Doping of Thiolate Protected Gold Clusters through Reaction with Metal Surfaces

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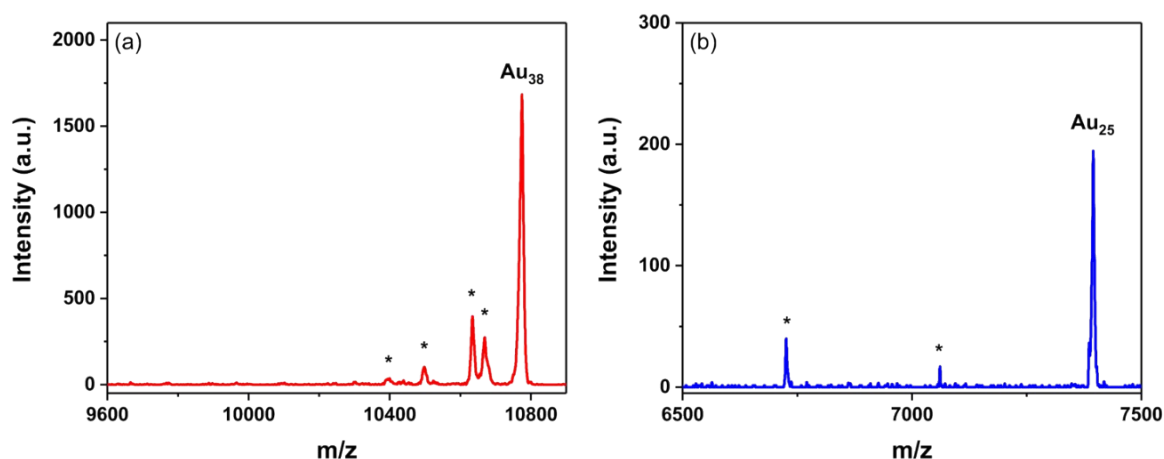Corresponding author: Thomas.Buergi@unige.ch

Figure S1. MALDI mass spectra of the pure $Au_{38}(2\text{-PET})_{24}$ (a) and $Au_{25}(2\text{-PET})_{18}$ (b) nanoclusters respectively. The peaks marked with an asterisk correspond to the different fragments of the clusters.
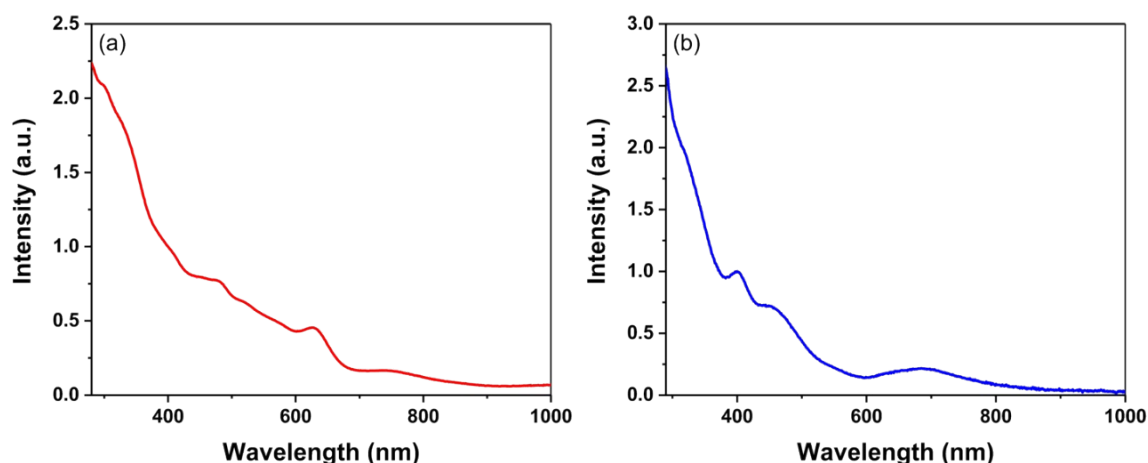
Figure S2. UV-Vis spectra of the pure $Au_{38}(2\text{-}PET)_{24}$ (a) and $Au_{25}(2\text{-}PET)_{18}$ (b) nanoclusters respectively. The spectra were normalized at 400 nm.

