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Rational synthesis, structural characterization and theoretical exploration on third-order nonlinear optical properties of isolated $\mathbf{Ag}_n$ ($n = 5, 8, 12$) alkynyl clusters

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ABSTRACT

Three silver(I) alkynyl compounds, $[Ag_5(C{\equiv}C^tBu)(CF_3COO)_7(nBu_4N)_3{\cdot}H_2O]$ (**1**), $[Ag_8(C{\equiv}C^tBu)_2(CF_3COO)_{10}(Et_3N)_4]$ (**2**), and $[Ag_{12}(C{\equiv}C^tBu)_6(CF_3COO)_8(nBu_4N)_2(Et_3N)_2(CF_3COO)_2]$ (**3**), have been obtained. Concomitantly, isolated $[Ag_5(C{\equiv}C^tBu)(CF_3COO)_7]^{3-}$, $[Ag_8(C{\equiv}C^tBu)_2(CF_3COO)_{10}]^{4-}$ and $[Ag_{12}(C{\equiv}C^tBu)_6(CF_3COO)_8]^{2-}$ clusters (**Ag_5**, **Ag_8** and **Ag_{12}** for short) appear in **1**–**3**, respectively. The synthesis of **1**–**3** demonstrates silver(I) alkynyls are better systems for the study of the template effect. ESI-MS analysis indicates compounds **1**–**3** can stably exist in methanol, and they have been proved to be potential wide gap semiconductor materials by the reflectance spectra. Notably, the second hyperpolarizabilities (γ values) of **Ag_5**, **Ag_8** and **Ag_{12}** have been studied by using time-dependent density functional theory (TDDFT) calculations and the finite filed (FF) approach combining CAM-B3LYP. The calculated results show that they can be applied as potential third-order nonlinear optical (NLO) materials owing to their second hyperpolarizabilities rising from 39.1×10^{-36}, 60.3×10^{-36} to 97.7×10^{-36} esu with the growth of the number of Ag atoms and C≡C groups.

1. Introduction

The keen interest has been taken in design and development of multinuclear transitionmetal (TM) clusters, which not only stems from their fascinating structures, but also originates from their anticipatory technological applications [1,2]. It is worth mentioning that the simple coinage-metal (Cu, Ag, and Au) alkynly compounds are a kind of typical multinuclear TM clusters [3]. They were originally studied by Nast and Schindel et al. half a century ago, and then have been widely discussed up to now [4]. In comparison with other coinage-metal alkynyl compounds, silver(I) alkynyl compounds have been actively researched. Because metal silver demands an acceptable price and shows versatile coordination modes as well as high binding ability to donor ligands [5]. In addition, alkynyl ligands can be identified as derivating from the prototypical $HC{\equiv}C^-$ ligand, which can serve as a good σ donor and modest π acceptor and displays a flexible coordination environment [6]. Therefore, metal-alkynyl σ, π and mixed (σ, π) bonds will be formed between metal silver centers and alkynyl ligands [7]. Furthermore, argentophilic Ag···Ag interactions can facilitate the aggregation of Ag centers during the formation of multinuclear silver(I) alkynyl compounds [8]. Although a series of silver(I) alkynyl compounds constructed from ^{t}BuC≡C$^-$ ligand with a great diversity of configurations ranging from 0D clusters, 1D chains to 2D networks have been documented [9–11]. While we have paid more attention to the 0D silver-rich alkynyl clusters induced by anions/cations templates which can exhibit more intriguing structures and characters [10,11b].

On the other hand, the design and synthesis of new materials with large NLO capability is an active field in modern chemistry, physics, and materials science [12], because these materials possess many potential applications in the area of opto-electronic technology [13]. Metal clusters can serve as excellent NLO materials, since they involve dπ–pπ delocalized systems and dπ–dπ conjugated systems [14]. Hou et al. have demonstrated that the NLO properties of metal clusters are affected by both of metal ions

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and organic ligands [15]. While heavy-metal ions play very important roles on the third-order NLO properties of metal clusters, and a larger NLO response can be produced because their incorporation introduces more sublevels into the energy hierarchy in order to permit more allowed electronic transitions to take place [16]. In addition, Humphrey et al. have reported the switchable third-order NLO properties induced by electron-rich iron/ruthenium arylalkynyl complexes [17], and they also have reported that different metals and conjugate degrees of alkynyl ligands have a great influence on the third-order NLO response [18]. Inspired by Hou and Humphrey's reports and in view of none of the third-order NLO research on the cage-like multinuclear metal clusters protected by shorter alkynyl ligands, our interest appeals to preparing the silver(I) alkynyl clusters containing heavy-metal silver(I) ion and $^{t}BuC{\equiv}C^{-}$ ligand and investigating their third-order NLO properties.

