

Synthesis, Structure, and Salt-Dependent Aggregation Properties of Water-Soluble Bipyridyl-Bridged Porphyrin Macrocycles

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Supramolecular self-assembly has proven to be a powerful strategy for constructing complex molecular architectures inaccessible via conventional chemical synthesis.^[1] Metal coordination, hydrogen bonding, Van der Waals interactions and the hydrophobic effect are well-established driving forces for self-assembly, yet the influence of salt concentration remains comparatively underexplored despite its relevance to many biological processes. In this work, we introduce nickel porphyrin macrocyclic dimer **2** which showed evidence of self-assembly above a critical salt concentration threshold.

Nickel porphyrin dimer **1** was synthesized through reductive homocoupling of 5,15-acetoxypropyl-10,20-bis-6-(methyl 2-chloronicotinate) nickel porphyrin using bis(1,5-cyclooctadiene)nickel(0) (Figure a). Deprotected dimer **2** was obtained by stirring **1** in a 3 M KOH_{aq}/THF biphasic solvent for 4 hours. When **2** was dissolved in 3M KOH_{aq}, the UV-Vis spectrum revealed splitting of the Soret band into two distinct peaks, consistent with excitonic interactions arising from long range J-type stacking of the porphyrin moieties. NaCl, NH₄Cl and NH₄HCO₂ each induced splitting of the Soret band at a concentration of 6.67 mM, suggesting that aggregation is governed by salt concentration rather than by specific ion interactions (Figure b). Dynamic light scattering measurements further demonstrated the formation of aggregates ranging from 100 to 1000 nm in diameter. To determine the structure of these aggregates, single-crystal X-ray diffraction measurements were performed, to reveal a hydrogen-bonded framework with orthogonal 1-D channels (Figure c). The UV-Vis diffuse reflectance spectrum differs from that recorded in solution, indicating that the mode of aggregation observed in the solid state does not directly mirror that in solution. The interplay between salt concentration and supramolecular organization, as well as the structure of the self-assembled species in solution and in the solid state, will be discussed.

1) Lehn J.-M., *Science* **2002**, 295, 2400.