Estimation of cluster amount needed

The amount of gold nanoclusters need for the reactions was chosen such that it equals the number of thiolate molecules covering the foil. The latter number was estimated from the known macroscopic surface area by assuming a (111) surface and a c (4 × 2) superlattice structure of the adsorbed thiolates (four thiolates per unit cell).[1]

$$N_{gold\ nanoclusters} = N_{thiolate\ molecules\ on\ the\ surface} \quad (1)$$

The number of thiolate molecules covering the foil's surface can be calculated as follows:

$$N_{thiolate\ molecules/cm^2} = \frac{N_{thiolate\ molecules\ in\ one\ unit\ cell}}{area\ of\ the\ unit\ cell} = \frac{4\ molecules}{0.866 \times 10^{-14} cm^2} = 4.62 \times 10^{14}\ molecules/cm^2 \quad (2)$$

$$Area\ of\ unit\ cell = a \times b = 10\ \text{Å} \times 8.66\ \text{Å} = 86.6\ \text{Å}^2 = 0.866 \times 10^{-14}\ cm^2 \quad (3)$$

Taking into account that the foil's surface area is set to around two cm² in all the experiments, one can calculate the number of thiolate molecules covering the surface and hence the corresponding number of clusters involved in the reaction.

In the case of the Au₂₅(2-PET)₁₈ cluster for example:

$N_{Au25\ nanoclusters} = N_{thiolate\ molecules} = 9.24 \times 10^{14}$ cluster (for 2 cm² foil).
$n_{Au25} = 1.53 \times 10^{-9}$ mol = 1.53 nmol

Nevertheless, in the reaction of the Au_{25} nanocluster with the Cu-2PET modified surface, a total instantaneous (within 2 minutes) decomposition of the cluster was observed when using the exact amount of Au_{25} required (Figure S3). This can be attributed to the instability of the heavily copper doped clusters.[2] Therefore, the reaction was performed by doubling the amount of the cluster needed.
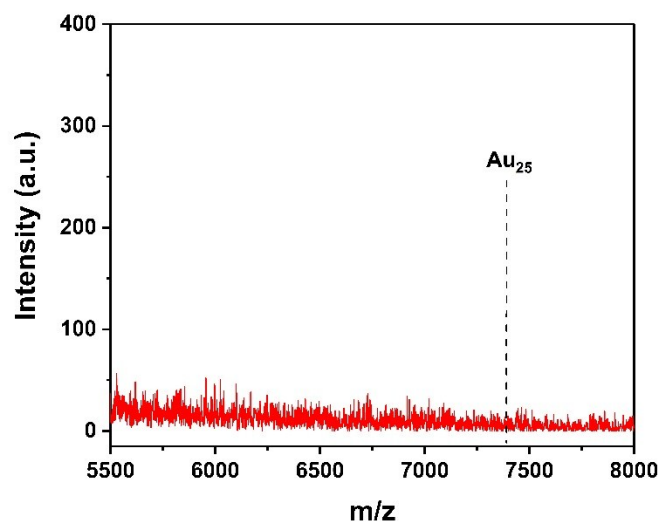
Figure S3. MALDI mass spectrum of the sample taken after two minutes during the reaction of the $Au_{25}(2\text{-PET})_{18}$ with the Cu surface modified by 2PET.

