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Amphiphilic Porphyrin Nanocrystals: Morphology Tuning and Hierarchical Assembly**

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The translation of molecular building blocks into well-defined solid-state structures in a hierarchical fashion (i.e., molecular scale → nanoscale → meso- and macroscale) is a key process in many bottom-up materials syntheses. Recent applications of this concept have resulted in new classes of materials that possess well-defined nanometer-sized domains that effect selective catalysis^[1] and separation,^[2] enable gas storage,^[3,4] and facilitate energy transfer.^[5] However, assembling such domains into mesoscopic^[6,7] or even macroscopic structures remains a major challenge. As the properties of nanomaterials created from small inorganic and organic building blocks can be readily tuned at a molecular level, much interest has been devoted to the assembly of these materials into ever-larger structures. Herein, we demonstrate a hierarchical strategy for producing mesoscopic (and larger) objects from discrete amphiphilic porphyrins. Crystal growth under highly “energetic” conditions (i.e., vigorous stirring and heating) was first employed to produce, in a scalable fashion, uniform nanocrystals the morphology of which can be easily modulated by crystal growth conditions as well as the structure of the porphyrin building blocks. These materials were then assembled into macroscopic prisms in the presence of a simple surfactant or selectively partitioned into hydrophobic patterns on glass surfaces. Because the porphyrin nanocrystals formed in the first step have enhanced photostability compared to their molecular constituents, the described hierarchical method for assembling them into larger objects should facilitate practical applications of porphyrin-based materials in transport,^[8] imaging,^[9] light-harvesting,^[10] or catalysis.^[11]

In many crystalline materials, the bonding between “molecular” partners is largely based on strong, directed interactions and the resulting solids are invariably obtained under non-agitated conditions over a long period. Large crystals (several micrometers or greater) are almost impossible

to obtain directly when the growth mixture is agitated or heated.^[12] Under such energetic conditions, however, nanocrystals can be grown more readily and assembled into larger structures. A related example is the seemingly chaotic formation of snowflakes, where macroscopic crystals with spectacular morphological diversity are formed from large number of hydrogen-bonded nanocrystalline subunits.^[13] While snowflakes come in infinitely diverse, non-reproducible morphologies, Nature can also generate reproducible and functional macroscopic objects via the hierarchical assembly of complementary nanoscale building blocks, as is well-known in the biomineralization of bones, teeth, and shells.^[14]

These simple but compelling ideas prompted us to ask whether larger amphiphilic molecules, particularly hydrophobic porphyrin building blocks that are also equipped with both hydrogen-donating and -accepting moieties, could be similarly and hierarchically assembled, first as nanocrystals and then as meso- and microscale crystalline objects. The amphiphilicity of such building blocks should allow them to undergo self-crystallization into particles with observable intermediate-range order without the need for a second metal-ion component.^[6] In addition, the weak nature and short distance of hydrogen bonds should facilitate the annealing of the growing nanoparticles into uniform, monodispersed crystals under highly energetic (e.g., vigorous stirring, high temperature) growth conditions, in contrast to the “more static” conditions traditionally employed for growing crystals of small molecules. Finally, the extended van der Waals interactions between porphyrin crystals, akin to those between graphene sheets in graphite, may eventually allow one to extend this assembly into the meso- and macroscale.

Porphyrins **1–3** (Fig. 1), possessing both 5,15-dipyridyl hydrogen-bond-acceptor units and Sn(OH)₂ centers that can serve as both hydrogen-bond donors and acceptors, satisfied our design criteria in an impressive fashion.^[15,16] Injection of 1 mM ethanol solutions of each of these porphyrins into stirring water at room temperature (rt) leads to initially homogeneous solutions, which eventually become cloudy with hydrophobic nanocrystals floating at the water/air interface (Supporting Information Fig. S1). As the injected amount increases, the crystals become larger but retain their original habits. Both the Sn(OH)₂ core and the pyridyl groups are critical to nanocrystal formation: injections of solutions of the non-metallated version of **2** as well as its non-pyridinated analogue **4** lead only to amorphous solids.

