Polymorphism of Phosphine-Protected Gold Nanoclusters: Synthesis and Characterization of a New 22-Gold-Atom Cluster

*Qian-Fan Zhang, Paul G. Williard, and Lai-Sheng Wang**

Department of Chemistry
Brown University
Providence, RI 02912, USA

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Md Bodiuzzaman
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Introduction

- Ligand-protected gold nanoclusters (AuNCs) have attracted tremendous interest recently, due to their potential applications in catalysis, biosensor, imaging, and molecular electronics.

- The quantum confinement effects of such small gold cores lead to discrete electronic states, which give rise to unique molecular-like electronic properties for AuNCs.

- Thiolate-protected AuNCs have all been found to have complicated gold-ligand interfaces, because of the formation of gold-thiolate staples.

- Phosphine-protected AuNCs tend to have simpler inter-faces with well-defined cores and ligand layers, due to the neutral charge state of phosphines and the weaker gold-phosphine bond.

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Communication

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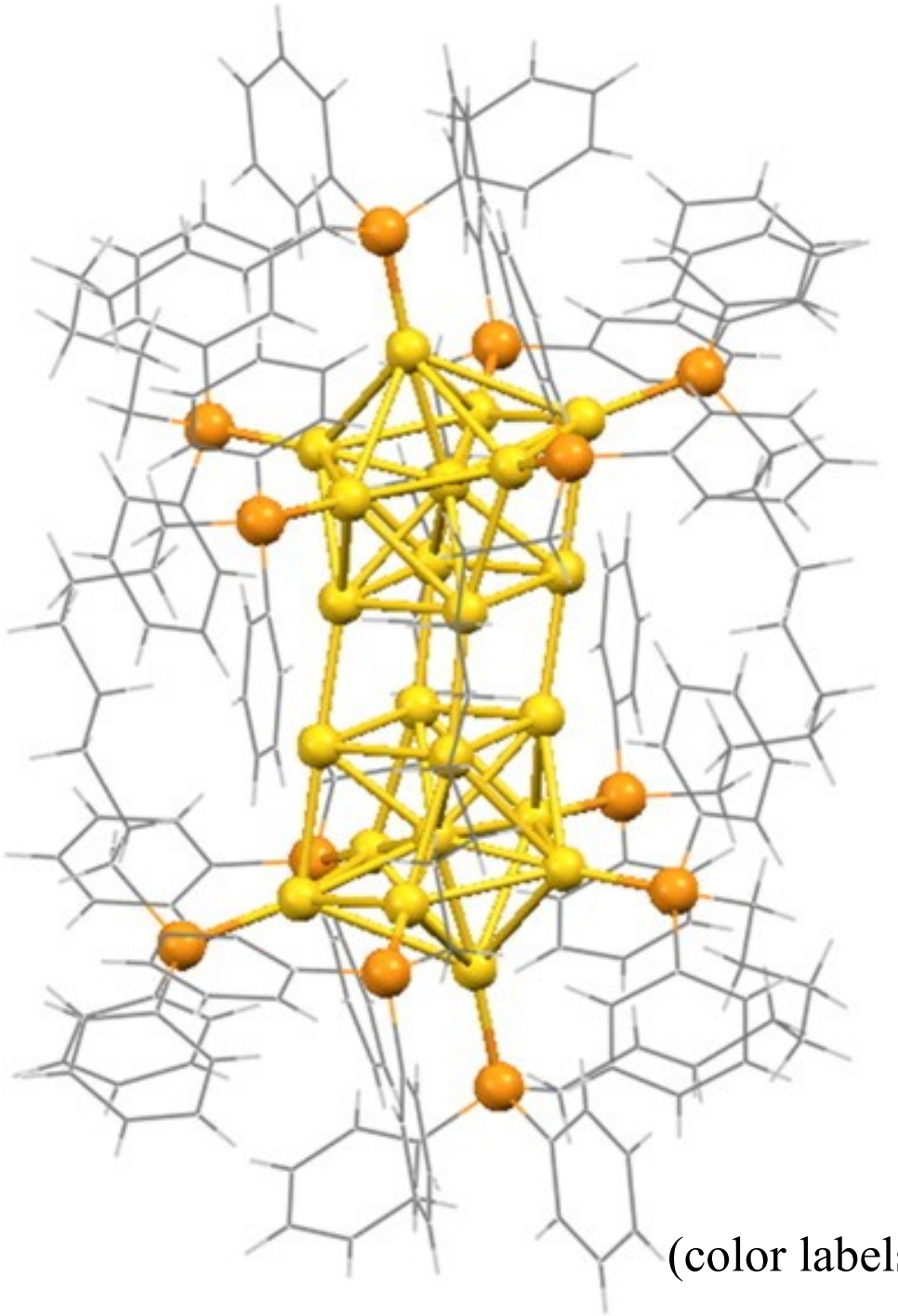
Controlling Gold Nanoclusters by Diphospine Ligands

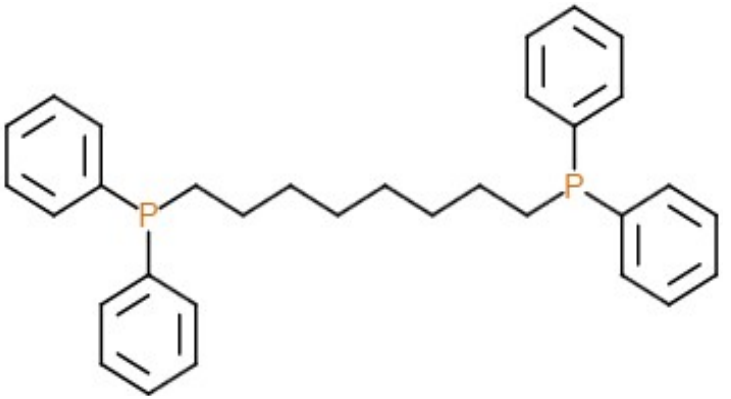
Jing Chen, Qian-Fan Zhang, Timary A. Bonaccorso, Paul G. Williard, and Lai-Sheng Wang*

Department of Chemistry, Brown University, Providence, Rhode Island 02912, United States

