Electronic Supplementary Information

Hydride-Induced Ligand Dynamic and Structural Transformation of Gold Nanoclusters during Catalytic Reaction*

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Supplementary Results and Discussion

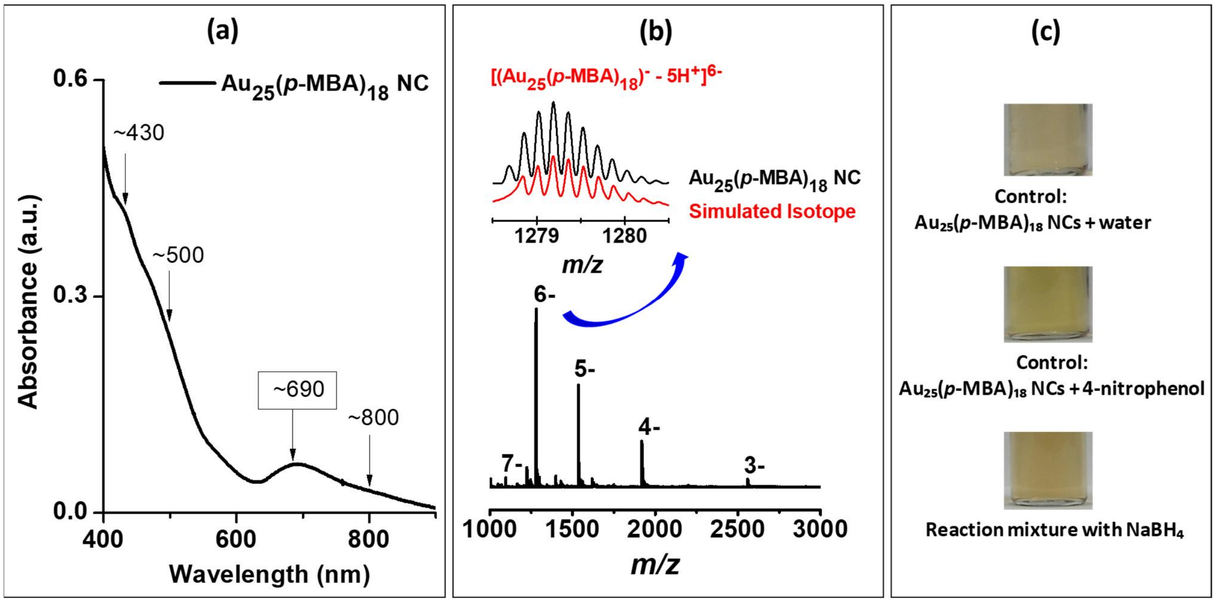

Fig. S1 (a) Characteristic UV-Vis absorption and (b) ESI mass spectrum of Au_{25}(*p*-MBA)$_{18}$ NCs. (c) Digital photos of the catalysts (Au_{25}(*p*-MBA)$_{18}$ NCs), the catalysts with 4-nitrophenol, and the reaction mixture (Au_{25}(*p*-MBA)$_{18}$ + 4-nitrophenol and $NaBH_4$).

UV-Vis absorption spectrum of the concentrated Au_{25}(*p*-MBA)$_{18}$ NCs shows that the clusters exhibit the characteristic UV-Vis absorption peaks (*i.e.,* ~430, ~500, ~690 and ~800) of Au_{25} NCs (Fig. S1a). The Au_{25}(*p*-MBA)$_{18}$ solution also has high purity (Fig. 1b). Images in Fig. 1c show the color of the catalysts in control experiments and the catalytic reaction. As the study was focusing on the structural transformation of Au_{25}(*p*-MBA)$_{18}$ NCs, the amount of the clusters used in the catalytic reaction was high. Therefore, the color of the reaction mixture after the catalytic reaction was not turned into colorless, but into brown Au_{25}(*p*-MBA)$_{18}$ NCs.

