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THE ELECTRONIC TRANSITIONS IN THE CYANINE DYE J-AGGREGATES, FORMED ON THE POLY(dA)-POLY(dT) POLYNUCLEOTIDE

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The carbocyanine dye Cyan βiPr selectively forms J-aggregates on the adenine-thymine sequences of DNA. The fluorescence quantum yield values of Cyan βiPr J-aggregates formed on poly(dA)-poly(dT) polynucleotide were determined for the aggregates of different degree of order and for different aggregate absorption bands. It was established that the J-aggregate quantum yield values are near to that of the dye monomer molecules fixed on poly(dA)-poly(dT). The ordering of the aggregate structure leads to the increase of J-aggregate quantum yield and to the decrease in the efficiency of the transition from the upper aggregate exciton zone to the lower one. The electronic transition processes in Cyan βiPr J-aggregates were discussed.

Keywords: J-aggregate; polynucleotide; cyanine dye; quantum yield

INTRODUCTION

Cyanine dyes are widely used as fluorescent probes for nucleic acids detection, so the study of cyanine dyes aggregation in presence of nucleic acids is very important. In [1] the J-aggregates of the carbocyanine dye Cyan βiPr (Fig. 1) formed on native DNA and on the polynucleotide poly(dA)-poly(dT) were described, and the helical structure of aggregates as well as their formation in the nucleic acid groove, was supposed. It was shown that these aggregates are selectively formed on AT-sequences of DNA, and the degree of order of the J-aggregate structure substantially

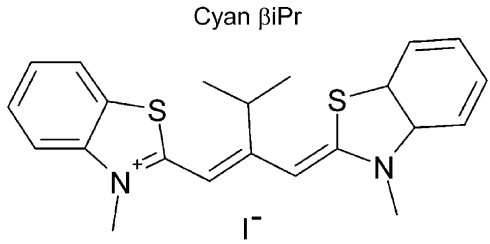

FIGURE 1 The chemical structure of carbocyanine dye cyan βIPR.

depends on the dye to nucleic acid base pairs concentrations ratio. At low dye to polynucleotide concentrations ratio, Cyan βiPr is fixed on poly(dA)-poly(dT) in the monomeric form (with maximum at about 547 nm), under increasing dye concentration the aggregate band appears (at about 600 nm), at further increase of dye concentration one more aggregate band become distinguished (at about 570 nm). [1] By a more detailed concentration dependence experiment described in [2] it was shown, that the increase in dye to polynucleotide concentrations dependence leads to narrowing and better separation of the two aggregate bands, called J1 (near 570 nm) and J2 (near 600 nm). Moreover, the increase in dye concentration shifts the J2 band to the longwave region, while the maximum of J1 band does not shift. The conclusion was made that the number of dye molecules in an aggregate as well as the degree of order of an aggregate grows at the increase of the dye to polynucleotide concentration ratio. Basing on the polarisation measurements, it was also supposed in [2] that the band J1 corresponds to the absorption transition, perpendicular to the nucleic acid axis (and hence to that of the helical aggregate), and the J2 band corresponds to the parallel one. In the presented paper, the electronic transitions in the Cyan βiPr J-aggregates formed on poly(dA)-poly(dT) were further studied and discussed.

EXPERIMENTAL

The carbocyanine dye Cyan βiPr was synthesised by S.S. Lukashov (Institute of Molecular Biology and Genetics of NAS of Ukraine). Polynucleotide poly(dA)-poly(dT) was purchased from "Sigma" (USA). The 0.05 M TRIS-HCl buffer (pH 7,9) was used as a solvent. The samples were prepared as described in [2] immediately before measurements.

The absorption spectra were obtained with the help of the spectrophotometer Specord M 40 (Carl Zeiss, Germany). The fluorescence spectra were recorded on the Cary Eclipse fluorescence spectrophotometer

(Varian, Australia). The quantum yields were determined using Rhodamine 6G solution in ethanol as reference, the quantum yield of which is known to be equal to 0.97 [3].

