Supporting Information

The Missing Link: $Au_{191}(SPh\text{-}tBu)_{66}$ Janus Nanoparticle with Molecular and Bulk-Metal-like Properties

Naga Arjun Sakthivel,[†] Masoud Shabaninezhad,[⸸] Luca Sementa,[⊥] Bokwon Yoon,[§] Mauro Stener,[⊤] Robert L. Whetten,[‡] Guda Ramakrishna,[‖] Alessandro Fortunelli,[⊥] Uzi Landman,[§] and Amala Dass[*,†]

[†] Department of Chemistry and Biochemistry, University of Mississippi, Oxford, Mississippi 38677, United States

[‡] Department of Applied Physics and Materials Science, Northern Arizona University, Flagstaff, Arizona 86011, United States

[§] School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

[⊥] CNR-ICCOM & IPCF, Consiglio Nazionale delle Ricerche, Pisa, I-56124, Italy

[‖] Department of Chemistry, Western Michigan University, Kalamazoo, Michigan 49008, United States

[⸸] Department of Physics, Western Michigan University, Kalamazoo, Michigan 49008, United States

[⊤] Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste, Trieste I-34127, Italy

*corresponding author: amal@olemiss.edu

Table of contents

Experimental Details

Materials. Hydrogen tetrachloroaurate(III) ($HAuCl_4.3H_2O$) (Alfa Aesar ACS grade), tetra octylammonium bromide (TOABr) (Acros), sodium borohydride ($NaBH_4$) (Sigma Aldrich, 99%), 4-tert-butylbenzenethiol (TBBT) (TCI America, >97%), cesium acetate (Acros, 99%), anhydrous ethyl alcohol (Acros, 99.5%), and trans-2-[3[(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB matrix) (TCI America) were used as received. HPLC grade solvents ethyl acetate (EtOAc), methylene chloride (DCM), tetrahydrofuran (THF), toluene, methanol, and butylated hydroxytoluene stabilized tetrahydrofuran (THF-BHT) were purchased from Fisher Scientific. All materials were used as received.

Methods

Synthesis, Isolation, and Crystallization. $Au_{191}(TBBT)_{66}$ nanocrystals was prepared in three steps by modified version of a previous report.[1-2] 0.5 g $HAuCl_4 \cdot 3H_2O$ and 0.7 g TOABr was dissolved in 50 mL ethyl acetate in a 200 mL round bottom flask and stirred vigorously for 2 h. Then, 0.6 mL TBBT ligand (Au:TBBT = 1:2.74) was added to the reaction mixture and stirred for 4 h. The reaction was reduced with 0.48 g $NaBH_4$ dissolved in 10 mL ice cold water (Au:$NaBH_4$ = 1:10). The reaction was stopped after 24 h and the solvent was removed by rotary evaporation. The crude product was washed with methanol and water to remove excess thiol and other byproducts. The crude product was extracted with toluene. It was etched with excess TBBT at 90 °C for ~18 h. Methanol and water were added to the etched product and centrifuged (4400 rpm, 5 min) to precipitate the products. The etched product was washed with methanol to remove excess thiols. The etched product was extracted using DCM. $Au_{191}(TBBT)_{66}$ was then isolated by using size exclusion chromatography (SEC) as detailed elsewhere.[1] The yield of the compound was 0.5% (on Au mole basis). The composition and purity of the compound was determined by Electrospray ionization (ESI-MS) and Matrix assisted laser desorption ionization (MALDI-MS) mass spectrometry, respectively (Figure 6 main text). These nanocrystals are very stable under ambient conditions. $Au_{191}(TBBT)_{66}$ single crystals were obtained by slow evaporation of a SEC fraction dissolved in hexane. $Au_{133}(TBBT)_{52}$ and $Au_{279}(TBBT)_{84}$ were prepared following the protocols as reported in ref.[3] and ref.[1] , respectively.

Instrumentation. MALDI-MS data was acquired using a Voyager DE PRO mass spectrometer from applied Biosystems. The sample was dissolved on toluene and spotted on MALDI plate with 20 mM DCTB matrix in toluene. ESI-MS data was collected using Waters Synapt HDMS system with THF as the solvent. UV−Vis−NIR absorption spectra was collected using a Shimadzu UV-1601 spectrophotometer (toluene as the solvent).

X-ray crystallography. A black tablet/plate-like crystal specimen (approximate dimension 0.067 mm × 0.033 mm × 0.026 mm) coated with Dow Corning high vacuum grease was mounted using a MiTeGen loop in a stream of liquid N_2 at 100 K. Single crystal X-ray diffraction data was collected using Rigaku Xtalab Synergy R-DW diffractometer with a rotating anode, Cu Kα (λ = 1.54184 Å) radiation source and hypix detector. The data were processed using CrysAlis^{Pro} v171.39.46 and the structure was

solved with SHELXT[4] and subsequent structure refinements were performed with SHELXL[5] using Olex2 program[6]. All Au and S atoms were readily located during structure solution. Carbon atoms were located through successive cycles of least-squares refinement. Around 90% of C atoms were located during least square refinements and -Ph*t*Bu ligand groups were completed by using FRAG/FEND command with experimental co-ordinates for -Ph*t*Bu groups. All non C and H atoms were refined anisotropically and the H atoms were added as riding atoms. The disordered solvent molecules in the unit cell was treated by using solvent mask option in Olex2 also known as PLATON SQUEEZE.[7]

Crystal structure for $C_{660}H_{858}Au_{191}S_{66}$; Formula weight 48528.84; Monoclinic; Space group C2/c; a = 45.2690(13) Å; b = 45.1575(5) Å; c = 63.9193(12) Å; α = 90°; β = 110.206(3)°; γ = 90°; Volume = 122624(5) Å^3; Z = 4; ρ_{calc} = 2.582 g/cm^3; μ = 42.945 mm^{-1}; F(000) = 80421.0; 2Θ range = 4.59° to 84.19°; 60109 reflections collected; 31565 unique (R_{int} = 0.0451); giving R_1 = 0.0573, wR_2 = 0.1407 for 31565 with [I > 2σ(I)] and R_1 = 0.0955, wR_2 = 0.1576 for all 60109 data. Residual electron density (e$^-$·Å^{-3}) max/min: 2.12/-1.60.

Transient absorption measurements. Femtosecond transient absorption measurements were carried out at the Center for Nanoscale Materials, Argonne National Laboratory. Briefly, a Spectra Physics Tsunami Ti:Sapphire, 75 MHz oscillator was used to seed a 5 KHz Spectra-physics Spit-fire Pro regenerative amplifier. 95% of the output from the amplifier is used to pump a TOPAS optical parametric amplifier, which is used to provide the pump beam in a Helios transient absorption setup (Ultrafast Systems Inc.). A pump beam of 370 nm was used for the measurements. The remaining 5% of the amplified output is focused onto a sapphire crystal to create a white light continuum that serves as the probe beam in our measurements (450 to 750 nm). The pump beam was depolarized and chopped at 2.5 kHz and both pump and probe beams were overlapped in the sample for magic angle transient measurements. No degradation of the sample was observed as revealed from optical absorption spectra before and after the measurements (see Figure S19). Species-associated spectra were obtained by fitting the principle kinetics deduced from single value decomposition analysis. The growth of the kinetics was included in the instrument response.

TDDFT studies. To shed more light and understanding on the electronic and optical properties of $Au_{191}(TBBT)_{66}$, we performed first-principles density-functional theory (DFT) and time-dependent DFT (TDDFT) simulations. To reduce computational effort, we transformed $Au_{191}(TBBT)_{66}$ into $Au_{191}(SPh)_{66}$, whose structural model was derived by taking the X-ray experimental coordinates of $Au_{191}(TBBT)_{66}$, turning the tert-butyl residues into hydrogens, freezing the (Au,S) skeleton, and locally relaxing the resulting $Au_{191}(SPh)_{66}$ compound using DFT and the Perdew–Burke–Ernzerhof (PBE) exchange-correlation (xc-)functional[8] augmented with Grimme-D3 empirical dispersion correction[9] (spin-unrestricted calculation). The charge state was taken to be +1. On this fixed geometry all the successive DFT and TDDFT simulations were conducted. The Cartesian coordinates of the $Au_{191}(SPh)_{66}$ used in the theoretical simulations are reported in Table S3.

First-principles density-functional theory (DFT) and time-dependent DFT (TDDFT) simulations were performed using the CP2K package[10] whose algorithms for solving the Kohn-Sham equations implements the mixed Gaussian and Plane Wave (GPW) approach (GPW) proposed in ref[11]. We employed DVZP primary Gaussian basis sets[12], GTH-pseudopotentials[13] and an auxiliary plane-wave basis set with a cutoff of 300 Ry. TDDFT simulations were conducted using a real-time (RT) approach and the VS98 xc-functional[14-16]. As discussed earlier[17], the VS98 xc-functional is considered the most accurate non-hybrid (and therefore computationally affordable on these large systems) xc-functional to simulate the optical response of MPC. The optical response of the cluster was obtained by following the evolutions of the system's electric dipole after perturbing the equilibrium state by electric fields with a strength of 0.0005 a.u polarized along different Cartesian directions. The dipole-dynamics, lasting 9 femto-sec, was sampled with time steps of 0.012 femto-sec. A time damping of 7.2 fs (corresponding to an FWHM of 0.25 eV) was chosen to broaden the simulated spectrum.

RT-TDDFT/VS98 photon-energy spectrum of $Au_{191}(SPh)_{66}$ together with the corresponding RT-TDDFT/VS98 photon-energy spectra of $Au_{279}(SPh)_{84}$ and $Au_{133}(SPh)_{52}$ is given in Figure S12C. For comparison with previous work, see the RT-TDDFT/PBE simulated spectra of these two latter compounds in Figure 3 of supplementary reference [2] and Figure 2 of supplementary reference [17], respectively, while the Z-components of the RT-TDDFT/VS98 spectra of these compounds were reported in Figure S3 of supplementary reference[17].

The single-electron excitation signed components of the TDDFT/PB86 optical response was also studied using ICM-OS plots [ICMOS[18], ICMRS[19]], which allow one to identify both the nature of the excited state and the contribution of the dipole matrix elements to the oscillator strength, especially their relative sign with respect to the corresponding density matrix elements. The corresponding ICM-OS(Y) plots at 2.21 eV are reported in Figure S13. In addition to the analysis in the main text fully in tune and rationalizing the transient spectroscopy observations of a mixed plasmonic/molecular of this clusters, it can be added, in passing, that the presence of appreciable negative contributions in the upper diagonal part of the ICM-OS plots suggest, that there is still room for re-birth effects[20].

RT-TDDFT/VS98 optical spectrum of $Au_{191}(SPh)_{66}$, projected onto atomic components (Mulliken charge analysis of the induced density) is shown in Figure 7 of main text. Figure S18 plots were obtained by representing the Mulliken induced charges with Gaussian charge distributions centered on the atoms.

To compare the electronic structure of $Au_{191}(SPh)_{66}$ with previous results, we report in Figure S20 the Density of States (DOS) obtained at the DFT level using the LDA xc-functional. This can be compared with Figure 2b and S2 of supplementary reference[17]. The DOS projected onto atoms is reported in Figure S20, where it is to be noted that the SCH moiety gives a smaller but non-negligible contribution around the Fermi level. For completeness, we also report in Figure S21 the DOS using the VS98

xc-functional, ie the xc-functional which has been used in the RT-TDDFT simulations of the optical spectra of the main text.

As an independent confirmation of our RT-TDDFT/VS98 analysis, we conducted TDDFT simulations in the frequency domain. TDDFT optical spectra were obtained via a complex polarizability algorithm[21] employing the ADF package[22], and the PB86 exchange-correlation potential[23-25] while the exchange-correlation kernel in the TDDFT part was approximated according to the Adiabatic LDA (ALDA)[26]. A Slater-type-orbital basis set of Doule-Zeta quality was employed. The Zero Order Regular Approximation (ZORA)[27] was employed to include relativistic effects, which are important for heavy elements such as gold. The imaginary frequency employed to introduce finite lifetime of the excited state was fixed to 0.075 eV. Due to computational issues, we managed to conduct these simulations using a limited DZV basis set, so that the present predictions can be only semi-quantitatively compared with those of the RT-TDDFT approach reported in the main text. The optical spectrum of $Au_{191}(SPh)_{66}$ as predicted by our TDDFT/PB86 approach, where a semi-quantitative agreement with the RT-TDDFT/VS98 simulations can be appreciated, although with the usual red-shift of the absorption peaks which is typical when using the PB86 xc-functional (Figure S22).

Electronic structure using DFT. Insights into the electronic structure and stability of the thiol-ligand-capped $Au_{191}(SR)_{66}^{+}$ nanomolecule (see Figure S9), have been gained through calculations using the density-functional theory (DFT) method, employing the Vienna ab-initio simulation package VASP.[28-31] The calculations employed a cubic supercell of size 45 Å X 45 Å X 45 Å, and for the singly charged cluster ions, a homogeneous neutralizing background charge has been used. The wavefunctions were expanded in a plane wave basis with a kinetic energy cut-off of 400 eV. The interaction between the atom cores and the valence electrons was described by the projector augmented-wave (PAW) potential[32] (which includes relativistic corrections) and the exchange-correlation functional was described by the Perdew-Wang PW91 generalized gradient approximation (GGA).[33-35] Van der Waals interactions have been included following reference[36]. Table S4 reports the Bader charge analysis[37-38] of $Au_{191}(SPh\text{-}t\text{Bu})_{66,}$ calculated (as noted above) for $Au_{191}(SR)_{66}^{+}$ in a neutralizing background.

Table S1. Crystal data and structure refinement for 191_66

Identification code	191_66
Empirical formula	$C_{660}H_{858}Au_{191}S_{66}$
Formula weight	48528.84
Temperature/K	100.0
Crystal system	monoclinic
Space group	C2/c
a/Å	45.2690(13)
b/Å	45.1575(5)
c/Å	63.9193(12)
α/°	90
β/°	110.206(3)
γ/°	90
Volume/Å^3	122624(5)
Z	4
ρ_{calc}g/cm^3	2.582
μ/mm^{-1}	42.945
F(000)	80421.0
Crystal size/mm^3	0.067 × 0.033 × 0.026
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	4.59 to 84.19
Index ranges	-37 ≤ h ≤ 38, -39 ≤ k ≤ 36, -55 ≤ l ≤ 50
Reflections collected	60109
Independent reflections	31565 [R_{int} = 0.0451, R_{sigma} = 0.0713]
Data/restraints/parameters	31565/330/1786
Goodness-of-fit on F^2	0.974
Final R indexes [I>=2σ (I)]	R_1 = 0.0573, wR_2 = 0.1407
Final R indexes [all data]	R_1 = 0.0955, wR_2 = 0.1576
Largest diff. peak/hole / e Å^{-3}	2.12/-1.60

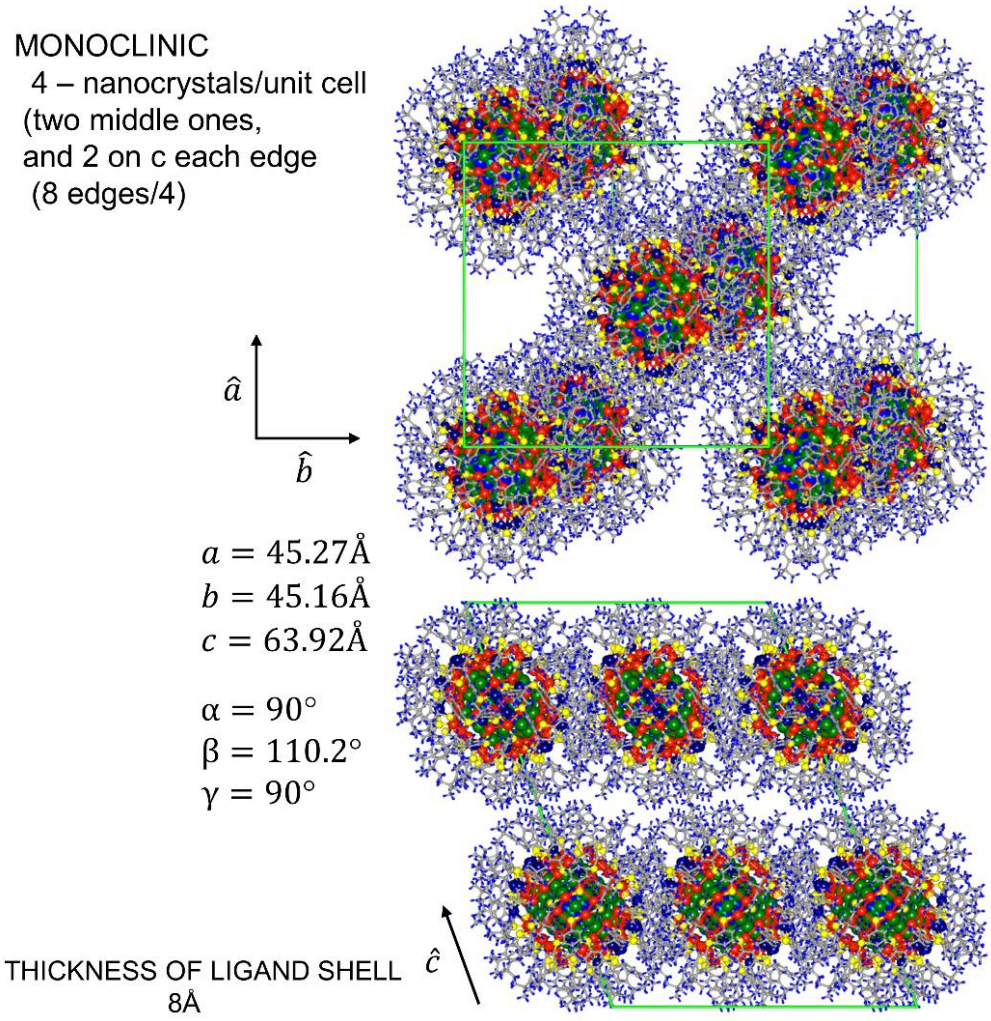

Figure S1. $Au_{191}(SPh\text{-}tBu)_{66}$ in the monoclinic unit cell.

