

## Influence of Substituent in Conjugated Chain of Molecules on Nanocomponents Composition of Polymethine Dye Films

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Molecular layers of polymethine dye long conjugation chain on glass contain several types of molecular nanocomponents. The number and type of the components depend on the thickness of a layer. In thin layers, only monomolecular components (all-trans-stereoisomers and cis-isomers) are present. We studied a series of four dicarbocyanines and determined the steric structure of the nanocomponents of the layers. The layers of less than 1 monolayer thick contain up to 4 monomeric components. For monocis- and dicis-isomers of the dyes studied, which are obtained from the all-trans form upon rotation of fragments of a molecule around different bonds in the conjugated chain, the steric models were constructed. It was shown that in the series of polymethine molecules differing in the substituents and their positions in the chain there is a correlation between the intensity of the absorption bands of the certain components and the steric hindrance of molecular isomers. The above correlation may be used for the determination of the steric structure of monomeric components of the layer.

**Keywords:** Polymethine, Cyanine, Isomer, Film.

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### 1. INTRODUCTION

Study of materials consisting of nano-size particles is the new rapidly developing direction of research, known as nanophotonics [1]. Evidently, the nanophotonic results may set a basis for future information technology, because they suggest the use of more compact elements, which operate at higher frequencies than the current devices. Molecular organic dye layers are promising media for these purposes [2]. The molecules of the above dyes have sizes on the order of several nanometers and therefore may be classed with nanoobjects. Correspondingly, their aggregates may be considered as molecular nanoclusters [3]. The component composition, photophysical and photochemical properties of molecular dye layers strongly differ from the properties of these compounds in solutions [4].

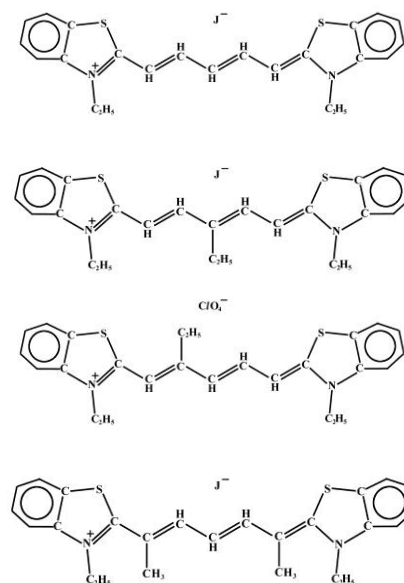
Molecular layers of polymethine compounds with long conjugation chain on glass contain several types of molecular nanocomponents [5]. The number and type of the components depend on the thickness of a layer. In thin layers, only monomolecular components (all-trans-isomers and cis-isomers) are present. Cis-isomers are formed from all-trans-isomer upon rotation around various bonds in the polymethine chain. The relative surface concentration of the stereoisomers is determined by the thickness of a layer. The spectral parameters of the components are significantly different. Further increase in the concentration of molecules in thick layers results in the formation of dimers and aggregates.

The study is concerned with the formation mechanisms of the equilibrium component composition of a molecular layer of polymethine dyes with substituents in conjugated chain. A series of four dicarbocyanines (unsubstituted DTDCI, and its derivatives differing in the substituents and their positions in the polymethine

chain) were investigated, steric structure of the nanocomponents of the layers were determined.

### 2. SAMPLES AND METHODS

As polymethine dye (PD) was chosen unsubstituted symmetric molecule DTDCI, and its derivatives differing in the methyl or ethyl substituents and their positions in the conjugated chain (Fig. 1).



**Fig. 1** – From top to bottom structure of PD1, PD2, PD3, PD4

Samples were prepared by the spin coating method including spreading of an ethanol solution of dye onto a rotating glass substrate. The surface concentration of monomolecules in the layer varies linearly with the

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concentration of a spread solution.

