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Super-Helix Formation Induced by Cyanine J-Aggregates onto Random-Coil Carboxymethyl Amylose as Template

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Abstract: The J-aggregation of Cyanine-1dye in the presence of carboxymethyl amylose (CMA) is described. The J-aggregation requires a large excess CMA concentration; the J-band maximum appears in the concentration range, [CMA]/[dye] = 10−50, depending on the degree of substitution (DS) of carboxylation, where [CMA] is the concentration of polymer repeat units. An extraordinarily large induced circular dichroism (CD) is observed from J-aggregates of the achiral cyanine dye in association with a random coil CMA, suggesting that the CMA is transformed into a helix. The magnitude of CD intensity increases with increasing DS of CMA and pH up to neutral (where a maximum J-aggregation occurs), while the CMA-bound dye monomer and H-aggregates (occurring at pH ≥ 9) exhibit no induced CD. The trend in the CD intensity (of the J-aggregates) is in parallel with the fluorescence intensity of the J-aggregates. This suggests that binding of the J-aggregates onto the template CMA is sterically controlled by the asymmetric environment of glucose residues (of CMA) so that more twisting power is exerted with increasing DS (of CMA), rendering the cyanine dye/CMA complex a more rigid (a high fluorescence intensity) super-helix. This is also revealed by the AFM image of a long strand.

Introduction

There has been growing interest in J-aggregation of cyanine dyes onto ordered polymers templates due to the noncovalent binding and their unique photophysical properties. Such organization/function resembles the light-harvesting photosynthetic antenna molecules (biological pigments) bound to protein matrixes.[1] The antenna role anticipated for the J-aggregates is associated with the very large absorption cross-section and the ability of fast, efficient excitation energy migration over many molecules. The characteristic sharp low-energy absorption of J-aggregates is the result of exciton delocalization over a wide range of molecular building blocks of the noncovalent assembly.[2] This promotes the efficient transport of excitation energy and a high optical polarizability in the J-aggregates, thereby creating distinctive photophysical and nonlinear optical (NLO) properties,[3] which provide a great opportunity for technical applications in the field of optical communications.

Cyanine-1

CMA: R =CH$_2$COOH(Na)
x = 1-y (y = 0 − 0.94)
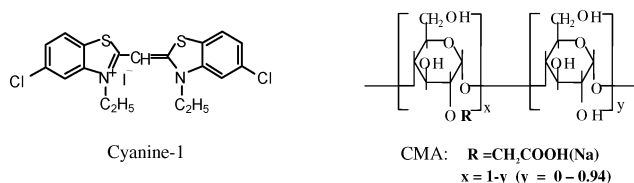
We were interested in developing a supramolecular device based on cyanine dye (Cyanine-1) J-aggregates as a photoactive functional surface on helical amylose because they are potentially a receptor or a sensing unit for biological molecules as well as a photosensitizer for artificial photosynthetic devices.[4] It is of great advantage for such applications if the polymer template has a inclusion capability like amylose such that a photoactive chromophore (a third component) in inclusion can communicate photoelectronically across the helix with the bound J-aggregates onto the helical exterior. However, the J-aggregation does not occur with neutral amylose, but it does occur with carboxymethylated amylose (CMA). CMA is a chiral polymer, but the conformation is a heavily disrupted helix or random coil in water[5] due to the electrostatic repulsion, which depends on the degrees of anionic "loading" and carboxylic substitution (DS), and the solution pH. In our investigation to develop self-

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(1) (a) Ritz, T.; Damjanovic, A.; Schulten, K. *ChemPhysChem* **2002**, *3*, 243−248. (b) van Amerongen, H.; Valkunas, L.; van Grondelle, R. *Photosynthetic Excitons*; World Scientific: Singapore, 2000.
(2) (a) Fidder, H.; Terpstra, J.; Wiersma, D. A. *J. Chem. Phys.* **1991**, *94*, 6895−6097. (b) Moll, J.; Daehne, S.; Durrant, J. R.; Wiersma, D. A. *J. Chem. Phys.* **1995**, *102*, 6362−6370.
(3) (a) Bognadov, V. L.; Viktorova, E. N.; Kulya, S. V.; Spiro, A. S. *JRTP Lett.* **1991**, *53*, 105−108. (b) Kobayashi, S.; Sasaki, F. *Nonlinear Opt.* **1993**, *4*, 305−309.
(4) (a) Kim, O.-K.; Choi, L.-S.; Zhang, H.-Y.; He, X.-H.; Shih, Y.-H. *J. Am. Chem. Soc.* **1996**, *118*, 12220−1222. (b) Kim, O.-K.; Je, J.; Baldwin, J.; Kooi, S.; Pehrsson, P. E.; Buckley, L. J. *J. Am. Chem. Soc.* **2003**, *125*, 4426−4427. (c) Kim, O.-K.; Je, J., unpublished results.
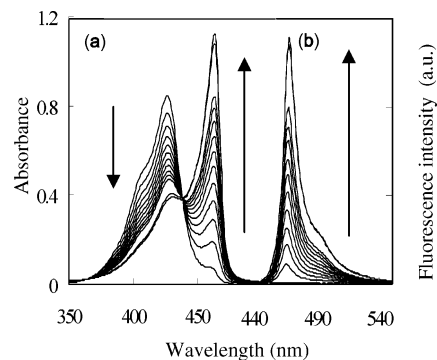(5) Dubin, P. L.; Brant, D. A. *Macromolecules* **1975**, *8*, 831−842.

assembled J-aggregates in the presence of CMA, we discovered an unusual super-helix formation, occurring concurrently with cyanine J-aggregation onto the CMA.

