Metal Exchange Method Using Au25 Nanoclusters as Templates for Alloy Nanoclusters with Atomic Precision

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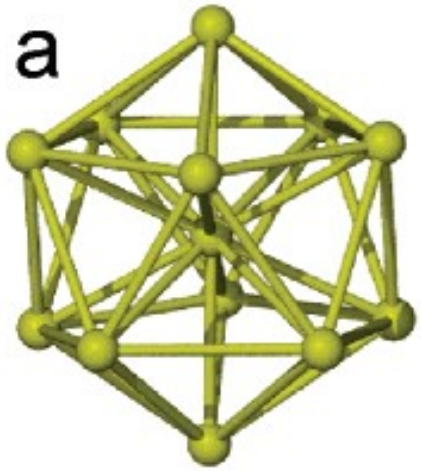
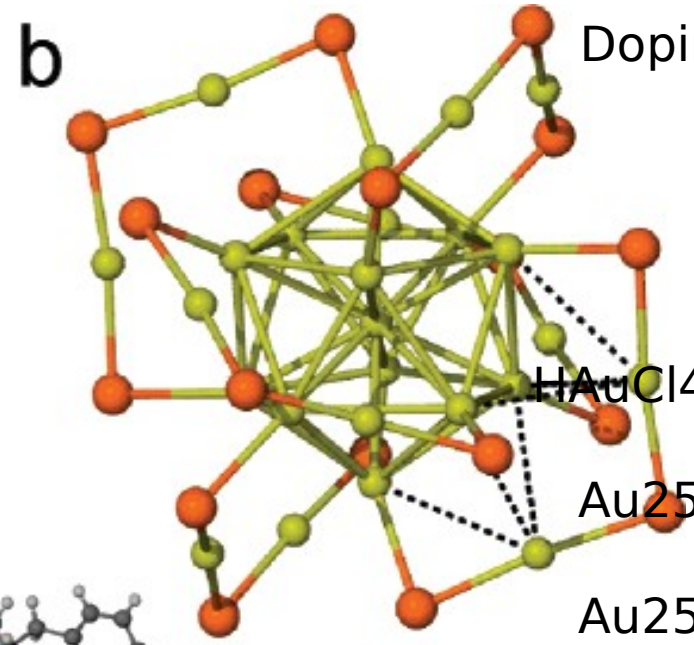
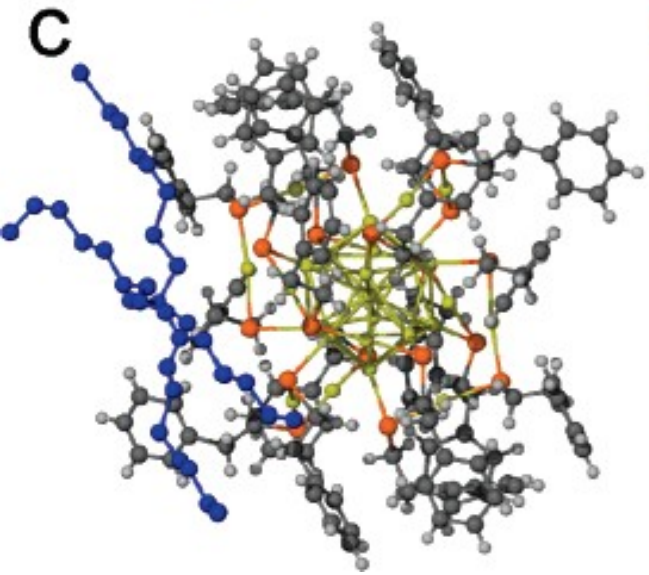
Crystal structure of Au25(SR)18-