Total structure of the $Au_{22}(L8)_6$ cluster

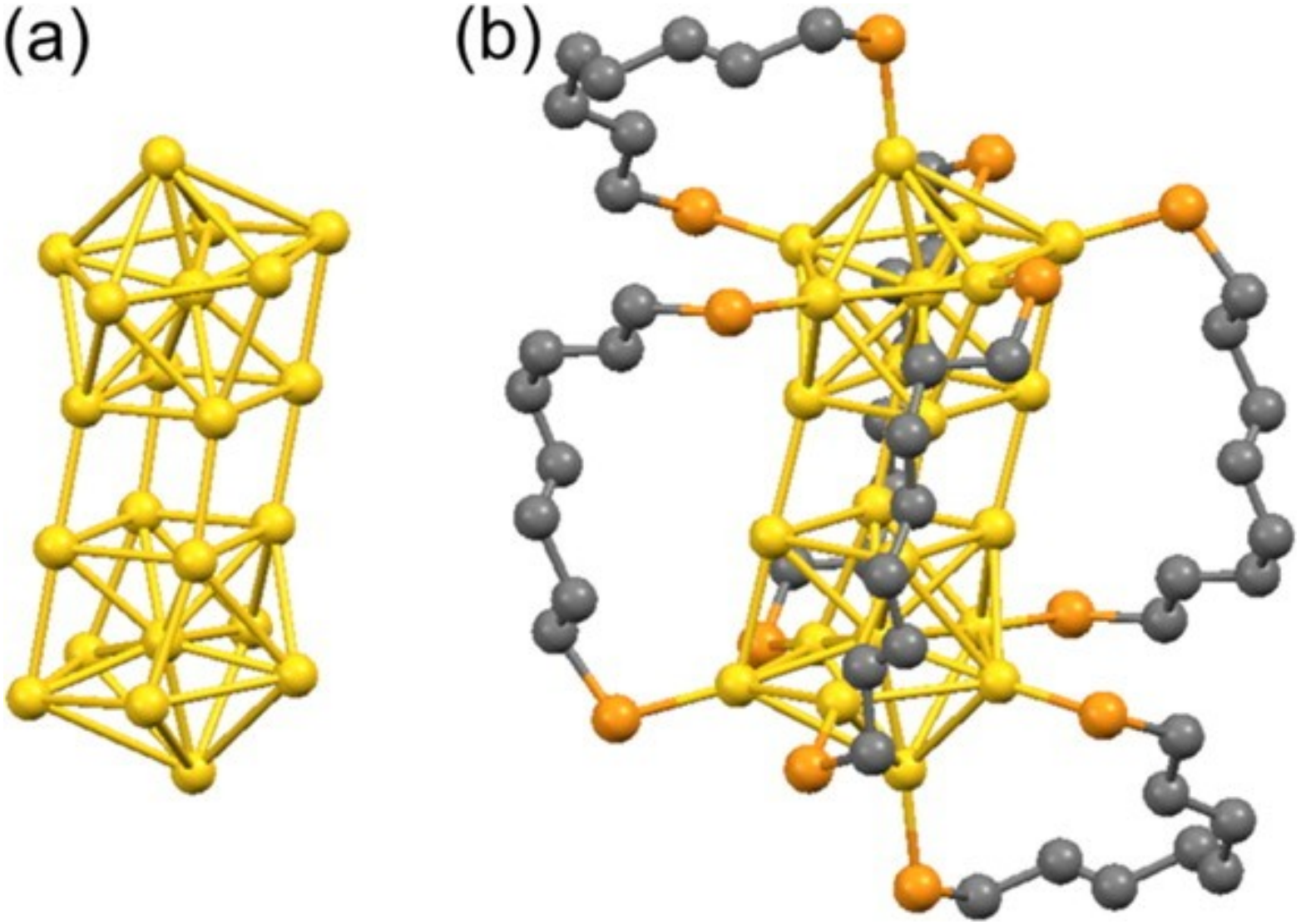


L8 = 1,8-bis(diphenylphosphino) octane (DPPO)

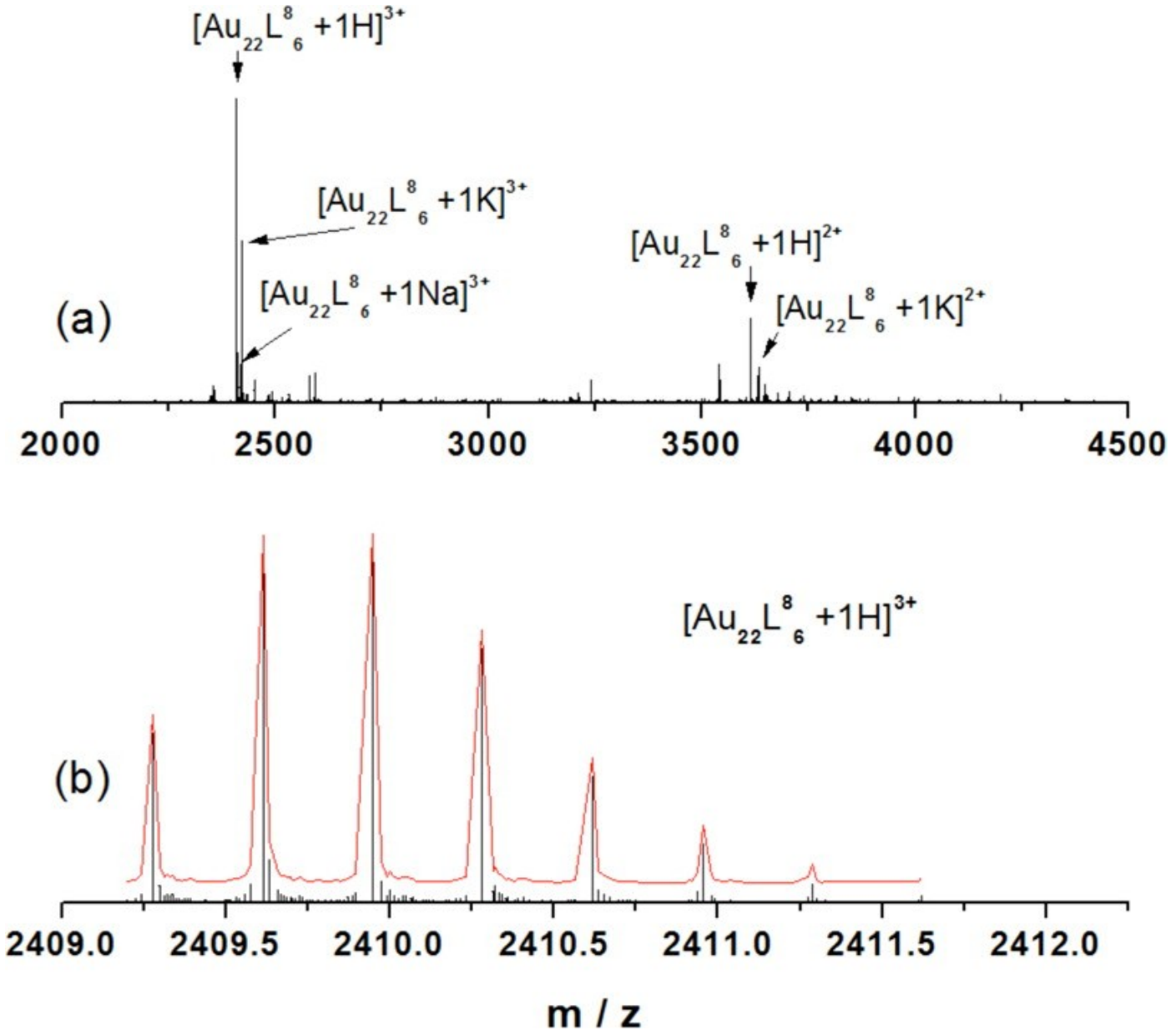


(color labels: yellow = Au; orange = P; gray = C).