In this paper, we discuss spectroscopic properties of Cyanine-1 J-aggregates in the presence of CMA with respect to solvent effects, CMA concentration, and its DS, and we also discuss the observation of an unusual conformational transition of CMA from a random coil to a very stable, rigid super-helix formation through in-situ J-aggregation of the achiral cyanine dye onto CMA. By contrast, this does not occur when H-aggregates or the monomer dyes associate with CMA. While there are several reports in the literature dealing with cyanine dye J-aggregation in the presence of polyelectrolytes,[6] they are largely lacking in molecular details. To the best of our knowledge, it has not been known that cyanine J-aggregation induces a helical transformation of the host polymer template. This helical transition is evidenced by an extraordinarily large circular dichroism (CD) of the cyanine dye J-aggregates bound to CMA and also by atomic force microscopy (AFM) images as long helical rods. The underlying concept is new and clearly different from what is known for induced chirality to bound dyes by a helical polymer[7] and to a polymer by bound chiral dyes.[8]

Results and Discussion

J-aggregation is understood as occurring due to the end-to-end stacking of dye monomers, and the aggregate absorption is known typically as a sharp, narrow band red-shifted from that of the monomer, while H-aggregates are due to a face-to-face stacking of monomers and appear most commonly as a broad blue-shifted band relative to the monomer band. Many cyanine dyes are capable of forming J-aggregates spontaneously in a relatively narrow concentration range in solution, but some are sensitive to solvent composition and ionic strength.[9] More complex behavior occurs in interfacial systems such as surfactant, polymer, double-helix DNA, or soluble clay, where the aggregation is governed[10] by the extent of surface charge, steric factors, or hydrophobic forces such that a variety of changes are expected to occur in J-aggregates structure. This may, in turn, induce changes in the morphology of the host template via cooperative interactions. However, this effect has been little explored.
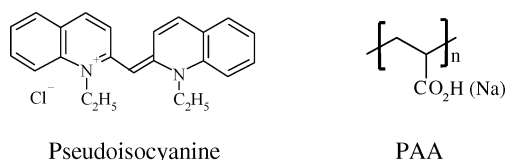
Cyanine-1 J-aggregation in the presence of CMA is strongly affected by external conditions such as solvent, CMA concentration, pH, as well as DS of CMA. The J-band absorption

(6) (a) Higgins, D. A.; Kerimo, J.; vanden Bout, D. A.; Barbara, P. F. *J. Am. Chem. Soc.* **1996**, *118*, 4049−4058. (b) Peyratout, C.; Donath, E.; Daehne, L. *J. Photochem. Photobiol., A* **2001**, *142*, 51−57.

(7) (a) Pasternack, R. F.; Giannetto, A.; Pagano, P.; Gibbs, E. J. *J. Am. Chem. Soc.* **1991**, *113*, 7799−1800. (b) Koti, A. S. R.; Periasamy, N. *Chem. Mater.* **2003**, *15*, 269−371.

(8) (a) Maeda, K.; Morino, K.; Okamoto, Y.; Sato, T.; Yashima, E. *J. Am. Chem. Soc.* **2004**, *126*, 4320−4342. (b) Schlitzer, D. S.; Navak, B. *J. Am. Chem. Soc.* **1998**, *120*, 2196−2197. (c) Egan, V.; Bernstein, R.; Hohmann, L.; Tran, T.; Kaner, R. B. *Chem. Commun.* **2001**, 801−802.

(9) (a) von Berlepsch, H.; Kirstein, S.; Boettcher, C. *Langmuir* **2002**, *18*, 7699−7705. (b) De Rossi, U.; Daehne, S.; Meskers, S. C. J.; Dekkers, P. J. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 760−763.

(10) (a) von Berlepsch, H.; Boettcher, C.; Ouart, A.; Regenbrecht, M.; Akari, S.; Keiderling, U.; Schnablegger, H.; Daehne, S.; Kirstein, S. *Langmuir* **2000**, *16*, 5908−5916. (b) von Berlepsch, H.; Kirstein, S.; Hania, R.; Didraga, C.; Pugzlys, A.; Boettcher, C. *J. Phys. Chem. B* **2003**, *107*, 14176−14184. (c) Niiesch, F.; Moser, J. E.; Shklover, V.; Graetzel, M. *J. Am. Chem. Soc.* **1996**, *118*, 5420. (d) Wang, M.; Silva, G. L.; Armitage, B. A. *J. Am. Chem. Soc.* **2000**, *122*, 9977−9986. (e) Garoff, R. A.; Litzinger, E. A.; Connor, R. E.; Fishman, I.; Armitage, B. A. *Langmuir* **2002**, *18*, 6330−6337. (f) Lu, L.; Jones, R. M.; McBranch, D.; Whitten, D. *Langmuir* **2002**, *18*, 7706−7713.

Figure 1. UV−vis absorption (a) and fluorescence (excitation at 460 nm) (b) titration of CMA to Cyanine-1 dye in 20% methanol−water mixture; [Cyanine-1] = 1 × 10^{-5} M, [CMA] = 0 to 30 × 10^{-5} M.
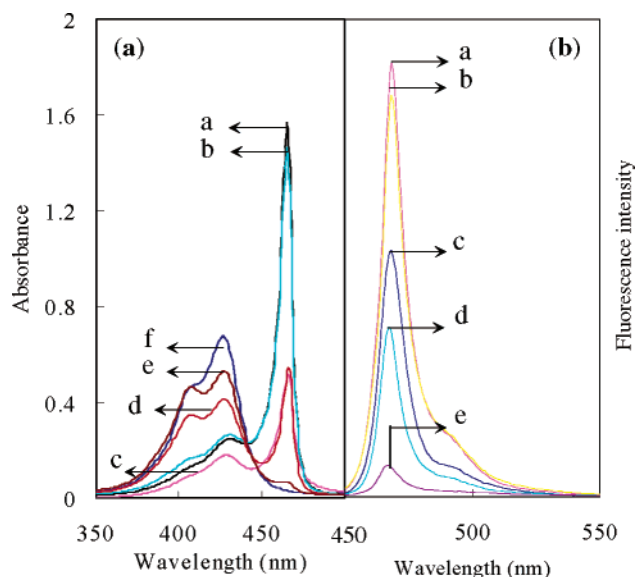
appears as a narrow, sharp peak even at a very low dye concentration (1×10^{-5} M), as long as the CMA concentration ($(1-5) \times 10^{-3}$ M) is high enough for the interactions. The fluorescence emission band of the J-aggregates is a sharp peak separated by only a few nanometers from the absorption band. In most cases, the spectral feature of the fluorescence reflects the absorption spectra except for the system comprising the high DS (=1.53) CMA. The CD spectra of the J-aggregates show typically a sharp doublet of positive and negative signs with large amplitude, depending on DS and pH. It is also noted that for a given DS of CMA, the CD intensity is in parallel with the fluorescence intensity.

