



HAL
open science

Effects of Single Platinum Atom Doping on Stability and Nonlinear Optical Properties of Ag 29 Nanoclusters

Hussein Fakhouri, Estelle Salmon, Xiao Wei, Stéphane Joly, Christophe Moulin, Isabelle Russier-Antoine, Pierre-François Brevet, Xi Kang, Manzhou Zhu, Rodolphe Antoine

► **To cite this version:**

Hussein Fakhouri, Estelle Salmon, Xiao Wei, Stéphane Joly, Christophe Moulin, et al.. Effects of Single Platinum Atom Doping on Stability and Nonlinear Optical Properties of Ag 29 Nanoclusters. *Journal of Physical Chemistry C*, 2022, 126 (49), pp.21094-21100. 10.1021/acs.jpcc.2c06836 . hal-04447551

HAL Id: hal-04447551

<https://hal.science/hal-04447551>

Submitted on 8 Feb 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Effects of Single Platinum Atom Doping on Stability and Nonlinear Optical Properties of Ag₂₉ Nanoclusters

Hussein Fakhouri,^a Estelle Salmon,^a Xiao Wei,^b Stéphane Joly,^a Christophe Moulin,^a Isabelle Russier-Antoine,^a Pierre-François Brevet,^a Xi Kang,^{b,*} Manzhou Zhu^{b,*} and Rodolphe Antoine^{a,*}

^a *Univ Lyon, Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, F-69622, LYON, France.*

*Email : rodolphe.antoine@univ-lyon1.fr.

^b *Department of Chemistry and Centre for Atomic Engineering of Advanced Materials, Key Laboratory of Structure and Functional Regulation of Hybrid Materials of Ministry of Education, Institutes of Physical Science and Information Technology and Anhui Province Key Laboratory of Chemistry for Inorganic/Organic Hybrid Functionalized Materials, Anhui University, Hefei, Anhui 230601, China.*

*Email : kangxi_chem@ahu.edu.cn, zmz@ahu.edu.cn

ABSTRACT : The properties of atomically precise noble metal nanoclusters can be modified by the addition of other metals, which may offer augmented characteristics, making them more suitable for real-life applications. In this work, we report the effects of single-platinum atom doping of a class of atomically precise silver nanoclusters protected by dithiolated ligands on their optical properties both in linear and nonlinear optical (NLO) regimes and on their stability over time. Pt doping of Ag₂₉ preserves their NLO properties (in particular two-photon excited photoluminescence).

INTRODUCTION

Atomically precise nanoclusters, having well-defined structures and chemical composition, have emerged as an intriguing class of nanomaterials endowed with vast application potential.¹⁻² Nanoclusters are in the size regime where each atom counts and therefore their properties may be affected by substituting one atom for an atom of another metal. “Alloying” (e.g. doping homometallic nanoclusters with one or several other metals) is a powerful strategy for dictating the geometric and electronic structures of nanoclusters and to obtain clusters with desired properties.³⁻⁴ As per surge of literature reports, doping of atomic clusters with heteroatoms in various cases have been demonstrated to lead to augmented luminescence quantum yield, enhanced catalytic activity or greater temporal stability of the clusters.⁵⁻⁷ Hence, doping of nanoclusters has been identified as a versatile approach to tune the optical and physicochemical properties of clusters for improved application potential. Theoretically investigating the alloying effect on nanocluster properties has provided fundamental insight in the structure–property relationships. Recently, Shihui Liu conducted a TDDFT study on the excited states and charge redistribution in response to the light absorption on single-atom doped Au₂₅ nanoclusters, highlighting different absorption features upon doping with Ag, Cu, Pd, or Pt.⁸ The nature and position of lowest excited electronic states are also sensitive to silver doping.⁹ Other factors like relativistic effects (mainly due to the Au atoms), the exact position of metal dopants and heteronuclear Au–Ag bonds¹⁰ can affect the fluorescence intensity of gold-doped nanoclusters.¹¹

While most of doping of nanoclusters with heteroatoms was done with the highly stable single thiolated (SR) Au₂₅SR₁₈,¹²⁻¹⁸ and Ag₂₅SR₁₈,¹⁹⁻²⁰ dithiolated (SSR) Ag₂₉SSR₁₂ nanocluster²¹⁻²⁶ is another interesting candidate for doping strategies.¹¹ The use of dithiolated molecules allow for exploring different staple motifs (as compared to those obtained with single thiolated molecules)

and therefore adds some versatility to doping strategies. Several experimental studies showed that doping of silver nanoclusters with dithiolated molecules with heteroatoms present enhanced catalytic activity, photoluminescence (PL), stability, and due to synergistic effects.²⁷ Van der Linden et al. demonstrated such enhanced PL and stability, by doping Ag₂₉ nanoclusters capped with lipoic acid with Au.²⁸ On the other hand, Bootharaju et al. were able to do doping of Ag₂₉ cluster with a single Pt atom, i.e. leading to enhanced excited-state lifetime and PL intensity.²⁹

Also the exact spatial position of metal dopants and the heteronuclear bimetallic bonds have a profound effect on the nanocluster's properties in particular their optical properties.¹⁰⁻¹¹ Moreover, doping of metal nanohybrid systems with another metal has been demonstrated to lead to enhanced nonlinear optical properties. In particular silver doped gold-cysteine supramolecular assemblies,³⁰ as well as silver-doped gold nanoclusters display efficient nonlinear optical signals (both two-photon excited fluorescence and second harmonic response).³¹⁻³² Recently, a series of Ag_{25-x}Au_xDMBT₁₈ nanoclusters where x=0, 1, and 5-10 were synthesized. For Ag₂₄Au₁DMBT₁₈, it was demonstrated that the presence of the central Au dopant strongly influences linear and non-linear optical properties, increasing photoluminescence upon both one- and two-photon excitations, with respect to un-doped silver nanoclusters.²⁰ Indeed, the central silver atom replacement with Au atom leads to localization of electron charge in the icosahedral center inducing changes in electronic structure of Ag₂₄Au₁.

