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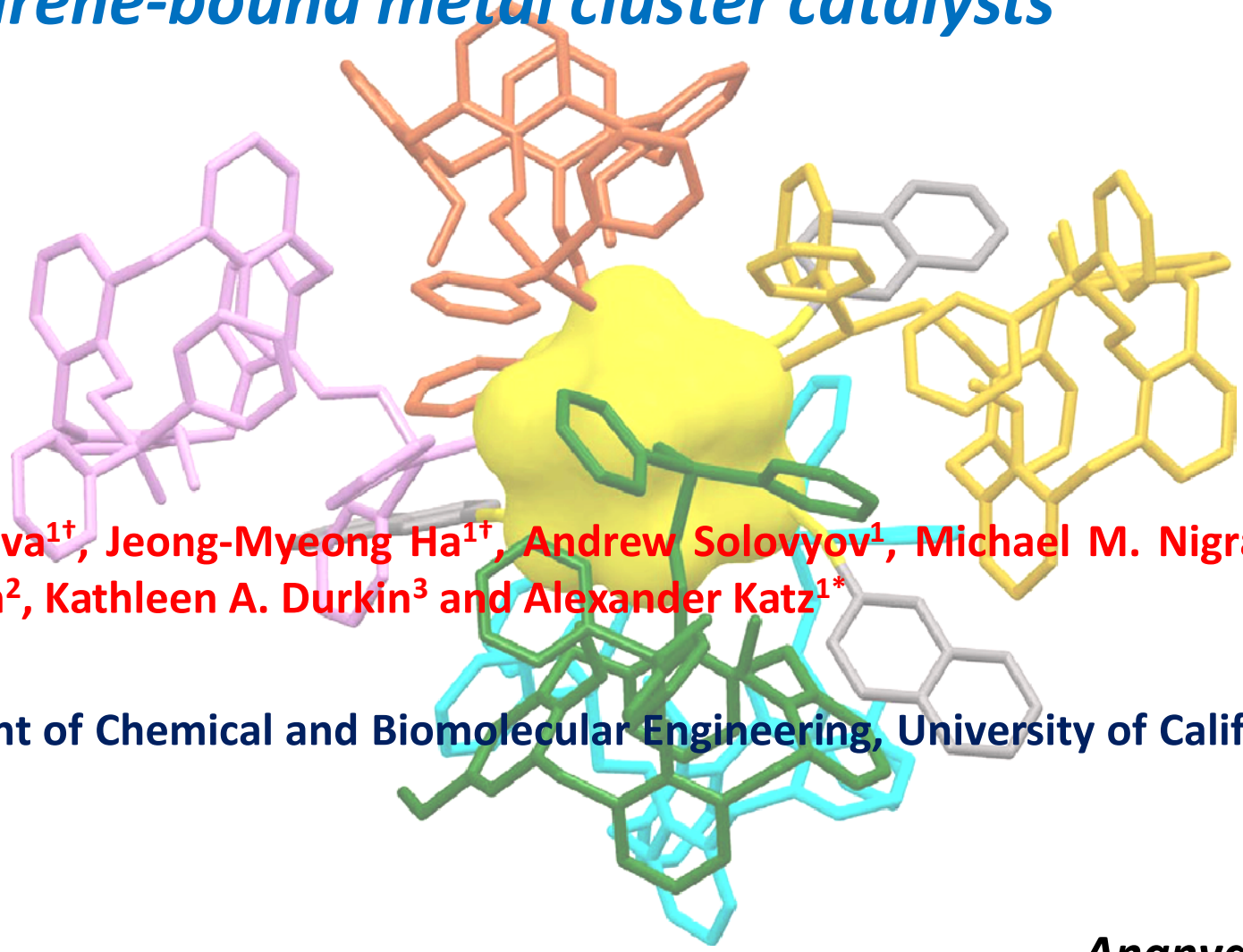
nature chemistry

A bioinspired approach for controlling accessibility in calix[4]arene-bound metal cluster catalysts



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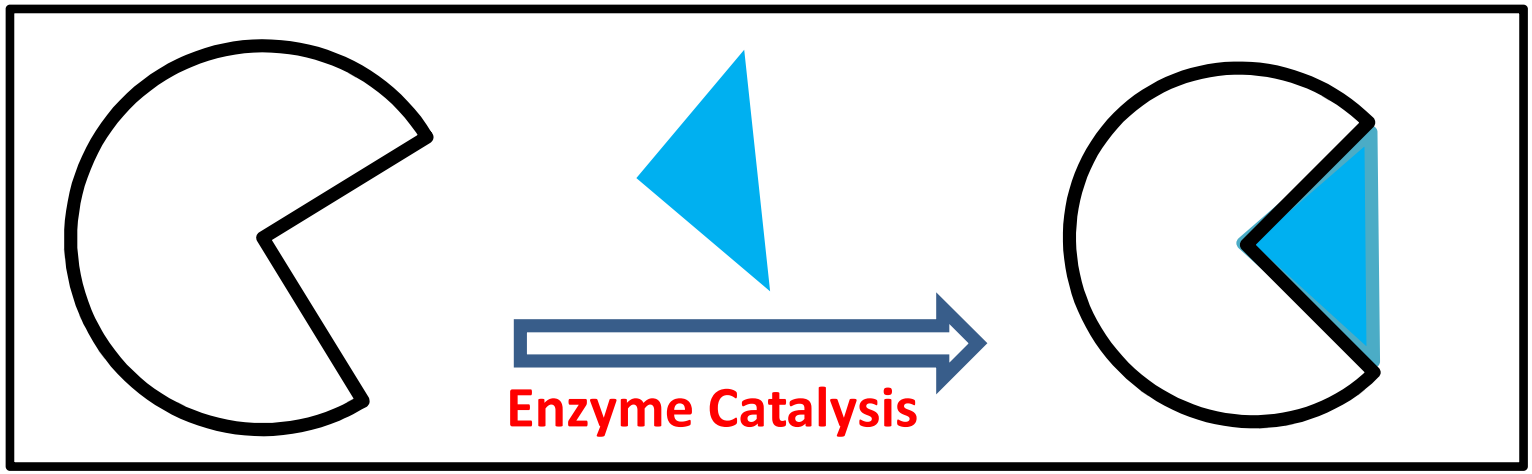


Question:

How enzymes are able to maintain coordinative unsaturation at active sites in the presence of inhibitors on the protein backbone, and in such close proximity?

