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Communication

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Doping-Induced Anisotropic Self-Assembly of Silver Icosahedra in $[Pt_2Ag_{23}Cl_7(PPh_3)_{10}]$ Nanoclusters

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Introduction

- Atomically precise nanoclusters have recently garnered significant attention because of the potential applications of their optical and physicochemical properties, which led to their use in catalysis, bioimaging and biosensing, and light energy conversion.

- Most of the current research has focused mainly on Au NCs (e.g., Au_{18}, Au_{25}, Au_{38}, Au_{102} , Au_{144}, Au_{246} and Au_{133}) due to their high stability, while properties of analogous Ag NCs are largely unexplored.

- Nevertheless, a handful of Ag NCs such as Ag_{25}, Ag_{29}, Ag_{44}, Ag_{67}, Ag_{136} and Ag_{374}, including their X-ray crystal structures, have been reported.

- The majority of metal NCs reported are isotropic and approximately spherical. In addition to anisotropy and metal nuclearity, NCs containing self-assembled metal nanobuilding blocks are highly desired for applications as they would provide distinct surface structures.

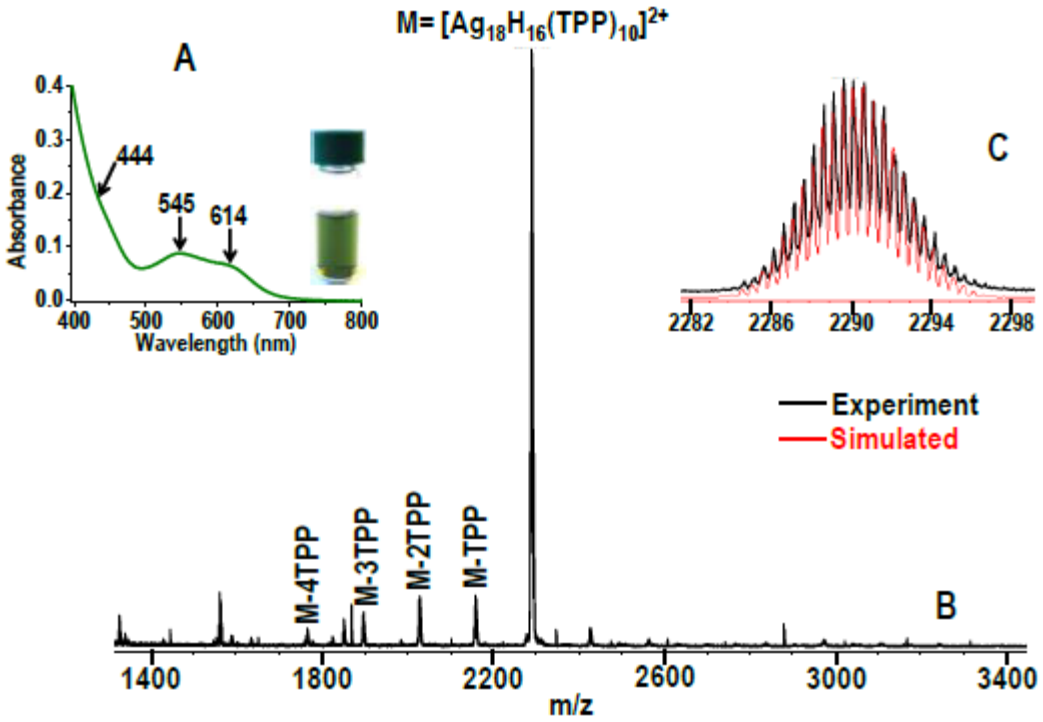
In this paper

- They designed a single-step reaction to synthesize a heteroatom-doped Ag NC, comprising self-assembled Ag building blocks, by using Pt as the dopant and a labile phosphine, PPh_3, and simple Cl^- as ligands.

- The use of labile ligands (e.g.,phosphines) and non-bulky ligands (e.g., halides) for these self-assembled nanostructures would make their surface more accessible.

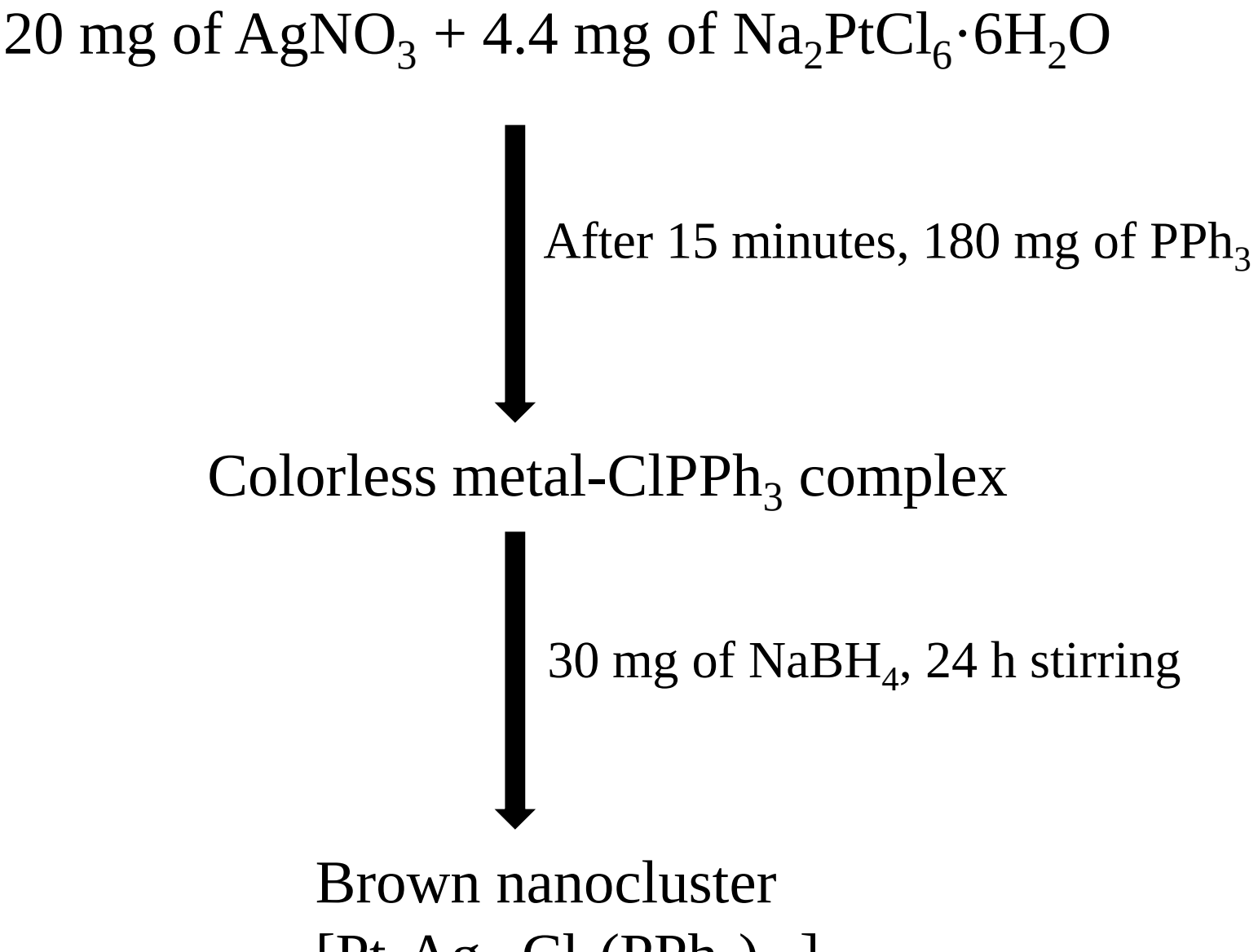
A New Class of Atomically Precise, Hydride-Rich Silver Nanoclusters Co-Protected by Phosphines