In this paper, three 0D multinuclear silver(I) alkynyl compounds, namely, $[Ag_5(C{\equiv}C^{t}Bu)(CF_3COO)_7(nBu_4N)_3{\cdot}H_2O]$ (**1**) [11a], $[Ag_8(C{\equiv}C^{t}Bu)_2(CF_3COO)_{10}(Et_3N)_4]$ (**2**), and $[Ag_{12}(C{\equiv}C^{t}Bu)_6(CF_3COO)_8(nBu_4N)_2(Et_3N)_2(CF_3COO)_2]$ (**3**), have been obtained by changing reaction conditions. It provides a possibility to analyze the influencing factor on the third-order NLO response from **Ag_5**, **Ag_8** to **Ag_{12}**, due to their structural similarity. Herein, the second hyperpolarizabilities γ values of the **Ag_5**, **Ag_8** and **Ag_{12}** have been studied by using time-dependent density functional theory (TDDFT) calculations [19,20] and the finite filed (FF) approach [21] combining CAM-B3LYP method. It is well known that the size of the metal clusters and the chain length of polyyne ligands can influence the NLO response [22]. In detail, Thomas's study reveals the distinct evolution of the third-order NLO properties as the cluster progress in size from Au_{25}, Au_{38} to Au_{144} nanocluster. Xu's investigation indicates that increasing the length of $Au_{n-m}M_m$ (M = Ag, Cu; m = 1, 2) clusters can augment the first hyperpolarizabilities (β values). The phenomenon that the β value is enhanced as the chain length of polyyne increases has been documented by Champagne. Given, the third-order NLO response enhanced from **Ag_5** (39.1×10^{-36} esu), **Ag_8** (60.3×10^{-36} esu) to **Ag_{12}** (97.7×10^{-36} esu) in our investigation can be tentatively attributed to the increase of the number of Ag atoms and C≡C groups.

2. Experimental section

2.1. Materials and measurements

In this paper, all reagents and solvents for synthesis were obtained from commercial sources and used without further purification, such as 3, 3-Dimethyl-1-butyne (Aladdin, >95%). All other reagents were of analytical grade and used as received. $[AgC{\equiv}C^{t}Bu]_n$ [11], $(nBu_4N)_4[Mo_8O_{26}]$, and $(nBu_4N)_2[W_6O_{19}]$, were synthesized according to the literatures [23]. Single-crystal X-ray diffraction data for **1**–**3** were recorded on a Bruker Apex CCD II area-detector diffractometer with graphite-monochromated Mo-Ka radiation (λ = 0.71073 Å) at room temperature. Absorption corrections were applied using multi-scan technique and performed by using the SADABS program. Their structures were solved by Direct Method of SHELXS-97 and refined by full-matrix least-square techniques using the SHELXL-97 program within WINGX [24]. Elemental analyses (C, H, and N) were performed on a Perkin–Elmer 2400 CHN elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range of 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Mass spectra were carried out on a Bruker Daltonics flex Analysis instrument. Diffuse reflectivity was measured from 200 to 800 nm using barium sulfate ($BaSO_4$) as a standard with 100% reflectance on a Varian Cary 500 UV–Vis spectrophotometer.

Caution! *Owing to silver(I) alkynyls have the potential explosive nature, great care should be taken, handled with care and only small amounts should be used.*

