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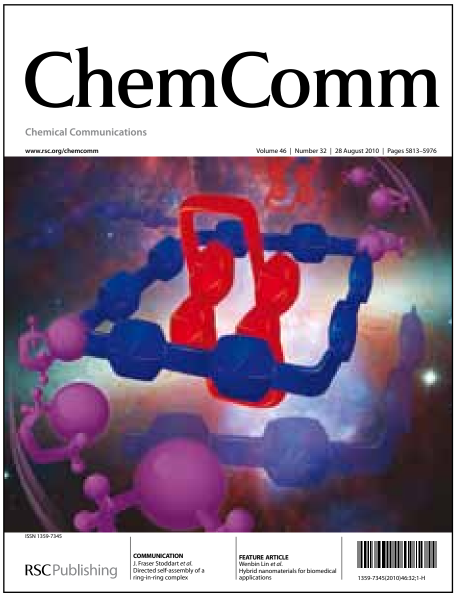

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ARTICLE TYPE

In-situ reversible conversion of porphyrin aggregate morphologies

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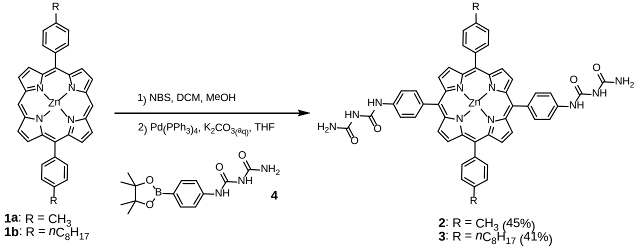
A porphyrin derivative possessing orthogonal self-assembly units displays in-situ reversible transformation of aggregate morphology between nano-rods and hollow spheres upon exposure to different solvents.

The design of well-defined self-assembled nanostructures based on specific supramolecular interactions between electroactive molecules is of interest for diverse applications such as field-effect transistors,[1] photovoltaics,[2] and sensors,[3] where the morphology of the active material plays a key role in determining the electrical properties of the final device. Organic materials with tailored functional groups capable of inducing the formation of nanostructures prior to or during deposition represent a route to supramolecular devices *via* a "bottom-up" approach, in which an ordered structural arrangement with nanometer precision over a large scale is constructed.[4] However, precise control of long-range order using non-covalent molecular interactions is still a challenge. Numerous factors, such as the nature and linking topology of the self-assembly motifs and the chemical structure of the functional core, as well as exterior factors such as solvent composition, aging time and deposition conditions, combine to form a complex ensemble from which the formation of specific nanostructures emerges. In some cases, it is possible to control the aggregation through an exterior stimulus. For example, a vesicle to nanofiber transformation could be reversibly induced by sonication and heating.[5] More generally, the addition of co-reagents,[6] pH modulation,[7] photochemical reaction,[8] or variation of solvent composition are used to induce transformation of aggregate structures.[9] Sometimes, reversible switching between dissolved and aggregated states can be promoted through solvent vapour annealing.[10] Despite the fact that the real-time interconversion between selected nanostructures is highly desired for potential application of soft materials,[11] the *in-situ* transformation of an aggregate's nano-morphology directly on a substrate is rare.[12]

Porphyrin derivatives decorated with self-assembly motifs have been widely used as molecular scaffolds for the construction of well-defined organic nanostructures such as fibres, sheets, rods, tubes, and cubes.[13] Herein, we report a porphyrin-based system that exhibits *reversible* solvent-induced transition between rod-like aggregates and hollow spherical structures directly on a substrate upon exposure to different solvents. The structure and synthesis of porphyrin derivatives **1** – **3** are shown in Scheme 1. Tetraphenylporphyrins **2** and **3** bearing bis-urea (biuret) substituents were obtained via NBS bromination of diphenylporphyrins **1a** and **1b** followed by Suzuki coupling with biuret boronic ester **4** in 45 and 41% yield, respectively (two steps).[14] Compared to **1b** possessing hydrophobic octyl side chains which promote self-assembly *via* van der Waals interactions, the biuret motifs are expected to induce self-assembly through hydrogen-bonding (H-B) interactions in aprotic media. In the case of **3**, possessing both octyl chains and biuret units, we may expect strong solvent-dependence of the self-assembly process.