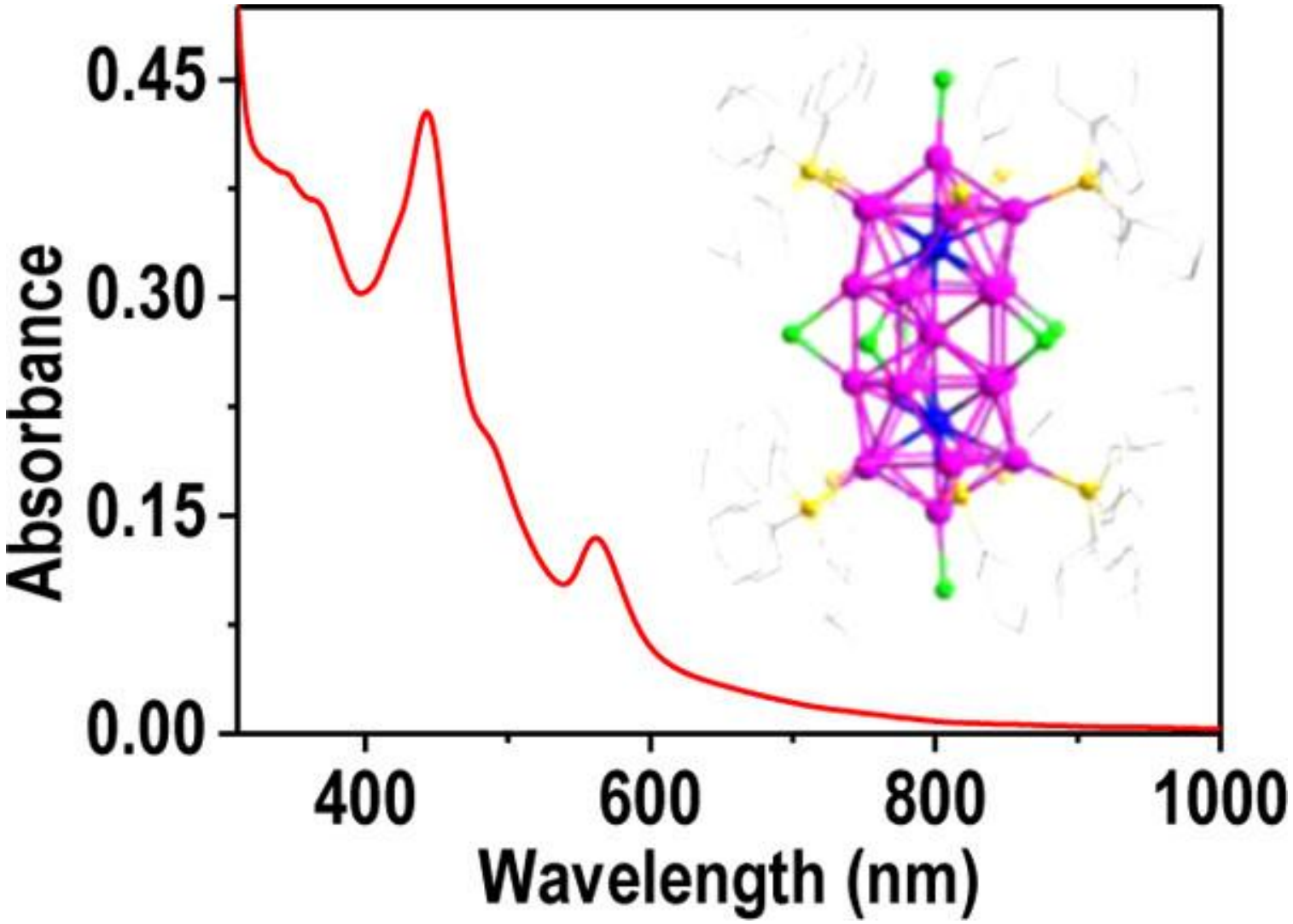
Megalamane S. Bootharaju, Raju Dey, Lieven E. Gevers, Mohamed N. Hedhili, Jean-Marie Basset, and Osman M. Bakr

