

AROMATICITY SWITCHING IN PORPHYRINOIDS

One of the ways to study the phenomenon of aromaticity is through the synthesis of new molecules, which are often specifically designed to test various aspects of the theory or to pose new problems. Aromaticity of porphyrinoids can be influenced by a variety of structural modifications, such as peripheral substitution, covalent linking of multiple macrocycles, ring expansion, and introduction of non-pyrrolic subunits. The latter approach is most readily realized by replacing one of the pyrrole rings of the porphyrin with a different hetero- or carbocyclic fragment. Such a modification can have a profound influence on the aromaticity of the macrocycle, as demonstrated by the investigated family of porphyrinoids including carbaporphyrinoids.

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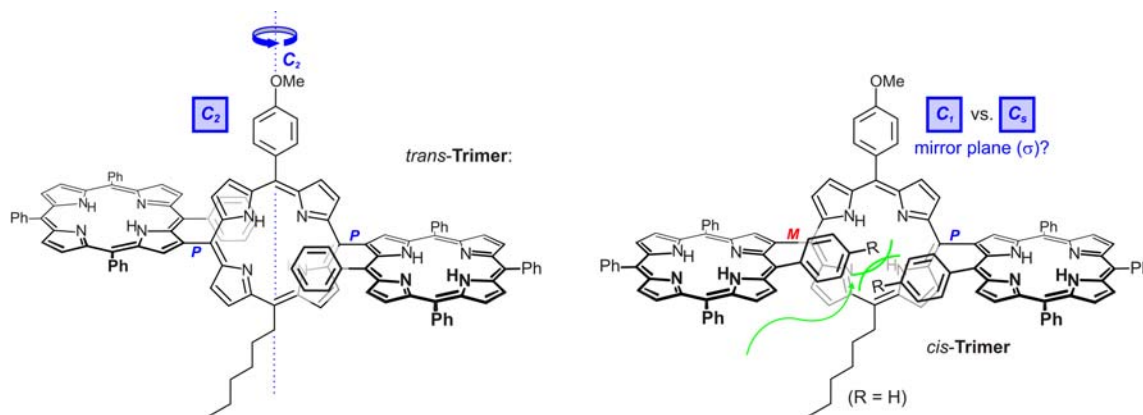
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Synthesis, Isolation and Stereostructures of Sterically Hindered Porphyrin-Trimers

Axially chiral, β ,*meso*-linked trimeric porphyrins have been synthesized for the first time in our group.¹ The novel porphyrin trimers show exciting stereochemical features. Linear trimers are formed as diastereomeric mixtures of two atropo-isomers ('*cis*' and '*trans*'), of which the *cis*-orientation of the central phenyl rings is sterically more demanding. Depending on the size of the *para*-substituents the – as such achiral – *cis*-configured triporphyrins can thus be forced into conformationally more or less stable chiral conformation! VT-NMR investigations clearly corroborate this unusual origin of chirality of trimeric porphyrin systems that has not been recognized before.



References:

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Mechanisms of Charge and Energy Transfer in Tetrapyrrole Supramolecular Assemblies

Because of their widespread importance in chemistry, biology, and nano-sciences the elucidation of charge and energy transfer in tetrapyrrole supramolecular structures is in the focus of research since decades. Therefore, the talk starts with a short review on our present understanding of electron and excitation energy transfer processes in molecular complexes. Then, the special features of tetrapyrroles when involved in such processes are underlined. Finally, some important examples are described comprising excitation energy and electron transfer in photosynthetic systems, exciton formation in dye aggregates, and the process of Foerster-transfer.

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Mixed Quantum Classical Computation of Excitation Energy Transfer and Optical Properties of Supramolecular Complexes

KEY WORDS: Chromophore complexes, Mixed quantum classical methodology, Intramolecular vibrations, Förster rates

Excitation energy transfer and optical properties of large chromophore complexes are calculated utilizing a mixed quantum classical methodology. The chromophore complex is formed by a butanediamine dendrimer to which four pheophorbide-a molecules are covalently linked. While all nuclear coordinates are described classically by carrying out room-temperature MD-simulations the electronic excitations are treated quantum mechanically utilizing a Frenkel-exciton model.