Scheme 1 Synthesis of porphyrin derivatives **2**, and **3**.

The aggregation behavior of **1b**, **2**, and **3** was studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM samples were prepared by evaporating a solution of molecules **1b**, **2**, or **3** (10 μL, 0.1 mM) onto a SiO$_2$/Si substrate (1 × 1 cm^2). Environmental SEM images (taken under 0.45 Torr H$_2$O or THF vapour, see SI) of the aggregates formed by **1b** and **2** are shown in Figure 1. For **1b**, deposition from THF solution leads to the formation of nanorods with *ca.* 50-nm width and *ca.* 700-nm length (Figure 1a),[9] whereas deposition from THF/MeOH (1:1) solution leads to the formation of a non-uniform sheet topology (Figure 1b). In contrast, the deposition of **2** from THF/MeOH solution (10:1, *v/v*) leads to the formation of spherical nanoparticles with a uniform diameter of *ca.* 200-nm (Figure 1c). The particles are hollow, as shown by TEM images (Figure 1c, inset, also Fig. S1 in ESI). The formation of self-assembled hollow spheres of **2** upon evaporation of the solvent is analogous to previously reported bis-biuret derivatives with a rigid conjugated core and is directly attributed to the presence of H-B interactions.[14, 15] In contrast to **1b**, increasing the proportion of methanol (e.g. THF/MeOH = 1:100 *v/v*) did not lead to changes in the aggregates' morphology, but had the effect of dispersing the aggregates which retained their hollow sphere morphology (Figure 1d). The increased dispersion is not related to the Marangoni effect[16] as there is only a slight difference in surface tension between THF and methanol (26.4 vs. 22.7 mN.m^{-1}, respectively).

Some understanding of how the intermolecular forces control aggregation can be gleaned from the solid-state structures of **1b**

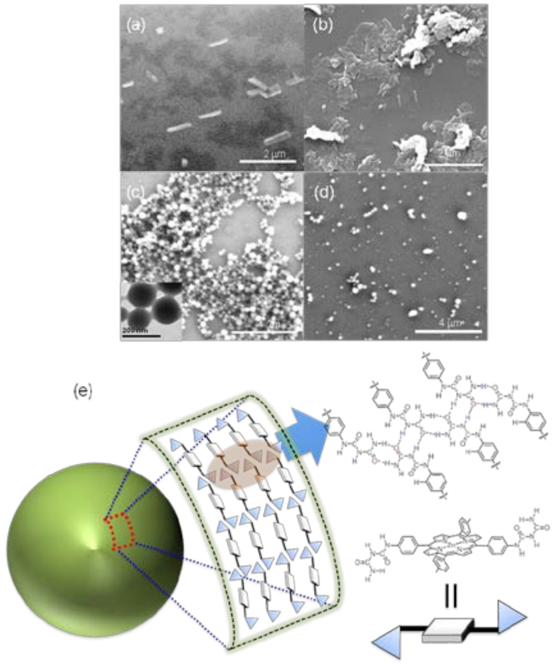


Fig. 1 SEM of **1b** (0.1 mM) prepared in (a) THF and (b) THF/MeOH (1:1, *v/v*) and **2** (0.1 mM) prepared in (c) THF/MeOH (10:1, *v/v*) and (d) THF/MeOH (1:100, *v/v*) at room temperature. The inset of (c): TEM of **2** prepared in THF/MeOH (10:1, *v/v*), showing hollow sphere structures. (e) Schematic representation of the proposed self-assembly of hollow spherical aggregates of **2**.