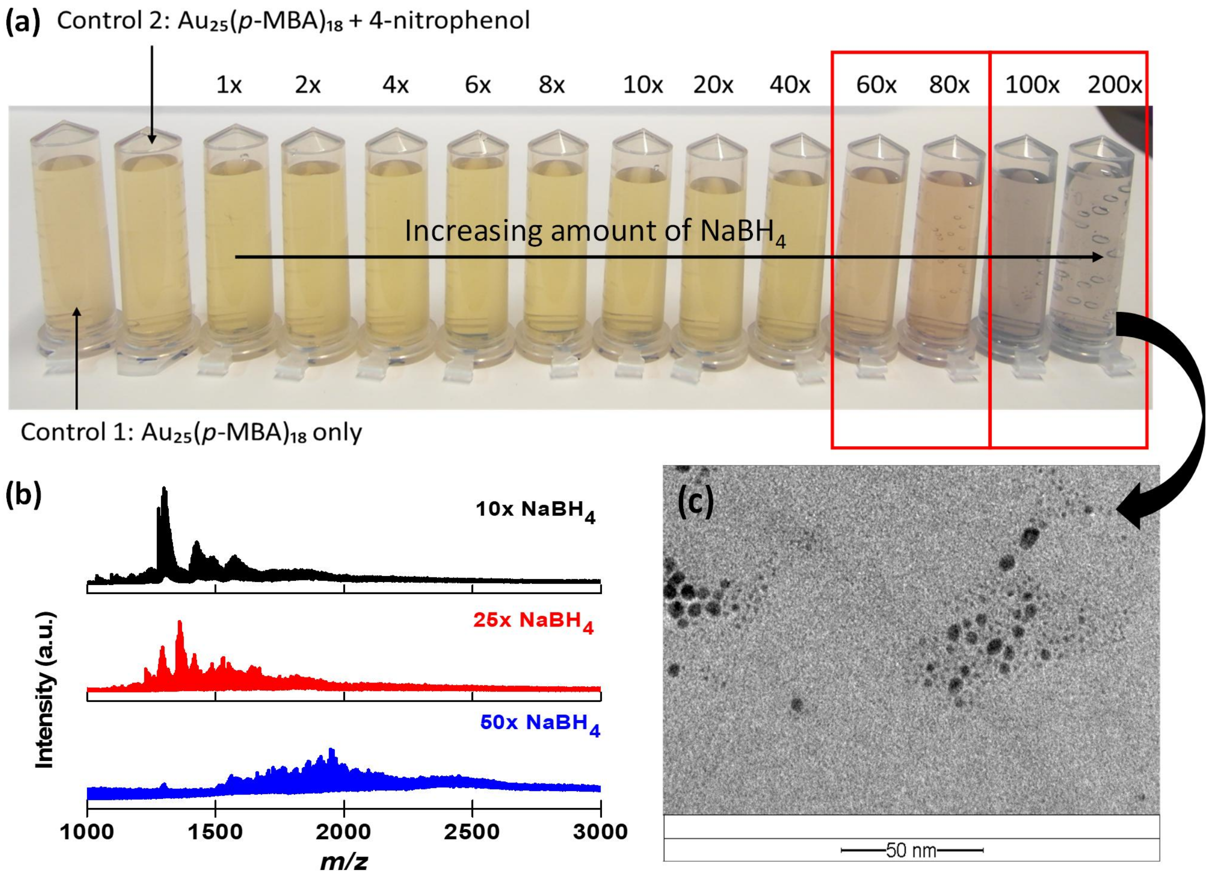

Fig. S2 (a) Images of the reaction solution after the reaction with increasing amount of $NaBH_4$. The reddish solution at 60x and 80x $NaBH_4$ and blackish solution at 100x and 200x $NaBH_4$ suggest formation of plasmon gold nanoparticles (Au NPs). (b) ESI-MS of reaction mixture after 15 minutes of reaction for 10x, 25x and 50x $NaBH_4$. (c) TEM images showing the aggregation of Au NCs into large Au NPs when adding a high amount of $NaBH_4$ (200x)

Based on the optimization study, we selected 25x of $NaBH_4$ as the optimum reaction conditions as the formation of large Au NPs is not obvious and the species of Au NCs can be well observed from the ESI-MS analysis.

Table S1 Detailed molecular formulas of the identified species before catalytic reaction.

#	m/z	Identified species before catalytic reaction
1	~ 503	$[Au(p\text{-MBA})_2]^-$
2	~ 699	$[(Au_4(p\text{-MBA})_4)^0 - 2H^+]^{2-}$
3	~ 874	$[(Au_5(p\text{-MBA})_5)^0 - 2H^+]^{2-}$
4	~ 1095 – 1110	$[(Au_{25}(p\text{-MBA})_{18})^- - (7 + x)H^+ + xNa^+]^{7-}$, x = 0-4
5	~ 1224 – 1235	$[(Au_{28}(p\text{-MBA})_{20})^0 - (7 + x)H^+ + xNa^+]^{7-}$, x = 0-3
6.1	~ 1278 – 1295	$[(Au_{25}(p\text{-MBA})_{18})^- - (5 + x)H^+ + xNa^+]^{6-}$, x = 0-4
7.1	~ 1534 – 1554	$[(Au_{25}(p\text{-MBA})_{18})^- - (4 + x)H^+ + xNa^+]^{5-}$, x = 0-4
8.1	~ 1918 – 1939	$[(Au_{25}(p\text{-MBA})_{18})^- - (3 + x)H^+ + xNa^+]^{4-}$, x = 0-4
9	~ 2558 – 2569	$[(Au_{25}(p\text{-MBA})_{18})^- - (2 + x)H^+ + xNa^+]^{3-}$, x = 0-1
10	~ 138	$[4\text{-nip} - H^+]^{1-}$
11	~ 277	$[2(4\text{-nip}) - H^+]^{1-}$
12	~ 2604 – 2623	$[(Au_{25}(p\text{-MBA})_{18})^- - (2 + x)H^+ + xNa^+ + (4\text{-nip})]^{3-}$, x = 0-1
13	~ 2657 – 2670	$[(Au_{25}(p\text{-MBA})_{18})^- - (2 + x)H^+ + xNa^+ + 2(4\text{-nip})]^{3-}$, x = 1-2

