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Aggregation and excitation trapping of 3,3'-diethyl-9-methylthiacarbocyanine iodide in disordered and uniaxially oriented polymer films

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ABSTRACT

Photophysical properties of 3,3'-diethyl-9-methylthiacarbocyanine iodide (MDTCI) in disordered and uniaxially stretched poly(vinyl alcohol) films (PVA) are reported at high dye concentration. Ground-state formation of fluorescent MDTCI aggregates at high concentration was observed in unstretched and stretched PVA films using steady-state and time-resolved spectroscopic methods. It was found that fluorescence of MDTCI aggregates is almost totally depolarized in disordered matrix, but it remains partly polarized in the stretched PVA film despite energy transfer from monomers. The differences between spectral properties of aggregates in both matrices may result from partial orientation of aggregate transition moment and its immobilization in polymer cage.

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1. Introduction

Nonradiative excitation energy transport and aggregation in disordered systems have been subjects of numerous studies [1–3]. These phenomena are among others responsible for concentration depolarization of fluorescence followed by its partial repolarization at highest concentrations in monomer – nonfluorescent ground state formed aggregates. Recently, however, fluorescent dimers of some rhodamines and flavinmononucleotide have been found while investigating their photophysical properties in solid polymer matrices and viscous solutions [4–10]. In such a case no fluorescence repolarization has been observed as energy transfer takes place from monomers to fluorescent dimers [5,8]. Also recent observations of other authors performed for several dyes exhibit the formation of fluorescent J aggregates in solid matrices [11–14]. Previously [15], while studying energy migration in one component MDTCI doped polymer films we observed the formation of red shifted fluorescence band, which could indicate the presence of aggregates. However, by now, we limited data analysis to lower concentrations, i.e., one component systems and no further studies of aggregate properties have been in this case undertaken. Moreover, the effect of aggregation and energy trapping by fluorescent aggregates in uniaxially stretched polymer films has not been studied at all by far. In this medium preferential mutual orientation of transition moments of interacting fluorophores is controlled by

mechanical stretching of the film in a certain direction. Therefore, stretched polymer film can be considered as an interesting system for studying mutual geometrical alignment of interacting fluorophores or their aggregates. This is possible, since the angular distribution of transition dipole moments can be related to the degree of stretching and/or linear dichroism using an appropriate distribution function [16–19]. As shown recently concentration depolarization of fluorescence can be very weak in uniaxially oriented polymer film despite effective energy migration, since fluorophores other than those primarily excited can partly preserve information on the orientation of the electric vector of the exciting light [20–25].

In this Letter, we report and discuss experimental results of steady-state and time-resolved fluorescence and steady-state fluorescence anisotropy spectra for 3,3'-diethyl-9-methylthiacarbocyanine iodide (MDTCI) in unstretched and stretched polyvinyl alcohol films at high dye concentration, where energy transfer and the formation of fluorescent aggregates take place.

2. Experimental procedures

Analytically pure 3,3'-diethyl-9-methylthiacarbocyanine iodide (MDTCI) and poly(vinyl alcohol) (PVA) were obtained from Fluka. MDTCI was dissolved in 5% water–ethanol solution of PVA at temperature $T = 323$ K to obtain homogeneous solution. Samples were left in a dust-free environment for a couple of days to allow water evaporation.

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Orientation of MDTCI absorption transition moment in PVA films was obtained by their uniaxial stretching. Optical density of samples used in fluorescence measurements was low enough to neglect reabsorption and secondary emission [26].

Absorption spectra were measured using Zeiss M-40 spectrophotometer. Steady-state fluorescence measurements were carried out at front face excitation and observation of the sample fluorescence using our spectrofluorometer [27]. Steady-state emission anisotropy measurements were performed using two channel single photon counting apparatus [28]. Time evolution of fluorescence spectra was measured using picosecond spectrofluorometer described recently [29].