(A) Absorption and Fluorescence Spectra of Cyanine-1 J-Aggregates. Solvent Effect on J-Aggregation of Cyanine-1 Dye. Cyanine-1 is less soluble in water than in MeOH and, in either case, exists predominantly as monomer ($\lambda_{max} = 425$ nm, $\epsilon = 7.4 \times 10^4$ cm^{-1} M^{-1} in MeOH) even at a relatively high concentration ($>1 \times 10^{-4}$ M). However, the discrete J-aggregation ($\lambda_{max} = 463$ nm) is observed upon addition of CMA (up to 3×10^{-4} M) to a dye solution (1×10^{-5} M), and the J-band is particularly pronounced in aqueous MeOH[11a] (Supporting Information S-1) by increasing the content up to 20 vol %, accompanied by a concomitant decrease of the monomer band as shown in Figure 1. Even in 20 vol % MeOH, when the dye concentration is equal to or higher than the CMA concentration, no J-aggregation is observable, regardless of DS of CMA. It is also noted that the shoulder at 399 nm, which appears always along with the monomer band in water as well as in a low MeOH solution (<30 vol %), diminishes with further increase in MeOH content in solution and disappears completely in a higher MeOH concentration ($\geq$50 vol %). This suggests that J-aggregation of the dye onto CMA is facilitated under the moderate solubility while it becomes destabilized in a high solubility condition; under the high solubility, the dye J-aggregates dissociate into the monomer,[9a] whereas under the low solubility, they tend to form aggregates (the shoulder at 399 nm), most likely dimeric H-aggregates.
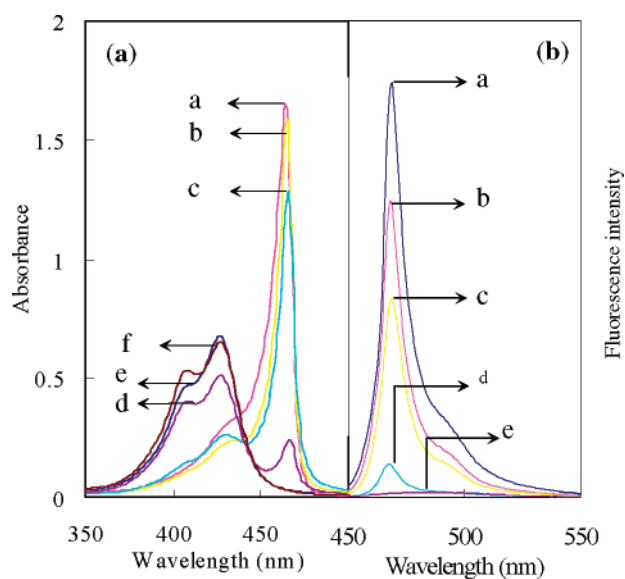

Pseudoisocyanine

PAA

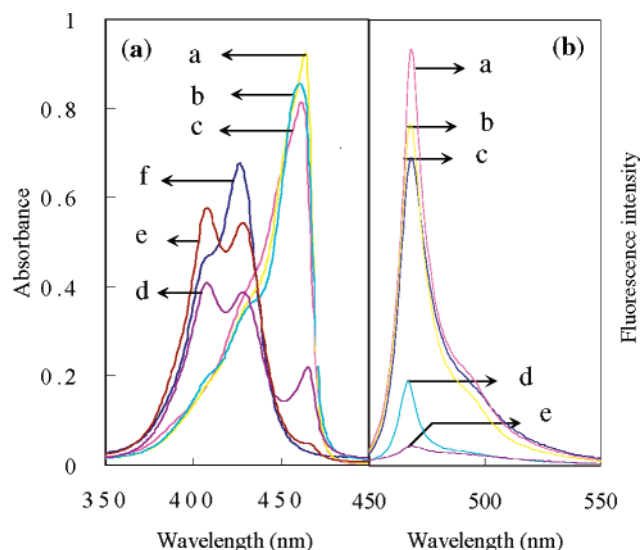(11) Supporting Information: (a) S-1; (b) S-2; and (c) S-3.

Figure 2. Concentration effect of CMA (DS = 0.06) on absorption (a) and fluorescence (ex. at 460 nm) (b) spectra of Cyanine-1 J-aggregates in water (pH = 6.8). [Cyanine-1] = 1×10^{-5} M, [CMA] = 1×10^{-4} M to 1×10^{-2} M; (a) 5×10^{-4} M, (b) 1×10^{-3} M, (c) 1×10^{-4} M, (d) 5×10^{-3} M, (e) 1×10^{-2} M, and (f) no CMA.

Figure 3. Concentration effect of CMA (DS = 0.37) on absorption (a) and fluorescence (ex. at 460 nm) (b) spectra of Cyanine-1 J-aggregates in water (pH = 7.0). [Cyanine-1] = 1×10^{-5} M, [CMA] = 1×10^{-4} to 1×10^{-2} M; (a) 1×10^{-4} M, (b) 5×10^{-4} M, (c) 1×10^{-3} M, (d) 5×10^{-3} M, (e) 1×10^{-2} M, and (f) no CMA.

