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Article

Doping Effect on the Magnetism of Thiolate-Capped 25-Atom Alloy Nanoclusters

Yingwei Li,[‖ Y.L. and S.B.] Saborni Biswas,[‖ Y.L. and S.B.] Tian-Yi Luo, Rosalba Juarez-Mosqueda, Michael G. Taylor, Giannis Mpourmpakis, Nathaniel L. Rosi, Michael P. Hendrich,* and Rongchao Jin*

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Introduction

- Ultrasmall Au NPs are known to be magnetic in nature.
- The magnetic properties in Au NP arises as size decrease due to the increase in the d-hole population of surface Au atom.
- $[Au_{25}(PET)_{18}]^0$, a 7e system NC is paramagnetic in nature due to 1 unpaired electron in its HOMO. Spin originates at the icosahedral Au_{13} kernel.
- The paramagnetic $[Au_{25}(PET)_{18}]^0$ can be manipulated by Ag doping.
- The ligand role in magnetism was explored using 2-ethylbenzenethiolate (*o*-EBT) protected NC, an aromatic homologue of 2-phenylethanethiol (PET).
- The study involves EPR spectroscopy.

Characterization of $[Au_{25-x}Ag_x(o\text{-EBT})_{18}]$

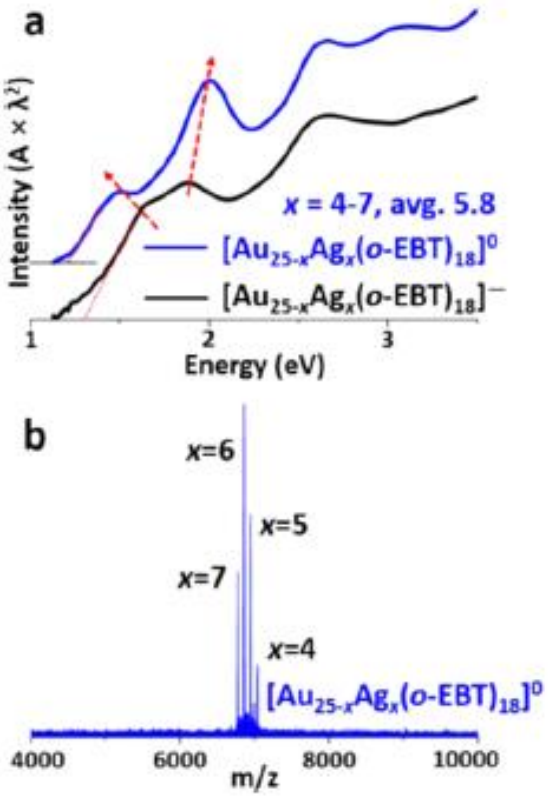


Figure 1. (a) UV−vis absorption spectra (on energy scale) of $[Au_{25-x}Ag_x(o\text{-EBT})_{18}]^q$ (q = −1 (black) and 0 (blue)); **(b)** ESI-MS spectrum of $[Au_{25-x}Ag_x(o\text{-EBT})_{18}]^0$.

