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A Reversible Self-assembling Light-Harvesting System Based on a Diphenylalanine – Porphyrin Motif

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Abstract

Herein we describe a very simple diphenylalanine-dipeptide construct to which a meso-tetraphenylporphyrin (TPP) has been attached and which self-assembles to fibrils, platelets or nanospheres depending on the solvent composition. The fibrils, gave intense excitonic couplets in the electronic circular dichroism (ECD) spectra. By slightly increasing the solvent polarity, these light-harvesting fibers disassemble to spherical structures with silent ECD spectra. A single crystal X-ray structure shows that a combination of hydrogen bonding with π -stacking of the porphyrin rings is responsible for the head-to-head arrangement which explains their excitonic coupling. By unraveling the exact supramolecular architecture our study may help devise artificial antenna systems with an on/off capability.

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Keywords

Self-assembling; dipheylalanine; porphyrin; nano-spheres; nano-fibers; chromophore

I. Introduction

Artificial self-assembling light-harvesting systems are of interest in dye-sensitized solar cells where a large photon capture cross section can assure that efficient energy transfer occurs to a large band-gap semiconductor. Presently, all artificial antenna systems, either assembled via covalent syntheses as in elegant dendrimeric architectures, or the self-assembling BChl c mimics, lead to large architectures which are unable to be dismantled, once they were formed.[1] Self-assemblies of short peptides such as diphenylalanine [(L)F(L)F] have been intensively studied in recent years and have shown promising luminescence or sensing applications.[2]

We have previously prepared diphenylalanine-porphyrin conjugates and have shown that these hybrid materials self-assemble upon drying into porous nanospheres.[3] By modifying the self-assembly conditions, and dissolving the porphyrin conjugates in dichloromethane which is then “injected” into a nonpolar solvent, we observed broadened, red-shifted and splitted Soret bands typical of porphyrinic J-aggregates. This porphyrin containing self-assembling antenna system can be reversibly assembled or disassembled by slightly changing only the solvent’s polarity. Furthermore we synthesized the unnatural [(D)F(D)F]-porphyrin conjugate and have studied with circular dichroism the transfer of chirality from the molecular to the supramolecular level.

II. Structure of Synthesized Compounds

The structure of the synthesized compounds is presented in Fig. 1. All of them were prepared in high yields after the covalent attachment of Fmoc-FF-OH or Boc-FF-OH with the amino group of the porphyrin chromophore via amide coupling.

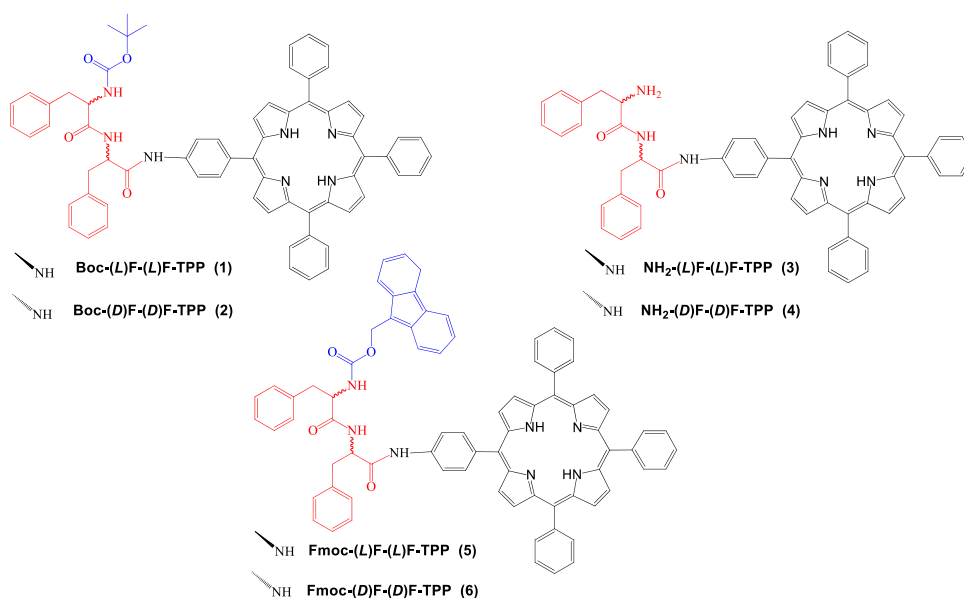


Fig. 1. The chemical structure of compounds addressed in this work

III. Self-assembly studies in solution

To study the properties of self-assembling porphyrinoid-amino acid bioconjugates, we performed absorption studies in solution, in the ground solid state and in the self-assembled orientation (Fig. 2). Due to the various morphologies of the nano-assemblies, we expected different spectra characteristics of the tested derivatives, as a result of their discrete electronic and stereochemical properties.

