

Transition of H- and J-aggregate of a Cyanine Dye Based on Cation Embedded in Aggregation

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J-aggregate of a cyanine dye induced by potassium ions from H-aggregate in solution, form a hypochromic complex by the addition of a nonionic ligand (18-crown-6 ether), and the spectral studies and NMR measurements indicate that the transition from J-aggregate to H-aggregate has been achieved.

Supramolecular chemistry and nanotechnology, together with their usage in the construction of functional assemblies and devices, have merged into a challenging field of study. Great progresses have been achieved in several aspects.^{1,2} Among them, the assembly of synthetic controllable molecular mechanical systems is one of the most attractive areas.³⁻⁵ As a kind of supramolecule, aggregates of cyanine dyes have been the focus on the scientific community for a long time because of their wide applications in technology.⁶ Further, the structure of aggregate could be manipulated by varying the concentration and/or temperature of the solution, adding inorganic salts or using template.⁷⁻⁹

Owing to hydrophobic character of the molecular frame, in most cases, some cyanine dyes exist in the form of aggregation which exhibit properties that the corresponding monomers do not show. Depending on the aggregated structure, a large bathochromic (J-aggregate) or hypsochromic (H-aggregate)¹⁰ shift is induced. Our previous work on the aggregate of a cyanine dye has revealed that in aqueous solution sodium cation can induce anionic cyanine dyes to transform from H-aggregates to J-aggregates.⁹ However, the reverse conversion from J-aggregates to H-aggregates has not yet been reported. In the present work, we try to develop a simple method to achieve the mutually structural conversion between J-aggregate and H-aggregate of a cyanine dye, 3,3'-di(3-sulfopropyl)-4,5:4',5'-dibenzo-9-methylthiacarbocyanine triethylammonium salt (abbreviated as MTC; chemical structure shown in the inset of Figure 1) based on molecular recognition of potassium ion embedded into two

adjacent molecules of the aggregates, which might be applied in building of supramolecular assembly.

In dimethyl sulfoxide, MTC only shows monomer's band located at 580 nm. However, different phenomena were observed in aqueous solution (Figure 1). In the absence of KCl, MTC exhibits a broad band at 514 nm, which could be assigned to the H-aggregate. Addition of KCl solution, the absorbance of H-aggregate reduced, and simultaneously, an intense, sharp peak located at 653 nm, due to J-aggregate, appeared. Further increasing the concentration of KCl, absorbance of H-aggregate decreased and disappeared finally indicating that the complete transition of H-aggregate transformed to J-aggregate at the circumstance of high ion strength.

The mechanism of salt-induced J-aggregation of cyanine dyes is the replacement of the organic cation of a cyanine dye by the metal ion of the added inorganic salt.¹¹ To further elucidate the effect of cations on the aggregation of MTC in aqueous solution, the ¹H NMR spectra of MTC in D₂O in the absence and presence of KCl and MTC in deuterated dimethyl sulfoxide (DMSO) have been measured at 298 K (Figure 2). As shown in Figure 2a, MTC shows a high-resolution ¹H NMR spectrum in DMSO-*d*₆ solution, which could be attributed to the contribution of monomer.¹² However, in D₂O, the ¹H NMR spectrum can be characterized by two broad peaks, which could be assigned to CH₃ (1.15 ppm) and CH₂ (3.06 ppm) of triethylammonium ion (HN(C₂H₅)₃⁺), respectively, except a single peak of the residual solvent. This result implies that MTC exists mostly in the form of aggregate in aqueous solution, and triethylammonium ion is partially involved in constructing the aggregates. The broad signals could be due to the magnetic dipolar interactions generated among the nuclei of the individual dye molecule in the aggregate.^{7,9} When KCl is introduced, the CH₃ and CH₂ signals exhibit highly resolved triplet and quartet patterns, respectively, suggesting that K⁺ have penetrated into the aggregates, replaced the triethylammonium ions. Further increasing KCl, the integral intensities ratio of the CH₃ to CH₂ signals remains constant

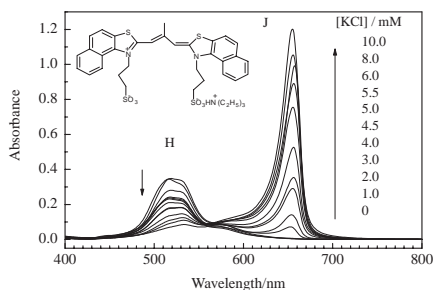


Figure 1. The absorption spectra of 7.3×10^{-6} M MTC with different concentration of KCl in aqueous solution.

