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Box-like gel capsule from heterostructure based on a core-shell MOF as template of crystal crosslinking

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New polymer capsules (PCs) were obtained using a crystal crosslinking (CC) method on core-shell MOFs crystals. The latter are based on the epitaxial growth of two isostructural coordination polymers that are then selectively crosslinked. Decomposition of the non-reticulated phase leads to new PC, possessing well-defined hollow cubic shape reflecting the heterostructure of the template.

Polymer capsules (PCs) consisting of a polymer shell and internal hollow core are promising for new drug delivery system, imaging, soundproof materials etc.¹ Conventionally, PCs are produced by several techniques such as emulsion polymerization,² seed polymerization,³ and suspension polymerization.⁴ In most cases, templates are used for building the hollow structure. For instance, Asher *et al.* reported the preparation of PCs using silica particles as template.^{3b} Alternatively, Okubo *et al.* have achieved PCs polymerization in a suspension,^{4a} using immiscible droplets behaving as template. For these techniques, polymerization of organic monomers or linear chains takes place at the surface of the used templates. Subsequently, removal of the templates leads to hollow polymeric materials. Since the size and shape of thus formed PCs reflect those of templates, the morphology of the templates plays a key role in the control of both size and shape of the resultant PCs. Previously described methodologies produce mono-dispersed PCs with imprinted size of the template.

Although controlling the shape of vesicular assemblies is of high interest, the preparation of PCs with well-defined polyhedral shape still remains a challenge.⁵ Indeed, almost all reported PCs display spherical or irregular shapes. PCs with controlled shape such as cubic or rectangular box are extremely rare: for example, some polyhedral polymer particles were prepared from polyhedral inorganic crystals as template,

however, the observed shape is not reproducible,⁶ or cubic particles building a close-packed “super crystal” were obtained, some of them exhibiting unique optical property due to their dense arrangement.⁷ In the present work, we report an unprecedented strategy for the preparation of PCs adopting a cubic shape and presenting cubic cavities.

Recently, we have reported a new method for the preparation of cubic robust polymeric shell based on crystal crosslinking (CC).⁸ Other groups have also used this CC approach for surface modification.⁹ Using a typical porous molecular crystal, *i.e.* metal-organic frameworks (MOFs),¹⁰ as template, applying the CC method, polymeric gels with ordered and reproducible shapes have been prepared. The CC method is based on a post-synthetic modification of MOF,¹¹ where azido groups, located on the walls of the MOF, are reticulated by multi-propargyl crosslinkers.⁸ The shape of thus formed polymeric gel perfectly reflects the shape of the initial MOF crystal. Thus, this methodology allows the control of the shape and size of polymeric gels, reflecting the well-defined polyhedral shape of the initial MOF crystal. Specifically, cubic polymeric gels were synthesized starting from crystals of MOF offering a cubic shape.⁸ We prepared several different polyhedral-shape polymeric gels, that all were homogeneously structured however with a limited variety of topologies. For example, preparing more complex heterostructures such as capsules was not possible using CC method. Indeed, Wöll and coworkers reported the preparation of a PC by using CC method for an MOF grown on magnetic nanoparticle, while it possessed spherical shape.^{9b} To achieve the goal for more complex heterostructures, another strategy should be developed. For this reason, we decided to use core-shell crystals, since several examples of molecular core-shell crystals based on hydrogen bonded networks with different shape have been reported.¹²

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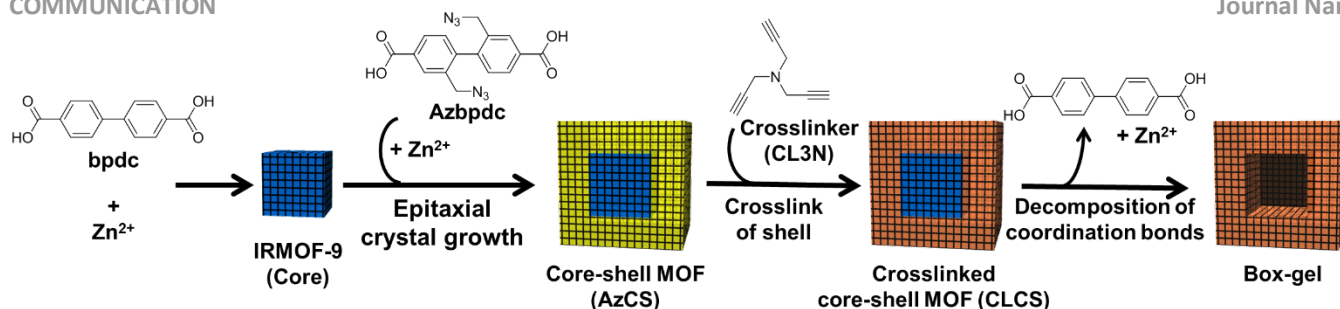


Fig. 1 Preparation of cubically hollowed cubic gels (**Box-gel**) via crosslinking crosslinking of the shell of a core-shell MOF.