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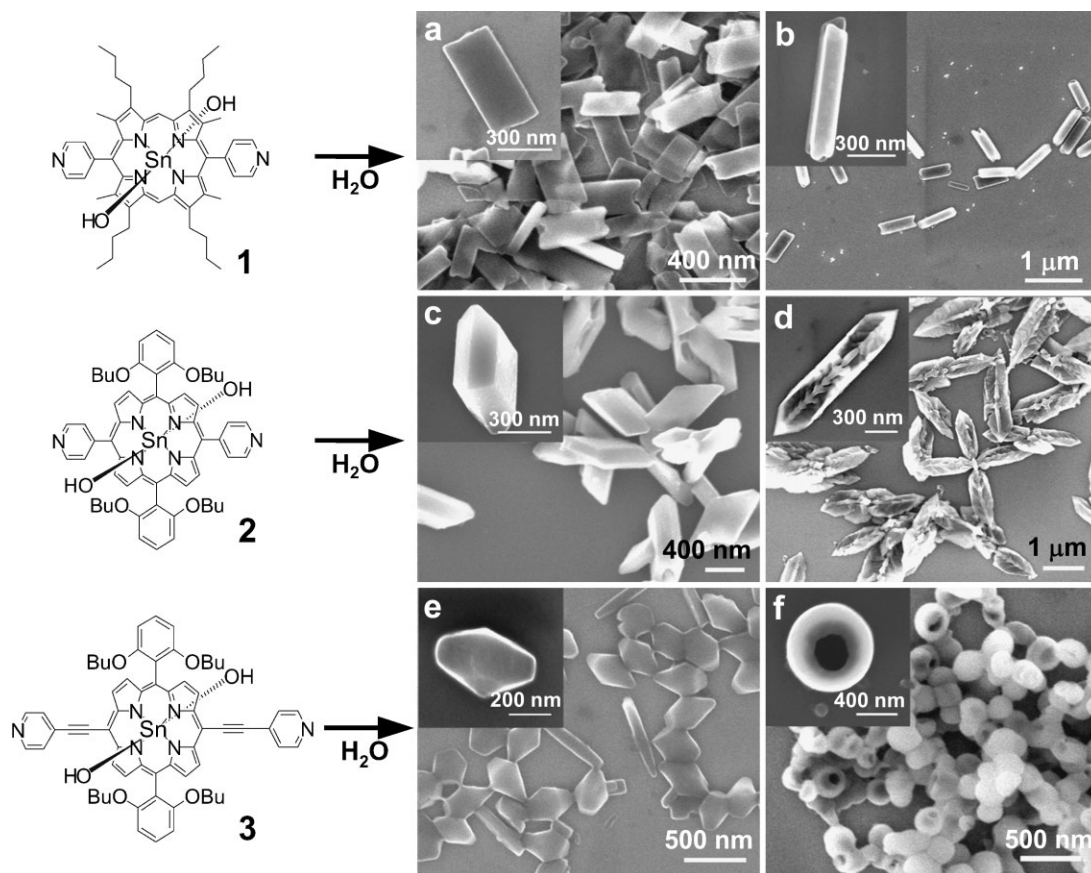


Figure 1. Schematic diagram illustrating the nanocrystallization of metalloporphyrins **1–3** in water. Shown on the right side of the arrows are the scanning electron microscopy (SEM) pictures of the different morphologies obtained under various conditions: a,c,e) room temperature (rt), stirring; b,f) 90 °C, stirring; d) 60 °C, stirring or 45 °C, microwave.

Scanning electron microscopy (SEM) examination of the nanocrystals obtained from **1** at rt reveals relatively monodisperse rectangular blocks (ca. 350 nm long, polydispersity index (PDI) = 0.21) with an average aspect ratio of 0.51 (Fig. 1a). When the ethanol solution of **1** is injected into water at 90 °C, the blocks are replaced by nanorods (Fig. 1b) displaying tighter size distributions (ca. 500 nm long, PDI = 0.16, aspect ratio = 0.24). In contrast, **2** affords truncated bipyramidal nanocrystals (Fig. 1c, ca. 630 nm long, PDI = 0.23) when the injection is carried out at rt and beautiful double-ended herringbone blades at 60 °C (Fig. 1d inset, ca. 1250 nm long, PDI = 0.05). The latter morphology can also be obtained at 45 °C under microwave irradiation, but with beautiful flower-like shapes interspersed among the blades (Fig. 1d).

