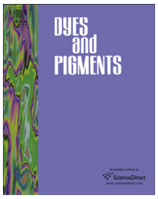
Dyes and Pigments 142 (2017) 255–261

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig



Tuning supramolecular chirality in *nano* and mesoscopic porphyrin J-aggregates

Roberto Zagami [a], Maria A. Castriciano [a, *], Andrea Romeo [a, b, *], Mariachiara Trapani [a], Rolando Pedicini [c], Luigi Monsù Scolaro [a, b]

[a] *CNR-ISMN, Istituto per lo Studio dei Materiali Nanostrutturati, c/o Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ad Ambientali, 98166, V.le F. Stagno D'Alcontres 31, Messina, Italy*

[b] *Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ad Ambientali, and C.I.R.C.M.S.B., University of Messina, V.le F. Stagno D'Alcontres 31, Vill. S. Agata, 98166, Messina, Italy*

[c] *CNR-ITAE Istituto di Tecnologie Avanzate per l'Energia, Via Salita Santa Lucia Sopra Contesse 5, 98126, Messina, Italy*

ARTICLE INFO

Article history:
Received 21 February 2017
Received in revised form
22 March 2017
Accepted 23 March 2017
Available online 24 March 2017

Keywords:
Nanoaggregates
Mesoscopic
Porphyrin
Chirality
Disassembling

ABSTRACT

In natural light-harvesting systems, chirality represents a crucial point being one of the recurrent motifs. The ability to tune supramolecular chirality both on nano and meso scale is a key topic on the design of mimetic antenna systems. Here we describe a non-covalent approach to achieve mesoscopic clusters, based on spermine and the diacid form of $TPPS_4$ porphyrin, having a sea urchin-like morphology, whose chirality can be induced by the presence of L- or D-tartrate under mild acidic conditions. The mechanism proposed for the formation of these clusters deals with the formation of peculiar optically active J-nanoaggregates, which serve as nuclei for further growth into mesoscopic structures. Poly(-vinylsulfonate) has been used to scavenge the polyamine and thereby foster disaggregation. The kinetics of this process show a biphasic behavior characterized by a rapid removal of spermine externally bound to porphyrin monomeric units followed by a stripping-out of the polyamine which is tightly bound to the J-nanoaggregates. A careful choice of experimental conditions allows precise control of the disaggregation kinetics, leading to the isolation of J-nanoaggregates. These latter species exhibit chirality even in the absence of a chiral inducer. This feature, together with the anomalous behavior of the CD signal of the mesoscopic aggregates containing optically active tartrate, have been explained in terms of screening hypochromism, differential scattering and structural rearrangements.

1. Introduction

Supramolecular aggregates of porphyrins and related macrocycles have been extensively investigated due to their similarity to biologically-relevant light harvesting antennas [1,2]. In particular, the so-called porphyrin "J-aggregates" have attracted a large interest [3–18]. These latter are molecular dyes aggregates noteworthy in displaying both a very intense and narrow absorption peak, namely known as a J-band, largely red-shifted with respect to monomer absorption. An intriguing property of these supramolecular assemblies of achiral monomers is the appearance of chirality induced by chiral biases such as: i) chiral templating agents [8,19,20], ii) vortex motion [21,22], iii) stirring [22–27], iv) application of rotational, gravitational and orienting forces [28] and v) weak thermal forces acting as an asymmetrical physical perturbation [29]. Tetra-anionic *meso*-tetrakis(4-sulfonatophenyl) porphyrin ($TPPS_4$) has been most extensively explored, and has been proved to form such J-aggregates consequent to acidification and/or by the interaction with cationic species [3,5,15,17,30–33]. A series of studies have demonstrated the presence in solution of assemblies whose size ranges from nano up to the micrometer scale [16,17,31]. Various spatial arrangements have been proposed, although most evidence points to a nanotube-like structure [30,34–39]. A transition between rod-like and fractal structures has also been proved, emphasizing a structure-dependent optical activity induced by a chiral template, thus raising an intriguing question about transmission of chirality from a local or molecular level up to the mesoscopic regime [31]. When spermine is used as a

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* Corresponding authors. CNR-ISMN, Istituto per lo Studio dei Materiali Nanostrutturati, c/o Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ad Ambientali, 98166, V.le F. Stagno D'Alcontres 31, Messina, Italy.

E-mail addresses: castriciano@pa.ismn.cnr.it (M.A. Castriciano), anromeo@unime.it (A. Romeo).

http://dx.doi.org/10.1016/j.dyepig.2017.03.047

cationic template, features of these fractal structures include a large enhancement of resonant Raman and Rayleigh light scattering, an unusually broad J-band, and a non-zero extinction coefficient throughout the visible range [33,40,41]. In the present paper, we describe the formation of chiral J-aggregates of $TPPS_4$ under mildly acidic conditions in the presence of spermine, with added optically active tartrate as chiral inducer. We also wanted to consider an equally important and largely unexplored area of supramolecular chemistry, assembly degradation. Compared to aggregation, the reverse process (disaggregation) has received little attention and it has been poorly described in the literature, thus far, for a very few examples [42–49].

In particular, neither aggregate properties nor solution conditions under which disruption of the self-assembled structures occurs, have been outlined. Consequently, further research is required due to the importance that chemical modulation takes in the disassembling of such supramolecular systems and notably for the implications in the study of aggregation diseases. In the present case, the mesoscopic networks can be easily converted back to the monomeric state through the isolation of J-nano-aggregates building blocks by adding a highly charged polyanion, thus revealing chiroptical properties of meso and nano structures.

