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Aggregation behaviour of two thiacarbocyanine dyes in aqueous solution

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Abstract

The J-aggregation behaviour of two cyanine dyes (3,3′-disulfopropyl-4,5,4′,5′-dibenzo-9-methyl-thiacarbocyanine triethylammonium salt (**MTC**) and 3,3′-disulfopropyl-4,5,4′,5′-dibenzo-9-phenyl-thiacarbocyanine triethylammonium salt (**PTC**)) has been investigated in the presence of dication chloride using absorption spectroscopy, ^{1}H and multinuclear NMR methods. The promotion efficiency on J-aggregation of the dye molecule and the magnitude of the effective coherence length of the J-aggregate were found to be dependent on the dyes' structure and their ability to coordinate with the metal ions. The interaction between the metal ions and the J-aggregates could be explained by the association between metal ions and J-aggregates, and the apparent association constants were obtained from the chemical shifts in NMR spectra of the metal ions.

Keywords: Thiacarbocyanine dye; Aggregation; Coherence length; Association constant; Multinuclear NMR; Chemical shift

1. Introduction

Cyanine dyes have been the object of continuous interest in the scientific community because of their application in the spectral sensitization of photographic emulsion [1] and wide-band semiconductors [2,3], information recording materials [4], nonlinear optical materials [5] and as fluorescence indicators in biological systems [6]. In aqueous solution, some cyanine dyes exhibit self-aggregation owing to the hydrophobic character of the molecular frame. The photophysical and photochemical properties of these aggregates have been studied in great detail and are often quite distinct from the monomeric dye. Depending on the aggregated structure, a large bathochromic (J-aggregate) or hypsochromic (H-aggregate) [7] shift is induced. More attention has been paid to J-aggregates because of their unique character and numerous applications.

J-aggregation of cyanine dyes was found to occur in aqueous solution under various conditions, for example, by adding salts, surfactants, polymers, polyelectrolytes and the introduction of a *meso*-substituent [8]. Numerous methods have been used to investigate the properties of J-aggregates including spectroscopy [9–11] and X-ray diffraction [12,13]. In addition, J-aggregate structures have been characterized by atomic force microscopy (AFM) [14,15], fluorescence microscopy [16], transmission electron microscopy [17–19] and near-field scanning optical microscopy [20].

Metal ions play important roles on the J-aggregates, but there has been no systematic study of the influence of metal ions on J-aggregation. In this paper, we explore the effects of metal dication chloride on the salt-induced J-aggregation of two cyanine dyes (**MTC** and **PTC**) using absorption spectrum, ^{1}H NMR as well as multinuclear spectroscopy.

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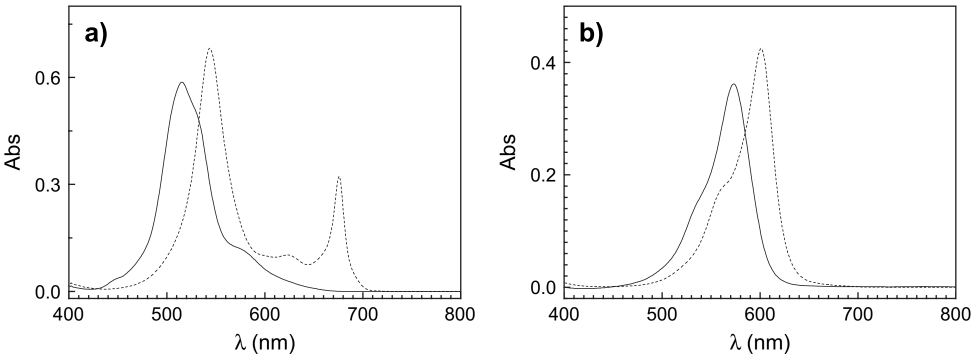

Fig. 1. Absorption spectra of 5.0 μM **MTC** (solid line) and 4.0 μM **PTC** (dash line) in (a) aqueous solution and (b) methanol.

