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Metal Nanoclusters

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Gold Doping of Silver Nanoclusters: A 26-Fold Enhancement in the Luminescence Quantum Yield

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Introduction

- ✓ Noble-metal nanoclusters (NCs), consisting of a precise number of metal atoms and ligands, exhibit unique molecular, optical, physicochemical properties because of their distinct electronic structures.

- ✓ Particularly NCs of gold, silver and their alloys are being investigated for light-energy conversion applications and catalytic activity.

- ✓ Luminescent NCs are in high demand and this origin of the luminescence is explained with some studies implicating LMCT or LMMCT.

- ✓ The pivotal roles of the nature of metal atoms and the ligands signify the opportunity to tune the photoluminescence (PL) quantum yield (QY) of NCs for practical applications.

- ✓ Thus in this direction two things can be done
  - surface functionalization of NCs with diverse protecting environments like polymers, thiols, and proteins.
  - Alloying or doping of the metal core of a NCs.

Background

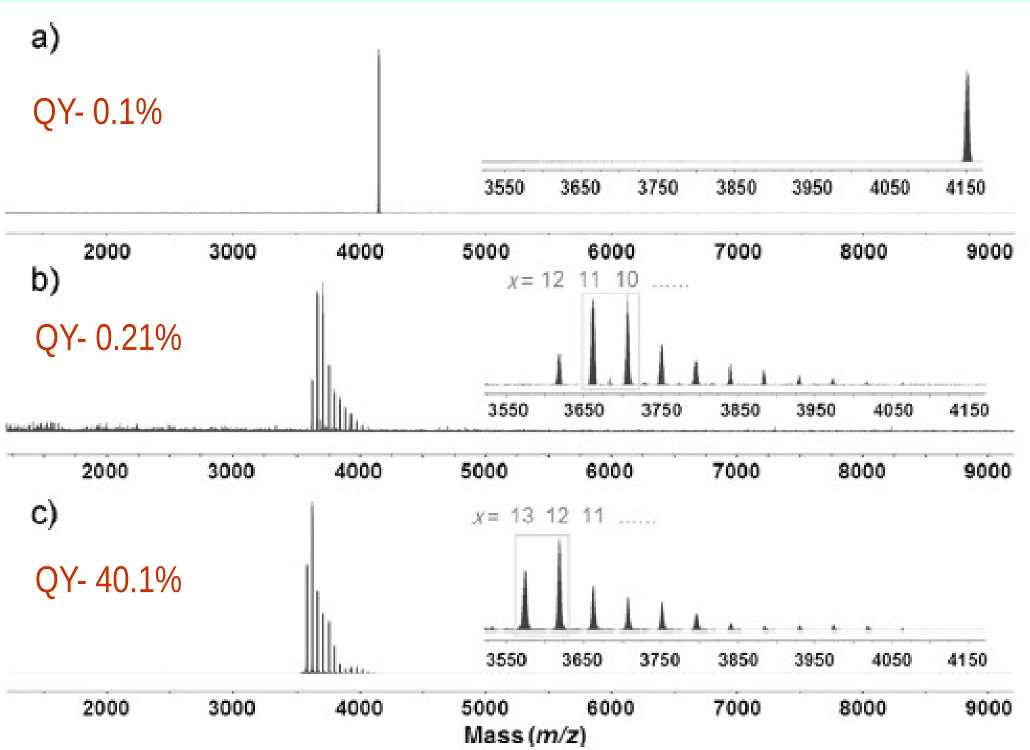
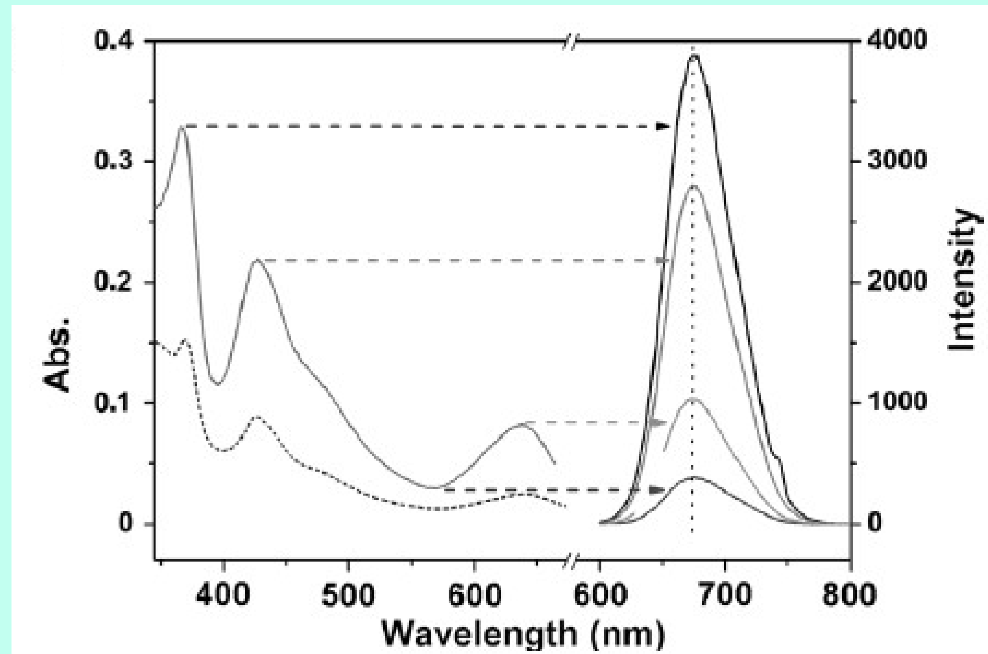


Figure 1. ESI mass spectra of: a) $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]^{2+}$, b) I, and c) II. The general formula of I and II is $[Ag_xAu_{25-x}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]^{2+}$, but with different *x* ranges.

II



PLE (——), UV/Vis (-----). UV/Vis and excitation spectra (left), and emission spectra (right) at different excitation wavelengths, as indicated by arrows.

Synthetic route

Au NP + Ag thiolate = I

Au_{11} NC + Ag thiolate = II

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Fluorescent Nanoclusters

A 200-fold Quantum Yield Boost in the Photoluminescence of Silver-Doped Ag_xAu_{25-x} Nanoclusters: The 13th Silver Atom Matters**

Shuxin Wang, Xiangming Meng, Anindita Das, Tao Li, Yongbo Song, Tiantian Cao, Xiuyi Zhu, Manzhou Zhu, and Rongchao Jin**