2. Experimental section

The porphyrin meso-tetrakis(4sulfonatophenyl)porphyrin was purchased from Aldrich Co. as tetrasodium salt (≥98% pure). Aqueous concentrated solutions of the porphyrin ($1–2 \times 10^{-4}$ M) were prepared in dust-free Millipore water, stored in the dark and used within a day of preparation. Porphyrin solution concentrations were determined spectrophotometrically in water at neutral pH and zero ionic strength by using the value of the molar extinction coefficient at the Soret maximum ($\varepsilon_{414} = 5.33 \times 10^5\ M^{-1}\ cm^{-1}$) [50]. Poly(sodium vinylsulfonate) (PVS) was purchased from Sigma–Aldrich Co. (molecular weight ranging from 4000 up to 6000, 25% by weight). Polyelectrolyte concentration, expressed as moles of sulfonate units per liter, was obtained by weighing. Each polymer chain has a length of about 100 Å and supports about 38 sulfonate residues, which are approximately 2.5 Å apart from each other [51]. To avoid or minimize dust contamination, special care was taken by filtering all the stock solutions through 0.22 μm Millipore filters. Spermine (1,12-diamino-4,9-diazadodecane) was purchased from Sigma. The pH values of the investigated samples were measured by using a Metrohm 744 pH meter (Metrohm, Herisau, Switzerland) by inserting a micro pH combined glass electrode. Samples of J-aggregated diacid $TPPS_4$ were prepared following a mixing protocol which involves the addition of a known volume of concentrated stock solution of spermine (100 μM) to a solution of porphyrin (3 μM) in 10 mM citrate or tartrate buffer at pH 3.2. In the case of disaggregation experiments promoted by the polymer and intended for the study of the effect of PVS load, in order to minimize any error, it was necessary to manage a starting J-aggregate system as reproducibly as possible. Taking advantage of the stability of the aggregated system within 24 h of its preparation, we proceeded to its formation in special vials taking into account a suitable volume of reagents such as to allow an adequate number of disaggregation experiments (typically at least a dozen). Milli-Q water was used throughout.

3. Results and discussion

At pH 3.2 in tartrate buffer (10 mM) the UV/Vis spectra of $TPPS_4$ (3 μM) show the presence of the diprotonated monomeric porphyrin with a B-band at 434 nm (Fig. 1a, dashed line). Under these mildly acidic conditions, $TPPS_4$ does not aggregate even after prolonged standing. However, upon addition of spermine (100 μM) evidence for extensive self-aggregation of the porphyrin is obtained: there is a marked decrease of the initial B-band concomitant with an increase of a new broad feature with maximum at 492 nm accompanied by a shoulder on its red-edge side (Fig. 1a, red solid line). Although found at this same characteristic wavelength, this feature differs considerably from the usual sharp band reported for $TPPS_4$ J-aggregates [12]. In addition, extinction throughout the entire visible range (to well above 800 nm) is observed. In Fig. 1b the corresponding kinetic profiles for the $TPPS_4$/spermine aggregation are reported, exhibiting a sigmoidal behavior characterized by the presence of an initial induction period in the early stage, a profile very similar to that observed for the aggregation of $TPPS_4$ in strongly acidic aqueous solutions [5]. Previous investigations have shown that this type of profile is strongly affected by the mixing order of the reagents which influences the dynamics of growth and eventually both morphology and size of the assemblies [32]. A kinetic analysis of the extinction/time traces at 434 and 492 nm has been performed by using an autocatalytic model that assumes a rate determining step in which a *"critical size"* assembly forms, catalyzing further growth [52]. The rate constants for the uncatalyzed pathway, k_0, and for the catalyzed pathway, k_c, have relative values of about 1:15 and are in the range typical reported in the literature for similar processes [53]. Therefore, experimental data suggest as the autocatalytic pathway becomes more relevant compared to the parallel uncatalyzed process, being the former essentially promoted by the formation of germinal nuclei. The latter, with time, become even larger as monomers self-assemble so leading to the formation of highly reactive units. In this regard, the critical size for the nuclei, m, is between 5 and 6 interacting units and the time exponent n, that indicates the evolution of the fractal growth, is about 6. These findings are in line with previous results, suggesting as small oligomers in which the spermine acts as sticky agent, should be suitable as critical nuclei in the growth of J-aggregates [32]. The formation of mesoscopic aggregates in which porphyrins are electronically coupled causes an almost complete quenching of fluorescence emission and gives rise to a large enhancement of the resonant light scattering [54] at the red-edge of the extinction peak (Fig. 1c). These aggregates are stable in solution for a day or more after their preparation. The observed optical features are very similar to those obtained using citrate buffer at lower pH and they have been explained in terms of dipole-dipole (rather than Frenkel exciton) coupling among individual porphyrins belonging to the extended network formed by the J-aggregates and spermine [33,40]. As expected for an achiral building block, when citrate is used as buffer, under the aforementioned experimental conditions, the obtained aggregates are not optically active as evidenced by silent circular dichroism spectra. In contrast, when L-tartrate buffer is used, quite strong bisignate CD signals having a positive Cotton effect are induced at 492 nm (J-band) and a somewhat weaker feature at 424 nm (H-band) is seen (Fig. 1d). The CD spectra obtained for the enantiomeric D-tartrate are almost mirror images as expected.

According to our previously reported model for this supramolecular system [32,33,40], nano-sized rod-like J-aggregates of the diacid $TPPS_4$ porphyrin are stabilized primarily via electrostatic interactions acting among adjacent porphyrins and involving the protonated cationic spermine. These nano-assemblies, together with porphyrin monomers, are embedded in a mesoscopic network in which spermine also plays an important role as bridging reagent. On the basis of this model, we thought it potentially enlightening to formulate a strategy to remove the cationic templating reagent and, thereby, disassemble the network. For this purpose we selected