification is presented.

Formula name	Aspicule Formula Name	Shell Name
$\text{Au}_{25}(\text{SMe})_{18}$	$\text{Au}_{25}(\text{SMe})_{18}$	$\text{Au@Au}_{12}@\text{Au}_{12}@\text{S}_6@\text{S}_{12}@\text{Me}_{18}$
$\text{Au}_{25}(\text{SMe})_{17}(\text{PET})_1$	$\text{Au}_{25}(\text{SMe})_{17}(\text{D1-3-PET})$	$\text{Au@Au}_{12}@\text{Au}_{12}@\text{S}_6@\text{S}_{12}@(\text{Me}_{17})((\text{D1-3})\text{-PET})$
$\text{Au}_{25}(\text{SMe})_{16}(\text{PET})_2$	$\text{Au}_{25}(\text{SMe})_{16}(\text{D1-3,D2-3-PET})_2$	$\text{Au@Au}_{12}@\text{Au}_{12}@\text{S}_6@\text{S}_{12}@(\text{Me}_{16})((\text{D1-3,D2-3})\text{-PET})_2$
$\text{Au}_{25}(\text{SMe})_{12}(\text{PET})_6$	$\text{Au}_{25}(\text{SMe})_{12}([\text{D1-D6}]\text{-3-PET})_6$	$\text{Au@Au}_{12}@\text{Au}_{12}@\text{S}_6@\text{S}_{12}@(\text{Me}_{12})([\text{D1-D6}]\text{-3-PET})_6$
$\text{Au}_{25}(\text{SMe})_{11}(\text{PET})_7$	$\text{Au}_{25}(\text{SMe})_{11}([\text{D1-D6}]\text{-3,D1-5-PET})_7$	$\text{Au@Au}_{12}@\text{Au}_{12}@\text{S}_6@\text{S}_{12}@(\text{Me}_{11})([\text{D1-D6}]\text{-3,D1-5-PET})_7$
$\text{Au}_{24}\text{Pd}(\text{SMe})_{18}$	$\text{Au}_{24}(i\text{-Pd})(\text{SMe})_{18}$	$\text{Pd@Au}_{12}@\text{Au}_{12}@\text{S}_6@\text{S}_{12}@\text{Me}_{18}$
$\text{Au}_{22}\text{Pd}_3(\text{SMe})_{18}$	$\text{Au}_{22}(i,\text{D1-2,D1-4-Pd})_3(\text{SMe})_{18}$	$\text{Pd@Au}_{12}@((\text{D1-2,D1-4})\text{-Pd})_2\text{Au}_{10}@\text{S}_6@\text{S}_{12}@\text{Me}_{18}$
$\text{Au}_{21}\text{Pd}_4(\text{SMe})_{18}$	$\text{Au}_{21}(i,2,\text{D1-2,D1-4-Pd})_4(\text{SMe})_{18}$	$\text{Pd}@((2)\text{-Pd})\text{Au}_{11}@((\text{D1-2,D1-4})\text{-Pd})_2\text{Au}_{10}@\text{S}_6@\text{S}_{12}@\text{Me}_{18}$

Supporting Information 7

Borromean-Rings Diagram with S-C Bond Directions for $\text{Au}_{25}(\text{SR})_{18}$

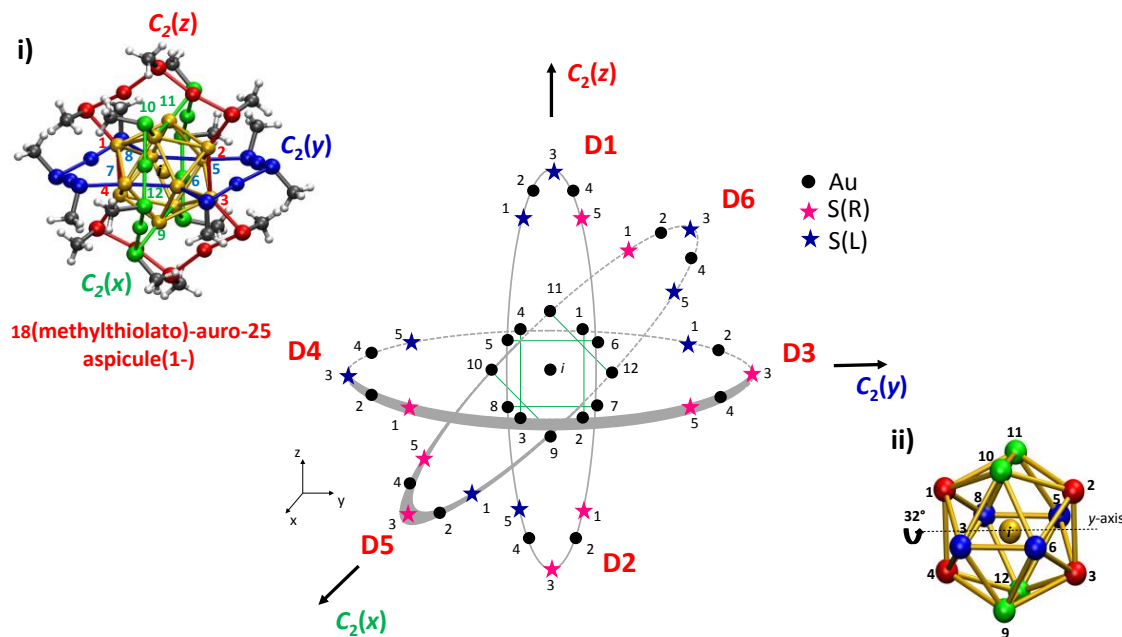


Figure S7. Borromean ring diagram for $\text{Au}_{25}(\text{SR})_{18}$ aspicule including S-C bond directions. Gold atoms are shown by black dots and sulfur atoms (ligands) by magenta and blue stars, respectively. The clockwise direction for each staple is defined by the path around the staple beginning at 1 and ending 5. The magenta stars correspond to an S-C bond direction which is parallel to the direction of a right-handed screw rotating in *clockwise* direction on that staple. The S(R) bond directions are in the z' direction on the $C_2(y)$ ring, the x' -direction on the $C_2(z)$ ring, and the y' -direction for the $C_2(x)$ ring. S(L) sulfur atoms are shown by blue stars are those for which the S-C bond direction is parallel to a right-handed screw rotating *anticlockwise*, and is opposite to the S(R) bond direction on each ring. We have assumed that C-S-Au bond angles are right angles for simplicity.

We may include S-C bond direction information for $\text{Au}_{25}(\text{SR})_{18}$ on a diagram similar to Manuscript Figure 1, and the result can be seen in Figure S7 above. We assumed that C-S-Au bond angles are right angles for simplicity. We indicate the direction of an S-C bond at a particular sulfur atom by the color of the star symbol used to represent it. Hence, blue and magenta stars indicate the direction of the sulfur-carbon (S-C) bond pointing in a clockwise screw and anticlockwise screw direction, respectively, with respect to the clockwise and anticlockwise directions around the staple. We specify the S-C bond directions by R (clockwise), and L (anticlockwise). We may form a prefix by concatenating the S-C bond directions for each ligand counting clockwise around a staple, eg. LRR indicates the S-C bond directions in positions 1(L), 3(R) and 5(R) on the staple. The staple locants of the staples which have a

specific S-C bond direction may be placed as a prefix to that S-C bond-direction-prefix *eg.* (D2,D3,D5)-LRR. We consider the name of $\text{Au}_{25}(\text{SMe})_{12}(\text{PET})_6$ with six substituents at the bridging ligand sites and include the S-C bond directions.

In the aspicule nomenclature, a name for $([\text{D1-D6}]-3)(\text{PET})_6, (\text{SMe})_{12}$ auro-25 aspicule(1-) including the S-C bond direction sequence together with the staple locants could be prefixed to the name to give ((D2,D3,D5)-LRR, (D1,D4,D6)-RLL)- $([\text{D1-D6}]-3)-(\text{PET})_6, (\text{SMe})_{12}$ -*i*-auro-25 aspicule(1-).