Background

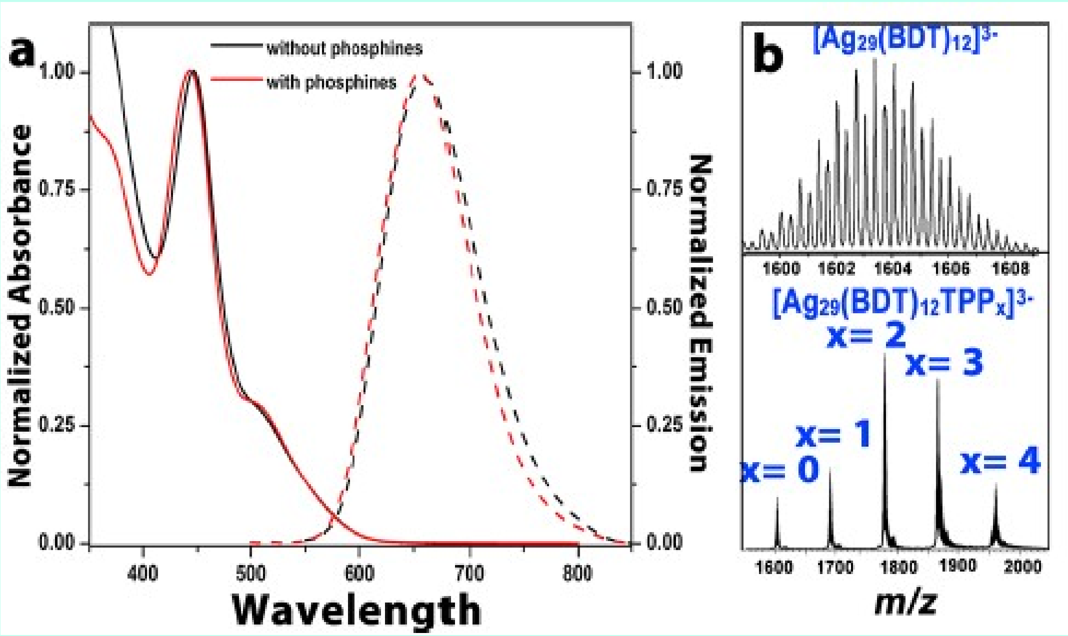


Figure 1. (a) UV−vis absorbance (solid) and emission (dashed) of $Ag_{29}(BDT)_{12}(TPP)_4$ NCs without (black) and with (red) phosphines. The excitation wavelength is at 450 nm. (b) ESI-MS of $Ag_{29}(BDT)_{12}$ without (upper panel) and with phosphines (bottom panel).

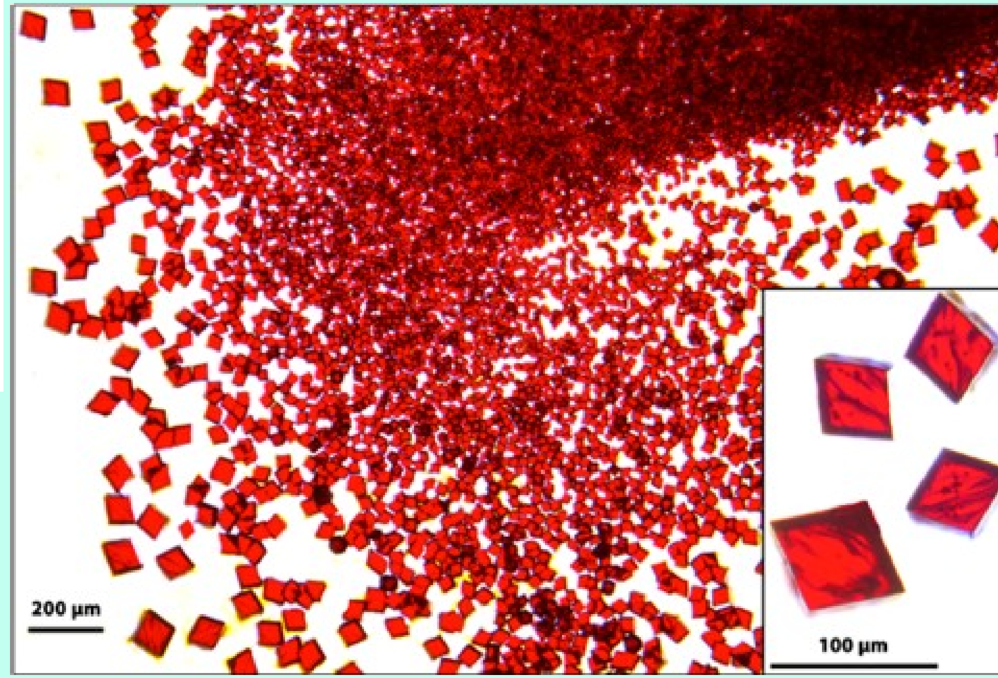
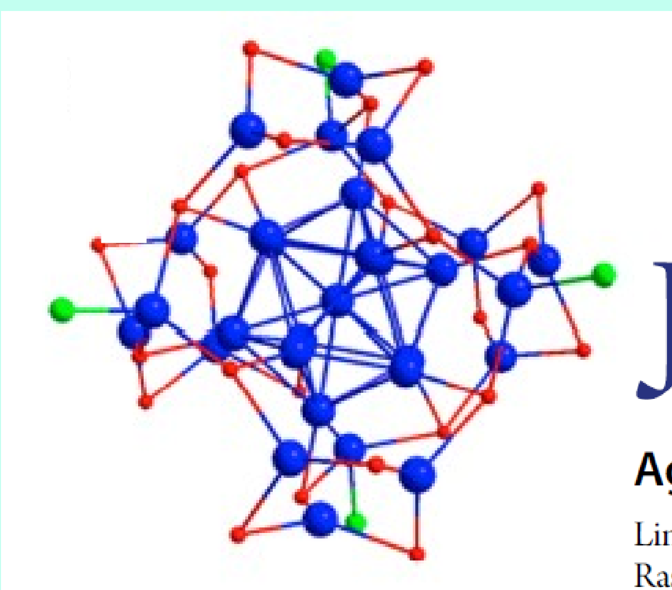


Figure 2. Optical microscopy image of self-assembled $Ag_{29}(BDT)_{12}TPP_4$ NCs. Inset shows separate rhombohedral single crystals.



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$Ag_{29}(BDT)_{12}(TPP)_4$: A Tetravalent Nanocluster

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In this paper

- They have demonstrated the PL QY enhancement of Ag_{29} NCs by doping with a distinct number of Au atoms while maintaining the Ag_{29} cluster's structural integrity.

- The PL QY is increased from 0.9 to 24% (26 times) and the fluorescence became visible to the naked eye, which would be useful for colorimetric and sensing applications.

- By Au doping, a significant enhancement in the ambient stability of Ag_{29} cluster is achieved.

