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A one-pot organometallic approach to access hybrid nanomaterials based on organophosphorus transition metal complexes covalently bonded to metal nanoparticles

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ABSTRACT

At the LCC-Toulouse-France, the *Engineering of Metal Nanoparticles* team develops efficient tools for the synthesis of finely controlled metal nanostructures in solution by applying a molecular chemistry approach based on the decomposition of organometallic complexes in the presence of a stabilizer (polymer, ligand, ionic liquid). This approach enables to prepare ultra-small monometallic or bimetallic (alloy, core-shell or surface-decorated) nanoparticles as well as supported nanoparticles (*i.e.* on silica or carbon supports). As described herein we are also developing hybrid nanomaterials consisted in the association of metal transition complexes to metal nanoparticles in order to explore their physicochemical properties.

1. INTRODUCTION

Metal-based nanoparticles (MNPs) and derived nanomaterials are well-recognized for their peculiar properties that find applications in numerous domains [1] including catalysis [2,3] and energy [4]. At the LCC-Toulouse-France, the *Engineering of Metal Nanoparticles* team has developed a performant toolbox for producing ultra-small (≤ 10 nm; most often 1-3 nm) and precisely defined NPs of different metals, with a narrow size distribution and a controlled composition [5]. This approach lies on the decomposition of organometallic or metal organic complexes in solution and in the presence of a stabilizer, at mild conditions of temperature and pressure (*i.e.* room temperature and 3 bar H₂). Olefinic complexes are preferred owing to the alkanes formed under H₂ -as only byproducts- do not interact with the metal surface. The stabilizer being another key-parameter for the control of the NP characteristics, we have studied the ability of ligands with various anchoring groups to stabilize small NPs and their influence on the MNP surface properties [6]. This led to various ligand-capped monometallic or bimetallic (alloy, core-shell or surface-decorated) MNPs in solution or supported conditions (*i.e.* on silica or carbon supports) with interesting properties in of catalysis [7] or energy [8]. If efficient synthesis tools for the design of multifunctional metal NPs *via* the coordination of specific stabilizing ligands at their surface, similar studies involving transition metal complexes (TMCs) are still in their infancy. Recently, we have been interested in grafting TMCs to metal NPs, either through a post-functionalization [9] or a direct synthesis [10] route, with the aim to explore the physico-chemical properties of the resulting hybrid nanomaterials. Our recent developments concern the utilization of organophosphorus polypyridyl ruthenium complexes [11] as stabilizing agents of metal NPs.

2. TOWARDS TMCs-MNPs HYBRID NANOMATERIALS

The one-pot synthesis and characterization of a novel hybrid nanomaterial where an organophosphorus polypyridyl ruthenium complex is covalently coordinated to the surface of RuNPs are hereafter described.

2.1. Synthesis conditions for the preparation of [Ru1]-RuNPs hybrid nanomaterial

In a Fischer Porter reactor, a THF solution containing the organometallic precursor $[(\text{Ru}(\text{COD})(\text{COT}))]$ and 0.1 molar eq. of the mononuclear cationic organophosphorus polypyridyl ruthenium complex $[(\text{bpy})_2\text{Ru}(\text{PPh}_2\text{Me})\text{Cl}]^+\text{PF}_6^-$ ([Ru1], [12]) was exposed to 3 bar of H_2 at room temperature (r.t.) under vigorous stirring for 24h (Fig. 1). The initial orange solution rapidly turned black indicating the formation of nanoparticles. Excess H_2 and solvent were then eliminated under vacuum, which led to the formation of a black solid and a red supernatant. Purification treatment including filtration, THF washings and drying under vacuum allowed getting a fine black powder.

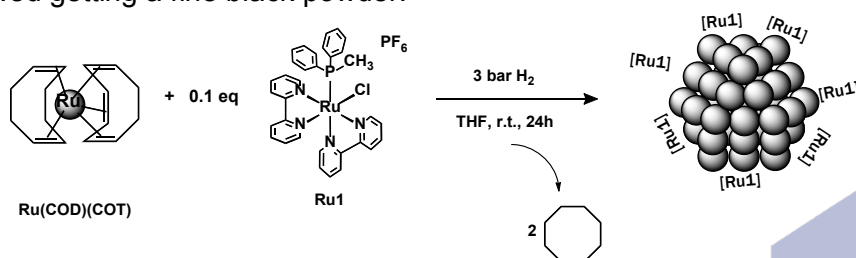


Figure 1. Synthesis of [Ru1]-RuNPs hybrid nanomaterial.

