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ARTICLE

Atomically Precise, Thiolated Copper−Hydride Nanoclusters as Single-Site Hydrogenation Catalysts for Ketones in Mild Conditions

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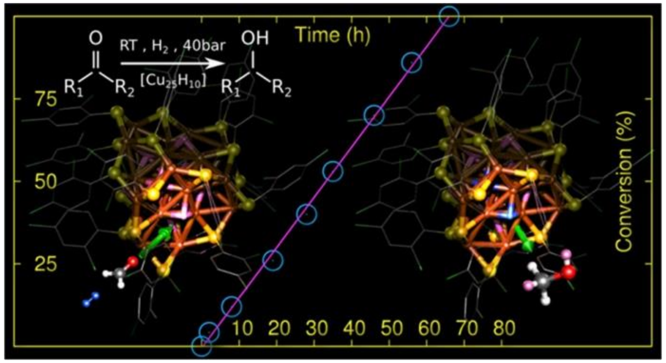


Md Bodiuzzaman
01-06-2019

Relevance to our group

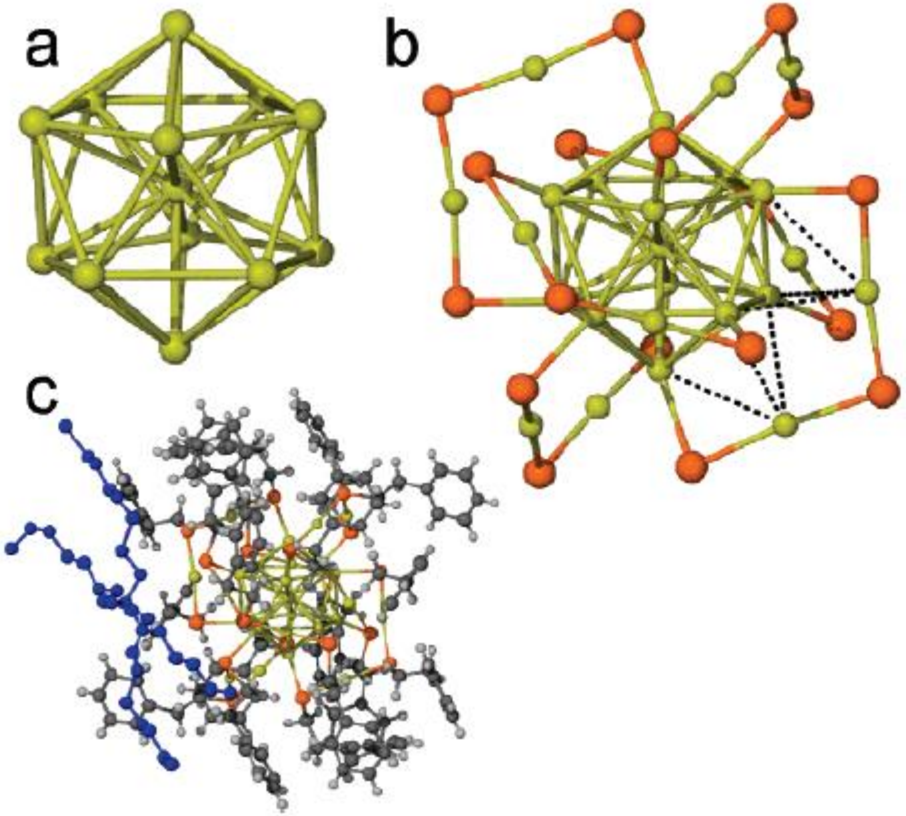
In previous years, the composition, structure, and electronic properties of several ligand-stabilized clusters have been investigated. In contrast to the increasing number of gold and silver nanoclusters, studies on copper clusters remain relatively few.

Copper nanomaterials have been identified to be good catalysts for electroreduction and several diverse organic reactions such as hydrogenation of CO, hydroamination of alkenes and alkynes, and chemoselective hydrogenation of unsaturated ketones to unsaturated alcohols.

J|A|C|S
COMMUNICATIONS

Crystal Structure of the Gold Nanoparticle $[N(C_8H_{17})_4][Au_{25}(SCH_2CH_2Ph)_{18}]$

Michael W. Heaven, Amala Dass, Peter S. White, Kennedy M. Holt, and Royce W. Murray*
Kenan Laboratories of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290