Reaction Time (min)	$\bar{x}$	N of Au atoms exchanged (10^{14})	N of Au Monolayers
0	0	0	0
2	0.9913	9.1214	0.3317
60	1.4624	13.4558	0.4894
180	2.3496	21.6190	0.7863
300	3.0247	27.8303	1.0122
480	3.5329	32.5067	1.1823
1500	4.9766	45.7901	1.6655

Table S1. Variation in the number of gold atoms exchanged and the number of gold monolayers deposited on the surface of the silver foil during the reaction of Au_{25} nanocluster with Ag surface modified by-2PET.

$$N_{Au\ atoms\ exchanged} = \bar{x} \times nb\ of\ gold\ nanocluster\ reacting\ \ (eqt.\ 1)\ \text{(4)}$$

$$N_{Ag\ atoms\ on\ the\ surface} = Area\ of\ the\ foil\ \times\ N_{Ag\ atoms\ on\ Ag\ (111)\ surface}/surface\ area\ \text{(5)}$$

$$N_{Au\ monolayers\ deposited\ on\ foil\ surface} = \frac{N_{Au\ atoms\ exchanged}}{N_{Ag\ atoms\ on\ surface}}\ \text{(6)}$$

Where:

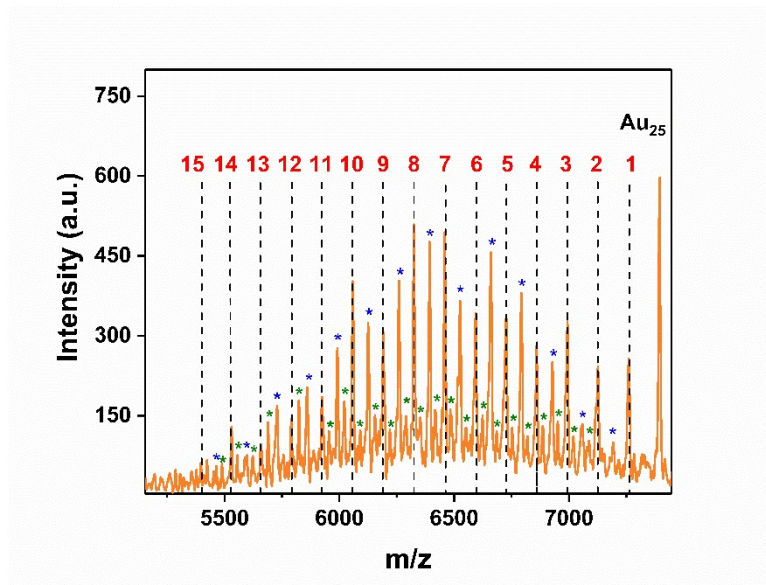$$N_{Ag\ atoms\ on\ Ag\ (111)\ surface} = 13.8 \times 10^{14}\ atoms/cm^2\ \text{[3]}\ \text{and Area of the foil} = 1.99\ cm^2$$

Figure S4. MALDI mass spectrum of $Au_{25-x}Cu_x(2\text{-PET})_{24}$ doped nanoclusters. Number of copper atoms incorporated is marked in red above the corresponding peaks. The peaks marked with a blue correspond to the loss of a Cu atom from each of the doped species. The peaks marked with a green asterisk correspond to the loss of a S atom from the doped species and the fragments (marked in blue) respectively. The sample was taken at one hour reaction time.
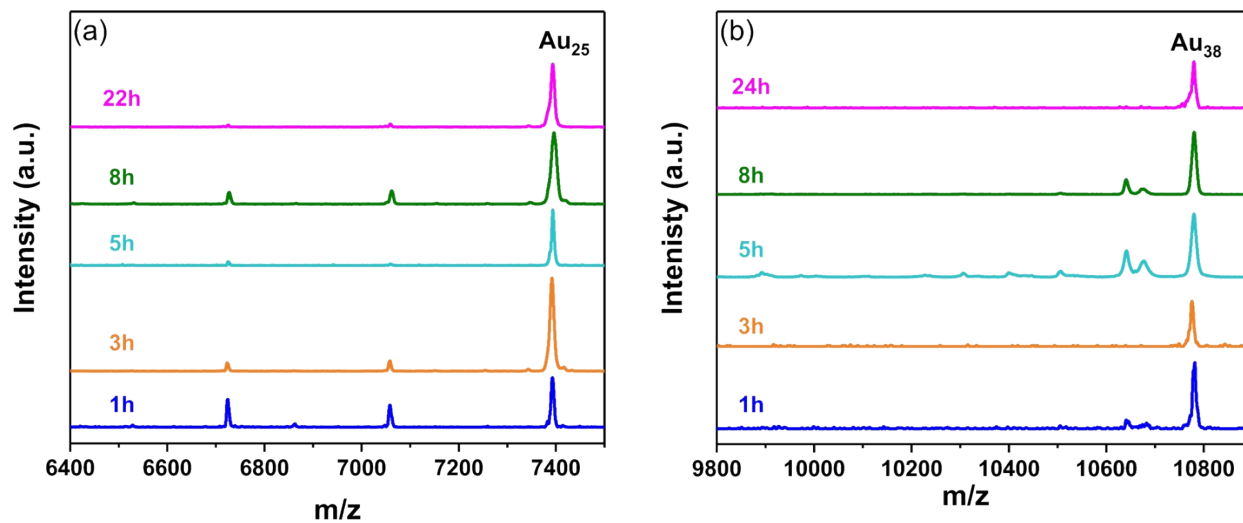