View:

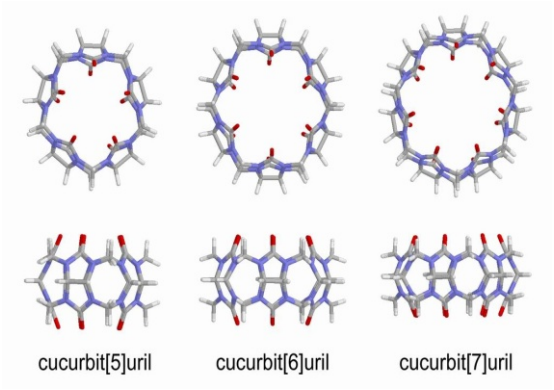
Protein backbone consists of a series of conjoined, rigid, nanoscale segments which could form a cage structure to surround each metal-cluster active site with an effective mesh size large enough to be penetrable to small molecules but not to other rigid protein segments.

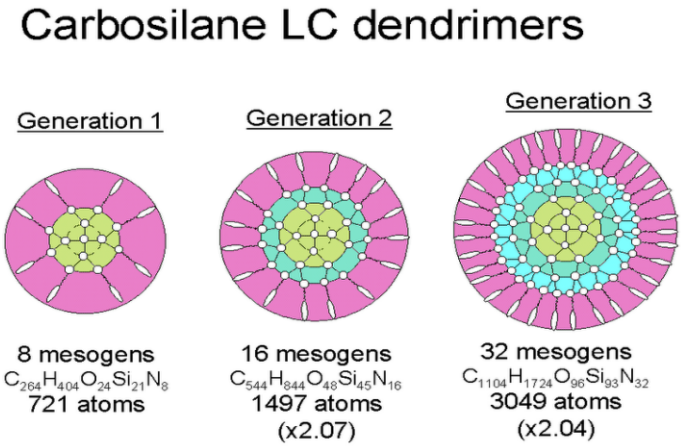
Goal :

Translate this mechanism to the realm of synthetic metal clusters, using calix[4]arene macrocycles as crude mimics of rigid protein backbo

Previously used ligands:

Cucurbituril, β-cyclodextrin, Dendron, Dendrimer and Polymer based ligands

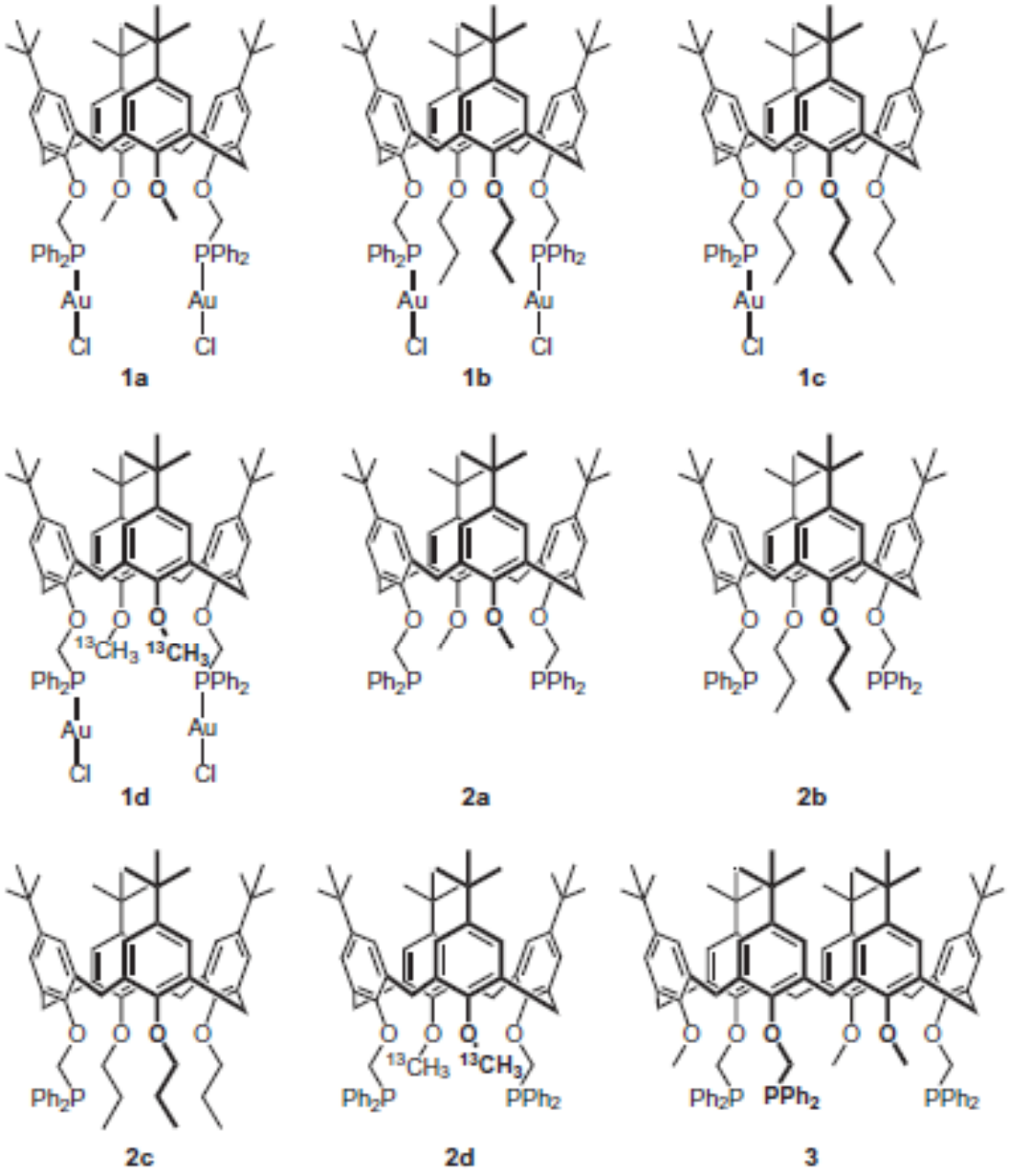




Criteria:

❖*Using organic ligands to ultimately control the electronic and catalytic properties of a metal-cluster active site requires the design and synthesis of specific ligands for the metal surfaces.*

❖*The ligands must have precisely positioned functional groups through which their interaction with the metal surfaces can be precisely controlled, and must allow accurate measurement of the surface accessibility of the resulting metal cluster–ligands systems.*



