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# Straightforward Self-Assembly of Porphyrin Nanowires in Water: Harnessing Adamantane/β-Cyclodextrin Interactions

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***Abstract:*** A convenient approach for the self-assembly of well-defined porphyrin nanowires in water, wherein the individual monomers do not aggregate *via* π−π interactions, is disclosed. These unidirectional and heteromeric assemblies are instead composed of robust β-CD/adamantane host/guest interactions. A combination of surface microscopies and fluorescence energy transfer experiments were conducted on the nanowires demonstrating their stability and resistance to disassembly.

The construction of porphyrinic nanostructures of well-defined shapes and sizes has received much interest due to their attractive photophysical, photochemical, and electronic properties.[1] While a variety of noncovalent interactions (including metal coordination and hydrogen bonding) have been used to self-assemble porphyrin nanostructures in organic solvents,[2] the preparation of analogously well-defined porphyrinic nanomaterials in water—a solvent of growing importance from biocompatibility and environmental standpoints—is rare and has largely been limited to the use of electrostatic forces in combination with π−π interactions.[3] However, π−π aggregation of porphyrins in water is a major reason for the formation of unwanted irregular aggregates and insoluble precipitates. We were thus interested in developing complementary aqueous assembly strategies that lead to high-definition porphyrin arrays *inter alia* by minimizing π−π aggregation.

We have recently reported the synthesis of porphyrin **1** (Figure 1) that does not undergo π−π aggregation because it is functionalized with eight bulky permethylated β-cyclodextrin (PMβ-CD) units.[4] Furthermore porphyrin **1** was specifically designed (by placing the β-CD units on each *meta* position of the *meso*-phenyl rings) to project four β-CD arms from each of its two faces. With this communication, we have prepared complementary (free-base) porphyrin **2** that projects four adamantane arms from its two faces. Moreover, we report the purely aqueous self-assembly of porphyrin **1** and **2** into a striking high-aspect ratio (single-molecule wide) nanowire **3** that forms through robust 1:1 β-CD/adamantane host−guest couples[5] (Figure 1).

In addition to investigating nanowire formation *via* transmission electron microscopy (TEM) and scanning tunneling microscopy (STM) studies, the binary nature of array **3** has enabled the study of intersubunit energy transfer (from donor **1** to acceptor **2**) using variable temperature steady-state fluorescence and time-correlated single photon counting experiments. These solution-based studies not only support the formation of an aqueous assembly but also demonstrate its remarkable stability, even to heating at 80 °C in the presence of excess disassembling agents (free PMβ-CD or adamantane carboxylate). This work demonstrates the versatility of using host−guest driven self-assembly to drive the formation of robust porphyrin nanowires in water without using π−π interactions.

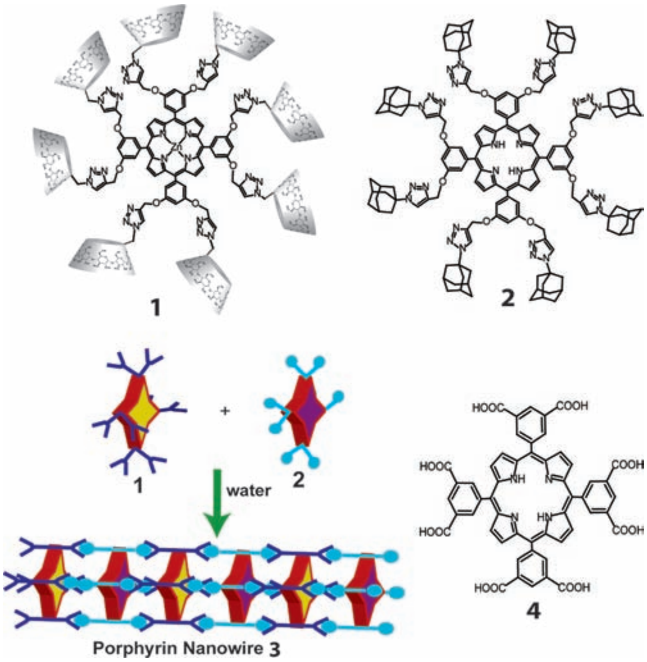

***Figure 1.*** Chemical structures of porphyrins **1**, **2**, and **4** and the aqueous assembly of nanowire **3** (*via* contiguous repeats of four β-CD/adamantane couples).

Porphyrin **2** was prepared *via* click reaction between 1-azidoadamantane and octaalkynyl Zn-porphyrin followed by demetalation with HCl.[6] Although porphyrin **2**, by itself, is not soluble in water, addition of **2** to an aqueous solution of porphyrin **1** followed by stirring for 24 h resulted in solubilization of **2** as gauged by the presence of characteristic absorption bands attributed to free-base porphyrin **2** (see Supporting Information (SI), Figure S3), suggesting the formation of a putative supramolecular assembly wherein the β-CD arms of porphyrin **1** sequester the hydrophobic adamantane arms of **2** to engender aqueous solubility to the latter macrocycle.