Figure S5. MALDI mass spectra of the samples taken at different times during the reaction of Cu surface (no pre-adsorbed thiol) with $Au_{25}(2\text{-PET})_{18}$(a) and $Au_{38}(2\text{-PET})_{24}$ nanoclusters (b) respectively.
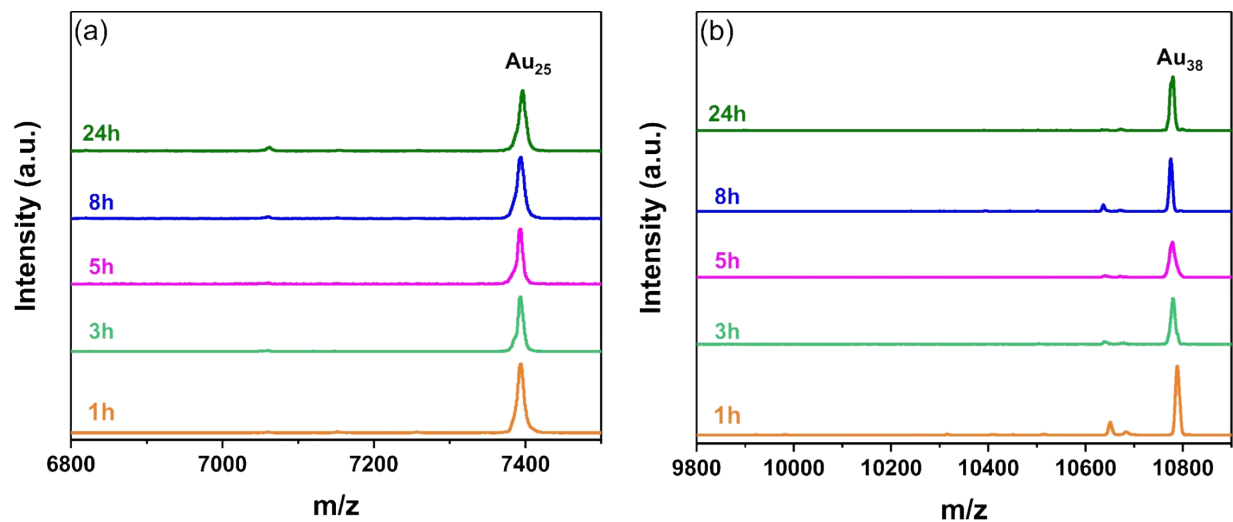
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Figure S6. MALDI mass spectra of the samples taken at different times during the reaction of the Cd surface (no pre-adsorbed thiol) with $Au_{25}(2\text{-PET})_{18}$ (a) and $Au_{38}(2\text{-PET})_{24}$ (b) nanoclusters, respectively.
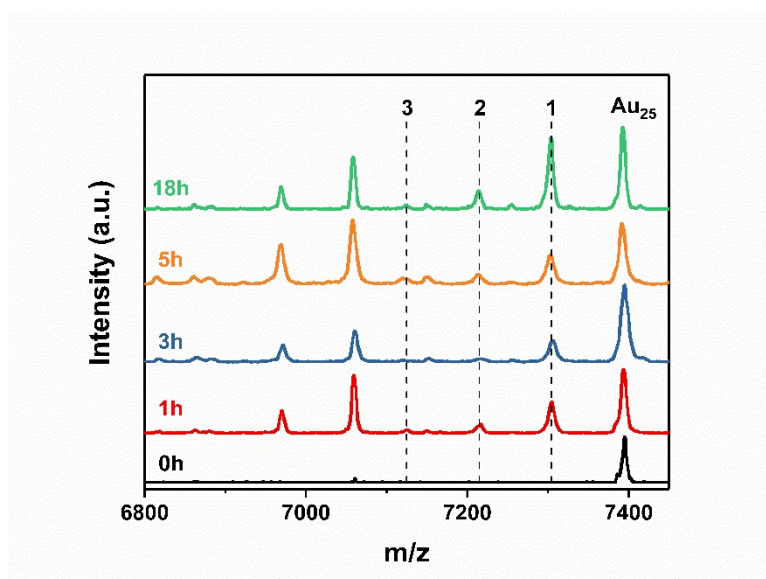