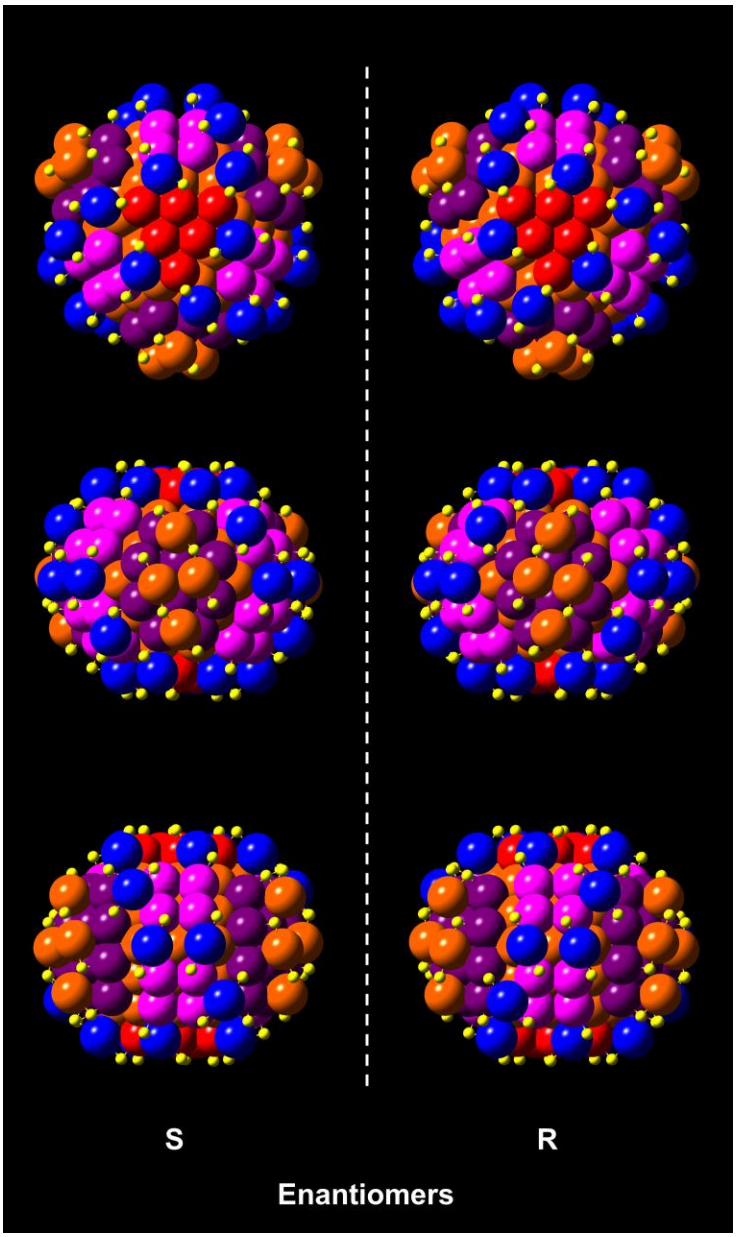

Figure S2. Enantiomers (S and R) of the $Au_{191}(TBBT)_{66}$ nanomolecule. top to bottom: Top -- triangular {111} facet viewed along C_3 axis; Middle -- trapezoidal {111} facet viewed along C_2 axis; Bottom -- {100} facets viewed along C_2 axis. Only Au and S atoms are shown for clarity); the Au atoms are depicted by the larger balls, and the S atoms are shown as small yellow balls.

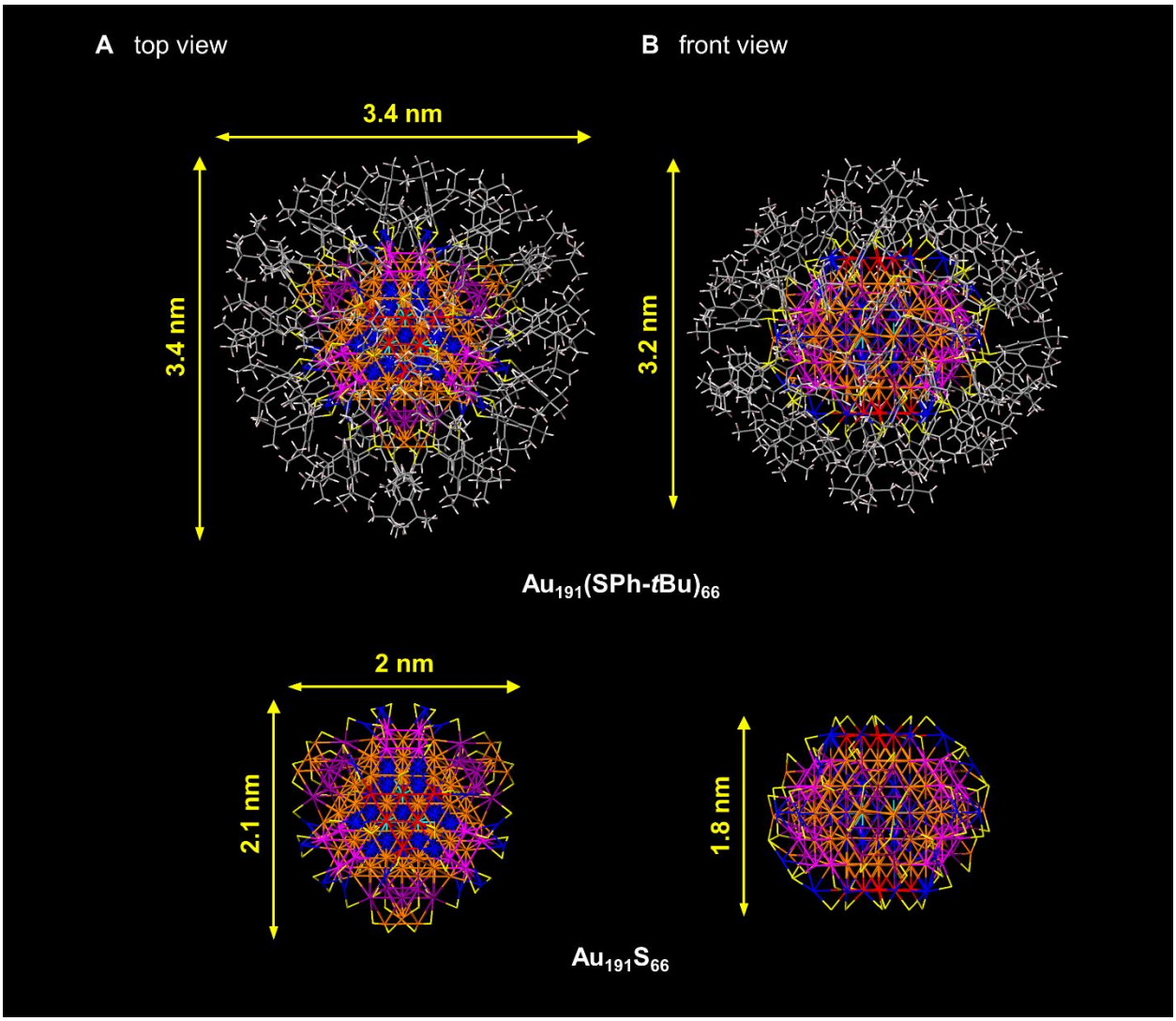

Figure S3. Dimensions of the TBBT-capped Au_{191} nanocrystals. (A) Top view and (B) front view of the nanocrystals with Ph-*t*Bu groups and Au-S core, respectively. Layer-wise dimensions of the metal core: 26-atom HCP kernel: 0.47 nm x 0.74 nm x 0.85 nm; 89-atom inner-core ; 0.94 nm x 1.24 nm x 1.42 nm; 155-atom core: 1.41 nm x 1.52 nm x 1.62 nm.

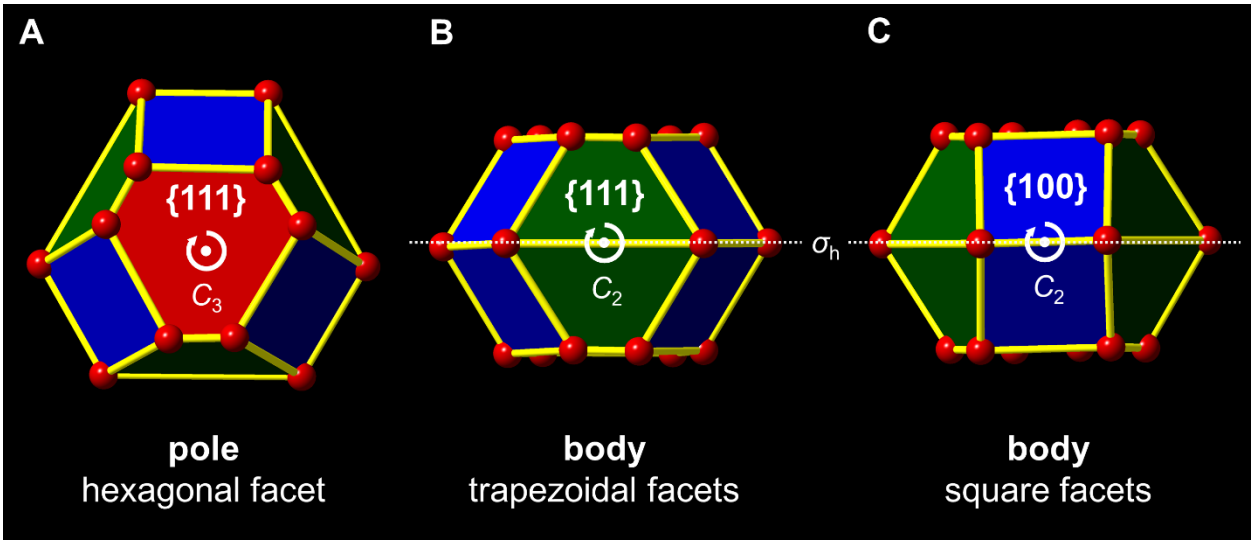

Figure S4. Morphology of the D_{3h}-Au_{89} inner-core. The inner-core viewed along (A) {111) pole (Red – hexagonal facets), (B) {111} body (olive - trapezoidal facets), and (C) {100} body facets (blue - square facets). C_3 and C_2 are the three-fold and two-fold rotational axes, respectively. Dotted line in (B) and (C) - σ_h is the mirror plane perpendicular to principal C_3 rotational axis. It is also the twin plane.

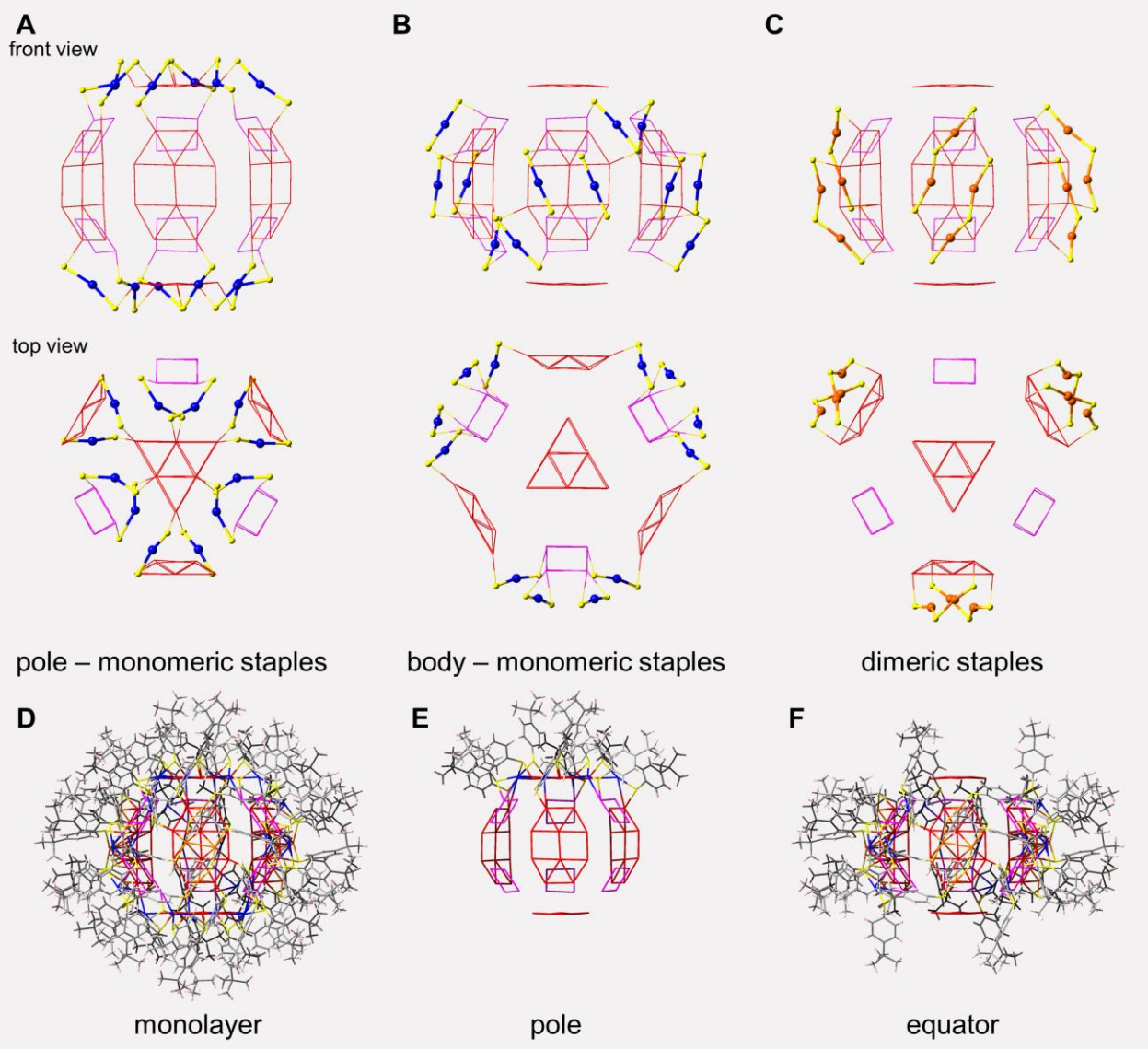

Figure S5. Staple motifs and TBBT monolayer on the Au_{191} nanoparticle. Monomeric staples on (A) poles and (B) body. (C) dimeric staples. TBBT monolayer on (D) Au_{66} surface atoms, (E) pole and (F) equatorial position. Orange – dimeric staple Au, blue – monomeric staple Au, yellow – S. Red – {111} facet Au and magenta – {100} facet Au. Grey – C and light yellow – H.

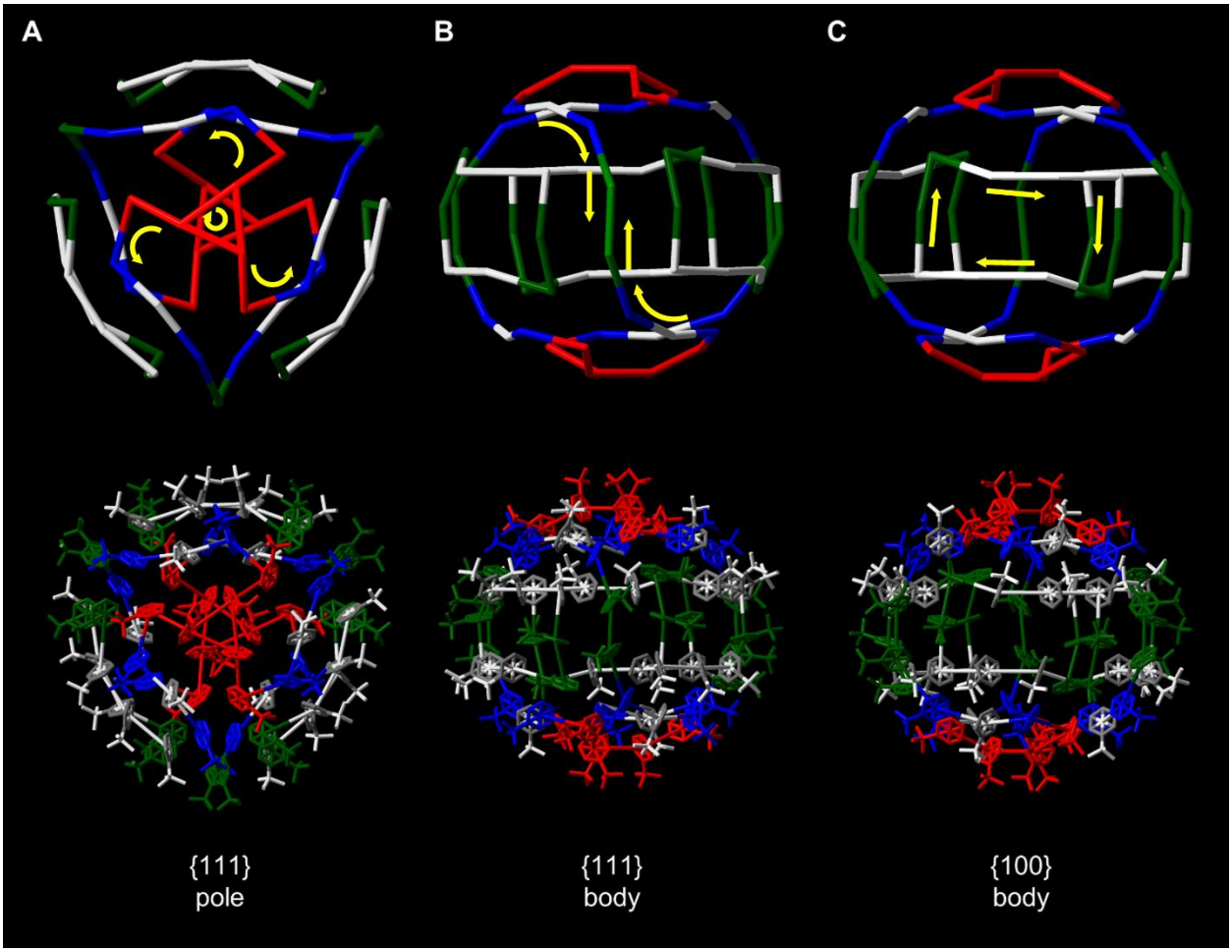

Figure S6. Clathrin cage-like structure in ligand-ligand interactions. Viewed along (A) {111) pole, (B) {111} body, and (C) {100} body facets. Top row shows the cage-like view of phenyl-phenyl interactions and bottom row displays the corresponding cage with TBBT ligands. Yellow arrows (in top row) indicate the direction of phenyl-phenyl interactions. Hydrogen atoms are excluded for clarity. TBBT ligands are color coded as follows: red, poles; blue, monomeric staple ligands extending out of poles; olive, dimeric staples; and white, monomeric staples on {100}8 facets. (the color code is similar to the Figure 3 in main text) The cage-like view was constructed by tracing the centers of phenyl ring in the phenyl-phenyl interactions.