Doping of other metals into Au25(SR

Ag, Cu
Pt, Pd

HAuCl4 + Ag+/Cu2+ salts + R-SH + N

Au25(SR)18 + Ag+/Cu2+ salts

Au25(SR)18 + Ag44(FTP)30

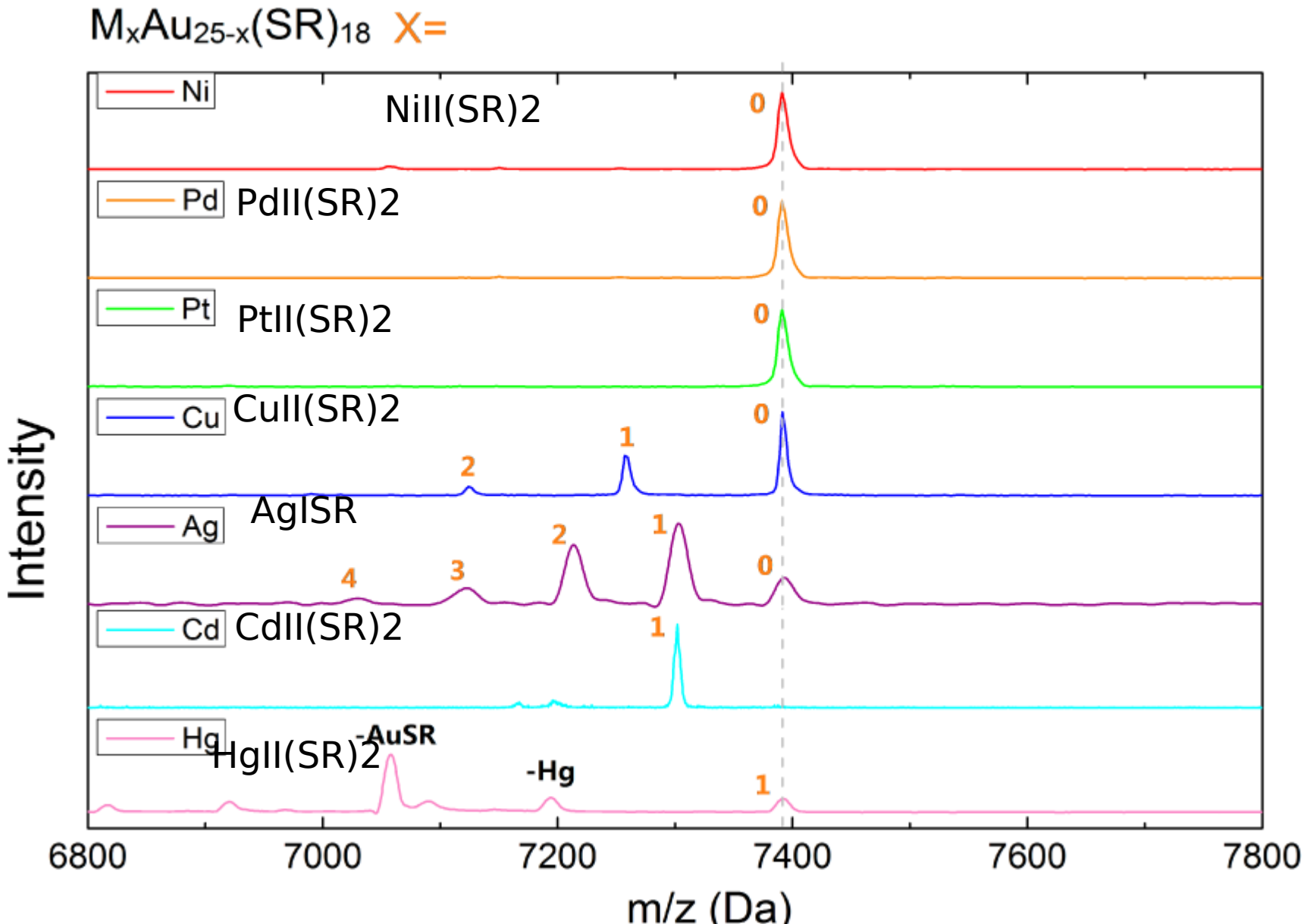
$$n^* = N\,vA - M - z$$

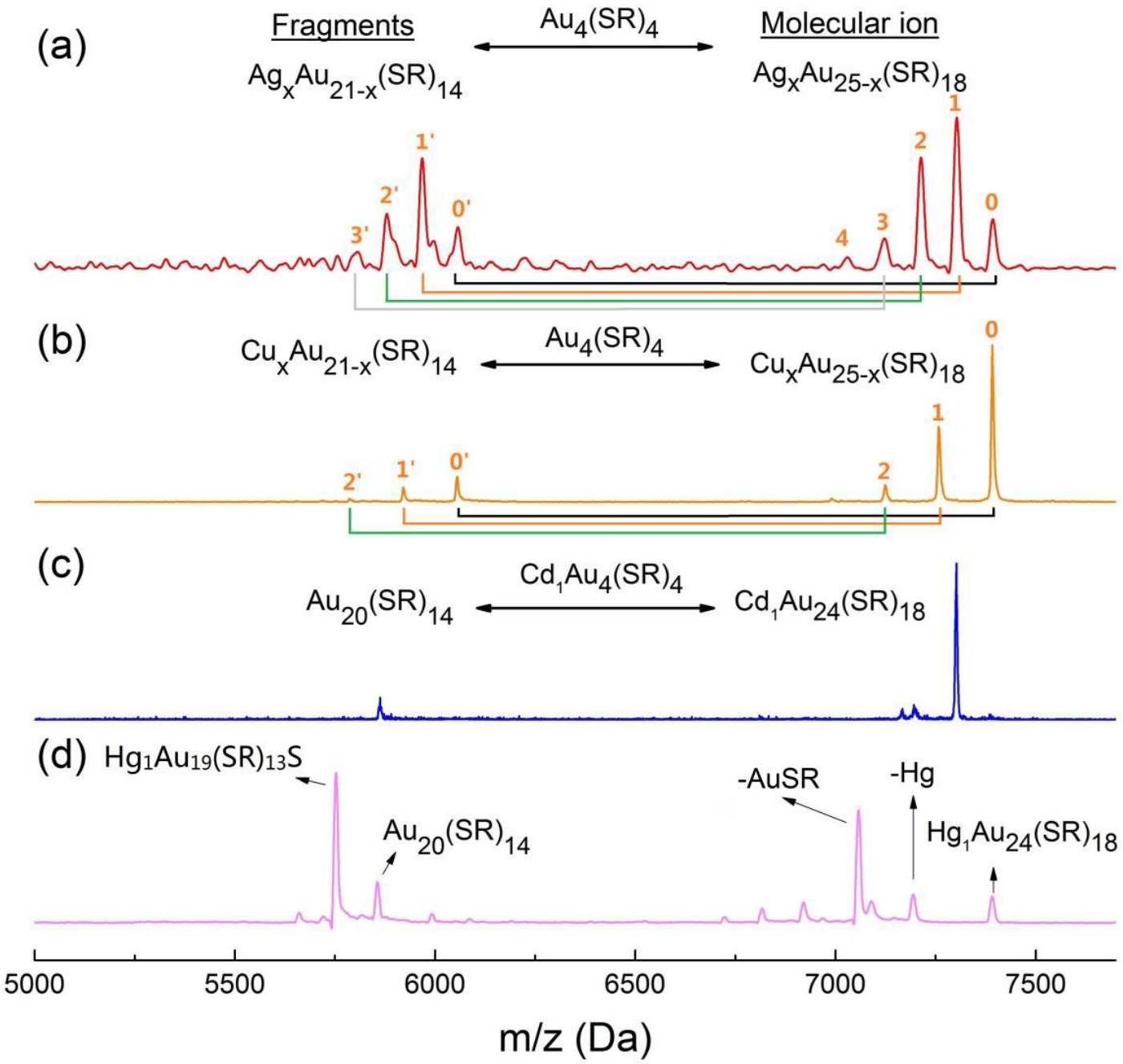
n = magic electron number (8)*
N = number of metal atoms of A (25)
vA = atomic valence of metal atom A (1)
M = number of electron localizing/withdrawing ligands (18)
Z = overall charge of cluster (-1)