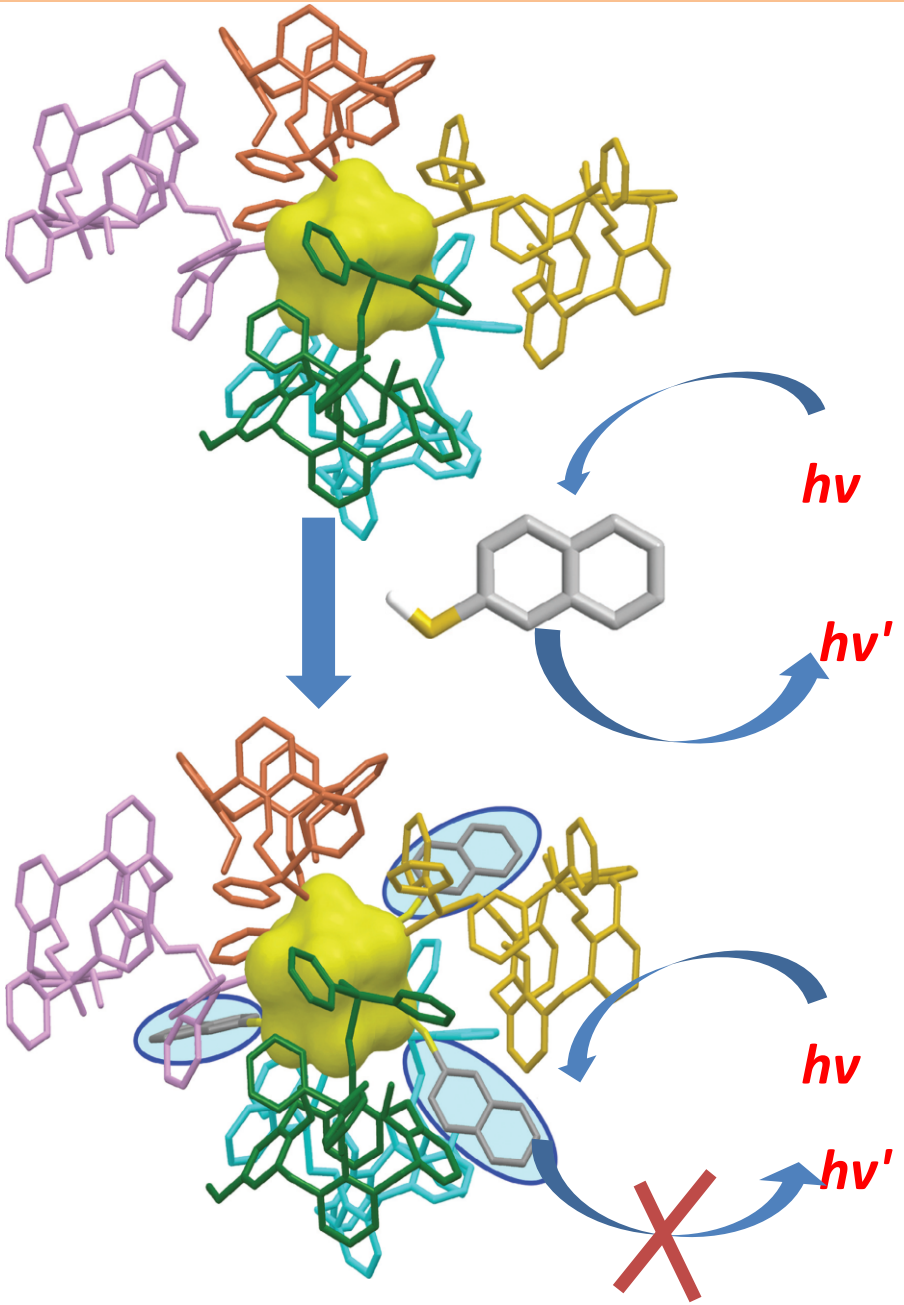
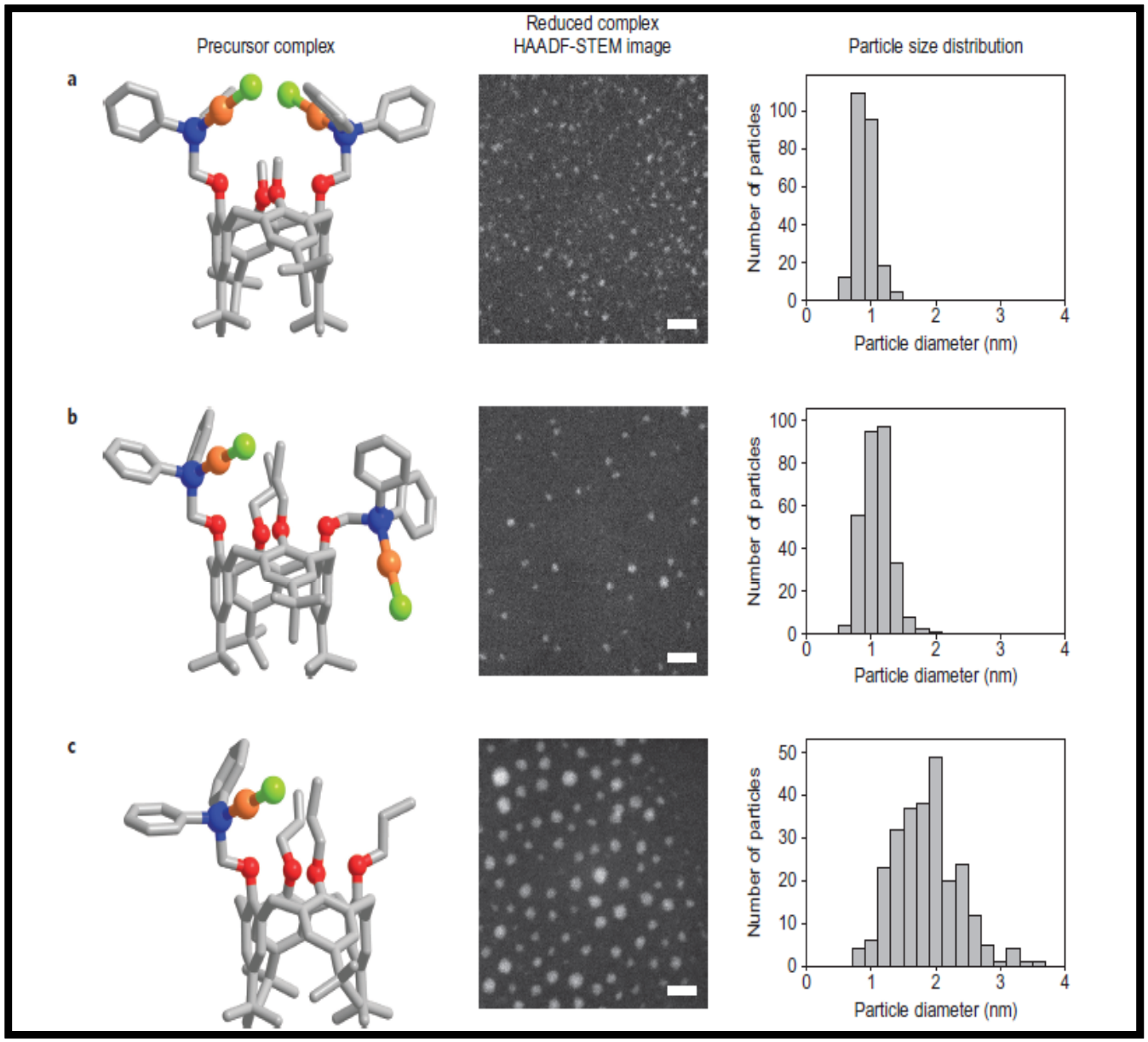
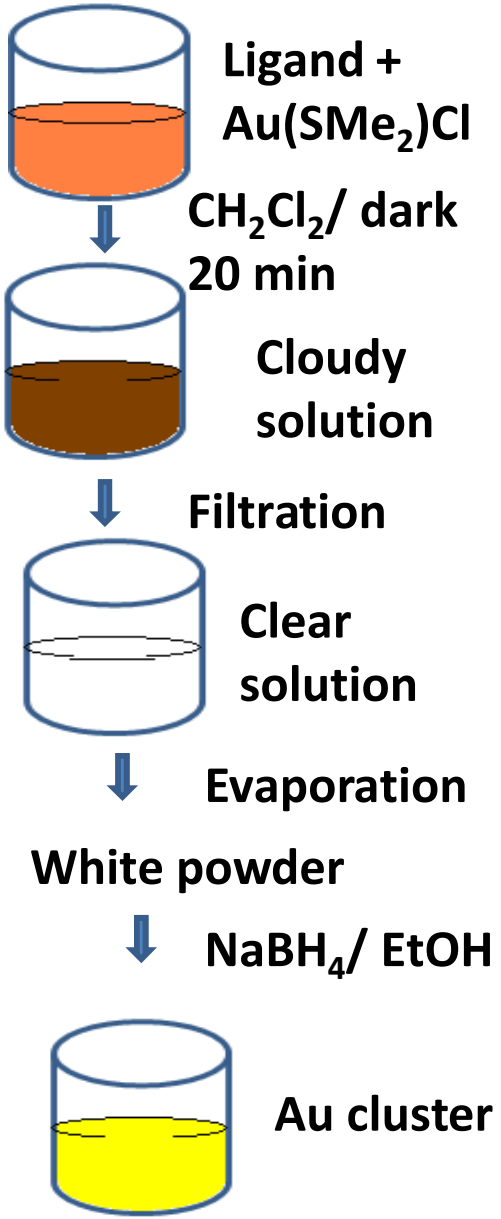