Single platinum atom doping to gold or silver clusters was found also to strongly affect optical properties in particular for efficient photoluminescence and photocatalysis³³ or for enabling near-infrared-to-blue photon upconversion with PtAg₂₄SR₁₈ nanoclusters.³⁴ In this work, we aim at exploring the effect of a single Pt doping of Ag₂₉ nanoclusters on their photoluminescence (both upon one- and two-photon excitation), second harmonic generation and their stability. Single Pt

doping of Ag₂₉ nanoclusters was done using both hydrophilic lipoic acid (DHLA) ligands (Ag₂₉DHLA₁₂) and hydrophobic 1,3-benzenedithiol (BDT) ligands (Ag₂₉BDT₁₂). In particular, we show that single Pt doping of Ag₂₉DHLA₁₂ nanoclusters significantly increases their stability and preserves their NLO properties (in particular two-photon excited photoluminescence) allowing live cell multiphoton confocal imaging to be reported.

METHODS

Nanoclusters synthesis.

Preparation of Ag₂₉DHLA₁₂

100 mg of (±)- α -lipoic acid was dissolved in 5 ml of MeOH and 10 ml of water followed by the addition of 2 equivalent (in mol) of tetramethylammonium borohydride (CH₃)₄N(BH₄) for 30 minutes, then solution was ultrasonicated for 1 hour to remove the excess of reducer. 41 mg of silver nitrate was dissolved in 15 ml of milliQ water and added to the solution, 1 ml of NH₄OH (10%) is added to the solution, followed by 85 mg of (CH₃)₄N(BH₄) and stirred at 50°C for 1 hour. Then, 1 equivalent of (CH₃)₄N(BH₄) (42.5 mg) is added and left for another 1 hour. The water quantity was reduced to 1 ml using rotatory evaporator to help the precipitation with EtOH. 5 ml of EtOH and 20 ml of Et₂O was added followed by 20 μ l of glacial acetic acid and centrifuged at 5000 rpm for 5 min. The precipitant was then dissolved in a minimum of water/NH₄OH (10%) followed by 5 ml of ethanol and 20 ml of diethyl ether (repeated 3 times). The last centrifugation was done by adding only diethyl ether and the precipitant was collected and dried under vacuum overnight and stored at the freezer for later use.

Preparation of Pt₁Ag₂₈DHLA₁₂

The synthesis of $\text{Pt}_1\text{Ag}_{28}\text{DHLA}_{12}$ was similar to the as prepared $\text{Ag}_{29}\text{DHLA}_{12}$ nanoclusters with a small modification. A ratio of silver/platinum is used when adding the metal salt in the previous synthesis, 31mg/11mg (silver nitrate/ dihydrogen Hexachloroplatin (IV)) was dissolved in 15 ml of milliQ water and added to the solution.

Preparation of $\text{Ag}_{29}\text{BDT}_{12}(\text{PPh}_3)_4$

The preparation of $\text{Ag}_{29}\text{BDT}_{12}(\text{PPh}_3)_4$ was based on the reported method of the Bakr group.³⁵

Preparation of $\text{Pt}_1\text{Ag}_{28}\text{BDT}_{12}(\text{PPh}_3)_4$

The preparation of $\text{Pt}_1\text{Ag}_{28}\text{BDT}_{12}(\text{PPh}_3)_4$ was based on the reported method of the Bakr group.³⁶

Preparation of $\text{Au}_x\text{Ag}_{29-x}\text{BDT}_{12}(\text{PPh}_3)_4$

The preparation of $\text{Au}_x\text{Ag}_{29-x}\text{BDT}_{12}(\text{PPh}_3)_4$ was based on the reported method of the Bakr group.²⁴

Instrumentation.

Electrospray Ionization Mass Spectrometry (ESI-MS). For nanoclusters protected by DHLA, ESI-MS was performed on a commercial quadrupole time-of-flight (micro-qTOF, Bruker-Daltonics, Bremen, Germany, mass resolution 10000). The samples were prepared to a final concentration of approximately 50 μM . The samples were analyzed in negative ion mode; each data point was the summation of spectra over 5 min. For nanoclusters protected by BDT, ESI-MS measurements were performed using a Waters XEVO G2-XS QT MS instrument. The sample was directly infused into the chamber at 5 $\mu\text{L}/\text{min}$. For preparing the ESI samples, the nanocluster samples were dissolved in CH_2Cl_2 or DMF (1 mg/mL) and diluted (v/v = 1:1) by CH_3OH . The ESI-MS test of $\text{Ag}_{29}\text{BDT}_{12}(\text{PPh}_3)_4$ and $\text{Pt}_1\text{Ag}_{28}\text{BDT}_{12}(\text{PPh}_3)_4$ was tested in the

negative mode. The mass signal of $[\text{Ag}_{29}\text{BDT}_{12}(\text{PPh}_3)_4]^{3-}$ locate around 1953 Da.³⁵ The mass signal of $\text{Pt}_1\text{Ag}_{28}\text{BDT}_{12}(\text{PPh}_3)_4]^{4-}$ locate around 1487 Da.³⁶

UV/Vis and PL spectra. For UV/Vis spectra, the sample is illuminated with a continuous spectrum using halogen lamp coupled to an AvaLight DH-S deuterium lamp, the transmitted light is collected and analyzed with AvaSpec-2048FT spectrophotometer.

PL spectra were recorded using a commercial spectrofluorometer from Horiba Jobin Yvon controlled by the FluorEssence software (Fluoromax 4 spectrophotometer) with Xenon arc lamp for the light source. The instruments enable the estimation of the quantum yield (ϕ_F) using an external reference, 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran, (DCM) in methanol in our case, using the following equation:

$$\phi_F = \phi_R \frac{n_F^2 I_F A_R}{n_R^2 I_R A_F} \quad (1)$$

Where R stand to the reference, F for the sample, I is the fluorescence intensity and A is the absorption at the excitation wavelength and n is the refractive index of the solvent.