The absorption spectra of polymethine dye layers were obtained from their extinction spectra and separated onto the spectra of single molecular configurations. The spectrum of each configuration was in the form of three Gaussian functions describing the most probable transitions between the ground electronic state and the vibrational sublevels of the first excited state.

### 3. RESULTS

All-trans-isomer is prevailing steric structure of polymethine molecules in the ethanol solution (Fig. 2). Shape and position of the absorption bands of studied PD solution differ slightly. It's mean weak influence of substituents on the  $S_0 \rightarrow S_1$  transition in the molecules.

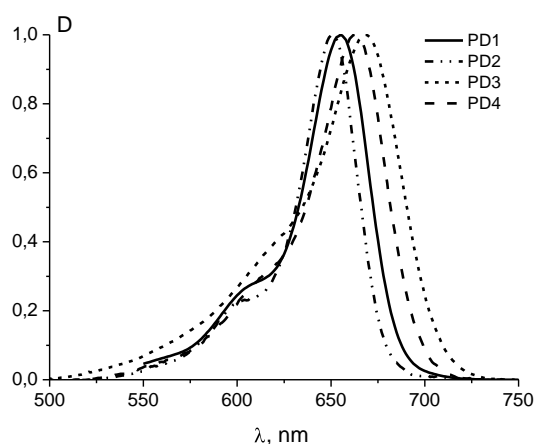
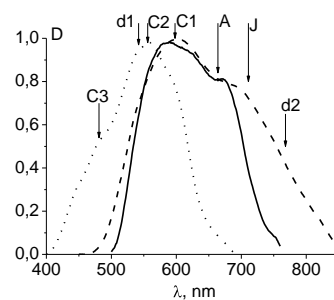
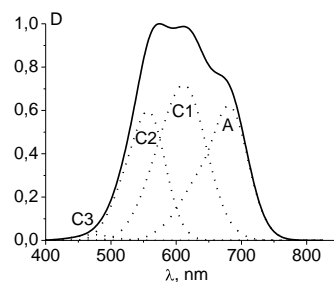


Fig. 2 – Normalized absorption spectra of PD solutions

Shape and position of absorption spectrum of PD1 layer depend on the thickness of a layer, in particular on the surface concentration of molecules (Fig. 3). The wavelength of the absorption maximum A is close to the maximum of the band of the  $S_0 \rightarrow S_1$  transition of the all-trans-isomer in ethanol solution. Therefore, the band A may be assigned to the all-trans isomer. The widths of Gaussian contours of all-trans isomer in layer are larger than in solution. This difference depends on the thickness of the layer and is likely to reflect the changes in the degree of inhomogeneous broadening in the spectra of layers of different thicknesses. The bands in the shorter wavelength region with respect to the all-trans isomer absorption maximum correspond to the cis-isomers of different structures ( $C_i$ ), which are formed upon rotation of the fragment of a molecule relative to different bonds of the conjugation chain. As the layer thickness (the number of conventional monolayers, which was calculated from the volume concentration of the monomers in the composition of all components of the layer) increases, the relative concentrations of the cis-isomers decrease and the number of all-trans isomers increases. Further increase in the concentration of molecules in thick layers results in the formation of dimers (d) and aggregates (J).

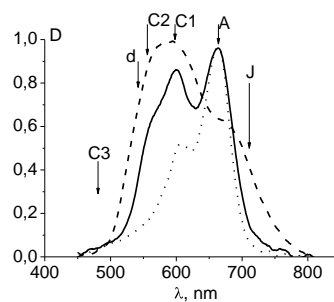


a

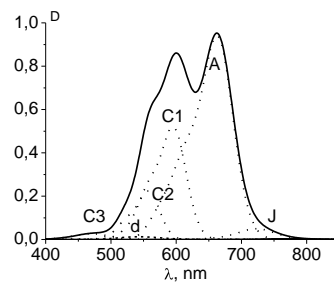


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Fig. 3 – (a) Normalized absorption spectra of PD1 layers differing in thickness;  $D_{max} = 0.003$  (dotted), 0.005 (solid), 0.04 (dashed); absorption maxima of the molecular components are indicated by the arrows: A – all-trans- and C1, C2, C3 – cis-isomers, d1, d2 – two bands of dimer; J – J-aggregate. (b) Normalized absorption spectrum of PD1 layer and its separation onto the spectra of nanocomponents