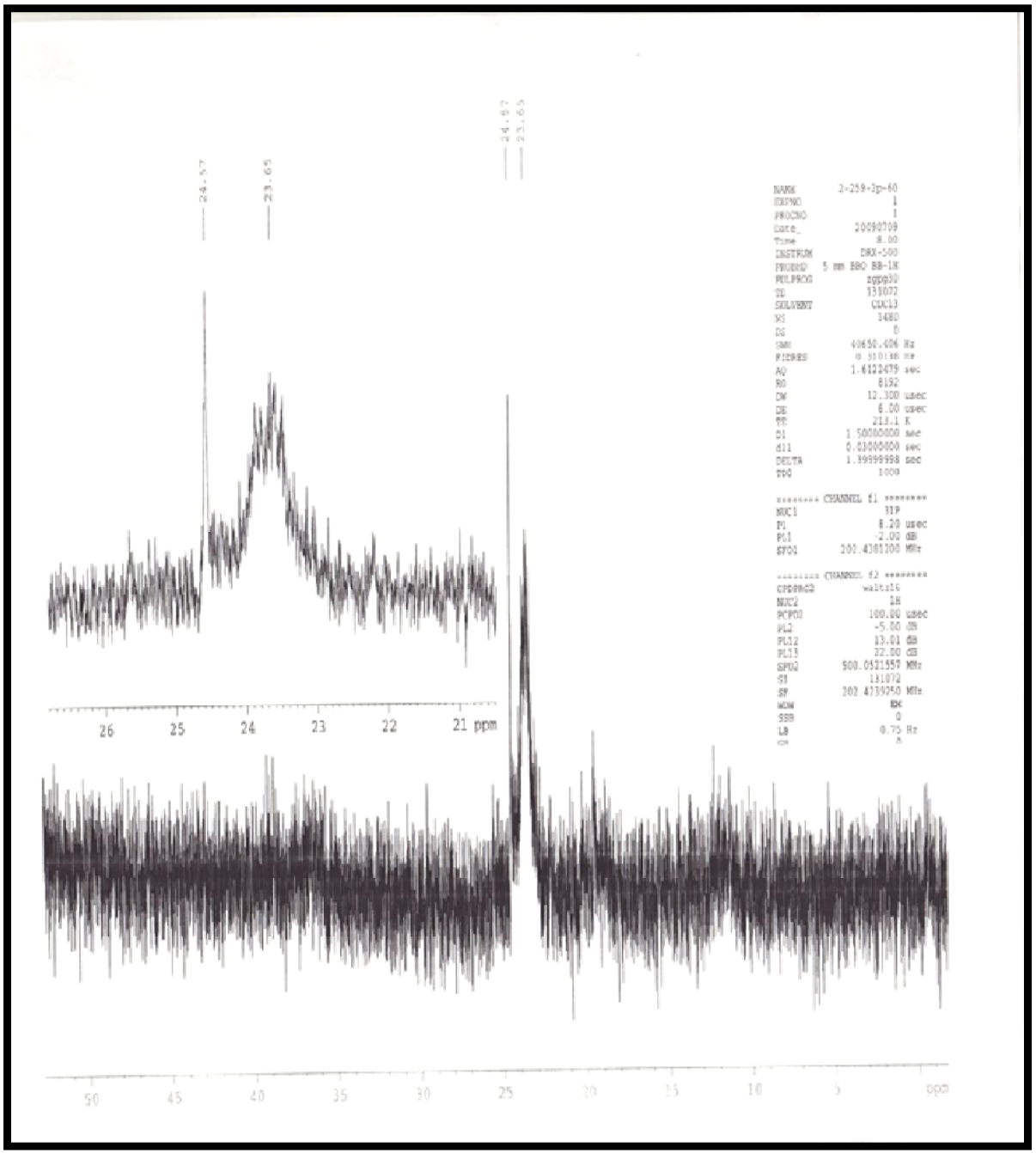
Illustration of comparative synthetic approach adopted to control the accessibility of gold clusters through bulky calix[4]arene ligands.