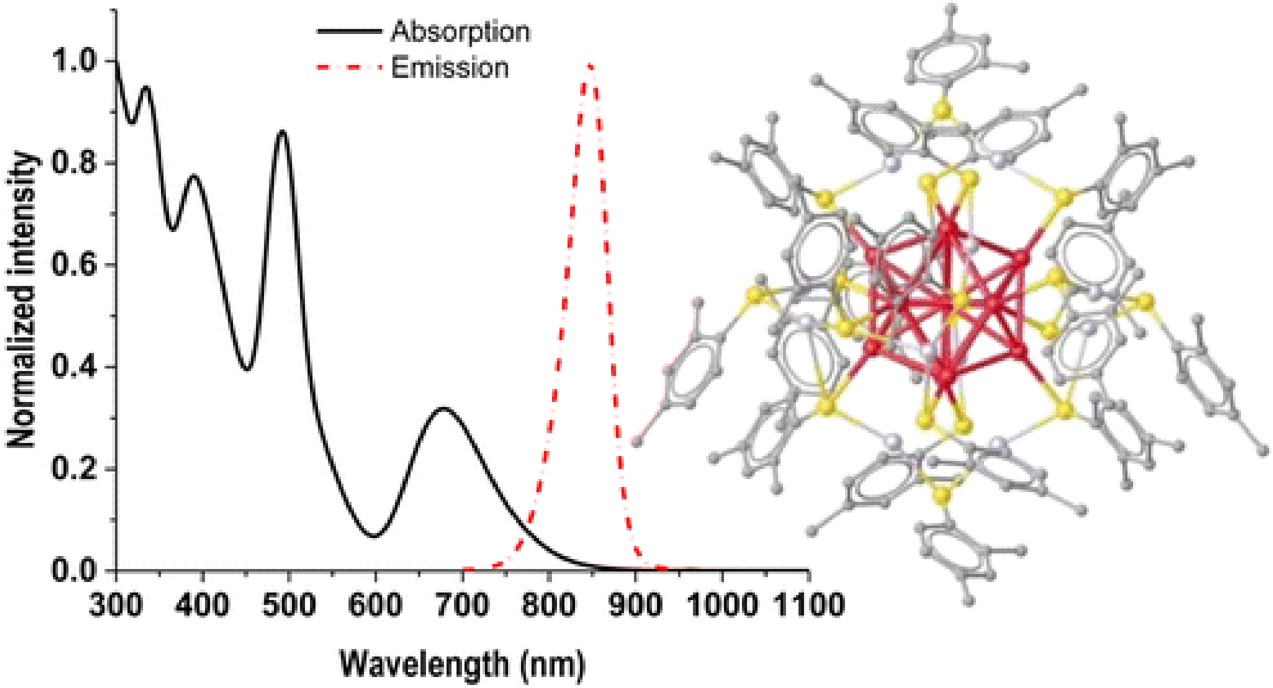


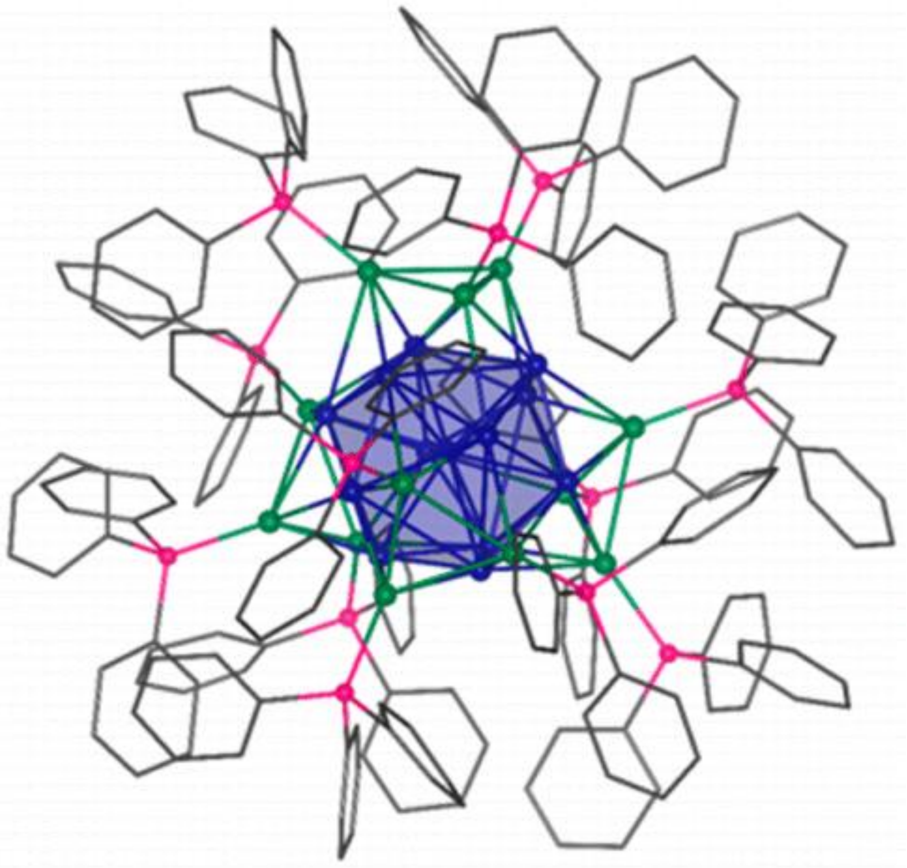
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

$[Ag_{25}(SR)_{18}]^{-}$: The ‘Golden’ Silver Nanoparticle

Chakra P Joshi, Megalamane S. Bootharaju, Mohammad J. Alhilaly, and Osman M. Bakr





$[Cu_{25}H_{22}(PPh_3)_{12}]^+$

$$\begin{array}{c} 24\ Cu(OAc) + CuCl \\ +\ 12\ PPh_3 + 13\ Ph_2SiH_2 \end{array} \xrightarrow[-\ 12\ Ph_2Si(OAc)_2,\ -\ H_2]{C_6H_6,\ RT,\ 14\ h} \begin{array}{c} [Cu_{25}H_{22}(PPh_3)_{12}]Cl\ (\mathbf{1}) \\ +\ [Cu_{18}H_{17}(PPh_3)_{10}]Cl\ (\mathbf{2}) \\ +\ Cu^0 \end{array}$$

Nguyen, T. A.; Jones, Z. R.; Goldsmith, B. R.; Buratto, W. R.; Wu, G.; Scott, S. L.; Hayton, T. W. A Cu_{25} Nanocluster with Partial Cu(0) Character. *J. Am. Chem. Soc*. **2015**, 137, 13319−13324.

- In this paper, they have reported the synthesis, crystallographic structure, and characterization of a thiolated copper nanocluster comprising 25 Cu atoms with 18 thiolate ligands, however, embedded with 10 hydride ions.

- In contrast to the Au_{25} and Ag_{25} clusters, which exist as monoanions, the Cu_{25} cluster exists as a trianion, viz. $[Cu_{25}H_{10}(SPhCl_2)_{18}]^{3-}$, labeled as **1**.

- A complete atomistic picture for understanding the interaction between reactant molecules and the highly stable, supposedly chemically passivated clusters, however, has been lacking.

- In this study, they demonstrated, using a combination of experiments and first-principles calculations, that cluster **1** performs as a catalyst for the hydrogenation of ketones to corresponding alcohols at room temperature, even with all ligands perfectly intact and gain an atomistic understanding of the catalytic mechanism by a fully protected cluster.