Concentration Effect of CMA on the J-Aggregation. We have investigated the concentration effect of CMA (differing in DS) on the cyanine dye J-aggregation in water. As shown in Figures 2a, 3a, and 4a, as long as CMA concentration is kept high ($(1-5) \times 10^{-4}$ M), the J-aggregation occurs at a very low dye concentration (1×10^{-5} M). A similar J-aggregation behavior was reported[6] with pseudoisocyanine in the presence of poly(styrenesulfonic acid). For CMA with DS = 0.06 (Figure 2a) and DS = 1.53 (Figure 4a), the J-band absorption increases with increasing CMA concentration relative to the dye concentration (fixed), reaching a maximum at [CMA]/[dye] ≈ 10−50 (at pH = 6−7); however, in the latter the J-band is relatively broader. For CMA with DS = 0.37 (Figure 3a), the maximum

Figure 4. Concentration effect of CMA (DS = 1.53) on J-band absorption (a) and fluorescence (ex. at 420 nm) (b) spectra of Cyanine-1 J-aggregates in water (pH = 7.0). [Cyanine-1] = 5×10^{-5} M, [CMA] = 1×10^{-4} M to 1×10^{-2} M; (a) 5×10^{-4} M, (b) 1×10^{-3} M, (c) 1×10^{-4} M, (d) 5×10^{-3} M, (e) 1×10^{-2} M, and (f) no CMA.

is reached at lower [CMA]. This concentration dependence of the J-band maximum is precisely reflected in the fluorescence and CD intensities (vide infra). Furthermore, the J-band absorption increases significantly with increasing DS of CMA such that the highest J-band absorption is attained at DS = 0.25 (vide infra) but decreases gradually with further increase in the DS. It is also noted that the J-aggregation in the presence of a lower DS (0.06) CMA requires a relatively higher CMA concentration as compared to that required for a higher DS (0.37) CMA[11b] (Supporting Information S-2), for example. As a result, the total number of carboxylic groups present in the respective CMA concentrations (at their J-band maxima) becomes about the same. Again, regardless of the difference in the proximity of carboxylic groups in CMA chain, DS, the J-aggregation still requires an order of magnitude high CMA concentration. The variation in the carboxylics proximity may contribute differently to the size of the J-aggregates, but their self-assembly pattern seems to be identical as long as their DS of the CMA is relatively low. However, when DS of CMA is very high (DS = 1.53), the characteristic J-band shape as a narrow and sharp peak (fwhm: 10 nm) becomes broadened (fwhm: 26 nm) with a noticeable decrease in absorption (Figure 4a). Such a broadening of J-band extended toward the higher energy side and overlapped partly with the monomer band may indicate that the J-band has a higher energy component, which differs in the molecular packing.[9a] More specifically, this may be the consequence of disorientation in the dye assembly, such as head-to-head alignment between adjacent dye molecules.[12] The broadening in the absorption band of the J-aggregates is reflected in its fluorescence spectrum (vide infra). In addition, viewing that the J-band maximum requires a large excess CMA concentration such as [CMA]/[dye] ≥ 10, regardless of DS of CMA, while no J-aggregation occurs when the CMA concentration is either equal to or smaller than that of dye concentration,

(12) (a) Chowdhury, A.; Wachsmann-Hogiu, S.; Bangal, P. R.; Raheem, I.; Peteanu, L. A. *J. Phys. Chem. B* **2001**, *105*, 12196−12201. (b) *Circular Dichroism −Principle and Applications*, 2nd ed.; Berova, N., Nakanishi, K., Woody, R. W., Eds.; Wiley-VCH: New York, 2000; Chapter 12.

it is likely that the J-aggregates exist in a number of small domains along the CMA chain.

Cyanine J-aggregates templated to CMA exhibit a very strong fluorescence emission (λ_{em} = 470 nm), as shown in Figures 2b and 3b, and their fluorescence intensity depends strongly on the CMA concentration, following exactly the same trend in their absorption spectra, as long as DS of CMA is relatively small. By contrast, in the case of the high DS (=1.53) CMA, the fluorescence intensity of the J-aggregates is unexpectedly strong (Figure 4b), almost comparable to those in low DS counterparts, and, furthermore, their quantum yield is very high[13] (Φ_f = 0.43 in the CMA (DS =1.53), unlike in soluble clay (Φ_f = 0.08) and in aqueous MeOH (Φ_f = 0.004).[10e] This may be that the physical size of the J-aggregates is rather small, and the assembly structure is somewhat disoriented, but the J-aggregates are more densely distributed along the CMA chain. Although there is little known about fluorescence properties of cyanine J-aggregates[14] relative to the aggregate structures, the inconsistency between the large fluorescence emission and the unusually broad and low J-band absorption (Figure 4a) in the high DS (=1.53) CMA can be attributed to the presence of a substantial energy gap (Davydov splitting) in the excitonic coupling of two adjacent dye molecules, due to the disordering[10b,12b] in the J-aggregates. Whichever the case, the common feature of Cyanine-1 J-aggregation is that where the dye concentration is equal to or higher than the CMA concentration, no or negligible J-aggregation occurs. On the other hand, when CMA concentration is in a large excess (>500-fold) relative to dye concentration, the monomeric dye and dimeric or higher H-aggregates predominate.