For Au25(SR)18-, 8 = (25 x 1)-18-(-1)

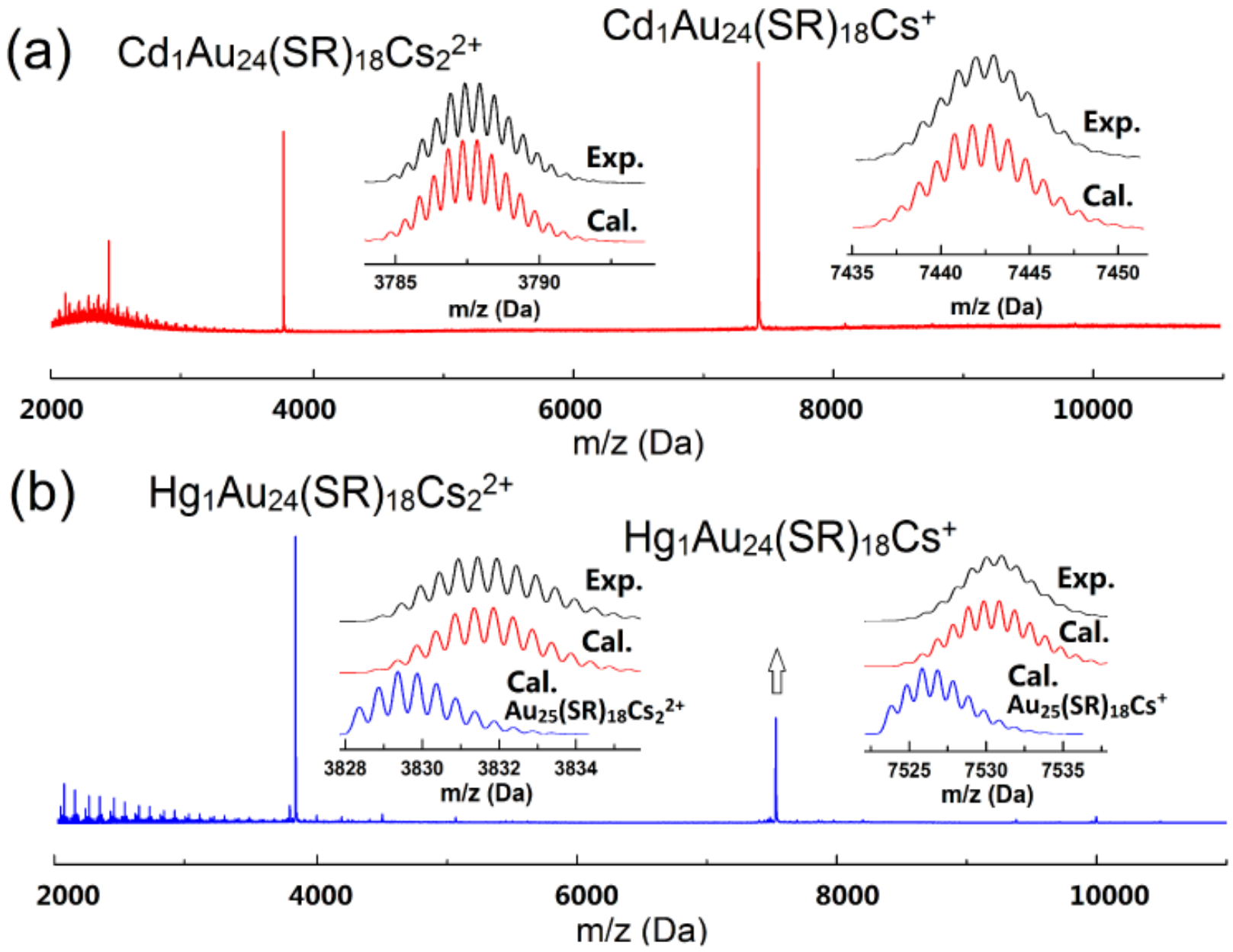
Murray, R. W. *et. al.* J. Am. Chem. Soc. 2008, 130, 3754-3755