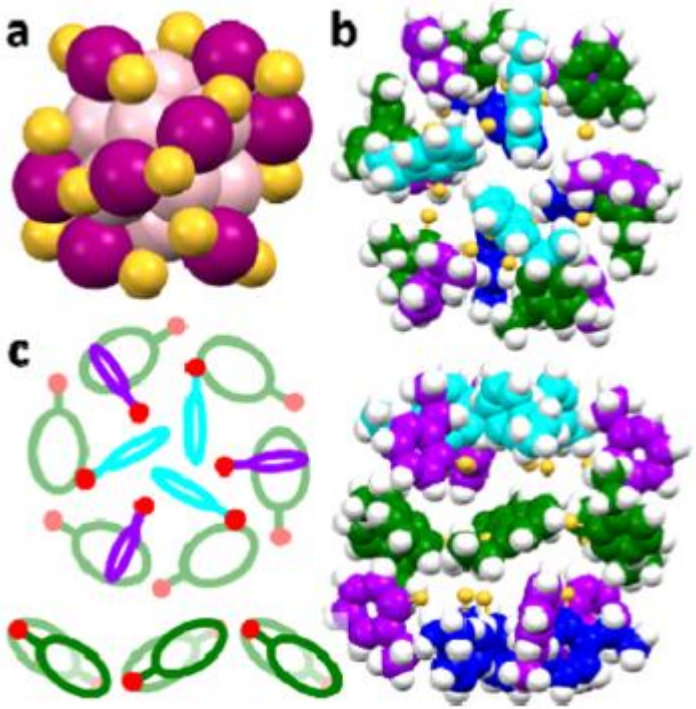


Figure 2. (a) Crystal structure and **(b)** top and side views of the ligand shell of $[Au_{25-x}Ag_x(o\text{-EBT})_{18}]^0$ (av. x = 5.8). **(c)** o-EBT ligand arrangement in the ligand shell. Color labels: magenta = Au, pink = Au/Ag, yellow = S, cyan/purple/green = C, and white = H.

Studies on $[Au_{25-x}Ag_x(PET)_{18}]$ NC system

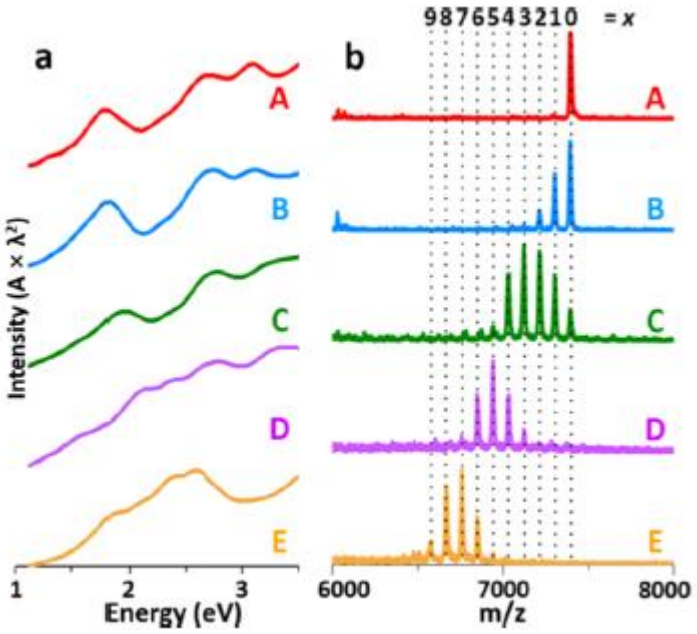


Figure 3. (a) UV–vis absorption spectra (on energy scale) and **(b)** MALDI-MS spectra of $[Au_{25-x}Ag_x(PET)_{18}]^-$.
Sample A: x = 0; **B**: x = 0–2 (av 0.58); **C**: x = 0–6 (av 2.39); **D**: x = 3–7 (av 4.89); and **E**: x = 5–9 (av 7.23),

