THE JOURNAL OF PHYSICAL CHEMISTRY B

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Cyanine-Based J-Aggregates as a Chirality-Sensing Supramolecular System

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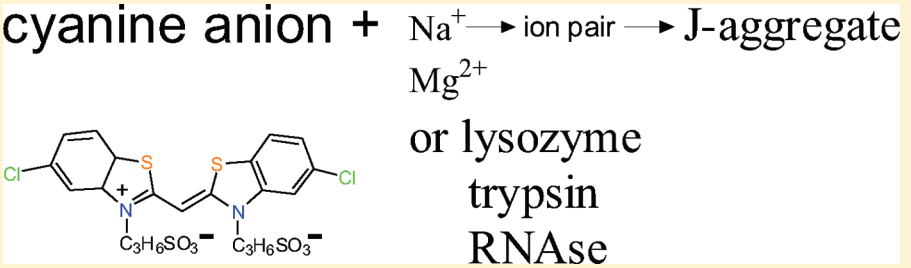
ABSTRACT:



J-aggregates are formed for 3,3′-disulfopropyl-5,5′-dichlorothiacyanine (Tc) and 3,3′-disulfobutyl-5,5′-diphenyl-9-ethyloxacarbocyanine (Oc) in aqueous solution in the presence of NaCl, $Mg(NO_3)_2$, D/L-tartaric acids, asparagine, proline, DNA, and proteins, such as lysozyme, trypsin, RNase, and gelatin. J-aggregates, which are formed in the presence of chiral additives, are optically active and characterized by sigmoidal kinetics with half-times of 10−1000 s, resonance fluorescence, and large CD amplitudes being up to 2° for Tc. Generally, the induced CD signals of the J-aggregates of both dyes are bisignate and the sign corresponds to that of the additive. The transfer of chirality information occurs in the course of the J-aggregation.

INTRODUCTION

J-aggregation was originally discovered by Jelley and Scheibe.[1] A frequently studied dye is pseudocyanine (PIC, 1,1′-diethyl-2,2′-cyanine).[1−6] However, relatively large PIC concentrations of 0.2−2 mM are required, whereas for other cyanine dyes J-aggregates are formed at much lower concentrations upon addition of metal ions.[6−12] J-aggregation which takes place for cyanine dyes in aqueous solution in the absence of additives is commonly denoted as self-aggregation.[5,6] A J-aggregate has been reported for 3,3′-disulfopropyl-5,5′-dichlorothiacyanine (Tc) under specific conditions[11−15] as well as for 3,3′-disulfobutyl-5,5′-diphenyl-9-ethyloxacarbocyanine (Oc). The specificity of thiacarbocyanine dyes is that dimers are building blocks of J-aggregation, in contrast to imidacarbocyanine and oxacarbocyanine, where monomers are building blocks.[10,16−22] Formation of J-aggregates can be induced by a variety of macromolecules, such as DNA, carboxymethyl amylose, polyelectrolytes, gelatin, albumins, and proteins,[23−33] as well as upon adoption to a Langmuir film.[34] A further specificity of certain J-aggregates is their optical activity which is commonly observed by circular dichroism (CD) spectroscopy.[2] This chirality takes place in the presence of an appropriate template or chiral additives. However, for J-aggregates of certain dyes, CD spectra have also been found in the absence of a template or any chiral auxiliaries.[2,3,10,16,18] Convincing reasons were not found as of yet.

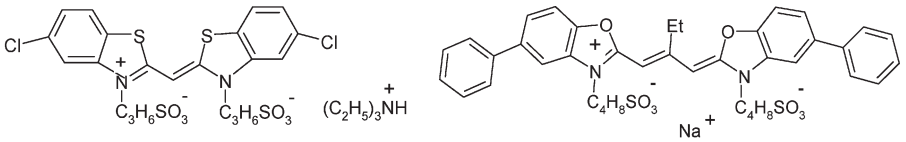
In recent years, chirality as a fundamental phenomenon has attracted much attention in some practical applications such as catalysis,[35] nonlinear optics,[36] polymer and material science,[37] molecular devices,[38] and molecular and chiral recognition.[39] A proposal to design a specific receptor which allows "read-out" of chiral information is very important. A supramolecular system appears to be the most fruitful chirality-sensing system.[40] For example, porphyrin-based supramolecular systems are able to sense different types of chirality: a point-chirality,[41] conformational,[42] and macroenvironmental chirality.[43] J-aggregates of cyanine dyes with versatile supramolecular structure are expected to serve as a chirality-sensing system. We have demonstrated that J-aggregates of anionic alkyl meso-thiacarbocyanines are able to "read-out" conformational chirality of a secondary structure of certain proteins.[26]