2. Experimental

2.1. Materials

The cyanine dyes, **MTC** and **PTC** were synthesized according to the methods suggested by Hamer [21] and Ficken [22]. Analytical grade $MgCl_2$, $CaCl_2$, $ZnCl_2$ and $CdCl_2$ were purchased from Beijing Chem. Co. Deuterated DMSO and water were purchased from Sigma–Aldrich.

2.2. Instrumentation

The absorption spectra were performed in UV-1601PC spectrophotometer. All of the spectral experiments were carried out in 1 cm quartz cells.

^1H, ^{25}Mg and ^{43}Ca NMR spectra were recorded on a Bruker Avance 600 spectrometer at 600.13 MHz, 36.74 MHz, and 40.39 MHz, respectively. ^{67}Zn and ^{113}Cd NMR spectra were obtained on a Bruker DMX 300 at 18.78 MHz and 66.61 MHz. Chemical shifts of ^1H NMR signals were expressed in δ (ppm) referenced to the residual solvent signals ($\delta = 4.70$ ppm for D_2O and 2.50 ppm for DMSO) at 298 K. The chemical shifts of ^{25}Mg, ^{43}Ca, ^{67}Zn and ^{113}Cd NMR signals were expressed in δ (ppm) related to their corresponding saturated solution.

3. Results and discussion

3.1. Absorption spectra

In aqueous solution, the absorption spectrum of **MTC** exhibits a short-wavelength maximum at 514 nm and a long-wavelength shoulder at 574 nm, which could be attributed to the band of H-aggregate and monomer, respectively, while that of **PTC** shows three bands at 545, 624 and 678 nm, assigned to the H-aggregate, monomer and J-aggregate, respectively (Fig. 1a) [23,24]. Compared with their absorption spectra in methanol (Fig. 1b), the predominant aggregation of **MTC** and **PTC** in aqueous solution could be ascribed to the intrinsic hydrophobic properties of the naphthothiazole group [25] and the *meso*-substituent group in the molecular frame [26]. Although both **MTC** and **PTC** exhibit strong tendency to aggregate, their aggregation behaviors are different: in the absence of salt, **MTC** prefers to form H-aggregate while **PTC** tends to form both H- and J-aggregates because of the influence of different *meso*-substituents. It is well known that, in aqueous solution, the size and shape of *meso*-substituents play important roles in determining the arrangement of dye molecules in aggregates [11]. As can be seen, both **MTC** and **PTC** are cationic in the heterocycle and polymethine bridge, while substituents on the heterocycle nitrogen are anionic. Due to the electrostatic interaction,

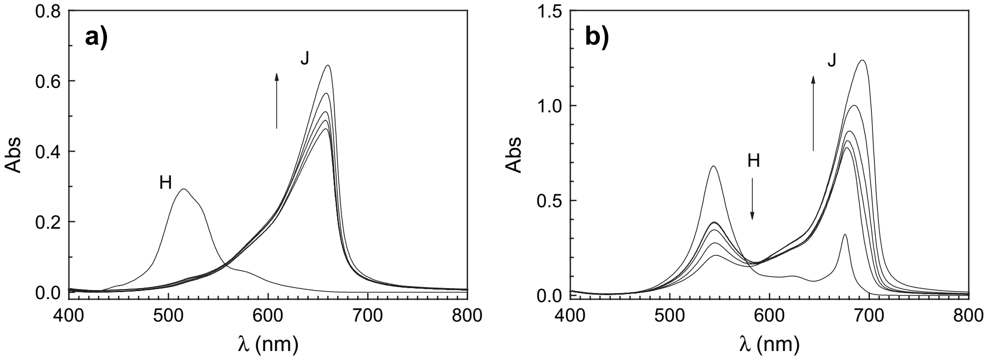

Fig. 2. The absorption spectra of (a) 5.0 μM **MTC** and (b) 4.0 μM **PTC** in aqueous solution with different concentrations of $MgCl_2$.

