Electronic Supplementary Information

The smallest triple-ring tubular gold clusters $M_2@Au_{15}$ with M = Mo, W: Stability, electronic property and nonlinear optical response

Nguyen Thi Bao Trang,[1] Minh Triet Dang,[1] Nguyen Thanh Si,[2] Tran Thi Ngoc Thao,[3] Pham Thi Bich Thao,[3] Minh Tho Nguyen,[4,5,*] Pham Vu Nhat[6,*]

[1] *School of Education, Can Tho University, Can Tho, Viet Nam*

[2] *Institute of Environmental Science and Technology, Tra Vinh University, Tra Vinh, Vietnam*

[3] *Department of Physics, Can Tho University, Can Tho, Viet Nam*

[4] *Laboratory for Chemical Computation and Modeling, Institute for Computational Science and Artificial Intelligence, Van Lang University, Ho Chi Minh City, Viet Nam. Email:* ***minhtho.nguyen@vlu.edu.vn***

[5] *Faculty of Applied Technology, School of Technology, Van Lang University, Ho Chi Minh City, Viet Nam*

[6] *Molecule and Materials Modeling Laboratory and Department of Chemistry, Can Tho University, Can Tho, Viet Nam. Email:* ***nhat@ctu.edu.vn***

Computational Methods.

In order to examine the LO and NLO responses of the clusters considered, we compute the permanent dipole moment (μ), along with polarizability (α), first and second hyper-polarizability (β and γ) in their ground state structures. The mathematical formulas for μ, α, β and γ parameters are given by equations (1) – (8) in the Supplementary Information (SI) file (cf. ref. 34 in the main text):

$$\alpha_{iso} = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right) \quad (1)$$

$$\alpha_{aniso} = \left[\frac{\left(\alpha_{xx} - \alpha_{yy}\right)^2 + (\alpha_{xx} - \alpha_{zz})^2 + \left(\alpha_{yy} - \alpha_{zz}\right)^2 + 6\left(\alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{yz}^2\right)}{2}\right]^{1/2} \quad (2)$$

$$\beta_{tot} = \left[\beta_x^2 + \beta_y^2 + \beta_z^2\right]^{1/2} \quad (3)$$

$$\beta_i = \frac{1}{3}\sum_j \left(\beta_{ijj} + \beta_{jji} + \beta_{jij}\right), \quad i,j = \{x,y,z\}$$

$$\beta_{\parallel} = \frac{3}{5}\sum_i \frac{\mu_i \beta_i}{|\mu_i|} \tag{4}$$

$$\beta_{\perp(z)} = \frac{1}{5}\sum_j \left(2\beta_{zjj} - 3\beta_{jzj} + 2\beta_{jjz}\right) \tag{5}$$

$$\gamma_{tot} = \left(\gamma_x^2 + \gamma_y^2 + \gamma_y^2\right)^{1/2} \tag{6}$$

$$\gamma_{\parallel} = \gamma_x + \gamma_y + \gamma_z \tag{7}$$

$$\gamma_i = \frac{1}{15}\sum_j \left(\gamma_{ijji} + \gamma_{ijij} + \gamma_{iijj}\right), \quad i,j = \{x,y,z\}$$

$$\gamma_{\perp} = \frac{1}{15}\sum_i \sum_j \left(2\gamma_{ijji} - \gamma_{iijj}\right), \quad i,j = \{x,y,z\} \tag{8}$$

where α_{ij}, β_{ijk}, and γ_{ijkl} are the tensor components of polarizability, first hyperpolarizability and second hyperpolarizability, respectively.

Table S1. Local and total spin magnetic moment of $Mo_2@Au_{15}$, $W_2@Au_{15}$ and Au_{15} species obtained by TPSS/ cc-pVDZ-PP computations.

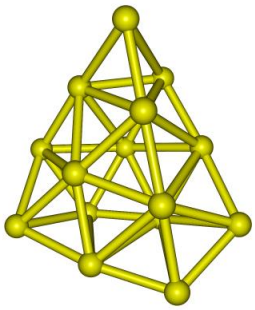
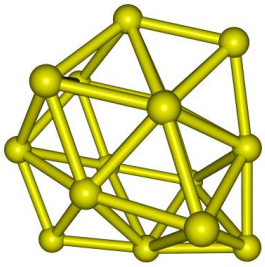
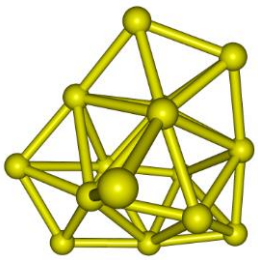
No.	$Mo_2@Au_{15}$		$W_2@Au_{15}$		Au_{15}
1	Au	0.02	Au	0.03	0.05
2	Au	0.03	Au	0.02	0.10
3	Au	0.02	Au	0.03	0.07
4	Au	0.02	Au	0.03	0.03
5	Au	0.02	Au	0.04	0.08
6	Au	0.02	Au	0.04	0.08
7	Au	0.01	Au	0.03	0.08
8	Au	0.02	Au	0.03	0.02
9	Au	0.02	Au	0.03	0.05
10	Au	0.02	Au	0.03	0.06
11	Au	0.02	Au	0.03	0.02
12	Au	0.02	Au	0.03	0.03
13	Au	0.01	Au	0.02	0.13
14	Au	0.02	Au	0.02	0.16
15	Au	0.02	Au	0.03	0.07
16	Mo	0.33	W	0.28	-
17	Mo	0.33	W	0.28	-
Total		1.00		1.00	1.00