Core structure of the $Au_{22}(L8)_6$ cluster

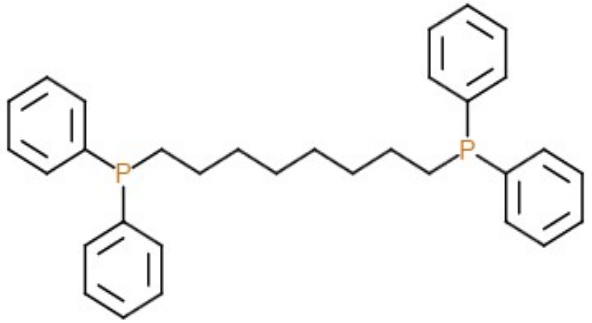


(color labels: yellow = Au; orange = P; gray = C).

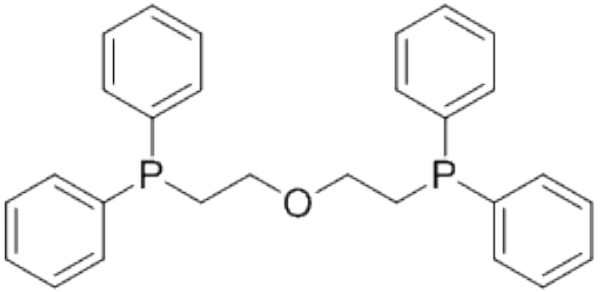


(a) Mass spectrum of the Au22 cluster. (b) The measured (black) and simulated (red) isotopic patterns of [Au22 (L8)6 + 1H]3+.

Here they report the synthesis of a new Au 22 cluster using the bis(2-diphenyl-phosphino)ethyl ether (dppee) ligand, which has a slightly shorter chain length than the dppo ligand and can be viewed as replacing four CH2 groups in dppo by an ether group.



DPPO



DPPEE

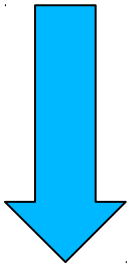
The new Au 22 cluster is found to be coordinated by seven dppee ligands, $Au_{22}(dppee)_7$, and can be obtained with relatively high yield and purity.

The $Au_{22}(dppee)_7$ cluster has been characterized by UV-Vis-NIR, collision-induced dissociation (CID), and 31 P-NMR and compared with the previous $Au_{22}(dppo)_6$ cluster.

The new $Au_{22}(dppee)_7$ nanocluster has a totally different core structure from the previous $Au_{22}(dppo)_6$ cluster.

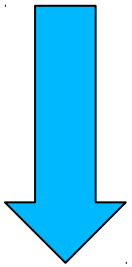
Synthesis of Au_{22} $(dppee)_7$ Nanocluster

