

Supporting information

Au₁₃₇(SR)₅₆ Nanomolecules: Composition, Atomic Structure, Optical Spectroscopy and Electrochemistry

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Table S1: Reproducibility table for Au₁₃₇(SR)₅₆

Methods and Experimental

Figure S1: UV-vis spectra of Au₁₃₇(SR)₅₆ recorded in toluene, at different dilutions.

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Figure S3: ESI-MS spectrum of Au₁₃₇(SR)₅₆ showing different charge states.

Figure S4: Powder XRD pattern of Au₁₃₇(SR)₅₆ nanomolecules compared with Au₁₄₄(SR)₆₀, Au₆₇(SR)₃₅, Au₃₆(SPH)_{23/24} and bulk Au *fcc*.

Figure S5: Positive and negative ESI spectra of Au₁₃₇(SCH₂CH₂Ph)₅₆. Peaks with relatively smaller intensity are being assigned to several species indicated by (Au, ligands).

Table S1: Reproducibility: Table showing the list of 29 experiments in which Au₁₃₇(SR)₅₆ was observed.

#	Sample name	Date of analysis	Reactions conditions	Au ₁₃₇ (SR) ₅₆
1	AD1-35-5 min	04/03/2010	Synthesis, Au:C6::1:5	Observed in ESI
2	AD1-37-C	04/03/2010	Synthesis, Au:PC2	Observed in ESI
3	AD1-25-A-22H	04/03/2010	Synthesis, Au:PC2::1:5	Observed in ESI
4	AD1-41-A-24H-INSOL	04/03/2010	Synthesis, Au:PC2::1:3	Observed in ESI
5	SB1-5CONC-WASH	04/03/2010		Observed in ESI
6	VJ3-31-A-20h	01/20/2013	Etching after Au:PC2::1:3, Tol, Two phase	Observed in ESI
7	VJ2-35-B-Insol1	01/31/2013	Etching after, Au:PC2::1:11, Tol, Two phase	Observed in ESI
8	VJ3-23-A-Reetch	01/06/2013	Etch w/PC2 after 1 :6 ::Au:C6,Tol, 2-phase	Observed in ESI
9	VJ3-9-b-ET-15h	12/23/2012	Etching after,1:5 :: Au:PC2.	Observed in ESI
10	VJ3-17-B-ET-15h	11/16/2012	Etching after, Au:PC2::1:2.	Observed in ESI
11	VJ3-16-B-Insol1	11/16/2012	Synthesis using, Au:PC2 :: 1:2.	Observed in ESI
12	VJ2-87-B-ET-36h	05/25/2012	Etching after, Au:PC2::1:2.	Observed in ESI
13	VJ2-23-A-Insol2	09/01/2011	Synthesis using, Au:PC2::1:5.	Observed in ESI
14	VJ2-28-A-ET	09/19/2011	Etching after, Au:PC2::1:5.	Observed in ESI
15	VJ2-20-A-Au144	08/24/2011	Synthesis using, Au:PC2::1:5.3	Observed in ESI
16	VJ2-32-B-Insol3-Au144	05/11/2011	Synthesis using, Au:PC2::1:5	Observed in ESI
17	CK3-11B-Etch-final	02/13/2013	Etching after Alloy:PC2::1:11, Tol, 2-phase	Observed in ESI
18	CK1-140-A-AC-2 mL	02/11/2013	Etching after Alloy:PC2::1:11, Tol, 2-phase	Observed in ESI
19	CK1-100D-Insol	03/10/2011	Etching after Alloy:PC2::1:11, Tol, 2-phase	Observed in ESI
20	ACD1_179A-crude	04/30/2012	Synthesis using Au:PC2::1:3.5	Observed in ESI
21	ACD2_01A	05/25/2012	Synthesis using Au:PC2::1:2	Observed in ESI
22	ACD2_01B	05/25/2012	Synthesis using Au:PC2::1:6	Observed in ESI
23	ACD2_05A	05/29/2012	Synthesis using Au:PC2::1:11	Observed in ESI
24	ACD2_21A	01/28/2013	Synthesis using Au:C6::1:15	Observed in ESI
25	ACD2_24	02/13/2013	Synthesis using Au:C6::1:20,	Observed in ESI
26	PN1-99-B	08/31/2012	Synthesis using Au : C6 :: 1 : 3	Observed in ESI
27	PN1-95-C-sol	05/22/2011	Solvent fraction of sample	Observed in ESI
28	DC1-24-C4	05/30/2012	Direct synthesis, C4, 1:3	Observed in ESI
29	DC1-36-C4	08/27/2012	Direct synthesis, C4, 1:3	Observed in ESI