Remarkably, nanocrystals from **2** exhibit the same powder X-ray diffraction (PXRD) patterns (Fig. 2), regardless of their macroscopic morphologies, indicating identical “unit cells” for the various forms. This observation also holds for the two types of nanocrystals from **1** (Supporting Information Fig. S2). The PXRD patterns for the nanocrystalline forms of **2** are remarkably similar to that obtained from a single crystal of **2** grown under non-agitated conditions by layering an ethanolic solution of the porphyrin on water (Fig. 2). The single-crystal X-ray structure of **2** (Fig. 3) shows two crystallographically

independent porphyrin molecules alternating in a pseudo-herringbone fashion where the porphyrin plane of one molecule forms a dihedral angle of 72° with respect to that of the adjacent porphyrin molecule (along *a*-axis). One of the two porphyrins has both of its OH groups involved in H-bonding while the other only has its pyridyl groups participating. Given the linear arrangement of the dipyrrolyl moieties and the orthogonal Sn(OH)₂ centre in **2**, this geometry is reminiscent of, but more flexible than, that observed by Shelnutt and coworkers for (pyridyltriphenylporphyrin)tin (SnPyTriPP),^[15] allowing for the accommodation of one water molecule between the two porphyrins. The (2,6-dibutoxy)phenyl substituents in **2** pack so as to render two faces of the crystal hydrophobic while the orthogonal HO–Sn–OH moiety makes the remaining face more hydrophilic (Fig. 3, looking down the *a*-axis), suggesting a natural tendency for crystal growth in water to occur faster along the hydrophilic direction, where water molecules can most readily be recruited as structural components and/or exposure of the hydrophobic residues to the aqueous surroundings can be limited.

Compound **3**, having a longer pyridyl-to-pyridyl distance than both **1** and **2**, leads to oval-shaped flat crystals that are ca. 280 nm long (Fig. 1e, PDI = 0.15). At elevated temperature

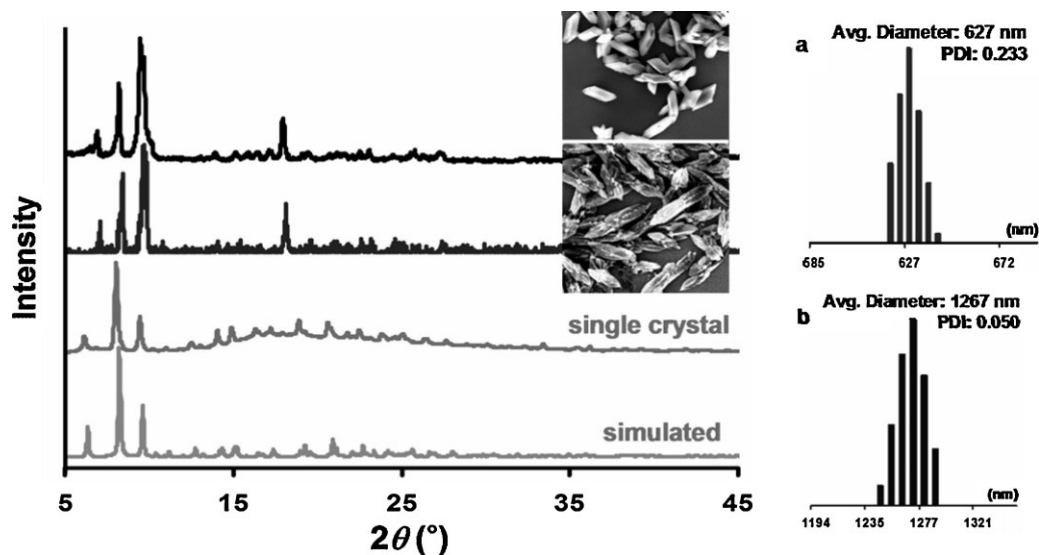


Figure 2. Left: PXRD patterns for the two nanocrystal morphologies of **2** as well as that from a single-crystal sample of **2**. Also shown is the simulated PXRD pattern obtained from the X-ray crystal structure of **2**. Right: Dynamic light scattering distribution plots for the aforementioned two nanocrystal morphologies obtained from **2**: a) obtained at rt, stirring; b) obtained at either 60 °C, stirring or 45 °C, microwave (see Supporting Information Fig. S15 for color figure).