TEM studies were performed to probe the nature of the self-assembly. As shown in Figure 2a, the TEM image of an aqueous solution of **3** ($1 \times 10^{-6}$ M) displays micrometer-long wires that are ca. 100 nm in width. Moreover, when a lower concentration of the porphyrin assembly ($1 \times 10^{-7}$ M) was probed by TEM (Figure 2b), much smaller unidirectional wires are observed consisting of a chain of interlocked dark spots. The diameter of this latter system (~3.5 nm) is consistent with a single molecule wide array **3**

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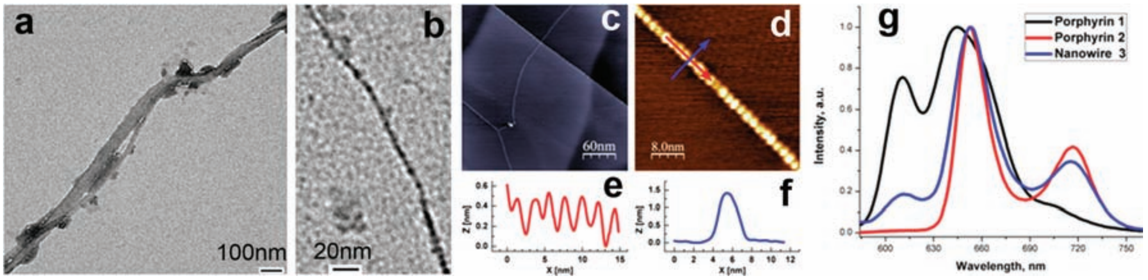

***Figure 2.*** TEM images of porphyrin nanowire **3** (a) at ($1 \times 10^{-6}$ M) and (b) at ($1 \times 10^{-7}$ M). STM images of porphyrin nanowire **3** on graphite. Image sizes are $300 \times 300$ nm$^2$ (c) and $40 \times 40$ nm$^2$ (d), $V_{\text{sample}} = +1.3$ V, and $I_{\text{tunnel}} = 0.5$ nA. The colored arrows indicate the positions where the line profiles (e) and (f) were taken. (g) Normalized fluorescence spectra of porphyrin **1**, nanowire **3** (both in water), and porphyrin **2** (in dichloromethane) (excitation wavelengths are 440, 440, and 420 nm, respectively).

composed of repeating porphyrin units. These TEM studies indicate the formation of discrete nanowires and higher-order bundles of nanowires at low and higher concentrations, respectively.

In an effort to obtain further evidence for the formation of nanowire **3** and to elucidate the periodicity of the array, STM measurements were undertaken. These measurements clearly display structures of wire-like morphology with lengths in the hundreds of nanometer regime (Figure 2c). A closer look at these unidirectional nanowires shows a repeating chain of bright protrusions that have a periodicity of 2 nm, an apparent height of 1.4 nm, and a diameter of 3 nm (Figure 2d−f). These dimensions compare well with the above-mentioned TEM images and with a suggested model (see SI, Figure S9) that assumes a 4-fold bundle structure where each bright spot represents the four 1:1 inclusion complexes between PM$\beta$-CDs of **1** and the adamantane arms of porphyrin **2**.

Since the above-mentioned surface characterization studies provide evidence for a defined supramolecular array with an interchromophore spacing of 2 nm, we were keen to explore the formation of nanowire **3** in solution through fundamental energy transfer studies (from donor **1** to acceptor **2**). As shown in Figure 2g, excitation of the assembly at 440 nm (where zinc porphyrin **1** is the dominant chromophore) in water at 25 °C resulted in an emission profile that is dominated by free base porphyrin **2**, with only a rather minor emission from Zn-porphyrin **1**. In contrast, steady state fluorescence experiments with a 1:1 mixture of porphyrin **1** and control porphyrin **4** (Figure 1; that cannot form inclusion complexes with the PM$\beta$-CD arms of **1**) do not exhibit appreciable zinc to free-base energy transfer (see SI, Figure S4). Taken together, these results suggest an efficient energy transfer event from porphyrin **1** to **2** which can be best explained by the formation of nanowire **3**. The rate and efficiency of energy transfer ($3.13 \times 10^9$ s$^{-1}$ and 81%, respectively)[7] were estimated by time-correlated single-photon counting (TCSPC) measurements (see SI, Figure S5).

Each $\beta$-CD/adamantane interaction in isolation is characterized by a significant binding constant ($\sim 10^4$ M$^{-1}$) in water.[8] Since nanowire **3** is composed of sequential repeats of four of these interactions, we were keen to probe its robustness. Thus variable-temperature fluorescence experiments were performed to determine whether the energy transfer process was intact at higher temperatures.[6] Interestingly, no significant change in the fluorescence spectra of **3** was observed even under rather harsh conditions (i.e., heating at 80 °C in the presence of excess PM$\beta$-CD or 1-adamantane carboxylate). These experiments (SI, Figures S10−15) indicate the substantial strength of nanowire **3**, most likely attributed to the multivalent nature of the assembly.[9]

In conclusion, we have disclosed a self-assembly procedure that harnesses host−guest interactions between complementary porphyrins to form well-defined porphyrin nanowires in water. Given the modularity (for e.g., electronically identical monomers can be used to develop homomeric porphyrin nanowires), water solubility, and resistance to disassembly of the present system, it is expected that alternate arrays with interesting electronic, catalytic, or photodynamic properties could be achieved. We are currently investigating these avenues.

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**Supporting Information Available:** Experimental details, characterization data, UV−vis and fluorescence spectra, TCSPC results, and molecular models. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) This value may represent a minimum energy transfer rate constant; see Supporting Information for details.

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