Functional Metal-Organic Nanoparticles

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Functional micro- and nanoparticles are of increasing interest in a variety of scientific fields such as storage, photonics, electronics, cell biology, biotechnology, diagnostics, nanoanalytics, and pharmaceutics. Therefore, widespread attention has been recently paid to new strategies for fabricating particles with novel compositions and properties. Metal-organic solids are hybrid materials created by the association of metal ions and organic ligands, which have already shown a wide range of promising properties in gas sorption, sensing, catalysis, ion exchange, magnetism, optics, etc. Because of the vast range of properties, one of the actual challenges is the miniaturization of these systems to design and fabricate novel metal-organic particles nanoparticles (MONPs). To date, two possible routes to fabricating MONPs have been explored. One involves the use of microemulsion techniques, which have already enabled the synthesis of Prussian blue- and triazol-based magnetic nanoparticles, and Gd(III) nanorods that can be used as multimodal contrast enhancing agents.[1] The second is based on precipitation processes, such as antisolvent technology with supercritical fluids.[2] Based on this principle, a method consisting on both coordination polymerization and precipitation in a poor solvent has recently allowed the synthesis of colloidal amorphous particles from infinite coordination polymers that show interesting optical properties and ion-exchange capabilities.[3,4] The presented work has been inspired by the latter route, and shows that a simple precipitation process can lead to functional nanoparticles from magnetic metal-organic clusters.

In a first step, we have demonstrated how through pre-synthesized magnetic building blocks and by a simple precipitation process, magnetic metal-organic nanoparticles can be fabricated. This process consist on a direct precipitation of $Mn_{12}O_{12}$ clusters in a mixture of acetonitrile and toluene that lead to the first example of sub-50 nm spherical Mn_{12}-based particles.[5] The integrity of these clusters is not affected in the fabrication process, and the single molecule magnet behaviour, which is typical for these well-known clusters, is maintained. Moreover, the small size as well as the amorphous character of these particles allows to obtain very important information to correlate the environment of Mn_{12} clusters (i.e. crystalline, nanostructured or amorphous character) with their magnetic properties.[6]

This approach has also been extended to other magnetic systems. The association of an electroactive building block, such as [Co^{III}(3,5-DBSQ)(3,5-DBCat)], with the adequate bridging ligand creates the first example of nanoparticles that exhibit valence tautomeric properties.[7] As shown in Figure 1, these particles interconvert reversibly between two different magnetic states induced by a temperature modification: from the low-spin ls-[Co^{III}(3,5-DBSQ)(3,5-DBCat)] to the high-spin hs-[Co^{II}(3,5-$DBSQ)_2$] through a reversible intramolecular transfer involving the metal ion and the redox-active ligand.

In addition to the intrinsic properties of the particles, the interest of these MNOPs comes from their high capacity to encapsulate external bodies, i. e. molecules, nanoparticles, and consequently, to introduce a novel property. A detailed study of the encapsulation of fluorescent molecules and magnetic inorganic particles will be presented.

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Figures:

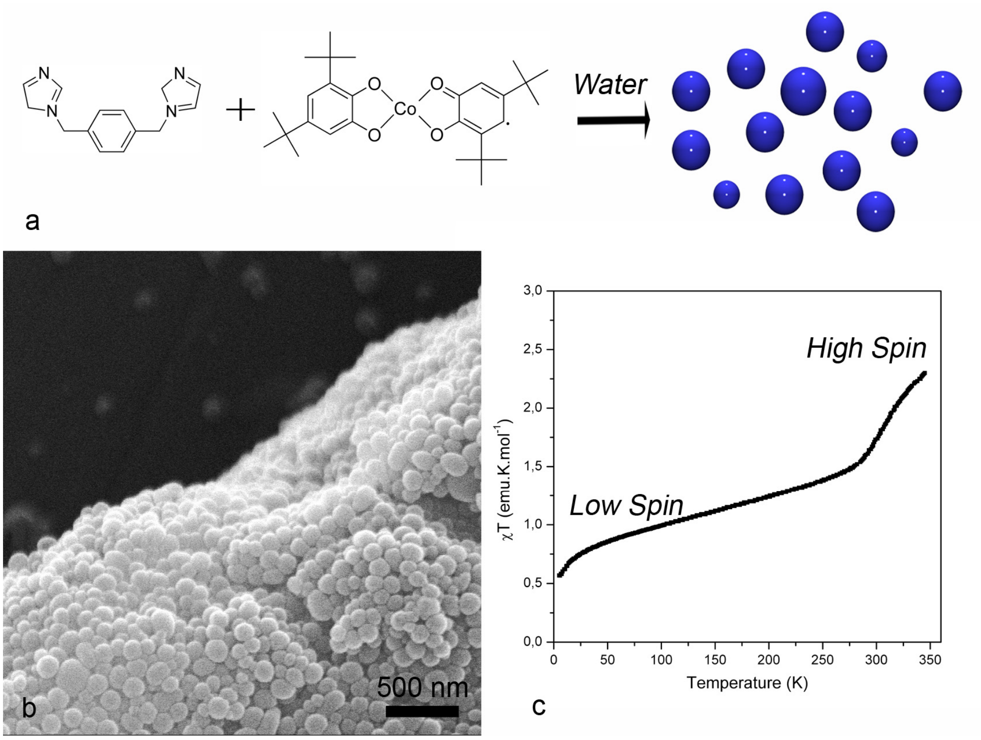

Figure 1: (a) Schematic illustration describing the coordination polymerization procedure followed to obtain valence tautomeric NMOPs. (b) SEM image of nanoparticles created by infinite coordination polymerization of $[Co^{III}$(3,5-DBSQ)(3,5-DBCat)] through Bix ligands. (c) XT values as a function of the temperature for the amorphous $[Co^{III}$(Bix)(3,5-DBSQ)(3,5-DBCat)] metal-organic nanospheres