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Morphogenesis of polyoxometalate cluster-based materials to microtubular network architectures†

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Pressed pellets of polyoxometalate (POM)-based materials are shown to undergo morphogenesis to produce microtubular network architectures without the need for a large single crystal precursor. The compression of the POM material into a pellet lowers the solubility sufficiently to allow tube initiation and growth from POMs that would otherwise be too soluble in their native crystalline state, thus yielding hollow, highly controllable, tubes of diameter 10–100 μm .

Polyoxometalates (POMs) represent an ever-growing class of structurally well-defined clusters, with applications in molecular magnetism, catalysis and even medicine.^{1–7} As highly anionic molecules, they can interact in the solid state with alkali metals or organic cations to form a wide range of micron or even nano-scale systems.⁸ The overwhelming majority of such architectures are made by co-crystallization of a cation with the POM, leading to a well-defined, thermodynamically stable product.⁹ In contrast, it has been shown, by us, that a suitable POM species can form micron scale tubes¹⁰ upon co-precipitation with an organic cation in aqueous solution while the whole system is maintained in a far-from-equilibrium state *via* a continuous osmotic pumping mechanism, see Fig. 1.^{11–15}

The assembly process relies upon the slow dissolution of a sparingly soluble crystalline POM species into a solution containing a sufficiently high concentration of the organic cations. A semi-permeable membrane is formed around the crystal by the precipitation of the insoluble aggregate that results from ion exchange of the anionic POM fragments and the organic cations. As the crystal continues to dissolve, water is drawn in *via* osmosis and the pressure across the membrane increases. This leads eventually to a rupture of the membrane and a plume of dissolved POM material is expelled through the aperture, whereupon further aggregation and precipitation with cations from solution leads to an extended hollow structure, which continues to grow until the POM is exhausted or another rupture allows the pressure to release elsewhere (Fig. 1).¹⁶ In order for tube growth to initiate, the initially

formed membrane must completely encapsulate the POM crystal, so that the osmotic pressure that drives the growth can develop. If the POM is too soluble, the rate of dissolution will overtake the aggregation and the closed membrane will not form, and until now, it was thought that the growth of the tubular architectures was only possible if crystalline POM precursors were utilized.

Herein, we show that it is possible to substitute large single crystals of the POM-based materials with compacted crystalline and non-crystalline precursors, thereby allowing the extension of this morphological transformation beyond the use of large single crystals. This is achieved by pressing a powder of the POM material into a pellet, see Fig. 2. Furthermore, this allows us to grow tubes from POM materials that are otherwise too soluble in their native crystalline form.

To the best of our knowledge, this is the first time in such chemistry that micron-sized tubular structures have been synthesized starting from a pressed solid thereby fundamentally extending the utility and application of this phenomenon first presented by us in 2009.⁸ The POMs used in this study were carefully chosen from the literature to ensure that they would include variety in structure, charge and composition, to underline that the phenomenon of tube growth can be generalized to all POM species, given the right solubility conditions (Fig. 3). Particular attention was given to the species $[\text{H}_3\text{PW}_{12}\text{O}_{40}]$ (**D**)

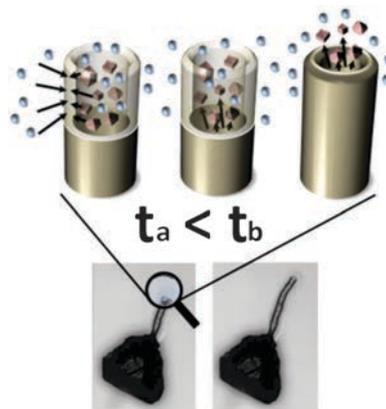


Fig. 1 Photographs of a tube growing from a crystal of a POM with a graphical representation of the growing tube (cations: blue spheres, POMs: pink polyhedra). T_a and t_b stand for two different times of the growth process with $t_a < t_b$.

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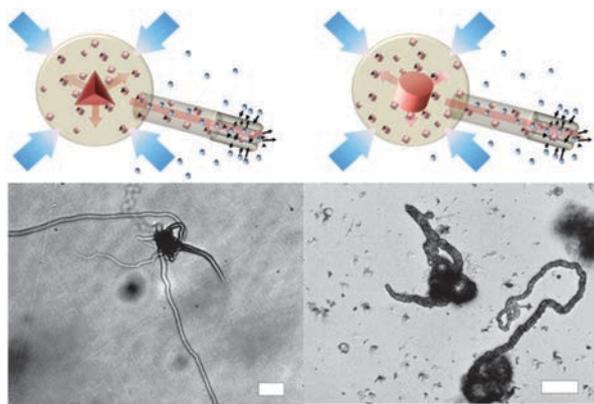


Fig. 2 Scheme highlighting the mechanisms of formation involved in microtube growth based on POM crystals (left) or pressed pellets (right). The tubular structures formed are amorphous, hollow and with a range of diameters between 2–100 μm . Scale bars are 50 μm .