Figure S7. MALDI mass spectra of the samples taken simultaneously with the studied foils at different times during the reaction of $Au_{25}(2\text{-PET})_{18}$ nanocluster with the Ag foil modified by 2-PET. The number of doped Ag atoms is marked in black above the corresponding peak and it is noticed that the doping herein is slower than before due to the gradual removal of the foil pieces from the reaction mixture.
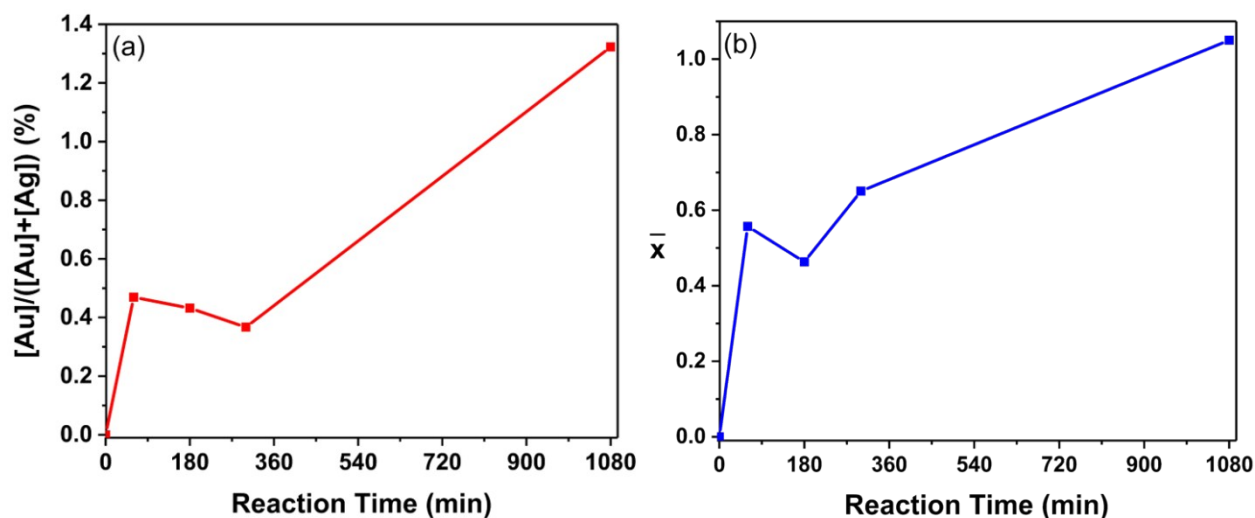
Figure S8. (a) Variation in the [Au]/([Au]+[Ag]) ratio on the surface of the silver foils removed at different reaction times during the reaction between $Au_{25}(2\text{-PET})_{18}$ nanocluster with the Ag foil modified by 2-PET. (b) Variation in the average number of doped Ag atoms ($\bar{x}$) during the reaction as obtained from the MALDI mass spectra in figure S7.