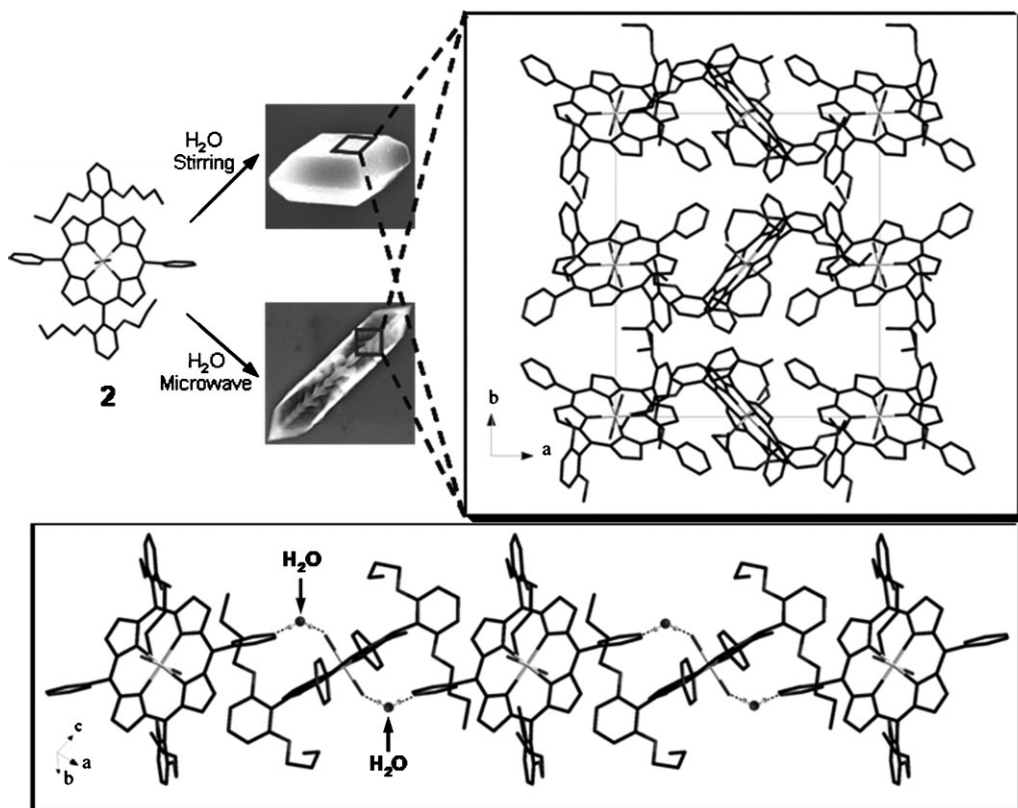


Figure 3. Packing-diagram representation of the X-ray structure of **2** (right top panel) showing water-mediated H-bonding pattern between adjacent porphyrin layers (bottom panel, hydrogen-bonded H_2O = grey, other hydrogen atoms are omitted for clarity). This arrangement suggests the presence of hydrophobic and hydrophilic faces that corresponds to the difference in crystal growth behaviors (left top panel) (see Supporting Information Fig. S16 for color figure).

(90 °C), these ovals turn into beautiful amorphous hollow spheres (Fig. 1f, ca. 350 nm, PDI = 0.28). That **1**, **2**, and **3** can be induced to produce nanomorphs with widely different morphologies (Supporting Information Fig. S2) and crystallinities (Supporting Information Fig. S3) depending on growth conditions points to synthesis as a tool for manipulating reproducible nanoparticle morphologies that is not available with simpler building blocks such as water: by adjusting the relative positions and distances between hydrogen-bonding moieties in a porphyrin building block, different unit cells and a wide range of nanoscopic crystalline shapes should be accessible. Additionally, the amphiphilic nature of metalloporphyrin building blocks such as **1–3** allows them to readily participate in several interactions – with molecules of the same type, as well as with water – under turbulent conditions to yield a diverse array of nanocrystal and/or nanoparticle morphologies.