Table S2. Wavelength (nm), energy (eV) and absorption coefficient (cm^{-1}) of typical absorption peaks in UV–Vis region.

Species	Energy	Wavelength		Transitions	Absorption coefficient (10^3)
		First peak	Significant peaks		
$Mo_2@Au_{15}^-$	1.58	785		HOMO-2 → LUMO+2	14.55
	4.30		288	HOMO-8 → LUMO+13	84.37
	3.97		312	HOMO-5 → LUMO+13	63.85
	1.90		652	HOMO-3 → LUMO+4	21.65
$Mo_2@Au_{15}$	1.60	777		HOMO → LUMO+4	11.62
	3.42		362	HOMO-11 → LUMO+5	31.45
	3.138		395	HOMO-11 → LUMO+3	31.42
	1.96		631	HOMO-5 → LUMO	19.85
$Mo_2@Au_{15}^+$	1.59	781		HOMO-3 → LUMO+1	14.24
	4.60		272	HOMO-9 → LUMO+11	53.20
	3.58		346	HOMO-10 → LUMO+8	38.85
	2.01		617	HOMO-4 → LUMO+2	19.38
$W_2@Au_{15}^-$	1.41	882		HOMO-2 → LUMO	1.42
	4.16		298	HOMO-7 → LUMO+13	83.04
	3.94		315	HOMO-11 → LUMO+12	47.97
	2.10		591	HOMO-5→ LUMO	22.23
	1.69		734	HOMO-4 → LUMO+2	17.39
$W_2@Au_{15}$	1.58	784		HOMO → LUMO+4	2.35
	3.38		367	HOMO-8 → LUMO+9	39.34
	3.58		346	HOMO-11 → LUMO+6	19.36
	2.17		571	HOMO-5 → LUMO	15.78
$W_2@Au_{15}^+$	1.30	954		HOMO-5 → LUMO+10	1.16
	3.50		355	HOMO-7 → LUMO	57.71
	1.81		689	HOMO-3 → LUMO+3	11.99
	2.16		574	HOMO-4 → LUMO+1	12.81

Au_{17}^-	2.86	434		HOMO-4 → LUMO+7	31.05
	4.24		292	HOMO-6 → LUMO+9	118.82
	3.90		318	HOMO-8 → LUMO+8	88.47
	3.08		402	HOMO-8 → LUMO+5	40.17
Au_{17}	2.25	550		HOMO-3 → LUMO	4.24
	3.52		352	HOMO-1 → LUMO+9	78.86
	3.65		340	HOMO-18 → LUMO+5	74.94
	3.01		412	HOMO-5 → LUMO+4	42.68
Au_{17}^+	1.65	753		HOMO-4 → LUMO	2.70
	4.03		308	HOMO-2 → LUMO+9	60.83
	4.475		277	HOMO-6 → LUMO+9	60.49
	3.187		389	HOMO-8 → LUMO+5	37.64

Table S3. Geometries and Cartesian coordinates (angstrom) of ground-state Au_n^q clusters (n = 15, 17)

