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Hantzsch dihydropyridines: Privileged structures for the formation of well-defined gold nanostars

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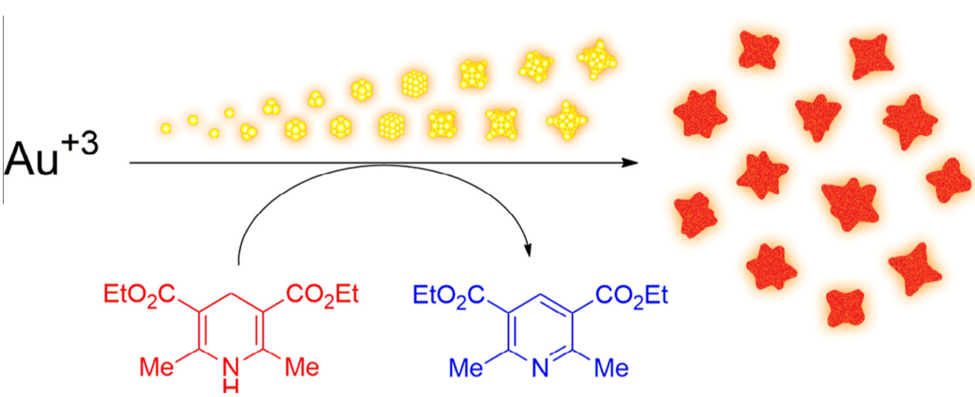
GRAPHICAL ABSTRACT



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ABSTRACT

Anisotropic and branched gold nanoparticles have great potential in optical, chemical and biomedical applications. However their syntheses involve multi-step protocols and the use of cytotoxic agents. Here, we report a novel one-step method for the preparation of gold nanostructures using only Hantzsch 1,4-dihydropyridines as mild reducing agents. The substituent pattern of the dihydropyridine

Abbreviations: AuNP, Gold nanoparticle; DHP, 2,6-Dimethyl-3,5-diethoxycarbonyl-1,4 dihydropyridine; Ph-DHP, 4-Phenyl-2,6-dimethyl-3,5-diethoxycarbonyl-1,4 dihydropyridine; N-DHP, 1-Benzyl-1,4-Dihydronicotinamide; Pyr, 2,6-Dimethyl-3,5 diethoxycarbonylpyridine; LMW, low molecular weight peptide; HMW, high molecular weight peptide.

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This paper is dedicated to the memory of our dear friend Professor Luis J. Núñez-Vergara, a great person and researcher, who made of the fairness, the respect and the friendship his philosophy of life.

Keywords:
Dihydropyridines
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nucleus was closely related to the ease of formation, morphology and stability of the nanoparticles. We observed nanostructures such as spheres, rods, triangles, pentagons, hexagons, flowers, stars and amorphous. We focused mainly on the synthesis and characterization of well-defined gold nanostars, which were produced quickly at room temperature (25 °C) in high yield and homogeneity. These nanostars presented an average size of 68 nm with mostly four or six tips. Based on our findings, we propose that the growth of the nanostars occurs in the (1 1 1) lattice plane due to a preferential deposition of the gold atoms in the early stages of particle formation. Furthermore, the nanostars were easily modified with peptides remaining stable for more than six months in their colloidal state and showing a better stability than unmodified nanostars in different conditions. We report a new approach using dihydropyridines for the straightforward synthesis of gold nanostructures with controlled shape, feasible for use in future applications.