RESULTS AND DISCUSSION

The fluorescence quantum yield values of the dye Cyan *β*iPr in monomer form (both in free state and fixed on poly(dA)-poly(dT)) and of its J-aggregates formed on poly(dA)-poly(dT) at different degree of order of these aggregates (see Fig. 2), as well as excited in both aggregate absorption bands J1 and J2 are presented in the Table 1.

It is seen from the Table 1 that the aggregate quantum yield has the values between 0,024 and 0,11, being thus of the same order as the quantum yield of the dye monomer fixed on the poly(dA)-poly(dT). At the same time, the quantum yield of the free dye is about two orders of magnitude less than that of both J-aggregate and monomer dye fixed on

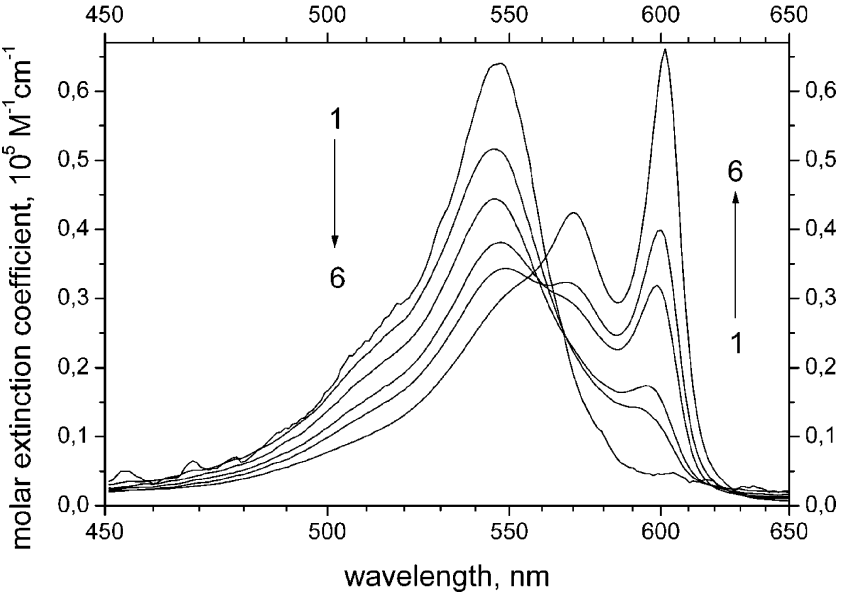

FIGURE 2 The absorption spectra of the dye Cyan *β*iPr in the presence of $2{,}3 \cdot 10^{-5}$ M of base pairs poly(dA)-poly(dT). The dye concentrations are $6{,}25 \cdot 10^{-7}$ M (1), $3{,}75 \cdot 10^{-6}$ M (2), $5 \cdot 10^{-6}$ M (3), $7{,}5 \cdot 10^{-6}$ M (4), 10^{-5} M (5) and $2 \cdot 10^{-5}$ M (6).

TABLE 1 The Fluorescence Quantum Yields (φ) of Monomer Dye Cyan βiPr (Free and Fixed on poly(dA)-poly(dT)) and its J-aggregates of Different Degree of Order; and the Efficiency $K_{J1\text{-}J2}$ of the Transition from the Upper Aggregate Exciton Zone to the Lower One