pH Effect of CMA and PAA on the J-Aggregation. It can be understood that cyanine J-aggregation involves carboxylic groups of the CMA template. For a comparative study, we have investigated poly(acrylic acid), PAA, a common polyacid as template for the cyanine J-aggregation, focusing on the role of chain flexibility and the close proximity of carboxylic groups as opposed to CMA. The J-aggregation in PAA (at pH = 5.2) occurs at a much lower concentration relative to CMA and in a narrow concentration range[11c] (Supporting Information S-3); it occurs only in the range of [PAA]/[dye] = 5−10, but either below or above the concentration range, the J-aggregation occurs negligibly. At high PAA concentrations, in particular, such as [PAA]/[dye] > 100, dimeric or higher aggregates (λ_{max} = 400 nm) prevail, being assignable to H-aggregates due to the absence of fluorescence.[6b] These are the distinctive differences from the case of CMA. However, the J-band in PAA resembles one in the high DS (=1.53) CMA but is more intensified. The J-band is dominated by high-energy components whose broad absorption appears at λ_{max} = 450 (instead of at λ_{max} = 465 nm in CMA) with a marked decrease in the absorption intensity, as compared to that in the CMA at the same concentration. This can be explained based on the same reason mentioned for CMA of the high DS that the self-assembly (toward the J-aggregation) of cyanine dye undergoes disordering and/or disorientation by locally high competitive electrostatic forces, besides the chain flexibility of PAA. While the fluorescence emission (Φ_f =
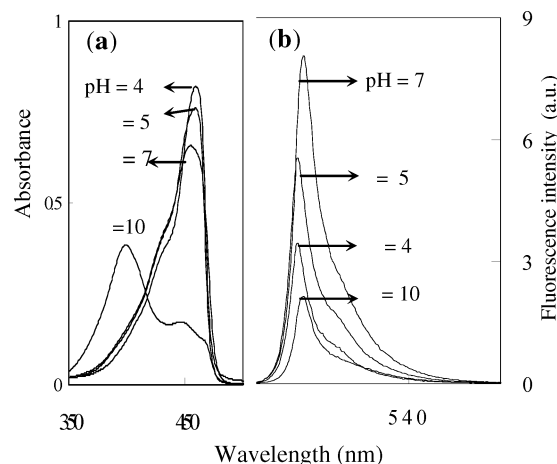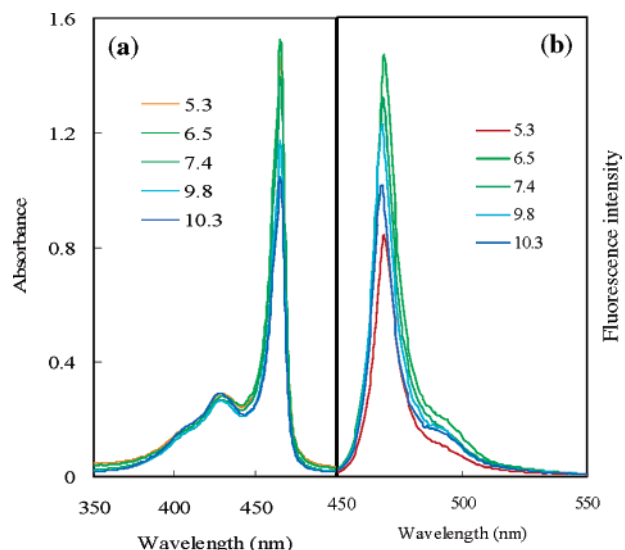

Figure 5. pH dependence of absorption (a) and fluorescence (b) spectra of Cyanine-1 J-aggregation in CMA (DS = 1.53) in water; [Dye] = 1 × 10^{-5} M, [CMA] = 5 × 10^{-4} M.

0.03)[13] of the J-aggregates in PAA is rather broad[11c] (Supporting Information S-3), the intensity is fairly strong, reminiscent of the J-aggregates with the high DS (=1.53) CMA. It is worth further noting that the absorption and fluorescence spectra of the J-aggregates in PAA are extremely sensitive to the local environment such that a relatively small change in the PAA concentration brings about a drastic shift of the J- to H-aggregates. More notably, when the pH (= 5.2) of the same PAA solution (1 × 10^{-4} M) is increased to >9, the J-band is completely disappeared and transformed almost all into a strong H-aggregates band even at the optimal J-aggregation condition [PAA]/[dye] =10.

In the present CMA system, the cyanine J-band maximum appears at [CMA]/[dye] = 10−50 ([dye] = 1 × 10^{-5} M), which is a significantly higher polymer concentration as compared to that of PAA (pH = 5.2), where the optimum ratio is 10. This difference may be attributable to the high proximity of carboxylates as well as chain flexibility (of PAA). Although the optimal concentration ratio varies somewhat depending on the pH and DS of CMA (vide infra), the maximum J-aggregation is attained always at a pH 5−7. Figure 5a and b shows pH dependence of absorption and fluorescence spectra of the J-aggregates in CMA of DS = 1.53, respectively, illustrating the maximum J-band absorption at pH around 5, while the largest fluorescence emission is at a pH around 7. However, there is a marked contrast in the J-aggregation dependence on high pH between the highest DS (=1.53) and the lowest DS (=0.06) CMAs; unlike in the former, in the latter, the J-band maximum appears at pH ≈ 6.5, and even at a high pH > 9, the J-aggregation prevails and the H-aggregation is not occurring (Figure 6a and b), revealing a strong fluorescence emission. This means that when CMA has a very low DS (where carboxylic functionalities are remotely separated from each other), the charge interruptions to the J-aggregates by nearby carboxylates are drastically diminished, particularly due to the chain rigidity of CMA. This could be the reason for the pH differences at their J-band maxima between the high DS (1.53) and the low DS (0.06) CMA; in the former, the J-aggregation is more stable in the acidic side (at pH ≈ 5) than in the neutral state that favors the latter. In view that the J-aggregation occurs dominantly at or near neutral pH, it can be safely said that the J-aggregation is not simply driven by the electrostatic force

(13) The quantum yield (Φ_f = 0.430) of the J-aggregation in CMA (1.53 DS) was determined at pH 7 using fluorescein as the standard. The quantum yields for the J-aggregation in CMA-free solution (Φ_f = 0.002) and in PAA (Φ_f = 0.03 at pH 5) were measured under the same condition.

