Synthesis and self-assembly of giant porphyrin discs†

Marga C. Lensen, Sandra J. T. van Dingene, Johannes A. A. W. Elemans, Harm P. Dijkstra, Gerard P. M. van Klink, Gerard van Koten, Jan W. Gerritsen, Sylvia Speller, Roeland J. M. Nolte and Alan E. Rowan

NSRIM Center, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands.
E-mail: jelemans@sci.kun.nl, E-mail: rowan@sci.kun.nl; Fax: (+31) 24 365 2929; Tel: (+31) 24 365 2238
Debye Institute, Department of Metal-Mediated Synthesis, Utrecht University, The Netherlands.

First published as an Advance Article on the web 23 February 2004

A giant porphyrin disc (Mw = 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. 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. 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. 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 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. 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/
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). 1H-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 1H-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. 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 domains (> 400 \times 400 \text{nm}^2) 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.

Notes and references