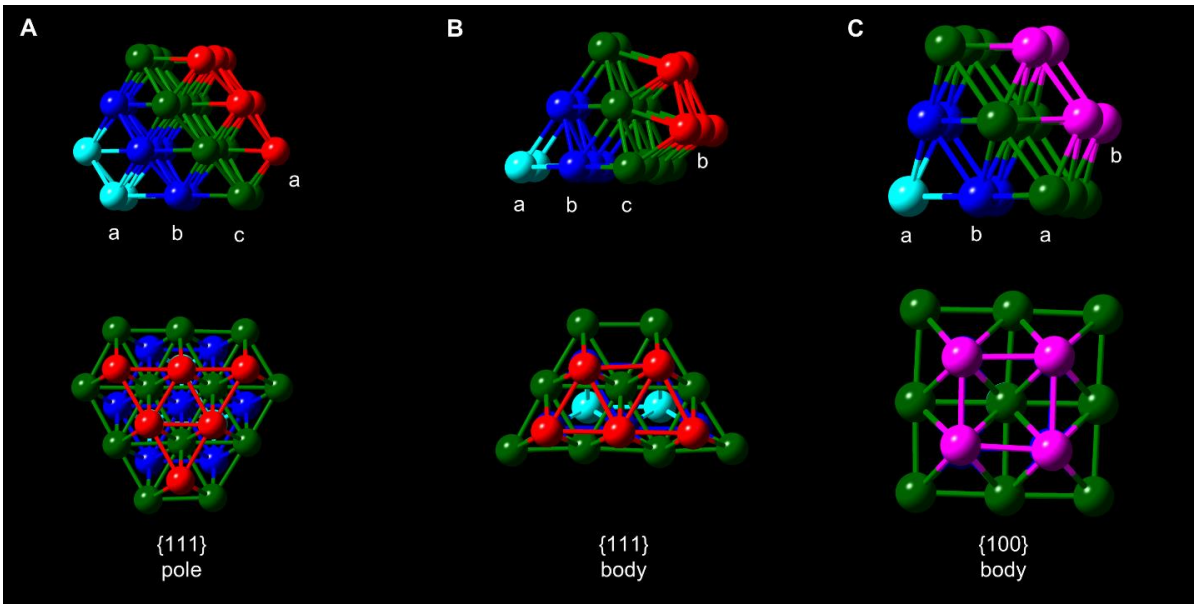

Figure S7. Stacking pattern of Au atoms from center to surface shown as sectional views in Au_{155} core. The figure depicts the 'growth' from the center to the surface shown as sectional views along: (A) {111} poles, (B) {111} body and (C) {100} body facets. The stacking sequence follows {abca}, {abcb} and {abab} sequence along the (A) {111} poles, (B) {111} body and (C) {100} body facets, respectively. Gold atoms: cyan, core-center atoms; blue, 23-atom shell; olive, 63-atom shell; red, {111} surface facets; magenta, {100} surface facets.

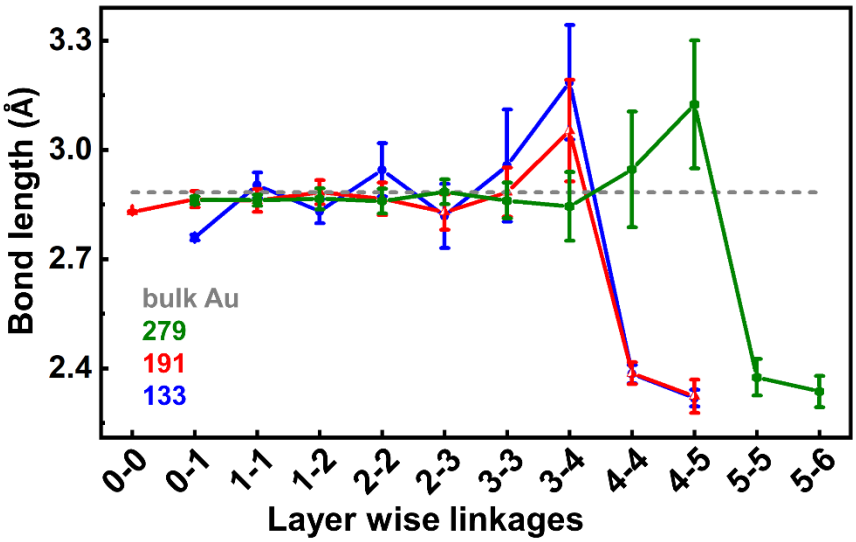

Figure S8. Bond length comparison from center to staple motifs in Au_{133}, Au_{191} and Au_{279}. X-axis: 0-0 – center to center, 0-1 – center to shell 1, 1-1 – shell 1 to shell 1, … 4-4 – shell 4 to shell 4. 3-4 (for Au_{133} and Au_{191}) and 4-5 (for Au_{279}) are the anchoring pad Au to staple Au site distances. 4-4 (for Au_{133} and Au_{191}) and 5-5 (for Au_{279}) is the anchoring pad Au to staple sulfur distances. 4-5 (for Au_{133} and Au_{191}) and 5-6 (for Au_{279}) is the staple Au site to staple sulfur distances. The plot includes the average bond length with standard deviation. blue filled sphere, Au_{133}; red filled triangle, Au_{191}; olive filled hexagon, Au_{279}; gray dashed line, bulk Au-Au bond distance. Table S2 lists the bond length analysis.

Table S2. Bond length analyses of $Au_{191}S_{66}$ nanocrystal

Connectivity	*N*	Mean (Å)	SD	Range (Å)
Au0-Au0	3	2.830	0.002	2.829 - 2.833
Au0-Au1	30	2.865	0.023	2.839 - 2.904
Au1-Au1	57	2.861	0.031	2.755 - 2.899
Au1-Au2	132	2.884	0.033	2.809 - 2.949
Au2-Au2	159	2.866	0.045	2.773 - 2.958
Au2-Au3	222	2.829	0.048	2.720 - 2.938
Au3-Au3	93	2.884	0.067	2.748 - 3.067
Au3-Au(St)	96	3.053	0.139	2.840 - 3.344
Au2-Au(St)	30	3.051	0.189	2.900 - 3.430
St-St	3	3.066	0.011	3.050 - 3.074
Au3-S	60	2.387	0.030	2.345 - 2.458
Au(St)-S	72	2.324	0.046	2.207 - 2.447
Core	696	2.859	0.051	2.720 - 3.067
Core w. Au(st)	825	2.890	0.103	2.720 - 3.430

Au0 – central Au atoms, Au1 – shell 1, Au2 – shell 2, Au3 – shell 3, Au(St) – staple Au atoms, St-St – bond between dimeric staple Au atoms, S – sulfur in thiolate group, core – bond length of Au_{155} core, and core w. Au(St) – bond length of Au_{191} atoms. N – number of bonds, Mean – average bond distance, and SD – standard deviation.

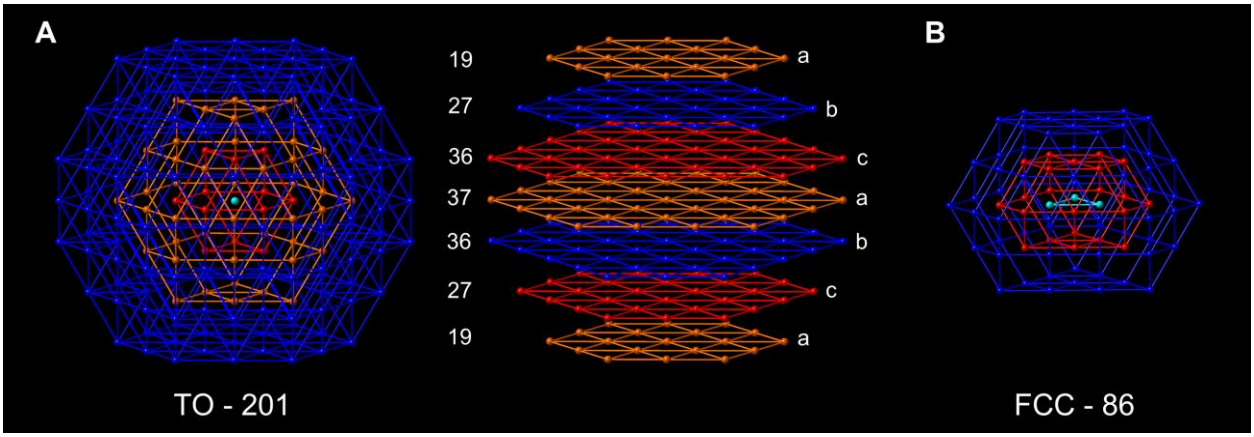

Figure S9. TO-201 and Three fused cuboctahedra. (A) Core-shell Au atom arrangement from center to surface in TO-201 core and 7-layer FCC arrangement along {111} facets. (B) 86-atom FCC polyhedra formed by fusing three 55-site cuboctahedra.

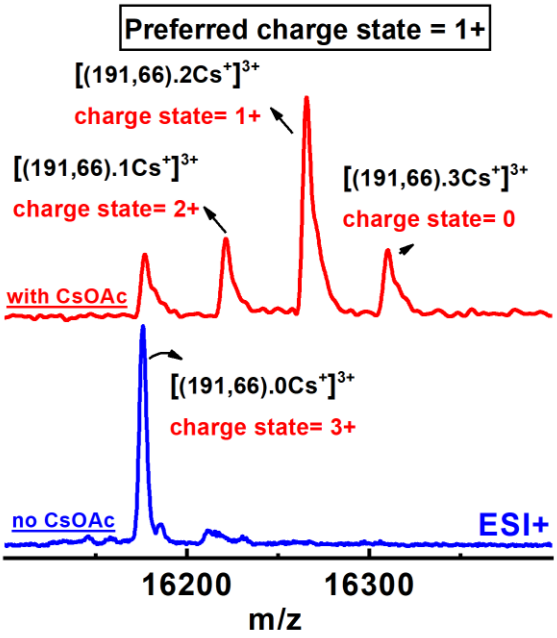

Figure S10. $Au_{191}(TBBT)_{66}$ preferred charge state analysis. Au_{191} sample was analyzed with and without Cesium acetate (CsOAc) to determine the preferred inherent charge state of the nanomolecule. CsOAc helps facilitate ionization of neutral compound by forming adducts. The mass spectrum in the 3+ m/z range is shown in the graph. In the presence of Cs+, it can be readily observed that (191,66) takes two Cs+ adducts and forms the intense 3+ peak, indicating its preferred charge state of 1+.

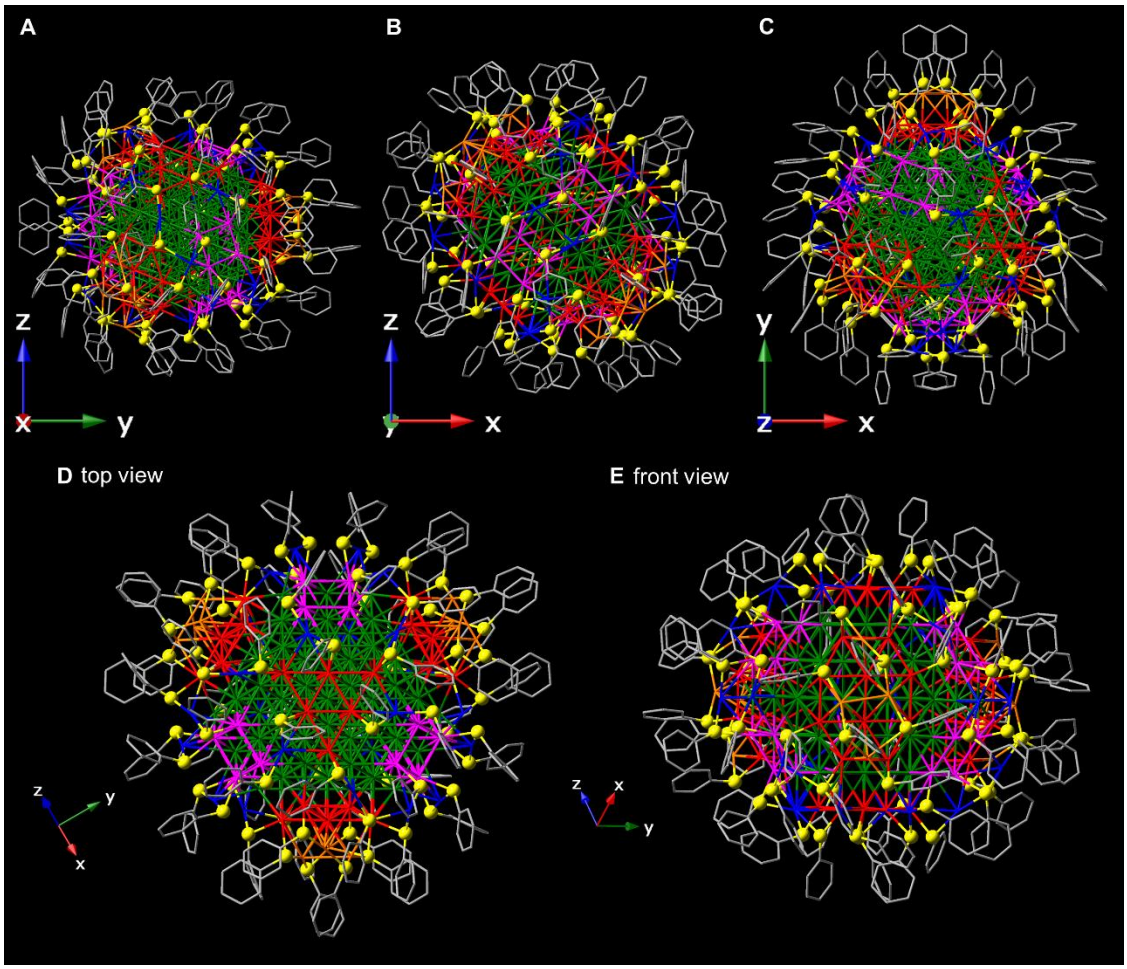

Figure S11. $Au_{191}(SPh)_{66}$ orientation of Cartesian axes. The nanocrystal is viewed along: (A) X, (B) Y, and (C) Z Cartesian coordinates axes. (D) top (pole) and (E) front views (equator) of the nanocrystal. H atoms excluded for clarity. Longest dimension along X, Y and Z axes are ~2.6 nm, ~2.9 nm and ~2.6 nm, respectively. Gold atoms: olive, 89-atom inner core; red, {111} facets; magenta, {100} facets. Yellow, S; light gray, C. The figure displays the Cartesian axes orientation with structure to correlate the X, Y and Z components of optical response in TDDFT studies (see Figure 7C of main text).

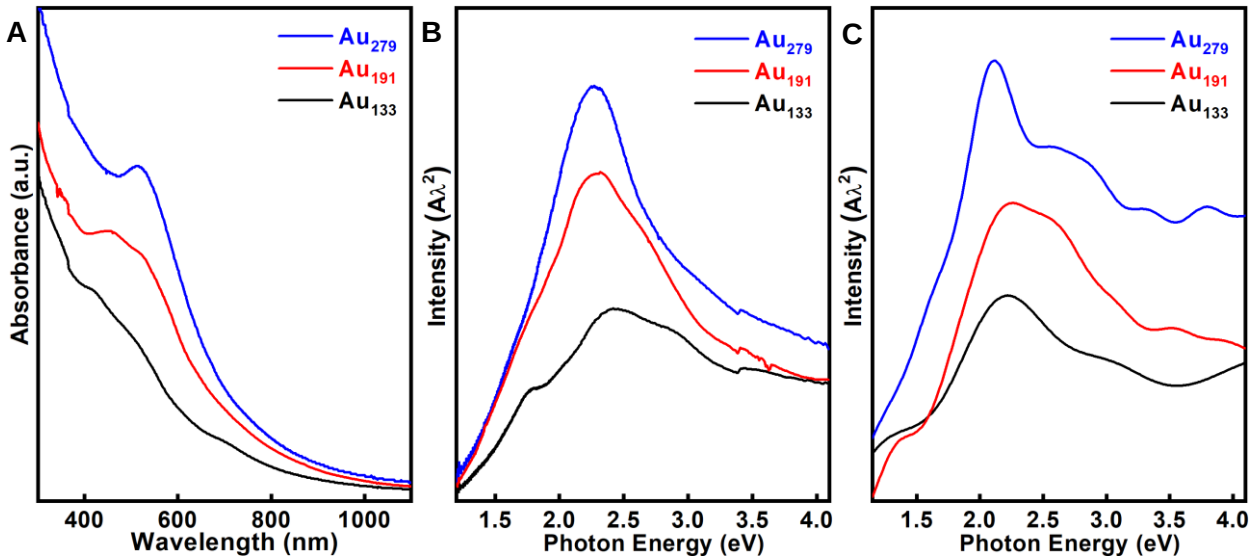

Figure S12. Absorption spectra as a function of size. (A) Experimental UV-visible absorption and (B) photon energy spectra, and (C) TDDFT/VS98 simulated photon energy spectra of $Au_{191}(TBBT)_{66}$ in comparison with $Au_{133}(TBBT)_{52}$ and $Au_{279}(TBBT)_{84}$. The TDDFT simulated photon energy spectra in (C) predicts the optical response of three AuNMs. Their appearance agrees with the (B) experimental photon energy plot from (A) absorption spectra.