(14) (a) Horng, M.-L.; Quitevis, E. L. *J. Phys. Chem.* **1993**, *97*, 12408−12415. (b) Moll, J.; Daehne, S. *J. Chem. Phys.* **1995**, *102*, 6362−6370.
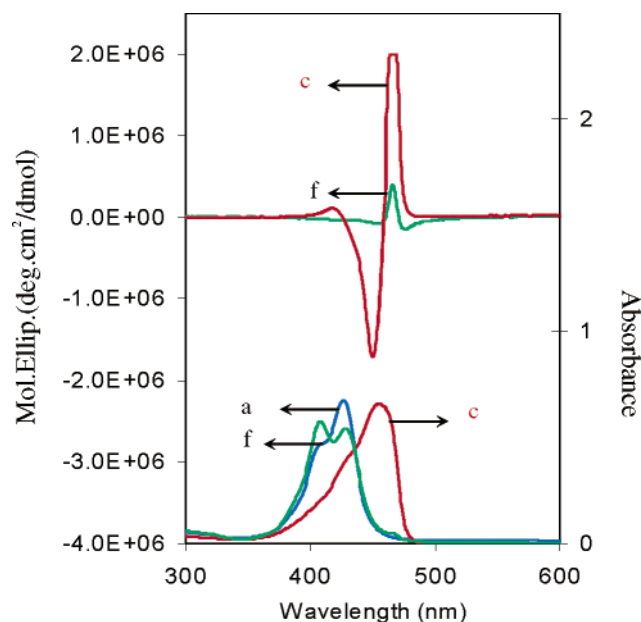
Figure 6. pH dependence of absorption (a) and fluorescence (ex. 420 nm) (b) spectra of Cyanine-1 J-aggregation in CMA (0.06 DS) solution; [CMA (0.06 DS)] $= 5 \times 10^{-4}$ M and [Cyanine-1] $= 1 \times 10^{-5}$ M.
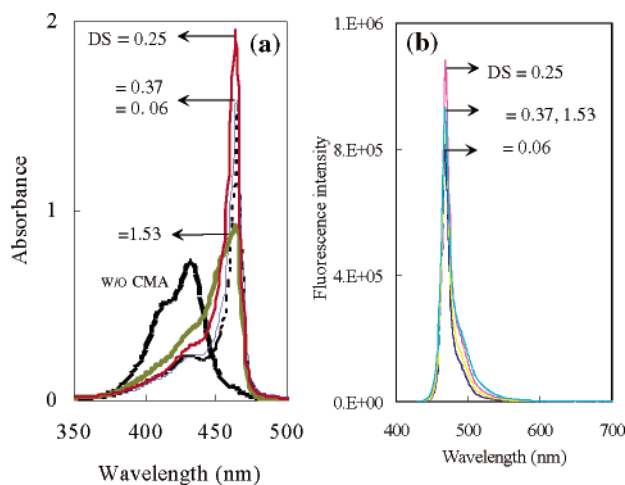
Figure 7. DS effect of CMA on J-band absorption (a) and fluorescence intensity (b) of Cyanine-1 J-aggregates in water (pH 6−7); [Cyanine-1] $= 1 \times 10^{-5}$ M and [CMA] $= 5 \times 10^{-4}$ M.

Figure 8. Dependence of CD intensity (and absorption) of cyanine J-aggregates ($\lambda_{max} = 465$ nm) on CMA concentration: [Cyanine-1] $= 1 \times 10^{-5}$ M, and [CMA (1.53 DS)] $= 0$ (a); 5×10^{-4} M (c); 1×10^{-2} M (f).

between polyacids and the cationic cyanine dye but is likely to involve ion−dipole interaction and/or H-bonding.[10b]

DS Effect of CMA on J-Aggregation. As shown in Figure 7a, absorption of J-aggregates increases with increasing DS up to the DS $= 0.25$ and decreases gradually with a further increase in DS of CMA under the fixed CMA concentration (5×10^{-4} M) and at pH $= 6−7$. The fluorescence intensity (Figure 7b) of the J-aggregates follows closely the trend in the absorption, except for the case of the high DS (1.53) CMA. As described above, while the J-band absorption in the high DS CMA is unexpectedly low and unusually broadened as compared to those in low DS CMA, its fluorescence intensity is nearly comparable to those of the low DS counterparts. Such anomaly in the J-aggregation in the presence of CMA of the high DS has a resemblance to the behavior in PAA. However, the broadening of the J-band is far more pronounced in PAA than in the CMA, extending to the monomer band. Such a common feature in these polyacids is likely to result from the presence of the high carboxylic density along the polymer backbone such that even at an optimal pH (5−7), the J-aggregation undergoes significant

perturbation in the self-ordering by functional intervention of the neighboring carboxylics. Therefore, as far as the cyanine J-aggregation is concerned, such a high-density polyacid is not the best host template, and for CMA as template the DS is not an important parameter, unless it induces unusual conformational changes through interactional complementarity between the associating partners.

(B) Super-Helix Formation Induced by the J-Aggregation in CMA. Circular Dichroism (CD) of Cyanine J-Aggregates. Cyanine-1 is achiral, and its J-aggregates formed by itself (without CMA) or in the presence of a common polyacid exhibit no CD. Surprisingly, the cyanine J-aggregates formed onto a nonhelical CMA demonstrate a very stable[15] and well-resolved CD. The induced optical activity splits the absorption band of the J-aggregates into two intense CD peaks of opposite sign (Figures 8−10), changing from positive to negative Cotton effect precisely at the absorption maximum (indicative of a right-handed helix).[12b] As such, the observed CD indicates the result of the CMA-bound cyanine J-aggregation, and the J-aggregation is dependent on the CMA concentration (Figures 2−4) and, therefore, the CD intensity (of the J-aggregates) is expected to follow the same trend of dependency (Figure 4) on the CMA concentration. This is clearly demonstrated by Figure 8 as such that the largest CD intensity is attained at the concentration where the largest J-band maximum occurs. In contrast, even in the presence of CMA, the CD was not observed from the CMA-bound dye monomer (occurring in a high CMA concentration $>1 \times 10^{-2}$ M) and H-aggregates (occurring in CMA at a pH > 9). Furthermore, the CD intensity is sensitive to pH and increases with increasing pH up to around neutral, then decreases with further increasing pH > 9 (Figure 9). As described above, the fluorescence intensity ($\Phi_f = 0.43$)[13] of the J-aggregates in