The growth process leading to the diverse nanocrystalline morphologies reported herein for **1–3** bears striking similarity to the formation of snowflakes in its seemingly chaotic nature: agitation, in the form of either stirring or heating, is critical to induce nanocrystal growth.^[17] Immediately after the injection of ethanol solutions of these porphyrins into water, the individual porphyrin molecules are still solvated by a water-miscible ethanol shell and remain in a metastable state, akin to the metastable supersaturation of water vapor in a cloud before a snow shower. Stirring disrupts this arrangement, removes the protective alcohol shells, and causes the porphyrin to aggregate as nanocrystals. However, as the porphyrin rings possess bulky hydrophobic groups that cannot be densely packed, a small amount of water may be necessary to fill the space and bridge the layers, as in the case of **2**. After nucleation, crystal growth on the hydrophilic faces (but not the hydrophobic faces) is governed by diffusion of partially solvated porphyrin molecules to the surface of the seed crystals. Because the porphyrin building blocks have large hydrophobic cores, minimization of hydrophobic interactions leads to crystal surfaces with variable hydrophobicity, and the nanocrystal grows fastest from the most hydrophilic surface. To remain in solution, the growth must be faster in the more hydrophilic domains so as to out-compete the precipitation/aggregation tendency of the hydrophobic face (vide infra). Agitation of the reaction mixture can bring fresh supplies of the building blocks towards the growth sites as well as change the “local growth” direction, as in the case of **2**, leading to local branching features on the crystal surfaces. When the crystals reach a certain size, hydrophobic tendencies win over growth and they come out of solution.

In general, increasing the amount of porphyrin injected into water, whether through increased injection volume or concentration, leads to larger particles (Supporting Information Figs. S7–S10). This trend is clearest for **2** where the porphyrin is overall more soluble. Higher temperature favors larger crystals, suggesting that the growth occurs through either increased “particle solubility” at higher temperature or a very fast Oswald ripening process.^[18] Both mechanisms are consistent with the observation that PDIs obtained at higher

temperature are narrower than those obtained at rt. Additionally, the overall uniform shapes and narrow PDIs for all the materials reported herein point to a faceting/branching process that is more controlled than that which occurs in snowflake formation. First, the faceting growth patterns for nanocrystals of **1–3**, up to the 1 μm scale, are more likely to be controlled by the large hydrophobic surfaces of the porphyrin building blocks than other features, enabling better molecular stacking and constraining unstable dendrite formation. When the nanocrystal grows to the micrometer-size, the hydrophobic forces become large enough so that crystals “float out” on top of the growth solution, as indeed observed (Supporting Information Fig. S1). This separation process limits crystal growth and provides near-monodisperse crystals before branching^[19] can set in.

While nanoparticles have recently been made from coordination complexes, either with^[17] or without^[20] stabilizer, they are often amorphous and limited to solid spherical shapes. Within the nanoscale evolution of growth shown herein, one can access both crystalline and amorphous materials depending on the growth conditions. The crystal population can evolve to include combinations of morphologies (Supporting Information Figs. S9 and S10), but these habits do not interconvert – just as one snowflake cannot be directly transformed into another. In our hands, the room temperature-formed blocks of **1** do not convert to the rod form upon extended heating, suggesting a truly kinetically controlled process that is not governed by Ostwald ripening. However, these rectangular blocks can be redissolved by addition of organic solvent to the growth mixture and converted into the rod form with heating, analogous to the natural process where a snowflake is sublimed into water vapor and recondensed into a new one. Aside from this similarity, the protocol presented herein affords controls and advantages that do not exist in chaotic natural processes: the conditions within the flask can be tuned and scaled up to give macroscopic quantities of nanocrystals of similar morphology, making the methodology a practical one for producing large quantities of nanomaterials.