Supporting Information 8

Borromean-Rings Diagram of $\text{Au}_{25}(\text{SR})_{18}$ with Hybrid Directional Locants

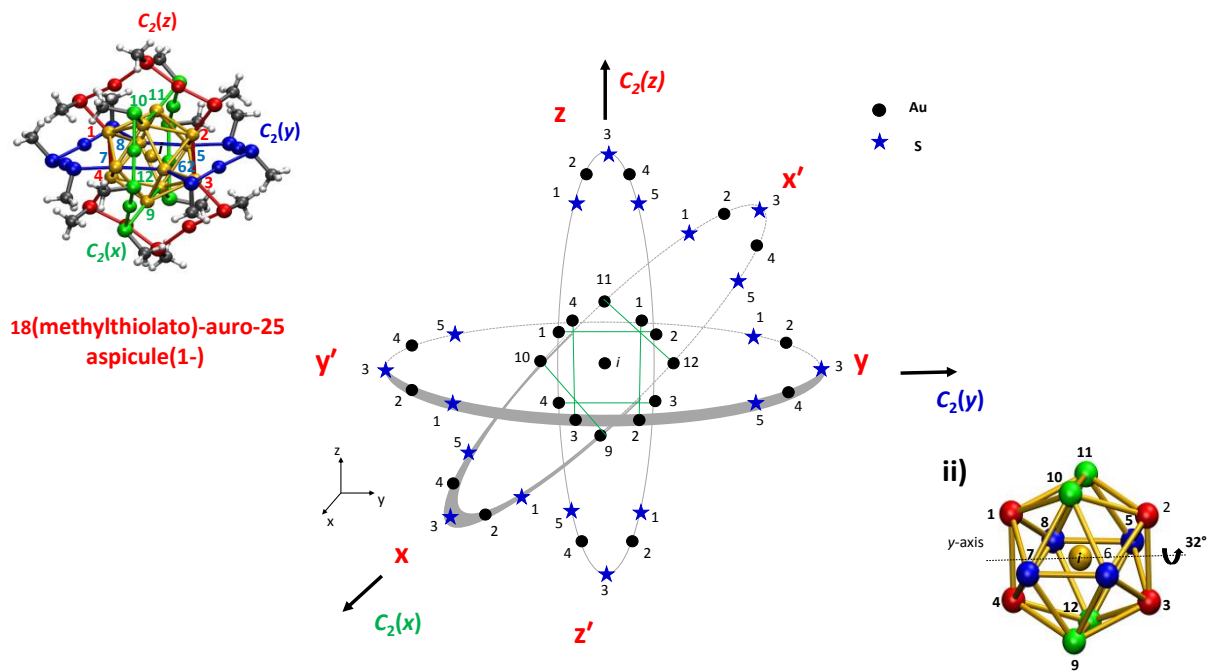


Figure S8. Borromean-Rings diagram of $\text{Au}_{25}(\text{SMe})_{18}$ with *hybrid-directional locants* for the staples. Gold atoms are shown by black dots and SMe ligands by the blue stars. The Cartesian direction associated with each of the staples is marked alongside the relevant staple. Insets (i) shows the 3D ring structure within $\text{Au}_{25}(\text{SMe})_{18}$ and inset (ii) the core icosahedron, respectively.

We introduce just such a hybrid-directional locant scheme for $\text{Au}_{25}(\text{SR})_{18}$. Instead of using the staple type and number (eg. D1, D2, etc.) to specify staple locants we use the direction the central sulfur that the staple points in, according to a Cartesian axis system superimposed on at least one symmetry axis of the aspicule. In the case of $\text{Au}_{25}(\text{SR})_{18}$ we may associate the three C_2 axes of symmetry with a set of Cartesian axis as oriented in supporting information 1. This locant scheme is suitable for smaller aspicules with upto approximately 44 metal atoms and is convenient as it allows the structure to be visualized with or without the aid of a diagram. We note that labeling atoms using directions for $\text{Au}_{102}(\text{SR})_{44}$ and $\text{Au}_{144}(\text{SR})_{60}$ is impractical as the number of staples is large and they are spread out over a wide range of directions.

Figure S8 shows Figure 1 from the manuscript with the positions labelled using Cartesian directions. In this locant scheme, the locants for the core atoms are simply the number which labels them; however, the locants of the staple atoms are formed by combining the direction of the staple with the number of the staple atom counting clockwise from the first sulfur atom on its left side. For example, x3 indicates the bridging sulfur on the x-direction staple, and x1 and x5 indicate the non-bridging sulfurs on that staple. We do not insist on italics to specify the

Cartesian directions in the locants. The name hybrid directional locant stems from this combination of the use of both numerals and Cartesian axis directions such as x , y and z . An example of a name for a ligand substitution on the bridging ligands in the x and x' direction would be (x3,x'3)-(PET)₂(SMe)₁₆-auro-25 aspicule(1-). We remark that this method of providing locants has the advantage that the position of the substituent is very easy to identify compared to existing locant systems and could be applied to other classes of molecules.

Supporting Information 9

Tables of Names for $\text{Au}_{25}(\text{SR})_{18}$, $\text{Au}_{38}(\text{SR})_{24}$ and $\text{Au}_{102}(\text{SR})_{44}$

Table S3: Table of aspicule names for $\text{Au}_{25}(\text{SMe})_{18}$ and some examples of names for ligand-exchange and alloy modifications. The (SR) terminology for the ligands has been used here. Only one of the names of the isomers of a given formula name of a modification is presented.

Formula Name	Aspicule Name
$\text{Au}_{25}(\text{SMe})_{18}$	(SMe) ₁₈ -auro-25 aspicule(1-)
$\text{Au}_{25}(\text{SMe})_{17}(\text{PET})_1$ 1 bridging PET ligand	(D1-3)-(PET) ₁ -(SMe) ₁₇ -auro-25 aspicule(1-)
$\text{Au}_{25}(\text{SMe})_{16}(\text{PET})_2$ Two bridging PET ligands (<i>trans</i>)	(D1-3,D2-3)-(PET) ₂ -(SMe) ₁₆ -auro-25 aspicule(1-)
$\text{Au}_{25}(\text{SMe})_{16}(\text{PET})_2$ Two bridging PET ligands (<i>cis</i>)	(D1-3,D3-3)-(PET) ₂ -(SMe) ₁₆ -auro-25 aspicule(1-)
$\text{Au}_{25}(\text{SMe})_{12}(\text{PET})_6$ Six bridging PET ligands	([D1-D6]-3)-(PET) ₆ -(SMe) ₁₂ -auro-25 aspicule(1-)
$\text{Au}_{25}(\text{SMe})_{11}(\text{PET})_7$ Six bridging ligands and one non-	([D1-D6]-3,D1-5)-(PET) ₇ -(SMe) ₁₁ -auro-25 aspicule(1-)
$\text{Au}_{24}\text{Pd}(\text{SMe})_{18}$ One central Pd atom	(SMe) ₁₈ - <i>i</i> -monopalladoauro-25 aspicule(1-)
$\text{Au}_{22}\text{Pd}_3(\text{SMe})_{12}(\text{PET})_6$ Three Pd atoms: one central, two in core. Six bridging ligands	([D1-D6]-3)-(PET) ₆ -(SMe) ₁₂ -(<i>i</i> ,1,2)-tripalladoauro-25 aspicule(1-)
$\text{Au}_{21}\text{Pd}_4(\text{SMe})_{12}(\text{PET})_6$ Four Pd atoms: one interstitial, two in the core and one on a staple. Six PET bridging ligands	([D1-D6]-3)-(PET) ₆ -(SMe) ₁₂ -(<i>i</i> ,1,2,D1-2)-tetrapalladoauro-25 aspicule(1-)

Table S4: Table of aspicule names for $\text{Au}_{25}(\text{SMe})_{18}$ and some examples of names for ligand-exchange and alloy modifications. The IUPAC terminology names for the ligands has been used here. Only one of the names of the isomers of a given formula name of a modification is presented.