 Au_{15}^-	79	-2.944204000	-1.411442000	1.140413000
	79	-0.477067000	-2.449608000	0.839939000
	79	-4.328734000	-0.756278000	-1.237105000
	79	-2.828730000	1.180419000	-0.015206000
	79	-1.647814000	-0.999381000	-1.458712000
	79	-0.109066000	1.268660000	-1.172913000
	79	2.022585000	-3.332235000	0.230818000
	79	1.030887000	-1.214537000	-1.362195000
	79	1.837419000	-0.797320000	1.392233000
	79	-1.015971000	3.017259000	0.731655000
	79	2.673878000	1.159814000	-0.947753000
	79	3.713848000	-1.305265000	-0.703508000
	79	1.397470000	3.593428000	-0.603407000
	79	-0.769856000	0.215908000	1.640585000
	79	1.445356000	1.830578000	1.525157000
 Au_{15}	79	0.000000000	3.684595000	-0.109320000
	79	1.517959000	-1.361336000	-0.326770000
	79	1.517959000	1.361336000	-0.326770000
	79	2.020692000	0.000000000	2.036448000
	79	0.000000000	1.962994000	2.022660000
	79	1.480664000	0.000000000	-2.738139000
	79	-1.517959000	1.361336000	-0.326770000
	79	-1.517959000	-1.361336000	-0.326770000
	79	-2.020692000	0.000000000	2.036448000
	79	-1.480664000	0.000000000	-2.738139000
	79	0.000000000	2.343612000	-2.532804000
	79	0.000000000	-2.343612000	-2.532804000
	79	0.000000000	-1.962994000	2.022660000
	79	0.000000000	0.000000000	3.949389000
	79	0.000000000	-3.684595000	-0.109320000
 Au_{15}^+	79	3.758533000	-0.078485000	-0.276652000
	79	2.758785000	-2.692487000	-0.232294000
	79	1.457397000	-0.637101000	1.138959000
	79	1.400150000	-0.655316000	-1.659148000
	79	0.051674000	-2.769312000	-0.253838000
	79	2.188067000	2.106355000	-0.202582000
	79	0.010657000	-0.108178000	3.376510000
	79	-0.070648000	1.685919000	1.345292000
	79	-0.017091000	1.619920000	-1.776230000
	79	-1.432446000	-0.727531000	1.161217000
	79	-1.367551000	-0.694865000	-1.643844000
	79	-2.661738000	-2.792340000	-0.245717000
	79	-0.062507000	3.887645000	-0.205719000
	79	-2.277160000	2.058141000	-0.265742000
	79	-3.736123000	-0.202366000	-0.260213000
	79	2.164167000	1.434609000	-0.592341000
	79	-1.366821000	-2.317775000	1.923931000
	79	-2.164167000	-1.434609000	-0.592341000

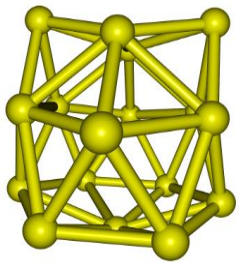
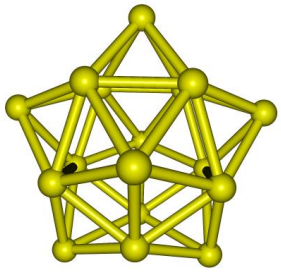
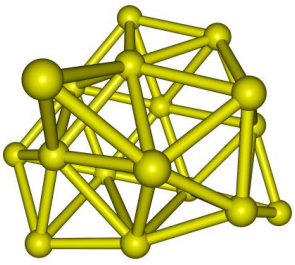
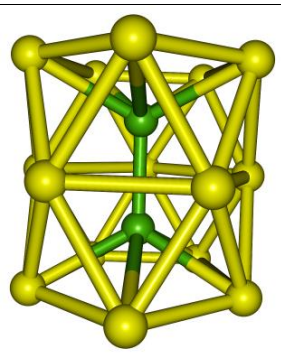
 Au_{17}^{-}	79	0.000000000	-1.427130000	-2.425399000
	79	1.366821000	-2.317775000	1.923931000
	79	2.164167000	-1.434609000	-0.592341000
	79	2.293379000	0.000000000	-2.941478000
	79	-2.741126000	0.000000000	1.702998000
	79	1.366821000	2.317775000	1.923931000
	79	2.741126000	0.000000000	1.702998000
	79	0.000000000	1.427130000	-2.425399000
	79	0.000000000	3.175160000	-0.339440000
	79	-2.293379000	0.000000000	-2.941478000
	79	0.000000000	-3.175160000	-0.339440000
	79	0.000000000	0.000000000	2.680280000
	79	-1.366821000	2.317775000	1.923931000
	79	-2.164167000	1.434609000	-0.592341000
 Au_{17}	79	0.000584000	-0.004088000	2.942091000
	79	1.401061000	-1.882876000	-1.448026000
	79	-2.273633000	3.073080000	0.000000000
	79	-0.048477000	2.369405000	1.482728000
	79	-2.206409000	0.681164000	1.415918000
	79	2.177488000	0.774550000	-1.416379000
	79	2.177488000	0.774550000	1.416379000
	79	3.638060000	-1.120521000	0.000000000
	79	-1.323843000	-1.940985000	1.451228000
	79	1.401061000	-1.882876000	1.448026000
	79	2.145113000	3.166615000	0.000000000
	79	-1.323843000	-1.940985000	-1.451228000
	79	0.000584000	-0.004088000	-2.942091000
	79	-2.206409000	0.681164000	-1.415918000
	79	0.077488000	-3.840385000	0.000000000
	79	-3.587837000	-1.273129000	0.000000000
	79	-0.048477000	2.369405000	-1.482728000
 Au_{17}^{+}	79	-1.891685000	1.220144000	3.064694000
	79	-2.881988000	-2.845755000	-0.050563000
	79	-2.232564000	-0.356569000	0.915966000
	79	-3.952266000	-0.533920000	-1.263903000
	79	-0.253965000	-2.618226000	0.609261000
	79	-0.384921000	1.845720000	0.864233000
	79	0.136982000	-0.505534000	2.386944000
	79	-2.233444000	1.552938000	-1.327380000
	79	-1.274755000	-1.137246000	-1.652211000
	79	2.267716000	-1.651297000	1.182108000
	79	2.008253000	2.846355000	-0.333546000
	79	-0.476361000	3.639548000	-1.242517000
	79	0.483100000	0.965399000	-1.711381000
	79	2.273711000	1.080794000	1.780675000
	79	1.356626000	-1.647731000	-1.563654000
	79	3.122555000	0.367823000	-0.754383000
	79	3.933007000	-2.222442000	-0.904342000