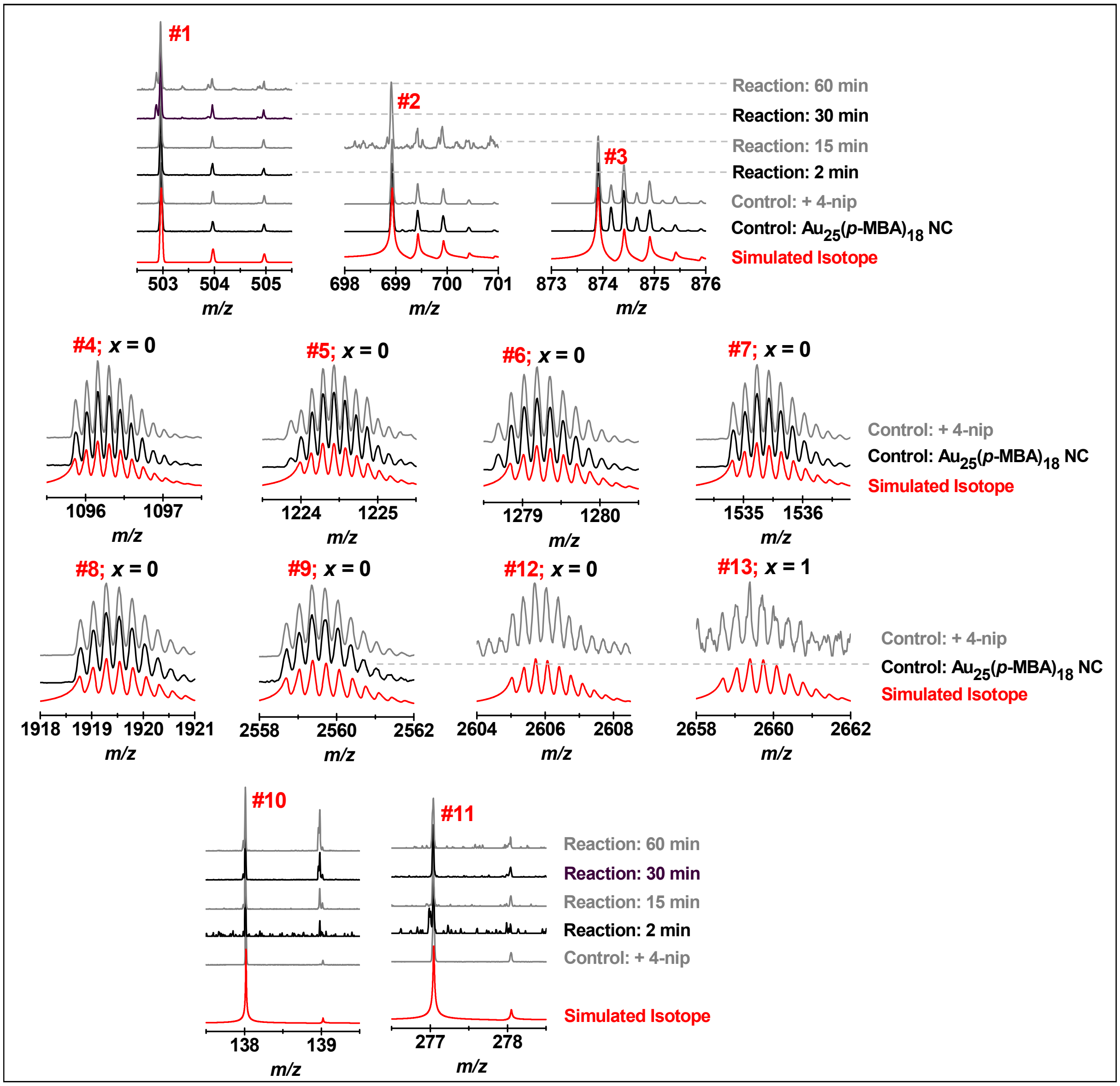

Fig. S3 ESI mass spectra of the identified species #1-13 (before catalytic reaction) with their simulated isotope patterns. Their molecular formulas can be referred to Table S1.

Table S2 Detailed molecular formulas of the identified species after 2 minutes of reaction.