Au_2Cl_2 (dppee) dissolved in DCM

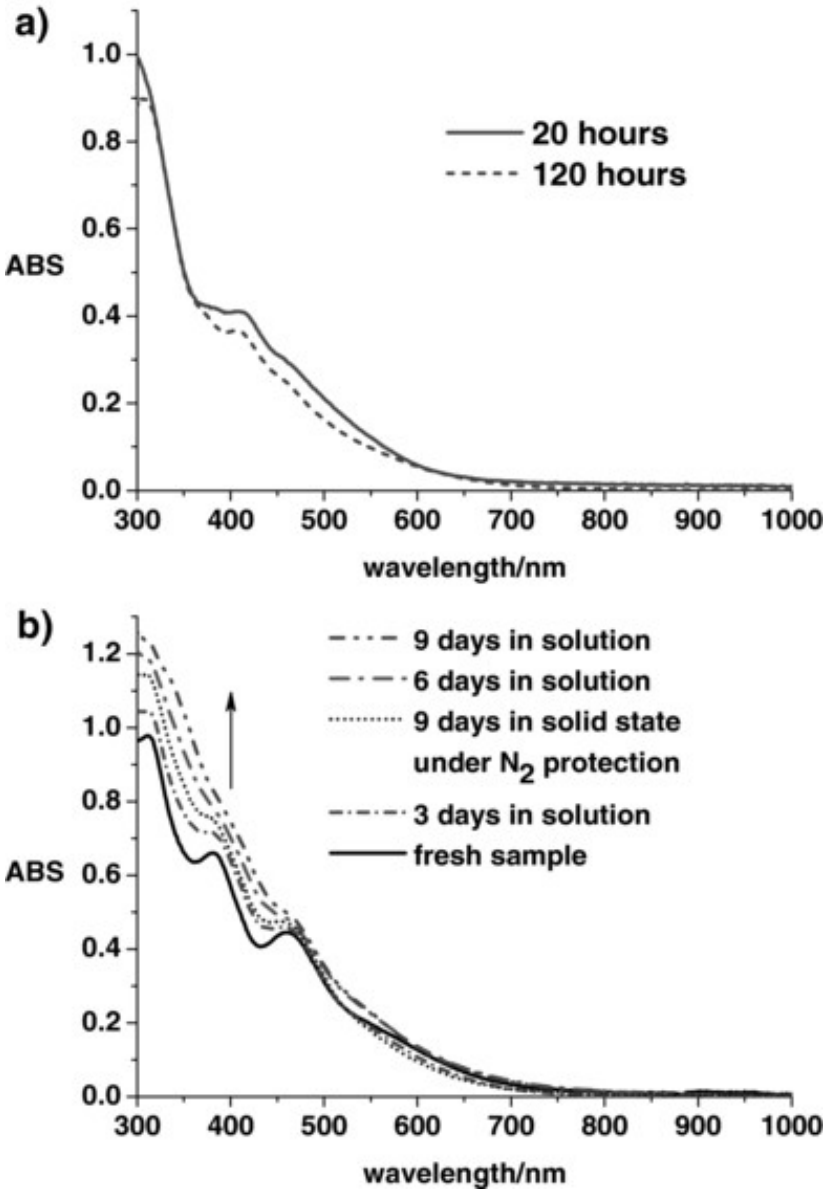


10 min stirring
NaBH4 in EtOH

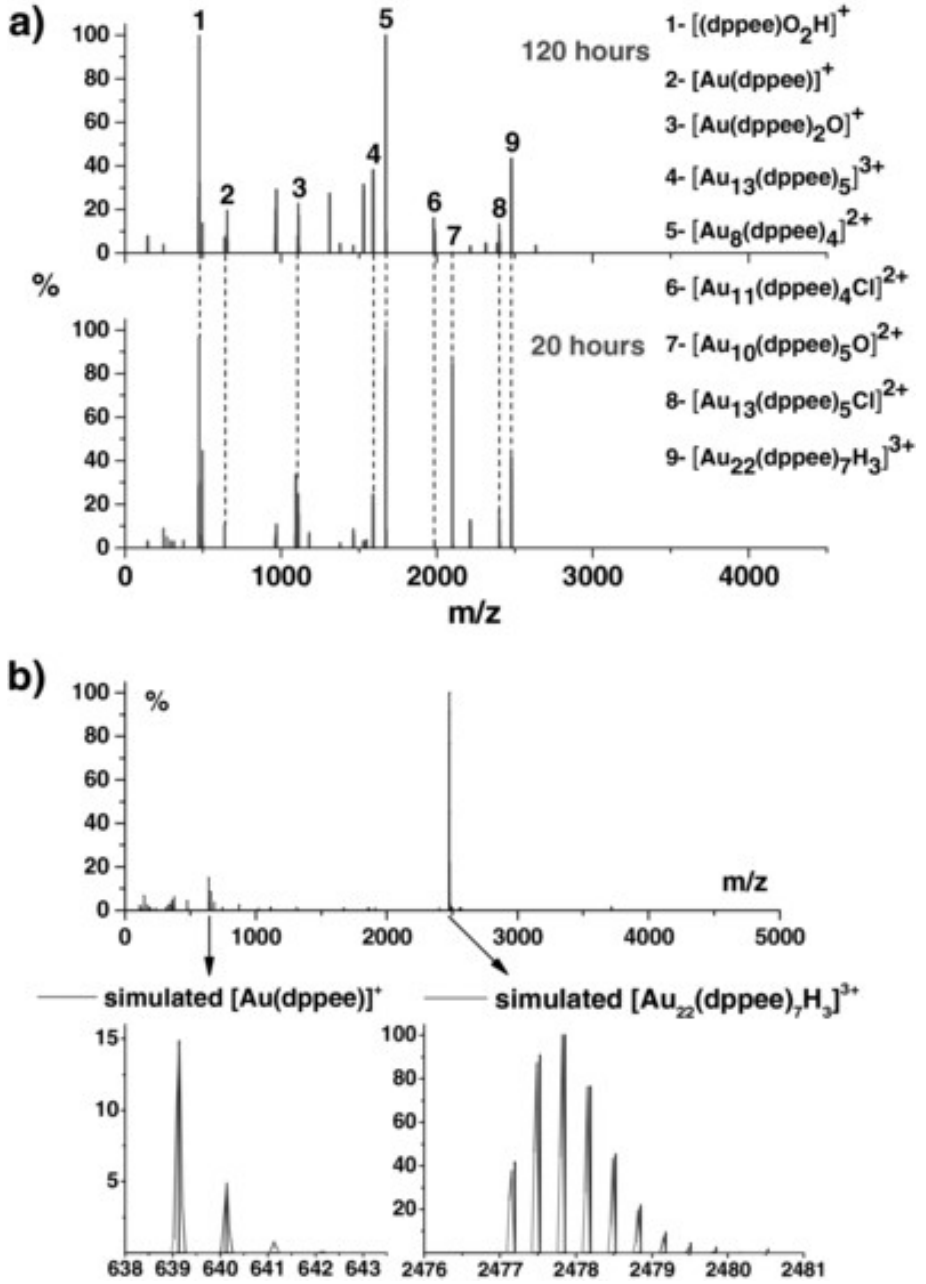
Crude product after 20 h



Purified by silica gel column chromatography
(DCM/ethyl acetate/methanol)



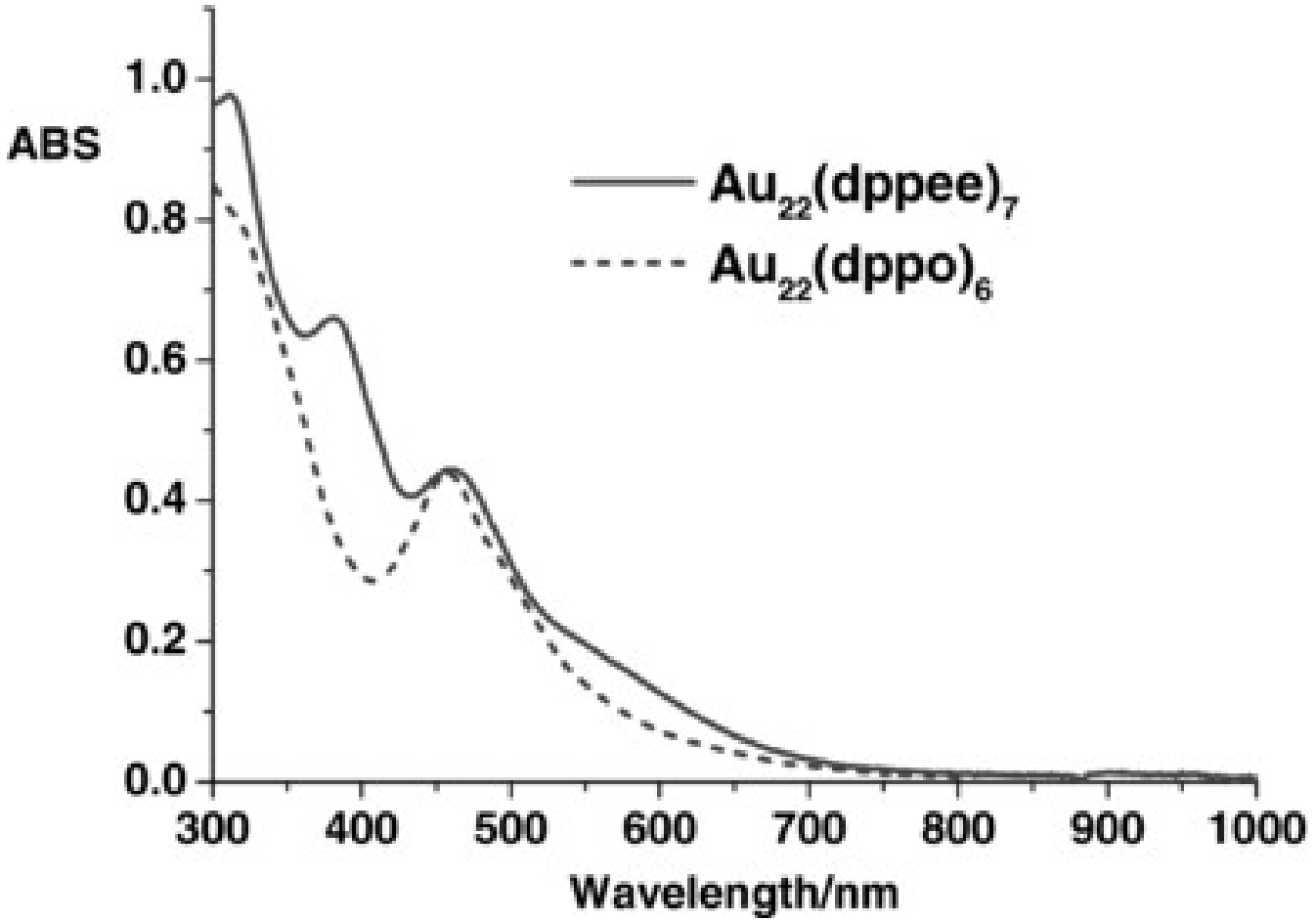
a) UV-Vis-NIR of the crude products during the syntheses of $Au_{22}(dppee)_7$ with different reaction times. b) UV-Vis-NIR spectra of pure $Au_{22}(dppee)_7$ after column separation in CH_2Cl_2.