Table S4. Geometries and Cartesian coordinates of $Au_{15}Mo_2^q$ isomers (angstrom).

 **Mo·I**	Anion	79	0.000000000	-2.409817000	2.432655000
		79	0.000000000	2.573277000	0.000000000
		79	-1.416455000	1.949583000	-2.432655000
		79	1.416455000	1.949583000	-2.432655000
		79	-2.291872000	-0.744674000	2.432655000
		79	-2.291872000	-0.744674000	-2.432655000
		79	-1.512534000	-2.081825000	0.000000000
		79	2.291872000	-0.744674000	-2.432655000
		79	0.000000000	-2.409817000	-2.432655000
		79	-2.447332000	0.795186000	0.000000000
		79	2.291872000	-0.744674000	2.432655000
		79	1.416455000	1.949583000	2.432655000
		79	1.512534000	-2.081825000	0.000000000
		79	2.447332000	0.795186000	0.000000000
		79	-1.416455000	1.949583000	2.432655000
		42	0.000000000	0.000000000	-1.225500000
		42	0.000000000	0.000000000	1.225500000
	Neutral	79	2.152112000	1.036286000	2.473874000
		79	-2.311274000	-1.148813000	0.000000000
		79	-1.183348000	-2.092707000	-2.416831000
		79	-2.379120000	0.445358000	-2.365895000
		79	1.617737000	-1.757239000	2.471307000
		79	1.617737000	-1.757239000	-2.471307000
		79	2.549165000	-0.469717000	0.000000000
		79	-0.340208000	2.373622000	-2.436089000
		79	2.152112000	1.036286000	-2.473874000
		79	0.420433000	-2.546517000	0.000000000
		79	-0.340208000	2.373622000	2.436089000
		79	-2.379120000	0.445358000	2.365895000
		79	1.312949000	2.225484000	0.000000000
		79	-1.711943000	1.929198000	0.000000000
		79	-1.183348000	-2.092707000	2.416831000
		42	0.005947000	-0.000259000	-1.207595000
		42	0.005947000	-0.000259000	1.207595000
	Cation	79	2.070188000	1.153320000	2.514083000
		79	-2.233659000	-1.306044000	0.000000000
		79	-1.087441000	-2.137014000	-2.414392000
		79	-2.405204000	0.316495000	-2.316984000
		79	1.681619000	-1.671915000	2.510298000
		79	1.681619000	-1.671915000	-2.510298000
		79	2.587006000	-0.325573000	0.000000000
		79	-0.490697000	2.337008000	-2.449462000
		79	2.070188000	1.153320000	-2.514083000
		79	0.623575000	-2.505814000	0.000000000