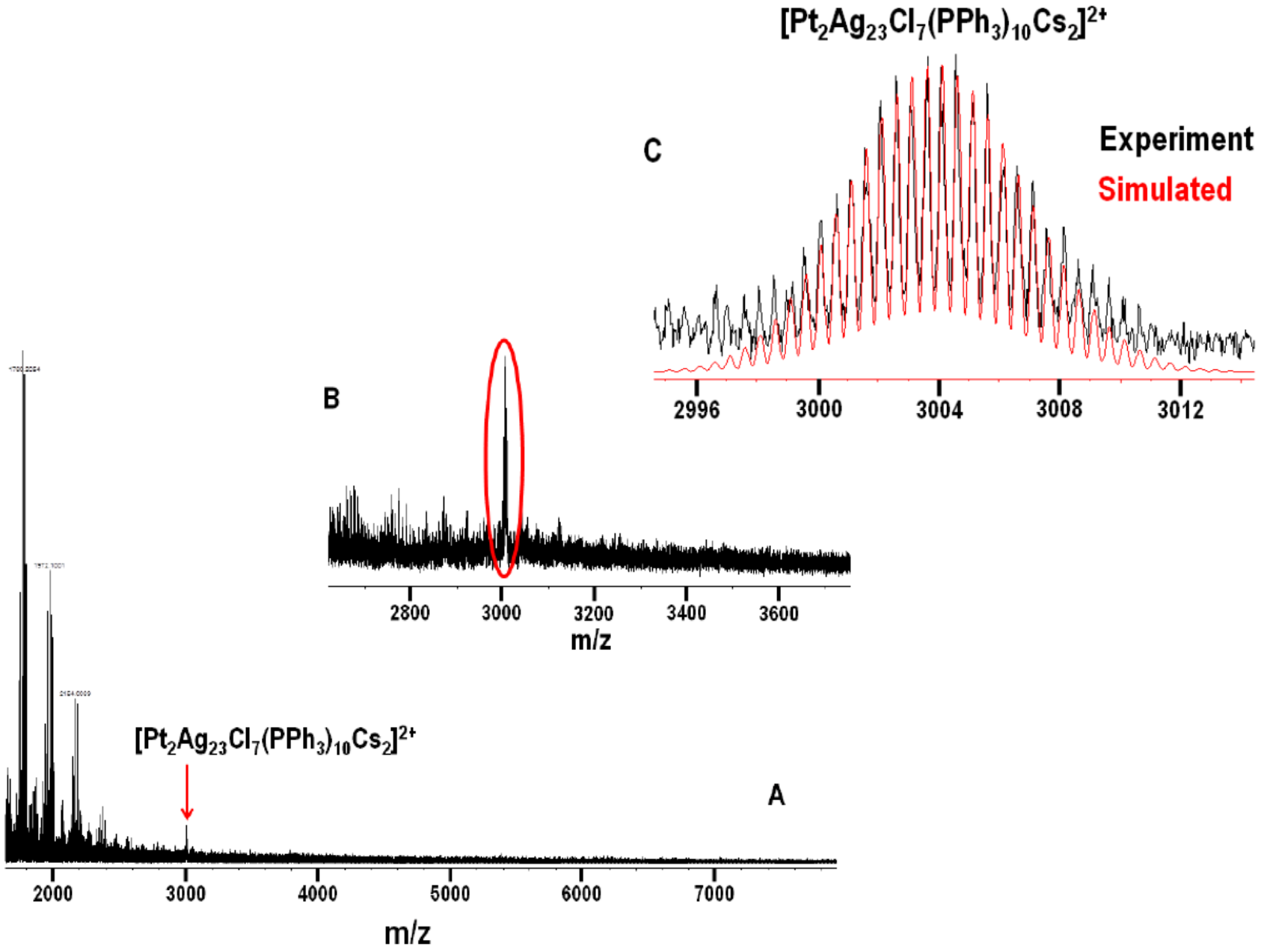


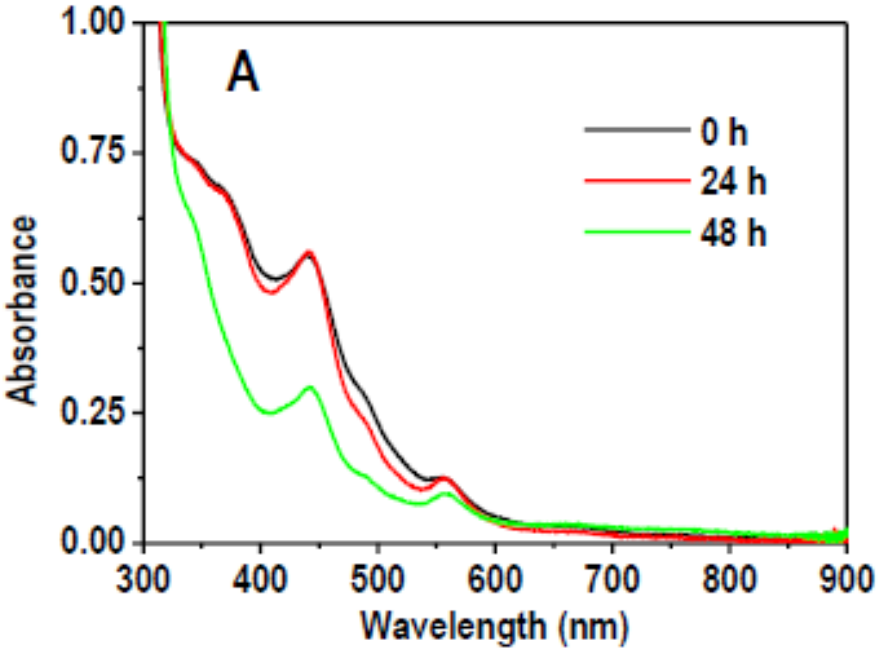
J. Am. Chem. Soc. 2016, 138, 13770−13773