MTC can form H-aggregate by close packing of two adjacent molecules with no or little displacement between adjacent molecular planes in aqueous solution. However, the electrostatic interaction between adjacent **PTC** molecules is weaker than **MTC** because the bulky phenyl substituent protrudes from the molecular frame and hinders the close packing of molecular frame; the steric hindrance of phenyl group leads **PTC** molecules to form J-aggregate by arranging with a larger displacement. As a result, it is reasonable that in aqueous solution **PTC** exists as both H-aggregate and J-aggregate.

By adding chloride salts into the aqueous **PTC** and **MTC** solutions, interestingly, two different aggregation behaviors were observed. One example is shown in Fig. 2. In aqueous **MTC** solution, adding $MgCl_2$ led to the decrease of the absorbance of H-aggregate while a new intense and sharp peak at 653 nm, due to the J-aggregate, appeared. Further increasing of the concentration of $MgCl_2$ resulted in complete disappearance of the peak of H-aggregate and increase of the peak of J-aggregate, which indicate that the full transformation of H-aggregate to J-aggregate occurs; while for aqueous **PTC** solution, the peak of H-aggregate also decreases but does not disappear completely even under the condition of high concentration of $MgCl_2$ as that of **MTC**.

The promotion efficiency on J-aggregation is mainly determined by the ability of the ions to form ion-pairs with the anionic dye [27]. As shown in Fig. 1b, in methanol the λ_{max} of **PTC** is at 600 nm, 26 nm bathochromic shift compared with the λ_{max} of **MTC** at 574 nm. The spectral character may be assigned to the delocalization of π electrons in the molecular frame of **PTC**, which is much stronger than that of **MTC** because of the conjugated effect of the *meso* phenyl in **PTC**. Therefore, **MTC** should exhibit higher capacity to form ion-pairs with magnesium dication than **PTC**. This result is slightly different from our previous report [23] that the addition of NaCl has fully promoted **PTC** to J-aggregate, which could be explained by the salting-out effect because of the high concentration of NaCl under the previous experimental condition [28]. Similar phenomena with $MgCl_2$ were also observed when $CaCl_2$, $ZnCl_2$ or $CdCl_2$ solution was added.

Based on the absorption spectral data of **MTC** and **PTC** in methanol and in aqueous solution, the effective coherence length of the J-aggregates (N (J)) could be estimated using the following equation [29]:

Table 1
The N(J) of **MTC** and **PTC** with different dications together with the ionic parameter under similar condition

Cations	MTC	PTC
Free[a]	4.0	5.0
Mg^{2+}	1.8	2.0
Ca^{2+}	2.2	2.2
Zn^{2+}	2.6	3.0
Cd^{2+}	4.2	4.6

[a] Obtained from Ref. [23].

$$N(\mathrm{J})^{1/2} = \Delta\nu_{1/2}(\mathrm{M})/\Delta\nu_{1/2}(\mathrm{J}) \quad (1)$$

where $\Delta\nu_{1/2}(\mathrm{M})$ and $(\Delta\nu_{1/2}(\mathrm{J}))$ are the bandwidths of the monomer absorption band measured in methanol and that of the J-aggregate absorption band of corresponding molecules in aqueous solution, respectively. The calculated values of N(J) for both **MTC** and **PTC** with different dications under similar conditions are listed in Table 1.

From Table 1, the effective coherence length, N(J), decreases of the J-aggregates in the presence of chloride salts, the reason for that phenomena is that N(J) is a measurement of the number of monomer units over which the exciton wave function is delocalized and the delocalization range is determined by the relative magnitude of the intermolecular coupling compared to the energetic disorder [30].

For the metal ions used in the experiment, the charges are identical to each other but are different in electronic structures. The difference in N(J) for different dication metal should be due to the electronic structures rather than the charge. Therefore, one may expect that the ability of the coordination of dye molecule to the metal ions would affect the N(J) because formation of J-aggregate is also affected by the ability of coordination of dye molecules to the metal ions [8,27].

Looking at the absorption spectra (Fig. 3) of the J-aggregates of **MTC** or **PTC** induced by Mg^{2+}, Ca^{2+}, Zn^{2+} and Cd^{2+}, one can found that the cations have no effect on the position of the maximum of the J-aggregate, which is consistent with the previous reports [28].