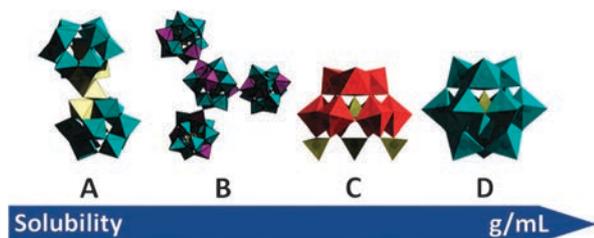


Fig. 3 Structural representation of the POM species used in this study (associated cations are not shown). $\text{Na}_4\text{H}_3(\text{C}_6\text{H}_{11}\text{N}_2)_{13}[(\text{SiW}_{10}\text{O}_{36})_2(\text{Ni}_4\text{O}_6)] \cdot 12\text{H}_2\text{O}$ (A), $(\text{C}_4\text{H}_{10}\text{NO})_{40}[\text{W}_{72}\text{Mn}_{12}\text{O}_{268}\text{Si}_7] \cdot 48\text{H}_2\text{O}$ (B), $\text{Na}_{15}[(\text{PO}_2)_3\text{PNb}_9\text{O}_{34}]$ (C), $[\text{H}_3\text{PW}_{12}\text{O}_{40}]$ (D). Polyhedra are colored according to the nature of the central atom. Teal: W, red: Nb, purple: Mn, yellow: Ni, ochre: P, gold: Si. The calculated solubility (in g mL^{-1}) of the different species are A (0.016), B (0.026), C (0.029) and D (0.19), with experimental details discussed in the ESI†

and $\text{Na}_{15}[(\text{PO}_2)_3\text{PNb}_9\text{O}_{34}]$ (C) as they are known to be too soluble in their crystalline form to grow tubes.¹⁶

It is interesting to note that there is little or no difference in solubility between a pure POM starting material in crystalline form and the same POM in the shape of a hard pellet from pressed powder. Thus, there is no immediate interest in pressing pellets of pure POM materials, other than to confirm that tube growth still occurs for materials of sufficiently low solubility. However, if the soluble POM is mixed with another less soluble additive, which is innocent towards cation exchange reactions, the resulting pellet of this mixture can grow tubes. The additive acts as a retardant to POM dissolution and reduces the rate of POM release sufficiently to allow initial membrane formation. Starch (*amylum*) is a cheap, slightly water soluble, non-aromatic and neutral molecule, which does not react with POMs to form microtubes. It has a solubility of 0.04 g mL^{-1} in water (20 °C), and, as such, is a perfect candidate to be mixed with POMs, allowing the mixed pellet to be sufficiently insoluble to grow tubes. Another route that has been considered involved the use of bulky molecules such as *tert*-butyl ammonium (TBA) to act as a thickener and retardant in the pellet. Association of such molecules as counter ions in POM chemistry has been known for a long time, imparting

excellent organic solubility of these molecules whilst making them poorly soluble in water.¹⁷ Tube growth was indeed observed with such pellets, but control experiments show that TBA is not innocent towards the reaction as it can act as the required cation to form microtubes with dissolved POMs instead of the desired cation source. In this particular case, a pellet made of a 1 : 1 ratio between POM and TBA can be seen as a narrower example of the “seed experiment” described by us in previous work.¹⁶

The proportion of POM and additive in the pellet is critical in determining the success of tube growth. Pellets with a POM:starch ratio of 1 : 2, 1 : 1 and 2 : 1 (by mass) were produced on a standard IR pellet press, with amorphous solids carefully ground, mixed and compressed three times at the pressure of 10000 Kg cm^{-2} to ensure maximum homogeneity and minimum residual hydration. Small fragments of the resulting pellet were then immersed in aqueous solutions of the organic molecule (methyl-dihydrophenanthridinium bromide; Me-DIP Br) at different concentrations ($2 \times 10^{-2} - 2.5 \times 10^{-3} \text{ mol L}^{-1}$). These conditions and concentrations are known to be suitable from previous crystal-based tube growth experiments.⁸ Results of the pellet experiments are summarized below in Table 1.

Several conclusions regarding tube formation can be extracted from the table above for POMs that were too soluble for tube growth in the pure form (C). Pellets made of 2 : 1 POM:starch were also too soluble, and no tube growth was observed. In these cases, the solid was rapidly dissolved into the aqueous solution, but the membrane formation did occur.¹⁶ Here, the pellet was not encapsulated by a closed shell and so tube initiation was not observed. On the other hand, pellets made with a 1 : 2 ratio of POM:starch also did not form tubes at low concentrations, but grew poorly resolved tubes only in a concentrated solution of DIP-Me Br. In this case, the pellet seemed to not contain/release enough active material to properly form an encapsulating membrane (see ESI† for pictures), although the release rate for the POM was certainly sufficiently reduced to be within the thresholds of tube growth, only pellets with the POM:starch ratios of 1 : 1 were able to show spatially resolved tube growth. A carefully ground mixture composed of equal masses of POM and starch is therefore believed to be the best compromise between the requirements of decreasing the overall rate of release for the POM compound while still delivering sufficient active material to form the initial membrane.