NLO Measurements. 2PEPL cross sections were measured using the reference method with multiphoton confocal instrument. The setup for two-photon excited photoluminescence (2PEPL) has been described in detail in previous works.¹⁰

The 2PEPL cross sections are extracted using the reference method and is calculated using fluorescein as a reference according to the equation:

$$\sigma_{2PEPL} = \frac{\sigma_2^{ref} c^{ref}}{c} \frac{I}{I_{ref}} \quad (2)$$

Where σ_2 is the two-photon excited fluorescence cross section, c is the concentration, and I is the fluorescence intensity. Here ref donates to the different coefficients of the reference used. The reference used for the experiments was the fluorescein with a low concentration to obtain two-photon emission yields compatible with gold NCs yield. At 780nm, σ_2 of the fluorescein is 33.3 GM.³⁷

TPA cross sections could be calculated using QYs (Φ), and assuming that 1P QY = 2P QY using the following formula :

$$\sigma_{TPA} = \frac{\sigma_{2PEPL}}{\Phi} \quad (3)$$

This assumption is commonly accepted in photochemistry community (Kasha's rule and Vavilov's rule).

For hyper Rayleigh scattering (HRS), the output of a femtosecond Ti:Sapphire laser (Spectra, Tsunami pumped with a Millennia) with a pulse duration of about 120 fs centered at the wavelength of 800 nm was used to generate incoherent second harmonic scattered light from the sample cell. In order to control the energy of the light impinging onto the sample, the beam was passed through a half wave plate followed by a polarizing cube. The fundamental beam was vertically polarized and focused using a low NA microscope objective (X16, NA=0.32). The

optical cell was made from fused silica and had an optical path of 5 mm. The focus was nevertheless no more than 2 mm away from the cell walls from alignment convenience. The second harmonic light scattered at right angle at 400 nm was then send to a spectrometer (SPEX, 500M) and detected with a CCD camera (Andor, Du40). Data were then treated for spectral cleaning and spurious PL rejection. The first hyperpolarizability of the different nanoclusters was obtained using the external reference method were the output scattered harmonic intensity is recorded as a function of the input power of the fundamental intensity and plotted as a function of the square root of this fundamental intensity. Linear plots were thus obtained and slopes compared to a reference. We used several countings to extract an error bar. Here, we used neat water as the reference, the first hyperpolarizability of which is taken as 0.087×10^{-30} esu.³⁸

RESULTS AND DISCUSSION

In the work, Pt doping at the single atom level of the as synthesized Ag₂₉ nanoclusters was performed. Details of the doping process are given in the Supporting Information. Evidence of doping of Pt atoms into the system of Ag₂₉ clusters (with the appearance of PtAg₂₈SSR₁₂ nanoclusters, with SSR = DHLA or BDT) was obtained from ESI-MS analysis as shown in Figure S1 for Ag₂₉DHLA₁₂ nanoclusters.

Ag clusters prepared with lipoic acid (DHLA) as the ligand are generally observed with atomic precision (and assigned as Ag₂₉DHLA₁₂).^{23, 26} Although quite appealing since highly luminescent, degradation over time of as-synthesised clusters was a general trend and results in aggregation and possibly oxidation.²⁶ Clearly, such degradation can be easily followed by looking at changes in absorption spectra. Figure 1a) and b) display the UV/Vis absorption spectrum of Ag₂₉ nanoclusters from fresh solutions and aged solutions (after two weeks).

Clearly, the typical absorption bands observed for the fresh solution are strongly decreased for the aged solution (and also the photoluminescence intensity, compare insets in fig. 1a) and 1b)). During degradation, absorption spectrum becoming less pronounced is a clear signature of degradation as demonstrated by Van der Linden et al.²⁶ Single platinum doping on Ag₂₉ nanoclusters has a strong effect on the stability of nanoclusters. As shown in Figure 1c) and 1d), absorption and photoluminescence spectra are unmodified between fresh and aged solutions. This can be explained by bond lengths and strengths that are modified by introduction of Pt dopant atom in the Ag₂₉ metal core, as evidenced by X-ray spectroscopies.²⁸ In addition, Basset et al. synthesized [PtAg₂₈BDT₁₂TPP₄]⁴⁻.²⁹ The Pt dopant in PtAg₂₈ was found to occupy the center position of the icosahedron core. PtAg₂₈ possesses a closed-shell electronic configuration, showing enhanced stability,

