Molecular Engineering
of Extended Multiporphyrinic Architectures : toward the Control of their Physico-Chemical Properties.

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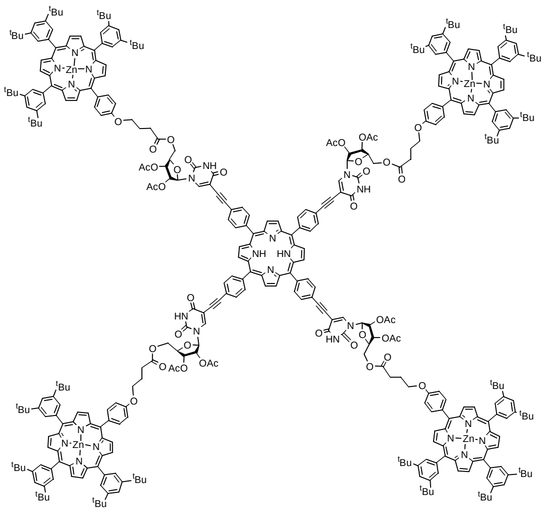
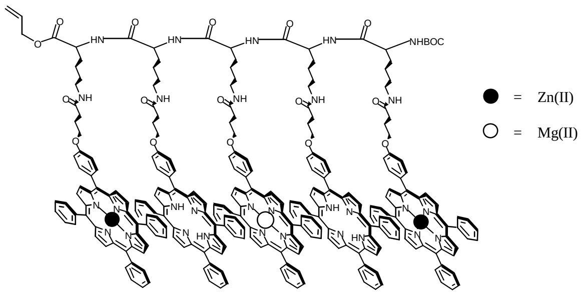
In natural photosynthetic systems, the solar energy is collected by pigment molecules attached to the light harvesting complexes. In these units, the chlorophylls are held in a favored spacing and orientation by fairly short α-helical polypeptides.[1] When a photon hits one of the chlorophylls, the absorbed 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. Two key points need to be highlighted in the light harvesting antenna of the natural photosynthetic system : i) the multiplication of the number of pigment molecules absorbing photons for just one reaction center capable of converting light into chemical energy increases the probability to generate an excited state and thus to observe energy transfer. Such a phenomenon is called antenna effect. ii) 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 synthesis of artificial light harvesting complexes[2] as well as for the elaboration of photonic and electronic wires.[3]

The star-like pentaporphyrin represented below, consti- tuted of 4 Zn(II) porphyrins linked to a free-base one *via* nucleosidic spacers, has been synthesized and studied.[4]



As reasonably expected, the fluorescence of the four peripheral porphyrins of this pentaporphyrin is substancially quenched by the free-base core, while the latter central chromophore behaves as an encapsulated, redox silent molecule. These observations demonstrate a duality of the physico-chemical properties of the pentaporphyrin. Indeed, beside the expected - and actually observed - antenna effect, this pentaporphyrin exhibits also the characteristics to prevent electron transfers with the central porphyrin, an unexpected feature in a molecule whose arborescent shape resembles a first generation dendrimer.

An octapeptide derived from the L-lysine and functionalized with porphyrins has also been prepared.[5] Beyond a certain degree of oligomerisation, it is reasonable to expect the development of a secondary structure such as α-helices which would force the porphyrins to arrange in a defined spatial arrangement. Due to the overlap of the porphyrins in such a conformation, the chromophores may undergo a sufficient electronic coupling to favor a good exciton migration. In lower oligomers bearing Zn(II) porphyrins, we intend to take advantage of the axial coordination of the central metal in the porphyrins to force the parallel orientation of the chromophores and hence to favor the desired conformation.



Furthermore, the pentapeptide bearing a defined sequence of metallated chromophores and represented above has been prepared, as presumed redox switching device.[6] Increasing efforts are devoted in our group to these homo- and hetero-peptides bearing a defined sequence of pendant metallated porphyrins, expected to be good candidates as molecular wires endowed with exciton migration or switching capabilities.

Acknowledgements

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