Formula Name/Substituent details	Aspicule Name
$\text{Au}_{25}(\text{SMe})_{18}$	18(methylthiolato)-auro-25 aspicule(1-)
$\text{Au}_{25}(\text{SMe})_{17}(\text{PET})_1$ One bridging PET ligand	(D1-3)-mono(2-phenylethanethiolato),17(methylthiolato)-auro-25 aspicule(1-)
$\text{Au}_{25}(\text{SMe})_{16}(\text{PET})_2$ Two bridging PET ligands (<i>trans</i>)	(D1-3,D2-3)-di(2-phenylethanethiolato),16(methylthiolato)-auro-25 aspicule(1-)
$\text{Au}_{25}(\text{SMe})_{16}(\text{PET})_2$ Two bridging PET ligands (<i>cis</i>)	(D1-3,D3-3)-di(2-phenylethanethiolato),16(methylthiolato)-auro-25 aspicule(1-)
$\text{Au}_{25}(\text{SMe})_{12}(\text{PET})_6$ Six bridging PET ligands	([D1-D6]-3)-hexa(2-phenylethanethiolato),dodeca(methylthiolato)-auro-25 aspicule(1-)
$\text{Au}_{25}(\text{SMe})_{11}(\text{PET})_7$ Six bridging and one non-bridging PET ligand	([D1-D6]-3,D1-5)-hepta(2-phenylethanethiolato),unadeca(methylthiolato)-auro-25 aspicule(1-)
$\text{Au}_{24}\text{Pd}(\text{SMe})_{18}$ One central Pd atom	18(methylthiolato)-(i)-monopalladoauro-25 aspicule(1-)
$\text{Au}_{22}\text{Pd}_3(\text{SMe})_{12}(\text{PET})_6$ Three Pd atoms: one central, two in core. Six PET bridging ligands	([D1-D6]-3)-hexa(2-phenylethanethiolato),dodeca(methylthiolato)-(i,1,2)-tripalladoauro-25 aspicule(1-)
$\text{Au}_{21}\text{Pd}_4(\text{SMe})_{12}(\text{PET})_6$ Four Pd atoms: one central, two in the core and one on a staple. Six PET bridging ligands	([D1-D6]-3)-hexa(2-phenylethanethiolato),dodeca(methylthiolato)-(i,1,2,D1-2)-tetrapalladoauro-25 aspicule(1-)

Table S5: Table of names for supramolecular adducts formed between β -CD and $\text{Au}_{25}(\text{BBSH})_{18}$. We provide example names for one possible isomer for each number of attached β -CDs (from 1 to 4). The positions for the four β -CD attached structure are taken from Mathew et al.⁵. Only one of the names of the isomers of a given formula name of a modification is presented. The (SR) terminology for the ligands has been used here.

Formula Name	Aspicule name
$\text{Au}_{25}(\text{BBSH})_{17}(\text{BBSH} \cap \text{CD})_1$	(D1-3)-(BBSH $\cap$ CD) ₁ , (BBSH) ₁₇ -auro-25 aspicule(1-)
$\text{Au}_{25}(\text{BBSH})_{16}(\text{BBSH} \cap \text{CD})_2$	(D1-3, D2-3)-(BBSH $\cap$ CD) ₂ , (BBSH) ₁₆ -auro-25 aspicule(1-)
$\text{Au}_{25}(\text{BBSH})_{15}(\text{BBSH} \cap \text{CD})_3$	(D3-3, D4-1, D4-5)-(BBSH $\cap$ CD) ₃ , (BBSH) ₁₅ -auro-25 aspicule(1-)
$\text{Au}_{25}(\text{BBSH})_{14}(\text{BBSH} \cap \text{CD})_4$	(D6-1, D2-5, D2-1, D3-5)-(BBSH $\cap$ CD) ₄ , (BBSH) ₁₄ -auro-25 aspicule(1-)

Table S6: Table of names for some possible conjugated FITC complexes with $\text{Au}_{25}(\text{SR})_{18}$ with dansyl glutathione (SDG) ligands. We provide example names for one possible structural isomer for several numbers of conjugated FITCs. In the ligand name, SDG-FITC, the dash indicates the SDG ligand is conjugated with FITC. Only one of the names of the isomers of a given formula name of a modification is presented.

Formula Name	Aspicule name
$\text{Au}_{25}(\text{SDG})_{18}(\text{FITC})_1$	(D1-3)-(SDG-FITC) ₁ , (SDG) ₁₇ -auro-25 aspicule(1-)
$\text{Au}_{25}(\text{SDG})_{18}(\text{FITC})_2$	(D1-3, D2-3)-(SDG-FITC) ₂ , (SDG) ₁₆ -auro-25 aspicule(1-)
$\text{Au}_{25}(\text{SDG})_{18}(\text{FITC})_3$	(D1-3, D3-3, D5-3)-(SDG-FITC) ₃ , (SDG) ₁₅ -auro-25 aspicule(1-)
$\text{Au}_{25}(\text{SDG})_{18}(\text{FITC})_6$	([D1-D6]-3)-(SDG-FITC) ₆ , (SDG) ₁₂ -auro-25 aspicule(1-)

Table S7: Aspicule structural names with staple-core locants for ligand-exchanged and alloy-modifications of $\text{Au}_{25}(\text{SR})_{18}$. Only one of the names of the isomers of a given formula name of a modification is presented.

Formula Name/Substituent positions	Structural Aspicule Name
$\text{Au}_{25}(\text{SMe})_{18}$	D1(1,2):D2(3,4):D3(5,6):D4(7,8):D5(9,10):D6(11,12)-(1,3,5-SMe-2,4-Au) ₆ -auro-25 aspicule(1-) (<i>i@I,3C₂</i>)
$\text{Au}_{25}(\text{SMe})_{17}(\text{PET})_1$ One bridging PET ligand	D1(1,2)-(3-PET,1,5-SMe-2,4-Au) ₂ ,D2(3,4):D3(5,6):D4(7,8):D5(9,10):D6(11,12)-(1,3,5-SMe-2,4-Au)-auro-25 aspicule(1-) (<i>i@I,3C₂</i>)
$\text{Au}_{25}(\text{SMe})_{16}(\text{PET})_2$ Two bridging PET ligands (<i>trans</i>)	D1(1,2):D2(3,4)-(3-PET,1,5-SMe-2,4-Au) ₂ ,D3(5,6):D4(7,8):D5(9,10):D6(11,12)-(1,3,5-SMe-2,4-Au) ₄ -auro-25 aspicule(1-) (<i>i@I,3C₂</i>)
$\text{Au}_{25}(\text{SMe})_{16}(\text{PET})_2$ Two bridging PET ligands	D1(1,2):D4(7,8)-(3-PET,1,5-SMe-2,4-Au) ₂ ,D2(3,4):D3(5,6):D5(9,10),D6(11,12)-(1,5-SMe,3-PET-2,4-Au) ₄ -auro-25 aspicule(1-) (<i>i@I,3C₂</i>)
$\text{Au}_{25}(\text{SMe})_{12}(\text{PET})_6$ Six bridging PET ligands	D1(1,2); ... ;D6(11,12)-(3-PET,1,5-SMe-2,4-Au) ₆ -auro-25 aspicule(1-) (<i>i@I,3C₂</i>)
$\text{Au}_{25}(\text{SMe})_{11}(\text{PET})_7$ Six PET bridging ligands and one PET non-bridging ligand	D1(1,2)-(1-SMe,3,5-PET-2,4-Au),D1(1,2); ... ;D6(11,12)-(3-PET,1,5-SMe-2,4-Au) ₅ -auro-25 aspicule(1-) (<i>i@I,3C₂</i>)
$\text{Au}_{24}\text{Pd}(\text{SMe})_{18}$ One interstitial Pd atom	D1(1,2):D2(3,4):D3(5,6):D4(7,8):D5(9,10):D6(11,12)-(1,3,5-SMe-2,4-Au) ₆ -monopalladoauro-25 aspicule(1-) (<i>i@I,3C₂</i>)
$\text{Au}_{22}\text{Pd}_3(\text{SMe})_{12}(\text{PET})_6$ Three Pd atoms, one central, and two in the core	D1(1,2); ... ;D6(11,12)-(3-PET,1,5-SMe-2,4-Au) ₆ -(<i>i,1,2</i>)-tripalladoauro-25 aspicule(1-) (<i>i@I,3C₂</i>)
$\text{Au}_{21}\text{Pd}_4(\text{SMe})_{12}(\text{PET})_6$ Four Pd atoms, one central, two in the core and one on a staple. Six PET bridging ligands.	D1(1,2)-(3-PET,1,5-SMe-2-Pd,4-Au) ₁ ,D2(3,4):D3(5,6):D4(7,8):D5(9,10):D6(11,12)-(1,5-SMe,3-PET-2,4-Au) ₅ -(<i>i,1,2,D1-2</i>)-tetrapalladoauro-25 aspicule(1-) (<i>i@I,3C₂</i>)

Table S8: Aspicule names for $\text{Au}_{25}(\text{SR})_{18}$, $\text{Au}_{38}(\text{SR})_{24}$ and $\text{Au}_{102}(\text{SR})_{44}$ and one modification of each. Only one of the names of the isomers of a given formula name of a modification is presented.

