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Facile Light-Triggered One-Step Synthesis of Small and Stable Platinum Nanoparticles in an Aqueous Medium from a β-Cyclodextrin Host–Guest Inclusion Complex[†]

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It is shown, for the first time, that small (ca. 2 nm) and stable platinum nanoparticles can be easily obtained in one step through visible light irradiation of a host–guest inclusion complex between β-cyclodextrin and platinum acetylacetonate in a water solution. The exclusive control of the reaction by an external trigger, the removal of the undesired reaction products without any manipulation of the sample, and the absence of ionic repulsions between the metal nanoparticles represent the main remarkable advantages offered by this synthetic methodology.

In the emerging and fascinating world of nanostructured materials, metal nanoparticles are continuing to receive a great deal of both academic and industrial interest by virtue of their unique optical, electronic, magnetic, and catalytic properties.[1] These multifunctional physicochemical characteristics make nanoparticles very appealing for a variety of applications in multidisciplinary fields spanning from molecular electronics to biomedicine.[2] Therefore, the development of simple synthetic protocols for these nanosystems represents nowadays a research area of considerable relevance.

Many practical applications necessitate metal nanoparticles to be dispersible in water with preservation of their physicochemical properties over a long period of time.[3] The obtainment of these crucial prerequisites is, in general, a difficult task. In fact, in contrast to organic solvents, synthetic procedures in a water solution present several difficulties mainly related to effective ionic interactions and the presence of reactants and stabilizers that are difficult to remove.[4] Because of their excellent catalytic activity, Pt nanoparticles have been the object of intensive investigations over the years.[5] Furthermore, because these nanoparticles are characterized by negligible plasmon absorption into the visible region,[6] they represent ideal platforms for the fabrication of hybrid optical nanodevices by the self-assembling of functional chromogenic units.[7] Although a number of processes have been developed for the synthesis of Pt nanoparticles in different environments,[8] only a few synthetic methodologies have addressed the preparation in an aqueous medium. Most of them are based on the use of dendrimers, surfactants, and thiol derivatives and involve the chemical reduction of aqueous soluble platinum salts.[9]

In this contribution, we report a facile, one-step synthesis of small (ca. 2 nm) and stable platinum nanoparticles in

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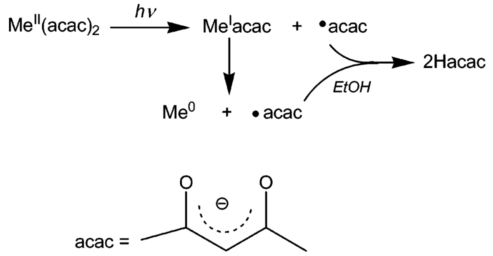
Scheme 1



water, exclusively triggered by visible light and involving a host−guest inclusion complex between β-cyclodextrin (β-CD) and platinum acetylacetonate, Pt(acac)$_2$, as the only chemical reactant. Our interest in this work has been stimulated by the merging of three key factors: (i) the recently reported capability of unmodified CDs to solubilize metal nanoparticles in a water solution,[10] (ii) the well-known photoreactivity of transition-metal β-diketonates, which, in an ethanol or dichloromethane solution, yield colloidal metal and β-diketones,[11] and (iii) our continuous attention over the years in exploring peculiar aspects related to the photoreactivity of β-CD host−guest complexes.[12]

The main steps leading to the colloidal metals are sketched in Scheme 1 for the sake of clarity.

They involve the homolytic cleavage of the metal−ligand bond, followed by hydrogen abstraction from the solvent by the ligand-centered radical.[11] Different from β-diketonate complexes with metals such as Cu, Ni, and Pd, Pt(acac)$_2$ undergoes photodecomposition with comparable efficiency upon irradiation with both UV and visible light because of the absence of low-lying d,d states, which deactivate the reactive π,π^* state.[11a]

Pt(acac)$_2$ is completely insoluble in an aqueous solution. On the other hand, it is fairly soluble in the presence of 10^{-2} M β-CD, as confirmed by the absorption spectrum shown in Figure 1, which is basically similar to that obtained in ethanol. This is due to the formation of an inclusion complex whose existence is further supported by the induced circular dichroism (ICD) measurements. Indeed, as shown in the inset of Figure 1, an ICD signal with bands fairly well-corresponding to those observed in the absorption spectrum arises as a consequence of the incorporation of the nonchiral Pt(acac)$_2$ within the optically active β-CD cavity.