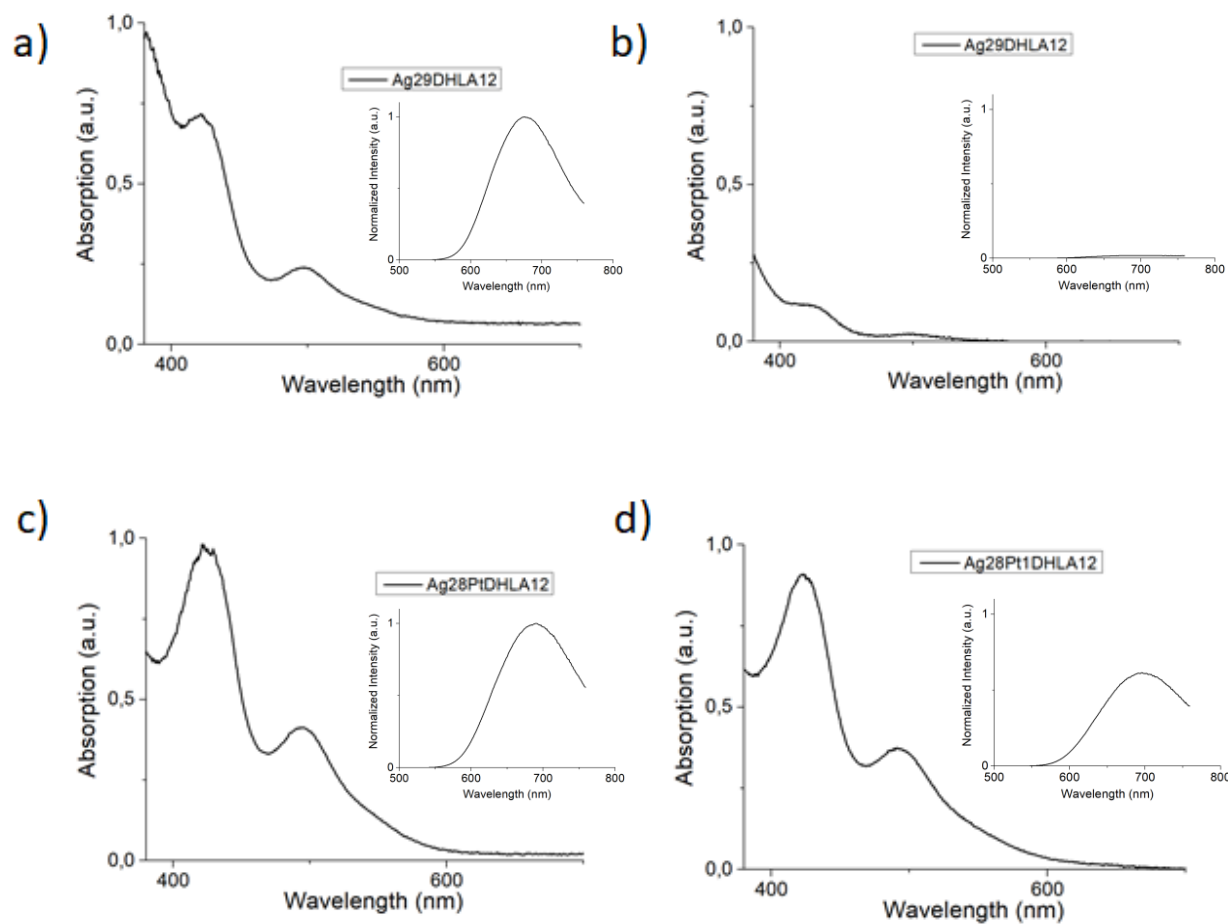
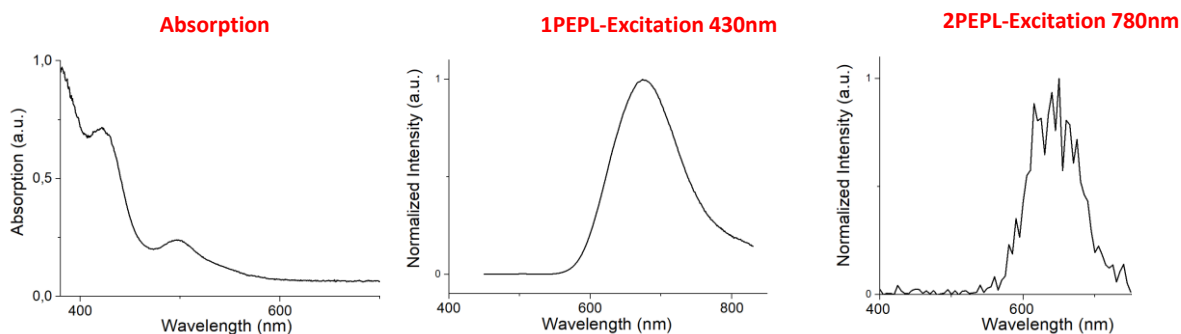


Figure 1 : UV-Vis absorption spectra (and the corresponding PL spectra in insets) of fresh solutions of nanoclusters (a and c), and aged solutions of nanoclusters (b and d). Aged solutions are solution after 2 weeks. All samples were purified and we collect the powder and stored in the freezer in the same conditions. Water was used as solvent for Ag₂₉DHLA₁₂. Concentration of nanoclusters is 100 μ M.

Ag₂₉DHLA₁₂



PtAg₂₈DHLA₁₂

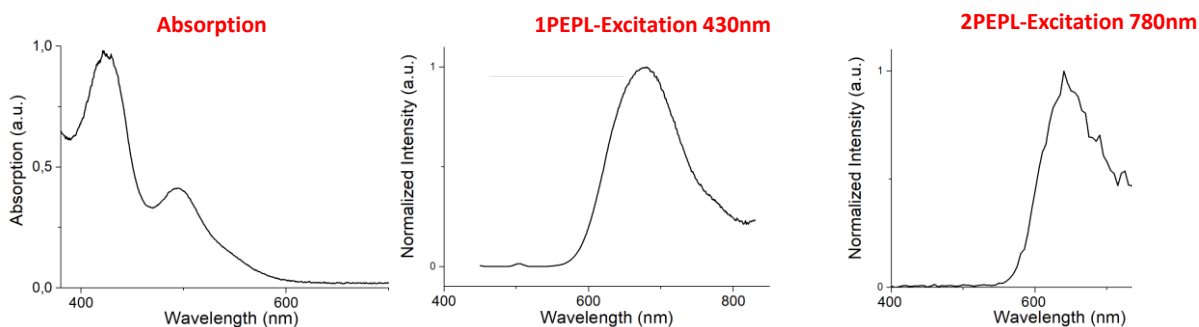


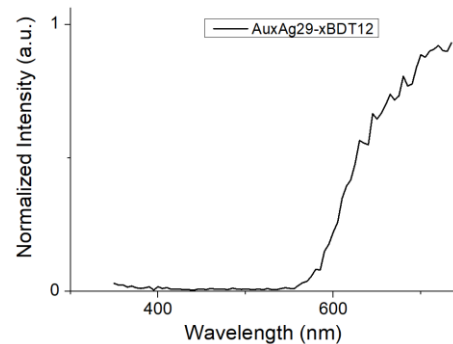
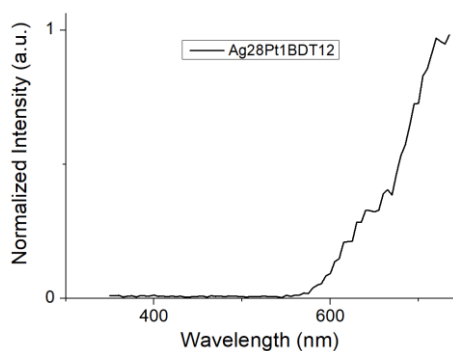
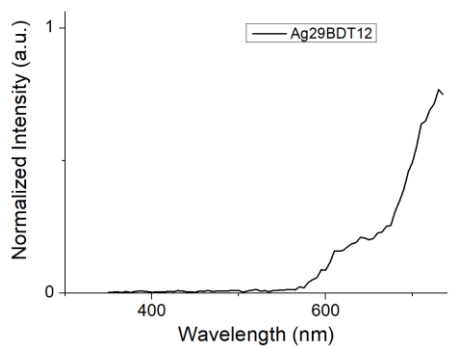
Figure 2: Spectroscopic characterization of the synthesized Ag₂₉ and PtAg₂₈ clusters protected by DHLA dispersed in water. Absorption spectrum (left panel) concentration is 100 μ M, one-photon excited photoluminescence (1PEPL) spectrum (middle panel) with excitation at 430 nm. Concentration is 10 μ M and two-photon excited photoluminescence (2PEPL) spectrum (right panel) with excitation at 780 nm concentration is 970 μ M. The sharp drop observed after 750 nm on the lower right (2PEPL spectrum) is due to filter effect. Water was used as solvent for Ag₂₉DHLA₁₂.