2.2. Characterization of [Ru1]-RuNPs hybrid nanomaterial

First, together with the red color observed, ^1H and ^{31}P NMR spectra recorded from the supernatant showed that the byproducts present were 1) unreacted [Ru1] complex and 2) cyclooctane (resulting from decomposition of $[(\text{Ru}(\text{COD})(\text{COT}))]$). Besides confirming the decomposition of the RuNP precursor, these results indicated that the 0.1 eq. of introduced [Ru1] complex was not totally integrated in the final nanomaterial. Second, TEM (transmission electron microscopy) analysis performed on two grids - one prepared from the crude colloidal suspension in THF and second one from the purified sample re-dispersed in acetonitrile - evidenced some differences in terms of dispersion. THF suspension contains regular spherical aggregates of ca. 350 nm (Fig 2a) composed of individual small NPs whose precise size was difficult to estimate due to their close proximity (Fig 2b). In the contrary, the acetonitrile dispersion contains small and well-dispersed individual NPs with a size distribution centered at ca. $1.4 \text{ nm} \pm 0.6$ (Fig. 2c,d). It is important to note that a great majority of particles have a size close to the calculated mean size thus indicating that the reaction conditions applied led to an effective size control. The difference in dispersion observed can be explained by a difference of solubility of the nanomaterial in THF and acetonitrile. A parallel can be made with the behavior of the [Ru1] complex in the same solvents since it is more soluble in acetonitrile which is a more polar solvent than in THF due to its ionic character. The better dispersion of the particles in acetonitrile clearly indicates a transfer of solubility properties from [Ru1] to [Ru1]-RuNPs hybrid nanomaterial.

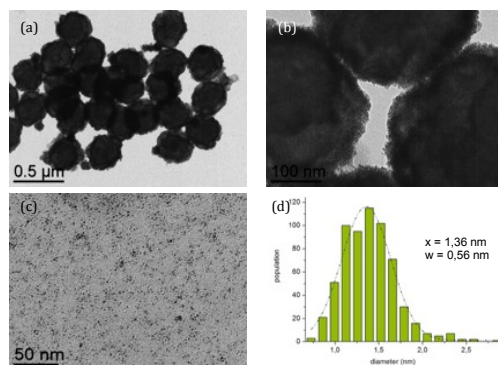


Figure 2. TEM pictures of [Ru1]-RuNPs in crude colloidal THF suspension (a) and (b) and after redispersion in acetonitrile (c) and size histogram built from c image (d).

Liquid and solid-state NMR (^1H , ^{13}C , ^{31}P and ^{19}F) investigations on purified [Ru1]-RuNPs sample provided accurate information on the structure of the hybrid nanomaterial. Together with the signature of a preserved complex, NMR results indicate the presence of [Ru1] species directly coordinated at the RuNP surface (inner layer) as well as that of non-directly coordinated ones (outer layer). Also, ^{31}P and ^{19}F NMR data revealed that PF_6^- anions are totally solvated and located away from the influence of RuNPs. Remarkably, extended information on the hybrid structure derives from 2D DOSY NMR data where two different diffusion coefficients, namely $D_1=3.6 \cdot 10^{-10} \text{ m}^2/\text{s}$ and $D_2=9.9 \cdot 10^{-10} \text{ m}^2/\text{s}$ ([Ru1] $D=1.3 \cdot 10^{-9} \text{ m}^2/\text{s}$) can be seen (Fig. 3). D_1 corresponds to the [Ru1]-RuNPs hybrid material involving [Ru1] complex coordinated to the RuNP surface. D_2 evidences [Ru1] species in dynamic exchange between free and outer-sphere complexes in solution. By applying the Stokes-Einstein equation, D_1 of [Ru1]-RuNPs provides a ca. 3 nm hydrodynamic diameter against ca. 0.84 nm for the free [Ru1]. Given the mean size of 1.4 nm determined by TEM analysis for the metal cores, one can estimate that the size of the [Ru1]-RuNPs hybrid nanomaterial made of Ru cores surrounded by a layer of [Ru1] complexes would be ca. 3.0 nm, which matches well with the value deduced from D_1 .

