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# Effects of Single Platinum Atom Doping on Stability and Nonlinear Optical Properties of Ag<sub>29</sub> Nanoclusters

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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 Ag<sub>29</sub> 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.<sup>1-2</sup> 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.<sup>3-4</sup> 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.<sup>5-7</sup> 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 Au<sub>25</sub> nanoclusters, highlighting different absorption features upon doping with Ag, Cu, Pd, or Pt.<sup>8</sup> The nature and position of lowest excited electronic states are also sensitive to silver doping.<sup>9</sup> Other factors like relativistic effects (mainly due to the Au atoms), the exact position of metal dopants and heteronuclear Au–Ag bonds<sup>10</sup> can affect the fluorescence intensity of gold-doped nanoclusters.<sup>11</sup>

While most of doping of nanoclusters with heteroatoms was done with the highly stable single thiolated (SR) Au<sub>25</sub>SR<sub>18</sub>,<sup>12-18</sup> and Ag<sub>25</sub>SR<sub>18</sub>,<sup>19-20</sup> dithiolated (SSR) Ag<sub>29</sub>SSR<sub>12</sub> nanocluster<sup>21-26</sup> is another interesting candidate for doping strategies.<sup>11</sup> 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.<sup>27</sup> Van der Linden et al. demonstrated such enhanced PL and stability, by doping Ag<sub>29</sub> nanoclusters capped with lipoic acid with Au.<sup>28</sup> On the other hand, Bootharaju et al. were able to do doping of Ag<sub>29</sub> cluster with a single Pt atom, i.e. leading to enhanced excited-state lifetime and PL intensity.<sup>29</sup>

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.<sup>10-11</sup> 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,<sup>30</sup> as well as silver-doped gold nanoclusters display efficient nonlinear optical signals (both two-photon excited fluorescence and second harmonic response).<sup>31-32</sup> Recently, a series of Ag<sub>25-x</sub>Au<sub>x</sub>DMBT<sub>18</sub> nanoclusters where x=0, 1, and 5-10 were synthesized. For Ag<sub>24</sub>Au<sub>1</sub>DMBT<sub>18</sub>, 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.<sup>20</sup> 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 Ag<sub>24</sub>Au<sub>1</sub>.

Single platinum atom doping to gold or silver clusters was found also to strongly affect optical properties in particular for efficient photoluminescence and photocatalysis<sup>33</sup> or for enabling near-infrared-to-blue photon upconversion with PtAg<sub>24</sub>SR<sub>18</sub> nanoclusters.<sup>34</sup> In this work, we aim at exploring the effect of a single Pt doping of Ag<sub>29</sub> nanoclusters on their photoluminescence (both upon one- and two-photon excitation), second harmonic generation and their stability. Single Pt

doping of Ag<sub>29</sub> nanoclusters was done using both hydrophilic lipoic acid (DHLA) ligands (Ag<sub>29</sub>DHLA<sub>12</sub>) and hydrophobic 1,3-benzenedithiol (BDT) ligands (Ag<sub>29</sub>BDT<sub>12</sub>). In particular, we show that single Pt doping of Ag<sub>29</sub>DHLA<sub>12</sub> 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 Ag<sub>29</sub>DHLA<sub>12</sub>**

100 mg of (±)- $\alpha$ -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 (CH<sub>3</sub>)<sub>4</sub>N(BH<sub>4</sub>) 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 NH<sub>4</sub>OH (10%) is added to the solution, followed by 85 mg of (CH<sub>3</sub>)<sub>4</sub>N(BH<sub>4</sub>) and stirred at 50°C for 1 hour. Then, 1 equivalent of (CH<sub>3</sub>)<sub>4</sub>N(BH<sub>4</sub>) (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 Et<sub>2</sub>O was added followed by 20  $\mu$ l of glacial acetic acid and centrifuged at 5000 rpm for 5 min. The precipitant was then dissolved in a minimum of water/NH<sub>4</sub>OH (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 Pt<sub>1</sub>Ag<sub>28</sub>DHLA<sub>12</sub>**