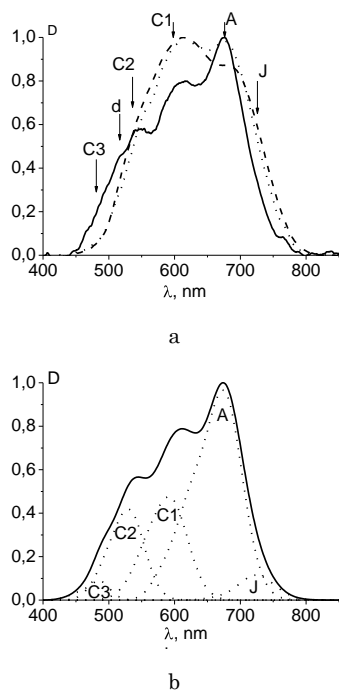


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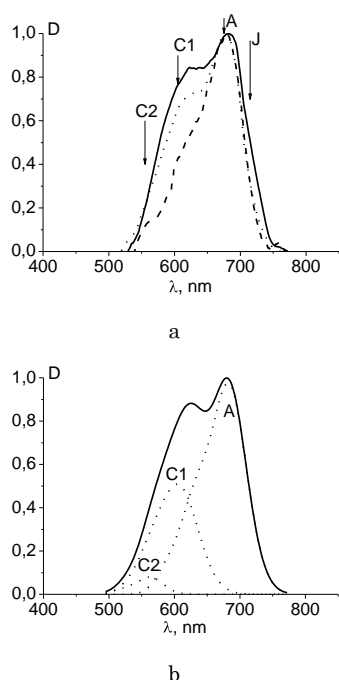


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Fig. 4 – (a) Normalized absorption spectra of PD2 layers differing in thickness;  $D_{max} = 0.003$  (dotted), 0.007 (solid), 0.026 (dashed); absorption maxima of the molecular components are indicated by the arrows: A – all-trans- and C1, C2, C3 – cis-isomers, d – dimer; J – J-aggregate. (b) Normalized absorption spectrum of PD2 layer and its separation onto the spectra of nanocomponents



**Fig. 5** – (a) Normalized absorption spectra of PD3 layers differing in thickness;  $D_{max} = 0.003$  (solid),  $0.011$  (dotted),  $0.036$  (dashed); absorption maxima of the molecular components are indicated by the arrows: A – all-trans- and C1, C2, C3 – cis-isomers, d – dimer; J – J-aggregate. (b) Normalized absorption spectrum of PD3 layer and its separation onto the spectra of nanocomponents



**Fig. 6** – (a) Normalized absorption spectra of PD4 layers differing in thickness;  $D_{max} = 0.001$  (solid),  $0.005$  (dotted),  $0.04$  (dashed); absorption maxima of the molecular components are indicated by the arrows: A – all-trans- and C1, C2 – cis-isomers, J – J-aggregate. (b) Normalized absorption spectrum of PD4 layer and its separation onto the spectra of nanocomponents

The increase of thickness of PD2 layer leads to increase in the relative concentrations of cis-isomers (C1 and C2) and to reduce of all-trans-molecule relative concentration (Fig. 4). Similar results were obtained for PD3 (Fig. 5).

All-trans-isomers presents mainly in layer of PD4 (Fig. 6), which has two substituents in the conjugated chain. With increasing layer thickness appear bands of two cis-isomers C1 and C2, band of C3 form wasn't observed in spectrum.

#### 4. DISCUSSION

The results for the thin layers containing only monomeric components were compared with the presence of steric hindrance in stereoisomers differing in structure (Table 1). The spatial hindrances were determined by constructing geometric models of dye stereoisomers in the ChemDraw program. This comparison makes possible to determine the structure of monomeric cis-isomers (C1, C2, and C3) in the study (Table 2).