Methods

Chemicals: phenylethanemercaptan (SAFC, $\geq 99\%$), hexanethiol (fluka), n-butanethiol (acros), sodium borohydride (Acros, 99%), trans-2-[3[(4-tertbutylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB matrix) (Fluka $\geq 99\%$) were purchased from Aldrich. Tetrahydrofuran (stabilized) and other solvents like toluene, methanol, acetonitrile and acetone were used from fisher as received. Biorad-SX1 beads (Biorad) were used for the SEC.

Equipment: UV-visible absorption spectra were recorded in toluene on a Shimadzu UV-1601 instrument. Matrix assisted laser desorption time-of-flight (MALDI TOF) mass spectra were collected on a Bruker Autoflex 1 mass spectrometer in linear positive mode using nitrogen laser (337 nm) with DCTB as a matrix. ESI-MS spectra were acquired on Waters SYNAPT HDMS instrument. The instrument was calibrated using $\text{Au}_{144}(\text{SR})_{60}$ ions, which are closer to the mass of $\text{Au}_{137}(\text{SR})_{56}$. Electrochemical measurements were performed on a CHI 620 instrument using 3 mg of title compound in 0.75 mL of anhydrous THF solution with 0.5 mM TBAPF₆ as supporting electrolyte under nitrogen atmosphere. Powder XRD measurements were performed on a Bruker D8-Focus XRD instrument on a quartz substrate. 4 mg of sample was dissolved in minimal amount of toluene and deposited on the substrate and air-dried.

Experimental

Step 1: Synthesis of crude product

Using two phase Brust-Schiffrin method crude product was prepared. Briefly, 1:3 :: gold : thiol was used and reaction was performed in toluene. First, 0.1 g of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in 10 mL distilled water was mixed with 0.16 g of Tetraoctylammoniumbromide (TOABr) in 20 mL toluene. After 30 min of stirring the gold salt transferred to the organic phase evidenced by clear aqueous layer. The organic phase was separated and 105 μL of phenylethanethiol was added. After 1 h of thiol addition, 0.1 g NaBH_4 in 10 mL ice-cold water was added instantaneously to the reaction flask. Up on addition of reducing agent the reaction mixture turned dark in color indicating the formation of nanoparticles. The reaction was stopped after 3 h of NaBH_4 addition and processed.

Step 2: Separation by SEC

Size exclusion chromatography was used for the isolation of $\text{Au}_{137}(\text{SR})_{56}$. Biorad S-X1 beads were soaked in stabilized THF overnight and packed in the column. The sample was dissolved in minimal amount of stabilized THF and loaded on to the column. Several fractions were collected and analyzed by both MALDI-TOF mass spectrometry and ESI-MS. After first SEC, fractions containing $\text{Au}_{137}(\text{SR})_{56}$ as the major species were combined and re-run through the SEC column. After second SEC some of the fractions collected were found to be pure $\text{Au}_{137}(\text{SR})_{56}$ up on ESI analysis.

Figure S1: UV-vis-NIR spectra of $\text{Au}_{137}(\text{SR})_{56}$ recorded in toluene at several dilutions. The characteristic features are present at different dilutions.

