

SPECTROSCOPIC INVESTIGATION OF J-AGGREGATE FORMATION OF CYANINE DYES IN AQUEOUS SOLUTIONS OF INORGANIC SALTS

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Abstract

The effect of monovalent, divalent and trivalent metal cations of the types; Na⁺, K⁺, Cs⁺, Mg²⁺, Ca²⁺, Sr²⁺, Zn²⁺, Cd²⁺, and Al³⁺, on the aggregation behavior of the cyanine dye, 3,3'-disulfobutyl-5,5'-dichlorothiacarbocyanine triethylammonium salt, (NK-3796) in aqueous solution were investigated using UV-vis spectrophotometry. The results revealed that the dye forms J-aggregates upon incremental addition of aqueous salt solutions of the above metal ions to the monomer/dimer equilibrium of the dye in solutions. The appearance of a single, red-shifted band at 652 nm in the UV-vis spectra suggests that dye molecules are quantitatively converted to J-aggregates in the presence of these inorganic salts. The monovalent cations produce a narrow absorbance band while the divalent cations produce a wider band. The AlCl₃ salt effect is very much like that of the divalent cations except that the J-band produced in this case is even wider. Neither the cationic size nor the type of the anion seem to have any significant effect on the formation of the aggregates.

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Introduction

A wide variety of aromatic organic compounds and dyes exhibit a spontaneous self-assembly phenomenon that results in forming macro-structures of unique photophysical properties. Cyanine dyes are known for their ability to form H-aggregates and J-aggregates on solid substrates and on interphases and even in aqueous solutions containing larger size particles with a surface charge density¹⁻⁵. The J-aggregate can be looked at as two-dimensional brick-stone arrangements of the dye molecules. It normally occurs because of π - π interactions between polarizable centers of the molecules. J-aggregates are characterized by an intense and sharp absorption and emission band (J-band, 10-20 nm in width) red shifted (longer wavelength, ~100 nm) from the monomer band. The H-aggregates band however, is broader in nature and it is blue-shifted compared to the monomer band. Molecular aggregates' bonding by non-covalent interactions have generated interest in the scientific community for their remarkable and unusual spectroscopic and non-linear optical properties that are distinctly different from those of the individual molecules that constitute the aggregates⁶⁻⁹. J-aggregates are representative of polymer-type assemblies, which are composed of thousands of dye monomers¹⁰. The presence of various aqueous catalysts, supporting surfaces, and polymeric substrates can facilitate the formation of J-aggregates. Their formation is accompanied by a drastic change in both absorbance and fluorescence bands. Unique optical spectral features of the aggregates, make the cyanine dyes excellent candidates in many technological fields such as optical storage, light harvesting and ultrafast optical switching devices, photography, sensors and molecular devices¹¹. This wide range of applications of the aggregates from cyanine dyes provides the motivation to better understand the properties of the J-aggregates and explore the mechanisms involved in their production^{12,13}. This study focuses on the influence of inorganic salts of monovalent, divalent and trivalent metal cations on the cyanine dye; 3,3'-disulfobutyl-5,5'-dichlorothiacarbocyanine triethylammonium salt (NK-3796, Figure 1) in aqueous solutions, and their impacts on the

dye's behavior. It reports on the spontaneous self-assembly of the cyanine dye as a function of the type and concentration of cationic metal ions in aqueous solutions. It also compares the effects of differently charged metal cations on the morphology of the aggregates produced.

Experimental Procedure

NK-3796 dye was purchased from Hayashibara Biochemical Laboratory and used as received. A 1.94×10^{-5} M stock solution of (NK-3796) was prepared in deionized water at room temperature. The absorbance of the dye in solution was recorded using an HP Agilent Cary UV-Vis spectrophotometer. Monovalent cationic salts of sodium chloride, potassium chloride and cesium chloride and divalent cationic salts of magnesium chloride, calcium chloride, strontium chloride and barium chloride were tested for their effect on the aggregation behavior of the dye in aqueous solutions. In addition, zinc chloride and cadmium chloride were also tested for their ability to catalyze the formation of dye aggregates. All salt solutions used were saturated aqueous solutions and were prepared freshly before use. The selected salt solution was added in 25- μ L increments to 2.5 mL of the dye solution in the cuvette. Then the absorbance of the dye was recorded after each incremental addition of salt solutions. The addition of the salt solutions was contin-

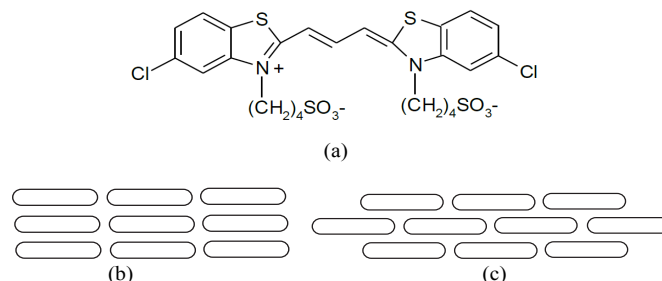


Figure 1. (a) The Structural formula of (NK-3796) and the stacking scheme of, (b) H-aggregates and (c) J-aggregates of the dye.

ued until there was no further noticeable change in the absorbance spectra of the dye.

