



Directed Assembly of Inorganic Polyoxometalate-based Micrometer-Scale Tubular Architectures by Using Optical Control**

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The self-assembly of supramolecular architectures to produce functional systems and devices is a key goal where molecular design, self-assembly, and materials design need to be combined together.^[1–3] In polyoxometalate chemistry we have taken the challenge to understand the assembly of clusters from the molecular to the nanoscale, by using a range of approaches including control of the available species and the use of macroscale flow systems.^[3] This type of control is vital, especially if the link from the nanoscale to the mesoscale (and beyond) is to be made.^[4] Nature can solve this problem by constructing a scaffold to direct the assembly processes.^[5] By using this strategy, scaffolding allows complex structures to be assembled and self-correction ensures the formation of precise, highly complex architectures. However, even these systems displace the problem to the design of the scaffold that must be replaced in synthetic systems. Routes to accomplish this from the bottom up are limited because controlling the structures formed on longer length scales is extremely demanding.^[6,7] The associated dynamic range currently requires specialist equipment for fabrication, and reliable new material and device architectures are difficult and time consuming to fabricate.^[8,9] As such, the discovery of a strategy for the controllable and reliable fabrication of materials that bridges the gap between bottom-up self-assembly and top-down control would revolutionize the design and fabrication of mesoscopic materials.

Herein we report the use of local convective flow fields to direct the bottom-up growth of self-assembling nanometer-sized inorganic building blocks into micrometer-sized tubes,^[10–12] by injecting solutions of polyoxometalate clusters into a bulk solution containing a large organic cation.^[13–17] The resulting millimeter-sized network materials can be structured from the top down, by using polyoxometalate clusters assembled from the bottom up (Figure 1). The basic building

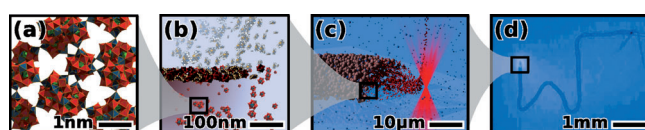


Figure 1. Schematic showing the assembly of the nanometer-sized polyoxometalate (POM) clusters (a) to form a membrane when they come into contact with cationic dye molecules (b). The formation of a tube is shown (c) along with a photograph of an individual micrometer-scale tube, which was written using laser control (d).

blocks for our self-assembled structures are nanoscale polyoxometalate (POM) cluster anions. This versatile class of molecular metal oxide anions has a general formula of $\{MO_x\}_n$ where M is Mo, W, V, and sometimes Nb and x can be 4–7. POMs have much in common with bulk transition metal oxides, and their molecular nature has led to many useful applications as redox, catalytic, and nanoscale materials.^[13–17] A large range of cation/anion combinations are possible and the morphological transformation of crystalline materials by cation exchange shows potential for nonequilibrium manipulation of such processes.^[10,12]

The flow patterns are created by using laser heating in a microscope, and we can easily reconfigure them on the fly either by direct user input or autonomous computer control, to produce a rich variety of architectures. The controllable micro-networks naturally form hollow tubes, allowing material to flow through them during and after fabrication, thus raising the prospect of harnessing this feature in the development of synergistic materials with embedded device functionality. By using localized flow patterns rather than bulk flow methods,^[10] we are able to control multiple microstructures in different directions simultaneously, allowing controlled merging events to occur at predefined locations.

The self-assembly of these cluster anions into a membrane by a “chemical garden”^[11] like mechanism is the first step towards constructing a network. Ion exchange and aggregation occurs at the interface between a solution of POM and a solution containing large cations (such as the dye solution used here), forming a membrane that is impermeable to the

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large ions. When the POM solution is injected into the dye solution through a microcapillary, the membrane forms a tube that grows as more POM solution is pushed out of its open end (see Figure 2 and the Supporting Information, Video 2).

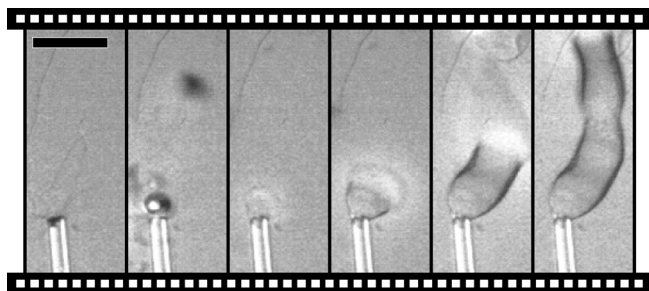


Figure 2. Time lapse (from Video 2 in the Supporting Information) showing the use of a laser spot to remove a plug of polyoxometalate material and initiate growth of a tube from a preloaded glass capillary. Scale bar 200 μm .