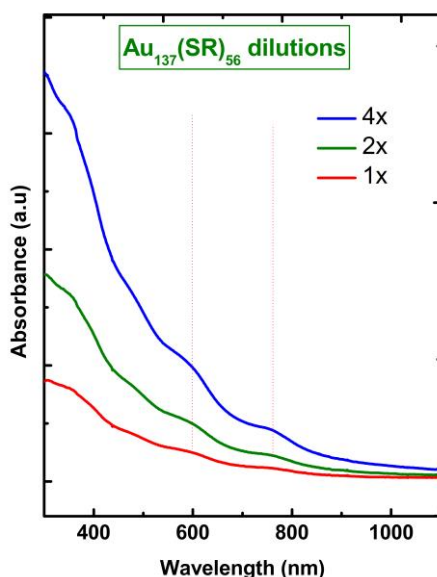


Figure S2: UV-vis spectrum of $\text{Au}_{137}(\text{SCH}_2\text{CH}_2\text{Ph})_{56}$ compared with that of $\text{Au}_{137}(\text{SC}_4\text{H}_9)_{56}$. The characteristic features of the nanomolecule are consistent, further confirming the assigned composition. The absorbance spectra are offset for better clarity.

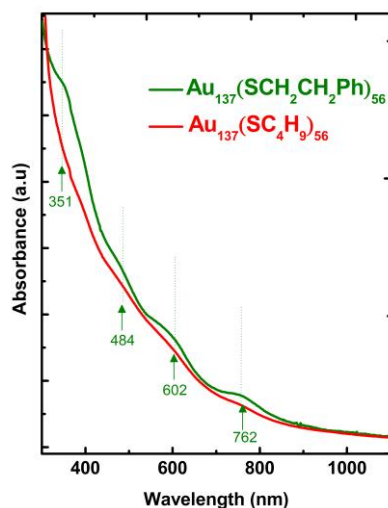


Figure S3: ESI spectrum of $\text{Au}_{137}(\text{SC}_6\text{H}_{13})_{56}$ and $\text{Au}_{144}(\text{SC}_6\text{H}_{13})_{60}$ showing 1+, 2+ and 3+ peaks. The red peaks correspond to $\text{Au}_{144}(\text{SC}_6\text{H}_{13})_{60}$ and olive peaks correspond to $\text{Au}_{137}(\text{SC}_6\text{H}_{13})_{56}$ nanomolecules.