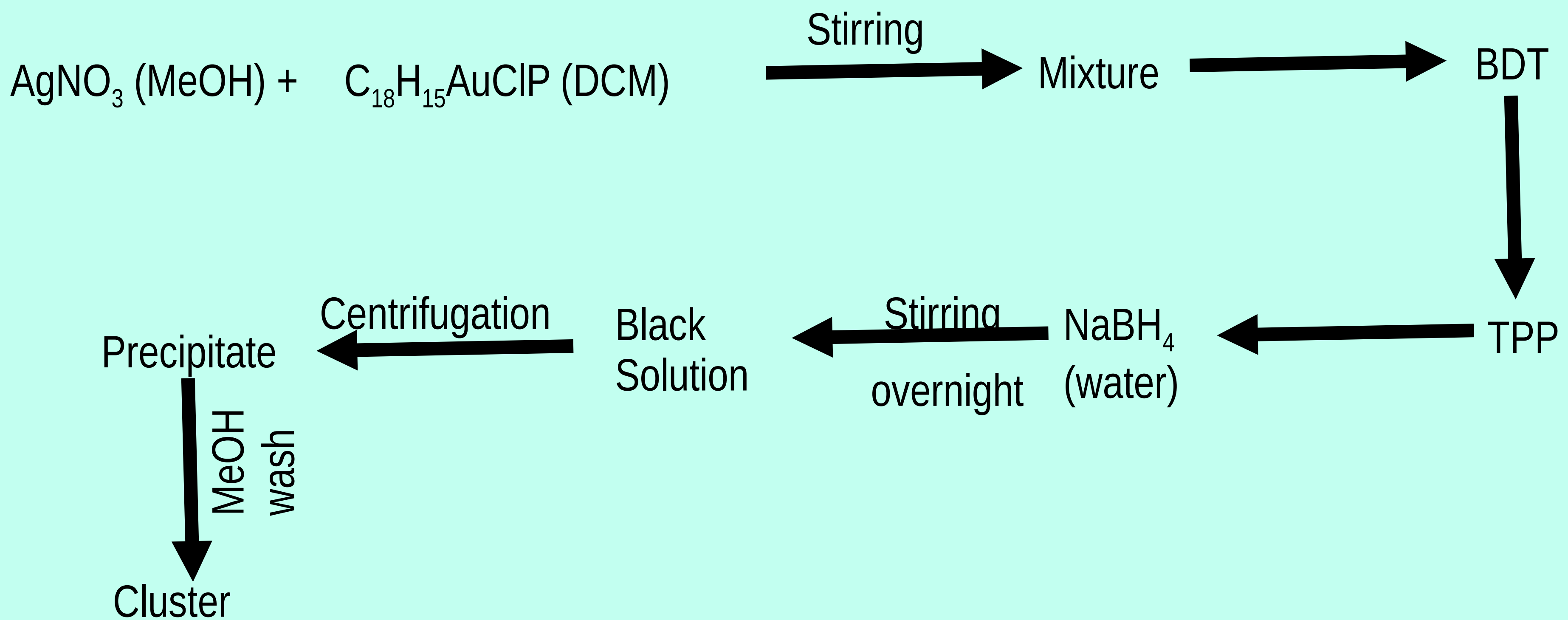
- Single-crystal analysis coupled with mass spectrometry, transient absorption spectroscopy, and nuclear magnetic resonance (NMR) provides insights into the PL enhancement mechanism and probable locations of Au atoms in the doped clusters.

Synthesis of Au-doped Ag_{29} NCs

Table 1. Different mmol of Ag and Au precursors.

mmol	0% Au	10% Au	20% Au	30% Au	40% Au
$AgNO_3$	0.118	0.106	0.094	0.082	0.071
$C_{18}H_{15}AuClP$	0	0.0118	0.0236	0.0354	0.0472

Total metal ion concentration 0.118 mmol



ESI-MS

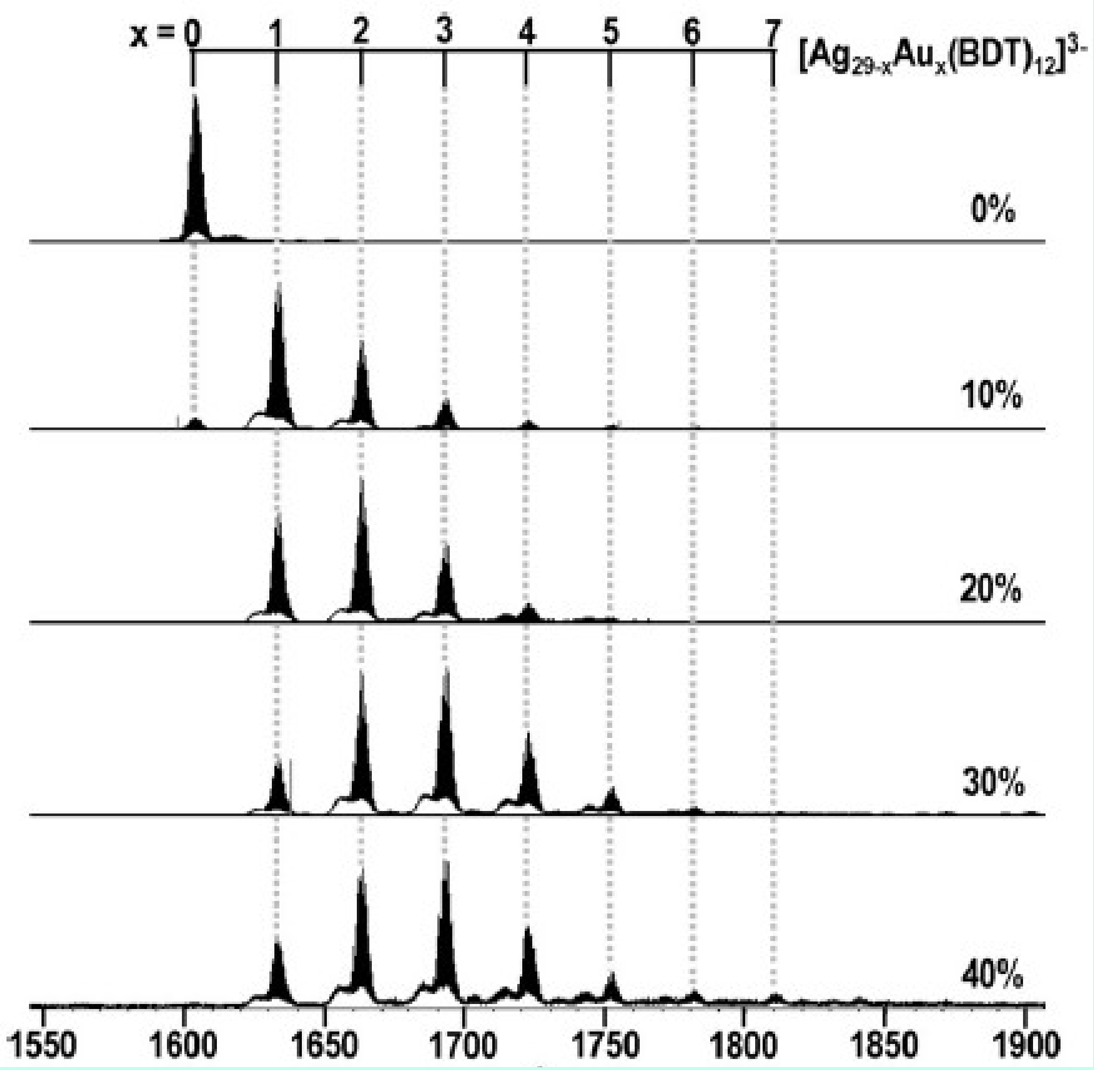
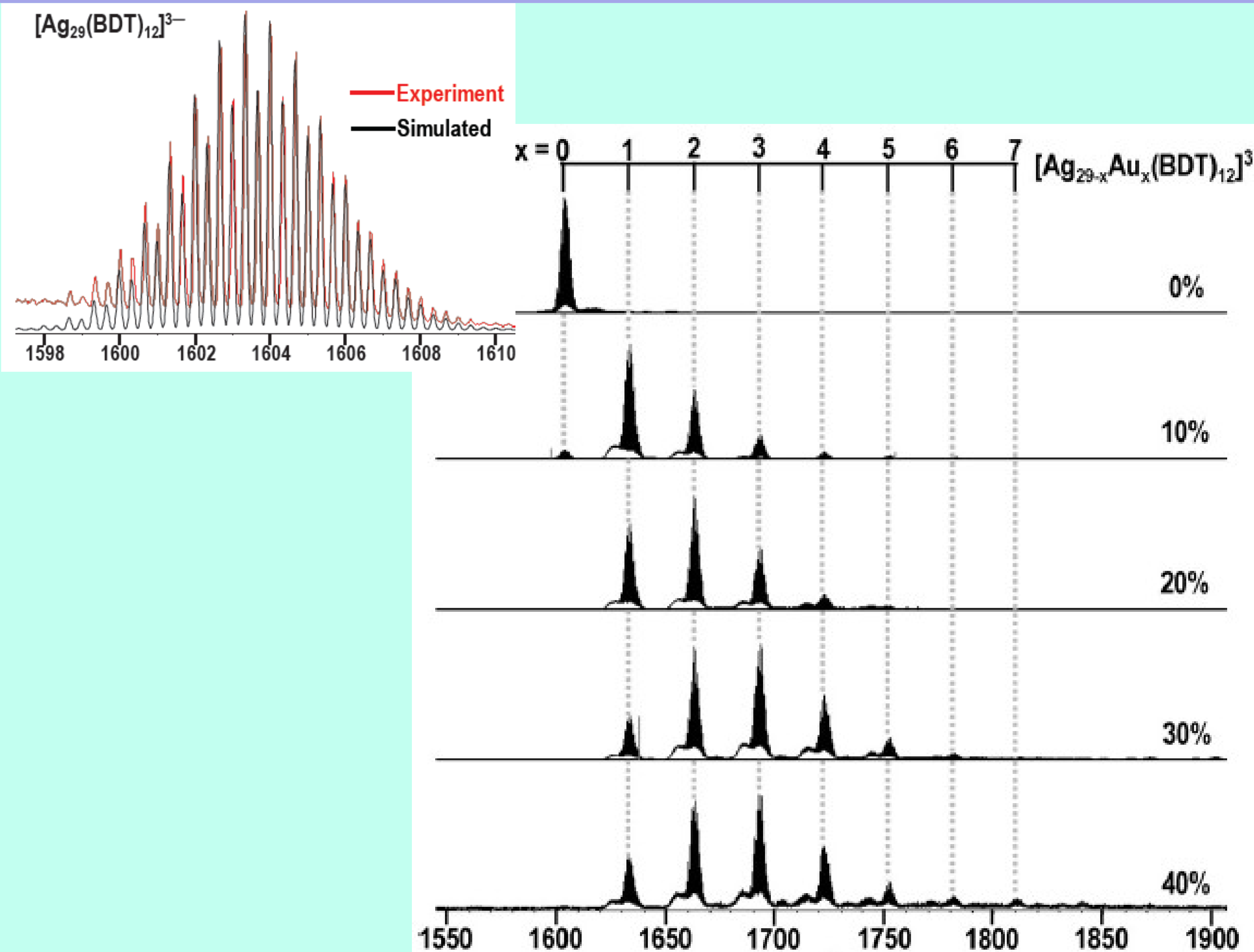