Beyond the obvious organizational, alignment, and orientational benefits, assembling **1** into nanocrystals increases its stability against photo-bleaching, likely by limiting exposure to dissolved O₂.^[21] For example, exposure of a solution of **1** in 25% ethanol/water to a handheld UV lamp (Hg-filtered at 254 nm, 60 Hz) in the presence of air over a 14 h period completely degrades the chromophore. In contrast, a similarly concentrated solution of nanocrystals of **1** in water retained more than 50% of its initial absorptivity after equivalent UV exposure (Supporting Information Fig. S11). This enhanced stability could be important in applications such as molecular photovoltaics^[22] or nanoparticle-based medical imaging (luminescence imaging).^[9]

As the nanoplates made from porphyrin **1** feature both hydrophilic and hydrophobic faces, they can be induced to further assemble into macroscopic structures in the presence of other hydrophobic agents. Exposing a freshly made colloidal solution of **1** to the common surfactant cetyltrimethylammonium

bromide (CTAB), followed by a brief microwave irradiation, led to the self-assembly of the resulting porphyrin nanoplates into micrometer-size triangular columns (Fig. 4), whose size and aspect ratio can be readily modulated via the concentrations of CTAB (see Supporting Information Fig. S12). The main driving force for such macroscopic assembly are likely the strong hydrophobic–hydrophobic interactions between the long alkyl chains of CTAB in water, assisted by weaker hydrophobic–hydrophobic attractions between the plates. When CTAB is added to the nanoparticle suspensions, the hydrophilic ammonium end of CTAB molecules interacts

strongly with the hydrophilic faces of the nanoplates, effectively coating these surfaces with a layer of highly hydrophobic hydrocarbon tails. To minimize the interaction with water, the CTAB-modified edges of the plates come together, forming a bilayer of alkyl chains between the plates, akin to the lipid bilayer in cell membrane (Fig. 4, top row). This layer is “annealed” by microwave irradiation, allowing for the assembly of a small stack of plates into large sheets that can then serve as the “seed” surface for recruiting additional nanoplates and sheets, eventually forming trigonal prismatic rods (Fig. 4). In analogy to biological mineralization, the

triangular column structures described herein comprise true superstructures assembled from two different primary building blocks: porphyrin nanocrystals and CTAB “glue”. This is made possible based on two different types of hydrophobic interactions: a stronger one between the CTAB-modified edges, which “seeds” the assembly, and a weaker one between the naturally hydrophobic faces of the nanoplates, which drives the subsequent mesoscopic growth.

The assembly of nanoplates of **1** into macroscopic rods of overlapping sheets, is remarkably similar to the protein-mediated nacre growths in mollusk shell,^[23] albeit at a smaller scale. The latter is essentially a hierarchical organization of CaCO₃ nanocrystals into macroscopic overlapping sheets in the presence of a layer of proteins, resulting in permanent structures with enhanced mechanical properties.^[24,25] In this analogy, CTAB serves as our amphiphilic glue for the assembly of (porphyrin)Sn nanocrystals into macroscopic objects. Consistent with this reasoning, exposure of OTS-patterned glass to a suspension of nanoplates of **1** under microwave irradiation resulted in exclusive deposition of the plates on the 3 μm OTS-patterned, hydrophobic strips (Fig. 5). Similar results were obtained with OTS patterns deposited on SiO₂/Si (Supporting Information Fig. S13), but now via direct heating.

