Metal-organic spheres as new functional micro- and nanomaterials for encapsulation

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Encapsulation of functional species into micro- and nanometer sized matrices hold great promise in areas of drug-delivery and cosmetics,[1] medical diagnostics[2] and materials science.[3] Throughout history, big efforts have been dedicated to design and fabricate encapsulating materials that satisfy all specificities and critical properties needed for each intended application. To date, a number of capsules, such as liposomes,[4] cyclodextrin,[5] chitosan,[6] organic polymeric particles,[7] dendrimers[8] and carbon or silicate-based hollow spheres,[9] have been used. Thus far, however, the use of metal-organic micro- and nanoparticles as encapsulating matrices has not been explored. Metal-organic solids created by the association of metal ions and multitopic organic ligands are a very promising type of materials because of their broad compositional and structural diversity, low cost and easy-made production, and their wide range of potential properties and applications that include gas sorption, catalysis, ion exchange, sensing, drug-delivery, magnetism, fluorescence, non-linear optics, etc.[10] Because of this rich range of properties, we envisage the use of conventional metal-organic chemistry for fabricating functional matrices that display the intrinsic properties of such molecular materials.

Prior to this work, advances have been done on the miniaturization of metal-organic materials down to the micro- and nanometer scale. For instance, Gd(III) nanorods that can act as potential multimodal contrast enhancing agents and sub-50 nm Prussian blue- and triazol-based magnetic particles have been obtained by means of microemulsion-based techniques.[11,12] More recently, an alternative promising methodology has been reported by Mirkin's and Wang's groups.[13,14] This strategy, which is based on infinite coordination polymerization followed by precipitation in a poor solvent, allows the straightforward fabrication of cross-linked sub-micron functional metal-organic spheres. For example, this approach has been exploited to synthesize fluorescent metal-organic spheres that show selective cation-exchange and hydrogen storage properties, as well as others with an interesting valence tautomeric behaviour.[15]

Inspired by this fabrication process, herein we show a new and versatile methodology for encapsulating desired species into metal-organic polymeric micro- and nanospheres.[17] This new encapsulation method is based on a one-step strategy, depicted in Figure 1a: blue fluorescent metal-organic spheres (hereafter referred to as **ZnBix** spheres, Figure 1b) can be formed by infinite coordination polymerization of Zn(II) metal ions and 1,4-bis(imidazol-1-ylmethyl)benzene organic ligands followed by a fast precipitation to mechanically trap the desired functional species that are present in the reaction mixture. By using this methodology, a wide range of functional species, such as magnetic nanoparticles, gold nanoparticles, organic dyes, and luminescent quantum dots (QDs), has already been encapsulated (Figure 1c-e). In this way, a new type of multifunctional materials, which combine the inherent properties of both **ZnBix** spheres and the encapsulated substances, can be designed. For example, as shown in Figure 1e, **ZnBix** spheres encapsulating QDs are fluorescent in the blue (fluorescence properties of the metal-organic matrix) and red (fluorescence properties of encapsulated QDs) regions of the spectrum.

Based on these promising results, our current motivation is to study the potential of these micro- and nanomaterials for medical applications. Thus, preliminary studies of encapsulation and further *in vitro* controlled release of several drugs will be presented.

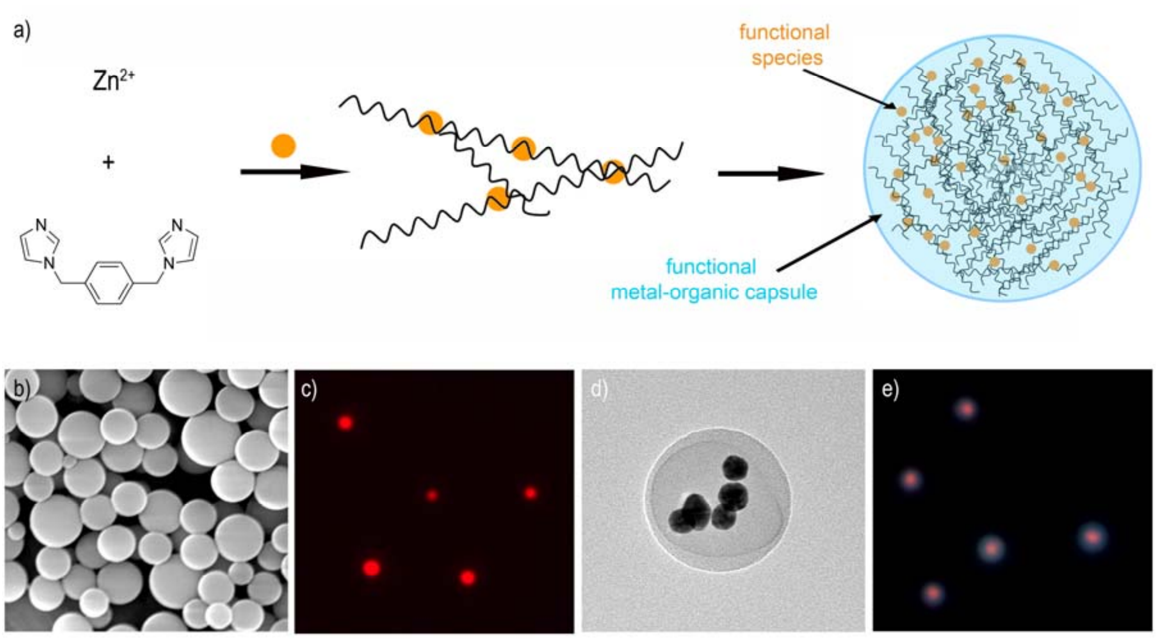

Figure 1. (a) Schematic illustration describing the simultaneous formation and encapsulation of functional species into **ZnBix** spheres. (b) SEM image of **ZnBix** spheres. (c) Fluorescence optical microscope images of Rhodamine@**ZnBix**, (d) Transmission Electron Microscope images of AuNP@**ZnBix**, (e) Fluorescence optical microscope images of QDs@**ZnBix.**

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