Figure 1. Negative mode ESI MS of $[Ag_{29}(BDT)_{12}]^{3-}$ (0% Au) and its Au-doped NCs $[Ag_{29-x}Au_x(BDT)_{12}]^{3-}$, $x = 1–7$ synthesized by varying the amount (mmol%) of doped Au.

ESI-MS



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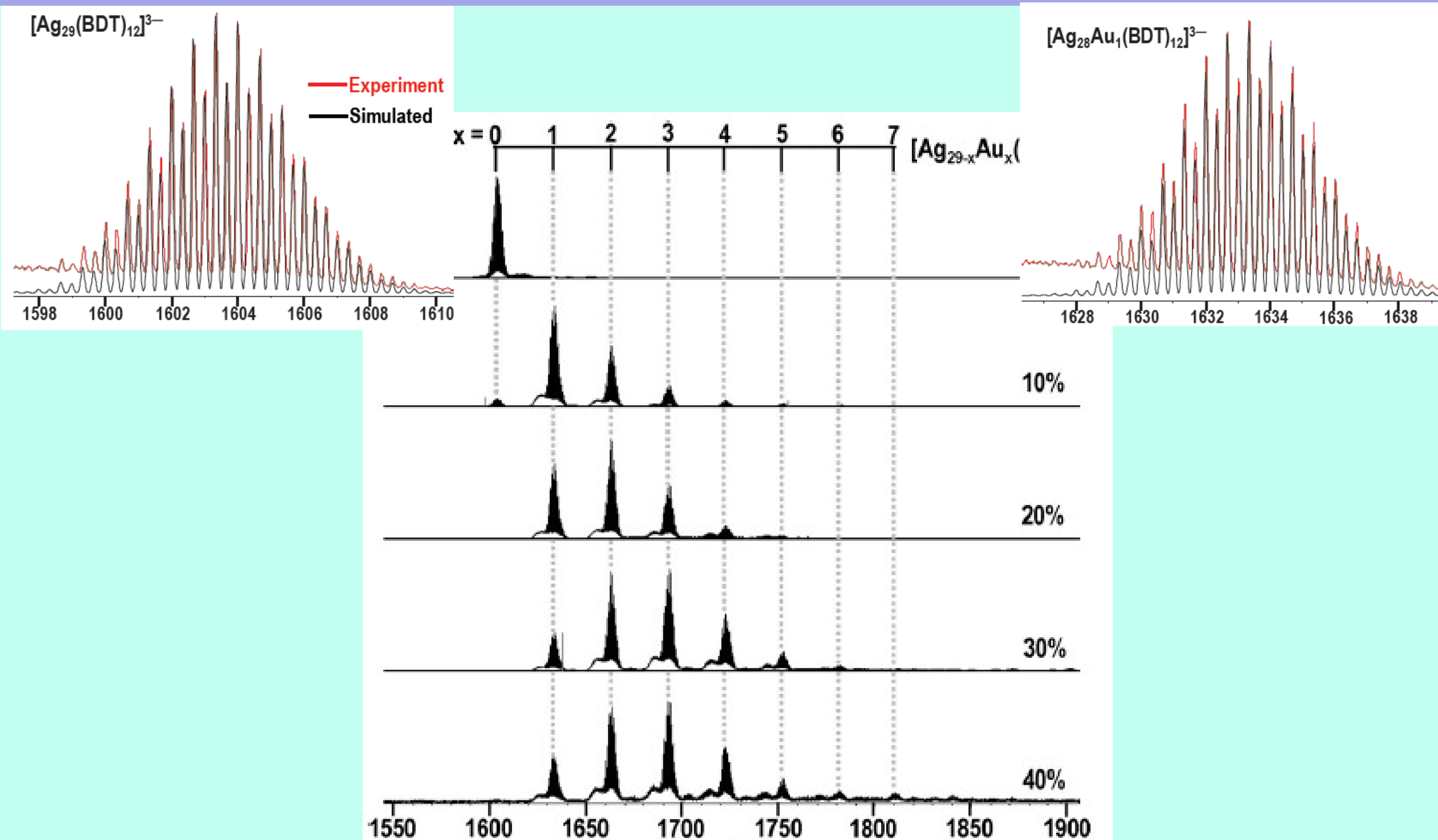