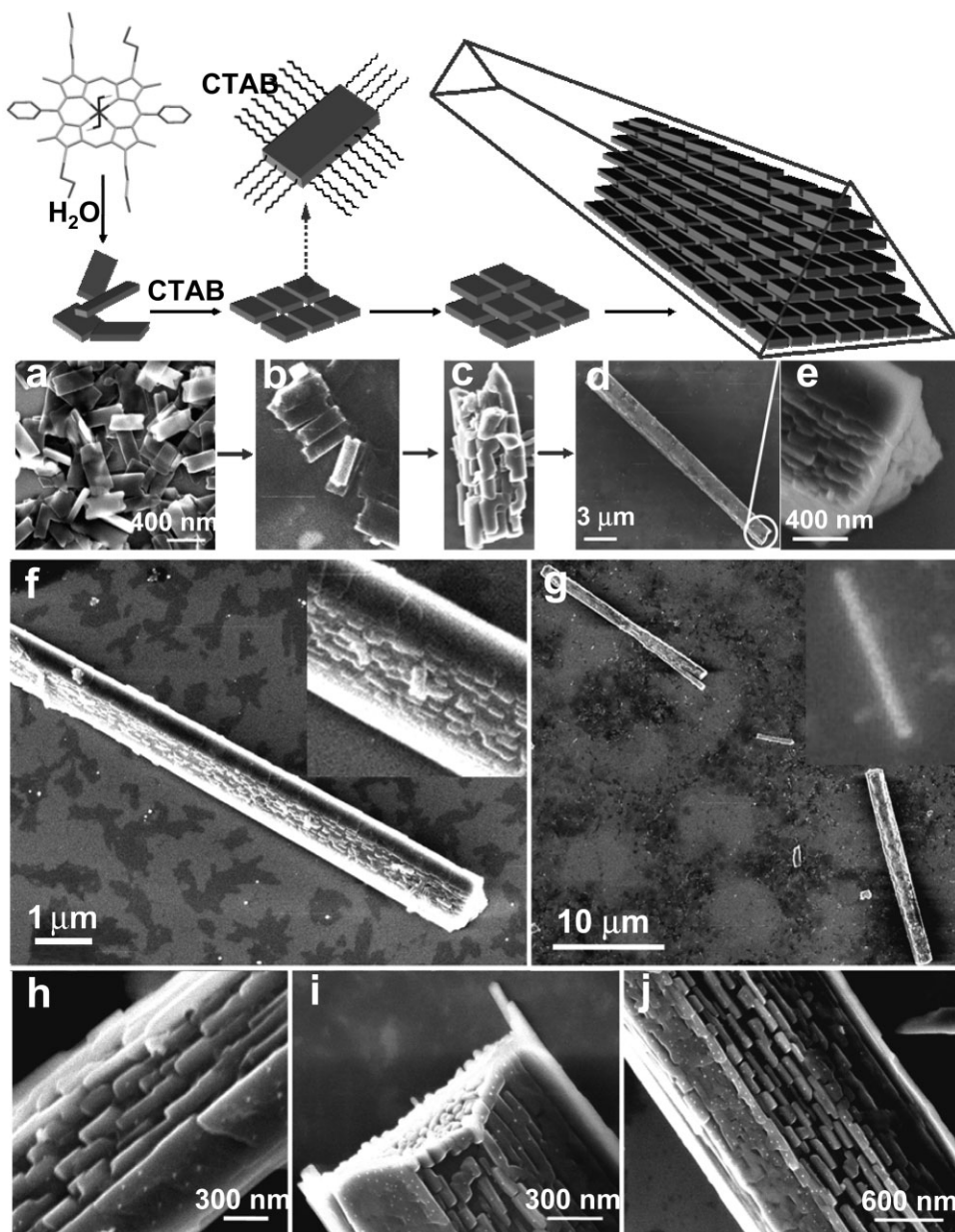


Figure 4. Top row: Schematic representation of CTAB-assisted assembly of porphyrin nanoplates **1**. Bottom three rows: a–e) SEM images of the nanoparticles after each assembly steps. f–j) SEM images of the triangular column made from nanoplates (see Supporting Information Fig. S17 for color figure).