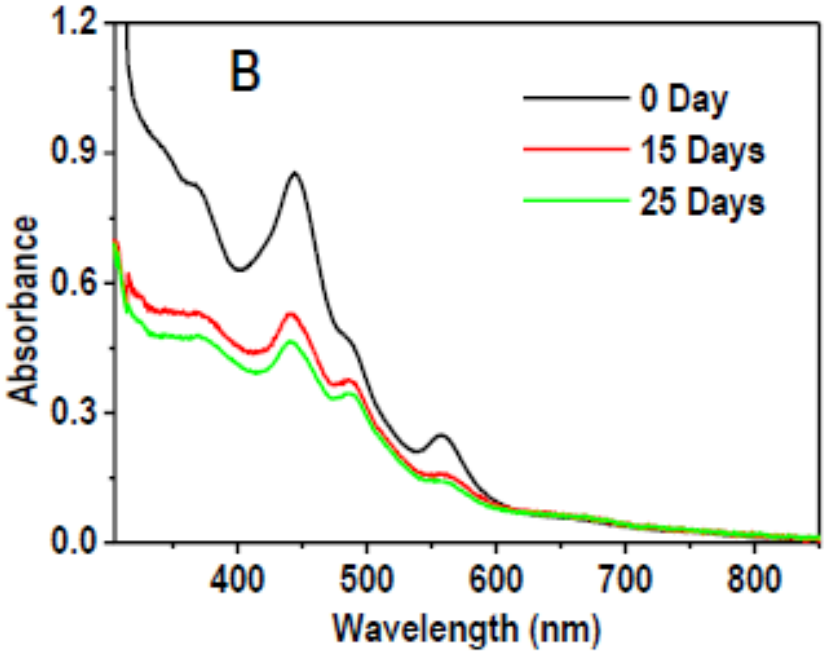
Synthesis

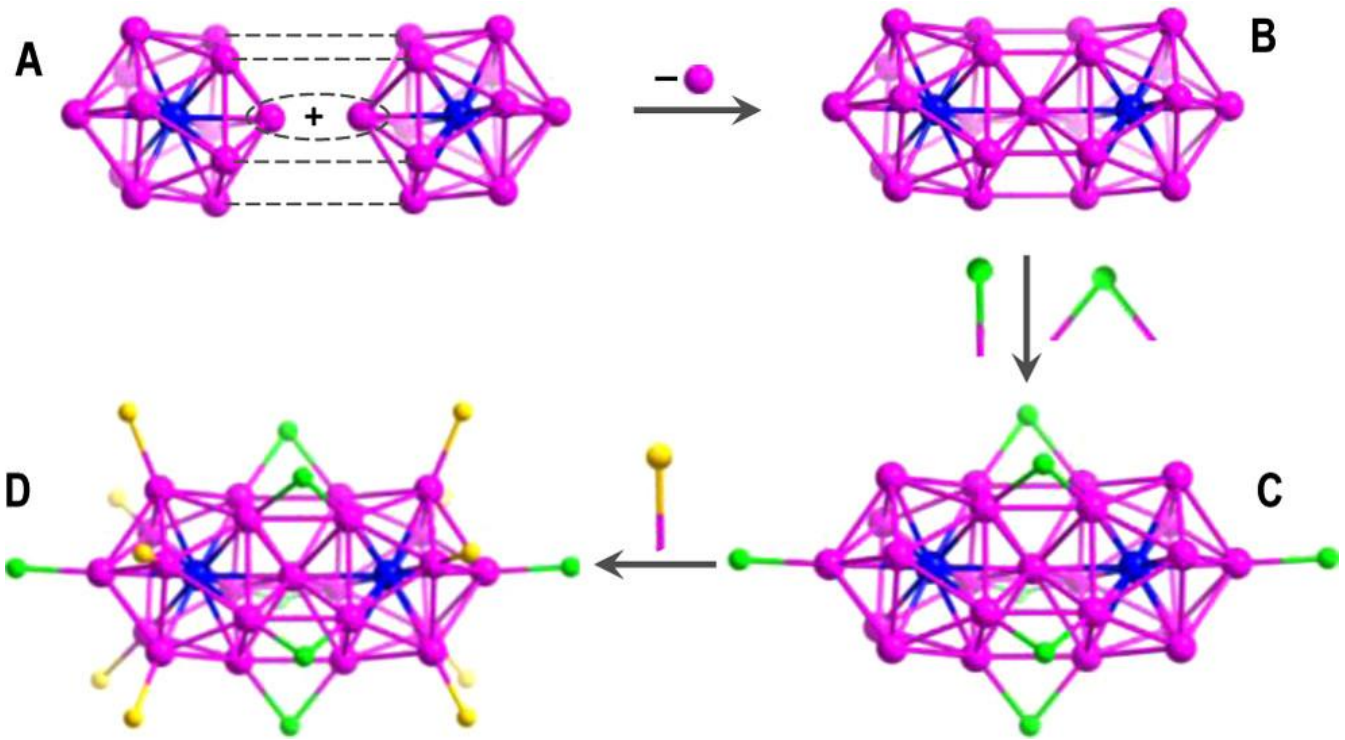

20 mg of $AgNO_3$ + 4.4 mg of $Na_2PtCl_6 \cdot 6H_2O$
After 15 minutes, 180 mg of PPh_3
Colorless metal-$ClPPh_3$ complex
30 mg of $NaBH_4$, 24 h stirring
Brown nanocluster
$[Pt_2Ag_{23}Cl_7(PPh_3)_{10}]$