		79	-0.490697000	2.337008000	2.449462000
		79	-2.405204000	0.316495000	2.316984000
		79	1.250159000	2.266389000	0.000000000
		79	-1.775586000	1.875252000	0.000000000
		79	-1.087441000	-2.137014000	2.414392000
		42	0.010884000	0.000004000	-1.189819000
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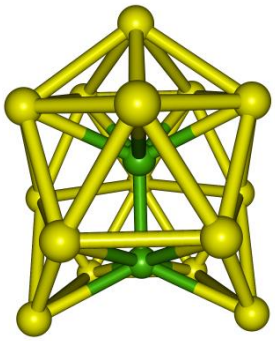
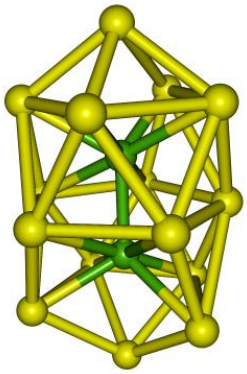
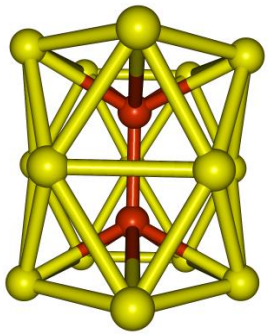
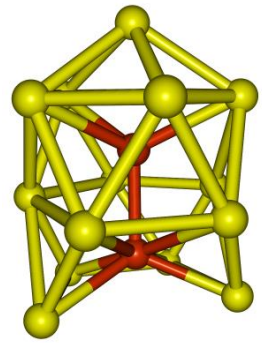
 **Mo·II**	Anion	79	0.051727000	-1.433650000	2.351222000
		42	0.726972000	-0.000003000	-0.048569000
		79	1.529386000	-1.411424000	-2.250816000
		79	-2.367424000	-2.433143000	1.481610000
		79	-0.506139000	-2.466196000	-0.633516000
		79	2.541460000	0.000005000	2.046554000
		79	0.051725000	1.433660000	2.351216000
		79	2.121665000	-2.274779000	0.459983000
		79	3.527717000	0.000000000	-0.739601000
		79	-2.367428000	2.433145000	1.481604000
		79	-3.144364000	-1.433469000	-1.080687000
		79	2.121662000	2.274781000	0.459974000
		42	-1.589510000	0.000000000	0.631411000
		79	-0.506140000	2.466193000	-0.633520000
		79	-0.980300000	-0.000003000	-2.272377000
		79	-3.144365000	1.433463000	-1.080690000
		79	1.529384000	1.411418000	-2.250820000
	Neutral	79	-0.092820000	1.459638000	2.316008000
		42	-0.701457000	0.000001000	-0.023466000
		79	-1.556436000	1.407140000	-2.222952000
		79	2.367485000	2.389621000	1.551188000
		79	0.528956000	2.450522000	-0.659094000
		79	-2.525822000	-0.000002000	2.021176000
		79	-0.092819000	-1.459641000	2.316006000
		79	-2.096207000	2.298603000	0.438136000
		79	-3.521763000	0.000000000	-0.679988000
		79	2.367488000	-2.389618000	1.551187000
		79	3.150574000	1.445999000	-1.097738000
		79	-2.096206000	-2.298604000	0.438133000
		42	1.619442000	0.000001000	0.600359000
		79	0.528958000	-2.450521000	-0.659094000
		79	0.956430000	-0.000001000	-2.298979000
		79	3.150575000	-1.445997000	-1.097738000
		79	-1.556436000	-1.407139000	-2.222953000
	Cation	79	-0.094817000	1.470833000	2.318915000
		42	-0.680316000	0.000002000	-0.028474000
		79	-1.584477000	1.408175000	-2.218244000
		79	2.355634000	2.367231000	1.548779000
		79	0.528552000	2.448388000	-0.709465000
		79	-2.503294000	-0.000002000	2.015415000

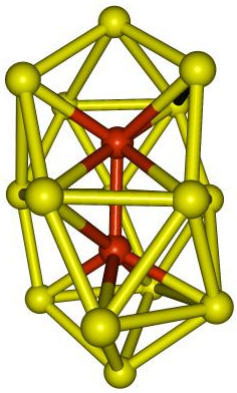
		79	-0.094817000	-1.470834000	2.318913000
		79	-2.080786000	2.301400000	0.454678000
		79	-3.521369000	0.000000000	-0.657490000
		79	2.355635000	-2.367230000	1.548778000
		79	3.162537000	1.442185000	-1.074618000
		79	-2.080786000	-2.301399000	0.454677000
		42	1.584944000	0.000001000	0.601677000
		79	0.528552000	-2.448387000	-0.709465000
		79	0.970435000	-0.000002000	-2.302751000
		79	3.162538000	-1.442184000	-1.074618000
		79	-1.584477000	-1.408174000	-2.218244000
 **Mo·III**	Anion	79	-2.547939000	-0.322711000	2.256756000
		79	-0.004498000	0.787352000	2.425667000
		79	-2.652498000	0.084927000	-2.251009000
		79	0.076421000	-1.963792000	-1.412970000
		79	0.022750000	0.753042000	-2.415390000
		79	-0.125944000	-1.950493000	1.458278000
		79	-2.499319000	-2.215975000	-0.213205000
		42	-1.242221000	0.138549000	-0.006333000
		42	1.242203000	0.118736000	0.031087000
		79	2.461647000	-2.231145000	0.339625000
		79	-2.698767000	2.322582000	0.134180000
		79	2.693020000	0.289145000	2.241570000
		79	2.725748000	2.262820000	-0.316408000
		79	2.527996000	-0.464599000	-2.224424000
		79	0.020267000	2.612686000	-0.037866000
		79	4.259376000	-0.085067000	-0.051199000
		79	-4.258252000	-0.015556000	0.053234000
	Neutral	79	2.274194000	-1.682812000	-1.922214000
		79	-0.397570000	-0.925308000	-2.322768000
		79	2.724029000	0.976154000	1.797013000
		79	0.389680000	-0.519034000	2.411683000
		79	0.232158000	2.223885000	1.250116000
		79	0.040694000	-2.477762000	0.151221000
		79	2.634508000	-1.845141000	1.047956000
		42	1.223653000	0.043863000	-0.231754000
		42	-1.182590000	0.065773000	0.171243000
		79	-2.278130000	-1.143292000	2.224222000
		79	2.416972000	2.327241000	-0.834628000
		79	-2.600160000	-2.051986000	-0.646959000
		79	-2.747358000	0.651059000	-1.935699000
		79	-2.435648000	2.344085000	0.563516000
		79	-0.233373000	1.945750000	-1.683688000
		79	-4.120381000	0.077678000	0.469120000
		79	4.078554000	0.041195000	-0.536718000
	Cation	79	2.087862000	2.557657000	-0.290876000
		79	-0.324185000	2.336822000	1.149334000

