Electronic Supplementary Material (ESI) for Chemical Communications

Morphogenesis of polyoxometalate cluster-based materials to microtubular network architectures

Antoine G. Boulay, Geoffrey J. T. Cooper and Leroy Cronin*

WestCHEM, School of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland, UK. Email: Lee.Cronin@glasgow.ac.uk; web: http://www.croninlab.com

Materials

All reagents and chemicals were supplied by Sigma Aldrich Chemical Company Ltd. and Alfa Aesar. Unless stated otherwise, the materials were used without further purification.

Instrumentation

Optical Microscopy: Experiments involving microscopy were conduct at room temperature and under air using plastic well or glass slides with an Olympus IX81 inverse microscope. Snapshots were taken, analysed and processed through the Cell^r Software. Measurements were made directly on the frames using the built-in add-on.

Pellet Press: Pellets were pressed using a 15 ton Specac hydraulic pellet press. 100 mg of product were carefully ground using a mortar and pestle before introducing the powder into the apparatus. The set up was pressed at 10 tons for a minute three times in a row to ensure minimal residual hydration.

Typical tube growth experiment usign a pellet as POM source

Using a pellet of POM pressed according to the method described above, bits of the pellet were carefully chopped off using a scalpel. After deposition on a microscope slide, 0.5 mL of an aqueous solution containing Me-DIP Br (concentration $2x10^{-2}$ $mol.L^{-1}$) was added on top of it and progress was monitored through the micrscope.

Control Experiments: Pellets made of pure POM and pure Starch

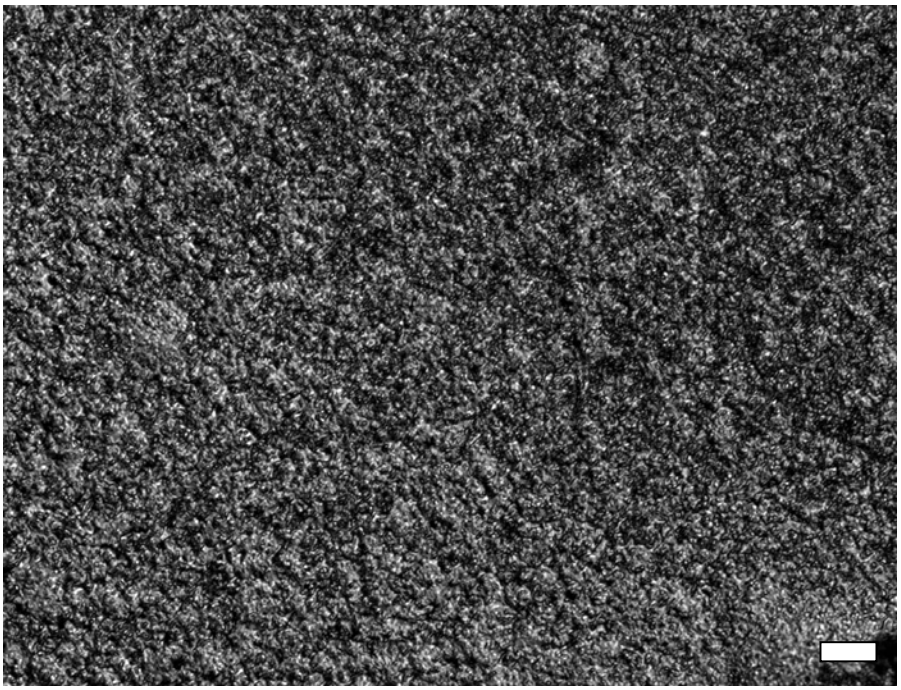

Fig. S1: Dissolution of a pellet made of pure Starch into a solution of Me-DIP Br (concentration $2x10^{-2}$ mol/L). Scalebar is 100 μm long.