Under near-UV/visible light, solution of Ag₂₉ and platinum-doped Ag₂₉ clusters showed strong red photoluminescence (one-photon excited photoluminescence (1PEPL), see Figure 2). However, Pt-doping does not increase PL signal intensity, and PL spectra are very similar to those of undoped Ag₂₉ nanoclusters. In the current study, we also investigated the two-photon excited photoluminescence (2PEPL) spectra of Pt-doped Ag₂₉ nanoclusters and compared with that of undoped Ag₂₉ nanoclusters (see Figures 2 and 3). Both Ag₂₉ and platinum-doped Ag₂₉ nanoclusters showed strong 2PEPL spectra in the red. 2PEPL cross-section can be as high as 0.13 ± 0.05 GM (see Table 1). However, Pt-doping does not increase significantly cross sections

(see Table 1), and 2PEPL spectra are very similar to those of undoped Ag₂₉ nanoclusters. The same trend is observed when gold is used as dopant (instead of Pt) for Ag₂₉ nanoclusters (see Table 1, Au_xAg_{29-x}BDT₁₂). However, we would like to point that 2PEPL cross sections of these silver nanoclusters are quite large as compared to reported values for gold nanoclusters.³⁹ On the other hand, Oh et al.⁴⁰ found that AuNC protected by PEG-modified thioctic acid ligands presented large two-photon excited fluorescence cross sections (several tens of GM) and also found that the addition of just a few dopant Ag atoms per AuNC protected by PEG-modified thioctic acid ligands yielded significant enhancement in QY (>10%) along with improved long-term photostability.⁴¹

Interestingly a solvent effect has been observed in the 2PEPL spectra of platinum doped Ag₂₉ clusters protected by BDT. A red shift (of more than 50 nm) of 2PEPL spectra is observed when clusters are diluted in THF as compared to DMF solvent. Fig. S2 presents solvent dependent 1PEPL spectra of different clusters, which are found to be similar to that for 2PEPL. Therefore such red-shift that may be related by a stronger stabilization of ground state than those of excited state, due to different dielectric constants between THF and DMF.

a) THF



b) DMF

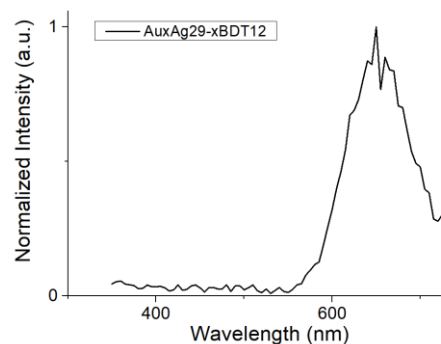
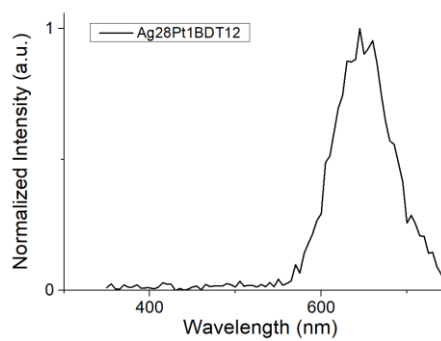
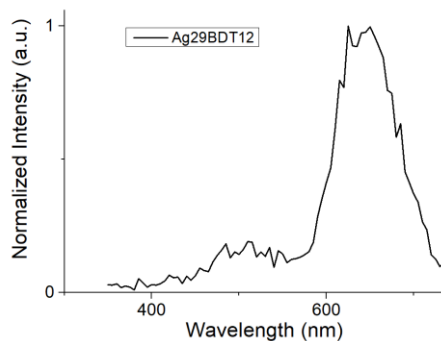


Figure 3 : 2PEPL spectra with excitation at 780 nm of the synthesized Ag₂₉, PtAg₂₈ and Au_xAg_{29-x} clusters protected by BDT dispersed in a) THF and b) DMF. The sharp decrease of 2PEPL signal of nanoclusters in THF is due to filter effect that cuts the excitation laser signal.

Table 1: 2PEPL and TPA cross sections for silver-based nanoclusters (in DMF for BDT ligands and in water for DHLA ligands). 1PL QY is the one photon excited quantum yield.

Compounds	2PEPL cross section (GM)	QY(%)	TPA cross section (GM)
Fluorescein	33,3	90	37
Ag ₂₉ BDT ₁₂	0,13	1.51	8.6
Ag ₂₈ Pt ₁ BDT ₁₂	0,08	1.5	5.3
Au _x Ag _{29-x} BDT ₁₂	0,14	18.1	0.8
Ag ₂₉ DHLA ₁₂	0,06	0.5	12
Ag ₂₈ Pt ₁ DHLA ₁₂	0,06	0.15	40

