

Final Report

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Introduction

Since the discovery of conducting polymers organic electronics became a growing field of academic and industrial research. Due to low manufacturing costs and advantageous mechanic properties of organic electronic devices, they can complement the existing silicon based technology. Organic π -conjugated molecules are already used in organic thin-film transistors or bulk-heterojunction photovoltaic.

Most of the applied π -systems so far are linear conjugated molecules. Cyclic compounds having a fully conjugated π -system have recently attracted a lot of attention due to their unique properties. They can be regarded as a model for infinitely conjugated π -systems, lacking of endgroup-effects and possessing an inner cavity. This leads to unusual optical, electrical and magnetic properties compared to the corresponding linear oligomers. Over the last two decades there has been huge progress in synthesis and characterization of conjugated macrocycles composed of units like benzene, thiophene, acetylene or their combinations.^[1]

While the majority of the conjugated cyclic systems have an axial π -system molecules showing a radial π -system are of particular interest. Anderson's group recently described the template directed synthesis and characterization of porphyrin nanorings consisting of 6, 8, and 12 porphyrin units.^[2,3] These are huge fully conjugated cycles with a radial π -system. As described for cycloparaphenylenes^[4] the deviation of the π -orbital properties from the linear oligomers is increasing by decreasing ring size. The porphyrin 6-ring has the most strained and stiffest geometry of the porphyrin nanorings synthesised so far. Investigation of the π -system by voltammetry, optical spectrometry, and quantum-chemical calculations as well as a crystal structure show that this 6-porphyrin nanoring behaves as a single π -system, not as an assembly of six discrete porphyrin chromophores.^[3]

Aim of this project was to get a deeper understanding of the π -delocalisation in the porphyrin nanorings with focus on the porphyrin-6-ring. An informative method for the investigation of the π -delocalisation in extended π -system is to oxidize the molecule and to explore the resulting radical cation. The Optical properties of radical cations can provide information about relative energy and symmetry of π -orbitals. Even more information can be acquired by electron paramagnetic resonance (EPR) measurements on radical species. The bandshape of continuous wave (CW)-EPR signals can provide information on the π -delocalisation by means of the hyperfine coupling of the unpaired electron with nuclei having a nuclear spin. In general the bandwidth of the EPR signal is decreasing by increasing π -system because the individual hyperfine couplings become smaller. Theories for the quantification of the π -delocalisation have been developed for conjugated polymers^[5] and have already been used for the investigation of conjugated porphyrin systems.^[6]

To carry out experiments on radical cations it is necessary

to find conditions to prepare radical cations that are reasonably stable in the timescale the experiments are performed. The reversibility of the oxidation must be proved by reduction back to the starting material, to be sure that the species measured is the expected radical cation and not a decomposition product. To establish a relation between porphyrin nanorings and the corresponding linear oligomeres series of rings and oligomers of different size need to be synthesised and investigated.

Results and Discussion

Porphyrin derivatives having 3,5-bis-trihexylsilyl-phenyl substituents in meso-positions^[7] (figure 1) fulfill above conditions. A series of linear porphyrin oligomers from monomer to hexamer ***l-PN*** ($N = 1-6$) as well as the cyclic hexamer with ***c-P6***·***T6*** and without template ***c-P6*** were synthesised. Stable radical cations that can be reduced reversibly could be generated. The huge number of alkyl chains provide excellent solubility in un-polar solvents and aggregation of the sample molecules can be excluded.