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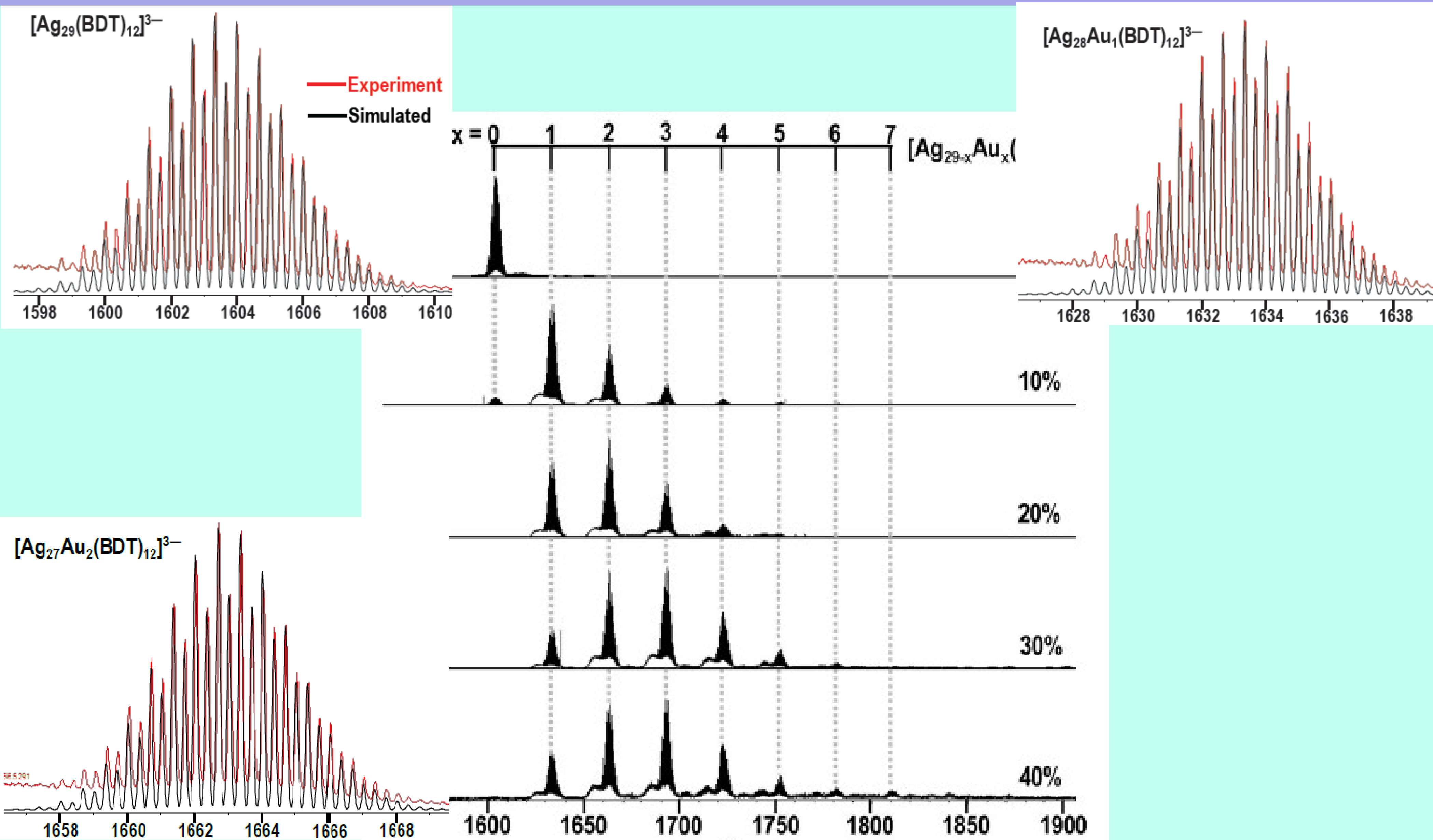

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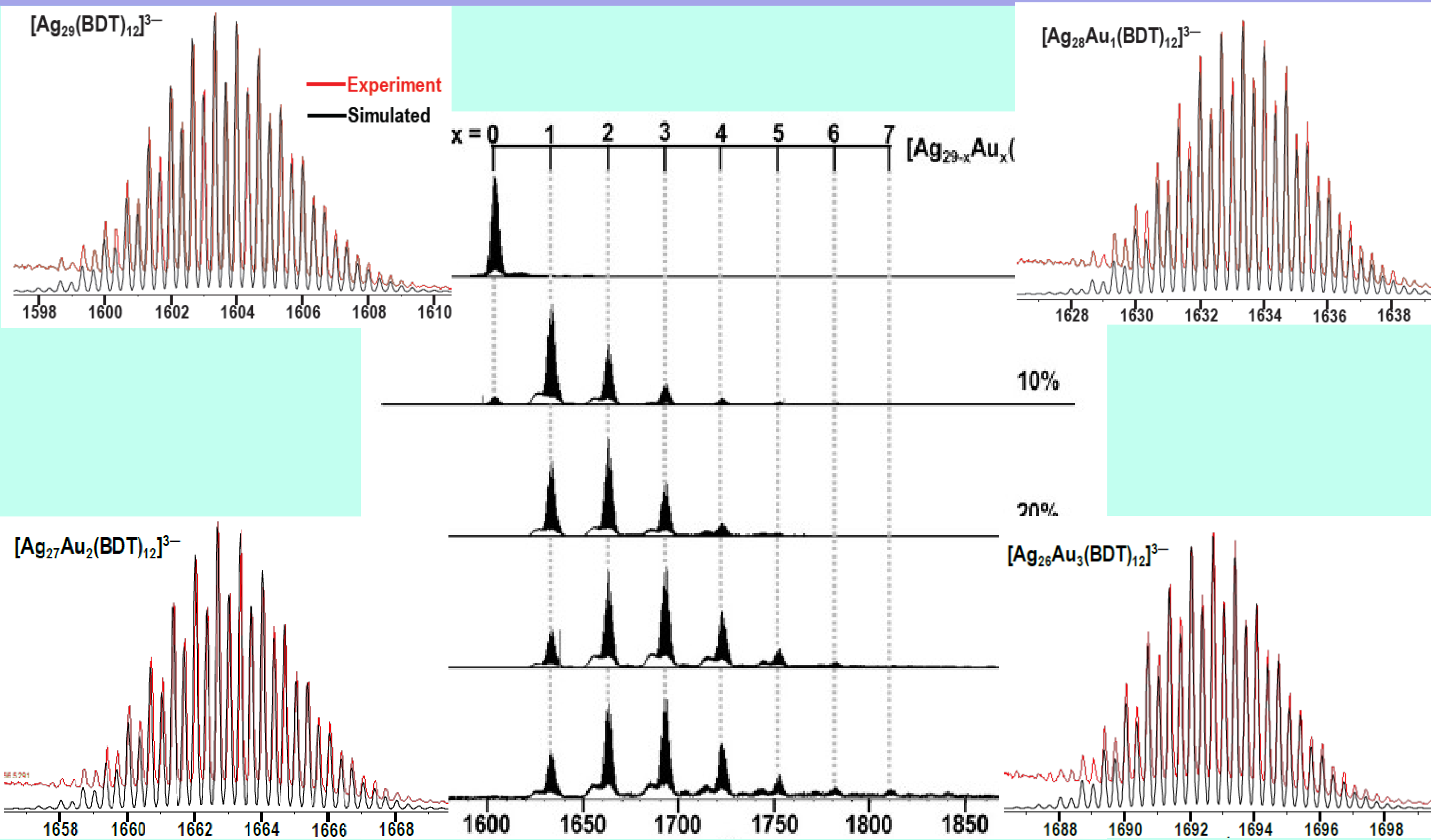