Reaction Time (min)	[S]/[Ag] (%)
60	7.84
180	5.63
300	8.1
1080	12.44

Table S2. Variation in the [S]/[Ag] ratio (%) on the surface during the reaction of $Au_{25}(2\text{-PET})_{18}$ nanocluster with the Ag foil modified by 2-PET. The sulphur/silver atomic concentration ratio (%) on the reference foil is 9.14 %.
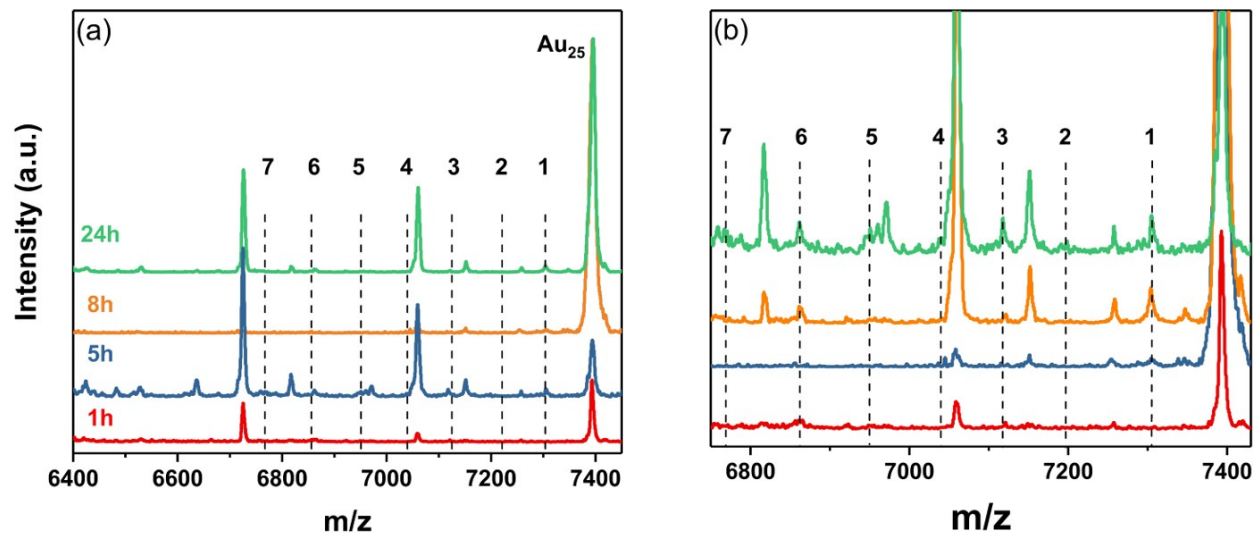