$\text{Au}_{137}(\text{SC}_6\text{H}_{13})_{56}$ in different charge states

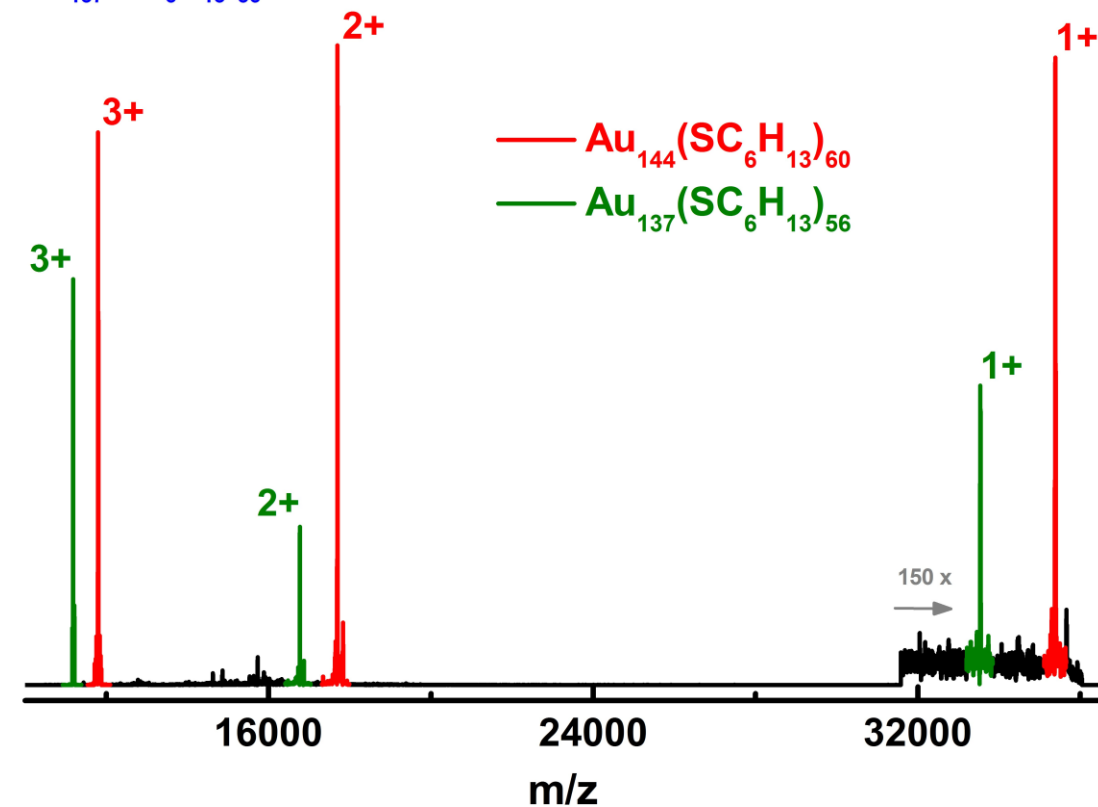
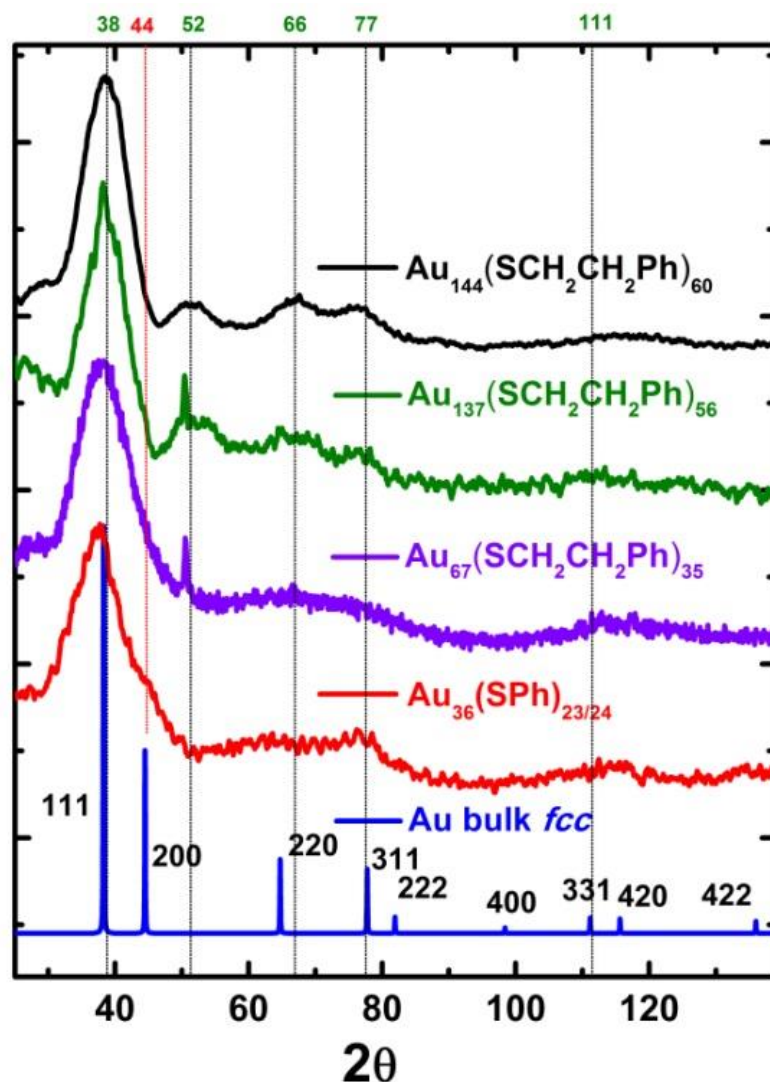
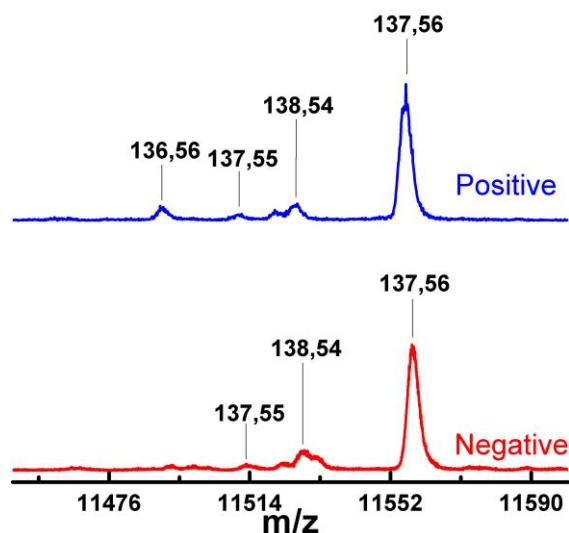


