Growth of Narrowly Dispersed Porphyrin Nanowires and Their Hierarchical Assembly into Macroscopic Columns

Suk Joong Lee, Joseph T. Hupp*, and SonBinh T. Nguyen*

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208

Received March 8, 2008; E-mail: j-hupp@northwestern.edu; stn@northwestern.edu

Over the past decade, the promise of functional materials with applications in catalysis,[1] separations,[2] storage,[3] and energy transfer[4] has turned molecular-level synthesis and design of materials into one of the most exciting frontiers in modern chemistry. In particular, macroscopic materials created from small molecules often show unique and/or enhanced properties beyond those of their molecular components.[5] Among the known molecular building blocks, porphyrins constitute a highly attractive class of "synthons" for functional nanomaterials due to their unique photonic[6] and electronic[7] properties, which can be rationally modified by synthetic manipulations. However, examples of well-defined, molecularly assembled porphyrinic materials[8] that can be systematically built up from the nano- to microscale in a hierarchical and controlled fashion are rare. For example, although the growth of porphyrin nanowires[9] has been successfully demonstrated, precise control of length and aspect ratio remains challenging. Herein, we report the synthesis of narrowly dispersed porphyrin nanowires whose lengths can be finely tuned using an amphiphilic polymer surfactant, Pluronic F127.[10] The surfactant was utilized as a template to precisely set the dimensions of porphyrin nanowires. By controlling temperature and concentrations, the lengths of the nanowires can be systematically varied while keeping widths unchanged.

We recently demonstrated a hierarchical strategy for producing meso- and macroscopic objects from discrete (porphyrin)Sn nanoplates.[11] In further exploration of this approach, we have discovered that the aspect ratio of these nanorods can be systematically modulated by adjusting reaction conditions (Figure 1). At high temperature, rapid injection of an ethanolic solution of amphiphilic porphyrin **1** into water quickly yields crystalline monodispersed square-faced rods that are ~500 nm long with an average aspect ratio of 0.24 (Figure 1, left column). As they grow, these amphiphilic nanocrystalline aggregates become more hydrophobic and precipitate from the aqueous medium. In this manner, the sizes of resulting particles are controlled by the ability of the aqueous solution to support the particles, leading to a narrowly dispersed population of rods. This observation prompted us to hypothesize that, if the porphyrin aggregates could be maintained in solution for a longer period during growth, larger, but still narrowly dispersed, nanostructures would result.

Although the porphyrin template can be synthetically tuned to afford higher aqueous solubility, the difficulties commonly encountered in porphyrin synthesis render this strategy unattractive. As such, we turn to amphiphilic Pluronic polymer surfactants as a more facile means for maximizing the solubility of porphyrin nanoparticles in water during crystal growth.[12] Because these nanocrystals are grown from amphiphilic building blocks **1**, the surfactants may favorably interact with the growing particles, prolong their solution lifetime, and sustain growth to larger objects while maintaining the narrow distribution. We were pleased to find that this approach works beautifully. Upon injecting a 0.05 mM ethanolic solution of **1** into a hot solution of the commercially available triblock copolymer Pluronic F127[11,13] and allowing the resulting mixture to cool to room temperature, narrowly dispersed square-faced nanowires are obtained that are ~9.2 µm in length and ~130 nm in width (Figure 1, right column; also see Supporting Information (SI)). The widths of these nanowires are remarkably similar to those of the nanorods (Figure 1, left column) that were synthesized in the absence of Pluronic F127. The two materials exhibit the same powder X-ray diffraction (PXRD) patterns (see SI), indicating identical "unit cells" despite their different macroscopic morphologies.

When the concentration of Pluronic F127 was varied, the lengths of porphyrin nanowires changed dramatically while their widths remained constant. As shown in the right column of Figure 1, narrowly dispersed nanowires with lengths ranging from 0.8 ± 0.1 to 12.4 ± 1.5 µm can be obtained over a 0.5 mM concentration range of Pluronic F127. Remarkably, the widths of these nanowires are maintained in the constant range of 100−150 nm up to 0.5 mM of Pluronic F127, where the wires doubled in width (see SI). To the best of our knowledge, this type of systematic length variation (Figure 1, plot in right column) has not been documented for the synthesis of molecular-based materials in bottom-up fashion.

Pluronic F127 triblock copolymers are known to form a cylindrical micellar phase at high temperature that organized into hexagonal pattern
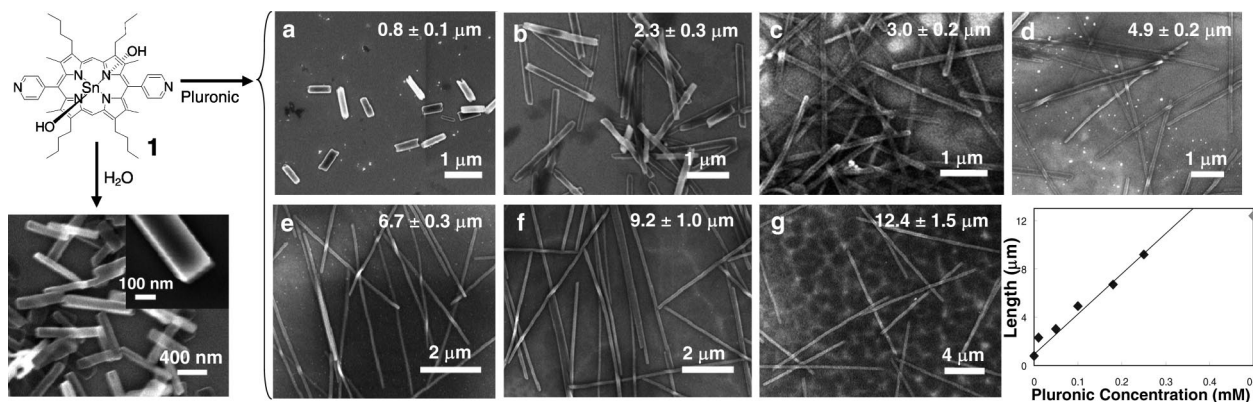