Results and Discussion

A distinguished sharp absorbance band centered around 652 nm is observed when salt solutions of main group elements are added to the cyanine dye in water. This band signifies the formation of the J-aggregates of the dye in solution. The intensity of this band increases as the concentration of the salt in solution increases, indicating that the number of aggregates formed is dependent on the salt concentration. During this process, both the monomers and dimers of the dye are converted to J-aggregates as the intensity of the absorbance of the monomers/dimers (562 nm) decreases. The intensity of the J-band centered at 652 nm grows after each incremental addition of salt solutions (Figures 2 and 3). This suggests that the formation of J-aggregates of the cyanine dye is catalyzed by the addition of these inorganic salts.

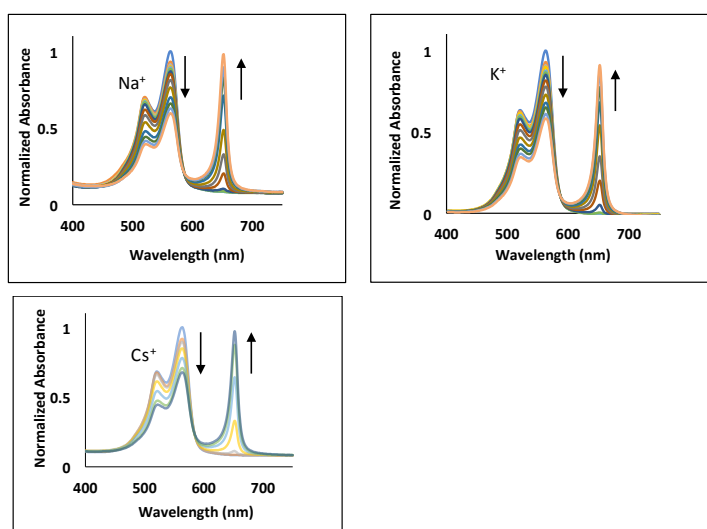


Figure 2: Normalized absorbance of NK-3796 ($1.94 \times 10^{-5} \text{M}$) as saturated solutions of NaCl, KCl and CsCl were added in 25 μL increments.

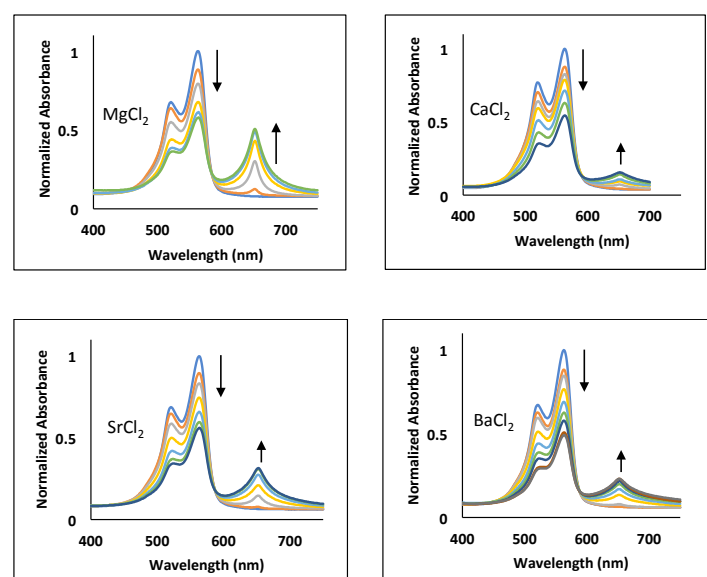


Figure 3: Normalized absorbance of NK-3796 ($1.94 \times 10^{-5} \text{M}$) as saturated solutions of MgCl_2 , CaCl_2 , SrCl_2 and BaCl_2 were added in 25 μL increments.