	φ			
Sample	Monomer band	J1-band	J2-band	$K_{J1\text{-}J2}$
$2{,}5 \cdot 10^{-6}$ M Cyan βiPr free	0,0009			
$6{,}25 \cdot 10^{-7}$ M Cyan βiPr+ $2{,}3 \cdot 10^{-5}$ M poly(dA)-poly(dT)	0,07			
$3{,}75 \cdot 10^{-6}$ M Cyan βiPr+ $2{,}3 \cdot 10^{-5}$ M poly(dA)-poly(dT)			0,024	
$5 \cdot 10^{-6}$ M Cyan βiPr+ $2{,}3 \cdot 10^{-5}$ M poly(dA)-poly(dT)			0,03	
$7{,}5 \cdot 10^{-6}$ M Cyan βiPr+ $2{,}3 \cdot 10^{-5}$ M poly(dA)-poly(dT)		0,038	0,043	0,88
10^{-5} M Cyan βiPr+ $2{,}3 \cdot 10^{-5}$ M poly(dA)-poly(dT)		0,041	0,048	0,85
$2 \cdot 10^{-5}$ M Cyan βiPr+ $2{,}3 \cdot 10^{-5}$ M poly(dA)-poly(dT)		0,056	0,11	0,51

polynucleotide. It was suggested in [4] that the main mechanism of nonradiative electronic excitation energy deactivation of Cyan βiPr monomers in free form is the rotation of the dye heterocycles around the polymethine chain in an excited state, forming thus the nonfluorescent conformation. The fixation of the dye monomer molecule on the nucleic acid strongly decreases the rotation probability, and other nonradiative deactivation mechanisms become predominant, the most possibly these of internal conversion and intersystem crossing [4]. The fact that the quantum yield values of J-aggregate and of the dye monomer molecule fixed on the polynucleotide are of the same order of magnitude may mean that the mechanisms of the nonradiative deactivation of electronic excitation energy of the both systems have the same nature.

The increase in dye to polynucleotide concentrations ratio, and hence the growth of the number of molecules in an aggregate and of the degree of order of the aggregates (see Fig. 2), leads to the increase in J-aggregate fluorescence quantum yield. This may be explained by the ordering and confinement of energy levels structure of an aggregate,

confining also the places of crossing of the hypersurfaces of ground and excited electronic energy states of J-aggregate, thus reducing the internal conversion probability.

It is also remarkable that the quantum yield of the J-aggregate fluorescence excited in J1 band (φ_{J1}) is less than that excited in J2 band (φ_{J2}). This result is in agreement with the assumption made by us earlier [1,2] that the bands J1 and J2 of the aggregate correspond to the electronic transitions to two different Davidov-splitted exciton zones. Basing on the fact that the J-aggregate fluorescence spectrum contains only one band and is reflection symmetric to the J2 absorption band, we supposed earlier [2] that the excitation of the upper J-aggregate exciton zone (corresponding to J1 band) passes nonradiatively to the lower one (corresponding to J2 band), and from this lower zone can be fluorescently deactivated. According to such model it is obvious that φ_{J1} cannot be higher than φ_{J2}. Besides, φ_{J1} could be presented as $\varphi_{J1} = K_{J1\text{-}J2} \times \varphi_{J2}$, where $K_{J1\text{-}J2}$ is the efficiency of the transition from the upper exciton zone to the lower one. $K_{J1\text{-}J2}$ can be found as the ratio $\varphi_{J1}/\varphi_{J2}$ (Table 1). It is seen from the table that the efficiency $K_{J1\text{-}J2}$ has the values between 0,51–0,88 for the studied cases. Hence, the value of rate of the transition from the upper exciton zone to the lower one is comparable with the sum of rates of other deactivation processes owing to which the excitation passes from the upper exciton zone to the ground electronic state avoiding the lower exciton zone. The examples of such processes could be the internal conversion directly to the ground state or the intersystem crossing.

The (Table 1) also shows that the value of $K_{J1\text{-}J2}$ decreases with an increase of the number of molecules in an aggregate. One of the possible reasons of such dependence could be the fact that the higher is the number of molecules in an aggregate, the higher is the degree of order of an aggregate, and hence the better is the separation of the J1 and J2 bands in an aggregate absorption spectrum. The narrowing and better separation of the two aggregate absorption bands means also the separation of the two exciton zones and hence the more difficult transition between them.

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