Formula Name	Aspicule name
$\text{Au}_{25}(\text{SMe})_{18}$	(SMe) ₁₈ -auro-25 aspicule(1-)
$\text{Au}_{23}\text{Pd}_2(\text{SMe})_{16}(\text{PET})_2$ Two PET on the bridging ligands opposite each other, and 2 Pd in the core.	(D1-3,D2-3)-(PET) ₂ , (SMe) ₁₆ -(i,2)-dipalladoauro-25 aspicule(1-)
$\text{Au}_{38}(\text{SMe})_{24}$	(SMe) ₂₄ -(i ₁ , i ₅)-auro-38 aspicule(0)
$\text{Au}_{36}\text{Pd}_2(\text{SMe})_{20}(\text{PET})_4$ Two Pd in interstitials, Two PET ligands in bridging positions on dimer staples and two on monomer staples	(D1-3,D2-3,M1-1,M2-3)-(PET) ₄ , (SMe) ₂₀ -(i ₁ , i ₅)-dipalladoauro-38 aspicule(0)
$\text{Au}_{102}(\text{SMe})_{44}$	(SMe) ₄₄ -auro-102 aspicule(0)
$\text{Au}_{100}\text{Pd}_2(\text{SMe})_{40}(\text{PET})_4$ Two Pd in MD core. Two PET ligands at bridging positions of the dimer staples and two on monomer ligands of the N Au ₁₅ cap.	(D1-3,D2-3,M1-1,M2-3)-(PET) ₄ , (SMe) ₄₀ -(1,42)-dipalladoauro-102 aspicule(0)

Table S9: Compact aspicule structural names for $\text{Au}_{25}(\text{SR})_{18}$, $\text{Au}_{38}(\text{SR})_{24}$ and $\text{Au}_{102}(\text{SR})_{44}$ and one modification of each. Only one of the names of the isomers of a given formula name of a modification is presented.

Formula Name/substituent positions	Compact Aspicule Structural Name	Aspicule name
$\text{Au}_{25}(\text{SMe})_{18}$	[D1-D6]-(1,3,5-SMe-2,4-Au) ₆ -auro-25 aspicule(1-) (<i>i@I,C₂</i>)	(SMe) ₁₈ -auro-25 aspicule(1-)
$\text{Au}_{23}\text{Pd}_2(\text{SMe})_{16}(\text{PET})_2$ Two Pd in the core. Two PET at the bridging ligands	D1,D2-(3-PET,1,5-SMe-2,4-Au) ₂ ,[D3-D6]-(1,3,5-SMe-2,4-Au) ₄ -(<i>i,2</i>)-dipalladoauro-25 aspicule(1-) (<i>i@I,C₂</i>)	(D1-3,D2-3)-(PET) ₂ , (SMe) ₁₆ -(<i>i,2</i>)-dipalladoauro-25 aspicule(1-)
$\text{Au}_{38}(\text{SMe})_{24}$	[D1-D6]-(1,3,5-SMe-2,4-Au) ₆ ,[M1-M3]-(1,3-SMe-2-Au) ₂ -auro-38 aspicule(0) (<i>TBP@BIC₁₈,C₃</i>)	(SMe) ₂₄ -auro-38 aspicule(0)
$\text{Au}_{36}\text{Pd}_2(\text{SMe})_{22}(\text{PET})_2$ Two Pd atoms in the icosahedra centres. Two PET ligands in bridging positions of two dimer staples	D1,D2-(3-PET,1,5-SMe-2,4-Au) ₂ ,[D3-D6]-(1,3,5-SMe-2,4-Au) ₄ ,[M1-M3]-(1,3-SMe-2-Au) ₃ -(<i>i₁,i₅</i>)-dipalladoauro-38 aspicule(0) (<i>TBP@BIC₁₈,C₃</i>)	(D1-3,D2-3)-(PET) ₂ , (SMe) ₂₂ -(<i>i₁,i₅</i>)-dipalladoauro-38 aspicule(0)
$\text{Au}_{102}(\text{SMe})_{44}$	[M1-M19]-(1,3-SMe-2,4-Au) ₁₉ ,D1,D2-(1,3-SMe-2,4-Au) ₂ -auro-102 aspicule(0) (<i>PBP@MD₄₂@(N-RID₁₅,S-RID₁₅),C₅</i>)	(SMe) ₄₄ -auro-102 aspicule(0)
$\text{Au}_{100}\text{Pd}_2(\text{SMe})_{40}(\text{PET})_4$ Two Pd atoms in the MD core. Two PET ligands at bridging ligands of the dimer staples and two on different monomer staples in different positions.	M1-(1-PET,3-SMe-2-Au),M2-(3-PET,1-SMe-2-Au),[M3-M19]-(1,3-SMe-2-Au) ₁₇ ,D1,D2-(3-PET,1,5-SMe-2,4-Au) ₂ -(1,42)-dipalladoauro-102 aspicule(0) (<i>PBP@MD₄₂@(N-RID₁₅,S-RID₁₅),C₅</i>)	(D1-3,D2-3,M1-1,M2-3)-(PET) ₄ , (SMe) ₄₀ -(1,42)-dipalladoauro-102 aspicule(0)

Table S10: Aspicule structural names and aspicule names for Au₂₅(SR)₁₈, Au₃₈(SR)₂₄ and Au₁₀₂(SR)₄₄ and one modification of each. The ligand-staple names have been shown in bold for clarity. Only one of the names of the isomers of a given formula name of a modification is presented.

Formula Name	Aspicule Structural Name	Aspicule Name
Au ₂₅ (SMe) ₁₈	D1(1,2):D2(3,4):D3(5,6):D4(7,8):D5(9,10)- (1,3,5-SMe-2,4-Au) ₆ -auro-25 aspicule(1-) (<i>i</i> @ <i>I</i> ,3 <i>C</i> ₂)	(SMe) ₁₈ -auro-25 aspicule(1-)
Au ₂₃ Pd ₂ (SMe) ₁₆ (PET) ₂ Two PET ligands on the bridging positions, and two Pd atoms in the core	D1(1,2):D2(3,4)- (1,3,5-SMe-2-Au,4-Pd) ₂ , D3(5,6):D4(7,8):D5(9,10):D6(11,12)- (1,3,5-SMe-2,4-Au) ₄ -(<i>i</i> ,2)-dipalladoauro-25 aspicule(1-) (<i>i</i> @ <i>I</i> ,3 <i>C</i> ₂)	(D1-3,D2-3)-(PET) ₂ ,(SMe) ₁₆ -(<i>i</i> ,2)-dipalladoauro-25 aspicule(1-)
Au ₃₈ (SMe) ₂₄	D1(1,9):D2(2,10):D3(3,8):D4(14,22):D5(15,23)- (1,3,5-SMe-2,4-Au) ₆ ,M1(4,18):M2(5,19):M3(6,20)- (1,3-SMe-2-Au) ₃ -auro-38 aspicule(0) (<i>TBP</i> @ <i>BIC</i> ₁₈ , <i>C</i> ₃)	(SMe) ₂₄ -auro-38 aspicule(0)
Au ₃₆ Pd ₂ (SMe) ₂₂ (PET) ₂ Two Pd atoms in central positions, Two PET in dimer staples	D1(1,9):D2(2,10)- (3-PET,1,5-SMe-2,4-Au) ₂ ,D3(3,8):D4(14,22):D5(15,23)- (1,3,5-SMe-2,4-Au) ₄ ,M1(4,18):M2(5,19):M3(6,20)- (1,3-SMe-2-Au) ₃ -(<i>i</i> ₁ , <i>i</i> ₅)-dipalladoauro-38 aspicule(0) (<i>TBP</i> @ <i>BIC</i> ₁₈ , <i>C</i> ₃)	(D1-3,D2-3,M1-1,M2-3)-(PET) ₂ ,(SMe) ₂₂ -(<i>i</i> ₁ , <i>i</i> ₅)-dipalladoauro-38 aspicule(0)
Au ₁₀₂ (SMe) ₄₄	M1(N1,N7):M2(N2,N9):M3(N3,N11):M4(N4,N13):M5(N5,N15):M6(N6,31):M7(N10,26):M8(N14,30):M6(17,18):M2(1,22):M8(25,26):M12(17,S15):M13(19,S7):M14(23,S11):M15(S6,S2):M16(S8,S3):M17(S10,S4):M18(S12,S5):M19(S14,S1)- (1,3-SMe-2-Au) ₁₉ ,D1(N8,S9):D2(N14,S13)- (1,3,5-SMe-2,4-Au) ₂ -auro-102 aspicule(0) (<i>PBP</i> @ <i>MDS</i> ₄₂ @(<i>N-RID</i> ₁₅ , <i>S-RID</i> ₁₅ , <i>C</i> ₅))	(SMe) ₄₄ -auro-102 aspicule(0)
Au ₁₀₀ Pd ₂ (SMe) ₄₀ (PET) ₄ Two Pd in the MD core. Two PET ligands on bridging ligands of the dimer staples and two PET ligands on different positions of monomer staples.	M1(N1,N7):M2(N2,N9)- (1-PET,3-SMe-2-Au) ₂ ,D1(N8,S9):D2(N14,S13)- (3-PET,1,5-SMe-2,4-Au) ₂ ,M3(N3,N11):M4(N4,N13):M5(N5,N15):M6(N6,31):M7(N10,26):M8(N14,30):M9(17,S15):M10(19,S7):M11(23,S11):M12(17,S15):M13(19,S7):M14(23,S11):M15(S6,S2):M16(S8,S3):M17(S10,S4):M18(S12,S5):M19(S14,S1)- (1,3-SMe-2-Au) ₁₇ -(1,42)-dipalladoauro-102 aspicule(0) (<i>PBP</i> @ <i>MD</i> ₄₉ @(<i>N-RID</i> ₁₅ , <i>S-RID</i> ₁₅ , <i>C</i> ₅))	(D1-3,D2-3,M1-1,M2-1)-(PET) ₄ ,(SMe) ₄₀ -(1,42)-dipalladoauro-102 aspicule(0)