		79	2.742571000	-1.921606000	-0.552535000
		79	0.237414000	-1.597052000	-1.815153000
		79	0.324399000	-2.339257000	1.144298000
		79	-0.237293000	1.600548000	-1.812172000
		79	2.289313000	0.388724000	-2.246901000
		42	1.166218000	0.134485000	0.174147000
		42	-1.166207000	-0.134665000	0.173875000
		79	-2.289164000	-0.384354000	-2.247747000
		79	2.614638000	-0.777914000	2.186799000
		79	-2.742289000	1.922932000	-0.548785000
		79	-2.614952000	0.773485000	2.188169000
		79	-2.087972000	-2.556883000	-0.295701000
		79	-0.000234000	-0.003133000	2.762897000
		79	-4.027178000	-0.528848000	0.095953000
		79	4.027064000	0.528974000	0.097395000

Table S5. Geometries and Cartesian coordinates of $Au_{17}W_2^q$ isomers (angstrom).

 **W·I**	Anion	79	0.000000000	-2.407550000	2.466878000
		79	0.000000000	2.530729000	0.000000000
		79	-1.415123000	1.947749000	-2.466878000
		79	1.415123000	1.947749000	-2.466878000
		79	-2.289717000	-0.743974000	2.466878000
		79	-2.289717000	-0.743974000	-2.466878000
		79	-1.487525000	-2.047403000	0.000000000
		79	2.289717000	-0.743974000	-2.466878000
		79	0.000000000	-2.407550000	-2.466878000
		79	-2.406867000	0.782038000	0.000000000
		79	2.289717000	-0.743974000	2.466878000
		79	1.415123000	1.947749000	2.466878000
		79	1.487525000	-2.047403000	0.000000000
		79	2.406867000	0.782038000	0.000000000
		79	-1.415123000	1.947749000	2.466878000
		74	0.000000000	0.000000000	-1.279042000
		74	0.000000000	0.000000000	1.279042000
	Neutral	79	-0.441060000	-2.349314000	2.485626000
		79	0.506690000	2.485067000	0.000000000
		79	-1.101389000	2.133066000	-2.448579000
		79	1.681250000	1.701531000	-2.497655000
		79	-2.396901000	-0.344912000	2.396597000
		79	-2.396901000	-0.344912000	-2.396597000
		79	-1.745489000	-1.836672000	0.000000000
		79	2.117425000	-1.118812000	-2.498769000
		79	-0.441060000	-2.349314000	-2.485626000
		79	-2.226997000	1.207051000	0.000000000
		79	2.117425000	-1.118812000	2.498769000
		79	1.681250000	1.701531000	2.497655000

		79	1.193906000	-2.248285000	0.000000000
		79	2.530690000	0.354370000	0.000000000
		79	-1.101389000	2.133066000	2.448579000
		74	0.012037000	-0.002483000	-1.262530000
		74	0.012037000	-0.002483000	1.262530000
	Cation	79	2.486792000	2.240348000	-0.812050000
		79	0.000000000	-2.365000000	0.938067000
		79	-2.486792000	-2.240348000	-0.812050000
		79	-2.546800000	-1.436001000	1.888851000
		79	2.322139000	0.000000000	-2.437061000
		79	-2.322139000	0.000000000	-2.437061000
		79	0.000000000	1.593663000	-1.965238000
		79	-2.546800000	1.436001000	1.888851000
		79	-2.486792000	2.240348000	-0.812050000
		79	0.000000000	-1.593663000	-1.965238000
		79	2.546800000	1.436001000	1.888851000
		79	2.546800000	-1.436001000	1.888851000
		79	0.000000000	2.365000000	0.938067000
		79	0.000000000	0.000000000	2.583123000
		79	2.486792000	-2.240348000	-0.812050000
		74	-1.248129000	0.000000000	0.020357000
		74	1.248129000	0.000000000	0.020357000
 **W·II**	Anion	79	0.014467000	1.452380000	2.230385000
		74	-0.864831000	-0.000395000	-0.048353000
		79	-1.652559000	1.397351000	-2.237830000
		79	2.510787000	2.346872000	1.408330000
		79	0.449767000	2.412452000	-0.622133000
		79	-2.489347000	0.007492000	2.167203000
		79	0.020020000	-1.421539000	2.252299000
		79	-2.213646000	2.258475000	0.502101000
		79	-3.641469000	-0.007376000	-0.632583000
		79	2.503348000	-2.344355000	1.418864000
		79	3.148504000	1.445954000	-1.188163000
		79	-2.202985000	-2.257669000	0.522966000
		74	1.626324000	-0.000222000	0.519643000
		79	0.451487000	-2.416730000	-0.609415000
		79	0.892397000	-0.005101000	-2.243035000
		79	3.147523000	-1.451841000	-1.182378000
		79	-1.651590000	-1.415786000	-2.228072000
	Neutral	79	2.233235000	-0.020335000	1.451569000
		74	-0.036644000	-0.818978000	0.000000000
		79	-2.192356000	-1.683996000	1.415958000
		79	1.491312000	2.489083000	2.308083000
		79	-0.649132000	0.483058000	2.412444000
		79	2.107522000	-2.497115000	0.000000000
		79	2.233235000	-0.020335000	-1.451569000
		79	0.494677000	-2.158079000	2.292758000