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.<sup>35</sup>

#### **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.<sup>36</sup>

#### **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.<sup>24</sup>

### **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  $\mu\text{M}$ . 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  $\text{CH}_2\text{Cl}_2$  or DMF (1 mg/mL) and diluted (v/v = 1:1) by  $\text{CH}_3\text{OH}$ . 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.<sup>35</sup> The mass signal of  $[\text{Pt}_1\text{Ag}_{28}\text{BDT}_{12}(\text{PPh}_3)_4]^{4-}$  locate around 1487 Da.<sup>36</sup>

**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 ( $\phi_F$ ) 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.<sup>10</sup>



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  $\sigma_2$  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,  $\sigma_2$  of the fluorescein is 33.3 GM.<sup>37</sup>

TPA cross sections could be calculated using QYs ( $\Phi$ ), 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  $0.087 \times 10^{-30}$  esu.<sup>38</sup>

## RESULTS AND DISCUSSION

In the work, Pt doping at the single atom level of the as synthesized Ag<sub>29</sub> nanoclusters was performed. Details of the doping process are given in the Supporting Information. Evidence of doping of Pt atoms into the system of Ag<sub>29</sub> clusters (with the appearance of PtAg<sub>28</sub>SSR<sub>12</sub> nanoclusters, with SSR = DHLA or BDT) was obtained from ESI-MS analysis as shown in Figure S1 for Ag<sub>29</sub>DHLA<sub>12</sub> nanoclusters.

Ag clusters prepared with lipoic acid (DHLA) as the ligand are generally observed with atomic precision (and assigned as Ag<sub>29</sub>DHLA<sub>12</sub>).<sup>23, 26</sup> Although quite appealing since highly luminescent, degradation over time of as-synthesised clusters was a general trend and results in aggregation and possibly oxidation.<sup>26</sup> 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 Ag<sub>29</sub> 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.<sup>26</sup> Single platinum doping on Ag<sub>29</sub> 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 Ag<sub>29</sub> metal core, as evidenced by X-ray spectroscopies.<sup>28</sup> In addition, Basset et al. synthesized [PtAg<sub>28</sub>BDT<sub>12</sub>TPP<sub>4</sub>]<sup>4-</sup>.<sup>29</sup> The Pt dopant in PtAg<sub>28</sub> was found to occupy the center position of the icosahedron core. PtAg<sub>28</sub> possesses a closed-shell electronic configuration, showing enhanced stability,