3. Results and discussion

Previously [30], selected photophysical properties of MDTCI were studied. It has been found that the absorption transition moment is parallel relative to the long molecular axis based on linear dependence between the linear dichroism R_D and the stretching factor R_S . Using different approaches (i.e., Kowski–Gryczyński model [18,19] and Monte–Carlo approach [30]) it has been estimated that the absorption and emission transition moments are almost parallel ($3^\circ \leq \beta \leq 9^\circ$). It occurs that disordered and partly ordered systems studied here differ the most in emission anisotropy values. We have measured limiting emission anisotropy of MDTCI $r_0 = 0.32$ for disordered sample and $r_0 = 0.83$ for the ordered one (linear dichroism ratio $R_D = 4.8$). Therefore, it is expected that the measurement of emission anisotropy should also provide the most valuable information on fluorescence properties of MDTCI concentrated system. Significant increase of the averaged orientation factor $\langle \kappa^2 \rangle$ in the stretched polymer film compared to the unstretched film should also be underlined. This increase is due to highly non-random distribution of long molecular axes (and of course transition moments) of MDTCI in stretched PVA films. The values of $\langle \kappa^2 \rangle$ were obtained using Monte–Carlo calculation method. The detailed effect of linear dichroism ratio R_D on the values of $\langle \kappa^2 \rangle$ is presented in Fig. 1. The procedure of $\langle \kappa^2 \rangle$ calculations used in this work is similar to that reported in [31] for two and three component systems. The simulation is carried out in a unit cube, the linear dimensions of which change with the film uniaxial stretching. Since the volume of the initial cube and final cuboid are assumed equal, the dimensions of the cube and cuboid fulfill the following relations:

$$x_{ij} \rightarrow x_{ij}/\sqrt[3]{R_S}, y_{ij} \rightarrow y_{ij}/\sqrt[3]{R_S}, z_{ij} \rightarrow z_{ij}\sqrt[3]{R_S^2}, \quad (1)$$

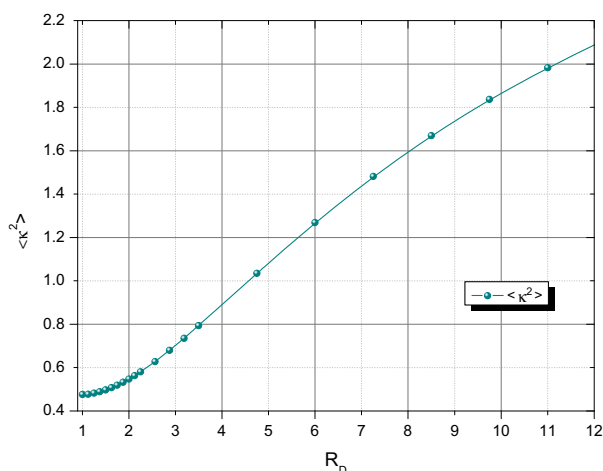


Fig. 1. The dependence of averaged orientation factor on R_D . Calculations were performed using Monte–Carlo technique.

where x_{ij} , y_{ij} , z_{ij} denote the components of vector \mathbf{r}_{ij} . Adopting Tanizaki function [16] for the description of the angular distribution of absorption transition moments at a given R_D , final result for mean orientation factor is achieved by averaging the real orientation factor over all configurations of interacting pairs. The increased values of $\langle \kappa^2 \rangle$ are practically exclusively responsible for much higher critical distance R_0^{MM} for energy migration between MDTCI monomers in partly ordered polymer matrix [32]

$$R_0^{MM} = \left[\frac{9 \langle \kappa^2 \rangle (\ln 10) \eta_{OM} I_{MM}}{128 \pi^5 n^4 N'} \right]^{1/6}, \quad (2)$$

where

$$I_{MM} = \int_0^\infty f_D(\nu) \varepsilon_A(\nu) \nu^{-4} d\nu, \quad (3)$$

is the spectral overlap integral between fluorescence and absorption band for monomer molecule. As a result of the orientation factor change from $\langle \kappa^2 \rangle = 0.476$ for disordered system to $\langle \kappa^2 \rangle \approx 1.04$ for the ordered system, the respective values of critical distance increased from $R_0^{MM} = 39.6$ Å for disordered system to $R_0^{MM} = 45.3$ Å for the ordered one.

