

1. Molecular Wires with Pendant Porphyrins :

Studies of exciton migration, conception of redox molecular switches and of novel type of glues.

We are interested in *controlling the spatial organization of porphyrins to enables exciton migration through the pool of chromophores* and mimicking the light harvesting antennae of the photosynthetic system. In the 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 parallel orientation by fairly short α -helical polypeptides. When a photon hits one of the chlorophylls, the absorbed energy spreads extremely rapidly to the others until the reaction center is reached. Succeeding in organizing the porphyrins in a similar way as nature does should provide information about the relation existing between the orientation of the chlorophylls and the efficiency of nature in transferring an excited state over a very long distance and with minimal loss of energy. We therefore developed porphyrin-functionalized α -polypeptides, in which *a polypeptidic backbone was chosen because it seems reasonable to expect, after a certain degree of oligomerisation, the establishment of a secondary helical structure*. Our poly-L-lysine functionalized with eight porphyrins adopts a right-handed 3_{10} helical conformation, as demonstrated by VCD (Vibrational Circular Dichroism) in collaboration with Prof. Timothy Keiderling from the University of Illinois at Chicago, which demonstrates the validity of the concept. Such a conformation, favored by the natural tendency of the porphyrins to aggregate, induces an overlap of the chromophores, which thus present sufficient electronic coupling to promote a good exciton migration within the molecular wire (studies realized in collaboration with Prof. Tetsuro Majima from SANKEN in Osaka, Japan).

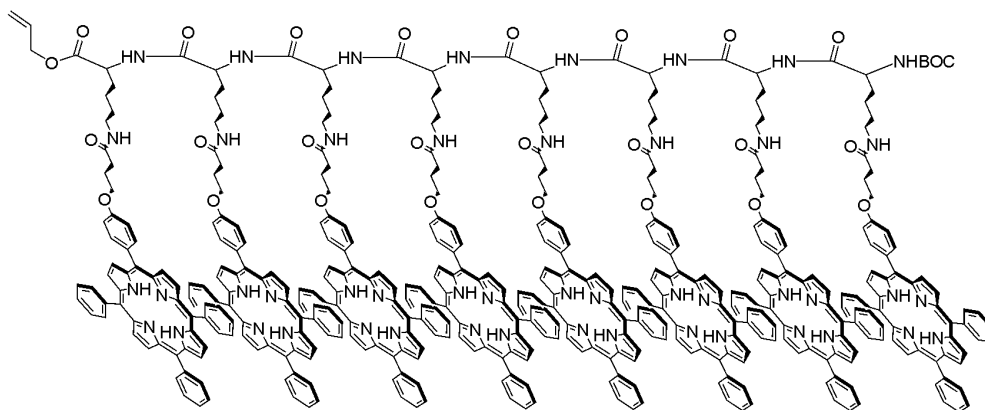


Figure. Octapeptide with pendant porphyrins.

The processing of information at the molecular level, and the controlled elaboration of nano-materials such as photonic or electronic wires capable of excited-state energy transfer or electron-transfer processes are nowadays attracting growing interest. In particular considerable efforts are dedicated to the *elaboration of molecular switches through the development of new bi-functional compounds able to properly generate or inhibit a signal in a controlled manner*. Such a signal may be, for instance, the emission of an electromagnetic wave by pigment molecules such as porphyrins, which thus appear as good candidates for the elaboration of photonic logical gates. In such wires, directing the excited-state energy transmission towards a non-luminescent bi-functional switch site and gating the energy transfer process towards this component of the molecule will allow the

emission to be switched on/off in a controlled manner. In this spirit, we took advantage of peptidic synthesis to synthesize a pentapeptide bearing a defined sequence a metallated and free-base porphyrins. The redox switching capabilities of this pentapeptide were studied in collaboration with Dr. Paola Ceroni (University of Bologna, Italy).

These polypeptides with pendant porphyrins also found applications as organic photovoltaic cells and for the successful purification of Single-Walled Carbon Nanotubes (studies realized in collaboration with Prof. Shunichi Fukuzumi, Univeristy of Osaka, Japan).