(15) There was no change observed in the CD spectra of the Cyanine-1 J-aggregates onto CMA in water, at room temperature for several months. Also, when the pH of the sample solution was raised from 7 to 9, the CD spectra remain almost unchanged for at least several weeks. Such helical stability is associated with the strongly intertwining cooperativity between the dye and CMA, which protects against the solvent.[16]
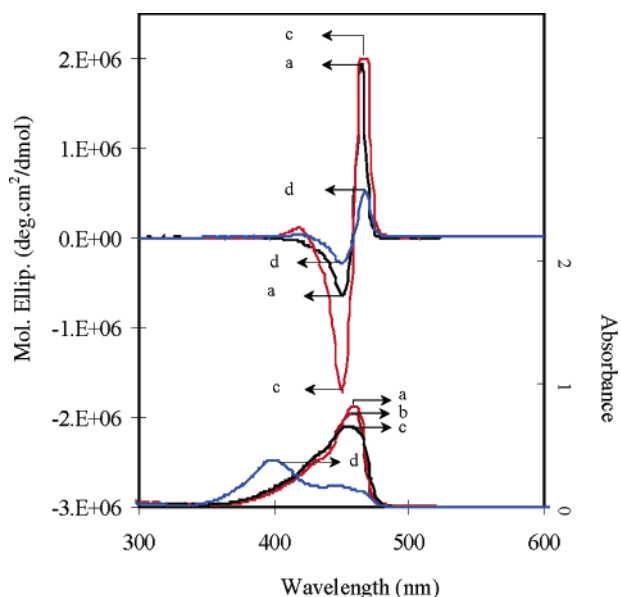
Figure 9. pH dependence of the CD intensity and the J-band maximum of Cyanine-1 J-aggregates in CMA (DS = 1.53) in water. [Cyanine-1] = 1 × 10^{-5} M, [CMA (DS = 1.53)] = 5 × 10^{-4} M; pH: (a) 4.2; (b) 5.3; (c) 7.0; (d) 10.2.
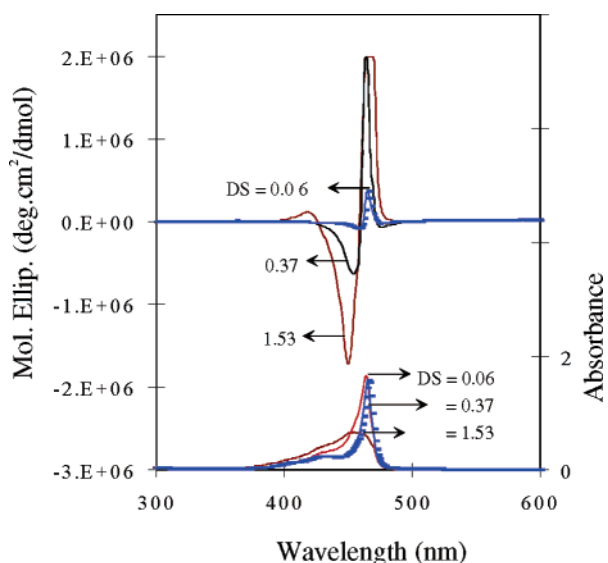
Figure 10. DS effect of CMA on the CD intensity and the J-band maximum of Cyanine-1 J-aggregates in water (pH = 6.8−7.0); [Cyanine-1] = 1 × 10^{-5} M and [CMA] = 5 × 10^{-4} M.

CMA (DS = 1.53) is strongly pH-dependent, being the largest at neutral pH (Figure 5b). Thus, it is worth noting that the CD intensity of the J-aggregates is closely related to their fluorescence intensity. The CD intensity of the J-aggregates is also strongly affected by DS of CMA such that it increases with increasing DS (Figure 10); an exceptionally large CD signal $(2.8 \times 10^6$ (deg cm^2/dmol)) was observed with the highest DS (=1.53) of CMA at neutral pH, which is 1 order of magnitude larger than that with the lowest DS (=0.06) CMA. Such a high CD intensity is 2 orders of magnitude larger than the induced CDs observed commonly for optically active dye-bound polymer systems.[8]

Because without CMA the cyanine J-aggregates reveal no induced CD (vide supra), the induced CD can be attributed due to the CMA. This is reminiscent of the induced CD of porphyrin

J-aggregates templated by α-helical (at pH < 6) poly(L-glutamic acid).[7,17] The question is how the helical transition of CMA (p$K_a \approx 4.9$) takes place from a random-coil state. Considering the fact that such a high magnitude of the induced CD is observable only when bound dyes are heavily twisted by the chiral host,[18] along with our observation that the CD intensity increases with increasing DS of CMA, it is most likely that the higher DS (of CMA) exerts more twisting power onto the J-aggregates and, in turn, to themselves. The cyanine J-aggregates with the high DS (=1.53) CMA are partly disordered (vide supra), but the large carboxylic density along the CMA chain may induce enhanced complementarity with the bound dyes.

Because the cyanine J-aggregation takes place through the binding of the dye to CMA and subsequent self-organization, the cyanine J-aggregates undergo steric influence of CMA monomer unit, glucose residue. CMA is a macroscopically nonchiral template, but the local asymmetric environment on glucose unit can execute steric control on the orientation of dye molecules in the assembly process (of the J-aggregates) such that a strong intermolecular twisting force develops between the interacting partners. This results in the macroscopic chirality in the J-aggregates and in CMA itself as well, forming an unusually stable[15] super-helix. As such, the strong, intense fluorescence and the extremely large and stable induced-CD of the J-aggregates are the consequence of the rigidity developed in the super-helix. This is contributed at least partly by the charge screening effect[16] of the bound J-aggregates, which reduces the impact of the repulsive forces between carboxylates on CMA. With such cooperative interactions, the super-helix becomes strongly resistant to unfolding thermally as well as by solvents.

The present cyanine dye is assumed to be somewhat twisted around the central methine group as in pseudoisocyanine dye.[6a] One can argue the possibility of spontaneous generation of optical activity in the J-aggregates bound to a polymer, not specifically with CMA. However, the J-aggregates with PAA, for example, show no chirality.