Also, the effect of chemical substitution based platinum doping on the hyperpolarizability (β) value of Ag₂₉ nanoclusters was evaluated (see Figs. S3 and S4). Intriguingly, similar β values of $\sim 58 \pm 12 \times 10^{-30}$ esu for Ag₂₉ and PtAg₂₈ nanoclusters protected by DHLA were found. In contrast we observed a reduced hyperpolarizability value of $82 \pm 30 \times 10^{-30}$ esu for PtAg₂₈ nanoclusters protected by BDT as compared to $162 \pm 60 \times 10^{-30}$ esu for pure Ag₂₉ nanoclusters protected by BDT (see Supporting information for raw data and details on the methods used to extract hyperpolarizability (β) values). We would like to point out that measurements were done in water for Ag₂₉ and PtAg₂₈ nanoclusters protected by DHLA and in DMF for Ag₂₉ and PtAg₂₈ nanoclusters protected by BDT. We tried determine the hyperpolarizability with THF solvent, but unstable signal was observed. Thus, single doping of Pt atom does not influence significantly the hyperpolarizability of Ag₂₉ nanoclusters. Since hyperpolarizability (β) is sensitive to symmetry-breaking in nanosystems, we can speculate that since β values for Ag₂₉ and PtAg₂₈ nanoclusters protected by DHLA are similar, then Pt atom is certainly located in the center of the Ag₂₉ metal core (and do not affect the centro-symmetry of the metal core structure). From an

analytical point-of-view, measuring hyperpolarizability for doped metal nanoclusters seems to be an efficient probe to locate the hetero-atom position in the metal kernel. Indeed, Knoope and coworkers have shown that when hetero-atom doping is not at the center of the metal kernel, strong increase in hyperpolarizability was observed.³² Since PtAg₂₈DHLA₁₂ are water-soluble, present good stability, we demonstrate its applicability for in vitro imaging. Figure S5 shows the two-photon excited photoluminescence image of HeLa cells incubated with PtAg₂₈DHLA₁₂ nanoclusters under excitation of femtosecond laser pulses at 780 nm with concentrations ranging from 30 to 900 μM. No auto-fluorescence from the cells was observed under the same experimental conditions (See control in Figure S5). MTT viability assay for HeLa cells incubated with A PtAg₂₈DHLA₁₂ silver NCs with different concentration is displayed in Fig. S6. LD50 is reached for NCs concentrations higher than 900μM.

CONCLUSION

In summary, the effects of single-platinum doping of a class of Ag₂₉ nanoclusters (protected either by hydrophilic DHLA or hydrophobic BDT ligands) were evaluated on their photoluminescence (both upon one and two photon excitation), second harmonic generation and their stability. Pt doping of Ag₂₉DHLA₁₂ nanoclusters significantly increases their stability and preserves their NLO properties (in particular their two-photon excited photoluminescence). Similar trends are observed when BDT is used as ligands. Thanks to their strong stability, water-solubility, and due to 2PEPL signals, we have reported two-photon excitation live cell fluorescence imaging with such nanoclusters.

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/>.

Methods for cell culture and bio-imaging. ESI-MS spectra of nanoclusters, one-photon excited fluorescence spectra of nanoclusters in DMF and THF. HRS line intensity of nanoclusters in aqueous solutions as a function of laser power. Two-photon excited photoluminescence image of HeLa cells incubated with nanoclusters and MTT viability assay for HeLa cells incubated with NCs with different concentration.

AUTHOR INFORMATION

Corresponding Authors

Rodolphe Antoine

Univ Lyon, Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, F-69622, LYON, France. rodolphe.antoine@univ-lyon1.fr.

Xi Kang

Department of Chemistry and Centre for Atomic Engineering of Advanced Materials, Key Laboratory of Structure and Functional Regulation of Hybrid Materials of Ministry of Education, Institutes of Physical Science and Information Technology and Anhui Province Key Laboratory of Chemistry for Inorganic/Organic Hybrid Functionalized Materials, Anhui University, Hefei, Anhui 230601, China.

kangxi_chem@ahu.edu.cn

Manzhou Zhu

Department of Chemistry and Centre for Atomic Engineering of Advanced Materials, Key Laboratory of Structure and Functional Regulation of Hybrid Materials of Ministry of Education, Institutes of Physical Science and Information Technology and Anhui Province Key Laboratory of Chemistry for Inorganic/Organic Hybrid Functionalized Materials, Anhui University, Hefei, Anhui 230601, China.

zmz@ahu.edu.cn

Authors

Hussein Fakhouri

Univ Lyon, Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, F-69622, LYON, France.

Estelle Salmon

Univ Lyon, Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, F-69622, LYON, France.

Xiao Wei

Department of Chemistry and Centre for Atomic Engineering of Advanced Materials, Key Laboratory of Structure and Functional Regulation of Hybrid Materials of Ministry of Education, Institutes of Physical Science and Information Technology and Anhui Province Key Laboratory of Chemistry for Inorganic/Organic Hybrid Functionalized Materials, Anhui University, Hefei, Anhui 230601, China.

Stéphane Joly

Univ Lyon, Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, F-69622, LYON, France.

Christophe Moulin

Univ Lyon, Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, F-69622, LYON, France.

Isabelle Russier-Antoine

Univ Lyon, Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, F-69622, LYON, France.

Pierre-François Brevet

Univ Lyon, Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, F-69622, LYON, France.

NOTES

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

X. K. acknowledges the financial support of the NSFC (22101001). H. F. acknowledges the STIM-REI project, Doctoral study of Biophysics at the University of Split as well as Prof. Miroslav Radman at MedILS and Split-Dalmatia County for support.