Chiroptical properties of J-aggregates of benzothiazole-derived tricationic dicarbocyanine dyes reflect a helical structure of DNA.[30] J-aggregates of Tc onto carboxymethyl amylose result in the formation of the super helix which produces an extraordinarily large induced CD signal.[32] Point-chirality sensing has been shown for J-aggregates of 3,3′-bis(3-carboxypropyl)-5,5′,6,6′-tetrachloro-1,1′-dioctylbenzimidacarbocyanine when long-chained chiral alcohols are incorporated into J-aggregates by hydrophobic forces.[20]

In this paper, the spectral absorption and CD properties of the J-aggregate of Tc and Oc were studied in aqueous solution in the presence of different chiral additives, namely, D/L-tartaric acids, amino acids, DNA, and proteins. The principal result of this work

Received: December 21, 2010
Revised: February 7, 2011
Published: March 15, 2011

Chart 1



Tc Oc

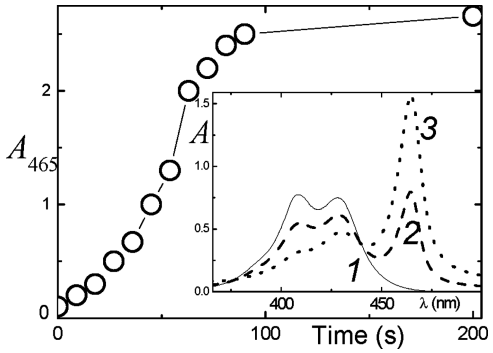


Figure 1. Time dependence of A_{465} of Tc (10 μM) in the presence of 1 mM $Mg(NO_3)_2$. Inset: absorption spectra at 0, 50, and 300 s after mixing, *1*−*3*, respectively.

is that J-aggregates of both dyes formed in the presence of chiral additives are able to sense their chirality. This has made it possible to use J-aggregates as a sensor of point-chirality and conformation chirality.

EXPERIMENTAL SECTION

Dyes Tc and Oc, dimethyl sulfoxide (DMSO), proteins, and the other additives or salts were used as received. Double-stranded calf thymus DNA was from Merck; the concentration was determined from absorption using $\varepsilon_{260} = 1.3 \times 10^4\ M^{-1}\ cm^{-1}$ expressed in numbers of base pairs. The UV−vis absorption spectra were recorded on a diode array spectrophotometer (HP, 8453). A spectrofluorimeter (Cary, Eclipse) was employed to measure the fluorescence spectra. The CD spectra were recorded by a Jasco J-715 spectrometer. The stock solution of dyes in DMSO was buffer-free and mixed with water so that the DMSO concentration in a mixture was mostly 0.5 vol % (0.04 M). Water was from a Millipore (milli Q) system. The pH was typically 6 and shifted by addition of protons ($HClO_4$) or hydroxyl ions (NaOH). The molar absorption coefficient of monomeric Tc[13] and Oc in methanol solution is $\varepsilon_{430} = 8.3 \times 10^4\ M^{-1}\ cm^{-1}$ and $\varepsilon_{500} = 9.7 \times 10^4\ M^{-1}\ cm^{-1}$, respectively. The results refer to air saturation and 24 °C unless indicated otherwise. The presence or absence of oxygen did not have any effect.

RESULTS AND DISCUSSION

Absorption and Fluorescence Properties in the Presence of Metal Ions. The absorption spectrum of Tc in aqueous solution at pH 6 contains the dimer and monomer bands with maxima at λ_D = 408 nm and λ_M = 428 nm, respectively. A new band at λ_J = 465 nm appears upon addition of NaCl (not shown) or $Mg(NO_3)_2$ (Figure 1). The salt-induced 465 nm peak is denoted here as a J-aggregate. The increase of the absorbance of

Table 1. Kinetic Data upon Formation of Metal-Ion-Induced J-Aggregates of Tc[a]

additive	[salt] (mM)	$t_{1/2}$ (s)	$(dA_J/dt)_{max}$ (s^{-1})	A_J/A_M
NaCl	20	>500		<0.2
	40	30	0.03	1
	80	50		1
$Mg(NO_3)_2$	1	30	0.03	2
	3	80		1

[a] Using [Tc] = 12 μM and pH 6.