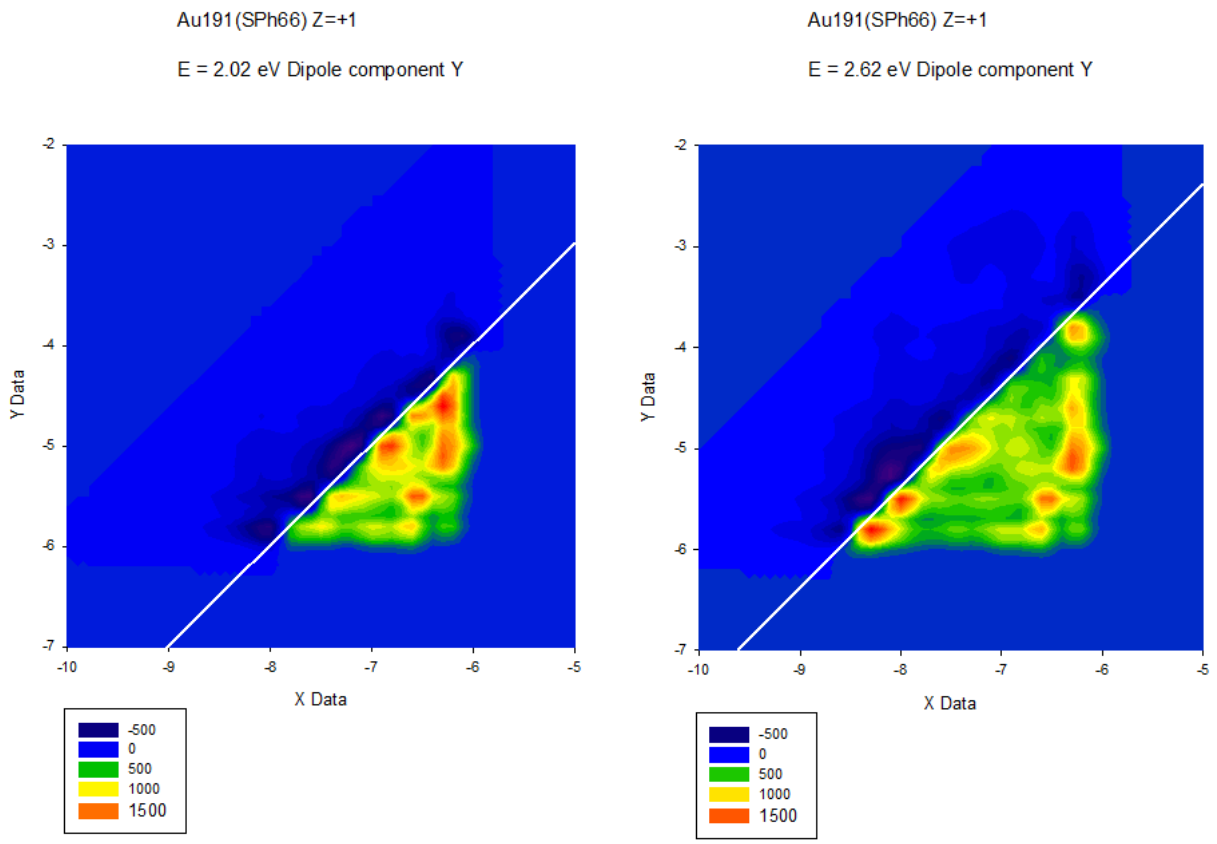

Figure S13. ICM-OS analysis. Y electric-dipole component of the $[Au_{191}(SPh)_{66}]^+$ cluster at 2.02 eV (left) and 2.62 eV (right) from TDDFT/PB86 simulations. It confirms some incipient, but not fully developed, pre-plasmonic features, with low intensity at 2.02 eV. It can be added, in passing, that the presence of appreciable negative contributions in the upper diagonal part of the ICM-OS plots suggest, that there is still room for re-birth effects.

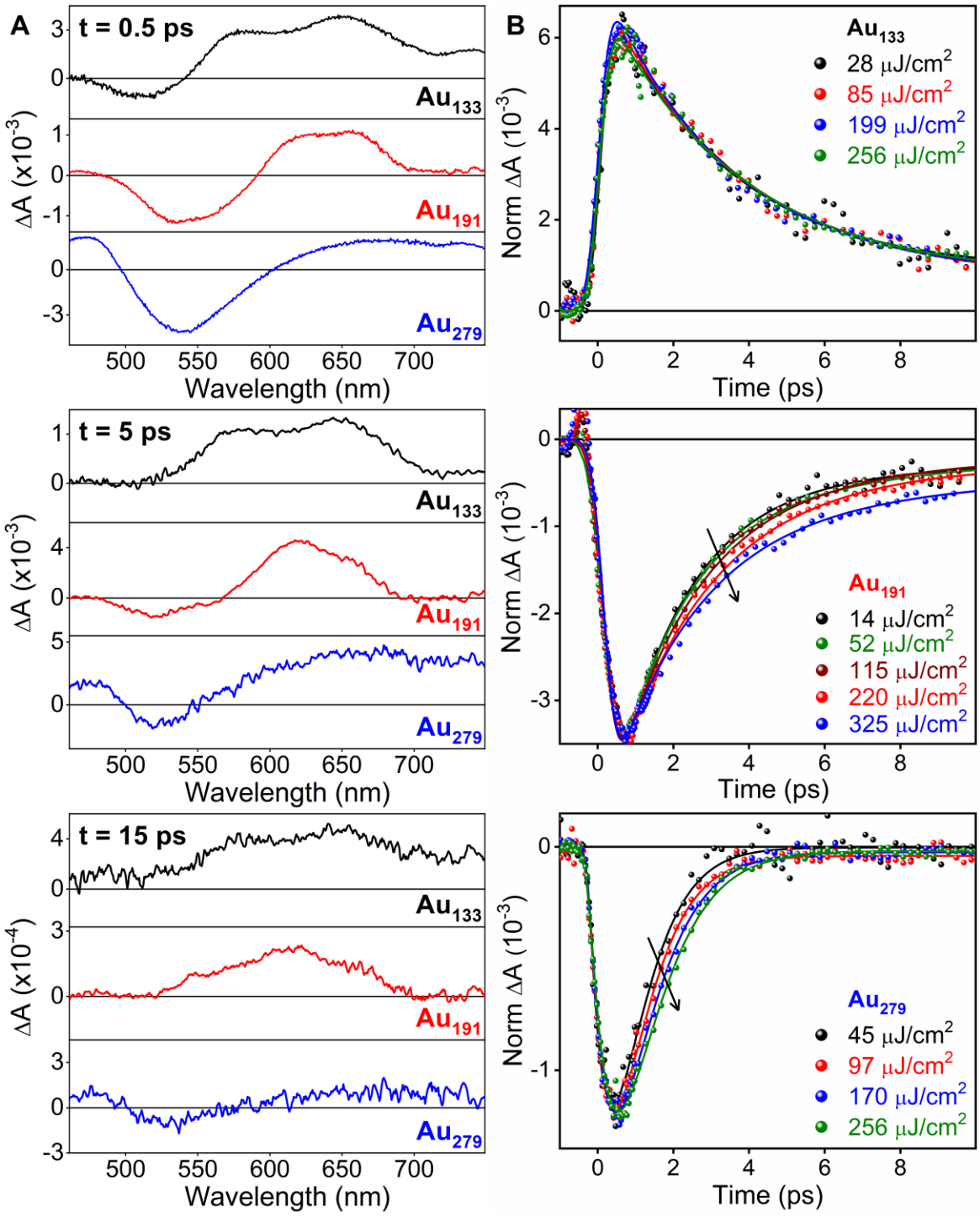

Figure S14. Transient absorption studies. Au_{133}, Au_{191} and Au_{279} (A) TA spectra at different time delays, and (B) Pump power dependent excited state decay kinetic study. Au_{133}, Au_{191} and Au_{279} kinetics at 650, 538 and 540 nm, respectively.

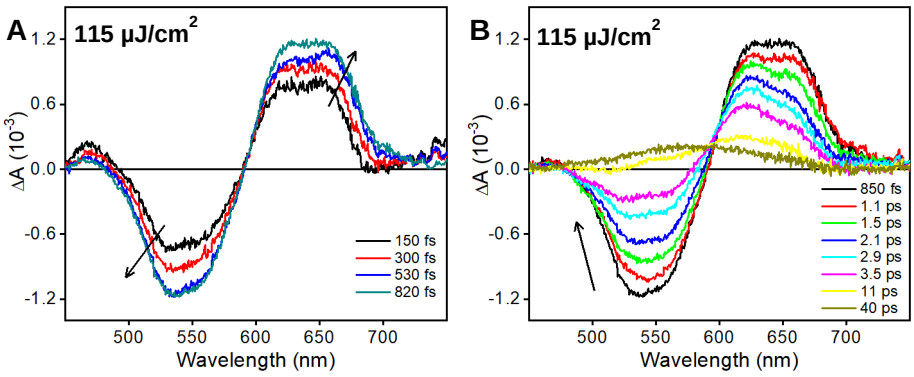

Figure S15. Transient absorption spectra at different time delays. (A) 150 fs to 820 fs, (B) 820 fs to 40 ps.

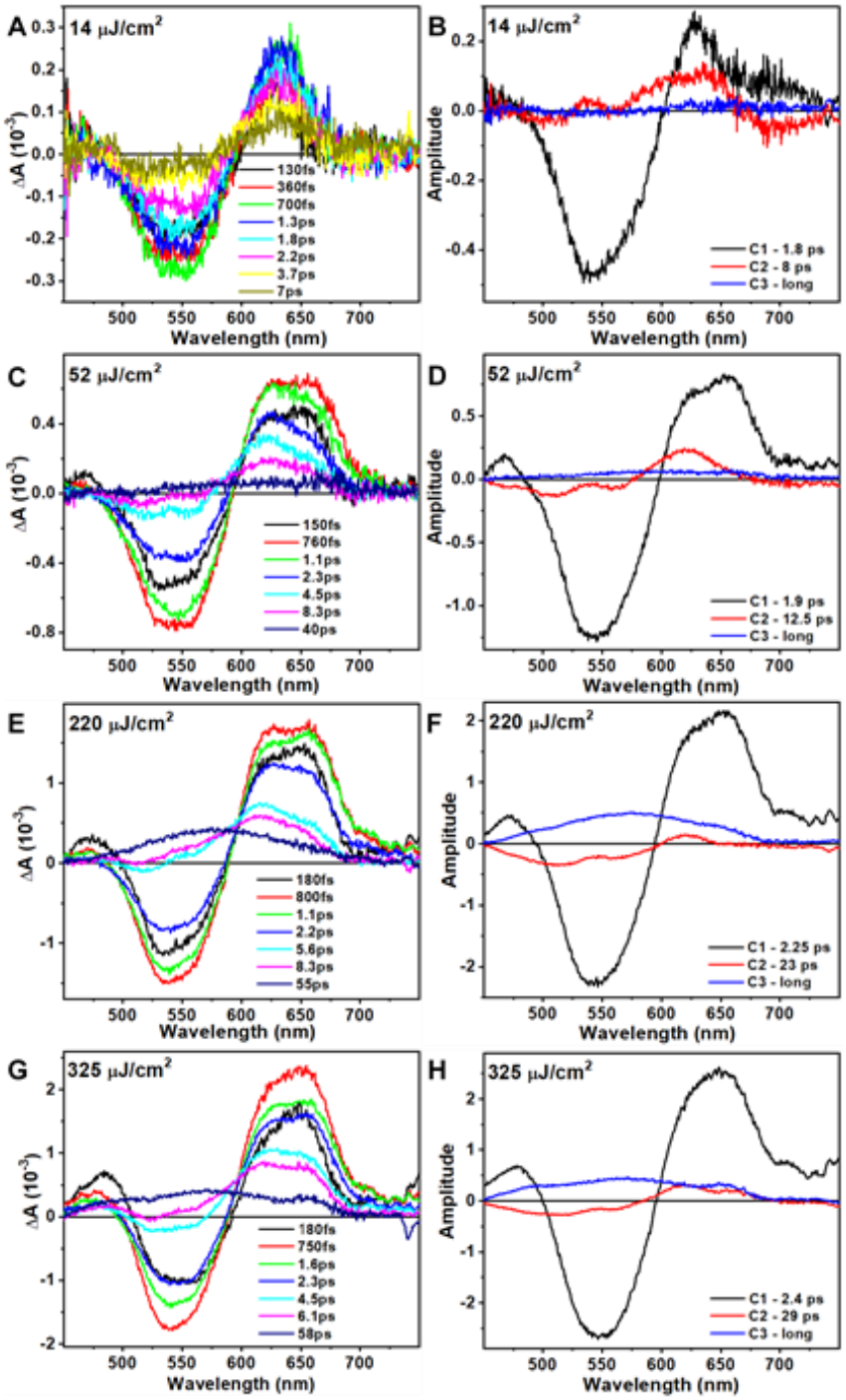

Figure S16. Transient absorption spectra at different pump fluence. (A) 14 μJ/cm^2, (C) 52 μJ/cm^2, (E) 220 μJ/cm^2 and (G) 325 μJ/cm^2. Corresponding species associated spectra obtained from global fit analysis for Au_{191} at different pump fluence: (B) 14 μJ/cm^2, (D) 52 μJ/cm^2, (F) 220 μJ/cm^2 and (H) 325 μJ/cm^2. The longer time delay spectral features at different fluences are similar to one another but markedly different from other plasmonic AuNPs showing the presence of molecule-like nature.

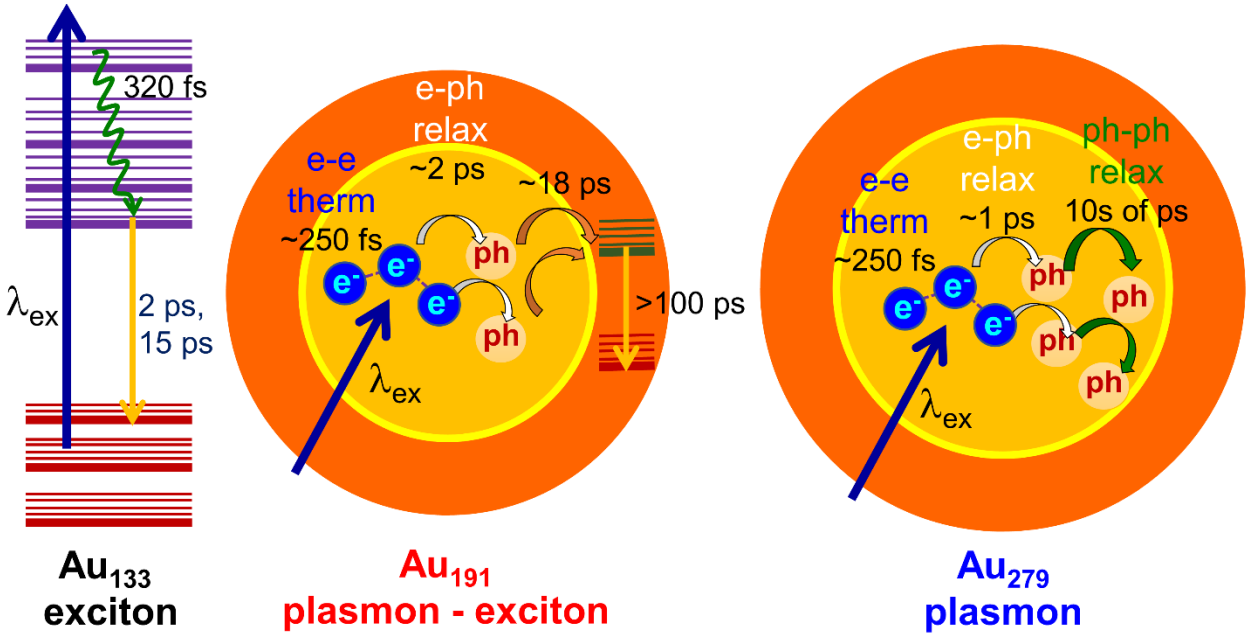

Figure S17. Electron dynamics in molecule to metal transition. (from Au_{133} to Au_{191} to Au_{279} shown as a schematic representation of experimental TA spectra). Colors in Au_{191} and Au_{279} are orange - core and dark orange – ligand shell of the NPs. Au_{133} shows an excitonic behavior typical for molecule-like compounds, Au_{191} shows a mixed metallic and molecular behavior, and Au_{279} exhibits plasmonic nature characteristic of metallic NPs. The samples are pumped to an excited using a laser of certain wavelength (λ_{ex}). The plasmonic NPs undergo processes such as electron-electron thermalization (e-e therm), electron-phonon relaxation (e-ph relax), and phonon-phonon relaxation (ph-ph relax) as they return to ground state. Species associated spectra for Au_{133} can be found in Figure S6 of ref.[17].

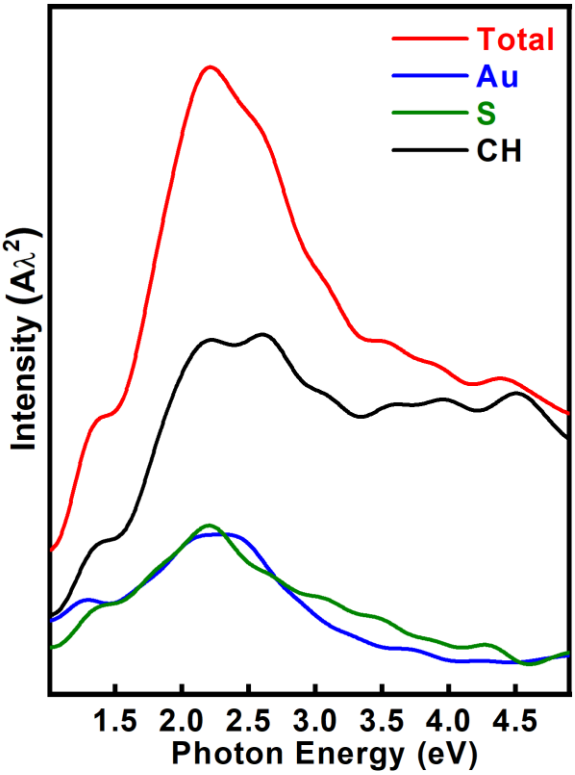

Figure S18. Decomposition of the optical response of $Au_{191}(SPh)_{66}$ simulated via TDDFT/VS98 into contributions associated with the different atomic components: Au, S, and CH.