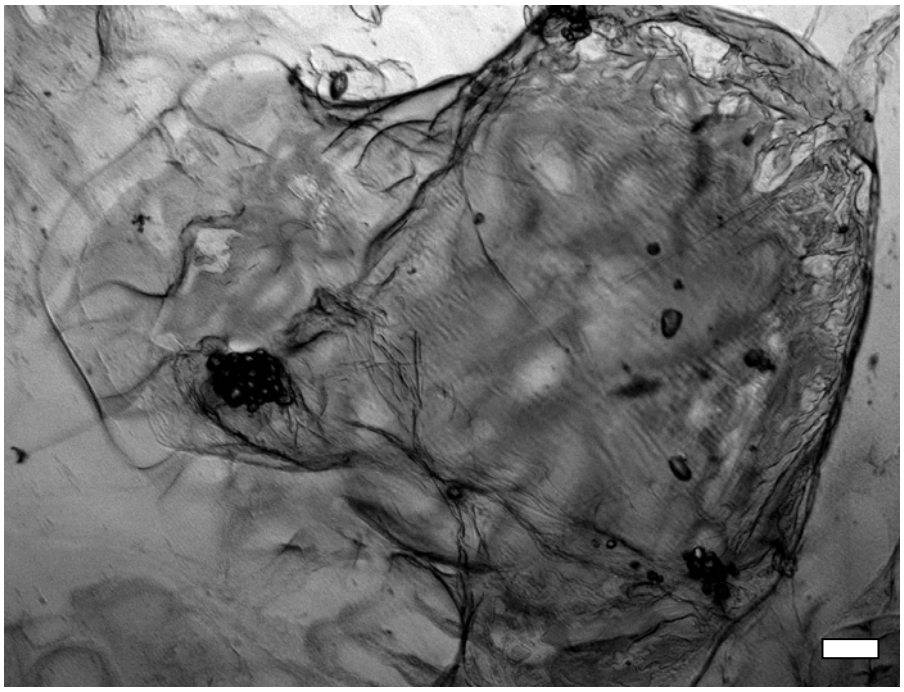

Fig. S2: Dissolution of a pellet made of pure Phosphotungstic acid (**D**) into a solution of Me-DIP Br (concentration $2x10^{-2}$ mol/L). Scalebar is 100 μm long.

Tubes made out of a 1:1 POM:TBA pellet

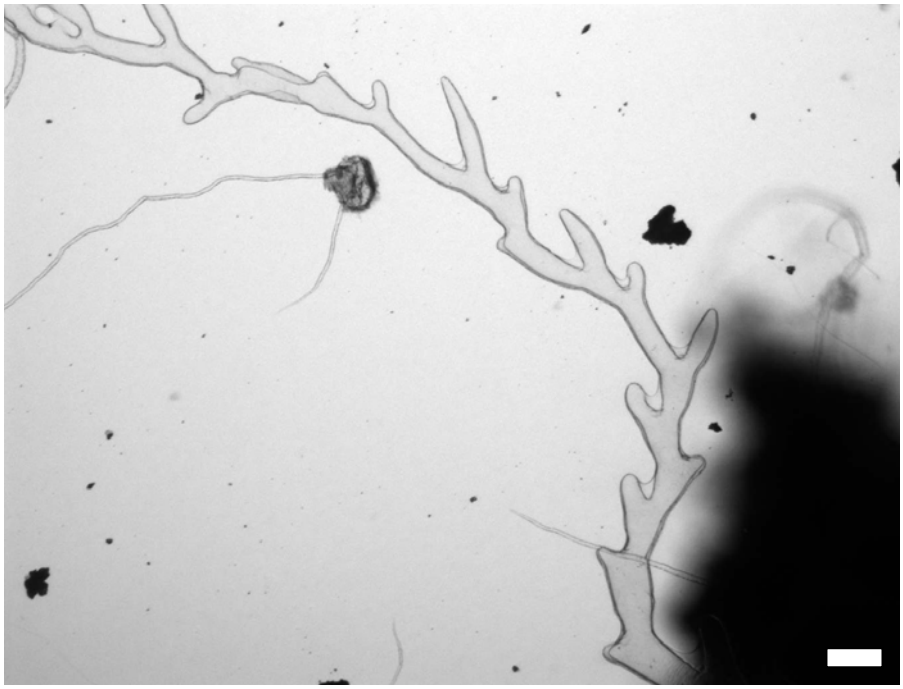

Fig. S3: Dissolution of a pellet made of 1:1 Phosphotungstic acid (**D**):*tert*-butylammonium into a solution of Me-DIP Br (concentration $2x10^{-2}$ mol/L). Scalebar is 100 μm long.