Supporting Information 10

Table of Crystal Structures and their Corresponding Nomenclature Names

Table S11: A list of crystal structures together with their aspicule names for $\text{Au}_M(\text{SR})_N$ is shown below. Both aspicule names with (SR) notation for the ligands and with their IUPAC name are given. A few structurally related compositions containing silver, selenium and chlorine, have also been included in this table. In the case of charged species, the counterion is shown in brackets after the aspicule name. Modifications of these structures may be specified using the locant prefixes as shown in Tables S3-S8. Aspicule structural names with information on the staple type and arrangement and the core shape may be formed from these names in a similar way to those shown in Tables S7, S9, and S10. This table has been based on inputs from the literature³.

No	Crystal structure	Aspicule Name	Ref.
1	$\text{Au}_{10}(\text{TBBT})_{10}$	(TBBT) ₁₀ -auro-10 aspicule(0)	6
		10(4-tert-butylbenzenethiolato)-auro-10 aspicule(0)	
2	$\text{Au}_{18}(\text{CHT})_{14}$	(CHT) ₁₄ -auro-18 aspicule(0)	7
		14(1-cyclohexanethiolato)-auro-18 aspicule(0)	
3	$\text{Au}_{20}(\text{TBBT})_{16}$	(TBBT) ₁₆ -auro-20 aspicule(0)	8
		16(4-tert-butylbenzenethiolato)-auro-20 aspicule(0)	
4	$[\text{Au}_{23}(\text{CHT})_{16}]^{1-}$	(CHT) ₁₆ -auro-23 aspicule(1-) (TOAA)	9
		16(1-cyclohexanethiolato)-auro-23 aspicule(1-)	
5	$\text{Au}_{24}(\text{ADT})_{16}$	(ADT) ₁₆ -auro-24 aspicule(0)	10
		16(1-adamantanethiolato)-auro-24 aspicule(0)	
6	$\text{Au}_{24}(\text{SePh})_{20}$	20(SePh)-auro-24 aspicule(0)	11
		20(phenylselenolato) auro-24 aspicule(0)	
7	$[\text{Au}_{25}(\text{PET})_{18}]^{1-}$	(PET) ₁₈ -auro-25 aspicule(1-) (TOAA)	12,1
		18(2-phenylethanethiolato)-auro-25 aspicule(1-) (TOAA)	
8	$[\text{Ag}_{25}(\text{PET})_{18}]^{1-}$	(PET) ₁₈ -argento-25 aspicule(1-) (TOAA)	13
		18(2-phenylethanethiolato)-argento-25 aspicule(1-) (TOAA)	
9	$[\text{Au}_{25}(\text{SePh})_{18}]^{1-}$	(SePh) ₁₈ -auro-25 aspicule(1-)	14
		18(phenylselenolato)-auro-25 aspicule(1-) (TOAA)	
10	$\text{Au}_{28}(\text{TBBT})_{20}$	(TBBT) ₂₀ -auro-28 aspicule(0)	15
		20(4-tert-butylbenzenethiolato)- auro-28 aspicule(0)	
11	$\text{Au}_{30}(\text{TBT})_{18}$	(TBT) ₁₈ -auro-30 aspicule(0)	16
		18 (2-methylpropane-2-thiolato)-auro-30 aspicule(0)	
12	$\text{Au}_{36}(\text{TBBT})_8\text{Cl}_{20}$	(Cl) ₂₀ , (TBBT) ₈ -auro-36 aspicule(0)	17
		20(chlorido), 8(4-tert-butyl-benzenethiolato)-auro-36 aspicule(0)	
13	$\text{Au}_{36}(\text{TBT})_{24}$	(TBT) ₂₄ -auro-36 aspicule(0)	18
		24(2-methylpropane-2-thiolato)-auro-36 aspicule(0)	
14	$\text{Au}_{38}(\text{PET})_{24}$	(PET) ₂₄ -auro-38 aspicule(0)	19
		24(2-phenylethanethiolato)-auro-38 aspicule(0)	

15	$\text{Au}_{38}\text{S}_2(\text{PET})_{20}$	$(\text{PET})_{20}, \text{S}_2\text{-auro-38 aspicule}(0)$	20
		$20(2\text{-phenylethanethiolato}), \text{di(sulfido)-auro-38 aspicule}(0)$	
16	$\text{Au}_{40}(\text{o-MBT})_{28}$	$(\text{o-MBT})_{28}\text{-auro-40 aspicule}(0)$	21
		$28(2\text{-sulfanylbzenethiolato)-auro-40 aspicule}(0)$	
17	$\text{Au}_{52}(\text{TBBT})_{32}$	$(\text{TBBT})_{32}\text{-auro-52 aspicule}(0)$	22
		$32(4\text{-tert-butylbenzenethiolato)-auro-52 aspicule}(0)$	
18	$\text{Au}_{68}(\text{3-MBA})_{34}$	$(\text{3-MBA})_{34}\text{-auro-68 aspicule}(0)$	23
		$34(3\text{-mercaptobenzoic acid)-auro-68 aspicule}(0)$	
19	$\text{Au}_{102}(\text{p-MBA})_{44}$	$(\text{p-MBA})_{44}\text{-auro-102 aspicule}(0)$	24
		$44(\text{p-mercaptobenzoic acid)-auro-102 aspicule}(0)$	
20	$\text{Au}_{130}(\text{TBT})_{50}$	$(\text{TBT})_{50}\text{-auro-130 aspicule}(0)$	25
		$50(2\text{-methylpropane-2-thiolato)-auro-130 aspicule}(0)$	
21	$\text{Au}_{133}(\text{TBT})_{52}$	$(\text{TBT})_{52}\text{-auro-133 aspicule}(0)$	26, 27
		$52(2\text{-methylpropane-2-thiolato)-auro-133 aspicule}(0)$	
22	$\text{Au}_{144}(\text{PET})_{60}$	$(\text{PET})_{60}\text{-auro-144 aspicule}(0)$	28
		$60(2\text{-phenylethanethiolato)-auro-144 aspicule}(0)$	

Supporting Information 11

Isomers with Two-Substituents of Ligand-Exchanged and Alloyed $\text{Au}_{25}(\text{SR})_{18}$

For two ligand exchanges of $\text{Au}_{25}(\text{SMe})_{16}(\text{PET})_2$, we counted 15 symmetry-unique isomers and these are shown in **Figure S9**. In the case of alloying, we found that $\text{Au}_{23}\text{Pd}_2(\text{SMe})_{18}$ has 28 symmetry-unique alloy isomers, and we have shown a selection of eighteen these in Figure S10 and provided locants for the substituent atoms for all the isomers in Table S12. The three-ring diagram of $\text{Au}_{25}(\text{SR})_{18}$ is a useful device for both representing and finding the possible isomers taking into account the $d\text{O}_h$ symmetry elements. Using the Borromean-rings diagram of $\text{Au}_{25}(\text{SR})_{18}$ we can easily identify structures that are equivalent under the C_2 and C_3 rotation operations in the reduced point group of the modified configuration. We checked for chiral isomers of the modified aspicule (which are symmetry-non-equivalent) by testing whether the mirror image was superimposable on the modified aspicule, where this image was obtained by reflection in a plane parallel to the mirror plane of the symmetry element which is broken by the modification. For clarity, when considering ligand exchanges one need not show the Au atoms on the diagram, and when considering alloy exchanges one can dispense with showing the S atoms.