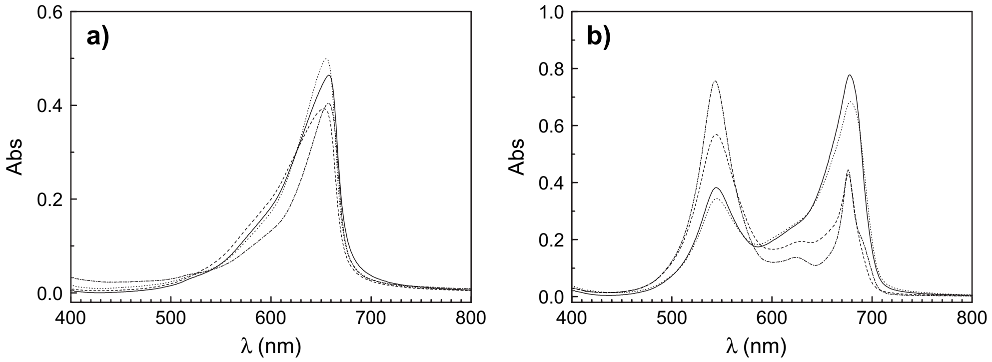

Fig. 3. The effect of different ions (0.5 M) on the J-aggregation: (a) 5.0 μM **MTC** and (b) 4.0 μM **PTC**.

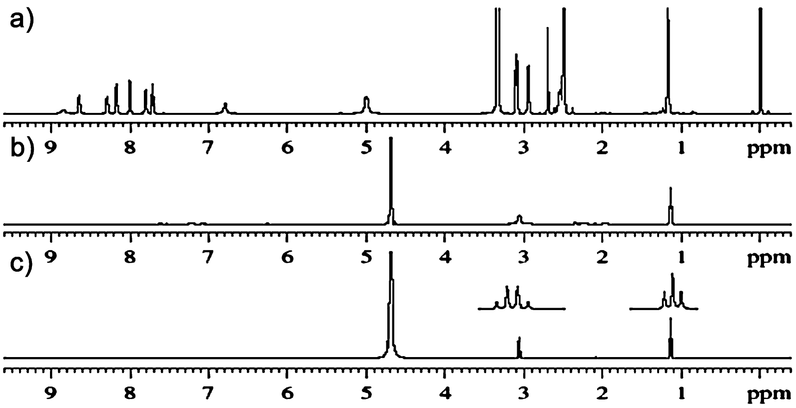

Fig. 4. The ^1H NMR spectra of **MTC** in: (a) DMSO-d_6, (b) D_2O and (c) D_2O with 0.2 M $MgCl_2$.

3.2. NMR measurements

Replacement of the inherent organic cation in the dye by the metal ion of the added salt is thought to be the reason for the salt-induced J-aggregation [27]. Our measurement of *N*(J)s of two cyanine dyes supports this deduction. In order to further elucidate the mechanism that metal ion promotes J-aggregation, the measurements of ^1H NMR spectra have been carried out.

Fig. 4 shows the ^1H NMR spectra of **MTC** in DMSO-d_6, in D_2O without and with $MgCl_2$. In the DMSO-d_6 solvent, a well-resolved ^1H NMR spectrum (Fig. 4a) is observed, attributed to the contribution of the monomer [13]. However, in D_2O solution (Fig. 4b), there are only two broad peaks assigned to CH_3 (1.15 ppm) and CH_2 (3.06 ppm) of triethylammonium ion ($(HN(C_2H_5)_3^+$), respectively, other resonance peaks almost disappear, which is due to the magnetic dipolar interactions generated among the protons of the individual dye molecule in the aggregate [13], except for a single peak of the residual solvent at 4.70 ppm. When inorganic salt was added to the D_2O solution of **MTC**, the methyl and methylene signals of triethylammonium ion exhibit highly resolved triple and quartet patterns (Fig. 4c), indicating the triethylammonium ions has been replaced by metal cation and move freely. Increasing the concentration of the salt, the integral intensity ratio of the signal of CH_3 to CH_2 remains constant (3/2). This result provides a strong support to our statement that, in salt-induced J-aggregation, the metal cation has replaced the triethylammonium cation and bound to the dye anions in the J-aggregates, reduce the electrostatic repulsion between dye anions, and thus facilitate their J-aggregation. This process could be simply expressed as:

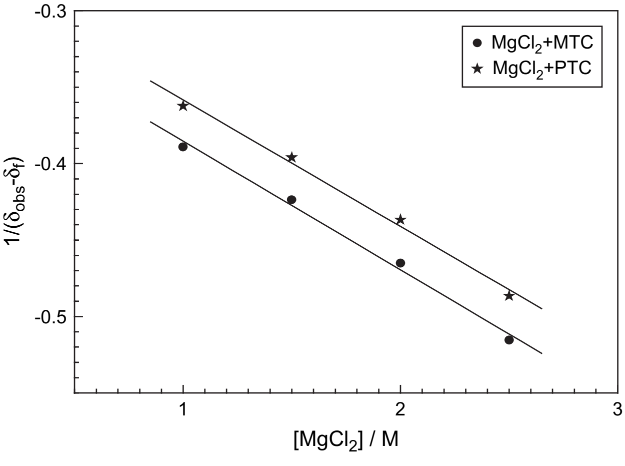

Fig. 5. The dependence of $1/(\delta_{obs} - \delta_f)$ on the concentration of **PTC**/$MgCl_2$ and **MTC**/$MgCl_2$ systems.

$$M^{2+} + J^- - \left(HN(C_2H_5)_3\right)^+ \xrightarrow{K} J^- - M^{2+} + \left(HN(C_2H_5)_3\right)^+ \quad (2)$$

where *K* is the apparent association constant. Therefore, one may expect the chemical shift of the metal ions would be affected by the presence of dye. Because triethylammonium cation does not involve in the J-aggregate structure in the presence of inorganic salts, the above equilibrium could be simplified as:

$$M^{2+} + J^- \xrightarrow{K} J^- - M^{2+} \quad (3)$$

Therefore, the observed chemical shift (δ_{obs}) of the metal ions can be expressed by the weighted mean of the chemical shift of free (δ_f) and associated (δ_a) dications by the equation:

$$\delta_{obs} = (1 - \alpha)\delta_f + \alpha\delta_a \quad (4)$$

where α is the degree of association between J-aggregates and metal ions. Under the experimental condition, the concentration of metal dication is much greater than that of J-aggregate, α could be expressed as:

$$\alpha = K \times [M]/(1 + K \times [M]) \quad (5)$$

Table 2
The values of *K* with **MTC** and **PTC** associated with metal ions

Cations	Metallicity[a]	K/M^{-1} (**MTC**)	K/M^{-1} (**PTC**)
Mg^{2+}	1.31	1.99	2.51
Ca^{2+}	1.00	2.42	3.29
Zn^{2+}	1.65	1.76	2.38
Cd^{2+}	1.69	0.68	1.45

[a] Obtained from Ref. [31].

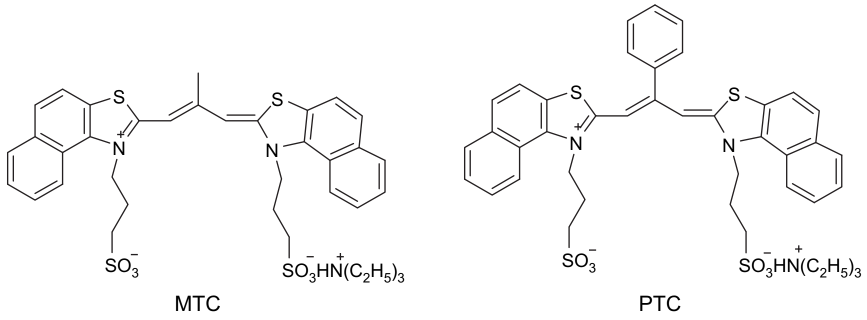

Chart 1. The structural formula of **MTC** and **PTC**.