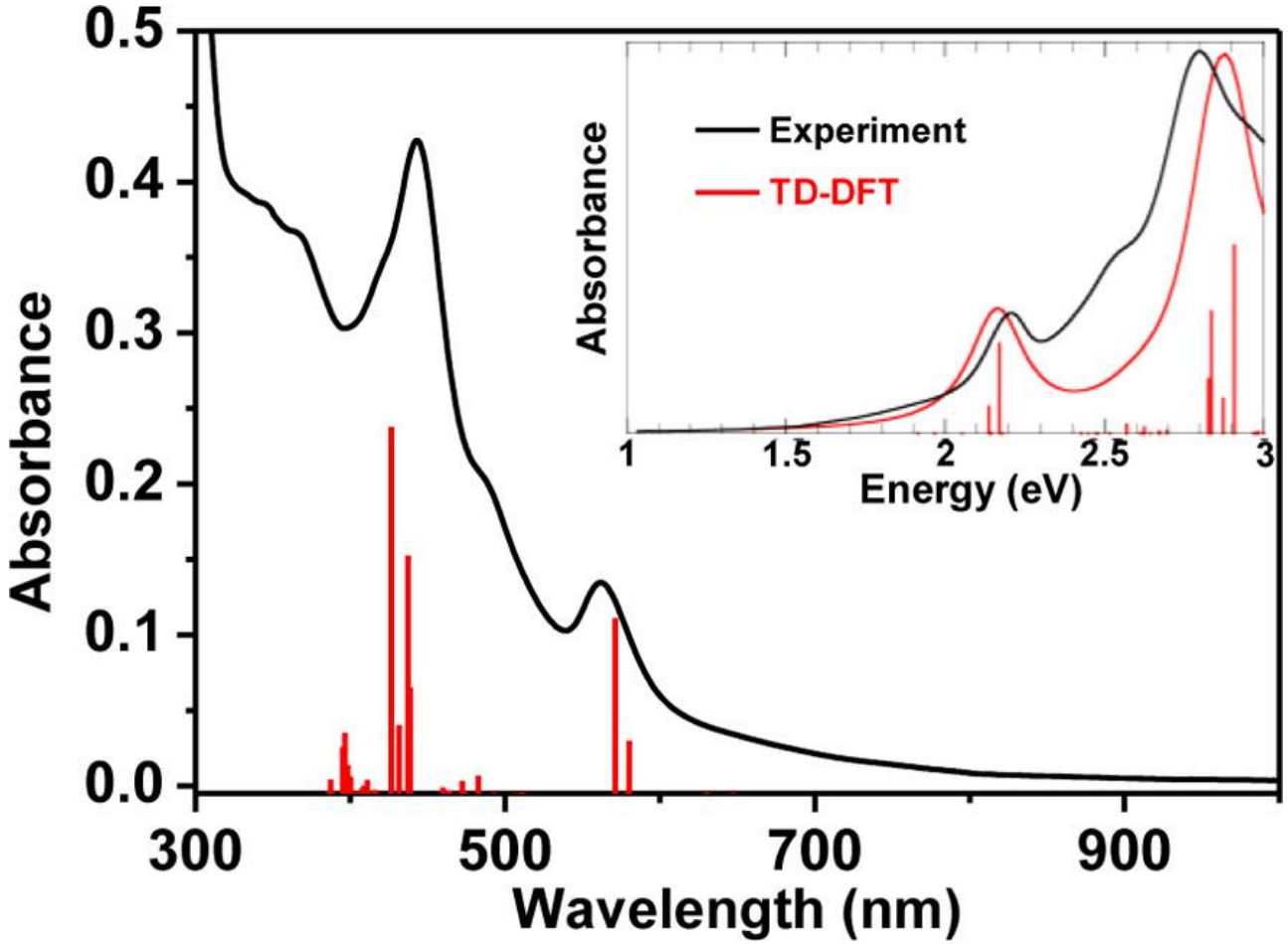




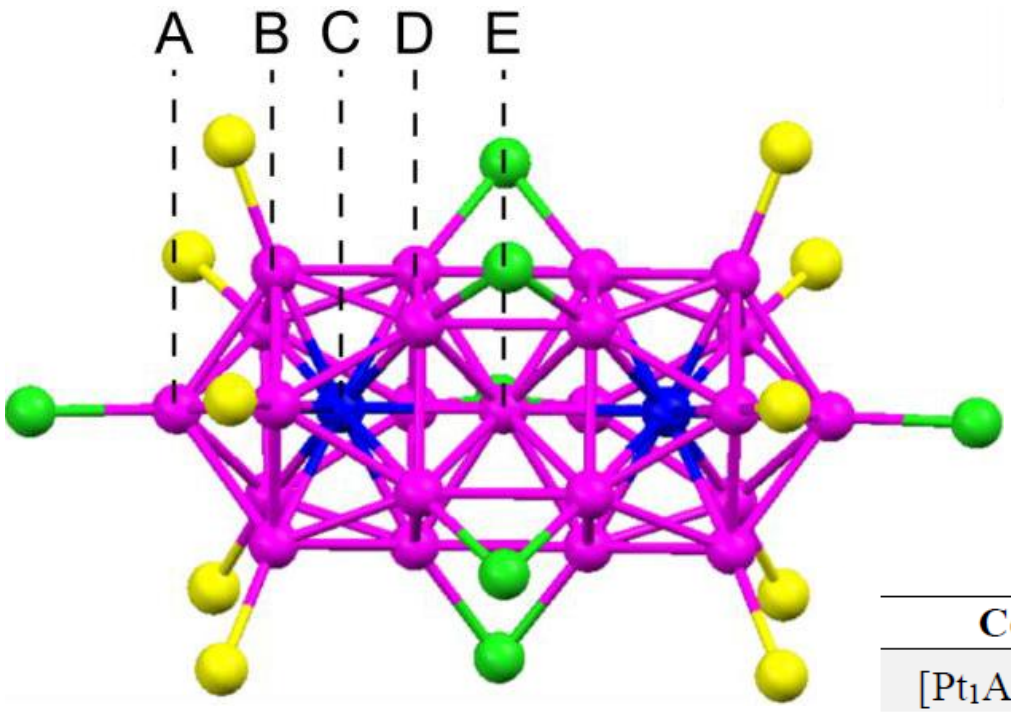




(A) Vertex Ag atoms of two $PtAg_{12}$ icosahedra being shared and connected are shown with a dotted ellipse and dotted lines, respectively. (B) Biicosahedral Pt_2Ag_{23} rod. (C) Bridging and terminal chlorides bind with the structure shown in (B) to form $Pt_2Ag_{23}Cl_7$. (D) Capping with the 10 P atoms of 10 PPh_3 ligands gives $Pt_2Ag_{23}Cl_7P_{10}$.
Color legends: cyan, Ag; blue, Pt; yellow, P; green, Cl; and gray, C. H atoms of ligands are omitted for clarity.



Experimental UV–vis spectrum of $[Pt_2Ag_{23}Cl_7(PPh_3)_{10}]$ (black) compared with the excitation energies and oscillator strengths calculated by TD-DFT for $[Pt_2Ag_{23}Cl_7(P(CH_3)_3)_{10}]$ (red). Inset: corresponding UV–vis data on the energy scale.



Composition	Pt positions	E_{mix}, eV
$[Pt_1Ag_{24}Cl_7(PPh_3)_{10}]$	A	-0.19
	B	-1.03
	C	-2.04
	D	-0.03
	E	-0.29
$[Pt_2Ag_{23}Cl_7(PPh_3)_{10}]$	B+C	-3.19
	C+C	-4.20
	C+E	-2.45
$[Pt_3Ag_{22}Cl_7(PPh_3)_{10}]$	B+C+C	-4.11
	C+C+E	-3.65

In summary, they have successfully synthesized a novel rod shaped diplatinum-doped silver nanocluster , $[Pt_2Ag_{23}Cl_7(PPh_3)_{10}]$, through the doping strategy.

Its crystal structure shows two Pt-centered Ag icosahedra self-assembled by vertex sharing.

The chloride ligands were found to protect the cluster through bridging and terminal binding modes.

Click Chemistry

Click Chemistry is a term that was introduced by K. B. Sharpless in 2001 to describe reactions that are high yielding, wide in scope, create only byproducts that can be removed without chromatography, are stereospecific, simple to perform.

This concept was developed in parallel with the interest within the pharmaceutical, materials, and other industries in capabilities for generating large libraries of compounds for screening in discovery research.