100 mg of $Cu(OAc)_2 \cdot H_2O$ + 32 mg of PPh_4Br

↓ 30 µL $HSPhCl_2$

Formation of thiolate

↓ 90 mg $NaBH_4$

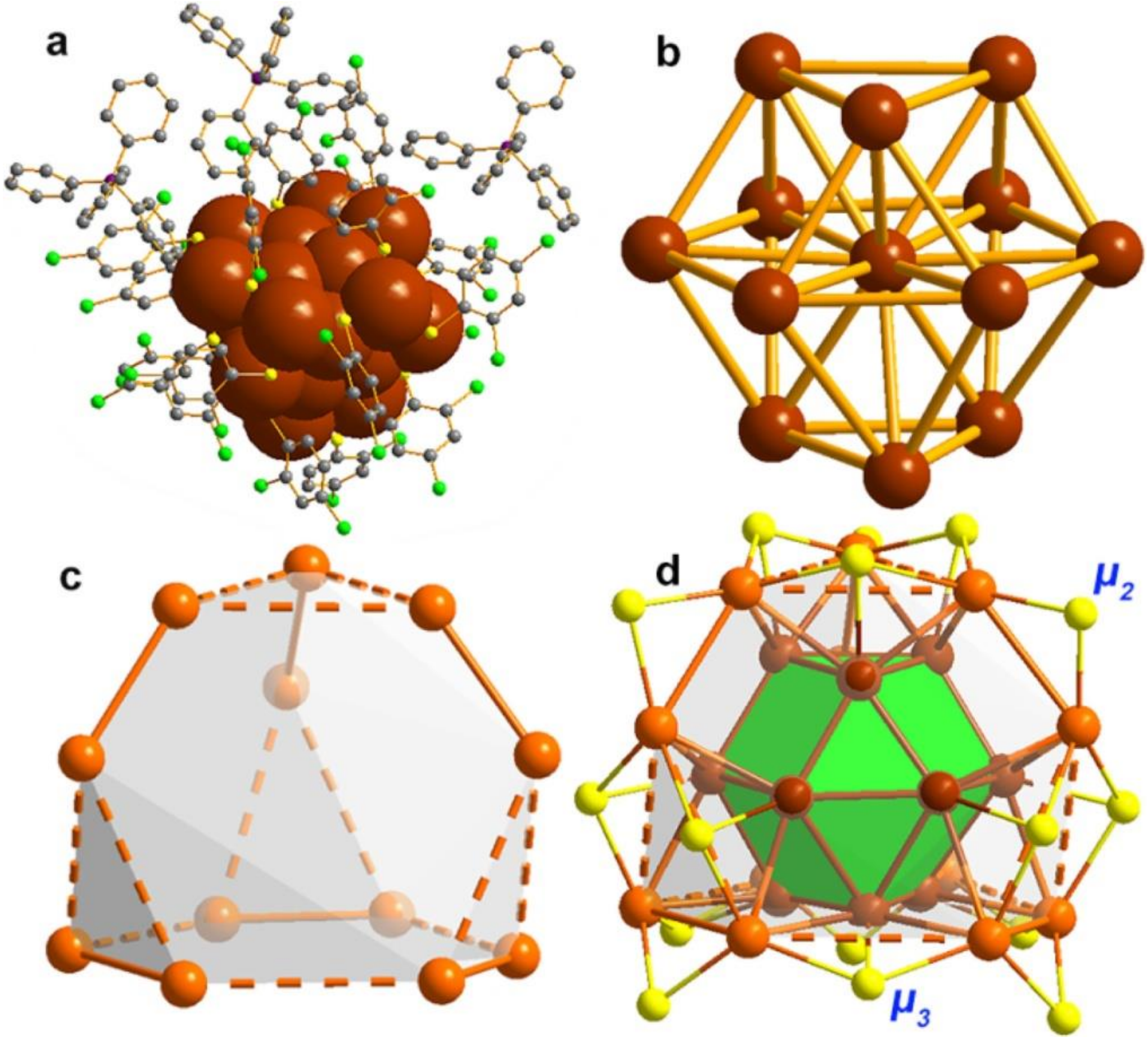
Reaction mixture was stirred
for 3 h at room temperature