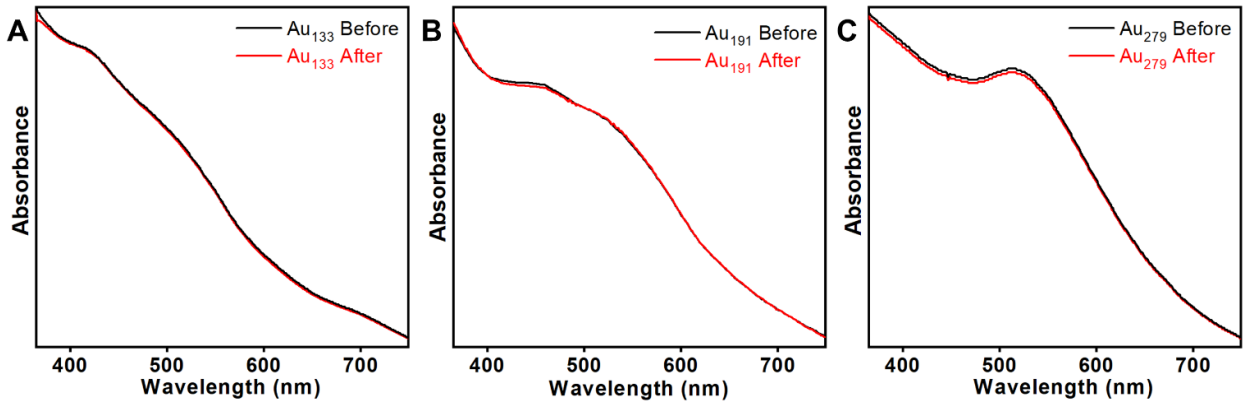

Figure S19. Optical absorption spectra before (black) and after (red) transient absorption experiments of (A) Au_{133}, (B) Au_{191}, and (C) Au_{279}. As can be seen from the figure, the absorption spectrum is quite unchanged. Also, the measurements were repeated on the same sample at different pump power and repeated for three times. All the times, the data was repeated and no change in transient absorption signal was observed for all investigated clusters.

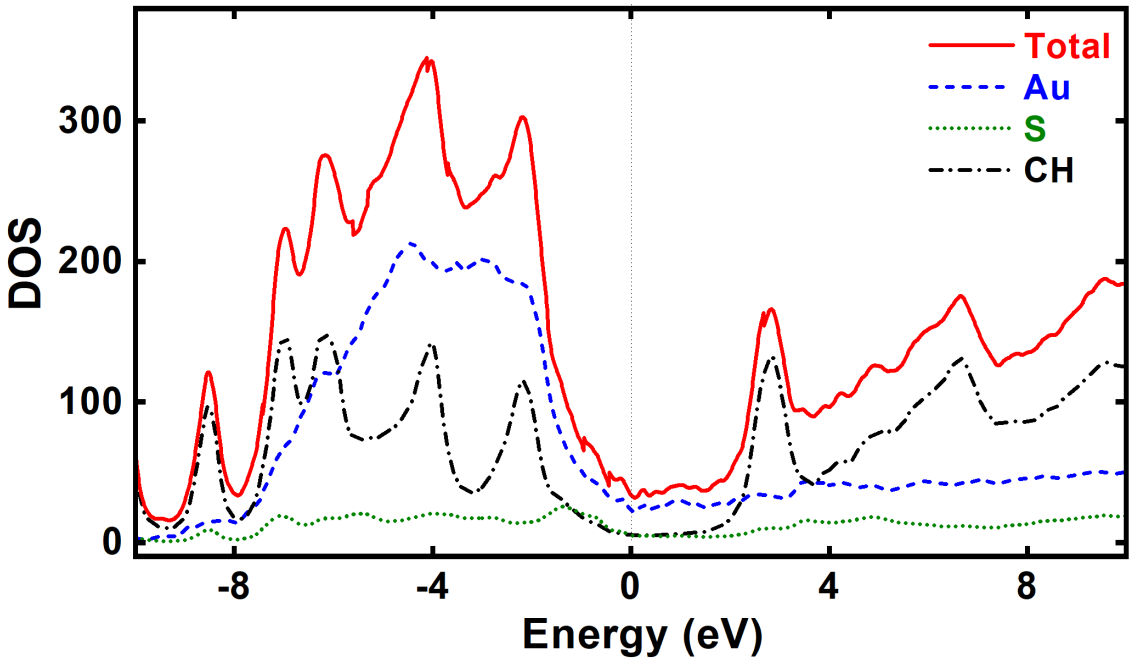

Figure S20. LDA VWN partial DOS analysis of the $[Au_{191}(SPh)_{66}]^+$ nanomolecules. The dotted vertical line represents the Fermi level.

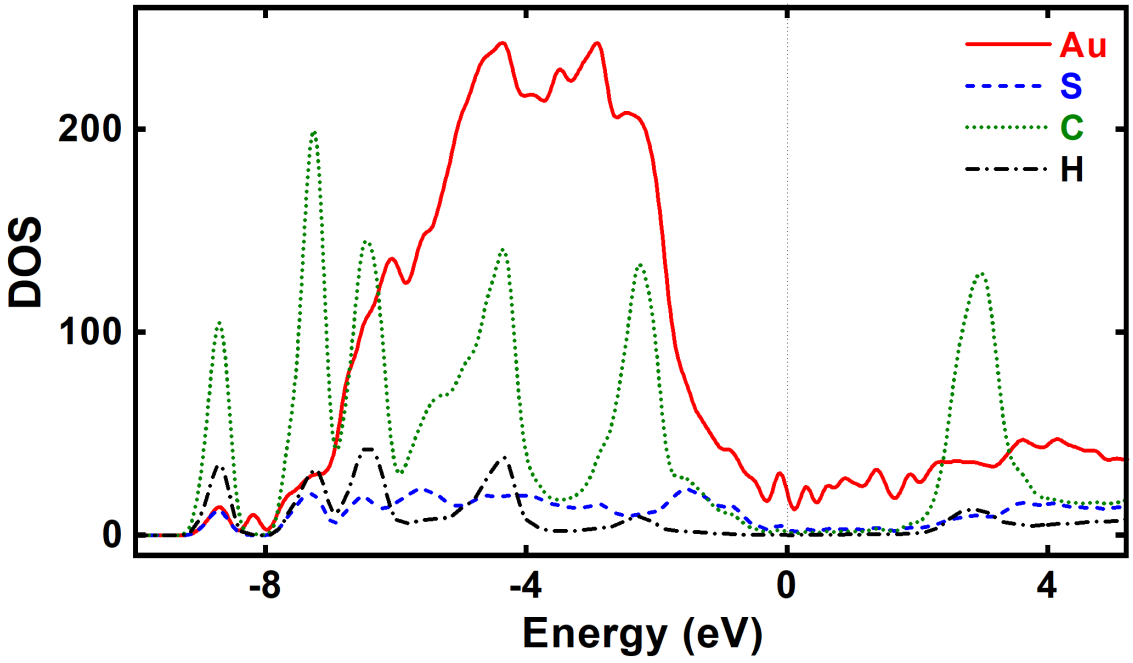

Figure S21. VS98 partial DOS analysis of the $[Au_{191}(SPh)_{66}]^+$ nanomolecules. The dotted vertical line represents the Fermi level.

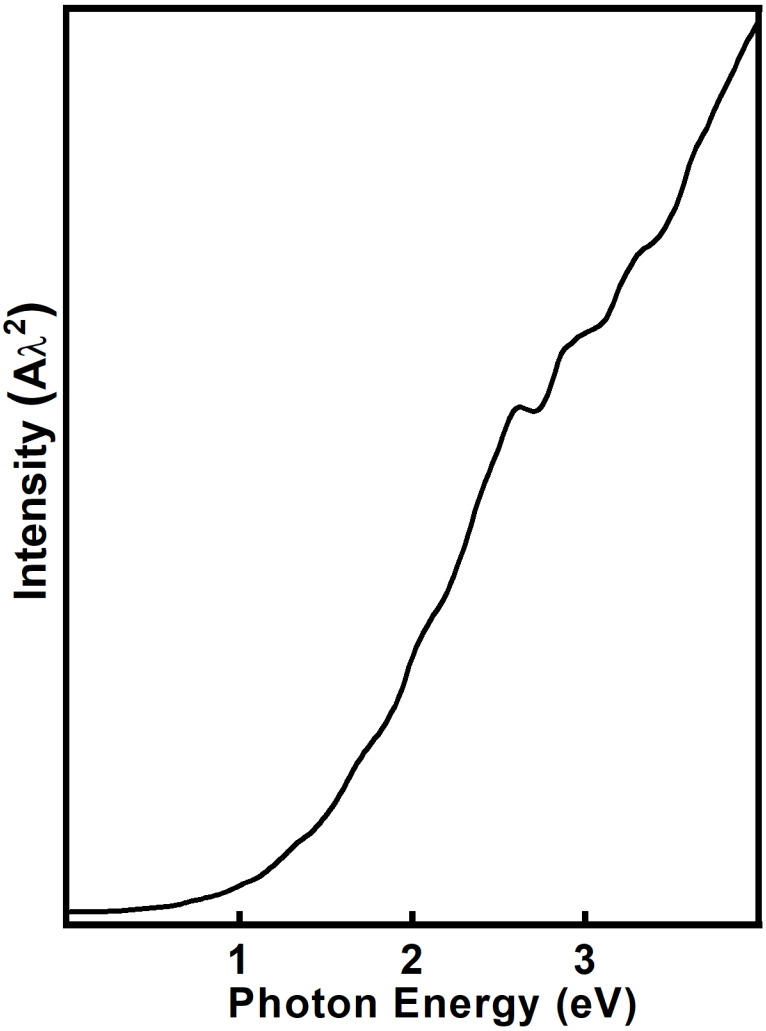

Figure S22. $Au_{191}(SPh)_{66}$ absorption using TDDFT/PB86 xc-functional. The optical spectrum of $Au_{191}(SPh)_{66}$ as predicted by our TDDFT/PB86 approach, where a semi-quantitative agreement with the RT-TDDFT/VS98 simulations can be appreciated, although with the usual red-shift of the absorption peaks which is typical when using the PB86 xc-functional.

Table S3. Cartesian coordinates of $Au_{191}(SPh)_{66}$

Au	19.7483450000	22.0400210000	15.6706130000
Au	19.1548580000	22.8691130000	12.9880620000
Au	17.1151250000	22.8889820000	14.9963760000
Au	18.1249060000	25.3378730000	14.0030160000
Au	17.7671770000	22.0436340000	17.6969240000
Au	21.8249210000	22.0368600000	13.6323060000
Au	18.7731250000	24.5241350000	16.6807690000
Au	18.5520960000	22.0336990000	10.3061100000
Au	19.7812670000	26.9761870000	15.6328230000
Au	20.1813930000	25.3884500000	12.0438900000
Au	20.8244850000	24.5214260000	14.6814520000
Au	20.3955200000	21.1919630000	18.4065520000
Au	19.1242690000	27.7709590000	12.9358740000
Au	16.4646960000	27.0037330000	12.3000280000
Au	17.1151250000	17.8363090000	14.9963760000
Au	17.4178230000	19.5012660000	11.2748760000
Au	20.7577770000	19.5662930000	14.5908740000
Au	21.8706220000	27.0570190000	13.6545010000
Au	20.4385080000	26.1710290000	18.3315700000
Au	16.1314980000	30.2586860000	16.1007100000
Au	17.5155320000	24.5453590000	11.3402600000
Au	18.5495610000	27.0064430000	10.2281290000
Au	19.0731240000	17.9157870000	13.0342500000
Au	18.0584920000	20.4057710000	13.9928190000
Au	18.8113710000	19.4967510000	16.6801690000
Au	16.7371210000	29.4842350000	18.7982580000
Au	20.0538600000	20.3804830000	11.9599100000
Au	18.3569740000	21.1937690000	20.3476830000
Au	21.2369740000	22.9336880000	11.0589280000
Au	23.5020740000	23.7122030000	15.2831070000
Au	17.1151250000	27.8251480000	14.9963760000
Au	21.4213060000	23.6995590000	17.3574060000
Au	16.8900410000	23.7180740000	8.7212930000
Au	18.7525530000	29.4995880000	16.6591750000
Au	20.7354750000	29.4973310000	14.6022720000
Au	19.3984430000	23.7307180000	19.3543230000
Au	23.9569350000	23.1748290000	10.3978880000
Au	21.2238130000	27.8554040000	10.9335580000
Au	22.3768700000	21.2755050000	16.3022610000
Au	18.3978830000	26.2572800000	20.3656790000
Au	22.9319790000	24.5860010000	12.6821360000
Au	21.4385210000	18.7742310000	17.2368350000
Au	18.0799500000	32.2392940000	16.0599190000
Au	21.3729290000	28.6212750000	17.2908220000
Au	19.6079770000	24.5029110000	9.3535400000
Au	19.8438780000	17.1119830000	15.7210010000
Au	22.1996930000	25.4178020000	10.0187790000
Au	19.0873740000	22.4667590000	7.6217580000
Au	24.5118170000	26.2184450000	14.3587300000
Au	20.1748580000	30.2329460000	11.9251180000
Au	19.5672070000	29.4756550000	9.2773580000
Au	23.4377260000	19.8426570000	14.2033680000
Au	14.7584820000	18.7579740000	10.6396290000
Au	24.5676560000	22.2599380000	13.0594440000

Au	19.7605090000	18.1763450000	10.2527230000
Au	21.8945450000	23.1531530000	8.3817750000
Au	16.4716320000	17.0672770000	12.3156240000
Au	20.8384850000	20.6026580000	9.3151490000
Au	20.5118430000	26.9721230000	8.2642030000
Au	16.0575420000	19.8851050000	21.4454180000
Au	22.9002570000	20.7232280000	11.3378600000
Au	21.7674420000	18.2273730000	12.3174240000
Au	18.8332780000	31.4264590000	18.6980820000
Au	19.3787900000	28.7030100000	19.3585220000
Au	22.5233430000	26.1457410000	16.3052600000
Au	23.0541970000	25.3794180000	19.0190040000
Au	19.9229470000	22.8921430000	21.9205030000
Au	23.3902820000	28.7048160000	15.2855060000
Au	13.1857230000	25.3423890000	8.9942270000
Au	17.9642210000	26.1236140000	7.6673470000
Au	14.1476390000	32.1819440000	16.0335260000
Au	16.1405950000	32.2239400000	18.1042250000
Au	24.0071160000	22.9029810000	17.8984750000
Au	22.8631500000	29.4855900000	12.7043300000
Au	23.8676910000	27.0362470000	11.6341890000
Au	22.0713090000	22.9201410000	19.9835710000
Au	16.4031800000	31.5673500000	21.6169770000
Au	20.8962940000	31.2666010000	16.6621740000
Au	17.3912520000	28.6167590000	21.4058280000
Au	18.6037480000	15.0984100000	13.6748960000
Au	22.2724670000	30.9884310000	10.0313760000
Au	20.3978330000	19.9677430000	6.5408200000
Au	23.5982910000	27.5018210000	8.4843500000
Au	21.9707390000	27.8545010000	19.9025910000
Au	23.9902840000	20.8045120000	8.5779270000
Au	16.6425400000	16.5244840000	9.5143010000
Au	26.2509700000	25.4801190000	11.8879270000
Au	25.4782050000	19.5906780000	12.0072990000
Au	15.1346380000	25.4476060000	6.9313250000
Au	18.9659960000	20.2219800000	23.0212370000
Au	24.2275440000	27.7772810000	18.0412410000
Au	26.2909840000	22.9233020000	15.7827860000
Au	22.5798210000	18.1510570000	9.2245710000
Au	19.8517750000	34.0022430000	17.4977720000
Au	23.1052290000	20.4035130000	19.1521720000
Au	20.9268020000	30.5084070000	21.0933030000
Au	16.2266850000	34.5752910000	16.2356770000
Au	14.4819040000	22.0400210000	14.3221390000
Au	15.0753920000	22.8691130000	17.0046910000
Au	16.1053430000	25.3378730000	15.9897360000
Au	16.4630730000	22.0436340000	12.2958290000
Au	12.4053290000	22.0368600000	16.3604470000
Au	15.4571250000	24.5241350000	13.3119830000
Au	15.6781540000	22.0336990000	19.6866430000
Au	14.4489820000	26.9761870000	14.3599300000
Au	14.0488570000	25.3884500000	17.9488630000
Au	13.4057650000	24.5214260000	15.3113000000
Au	13.8347300000	21.1919630000	11.5862000000
Au	15.1059800000	27.7709590000	17.0568780000
Au	17.7655530000	27.0037330000	17.6927250000

Au	16.8124270000	19.5012660000	18.7178770000
Au	13.4724720000	19.5662930000	15.4018780000
Au	12.3596270000	27.0570190000	16.3382520000
Au	13.7917410000	26.1710290000	11.6611820000
Au	18.0987510000	30.2586860000	13.8920430000
Au	16.7147180000	24.5453590000	18.6524930000
Au	15.6806890000	27.0064430000	19.7646240000
Au	15.1571260000	17.9157870000	16.9585020000
Au	16.1717570000	20.4057710000	15.9999340000
Au	15.4188780000	19.4967510000	13.3125830000
Au	17.4931280000	29.4842350000	11.1944950000
Au	14.1763900000	20.3804830000	18.0328430000
Au	15.8732760000	21.1937690000	9.6450690000
Au	12.9932760000	22.9336880000	18.9338250000
Au	10.7281750000	23.7122030000	14.7096460000
Au	12.8089430000	23.6995590000	12.6353470000
Au	17.3402090000	23.7180740000	21.2714600000
Au	15.4776960000	29.4995880000	13.3335780000
Au	13.4947740000	29.4973310000	15.3904810000
Au	14.8318060000	23.7307180000	10.6384290000
Au	10.2733150000	23.1748290000	19.5948650000
Au	13.0064360000	27.8554040000	19.0591950000
Au	11.8533790000	21.2755050000	13.6904920000
Au	15.8323670000	26.2572800000	9.6270740000
Au	11.2982710000	24.5860010000	17.3106170000
Au	12.7917290000	18.7742310000	12.7559180000
Au	16.1503000000	32.2392940000	13.9328330000
Au	12.8573200000	28.6212750000	12.7019310000
Au	14.6222720000	24.5029110000	20.6392130000
Au	14.3863710000	17.1119830000	14.2717510000
Au	12.0305560000	25.4178020000	19.9739740000
Au	15.1428760000	22.4667590000	22.3709940000
Au	9.7184320000	26.2184450000	15.6340220000
Au	14.0553920000	30.2329460000	18.0676340000
Au	14.6630430000	29.4756550000	20.7153940000
Au	10.7925240000	19.8426570000	15.7893850000
Au	19.4717680000	18.7579740000	19.3531240000
Au	9.6625940000	22.2599380000	16.9333080000
Au	14.4697410000	18.1763450000	19.7400300000
Au	12.3357050000	23.1531530000	21.6109780000
Au	17.7586180000	17.0672770000	17.6771290000
Au	13.3917650000	20.6026580000	20.6776040000
Au	13.7184060000	26.9721230000	21.7285500000
Au	18.1727070000	19.8851050000	8.5473350000
Au	11.3299930000	20.7232280000	18.6548920000
Au	12.4628070000	18.2273730000	17.6753290000
Au	15.3969720000	31.4264590000	11.2946710000
Au	14.8514590000	28.7030100000	10.6342300000
Au	11.7069060000	26.1457410000	13.6874930000
Au	11.1760530000	25.3794180000	10.9737480000
Au	14.3073030000	22.8921430000	8.0722490000
Au	10.8399670000	28.7048160000	14.7072460000
Au	21.0445260000	25.3423890000	20.9985260000
Au	16.2660290000	26.1236140000	22.3254050000
Au	20.0826100000	32.1819440000	13.9592270000
Au	18.0896540000	32.2239400000	11.8885270000

