

Case history of porphyrin J-aggregates: a personal point of view

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ABSTRACT: The formation and structure of the title aggregates are paradigms of the self-assembly of amphiphilic molecular building blocks in supramolecular chemistry. This review summarizes the research in the University of Barcelona on the homoassociation of the water soluble *meso* 4-sulfonatophenyl- and phenyl substituted porphyrins.

KEYWORDS: aggregation, exciton coupling, porphyrinoids, self-assembly, spontaneous symmetry breaking, supramolecular chirality.

INTRODUCTION

Our interest in amphiphilic *meso*-substituted porphyrinoids as building blocks for supramolecular structures arose at the beginning of the nineties as a lateral consequence of our previous work on the chemistry of linear tetrapyrroles [1]. The nice and expected zwitterionic behavior of sulfonato-substituted tripyrrinones [2] (published later in 1996) lead us to spectrometric pK_a measurements of the analogous series of the *meso*-substituted 4-sulfonatophenyl- and phenyl substituted porphyrins (Fig. 1) in order to study the electronic effect of the sulfonato substituents on the basicity of the pyrrolic nitrogens. The first member of the series, *meso*-tetrakis(4-sulfonatophenyl)porphyrin (TPPS₄), was already available in our laboratory because the preparation of the homologous series was one of the objectives of an industrial research project directed towards the preparation of metalloporphyrins as synthetic analogs of superoxide dismutase [3]. TPPS₄ was also being used in our group as a bulky anionic dopant for polypyrrole [4]. The first experiment showed that the spectrometric pK_a measurements were interfered by the formation of species

other than the diprotonated porphyrin in acidic media. A literature search indicated that these aggregated species, characterized by a strong bathochromic shifted B (Soret) and Q bands, had already been detected in the seventies by other authors [5]. These first reports considered that the shifted absorptions corresponded to dimeric structures and the aggregation behavior was considered to be “very complicated”, a fact confirmed by our present yet incomplete understanding of the aggregation process in spite of the many and significant contributions by other groups researching the topic [6]. Probably, the objective of these first reports [5] was the study of water soluble porphyrins, but Pasternack had already recognized the interest of these compounds as amphiphiles [6c, d]. The simple use of thin UV-vis cuvettes which are not so common some years ago in organic chemical laboratories allowed us to report the dependence of the UV-vis spectra of TPPS₄ in acidic media with concentration in the range of several order of magnitude. This was presented as a graphic (Fig. 2) showing the effect of concentration on the absorption spectrum that constituted the central point of our first publication in this topic [7a]. Presenting in the same figure all the UV-vis spectra reported in [7a] (Fig. 2). Without the availability of digital spectrometer data and in the absence of digital scanners and adequate PC drawing software [8], it was a boring and time-consuming task. However, the extended use posteriorly of the same

◇SPP full member in good standing

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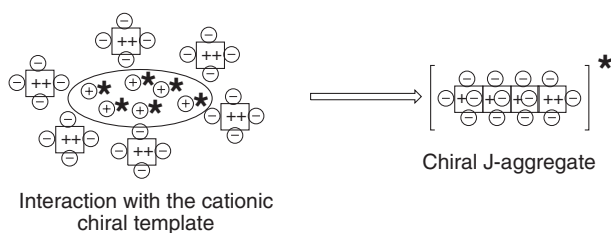


Fig. 6. Initiation of the aggregation and chirality transfer by interaction of the H_2TPPS_4 monomers with a chiral cationic polyelectrolyte as proposed in reference [71]