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UV/Vis and PL spectroscopy

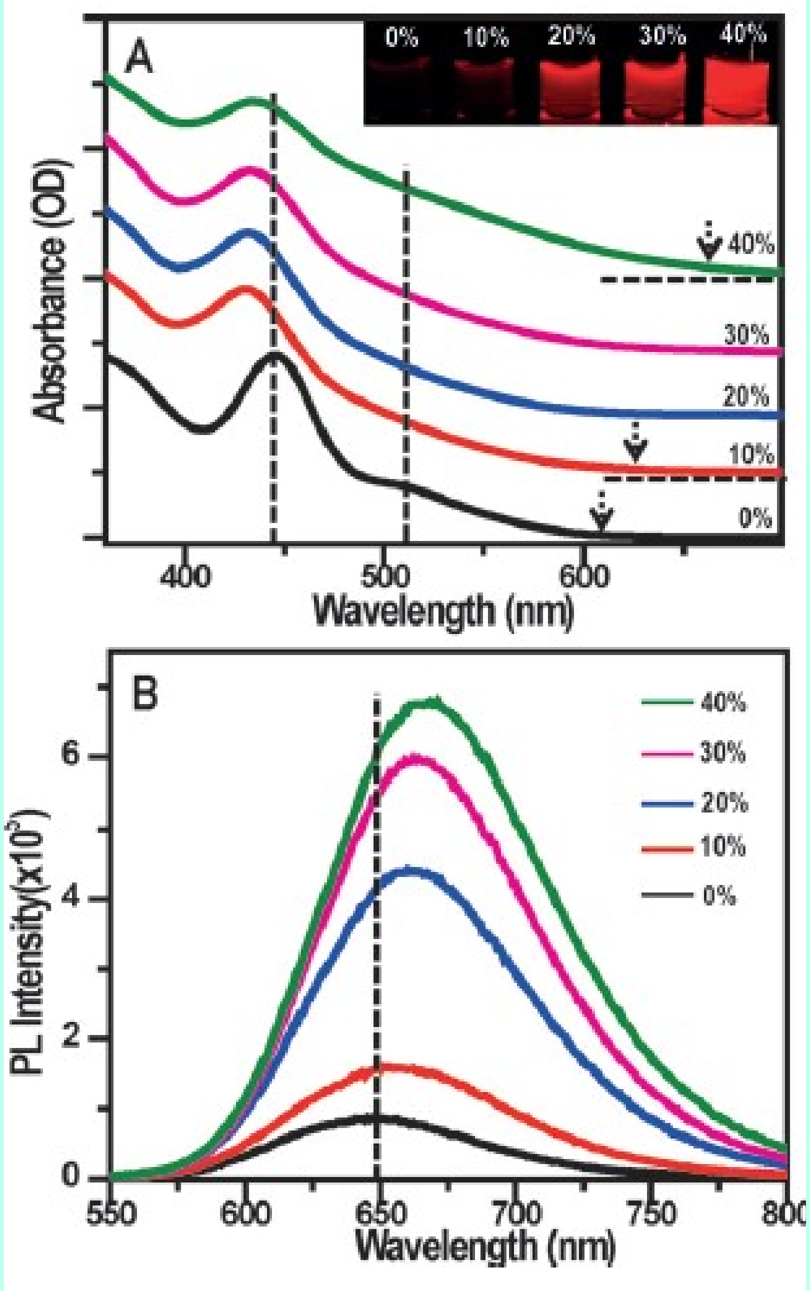


Figure 2. A) UV/Vis and B) PL spectra of Ag_{29} and Au-doped Ag_{29} clusters synthesized using different amounts (mmol%) of Au. Inset: a photograph of Ag_{29} and Au-doped Ag_{29} clusters under a UV lamp (using 365 nm light).

Transient Absorption and TCSPC

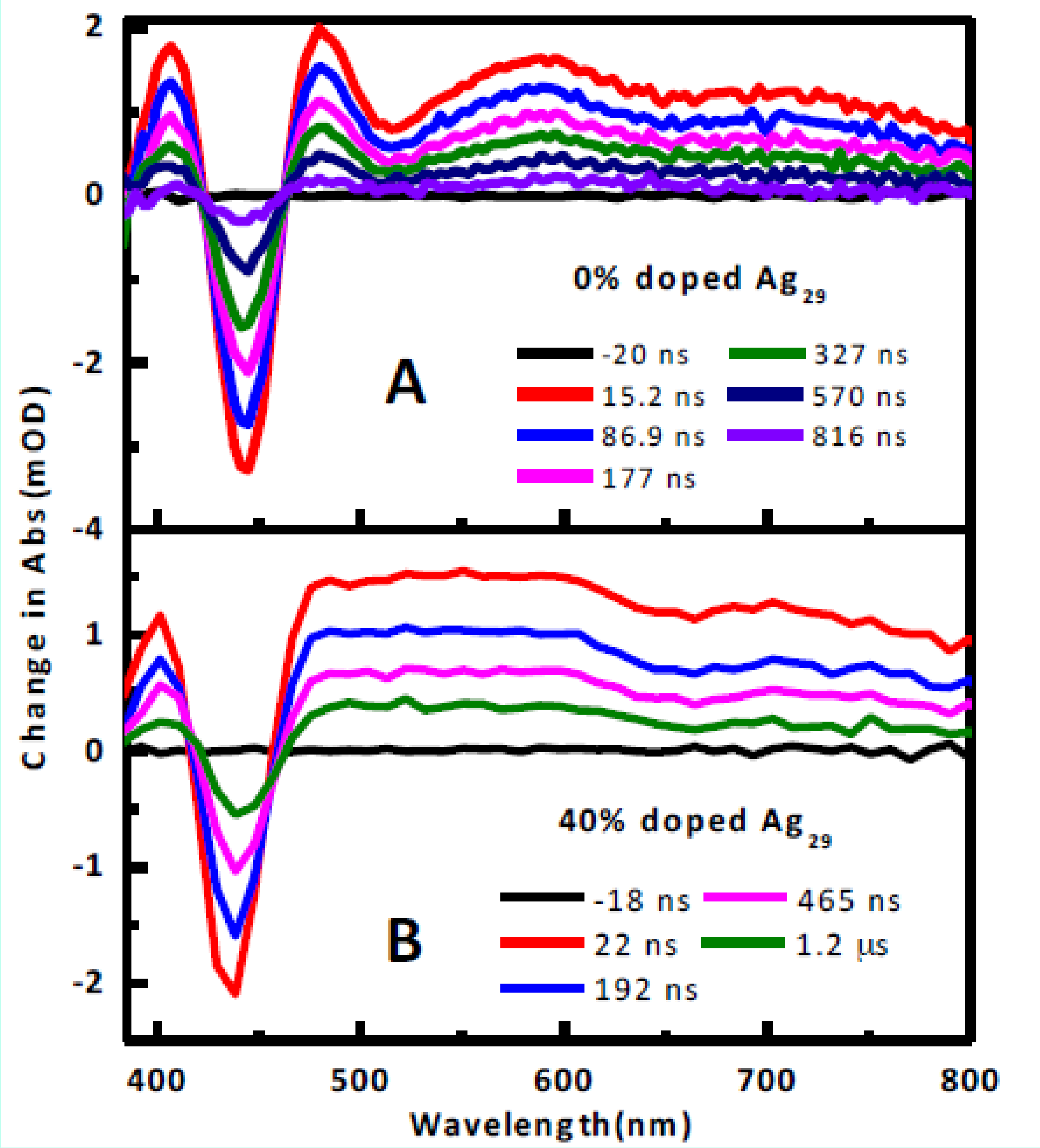


Figure S3. Transient absorption spectra of $Ag_{29}(BDT)_{12}(TPP)_4$ and its Au-doped NCs (40 mmol% sample).

