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# Synthesis and self-assembly of giant porphyrin discs†

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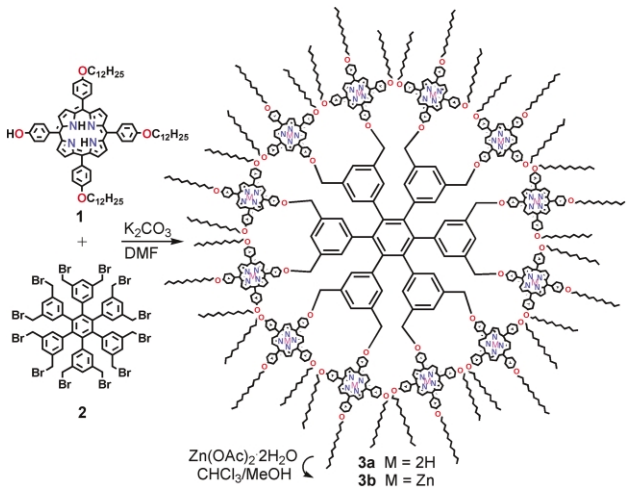
**A giant porphyrin disc ($M_w$ = 15 kDa) has been synthesized and its self-assembly behaviour at an interface studied by liquid STM which reveals the presence of huge domains (> 400 × 400 nm²) of very well ordered and molecularly resolved columnar stacks.**

Nowadays, one of the most appealing topics in the field of supramolecular chemistry is the (non-covalent) synthesis of multi-porphyrin arrays.[1] These arrays are ideal model systems, not only for the study of energy transfer mechanisms and as mimics of the natural photosynthetic system, but they can also be foreseen as functional components in nanodevices.[2] We have been working on the construction of a family of disc-like porphyrin arrays *via* covalent synthesis, which can further self-assemble into well-defined nanometre-sized aggregates in solution and at solid/liquid interfaces.[3,4] Their aggregation behaviour is governed by strong intermolecular π–π-interactions. In order to create columnar porphyrin arrays with an even higher stability and definition, we here present the design, synthesis, and self-assembly behaviour of a novel disc-like porphyrin dodecamer **3** (Scheme 1). This molecule, in which 12 porphyrins are arranged in a circular fashion around a rigid central core, has an extended π-surface with a diameter of 4 nm.

Dodecamer **3a** was prepared by a 12-fold nucleophilic substitution of **2**[5] with porphyrin **1** in hot DMF and was obtained in a remarkably high yield of 55%, which suggests that a significant templating occurs involving favoured coupling of a porphyrin molecule to the core when other porphyrin moieties are already attached.[3a] Zinc derivative **3b** was synthesized by reaction of **3a** with zinc acetate in a mixture of chloroform and methanol (2 : 1 v/v). MALDI-TOF MS (*m*/*z* = 14895 for **3a** and 15721 for **3b**) and elemental analysis confirmed the identity and purity of both **3a** and **3b**.




**Scheme 1** Synthesis of porphyrin dodecamers.

† Electronic supplementary information (ESI) available: experimental procedures and characterization data, NMR- and UV/Vis-titration data. See http://www.rsc.org/suppdata/cc/b4/b401324g/

The resonances in the $^1$H-NMR spectra of **3a** and **3b** are severely broadened as compared to the spectra of **1** and **2**. The considerably upfield shifted resonances of the *cis*-phenyl protons ($\Delta\delta$ = −1.2 ppm for H4, −0.7 for H6, −1.0 for H5 and −0.6 for H7, respectively, see Fig. 1) and of the $OCH_2$ protons of the *cis*-alkyl substituents ($\Delta\delta$ = −0.9 ppm for H32 and −1.43 for H18, respectively), as compared to **1**, indicate strong shielding of these protons by a neighbouring porphyrin plane. In contrast, the signals of the *core*-phenyl protons and *link*-benzyl protons are shifted downfield ($\Delta\delta$ = +0.9 ppm for Ha, +1.4 for Hc and +1.3 for Hb, respectively) compared to the dodecakis(methoxy) derivative of **2**.† Based on the 1D and 2D $^1$H-NMR experiments (COSY, NOESY), molecular modeling indicated that in solution both **3a** and **3b** adopt a unique 'yo-yo'-like shape, in which two disks each of 6 porphyrin moieties are stacked in an off-set fashion (Fig. 1).