Control experiment: Tubes made out of a 1:1 POM:TBA pellet in pure water

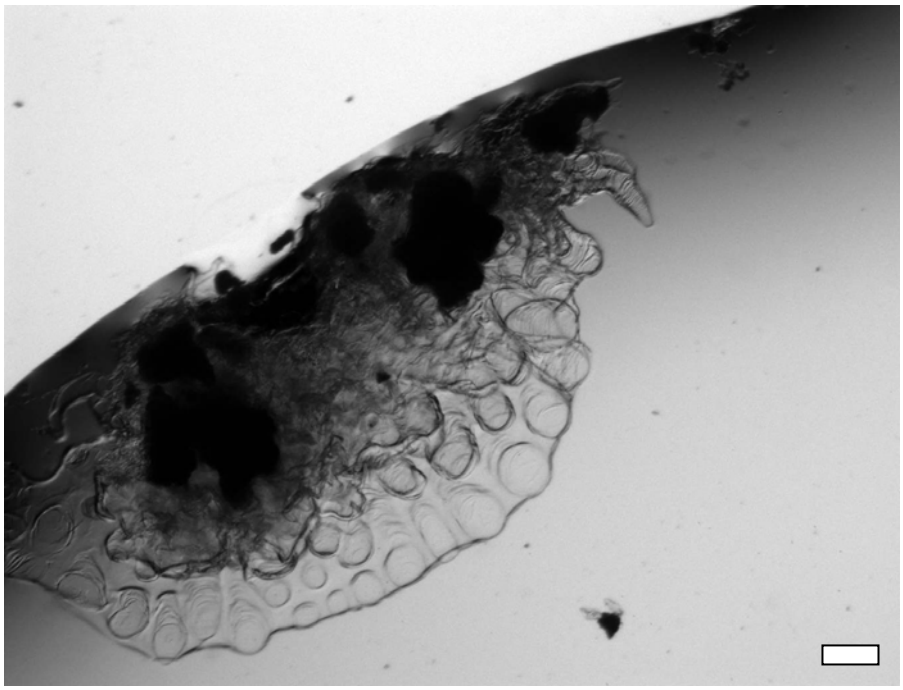

Fig. S4: Dissolution of a pellet made of 1:1 Phosphotungstic acid (**D**): *tert*-butylammonium in pure water. Membrane formation highlights the non-innocence of TBA towards tube growth. Scalebar is 100 μm long.

Tube growth assays at different Cation concentrations

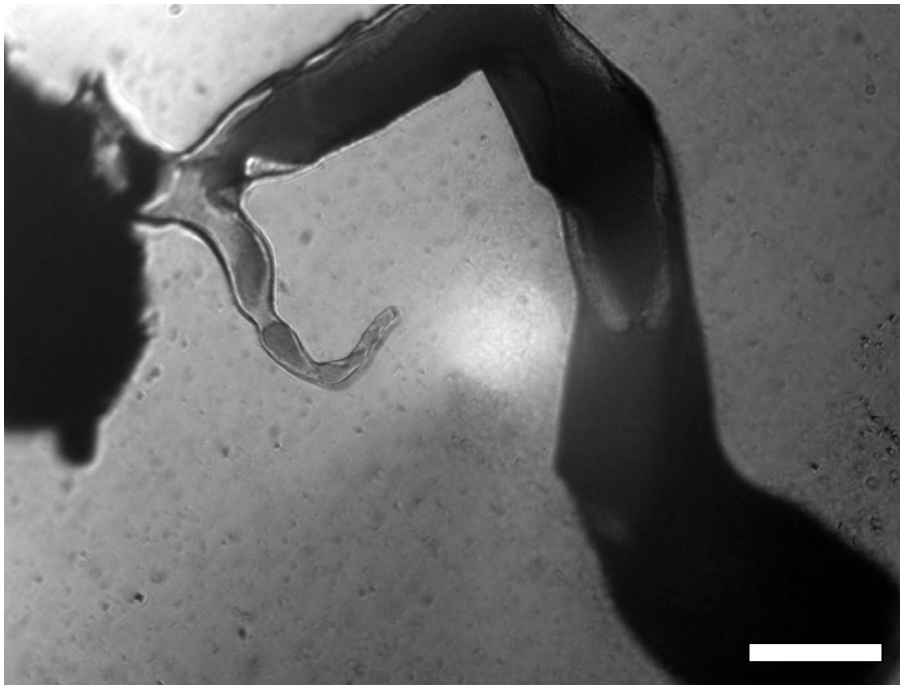

Fig. S5: Dissolution of a pellet made of 1:1 $Na_4H_3(C_6H_{11}N_2)_{13}[(SiW_{10}O_{36})_2(Ni_4O_6)].12H_2O$ (**A**):Starch in a solution of Me-DIP Br (concentration $6x10^{-3}$ mol/L). Scalebar is 50 μm long.

