Water-soluble nanorods self-assembled *via* pristine C_{60} and porphyrin moieties†

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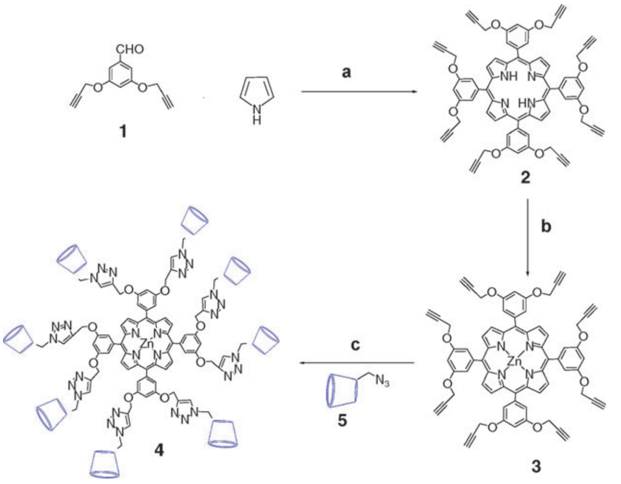
A novel water-soluble nanorod is discussed, which is prepared *via* the self-assembly of pristine C_{60} and a double-sided porphyrin projecting four β-cyclodextrins from each face.

The design of molecules imbued with specific structural information that encodes their spontaneous assembly into organized nanoscale structures is a salient goal in supramolecular chemistry[1] and is critical for further advancements in the bottom-up approach to nanofabrication.[2] From this point of view, supramolecular structures consisting of fullerene C_{60} and porphyrin subunits are particularly attractive for the fabrication of functional nanomaterials, given the potential light-harvesting and photo-induced electron transfer properties of their constituents.[3]

While elegant nanostructures composed of a C_{60}–porphyrin self-assembly have been studied in low dielectric solvents,[4] the development of such architectures in water—an attractive solvent from environmental, economic and biocompatibility points of view—remains a formidable challenge.[5] The reason for this difficulty is due to the low solubility of both components in water and their tendency to form ill-defined homomeric aggregates with diminished photophysical properties.[6] Furthermore, the few water-soluble C_{60}–porphyrin nanostructures developed thus far are largely based on either favorable van der Waals interactions between C_{60} and the porphyrin plane, or *via* axial coordination to metallated porphyrins. Hence, in order to enhance the repertoire of potential nanostructures that can be prepared, alternative modes of self-assembling porphyrin and C_{60} modules are required.

Our strategy to answer this problem exploits the unique ability of β-cyclodextrin (β-CD) to encapsulate pristine C_{60} in a 2 : 1 stoichiometry.[7a] While this ternary supramolecular motif has been used to assemble higher-order structures,[7b,c] to the best of our knowledge, there has been no exploration of using this motif to assemble porphyrin–C_{60} nanoscale architectures. In this communication, we detail the synthesis and assembly studies of "double-sided" zinc porphyrin derivative **4** (Scheme 1), judiciously designed to project four β-CDs from each of its two faces. Such functionalization not only enhances aqueous solubility and precludes porphyrin-based stacking interactions, but importantly also facilitates directional host–guest inclusion complexation with pristine C_{60}. In particular, the resultant self-assembly, while generated in DMF–toluene, is water soluble and forms unidirectional C_{60}–porphyrin nanorod **6** (Fig. 1) by exploiting repeats of four 2 : 1 β-CD–C_{60} interactions. The formation of nanorod **6** and its higher-order assembly has been extensively characterized *via* analytical and microscopic techniques, including dynamic light scattering (DLS), scanning tunneling microscopy (STM), transmission electron microscopy (TEM), and scanning electron microscopy (SEM).



Scheme 1 The synthesis of porphyrin **4**. *Conditions:* (a) propionic acid, reflux; (b) $Zn(OAc)_2$ in $CHCl_3$–methanol (10 : 1); (c) 6-azido-6-deoxy-PMβ-CD (**5**), sodium ascorbate, $CuSO_4$ in THF–H_2O.

A central feature of our assembly design is octadentate tetraphenylporphyrin derivative **4**, with permethylated β-cyclodextrin (PMβ-CD) substituents on each *meta*-position of the phenyl rings. It was expected that torsional strain would place the plane of the *meso*-phenyl rings close to perpendicular to the plane of the porphyrin macrocycle, thereby resulting in a double-sided porphyrin that projects four PMβ-CD units from each face. Furthermore, PMβ-CD was specifically chosen because methylation has been reported[8] to increase the effective diameter of the hydrophobic cavity of β-CDs, thereby better facilitating fullerene inclusion.