UV/Vis spectroscopy of **3a** in chloroform revealed an overall broadening, but not a shift of the Soret absorption (at 423 nm) as compared to a monomeric reference porphyrin. This indicates that at micromolar concentrations there is no apparent aggregation of the molecules. From a concentrated solution in 1-phenyloctane, however, the disc-like molecules appeared to self-assemble at a solid/liquid interface. Scanning tunneling microscopy (STM) studies revealed that **3a** forms stable monolayers at the HOPG/solution interface (Fig. 3a) in which the individual dodecamers, despite their large diameter (4–8 nm), could be clearly distinguished. The observation that the molecules on the surface are 'edge-on' oriented and not parallel, which is the most common orientation observed for porphyrins on HOPG,[6] indicates the presence of strong intermolecular π–π-interactions. Surprisingly, molecules of zinc derivative **3b** did not form stable adlayers at the solid/liquid interface. This is tentatively attributed to the axial coordination of water molecules to the zinc ions as a result of which stacking is inhibited. We have shown previously that aggregation of zinc porphyrin hexamers can be induced by the addition of the bidentate ligand 1,4-diaza[2.2.2]bicyclooctane (DABCO) to the solution of these porphyrins.[4] The binding of DABCO to **3b** was

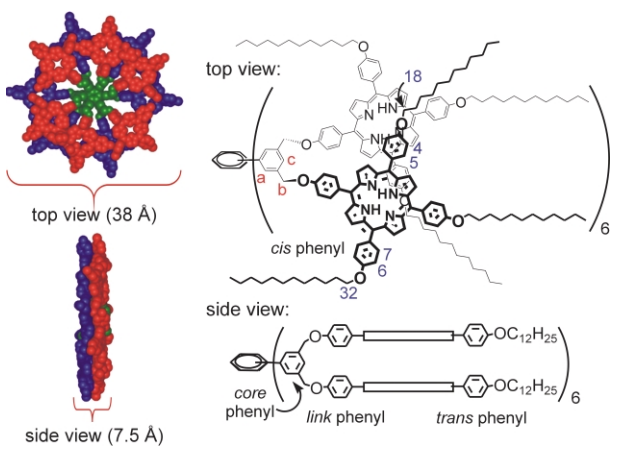



**Fig. 1** Left: proposed 'yo-yo'-like shape of **3a** in solution (alkyl tails have been omitted for clarity). Right: proton designations and proposed respective orientation of two porphyrin moieties within **3a** as derived from 1D and 2D NMR.

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investigated by UV/Vis and NMR titrations in chloroform. Upon binding of DABCO, the Soret band shifted from 424 to 427 nm, indicative of the formation of a DABCO : **3b** complex (Fig. 2a). In the spectra one isosbestic point was present (Fig. 2b, inset) which suggests the formation of only one distinct porphyrin species during the titration. The titration curve displayed an inflection point after the addition of ~6 equivalents of DABCO, a stoichiometry at which a sandwich-like DABCO : **3b** complex is most feasible, and leveled off after the addition of ~12 equivalents (Fig. 2b). $^1$H-NMR titrations of DABCO and **3b** showed a resonance of the DABCO protons at −4.9 ppm (Fig. 2c, top), which indicates that the ligand molecules bind in between two porphyrin moieties in a sandwich-like geometry, either in an intra- or intermolecular fashion (Fig. 2a). Both the peak width (at half height) and the upfield shift of the DABCO protons are minimal when ~6 molecules of DABCO are bound (Fig. 2c, bottom). In addition, the $^1$H-NMR resonances for the porphyrins and tails became more symmetric, indicative of a change in the porphyrin arrangement from an offset to a cofacial geometry. After the addition of more than 6 equivalents of DABCO, it was expected that the excess ligands would compete with the ones bound in the sandwich complex.[7] The peak at −4.9 ppm indeed broadened, but remained visible, even after the addition of a 500-fold excess of DABCO or after dilution to 0.17 mM (two processes which are expected to shift the equilibrium towards a 1 : 1 complex, Fig. 2a bottom). In addition, the cofacial arrangement of the porphyrins appeared to be retained. These results suggest that the sandwich complex which is formed after the addition of 6 equivalents of DABCO is exceptionally stable. STM was used to directly observe the complexes. Whereas **3b** alone did not form stable monolayers at the HOPG/solution interface, the addition of an excess of DABCO to the solution of **3b** caused the instantaneous formation of huge

