

A Labile Metallo-Porphyrin as Tool to Control J-Aggregates Chiroptical Properties

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The zinc(II) metal derivative of 5,10,15,20-*tetrakis*(4-sulfonatophenyl)porphyrin (TPPS₄) is quite labile and readily demetallates under acidic conditions, affording the parent diacid porphyrin in a monomeric form. The rate of this process is first order on [ZnTPPS₄] and second order on [H⁺], allowing a precise control of the monomer release in solution. Under high ionic strength, this latter species is able to self-assemble into J-aggregates, whose kinetics of growth are largely modulated by pH. The aggregation kinetics have been treated according to a well-established model, in which the formation of an initial nucleus is the rate determining step preceding the autocatalytic growth of the whole assembly. The extinction spectra of the aggregates suggest the occurrence of a dipolar coupling mechanism very similar to that operating in metal nanoparticles. Spontaneous symmetry breaking takes place in these aggregates as evidenced by unusual circular dichroism spectra. The intensity and sign of the effect is controlled by the aggregation rate and therefore can be tuned through a proper choice of initial conditions.

Keywords: Porphyrins ; J-Aggregates ; Symmetry breaking ; Demetallation kinetics ; Aggregation kinetics ; Chiral supramolecular assemblies

J-aggregates are supramolecular systems in which the constituent chromophore units are laterally arranged. Apart the occurrence of a specific J-band in the UV/Vis spectra, bathochromically shifted with respect to the free monomer, a series of peculiar opto-electronic and chiroptical properties attracted the interest of many researchers on these species in the last decades ^{[1][2]}. Usual candidates to build such structures are aromatic compounds, e.g. porphyrins and, among them the water soluble 5,10,15,20-*tetrakis*(4-sulfonatophenyl)porphyrin (TPPS₄) has been intensely studied. Such interest arises from the possibility of obtaining a variety of supramolecular architectures whose size spans from the nano- up to the microscale. ^{[3][4][5][6][7]} Chirality can be induced in these species by imposing external chemical (small chiral molecules or polymers) ^{[8][9][10][11][12]} or physical chiral bias (hydrodynamic flows, vortexes or combination of gravitational and rotational forces) ^{[13][14][15][16][17][18]}. More intriguingly, spontaneous symmetry breaking can also occur in the absence of any bias, leading to a search for the intimate causes of such phenomenon ^{[19][20][21]}. Kinetic studies on the self-assembly formation pointed out the role of aggregation rates and the mixing protocol on the intensity of the circular dichroic signals ^[22]. Furthermore, these findings suggest that the interplay of local concentration and temperature gradients, mixing techniques, and also aging of reagents could have a deep impact on the reproducibility of the experiments, since the distribution of species in solution at the beginning of aggregation could be unpredictable (monomers, dimers, oligomers etc.). In complex systems, all these factors are able to change the aggregation pathway and eventually influence the resulting structure of the final supramolecular assembly ^[23]. For these reasons, it is very important to develop approaches to minimize the potential sources of uncertainty. In a previous study, we showed that controlled amounts of the zinc(II) metal derivative of TPPS₄ when added to the metal-free porphyrin decrease consistently the formation of J-aggregates and influence their chiroptical properties ^[24]. This particular metal complex is quite labile under acidic conditions and the metal ion can be easily removed, ^[25] affording an easy and convenient way to obtain in situ the monomeric diacid H₂TPPS₄, that is the building block for the subsequent aggregate growth (see Scheme 1).

Scheme 1. Pictorial sketch of the basic strategy to growth J-aggregates of the diacid H₂TPPS₄ by demetallation of ZnTPPS₄ under acidic conditions.

This particular metal complex offers three main advantages: i) since the rate of zinc(II) extrusion from the porphyrin core is first order on [ZnTPPS₄] and second order on [H⁺], the proper choice of pH and ionic strength conditions allows a fine time-control on the initial concentration of monomeric diacid H₂TPPS₄. Actually, by lowering the pH the demetallation becomes fast with respect to the J-aggregate formation, disentangling the two processes; ii) zinc(II) is usually a penta-coordinated metal ion and the presence of an axial ligand (usually water) on top of the porphyrin plane hinders formation

of dimers or oligomers for this porphyrin; iii) the difference always observed in kinetics and optical activity when using different mixing protocols is removed. Purrello et al. exploited this strategy to induce chirality into a porphyrin supramolecular assembly pre-organized onto a polymeric support [26].

In this report, we have performed a detailed kinetic study of the demetallation of ZnTPPS₄ and the subsequent aggregation into J-aggregates of the diacid H₂TPPS₄ generated in situ as function of pH and ionic strength. The main spectroscopic and chiroptical features of the J-aggregates have been related to the experimental conditions, suggesting an effective role of zinc cations.

Kinetic analysis

Our kinetic experiments have shown that when ZnTPPS₄ is used as starting material, the rates are independent on the mixing order, and sigmoidal profiles for extinction vs time have been observed in all cases. A precise control on the release of metal free porphyrin could be achieved at pH higher than 1, a condition that requires rather high ionic strength to trigger aggregation. Since both the demetallation and aggregation rates could be influenced by the nature of the various species in solution, we used H₂SO₄ as acid to initiate both process and ZnSO₄ to ensure the proper ionic strength. The spectral changes in the extinction spectra show the conversion of the starting ZnTPPS₄ into the intermediate diacid H₂TPPS₄ that eventually converts to J-aggregates. An analysis of the spectral changes allowed the calculation of the relevant kinetic parameters for both processes. The removal of the metal ion from its porphyrin complex follows the rate law: $rate = k_2 [ZnTPPS_4][H^+]^2$, with $k_2 = 5.5 \pm 0.4 \text{ M}^{-2} \text{ s}^{-1}$ at 298 K, in line with the literature [27]. The subsequent aggregation kinetics have been treated according to an established model proposed by Pasternack et al [28]. The rate determining step is the formation of a nucleus containing m porphyrin units, that initiates the autocatalytic growth of the final assembly following a time-dependent process. The values of the catalytic rate constant k_c monotonically increase on increasing both $[H^+]$ and ionic strength, while the value of m indicates a trimer or a tetramer as the initial nucleus.

Chiroptical properties

Samples of the prepared J-aggregates exhibit rather peculiar spectroscopic features: i) a broad J-band, suggesting a dipolar coupling mechanism, instead of the usual Frenkel exciton model [29][30][31], ii) resonance enhanced light scattering (RLS) corresponding to the absorption bands due to their size and the strong electronic coupling among the monomers [32]. The increase of intensity of RLS on increasing $[H^+]$ and ionic strength suggests that aggregates become larger at lower pH and higher ionic strength. As already reported in literature, spontaneous symmetry breaking can occur in these systems, leading to the observation of circular dichroism (CD) spectra [20][21]. On increasing $[H^+]$ or the ionic strength, i.e. increasing the aggregation rates (see Figure 1), the absolute intensity of the dissymmetry g -factor decreases and the bands eventually switch from negative to positive Cotton effect.

Figure 1. Plot of dissymmetry g -factor as function of the corresponding rate constants k_c and two representative CD spectra for positive and negative Cotton effect (inset).

All our experimental evidence points to a specific role played by the zinc(II) ions, at molecular level and on the mesoscopic structure of the aggregates, in analogy to other polycationic species [29][30][31]. At difference with J-aggregates prepared by simply adding inorganic acids, the sign of the Cotton effect in these species can be changed from negative to positive by varying pH and ionic strength [19][22]. All together, these findings shed further light onto these fascinating supramolecular assemblies and pave the way to new approaches in order to modulate their spectroscopic and chiroptical properties for potential applications.

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