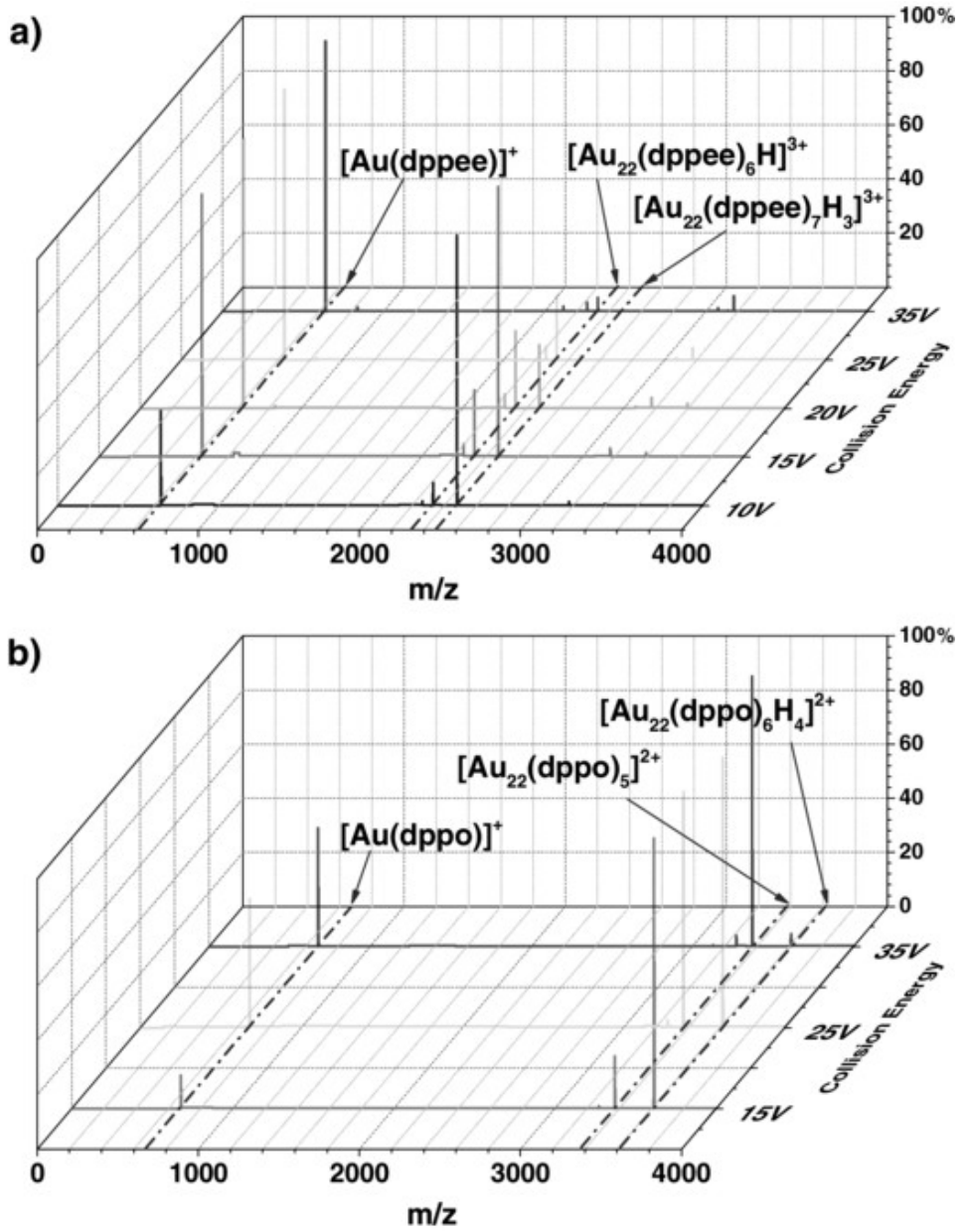
a) Electrospray mass spectra of the crude products during the syntheses of $Au_{22}(dppee)_7$ with different reaction times. b) Electrospray mass spectra of pure $Au_{22}(dppee)_7$ after column separation, as well as the experimental and simulated isotopic distributions of the two major peaks.

The new $Au_{22}(dppee)_7$ nanocluster has the same gold core size as the previously reported $Au_{22}(dppo)_6$ cluster.