#	m/z	Identified species after 2 minutes of reaction
a	~ 108	$[\text{4-amp} - H^+]^{1-}$
b	~ 153	$[p\text{-MBA} - H^+]^{1-}$
c	~ 351	$[Au(p\text{-MBA})H]^-$
d1	~ 1433 – 1445	$[(Au_{24}(p\text{-MBA})_{16})^{2-} - (3 + x)H^+ + xNa^+]^{5-}$, x = 0-2
d2	~ 1482 – 1493	$[(Au_{25}(p\text{-MBA})_{16}\mathbf{H}_h)^q - xH^+ + yNa^+]^{5-}$, $[h,q,y,z]$ = [0,7,2,0], [-,6,2,2], [+,9,3,0], [-,7,3,4], [0,9,4,0] and [-,8,4,2]
d3	~ 1500 – 1510	$[(Au_{24}(p\text{-MBA})_{17}\mathbf{H}_h)^+ - (6 + x)H^+ + xNa^+]^{5-}$, $[h,x]$ = [8,0], [8,4] and [9,4]
d4	~ 1547 – 1560	$[(Au_{25}(p\text{-MBA})_{18}\mathbf{H}_2)^- - (4 + x)H^+ + xNa^+]^{5-}$, x = 3-5
d5	~ 1564 – 1574	$[(Au_{25}(p\text{-MBA})_{18}\mathbf{H})^- - (4 + x)H^+ + xNa^+]^{5-}$, x = 7-8
d6	~ 1574 – 1598	7 = $[(Au_{25}(p\text{-MBA})_{18})^- - (4 + x)H^+ + xNa^+]^{5-}$, x = 9-14
d7	~ 1667 – 1681	$[(Au_{23}(p\text{-MBA})_{14}\mathbf{H}_4)^- - (3 + x)H^+ + xNa^+]^{5-}$, x = 0,2,6-8
d8	~ 1716 – 1741	$[(Au_{23}(p\text{-MBA})_{15}\mathbf{H}_h)^0 - (2 + x)H^+ + xNa^+]^{4-}$, x = 2,4,6 for h = 4 and x = 5 for h = 2
d9	~ 1744 – 1818	$[(Au_{23}(p\text{-MBA})_{16}\mathbf{H}_h)^- - (3 + x)H^+ + xNa^+]^{4-}$, x = 0-5,7,11 for h = 4 and x = 6-10,12-13 for h = 2
d10	~ 1820 – 1862	$[(Au_{25}(p\text{-MBA})_{15}\mathbf{H}_h)^0 - (4 + x)H^+ + xNa^+]^{4-}$, x = 3-5,7,9 for h = 4 and x = 6,8,10 for h = 2
d11	~ 1863 – 1883	$[(Au_{25}(p\text{-MBA})_{16}\mathbf{H}_h)^+ - (5 + x)H^+ + xNa^+]^{4-}$, x = 4,7 for h = 2 and x = 5 for h = 4
d12	~ 1924 – 1966	$[(Au_{25}(p\text{-MBA})_{18}\mathbf{H}_h)^- - (3 + x)H^+ + xNa^+]^{4-}$, x = 1,5,7 for h = 4 and x = 6,8 for h = 2

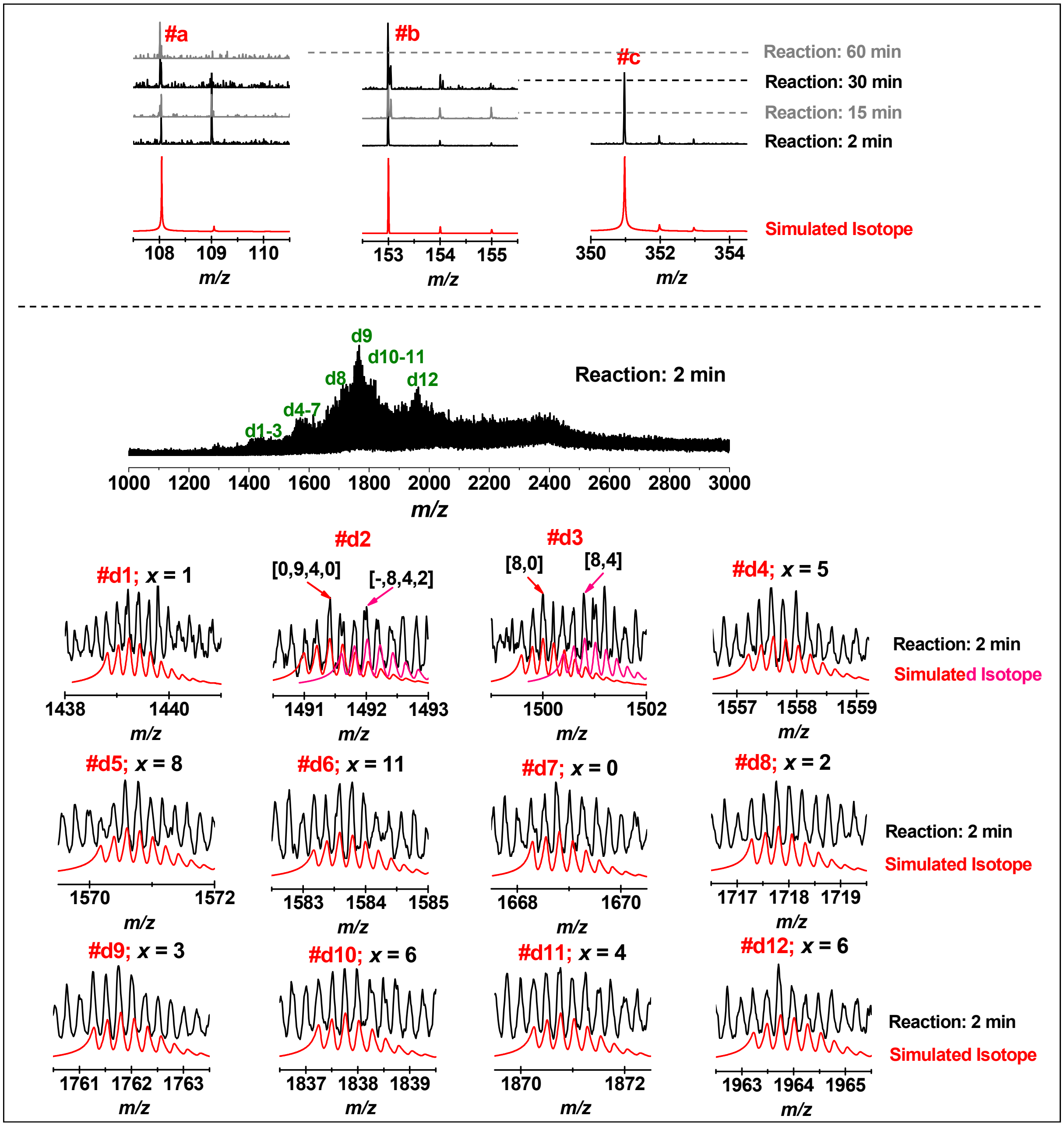

Fig. S4 ESI mass spectra of the identified species #a-c and the detailed identified species of #d with their simulated isotope patterns. Their molecular formulas can be referred to Table S2.