formation of optically active J-aggregates corresponds to a spontaneous mirror symmetry breaking (SMSB) process similar to those of the crystallization of achiral compounds, yielding racemic conglomerates of enantiopure crystals, where the formation of detectable enantiomeric excess (stochastically of one of the other chirality sign) is often detected. In the interaction with biopolymers, and with some chiral compounds, a transfer of the chirality sign has been observed [6f, q]. However, in the case of the more studied H_2TPPS_4 J-aggregates, also in the absence of any chiral induction, the same chirality sign in the CD spectra has been obtained in the high majority of the published reports. This, together with the difficulty of interpreting the CD signal of anisotropic samples, had led to skepticism of the real circular dichroic character of these signals. However, we have demonstrated recently that the bias towards one chirality sign is a consequence of the detection of traces of chiral compounds in ultrapure water [71]. This high sensitivity to chiral polarizations is a characteristic of the SMSB processes. In this respect, the most dramatic result is that the hydrodynamic chiral flow of stirring vortexes can suffice to select the final chiral sign outcome. We have reported the irreversible chiral sign induction by the direction of the stirring vortex during the formation of the H_2TPPS_3 J-aggregates [7d, e–g, j], but negative results have been obtained in the case of the rest of compounds of the homologous series. However, recently, in collaboration with the group of Prof. R. Purrello (Catania) we have detected, in the direct measurement of the CD spectra in stirred solutions, that huge reversible CD signals arise in the case of the J-aggregates solutions of $TPPS_1$, $TPPS_{20}$ and H_2TPPS_4 [7n]. This suggests that the appearance of stationary chiral states by mechanical effects on these J-aggregates is a more common phenomenon than the irreversible formation of chiral structures (case of H_2TPPS_3). In the case of the J-aggregates of H_2TPPS_3 , the irreversible effect of the stirring vortex is summarized in Fig. 5, which indicates that the stirring vortex leads to long order folding and to an enantiomeric excess of one folding direction during the formation of the more stable *meso* form (folded structures). Therefore, the formation of folded structures would be related to the plasticity of the material and the reversible effect (*i.e.* leading to a mechanochiral stationary state) would be related to the elasticity. Obviously,

the adequate size, shape, and mechanical modulus of the particles must be limiting conditions for the detection of such effects.

However, the interpretation of these experimental results is handicapped by the difficulty of interpreting the dichroic spectra of anisotropic and oriented species. We address the interested reader to a recent discussion of the conditions for detecting such mechanochiral effects [70].

An important point for further research is to elucidate if the detected chirality is the consequence of chiral distortions in the soft-matter structure or chiral ordering in the 2D/3D packing of the initial linear J-aggregate chain. In this respect, the point group S_4 of the achiral monomer (H_2TPPS_4) in the 1D chain changes to a chiral C_2 through the conformational changes on the opposite aryl substituents, but probably the enantiomers alternate in the chain giving a centrosymmetric ordering, which implies a symmetry decrease in respect to the initial monomer. Depending on the packing between the centrosymmetric chains, achiral or chiral *meso* forms would be obtained. Another interesting point to clarify is the role of the symmetry of the implied chromophore in the exciton, since the geometry corresponds to point groups related to the achiral D_{2d} which can show chirality in some directions and therefore unexpected chiral exciton coupling phenomena [19].

FINAL REMARKS

The initial interest on these J-aggregates was in relation to the application of energy and electron transfer processes in nanostructured materials [20]. In this respect there is the industrial precedent of the use of cyanine dye J-aggregates as photosensitizers in classical photography, now in fast regression. However, this has not found a similar practical application for the porphyrin J-aggregates, in spite of the evident interest of the photophysical and photochemical properties of the porphyrin chromophore. We think that the principal handicap arises from the water solubility of the title aggregates. However, recent results indicate that strong interactions can occur between the porphyrin and some surfaces. An intense research in this direction could change the present sterility into practical applications. Up to now, the important contribution of the research in the J-aggregates of porphyrins is in the understanding of the self-assembly process by the study of this “simple complex system”.

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and H₂TPPS₃ J-aggregates. Part of this research has been financed by the Spanish Government (AYA2006-1648-C02-01). The recent collaborations with Prof. Roberto Purrello and Prof. Giovanna Mancini have been possible through the COST Action D27 (WG0004-02) of the European Union.

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- The project (EUREKA EU-437-SODA; 1991–1992) was closed before the test for the Mn porphyrinates of the title porphyrins, which later were demonstrated to show the searched superoxide dismutase activity (Batinic-Haberle I and Fridovich I). This example exemplifies how difficult it is to reconcile industrial objectives with research work in public institutions.
- Work performed by Urmas Johanson (visiting Estonian student) which, due to our fault, remains unpublished. This example exemplifies the difficulty in using for publication the work performed by talented students in short research laboratory stages.
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