Figure S4: Powder XRD pattern of $\text{Au}_{137}(\text{SR})_{56}$ nanomolecules compared with $\text{Au}_{144}(\text{SR})_{60}$, $\text{Au}_{67}(\text{SR})_{35}$, $\text{Au}_{36}(\text{SPh})_{23/24}$ and bulk Au *fcc*.



The atomic structure of $\text{Au}_{137}(\text{SR})_{56}$ was studied using powder X-ray diffraction^{1,2} by depositing a solution of the title nanomolecule on a quartz substrate. Powder XRD pattern in Figure 3 of [137,56], olive curve shows a sharper, intense peak at 2θ value of 38° and four broader features at 52° , 66° , 77° , and 111° . The powder XRD pattern was compared with that of $\text{Au}_{36}(\text{SR})_{23/24}$, $\text{Au}_{67}(\text{SCH}_2\text{CH}_2\text{Ph})_{35}$, and $\text{Au}_{144}(\text{SCH}_2\text{CH}_2\text{Ph})_{60}$. All of these have the peak at 38° , which corresponds to Au interatomic distances of the nearest neighbors. The features at 52° , 66° , and 77° are present in 67, 137 and 144-atom nanomolecules. However, the feature at 52° is present only in the 137 and 144-atom species, showing the presence of related lattice planes, suggesting similarities in their atomic structure. $\text{Au}_{36}(\text{SPh})_{23/24}$ shows a clear shoulder at the 44° that corresponds to the (200) fcc plane.^{3,4} The XRD pattern of [137,56] does *not* match with the bulk Au *fcc* structure (Figure 3 blue lines) or the Au_{36} -atom fcc nanomolecule, clearly showing the *non-crystallographic* nature of the 137-atom core. Due to (a) the non-*fcc* nature and (b) the position of the 137-atom falling in between 102 and 144-atom core, it is likely that the core may adopt either marks decahedral,² *m-Dh* or icosahedral, *1h* non-crystallographic core.⁵

Figure S5: Positive and negative ESI spectra of $\text{Au}_{137}(\text{SCH}_2\text{CH}_2\text{Ph})_{56}$. Peaks with relatively smaller intensity are being assigned to several species indicated by (Au, ligands).