Salts increase the dielectric constant of the solution which in turn decreases the electrostatic repulsions between dye ions. As a result, aggregates form in solution^{14,15}. The type and the number of aggregates formed depends on the concentration and the charge of the metal cation in the salt, but not on its ionic size, charge density, or the nature of the anion of the salt. For example, the main group salts such as NaCl, KCl and CsCl all show the same effect on the aggregation of the dye. They all promote the formation of J-aggregates quantitatively as a single isosbestic point is observed in all the recorded spectra of the three salts (Figure 2). In the case of the chloride salts of Magnesium, Calcium, Strontium, and Barium, the J-band observed is broader in nature and less intense but appears at the same wavelength as that of the monovalent cations (Figure 3). According to previous studies¹⁶⁻¹⁹, the shape and the broadness of the J-band is dependent on the electronic coupling and exciton coherence between the monomeric molecules forming the aggregates. However, the possibility of coexistence of the dye monomers with the J-aggregates could also cause broadening in the band¹⁹. Therefore, the absorption spectrum of the monomer in the region near the J-band has a crucial effect on the shape and width of the J-band. This leads us to believe that the J-aggregates induced by divalent and trivalent cations vary in their structures compared to those produced when monovalent cations are used. As a result, the nature and the strength of electronic coupling between the aggregated dye molecules varies, and this leads to the distinction of the J-band observed in the absorption spectra.

This study also investigated if transition metal ions have the same effect on the dye in solutions as the main group metal ions. The effect of ZnCl_2 and CdCl_2 were studied using the same methodology above. The results from these two experiments indicate that the Zn^{2+} and Cd^{2+} cations have the same effect on J-aggregates formation as the main group divalent chloride salts (Figure 4).

The effect of AlCl_3 (as a trivalent main group cation) on the dye aggregation was also tested. Its effect resembles that of the divalent cations, but the absorbance of the J-band is even wider and less intense (Figure 5). The results from this experiment agree with the reported effects of Eu^{3+} and Tb^{3+} ions on the rate of aggregation of a similar cyanine dye¹⁰.

In conclusion, metal cations in solution catalyze the self-assembly of cyanine dye into J-aggregates. As the concentration of metal ions in a solution increases, the amount of J-aggregates formed also increases; this is because the metal ions of the salt act as a driving force for the self-assembly of dye molecules into J-aggregates, with the most efficient aggregation occurring at near-equivalent molar ratios of dye to salt. The morphology of

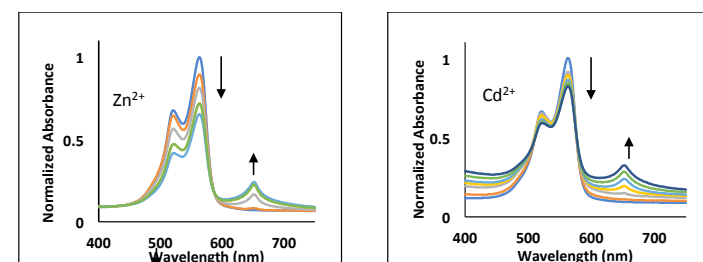


Figure 4: Normalized absorbance of NK-3796 ($1.94 \times 10^{-5} \text{M}$) as saturated solutions of ZnCl_2 and CdCl_2 were added in 25 μL increments.

the J-aggregates produced depends primarily on the charge of the cation (+1, +2 or +3) but not on the cationic size or its type. The anion of the salt has no effect on the aggregation phenomena of this cyanine dye.

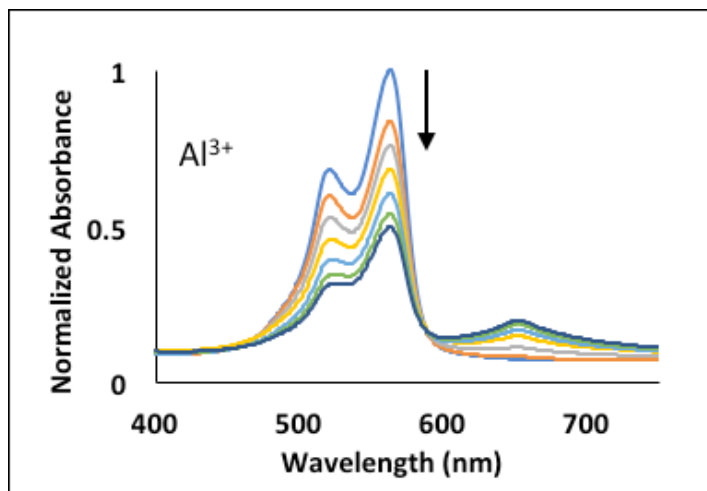


Figure 5: Normalized absorbance of NK-3796 ($1.94 \times 10^{-5} \text{M}$) as a saturated solution of AlCl_3 were added in 25 μL increments.

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