Au	10.2231330000	22.9029810000	12.0942780000
Au	11.3671000000	29.4855900000	17.2884230000
Au	10.3625590000	27.0362470000	18.3585640000
Au	12.1589400000	22.9201410000	10.0091810000
Au	17.8270700000	31.5673500000	8.3757760000
Au	13.3339550000	31.2666010000	13.3305790000
Au	16.8389970000	28.6167590000	8.5869250000
Au	15.6265020000	15.0984100000	16.3178570000
Au	11.9577820000	30.9884310000	19.9613770000
Au	13.8324160000	19.9677430000	23.4519330000
Au	10.6319590000	27.5018210000	21.5084030000
Au	12.2595100000	27.8545010000	10.0901620000
Au	10.2399660000	20.8045120000	21.4148250000
Au	17.5877100000	16.5244840000	20.4784520000
Au	7.9792790000	25.4801190000	18.1048250000
Au	8.7520450000	19.5906780000	17.9854540000
Au	19.0956120000	25.4476060000	23.0614280000
Au	15.2642540000	20.2219800000	6.9715150000
Au	10.0027060000	27.7772810000	11.9515120000
Au	7.9392660000	22.9233020000	14.2099660000
Au	11.6504280000	18.1510570000	20.7681820000
Au	14.3784740000	34.0022430000	12.4949810000
Au	11.1250200000	20.4035130000	10.8405810000
Au	13.3034480000	30.5084070000	8.8994500000
Au	18.0035650000	34.5752910000	13.7570760000
S	22.9347110000	21.7884940000	6.7117780000
S	26.7929580000	22.9174310000	13.4607470000
S	23.4718910000	17.2546810000	11.0331340000
S	20.7576990000	15.2406560000	14.5824760000
S	22.8660400000	29.3117330000	21.5227990000
S	15.3184820000	33.0552900000	20.1731250000
S	24.8747030000	28.5169610000	10.0013830000
S	14.3455330000	16.7263380000	9.4837080000
S	21.9414680000	33.0733530000	17.7497110000
S	19.3429570000	32.2018130000	20.9109470000
S	18.9363850000	15.9722080000	9.7650400000
S	17.1014510000	30.0884420000	23.2497820000
S	16.4774290000	14.6716720000	12.8668910000
S	26.7116060000	26.7964610000	13.7186850000
S	20.4731630000	21.7839780000	23.9162210000
S	25.4243150000	25.9520150000	19.1473730000
S	17.3938980000	18.5010280000	22.8364820000
S	25.6048750000	18.8938980000	14.2165650000
S	25.7991670000	20.1628240000	9.7896340000
S	21.4888600000	30.3051980000	8.0080650000
S	17.0460060000	25.3423890000	5.6026460000
S	24.6930950000	29.8084660000	16.9399070000
S	21.6527500000	18.0810630000	7.1322770000
S	19.1608280000	21.5943170000	5.4406850000
S	12.9632890000	26.4532630000	6.8803370000
S	13.9951490000	34.5229090000	15.6262240000
S	26.3469420000	22.6600340000	18.0796310000
S	23.6951610000	18.4603860000	17.9416650000
S	23.0191740000	21.2195090000	21.4388200000
S	25.8721550000	24.5250380000	9.8496200000
S	17.9533610000	35.3718700000	17.5157680000

S	23.3452130000	31.6960490000	11.9431140000
S	22.3562650000	26.6564720000	6.7459700000
S	11.2955380000	21.7884940000	23.2809750000
S	7.4372910000	22.9174310000	16.5320050000
S	10.7583580000	17.2546810000	18.9596190000
S	13.4725500000	15.2406560000	15.4102760000
S	11.3642100000	29.3117330000	8.4699530000
S	18.9117670000	33.0552900000	9.8196270000
S	9.3555460000	28.5169610000	19.9913690000
S	19.8847160000	16.7263380000	20.5090440000
S	12.2887810000	33.0733530000	12.2430420000
S	14.8872930000	32.2018130000	9.0818060000
S	15.2938650000	15.9722080000	20.2277120000
S	17.1287990000	30.0884420000	6.7429710000
S	17.7528200000	14.6716720000	17.1258620000
S	7.5186440000	26.7964610000	16.2740680000
S	13.7570870000	21.7839780000	6.0765320000
S	8.8059340000	25.9520150000	10.8453790000
S	16.8363510000	18.5010280000	7.1562710000
S	8.6253740000	18.8938980000	15.7761880000
S	8.4310820000	20.1628240000	20.2031180000
S	12.7413900000	30.3051980000	21.9846880000
S	17.1842430000	25.3423890000	24.3901070000
S	9.5371550000	29.8084660000	13.0528460000
S	12.5775000000	18.0810630000	22.8604760000
S	15.0694210000	21.5943170000	24.5520670000
S	21.2669600000	26.4532640000	23.1124150000
S	20.2351010000	34.5229090000	14.3665290000
S	7.8833070000	22.6600340000	11.9131210000
S	10.5350880000	18.4603860000	12.0510880000
S	11.2110750000	21.2195090000	8.5539330000
S	8.3580950000	24.5250380000	20.1431330000
S	16.2768890000	35.3718700000	12.4769850000
S	10.8850370000	31.6960490000	18.0496390000
S	11.8739850000	26.6564720000	23.2467830000
C	20.7578523646	11.1708996088	15.3787938865
C	21.3827253446	13.5280140085	16.7008673462
C	21.5940462483	12.3124714091	17.3437663956
C	20.5461411852	12.3888838325	14.7285186795
C	21.2859351203	11.1250072289	16.6754535677
C	20.8736349923	13.5755570497	15.3979683059
C	25.1834489933	32.0310795329	19.4968268622
C	25.4939837469	30.0287918238	21.4143273234
C	26.6021701842	30.7805434666	21.0020163905
C	24.0773489270	31.2750961834	19.8933430208
C	26.4485598476	31.7923491063	20.0471575447
C	24.2252836466	30.2769488418	20.8619917437
C	22.4742513798	34.8195340160	21.2370375906
C	19.7415616171	34.8552876442	20.5589087232
C	20.4934348995	36.0232960224	20.5406209687
C	21.7287503509	33.6315326829	21.2636776298
C	21.8542720440	36.0069749917	20.8650341438
C	20.3709853118	33.6492641301	20.9082794140
C	20.6593274311	33.8593012816	6.1918591677
C	20.5220478699	31.1408073517	5.6448036802
C	20.1328653113	32.0685551381	4.6794216636

C	21.0508838971	32.9479876225	7.1724916690
C	20.2090718020	33.4426376061	4.9329531377
C	20.9821916531	31.5800872138	6.8956858705
C	21.4039198514	14.7138958721	6.8653782726
C	18.6355243140	14.9427450350	7.1706592286
C	19.1878587761	14.7266548003	5.9048219387
C	20.8659357860	14.9177713776	8.1356086381
C	20.5764550417	14.6852950756	5.7398413582
C	19.4886217895	15.1644122928	8.2678482057
C	24.6874613883	16.6334185651	4.8759370907
C	22.8844576285	18.7664269214	4.7501104939
C	23.7331521118	18.4967963839	3.6790290937
C	23.8870413878	16.9374304246	5.9853898242
C	24.6043770524	17.4027313430	3.7151766616
C	22.9346203155	17.9666840459	5.9000987083
C	29.5953665438	20.3306567110	11.9684515120
C	28.6255276050	21.0715839464	14.4844816832
C	29.6528550396	20.1210211081	14.3843852401
C	28.5250039701	21.2431587822	12.0673149748
C	30.0818204884	19.7097053574	13.1204070186
C	28.0634004220	21.6346737908	13.3335791103
C	27.9172857449	16.6946363452	9.2964072289
C	26.6605681599	18.5904830196	7.6684477582
C	27.2779643428	17.4745961823	7.1005572879
C	27.1816714401	17.7356645839	9.8771700773
C	27.9640694451	16.5558057670	7.9051602545
C	26.5978918152	18.7214998642	9.0651290171
C	28.9118974301	28.4516844558	10.4879761926
C	27.0781452537	27.3542943413	8.6838198394
C	28.4459527249	27.1142772771	8.5405900593
C	27.5348195034	28.6841832097	10.6553926311
C	29.3932043494	27.6616887268	9.4314487644
C	26.6167016002	28.1376014878	9.7496840660
C	27.3659527647	31.8790772191	12.2827206034
C	25.5213972162	32.1735757210	10.2069902911
C	26.8879851811	32.3778845726	9.9734736084
C	26.0133878383	31.6370722833	12.5149845060
C	27.8191568241	32.2490934860	11.0107900805
C	25.0741987763	31.8116485827	11.4884297585
C	28.6837489938	29.2966948041	17.4636518733
C	26.9486060429	29.6264868703	15.3178643611
C	28.3213005735	29.5235012495	15.0935689602
C	27.3097484137	29.4000579670	17.7034893159
C	29.2111349365	29.3641094681	16.1639540857
C	26.4392965152	29.5767847679	16.6194868392
C	21.8407388798	22.3513527709	2.5403443655
C	20.9159066236	23.7007671981	4.7857458619
C	21.8834023475	24.2842208382	3.9560997390
C	20.8360220155	21.7769937298	3.3109093187
C	22.3585912203	23.6148799163	2.8279575609
C	20.4037561296	22.4298189494	4.4844131676
C	21.2390739796	28.2041493378	3.1662873362
C	23.4343908105	28.4701355432	4.8942292836
C	23.4306327177	29.1076521420	3.6586846309
C	21.2179182170	27.6046894171	4.4435671466
C	22.3493165627	28.9588176655	2.7730688628

C	22.3290066770	27.7049778766	5.2902677761
C	25.8352660512	24.5508642865	5.8309801663
C	25.1401384213	21.9591156033	5.0387617173
C	26.3159153779	22.5535608618	4.5656301641
C	24.6952508624	23.9462085625	6.3662658968
C	26.6629617116	23.8574552165	4.9380028381
C	24.3513700819	22.6419305585	5.9887620493
C	29.7336779184	23.3690641250	9.4462124494
C	27.2318521828	22.6718155413	8.3265502963
C	28.4170672517	22.0931208707	7.8661784557
C	28.5381586798	23.9353453641	9.9276478623
C	29.6798513469	22.4367661840	8.4007469544
C	27.2930237605	23.6072253112	9.3703998381
C	24.0668401320	16.4086832608	21.4424540984
C	23.6812811946	15.7414519551	18.7405135546
C	23.7705678731	14.7353675338	19.7141986363
C	23.9892623318	17.4067587404	20.4803137449
C	23.9419950611	15.0636926012	21.0655572526
C	23.7611404670	17.0990395335	19.1324403221
C	18.0702677388	12.4578956792	9.8397877222
C	15.5177635575	13.2273088312	10.7302905829
C	15.6625991220	12.4965844615	9.5429974489
C	17.9324078523	13.1776892378	11.0284500651
C	16.9381137112	12.1914099310	9.0652162585
C	16.6608046116	13.5521162812	11.4751522500
C	15.2328684517	17.6896914807	26.2322972459
C	17.6549294788	18.9260994658	25.6254610247
C	17.2234716760	18.8506190736	26.9710378517
C	15.6638388104	17.7675486653	24.9120153431
C	15.9952883363	18.2507086143	27.2665856569
C	16.8654194578	18.4155361690	24.5839329711
C	22.1524797284	13.3088177061	11.3209645298
C	24.2454674628	14.7148607028	10.1250759339
C	24.1712416467	13.3150724864	10.0182056085
C	22.2053878346	14.7089998555	11.4336941485
C	23.1315016991	12.5862702782	10.6212098496
C	23.2631042508	15.4165617466	10.8467422965
C	30.0824845285	25.0964949828	15.3918919581
C	27.5388161674	25.9098713953	16.1503909634
C	28.4050430911	25.3651760532	17.0980806702
C	29.2774434891	25.7097244929	14.4343205322
C	29.6864132266	24.9384412989	16.7203647505
C	27.9610017402	26.0662674682	14.8163561504
C	26.6201856347	21.0443282951	23.2723655528
C	25.2529814073	22.9103975196	21.6906514702
C	26.5228213965	23.2137589927	22.1964346373
C	25.3525065715	20.7353600674	22.7667746578
C	27.1921698229	22.2899277268	23.0006160255
C	24.6589564900	21.6701727476	21.9737019175
C	17.5636003359	28.9412015999	3.7330146611
C	15.7303028479	26.8504348877	3.7397091184
C	15.6272685666	27.8530778454	2.7727325914
C	17.7140969414	27.8965256644	4.6536296007
C	16.5524829900	28.9067892487	2.7646740663
C	16.8057487871	26.8303403182	4.6421059662
C	10.4775764301	23.8440812024	4.8731176929

C	11.5279454899	26.4175502106	4.6641731115
C	10.6914234880	25.9230724172	3.6694882613
C	11.2949744749	24.3480631207	5.9018826009
C	10.1826321015	24.6215764962	3.7526063042
C	11.8632054096	25.6228446448	5.7695069004
C	13.9215483109	16.8657090410	5.4063420591
C	12.8841748032	18.1954426560	7.6308994862
C	12.4509233661	18.5267414455	6.3425387735
C	14.3402669079	16.5141194671	6.6946105870
C	12.9712088217	17.8751199035	5.2145744114
C	13.8273248070	17.1739701208	7.8197615454
C	20.7212734000	30.1050770518	25.0634877240
C	18.7817000169	31.9871046876	24.3531343239
C	19.9040337214	32.3847303911	25.0860173342
C	19.6109022936	29.7015673650	24.3138063437
C	20.8854684749	31.4449561415	25.4196235755
C	18.6295574566	30.6430825782	23.9758821962
C	12.0739915422	35.8095348743	18.9706603544
C	13.3581890585	37.0728565794	16.7809442343
C	12.7641444461	37.7903282390	17.8075448263
C	12.6614495421	35.0194163901	17.9744784457
C	12.1259635125	37.2111637481	18.9015838574
C	13.3041520255	35.6489813460	16.8902286313
C	16.9338118824	36.0411611923	22.4295741709
C	15.5596357270	35.9349953641	20.0051885400
C	15.9443042002	37.1994009052	20.5397847450
C	16.5338722335	34.8233131035	21.9122459057
C	16.6401655019	37.2570725014	21.7581490833
C	15.8490229279	34.7457187421	20.6925821183
C	27.6170090468	27.3371713962	22.2116055947
C	25.0042761606	26.3866260918	21.8940121735
C	25.4938007914	26.7070939946	23.1626318882
C	27.1439466926	27.0147598639	20.9391880295
C	26.8036841300	27.1693408234	23.3331344477
C	25.8413539533	26.5162450325	20.7749740597
C	19.4950012182	39.0697799149	16.8429485622
C	17.0050027346	37.7263324754	16.8078806721
C	17.0587388797	39.1139006096	16.6151024700
C	19.4654466825	37.6664387506	17.0402741418
C	18.3021303048	39.7535382280	16.6295100237
C	18.2037782087	37.0800097371	17.0561647147
C	17.7468987573	22.8319175795	26.8135441625
C	20.4231818399	23.3204038684	26.1450196299
C	19.8558862043	23.9383742692	27.2536937236
C	18.2908407631	22.2636776218	25.6461207264
C	18.5049783367	23.7349217182	27.5425852493
C	19.6253971501	22.5207999787	25.3043743938
C	24.1127404965	35.8050291625	15.7406330324
C	23.5608879557	33.0379610238	15.4711085811
C	24.3979434860	33.6936768179	14.5669376541
C	23.3006314076	35.1372242077	16.6671015038
C	24.6710295314	35.0547663876	14.6932736123
C	23.0074228036	33.7742669793	16.5255500600
C	26.9194335349	15.1591654206	13.8909582006
C	24.4480620390	16.4515969169	14.3802252951
C	24.5102844076	15.0614126959	14.3542664790

C	26.8665822228	16.5535138218	13.8935565237
C	25.7372699673	14.4487755771	14.1089711766
C	25.6199665120	17.1616961129	14.1298303252
C	27.0343211490	19.1724898468	20.0062667720
C	26.9072916248	19.9831055759	17.3405321248
C	27.0180367778	18.6264139792	17.6544925511
C	26.9293854557	20.5313705514	19.6990823753
C	27.0464604019	18.2134653554	18.9886395277
C	26.7957020622	20.9356637787	18.3608071906
C	13.4732168369	11.1713149071	14.6147424569
C	12.8479290597	13.5273890363	13.2919995633
C	12.6370213835	12.3123579497	12.6493673496
C	13.6849664844	12.3886161907	15.2641254419
C	12.9450010834	11.1247011057	13.3175953944
C	13.3569569762	13.5756615557	14.5956589764
C	9.0465723180	32.0304712844	10.4967189170
C	8.7366204714	30.0296515046	8.5793033524
C	7.6276906605	30.7787334741	8.9909757927
C	10.1514421778	31.2748453851	10.0990789497
C	7.7816814241	31.7911999447	9.9457189903
C	10.0050672648	30.2783252436	9.1299421245
C	11.7564540663	34.8192329039	8.7554410871
C	14.4871693331	34.8551812496	9.4342388145
C	13.7380821481	36.0224077645	9.4522414254
C	12.5016565602	33.6327182001	8.7285264365
C	12.3760332253	36.0071373805	9.1282702089
C	13.8593368250	33.6493681975	9.0855745731
C	13.5710724477	33.8588336526	23.8015798233
C	13.7086568455	31.1398886977	24.3485402433
C	14.0970700952	32.0677378349	25.3135705839
C	13.1782494566	32.9480697944	22.8204623040
C	14.0218175073	33.4421285372	25.0600845766
C	13.2477771323	31.5792796555	23.0975726884
C	12.8262971146	14.7126368632	23.1271502776
C	15.5957718912	14.9439351477	22.8219623094
C	15.0425823756	14.7261712589	24.0874468843
C	13.3631813280	14.9191935473	21.8565973427
C	13.6541126418	14.6842177117	24.2527975580
C	14.7415297038	15.1683664443	21.7259895169
C	9.5464109220	16.6319075538	25.1214564177
C	11.3478847650	18.7667440295	25.2451573588
C	10.5005331988	18.4956470615	26.3170987737
C	10.3454385700	16.9358792702	24.0104543409
C	9.6297298667	17.4011336410	26.2820770633
C	11.2971462947	17.9667883073	24.0947967434
C	4.6341074151	20.3318371114	18.0224040719
C	5.6039314662	21.0734393989	15.5071183554
C	4.5765322879	20.1226376162	15.6064489368
C	5.7044973486	21.2434414961	17.9232873114
C	4.1474610122	19.7112645474	16.8701052290
C	6.1661909734	21.6369733111	16.6578058094
C	6.3132396753	16.6954966334	20.6999686209
C	7.5783061438	18.5878171637	22.3259910086
C	6.9612885288	17.4720180647	22.8942546397
C	7.0475560021	17.7371369404	20.1176028926
C	6.2710444235	16.5552140841	22.0910567560