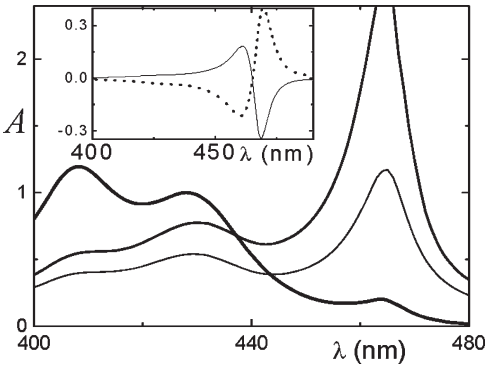


Figure 2. Absorption spectra of Tc (12 μM) in aqueous solution in the presence of 0.1 M D-tartaric acid at 0, 50, and 300 s after mixing. Inset: CD spectra in the presence of 0.1 M D- (dotted) and L-tartaric acid (full) after 300 s.

the J-band at 465 nm (A_J) occurs at the expense of the D- and M-bands. Evidence in favor of the formation of J-aggregates follows from the observation of resonance fluorescence centered at 470 nm and resonance light scattering (not shown). The fluorescence excitation spectrum of the J-aggregate coincides with the absorption band.

The kinetics for formation of the J-aggregate of Tc are in most cases of sigmoidal type. The time courses of conversion of monomer and dimer to the J-aggregate can be defined by a characteristic time t_J (time for 50% of maximum conversion). This time course is reminiscent of that of other cyanine dyes in aqueous solution.[10] The rate, i.e., the maximum derivative $(dA_J/dt)_{max}$, is a second method of characterization of the kinetics. For Tc and the two metal ions, $(dA_J/dt)_{max} = 0.03\ s^{-1}$ (Table 1), similar to other cyanine dyes.[7,25] Thus, Tc demonstrates the ability to form J-aggregates analogously to that of thiacarbocyanines and one might suggest that the basic unit of the J-aggregate is a dimer rather than a monomer.[8] Several absorption and fluorescence properties of Oc in the presence of metal ions have been presented elsewhere.[10]

dx.doi.org/10.1021/jp1121118 |J. Phys. Chem. B 2011, 115, 3379–3384

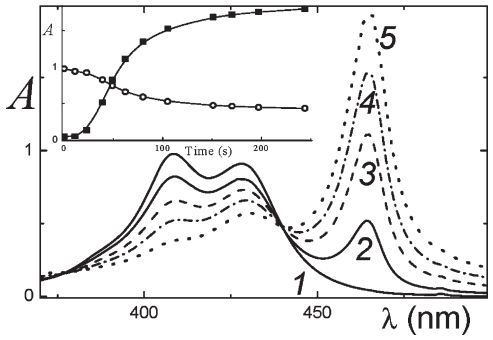


Figure 3. Absorption spectra of Tc (12 μM) in the presence of 2 μM lysozyme at pH 5.5 at 0, 50, 65, 100, and 250 s after mixing, *1*−*5*, respectively. Inset: time dependences of A_{408} (circles) and A_{465} (squares).

Table 2. Kinetic Data upon Formation of Lysozyme-Induced J-Aggregates of Tc[a]

[protein] (μM)	$t_{1/2}$ (s)	$(dA_J/dt)_{max}$ (s^{-1})	A_J/A_M
0.1	140	0.0006	0.20
0.4	110	0.003	0.7
0.5	120	0.0065 (0.0036)[b]	3
1	95	0.009	2
2	65	0.011	3
4	80	0.0082	1.5

[a] Using [Tc] = 12 μM and pH 6. [b] Heated for 30 min at 56 °C.