Ranging in diameter from tens to hundreds of μm , these hollow microstructures form the basis of the network architectures. Tube growth is mostly constrained to the sample surface since the POM solution is more dense than the bulk phase. The capillary is not only used to initiate the growth of the inorganic material, but also to connect the micrometer-scale tube to the external environment. The use of solutions in capillaries, as opposed to crystalline materials, gives total control over where and when tube growth will occur, as well as reducing the limitations of solubility and allowing tube growth with almost any POM. Additionally, the ability to preload the capillary with a number of different materials gives access to a large library of functional clusters to incorporate into these modular inorganic materials.

To fabricate a predefined network of tubes, the preloaded glass microcapillaries are mounted on a microscope slide and immersed in the cation solution. The cationic polyaromatic dye molecule methylene blue (3,7-bis(dimethylamino)-phenothiazin-5-ium chloride) is used in conjunction with other cationic molecules, such as dihydro-imidazo-phenanthridinium (DIP) compounds or polymeric poly(*N*-[3-(dimethylamino)propyl]methacrylamide). The capillaries are initially sealed at their tips with a plug of crystallized material, which can be dissolved by heating with the laser spot (shown in Figure 2). Thus, the growth process does not start until it is required. Several needles can be placed in a sample and initiated at different times, thus allowing us to produce complex network architectures with multiple inputs and outputs (see Video 3 in the Supporting Information). The membrane forms around the POM solution leaving the open end of the tube and manipulation of this outflow allows the speed, size, and direction of the tube's growth to be set by the user, thus enabling predefined patterns of these materials to be grown by user or computer control.

The tube can be steered by creating a local flow in the sample, and this is achieved by using a laser coupled into the microscope through which the sample is observed. Heating a small volume of the solution with a focused 670 nm laser,

which is strongly absorbed by the dye, sets up a convection current (see Figure 3). Near the surface of the slide, this flow pattern draws fluid towards the focused spot and when positioned near to a growing tube, the plume of ejected POM

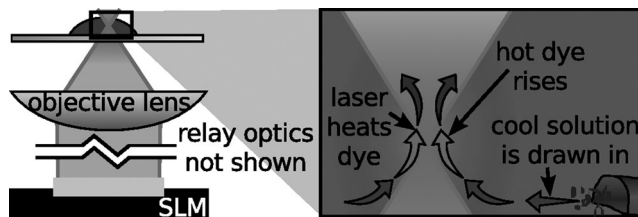


Figure 3. A spatial light modulator (SLM) is used to create multiple, controllable laser focused spots in the sample. These focused laser spots heat the dye solution, causing convection currents that create a flow towards the laser spots on the surface of the slide.

solution, and thus the direction of growth, will be oriented towards the laser focus. The laser is controlled using a spatial light modulator (SLM) that can project multiple foci into the sample, each of which can be controlled independently in three dimensions. The SLM is placed in a pupil plane of the system, in the same configuration usually found in holographic optical tweezers.^[18–20]

Growing a specific structure requires accurate positioning of the laser spots by a user who can react to the progress of the system, and this depends critically on the computer interface used to control the SLM. We display the microscope image on a touchscreen tablet (Apple iPad), along with markers representing the laser spots.^[21] These markers can be dragged around the screen, that is, the user's fingers move the laser spots, and touchscreen gestures allow the spots to be created, removed and defocused. Out-of-focus spots allow sufficient flow for guiding the growth, without boiling the solution, while in-focus spots can rupture membrane walls and unblock sealed needles.

Joining two growing tubes in a controlled way is impossible with only global control such as bulk flow. However, with multiple laser foci it is possible to create more complex flow patterns and thus direct more than one growth simultaneously to form a junction or network branch (see Videos 1 and 3 in the Supporting Information). Junctions can be formed either by causing a collision of two growing ends to create a Y junction, or by puncturing an existing tube with a focused spot to create a T junction (Figure 4g–i). Furthermore, merged junctions can be made between tubes constructed from different POM materials (e.g. Mo-based or W-based), where the resulting networks comprises a mixture of POMs. Combined with control over the direction of growth, these techniques allow us to create a range of configurations for building structures and devices (Figure 4). The presented platform is easily scalable, and architectures with a large number of network branches can be obtained by activating preloaded capillaries with the laser when needed.

