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Self-association of 5,10,15,20-tetrakis-(4-sulfonatophenyl)-porphyrin tuned by poly(decylviologen) and sulfobutylether-β-cyclodextrin

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ABSTRACT

With the aim of achieving supramolecular structures containing dyes with controlled state of aggregation, the formation of ternary complexes between 5,10,15,20-tetrakis-(4-sulfonatophenyl)-porphyrin, poly(decylviologen), and sulfobutylether-β-cyclodextrin at low excess of the cyclodextrin is described. By controlling the stoichiometry of the reactants, both non-fluorescent H-aggregates of the dye and stabilized fluorescent monomers may be obtained. The dye undergoes self-aggregation in the presence of the flexible, cationic polymer, and by addition of the negatively charged cyclodextrin the aggregates are cleaved. The cyclodextrin primarily induces the inclusion of 5,10,15,20-tetrakis-(4-sulfonatophenyl)-porphyrin in its cavity, and the ensemble is stabilized by the polymer by means of electrostatic, hydrophobic, and/or aromatic–aromatic interactions. The ternary complex thus produced tends to nanofiber formation, as seen by FE-TEM.

1. Introduction

The self-aggregation tendency of aromatic dyes such as xanthene dyes and porphyrins at increasing concentrations in aqueous solution is well known [1–15]. Dispersion forces and aromatic–aromatic interactions stabilize the aggregates. Higher order aggregates of charged dyes can be found on complementary charged surfaces. The charge compensation produced on these environments minimizes the charge repulsion, produces a higher local concentration of dyes, and the dyes self-aggregate, frequently undergoing cooperative binding [16]. Examples of dye self-aggregation in the presence of polyelectrolytes are methylene blue (MB) [11] and the tetra-anionic form of 5,10,15,20-tetrakis-(4-sulfonatophenyl)-porphyrin (H_2TPPS^{4-}) [4,6] interacting with the polyanion poly(sodium vinylsulfonate) (PVS) and the polycation poly(allylamine) (PALA), respectively. The interaction of these dyes with these polyelectrolytes is considered non-site-specific, producing territorial binding, thus governed by long-range electrostatic interactions. That makes this interaction very sensitive to the presence of other ions in solution. As a consequence of this, the incorporation of such dye/polyelectrolyte complexes in solid materials by solvent evaporation or deposition techniques may find the drawback of dye release from the complexes, and a consequent crystallization, non-homogenous accumulation, polydisperse aggregation, or bad control of the dye distribution in the solid.

The formation of materials where the dyes are homogenously dispersed, together with furnishing a good control of the dye state of aggregation is then of interest. For many dye applications such as electron transfer agents in electronic devices [17], or photosensitizers in photodynamic therapy [18], aggregation may be an unwanted feature since it may reduce light harvesting and minimize the efficiency of energy transfer. However, recent studies highlight the potential of organic dyes aggregates for improving the global energy-conversion efficiencies of organic dye-sensitized solar cells and photocatalysts under the requirement of achieving a good control of the dye aggregation in the assembled structures [19,20]. It is by means of secondary interactions such as hydrogen bonding or aromatic–aromatic interactions, apart from primary long-range

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electrostatic interactions, that a good control of the assembled structures is achieved by ionic self-assembly (ISA) [21–28]. This property has been elegantly used to form interesting nanostructures between polyelectrolytes or dendrimers and dyes [25–28].

We have shown that when polyelectrolytes furnish complementary charged aromatic groups, interactions between the dyes and the polymeric aromatic groups are stabilized by short-range aromatic–aromatic interactions, which leads to site-specific binding [2,4,5,11,12,14,29–34]. The extent of binding and the state of aggregation of different dyes in the presence of such polyelectrolytes strongly depends on the structure of the polymer as a whole, and variables such as functional groups, localization of the charge, flexibility, hydrophobia, linear charge density, and linear aromatic density determine the behavior of the system [4,5,12,34]. Among aromatic polyelectrolytes, polyviologens are interesting polymers due to their electro- and photoactive properties. Viologens, 1,1′-disubstituted-4,4′-bipyridinium dications, are well known in both electrochemistry and photochemistry [35–38], in particular for their reversible redox behavior accompanied by a color change that make them useful for electrochromic displays [35,36]. Viologen derivatives are important molecules used in electronic devices as electron acceptors. Polyalkylviologens are particularly attractive due to the possibility of modulating the interunit spacing through changes of the alkyl chain length. They are usually prepared by the Menschutkin reaction of 4,4′-bipyridine and dihaloalkanes in aprotic solvent [39]. The resulting linear polymers are water-soluble. Ionic porphyrins are commonly used as water-soluble electron-transfer photosensitizers, and are often used in conjunction with viologens as electron acceptors [40,41]. Porphyrin-viologen pairs have been used for photoinduced electron transfer in a variety of solution-phase and supramolecular assemblies [42,43]. As aromatic cationic polyelectrolytes, polyalkylviologens produce strong binding to anionic porphyrins, which may be useful for the incorporation of the dye in different structures in a controlled manner. Therefore, designing strategies for the control of the dye state of aggregation in the presence of polyalkylviologens are of interest.