‘Click Reactions’

Cycloaddition : 1,3-dipolar cycloaddition
Diels-Alder

Nucleophilic substitution : Ring-opening of strained heterocycle electrophile
Epoxide, aziridine, aziridinium, episulfonium

Carbonyl chemistry (non aldol) : Formation of ureas, thioureas, aromatic heterocycles, Oxime ether, hydrazones, amides

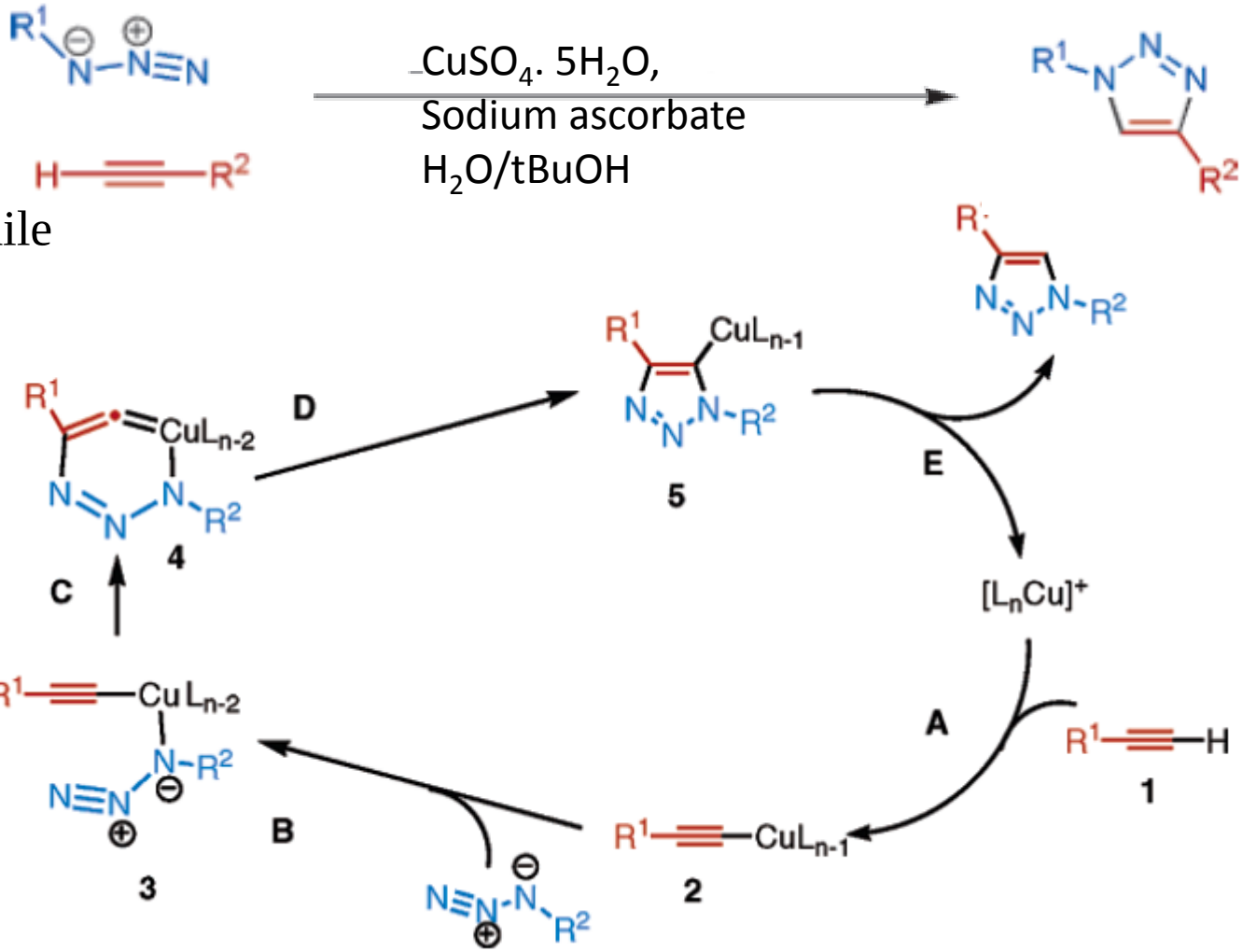
Addition to C-C multiple bond : epoxidation, dihydroxylation, aziridination, Michael addition

Protection reaction : Ms, Ts ...