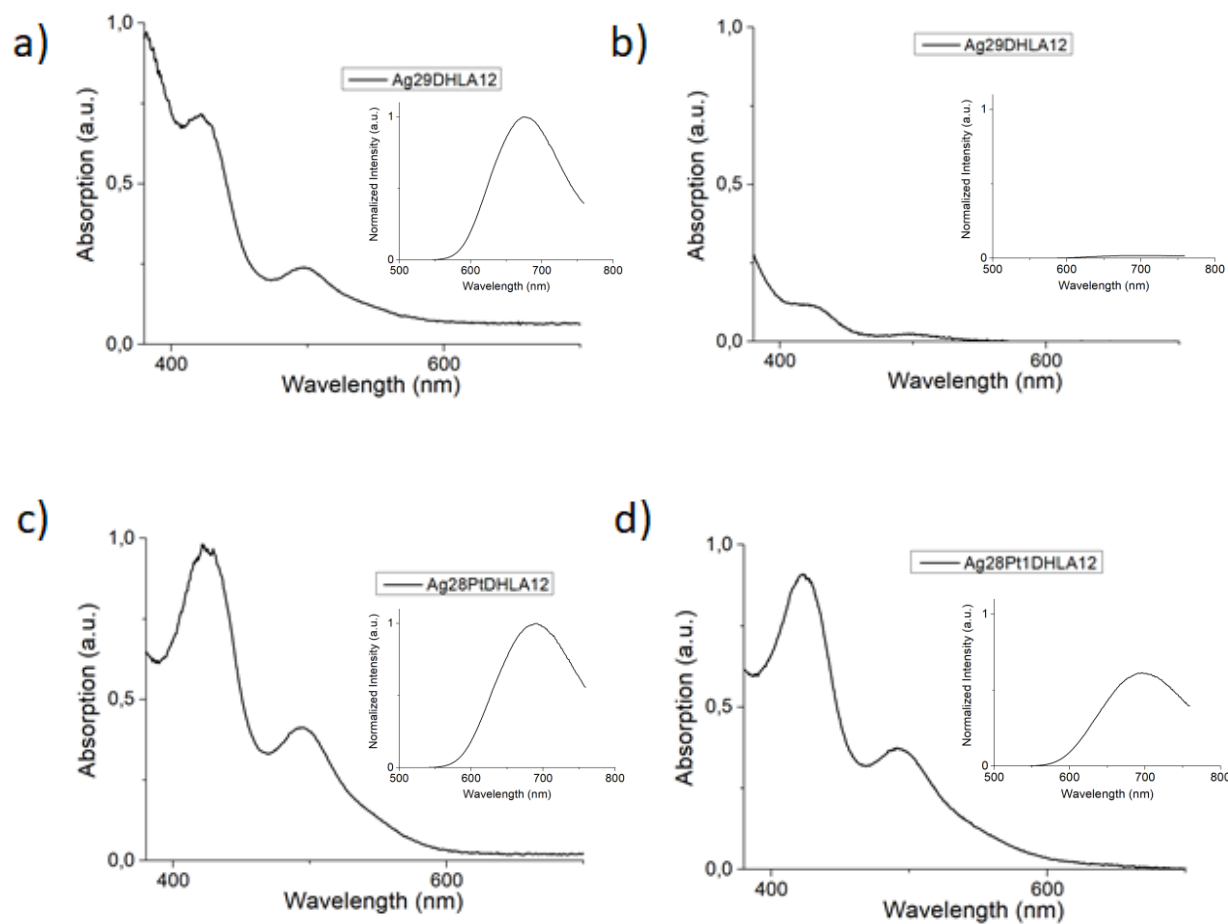
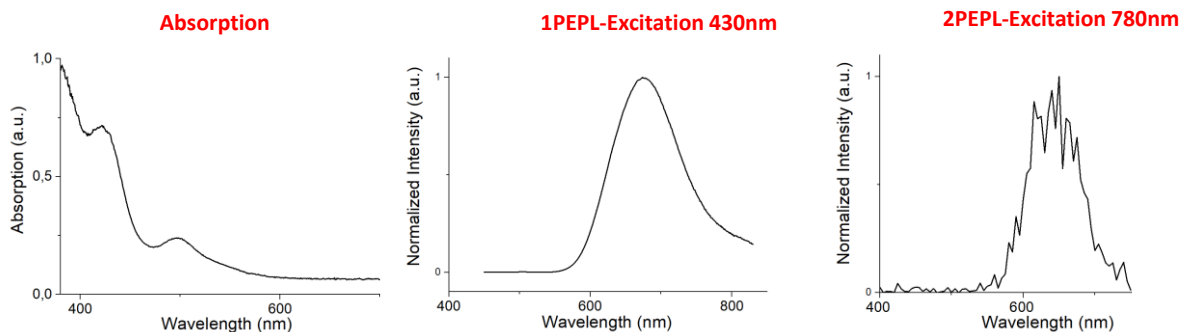


Figure 1 : UV-Vis absorption spectra (and the corresponding PL spectra in insets) of fresh solutions of nanoclusters (a and c), and aged solutions of nanoclusters (b and d). Aged solutions are solution after 2 weeks. All samples were purified and we collect the powder and stored in the freezer in the same conditions. Water was used as solvent for Ag<sub>29</sub>DHLA<sub>12</sub>. Concentration of nanoclusters is 100 $\mu$ M.

