Coordination Polymers

DOI: 10.1002/anie.200806069

Coordination Polymers: From Metal–Organic Frameworks to Spheres

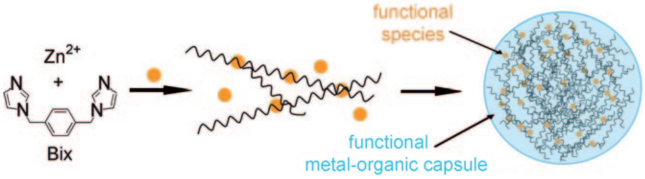
*Neil R. Champness**

coordination polymers · fluorescence · host–guest systems · magnetism · metal–organic frameworks

Research in the area of coordination polymers has been undertaken for over fifty years[1] but in recent years the term coordination polymer has been replaced more and more by the term metal–organic framework (MOF).[2] The study of metal–organic frameworks has grown so rapidly over the last ten years that it is now almost impossible to read one of the top chemistry or materials journals without encountering the latest development in the design and evaluation of the properties of these fascinating materials.[2] This interest has arisen thanks to two main features. Firstly, the combinations of building blocks, metal cations or clusters and multitopic bridging ligands, is almost limitless, which gives the imaginative researcher a large field of possibilities to explore. Secondly, the frameworks can be designed to be porous and thus act as hosts for guest species.[2] Many interesting properties arise from such systems but ultimately one limitation will always hold back such materials; they are macroscopic solid-state species that have very limited solution-based behavior.

A study by Maspoch and co-workers[3] elegantly demonstrates how the limitations of metal–organic frameworks can be overcome by the preparation of nano- and microscale spheres, from metal salts and ditopic ligands, and importantly illustrates the range of species that can be encapsulated within such materials. The synthesis of such metal–organic spheres has been reported by several groups,[4,5] notably by Oh and Mirkin,[4] but the latest study by Maspoch and co-workers demonstrates the full potential of these new materials and in particular reveals their encapsulation properties.

The metal–organic spheres are prepared by the addition of an aqueous solution of a Zn^{II} salt, in this case $Zn(NO_3)_2$, to an ethanolic solution of the bidentate bridging ligand 1,4-bis(imidazol-1-ylmethyl)benzene (bix; Scheme 1). Importantly, the preparation of the spheres differs from that used usually for analogous framework materials, in that the mixture is rapidly stirred for five minutes, which ultimately gives rise to the spherical morphology of the product material. Maspoch and co-workers also elegantly demonstrate that the spheres can be used to encapsulate a range of guests and even multiple species, providing a remarkably adaptive material whose properties can be tuned and even designed.



Scheme 1. Schematic representation of the formation of Zn(bix) spheres and concomitant encapsulation of guest species.

The encapsulation properties, as well as overall size, mark out these metal–organic spheres from other, seemingly related, metal–organic polyhedra that can be constructed from small numbers of metal cations and bridging ligands. Extensive studies of such compounds have been developed over a number of years[6] but these polyhedra typically have dimensions of a few nanometers and can only encapsulate individual or small numbers of guest molecules. The metal–organic spheres reported by Maspoch and co-workers range in size from about 100 nm to over 1 μm (Figure 1), orders of magnitude greater than metal–organic polyhedra, and significantly smaller than crystalline samples of analogous framework materials.

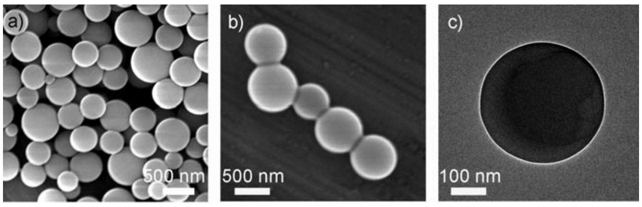


Figure 1. a, b) SEM micrographs of Zn(bix) spheres and c) high resolution TEM image of an individual sphere.

Owing to the dimensions of the metal–organic spheres, the resultant materials can encapsulate many guests and even combinations of guest species. Maspoch and co-workers demonstrate the encapsulation of 10 nm iron oxide nanoparticles, fluorescent organic dyes (fluorescein and Rhodamine B), and luminescent CdSe/ZnS quantum dots. The guests can be readily encapsulated by simply adding them

---

[*] Prof. Dr. N. R. Champness
School of Chemistry, University of Nottingham
University Park, Nottingham, NG72RD (UK)
Fax: (+44)115-951-3563
E-mail: Neil.Champness@nottingham.ac.uk

to a solution of the bix ligand prior to addition of the Zn^{II} salt that leads to the formation of the spheres.

