

Chiral Porphyrin Supramolecular Aggregates and Their Applications in Chemical Sensors

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The study of the formation of porphyrin aggregates characterized by supramolecular chirality is an important issue amenable to wide applications. One approach to prepare these architectures takes advantage by the presence of chiral substituents on the periphery of the macrocycles acting as specific chiral effectors during the molecular recognition event. We initially studied the aggregation properties of a tetraphenylporphyrin bearing a peripheral proline group in ethanol–water solvent mixtures (Figure 1 a). In pure ethanol the porphyrin is in monomeric form, while adding water as a co-solvent fosters a specific self-recognition path, promoting the formation of extended J-type aggregates, featuring supramolecular chirality.

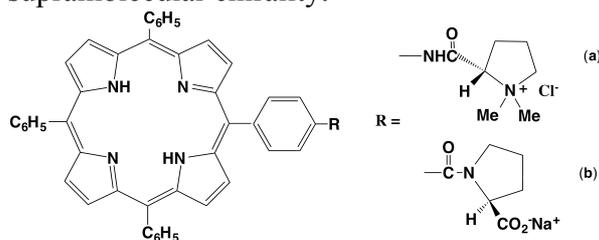


Figure 1

The behavior of these aggregates strongly depends on the peripheral proline substituents and on the relative electronic charge. Furthermore, we recently discovered that the aggregation of porphyrin derivatives bearing L- or D-prolinate enantiomers did not result, as instead expected, in architectures

featuring specular chiroptical properties, demonstrating the complexity of factors that steers the formation of these supramolecular architectures, also in the case of inherently chiral substrates.

The chirality exhibited by supramolecular assemblies of these porphyrin derivatives was preserved after the spontaneous deposition onto inorganic surfaces. However, the expected stereoselective properties are not found when the film is deposited onto the surface of quartz microbalance and exposed to vapors of chiral analytes. The implementation of these supramolecular aggregates possessing chiroptical properties as functional surface is probably thwarted by the lack of robustness and stability. Regardless of the different reasons accountable for this failure, it is clear that chiroptical activity is a necessary, but not sufficient condition for fabricating stereoselective solid state materials. A viable alternative could be found grafting the receptor molecules onto inorganic nanostructures and then coating the sensor surface with a thick film of such hybrid materials. We followed this approach with ZnO nanoparticles functionalized with porphyrin derivatives bearing an appended proline functionality on a *meso* phenyl position, having the aminoacidic carboxylic group that grafts the macrocycle at the oxide surface. Sensing properties of such hybrid materials have been extensively studied and results show that they have promising features for the development of reliable and efficient sensors based on the implementation of large chiral surfaces.