Table S3 Detailed molecular formulas of the identified species after 15 minutes of reaction.

#	m/z	Identified species after 15 minutes of reaction
e	~ 426	$[(Au_2(p\text{-MBA})_3)^{-} - H^+]^{2-}$
f	~ 601	$[(Au_3(p\text{-MBA})_4)^{-} - H^+]^{2-}$
g1	~ 1160 – 1182	$[(Au_{23}(p\text{-MBA})_{16})^{-} - (5 + x)H^+ + xNa^+]^{6-}$, x = 0,2-3,5
g2	~ 1482 – 1493	$[(Au_{25}(p\text{-MBA})_{16}\mathbf{H}_h)^0 - (6 + x)H^+ + xNa^+]^{6-}$, x = 0,2 for h = 1 and x = 1,3-4 for h = 0
g3	~ 1487, 1500	$[(Au_{25}(p\text{-MBA})_{16})^{2+} - (8 + x)H^+ + xNa^+]^{6-}$, x = 5-7
g4	~ 1547 – 1560	$[(Au_{25}(p\text{-MBA})_{17})^0 - (6 + x)H^+ + xNa^+]^{6-}$, x = 2-5
h1	~ 1278 – 1306	$[(Au_{25}(p\text{-MBA})_{18})^0 - (6 + x)H^+ + xNa^+]^{6-}$, x = 2-9
h2	~ 1307 – 1331	$[(Au_{25}(p\text{-MBA})_{17}\mathbf{H}_4)^0 - (6 + x)H^+ + xNa^+ + 2(4\text{-nip})]^{6-}$, x = 2-8
i1	~ 1344 – 1372	$[(Au_{26}(p\text{-MBA})_{19})^0 - (6 + x)H^+ + xNa^+]^{6-}$, x = 2-9
i2	~ 1377 – 1386	$[(Au_{28}(p\text{-MBA})_{18})^{2+} - (8 + x)H^+ + xNa^+]^{6-}$, x = 0-2
j	~ 1402 – 1430	$[(Au_{27}(p\text{-MBA})_{20})^0 - (6 + x)H^+ + xNa^+]^{6-}$, x = 2-9
k	~ 1468 – 1481	$[(Au_{28}(p\text{-MBA})_{20})^0 - (6 + x)H^+ + xNa^+]^{6-}$, x = 11-20
l1	~ 1517 – 1554	$[(Au_{25}(p\text{-MBA})_{17}\mathbf{H}_h)^0 - (5 + x)H^+ + xNa^+]^{5-}$, x = 3 for h = 1, x = 4,6,11 for h = 0 and x = 5,10 for h = 2
l2	~ 1556 – 1567	$[(Au_{25}(p\text{-MBA})_{18}\mathbf{H}_h)^q - xH^+ + yNa^+]^{5-}$, $[h,q,x,y]$ = [+,11,5,0], [-,10,6,1] and [0,12,7,0]
l3	~ 1586 – 1633	$[(Au_{26}(p\text{-MBA})_{18})^0 - (5 + x)H^+ + xNa^+]^{5-}$, x = 3-10
m1	~ 1635 – 1646	$[(Au_{27}(p\text{-MBA})_{18})^{-} - (4 + x)H^+ + xNa^+]^{5-}$, x = 5-7
m2	~ 1648 – 1664	$[(Au_{27}(p\text{-MBA})_{18})^0 - (5 + x)H^+ + xNa^+]^{5-}$, x = 8-11
m3	~ 1665 – 1685	$[(Au_{27}(p\text{-MBA})_{19})^0 - (5 + x)H^+ + xNa^+]^{5-}$, x = 5-9
n	~ 1700 – 1721	$[(Au_{27}(p\text{-MBA})_{20})^0 - (5 + x)H^+ + xNa^+]^{5-}$, x = 6-10