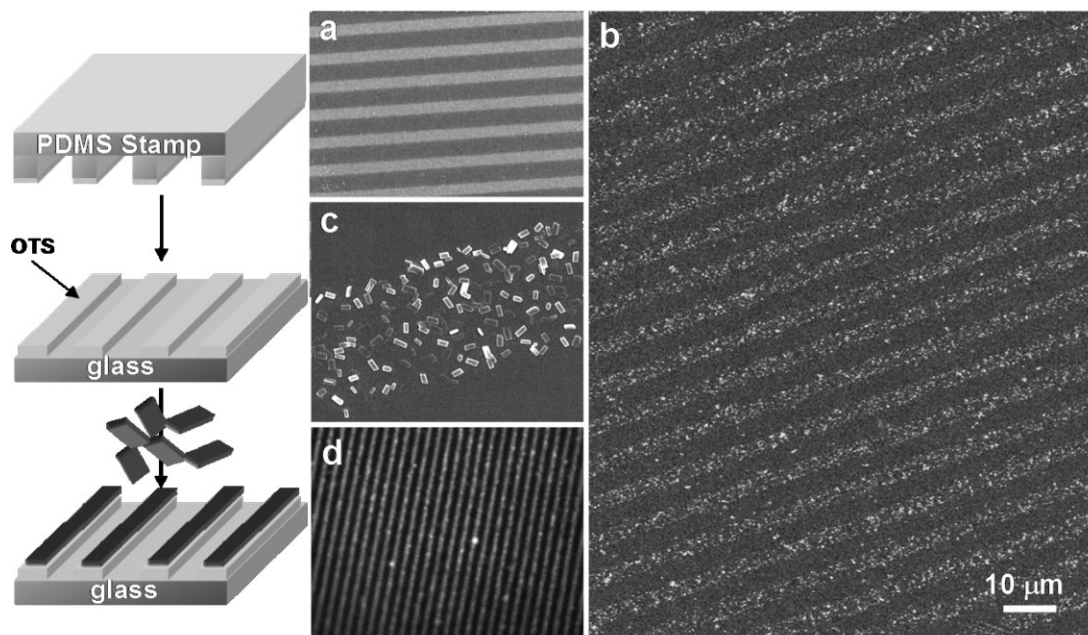


Figure 5. Left column: Schematic representation of interaction of nanoplates of **1** on OTS-patterned glass surface. Right two columns: SEM images of OTS-patterned glass (a) and nanoplates on patterned glass (b,c). Fluorescence microscopy image of nanoplates of **1** on OTS-patterned surface (d) (see Supporting Information Fig. S18 for color figure).

Although metastable inorganic colloids^[26] and porphyrin nanoparticles^[17,27] can be grown with specific shapes under high-energy conditions (vigorous stirring and/or high temperature), until recently reports of molecular crystal growth^[15] under such conditions have been scarce, with none progressing beyond the initial molecule-to-nanocrystal stage. As this new frontier in molecular materials emerges, exciting new nanoscale materials will be produced given the near-infinite functional diversity provided by synthetic chemistry; a feature that is not available in the natural environment.^[25] However, for these materials to become useful in practical applications, methods must be developed to assemble them into higher-order structures, beyond the nanoscale regime. In this spirit, the work described here represents a novel strategy for manipulating growth of molecular nanocrystals in solution under energetic growth conditions and subsequently assembling them into larger structures using amphiphilic surfactant glue. The method is scalable and the crystal shape can be tuned with the vast store of synthetic porphyrins, offering a wide diversity of nanomaterials with potential applications in energy conversions, imaging (vide supra), and catalysis. The plethora of functionalities accessible via synthetic chemistry, together with our ability to control nanocrystal growth followed by hierarchical assembly, should make the strategy described here a fertile venue for fabricating multifunctional nano-, meso-, micro-, and macro-structures from molecular building blocks and investigating the applications of these new nanomaterials in energy conversion, imaging, and catalysis.

Experimental

Methods: Isolation of all porphyrin nanoparticles after synthesis was easily carried out via centrifugation and decantation of the mother liquor.

Method A: An ethanol solution of porphyrin (200 μ L of a 1 mM solution) was injected into a vial containing magnetically stirred deionized water (10 mL) at rt. Stirring was maintained for ca. 2–20 min, after which colloidal porphyrin particles were obtained.

Method B: An ethanol solution of porphyrin (200 μ L of a 1 mM solution) was injected into a vial containing stirring deionized water (10 mL) at 90 °C. Colloidal porphyrin particles were obtained after approximately 30 s.

Method C: An ethanol solution of porphyrin (200 μ L of a 1 mM solution) was injected into a vial containing stirring deionized water (5 mL) at rt. Colloidal porphyrin particles were obtained after 1–2 min of microwave (45–50 W) irradiation at 45 °C.

Method for Triangular Column Assembly: Freshly prepared nanoplate colloids from method C using porphyrin **1** were treated with 5 mL of aqueous solutions of CTAB (0.2 mM) and triangular columns were obtained after 1–2 min of microwave (45–50 W) at 45 °C. Particles were imaged by scanning electron microscopy.

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