MALDI-MS of MxAu25-x(SR)18 (x as indicated in each spectrum) after reaction with different metal ions (NiII, PdII, PtII, CuII, AgI, CdII, and HgII, all in thiolate complexes) R = C2H4Ph




(a)
Fragments
$Au_4(SR)_4$
Molecular ion
$Ag_xAu_{21-x}(SR)_{14}$
$Ag_xAu_{25-x}(SR)_{18}$
1
2
0
1'
2'
0'
3'
4
3
(b)
$Cu_xAu_{21-x}(SR)_{14}$
$Au_4(SR)_4$
$Cu_xAu_{25-x}(SR)_{18}$
0
1
2
2'
1'
0'
(c)
$Au_{20}(SR)_{14}$
$Cd_1Au_4(SR)_4$
$Cd_1Au_{24}(SR)_{18}$
(d)
$Hg_1Au_{19}(SR)_{13}S$
$Au_{20}(SR)_{14}$
-AuSR
-Hg
$Hg_1Au_{24}(SR)_{18}$
5000
5500
6000
6500
7000
7500
m/z (Da)

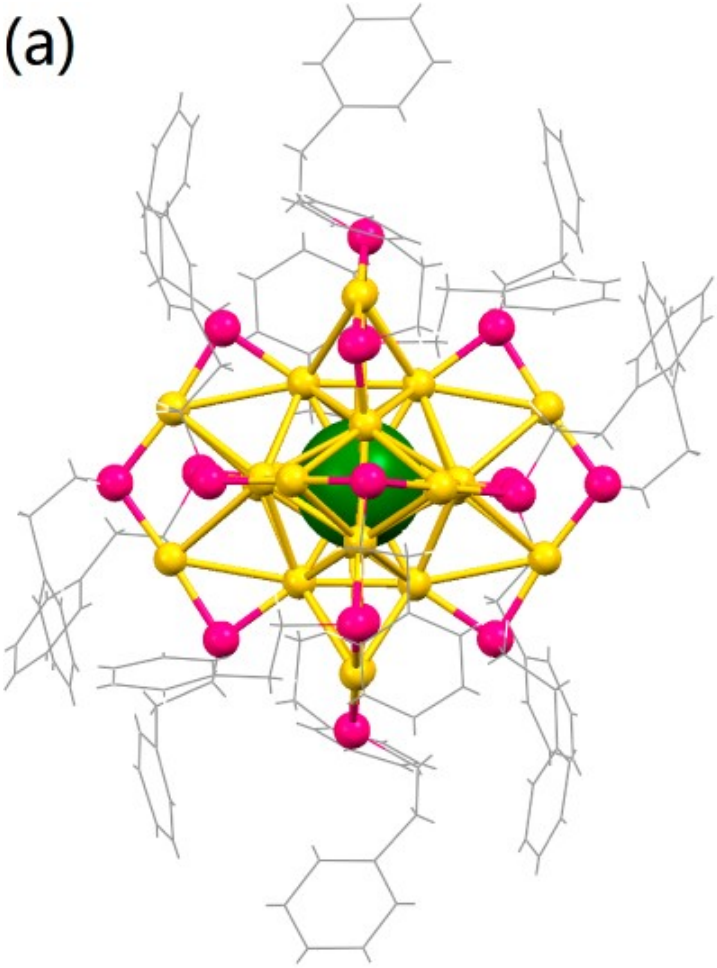
ESI mass spectrum of Cd1Au24(SC2H4Ph)18 NCs