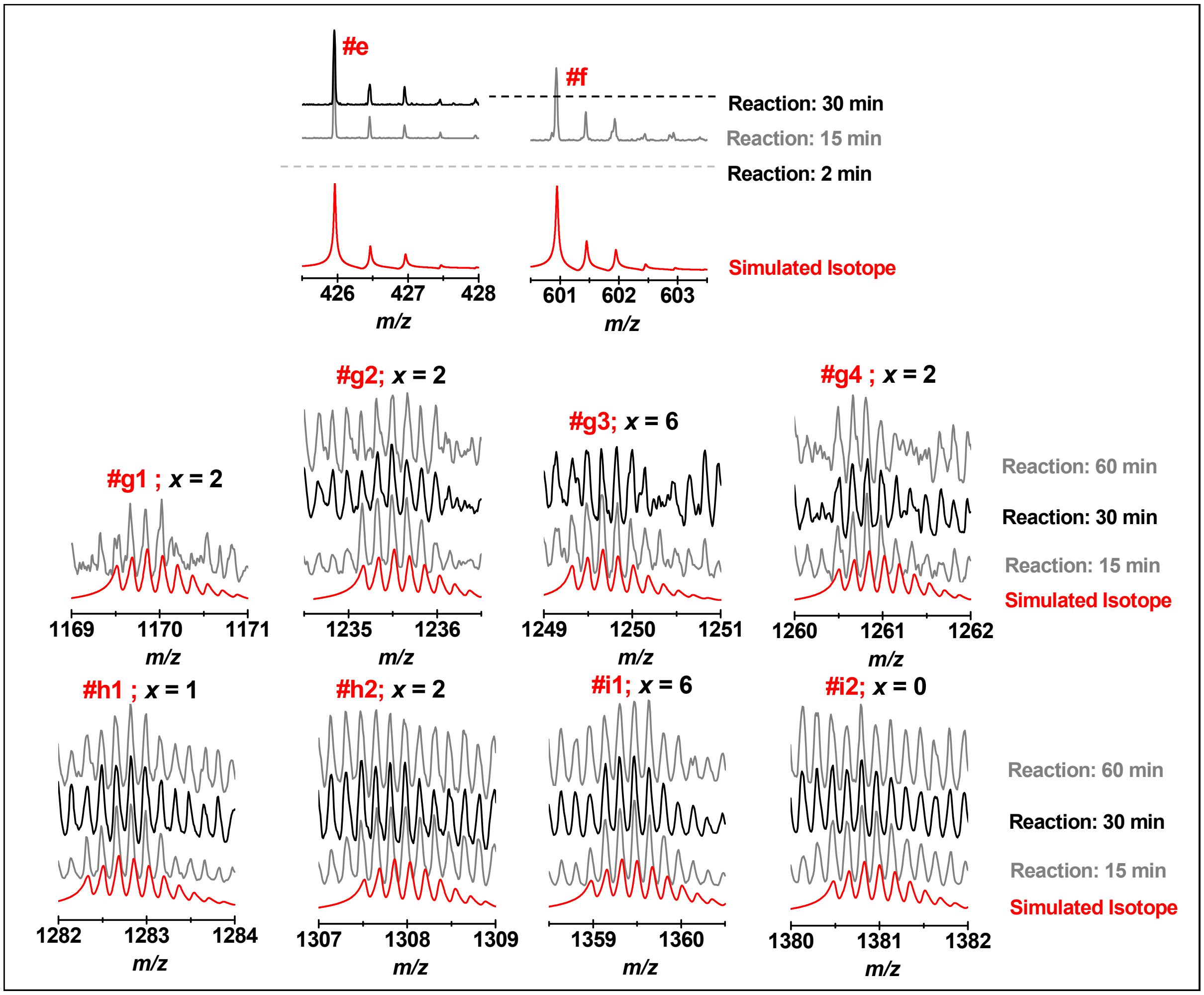

Fig. S5 ESI mass spectra of the identified species #e-i with their simulated isotope patterns. Their molecular formulas can be referred to Table S3.