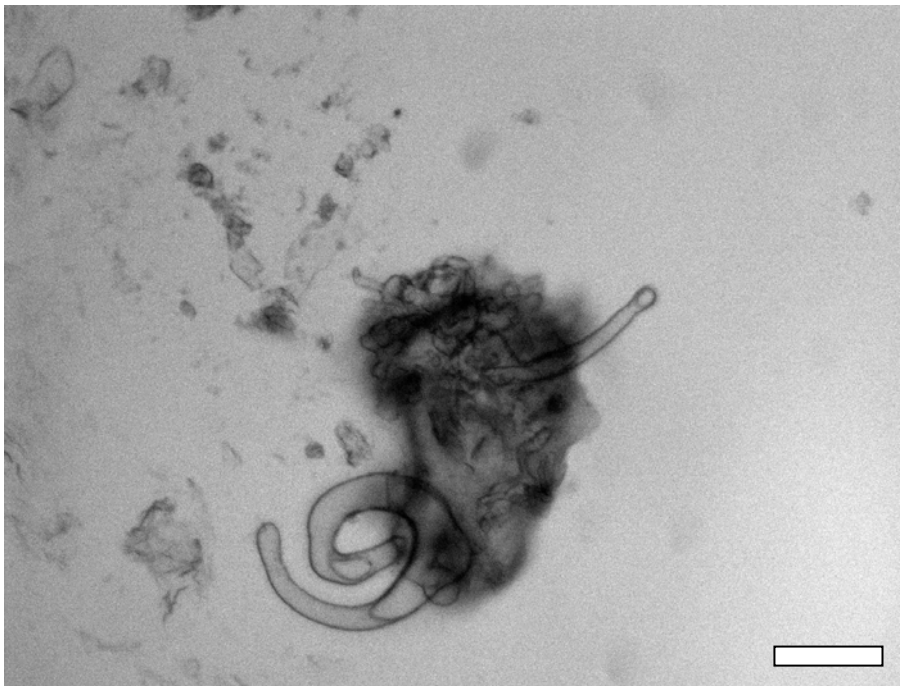

Fig. S6: Dissolution of a pellet made of 1:1 $Na_4H_3(C_6H_{11}N_2)_{13}[(SiW_{10}O_{36})_2(Ni_4O_6)].12H_2O$ (**A**):Starch in a solution of Me-DIP Br (concentration $2x10^{-2}$ mol/L). Scalebar is 100 μm long.

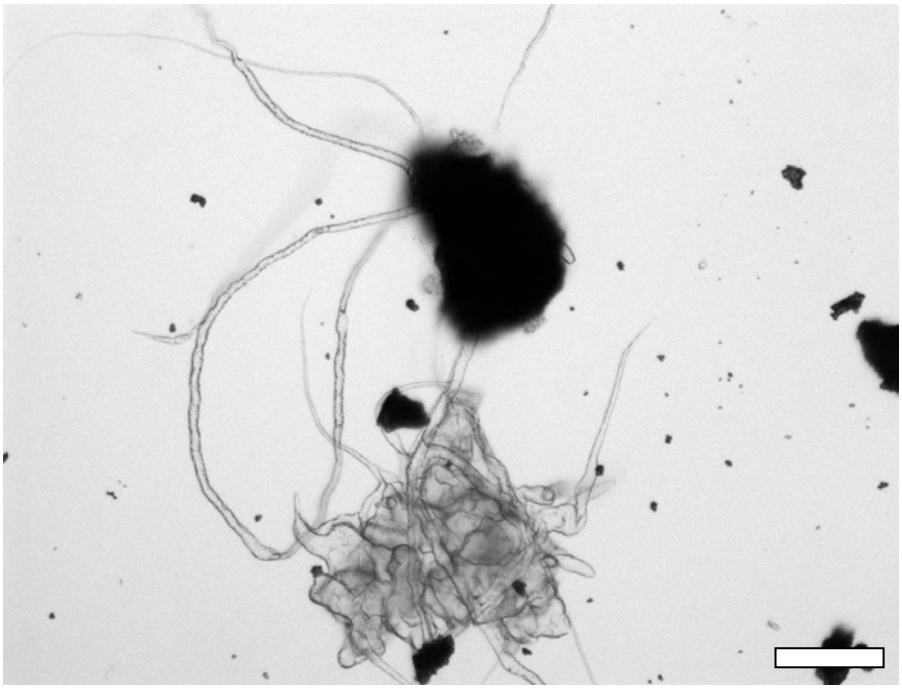

Fig. S7: Dissolution of a pellet made of 1:1 $(C_4H_{10}NO)_{40}[W_{72}Mn_{12}O_{268}Si_7].48H_2O.4(C_4H_9NO)$ (**B**):Starch in a solution of Me-DIP Br (concentration $6x10^{-3}$ mol/L). Scalebar is 200 μm long.