In addition, using the Molecular Tectonics approach,¹³ a large variety of molecular core-shell crystals based on the epitaxial growth of *isostructural* (isomorphous and isometric) H-bonded species have been obtained.¹⁴ In such architectures, one or several monocrystalline layers grows epitaxially around a core crystal with defined shape, leading to single crystalline species.

Several generations of core-shell crystals were obtained: generation 1 with only one single crystal-line layer and further generations using a core-shell crystals as seed crystals, leading to 2 or more crystalline layers on the core crystal. Few examples of core-shell crystals based on coordination polymers have also been reported.¹⁵ For example, Matzger *et al.* have reported a cubic core-shell MOF build from IRMOF-3 and MOF-5.¹⁶

In the present contribution, dealing with the design of PCs presenting new shapes, we propose to use the CC method applied to core-shell MOFs. As shown in Fig. 1, we intend to use two different molecular building blocks, leading to two *isostructural* coordination polymers, required for the formation of core-shell MOFs. Post synthetic modification performed on core-shell MOF, based on the click reaction, leads to a single layer (shell layer): crosslinked core-shell (**CLCS**) MOF (Fig. 1). Subsequently, the latter was decomposed, leading exclusively to a polymeric gel-type structure presenting the same complementary shape as the one of the seed crystal (**Box-gel**) (Fig. 1). This approach, including the core-shell MOFs construction, as well as the CC approaches, allows to convert the cubic core-shell MOFs heterostructure into a box-like polymeric gel presenting cubic shape and cubic voids (Fig. 1).

In order to build core-shell MOFs, the used ligand was 4,4'-biphenyldicarboxylic acid (**bpdc**) combined with Zn^{2+} . This forms the colourless core crystal IRMOF-9 (Fig. 2a). The shell was epitaxially grown around the core crystal,¹²⁻¹⁶ using the combination of azido-tagged **bpdc** (**Azbpdc**) and Zn^{2+} cations, which leads to $Zn_4O(Azbpdc)_3$ *isostructural* to IRMOF-9. The epitaxial growth occurs on all faces of IRMOF-9 cubic core crystals (Fig. 2b). For this purpose, **Azbpdc** and zinc nitrate were dissolved in DMF. The mixture was heated at 80 °C for 1 day providing a supersaturated solution of $Zn_4O(Azbpdc)_3$ (see experimental part in ESI). IRMOF-9 core-crystals were immersed in a solution of Az-IRMOF-9 and heated for 2 hours. This stepwise process afforded the core-shell MOF **AzCS**, and also Az-IRMOF-9 single crystals, that were manually separated (Fig. S1). Optical microscopy clearly evidenced the formation of the

core-shell MOF **AzCS** with different contrast, resulting from different refractive indices between core and shell (Fig. 2b). The presence of azido groups was confirmed by FT-IR, exhibiting a stretching band at 2097 cm^{-1} (Fig. 3b and Fig. S2). Furthermore, ¹H-NMR data of core-shell MOF **AzCS** decomposed in a 0.5 M $D_2SO_4/DMSO-d_6$ solution, exhibit both signals corresponding to **Azbpdc** and **bpdc** (Fig. 2c), with a **Azbpdc** to **bpdc** ratio of 1.8 : 1.0 (integral of signals for phenyl protons at 7.37 ppm for **Azbpdc** and at 7.89 ppm for **bpdc**). These results clearly indicate that the core-shell MOF **AzCS** contains both ligands **Azbpdc** and **bpdc**. As already shown,¹²⁻¹⁶ during the epitaxial crystal growth process, the shape of the seed (**Core**) crystal was transferred to the shell (Fig. S3), and the corresponding thickness can be tuned by modifying the synthetic conditions: size of core crystals, temperature, time, etc. Additional duration of crystallization of the shell increases the shell thickness (Fig. S4).