↓ Cleaned by MeOH/water

$[Cu_{25}H_{10}(SPhCl_2)_{18}]^{3-}$

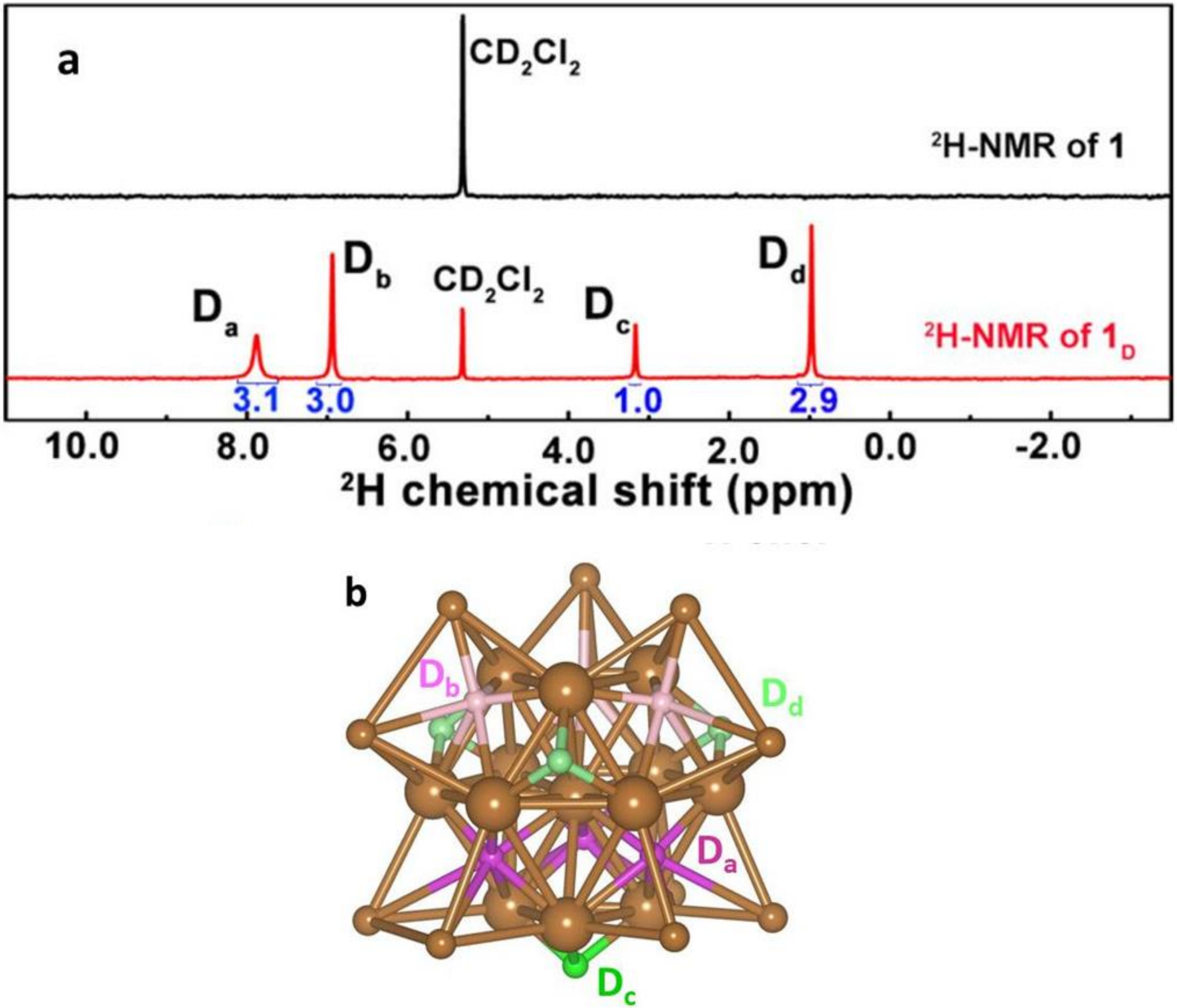
Crystallization

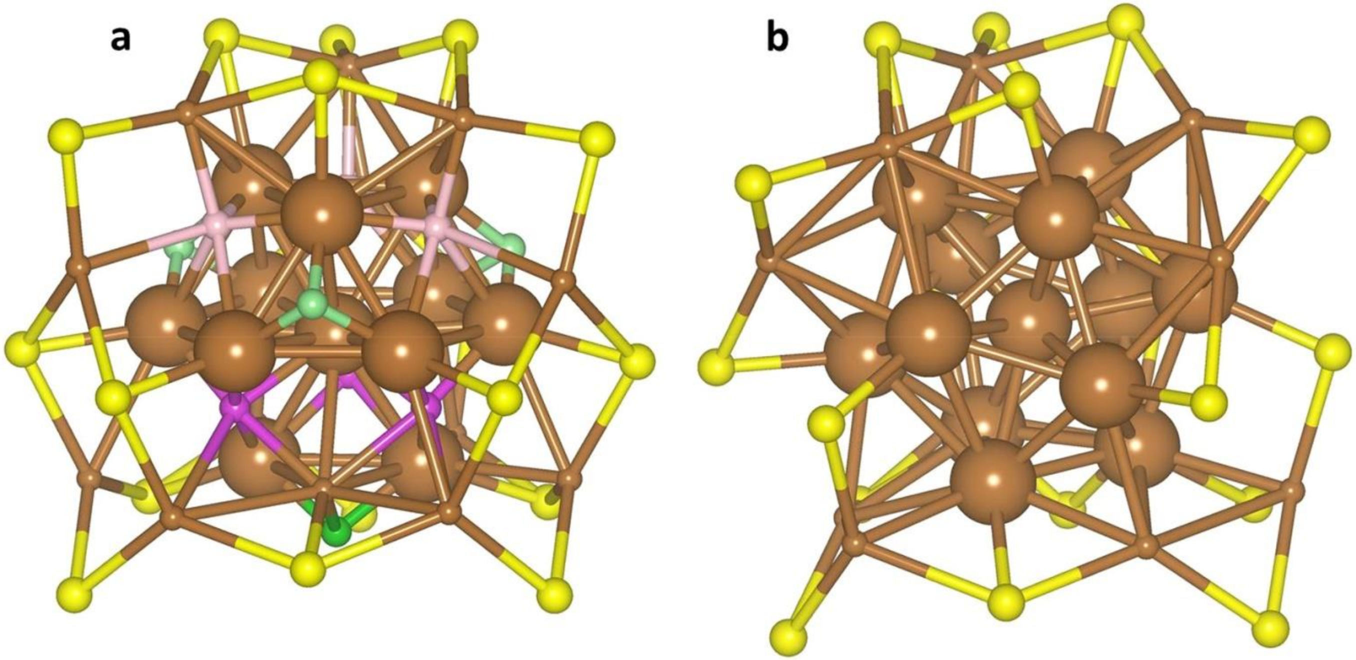
By diffusion with hexane into DCM solution at 4˚C for 1 week, bright-red single crystals were obtained