According results of study, all-trans-isomers, as well as mono-cis-isomers, bands are the most intense in spectra of polymethine dye layers. The linear dichroism method revealed that nanocomponents tilted with respect to the normal to the substrate. The tilt angles between the  $S_0 \rightarrow S_1$  transition dipole moment (which in the all-trans isomer is directed along the conjugation chain) of the components and surface normal are  $40 - 70$  degrees. It might be supposed that nanocomponent C1 formed by torsion of  $\alpha'$ -bond, C2 – by torsion of  $\beta'$ -bond. The most short-wavelength components C3 is  $\gamma/\beta$ -dicis-isomer.

#### 5. CONCLUSION

It was shown that the polymethine dye layers of less than 1 monolayer thick contain up to 4 monomeric components. The spectral shifts of the long-wave singlet bands of the isomers with respect to the all-trans isomer band ( $\Delta\nu_{ca}$ ) are within  $(1600 \div 6500) \text{ cm}^{-1}$ , depending on the type of the isomer. In a series of the dyes studied, the differences in  $\Delta\nu_{ca}$  between the same components are considerably lesser than those between the different components of the same layer. For monocis- and dicis-isomers of the dyes studied, which are obtained from the all-trans form upon rotation of fragments of a molecule around different bonds in the polymethine chain, the steric models were constructed. It was shown that in the series of polymethine molecules differing in the substituents and their positions in the conjugated chain there is a correlation between the intensity of the absorption bands of the certain components and the steric hindrance of molecular isomers. The above correlation may be used for the determination of the steric structure of monomeric components of the layer.

**Table 1** – Steric hindrance in PD. “?” means that the elements of the molecule do not overlap, but closely boarded to each other

	PD1	PD2	PD3	PD4	Band
Substituent	no	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	
Place in chain	–	10 (center)	9 or 11	8 and 12	
Stereostructure	Steric hindrance				
all-trans	no	no	no	no	A
(10-11) $\gamma$ -monocis	no	no	yes(9,?) no(11)	yes(?)	
(9-8) $\beta$ -monocis	no	yes	no(?)	no	C2
(2-8) $\alpha'$ -monocis	no	no	yes(9) no(11)	no	C1
(10-11,2-8) $\gamma\alpha$ -dicis	no	no	yes(9) no(11)	yes	
(10-11,9-8) $\gamma\beta$ -dicis	no	yes(?)	yes(9) no(11)	yes(?)	C3
(10-11,11-12) $\gamma\beta'$ -dicis	no	no	no	no	
(10-11,10-9) $\gamma\gamma$ -dicis	yes	yes	yes	yes	
(10-11,12-2') $\gamma\alpha'$ -dicis	no	no	yes	yes	

**Table 2** – Relative absorption maxima of nanocomponents in the normalized spectrum of the layer deposited from solutions with concentration  $\leq 70 \text{ cm}^{-1}$  (less than a monolayer), and the conjectural stereostructure of component

	PD1	PD2	PD3	PD4	conjectural stereostructure
Solution concentration ( $\text{cm}^{-1}$ )	62	34	32	47	
Number of monolayer	0.7	0.3	0.4	0.24	
$D_{\max}$ of layer	0.0027	0.0028	0.0019	0.0018	
$D_{\max}(\text{A})/D_{\max}$	$\sim 0$	1	1	1	all-trans
$D_{\max}(\text{C1})/D_{\max}$	0.7	0.2	0.35	0.3	$\alpha(2-8)$ -monocis
$D_{\max}(\text{C2})/D_{\max}$	0.7	0.06	0.72	0.31	$\beta(9-8)$ -monocis
$D_{\max}(\text{C4})/D_{\max}$	0.4	$\leq 0.03$	0.2	0	$(\gamma',\beta)$ (10-11,9-8)-dicis

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