The procedure used to the numbers and structures of the isomers was as follows: First we replaced two ligands (marked by an X) and then identified all the symmetry equivalent isomers to that configuration. The second step was to replace a different pair of ligands from all the previous symmetry equivalent isomers found in the previous steps, and then we repeated this step until there were no more possible symmetry-unique placements.

The whole procedure was repeated for the different classes of ligand placements, which consist of choosing the two ligands to be on the same staple, secondly, to both on a single ring which includes the staple and its coplanar pair, and then thirdly, on two perpendicular rings. The number of ligand isomers can be counted in the following way: there are six isomers on the same ring and nine isomers on perpendicular rings making a total of fifteen. The same procedure was used to enumerate the alloy isomers. The number of alloy isomers can be counted as follows: two involving the central atom, ten on the same ring, and sixteen on perpendicular rings making a total of 28. We neglected the S-C bond directions in this analysis, if they are included then there would be a greater number of different isomers. For six of the alloy isomers (Nos: 2, 10, 11, 12, 17 and 18 in Figure S10) which involve only substitution of two core atoms, the configuration of substituent atoms in the core icosahedron is visualized in Figure S11. These core alloy isomers may be distinguished as to whether the two substituent atoms are nearest neighbors, next-nearest neighbors, and third neighbors on opposite ends of a C_5 axis. It can be seen that although S11(b) and S11(c) appear to be equivalent in that the substituted atoms are nearest neighbors, they are in fact separate isomers since in (c) both substituent atoms are bonded to staples on different rings rather than the same ring, which makes their local bonding geometry slightly different. A similar case as S11(b) and S11(c) also occurs for the next-nearest neighbors S11(e) and S11(f).

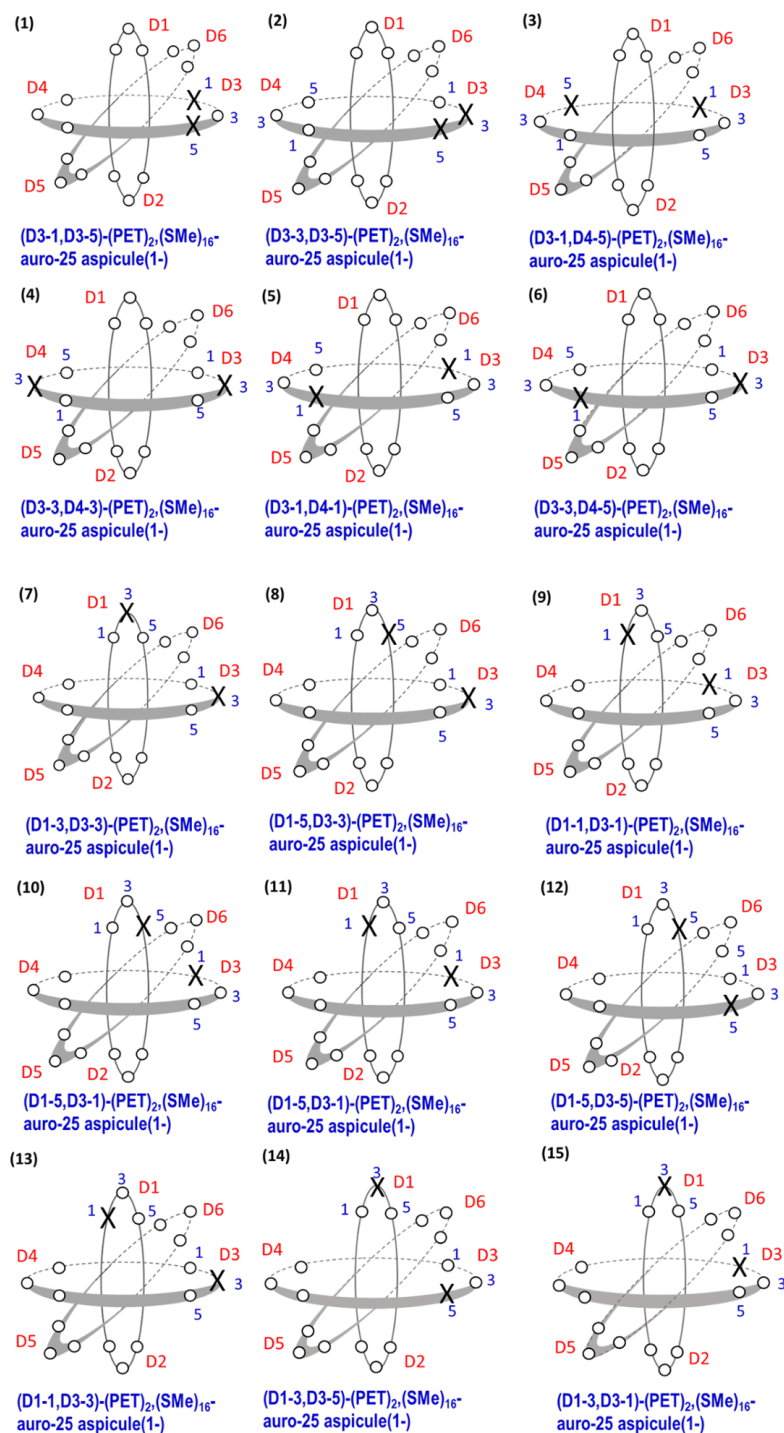
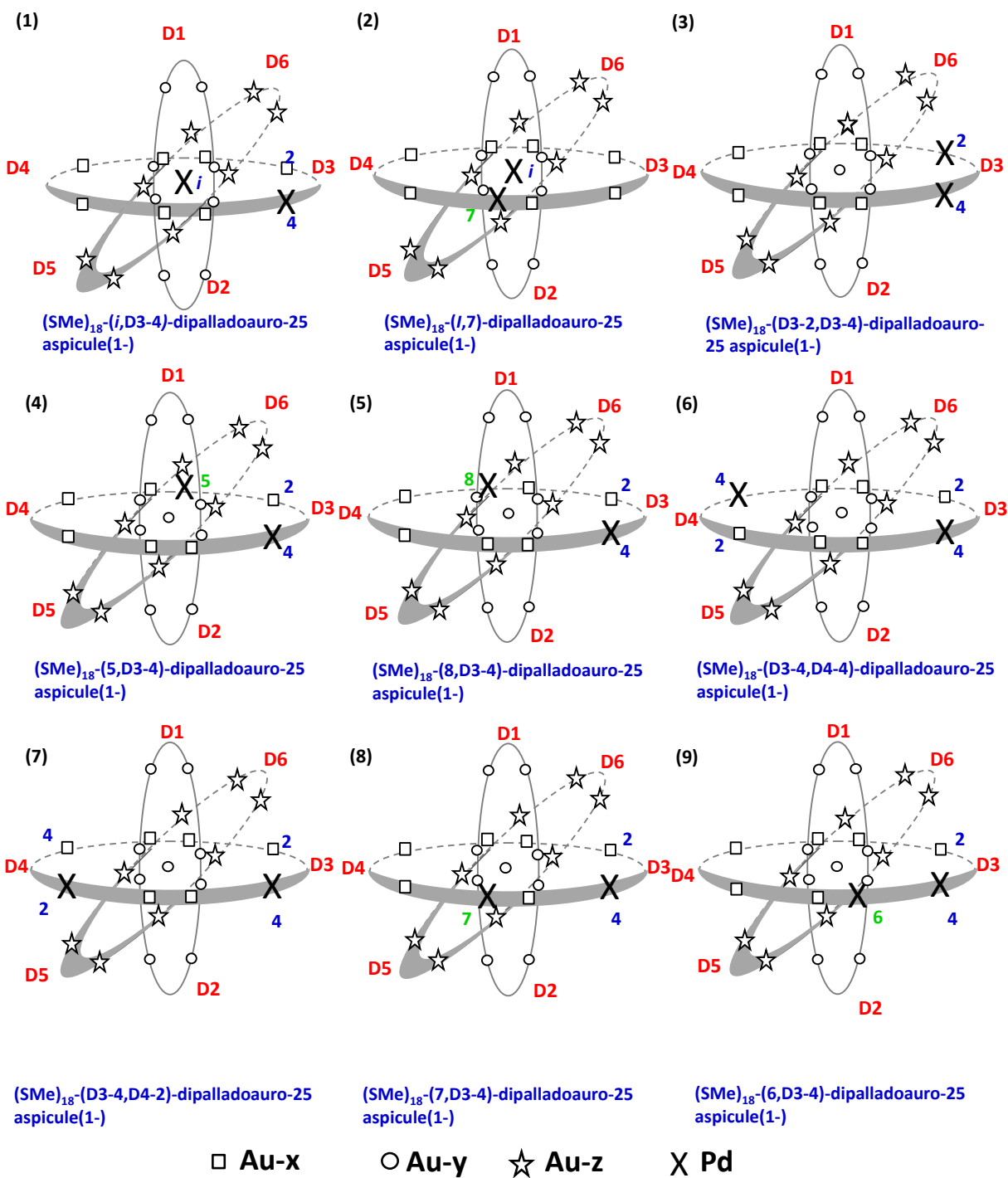