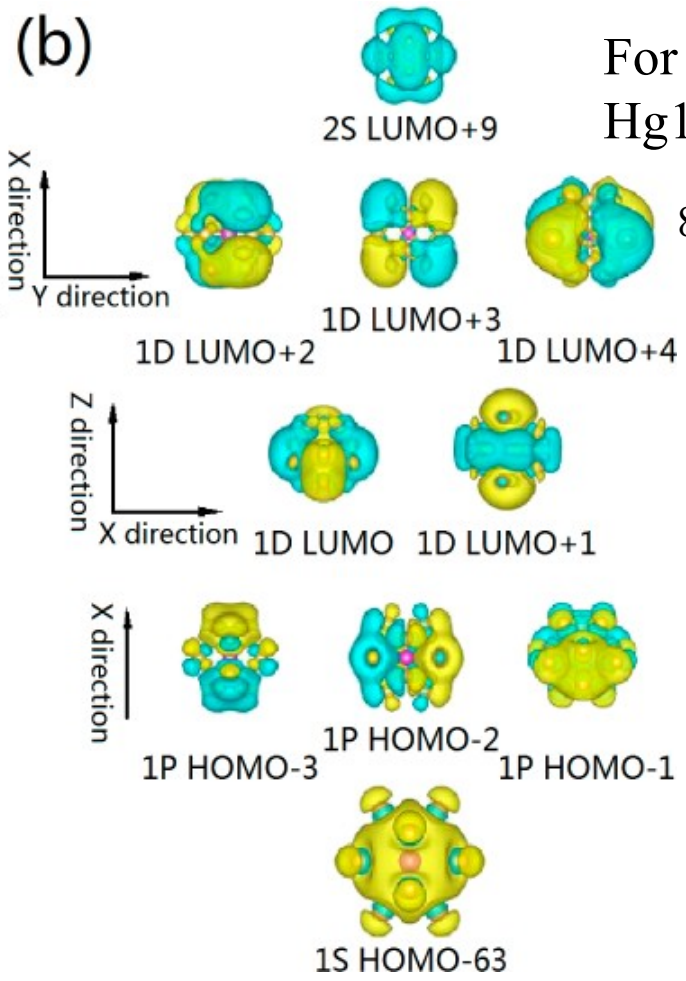


No TOA+ was observed

(a) Total structure of Cd1Au24(PhC2H4S)180 NCs. Colo labels: dark green = Cd; yellow = Au; magenta = S; all C and Hatoms are shown in wireframe. (b) Superatomic orbital of [Cd1Au12]6+

