

Electronic Supplementary Information

## **Structural Isomerism for Gold Nanoclusters**

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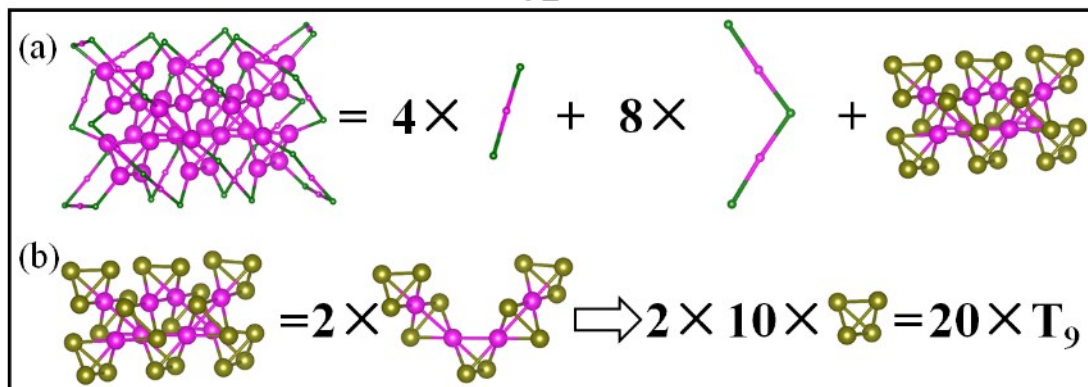
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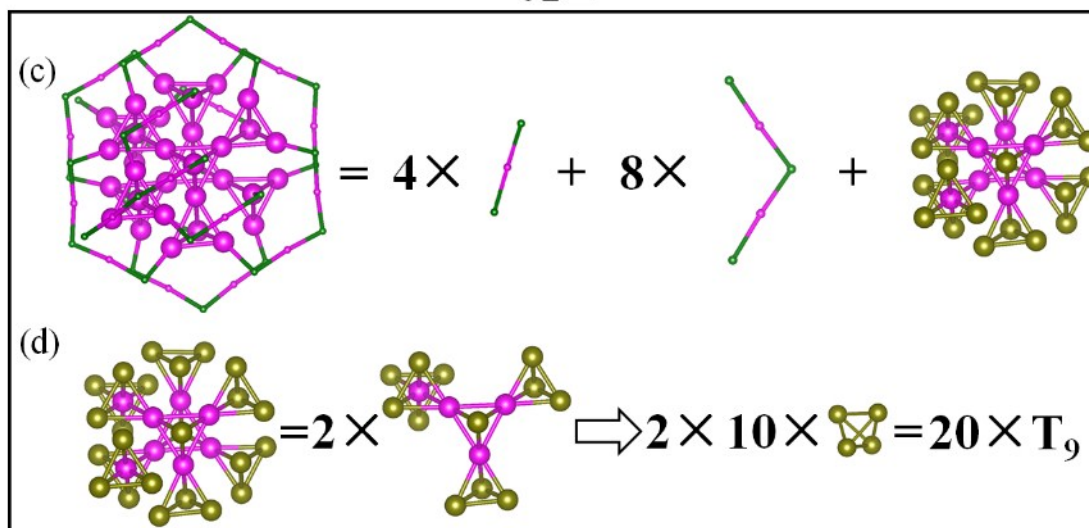
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### Au<sub>52</sub>\_iso1