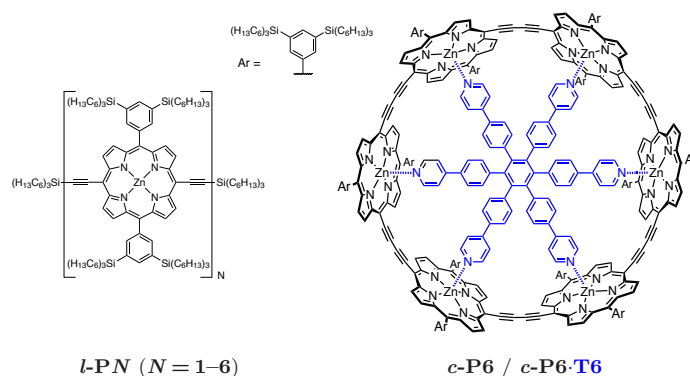


Figure 1: Structure of sample molecules: linear porphyrin oligomeres ***l-PN*** ($N = 1-6$) and porphyrin nanorings ***c-P6*** / ***c-P6***·***T6***

For comparison of the optical properties the absorption of porphyrin oligomers and nanorings in degassed dichloromethane were measured. The trend in the first electronic transition $S_0 \rightarrow S_1$ of the oligomer series ***l-P1*** to ***l-P6*** is the same as described for other derivatives, i.e., the Q-band is red shifted and intensified with increasing chain-length.^[8] By fitting the absorption energy to the function $E_{i(N)} = E_{i,\infty} + (E_{i,1} - E_{i,\infty}) \exp(-a_i \cdot (N - 1))$ introduced by Meier et al.^[9] the high degree of π -delocalisation can be demonstrated ($N =$ number of repeating units, $E_{i,1}$ and $E_{i,\infty} =$ absorption energy of the monomer ($N = 1$) and the polymer ($N \rightarrow \infty$) respectively, and a_i as parameter indicating how

fast the limit of convergence is approached). The absorption of the 6-rings **c-P6** and **c-P6·T6** can not directly be related with the oligomers since the $S_0 \rightarrow S_1$ transition is symmetry forbidden whereby the long wavelength absorption is dominated by the strongly allowed $S_0 \rightarrow S_2$ transition.^[3] But qualitative it can nicely be seen that the cyclic hexamer **c-P6** shows a bathochromically shifted absorption compared to the linear hexamer **l-P6** due to increased π -delocalisation in the ring. This effect can be further increased by freezing rotation around the alkyne bounds by introduction of the template in **c-P6·T6**.^[3]

The absorption of the oligomer radical cations show a bathochromically shifted Q band. Plotting the maxima of the longest wavelength peak vs. the reciprocal number of porphyrin units and fitting with above equation shows a high π -delocalisation in the radical cation oligomers that converges slightly slower than for the neutral species (figure 2). The longest wavelength absorption of the 6-ring radical cations **c-P6⁺** and **c-P6·T6⁺** have their maximum longer wavelength than the hexamer radical cation **l-P6⁺**. Again the ring with the stiffened **c-P6·T6⁺** shows a significant bathochromic shift in absorption compared to the more flexible **c-P6⁺**. Comparison of the absorption between **c-P6·T6⁺** and the other derivatives is only qualitative since the the coordination of the template's pyridines to the zinc also influences the optical properties.