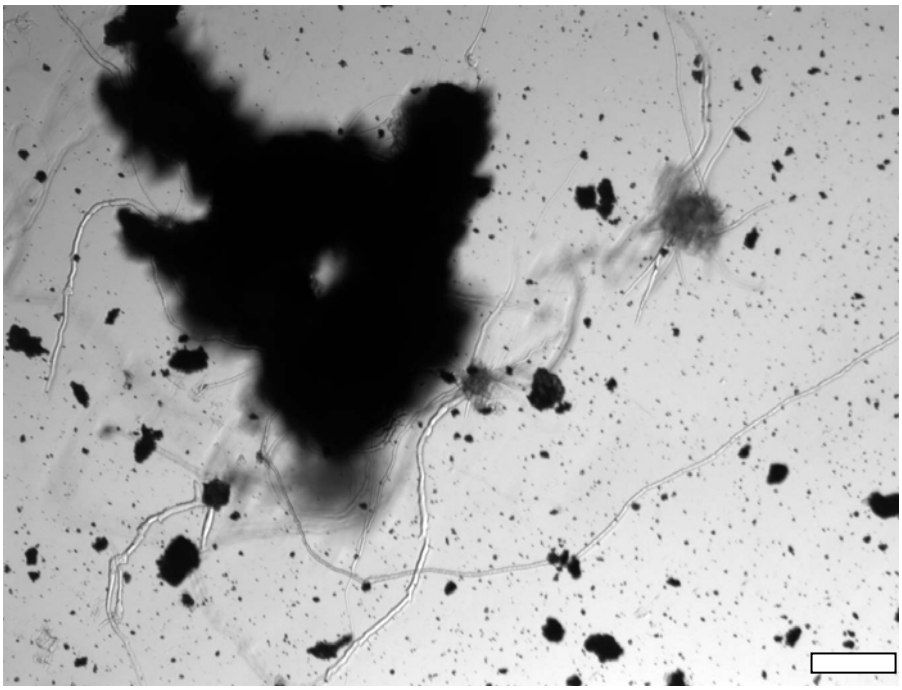

Fig. S8: Dissolution of a pellet made of 1:1 $(C_4H_{10}NO)_{40}[W_{72}Mn_{12}O_{268}Si_7].48H_2O.4(C_4H_9NO)$ (**B**):Starch in a solution of Me-DIP Br (concentration $2x10^{-2}$ mol/L). Scalebar is 50 μm long.

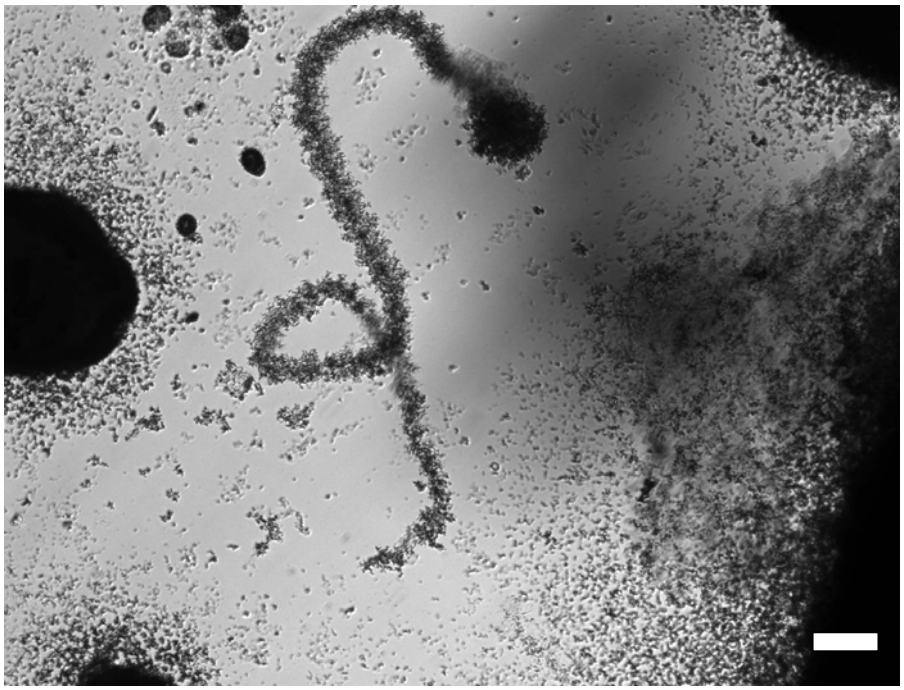

Fig. S9: Dissolution of a pellet made of 1:2 $Na_{15}[(PO_2)_3PNb_9O_{34}]$ (**C**):Starch in a solution of Me-DIP Br (concentration $2x10^{-2}$ mol/L). Scalebar is 50 μm long.