Then Eq. (5) could be rearranged to Eq. (6) [23] as:

$$\frac{1}{(\delta_{\mathrm{obs}}-\delta_{\mathrm{f}})}=\frac{1}{(\delta_{\mathrm{a}}-\delta_{\mathrm{f}})K\times[\mathrm{J}]}+\frac{[\mathrm{M}]}{(\delta_{\mathrm{a}}-\delta_{\mathrm{f}})\times[\mathrm{J}]} \tag{6}$$

If the change of the chemical shifts of the metal nuclei were due to the binding of metal cations to J-aggregates, a liner dependence of $1/(\delta_{\mathrm{obs}}-\delta_{\mathrm{f}})$ on the concentration of metal ions is expected. Indeed, the linearity of the double reciprocal plot was obtained based on our experiment results, which confirmed this behaviour and is shown in Fig. 5. Then, the value of K can be deduced from the plot. The calculated values are listed in Table 2. For comparison, the metallicity of the metal dications is included.

From Table 2, we can see that for both J-aggregates, the values of K increase in the order: $K(\mathrm{Ca}^{2+}) > K(\mathrm{Mg}^{2+}) > K(\mathrm{Zn}^{2+}) > K(\mathrm{Cd}^{2+})$, following the same order of the metallicity of metal dications. Because of the negative character of J-aggregate in solution, the driving forces of the association between the J-aggregate and metal ion should resulted from the electrostatic interaction. Therefore, for the same J-aggregate, the higher the metallicity of metal dication, the larger the association constant.

The plot of the coherence length (N(J)) vs the value of association constant (K) is shown in Fig. 6, which indicates that in gross, the larger the N(J), the smaller the K. The reason for that phenomenon is not clear and further exploration will be made in the near future.

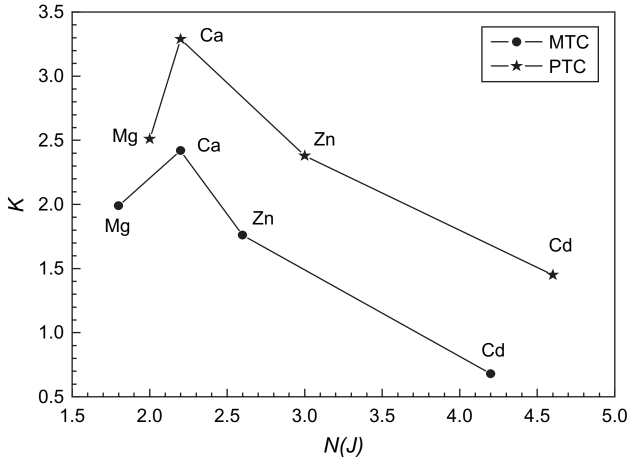

Fig. 6. The relationship between K and N(J) of **MTC** and **PTC**.

4. Conclusion

In summary, salt-induced J-aggregation behaviors of two thiacarbocyanine dyes with different *meso*-substituent have been investigated (Chart 1). In the presence of salt, the effective coherence length of the J-aggregates increases in the following order: $N(\mathrm{J})\ (\mathrm{Mg}^{2+}) < N(\mathrm{J})\ (\mathrm{Ca}^{2+}) < N(\mathrm{J})\ (\mathrm{Zn}^{2+}) < N(\mathrm{J})\ (\mathrm{Cd}^{2+})$. NMR experimental results reveal that the metal cations have replaced the original counter ion, triethylammonium cation, of dye anion in the J-aggregate, and such process might be regarded as an association reaction between metal cations and J-aggregate, where the electrostatic force plays the major role. The association constant decreases in the order: $K\ (\mathrm{Ca}^{2+}) > K\ (\mathrm{Mg}^{2+}) > K\ (\mathrm{Zn}^{2+}) > K\ (\mathrm{Cd}^{2+})$.

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