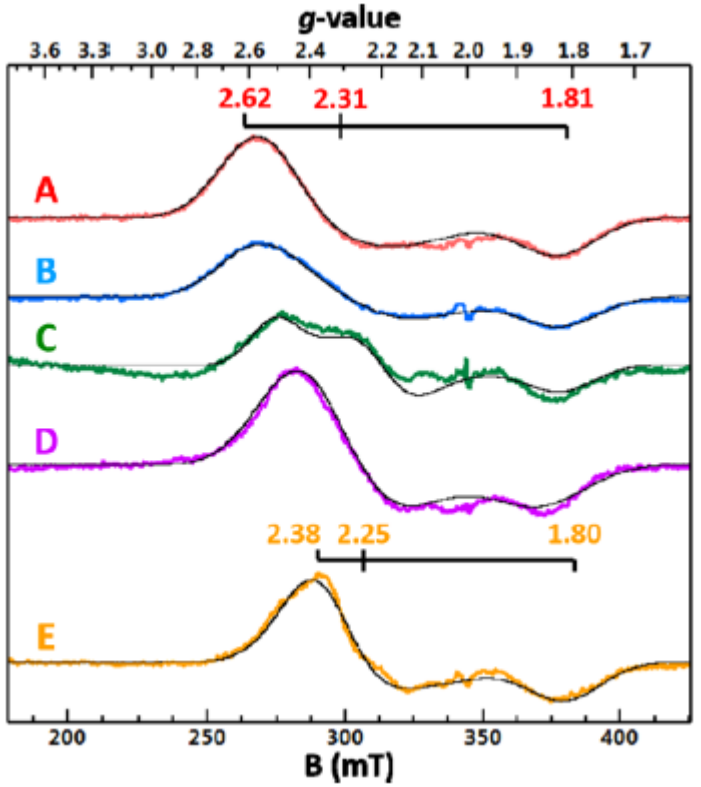


Figure 4. X-band (9.645 GHz) EPR spectra of $[Au_{25-x}Ag_x(PET)_{18}]^0$ with x ranging from 0 to 9 at 16 K. Microwave power 0.2 mW. The Ag dopant x is **(A)** 0, **(B)** 0–2, **(C)** 0–6, **(D)** 3–7, and **(E)** 5–9.

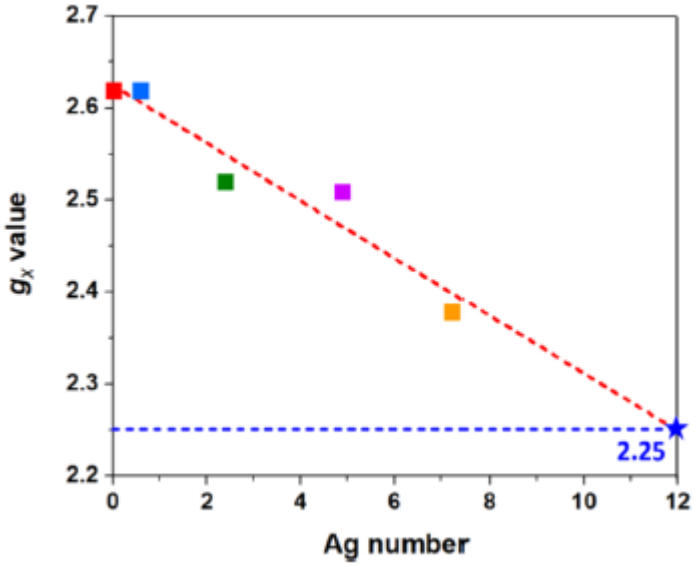


Figure 5. Plot of g_x *vs* the average Ag doping number in $Au_{25-x}Ag_x$ (or the $Au_{12-x}Ag_x$ shell since the center and exterior staple motifs contain gold exclusively) with maximum *x* being 12 and the corresponding fit.

