Nucleotidic and Peptidic Multi-Porphyrinic Devices: when the Desired Conformation is Determined by Chiral Flexible Linkers.

Nathalie SOLLADIE

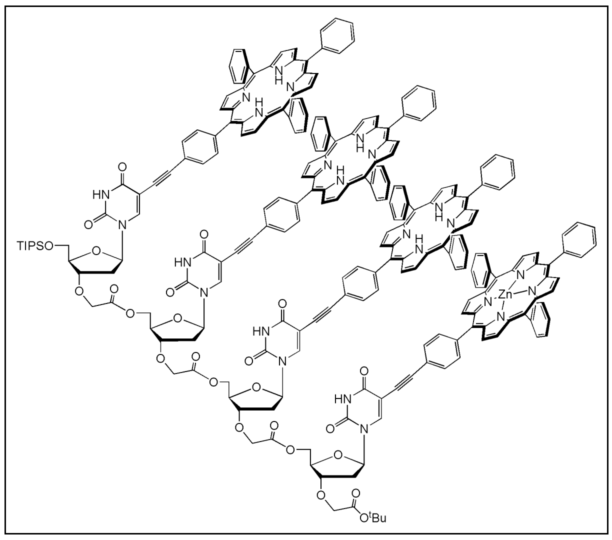
Groupe de Synthèse de Systèmes Porphyriniques,
Laboratoire de Chimie de Coordination du CNRS,
205 route de Narbonne, 31077 Toulouse cedex 4, France.
nathalie.solladie@lcc-toulouse.fr

In natural photosynthetic systems, the solar energy is collected by pigment molecules attached to the light harvesting complexes. In these units, the chlorophylls are held in a favored spacing and orientation by fairly short α-helical polypeptides.[1] When a photon hits one of the chlorophylls, the absorbed energy spreads extremely rapidly to the others until the reaction center is reached within the cell membrane, where the solar energy is converted into chemical energy used by the cell to grow. In this way, the energy contained in a single photon is conducted in a very short time and with minimal loss of energy from the point where it is absorbed to where it is needed. The extraordinary efficiency of the energy migration over long distances with minimal loss of energy is ascribed to the favored spacing and orientation of the chlorophylls which are held in an appropriate parallel conformation. Beyond the control of the structure of multi-chromophoric arrays, monitoring the spatial orientation of the chromophores in artificial light harvesting devices is a challenge of growing interest. Indeed, multi-porphyrinic arrays attract more and more attention for the elaboration of photonic and electronic wires.[2]

An octapeptide[3] and an hexadecapeptide[4] derived from the L-lysine and functionalized with porphyrins have been prepared. Beyond a certain degree of oligomerisation, we observed the development of a secondary structure such as a 3_{10} helix which forces the porphyrins to arrange in a defined spatial arrangement. Due to the overlap of the porphyrins in such a conformation, the chromophores undergo a sufficient electronic coupling to favor a good exciton migration.[5]

The ability of these peptides to accomodate guests was investigated through ligand binding studies carried out in dichloromethane with DABCO as bidentate base. The complexation of DABCO by these peptides was monitored by UV-visible spectrophotometric titration in CH_2Cl_2. We showed that the enhanced stability of the complexe octapeptide/DABCO can be ascribed to a pre-organization of the octapeptide forming cavities, and provides convincing evidence that the bidentate base is inserted into the cavities of the octapeptide via host/guest interactions.

We also investigated the ability of oligonucleotides to orientate porphyrins in space, and the capability of this type of backbone to generate multi-porphyrinic hosts able to complex multiple bidentate guests.



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