and **4**. Examination of the crystal structure of **1b** (Fig. S2) reveals that the porphirin cores in **1b** are not co-planar and that they are separated by a distance of 6.54 Å, whereas the octyl chains are in the all-*trans* configuration and interdigitated. This indicates that van der Waals interactions between octyl chains control intermolecular self-assembly in the crystal rather than co-facial π–π stacking as is often observed for planar π-cores with peripheral long chains.[17] Based on the crystal packing of **4** (Fig. S3), the biuret unit induces the formation of H-B ribbons. In the case of **2** which possess two biuret units at 180°, such ribbons would be interconnected and lead to the formation of sheets whose folding would result in hollow aggregates being formed (Figure 1e).

The deposition of compound **3** from solution of (THF/MeOH = 2:5 *v/v*) also led to the formation of rod-like aggregates (Figure 3a) similar to those obtained from **1b**. However, the addition of methanol did not result in a transformation of the aggregates as had been observed for **1b** in THF/MeOH = 1:1 (*v/v*) and distinct rod-like aggregates were still observed for **3** even at high methanol concentrations. Moreover, the average length of the rod-like aggregates (ca. 15 μm) was significantly longer than those of **1b** derived from THF. Treatment of the rod-like aggregates deposited onto the substrate with THF (10 μL)[18] led to their transformation into homogeneous spherical aggregates with an average diameter of *ca.* 200 nm (Figure 3b). The self-assembly behavior observed for **3** after THF treatment is the same as that of compound **2** deposited from THF solution, suggesting a similar process for the formation of the spherical aggregates in both cases. We thus conclude that the spherical aggregates derived from **3** present the octyl chains organized at the suprafacial and antarafacial positions of the 2D surface. The location of the octyl chains on the spherical surface would also account for the more dispersed nature of the aggregates in THF and suggests that they should be destabilized by the presence of a polar solvent. To verify this, the substrates containing the spherical aggregates were treated with (THF/MeOH = 2:5 *v/v*, 10 μL) to weaken the H-B interactions and enhance van der Waals forces between the octyl chains. In line with our expectations, rod-like aggregates once again re-emerged (Figure 3c). The process can be repeated (Figure 3d), successfully demonstrating the *in-situ* reversible conversion between self-assembled structures of different morphology.

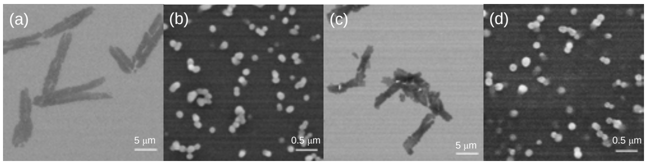


Fig. 3 Evolutionary SEM images (0.45 Torr H_2O or THF vapour, see SI) for morphology transition of **3** at room temperature. (a) As cast film from THF/MeOH (2:5, v/v). (b) The same substrate after treating with THF (10 μL). (c) After THF/MeOH (2:5, v/, 10 μL) treatment from (b). (d) After THF (10 μL) treatment from (c). All solvent treatments were directly done on the same substrate.

The electronic absorption spectra of **3** in THF and THF/MeOH (*v/v* = 2/5) and their corresponding aggregates (state I: sphere, II: rod) cast from solution (0.1 mM) are shown in Figure 4.

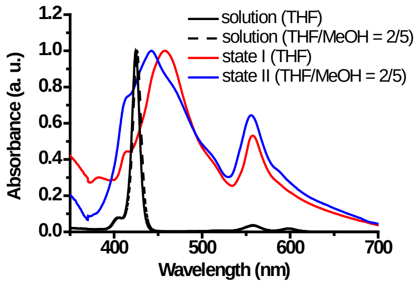


Fig. 4 Absorption spectra of **3** in THF (10^{-6} M, solid line) and THF/MeOH (v/v = 2/5) solution (4×10^{-6} M, dashed line) and their respective aggregates (states I and II) cast from their corresponding solutions (10^{-4} M).