1,3-dipolar cycloaddition

Dipole

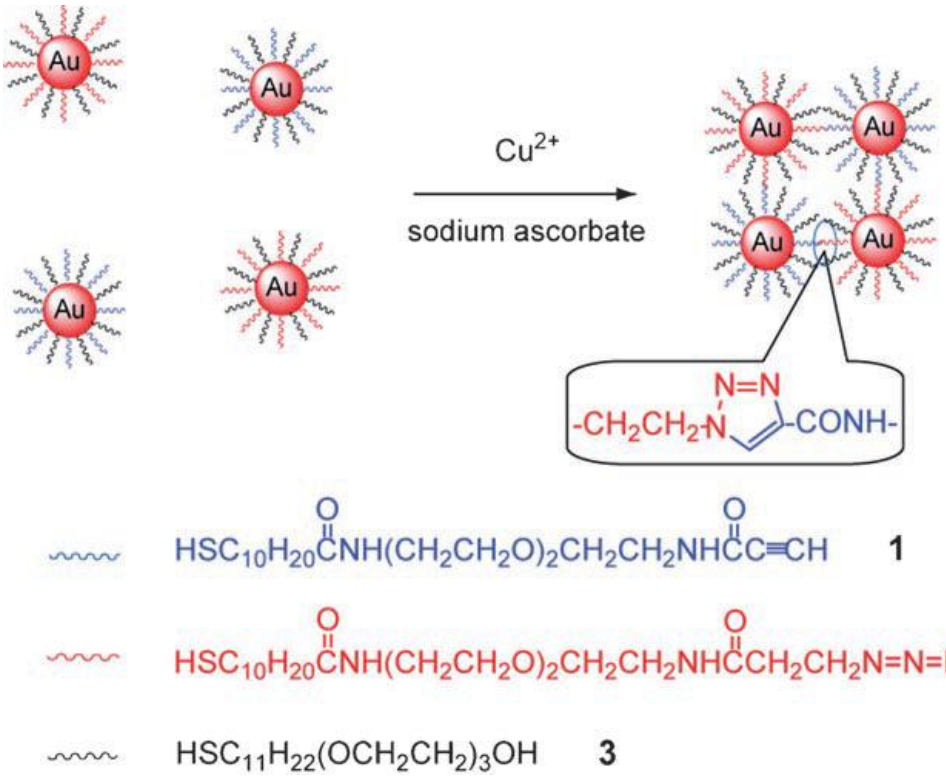
Dipolarophile



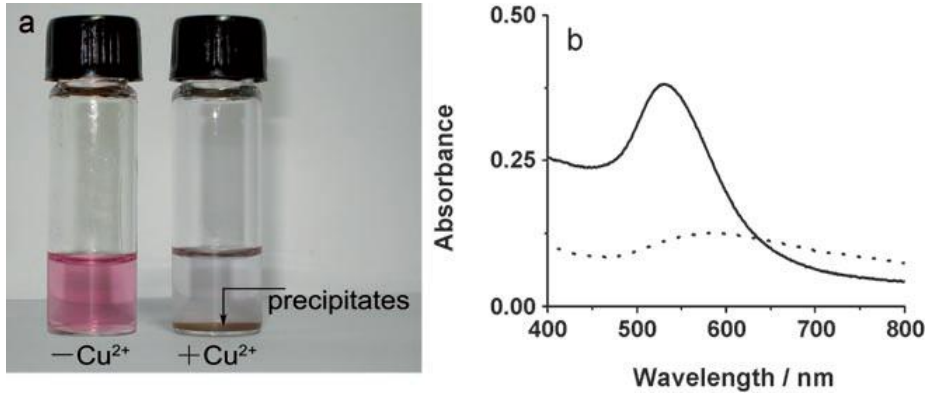
F. Himo, T. Lovell, R. Hilgraf, V. V. Rostovtsev, L. Noodleman, K. B. Sharpless, V. V. Fokin, *J. Am. Chem. Soc.*, **2005**, *127*, 210-216.

Visual Detection of Copper(II) by Azide- and Alkyne-Functionalized Gold Nanoparticles Using Click Chemistry

Yang Zhou, Shixing Wang, Ke Zhang, and Xingyu Jiang

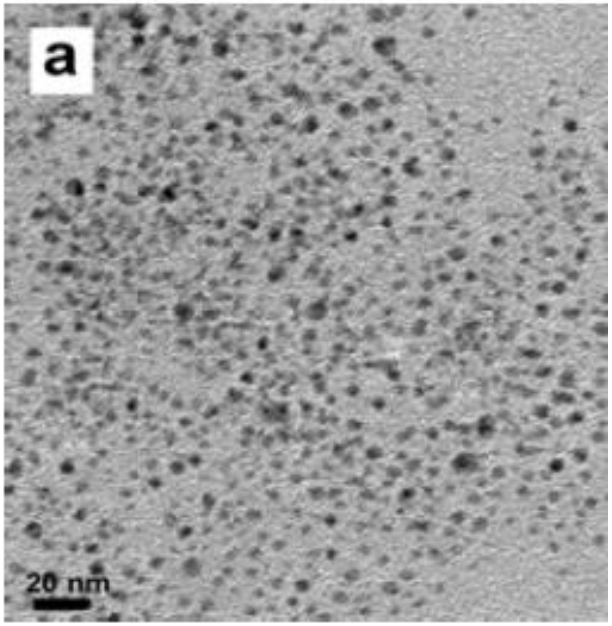


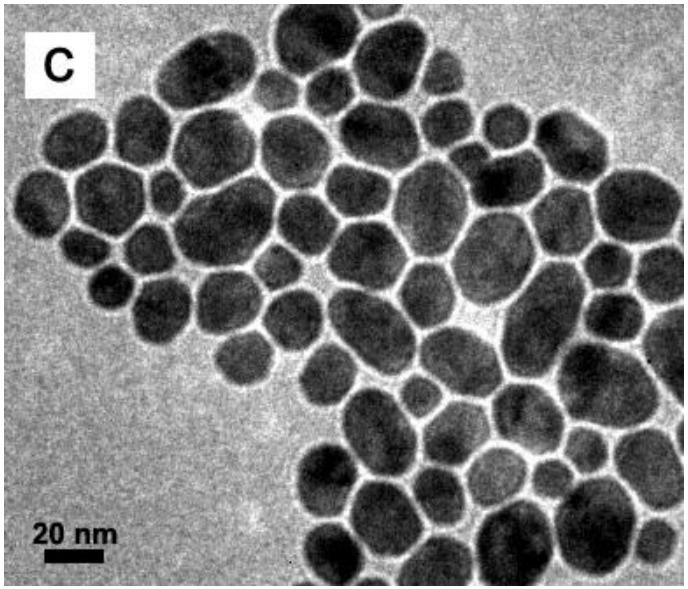
The detection of Cu^{2+} ions using click chemistry between two types of gold NPs, each modified with thiols terminated in an alkyne (1) or an azide (2) functional group.



(a) Photographs of the solution containing only the mixture of functionalized Au NPs (left) and the same mixture after the addition of Cu^{2+} (right); (b) UV/Vis spectra obtained from solutions of functionalized Au NPs and after 24 h in the presence of Cu^{2+} ions and sodium ascorbate. solid line: AuNPs, dotted line: Au NPs+Cu^{2+}