Fig. 2 shows absorption and fluorescence excitation spectra of MDTCI at low ($C = 0.0005$ M) and high ($C = 0.02$ M) concentration in unstretched (Fig. 2a) and stretched (Fig. 2b) PVA matrix. From both figures blue shift of the maximum of absorption spectra accompanied by absorption profile change can be seen for concentrated sample (from 562 nm for $C = 0.0005$ M to 550 nm for

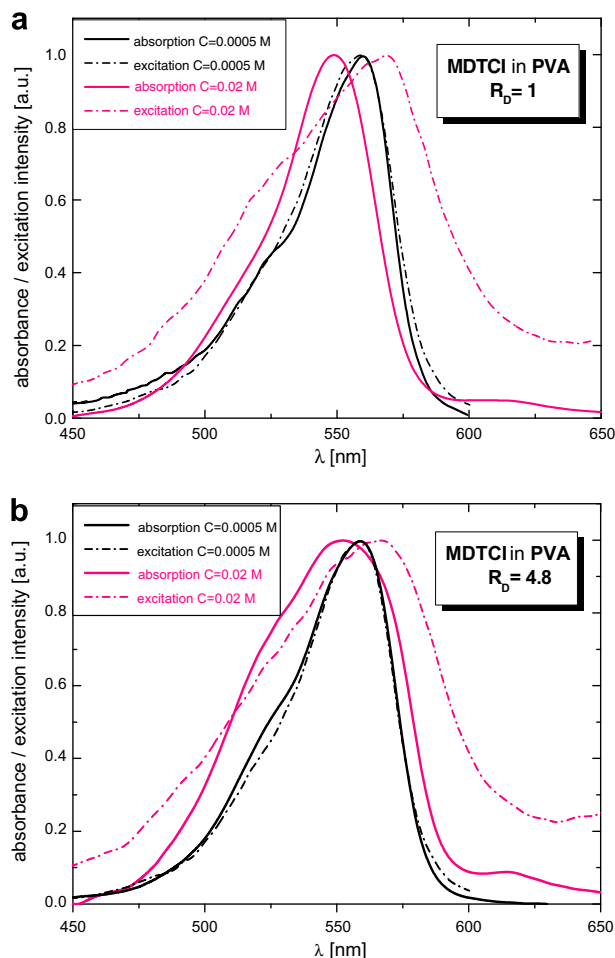


Fig. 2. Absorption and fluorescence excitation spectra of MDTCI at $C = 0.0005$ M and $C = 0.02$ M in unstretched (a) and stretched PVA matrix (b).

$C = 0.02$ M in the unstretched film and from 558 nm to 552 nm for respective samples in the stretched film). This blue shift is accompanied by visible broadening of excitation spectra at high concentration. The half-width of excitation spectra increases from 43 nm ($C = 0.0005$ M) to 83 nm ($C = 0.02$ M) for unstretched film and from 45 nm ($C = 0.0005$ M) to 85 nm ($C = 0.02$ M) for stretched film indicating the presence of a different from monomer fluorescent center. Simultaneously, the formation of a weak red shifted absorption band with the maximum at around 620 nm can be seen in both systems at high concentration. Such concentration dependent changes in absorption and excitation spectra indicate the formation of aggregates in the ground state able to emit their own fluorescence. Strong similarity between the absorption and fluorescence excitation spectrum can also be seen for low concentration $C = 0.0005$ M. No significant changes in this fluorescence excitation spectrum was found up to 0.002 M, which evidences that in this case only monomers contribute to fluorescence signal (one component system).

Fig. 3a and b presents, in turn, fluorescence and emission anisotropy spectra of MDTCI at low ($C = 0.0005$ M) and high ($C = 0.02$ M) dye concentration at $T = 293$ K in unstretched (a) and stretched (b) PVA matrix. With increase in concentration red shift of fluorescence band maximum and the formation of strong red fluorescence band with maximum at around 650 nm is visible in the case of disordered matrix (Fig. 2a). In the case of ordered matrix, long wavelength band is much weaker (the spectrum is only

broadened). In both cases the contribution of red band appears only at high MDTCI concentrations. This suggests that weaker aggregate fluorescence band in the stretched matrix results from its lower fluorescence quantum yield than in the unstretched film. The estimation of aggregate fluorescence quantum yield is a complex task as monomers and aggregates coexist in the matrix and can exchange excitation energy both in forward and in reverse direction [4]. We will show in a separate report that such an estimation is possible using best fitting of Monte–Carlo simulated concentration course of fluorescence quantum yield to experimental data by taking into account forward and reverse energy transport in disordered and partly ordered matrices.

