

Full Length Article

Self-assembly and photopolymerization of a novel quaternary-ammonium functionalized diacetylene on noble metal nanoparticles: A comparative study



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ABSTRACT

Stable hydrosols of gold and silver nanoparticles coated with the quaternary-ammonium group endowed diacetylene DAAMM (*N,N,N*-trimethyl-3-(pentacosa-10,12-diynamido)propan-1-ammonium) were obtained through a ligand-exchange reaction leaving the morphology of the pristine cores unmodified. Photopolymerization of the chemisorbed diacetylene shell occurred in both red and blue phases thanks to the presence of internal, H-bondable amide functions in the monomer chain, which are supposed to help the formation of a packed bilayer on the metal surfaces. Multidisciplinary characterization of the polymerized samples, including spectroscopic, morphological and thermal techniques, highlighted that differences occur in the polymerization process on gold and silver nanoparticles under different experimental conditions, suggesting a higher affinity of the trimethylammonium headgroup for gold substrates in acidic media.

With respect to the extensively investigated PCDA (pentacosa-10,12-diyanoic acid), DAAMM showed reduced capability of photogenerating thick polymer shells, especially in the more delocalized blue form, probably because of the inefficiency of the cationic monomer to form the multi-bilayered architecture typical of the highly-performing, carboxyl-terminated diacetylene. On the other end, the inner cross-linked structure gives to poly(DAAMM)-coated nanohybrids increased stability in water with respect to self-assembled counterparts deriving from saturated cationic surfactants, making them a promising sensing platform for rapid and cost effective assays of real samples.

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1. Introduction

Neutral and charged surfactants are widely used as stabilizers in the synthesis of noble metal nanoparticles (NPs) because their passivation of the metal surface was proved to be effective to rule growth and structure of the particles and to protect them against coagulation [1,2].

Among the charged surfactants exploited to the purpose, only a few are of the cationic type, even though the importance of the latter ones in biomedical and industrial field as well as in controlling the stability, size and shape of the produced nanoparticles is well-recognized [3]. Cationic surfactants are versatile in many aspects, as antibacterial and anti-electrostatic agents, corrosion inhibitors and structural or mesoporous templates [4–6]. In the

biomedical field, amine- and ammonium-based cationic surfactants have received a lot of attention as supramolecular vectors for gene delivery [7,8]. Moreover, because of the similarity in the chemical structure between cellular constituents and quaternary-ammonium amphiphiles, this class of cationic detergents shows a good biocidal activity [9], which is further enhanced by chemisorption on silver nanoparticles [3].

The quaternary-ammonium surfactants most commonly employed to produce stable, quite monodispersed silver and gold nanoparticles (AgNPs and AuNPs, respectively) are TOAB (tetraoctylammonium bromide) and CTAB (cetyltrimethylammonium bromide). In particular, the role played by CTAB as structure-directing agent in the synthesis of anisotropic gold nanostructures, especially nanorods (AuNRs), through a seeding growth approach is widely documented [10,11]. However, the use of cationic surfactants entails several drawbacks, including environmental pollution and a higher cost with respect to the anionic counterparts. As reagents, they can produce undesired precipitates of silver halides in the reaction medium when halo-

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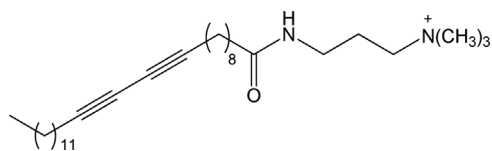


Fig. 1. Structural formula of DAAMM.

gens are employed as counterions [12–15]. As stabilizing agents in supramolecular architectures, they constantly exchange between solution and self-assemblies, thus inducing instability and toxicity in the systems. Incorporation of polymerizable motifs within the amphiphilic chains may overcome this drawback by generating inner crosslinked structures. Lately, photopolymerized micelles based on cationic diacetylenes were successfully exploited as plasmid-DNA delivery vectors [16] and as dual colorimetric and fluorescent sensors for ATP [17].

Diacetylene surfactants, that is asymmetrical diacetylenes bearing appropriate hydrophilic groups at one end (head) of the hydrocarbon chain (tail), are commonly employed in the fabrication of supramolecular nanoconstructs [18] because of their ability to generate quite rigid structures upon exposition to UV radiations [19]. In addition, the peculiar chromic behavior of polydiacetylenes (PDAs), deriving from the conjugated ene-yne backbone, confers optical properties to the new systems with potential applications as sensors [20,21] and molecular switches [22,23] or in optoelectronic [24,25] and drug delivery [26] devices to name a few. Furthermore, additional and/or improved characteristics can be added to the PDA-based assemblies by properly selected, post synthesis reactions. As an example, surface decoration of PDA vesicles with gold and silver nanoparticles of controllable size was successfully exploited to produce composite nanoconstructs with an excellent stability against mechanical disturbance and improved linear and nonlinear optical properties [27–29].

