

Publishable Summary

The project dealt with the synthesis and characterisation of double-strand porphyrin nanorings. Double-strand porphyrin nanorings consist of two fully π -conjugated porphyrin nanorings that are held together by coordinative interaction between the zinc-metal centres of the first nanoring with the pyridyl-substituents of the second porphyrin. This results in an edge-to-face arrangement setting up the conjugated π -systems orthogonal to each other. The double-strand formation allows fixing the conformation of the nanorings: one will be forced into a plane and the other one into a barrel-shape. Both conformations should exhibit enhanced effective conjugation compared to a corresponding free ring.

The arrangement of porphyrins in the double-strand nanoring resembles the arrangement of bacteriochlorophyll molecules in the light-harvesting systems (LH2) of purple bacteria. Therefore double-strand nanorings are expected to be interesting models for such natural systems allowing for further investigation and understanding of energy migration in photosynthetic systems.

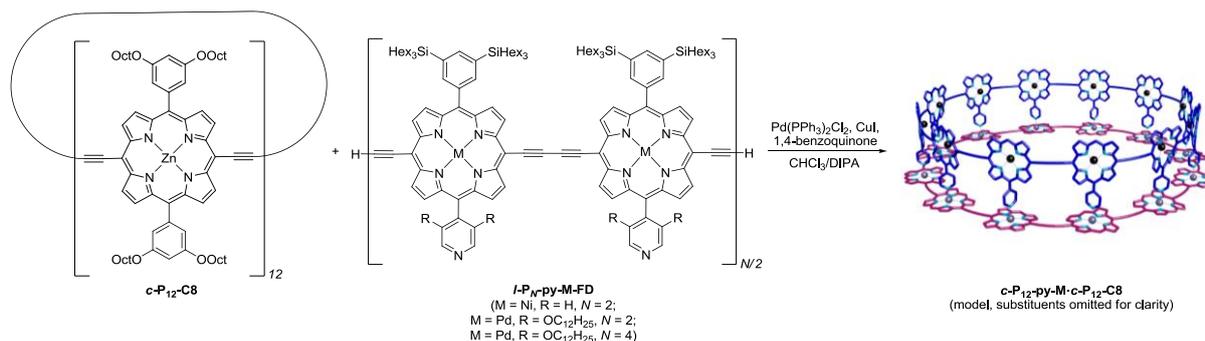
The synthetic approach to the double-strand geometry uses an existing zinc porphyrin-nanoring consisting of 12 porphyrin units *meso*-linked by butadiyne bridges as a template. A suitable dimer was designed that can bind to the initial 12-ring and form a complementary strand under Glaser coupling conditions. This dimer consists of two porphyrin units *meso*-linked by a butadiyne bridge. The opposite *meso*-positions are substituted with an ethynyl-group, that allows for the coupling to larger oligomers under Glaser coupling conditions. Each porphyrin further bears a pyridyl-substituent in one of the remaining *meso*-positions. This unit provides the coordinative binding interaction to the zinc porphyrin 12-ring. The remaining substituents are chosen according to their ability to ensure solubility and to avoid aggregation. The porphyrins host a metal that does not prefer binding a fifth N-ligand. According to these design elements the synthesis of two different porphyrin dimers was elaborated. Each dimer ***l*-P₂-py-M-FD** (Scheme 1) was synthesized in 9 steps.

To prove the binding abilities of the designed pyridyl-dimer it was combined with a linear zinc-porphyrin dimer. This resulted in double-strand formation which was analysed by UV-Vis and NMR. Titrations with competing ligands revealed the expected strong binding between the two types of dimers.

The combination of the dimer ***l*-P₂-py-M-FD** with the zinc-porphyrin 12-ring ***c*-P₁₂-C8** led to the formation of a 6:1 complex. Under Glaser coupling conditions this complex was transformed into the desired double-strand ring-ring complex with up to 30% yield. Extensive purification allows the separation of the desired complex from oligomeric side products. The double-strand complex was characterized by UV-Vis, GPC, MALDI-MS and solution SAXS (in cooperation with Marc Malfois at Diamond Light Source). The addition of a large amount of a competing ligand such as pyridine allowed the isolation of the newly formed 12-ring, which was further characterised by NMR, UV-Vis and MALDI-MS. Since a 10-ring was observed as a side product, the double-ring synthesis was as well performed by combining

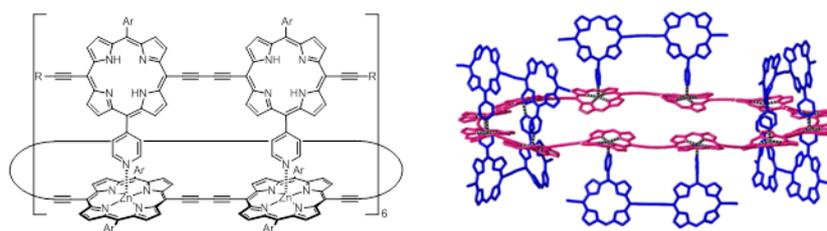
tetramer *l*-P₄-py-Pd-FD with *c*-P₁₂-C8. This prevented the formation of the 10-ring side product and simplified the purification.

The described double-ring synthesis offers a new templated approach to porphyrin nanorings. So far they have been synthesized using star-shaped templates. The described new approach now allows the use of an existing nanoring as a template to synthesize a new nanoring of the same size. This concept opens new avenues towards the self-replication of nanorings.



Scheme 1 Synthesis of double-strand porphyrin nanorings.

A 6:1 complex of a pyridyl-substituted free-base porphyrin dimer and a zinc porphyrin 12-ring was investigated (Scheme 2) by time-resolved fluorescence spectroscopy in cooperation with Professor Laura Herz and Dr Patrick Parkinson in Oxford University, Physics Department. The results reveal a very fast energy-transfer from the dimers to the 12-ring. The transfer-rate is comparable with energy-transfer rates observed in natural light harvesting systems. Therefore the double-strand porphyrin nanoring architecture might reveal further insight into understanding light harvesting systems and open new ways of mimicking such photosynthetic processes.



Scheme 2 6:1 complex of free base-porphyrin dimer with zinc porphyrin 12-ring, which was investigated by ultrafast fluorescence spectroscopy.