## Ag<sub>29</sub>DHLA<sub>12</sub>



## PtAg<sub>28</sub>DHLA<sub>12</sub>

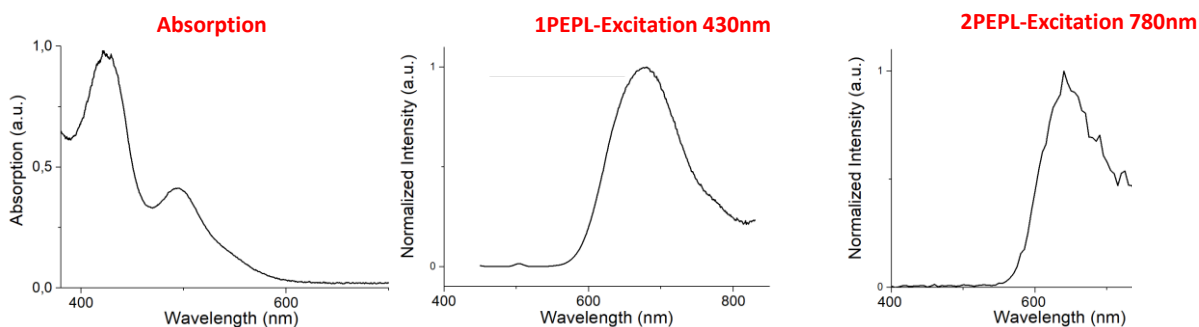


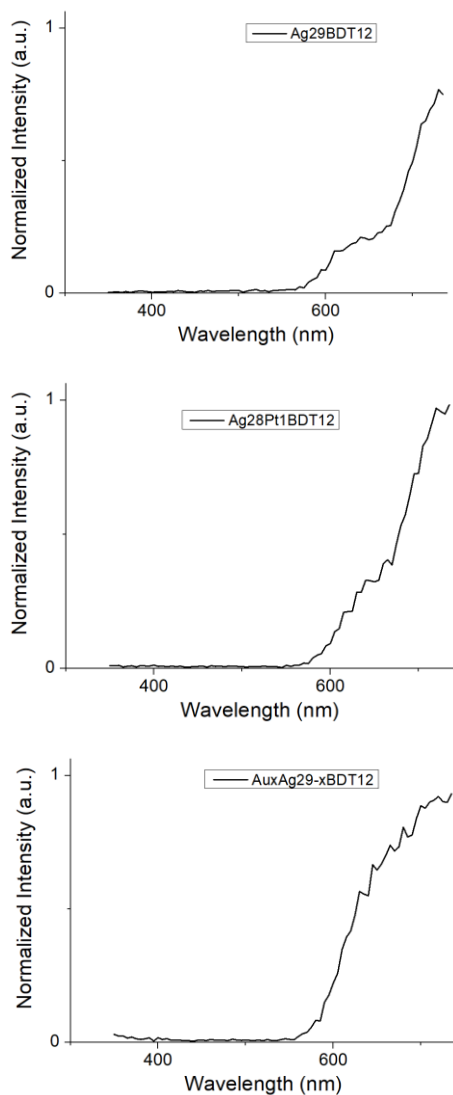
Figure 2: Spectroscopic characterization of the synthesized Ag<sub>29</sub> and PtAg<sub>28</sub> clusters protected by DHLA dispersed in water. Absorption spectrum (left panel) concentration is 100  $\mu$ M, one-photon excited photoluminescence (1PEPL) spectrum (middle panel) with excitation at 430 nm. Concentration is 10  $\mu$ M and two-photon excited photoluminescence (2PEPL) spectrum (right panel) with excitation at 780 nm concentration is 970  $\mu$ 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 Ag<sub>29</sub>DHLA<sub>12</sub>.

Under near-UV/visible light, solution of Ag<sub>29</sub> and platinum-doped Ag<sub>29</sub> 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 Ag<sub>29</sub> nanoclusters. In the current study, we also investigated the two-photon excited photoluminescence (2PEPL) spectra of Pt-doped Ag<sub>29</sub> nanoclusters and compared with that of undoped Ag<sub>29</sub> nanoclusters (see Figures 2 and 3). Both Ag<sub>29</sub> and platinum-doped Ag<sub>29</sub> nanoclusters showed strong 2PEPL spectra in the red. 2PEPL cross-section can be as high as  $0.13 \pm 0.05$  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 Ag<sub>29</sub> nanoclusters. The same trend is observed when gold is used as dopant (instead of Pt) for Ag<sub>29</sub> nanoclusters (see Table 1, Au<sub>x</sub>Ag<sub>29-x</sub>BDT<sub>12</sub>). 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.<sup>39</sup> On the other hand, Oh et al.<sup>40</sup> 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.<sup>41</sup>

Interestingly a solvent effect has been observed in the 2PEPL spectra of platinum doped Ag<sub>29</sub> 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