As an alternative to full user control, we can use image analysis to guide automated control of the laser spot, thus allowing us to grow predefined structures. Figure 5 shows one such structure, overlaid with the desired path (see also

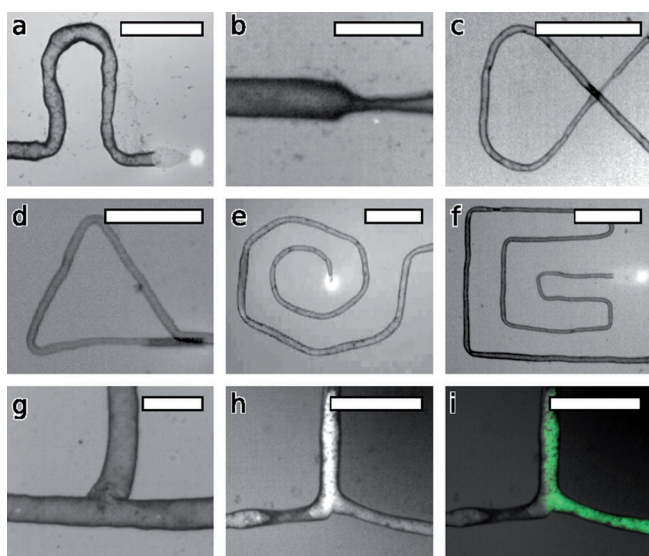


Figure 4. The holographic system can produce devices by using a number of basic components of the inorganic micro-networks: a) a sharp bend (scale bar: 100 μm); b) a change in diameter (scale bar: 100 μm); c) tubes crossing over one another (scale bar: 500 μm); d) a triangle motif (scale bar: 250 μm); e) a spiral pattern (scale bar: 500 μm); f) a nested pattern (scale bar: 500 μm); g) a T junction produced by puncturing a growing tube (scale bar: 100 μm); h) a Y junction produced by merging two tubes (scale bar: 250 μm); and i) a similar Y junction where green fluorescent dye (fluorescein) is introduced into one of the tubes (scale bar: 500 μm). The construction of several of these structural components is illustrated in Videos 1 and 4 (see the Supporting Information).

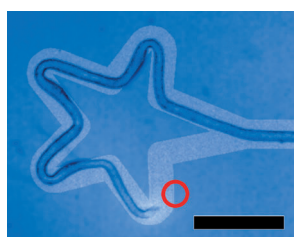


Figure 5. Automated control of the laser spot is possible, by using image analysis to track the end of the tube and keep the laser spot a constant distance ahead of the growth (circle). This enables us to assemble structures along predefined tracks (pale overlay). Scale bar: 500 μm .

Video 6 in the Supporting Information). This control method is achieved by simply placing the laser spot at a set distance ahead of the material growth, and relies on self-correction of the growth process (i.e. the convection pattern pulls the growing structure back towards the path if it deviates from the set course). Details of the control system are given in the Supporting Information.

In addition to the highly configurable network architectures and topologies, the diameter of a tube can be varied by changing the rate at which new material is added to its end, either with the laser-induced flow or by varying the driving hydrostatic pressure. This can create larger tube diameters for sorting or mixing, or constrictions to concentrate material into

a thinner tube (see Figure 4b). Also, because the POM solution enters the system through the microcapillary from a short length of flexible hose, the solution flows under gravity at low pressure, typically requiring the end of the supply hose to be raised by a few millimeters above the tip of the capillary. By using a micromanipulator to adjust the pressure head, it is possible to achieve fine control over the diameter of the growth as the flow rate, and hence the tube diameter, is proportional to the applied pressure (Figure 6).

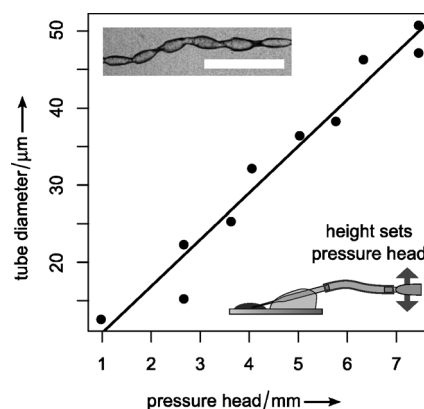


Figure 6. The flow rate, and hence the tube diameter, is proportional to the applied pressure. Raising or lowering the delivery hose adjusts the pressure and so the diameter is proportional to the height. The inset shows a micrograph of a tube where pressure control was used to change the diameter periodically (scale bar: 400 μm).

The resulting networks are made of hollow tubes, and this means they can be used as chemically active microfluidic devices, with the low Reynolds number flow characteristics expected for channels of their size.^[8,9] To observe this behavior, a POM solution was seeded with fluorescent beads and added to the inputs of a Y junction. Particle tracking of the beads showed the expected laminar flow patterns, as beads from the two arms of the device did not mix. Despite the tubes' rough appearance, their scale means that the flow patterns shown in Figure 7 and Video 5 (in the Supporting Information) are smooth. In addition, observing flow patterns of fluorescent dyes shows that by varying the pressures of two inputs flowing into a Y junction, the composition of the outflow solution can be controlled, thus