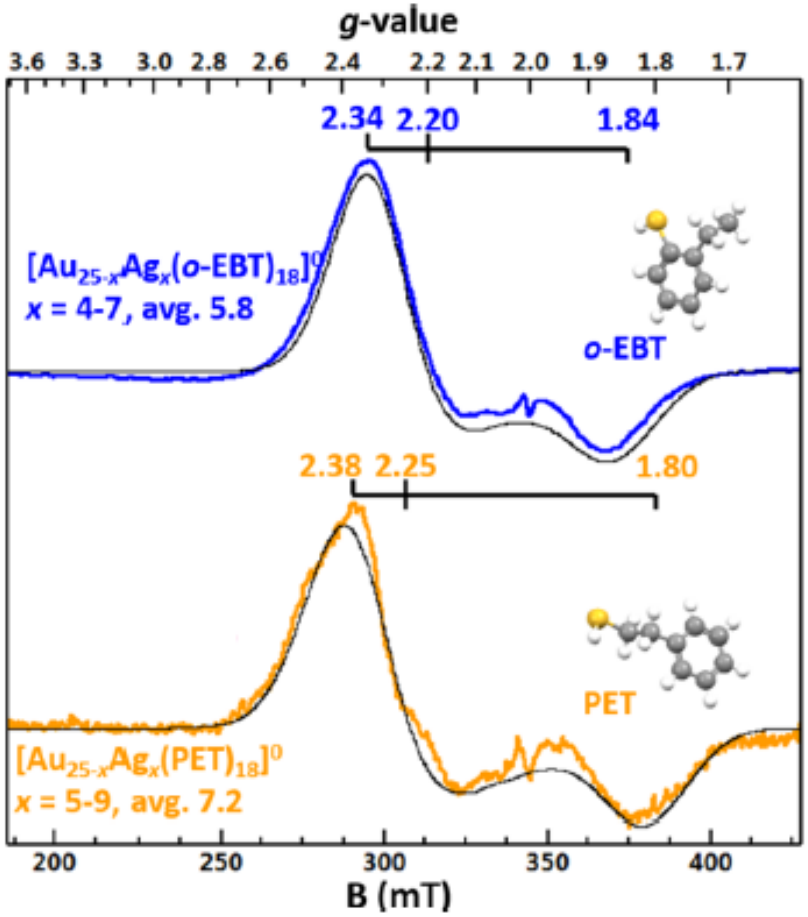
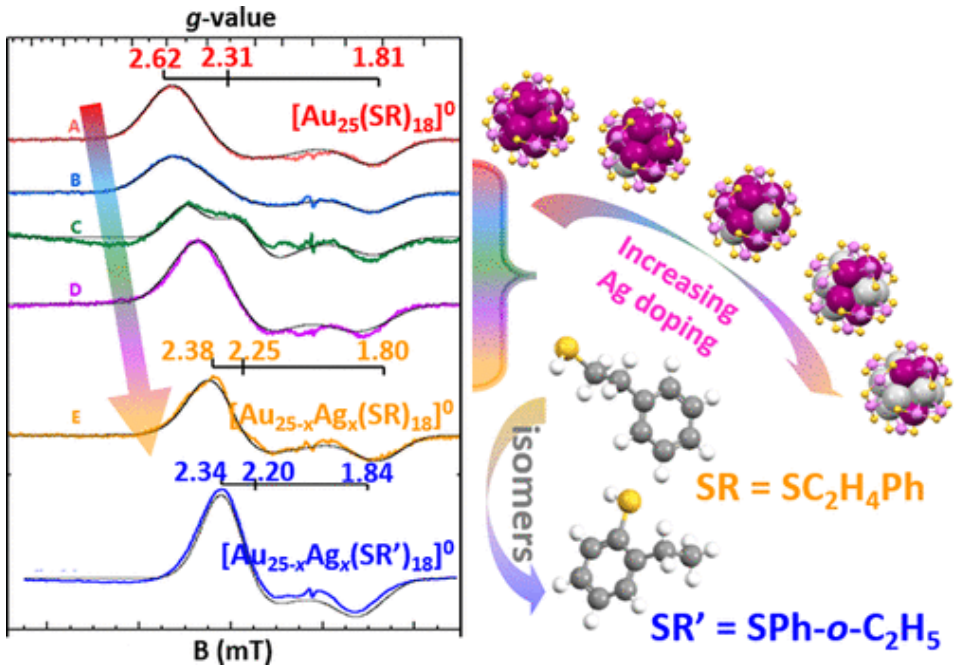


Figure 6. Comparison of the X-band EPR spectra of $Au_{25-x}Ag_x(o\text{-EBT})_{18}]^0$ (x = 4−7, av 5.8) with g = (2.34, 2.25, and 1.84) and $[Au_{25-x}Ag_x(PET)_{18}]^0$ (x = 5−9, av 7.2) with g = (2.38, 2.25, and 1.80) at 16 K and a microwave power of 0.2 mW. The ligand structures are shown aside.

Conjecture from the NC comparison

Factors that contribute to the axial splitting:

- Aromatic and non-aromatic ligands influence the electronic structure of the NC
- Metal kernel-capping ligand interactions might also influence the magnetism