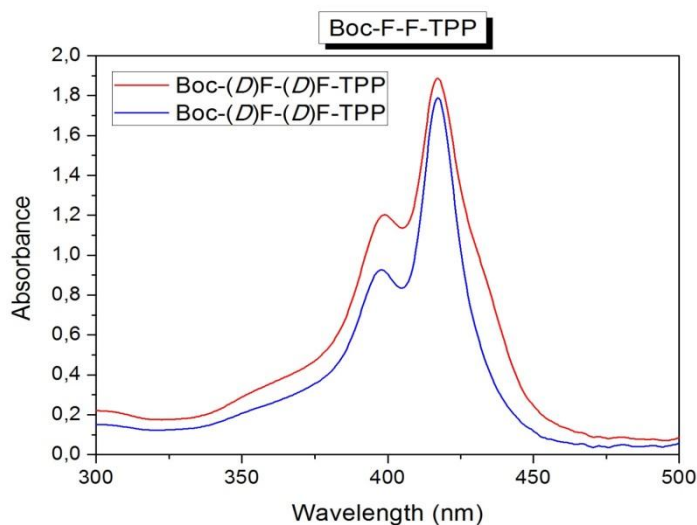


Fig. 2. The absorption spectra shows broad and split Soret bands typical of porphyrinic J-aggregates

IV. Morphology Studies

The diphenylalanine–porphyrin and phenylalanine–porphyrin conjugates were dissolved in various solvents, dried on glass slides, and studied by scanning electron microscopy (SEM) (Fig. 3).

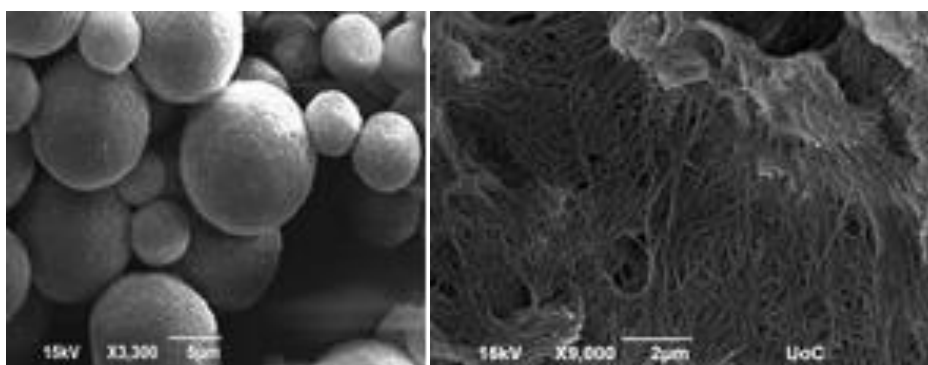


Fig. 3. Changes in the morphology with the solvent composition

V. Circular Dichroism experiments

Circular dichroism (CD) measurements were performed in order to study the chirality of the nanostructures (Fig. 4). Mirror-imaged Cotton effects were

observed for the unnatural F_D analogues, revealing that the chirality is translated from the molecular level to the supramolecular.

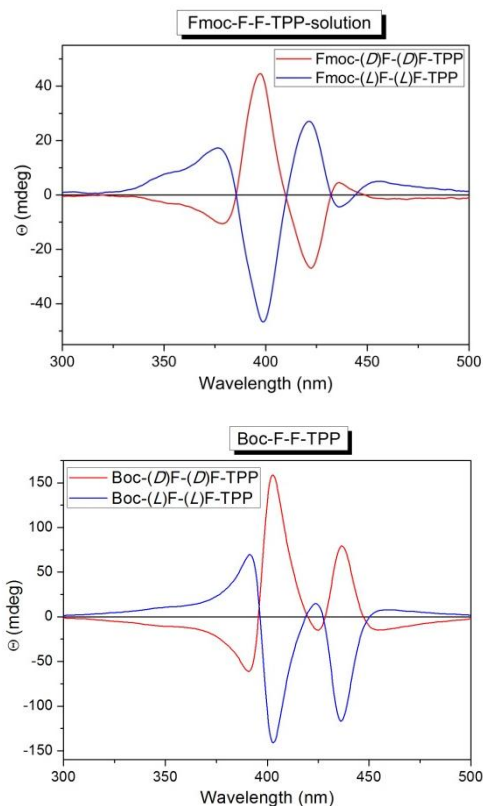


Fig. 4. CD spectra of Fmoc- (Top) and Boc- (Bottom) protected complexes

VI. Conclusion

We have reported herein diphenylalanine-porphyrin conjugates. All the synthesized compounds self-assemble upon drying into porous spheres with tunable size dependent on the solvent conditions. These compounds self-assemble in nonpolar solvents giving very intense CD signals; the protecting group influences the profile of the CD spectra. At a certain concentration film formation was observed on the walls of the cuvette, this film also gives CD signals. This is to our knowledge the first artificial antenna system which can be switched reversibly between a monomeric and a large aggregate by slightly changing only the solvent's polarity.

References

- [1] Balaban, T. S. "Tailoring Porphyrins and Chlorins for Self-Assembly in Biomimetic Artificial Antenna Systems", *Acc. Chem. Res.* 38 (2005): 612-623.
- [2] Gazit, E. "Self-assembled peptide nanostructures: the design of molecular building blocks and their technological utilization", *Chem. Soc. Rev.* 36 (2007): 1263-1269.
- [3] Charalambidis, G.; Kasotakis, E.; Lazarides, T.; Mitraki, A.; Coutsolelos, A. G. "Self-Assembly Into Spheres of a Hybrid Diphenylalanine–Porphyrin: Increased Fluorescence Lifetime and Conserved Electronic Properties", *Chem. Eur. J.* 17 (2011): 7213-7219.