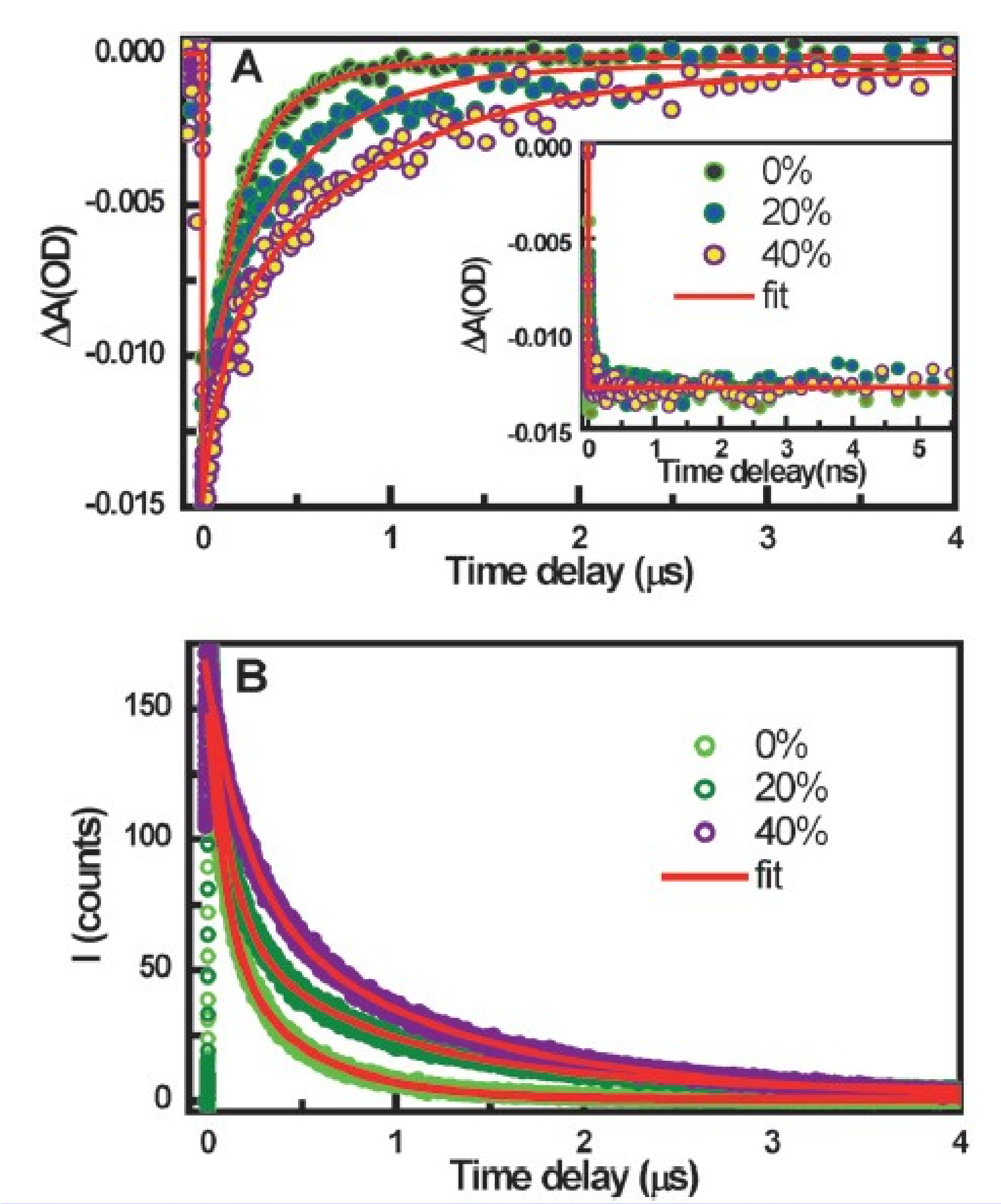
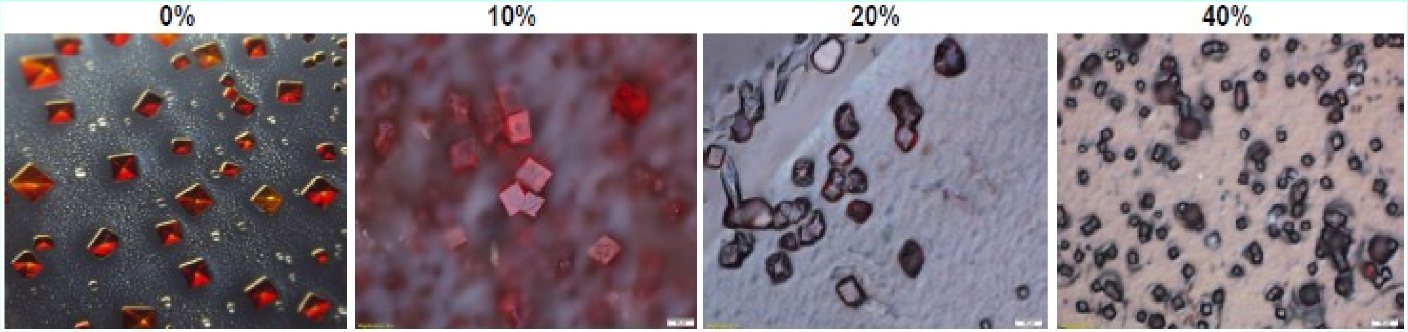


Figure 3. A) Transient kinetic traces corresponding to the GSB from the TA spectra of Ag_{29} and its Au-doped NCs. Inset: kinetics in 0.0–5.5 ns window. B) Kinetics of fluorescence excited-state decay of Ag_{29} and Au-doped clusters at the emission maxima measured by TCSPC. All the solid red lines are fits of the kinetic traces.