A new approach is introduced to account for the excitation energy fluctuation due to the intramolecular vibrations. This approach was used to calculate the linear absorbance of a single Pheo, resulting in a parameterfree calculation of the linewidth¹. Further it was used to directly calculate Förster rates² and nonlinear optical effects.

¹J. Megow et al., J. Chem. Phys. (in press).

²J. Megow et al., Chem. Phys. Chem. (submitted).

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Porphyrins as antimicrobial agents

The emergence of microbial resistance to many of the major classes of antimicrobial drugs is becoming an increasing problem in the clinic and environmental areas. Photodynamic antimicrobial chemotherapy is receiving considerable attention for its potentialities as a new form of antimicrobial treatment. In this communication we will discuss the state of porphyrinic derivatives as antimicrobial agents and will discuss some factors determining microbial inactivation efficiency by porphyrins [1].

[1] CMB Carvalho, JPC Tomé, MAF Faustino, MGPMS Neves, AC Tomé, JAS Cavaleiro, L Costa, E Alves, A Oliveira, Â Cunha and A Almeida, *J. Porphyrins Phthalocyanines*, 2009, **13**, 574.

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Porphyrin-functionalised polyacrylamide nanoparticles: tools for photodiagnosis and phototherapy

The use of nanoparticles as delivery agents for photosensitisers has recently become a focus of interest in the field of photodynamic therapy. The unique properties of nanoparticles allow to obtain photosensitising nanodevices with improved photostability, favourable circulation half-life, and ability to distribute to tumour tissue by escaping the blood stream through the gaps between the endothelial cells.¹ Thus, photosensitisers have been associated to nanoparticle to obtain multifunctional platform that found successful applications both as phototherapeutic/photodiagnostic agents,² and as probes to monitor intracellular processes.³ Polyacrylamide nanoparticles provide an ideal non-biodegradable, non-toxic, porous and transparent matrix for the conjugation of photosensitisers. The possibility of introducing different reactive functionalities on the surface of the polymer allows the derivatisation of the nanoparticles with photosensitisers either alone or in conjunction with targeting devices.

With the aim of generating phototherapeutic/photodiagnostic nanodevices, we undertook the synthesis of polyacrylamide nanoparticles bearing different reactive moieties for conjugation with water-soluble porphyrins. Here we report the synthesis, the preliminary studies of photodynamic efficiency evaluated *in vitro*, and the potential applications of these systems.

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A two-photon excitation study of natural photosynthetic antenna complexes

Carotenoids play crucial roles in photosynthesis as accessory light-harvesting pigments and photoprotectors. They possess a lowest excited singlet state, S_1 ($2^1A_g^-$), which is optically 'dark' for conventional spectroscopic techniques. We use two-photon excited (chlorophyll-) fluorescence (TPF) to investigate the role of these states in excitation energy transfer and dissipation in light-harvesting complexes. A TPF study of the plant major light-harvesting complex (LHC II) is provided and advantages as well as pitfalls of this approach are discussed. This research is supported by the DFG (SFB 429, TP A2).

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The *chlorina-f2* locus in barley determining chlorophyll *b*-content

Chlorophyll mutant research in barley isolated 14 alleles of the *chlorina-f2* locus (*fch2*) that are reduced in their chlorophyll *b*-content.

Synten analysis between barley and rice suggested *chlorophyllide a oxygenase* (*CAO*) as a possible candidate for *fch2*. *CAO* catalyzes the oxidation of chlorophyllide *a* to chlorophyllide *b*. Sequencing the putative *CAO*-gene of the *fch2*-mutants showed nonsense and missense mutations in 13 alleles.

Based on that we believe *fch2* to encode barley *CAO*, characterizing the recombinant enzyme will enable us to test this assumption. The many alleles of this locus will be used to analyze the structure-function relationship of the enzyme.