$$n^* = N\,vA - M - z$$

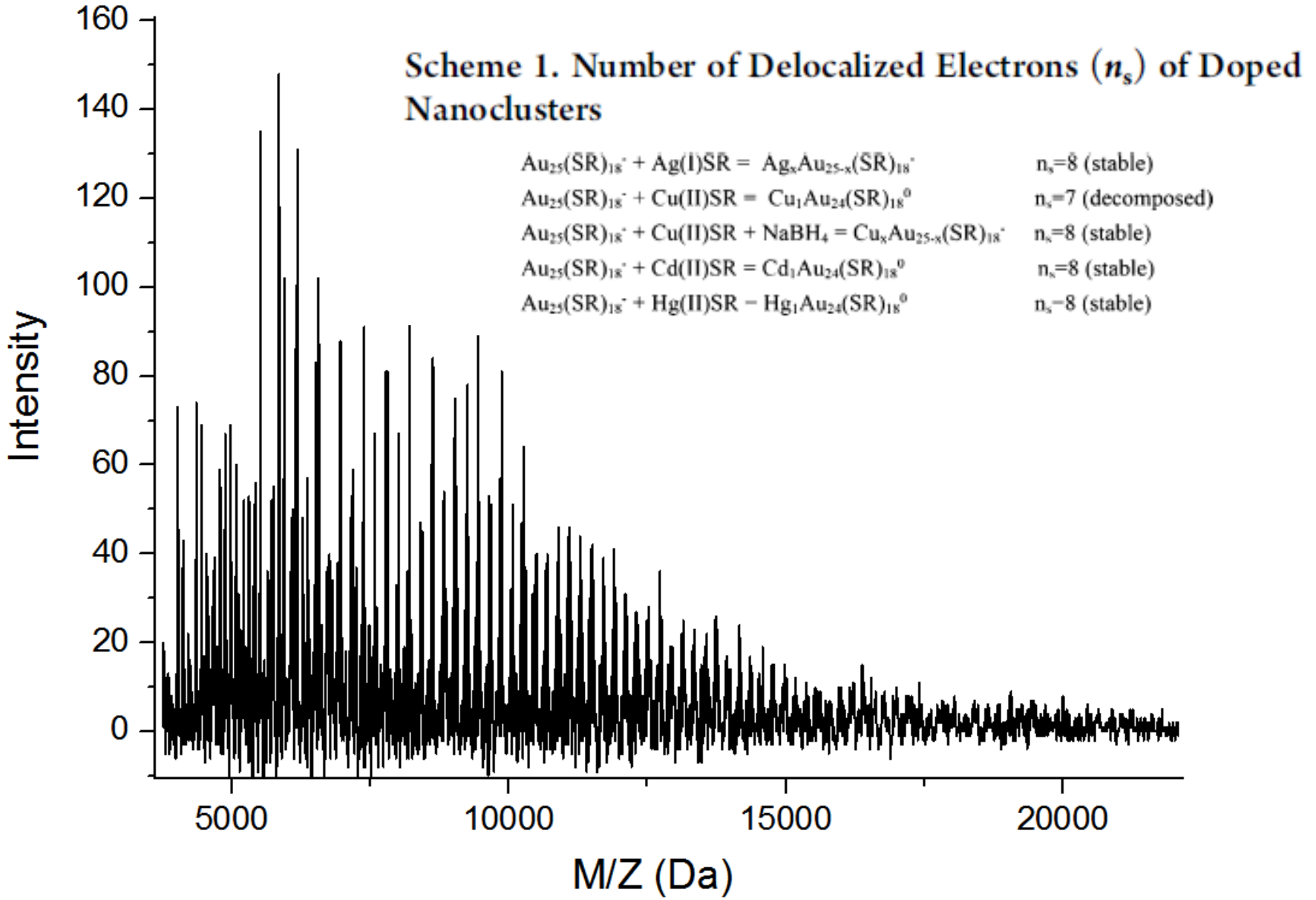




For Cd1Au25(SR)180,and Hg1Au24(SR)180

8 = (24 x 1) + (1 x 2) -18-(0)

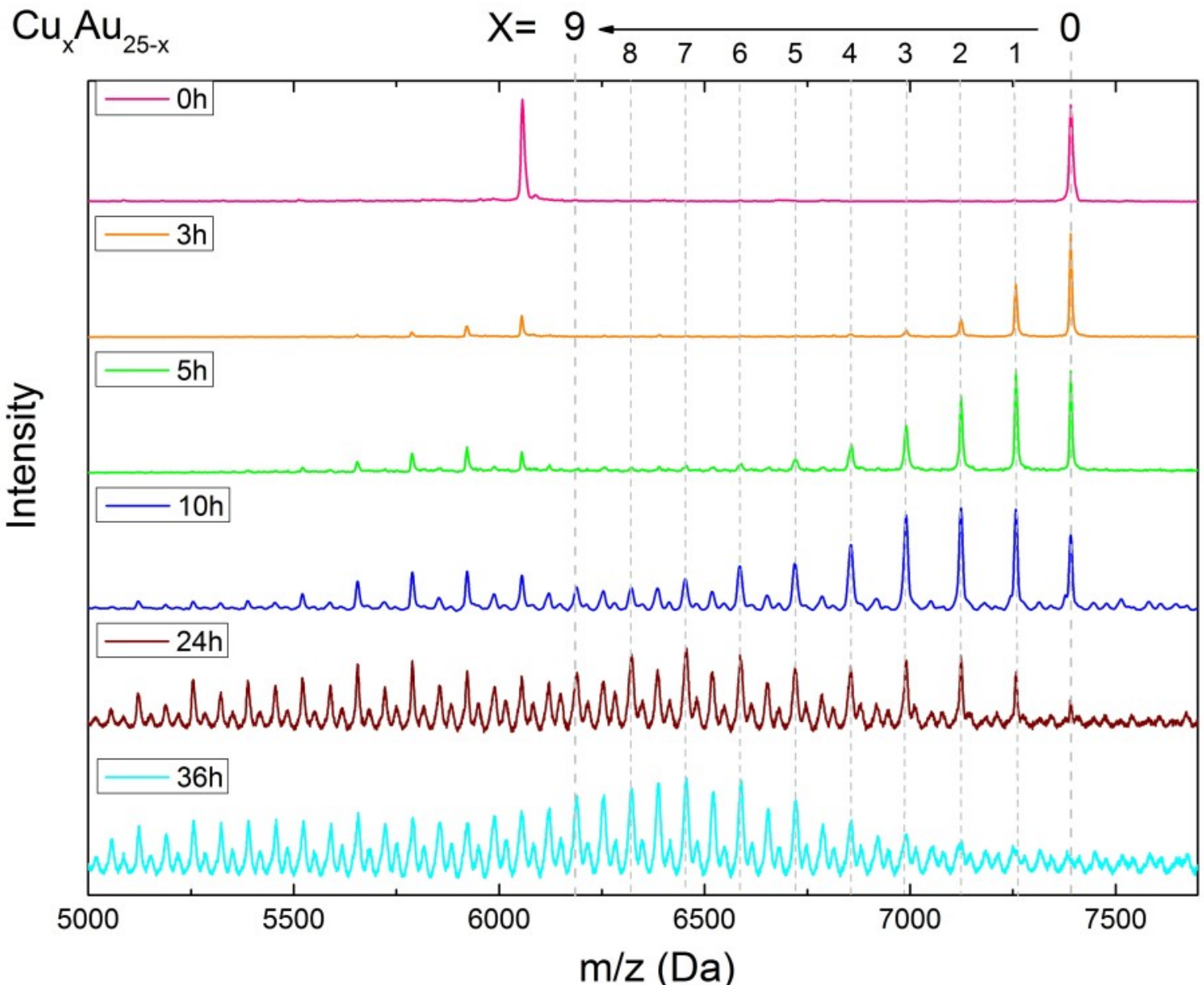
Negative mode MALDI-MS spectrumof Au25(SR)18-after reactionwith CuII(SR)2. Note: without addingNaBH4, the Au25NCs rapidly decomposed
R=C2H4Ph.