The core-shell MOF **AzCS** thus obtained was crosslinked using tripropargylamine (**CL3N**) as crosslinker, through a click reaction.⁸ Since azido groups were located on the shell of **AzCS**, this allowed the selective crosslinking of the shell without any change of the cubic shape of the core-shell MOF **AzCS** (Fig. 3a). The colour change observed for **AzCS** may be attributed to the presence of residual Cu^+ cations used as catalyst for crosslinking click reaction. This step leads to a crosslinked core-shell MOF (**CLCS**). FT-IR measurements during the crosslinking process show the disappearance of the azide stretching band at 2097 cm^{-1} (Fig. 3b), indicating the completion of the crosslinking process.

For core-shell MOF **AzCS** and **CLCS**, good matches were found between the recorded and simulated XRPD patterns using the single-crystal data measured for IRMOF-9, and az-IRMOF-9 (Fig. S5 and S6, Table S1), indicating the presence of a single phase in each layer. These structural results clearly evidenced that the crystal structure was retained during crosslinking of core-shell MOF **AzCS**.

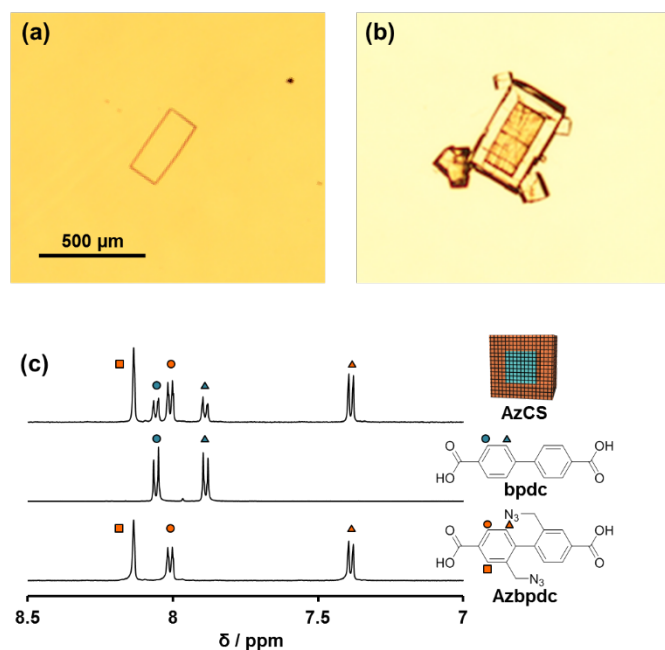


Fig. 2 Optical microscopy images of (a) IRMOF-9 seed crystal and (b) core-shell MOF AzCS. (c) ^1H NMR spectra of core-shell MOF AzCS decomposed in a 0.5 M $\text{D}_2\text{SO}_4/\text{DMSO}-d_6$ solution.

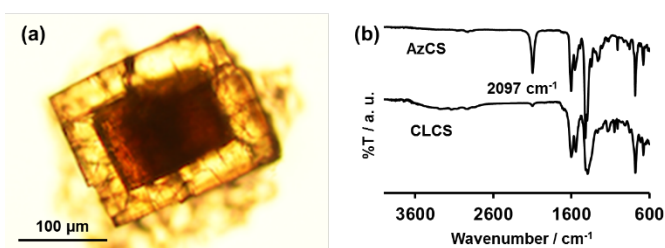


Fig. 3 (a) Optical microscopy image of CLCS. (b) FT-IR spectra of core-shell MOF AzCS and CLCS.

The last step for the formation of the box-like polymeric gel is based on the disruption of coordination bonds in **CLCS** core and shell phases, by immersion in a 0.5 M H_2SO_4 / DMSO solution (see experimental part in ESI). Optical microscopy evidenced that **CLCS** were gradually expanding their size during the process together with a change of colour (Fig. 4). However, the cubic shape was retained during the transformation, and, as expected, a hollow cubic material (**Box-gel**) were observed with empty spaces located in the core formed by IRMOF-9 seed-crystals. ^1H -NMR data performed in solution during the decomposition process confirmed the release of **bpdc** ligand, whereas **Azbpdc** ligand remained in the polymeric shell (Fig. S7). FT-IR measurements after decomposition of **CLCS** show the disappearance of C=O stretching band at 1392 cm^{-1} , indicating the disruption of coordination bonds between carboxylate and Zn^{2+} cations. Additional new signals appeared at 1705 cm^{-1} , attributed to C=O stretching bands of protonated carboxylic groups for reticulated Az-IRMOF-9, which also accounts for the release of Zn^{2+} cations (Fig. S2).