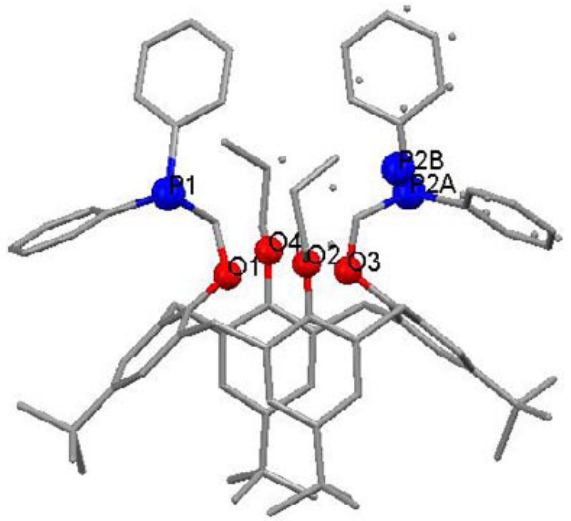
Structure of molecular precursors, and images and particle size distributions of gold clusters. a–c



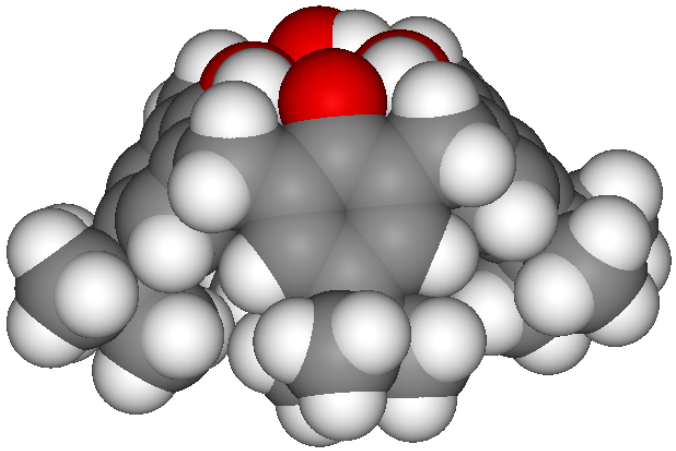
Scheme for preparation of gold cluster



^{31}P NMR spectrum of {Au-1}-2a at -60 °C



Single crystal X-ray crystallographic structure of *tert-butyl-calix[4]-(OR)$_2$(OCH$_2$PPh$_2$)$_2$ (R = C$_3$H$_7$-n)*



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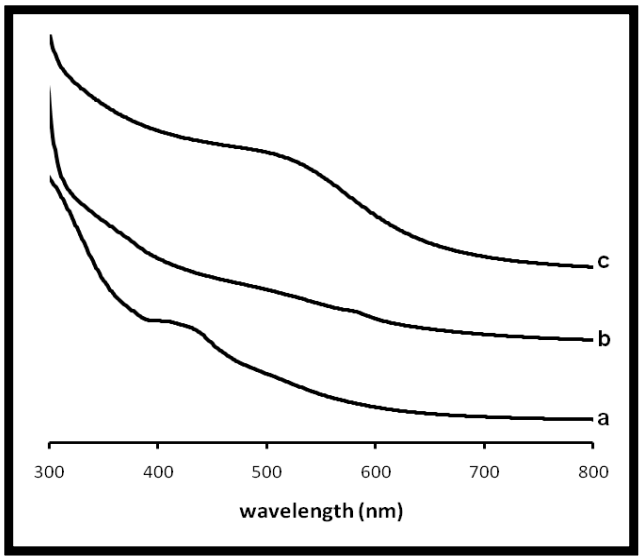
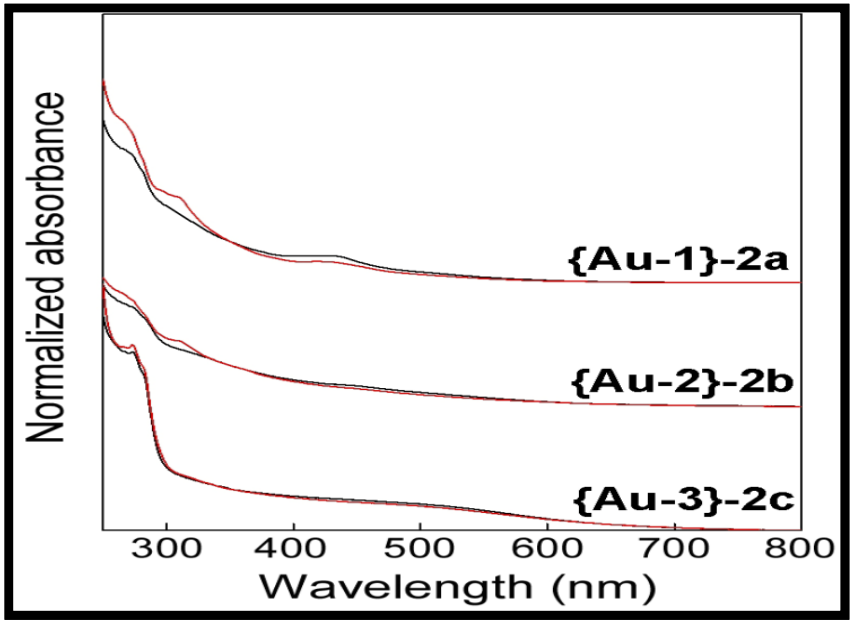
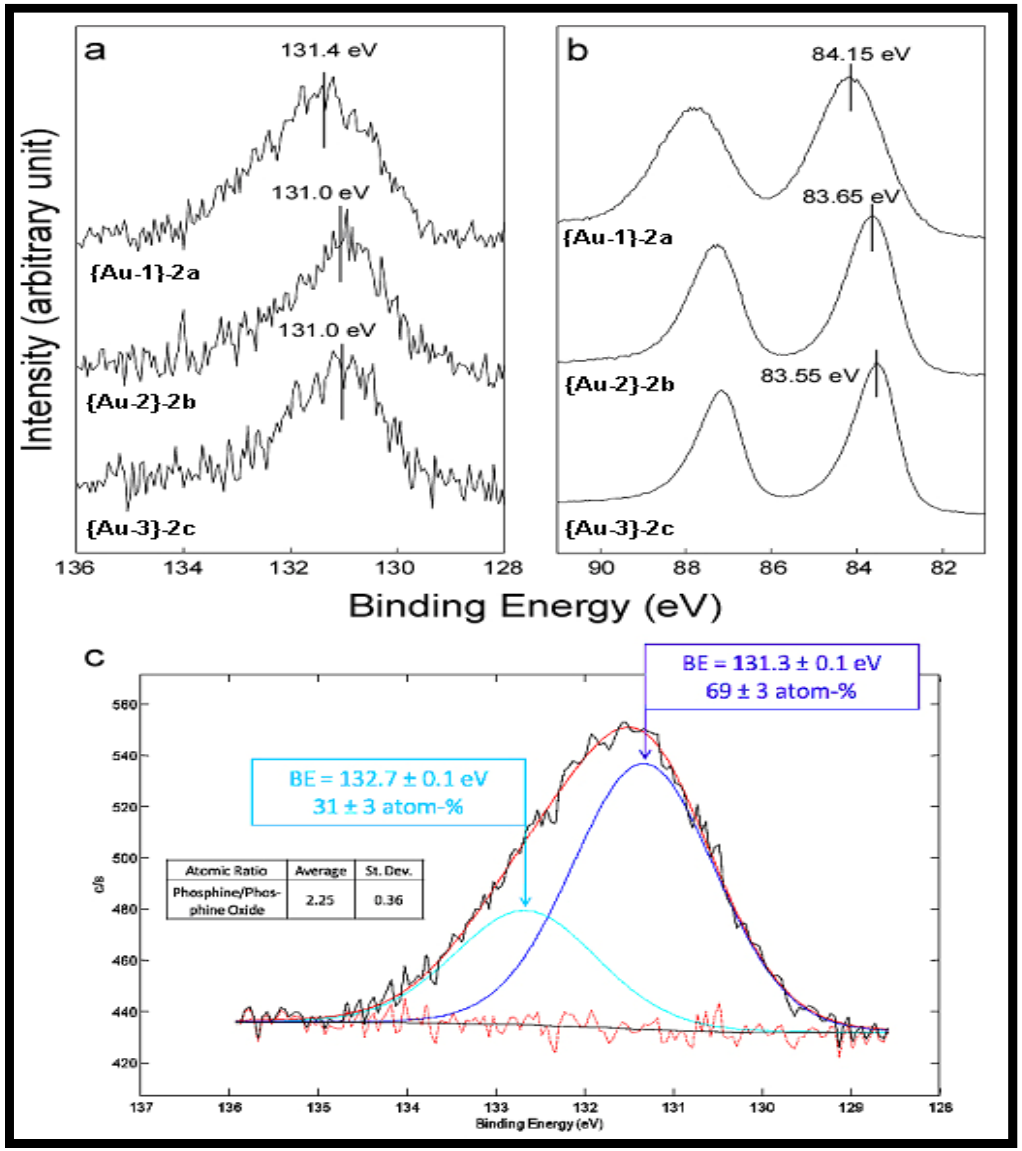