The synthesis of porphyrin **4** is outlined in Scheme 1 (*supra*) and features the highly efficient Huisgen [3 + 2] cycloaddition, which allows for the facile attachment of all eight PMβ-CD

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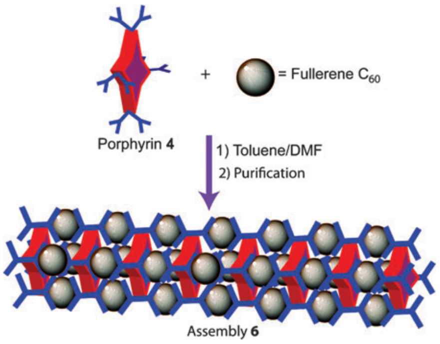

Fig. 1 The preparation of assembly **6** *via* inclusion complexation of pristine C_{60} by porphyrin **4**.

arms in a single step. Briefly, aldehyde **1** was prepared by the reaction of 3,5-dihydroxybenzaldehyde with propargyl bromide in excellent yield. Formyl derivative **1** was subsequently refluxed in the presence of pyrrole in propionic acid, followed by purification *via* column chromatography (silica gel column using methylene chloride as the eluent) to afford porphyrin **2** in 13% yield. Metallation of porphyrin **2** with zinc acetate afforded Zn porphyrin derivative **3** and the requisite double-sided porphyrin **4** was prepared by "clicking"[9] Zn porphyrin **3** with 6-azido-6-deoxy-PMβ-CD.[10]

Prior to investigating the potential of **4** to assemble in the presence of C_{60}, water-solubility studies were performed, with porphyrin **4** alone, using UV-vis spectroscopy. These experiments indicated that monomer **4** is indeed readily soluble in water. Furthermore, no porphyrin–porphyrin stacking interactions were observed (*i.e.*, the Soret band of **4** shows no broadening, even at 0.015 mM concentrations, and no absorption peaks characteristic for porphyrin aggregates were observed).[6] Encouraged by these preliminary studies, the self-assembly of porphyrin **4** in the presence of C_{60} was undertaken. Briefly, porphyrin **4** was incubated with 6 equiv. of fullerene C_{60} in a solution of toluene–DMF (a mixture that maximizes C_{60} solubility) for three weeks. Upon evaporation of the solvents, the resulting assembly was found to be soluble in water, and thus was dissolved in this same solvent and purified by filtration to remove any insoluble fullerene monomers and aggregates.

Preliminary evidence for the formation of a complex involving porphyrin **4** and C_{60} came from absorption studies. For instance, the FT-IR spectrum of assembly **6** (ESI, Fig. S1†) shows a characteristic peak at 527 cm^{-1} assigned to C_{60}.[4e] In addition, the electronic absorption spectrum of assembly **6** in water (ESI, Fig. S2†) displays broad bands (at 275 and 350 nm), albeit at low intensity, ascribed to C_{60}. In order to verify that these observed bands indeed correspond to C_{60}-based absorption, an aqueous solution of assembly **6** was extracted into toluene. The result of this experiment is illustrated in Fig. 2, clearly indicating the presence of C_{60} (*via* sharp absorptions bands at 278 and 332 nm) in the toluene layer.[4e] In contrast, an analogous extraction experiment with only porphyrin **4** does not show these dual absorption bands.

Although the aforementioned experiments demonstrate the presence of fullerene within assembly **6**, they do not, however, shed light on the size of the resulting supramolecular species. Hence, DLS studies were employed (ESI, Fig. S3†) that indicate, even at sub-micromolar concentrations of **6** (0.3×10^{-6} M), the presence of large aggregates with an average diameter of 263 nm.

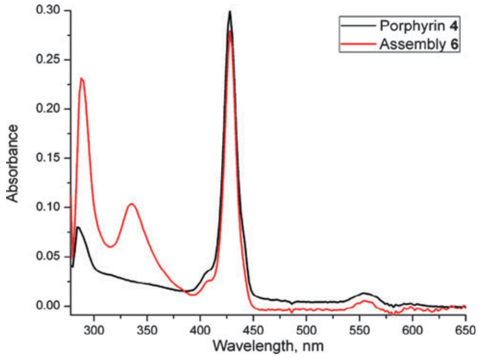

Fig. 2 UV-vis spectra of assembly **6** (red) and porphyrin **4** (black) upon extraction into toluene (from an aqueous solution).

In addition to the above mentioned solution phase studies, solid-state microscopies were undertaken to better characterize the nature of assembly **6**. The most telling information was gleaned from STM experiments. A dilute aqueous solution of assembly **6** (1×10^{-6} M) was deposited on a highly ordered pyrolytic graphite (HOPG) surface. Subsequent to evaporation of the solvent, STM investigations (Fig. 3a) displayed hundreds of nm long, one-dimensional nanorods, a finding not observed for porphyrin **4** alone. For the most part, these nanorods are located at steps of the HOPG substrate, probably because step edges provide more favorable binding sites than the flat terraces. As shown in the small-scale image in Fig. 3b, assembly **6** consists of a chain of bright protrusions. These protrusions have a periodicity of ∼2 nm, and an apparent height of 2.5 nm above the lower terrace next to the step edge (see line profiles in Fig. 3d and e).

