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Real-Time Direction Control of Self Fabricating Polyoxometalate-Based Microtubes

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Polyoxometalates (POMs), oxo-anion clusters of early transition metals, encompass a range of structure types with a large variety of interesting physical properties from catalysis to electronic bistability.[1] These clusters are particularly appealing for the design of advanced functional materials, since their physical properties can be manipulated across the length scales, on both the molecular level and the nano/microscale. To investigate this, we took our inspiration from nature[2] to see if a stepwise building block approach can be employed to achieve a type of morphogenesis between length scales involving POMs. There are several examples from the broader literature including the transformation of crystalline materials,[3] aggregation of nanoparticles,[5] interfacial self-assembly of polymers[6] and amphiphilic systems.[7]

Recently, a phenomenon has been seen by us[8] where micrometer-scale tubes (1−100 μm diameter) are spontaneously grown from a POM crystal[9] upon addition of an aromatic organic dihydroimidazolphenanthridinium cation (DIP, Figure 1).[10]

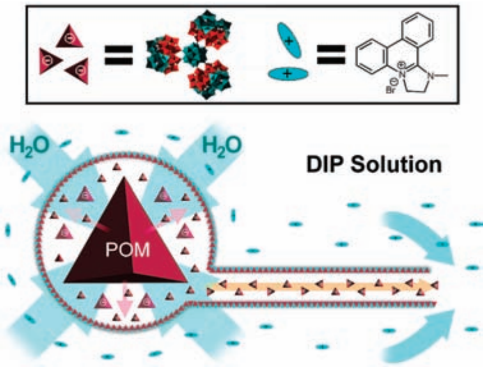

Figure 1. A schematic representation of the formation of micrometer-scale tubular structures from molecular building blocks, anionic POMs, and organic DIP cations. The arrows indicate the flow of DIP solution to the crystal and tube surface and the ingress of water into the membrane.

A semipermeable membrane forms around the crystal, that then begins to grow micrometer scale tubes with large aspect ratios with controllable rates and diameters. The growth process is driven by an osmotic pressure within the membrane sack around the crystal, which ruptures to release the pressure but then extends from the point of rupture, as new POM material combines with the surrounding cations, preventing equilibration of the system. The tubes are comprised of an amorphous mixture of POM-based anions and the organic cations, and initial work has indicated that they are both robust and highly controllable. For instance, the promise is that the tubes could be used either as microreactor components, taking advantage of the catalytic, redox, or optical properties of POMs,[11−13] or as autofabricated interconnects,[14] avoiding the problems of traditional manufacture.[15]

Herein, we describe a process whereby the tube diameter and direction of tube growth can be controlled reliably using concentration changes and applied potential across the bulk sample. This demonstrates that a variety of shapes and motifs can be achieved. Direction control experiments were carried out in flat bottomed round (14 mm diameter) reaction vessels with four perpendicular platinum wire electrodes (i.e., in a square motif) on the base (see Figure S1). Crystals (up to 2 mg, 0.09 mmol) of $(C_4H_{10}NO)_{40}$-$[W_{72}Mn_{12}O_{268}Si_7]\cdot 48H_2O$ (**1**, a POM cluster comprised of an infinite network of Keggin units)[9,16] were added to 0.5 mL of a 20 mM aqueous solution of the polyaromatic organic cation *N*-methyl dihydroimidazolphenanthridinium bromide (**2**, DIP-Me).[10] For the best control accuracy, crystals were introduced to the center of the reaction vessel. The reaction mixture was left undisturbed for several minutes, to allow tube growth to initiate, before further experiments were carried out.

To achieve direction control, a potential difference of 9 V was applied across opposite pairs of electrodes resulting in localized heating and thus, bulk flow of the solvent through convection. Solvent flow has been previously demonstrated to influence tube growth direction, and this overrides any tendency for the anionic POM material to undergo electrophoresis. In an electrophoresis mechanism, the growing microtubes would be expected to turn toward the anode, while in this case they are always observed to grow toward the cathode. Furthermore, a reduction in the effectiveness of direction control would be expected when a lower potential difference is applied, while in the presented system, control is completely lost below 8 V. Application of the potential caused some aggregation of organic material at the anode, but ^{1}H NMR studies of the starting material, and of the aggregated precipitate, show that the organic framework remains unaltered. However, there is a reduction in the lifetime of tube growth, and this is due to migration of the charged species toward the electrodes and consequent reduction of concentration in the area in which direction control experiments are carried out.

By carefully controlling the direction of the applied electric field and the duration for which it was applied, several different motifs were generated in the growing tube, and these fall into two categories. In the first, and most simple example, the growth is continuously switched between two directions which are opposite to one another, creating a tight wave-like shape with 180° bends (Figure 2a, top right). In the second, more advanced category, both sets of perpendicular electrodes are used to create either a zigzag pattern with 90° bends (Figure 2b) by switching between two directions or more complex motifs of 90° bends, for which the tube is steered in all four directions (Figure 2c,d).