The formation of MDTCI *J*-aggregates can be strongly supported by emission anisotropy studies. Selected results are also presented in Fig. 3a and b. Both for disordered system (triangles) and ordered system (squares) a rapid decrease of emission anisotropy can be observed when passing from the monomer fluorescence to the aggregate emission band, where emission anisotropy attains low value $r \approx 0.04$ in disordered system and significantly higher value $r \approx 0.18$ in ordered system. Strong fluorescence depolarization in the *J*-aggregate band is connected in both cases with excitation electronic energy transfer from monomers to fluorescent *J*-aggregates (energy acceptors) as well as with mutual alignment of transition moments inside the aggregate responsible for absorption and emission. Higher value of emission anisotropy in the stretched matrix can be connected with certain alignment of transition moments towards the direction of matrix stretching [15]. This can be also evidenced by low emission anisotropy values recorded in the aggregate band upon their direct excitation at 620 nm corresponding to the maximum of weak aggregate absorption band (triangles and squares for disordered and ordered system, respectively). Please, note that in the case of disordered system emission anisotropy values recorded upon 620 nm excitation (*J*-aggregate absorption band) are higher than those obtained for 520 nm excitation (monomer excitation), whereas, comparable emission anisotropy values are observed at both excitations for the uniaxially stretched film. These remarks indicate that the *J*-aggregate undergoes a structural change in the polymer matrix as a result of film stretching.

It seems also that time evolution of emission spectra can deliver interesting information on MDTCI *J*-aggregates. Fig. 4a and c shows such selected results for MDTCI in disordered and ordered PVA matrix. The observed difference in fluorescence profiles for 480 nm and 520 nm (Fig. 4a and b) at short time after excitation (0.95 ± 0.04 ns) results from different ratio of excited monomers to aggregates number. We have found that double exponential fluorescence intensity decay taken at 650 nm associated with the red band is fast no matter we deal with the stretched or unstretched sample (figure not shown due to space limitation). Mean fluorescence lifetimes of 95 ps and 110 ps were found for aggregates in stretched and unstretched sample at that observation wavelength, respectively. Mention should be made that in the case of stretched matrix (Fig. 4c) fluorescence aggregate band consists of two bands, one of which is spectrally closer to that of monomer ($\lambda_{\max} \approx 605$ nm) and the other one is shifted significantly to the red ($\lambda_{\max} \approx 700$ nm). This fact together with lower aggregate band intensity and shorter mean fluorescence lifetime suggests that the structure of MDTCI *J*-aggregates change upon matrix stretching.

4. Final remarks

Introductory spectroscopic results obtained for MDTCI in PVA at high concentrations demonstrate the ground state formation of fluorescent *J*-aggregates. Both steady-state and time-resolved data yield surprisingly different fluorescence characteristics of *J*-aggre-

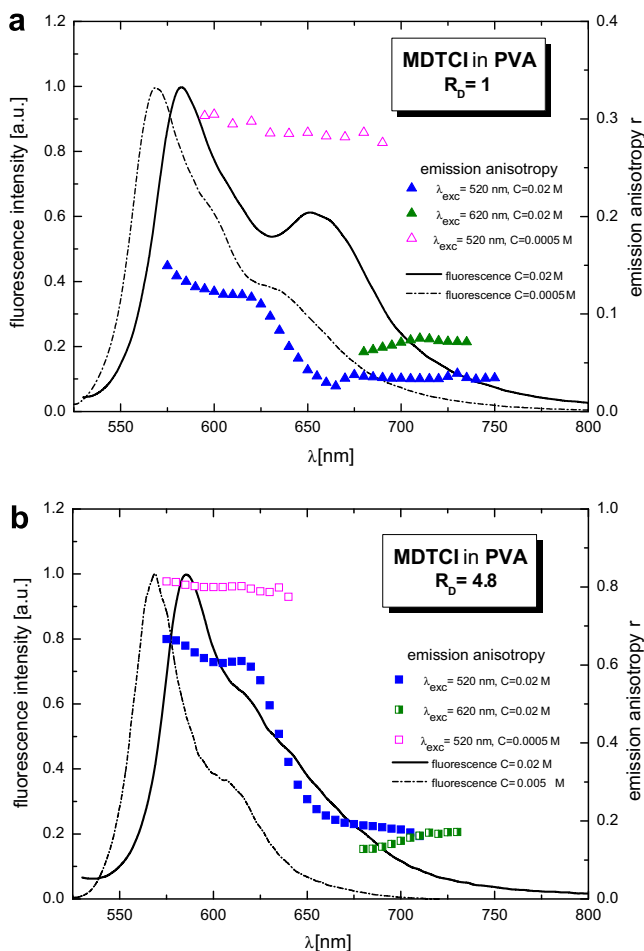


Fig. 3. Fluorescence and emission anisotropy spectra of MDTCI in disordered (a) and ordered (b) polyvinyl alcohol matrices for $C = 0.02$ M and $C = 0.0005$ M. The error of emission anisotropy measurement does not exceed 0.003, which is less than the linear dimension of data graphical symbols.