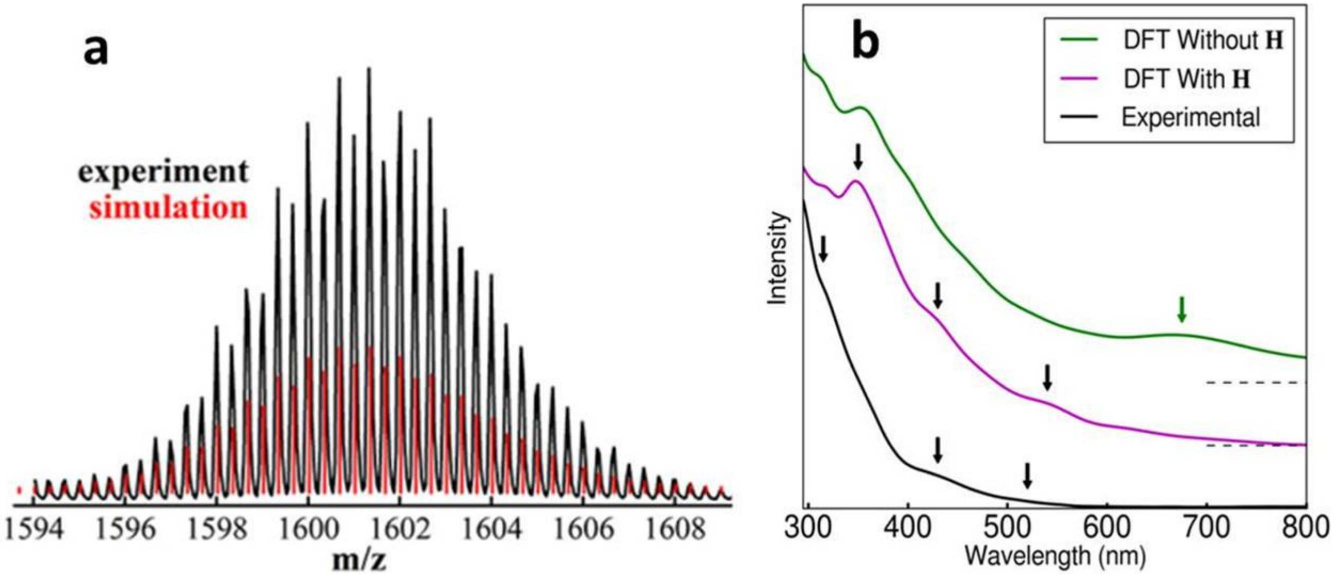


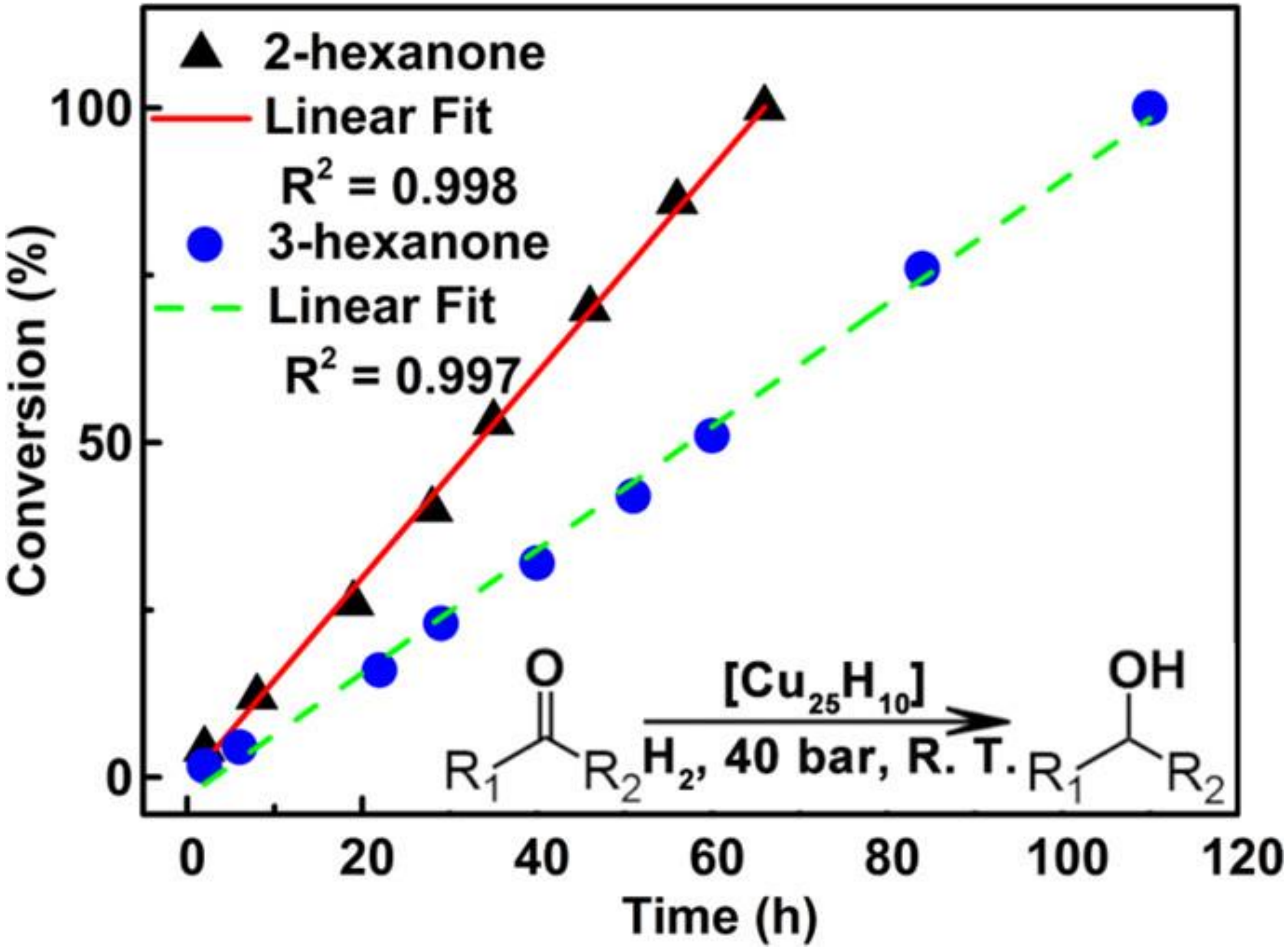
Structure of cluster **1** determined from X-ray diffraction results: (a) ball-and-stick view of **1** with space-filling metal core, 18 ligands (−SPhCl2) and three counterions [(PPh4)+]; (b) centered twinned cuboctahedron Cu@Cu12 inner core; (c) third layer forming a Cu12-truncated v3 tetrahedral shell; (d) metal atoms within the shell and in the two layers bridged by μ2 and μ3 S atoms.

Color code: dark-red and light-brown, Cu; gray, C; yellow, S; bright green, Cl; purple, P. Hydrogen atoms have been omitted for clarity.

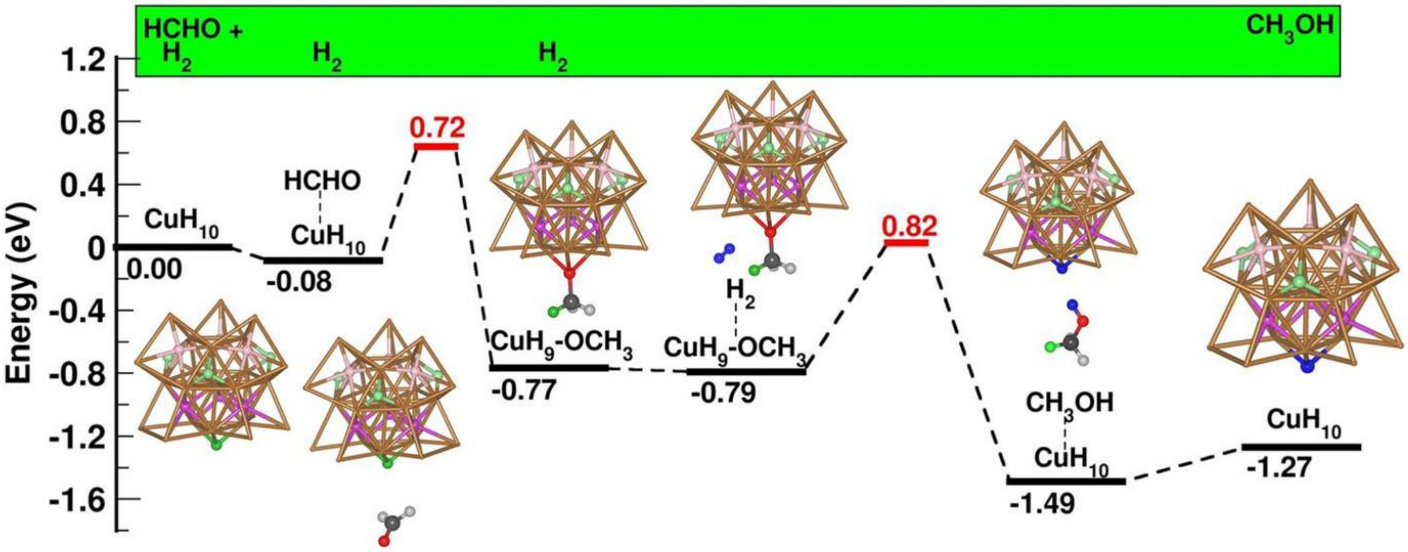

a
CD_2Cl_2
^{2}H-NMR of 1
D_a
D_b
CD_2Cl_2
D_c
D_d
^{2}H-NMR of 1_D
3.1
3.0
1.0
2.9
10.0
8.0
6.0
4.0
2.0
0.0
-2.0
^{2}H chemical shift (ppm)
b
D_b
D_d
D_a
D_c