ESI-MS analysis of $\text{Au}_{137}(\text{SR})_{56}$ nanomolecules

For the ESI analysis was performed on a Water Synapt HDMS ESI-MS mass spectrometer. The samples were dissolved in THF (~0.5 mg/mL) and directly injected into the mass spectrometer. No additional salts were added to aid ionization as the THF solution of the nanomolecules gave good signal intensity in both the positive and negative ionization modes.

Following are the instrument parameters used for acquiring the mass spectra

Positive Ionization Mode

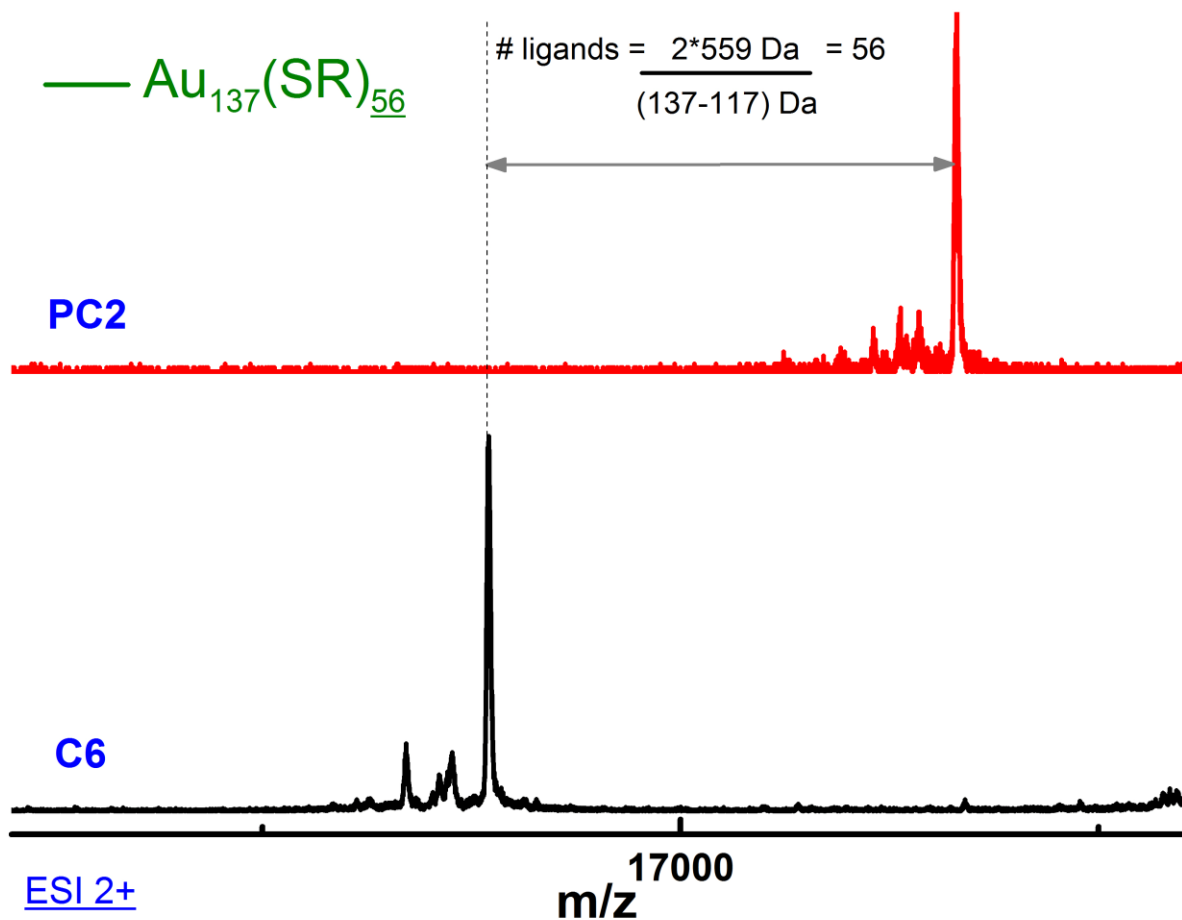
Polarity		ES+
Analyser		V Mode
Capillary (kV)	3.0	
Sampling Cone		138.0
Extraction Cone		7.4
Source Temperature (°C)		100
Desolvation Temperature (°C)		200
Desolvation Gas Flow (L/Hr)	550.0	
Trap Collision Energy	6.0	
Transfer Collision Energy		4.0
Trap Gas Flow (mL/min)		6.00
Source Gas Flow (mL/min)		33.90
Detector		1700