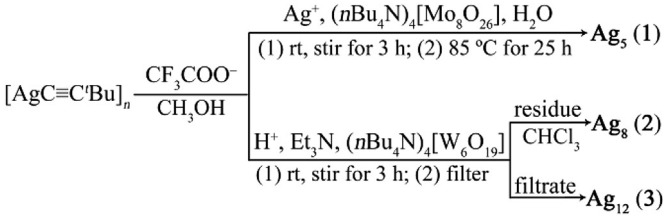
2.2. Synthesis

2.2.1. Synthesis of compounds **1**–**3**

*2.2.1.1. Synthesis of compound $[Ag_5(C{\equiv}C^{t}Bu)(CF_3COO)_7(nBu_4N)_3{\cdot}H_2O]$ (**1**).* $[AgC{\equiv}C^{t}Bu]_n$ (0.0391 g, 0.2069 mmol) was dissolved in a solution of $AgCF_3COO$ (0.0531 g, 0.2404 mmol) in methanol (8 mL) under ultrasonication. Then $(nBu_4N)_4[Mo_8O_{26}]$ (0.0400 g, 0.0186 mmol) and H_2O (0.3 mL) were added to the above resulting solution. The mixture was stirred for 3 h to give a white suspension (pH ≈ 2.3). The reaction mixture was transferred to a Teflon-lined stainless autoclave (25 mL) and kept at 85 °C for 25 h. After cooling to room temperature, the solution was filtered and the filtrate evaporated slowly at room temperature in an Erlenmeyer flask. A few days later, we have successfully achieved compound **1**. compound **1** was deposited as colorless schistose crystals. Yield: ca. 16% (based on Ag). Elemental analysis calcd (%) for $C_{68}H_{119}F_{21}O_{15}N_3Ag_5$: C, 37.86; H, 5.56; N, 1.95; found: C, 37.91; H, 5.43; N, 1.98. IR (KBr): ν = 2010 cm^{-1} (vs, C≡C); 1686 cm^{-1} (w, C=O) (Scheme 1).

*2.2.1.2. Synthesis of $[Ag_8(C{\equiv}C^{t}Bu)_2(CF_3COO)_{10}(Et_3N)_4]$ (**2**).* $[AgC{\equiv}C^{t}Bu]_n$ (0.0730 g, 0.3862 mmol) was dissolved in methanol (10 mL) under stir. Then CF_3COOH (0.2 mL, 0.0027 mmol), several drops Et_3N and $(nBu_4N)_2[W_6O_{19}]$ (0,0231 g, 0.0122 mmol) were in turn added under stir to form a white suspension. After stir for 3 h, the solution (pH ≈ 1.4) was filtered. And the filter residue was dissolved by chloroform (15 mL) to form the second resulting solution (pH ≈ 0.4). And then the second resulting solution was filtered again. We stored the second filtrate. And then the second filtrate evaporated slowly at room temperature in an Erlenmeyer flask. Two days later, we have unexpectedly achieved compound **2**. they were deposited as colorless rod-like crystals. Yield: ca. 19% (based on Ag). Elemental analysis (%) calcd for $C_{56}H_{82}F_{30}O_{20}N_4Ag_8$: C, 26.23; H, 3.22; N, 2.19; found: C, 26.31; H, 3.10; N, 2.22. IR (KBr): ν = 2026 cm^{-1} (vs, C≡C); 1682 cm^{-1} (*w*, C=O).

*2.2.1.3. Synthesis of $[Ag_{12}(C{\equiv}C^{t}Bu)_6(CF_3COO)_8(nBu_4N)_2(Et_3N)_2(CF_3COO)_2]$ (**3**).* The same procedure for synthesis of **3** was used as preparation for **2**. ($[AgC{\equiv}C^{t}Bu]_n$ (0.0730 g, 0.3862 mmol) was dissolved in methanol (10 mL) under stir. Then CF_3COOH (0.2 mL, 0.0027 mmol), several drops Et_3N and $(nBu_4N)_2[W_6O_{19}]$ (0.0231 g, 0.0122 mmol) were in turn added under stir to form a white suspension. After stir for 3 h, the solution (pH ≈ 1.4) was filtered.) A few weeks later, compound **3** crystallized in the filtrate after slow evaporation at room temperature in an Erlenmeyer flask. They were deposited as colorless bulk crystals. Yield: ca. 21% (based on Ag). Elemental analysis (%) calcd for $C_{100}H_{160}F_{30}O_{20}N_4Ag_{12}$: C, 33.34; H, 4.48; N, 1.56; found: C, 33.41; H, 4.37; N, 1.59. IR (KBr): ν = 2031 cm^{-1} (vs, C≡C); 1680 cm^{-1} (*m*, C=O).



Scheme 1. Synthetic procedures for compounds **1**–**3**.