a
b

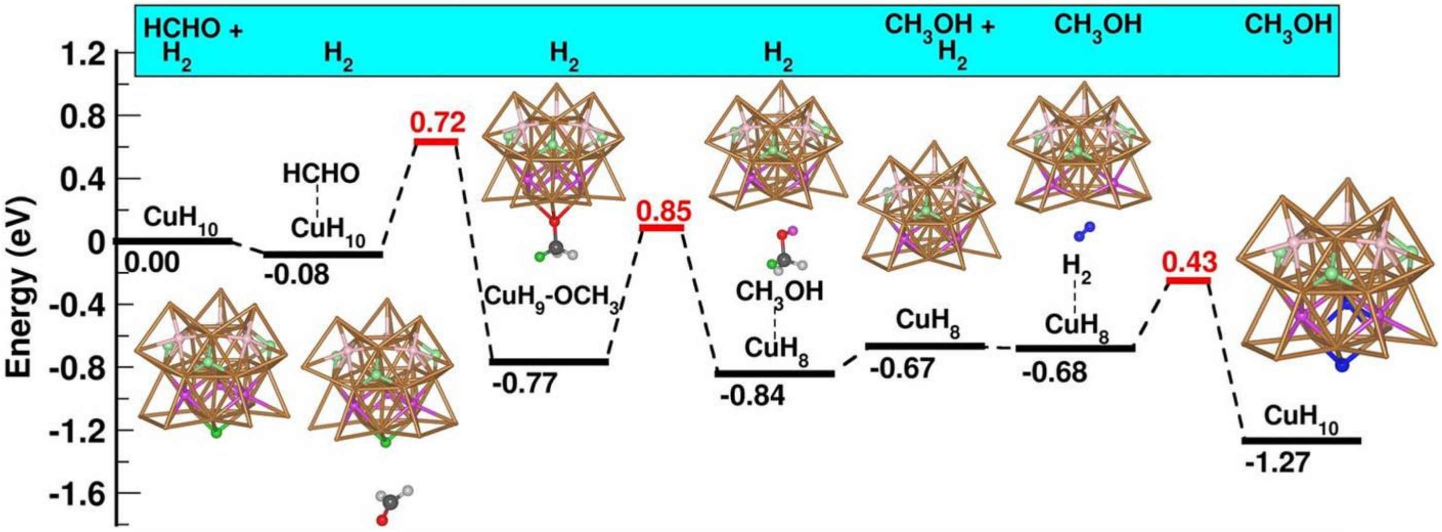

a
experiment
simulation
1594
1596
1598
1600
1602
1604
1606
1608
m/z
b
DFT Without H
DFT With H
Experimental
Intensity
300
400
500
600
700
800
Wavelength (nm)

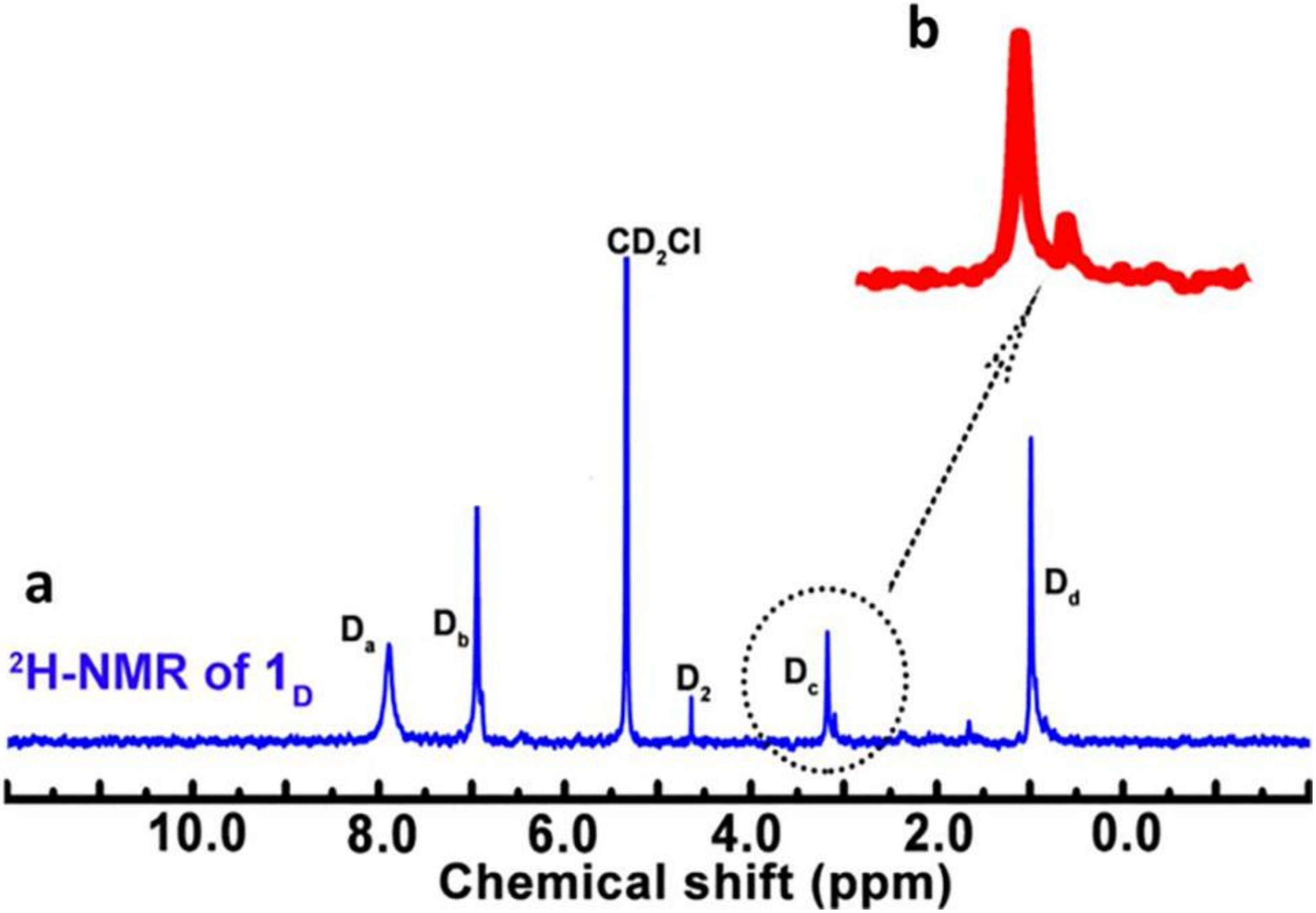

2-hexanone
Linear Fit
$R^2 = 0.998$
3-hexanone
Linear Fit
$R^2 = 0.997$
Conversion (%)
100
50
0
0
20
40
60
80
100
120
Time (h)
O
R_1
R_2
$[Cu_{25}H_{10}]$
H_2, 40 bar, R. T.
OH
R_1
R_2