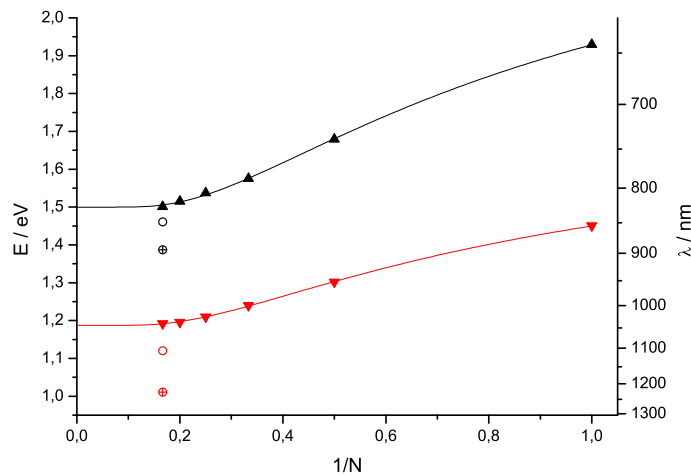


Figure 2: Absorption energies of the neutral (black) oligomers and nanorings (@ $\epsilon = 0.1 \cdot \epsilon_{\max}$) and of the radical cations (red) at the absorption maxima vs. reciprocal number of porphyrin units ($1/N$); oligomers **l-PN⁽⁺⁾** = triangles and nanorings **c-P6⁽⁺⁾** = hollow rings and **c-P6·T6⁽⁺⁾** = filled rings; solid lines are fits to $E_{i(N)} = E_{i,\infty} + (E_{i,1} - E_{i,\infty})\exp(-a_i \cdot (N - 1))$ with $E_{i,1} = 1.929$ eV (neutral) and 1.450 eV (radical cation).

X-band CW-EPR spectra of the porphyrin oligomer and nanoring radical cations were recorded at a modulation amplitude of 0.1 G (100 kHz). The hyperfine couplings of the monomer **l-P1⁺** and the dimer **l-P2⁺** radical cations are resolved and show an envelope line width of 5.46 G and 3.80 G respectively. For higher oligomers and nanorings the value of the hyperfine couplings decrease and are therefore not resolved any more.

This line width narrowing can be either due to coherent delocalisation of the electron or incoherent hopping on a time scale more rapid than that associated with the hyperfine interaction. Norris has predicted that in the limit of stochastic, near barrierless, one-dimensional charge hopping between N equivalent sites, the theoretical line width is given by $\Delta B_{PP}(N)$

$= \Delta B_{PP}(1)/N^{1/2}$.^[5,6] Figure 3 shows that the measured line widths of the oligomers nicely fit this function taking $\Delta B_{PP}(1) = 5.46$ G. The radical cation of the cyclic hexamer **c-P6⁺** shows a more narrow line width compared to the linear hexamer **l-P6⁺** while the line width of the template containing ring **c-P6·T6⁺** is slightly broader.

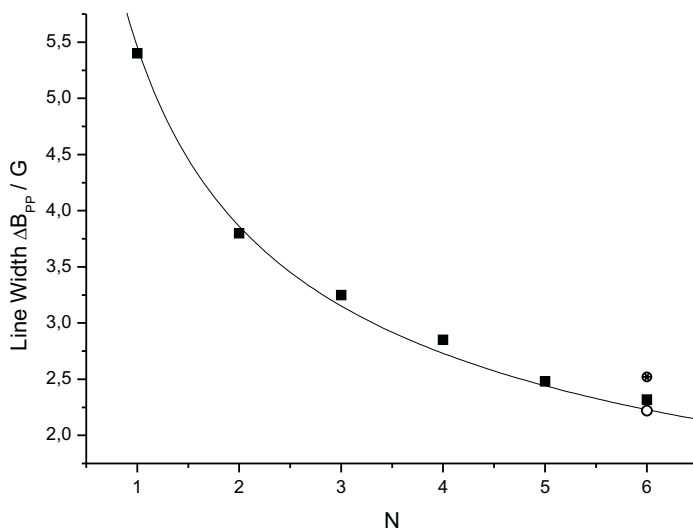


Figure 3: Plot of EPR peak-to-peak line width (ΔB_{PP} , of the radical cations of the oligomers (squares) and the nanorings **c-P6⁺** (hollow ring) and **c-P6·T6⁺** (filled ring) vs. number of porphyrin units (N). The solid line is a fit to $\Delta B_{PP}(N) = \Delta B_{PP}(1)/N^{1/2}$ ^[5] with $\Delta B_{PP}(1) = 5.46$ G.

In conclusion the cyclic conjugated systems show an even more delocalised π -system than the linear oligomers. This could be observed in absorption as well as in CW-EPR measurements. For a more detailed and quantitative understanding of the CW-EPR results obtained so far, pulsed-EPR measurements on this samples and quantum chemical calculations were performed and the evaluation is in progress.

References

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