Figure S9. (a) MALDI mass spectra of the samples taken (simultaneously with the studied foils) at different times during the reaction of $Au_{25}(2\text{-PET})_{24}$ nanocluster with the 2-PET free Ag-foil. The number of doped Ag atoms is marked in black above the corresponding peak. (b) Zoom in of the mass spectrum in the range 6750 - 7430 Da with the clear peaks of the different $Au_{25-x}Ag_x$ alloys formed.
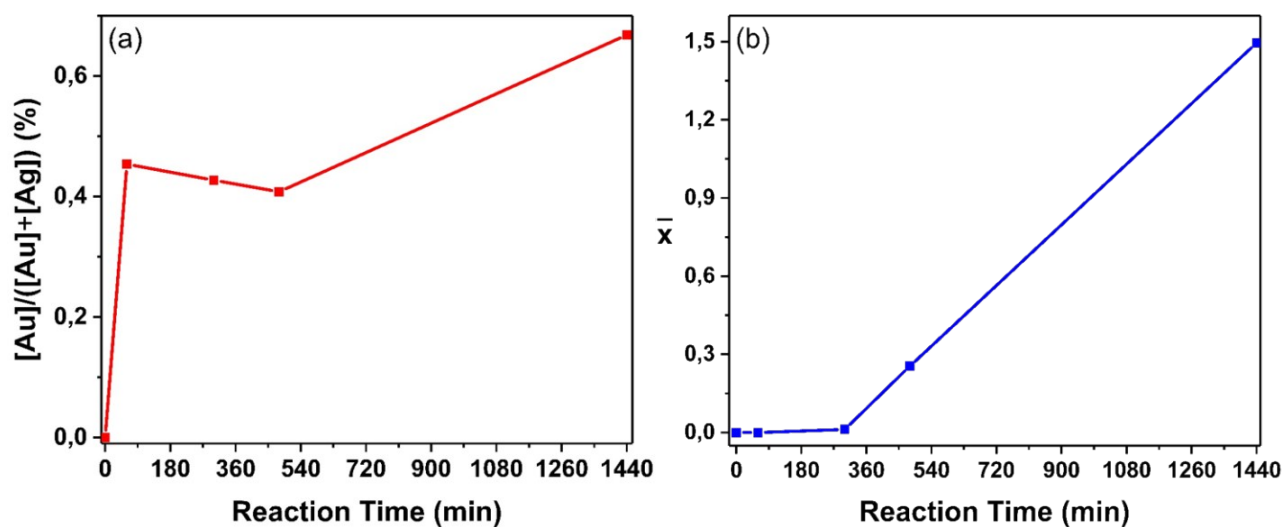
Figure S10. (a) Variation in the [Au]/([Au]+[Ag]) ratio on the surface of the silver foils removed at different reaction times during the reaction between $Au_{25}(2\text{-PET})_{18}$ nanocluster with the 2-PET free Ag-surface. (b) Variation in the average number of doped Ag atoms ($\bar{x}$) during the reaction as obtained from the MALDI mass spectra in Figure S9.

Reaction Time (min)	[S]/[Ag] (%)
60	9.11
300	2.57
480	5.39
1440	3.66

Table S3. Variation in the [S]/[Ag] ratio (%) on the surface during the reaction of $Au_{25}(2\text{-PET})_{18}$ nanocluster with the 2-PET free Ag-foil.
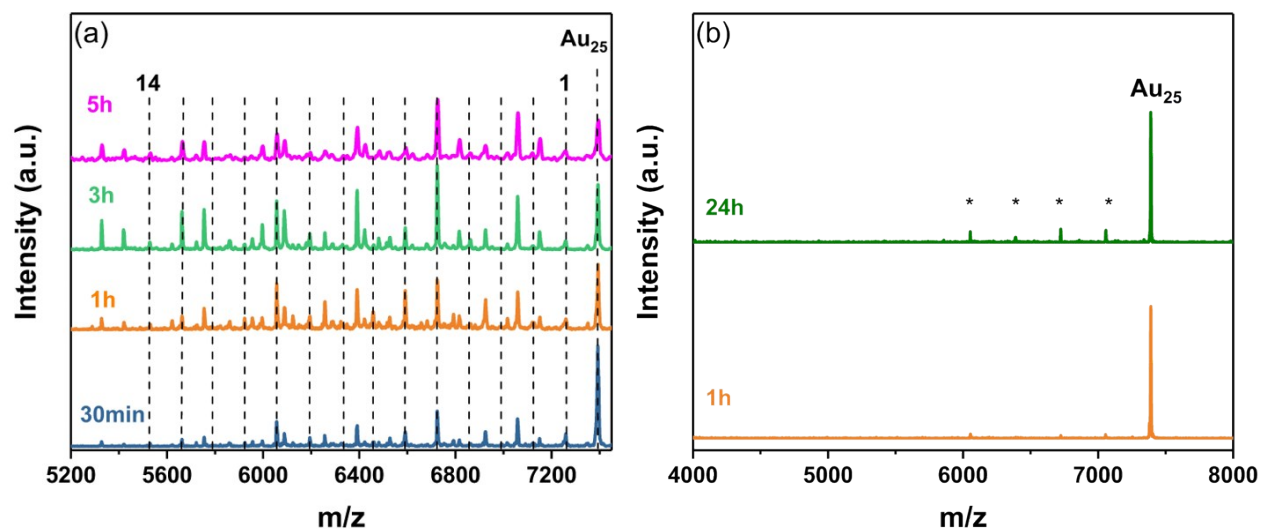