a. ***Route 1 involves one H from the cluster***

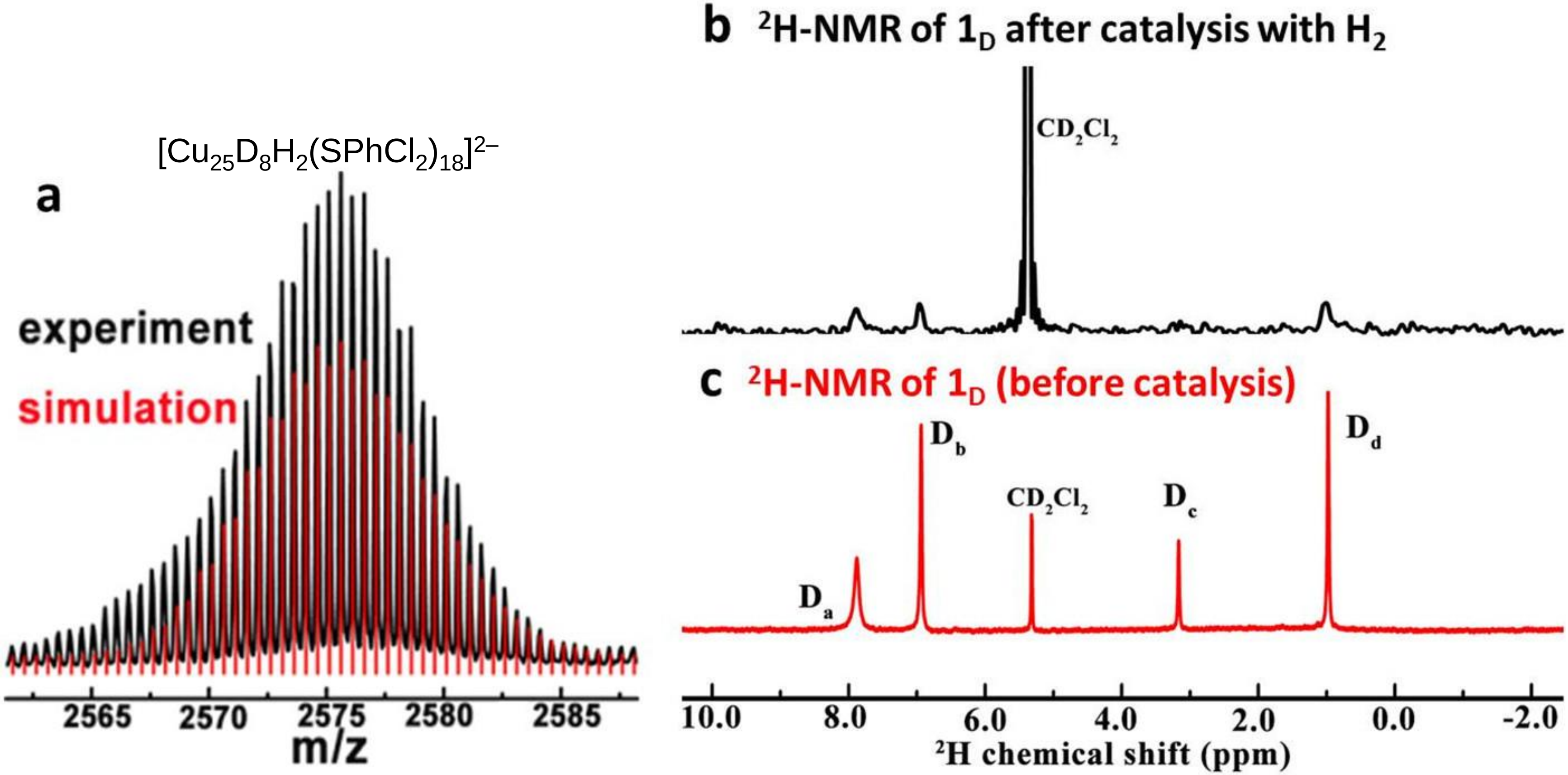


b. ***Route 2 involves two H from the cluster***

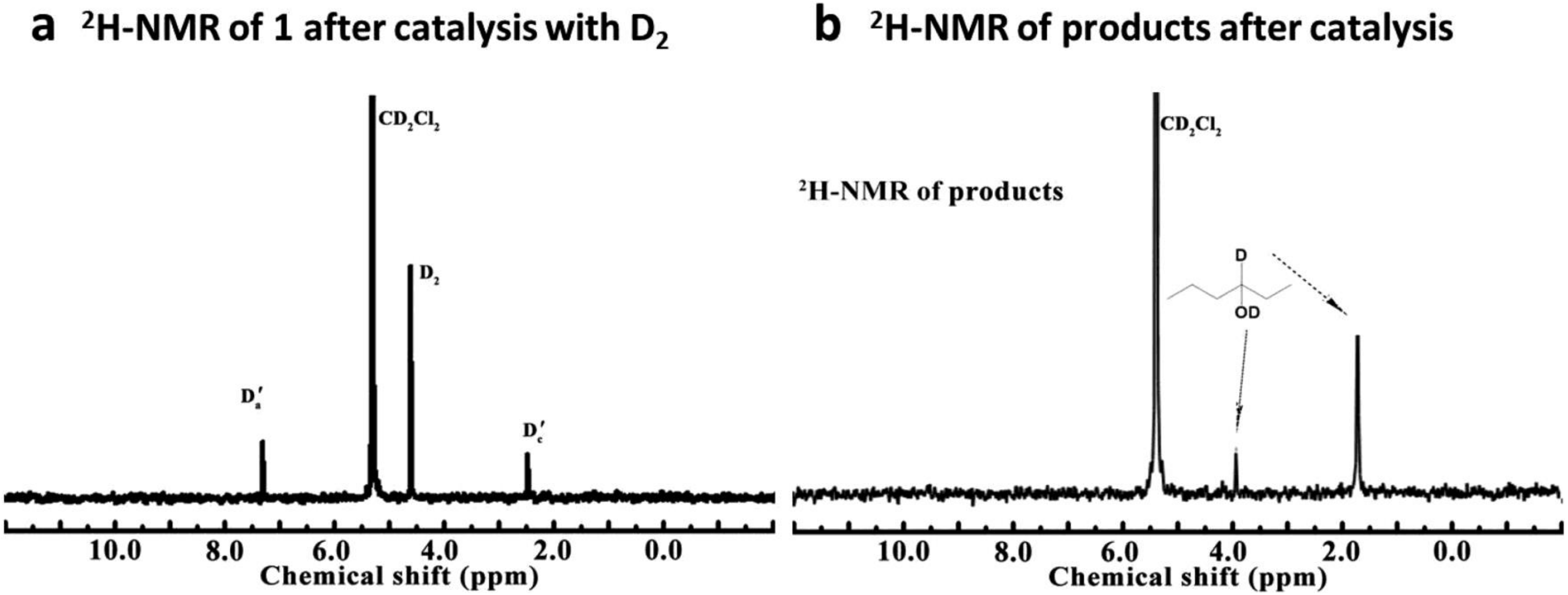




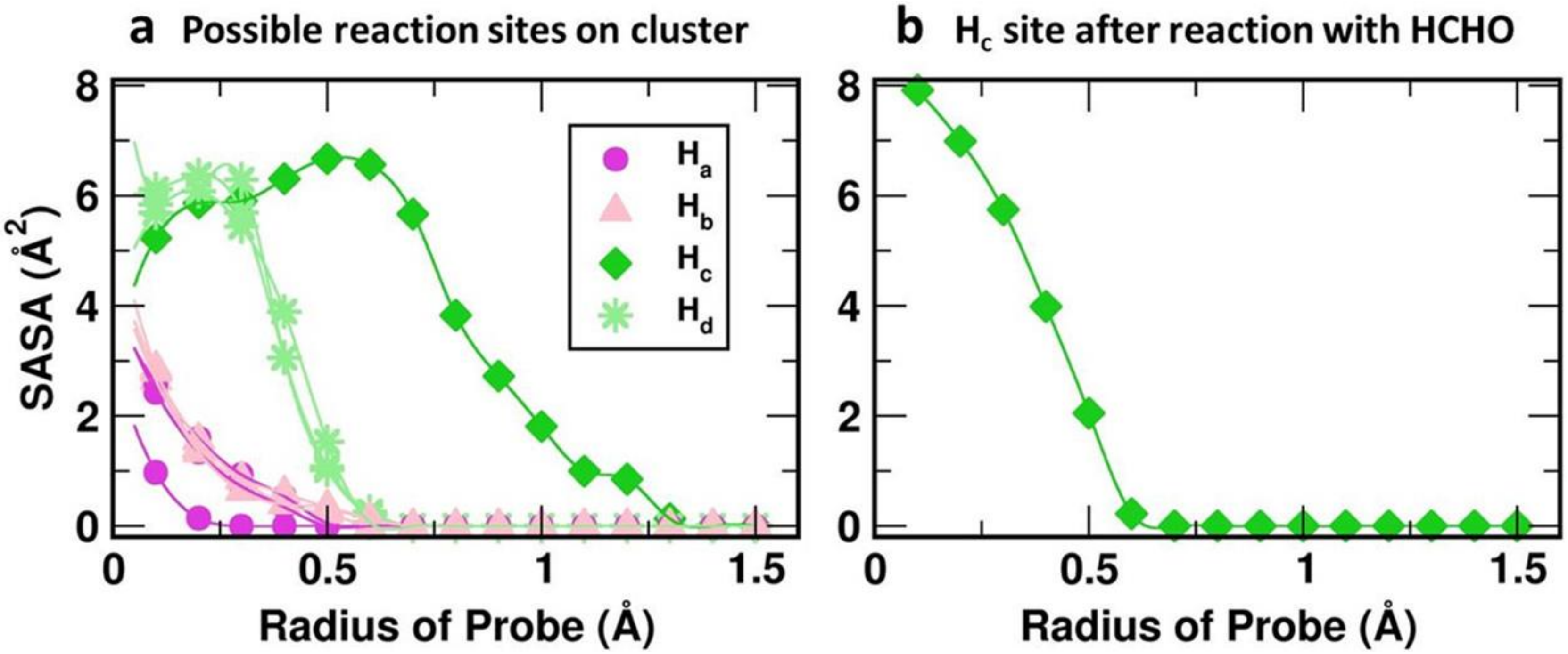
^{2}H NMR of **1D** with 3-hexanone in CH_2Cl_2. The interaction of the reactant molecule 3-hexanone with the **1D** cluster may be causing a chemical shift in the NMR peak for Dc. This seems to support our suggestion of a single-site mechanism for the catalytic reaction.



(a) ESI-MS spectrum of re-collected **1D** after the catalysis under H2 shows that two to four D atoms from the cluster have been replaced by two H atoms {simulation is for $[Cu_{25}D_8H_2(SPhCl_2)_{18}(PPh_4)]^{2-}$}, which suggests the occurrence of Route 2 mechanism. (b) 2H NMR spectra of **1D** after catalysis with H_2 can be compared with (c) spectra of **1D** before catalysis to highlight the disappearance of the Dc peak in (b); this clearly confirms our suggestion for a single-site mechanism. The Dc atom has definitely been replaced by a hydrogen atom during the catalytic process.



Reaction of **1** with ketone and D2. (a) 2H NMR of **1** after catalysis with D2 shows the appearance of two peaks that may be slightly right-shifted but correspond to Dc and Da atoms in the cluster. This confirms that two H atoms in the cluster have been replaced by two D atoms from molecular D2, supporting the Route 2 catalytic mechanism. (b) 2H NMR show that the alcohol product is deuterated.