C	7.6350811438	18.7216916410	20.9291093147
C	5.3190100294	28.4522398510	19.5039087426
C	7.1517170406	27.3548047805	21.3086531220
C	5.7845854168	27.1149074754	21.4516805325
C	6.6959530128	28.6839143151	19.3374487963
C	4.8377062070	27.6623819526	20.5609820020
C	7.6138040272	28.1378325767	20.2433388066
C	6.8640193305	31.8797488782	17.7109717628
C	8.7084565456	32.1744345912	19.7860065088
C	7.3426177675	32.3780217559	20.0201851578
C	8.2161720798	31.6373422154	17.4793017142
C	6.4111279287	32.2496480154	18.9832410797
C	9.1560132086	31.8127476828	18.5049924606
C	5.5474143400	29.2955553112	12.5284836069
C	7.2802656243	29.6268215138	14.6738378986
C	5.9089895856	29.5229445491	14.8991386296
C	6.9212675066	29.3993419272	12.2905410818
C	5.0196201310	29.3632979912	13.8285148078
C	7.7915138501	29.5773683762	13.3734765868
C	12.3900069477	22.3518326332	27.4522027144
C	13.3148793391	23.7029071046	25.2068015018
C	12.3478860566	24.2850321273	26.0375630354
C	13.3926665223	21.7758212860	26.6794089080
C	11.8726933269	23.6157234856	27.1651114348
C	13.8250233231	22.4303792971	25.5061947609
C	12.9944521701	28.2056642044	26.8221520189
C	10.7947659958	28.4685025971	25.1011229007
C	10.8007141801	29.1052720090	26.3374328374
C	13.0138935332	27.6061143967	25.5459535948
C	11.8849834479	28.9586728405	27.2194181495
C	11.9014609664	27.7057697663	24.7016088888
C	8.3949103473	24.5504047991	24.1626039147
C	9.0903480850	21.9586746893	24.9551915287
C	7.9151528565	22.5541691536	25.4285963945
C	9.5345965496	23.9465040023	23.6270127098
C	7.5676952038	23.8576260689	25.0561129315
C	9.8786043634	22.6421552044	24.0047088808
C	4.4957736134	23.3725969528	20.5474578176
C	6.9974129833	22.6722633773	21.6659747431
C	5.8119347672	22.0958764789	22.1273641956
C	5.6918975261	23.9364465965	20.0648095128
C	4.5494914091	22.4391347470	21.5913282381
C	6.9376786544	23.6052915772	20.6191113400
C	10.1633406729	16.4095752188	8.5501311827
C	10.5489168245	15.7425684093	11.2515878789
C	10.4593375291	14.7365811019	10.2783396126
C	10.2406916977	17.4070254001	9.5132897456
C	10.2878271925	15.0648623701	8.9273113631
C	10.4686602290	17.0997814467	10.8610616757
C	16.1619128788	12.4581127061	20.1544377339
C	18.7142151715	13.2271087247	19.2623865623
C	18.5694351792	12.4967095946	20.4496983124
C	16.2980427361	13.1776401679	18.9656186423
C	17.2939941073	12.1913193020	20.9288049202
C	17.5707256463	13.5520285210	18.5181494521
C	19.0002933057	17.6901073523	3.7638512500

C	16.5765927954	18.9252597764	4.3651381265
C	17.0088608735	18.8491548372	3.0190741599
C	18.5654548401	17.7687439109	5.0823307073
C	18.2384624075	18.2499902591	2.7278739320
C	17.3642812118	18.4158439137	5.4086568164
C	12.0768281123	13.3086168938	18.6724117690
C	9.9843026304	14.7154814749	19.8682960890
C	10.0589268336	13.3157609821	19.9754954080
C	12.0249040689	14.7087991568	18.5590493058
C	11.0977099445	12.5858838283	19.3715149087
C	10.9662394802	15.4171631374	19.1454506618
C	4.1478986747	25.0957299019	14.6030782599
C	6.6904803037	25.9086366222	13.8440348145
C	5.8246562274	25.3641236137	12.8945729066
C	4.9539560946	25.7103231528	15.5583385078
C	4.5427038891	24.9397036105	13.2737151221
C	6.2694915644	26.0686864379	15.1766432518
C	7.6098122496	21.0444467875	6.7214335128
C	8.9778847445	22.9098704790	8.3014314448
C	7.7073386143	23.2142297287	7.7974578134
C	8.8776246030	20.7368464980	7.2261137755
C	7.0378778866	22.2899936166	6.9931052129
C	9.5720990613	21.6705554535	8.0180331619
C	16.6657026327	28.9395785412	26.2633029423
C	18.5008492930	26.8486818889	26.2560348802
C	18.6024448275	27.8525162442	27.2223513672
C	16.5160649140	27.8957874657	25.3403082841
C	17.6777445995	28.9063263237	27.2297114240
C	17.4262372660	26.8309645072	25.3507900968
C	23.7516196688	23.8454261772	25.1232823170
C	22.6997215997	26.4195086658	25.3311436277
C	23.5363571743	25.9238378752	26.3267626505
C	22.9346952119	24.3472983722	24.0927736846
C	24.0457864237	24.6226141230	26.2438225021
C	22.3664326621	25.6230164231	24.2250451894
C	20.3065196749	16.8649811281	24.5875686444
C	21.3470802004	18.1946657626	22.3618917792
C	21.7775454041	18.5260417264	23.6523665034
C	19.8875933656	16.5119543695	23.2980934834
C	21.2591693232	17.8726199599	24.7796508068
C	20.4063228586	17.1707589782	22.1735425170
C	13.5077298487	30.1043487986	4.9310023790
C	15.4471810779	31.9861193388	5.6399679416
C	14.3256970450	32.3855633823	4.9083047593
C	14.6193505962	29.7023843003	5.6791632463
C	13.3448017017	31.4450078241	4.5739518597
C	15.6015057402	30.6427968271	6.0150031610
C	22.1562012162	35.8093991012	11.0215066302
C	20.8730195863	37.0729080572	13.2124678895
C	21.4659067760	37.7904965946	12.1848699162
C	21.5692082012	35.0194235297	12.0184077502
C	22.1051250769	37.2113100371	11.0918954444
C	20.9284524208	35.6485253188	13.1036478977
C	17.2980519285	36.0414575040	7.5621256493
C	18.6701557157	35.9344059427	9.9882043842
C	18.2867333476	37.1994164387	9.4540012763

C	17.6961578586	34.8232031971	8.0811865668
C	17.5909988285	37.2571052215	8.2349406862
C	18.3792908996	34.7453905042	9.3017161521
C	6.6132100660	27.3369036266	7.7817180882
C	9.2242646541	26.3870508244	8.0994331722
C	8.7364946666	26.7063744558	6.8303152848
C	7.0870168230	27.0141597760	9.0526025838
C	7.4258419413	27.1684671118	6.6604161968
C	8.3887880816	26.5159950519	9.2178911873
C	14.7341948290	39.0703955709	13.1504536582
C	17.2269304120	37.7259266634	13.1848162980
C	17.1702153022	39.1144160598	13.3764977937
C	14.7665565118	37.6658391530	12.9537630330
C	15.9300301503	39.7531094905	13.3635487979
C	16.0248739359	37.0798713024	12.9355127136
C	16.4778934392	22.8288283875	3.1688758821
C	13.8076954388	23.3222826784	3.8502372013
C	14.3693797594	23.9399845299	2.7409951470
C	15.9374515878	22.2610471989	4.3369675058
C	15.7203268875	23.7369743495	2.4469456116
C	14.6049788619	22.5221058463	4.6880647112
C	10.1179275585	35.8049935741	14.2527407471
C	10.6689318481	33.0392933942	14.5216742282
C	9.8327620882	33.6937794129	15.4255651939
C	10.9290766000	35.1368108651	13.3271422962
C	9.5597976066	35.0545443940	15.2995292635
C	11.2224092755	33.7742978033	13.4671372452
C	7.3107138140	15.1590554154	16.1017741835
C	9.7814892199	16.4516678818	15.6124160489
C	9.7189210245	15.0614257251	15.6387598191
C	7.3629380066	16.5537412462	16.0993506616
C	8.4926333824	14.4484194648	15.8845206367
C	8.6097630646	17.1623630358	15.8638056754
C	7.1945826627	19.1737874444	9.9867236346
C	7.3211123855	19.9838899758	12.6515814835
C	7.2113595750	18.6272293483	12.3384152306
C	7.2989160416	20.5324433562	10.2949040126
C	7.1832722570	18.2138627380	11.0040193061
C	7.4325696583	20.9378908395	11.6323755777
H	20.5032581571	10.2428270210	14.8661482416
H	21.5854832873	14.4815358984	17.2014345560
H	21.9787743061	12.3137229988	18.3634226083
H	20.1185583832	12.4084986328	13.7289477499
H	25.0476780860	32.7927455657	18.7316815800
H	25.6086034861	29.2478505656	22.1612338287
H	27.5774130342	30.5652653363	21.4293758792
H	23.1037040617	31.4492036525	19.4406756120
H	23.5273736197	34.8100778329	21.5118652032
H	18.6836684418	34.8684564358	20.3102462010
H	20.0205605472	36.9916164463	20.3080780434
H	22.1979963395	32.6901545748	21.5519844415
H	20.7039754224	34.9193726802	6.4290845783
H	20.4786760731	30.0757566642	5.4285752036
H	19.7725593769	31.7103857703	3.7185670637
H	21.3927525039	33.2953108408	8.1456028045
H	22.4808960557	14.6350500343	6.7470624900

H	17.5575326148	15.0495354105	7.2981694300
H	18.5460943335	14.6660557994	5.0249779471
H	21.5229621010	15.0042861133	8.9972608648
H	25.3698059406	15.7855038449	4.9160925557
H	22.1743871847	19.5918249915	4.7052116225
H	23.6848021120	19.1331130694	2.7952347523
H	23.9792451018	16.3848265625	6.9160802923
H	29.9282075131	20.0387568171	10.9742843585
H	28.3076780807	21.4311861522	15.4602249091
H	30.0155980683	19.6564542996	15.2987178505
H	28.1095704054	21.6863420821	11.1679177631
H	28.3844234874	15.9554863219	9.9419760929
H	26.1692446942	19.3281021994	7.0339539908
H	27.2453279381	17.3446676632	6.0209879524
H	27.0853939469	17.8001574425	10.9617864442
H	29.6257141936	28.8884909131	11.1902214655
H	26.3627998376	26.9174765952	7.9907642455
H	28.7789314435	26.4770794756	7.7247444716
H	27.1707463291	29.2888861123	11.4834400983
H	28.0805435847	31.7653286335	13.0982689459
H	24.7987438077	32.2793776844	9.3981957001
H	27.2078665020	32.6469548962	8.9688899217
H	25.6784797721	31.3170408441	13.4973490946
H	29.3886409501	29.1585669017	18.2877441057
H	26.2590195249	29.6935285191	14.4819112423
H	28.6779560987	29.5376387989	14.0662201429
H	26.9280437339	29.3398992383	18.7192529270
H	22.1843071734	21.8206060306	1.6552158773
H	20.5793515232	24.2137696050	5.6876217171
H	22.2925771355	25.2514240989	4.2331140554
H	20.4000821947	20.8315125036	2.9868610951
H	20.3515411569	28.1005987394	2.5506920303
H	24.2813772334	28.5554771531	5.5732629123
H	24.2930295486	29.7046045246	3.3713265566
H	20.3594040849	27.0101390796	4.7461372835
H	26.0860334367	25.5647279347	6.1378281649
H	24.8670164029	20.9474027769	4.7417973182
H	26.9398180679	22.0092386371	3.8565413350
H	24.0876621656	24.4711008980	7.1002565774
H	30.6835946136	23.6528660585	9.8948245106
H	26.2811837816	22.4114041287	7.8721056593
H	28.3494519901	21.3636106208	7.0624061443
H	28.5588053320	24.6615852190	10.7400589349
H	24.2105576427	16.6688552031	22.4888204658
H	23.5534076502	15.4668059170	17.6947254391
H	23.7069646773	13.6808184608	19.4191882111
H	24.0960408788	18.4513940695	20.7680389589
H	19.0666953507	12.2353039747	9.4671664042
H	14.5256888741	13.4762323520	11.0935878692
H	14.7851693526	12.2815259004	8.9368228651
H	18.8024449107	13.4208464979	11.6336213128
H	14.2785398200	17.2033426004	26.4195068182
H	18.6132501731	19.3867553228	25.3832517345
H	17.8518022913	19.2808664350	27.7450293800
H	15.0654965731	17.3219430370	24.1208964059
H	21.3443803734	12.7511180709	11.7966490912

H	25.0713800444	15.2429895892	9.6517356275
H	24.9407512445	12.7686244387	9.4720772302
H	21.4155514121	15.2197900614	11.9772802124
H	31.0751776828	24.7626878061	15.0920516004
H	26.5391588699	26.2229995729	16.4425402091
H	28.0804277292	25.2388301916	18.1275575264
H	29.6499126029	25.8519020562	13.4194475855
H	27.1367916508	20.3179951248	23.8952970861
H	24.7270814557	23.6232290738	21.0567078166
H	26.9696725280	24.1814080777	21.9727392706
H	24.9036991924	19.7642338970	22.9680115480
H	18.2426372183	29.7907487232	3.7737478510
H	15.0013523323	26.0488281887	3.7819639928
H	14.8259639169	27.8155195677	2.0353278662
H	18.5256311638	27.9095875003	5.3738413242
H	10.0819158489	22.8324797268	4.9476001761
H	11.9414135982	27.4208362742	4.6028983117
H	10.4640158843	26.5357978628	2.7981034869
H	11.5228117087	23.7449412669	6.7774455756
H	14.3885738494	16.3841499980	4.5548092879
H	12.5001343187	18.7331559365	8.4941602073
H	11.7436280341	19.3461847064	6.2274459751
H	15.0710209902	15.7176619610	6.8316952583
H	21.4873801142	29.3733278250	25.3105958294
H	18.0173100214	32.7086046003	24.0704372117
H	20.0249052649	33.4346881371	25.3487976141
H	19.4959628333	28.6630972744	24.0053336373
H	11.5880209368	35.2943250594	19.8005754434
H	13.8428599624	37.5114650694	15.9114114960
H	12.7964687694	38.8897188091	17.7508655245
H	12.6395896142	33.9296605069	18.0367904955
H	17.4781512379	36.0316557402	23.3715671924
H	15.0350742669	35.8993800128	19.0512126975
H	15.6934635648	38.0807385507	19.9643696762
H	16.7647801584	33.8954556028	22.4430584080
H	28.6273808646	27.7162177404	22.3293782417
H	23.9823637097	26.0291944491	21.7670270171
H	24.8477832150	26.5774083531	24.0253467661
H	27.7966603903	27.1353434424	20.0733627041
H	20.4507622568	39.5948259549	16.8657197323
H	16.0387677111	37.2222206982	16.8137712461
H	16.1374385559	39.6578112861	16.4440300472
H	20.3904743684	37.1434048056	17.2335609138
H	16.7228483888	22.6124933009	27.1169020254
H	21.4767241716	23.4567011237	25.9332764858
H	20.4685174709	24.5707828723	27.8955970111
H	17.6804979172	21.5992244100	25.0450938831
H	24.2718566436	36.8921625394	15.8195752771
H	23.3232516568	31.9823109976	15.3474920998
H	24.8199028628	33.1656120322	13.7237638742
H	22.8462553927	35.7120387335	17.4782262813
H	27.8679572938	14.6533066394	13.7181274302
H	23.5183808320	16.9801477424	14.5835064705
H	23.5977303616	14.5020100956	14.5216253582
H	27.7549124406	17.1613157277	13.7205169810
H	27.0795399156	18.8706573066	21.0509386507