1. Introduction

Gold nanoparticles (AuNPs) have fascinating optical, electronic, chemical and biological properties and thus are promising for chemical and biomedical applications [1–3]. In this regard, anisotropic and branched AuNPs (multi-pods, star-like, flower-like, urchin-like, among others) are of great interest because of their unique and fine-tuned properties which differ markedly from or are more pronounced than those observed for spherical AuNPs [4], as occurs with the Surface Enhanced Raman Spectroscopy (SERS) effect [5,6] and Near Infrared (NIR) absorption [7,8]. Therefore, branched AuNPs are ideal structures for cutting-edge applications in catalysis [9,10], optical sensing [11], biomedical labeling [12], cancer treatment [13], and as antibacterial agents [14]. A variety of reducing agents, capping agents, stabilizers, surfactants and growth-direction agents have been studied for use in the synthesis of anisotropic and branched AuNPs [15–22]. In many cases the preparation of these particles involves multi-step protocols with low yields, obtaining nanostructures difficult to functionalize [23–27], wherein the characteristics of the synthesis agents and conditions are critical for the formation, stabilization, final morphology and biocompatibility of the nanoparticles [28–31]. In this sense, the most popular methods for the synthesis of anisotropic nanoparticles in high yield are several-step protocols based on seed-mediated approaches using the cationic surfactant cetyltrimethylammonium bromide (CTAB), which is a well-known highly cytotoxic compound [32]. However, in recent years some authors have reported easier synthesis for the preparation of anisotropic gold nanoparticles in high yield, based on one-pot protocols, new mild reduction agents and/or green-chemistry methods free of toxic agents or pure organic solvents [16,33–36].

Furthermore, the Hantzsch 1,4-dihydropyridines, which are important pharmacological agents, have interesting redox properties and can be considered biomimetic reducing agents because of their structural similarity to NADH coenzyme [37–42]. In this regard, the electron transfer displayed by the dihydropyridines is strongly influenced by their substituent patterns [38–41]. Despite their well-known reducing properties, little attention has been devoted to the application of these molecules for the reduction of metallic ions and the growth of metallic nanoparticles [43,44]. Here, we report a novel one-step and surfactant-free synthesis for the preparation of gold nanostructures at 25 °C using only dihydropyridines as reducing agents of the tetrachloroauric acid (Fig. 1a). Studying different dihydropyridines and experimental conditions, we obtained nanostructures of several shapes and sizes. Given the interesting properties of the anisotropic AuNPs and the importance of their preparation in high yield and homogeneity, we focused mainly on the synthesis of well defined star-like AuNPs,

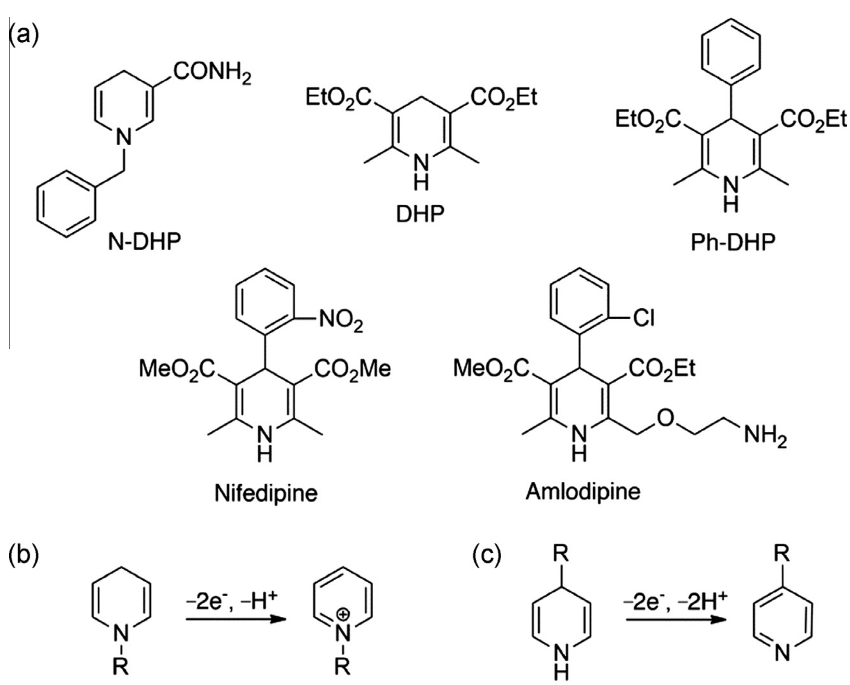

Fig. 1. (a) Chemical structures of the dihydropyridines assayed in the synthesis of gold nanostructures. Representative oxidation scheme of (b) N-substituted and (c) 4-substituted derivatives.