Figure 1. The syntheses of square-faced nanorods (bottom left panel) and porphyrin-based nanowires (right panels) from amphiphilic porphyrin **1** (top left panel). The SEM images shown in the right panels are for nanowires that were synthesized at various Pluronic concentrations: (a) 0, ((b) 0.01, (c) 0.05, (d) 0.1, (e) 0.18, (f) 0.25, and (g) 0.5 mM solutions of Pluronic F127 in water (see Figure S1 in the Supporting Information for thickness of the nanowires). The bottom right panel is a plot of the relationship between the lengths of nanowires versus concentration of Pluronic. The change in length becomes nonlinear after 0.25 mM.
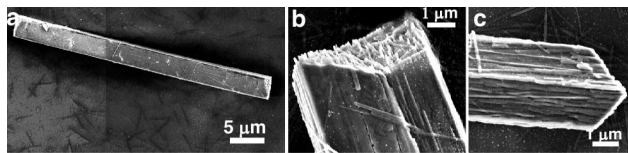
Figure 2. SEM images of macroscopic column assembled from (porphyrin)Sn nanowires in 0.1 mM aqueous solution of Pluronic F127.
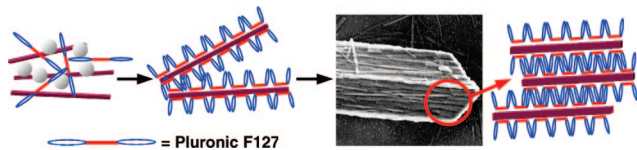

Figure 3. Schematic representation for Pluronic-assisted self-assembly of (porphyrin)Sn nanowires into macroscopic column. Red segments of the Pluronics indicate hydrophobic blocks; blue oval segments are hydrophilic.

with hydrophilic channels between the cylindrical micelles.[14] Presumably, when solutions of **1** are injected into this phase, the amphiphilic porphyrin molecules partition into the channels and crystallize into crystalline nanowires. Because the channels are filled with water, the crystallization process occurs in a similar manner as the growth of the nanorods[11] and affords materials with identical unit cell. On the other hand, the length of nanowires would depend on the average persistent length of the Pluronic F127 cylindrical micelles, which, in turn, is governed by the concentration of surfactant.[14] The high-temperature growth regime is critical to controlling the nanowire morphology of the porphyrin; injection of **1** into a room-temperature solution of Pluronic F127 only resulted in amorphous spheres (vide infra, see also SI), corresponding with the spherical micellar phase known to be occupied by Pluronic F127 at room temperature.[15]

When moderately dilute (0.05−0.25 mM) solutions of the colloidal nanowires in aqueous Pluronic F127 were kept at room temperature for an extended period (∼1 day), the nanowires self-assembled into rhombohedral macroscopic columns that are ∼30 μm in length and ∼3 μm in width (Figure 2). This assembly process can be accelerated with a short microwave pulse (0.5−1 min). Presumably, the main driving force for such macroscopic assembly is the gradual phase transition of the Pluronic F127 chains in water,[14,15] coupled with the strong attractions between the wires and the individual Pluronics polymer chains. As the hot Pluronic F127 solution cools to room temperature, its cylindrical micelles transition into a spherical micellar phase, which eventually break into small clusters/individual chains if the Pluronic concentration is below the critical micelle concentration (CMC) and/or temperature (CMT). Under these limits, the Pluronic chains interact strongly with porphyrin nanowires through the hydrophobic PPO blocks, effectively "decorating" the surfaces of the wires with the more hydrophilic PEO blocks. To maximize the interaction between Pluronic chains, the so-decorated porphyrin nanowires come together, cushioned by a bilayer of Pluronics between the nanowires, similar to the lipid bilayer in cell membrane (Figure 3).[16] This sequence of events is accelerated by microwave irradiation, allowing the nanowires to assemble into large bundles, eventually forming macroscopic columns (Figure 3). As expected, this behavior cannot be found with Pluronic solutions above 0.25 mM due to the high population of spherical micelles at concentrations above CMC (see also SI section VI).

In summary, we have demonstrated the hierarchical assembly of amphiphilic porphyrin **1** into narrowly dispersed nanowires and macroscopic bundles assisted by a monodisperse amphiphilic polymer surfactant. The exquisite phase transitions of the Pluronic polymer surfactants, as well as their remarkable uniform micellar phases, can be manipulated via concentrations and temperature to yield narrowly

dispersed nanowires with a high level of control of aspect ratios. These nanowires can be further assembled into secondary macroscopic columns with Pluronic surfactants as glue, akin to biomineralization processes[17] where inorganic nanocrystals are assembled together with protein "adhesives". This polymer-assisted hierarchical assembly strategy should lend itself readily to the preparation of other multifunctional materials from molecular building blocks and facilitate the investigations of these materials in applications concerning catalysis, separation, storage, and energy transfer.

Supporting Information Available: Complete experimental details, SEM images, and PXRD analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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