Negative Ionization Mode

Polarity		ES-
Analyser		V Mode
Capillary (kV)	2.2	
Sampling Cone		105.0
Extraction Cone		5.6
Source Temperature (°C)		90
Desolvation Temperature (°C)		200
Desolvation Gas Flow (L/Hr)	591.0	
Trap Collision Energy	6.0	
Transfer Collision Energy		4.0
Trap Gas Flow (mL/min)		5.30
Source Gas Flow (mL/min)		50.00
Detector		1650

Assignment of molecular composition

Figure S6. ESI-MS spectra of [137,56] NMs prepared using two ligands: PC2 (-SCH₂CH₂Ph) in red and C6 (-SC₆H₁₃) in black.



In figure S6, the peaks observed in both the spectra correspond to $\text{Au}_{137}(\text{SR})_{56}$. This assignment was made as follows. If both the peaks correspond to same nanomolecule then the observed mass difference is due to the mass difference of the ligand. In this case the mass difference of 559 m/z units was observed. As this is a doubly charged peak the actual mass difference would be $559 \times 2 = 1118$ Da. The mass difference between phenylethanethiol (137 Da) and hexanethiol (117) ligands would be 20 Da. Thus the number of total ligands would be

of ligands = total mass difference / mass difference of the ligands

In this case it would be $1118/20 = 55.9 \sim 60$ ligands. Once we know the number of ligands we can back calculate the number of metal atoms which is 137 in this case. Thus the composition of the observed nanomolecules would be $\text{Au}_{137}(\text{SR})_{56}$.

Yield of $\text{Au}_{137}(\text{SR})_{56}$

The typical yield of $\text{Au}_{137}(\text{SR})_{56}$ on Au atom basis is $\sim 2.9\%$. This yield is based on the pure Au_{137} that is isolated after multiple SEC runs. There is much more Au_{137} that is lost in the form of impure fractions. For example the fractions with greater amount of Au_{144} from the first SEC separation were not used for the next SEC separation. Thus the actual amount of Au_{137} formed in the reaction mixture is larger than $\sim 2.9\%$.

In the synthesis reactions, there is abundant amount of Au_{144} formed along with Au_{137} . Thus, the overall yield of nanoclusters formed from this synthesis is far higher than $\sim 2.9\%$. For increasing the yield of Au_{137} from the synthesis, the conditions should be optimized to yield higher amount of Au_{137} than Au_{144} .

Electrochemical Reduction of CO_2 with $\text{Au}_{137}(\text{PC2})_{56}$

A septum sealed 50 mL 3 neck flask was charged with 1.0 mg $\text{Au}_{137}(\text{PC2})_{56}$ and 0.8 mL of a 0.1 M NBu_4PF_6 DMF solution. Through each of the septum was placed an electrode (reference electrode = platinum wire, counter electrode = platinum coiled wire, working electrode = glassy carbon electrode). N_2 was rapidly bubbled through the solution for 5 minutes prior to collecting a CV scan at 0.1 V/s scanning in the negative direction first. The solution was then saturated with CO_2 by bubbling for 10 minutes prior to collecting a CV scan. To establish the voltamograph potential, ferrocene was then added as an internal reference and a second scan taken of the saturated CO_2 solution. The CO_2 in solution was then replaced with N_2 by bubbling N_2 through the solution for 5 minutes. The voltamograph returned to the original shape with ferrocene now present as a reference.

References

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