H	26.8436257216	20.2886281162	16.3020130946
H	27.0351580180	17.8964389565	16.8462614916
H	26.9059682107	21.2739563866	20.4897891600
H	13.7270257988	10.2432076531	15.1272877566
H	12.6458171636	14.4809207623	12.7913999743
H	12.2523674918	12.3141946060	11.6295008751
H	14.1122891163	12.4086580715	16.2639109191
H	9.1830864596	32.7925132597	11.2603914428
H	8.6229674910	29.2488947751	7.8333032123
H	6.6532549450	30.5638714103	8.5629285615
H	11.1244432798	31.4487054760	10.5505743880
H	10.7031995675	34.8104831384	8.4815065179
H	15.5452107423	34.8675978528	9.6828612281
H	14.2096689590	36.9909232503	9.6853221033
H	12.0328773876	32.6917718919	8.4412037180
H	13.5276871310	34.9195625816	23.5644588140
H	13.7518855355	30.0740896707	24.5655190686
H	14.4570574649	31.7101985444	26.2752307610
H	12.8386559929	33.2960215997	21.8458755958
H	11.7485895456	14.6352101630	23.2467618740
H	16.6747107346	15.0503034685	22.6936579703
H	15.6854627565	14.6658356756	24.9665131090
H	12.7044623937	15.0048316013	20.9940979052
H	8.8651141141	15.7825780056	25.0814909438
H	12.0571992255	19.5935226059	25.2893466004
H	10.5481754480	19.1333841613	27.1999302928
H	10.2532046106	16.3825968260	23.0791901868
H	4.3010671799	20.0401283271	19.0163336241
H	5.9206115232	21.4338832651	14.5313930091
H	4.2138050699	19.6586803950	14.6915327608
H	6.1196590141	21.6872863321	18.8224121640
H	5.8418744839	15.9582673576	20.0547944457
H	8.0754374240	19.3220049172	22.9600006469
H	6.9980381713	17.3406116181	23.9736617730
H	7.1394794165	17.8045878318	19.0322930160
H	4.6050423393	28.8896521533	18.8021200138
H	7.8669976220	26.9184307261	22.0015931075
H	5.4510145398	26.4779483279	22.2681829017
H	7.0607375808	29.2886078843	18.5096106374
H	6.1493577524	31.7655272028	16.8957472869
H	9.4315043571	32.2800542452	20.5943476656
H	7.0233168007	32.6480366007	21.0246856201
H	8.5513488150	31.3177470581	16.4965035002
H	4.8436149976	29.1571507719	11.7033858640
H	7.9698575308	29.6936026464	15.5092157012
H	5.5513435455	29.5386258693	15.9261875505
H	7.3036046885	29.3391405180	11.2758250733
H	12.0471647588	21.8203773412	28.3379244470
H	13.6509590303	24.2161905292	24.3038296138
H	11.9382003538	25.2519659133	25.7596592160
H	13.8291039361	20.8289727711	27.0028593311
H	13.8829515524	28.1029721561	27.4374917323
H	9.9462170310	28.5524634066	24.4230514359
H	9.9377185459	29.7005508721	26.6273780792
H	13.8725413843	27.0113883097	25.2431486427
H	8.1435457034	25.5642577234	23.8558353152

H	9.3640242403	20.9465902031	25.2528367327
H	7.2919635291	22.0100449996	26.1387601500
H	10.1425999310	24.4712987562	22.8923380576
H	3.5462117699	23.6558443243	20.0971563628
H	7.9479564537	22.4113485324	22.1209037614
H	5.8785421277	21.3645661815	22.9302656868
H	5.6716862570	24.6640785888	19.2527421896
H	10.0190026537	16.6696823596	7.5035960356
H	10.6766656445	15.4676295242	12.2967081243
H	10.5228104848	13.6826740689	10.5741443822
H	10.1328903471	18.4506753718	9.2249216212
H	15.1652718045	12.2350406068	20.5273714448
H	19.7064110950	13.4771740316	18.8984486191
H	19.4471205368	12.2814751037	21.0552103544
H	15.4271691162	13.4213156578	18.3596801102
H	19.9551864593	17.2040853393	3.5779893549
H	15.6180836114	19.3841273006	4.6057056778
H	16.3819459988	19.2789740745	2.2433921086
H	19.1618517705	17.3235142279	5.8732789377
H	12.8849383650	12.7522932301	18.1957207447
H	9.1580852619	15.2437510233	20.3424076368
H	9.2893892525	12.7690408080	20.5214456701
H	12.8148862310	15.2202384484	18.0146317044
H	3.1543199345	24.7622967994	14.9026513652
H	7.6895544663	26.2219669743	13.5501375673
H	6.1491697902	25.2396341113	11.8649008581
H	4.5818128627	25.8507926747	16.5725269352
H	7.0935367437	20.3188519068	6.0980714298
H	9.5030863006	23.6219369179	8.9353906985
H	7.2611614244	24.1814068419	8.0217113447
H	9.3252618192	19.7665256203	7.0244650092
H	15.9874152690	29.7905721795	26.2222510528
H	19.2292276794	26.0448931459	26.2151591757
H	19.4055768702	27.8151765585	27.9586932227
H	15.7032597822	27.9099701421	24.6197623680
H	24.1479885479	22.8335369552	25.0487222014
H	22.2861268378	27.4242756645	25.3914401963
H	23.7634913355	26.5374366429	27.1982462417
H	22.7076598236	23.7433688225	23.2156082896
H	19.8403109919	16.3818012315	25.4392292882
H	21.7309952291	18.7340873142	21.4980942849
H	22.4863237117	19.3445467131	23.7671997644
H	19.1556957102	15.7142900677	23.1607400573
H	12.7422894184	29.3725099905	4.6832329174
H	16.2110308387	32.7063854726	5.9218396941
H	14.2053113442	33.4349485961	4.6448290681
H	14.7339191611	28.6654123806	5.9884904224
H	22.6428987031	35.2933662036	10.1926607971
H	20.3881032600	37.5116353253	14.0809631220
H	21.4354339592	38.8899964815	12.2420648874
H	21.5908984542	33.9299259628	11.9567795915
H	16.7522266151	36.0313573563	6.6208971623
H	19.1947144556	35.8996721799	10.9416756480
H	18.5372862552	38.0811008023	10.0291870108
H	17.4650508826	33.8951633342	7.5516419125
H	5.6030590295	27.7147877853	7.6645632466

H	10.2448884823	26.0296714474	8.2254596356
H	9.3818272704	26.5766318006	5.9678836260
H	6.4357571677	27.1345023764	9.9175350176
H	13.7807458435	39.5947824625	13.1278660766
H	18.1903864880	37.2230284682	13.1783929942
H	18.0934189899	39.6575794228	13.5479071437
H	13.8396613050	37.1428348402	12.7601617717
H	17.5026583384	22.6113750021	2.8666066914
H	12.7549895807	23.4601604281	4.0653674403
H	13.7572304995	24.5759604163	2.1037157801
H	16.5475114455	21.5964530423	4.9348680518
H	9.9582002343	36.8914027344	14.1732089733
H	10.9071569458	31.9838204301	14.6444535221
H	9.4108843671	33.1661020419	16.2679309095
H	11.3830362115	35.7111248785	12.5156749539
H	6.3620206305	14.6539408043	16.2751433865
H	10.7125710519	16.9799534588	15.4092076099
H	10.6320029289	14.5020861835	15.4718034260
H	6.4750737651	17.1615135868	16.2719793227
H	7.1496192922	18.8723829801	8.9418850166
H	7.3852805989	20.2886236410	13.6902905314
H	7.1935399485	17.8970089458	13.1469789288
H	7.3228945555	21.2741521741	9.5043178805
H	5.3546883074	32.4329025578	19.1636843508
H	3.9592602482	29.2592072195	14.0087058224
H	3.9203731227	24.4380368653	12.5408414490
H	12.6675671576	18.1819525016	4.2177580301
H	17.0474544058	11.6675004182	8.1184447614
H	10.2461631914	14.3071052653	8.1559646279
H	18.5903724342	18.2022479681	1.6992838704
H	21.0067882638	14.6144852737	4.7425823562
H	25.2164478498	17.1660581537	2.8444722418
H	28.4565323405	15.6951927499	7.4553351986
H	30.8869420614	18.9755852357	13.0393754883
H	27.0729355971	17.1515958452	19.2290083006
H	25.7742507458	13.3612594030	14.0896829146
H	16.9493499037	38.2042397068	22.1878696643
H	14.3265852365	34.1687009515	25.8100385599
H	3.7818821628	27.4587843296	20.6890416011
H	3.6512145983	21.9769057045	21.9924159091
H	12.7937650731	10.1518196753	12.8437576196
H	21.4367500676	10.1512824045	17.1493348871
H	17.1847888870	11.6666074237	21.8757954827
H	13.2244743365	14.6143775023	25.2512273164
H	28.1760279163	22.5346597851	23.4005175011
H	24.6374058628	24.2221386243	27.0725249632
H	11.1356257377	11.4973889006	19.4381829909
H	7.0650316492	27.3982776415	5.6624315244
H	6.0553069087	22.5348913941	6.5948475377
H	3.3435778476	18.9768709727	16.9506776579
H	8.4554059262	13.3611352120	15.9042064292
H	7.1555584298	17.1533238726	10.7640584392
H	6.6558958563	24.3236618171	25.4202145944
H	11.8543968691	29.4260421643	28.2036068553
H	30.5776850674	21.9736046737	7.9994060272
H	27.5746952502	24.3233607625	4.5747204888

H	9.5922900938	24.2219037505	2.9250766013
H	23.9839682382	14.3053945351	21.8376413905
H	30.2731228513	29.2601758820	15.9819136866
H	18.3365673037	40.8347763747	16.4981816299
H	22.3870831834	36.9720624715	20.8721631758
H	19.9046765164	34.1683015757	4.1832208337
H	8.9476236839	35.5733191384	16.0381178739
H	9.0174512291	17.1642819207	27.1531138448
H	11.0906392706	24.0611635487	27.7774419634
H	15.8948710709	40.8347458874	13.4948435275
H	11.6605277860	37.7703435906	19.7017830004
H	22.5706989648	37.7700618261	10.2907608048
H	27.2956202282	32.3871417745	19.7155734428
H	28.8763671144	32.4323193382	10.8303713747
H	30.4494447716	27.4574363490	9.3030902220
H	27.1654119216	27.3994561214	24.3332750755
H	22.3809116729	29.4273973462	1.7901155543
H	17.2821212420	38.2032186653	7.8045043747
H	12.4884256043	31.7460403688	3.9736303998
H	21.5626567686	18.1800546919	25.7782855063
H	30.3100206081	24.4357935463	17.4540126335
H	6.9365821334	32.3847334778	10.2762752786
H	16.4696867089	29.7042461046	2.0279562933
H	11.8445331965	36.9701553853	9.1211271932
H	25.2830674627	35.5745810509	13.9534983939
H	23.0944198205	11.4977334956	10.5546646538
H	15.6452982435	18.2021990798	28.2967681312
H	21.7433276608	31.7466097773	26.0215426663
H	17.7620187118	29.7055856630	27.9668125687
H	18.0604499838	24.2384386121	28.3982552813
H	23.1410022011	24.0596790937	2.2174745827
H	16.1627101944	24.2431821634	1.5943178202
H	5.7793145205	15.6941744884	22.5409837670

Table S4. Bader charge analysis of $Au_{191}(SPh\text{-}tBu)_{66}$ (see Methods section, **"***Electronic structure using DFT")*

	Electron gain (+) or loss (-)	
3 Au	0.004	electron gain
23 Au	-0.188	electron loss
63 Au	0.084	electron gain
102 Au	-9.576	electron loss
66 S	7.414	electron gain
66 C_6H_4	5.493	electron gain
66 $C\text{-}(CH_3)_3$	-4.232	electron loss
$Au_{191}(SPh\text{-}tBu)_{66}$ charge	**-1.001**	**electron loss**

REFERENCES

1. Sakthivel, N. A.; Theivendran, S.; Ganeshraj, V.; Oliver, A. G.; Dass, A., Crystal Structure of Faradaurate-279: $Au_{279}(SPh\text{-}tBu)_{84}$ Plasmonic Nanocrystal Molecules. *J. Am. Chem. Soc.* **2017,** *139*, 15450-15459.
2. Dass, A.; Theivendran, S.; Nimmala, P. R.; Kumara, C.; Jupally, V. R.; Fortunelli, A.; Sementa, L.; Barcaro, G.; Zuo, X.; Noll, B. C., $Au_{133}(SPh\text{-}tBu)_{52}$ Nanomolecules: X-ray Crystallography, Optical, Electrochemical, and Theoretical Analysis. *J. Am. Chem. Soc.* **2015,** *137*, 4610-4613.
3. Nimmala, P. R.; Theivendran, S.; Barcaro, G.; Sementa, L.; Kumara, C.; Jupally, V. R.; Apra, E.; Stener, M.; Fortunelli, A.; Dass, A., Transformation of $Au_{144}(SCH_2CH_2Ph)_{60}$ to $Au_{133}(SPh\text{-}tBu)_{52}$ Nanomolecules: Theoretical and Experimental Study. *J. Phys. Chem. Lett.* **2015,** *6*, 2134-2139.
4. Sheldrick, G., SHELXT - Integrated Space-Group and Crystal-Structure Determination. *Acta Cryst.* **2015,** *A71*, 3-8.
5. Sheldrick, G., Crystal Structure Refinement with SHELXL. *Acta Cryst.* **2015,** *C71*, 3-8.
6. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009,** *42*, 339-341.
7. Spek, A., PLATON SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors. *Acta Cryst.* **2015,** *C71*, 9-18.
8. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996,** *77*, 3865-3868.
9. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H., A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010,** *132*, 154104.
10. Hutter, J.; Iannuzzi, M.; Schiffmann, F.; VandeVondele, J., CP2K: Atomistic Simulations of Condensed Matter Systems. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2014,** *4*, 15-25.
11. Lippert, B. G.; Parrinello, J. H.; Michele, A hybrid Gaussian and plane wave density functional scheme. *Mol. Phys.* **1997,** *92*, 477-488.
12. VandeVondele, J.; Hutter, J., Gaussian Basis Sets for Accurate Calculations on Molecular Systems in Gas and Condensed Phases. *J. Chem. Phys.* **2007,** *127*, 114105.
13. Goedecker, S.; Teter, M.; Hutter, J., Separable Dual-space Gaussian Pseudopotentials. *Phys. Rev. B* **1996,** *54*, 1703-1710.
14. Voorhis, T. V.; Scuseria, G. E., A novel form for the exchange-correlation energy functional. *J. Chem. Phys.* **1998,** *109*, 400-410.
15. Voorhis, T. V.; Scuseria, G. E., Erratum: “A novel form for the exchange-correlation energy functional” [J. Chem. Phys. 109, 400 (1998)]. *J. Chem. Phys.* **2008,** *129*, 219901.
16. Nazarov, V. U.; Vignale, G., Optics of Semiconductors from Meta-Generalized-Gradient-Approximation-Based Time-Dependent Density-Functional Theory. *Phys. Rev. Lett.* **2011,** *107*, 216402.
17. Sakthivel, N. A.; Stener, M.; Sementa, L.; Fortunelli, A.; Ramakrishna, G.; Dass, A., $Au_{279}(SR)_{84}$: The Smallest Gold Thiolate Nanocrystal That Is Metallic and the Birth of Plasmon. *J. Phys. Chem. Lett.* **2018,** *9*, 1295-1300.
18. Theivendran, S.; Chang, L.; Mukherjee, A.; Sementa, L.; Stener, M.; Fortunelli, A.; Dass, A., Principles of Optical Spectroscopy of Aromatic Alloy Nanomolecules: $Au_{36-x}Ag_x(SPh\text{-}tBu)_{24}$. *J. Phys. Chem. C* **2018,** *122*, 4524-4531.
19. Chang, L.; Baseggio, O.; Sementa, L.; Cheng, D.; Fronzoni, G.; Toffoli, D.; Aprà, E.; Stener, M.; Fortunelli, A., Individual Component Map of Rotatory Strength and Rotatory Strength Density Plots As Analysis Tools of Circular Dichroism Spectra of Complex Systems. *J. Chem. Theory Comput.* **2018,** *14*, 3703-3714.

20. Sementa, L.; Barcaro, G.; Dass, A.; Stener, M.; Fortunelli, A., Designing ligand-enhanced optical absorption of thiolated gold nanoclusters. *Chem. Commun.* **2015,** *51*, 7935-7938.
21. Baseggio, O.; Fronzoni, G.; Stener, M., A New Time Dependent Density Functional Algorithm for Large Systems and Plasmons in Metal Clusters. *J. Chem. Phys.* **2015,** *143*, 024106.
22. Baerends, E. J.; Ellis, D. E.; Ros, P., Self-consistent Molecular Hartree—Fock—Slater Calculations I. The Computational Procedure. *Chem. Phys.* **1973,** *2*, 41-51.
23. Becke, A. D., Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A* **1988,** *38*, 3098-3100.
24. Perdew, J. P., Density-functional approximation for the correlation energy of the inhomogeneous electron gas. *Phys. Rev. B* **1986,** *33*, 8822-8824.
25. Perdew, J. P., Erratum: Density-functional approximation for the correlation energy of the inhomogeneous electron gas. *Phys. Rev. B* **1986,** *34*, 7406-7406.
26. Gross, E. K. U.; Kohn, W., Time-Dependent Density-Functional Theory. In *Adv. Quantum Chem.*, Löwdin, P.-O., Ed. Academic Press: San Diego, California, 1990; Vol. 21, pp 255-291.
27. Lenthe, E. v.; Baerends, E. J.; Snijders, J. G., Relativistic Regular Two-Component Hamiltonians. *J. Chem. Phys.* **1993,** *99*, 4597-4610.
28. Kresse, G.; Hafner, J., Ab Initio Molecular Dynamics for Liquid Metals. *Phys. Rev. B* **1993,** *47*, 558-561.
29. Kresse, G.; Hafner, J., Ab Initio Molecular-Dynamics Simulation of The Liquid-Metal--Amorphous-Semiconductor Transition In Germanium. *Phys. Rev. B* **1994,** *49*, 14251-14269.
30. Kresse, G.; Furthmüller, J., Efficient Iterative Schemes for Ab Initio Total-Energy Calculations using A Plane-Wave Basis Set. *Phys. Rev. B* **1996,** *54*, 11169-11186.
31. Kresse, G.; Furthmüller, J., Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors using A Plane-Wave Basis Set. *Comp. Mat. Sci.* **1996,** *6*, 15-50.
32. Kresse, G.; Joubert, D., From Ultrasoft Pseudopotentials to The Projector Augmented-Wave Method. *Phys. Rev. B* **1999,** *59*, 1758-1775.
33. Perdew, J. P., *In Electronic Structure of Solids '91*. Akademie Verlag: Berlin, 1991.
34. Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C., Atoms, Molecules, Solids, and Surfaces: Applications of The Generalized Gradient Approximation for Exchange and Correlation. *Phys. Rev. B* **1992,** *46*, 6671-6687.
35. Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C., Erratum: Atoms, Molecules, Solids, and Surfaces: Applications of The Generalized Gradient Approximation for Exchange and Correlation. *Phys. Rev. B* **1993,** *48*, 4978-4978.
36. Grimme, S., Semiempirical GGA-type Density Functional Constructed with a Long-Range Dispersion Correction. *J. Comput. Chem.* **2006,** *27*, 1787-1799.
37. Bader, R. F. W., *Atoms in Molecules: A Quantum Theory*. Oxford University Press: New York, 1994; p 458.
38. Tang, W.; Sanville, E.; Henkelman, G., A Grid-based Bader Analysis Algorithm without Lattice Bias. *J. Phys.: Condens. Matter* **2009,** *21*, 084204.