Figure S11. MALDI mass spectra of the samples taken together with the studied foils at different times during the reaction of $Au_{25}(2\text{-PET})_{24}$ nanocluster with the 2-PET modified Cu surface (a) and 2-PET free Cu surface (b) respectively. From right to left, the dashed line marks the peak corresponding to the incorporation of an extra copper atom (a). Peaks marked with an asterisk correspond to the loss of an Au-L unit (b).
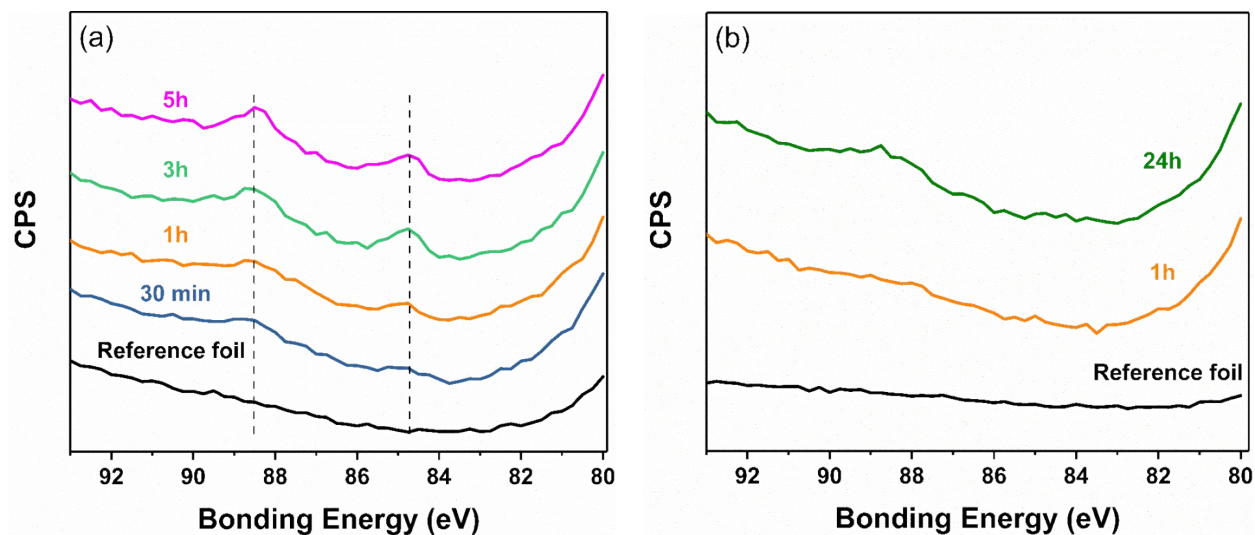
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Figure S12. XPS spectra of the copper substrates taken at different times during the reaction of the Au_{25}(2-PET)$_{18}$ nanocluster with the 2-PET modified Cu foil (a) and Cu foil (without pre-adsorbed 2-PET) (b). The black spectra correspond to the reference unreacted Cu foils modified by 2-PET (a), and 2-PET free (b) respectively.

1. P. Fenter, F. Schreiber, L. Berman, G. Scoles, P. Eisenberger and M. J. Bedzyk, *Surface Science*, 1998, **412-413**, 213-235.
2. Y. Negishi, K. Munakata, W. Ohgake and K. Nobusada, *J. Phys. Chem. Lett.*, 2012, **3**, 2209-2214.
3. M. Pedio, C. Cepek and R. Felici, *In Nobel Metals*, ed. Y. Su, Intech, China, 2012, ch.12, pp. 249-286.