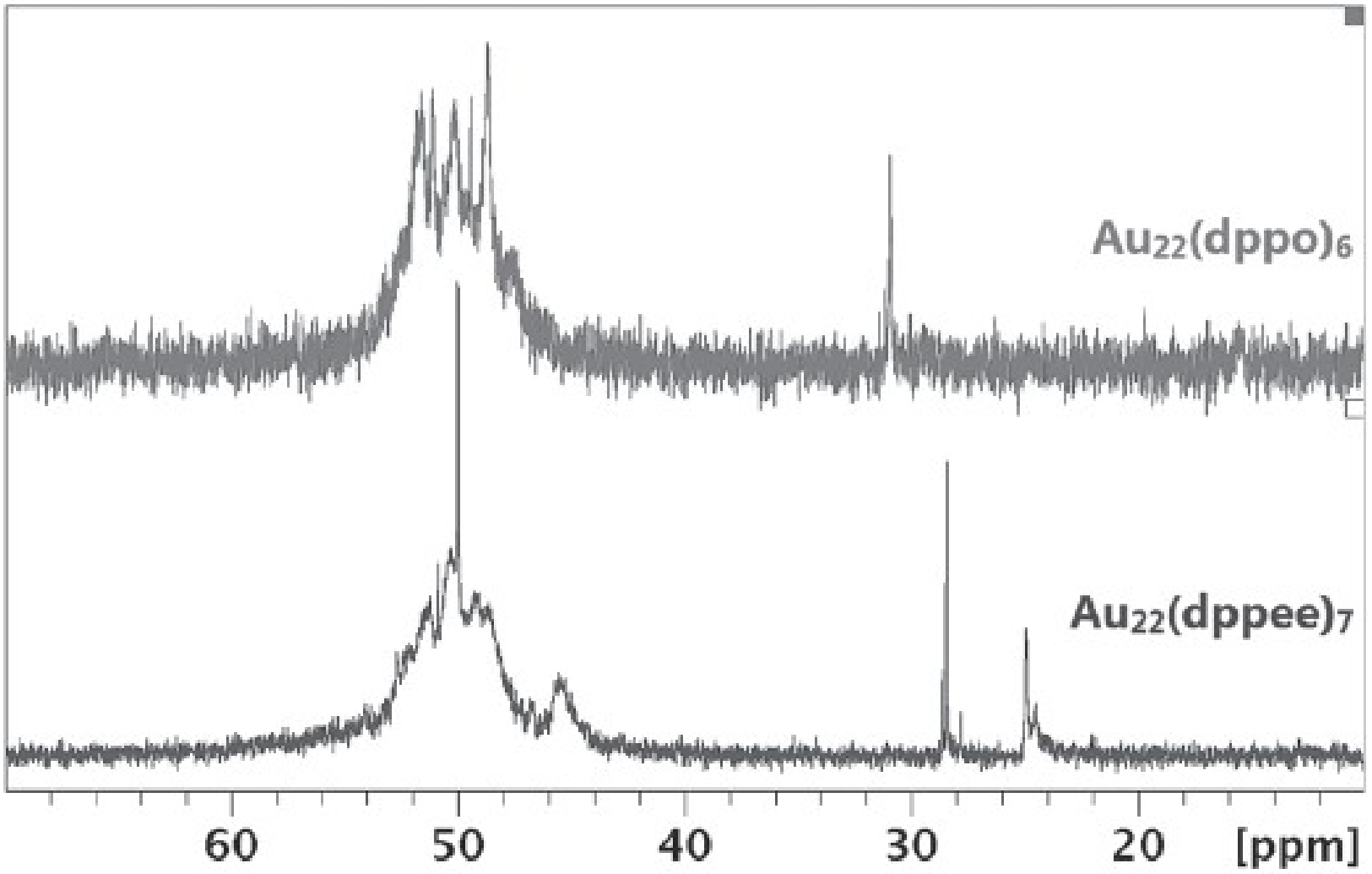
Do they have the same core structure?



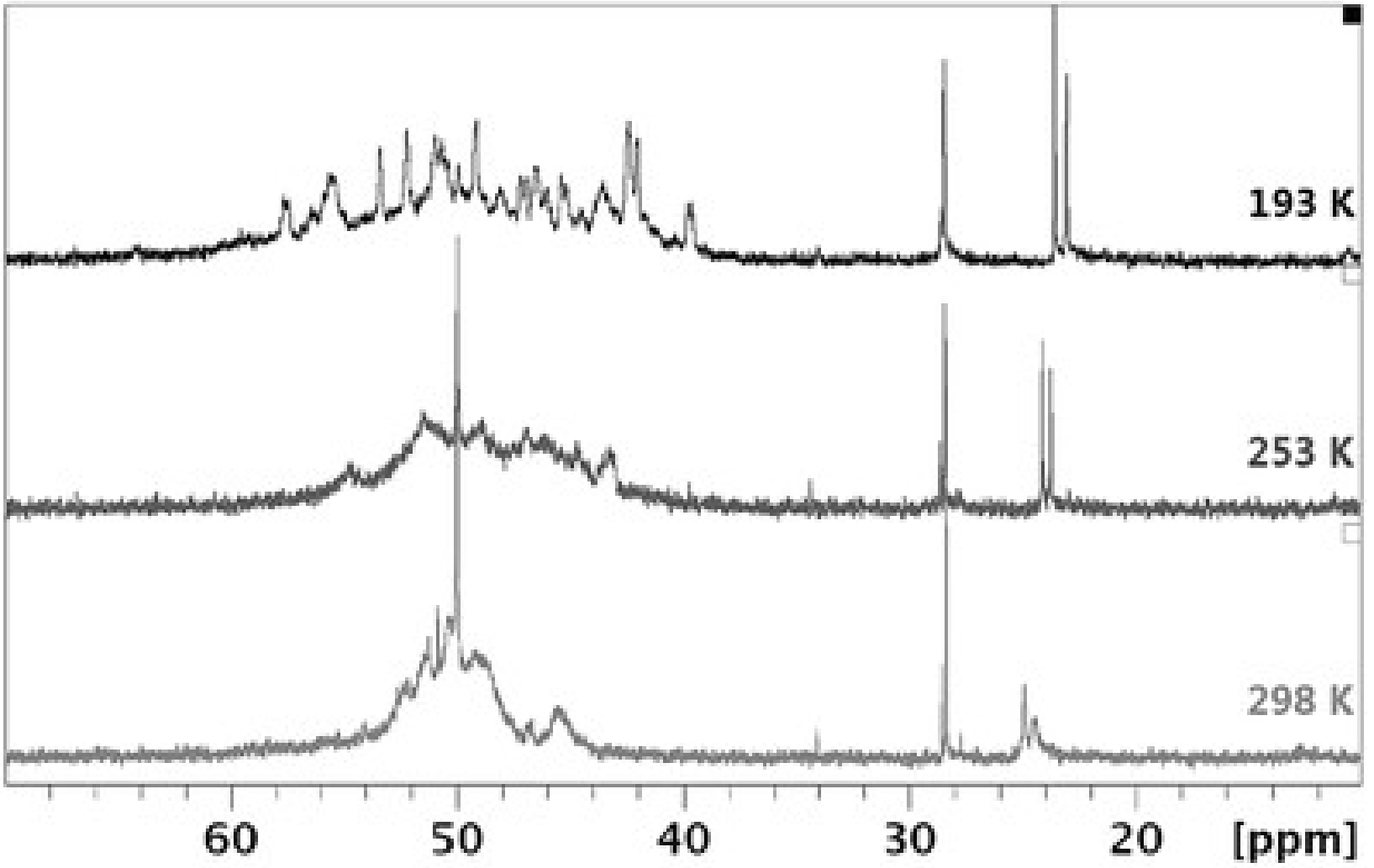
Comparison of the UV-Vis-NIR spectra of $Au_{22}(dppee)_7$ and $Au_{22}(dppo)_6$.