Figure S9. Ligand-exchanged isomers of $Au_{25}(SMe)_{16}(PET)_2$. The fifteen symmetry unique isomers are depicted in the following order: Isomers 1 and 2 have two PET ligands substituted on a D1 staple. Isomers 3, 4, 5, and 6 have PET ligands substituted on the $C_2(x)$ ring. Isomers 7 to 15, have PET ligands substituted on perpendicular $C_2(x)$ and $C_2(y)$ rings. An open circle indicates the sulfur bonded to methyl ligand R-groups, while a cross is used to denote a sulfur atom bonded to a PET ligand. The aspicule names for each isomer are shown underneath their respective diagrams.



Please see the caption on the next page.

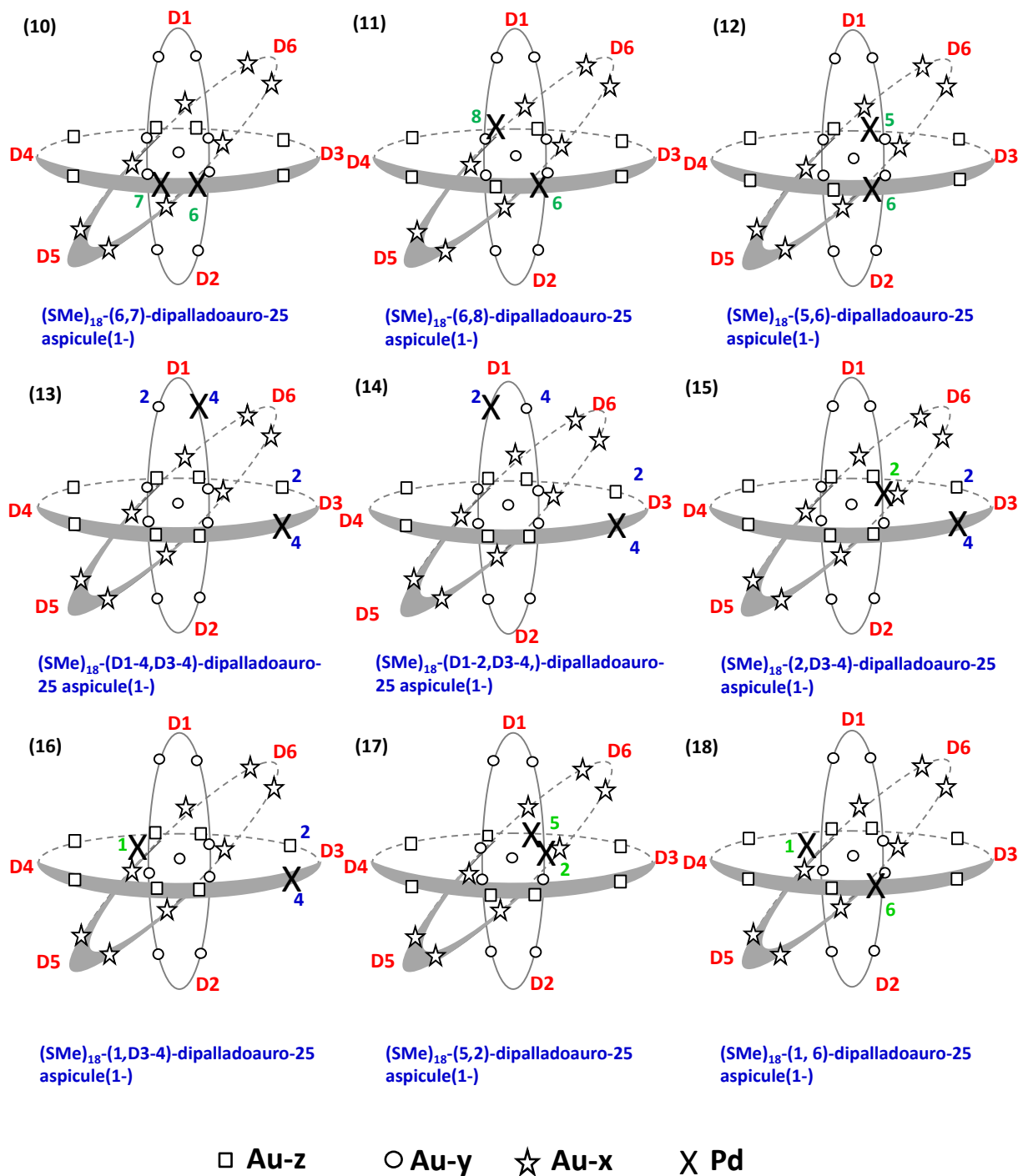


Figure S10. Alloy-exchanged isomers of $\text{Au}_{23}\text{Pd}_2(\text{SMe})_{18}$. A selection of 18 out of the 28 symmetry-unique isomers are depicted in the following order: (1) and (2) substitution of the two Pd atoms with one at the central position (*i*), (3)-(12) on the same $C_2(y)$ -ring, and (13)-(18) on perpendicular $C_2(y)$ and $C_2(z)$ rings. For clarity only the Au atoms have been shown and not the SMe ligands).

Table S12: Examples of locants of Pd atoms for the complete set of 28 symmetry-unique isomers of $\text{Au}_{23}\text{Pd}_2(\text{SMe})_{18}$. Isomers involving the central atom are Nos: 1 and 2, those involving the atoms on a single ring are Nos: 3-11 and No: 28. Isomers involving Pd atoms on perpendicular rings are Nos: 12-27.

Isomer number	Aspicule locants	Isomer number	Aspicule Locants	Isomer number	Aspicule Locants
1	(<i>i</i> ,D3-4)	14	(D1-2,D3-4)	27	6,D1-2
2	(<i>i</i> ,7)	15	(2,D3-4)	28	5,7
3	(D3-2,D3-4)	16	(D1-1,D3-4)		
4	(5,D3-4)	17	(5,2)		
5	(8,D3-4)	18	(1,6)		
6	(D3-4,D4-4)	19	(2,6)		
7	(D3-4,D4-2)	20	(D1-2,D3-2)		
8	(7,D3-4)	21	(D1-4,D3-2)		
9	(6,D3-4)	22	(1,D3-2)		
10	(6,7)	23	(2,D3-2)		
11	(6,8)	24	(6,D1-2)		
12	(5,6)	25	(5,D1-4)		
13	(D1-4,D3-4)	26	(6,D1-4)		

Supporting Information 12

Isomer Diagrams for Two Metal Atom Substituents in the Icosahedral Core of $\text{Au}_{25}(\text{SR})_{18}$