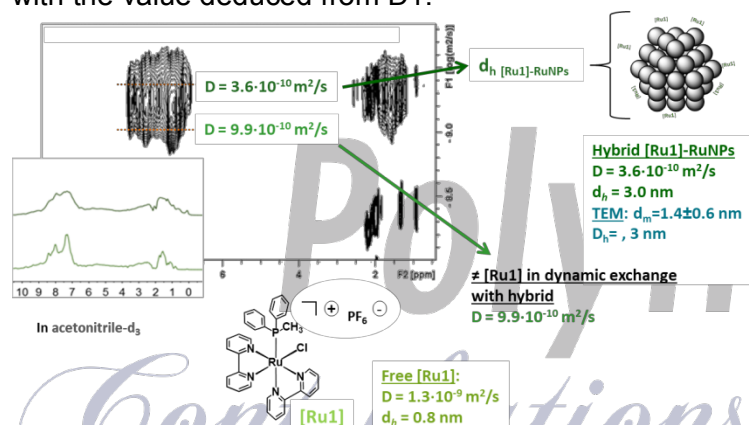


Figure 3. Diffusion coefficients determined from 2D DOSY ^1H NMR plot for [Ru1]-RuNPs compared to free [Ru1] complex (in CD_3CN).

2.3. Theoretical studies on [Ru1]-RuNPs hybrid nanomaterial

Density functional theory (DFT) calculations performed on a 1 nm hydrogenated ($0.8\text{H}/\text{Ru}_{\text{surf}}$) RuNP model ($\text{Ru}_{55}\text{H}_{35}$) [13] evidence that the coordination of [Ru1] complex at the RuNP surface occurs through the σ -donation of the chlorine lone pair atom, indicating the chlorine atom acts as a bridging ligand between [Ru1] and RuNP entities (Fig. 4). Moreover, the more stable hybrid conformer involves an additional aromatic π -type chelating interaction between one of the bipyridine ligands of [Ru1] complex and one ruthenium surface atom of the RuNPs and PF_6^- anion stands in the outer sphere of the [Ru1]-RuNPs hybrid nanomaterial.

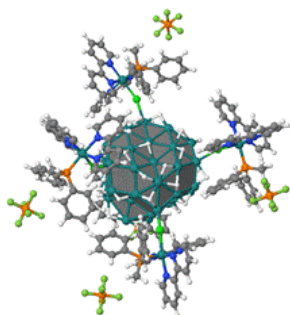


Figure 4. DFT modelling of [Ru1]-RuNPs hybrid nanomaterial showing the most stable coordination mode of the [Ru1] complex at the RuNP surface.

CONCLUSION

A novel hybrid nanomaterial made of organophosphorus polypyridyl ruthenium complexes, $[(bpy)_2Ru(PPh_2Me)Cl]^+PF_6^-$ ([Ru1]), covalently bonded at the surface of ruthenium nanoparticles (RuNPs), was synthesized in an one-pot procedure. NMR studies showed the direct coordination of [Ru1] complexes at the RuNP surface that form an inner stabilizing layer and the presence of [Ru1] complexes in an outer layer that electrostatically interact with their inner layer counterparts. Theoretical calculations evidenced : 1) the coordination of [Ru1] complex at the RuNP surface *via* its chlorine atom, thus binding the two entities of the hybrid nanomaterial, and 2) an aromatic π interaction between one of the phenyl groups of the [Ru1] and the NP surface that reinforces the stabilization of the hybrid. This type of connection is unprecedented in the domain of hybrid materials incorporating MNPs and TMCs. Given the known variation of the physicochemical properties of the organophosphorus polypyridyl ruthenium complexes as a function of the nature of the phosphorus ligand [11, 12], and those of the metal nanoparticles depending on the metal chosen [5], our synthesis approach may offer a vast family of hybrid nanomaterials that may be of interest in photophysics or electro(photo)catalysis for instance.

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