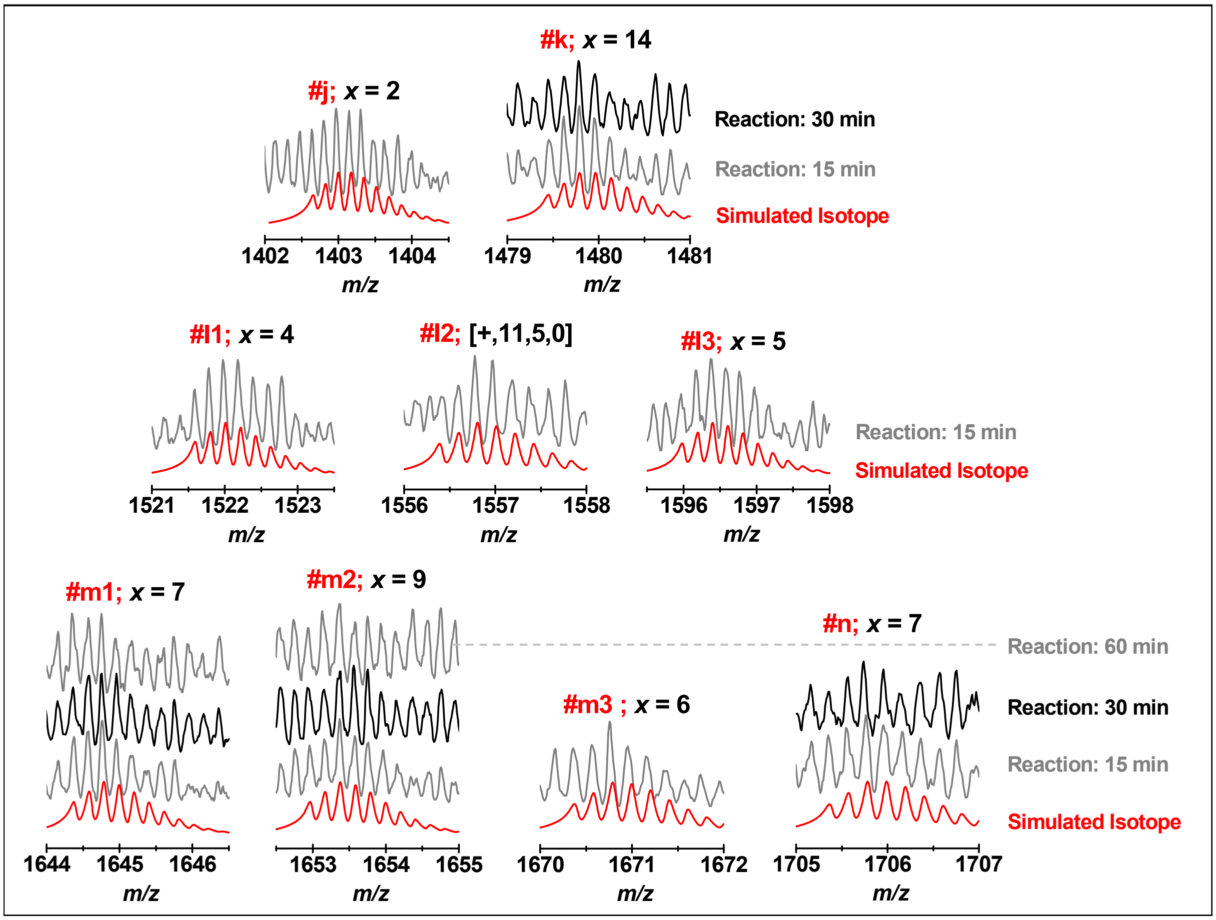

Fig. S6 ESI mass spectra of the identified species #j-n with their simulated isotope patterns. Their molecular formulas can be referred to Table S3.

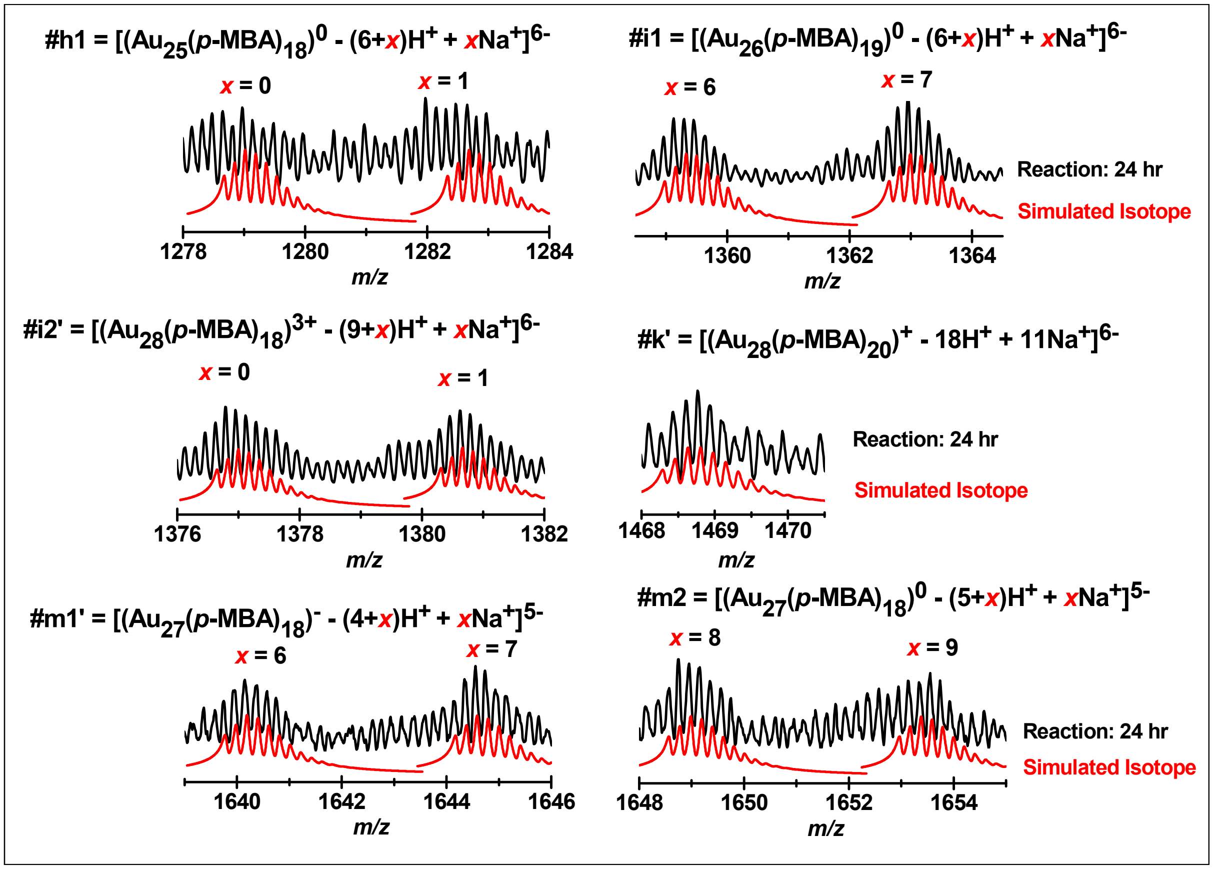

Fig. S7 ESI mass spectra of the identified species #h, i, k, and m (after 24 hours of reaction) with their simulated isotope patterns and molecular formulas.