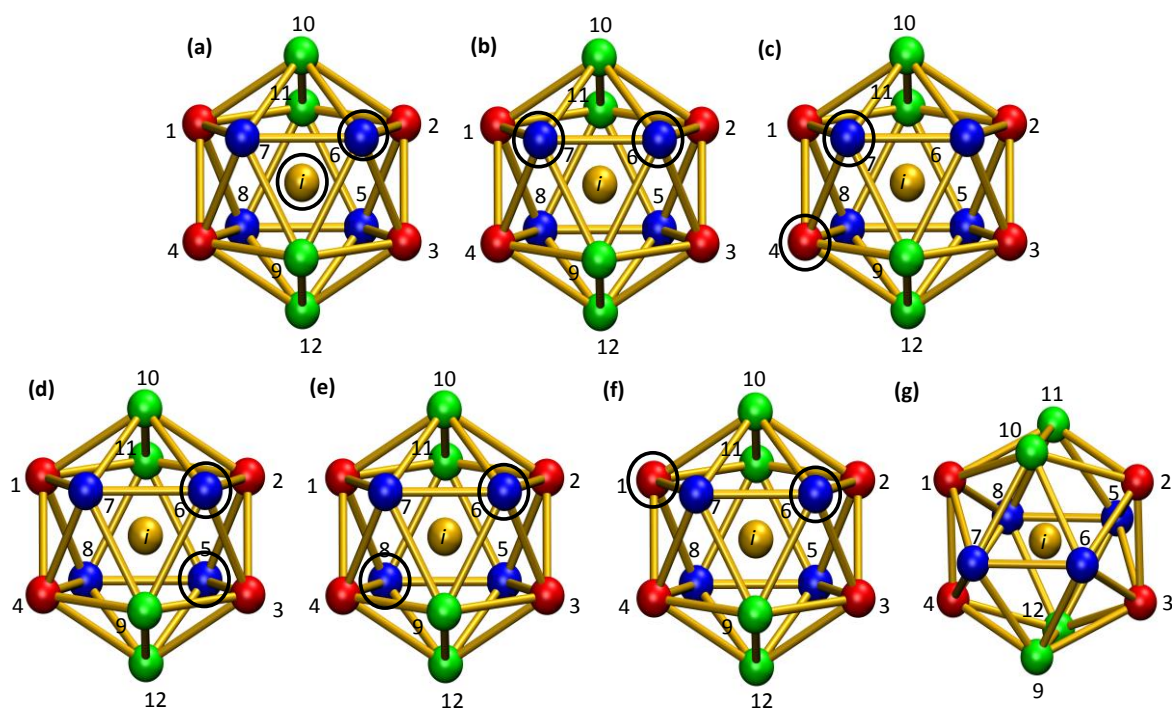


Figure S11. (a)-(f) Alloy isomers of $\text{Au}_{25}(\text{SR})_{18}$ aspicle with two metal (Pd) substituents in the core with nos. 2, 10, 11, 12, 17, 18, respectively in Figure S10. These six symmetry-unique isomers are shown by marking the positions of the substituent atoms using a thick black circle around the respective atom. The core atoms are colored red, green and blue according to inset of Figure 1 in the Manuscript, and the icosahedron is shown in its face projection. (g) The edge projection of an unmodified core icosahedron is shown for reference so that the positions may be understood as they appear on the diagrams of Figures S10.

Supporting Information 13

Staple to Core Connectivity Diagram of $\text{Au}_{102}(\text{SR})_{44}$ and its Standard Orientation and Locant Assignment

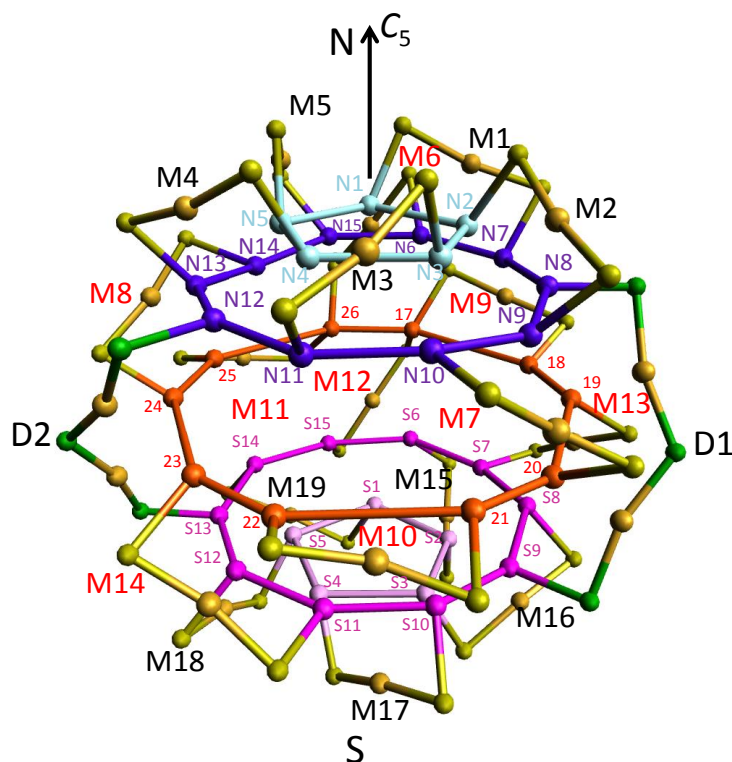


Figure S12. $\text{Au}_{102}(\text{SR})_{44}$ staples and their connectivity to the surface core atoms. The core atoms are shown as rings lying in planes perpendicular to the C_5 symmetry axis marked at the top of the figure. The core atom rings and their colors are the same as in Figure 4 in the Manuscript. Staple gold atoms are colored gold, monomer staple sulfur atoms yellow, while dimer staple sulfur atoms are colored green. The “North” and “South” hemispheres are labeled N and S respectively, and the prefixes N and S are also used in the locants of atoms of the respective Au_{15} polar caps. The arrow at the top indicates the principal C_5 symmetry axis.

The following two sections contain more details about the standard orientation and locant assignment of $\text{Au}_{102}(\text{SR})_{44}$ aspicule²⁹ which is described only briefly in the Manuscript.

(i) Standard orientation of $Au_{102}(SR)_{44}$

We select a standard orientation by placing the C_5 axis along the z-axis (vertical) as shown in **Figure S12** and secondly by using the asymmetry of the dimer and equatorial staple arrangement. Observing that the dimer staples slant at a fairly small angle from the vertical and are located on opposite sides and within one half of the $Au_{102}(SR)_{44}$ "globe", this asymmetry can be used to define the front and reverse of $Au_{102}(SR)_{44}$. The hemisphere with the dimer staples in it is taken to be the front half of $Au_{102}(SR)_{44}$.

(ii) Locant assignment of $Au_{102}(SR)_{44}$

The core atoms of the 49-atom Marks decahedron are numbered as in **Figure 4(A)**, following the core-ring locant scheme. The two Au_{15} polar caps are labelled as N(North) and S(South), and each polar cap consists of two rings of atoms. The N Au_{15} polar cap upper ring is shown in light blue and the lower ring in dark blue. The Au_{15} South polar cap upper ring is shown in purple and lilac for the lower ring. The numbering of the Au_{15} South (S) polar cap begins from the lower ring rather than the upper ring as an exception to the general rule due to the C_2 symmetry with the Au_{15} North (N) polar cap. The 49-atom Marks decahedron is divided into six planes of atoms, in which each ring (plane) of atoms in the Marks decahedron is colored differently to indicate its position, blues being used for the Northern hemisphere and reds being used in the Southern hemisphere, while orange represents the equatorial ring of atoms. This 49-atom structure may be further broken down into an outer 42-atom Marks decahedral shell and a central pentagonal bipyramid of atoms, whose atoms are numbered from i_1 to i_7 , once again following the core ring locant scheme.

For the purpose of assigning staple locants and staple core locants we may view the structure of the staples and the outer shell of core atoms in isolation. This structure includes the two Au_{15} polar caps and an equatorial ring of atoms of the Marks decahedron, to which the staples are connected to, as shown in **Figure 4(B)**. **Figure S9** above shows this structure and also the locants of the core atoms to which the staples bond to.

The color scheme below is used for the gold atoms present in the 19 monomer staples of **Figure 4(B)** which are divided into five groups of (1)-(5) below, with each group being distinguished by its different connectivity to the rings of core atoms:

(1) M1-M5 in dark blue bonded to N Au_{15} polar cap, (2) M6-M8 in cyan are three staples bonded from N Au_{15} polar cap to the orange equatorial ring of the Marks decahedron, (3) M9-M11 in orange for staples bonded solely to the equatorial ring of the Marks decahedron, (4) M12-M14, for staples bonded from the equatorial ring to the S polar Au_{15} cap structure, and finally (5) M15-M19 for those bonded solely to the S Au_{15} polar cap. The gold atoms in the sixth group comprising the two dimer staples are shown in gold, while dimer-staple sulfur atoms are shown in green and monomer-staple sulfur atoms are shown in yellow.

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