Interestingly, both spheres and guests maintain their physical properties following encapsulation. The Zn(bix) spheres exhibit strong blue fluorescence and this property is maintained even when guest species are encapsulated within the sphere. Thus, when iron oxide nanoparticles are encapsulated within Zn(bix) spheres they maintain their magnetic properties and the resulting nanoparticle-impregnated spheres display both Zn(bix)-based fluorescence and iron oxide-based magnetism. Similarly, spheres that have encapsulated fluorescent guest molecules display the fluorescence of both the Zn(bix) sphere and the guest species (Figure 2). Thus, Zn(bix) spheres with encapsulated fluorescein display both blue and green fluorescence. The encapsulation properties can even be extended to entrap two different species such that metal–organic spheres containing entrapped quantum dots and fluorescein can be prepared and display the inherent fluorescent properties of all three components, Zn(bix), quantum dots, and fluorescein, emitting in the blue, red, and green regions of the spectrum. The combination of the properties of the metal–organic sphere host with those of the guest species makes this an ideal and relatively facile approach to making multifunctional materials.

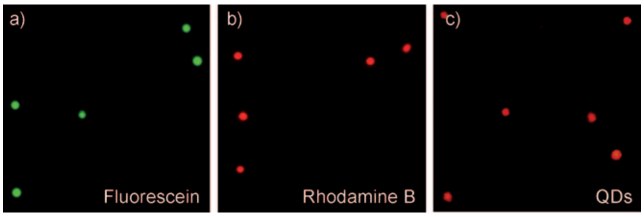


Figure 2. Fluorescence optical microscope images of Zn(bix) spheres encapsulating fluorescent guest molecules (fluorescein, rhodamine B) or quantum dots.

So what implications will these species have for multifunctional materials? To answer this question, one only has to consider the possible combinations of components, or building blocks, which can be exploited in such systems. Not only can the metal salt be varied, but an extremely diverse array of ligands can be exploited in the preparation of the metal–organic spheres. As has been developed with metal–organic frameworks over recent years,[2] the breadth of possibilities for building-block combinations is enormous. Similarly, if one considers the range of possible guest species that could be encapsulated within such spheres, the full range of possibilities becomes apparent. Indeed, the work of Maspoch and co-workers demonstrates the entrapment of a range of chemically distinct species, from inorganic iron oxide nanoparticles and quantum dots to organic dyes, such as fluorescein. Although not all combinations will be successful it is fair to consider that many promising multifunctional materials can be targeted using this approach. The results reported by Maspoch and co-workers will certainly stimulate the imagination of many researchers and we can look forward to many fascinating materials emerging from this field of research.

---

[1] W. J. Peard, R. T. Pflaum, *J. Am. Chem. Soc.* **1958**, *80*, 1593; F. W. Knobloch, W. H. Rauscher, *J. Polym. Sci.* **1959**, *38*, 261.

[2] a) X. Lin, J. Jia, X. Zhao, K. M. Thomas, A. J. Blake, G. S. Walker, N. R. Champness, P. Hubberstey, M. Schröder, *Angew. Chem.* **2006**, *118*, 7518–7524; *Angew. Chem. Int. Ed.* **2006**, *45*, 7358–7364; b) N. R. Champness, *Dalton Trans.* **2006**, 877–880; c) S. K. Ghosh, W. Kaneko, D. Kiriya, M. Ohba, S. Kitagawa, *Angew. Chem.* **2008**, *120*, 8975–8979; *Angew. Chem. Int. Ed.* **2008**, *47*, 8843–8847; d) A. D. Burrows, C. G. Frost, M. F. Mahon, C. Richardson, *Angew. Chem.* **2008**, *120*, 8610–8614; *Angew. Chem. Int. Ed.* **2008**, *47*, 8482–8486.

[3] I. Imaz, J. Hernando, D. Ruiz-Molina, D. Maspoch, *Angew. Chem.* **2009**, *121*, 2361–2365; *Angew. Chem. Int. Ed.* **2009**, *48*, 2325–2329.

[4] M. Oh, C. A. Mirkin, *Nature* **2005**, *438*, 651–654.

[5] a) I. Imaz, D. Maspoch, C. Rodriguez-Blanco, J. M. Perez-Falcon, J. Campo, D. Ruiz-Molina, *Angew. Chem.* **2008**, *120*, 1883–1886; *Angew. Chem. Int. Ed.* **2008**, *47*, 1857–1860; b) X. Sun, S. Dong, E. Wang, *J. Am. Chem. Soc.* **2005**, *127*, 13102–13103.

[6] a) K. Suzuki, J. Iida, S. Sato, M. Kawano, M. Fujita, *Angew. Chem.* **2008**, *120*, 5864–5866; *Angew. Chem. Int. Ed.* **2008**, *47*, 5780–5782; b) S. M. Biros, R. M. Yeh, K. N. Raymond, *Angew. Chem.* **2008**, *120*, 6151–6153; *Angew. Chem. Int. Ed.* **2008**, *47*, 6062–6064; c) D. J. Tranchemontagne, Z. Ni, M. O'Keeffe, O. M. Yaghi, *Angew. Chem.* **2008**, *120*, 5214–5225; *Angew. Chem. Int. Ed.* **2008**, *47*, 5136–5147.