X-ray crystal structures



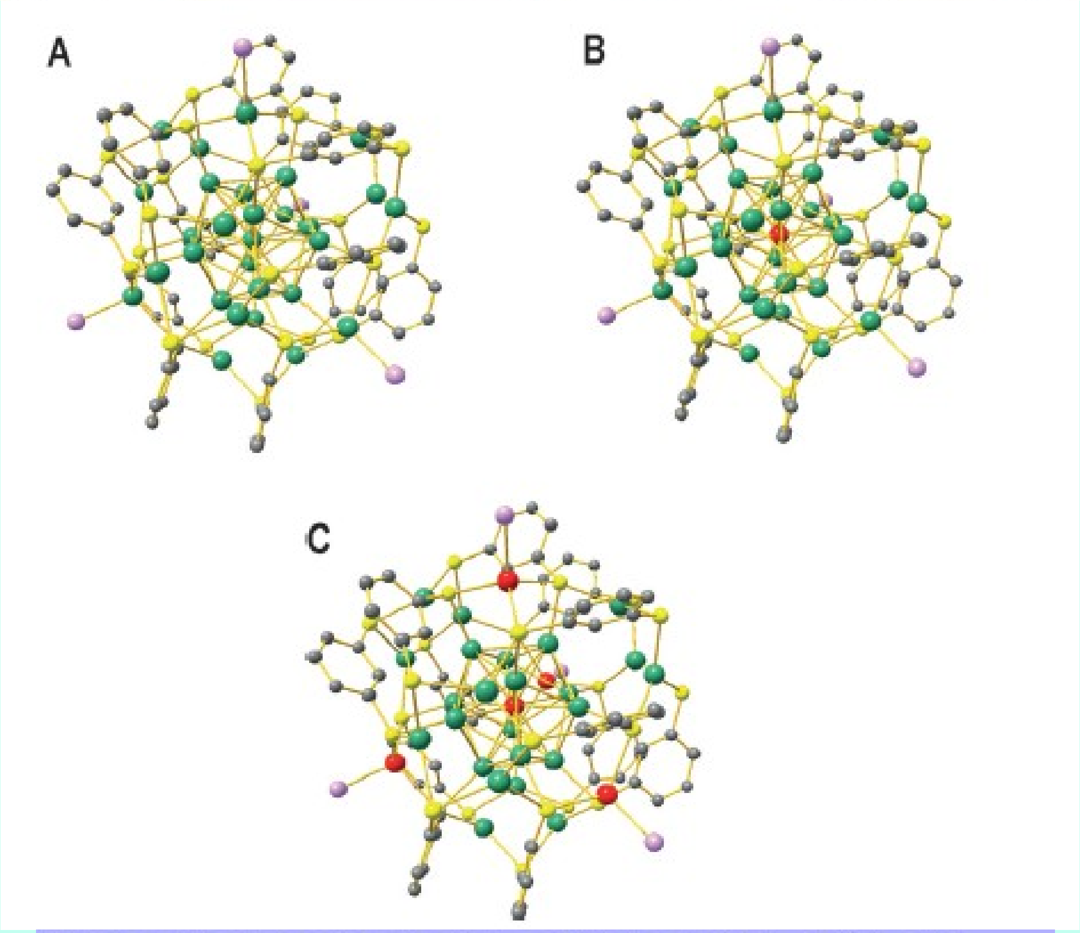


Figure 4. X-ray crystal structures of A) $Ag_{29}(BDT)_{12}(TPP)_4$ and B) $Ag_{28}Au(BDT)_{12}(TPP)_4$. C) Possible locations of Au atoms in $Ag_{29-x}Au_x(BDT)_{12}(TPP)_4$ clusters, $x = 1$–5. Color spheres: green, Ag; red, Au; yellow, S; pink, P; gray, C. For simplicity, H atoms are omitted.[22]

P NMR Spectra

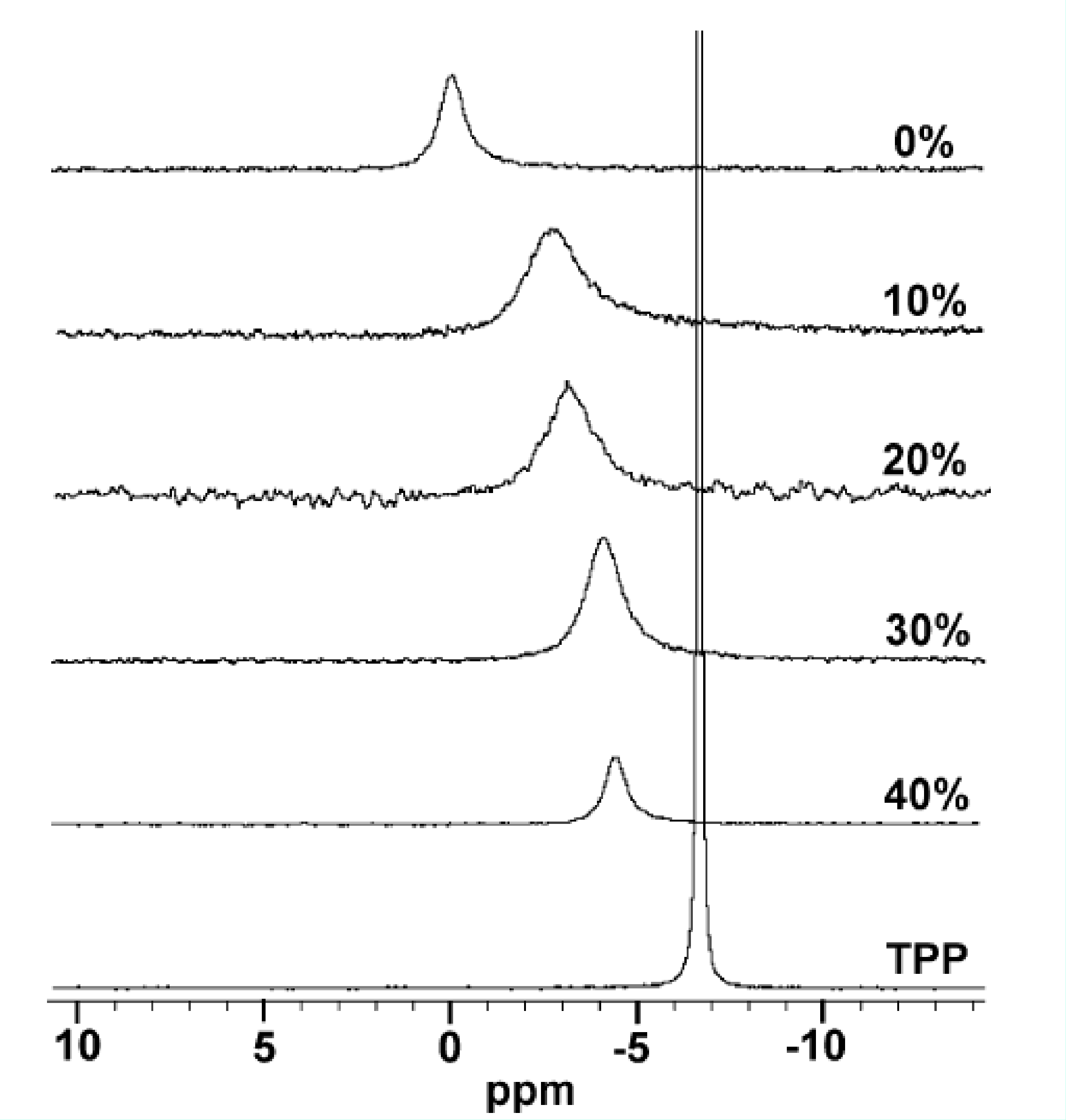


Figure 5. P NMR spectra of pure TPP, $Ag_{29}(BDT)_{12}(TPP)_4$, and $Ag_{29-x}Au_x(BDT)_{12}(TPP)_4$ clusters.

Conclusion

- They have successfully doped $Ag_{29}BDT_{12}TPP_4$ NCs with a discrete number of Au atoms to enhance the PL QY by 26 times .
- Doping of Ag_{29} NCs with Au atoms not only increased the PL intensity but also the ambient stability of the silver clusters.
- The detailed characterization using single crystal XRD, optical spectroscopy, mass spectrometry, and NMR spectroscopy provided insights into the PL enhancement mechanism and the possible locations of the Au heteroatoms within the Ag_{29} framework.
- This study opens a new path for creating highly luminescent noble-metal nanoclusters, for sensing and colorimetric applications.


Thank
You!!!