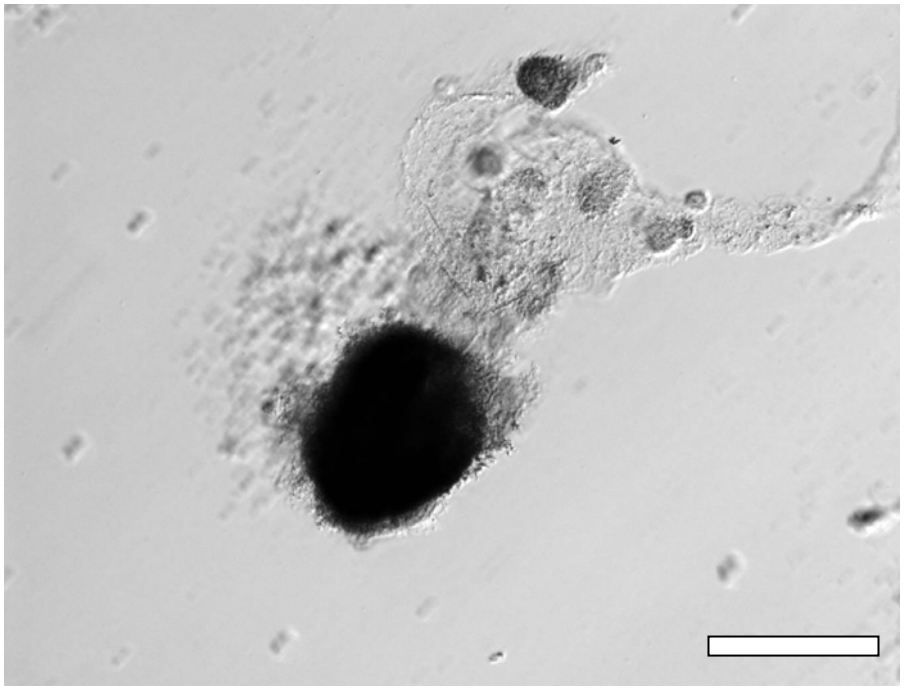

Fig. S10: Dissolution of a pellet made of pure $Na_{15}[(PO_2)_3PNb_9O_{34}]$ (**C**) in a solution of Me-DIP Br (concentration $2x10^{-2}$ mol/L). Scalebar is 50 μm long.

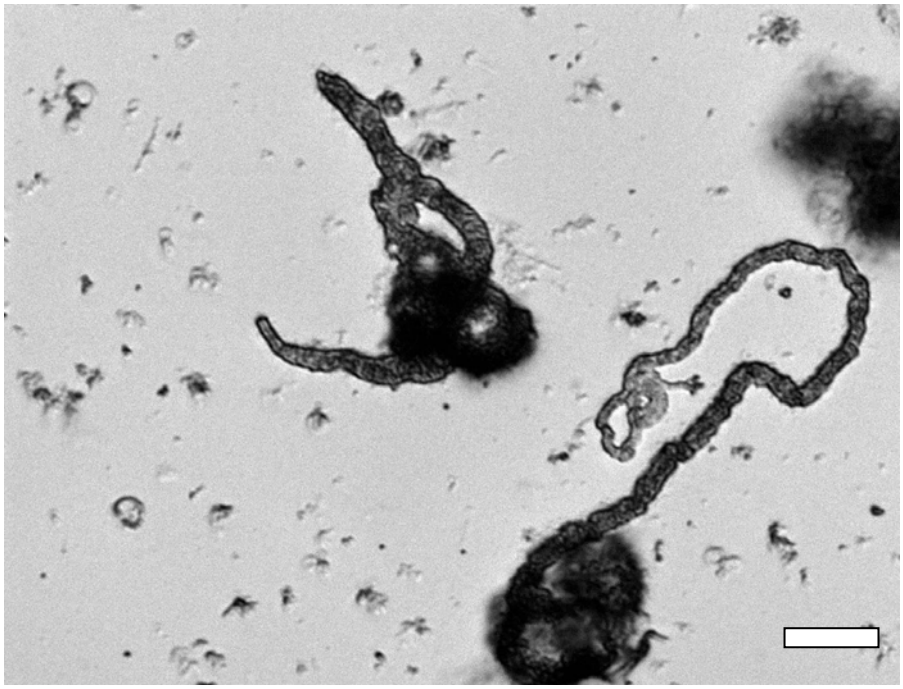

Fig. S11: Dissolution of a pellet made of 1:1 $Na_{15}[(PO_2)_3PNb_9O_{34}]$ (**C**):Starch in a solution of Me-DIP Br (concentration $6x10^{-3}$ mol/L). Scalebar is 50 μm long.