Point-Chirality Sensing. Formation of J-aggregates also occurs for Tc in the presence of D/L-tartaric acid (Figure 2). The absorption spectra are identical for the D and L forms, i.e., λ_J = 465 nm. In contrast to the conventional visible absorption spectra, the induced CD spectra of the J-aggregates are mirror images (Figure 2, inset) and the handedness of the J-aggregates corresponds to that of the added tartaric acid. Thus, the chiralities of tartaric acid and the Tc-induced J-aggregate are the same. Similar results have been obtained for Oc.[10] It is noteworthy that tartaric acid at a concentration of 0.1 M results in the decreasing of pH up to 1.5. Under these conditions, the tartaric acid is present in neutral, mono-, and doubly deprotonated forms and the concentration of those is much higher than that of Tc. This provides a basis to suggest that tartaric acid is able to interact with Tc in a supramolecular manner, namely, that the deprotonated form is involved in the electrostatic interaction with the delocalized positive charge of the chromophore. However, one cannot exclude that tartaric acid in the neutral form interacts with the SO_3^- group of the dye via the formation of H-bonds. The data obtained implies that J-aggregates as a supramolecular system might be used for recognition of the point-chirality. This conclusion is confirmed by the results obtained for the J-aggregates of Oc with amino acids. A small negative couplet was formed in the J-aggregate of Oc in the presence of unprotected asparagine or proline. We propose that the electrostatic interaction between amino acids and dye molecules results in the transfer of chiral information to the supramolecular J-aggregates.

Absorption and Fluorescence Properties of Tc in the Presence of Proteins. The formation of J-aggregates for both dyes was studied in the presence of lysozyme, trypsin, RNase, gelatin, and bovine serum albumin (BSA). In particular, J-aggregation was found

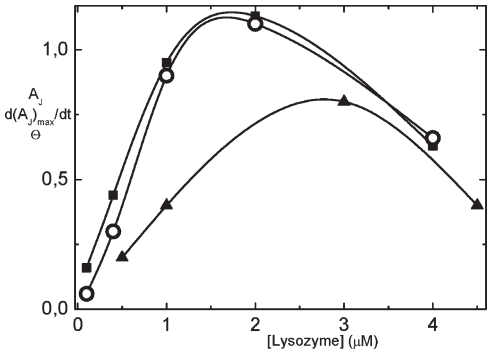


Figure 4. Dependencies of $(dA_J/dt)_{max}$ (in $s^{-1} \times 100$, circles), A_J^{max} (squares), and ellipticity (in degree × 2, triangles) of Tc (12 μM) at pH 6 on the lysozyme concentration.

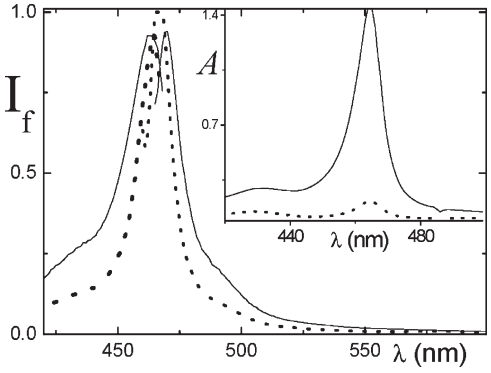


Figure 5. Fluorescence excitation (left, λ_{em} = 480 nm) and emission (right, λ_{ex} = 450 nm) spectra of Tc in the presence of 1 μM lysozyme; dotted lines refer to 9-fold dilution. Inset: corresponding absorption spectra.

for all proteins examined except for BSA. The kinetics of formation of the J-aggregates are in most cases of sigmoidal type. Examples of absorption spectra (Figure 3) and the kinetics of J-aggregation (Figure 3, inset) are shown for Tc in the presence of lysozyme. For Tc and lysozyme, characteristic times of t_J = 65−140 s and $(dA_J/dt)_{max}$ = 0.0006−0.01 s^{-1} were measured (Table 2). These values are similar to those with other cyanine dyes.[7,25,26] The spectroscopic and kinetic results are sensitive to the concentrations of the protein ([P]) and the dye. If [Tc] is below 5 μM, no J-aggregate was observed for [P] = 0.1−5 μM. If on the other hand [Tc] is 25 μM or larger, self-aggregation occurs. This strongly limits the regime of dye concentrations, which was kept at [Tc] = 10−20 μM (except for fluorescence). In the concentration range of 10−20 μM, the rate $(dA_J/dt)_{max}$ depends linearly on the concentration of Tc. The yield (A_J^{max}) and rate $(dA_J/dt)_{max}$ of J-aggregates both increase with the protein concentration, approach a maximum, and then decrease. The results obtained for lysozyme are presented in Figure 4. The position of absorption maxima of J-aggregates was varied in the range of 464−466 nm in the course of J-aggregation for different proteins.

In the presence of proteins, a strong fluorescence signal with a maximum at 470 nm was observed which is assigned to the J-aggregate (Figure 5). Moreover, the fluorescence excitation spectrum of the J-aggregate coincides with the absorption band.