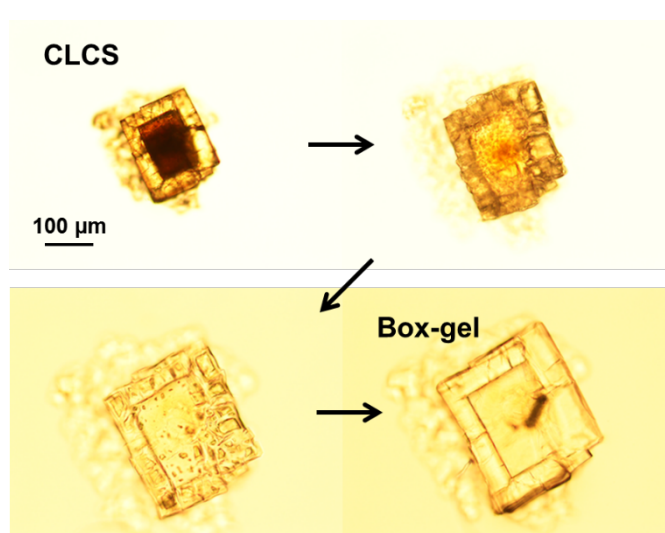


Fig. 4 Picture showing the evolution of the **CLCS** decomposition process by treatment with a 0.5 M H_2SO_4 / DMSO solution (see experimental part in ESI).

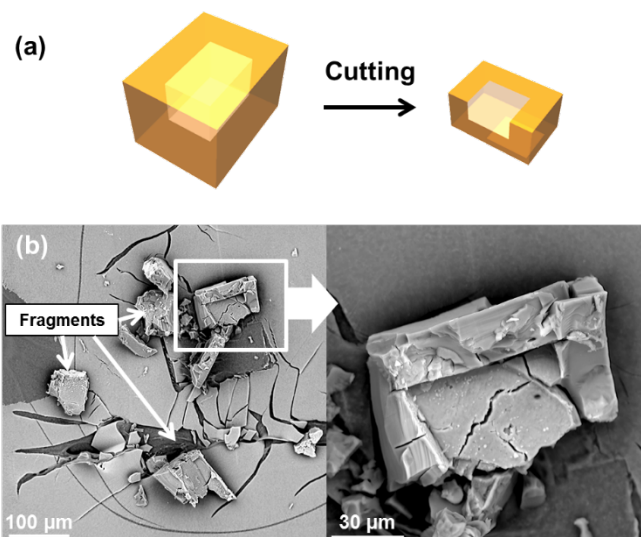


Fig. 5 SEM images of sliced **Box-gel**. (a) Slicing procedure (b) Cubically edged hollow observed inside the polymeric shell.

SEM observation was performed on sliced formed **Box-gel** as shown in Fig. 5a. Hollowed architectures presenting a cubic shell were indeed observed (Fig 5b). The thickness of the shell was estimated to be ca. $20\text{ }\mu\text{m}$ and a side of hollow to ca. $60\text{ }\mu\text{m}$. These results are in accordance with the microscopic picture of the shrunk **Box-gel** (Fig. S8). This direct observation proved that **Box-gel** indeed presents cubically hollowed cubic polymer shell. The thick shell effectively provided a rational sealability of **Box-gel** despite the observed cracks in Fig. 4, evidenced by a penetration test using fluorescent microbeads (Fig. S9).

In this investigation, using a crystal crosslinking (CC) method as post-synthetic modification on a core-shell crystal of MOF, we have demonstrated an original and unprecedented preparation of a new **Box-gel** architecture presenting a cubic

outer shape and an empty cubic inner shape. The well-defined cubic shape **Box-gel** architecture can be regarded as a unique Polymer Capsules (PC). The strategy used for the formation of **Box-gel** is a novel application of core-shell MOFs and it can be applied to a wide range of sizes of core-shell crystals, leading to a variety of **Box-gels**. Recently many attractive MOFs have been reported such as nano-sized MOF or monodispersed octahedral MOF¹⁷ that could be used for the formation of **Box-gels** of different sizes and shapes. Our approach could lead to a series of unique PCs such as nano PCs with octahedral shape, for example.

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