(C) AFM Image of Cyanine J-Aggregates/CMA Super-Helix. The helical transformation of a random-coil CMA in association with the cyanine dye J-aggregation was further confirmed by atomic force microscopy (AFM) imaging. Figure 11 shows AFM images of drop-cast solutions comprising the cyanine dye J-aggregates (A) in the presence of (1.53 DS) CMA, the CMA alone (B), and the dye alone (C) on a flat hydroxylated Si (001) surface. We have not observed any surface features when the CMA alone solution was deposited, and we only observed a textured surface when the dye alone solution was deposited. When the J-aggregates-forming dye/CMA mixture solution was deposited, we observed the formation of strand-like structures shown in (A). Such multiple structures give images of single, double, and multiple helices, providing a vague but periodic structure on the rigid-rod shape. A high-resolution

(16) Zanuy, D.; Csanovas, J.; Aleman, C. *J. Am. Chem. Soc.* **2004**, *126*, 704−705.
(17) (a) Bellacchio, E.; Lauceri, R.; Gurrieri, S.; Scolaro, L. M.; Romeo, A.; Purrello, R. *J. Am. Chem. Soc.* **1998**, *120*, 12353−12354. (b) Purrello, R.; Raudino, A.; Scolaro, L. M.; Bellachio, A. L. E.; Lauceri, R. *J. Phys. Chem. B* **2000**, *104*, 10900−10908.
(18) (a) Nakashima, N.; Ando, R.; Muramatsu, T.; Kunitake, T. *Langmuir* **1994**, *10*, 232−234. (b) Berthier, D.; Buffeteau, T.; Legar, J.-M.; Oda, R.; Huc, I. *J. Am. Chem. Soc.* **2002**, *124*, 13486−13494 and references therein.
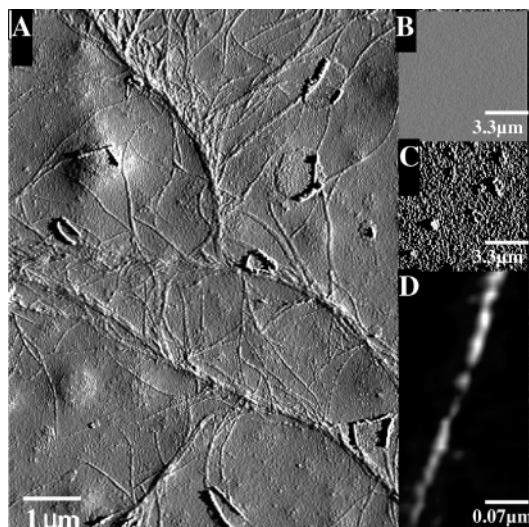
Figure 11. AFM images of drop-cast solutions (on a hydroxylated Si surface) from the following: (A) the J-aggregates-forming cyanine dye/CMA (DS = 1.53) mixture, (B) CMA alone, and (C) Cyanine-1 dye alone. (D) A high-resolution image of a single strand.

image of a single strand is shown in (D). Because the width of the strand is at the limit of the resolution of the AFM, the strands are probably a single intertwined super-helix formed between a random-coil CMA and bound J-aggregates of the achiral cyanine dye. The larger image (A) implies that a number of the strands intertwine to form a larger threadlike structure. It is difficult to observe a free single strand as all strands attach at one end to a large structure.

Polysaccharides have been known[19] to adopt a double or triple helix in the solid-state but are often present as aggregates. Such multiple helices, however, do not necessarily reflect their presence in solution. Most recently, an AFM study[20] developed an enhanced image for amylose as a single helix free of aggregation by making amylose as an inclusion complex with iodine or a surfactant. This means that the helical images of amylose are clearly noted when amylose helix is rigidified by inclusion, while, if not, aggregates are noted. This seems to be in agreement with our observations of the rigid super-helix.

Conclusion and Perspectives

In conclusion, the J-aggregation of Cyanine-1 (1×10^{-5} M) occurs only in a locally high concentration CMA (($10-50) \times 10^{-5}$ M) with an optimum range of [CMA]/[dye] = $10-50$; beyond that, however, the J-aggregates are dissociated to monomeric and/or converted to H-aggregates. The J-aggregation is also dependent strongly on pH and DS of CMA, producing

an optimum by increasing the pH from acidic to neutral and also by increasing the DS (of CMA), while a too high DS causes a disordering/disorientation in the J-aggregates. It was found that the J-aggregation of the cyanine dye onto CMA results in the formation of a super-helix. This is confirmed by an extraordinarily large, induced CD observed and also by their AFM images of twisted strands. The CD intensity (of the J-aggregates) depends also strongly on CMA concentration, pH, and DS (of CMA), following exactly the same trend as does the J-aggregation. The CD intensity and the fluorescence intensity of the J-aggregates, in particular, exhibit the same mode of dependency on pH, suggesting that the enhancement in the helical twist (CD intensity) and in the rigidity (fluorescence intensity) of the J-aggregates is the consequence of the super-helix formation. The AFM image reveals also that the cyanine J-aggregation has the rigid structure formation but either amylose alone or dye alone has no features.

The unusually stable CD of the J-aggregates over several months in water at room temperature suggests that the cyanine J-aggregates/CMA super-helix have an extraordinarily tight/rigid cooperative binding, which makes the helix strongly resistant to unfolding/dissociating by the solvent. It is easily understood that J-aggregates in such a form of super-helix are far more stable than those commonly forming J-aggregates in a polyacid. Furthermore, their high quantum efficiency (in water) coupled with a long fluorescence lifetime anticipated from the rigidity are very attractive photophysical properties for NLO and photonic wire materials. It is particularly interesting to note that regardless of the variation in DS, the random-coil CMA plays a role as chiral template for the cyanine J-aggregation. Even with the lowest DS (0.06), the resulting J-aggregates exhibit the same properties as those expressed by the J-aggregates with higher DS counterparts, although the intensity of the former is slightly less than that of the latter. From the broader application perspectives, the J-aggregates formed in the presence of CMA of the lowest DS (0.06) are particularly interesting because the low DS CMA has capability of a helical inclusion. This was indicated by our recent experiments. This opens a new potential for the development of uniquely new molecular devices such as for sensing devices, photo/electro-diodes, and an artificial photosynthetic reaction center, which are based on photo/electronic coupling across the helix.

Supporting Information Available: Experimental details and extended spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) McIntire, T. M.; Brant, D. A. *Bioplymers* **1997**, *42*, 133−146.
(20) Gunning, A. T.; Giardina, T. P.; Faulds, C. B.; Juge, N.; Ring, S. G.; Williamson, G.; Morris, V. J. *Carbohydr. Polym.* **2003**, *51*, 177−182.