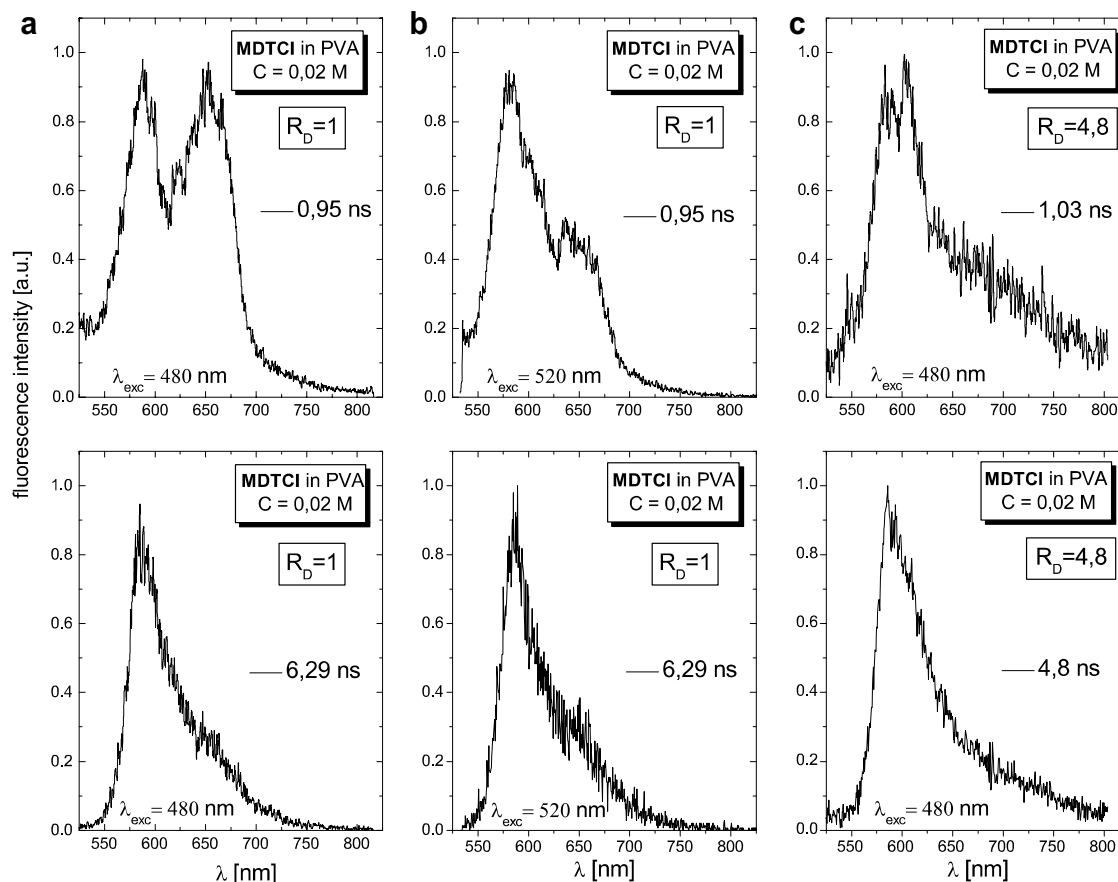


Fig. 4. Time evolution of MDTCI fluorescence spectra in unstretched (a, b) and stretched PVA matrix (c). (a, c) Excitation wavelength: 480 nm, (b) 520 nm.

gates in unstretched and partly ordered PVA films indicating that stretching the matrix affects the properties and structure of these *J*-aggregates. Further information on MDTCI *J*-aggregates in PVA will be reported soon. Among others the real absorption and emission spectra as well as fluorescence quantum yield of the aggregate will be reported. The nature of the *J*-aggregate as a trap of excitation energy (perfect or imperfect) as well as the conditions and extent of back energy transfer from *J*-aggregates to monomers will be discussed using Monte–Carlo approach.

Acknowledgments

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