REFERENCES

1. Chakraborty, I.; Pradeep, T., Atomically Precise Clusters of Noble Metals: Emerging Link between Atoms and Nanoparticles. *Chem. Rev.* **2017**, *117*, 8208-8271.
2. Jin, R.; Zeng, C.; Zhou, M.; Chen, Y., Atomically Precise Colloidal Metal Nanoclusters and Nanoparticles: Fundamentals and Opportunities. *Chem. Rev.* **2016**, *116*, 10346-10413.
3. Kang, X.; Li, Y.; Zhu, M.; Jin, R., Atomically Precise Alloy Nanoclusters: Syntheses, Structures, and Properties. *Chem. Soc. Rev.* **2020**, *49*, 6443-6514.
4. Kang, X.; Zhu, M., 12 - Alloy Nanoclusters-Synthesis Methods and Structural Evaluation. In *Luminescent Metal Nanoclusters*, Thomas, S.; Joseph, K.; Appukuttan, S.; Mathew, M. S., Eds. Woodhead Publishing: 2022; pp 349-384.
5. Ghosh, A.; Mohammed, O. F.; Bakr, O. M., Atomic-Level Doping of Metal Clusters. *Acc. Chem. Res.* **2018**, *51*, 3094-3103.
6. Yuan, X.; Dou, X. Y.; Zheng, K. Y.; Xie, J. P., Recent Advances in the Synthesis and Applications of Ultrasmall Bimetallic Nanoclusters. *Part. Part. Syst. Charact.* **2015**, *32*, 613-629.
7. Kwak, K.; Lee, D., Electrochemistry of Atomically Precise Metal Nanoclusters. *Acc. Chem. Res.* **2019**, *52*, 12-22.
8. Liu, S., Single-Atom Doping on Thiolate-Protected Gold Nanoclusters: A Tddft Study on the Excited States. *Mater. Res. Exp.* **2019**, *6*, 1150g3.
9. Muniz-Miranda, F.; Menziani, M. C.; Pedone, A., Influence of Silver Doping on the Photoluminescence of Protected Ag_nAu_{25-n} Nanoclusters: A Time-Dependent Density Functional Theory Investigation. *J. Phys. Chem. C* **2015**, *119*, 10766-10775.
10. Basu, S.; Bakulić, M. P.; Fakhouri, H.; Russier-Antoine, I.; Moulin, C.; Brevet, P.-F.; Bonačić-Koutecký, V.; Antoine, R., Rationale Strategy to Tune the Optical Properties of Gold Catenane Nanoclusters by Doping with Silver Atoms. *J. Phys. Chem. C* **2020**, *124*, 19368-19374.
11. Xie, X.-Y.; Xiao, P.; Cao, X.; Fang, W.-H.; Cui, G.; Dolg, M., The Origin of the Photoluminescence Enhancement of Gold-Doped Silver Nanoclusters: The Importance of Relativistic Effects and Heteronuclear Gold–Silver Bonds. *Angew. Chem. Int. Ed.* **2018**, *57*, 9965-9969.
12. Li, Q.; Wang, S. X.; Kirschbaum, K.; Lambright, K. J.; Das, A.; Jin, R. C., Heavily Doped Au₂₅-Xagx(Sc₆h₁₁)(18)(-) Nanoclusters: Silver Goes from the Core to the Surface. *Chem. Commun.* **2016**, *52*, 5194-5197.
13. Li, Y. W.; Biswas, S.; Luo, T. Y.; Juarez-Mosqueda, R.; Taylor, M. G.; Mpourmpakis, G.; Rosi, N. L.; Hendrich, M. P.; Jin, R. C., Doping Effect on the Magnetism of Thiolate-Capped 25-Atom Alloy Nanoclusters. *Chem. Mater.* **2020**, *32*, 9238-9244.
14. Liao, L. W.; Zhou, S. M.; Dai, Y. F.; Liu, L. R.; Yao, C. H.; Fu, C. F.; Yang, J. L.; Wu, Z. K., Mono-Mercury Doping of Au-25 and the Homo/Lumo Energies Evaluation Employing Differential Pulse Voltammetry. *J. Am. Chem. Soc.* **2015**, *137*, 9511-9514.
15. Pandeya, P.; Senanayake, R. D.; Aikens, C. M., Nonradiative Relaxation Dynamics in the Au₂₅-nAg_n(SH)(18) (-) (n=1, 12, 25) Thiolate-Protected Nanoclusters. *J. Chem. Phys.* **2021**, *154*, 184303.
16. Weng, S. Y.; Lv, Y.; Yu, H. Z.; Zhu, M. Z., The Ligand-Exchange Reactions of Rod-Like Au₂₅-Nmn (M=Au, Ag, Cu, Pd, Pt) Nanoclusters with Cysteine - a Density Functional Theory Study. *Chemphyschem* **2019**, *20*, 1822-1829.