		79	-0.571269000	-3.615009000	0.000000000
		79	1.491312000	2.489083000	-2.308083000
		79	-1.214615000	3.130449000	1.451860000
		79	0.494677000	-2.158079000	-2.292758000
		74	0.499181000	1.652604000	0.000000000
		79	-0.649132000	0.483058000	-2.412444000
		79	-2.295759000	0.850900000	0.000000000
		79	-1.214615000	3.130449000	-1.451860000
		79	-2.192356000	-1.683996000	-1.415958000
	Cation	79	0.031798000	1.353203000	2.295122000
		74	-0.805276000	-0.008115000	-0.050806000
		79	-1.732154000	1.453670000	-2.148753000
		79	2.459072000	2.274141000	1.500853000
		79	0.516172000	2.388717000	-0.736211000
		79	-2.474825000	0.061645000	2.096170000
		79	-0.056292000	-1.554299000	2.155471000
		79	-2.019955000	2.345826000	0.553676000
		79	-3.620761000	0.078368000	-0.522332000
		79	2.539558000	-2.224457000	1.539207000
		79	3.143130000	1.456280000	-1.210693000
		79	-2.236103000	-2.266825000	0.493594000
		74	1.629559000	0.001589000	0.460787000
		79	0.447106000	-2.435051000	-0.658774000
		79	0.848214000	-0.073444000	-2.314922000
		79	3.126585000	-1.455754000	-1.237606000
		79	-1.743660000	-1.395905000	-2.188836000
 **W·III**	Anion	79	-2.544139000	-1.697117000	1.517119000
		79	-0.010650000	-0.766775000	2.334217000
		79	-2.728202000	1.654065000	-1.553866000
		79	0.014481000	-0.730643000	-2.347629000
		79	-0.005391000	2.046792000	-1.492548000
		79	-0.005678000	-2.407136000	-0.021033000
		79	-2.555841000	-1.619081000	-1.595123000
		74	-1.292740000	0.080957000	-0.002903000
		74	1.291895000	0.079893000	0.001075000
		79	2.538012000	-1.698920000	-1.520858000
		79	-2.709882000	1.582806000	1.630507000
		79	2.563753000	-1.616692000	1.593158000
		79	2.730242000	1.635854000	1.568001000
		79	2.709347000	1.600859000	-1.616790000
		79	0.005363000	2.025803000	1.517733000
		79	4.284757000	-0.081482000	-0.020202000
		79	-4.285379000	-0.079001000	0.009027000
	Neutral	79	2.646192000	2.045095000	-0.660189000
		79	0.222984000	2.348972000	0.879497000
		79	2.493754000	-2.420439000	0.341508000
		79	-0.176982000	-1.454105000	-1.923803000

		79	-0.223831000	-2.342503000	0.894417000
		79	0.178709000	1.442189000	-1.932742000
		79	2.488424000	-0.560146000	-2.207572000
		74	1.271716000	-0.123630000	0.096591000
		74	-1.272075000	0.124636000	0.095373000
		79	-2.487553000	0.549302000	-2.211406000
		79	2.606583000	0.870345000	2.131212000
		79	-2.495390000	2.422090000	0.330322000
		79	-2.606365000	-0.862089000	2.134421000
		79	-2.645303000	-2.048279000	-0.651904000
		79	-0.001200000	0.009404000	2.590856000
		79	-4.184097000	0.211432000	0.052055000
		79	4.184411000	-0.212212000	0.053515000
	Cation	79	-2.715529000	0.781255000	-1.931206000
		79	-0.349956000	-0.756109000	-2.339880000
		79	-2.385477000	-1.218398000	2.155543000
		79	0.198911000	2.064691000	1.443275000
		79	0.353630000	-0.725645000	2.347236000
		79	-0.205397000	2.046142000	-1.469101000
		79	-2.481849000	2.278397000	0.680379000
		74	-1.242873000	0.027688000	0.180305000
		74	1.243641000	0.030087000	-0.182372000
		79	2.477917000	2.273355000	-0.718554000
		79	-2.626879000	-1.987094000	-0.858384000
		79	2.384293000	-1.268004000	-2.125842000
		79	2.631831000	-1.967165000	0.892296000
		79	2.714019000	0.817718000	1.917377000
		79	0.005473000	-2.483329000	0.013557000
		79	4.164592000	0.046275000	-0.384932000
		79	-4.166299000	0.043794000	0.380171000