Collision-induced dissociation of a) $[Au_{22}(dppee)_7H_3]^{3+}$ and b) $[Au_{22}(dppo)_6H_4]^{2+}$ at different collision energies.



Comparison of the ^{31}P-NMR of $Au_{22}(dppo)_6$ and $Au_{22}(dppee)_7$ at 293 K.



The ^{31}P-NMR of $Au_{22}(dppee)_7$ at 298, 253, and 193 K

Summary

A new $Au_{22}(dppee)_7$ nanocluster has been synthesized with high purity and high yield.

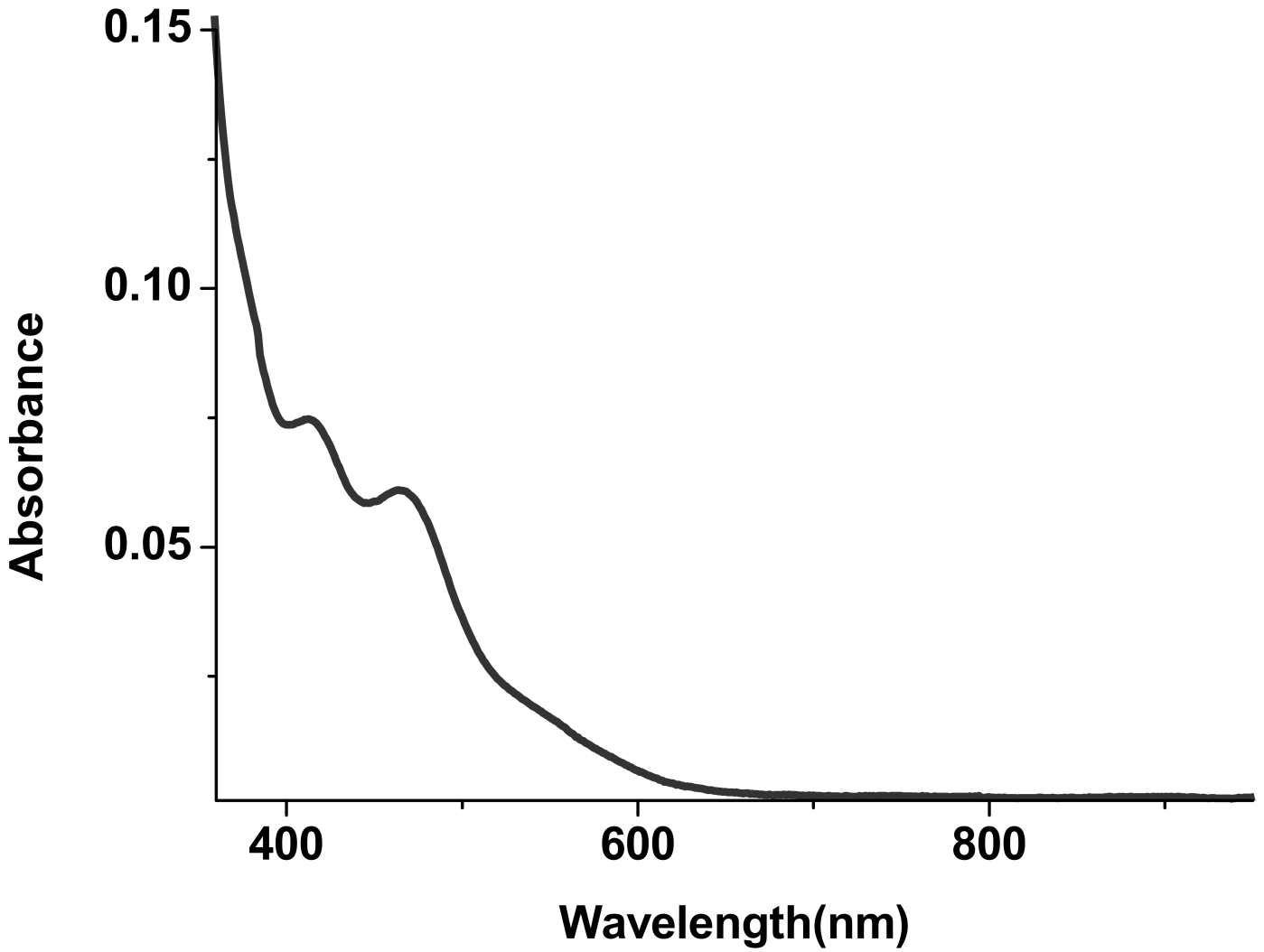
Its precise molecular formula was determined by high-resolution electrospray mass spectrometry.

Au_{22} $(dppee)_7$ has a different core structure, consisting of an Au 11 unit with additional Au atoms most likely as a new layer on its surface.

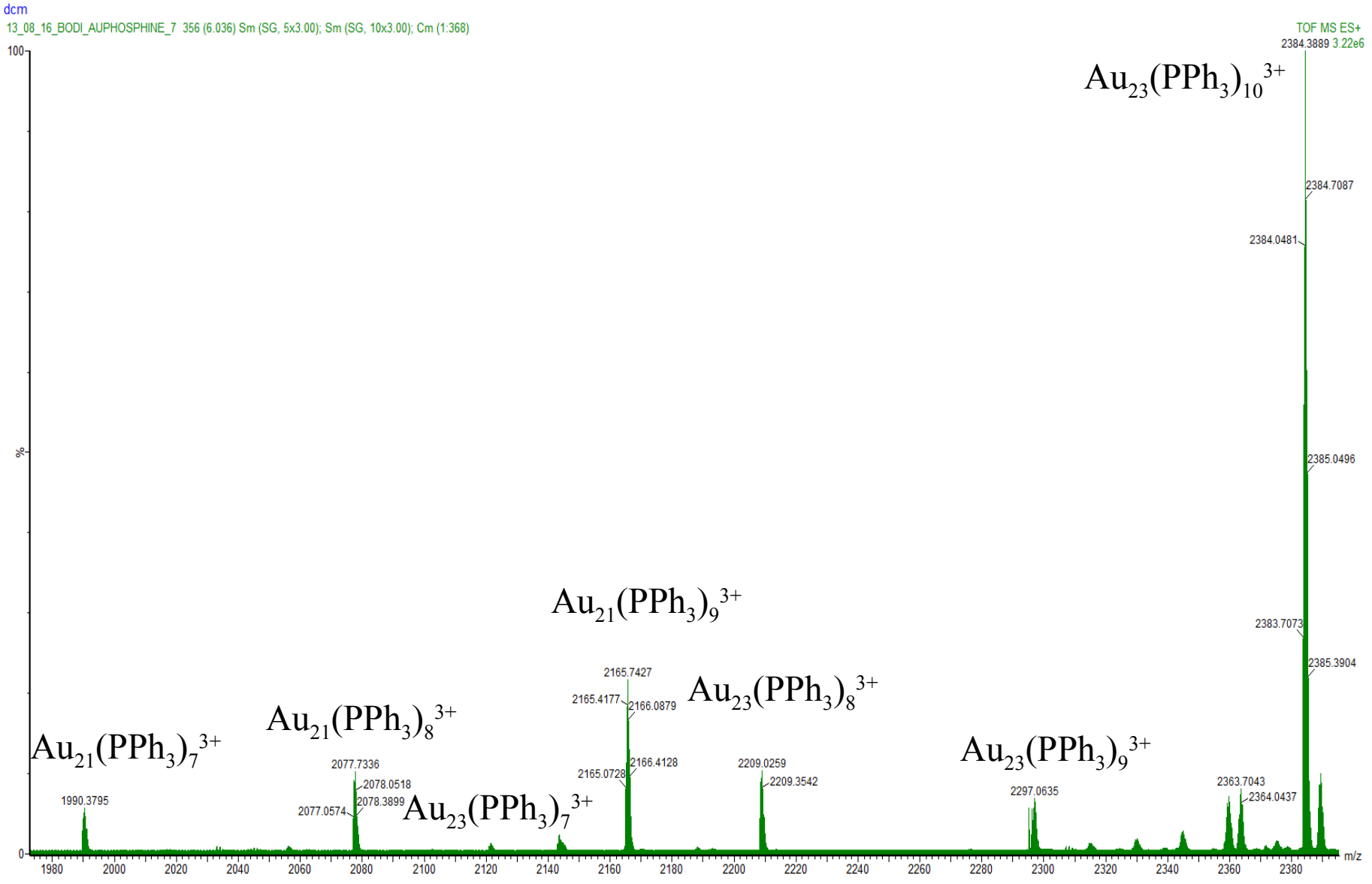
The current $Au_{22}(dppee)_7$ cluster and the previous $Au_{22}(dppo)_6$ cluster reveal that the Au22 nanoclusters exhibit interesting core isomers, depending on the ligands.