17. Xie, S. H.; Tsunoyama, H.; Kurashige, W.; Negishi, Y.; Tsukuda, T., Enhancement in Aerobic Alcohol Oxidation Catalysis of Au-25 Clusters by Single Pd Atom Doping. *ACS Cat.* **2012**, *2*, 1519-1523.
18. Yamazoe, S.; Kurashige, W.; Nobusada, K.; Negishi, Y.; Tsukuda, T., Preferential Location of Coinage Metal Dopants (M = Ag or Cu) in Au₂₅-X_m(Sc₂H₄Ph)(18) (-) (X Similar to 1) as Determined by Extended X-Ray Absorption Fine Structure and Density Functional Theory Calculations. *J. Phys. Chem. C* **2014**, *118*, 25284-25290.
19. Bootharaju, M. S.; Sinatra, L.; Bakr, O. M., Distinct Metal-Exchange Pathways of Doped Ag₂₅ Nanoclusters. *Nanoscale* **2016**, *8*, 17333-17339.
20. Pniakowska, A.; Kumaranchira Ramankutty, K.; Obstarczyk, P.; Perić Bakulić, M.; Sanader Maršić, Ž.; Bonačić-Koutecký, V.; Bürgi, T.; Olesiak-Bañska, J., Gold-Doping Effect on Two-Photon Absorption and Luminescence of Atomically Precise Silver Ligated Nanoclusters. *Angew. Chem. Int. Ed.* **2022**, *61*, e202209645.
21. Baksi, A.; Schneider, E. K.; Weis, P.; Chakraborty, I.; Fuhr, O.; Lebedkin, S.; Parak, W. J.; Kappes, M. M., Linear Size Contraction of Ligand Protected Ag-29 Clusters by Substituting Ag with Cu. *ACS Nano* **2020**, *14*, 15064-15070.
22. Juarez-Mosqueda, R.; Malola, S.; Hakkinen, H., Stability, Electronic Structure, and Optical Properties of Protected Gold-Doped Silver Ag₂₉-X_{aux} (X=0-5) Nanoclusters. *Phys. Chem. Chem. Phys.* **2017**, *19*, 13868-13874.
23. Russier-Antoine, I.; Bertorelle, F.; Hamouda, R.; Rayane, D.; Dugourd, P.; Sanader, Z.; Bonacic-Koutecky, V.; Brevet, P. F.; Antoine, R., Tuning Ag-29 Nanocluster Light Emission from Red to Blue with One and Two-Photon Excitation. *Nanoscale* **2016**, *8*, 2892-2898.
24. Soldan, G.; Aljuhani, M. A.; Bootharaju, M. S.; AbdulHalim, L. G.; Parida, M. R.; Emwas, A. H.; Mohammed, O. F.; Bakr, O. M., Gold Doping of Silver Nanoclusters: A 26-Fold Enhancement in the Luminescence Quantum Yield. *Angew. Chem. Int. Ed.* **2016**, *55*, 5749-5753.
25. Zeng, Y., et al., Impact of Ligands on Structural and Optical Properties of Ag-29 Nanoclusters. *J. Am. Chem. Soc.* **2021**, *143*, 9405-9414.
26. van der Linden, M.; Barendregt, A.; van Bunningen, A. J.; Chin, P. T. K.; Thies-Weesie, D.; de Groot, F. M. F.; Meijerink, A., Characterisation, Degradation and Regeneration of Luminescent Ag-29 Clusters in Solution. *Nanoscale* **2016**, *8*, 19901-19909.
27. Yang, J.; Pang, R.; Song, D.; Li, M.-B., Tailoring Silver Nanoclusters Via Doping: Advances and Opportunities. *Nanoscale Adv.* **2021**, *3*, 2411-2422.
28. van der Linden, M.; van Bunningen, A. J.; Amidani, L.; Bransen, M.; Elnaggar, H.; Glatzel, P.; Meijerink, A.; de Groot, F. M. F., Single Au Atom Doping of Silver Nanoclusters. *ACS Nano* **2018**, *12*, 12751-12760.
29. Bootharaju, M. S.; Kozlov, S. M.; Cao, Z.; Harb, M.; Parida, M. R.; Hedhili, M. N.; Mohammed, O. F.; Bakr, O. M.; Cavallo, L.; Basset, J.-M., Direct Versus Ligand-Exchange Synthesis of [Ptag₂₈(Bdt)₁₂(Tpp)₄]⁻ Nanoclusters: Effect of a Single-Atom Dopant on the Optoelectronic and Chemical Properties. *Nanoscale* **2017**, *9*, 9529-9536.
30. Fakhouri, H.; Perić, M.; Bertorelle, F.; Dugourd, P.; Dagany, X.; Russier-Antoine, I.; Brevet, P.-F.; Bonačić-Koutecký, V.; Antoine, R., Sub-100 Nanometer Silver Doped Gold-Cysteine Supramolecular Assemblies with Enhanced Nonlinear Optical Properties. *Phys. Chem.. Chem. Phys.* **2019**, *21*, 12091-12099.
31. Brach, K.; Olesiak-Banska, J.; Waszkielewicz, M.; Samoc, M.; Matczyszyn, K., DNA Liquid Crystals Doped with AuAg Nanoclusters: One-Photon and Two-Photon Imaging. *J. Mol. Liq.* **2018**, *259*, 82-87.

32. Van Steerteghem, N.; Van Cleuvenbergen, S.; Deckers, S.; Kumara, C.; Dass, A.; Häkkinen, H.; Clays, K.; Verbiest, T.; Knoppe, S., Symmetry Breaking in Ligand-Protected Gold Clusters Probed by Nonlinear Optics. *Nanoscale* **2016**, *8*, 12123-12127.
33. Hirai, H.; Takano, S.; Nakashima, T.; Iwasa, T.; Taketsugu, T.; Tsukuda, T., Doping-Mediated Energy-Level Engineering of M@Au₁₂ Superatoms (M=Pd, Pt, Rh, Ir) for Efficient Photoluminescence and Photocatalysis. *Angew. Chem. Int. Ed.* **2022**, *61*, e202207290.
34. Niihori, Y.; Wada, Y.; Mitsui, M., Single Platinum Atom Doping to Silver Clusters Enables near-Infrared-to-Blue Photon Upconversion. *Angew. Chem. Int. Ed.* **2021**, *60*, 2822-2827.
35. AbdulHalim, L. G.; Bootharaju, M. S.; Tang, Q.; Del Gobbo, S.; AbdulHalim, R. G.; Eddaoudi, M.; Jiang, D.-e.; Bakr, O. M., Ag₂₉(Bdt)₁₂(Tpp)₄: A Tetravalent Nanocluster. *J. Am. Chem. Soc.* **2015**, *137*, 11970-11975.
36. Bootharaju, M. S.; Kozlov, S. M.; Cao, Z.; Shkurenko, A.; El-Zohry, A. M.; Mohammed, O. F.; Eddaoudi, M.; Bakr, O. M.; Cavallo, L.; Basset, J.-M., Tailoring the Crystal Structure of Nanoclusters Unveiled High Photoluminescence Via Ion Pairing. *Chem. Mater.* **2018**, *30*, 2719-2725.
37. Albota, M. A.; Xu, C.; Webb, W. W., Two-Photon Fluorescence Excitation Cross Sections of Biomolecular Probes from 690 to 960 Nm. *Appl. Opt.* **1998**, *37*, 7352-7356.
38. Duboisset, J.; Matar, G.; Russier-Antoine, I.; Benichou, E.; Bachelier, G.; Jonin, C.; Ficheux, D.; Besson, F.; Brevet, P. F., First Hyperpolarizability of the Natural Aromatic Amino Acids Tryptophan, Tyrosine, and Phenylalanine and the Tripeptide Lysine–Tryptophan–Lysine Determined by Hyper-Rayleigh Scattering. *J. Phys. Chem. B* **2010**, *114*, 13861-13865.
39. Bonačić-Koutecký, V.; Antoine, R., Enhanced Two-Photon Absorption of Ligated Silver and Gold Nanoclusters: Theoretical and Experimental Assessments. *Nanoscale* **2019**, *11*, 12436-12448.
40. Oh, E., et al., Pegylated Luminescent Gold Nanoclusters: Synthesis, Characterization, Bioconjugation, and Application to One- and Two-Photon Cellular Imaging. *Part. Part. Syst. Charact.* **2013**, *30*, 453-466.
41. Oh, E.; Delehanty, J. B.; Field, L. D.; Mäkinen, A. J.; Goswami, R.; Huston, A. L.; Medintz, I. L., Synthesis and Characterization of Pegylated Luminescent Gold Nanoclusters Doped with Silver and Other Metals. *Chem. Mater.* **2016**, *28*, 8676-8688.

TOC Graphic