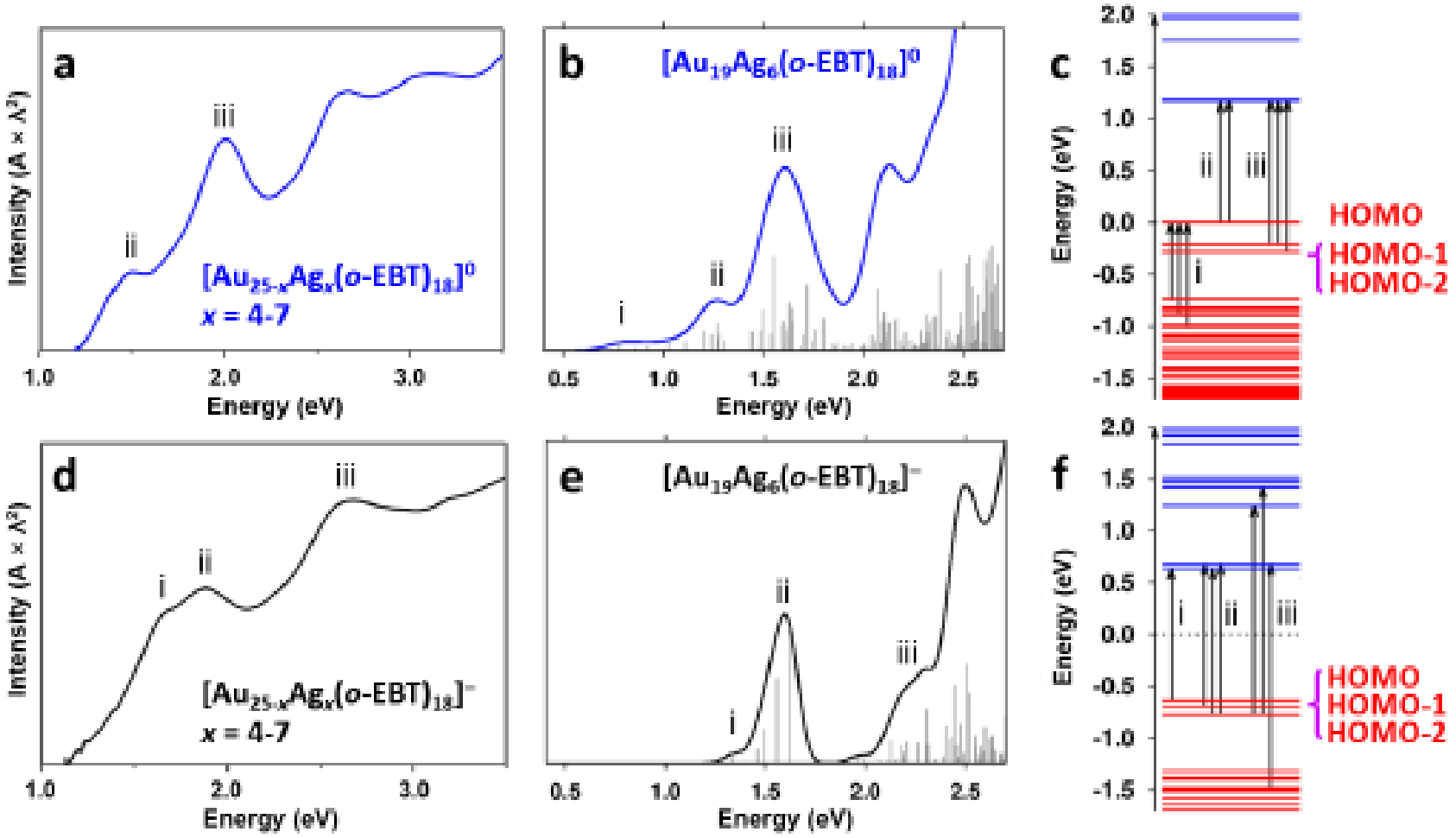


Conclusion

- A paramagnetic 7e $[M_{25}(SR)_{18}]^0$, where M=Au/Ag, can be manipulated using Ag doping.
- Ligand influence observed from the shift in *g*-value for o-EBT and PET capped $Au_{25-x}Ag_x$ NCs.
- In $[M_{25}(PET)_{18}]^0$ NC series, gradual and linear shift in g_x as Ag doing increases in M_{12} shell.
- The large difference in spin-orbit coupling for Ag and Au results in reduced axial splitting.
- 7e paramagnetic NC systems can be tailored with Ag doping.

Inspiration for Our Group

- As ~2 nm Au@DT NPs are known to be magnetic in nature. Can Au@DMBT or Au@BDT NPs be magnetic too ?
- If Yes, what happens when its doped?
- Choice of metals like Cu, Pd, and Pt can introduce different magnetism properties.


a
Intensity (A × λ²)
Energy (eV)
[Au25-xAgx(o-EBT)18]0
x = 4-7
i
ii
iii
b
[Au19Ag6(o-EBT)18]0
c
Energy (eV)
HOMO
HOMO-1
HOMO-2
d
[Au25-xAgx(o-EBT)18]−
e
[Au19Ag6(o-EBT)18]−
f