

Final Report

1. Publishable Summary

The project dealt with the synthesis of fully conjugated porphyrin oligomers and the spectroscopic characterization of their radical cations and photoexcited triplet states. Extensive studies have been devoted to monomeric porphyrin radical cations and their electronic structure, however, only little is known for porphyrin oligomers. We synthesized a porphyrin series comprising between one to six porphyrin units connected via butadiyne bridges in the meso position and investigated their spectroscopic properties upon one electron oxidation and photoexcitation. Curved π -systems have been shown to possess unique and different electronic properties than their linear analogues. Rigid porphyrin nanorings comprised of 6 porphyrin units have been investigated to obtain insights into their electronic structure. The second part of the project dealt with the development of new synthetic methodologies to extended porphyrin tubes and the investigation of their optoelectronic properties.

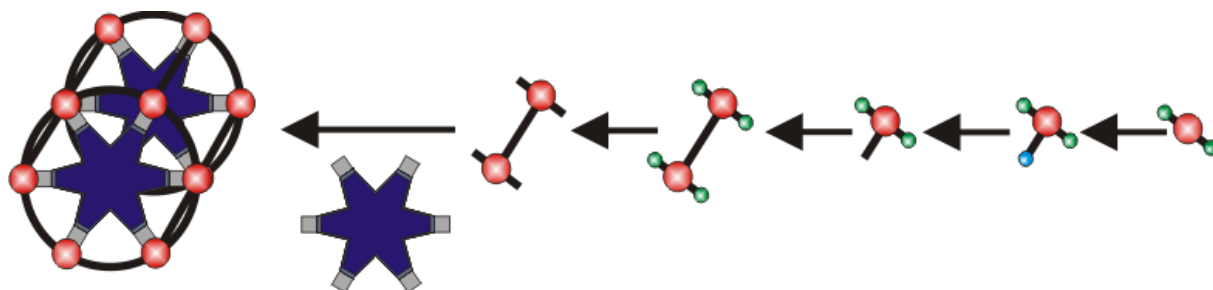
Charge circulation in porphyrin nanorings is expected to lead to unusual magnetic behavior, which could lead to a platform technology for organic-based magnetic data storage. Understanding these materials is relevant to mesoscopic physics, and to molecular-scale electronics, and may eventually lead to the synthesis of molecular solenoids and nano-electromagnets. The issue of charge delocalization in molecular nanorings is important because of the remarkable Aharonov-Bohm oscillations in mesoscopic metal rings.

Absorption and emission spectra show that **c-P6•T6** has a smaller HOMO-LUMO gap than the linear analogue **l-P6**. This is confirmed by electrochemical measurements; **c-P6•T6** shows six single-electron oxidation and reduction waves. Radical ions of conjugated porphyrin oligomers are easily generated in solution by chemical oxidation (e.g. with tris(4-bromophenyl)aminium hexachloroantimonate, BAHA). The spin state and electronic structure of these radical cations have been studied by EPR and ENDOR spectroscopy at X- and W-band both at rt and in the frozen glass. It was found that the line-width of the ESR signal is proportional to $N^{-0.5}$ at rt, where N is the number of porphyrin centers, confirming full delocalization or fast hopping of the spin. CW-EPR measurements conducted at cryogenic temperature find the peak-to-peak linewidth to stay constant, while changing from a Gaussian to a Lorentzian shape. ENDOR spectroscopy at low temperature unequivocally indicates that the spin is statically delocalized only through two porphyrin units in all systems, showing that the cw-EPR peak-to-peak linewidth is not an adequate property to probe spin delocalization. The near-IR and IR absorption spectra of these radical ions have been investigated at room temperature in a mixture of dichloromethane and tetrahydrofuran (10:1, v/v). Similar to studies on polymeric systems, the spin and charge distribution in porphyrin oligomers are not superimposable, because they are affected by different factors. Trends in the UV/Vis-NIR electronic transitions and the intervalence charge transfer bands allude to a static delocalization length of three units for the charge distribution in the studied porphyrin oligomers. Support for this assignment is provided by the IR spectra, where intensifications of butadiyne stretching vibrations of three to four orders of magnitude are found in comparison to the neutral oligomers, in good agreement with DFT calculations on these species. The

intensification of several IR vibrations can be ascribed to large charge fluxes within the oligomer radical cations due to the corresponding vibration.

Triplet excited states of porphyrins are generally found to be localized on one or two porphyrin units within oligomers and polymers. A similar conclusion has been drawn for the butadiyne-linked linear porphyrins, which are delocalized through two units. However, TR-EPR spectroscopy of the porphyrin nanoring shows full delocalization over six porphyrin units at cryogenic temperature. Furthermore, the delocalization of the linear systems can be extended by binding them to rigid and circular polypyridyl templates. Complete delocalization through three, four, and six units is found at cryogenic temperatures as judged by the zero-field splitting parameters of the triplet states for linear trimer, tetramer, and hexamer bound to a star shaped template, respectively. The oligomers stay attached to the template even at cryogenic temperatures as could be shown by low temperature UV/Vis-NIR spectroscopy.

Different morphologies of extended carbon species, like fullerenes, carbon nanotube, and graphene are known for their unique electronic characteristics. However, little is known of extended porphyrin structures. A porphyrin nanoring has been synthesized before by template assisted synthesis and we attempted to synthesize and characterize a monodisperse porphyrin nanotube through an analogous template assisted route. Using well-established synthetic methodology, we were able to synthesis the porphyrin dimer precursor in high quantities. Mixing of the four-fold ethyne-ended porphyrin dimer with a six-fold template under Glaser-coupling conditions gave a porphyrin nanotube for the first time. Optimization of the reaction conditions allowed us to increase the isolated synthetic yield to 40% (see scheme 1). The nanotube was characterized by NMR, UV/Vis, MALDI, and fluorescence spectroscopy.



Scheme 1. Synthetic route to the porphyrin nanotube. Red dots denote porphyrins. All substituents are attached to meso positions. One meso position is substituted with an aryl substituent bearing two THS sidegroups (not shown): short black lines are ethyne bonds, long black bonds denote butadiyne bonds, green and blue dots are protecting groups that are orthogonal towards each other. The star shaped structure is a rigid six fold pyridyl template.

In terms of electronic properties, the nanotube is found to be closely related to the nanoring. Its high symmetry is indicated by the low fluorescence quantum yield. Similar Herzberg-Teller vibrations are necessary to reduce the symmetry of the nanotube and allow emission of the first excited singlet state. The onset of the fluorescence is shifted to the red in comparison to the nanoring due to the extended delocalization of the singlet excited state in the nanotube. Reduction of the HOMO-LUMO gap, as measured by electrochemistry, hints towards the same direction of larger delocalization in the nanotube. In addition the radical cation of the nanotube is found to be delocalized through 12 porphyrin units at rt.