Experiments on pellet precursor: amorphous powder against crystal

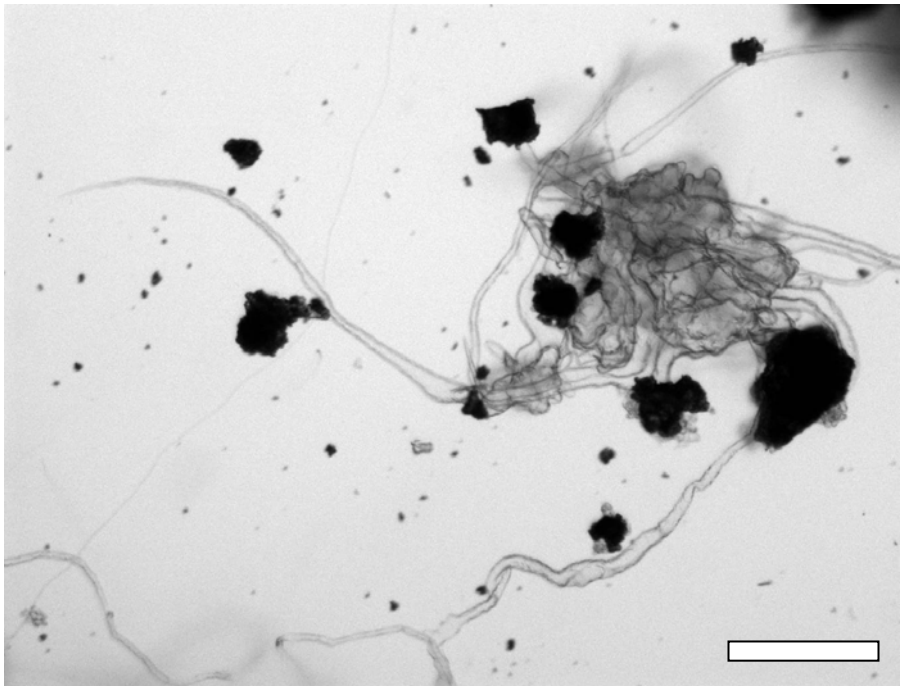

Fig. S12: Dissolution of a pellet made of 1:1 $(C_4H_{10}NO)_{40}[W_{72}Mn_{12}O_{268}Si_7].48H_2O.4(C_4H_9NO)$ (**B**):Starch in a solution of Me-DIP Br (concentration $2x10^{-2}$ mol/L), using ground crystals as the POM precursor. Scalebar is 100 μm long.

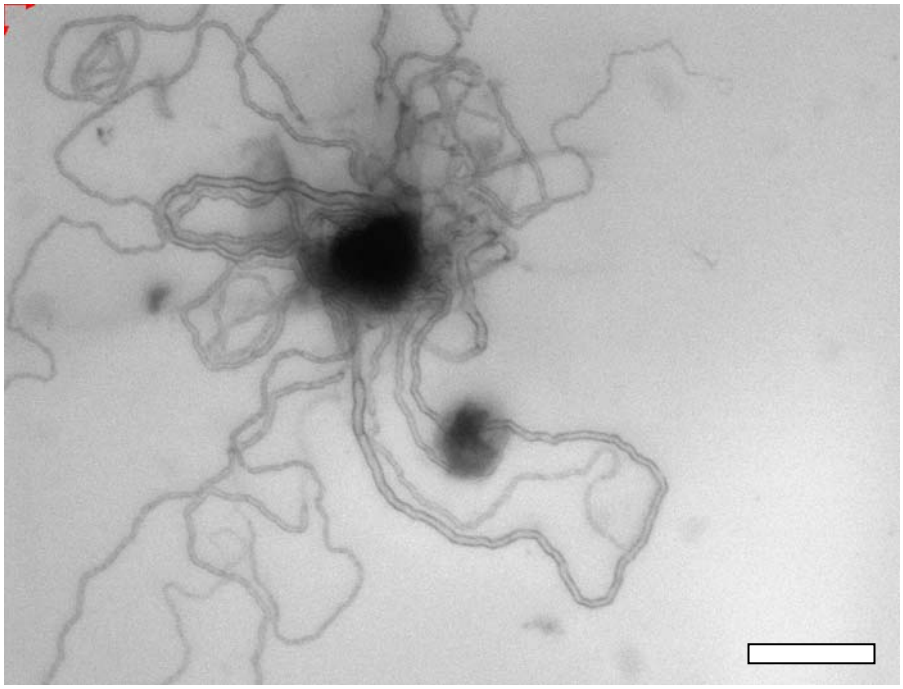

Fig. S13: Dissolution of a pellet made of 1:1 $(C_4H_{10}NO)_{40}[W_{72}Mn_{12}O_{268}Si_7].48H_2O.4(C_4H_9NO)$ (**B**):Starch in a solution of Me-DIP Br (concentration $2x10^{-2}$ mol/L), using amorphous powder as the POM precursor. Scalebar is 50 μm long.