Future direction

We have synthesized phosphine protected gold cluster following the same procedure used for $Ag_{18}H_{14}PPh3_{10}$. We have to optimise the reaction condition for better yield and purity.



ESI MS


dcm
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TOF MS ES+
2384.3889 3.22e6
Au23(PPh3)10 3+
2384.7087
2384.0481
2385.0496
2383.7073
2385.3904
Au21(PPh3)9 3+
2165.7427
2165.4177
2166.0879
Au23(PPh3)8 3+
Au21(PPh3)8 3+
Au21(PPh3)7 3+
2077.7336
2078.0518
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2078.3899
Au23(PPh3)7 3+
2165.0728
2166.4128
2209.0259
2209.3542
Au23(PPh3)9 3+
2297.0635
2363.7043
2364.0437
1990.3795
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1980
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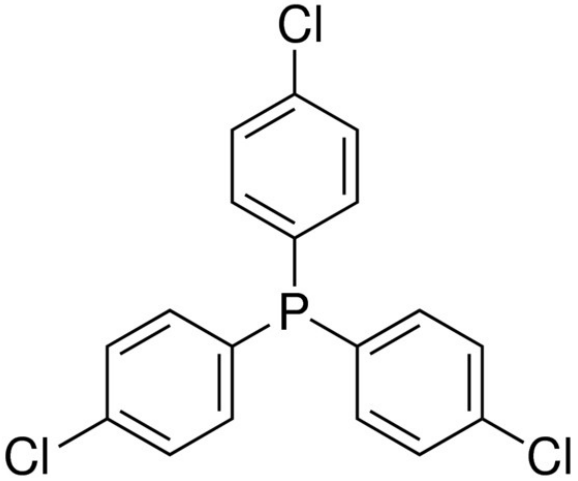
m/z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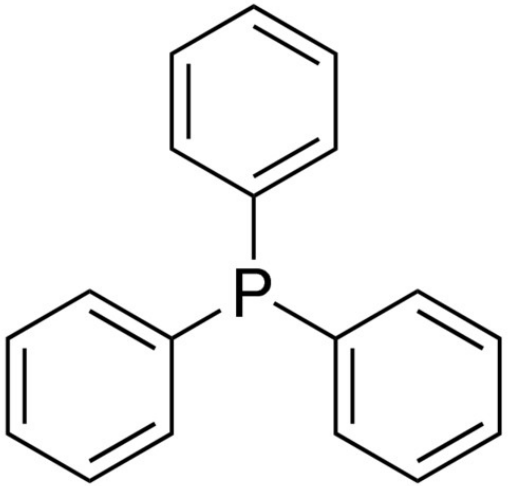
P
Cl
Cl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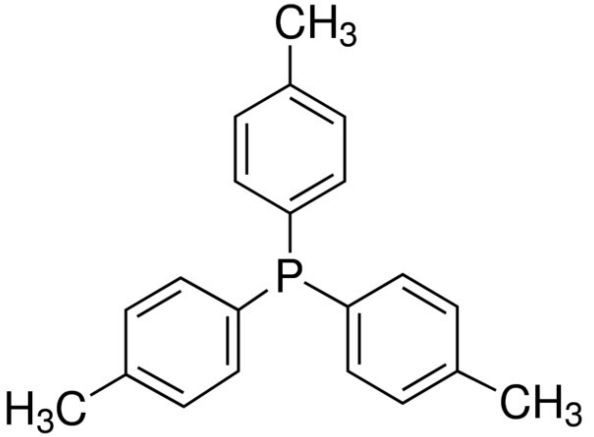
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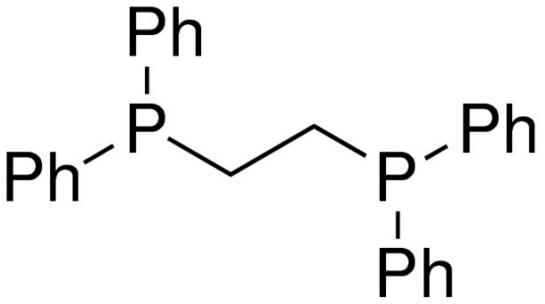
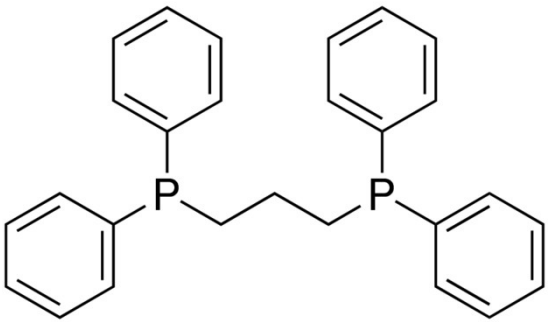
P
H3C
CH3


Ph
P
Ph
P
Ph
Ph


P
P