In solution, **3** possesses sharp absorption bands that are independent of solvent composition, suggesting isolated molecule behavior. Compared to solution, both the Soret and Q bands of the porphyrin cores are red-shifted and significantly broadened when deposited onto a quartz substrate. These spectral changes are commonly observed in porphyrin aggregates and assigned to the formation of *J*-type aggregates with a slipped-stacked geometry.[19] The Soret band of **3** in the aggregates is split into two peaks centred at 415 and 441 nm for state I and 415 and 459 nm for state II, respectively. The two peaks have been previously assigned to the optical transitions from the transition dipole moments oriented parallel (longer wavelength) and perpendicular (shorter wavelength) to the aggregation direction.[20] The parallel transition dipole is sensitive to the distance between the porphyrin cores,[21] suggesting that the inter-porphyrin distance is increased in the aggregates formed in state II with respect to those in state I.

To better understand the evolution of the aggregates of **3** upon solvent treatment, the process was followed using TEM. The transition from rod-like to spherical aggregates upon exposure to THF is shown in Figure 5. By treatment of the spherical aggregates (Figure 5b) twice with methanol (5 μL), most transform back to rod-like aggregates (Figure 5c, d). Within the same substrate, a small portion of architectures that may correspond to the transition from the spherical to the rod-like morphology are also observed. Their morphology suggests that the transition occurs by fusion of the spherical aggregates into needles (Figure 5e), which then grow in length. In addition, larger and more complex assemblies involving hierarchical aggregation of the rods onto thin sheets (Figures 5f~h) were also observed. This phenomenon resembles the merging behavior exhibited by **1b** aggregates in the presence of methanol. More importantly, the interconversion between vesicle and rod-like aggregates is reversible by switching between THF and methanol.

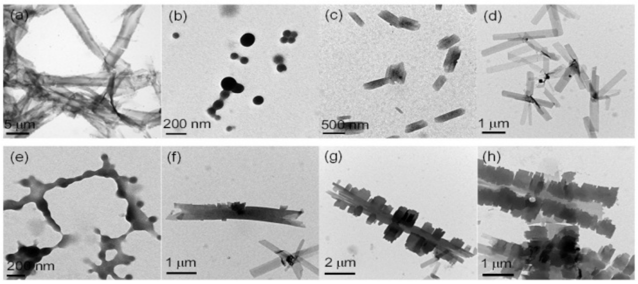


Fig. 5 Evolutionary TEM images for the transition of **3** at room temperature. (a) As cast film from THF/MeOH (2:5, *v*/*v*). (b) After THF (2 × 5 μL) treatment from as cast film. (c)-(h) show evolutionary progression of morphological transition from hollow spheres to sheet aggregates after MeOH (2 × 5 μL) treatment from (b). All solvent treatments were directly done on the same substrate.

In summary, we have developed a porphyrin derivative incorporating amphipathic groups whose self-assembly can be reversibly controlled through exposure to different solvents. Polar protic environments disrupt H-B interactions between the biuret groups and favor the hydrophobic interactions between the octyl chains (van der Waals forces), leading to the formation of rod-like aggregates. The reverse occurs in less polar aprotic media, which favor H-B over hydrophobic interactions and induce the formation of spherical aggregates. These results are in agreement with model systems that show that the rod-like and spherical aggregates arise from hydrophobic and H-B interactions, respectively. The switching between aggregate morphologies in **3** is thus understood on the basis of solvent favoritism for specific functional groups. Of particular interest is the fact that the process is entirely reversible and that it can be conducted directly onto the substrate analogously to solvent annealing procedures. Given the large difference in morphology between the spherical and rod-like aggregates, we believe the transition occurs via (partial) dissolution of the material in the liquid phase.

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† Electronic Supplementary Information (ESI) available: Synthesis, characterization, ^{1}H, ^{13}C NMR spectra for **5b**, **1b**, **2**, **3** , crystal structure parameters for **1b** (CCDC 881738) and **4** **(**CCDC 881739). See DOI: 10.1039/b000000x/

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