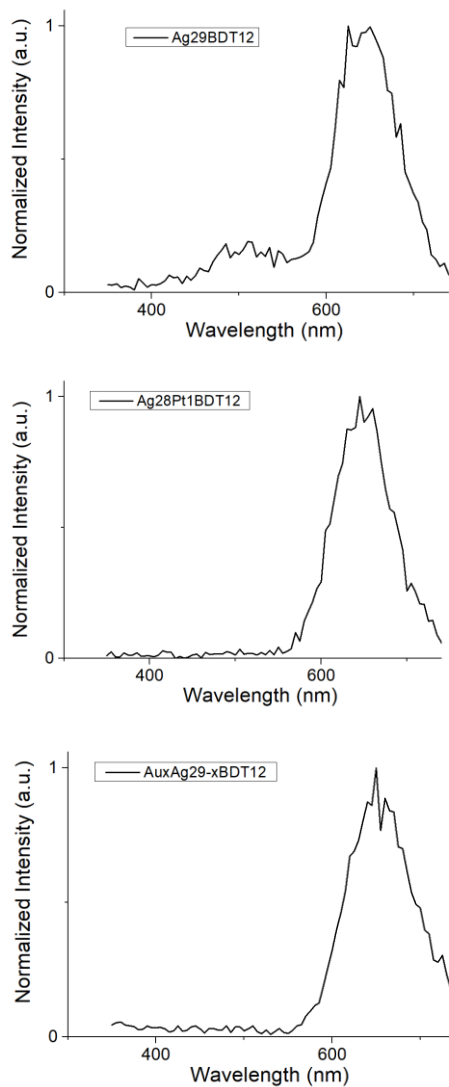


Figure 3 : 2PEPL spectra with excitation at 780 nm of the synthesized Ag<sub>29</sub>, PtAg<sub>28</sub> and Au<sub>x</sub>Ag<sub>29-x</sub> clusters protected by BDT dispersed in a) THF and b) DMF. The sharp decrease of 2PEPL signal of nanoclusters in THF is due to filter effect that cuts the excitation 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 <sub>29</sub> BDT <sub>12</sub>	0,13	1.51	8.6
Ag <sub>28</sub> Pt <sub>1</sub> BDT <sub>12</sub>	0,08	1.5	5.3
Au <sub>x</sub> Ag <sub>29-x</sub> BDT <sub>12</sub>	0,14	18.1	0.8
Ag <sub>29</sub> DHLA <sub>12</sub>	0,06	0.5	12
Ag <sub>28</sub> Pt <sub>1</sub> DHLA <sub>12</sub>	0,06	0.15	40

Also, the effect of chemical substitution based platinum doping on the hyperpolarizability ( $\beta$ ) value of Ag<sub>29</sub> nanoclusters was evaluated (see Figs. S3 and S4). Intriguingly, similar  $\beta$  values of  $\sim 58 \pm 12 \times 10^{-30}$  esu for Ag<sub>29</sub> and PtAg<sub>28</sub> nanoclusters protected by DHLA were found. In contrast we observed a reduced hyperpolarizability value of  $82 \pm 30 \times 10^{-30}$  esu for PtAg<sub>28</sub> nanoclusters protected by BDT as compared to  $162 \pm 60 \times 10^{-30}$  esu for pure Ag<sub>29</sub> nanoclusters protected by BDT (see Supporting information for raw data and details on the methods used to extract hyperpolarizability ( $\beta$ ) values). We would like to point out that measurements were done in water for Ag<sub>29</sub> and PtAg<sub>28</sub> nanoclusters protected by DHLA and in DMF for Ag<sub>29</sub> and PtAg<sub>28</sub> 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 Ag<sub>29</sub> nanoclusters. Since hyperpolarizability ( $\beta$ ) is sensitive to symmetry-breaking in nanosystems, we can speculate that since  $\beta$  values for Ag<sub>29</sub> and PtAg<sub>28</sub> nanoclusters protected by DHLA are similar, then Pt atom is certainly located in the center of the Ag<sub>29</sub> 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.<sup>32</sup> Since PtAg<sub>28</sub>DHLA<sub>12</sub> 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 PtAg<sub>28</sub>DHLA<sub>12</sub> nanoclusters under excitation of femtosecond laser pulses at 780 nm with concentrations ranging from 30 to 900  $\mu$ M. 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 PtAg<sub>28</sub>DHLA<sub>12</sub> silver NCs with different concentration is displayed in Fig. S6. LD50 is reached for NCs concentrations higher than 900 $\mu$ M.

## CONCLUSION

In summary, the effects of single-platinum doping of a class of Ag<sub>29</sub> 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 Ag<sub>29</sub>DHLA<sub>12</sub> 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.

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**NOTES**

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# TOC Graphic