The biocompatible cyclodextrins (CDs) are good hosts for inclusion complexes [44–48]. Low molecular-weight molecules containing hydrophobic groups of a defined size may form complexes with CDs by interaction with the hydrophobic internal face of the CD torus. Among these guest molecules, both substituted porphyrins [49–53] and viologen derivatives [49,54] have been described to be hosted by CDs. They can also form rotaxanes and pseudorotaxanes [55–60] by means of threading on polymeric chains, in some cases containing viologen units [58]. The CDs are able to spin around the axes of the polymer chains as well as move back and forth along the polymer backbones. These molecular architectures find potential applications in nanostructured functional materials, molecular switches, molecular logic gates, molecular wires, and memory devices, and contribute to advances in molecular electronics and the construction of artificial molecular machines. The low solubility in water of some CDs has limited their use in several applications such as pharmaceutical formulations. In this respect, sulfobutylether-β-cyclodextrin (SB-β-CD) overcomes this problem by bearing 6–9 negative charges per molecule that furnish high solubility in water.

The photosensitizer 5,10,15,20-tetrakis-(4-sulfonatophenyl)-porphyrin (TPPS) has interesting physicochemical properties concerning electronic transitions and acid–base equilibrium which are sensitive to its close environment. At pH 7, the basic form of TPPS (H_2TPPS^{4-}) is found, which bears four negative charges at its periphery, as can be seen in Fig. 1 [61,62]. In this paper, molecular association at pH 7 between H_2TPPS^{4-} and the viologen derivatives methylviologen (MV) and poly(decylviologen) (PV10) will be shown. The interaction between PV10 and SB-β-CD, and the interaction between H_2TPPS^{4-} and SB-β-CD will be also analyzed. Then, as an absolute novelty of the present work, the formation of a ternary complex produced by adding SB-β-CD to H_2TPPS^{4-}/PV10 complexes will be described, revealing monomeric H_2TPPS^{4-} imbibed in the H_2TPPS^{4-}/SB-β-CD/PV10 ternary complex, so that a good control of the state of aggregation of the dye can be achieved in these complexes. Ternary complexes that include CDs, poor water-soluble substances, and hydrophilic polymers have been described mainly to increase the solubility of poor water-soluble drugs and decrease the excess of CD needed to generate the drug/CD inclusion complex [63–66], and the hydrophilic polymers used are mainly uncharged polymers currently approved for pharmaceutical uses. However, the components of our research are all

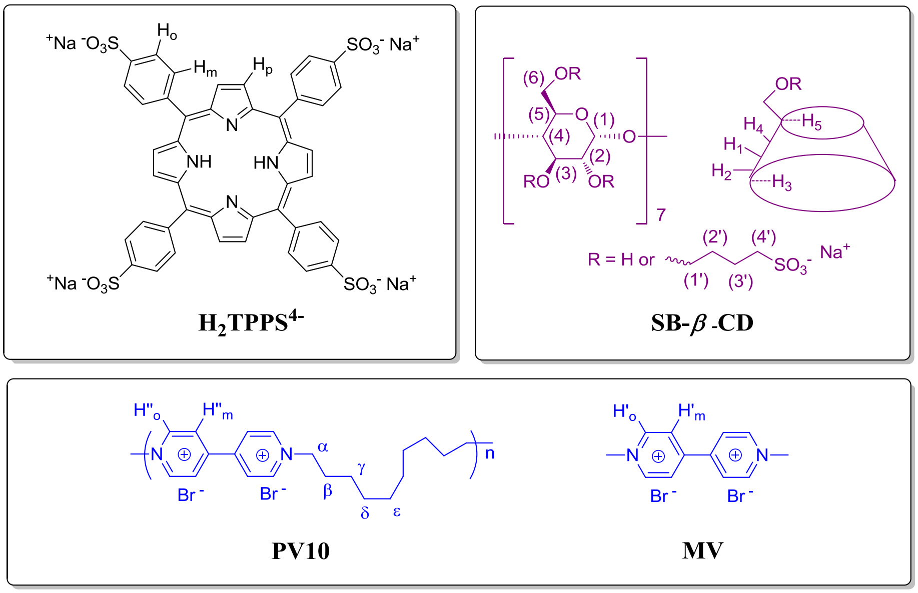

Fig. 1. Molecular structures.