UV-Visible spectra of (a) {Au-1}-2a, (b) {Au-2}-2b, and(c) {Au-3}-2c



UV-Vis spectra of gold clusters before (black) and after (red) addition of 40-fold excess 2NT

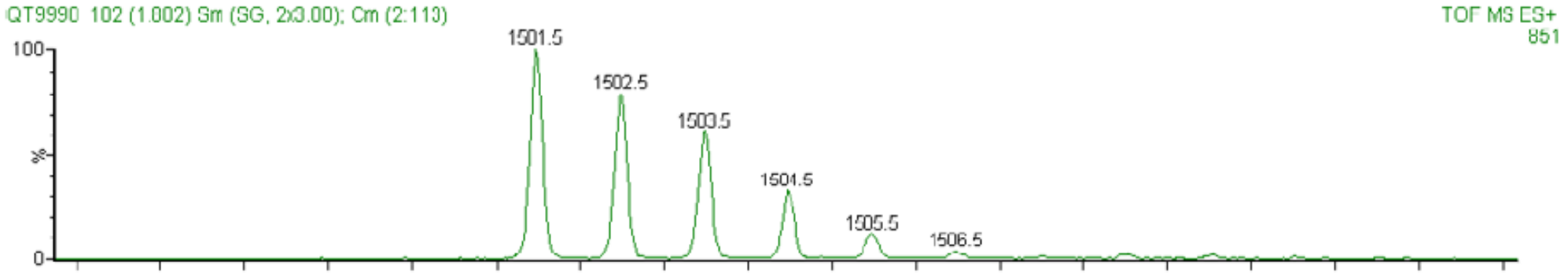


(a) P 2p and (b) Au 4f XPS results of {Au-1}-2a, {Au-2}-2b, and {Au-3}-2c. Deconvolution of {Au-1}-2a P 2p results in (a) is shown in (c). Binding energy is corrected by C 1s at 28

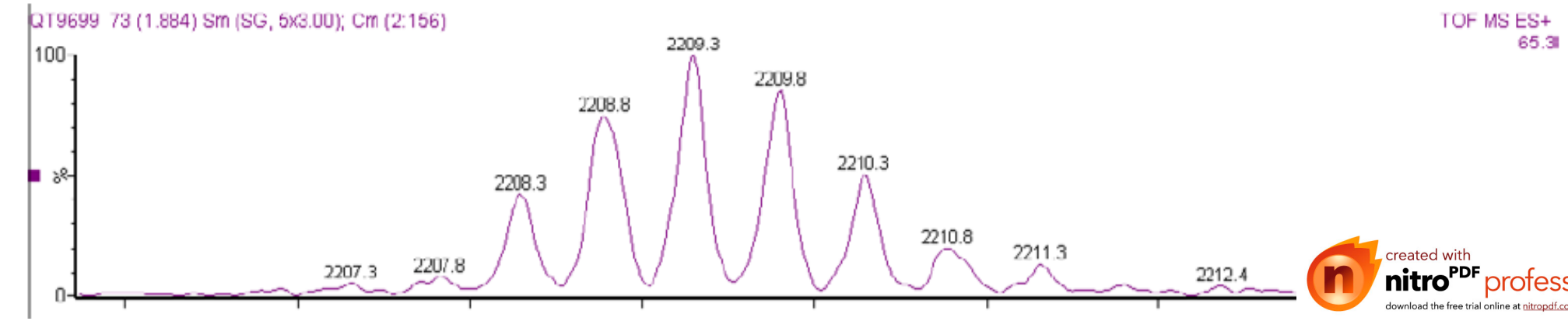
Table 1 | Summary of characterization data for gold clusters bound with lower-rim substituted calixarene-phosphine ligands.