In the past, our group was devoted to the study of the self-assembly of carboxylic-substituted diacetylenes on noble metal nanostructures in order to obtain novel hybrid materials with implemented linear and nonlinear optical properties [30–32]. In particular, optimum packing of PCDA around silver cores by stratification in multiple bilayers was achieved by properly selecting the synthesis procedure through a typical bottom-up approach [33]. Thanks to the experimental conditions adopted, the “pure” blue polymeric phase, that could be exploited for sensing and nonlinear optical devices, was obtained [34]. More recently, we focused our interest to the design and synthesis of novel quaternary-ammonium diacetylenes, characterized by different length and functionalization of the aliphatic chain, in order to investigate the influence of the cationic headgroup and the chemical nature of the tail on the polymerization behavior [35]. Intriguing results arose from the monomer DAAMM (Fig. 1) bromide in powders, in that it was demonstrated that the presence of internal, H-bondable amide groups in the tail can help the formation of a well-packed network among the hydrocarbon side segments, which in turn favors the polymer photogeneration also in the highly-conjugated blue phase.

Starting on these bases, in this paper the self-assembly of DAAMM bromide on silver and gold nanoparticles has been investigated with the aim of evaluating the effect exerted by the anchoring on different metal substrates on the topochemical polymerization of the diacetylene. The main proposal of this research was to produce supramolecular architectures of cationic surfactants, in which undesired and potentially toxic effects from exchange reactions with the environmental media are minimized by the inner cross-linked structure. To this purpose, a simple, reproducible strategy able to guarantee control of the molecular and spectroscopic properties of the resulting nanomaterial is proposed. In our opinion, the novel PDA-based nanohybrids could represent a versatile platform

for the development of polymerized assemblies with size and shape programmed at the nanoscale for technological applications. Moreover, by taking into account the emerging importance of cationic nanoconstructs in bioimaging and biomedical field, their stability in water makes them promising tools for in vivo testing.

To acquire further information on the polymeric shell structure, the study has been carried out as a function of strategic experimental parameters, such as irradiation timescale and pH values of the reaction medium, by means of spectroscopic (UV-vis, fluorescence, FT-IR), morphological (Field Emission Scanning Electron Microscopy, FESEM) and calorimetric (Thermal Gravimetric Analysis, TGA) techniques. A comparison of the results with those obtained from the reference, highly-performing PCDA under selected experimental conditions is also reported.

2. Experimental methods

2.1. Chemicals and solvents

The diacetylene monomer *N,N,N*-trimethyl-3-(pentacosyl-10,12-diyne)propan-1-ammonium (DAAMM) bromide was synthesized according to the procedure described in ref. [35].

All other reagents were commercial products used as received, excepting PCDA (pentacosyl-10,12-diyne acid), which was subjected to a purification procedure. In detail, the PCDA monomer, purchased from Lancaster, was purified to remove traces of any spontaneously-formed polymer through dissolution in ethanol followed by filtration with a 0.20- μm PTFE syringe filter. High molecular mass chitosan (Chit, acetylation degree = 22.8%, $M_w = 1.34 \times 10^6$ in terms of repeating units) was purchased from Fluka.

Solvents were spectroscopic grade and were used as received. All aqueous solutions were made with ultra-high-purity water, twice distilled prior to use.

2.2. Instrumentation

Photopolymerization was carried out by irradiating the samples in a Rayonet photochemical chamber reactor, operating at 254 nm and 35 W power, by keeping the samples at a 10-cm distance from the UV lamps. The experimental conditions were set up as published elsewhere [33,34] in order to compare the photopolymerization behavior of the DAAMM bromide with respect to the reference diacetylene PCDA.

Electronic absorption spectra were recorded at room temperature on a Perkin-Elmer Lambda 9 spectrophotometer using fused silica cuvettes of different pathlength.

Steady state fluorescence spectra were measured by using a Perkin Elmer MPF-44A spectrofluorimeter with excitation at 480 nm. Emission intensities were normalized at a constant value of the source intensity by means of a standard sample consisting of Rhodamine B embedded in a matrix of poly(methylmethacrylate).

FT-IR spectra were acquired by means of a Perkin Elmer Spectrum 65, operating in ATR mode on both hydrosols and solid samples.

The morphology of the polymerized colloids was assessed by a ZEISS SUPRA 40 VP Field Emission Scanning Electron Microscopy (FESEM), operating at 20 keV in back-scattered (QBSD mode) configuration.

Thermogravimetric analysis was carried out by a Mettler-Toledo TGA/DSC1 STARE System. Powders of the samples (6 ± 10 mg) were subjected to the following thermal program: 1) 20 °C \div 700 °C in nitrogen atmosphere (80 mL/min flow, 20 °C/min heating rate) 2) 700 °C \div 900 °C in air (80 mL/min flow, 20 °C/min heating rate).

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