Chiroptical Properties. Strong CD signals were observed for Tc in aqueous solution in the presence of lysozyme, trypsin,

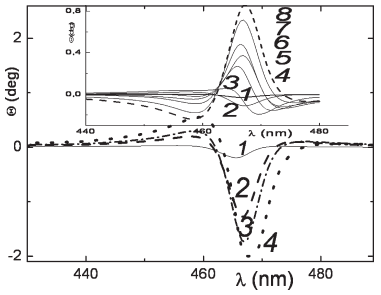


Figure 6. Time dependence of the CD spectra of Tc (12 μM) at pH 6 in the presence of 1 μM trypsin at 10, 60, 120, and 600 s, *1*−*4*, respectively. Inset: spectra at 0, 60, 120, 180, 240, 360, and 1200 s and 1.5 h, *1*−*8*, respectively.

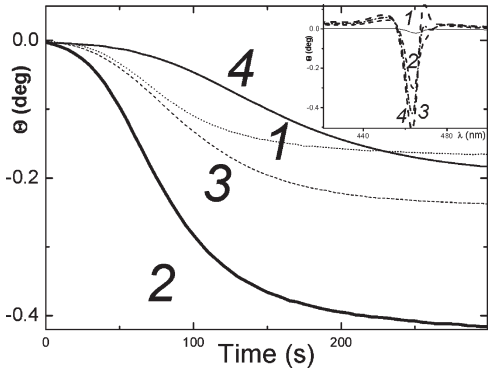


Figure 7. Time dependence of the CD signal at 465 nm of Tc (12 μM) at pH 6 in the presence of 4.4, 3.0, 2.2, and 1.5 μM lysozyme (*1*−*4*, respectively). Inset: spectra with 3 μM lysozyme at 10, 90, 300, and 2000 s, *1*−*4*, respectively.

Table 3. CD Signals upon Formation of J-Aggregates of Tc[a]

protein	[protein] (μM)	Θ (deg)	$t_{1/2}$ (s)
lysozyme	0.5	−0.1	200
	1.0	−0.2	160
	3.0	−0.4	100
	4.5	−0.2	90
RNase	1	−0.6	
trypsin	1	−0.2	

[a] Using [Tc] = 12 μM and pH 6.

RNase, and gelatin. Examples of the spectra and kinetics with trypsin, lysozyme, and RNase are shown in Figures 6−8, respectively. The amplitude of the ellipticity signal (Θ) strongly grows with time in a similar way as the A_J signal and reaches values of 0.1−2° which is much higher than those found for alkyl mesothiacarbocyanine.[26] The amplitude of Θ also depends on the protein concentration following exactly as the A_J does (Figure 4). In the first step of J-aggregation, the CD signal appears to be biphasic. After J-aggregation was completed, the signals become in some cases triphasic and the position of the major band is close to λ_J = 465 nm. The data of Θ are compiled in Table 3. In contrast, the negative bisignate CD signal of Oc and its 3,3′-bis[sulfopropyl] analogue in the presence of lysozyme is smaller and does not change with time (Figure 9). In the presence of gelatin, both dyes and the 3,3-bis[sulfopropyl]

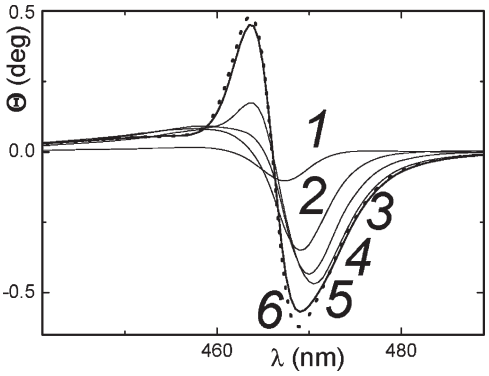


Figure 8. Time dependence of the CD spectra of Tc (12 μM) at pH 6 in the presence of 1 μM RNase at 10, 60, 120, 240, 600, and 1200 s, *1*−*6*, respectively.