In addition, the overall diameter and growth rate of the tube are not altered by the changes in direction, and this is consistent with a growth mechanism where the rate of growth is determined by the surface area of the parent crystal and the concentration of available cations (**2**). To demonstrate this, and to show that the tube diameter can also be controlled, the overall concentration of **2** was altered while the tube was growing. Increasing the concentra-

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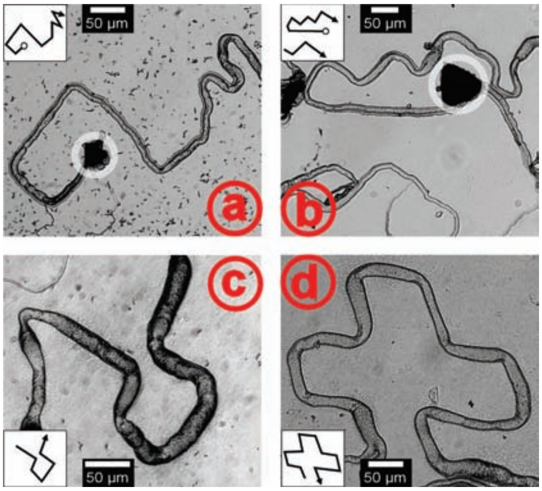

Figure 2. Motifs "drawn" by controlling the tube growth direction. (a) 90° bends followed by a series of 180° turns. (b) A series of 90° bends to make a zigzag motif. (c) 90° bends to form a square. (d) A series of 90° turns making a cross shape. Circles indicate the crystals from which tubes are growing. Inset diagrams show the direction of the tube growth.

tion of **2** caused the tube to become much narrower and to grow faster, while addition of water (thus decreasing the overall concentration of **2**) caused the tube to become much wider and to grow more slowly (Figure 3).

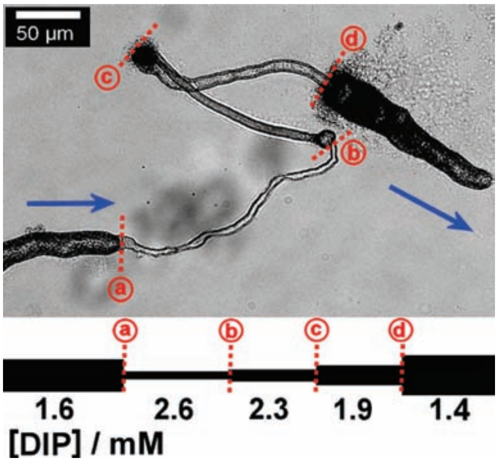

Figure 3. Size control of a growing tube by altering the available concentration of cations at points (a), (b), (c), and (d). The estimated concentrations at each point are shown in the lower section.

The tube diameter change was accompanied by a sharp change in direction, due to the bulk convective flow of the sample being altered by the addition of fluid. Analysis of the ratio between the diameter and growth rate showed that the area of tube surface grown per unit time was not constant as the concentration was changed, but it is also clear that the wall thickness of the slower growing tubes is much greater. This is because the rate of material outflow is roughly constant, being limited by the rate of dissolution of the parent crystal (**1**) and therefore the surface area of the membrane surrounding it.[8] Data collected for tubes grown at DIP concentrations between 1.0 and 3.5 mM showed that the average rate of tube growth (standardized for crystal surface area) was proportional to the concentration. Furthermore, rate data for the tubes in size control experiments were consistent with data collected at static concentrations of DIP (Figure 4).

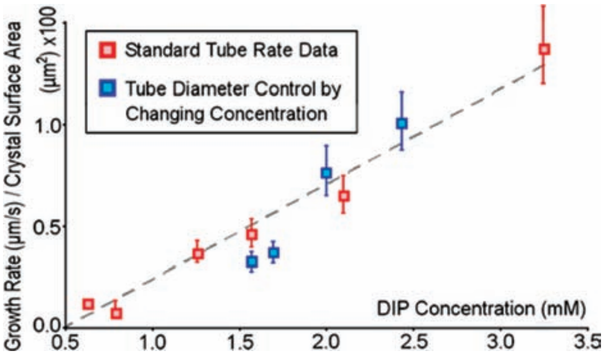

Figure 4. A plot of growth rate/crystal surface area against the overall concentration of DIP. Red squares show the linear trend increase in growth rate as the concentration is dropped, and blue squares show rate data for a tube where the concentration of DIP is varied while growing.

In conclusion, we have demonstrated the ability to control (and alter in real time)[17] the size and direction of polyoxometalate-based growing microtubes, and we have been able to fabricate several complex shapes and motifs. Future work with this system will focus on fully understanding the mechanism of tube growth and formation. In further studies, we will seek to exploit the control shown here to develop approaches to POM-tube based microsystem fabrication and also utilize the intrinsic catalytic properties of the clusters[18] for chemical transformations inside the tubes.

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Supporting Information Available: Schematic of experimental setup, full growth rate data, and real-time videos of tube size and direction control. This material is available free of charge via the Internet at http://pubs.acs.org.

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