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. 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 to see if a stepwise building block approach could 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, aggregation of nanoparticles, interfacial self-assembly of polymers and amphiphilic systems.

Recently, a phenomenon has been seen by us where micrometer-scale tubes (1–100 μm diameter) are spontaneously grown from a POM crystal upon addition of an aromatic organic dihydroimidazolphenanthridinium cation (DIP, Figure 1). 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 1H 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. 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 concentration of 2.
control experiments were consistent with data collected at static concentrations of DIP (Figure 4).

In conclusion, we have demonstrated the ability to control (and alter in real time)\(^\text{17}\) 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\(^\text{18}\) 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.

References


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