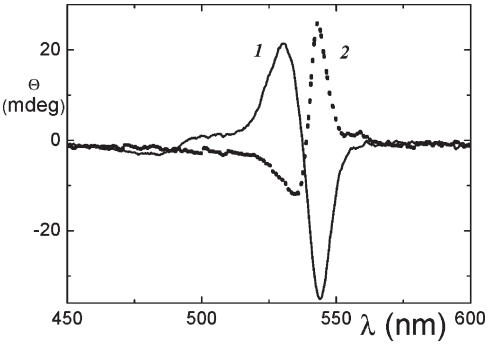


Figure 9. CD spectra of Oc (7 μM) at pH 6 in the presence of 1.5 μM lysozyme (*1*) and 0.01 wt % gelatin (*2*).

analogue of Oc show positive bisignate CD signals. Generally, the CD signals are bisignate, arising from excitonic interaction between dye molecules in the J-aggregate, and the sign of the induced CD signal corresponds to that of the secondary structure elements of proteins.

Temperature and pH Dependencies. A heating of the lysozyme solution (0.5 μM, 56 °C, 30 min) with the following cooling results in diminution of the protein CD signal at 300−220 nm (not shown). This points to a destruction of the chiral secondary structure of a protein. The latter is reflected on the efficiency of J-aggregation. J-aggregates of Tc formed in the presence of a temperature treated lysozyme solution show a decrease of A_J^{max} from 0.85 to 0.5 as well as two-folded diminution of $(dA_J/dt)_{max}$ (Table 2).

A variation of the pH value of the Tc/protein system results in changes of the yield A_J^{max}. For trypsin (2 μM), the value of A_J^{max} decreases down to 2.9, 1.6, and 0 for pH 2.2, 4.3, and 8.5, respectively. The influence of a base on the A_J value is depicted in Figure 10. Addition of NaOH to Tc/lysozyme leads to an increase of pH to 9.2 and results in neutralization of the positive charges of asparagine and lysine residues. This brings about a destruction of the J-aggregate. The pH dependence implies that the interaction between the anionic dye and a protein is due to Coulombic attractive forces with positively charged amino acid residues involved. It should be noted that the change of pH from 5.5 to 9.2 does not influence the CD spectra of lysozyme itself. This might point to the relative stability of the secondary structure of the protein molecule at this pH range. The time

dependence of A_J^{max} is described by two exponents with rate constants of 4×10^{-2} and 5×10^{-3} s^{-1}. Two components in the decay kinetics of the J-aggregate might imply the nonequivalence of the binding sites.

Binding Sites. It is noteworthy that the observation of protein-induced chirality of J-aggregates points to the presence of chiral elements in the secondary structure of the protein molecule, and electrostatic interaction of the dye with these elements is a prerequisite of J-aggregation. The secondary structure of the proteins under study is characterized by the presence of an α-helix which has a right-handed conformation, β-sheets (left-handed), and the polyproline helix structure. Negative bisignate CD signals of J-aggregates provide a basis for the assumption that the sites of the binding of both dyes with lysozyme, trypsin, and RNase are located on β-sheets. The content of β-sheets in trypsin, RNase, and lysozyme is 45, 35, and 12%, respectively.[26] The assumption is confirmed by the lack of dichroism with BSA which contains mostly right-handed α-helices and <1% β-sheets. Virtually no J-aggregates and consequently no CD signal were established for both dyes in the presence of BSA. From the results obtained, one might suggest that a right-handed α-helix does not induce J-aggregation. J-aggregates and positive induced CD signals are observed for both dyes in the presence of gelatin which represents an extended proline helix conformation. On the basis of the results obtained with the two cyanine dyes, it is reasonable to suppose that the extended elements of a secondary structure of proteins are favorable for formation of J-aggregates and the latter can be used as a tool to distinguish chiral elements of a secondary structure of proteins.

Close inspection of the ellipticity signals of a large number of measurements under well-defined conditions indicates changes of the shape of the CD signal in the course of J-aggregation. Two examples for trypsin under similar conditions are shown in Figure 6. We propose that protein-induced growing of a J-aggregate depends on the site of binding to various β-sheets. The latter is reflected in two exponents in the decay kinetics of the J-aggregate. Moreover, electrostatic interaction of anionic dyes with positively charged amino acid residues of proteins brings about a diminishing of the net charge of the protein that results in the conformation changes in its secondary structure. The latter is reflected in the fluctuation in the shape of the CD signal. It should be noted that the small (1−2 nm) shift in the visible absorption spectra is also observed in the course of J-aggregation.