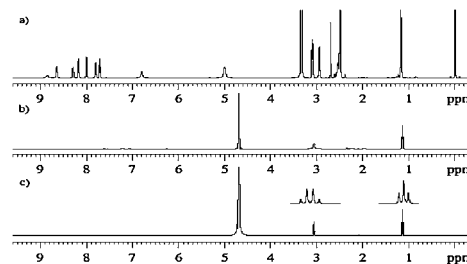


Figure 2. The ¹H NMR spectra of MTC a) in DMSO-*d*₆; b) in D₂O; c) in D₂O with 10 mM KCl.

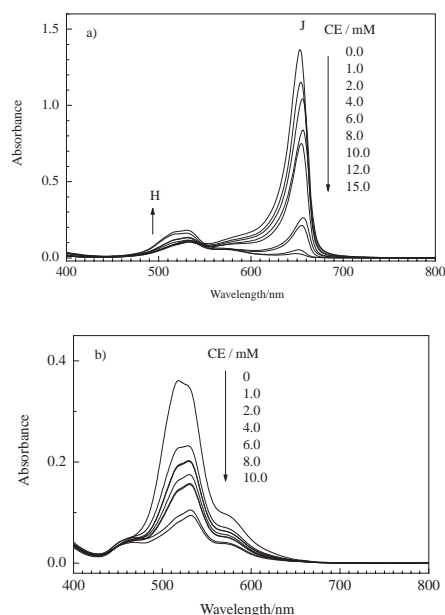


Figure 3. Effects of CE on the (a) J-aggregate (7.3×10^{-6} M MTC with 10 mM KCl) and (b) H-aggregate (7.3×10^{-6} M MTC).

(3/2), which agrees with the above interpretation.

When 18-crown-6 ether (CE) was added to the system of MTC and KCl, the absorbance of J-aggregate decreases and that of H-aggregate increases (Figure 3a). Increasing the concentration of CE, the absorbance of J-aggregate is reduced gradually, while that of H-aggregate is not enhanced a lot as expected. CE is well known to be an excellent nonionic ligand to K^+ .^{13,14} In the presence of CE, K^+ is expected to mainly form 1:1 crown complex and isolated from the aggregate, and thus facilitate the transformation from J-aggregate to H-aggregate. If it were the case, more notable enhancement of the absorbance of H-aggregate would be observed. However, the result shows it is not true, only minor enhancement of absorbance of H-aggregate was observed.

In order to understand what is happened in the system of MTC/KCl/CE, the titration of CE to H-aggregate has been carried out. Surprisingly, the addition of CE dramatically decreases the absorbance of the H-aggregate (Figure 3b) and no new band is observed. The spectral changes indicate that the complex formed by H-aggregates of MTC and CE probably had a much lower molar extinction coefficient than H-aggregate of MTC, or did not absorb in the visible region. However, this result is a little strange because CE is well known to be a good ligand to lots of ions and molecules but not to supramolecule.¹⁴ Further studies are necessarily required to clarify the intrinsic mechanism.

The observed spectral change of H-aggregates in MTC/KCl system in the presence of CE should be the contribution of both H-aggregate-CE complex and the H-aggregate transformed from J-aggregate. To further examine the interaction between MTC molecule, CE and K^+ , the chemical shifts (δ_K^+) of ^{39}K nuclei have been measured (see Supporting Information).¹⁵ One could

find that, under the certain concentration of KCl, the δ_K^+ of ^{39}K nuclei is up-field in the MTC/KCl system compared with that in MTC-free solution, indicating that K^+ is located very close to the center of the dye molecule in the J-aggregate and shielded by the dye molecules in the aggregate.¹⁰ This is in agreement with the 1H NMR results. When CE is added to the MTC/KCl solution, the δ_K^+ shows no notable change while the peak is very broad (see Supporting Information).¹⁵ The broader peak in ^{39}K NMR spectra, due to the exchange of K^+ between the free one and included one, indicates that the potassium ions were complexed with CE, which is consistent with the above assumption in the absorption spectra.

Based on the above results, an model is proposed to explain the transition between H- and J-aggregate by adjusting K^+ with CE: In aqueous solution, K^+ penetrates into H-aggregate, form ion-pair with the dye anion, and thus facilitates the J-aggregation; when K^+ is included by a strong ligand, e.g., CE, the dye molecule would rearrange to H-aggregate, at the same time, CE form a hypochromic complex with H-aggregate. By the competition of these two effects, the H-aggregate absorbance exhibits minor enhancement.

In summary, a simple method has been developed to transform between H- and J-aggregate by adjusting K^+ together with CE based on molecular recognition. Although not realizing the fully reversible transformation, our founding might help to assemble novel molecular devices.

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- 15 Supporting Information is also available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.