The aqueous solution (3 mL) of the host−guest complex was than irradiated with 420-nm light, and the course of the reaction was followed spectrophotometrically. As reported in Figure 2a, irradiation of the sample results in the quantitative disappearance of Pt(acac)$_2$ accompanied by the appearance of the typical absorption band of Hacac (see dotted spectrum, for comparison) and a weak structureless absorption extending in the visible region attributed to colloidal platinum.

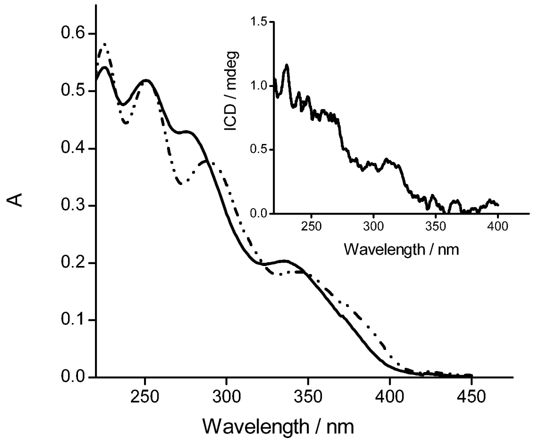


Figure 1. Absorption spectrum of Pt(acac)$_2$ in the presence of a 10^{-2} M β-CD aqueous solution (solid) and in ethanol (dotted). The inset shows the ICD spectrum of the β-CD−Pt(acac)$_2$ host−guest complex.

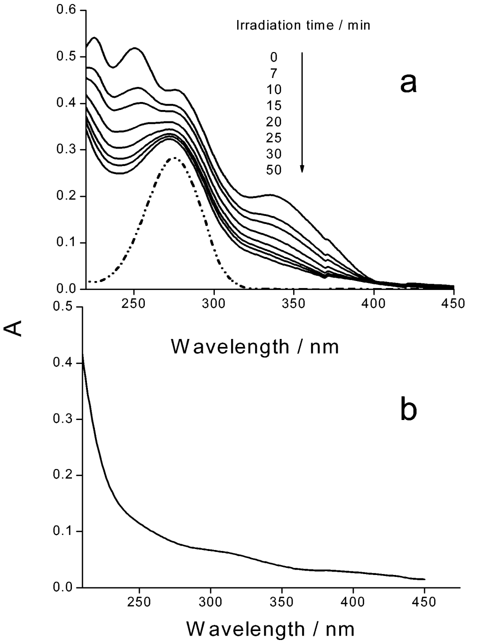


Figure 2. (a) Absorption spectral changes observed upon visible light irradiation of the β-CD−Pt(acac)$_2$ host−guest complex. The dotted line shows the absorption spectrum of Hacac in the presence of 10^{-2} M β-CD. (b) Absorption spectrum obtained after drying under vacuum at 75 °C for 2 h the final solution of the experiment reported in part a and resolubilizing the residual solid in the same volume before drying. The reference cell contained a 10^{-2} M β-CD aqueous solution.

Because Hacac does not absorb the exciting light, it is not photodecomposed during the photoreaction and can be easily removed from the reaction mixture by drying this latter under vacuum at 75 °C for 2 h. A control experiment carried out with a solution of Hacac in the presence of 10^{-2} M β-CD provided evidence for the quantitative release of all of the ligand from the Pt(acac) upon irradiation. The dried sample was then solubilized in the same volume of water as that at the beginning of the photolysis, and the absorption spectrum was recorded. As shown in Figure 2b, the spectrum obtained does not show any detectable signal associated with the

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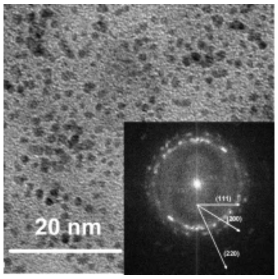

Figure 3. TEM micrograph of platinum nanoparticles obtained upon photolysis of the β-CD−Pt(acac)$_2$ host−guest complex. The inset reports the electron diffraction of the platinum nanparticles showing an fcc packing arrangement.