Chirality Sensing. J-aggregate chirality sensing is a process where, upon noncovalent interaction, asymmetry is transferred from a chiral molecule or system to an achiral J-aggregate. Cyanine dyes are characterized by a high polarizability, the presence of charged heterocyclic groups, and hydrophobic substituents. Owing to these versatile properties, cyanine dyes are able to interact with different chiral compounds in a supramolecular manner. Complexation of the dye with chiral species can bring about a sterical control on the orientation of the dye in the process of J-aggregation and result in the transfer of chirality information to the J-aggregate. In such a case, the protocol of J-aggregation plays an essential role. Namely, when J-aggregation is accomplished in the absence of any chiral auxiliaries, J-aggregates become more resistant and do not change their conformation on subsequent addition of a chiral compound. However, if a chiral compound is initially present in solution, the formed J-aggregate manifests the same chirality and the sign of the induced CD signal is the same as that of the additive.

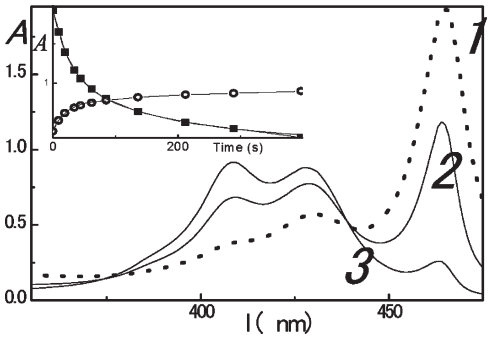


Figure 10. Absorption spectra of Tc (12 μM) in the presence of 2 μM lysozyme at pH 5.5 and 300 s after mixing and at 50 and 500 s after injection of OH^- (pH 9.2), *1*−*3*, respectively. Inset: time dependences of A_{408} (circles) and A_{465} (squares).

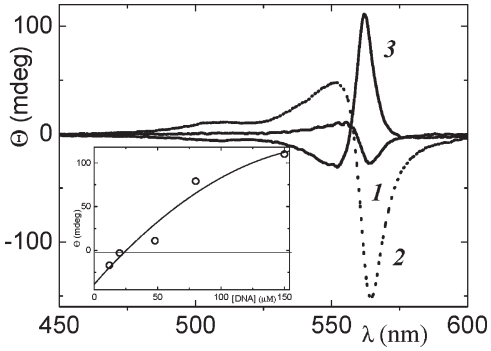


Figure 11. CD spectra of Oc (7 μM) at pH 6 in the presence of 10 mM NaCl (*1*), 10 mM NaCl + 150 μM DNA (*2*), and 150 μM DNA + 10 mM NaCl (*3*). Inset: dependence of the CD signal for 10 mM NaCl vs the DNA concentration.

Figure 11 shows specific results obtained for Oc. In one case, J-aggregation occurs on addition of NaCl; i.e., the cation causes a negative bisignate CD signal. Addition of 150 μM DNA results in an enhancement of Θ, and no change of the sign occurs. In a second case, the J-aggregation proceeds in the presence of DNA (150 μM), which was originally added to the Oc solution, but the negative bisignate signal reverses to a positive one. It should be noted that the sign reversion depends on the DNA concentration starting with the threshold concentration (Figure 11, inset). A similar influence of the protocolled procedure for J-aggregation was mentioned elsewhere.[20] Thus, J-aggregates formed in the presence of chiral auxiliaries might be the sensors of that chirality. Moreover, the essential advantage of a J-aggregate as a sensor is that it transcribes the chirality into a highly amplified CD signal in the visible region.

CONCLUSIONS

In this work, optically active J-aggregates for disulfopropyldichlorothiacyanine and disulfobutylmesoethyloxacarbocyanine were observed in aqueous solution at room temperature upon addition of D/L-tartaric acids, asparagine, proline, DNA, lysozyme, trypsin, RNase, and gelatin. Extended elements of a secondary structure of proteins (β-sheets, proline helix) are favorable for formation of the J-aggregates. The creation of chirality in a J-aggregate takes place in the course of J-aggregation. Bisignate CD signals of J-aggregates of both dyes examined

arise from excitonic interaction between the dye molecules in the J-aggregate and the sign of the induced CD signal, coinciding with that of the chiral additives. J-aggregates of cyanine dyes serve as a chirality-sensing supramolecular system and promise to be a powerful tool in recognition of point and conformation chirality.

■ ACKNOWLEDGMENT

We thank Professor Wolfgang Lubitz for his support and Mr. Leslie J. Currell and Andreas Göbels for technical assistance. A.K. C. is grateful to the Deutsche Forschungsgemeinschaft and the Russian Fund of Basic Researches (09-03-00170-a) for financial support.

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