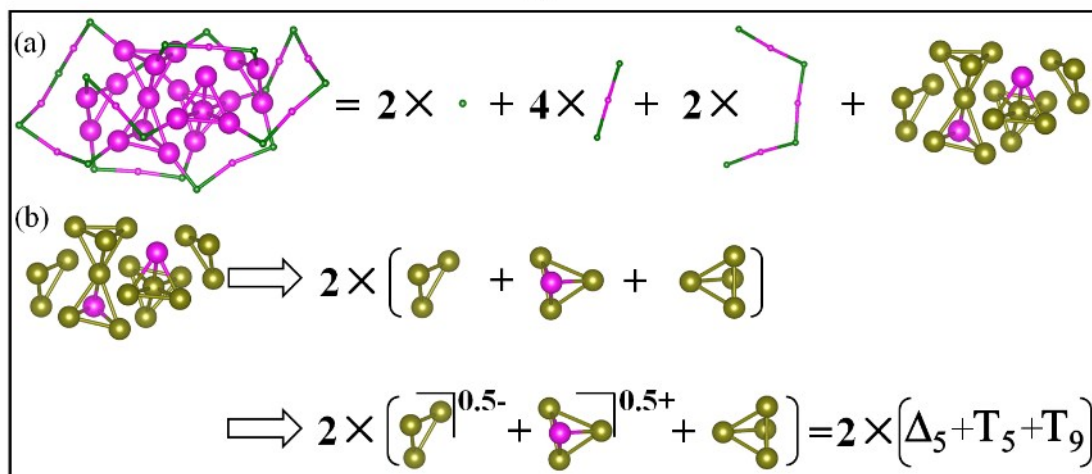


### Au<sub>52</sub>\_iso2

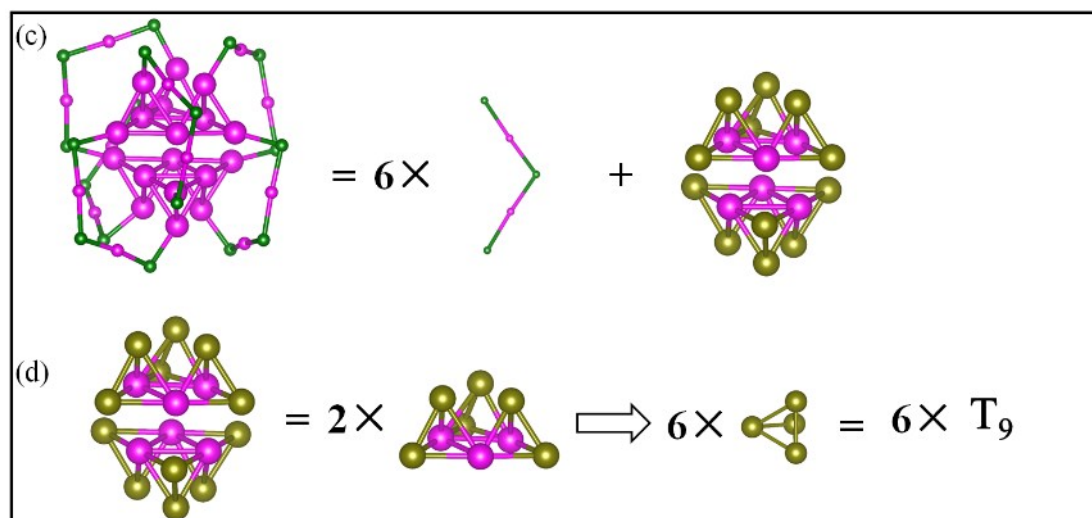


**Figure S1.** The structural decompositions of Au<sub>52</sub>(SR)<sub>32</sub> isomers Au<sub>52</sub>\_Iso1 (a and b) and Au<sub>52</sub>\_Iso2 (c and d). Magenta and dark yellow denote two possible valence states of Au atoms, i.e., 1e and 0.5e. S is represented in dark green. The R groups are omitted for clarity.