presence of Hacac but is exclusively characterized by a structureless absorption extending into the visible region, which is in full agreement with the spectra reported in the literature for other platinum nanoparticles.[6c,9b]

A transmission electron microscopy (TEM) micrograph on a representative sample prepared following the above procedure is displayed in Figure 3. The Pt nanoparticles are quite well-dispersed, exhibit a nearly spherical shape, and are characterized by an average diameter of 2.0 ± 0.8 nm. Electron diffraction (inset in Figure 3) shows that the nanoparticles are single crystals with face-centered-cubic (fcc) structure.[13]

These colloidal nanoparticles exhibited a good stability. Indeed, they remained well dispersed in water for several weeks with no relevant aggregation, as evidenced by the insignificant variation of the absorption spectrum and the particle size noted after this period of aging.

The role of the β-CD macrocycle in the formation of the Pt nanoparticles is manifold by virtue of the features of its unique microenvironment, indispensable for the one-step synthesis to occur. First, the nonpolar CD cavity allows the solubilization of the photoactive component. Second, the CD cage is well suited to effectively trap the reactive radical intermediates photogenerated. As reported in Scheme 1, the release of the free ligand involves H-abstraction by the ligand-centered radical. Because the occurrence of such a process from water is, of course, out of question because it is thermodynamically not favored, it is reasonable to conceive that the acac$^\bullet$ radical might lead to the formation of Hacac by decaying within the β-CD interior via an intracage H-abstraction reaction. This route is expected to be highly efficient because of the presence of 14 available hydrogen atoms bonded to secondary carbons and close to the radical center.[14] Third, the nonpolar β-CD interior is appropriate to effectively interact with the photoproduced metal nanoparticles. This interaction allows their solubilization in water and prevents agglomeration. In this regard, on the basis of the nanoparticles sizes, ca. 2 nm, and the internal diameter of the β-CD cavity, 0.78 nm, it is unlikely to explain both the small dimension of the metal nanoparticles and their stability as a result of the inclusion of the Pt atoms in the CD cavity. Rather, these properties seem more likely to be due to *hydrophobic−hydrophobic* interactions between the cavity and larger metal nanoparticles. This proposal is in accordance with what was recently observed by Luong and co-workers, who used different CDs to control the size of the Au nanoparticles formed by chemical reduction of Au salts solubilized in an aqueous medium.[10] Concerning this, it should be noted that solubilization of hydrophobic molecules by CDs does not necessarily imply molecular sizes compatible with the dimensions of the cavity. For example, it is well-known that very large aromatic hydrocarbons become soluble in the presence of CDs because of effective hydrophobic interactions involving the cavity and only some groups of such hydrocarbons.[15]

In summary, we have shown a very simple and effective method to produce small and stable Pt nanoparticles in a water solution. To the best of our knowledge, this represents *the first example* of the light-controlled preparation of metal nanoparticles from a host−guest inclusion complex of β-CD. This facile synthetic methodology presents the following, remarkable advantages. First, the exclusive control of the reaction by visible excitation produced by conventional lamps with moderate light intensity is environmentally and cheaply friendly, in contrast to the use of toxic chemicals and sophisticated laser sources, respectively. Second, the elimination of the reaction product does not require any manipulation of the sample. Third, different from metal nanoparticles prepared in water by using ionic surfactants as stabilizers,[16] the nanoparticles obtained in the presence of CD are not subject to ionic repulsions, which preclude chemical modification.

Studies currently underway in our laboratories have shown that, under appropriate experimental conditions, this facile protocol for the preparation of small-sized and stable metal nanoparticles in a water solution can be extended to other bis(β-diketonate) metal complexes. Hopefully, we believe this may open up new avenues for the achievement of colloidal systems in an aqueous medium that can be of potential interest in diverse technological areas.

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Supporting Information Available: Detailed experimental procedures containing the preparation of the host−guest inclusion complex and the irradiation conditions. This material is available free of charge via the Internet at htpp://pubs.acs.org.

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(13) Note that the highest nanoparticle concentration obtainable is, of course, strictly governed by the solubility limit of the photoactive complex in the CD cavity (ca. 10^{-4} M).

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