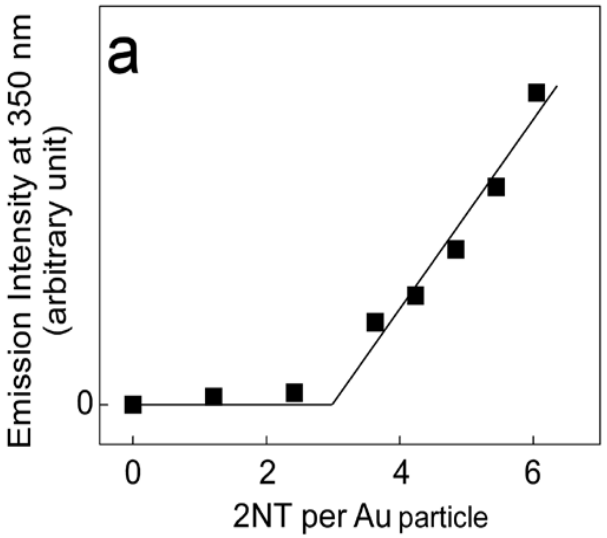
Gold cluster	Ligand	Diameter (nm*)	Au/P†	Au (wt%†)	Au 4*f* BE (FWHM) (eV§)	Total Au 2NT bound‖ (Surface Au 2NT bound)¶ (%)
{Au-1}-2a	2a	0.9±0.1	1.11±0.11	21‡	84.15 (1.64)	25.0 (25.0)
{Au-2}-2b	2b	1.1 ±0.2	1.78±0.09	38	83.65 (1.23)	6.3 (8.0)
{Au-3}-2c	2c	1.9 ±0.5	3.25±0.15	40	83.55 (1.11)	1.2 (2.1)
{Au-4}-2a	2a	4.1 ±0.9	N/D	N/D	N/D	0.0 (0.0)
{Au-4}-2c	2c	4.1 ±0.9	N/D	N/D	N/D	0.0 (0.0)
{Au-4}-3	3	4.1 ±0.9#	N/D	N/D	83.85 (1.09)#	1.4 (4.8)#

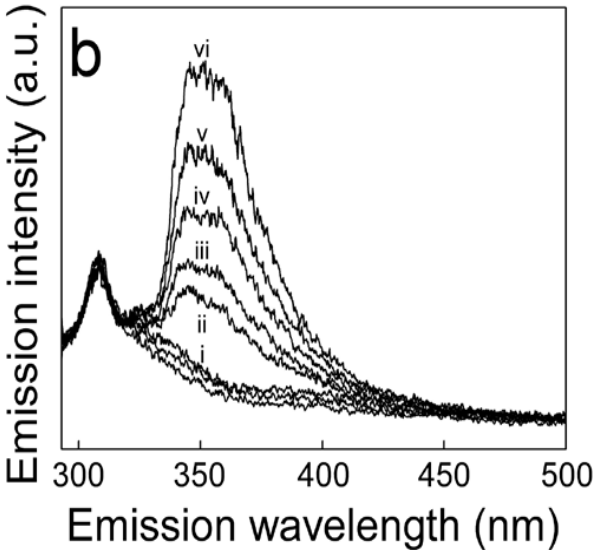
ESI mass spectra[M-Cl]$^+$ molecular ions of precursors 1a



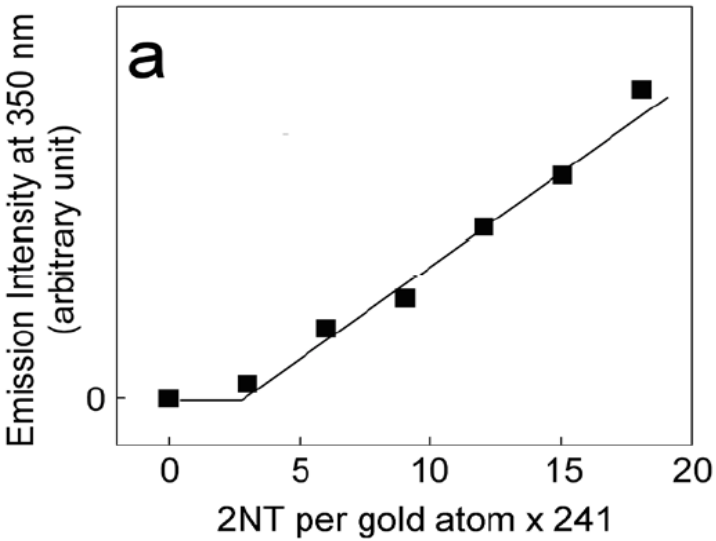
ESI mass spectrum showing a molecular ion fragment in {Au-1}-2a