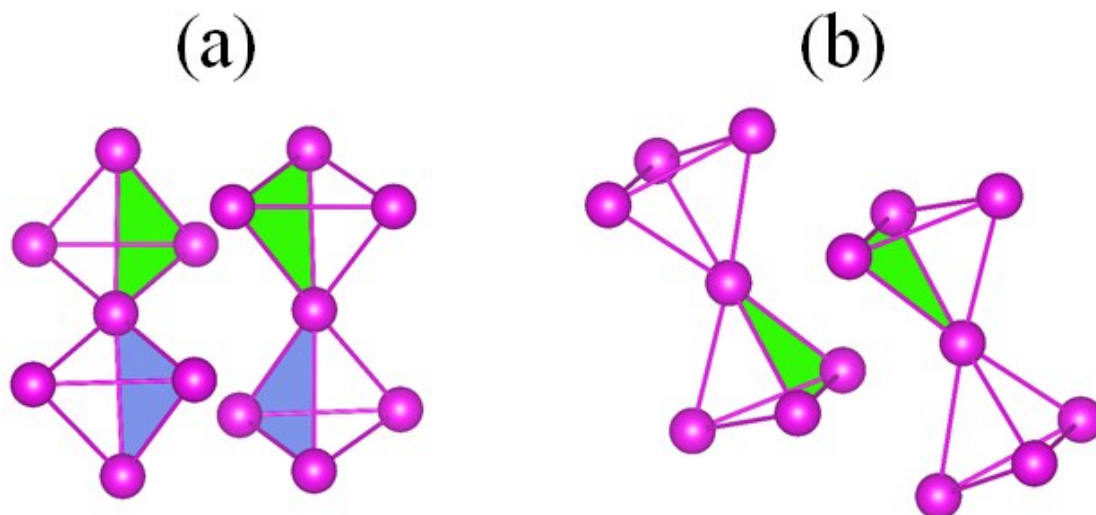
### Au<sub>30</sub>\_iso1



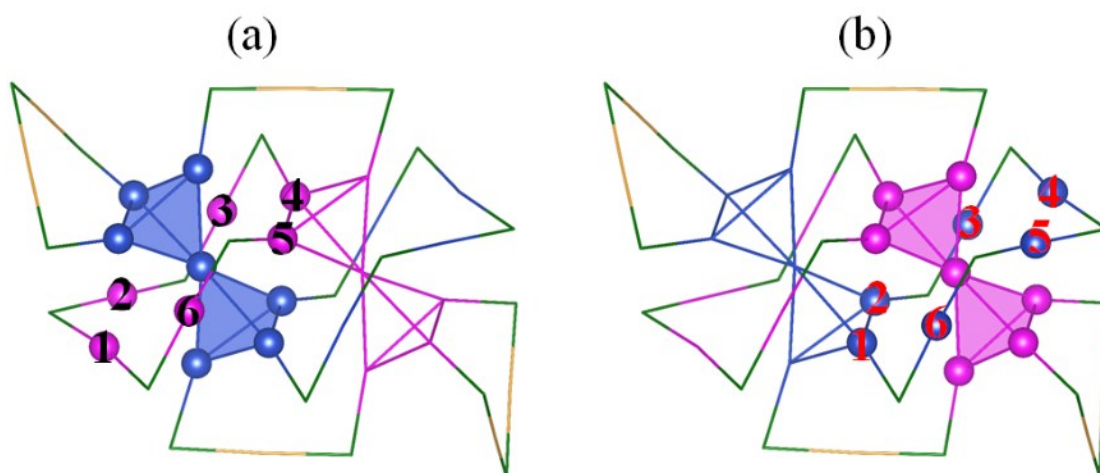
### Au<sub>30</sub>\_iso2



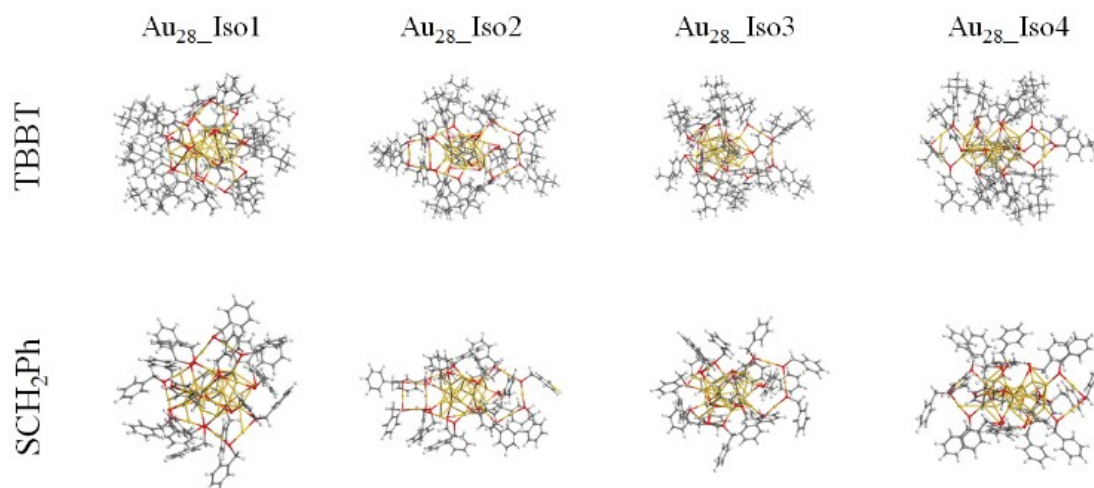
**Figure S2.** The structural decompositions of Au<sub>30</sub>(SR)<sub>18</sub> isomers Au<sub>30</sub>\_Iso1 (a and b) and Au<sub>30</sub>\_Iso2 (c and d). Magenta and dark yellow denote two possible valence states of Au atoms, i.e., 1e and 0.5e. S is represented in dark green. The R groups are omitted for clarity.



**Figure S3.** The structures of two type of Au<sub>14</sub> cores. The same color denotes one Au<sub>4</sub> unit in each Au<sub>7</sub> packing face to face with one Au<sub>4</sub> unit in another Au<sub>7</sub>.



**Figure S4.** (a) The blue  $\text{Au}_7$  and its six surrounded magenta Au atoms (marked by numbers 1, 2, 3,...6) to form a quasi-octahedral  $\text{Au}_{13}$  unit. (b) The magenta  $\text{Au}_7$  and its six surrounded blue Au atoms (marked by numbers 1, 2, 3,...6) to form a quasi-octahedral  $\text{Au}_{13}$  unit. The Au atoms are presented in yellow, wine, and blue, respectively. S is presented in dark green. The R groups are omitted for clarity.



**Figure S5.** The structures of  $\text{Au}_{28\_}\text{Iso1}$ ,  $\text{Au}_{28\_}\text{Iso2}$ ,  $\text{Au}_{28\_}\text{Iso3}$ , and  $\text{Au}_{28\_}\text{Iso4}$  with TBBT and  $\text{SCH}_2\text{Ph}$  ligands. Au, S, C, and H are in gold, red, dark grey, light grey respectively.

Table S1 The vdW and DFT energies of Au<sub>28</sub>\_Iso1, Au<sub>28</sub>\_Iso2, Au<sub>28</sub>\_Iso3, and Au<sub>28</sub>\_Iso4 with TBBT and SCH<sub>2</sub>Ph ligands.

	TBBT		SCH <sub>2</sub> Ph	
	vdW	DFT	vdW	DFT
Au <sub>28</sub> _Iso1	0.00	0.00	0.00	0.34
Au <sub>28</sub> _Iso2	0.80	0.53	0.64	0.03
Au <sub>28</sub> _Iso3	1.19	0.47	0.21	0.00
Au <sub>28</sub> _Iso4	0.50	1.32	0.68	0.21