The contrast in STM is not only a function of height but also of electronic structure, and tip convolution effects prevent accurate measurements of the dimensions of nanoscopic objects. Nevertheless, the periodicity as well as the measured

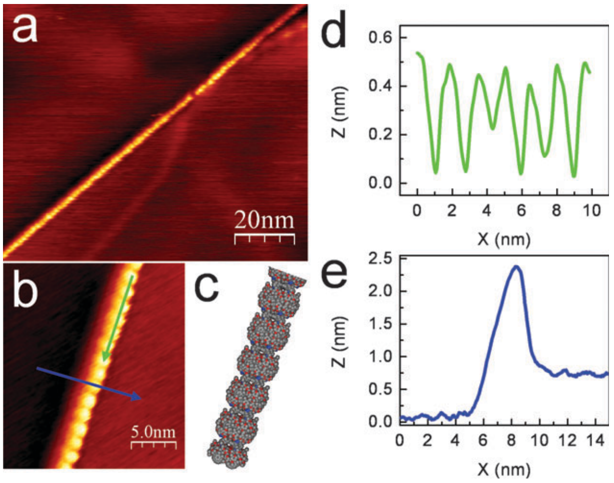

Fig. 3 STM images of assembly **6** on HOPG. (a) Image size 100 nm × 85 nm, sample bias voltage $V = +0.5$ V; tunneling current $I = 0.1$ nA); (b) 20 nm × 22 nm, $V = +0.5$ V; $I = 0.1$ nA. (c) Pictorial representation of assembly **6** and (d and e) line profiles of assembly **6** taken at the positions indicated by the arrows in (b).

height of the bright protrusions compare well with a suggested model that assumes a four-fold bundle structure (see Fig. 1 and 3c), where each bright spot[11] represents the four head-to-head PMβ-CD dimers (with each dimer encasing one C_{60} molecule). For example, the height of the nanorods (*ca.* 2.5 nm) is larger than the outer diameter of one PMβ-CD (*ca.* 1.6 nm) and thus supports a possible model that is two PMβ-CD units high. Likewise, the periodicity of $\sim$2 nm is consistent with repeats of head-to-head PMβ-CD dimers interdigitated by a porphyrin core with flexible linkers (see ESI, Fig. S4†).

Further evidence for a self-assembly consisting of four C_{60} molecules per unit of porphyrin **4** came from thermogravimetric analysis (TGA). Specifically, a sample containing only **4** loses 80% of its weight below 700 °C. On the other hand, a sample of assembly **6** loses only 63% of its weight below 700 °C (ESI, Fig. S5 and S6†). Thus, the remaining 17% that does not decompose under these experimental conditions is assigned to C_{60} (which is known to only decompose over 850 °C)[12]. This percentage is close to the theoretical value (18%) for four C_{60} molecules per unit of **4**.

With compelling evidence that assembly **6** forms a nanorod-type morphology at low concentrations, we were keen to discern the higher-order self-assembly of **6** in the solid-state. Thus, TEM studies were also performed. The sample for the TEM experiment was prepared by placing a drop of aqueous solution of assembly **6** (1×10^{-4} M) onto a carbon-coated copper grid, followed by evaporation of the aqueous solvent. As can be gathered from inspection of the TEM image of assembly **6** (Fig. 4a), several unidirectional structures with various lengths ranging from 300 to 500 nm are present. Based on the dimensions of assembly **6** (determined by STM studies) it is deduced that the long axes of these nanorods are formed by the inclusion complexation of approximately 150–250 units of porphyrin **4** with flanking fullerene C_{60} molecules.

In addition, SEM experiments were performed to determine whether porphyrin **4** (alone) and assembly **6** differed in their overall surface topology in terms of size and shape in the micron regime. As shown in Fig. 4b and c, both assembly **6** and porphyrin **4** display three-dimensional morphologies; however, the former forms significantly smaller macrostructures.

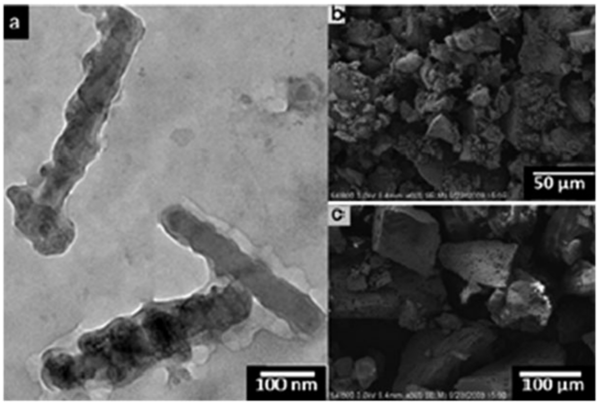

Fig. 4 TEM micrograph of assembly **6** (a), and SEM images of assembly **6** (b) and porphyrin **4** (c).

In conclusion, we have successfully designed and constructed a novel water soluble porphyrin–fullerene C_{60} nanorod *via* the inclusion complexation of a porphyrin-bridged octa-(β-CD) module **4** and pristine C_{60}. The nanorod structure is thought to be composed of sequential repeats of four 2 : 1 β-CD–C_{60} interactions. The development of other nanostructures based on water soluble porphyrins is currently under way in our laboratory.

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