Table S6. Cartesian coordinates of the dimers $\left(M_2@Au_{15}\right)_2$

$\left(\mathbf{Mo_2@Au_{15}}\right)_\mathbf{2}$	79	1.151767000	0.769652000	-2.336837000
	79	3.489859000	-0.818773000	2.486061000
	79	5.863301000	0.754167000	2.352957000
	79	5.863268000	-2.004791000	1.444334000
	79	1.151704000	2.460140000	0.009874000
	79	5.863170000	2.470987000	0.009890000
	79	3.489810000	2.123592000	-1.529913000
	79	5.863241000	-1.993110000	-1.460374000
	79	5.863284000	0.773051000	-2.346868000
	79	3.489809000	2.111308000	1.546884000
	79	1.151859000	-1.984787000	-1.454167000
	79	1.151840000	-1.996409000	1.438263000
	79	3.489863000	-0.798774000	-2.492450000
	79	3.489886000	-2.617424000	-0.010554000

	79	1.151735000	0.750962000	2.343065000
	42	4.813149000	0.000020000	0.000019000
	42	2.464391000	-0.000098000	0.000021000
	79	-1.151737000	-0.750959000	-2.343069000
	79	-1.151705000	-2.460141000	-0.009887000
	79	-1.151840000	1.996407000	-1.438265000
	79	-1.151858000	1.984785000	1.454166000
	79	-1.151765000	-0.769661000	2.336832000
	42	-2.464391000	0.000097000	-0.000022000
	42	-4.813148000	-0.000018000	-0.000012000
	79	-5.863279000	-0.773033000	2.346880000
	79	-5.863231000	1.993126000	1.460365000
	79	-5.863173000	-2.470983000	-0.009869000
	79	-5.863270000	2.004780000	-1.444346000
	79	-5.863310000	-0.754179000	-2.352943000
	79	-3.489883000	2.617425000	0.010537000
	79	-3.489809000	-2.123590000	1.529918000
	79	-3.489856000	0.798784000	2.492450000
	79	-3.489864000	0.818757000	-2.486064000
	79	-3.489815000	-2.111311000	-1.546877000
$(\mathbf{W_2@Au_{15}})_2$	79	-1.160956000	-2.447878000	0.033761000
	79	-3.526026000	2.584440000	-0.035402000
	79	-5.924369000	2.021386000	1.426469000
	79	-5.923905000	1.981493000	-1.481733000
	79	-1.161030000	-0.724333000	2.338088000
	79	-5.923839000	-0.732051000	2.363515000
	79	-3.526173000	-2.069986000	1.547960000
	79	-5.923770000	-0.796948000	-2.342504000
	79	-5.924129000	-2.473928000	0.034013000
	79	-3.526074000	0.832806000	2.446935000
	79	-1.160778000	-0.788180000	-2.317333000
	79	-1.160758000	1.960536000	-1.465968000
	79	-3.525991000	-2.111918000	-1.490346000
	79	-3.525996000	0.764931000	-2.469112000
	79	-1.160605000	2.000055000	1.411487000
	74	-4.918905000	-0.000051000	-0.000053000
	74	-2.466033000	-0.000001000	-0.000079000
	79	1.160605000	-2.000054000	-1.411487000
	79	1.161030000	0.724334000	-2.338086000
	79	1.160758000	-1.960537000	1.465968000
	79	1.160779000	0.788180000	2.317335000
	79	1.160956000	2.447879000	-0.033759000
	74	2.466033000	0.000001000	0.000081000
	74	4.918905000	0.000051000	0.000053000
	79	5.924129000	2.473927000	-0.034013000
	79	5.923771000	0.796945000	2.342504000
	79	5.923838000	0.732053000	-2.363515000

	79	5.923905000	-1.981495000	1.481730000
	79	5.924368000	-2.021384000	-1.426472000
	79	3.525996000	-0.764932000	2.469112000
	79	3.526173000	2.069986000	-1.547961000
	79	3.525991000	2.111919000	1.490347000
	79	3.526026000	-2.584440000	0.035400000
	79	3.526073000	-0.832805000	-2.446934000

0.0 **24.5**

Figure S1. Relative energy (kcal/mol) between the most stable structure (left) and a tube-like form (right) of the anion Au_{15}^{-}.