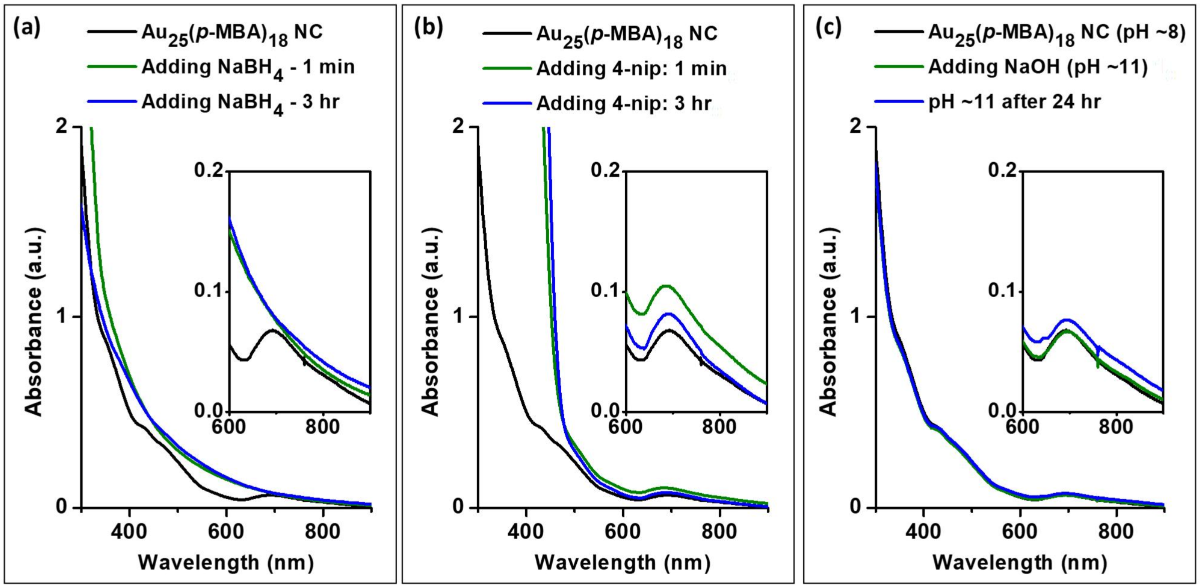

Fig. S8 Factors affecting ligand dynamic and structural transformation of Au_{25}(*p*-MBA)$_{18}$ NCs: (a) $NaBH_4$, (b) 4-nitrophenol, and (c) pH. Mixing condition: 500 rpm; Au_{25}(*p*-MBA)$_{18}$-to-$NaBH_4$ molar ratio of 1:93.75 and Au_{25}(*p*-MBA)$_{18}$-to-4-nitrophenol molar ratio of 1:187.5.

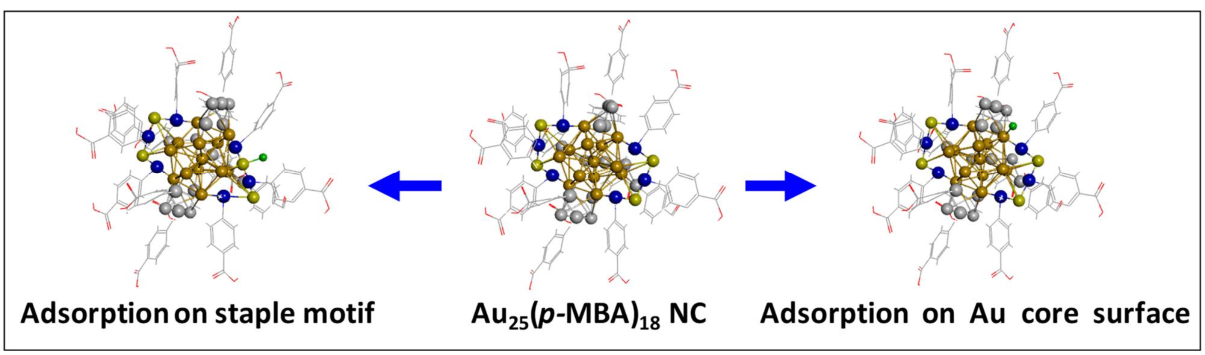

Fig. S9 Possible adsorption sites of hydrides on Au_{25}(*p*-MBA)$_{18}$ NCs. Some of the ligands and front staple motif were hidden to provide a clear view on the hydride adsorption. The green atoms represent the hydride. Other color codes: S atoms (blue), Au atoms at the Au core (gold) and Au atoms at the staple motifs (yellow). Some atoms were hidden or colored with white to increase the visibility of the staple motifs structure. The molecular structures were drawn using BIOVIA Discovery Studio 2016 and the structures were optimized using a generic forcefield, DREIDING.