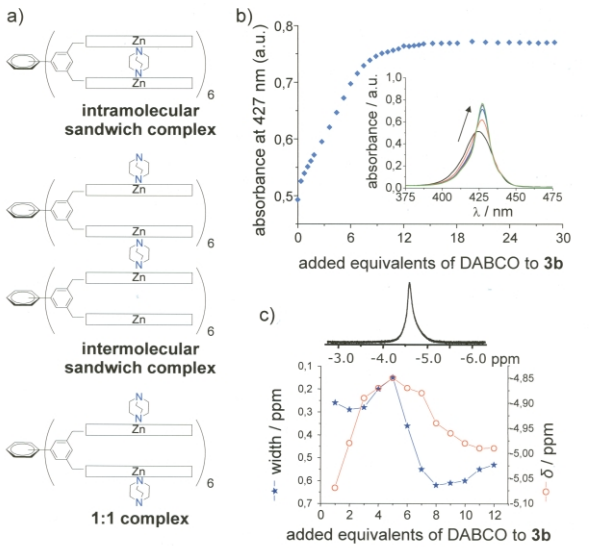


**Fig. 2** (a) Schematic representation of possible DABCO : **3b** complexes. (b) UV/Vis titration curve of the addition of DABCO to **3b** (0.14 μM) in chloroform. (c) Top: part of the $^1$H-NMR spectrum of **3b** with 6 equivalents of DABCO present. Bottom: peak width at half height and chemical shift upon the addition of DABCO to **3b** (0.69 mM) in chloroform.

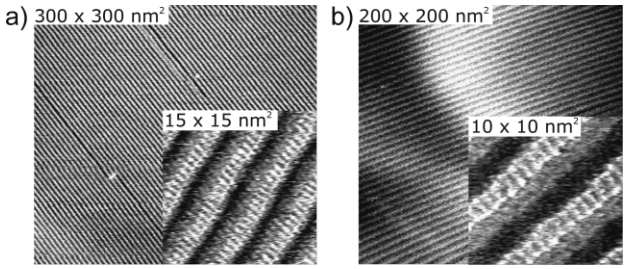


**Fig. 3** (a) STM topography of a monolayer of **3a** at the interface of 1-phenyloctane and HOPG where the molecules are positioned perpendicular to the surface in columnar arrays with a measured lamellar distance of 47 Å and at a mutual distance of 6.3 Å. The bright spots are domain boundaries. (b) STM topography of **3b** with excess DABCO. The measured lamellar distance is 44 Å and the distance between the molecules 8.2 Å. Insets: high-resolution images. $V_{bias}$ = −225 mV; $i_{set}$ = 1 pA.

domains (> 400 × 400 nm²) of stable lamellae of the supramolecular complex, in which the dodecamer molecules are arranged in a similar fashion as observed for **3a** (Fig. 3b). The individual dodecamers can be clearly discerned, and although the DABCO molecules cannot be resolved in the STM images, they are proposed to be bound in between the porphyrins. This coordination is further indicated by the fact that the molecules of **3b** are positioned at a slightly larger distance than those of **3a**. The dramatic effect of the addition of DABCO on the self-assembly behaviour of **3b** at a solid/liquid interface suggests that the ligand acts as a 'glue' to connect the dodecamers and freezes the dynamics within the monolayer.

We are currently investigating whether manganese derivatives of the porphyrin dodecamer can be assembled into columnar arrays in a similar fashion to create catalytically active surfaces.

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