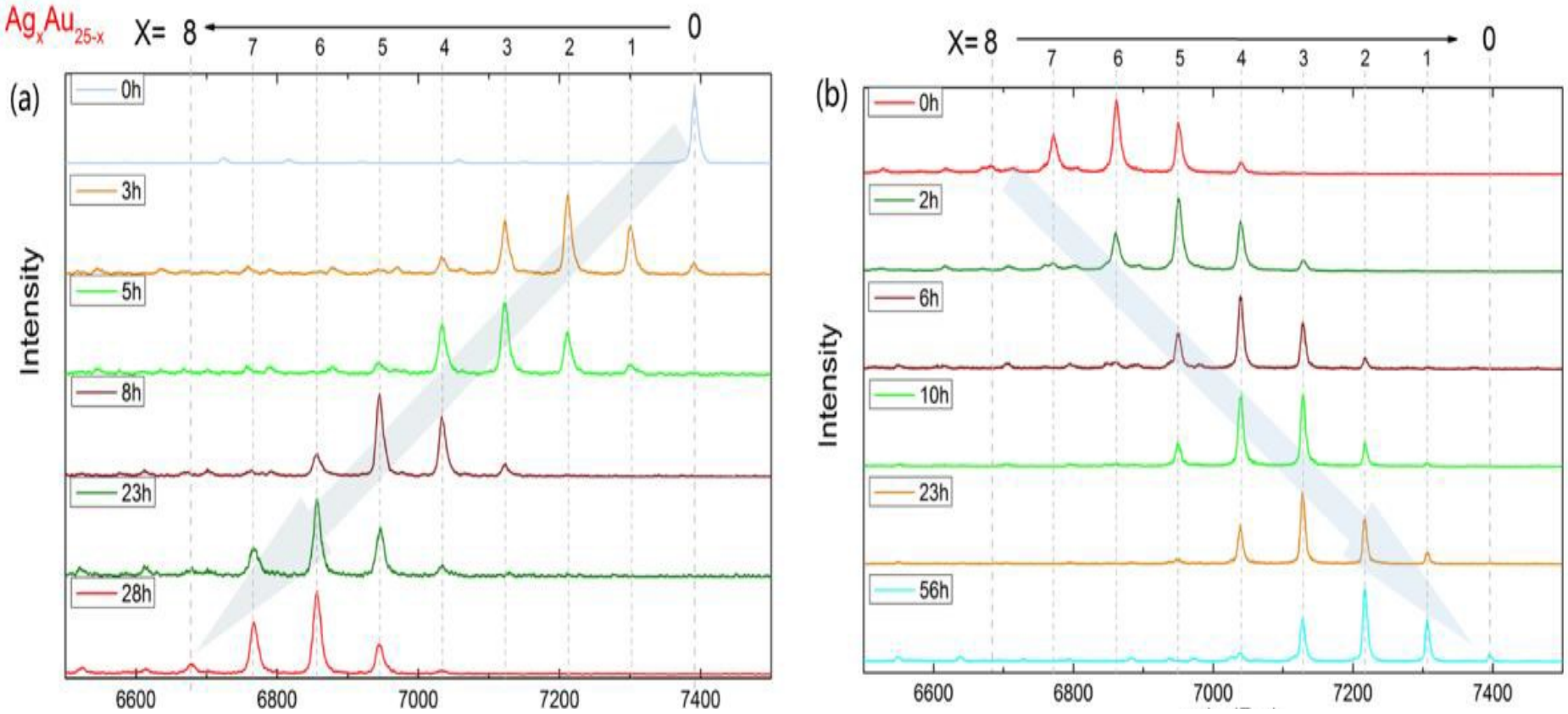


Scheme 1. Number of Delocalized Electrons (n_s) of Doped Nanoclusters

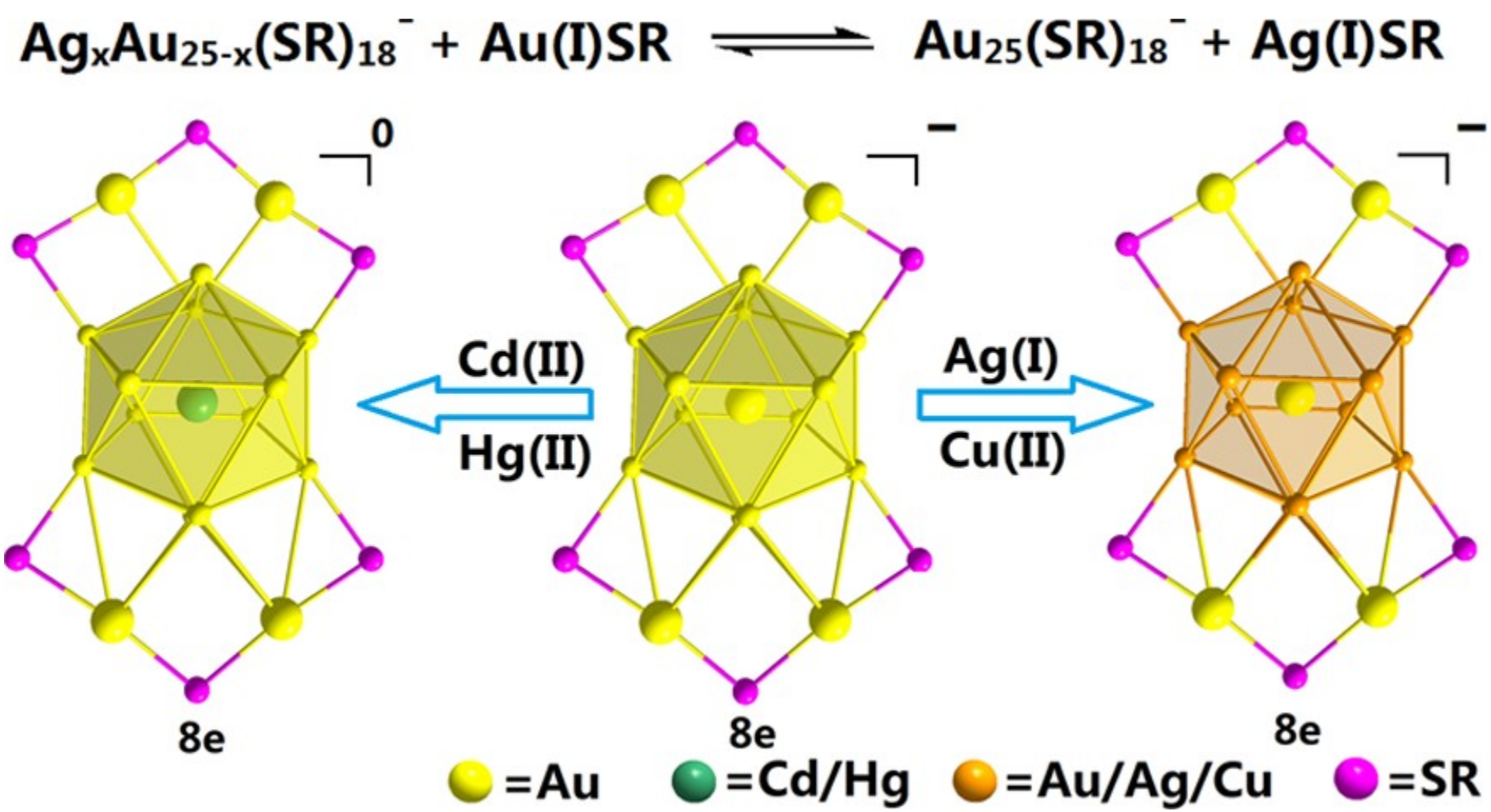
$Au_{25}(SR)_{18}^{-} + Ag(I)SR = Ag_xAu_{25-x}(SR)_{18}^{-}$	n_s=8 (stable)
$Au_{25}(SR)_{18}^{-} + Cu(II)SR = Cu_1Au_{24}(SR)_{18}^{0}$	n_s=7 (decomposed)
$Au_{25}(SR)_{18}^{-} + Cu(II)SR + NaBH_4 = Cu_xAu_{25-x}(SR)_{18}^{-}$	n_s=8 (stable)
$Au_{25}(SR)_{18}^{-} + Cd(II)SR = Cd_1Au_{24}(SR)_{18}^{0}$	n_s=8 (stable)
$Au_{25}(SR)_{18}^{-} + Hg(II)SR - Hg_1Au_{24}(SR)_{18}^{0}$	n_s=8 (stable)

Time-dependent MALDI mass spectra of CuxAu25-x(SR)18 in toluene after adding CuII(SR)2 complex. Note: solid NaBH4 was added
R=C2H4Ph




Ag$_x$Au$_{25-x}$
X= 8
0
7
6
5
4
3
2
1
(a)
0h
3h
5h
8h
23h
28h
Intensity
6600
6800
7000
7200
7400
X= 8
0
7
6
5
4
3
2
1
(b)
0h
2h
6h
10h
23h
56h
Intensity
6600
6800
7000
7200
7400

Metal Exchange Process of Nanoclusters Using Metal Complexes with the Metal Core Size Preserved



Summary and conclusions

- This metal exchange method for alloy NCs is, to a large extent, associated with electron shell closing and the NC's structural stability, but less on the metal activity.

- These findings shed some new light on the metal exchange process at the atomic level, and this approach holds promise in future development as a versatile method for synthesizing alloy NCs that contain both high- and low-activity metal atoms with precise control of metal composition, doping site, and dopant number for specific applications.

Future Aspects:

- Structure of MxAu25-x(SR)18 may vary depending in the source of M, presence or absence of reducing agents, etc.