Rate of growth recorded

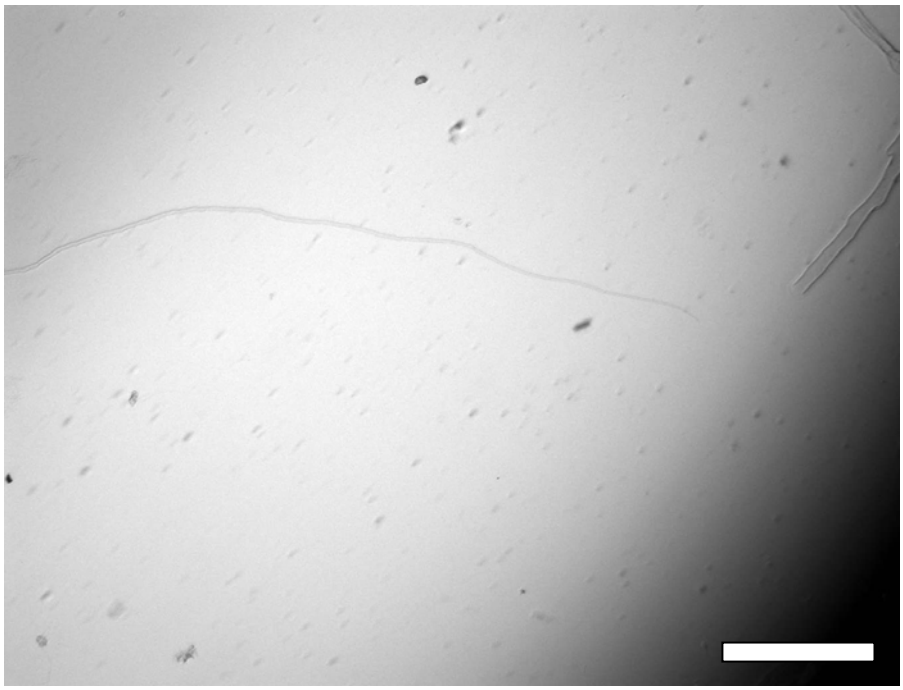

Fig. S14: Dissolution of a pellet made of 1:1 $(C_4H_{10}NO)_{40}[W_{72}Mn_{12}O_{268}Si_7].48H_2O.4(C_4H_9NO)$ (**B**):Starch in a solution of Me-DIP Br (concentration $2x10^{-2}$ mol/L), growth stage 1. Scalebar is 100 μm long.

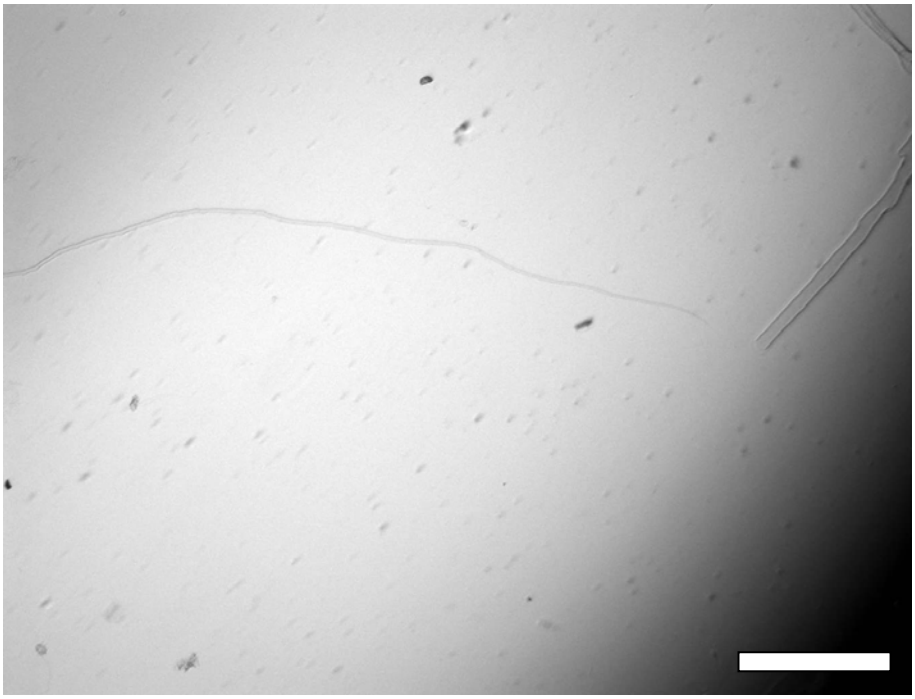

Fig. S15: Dissolution of a pellet made of 1:1 $(C_4H_{10}NO)_{40}[W_{72}Mn_{12}O_{268}Si_7].48H_2O.4(C_4H_9NO)$ (**B**):Starch in a solution of Me-DIP Br (concentration $2x10^{-2}$ mol/L), growth stage 2 (2 sec after stage 1). Scalebar is 100 μm long.

Tube diameter (μm)	Distance (μm)	Rate of growth (μm /s)
20	103	51.5
17	84	42
15	106	53
8	146	73
7.5	180	90
7.2	142	71
6.7	127	63.5

Table S1: Summary of the results obtained by measuring the rate of growth for POM **C** with a $[Ru^{II}(bpy)_3]^{2+}$ solution (concentration of $2x10^{-2}$ mol/L), for a time of 2 sec for each growth. The trend in the results shows larger tubes growing more slowly than smaller ones.

Solubility determination

To determine the solubility of the POM materials, each was dissolved in water to make a saturated solution. Solutions were gently warmed and material added until dissolution was incomplete and some solid remained. These were then stirred overnight and checked, to ensure there was still some solid material, before filtration of the solutions. Portions of each were then transferred to clean, dry, pre-weighed sample vials, which were then placed in a drying oven (at 80 °C) for 24 hours. Samples were weighed after this time and then returned to the oven for 5 hours before being weighed again, to ensure that dehydration was complete. Raw solubility data is shown in Table S2 below.

	Solubility (g/mL water)
A	0.016
B	0.026
C	0.029
D	0.19

Table S2: Averaged solubility data for POMs **A**-**D**.