(a) SASA analysis of the different H sites on the cluster $[Cu_{25}H_{10}(SCHCl_2)_{18}]^{3-}$ shows that clearly μ$_3$-H sites (Hc and Hd) are more accessible than μ$_6$-H sites (Ha and Hb), and the Hc site is most accessible among the μ$_3$-H sites. This explains why the catalysis proceeds *via* a single-site mechanism. (b) SASA analysis of the Hc site after the formation of the intermediate with the alkoxy group ($-OCH_3$) suggests that the site is no longer very accessible even for an incoming H_2 molecule to allow the Route 1 mechanism. This explains why Route 2 may be the preferred catalytic mechanism.

✓ In this work, they have synthesized and fully characterized an ambient-stable, atomically precise, thiolated $Cu_{25}H_{10}$ nanocluster by experimental and computational methods and showed that this cluster is an active catalyst for hydrogenation of ketones to corresponding alcohols in mild conditions.

✓ The 10 hydrogens found inside the copper core are in hydride form and play a crucial role in stabilizing the structure and acting as a hydrogen source in the catalytic reaction. Density functional theory computations predict a single-site mechanism that is confirmed by experimental data.

✓ Although the activity of the $Cu_{25}H_{10}$ cluster is below that of a typical industrial catalyst, this system offers important insight into understanding catalytic reactions at the atomistic level and at the same time sheds light on the controversial issue of how a ligand-protected metal cluster can have a catalytic function.


Thank You