

Synthesis and Characterization of Functional Organic and Supramolecular Nanomaterials

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Abstract:

Artificial photosynthetic systems offer a potential renewable energy source to manage the increasing global energy demand. Organized dye molecules, in particular *J*-type aggregates, exhibit efficient excitation-energy transfer suitable for light-harvesting antennas necessary in artificial photosynthetic systems. We designed and synthesized a porphyrin chromophore (**1S**) so as to self-assemble into a supramolecular polymer with a stable *J*-aggregate mode in solution. Ultraviolet-visible (UV-Vis), infrared (IR), nuclear magnetic resonance (NMR), and circular dichroism (CD) spectroscopic analyses were performed to investigate the aggregation properties.

Introduction:

Artificial photosynthesis represents another possibility to harness energy from the sun. In an artificial photosynthetic system, sunlight is absorbed by a light-harvesting antenna before being used to breakdown water into hydrogen and oxygen gas. Ideally a light-harvesting antenna is a chromophore that has a stable *J*-aggregate mode as well useful absorption properties such as broad spectral absorbance and high extinction coefficient [1]. Porphyrin is a conjugated cyclic compound that exhibits self-assembly properties fitting for a potential light-harvesting antenna. It can be synthetically functionalized to form a variety of different chemical structures depending on the application. A natural light-harvesting antenna, chlorophyll, is also a porphyrin derivative [2]. Two aggregation modes, *J*-aggregate and *H*-aggregate, are possible in porphyrin based systems. The *J*-aggregate forms with the porphyrin π systems overlapped partially and the *H*-aggregate is face-to-face stacks of the π systems. Although the *H*-aggregate is more thermodynamically stable, the *J*-aggregate has desirable light-harvesting properties necessary to transfer energy in artificial

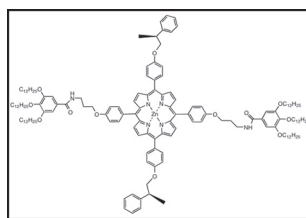


Figure 1: Chemical structure of **1S**.

photosynthesis. Compound **1S** was designed to form a supramolecular polymer with a stable *J*-aggregate mode in solution.

As seen in Figure 1, **1S** is based on a porphyrin ring with a zinc center. Chiral groups are included to introduce directionality to the aggregate, amide groups to allow for hydrogen bonding, and long alkyl chains to both increase the solubility in nonpolar solvents as well as allow for van der Waals interactions.

Experimental Procedure:

The target molecule was synthesized by a seven step series of reactions starting from pyrrole and ending with **1S**. All compounds were identified with ^1H NMR spectroscopy in CDCl_3 . The aggregation properties of **1S** were characterized with UV-Vis spectroscopy, IR spectroscopy, CD spectroscopy, and atomic force microscopy (AFM). Characterization measurements were taken with solutions of **1S** (10-100 μM) in methylcyclohexane (MCH) at 283-378 K.

Results and Conclusions:

The aggregation properties of **1S** in solution were measured by a combination of spectroscopic techniques. First UV-Vis spectral measurements were conducted to determine the stacking mode of the porphyrin molecules in a MCH solution. At concentration of 50 μM , both Soret and Q bands of the solution were red-shifted in comparison with those of monomeric **1S**, which indicated that the porphyrin molecules overlap in the *J*-aggregate mode. In addition, CD signal was observed with negative maxima at 433 nm, which corresponds to the absorption maximum for Soret band that arises in the UV-Vis spectra upon aggregation. These combined results imply that

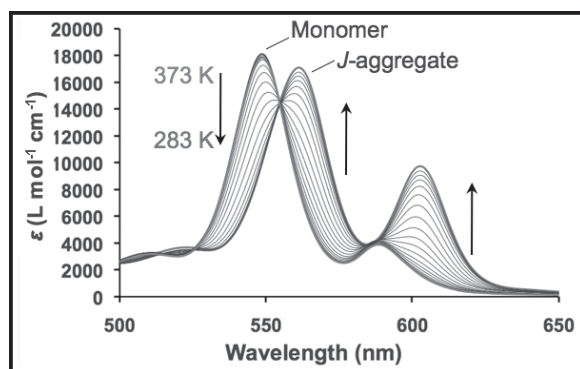


Figure 2: Temperature-dependent UV-Vis spectra of Q band to monitor the formation of J-aggregate in MCH ($C_T = 50 \mu\text{M}$).

the chiral groups induce a chiral excitonic coupling between the porphyrin π systems within the J-aggregate. IR spectral measurements confirmed both the N-H and C = O stretching vibration peaks were shifted to smaller wavenumbers. These results are indicative of hydrogen bonding between the amide groups of adjacent monomers.

Next the supramolecular polymerization mechanism was investigated with temperature-dependent UV-Vis spectroscopy (Figure 2). As the temperature was decreased from 373 K to 283 K (1 K min^{-1}), a shift of the Q band was induced with a sigmoidal transition that is characteristic of the isodesmic mechanism. This mechanism assumes that each species of aggregation (monomer, dimer, trimer, etc.) are formed with a same equilibrium constant (K_e).

Based on the isodesmic model, the equilibrium constant can be described using Equation 1, where the left side is a fraction of monomeric **1S**, and C_T is an initial concentration of **1S**

$$\frac{M}{C_T} = \frac{2C_T K_e + 1 - \sqrt{4C_T K_e + 1}}{2(C_T K_e)^2}$$

Equation 1: Isodesmic model for determining equilibrium constant.

[3]. The aggregation process was well fitted by an isodesmic analysis, which yielded equilibrium constants at various temperatures. A van't Hoff plot based on these values showed a linear relationship, from which the standard enthalpy change (ΔH°) and entropy change (ΔS°) were determined to be -88 kJ mol^{-1} and $-193 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively.

Furthermore, the aggregation shape was examined with AFM (Figure 3). The average aggregation height is 2 nm while the minimum distance across **1S** varies from 2.5-2.9 nm based on simulations. From this information, the aggregates lay approximately 50° to the surface and not perpendicularly. This stacking height further indicates that J-aggregates are formed in solution as well as on the substrate.

In conclusion, we successfully synthesized **1S** and characterized its aggregation behavior. From the results of various

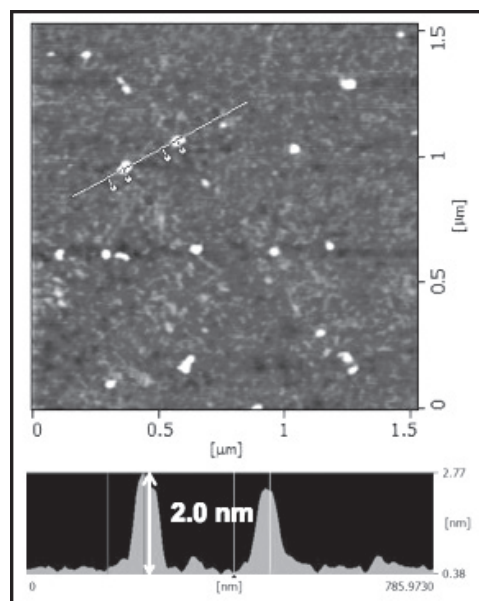


Figure 3: AFM height image of the J-aggregate spin-coated onto a silicon wafer from a MCH solution.

spectroscopic analyses, we revealed that **1S** could form a stable J-aggregate with the twisted absorption transition dipoles through π - π stacking and hydrogen bonding in MCH. The aggregation mechanism was well fitted by an isodesmic model so that the equilibrium constant and the thermodynamic properties were determined. Compound **1S** exhibits properties that are beneficial to the synthesis of a light-harvesting antenna.

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