Table 1 Summary of the results of tube growth experiments with different pellet compositions *versus* Me-DIP Br concentration. Red indicates absence of tube growth while green shows when it occurs. Orange indicates growth of poorly resolved tubes (see ESI† for pictures)

	A	B	D		
	1:1 Starch	1:1 Starch	1:1 TBA	1:1 Starch	Pure
Me-DIP Br 2.5 mM	Red	Red	Red	Red	Red
Me-DIP Br 6 mM	TUBES	TUBES	Red	Red	Red
Me-DIP Br 20 mM	TUBES	TUBES	TUBES	Red	Red
	C				
	1:1 TBA	1:2 Starch	1:1 Starch	2:1 Starch	Pure
Me-DIP Br 2.5 mM	Red	Red	Red	Red	Red
Me-DIP Br 6 mM	Red	Red	TUBES	Red	Red
Me-DIP Br 20 mM	TUBES	Red	TUBES	Orange	Orange

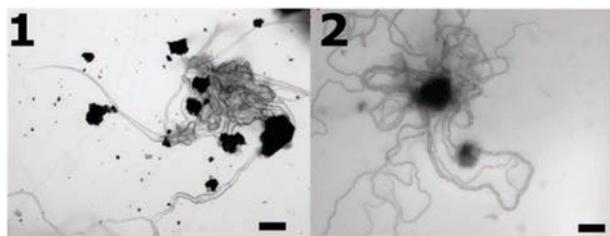


Fig. 4 Tubes grown using a pellet made of 1 : 1 mixture of POM **B** and starch. Scale bar is 50 μm . 1 (left) using crystals ground as source of **B** whereas amorphous powder is used in 2 (right).

Another set of experiments were designed using POM **B**, a material known to be available after synthesis both as single crystals or amorphous powder. Two pellets were pressed, using amorphous or crystalline POM samples, before being immersed in a $2 \times 10^{-2} \text{ mol L}^{-1}$ solution of Me-DIP Br. The tubes obtained in both case were similar in aspect ratio and diameter, suggesting that only the molecular composition of the POM material is relevant to the tube growth, not its original form. This is a particularly useful result for the future construction of POM-tube based devices, since many POM materials might take weeks (or months) to crystallize, while powders can often be obtained immediately after synthesis. Comparative pictures of the tubes formed are shown in Fig. 4.

The rate of growth of tubes from a pellet of POM **A** was recorded in a solution of $2 \times 10^{-2} \text{ mol L}^{-1}$ of $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$. Activation (initiation of tube growth) occurs within a time of 2 min as the pellet is solubilized. The amount of material released is higher than during tube growth based on a single crystal and the speeds of growth recorded were faster ($63.4 \mu\text{m s}^{-1}$ on average compared to $41 \mu\text{m s}^{-1}$), even considering the higher cation concentration in the medium compared to previously described experiments.¹⁶ Another explanation for faster tube growth lies in the fact that POM molecules are less ordered in a pellet rather than in a crystal, and so dissolution of the initial material is easier and occurs faster, releasing more material into solution in a shorter period of time. Complete rate of growth experiments are detailed in the ESI.†

In conclusion, we have shown that microtubes can be easily grown from pellets of powder or mixed materials *via* the same osmotic mechanism observed in crystal-based microtube growth. No critical differences were observed between tubular architectures produced in this way, with respect to those grown from large single crystals, reinforcing the idea that the mechanism involved in both reactions is the same. However, the rate of growth in this new method is significantly higher, partly due to the need of a more concentrated solution of cations. As expected, the solubility (release rate) of the POM is critical in determining whether tube growth will initiate.¹⁰ In addition, this work shows that the solubility of the crystalline POM form is no longer a barrier to growing tubes, as it is possible to obtain tubes from more soluble species simply by mixing with an innocent additive, such as

starch, and pressing a pellet. The role played by the additive is essential as it acts as a dissolution retardant, lowering the overall rate of pellet dissolution sufficiently to bring the rate of POM release within limits for tube growth initiation. The ability to grow tubes from more soluble POMs, or from those that do not crystallize readily, expands the generality of the tube growth phenomenon to all water soluble POM species. Further work will seek to produce new POM-based tubular architectures that show catalytic and other functional properties associated with their precursor materials, and the convenient new growth method described herein will facilitate control and construction of these architectures.

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