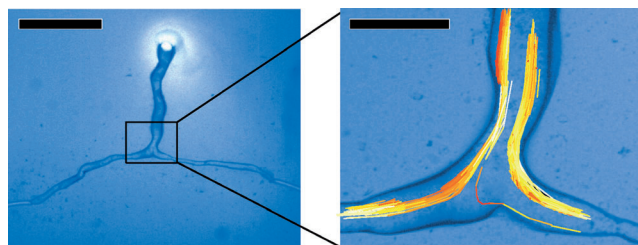


Figure 7. Bright-field micrograph of a Y-junction, showing particle tracks, colored according to speed of the flow, when fluorescent beads were flowed through the system (expansion). Scale bars are 1 mm and 200 μm for the wide view and expansion respectively. See Video 5 in the Supporting Information.

allowing solution outputs to be fine-tuned in the network of tubes (see Video 4 in the Supporting Information). In the context of developing devices it is worth pointing out that the self-assembled networks are found to be compatible with solutions of pH 1.0–6.5, and can withstand temperatures up to approximately 70 °C. The hollow architectures remain stable as long as they are not allowed to dry out, and this can be prevented by using a closed sample chamber (adding a cover-glass lid) or by encasing the whole device in an agarose gel matrix.

In conclusion, the directed assembly of inorganic micrometer-scale networks from molecular building blocks can be achieved from the top down by using a holographic optical system for tube control, as well as initiation of tube growth from a glass capillary. At the molecular scale we utilize bottom-up self-assembly of inorganic material to naturally form structures, which are directed using the convective flow produced by a focused laser. Multiple structures grown from glass microcapillaries can be controlled in their diameter, steered through specific paths, and merged to form networks and junctions, thus showing that complex material architectures can be formed. Not only do these networks have intrinsically hollow structures, but they can also be connected to the macroscale by leak-free interconnects and these structures support laminar flow within the tubes and junctions. The tablet computer interface allows the user to control the growing tubes in an intuitive way, and we have also shown that it is possible to autonomously control the fabrication of highly complex, predefined, structures. Furthermore, the available library of POM materials means that devices can incorporate many functional properties in the tube walls, thus demonstrating the potential of this directed self-assembly approach to connect bottom-up with top-down configurable assembly for the design of complex materials with embedded device functionality. It is worth pointing out that the work presented here represents the first effort to really control the architecture of the crystal gardens tube-by-tube, resulting in the prospect of real microdevice design, since the crystal-garden phenomenon was first studied over four centuries ago.^[22]

Experimental Section

All the experimental procedures are found in Supporting Information. The setup for growing tubes into a device comprised a 75 × 25 mm microscope slide, onto which preloaded glass capillaries were glued. The capillaries were pulled so as to have an aperture of approximately 50 μm and were glued at the other end to 1 mm inner diameter PVC tubing fitted with a dispensing needle for filling. Into these capillaries were loaded the relevant POM solutions at an overall concentration of 1.6 mg mL⁻¹ in water. The capillaries were then brought into contact with the microscope slide with their tips 200–400 μm apart, by using micromanipulators to position them while the glue set. To ensure that the POM solution was at positive pressure at the point of activation, the open ends of the tubing were held about 4 cm above the microscope stage and a droplet of the cation solution was then added, so as to cover the capillary tips. The standard cation solution comprised a mixture of methylene blue (0.19 mol) and poly(*N*-[3-(Dimethylamino)propyl] methacryl amide)—DP210 (2–10 mmol) in water. Although the methylene blue is sufficient to grow tubes, the addition of the polymeric cation leads to cross-linking of

POM fragments and thus more-stable tube structures. Tube growth was activated by raising the pressure and focusing the laser spot on the end of the capillary to dissolve or dislodge the blockage. The size and speed of the growing tube were adjusted by changing the pressure in the needle. This pressure could be set by adjusting the height of the supply hose above the sample, by using the micromanipulators to hold the ends of the hoses. The laser spot(s) for flow control were generated from a 500 mW, 670 nm diode pumped solid-state laser (MRL-H, Laser 2000). The beam passed through a 4x beam expander and illuminated a liquid crystal spatial light modulator (Boulder Nonlinear Systems XY series, 512 × 512 pixels). This SLM was used to steer and multiplex the laser beam, to create multiple controllable spots in the sample plane. The SLM was imaged onto the back aperture of the microscope objective by using a 200 mm lens and the microscope's tube lens (180 mm), and the beam was coupled into the microscope through the camera port. A custom camera tube containing a polarizing beam splitter allowed the laser to be used simultaneously with the camera. The direction of growth was controlled by using the laser spot to create localized convective flow patterns as described in the manuscript. For complex devices comprising junctions between several tubes, all the capillaries were placed in advance but the different tubes were activated as required. Hologram patterns for the SLM were generated by using Red Tweezers (available online), a control program for holographic optical tweezers written in LabVIEW and OpenGL. This allowed real-time generation of holograms. Multitouch control of the laser spots was achieved using iTweezers (application now available on iTunes).^[21]

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