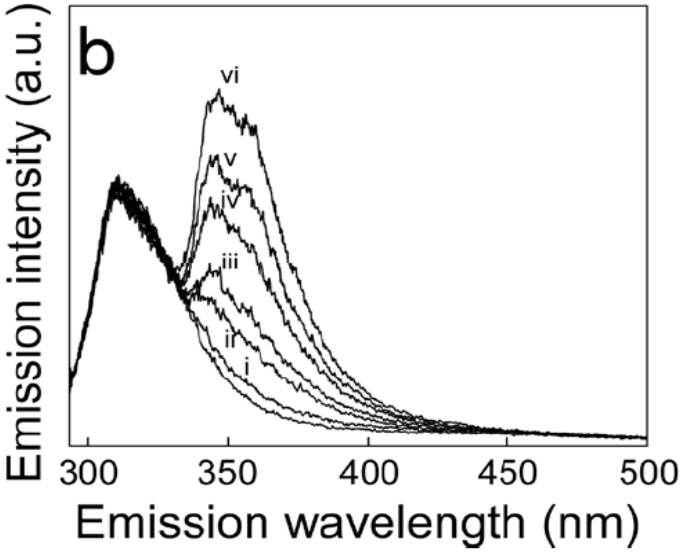




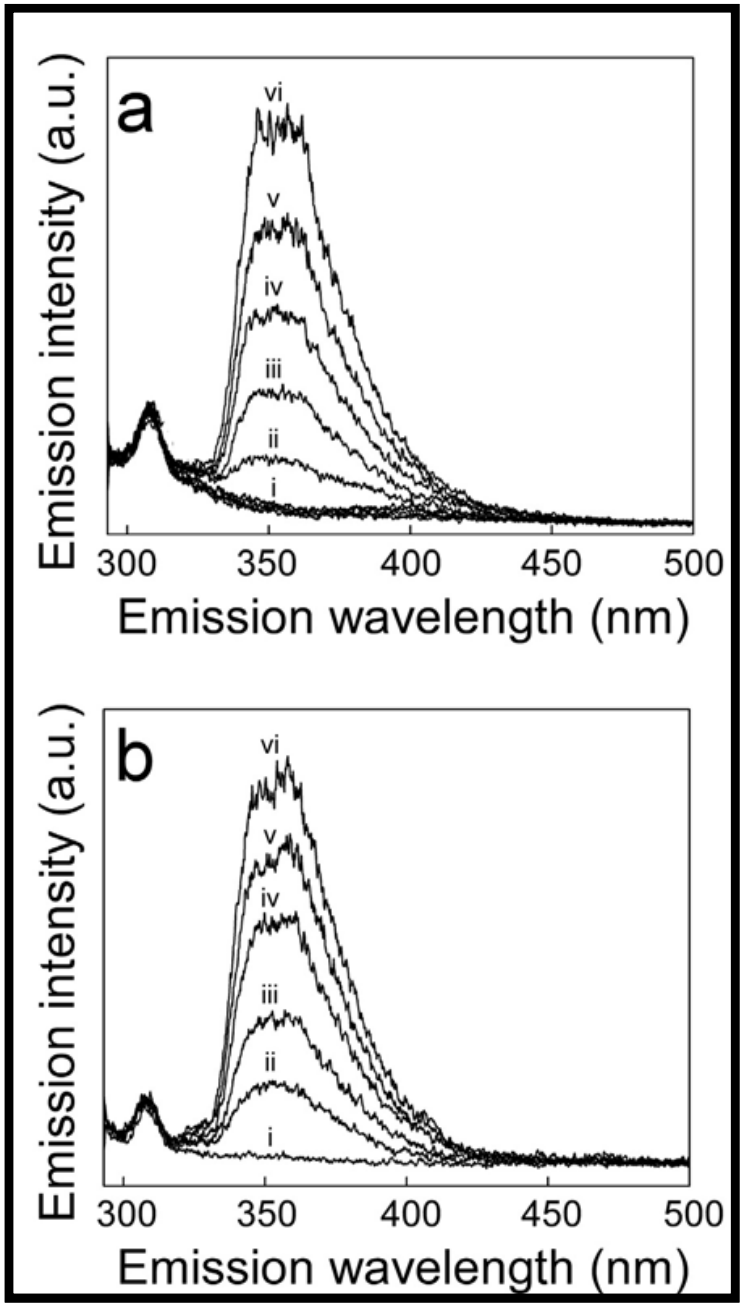


(a)Fluorescence emission intensity and (b) emission spectra of 2NT on {Au-2}-2b



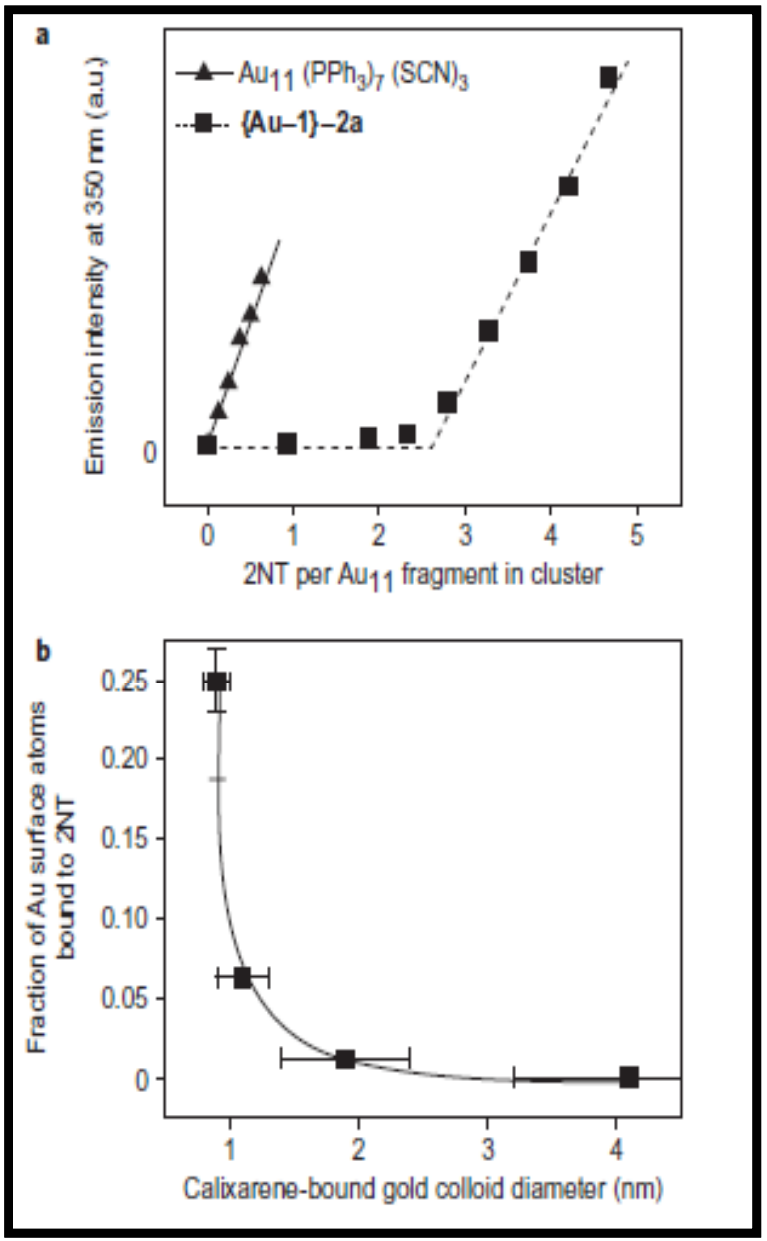


(a)Fluorescence emission intensity and (b) emission spectra of 2NT on {Au-3}-2c



Fluorescence emission spectra of 2NT on (a) {Au-1}-2a and (b) $Au_{11}(PPh_3)_7(SCN)_3$

a) Fluorescence emission intensity of 2NT on {Au–1}–2a (squares) and $Au_{11}(PPh_3)_7(SCN)_3$ (triangles) clusters



b) Fraction of gold surface atoms that are bound with 2NT (lower b[illegible]) versus cluster diameter

❖*The design and synthesis of organic ligand-bound gold clusters using a bioinspired approach is demonstrated, in which calix[4]arene phosphine ligands serve as crude macrocyclic mimics of rigid protein backbone segments.*

❖*The resulting electron-rich clusters show that using an organic ligand is a versatile approach to modify the electronic properties of the metal.*

❖*The calixarene-bound clusters demonstrate high levels of accessibility, with up to 25% of the total gold atoms binding chemisorption probe 2NT in cluster {Au–1}–2a, which is in contrast to a complete lack of accessibility observed in similarly sized Au_{11}-phosphine clusters as well as larger gold nanoparticles.*

❖*The observed abrupt increase in accessibility when the metal-core diameter is smaller than the calixarene ligand size suggests a new and general mechanism of accessibility in organic ligand-bound metal clusters.*

❖ ***surface-accessibility can be controlled by careful selection of the stabilizing ligands. This effect could represent a general mechanism for the reactivity of organic ligand bound metal clusters, and could potentially be used to control their surface accessibility. The next step will be to apply these clusters in a catalytic reaction.***

❖ ***As we are now using small protein like Lysozyme to establish the cluster formation mechanism, we can use this as a model for big proteins. We can extend this to see the catalysis in protein protected cluster as model.***

❖***Can cluster be the active site in protein protected clusters??***