Angew. Chem. Int. Ed. 2008, 47, 7454 –7456

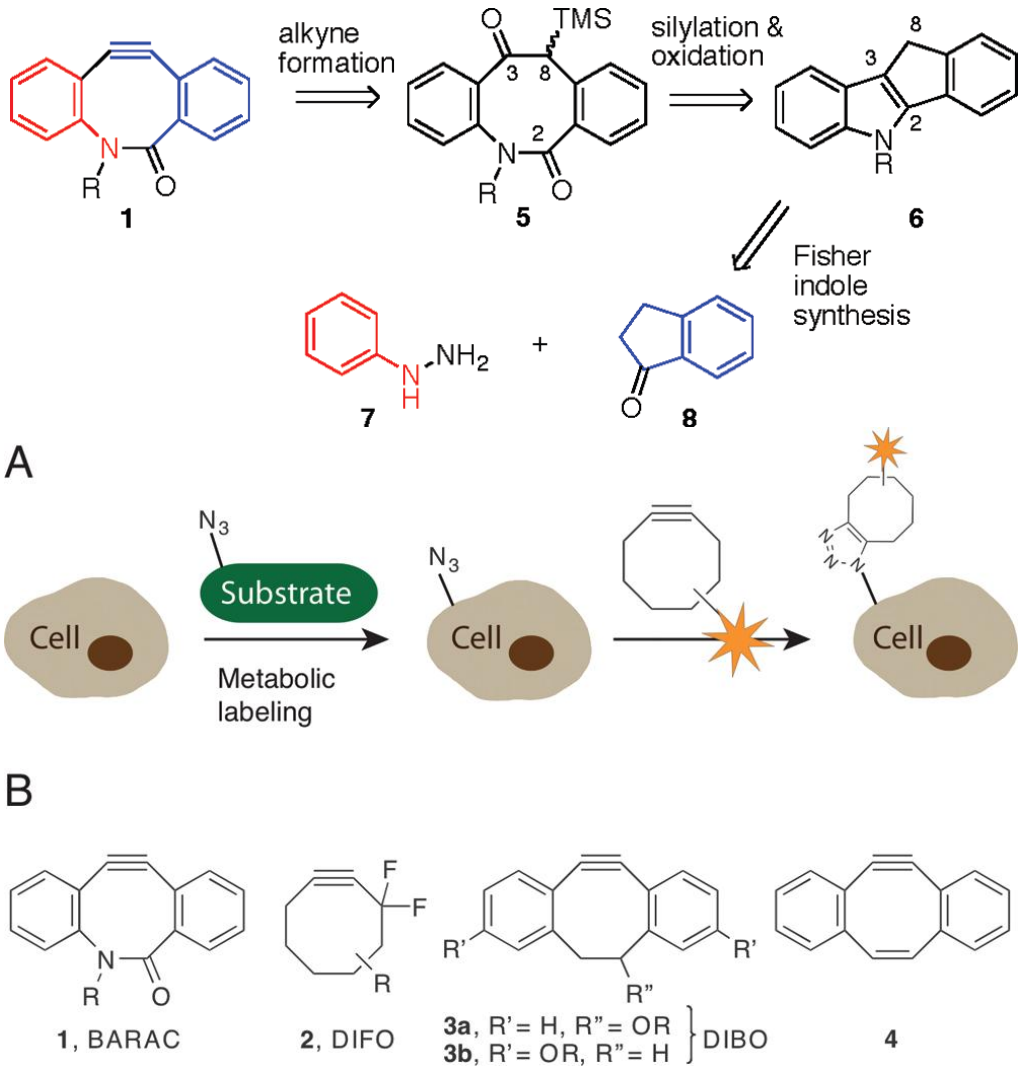




(a) The TEM image of the mixture of terminal alkyne-functionalized and azide-functionalized Au NPs,
(c) The TEM image of the precipitates of Au NPs

Rapid Cu-Free Click Chemistry with Readily Synthesized Biarylazacyclooctynones

John C. Jewett, Ellen M. Sletten, and Carolyn R. Bertozzi



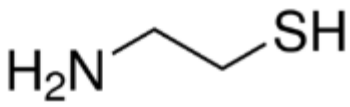
J. AM. CHEM. SOC. 2010, *132*, 3688–3690

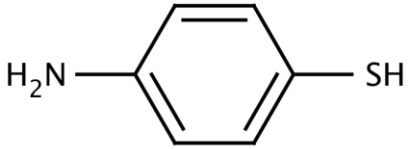
Cluster frameworks using copper free click chemistry

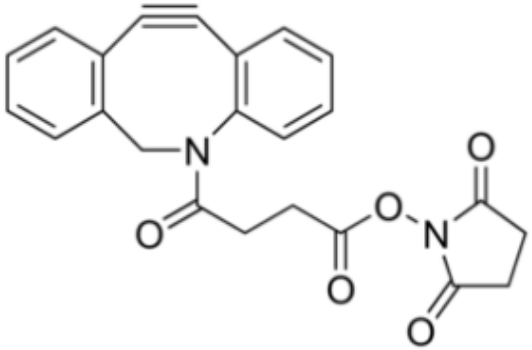
Step 1 : Synthesis of primary amine protected clusters

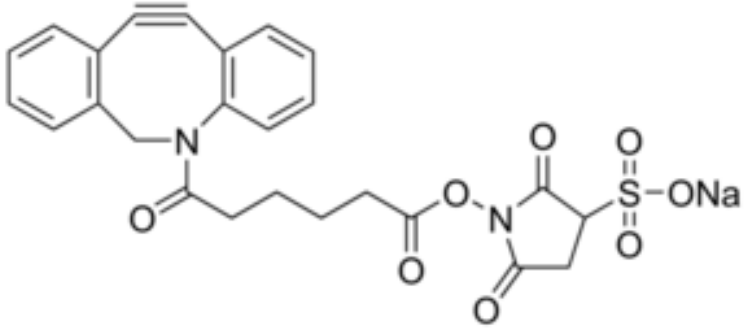
Step 2 : Conjugation with DBCO NHS ester/ conjugation to azide

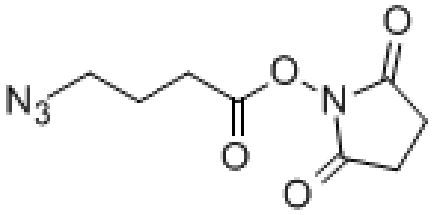
Step 3 : Using homo-bifunctional azide modified PEG molecules to form frameworks

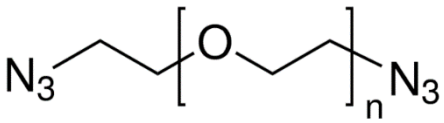






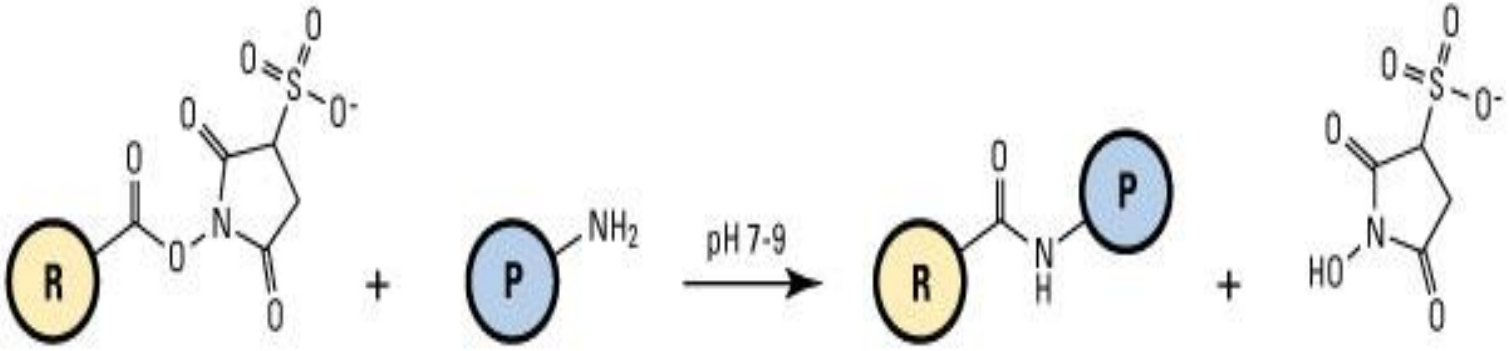






Mechanism

NHS ester to amine



Copper free click chemistry