

Enhanced light-induced director reorientation and dye aggregation in a nematic liquid crystal

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Our experimental and theoretical data suggest that the strong enhancement of light-induced director reorientation in a dye-doped nematic liquid crystal can be caused by aggregation of the dye molecules.

Наши экспериментальные и теоретические данные показывают, что сильное повышение фотоиндуцированной переориентации директора в нематическом жидком кристалле, допированном красителем, может быть обусловлено агрегацией молекул красителя.

Nematic liquid crystals (NLCs) show a giant optical nonlinearity as a result of the optical-field-induced director reorientation (DR) [1]. Janossy et al. [2] discovered that adding small amounts (~1 %) of a light absorbing dye to a nematic host can enhance the optical reorienting torque by a factor of 100. The proposed explanations assume that the dye is present in the NLC host as individual molecules ([1] and Refs. therein). This assumption is certainly valid when the interactions between the dye molecules are insignificant. However, these interactions might be strong in some solvents, giving rise to aggregation [3]. This work shows that dye aggregation can strongly enhance the light-induced DR.

We study the 5CB NLC (Merck) doped with an anthraquinone dye N,N'-(methylphenyl)-1,4-diamino-anthraquinone (D4) known to induce J'anossy effect [2]. Interaction between the dye molecules is evidenced by a strongly nonlinear dependence of the polarizability $\alpha = \alpha_L + \alpha'E^2$ on the dye concentration $c = (\text{number density of dye molecules})/\rho_0$ where $\rho_0 \approx 10^{27} \text{ m}^{-3}$ is number density of the 5CB molecules ($c = 0.01$ corre-

sponds to 1.78 wt. %); α_L and α' are independent of the field amplitude E . If the dye molecules do not interact, their contributions are additive and $\alpha \propto c$; for our system, we find $\alpha'(c)$ to be highly nonlinear.

First, we measured α' for 5CB+D4 for continuous laser generation TEM₀₀ single-mode CW He-Ne laser, $\lambda = 633 \text{ nm}$, 75 mW). The focused laser beam with Gaussian profile was normal to the NLC cell thickness of $h = 10 \text{ }\mu\text{m}$ with the homeotropic director \mathbf{n}_0 ($\mathbf{E} \perp \mathbf{n}_0$). We measured the intensity of light passing through the sample and a fixed diaphragm, vs the incident light intensity I (I was well below the DR threshold I_c at all the c 's values [4, 5]). The dependence $\alpha'_{633}(c)$ is strongly nonlinear, e.g., close to $c^{2.75}$ for $c \geq 0.002$, Fig. 1. To exclude the contribution from NLC, the same cells were irradiated with picosecond pulses at $\lambda = 532 \text{ nm}$: the absorption of 5CB at 532 nm is low and thus the optical response to picosecond pulses is weak [6]. A strongly nonlinear dependence $\alpha'_{532}(c)$ close to c^2 was observed in this case as well, Fig. 1. This nonlinearity of $\alpha'(c)$ indicates a domi-

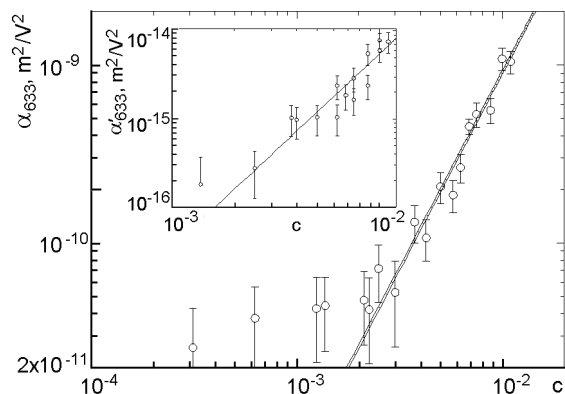


Fig. 1. Coefficient α'_{633} vs c ; solid line: $\alpha'_{633} \propto c^{2.75}$. Insert: α'_{532} vs c ; solid line: $\alpha'_{532} \propto c^2$. Homeotropic 10 μm cell.

nation of supramolecular units in the optical response. In contrast, the light absorption coefficient changes linearly with c for mW light intensities relevant to the effect.

In the models [1] of non-interacting dye molecules, the dye-induced torque on \mathbf{n}_0 is proportional to cI , and the threshold of light-induced DR I_c scales as $1/c$, so that $cI_c(c) = \text{const}$. We determined I_c for homeotropic cells of 5CB+D4 by measuring the on-axis transmittance vs. I [5] and found that $I_c(c) \propto 1/c$ only at relatively high concentrations, $c \geq 0.006$ (see also [7]). For lower concentrations, $0.0007 \leq c \leq 0.006$, the trend is different, $I_c \propto c^{-\beta}$, with $\beta \sim 1.5-2$, Fig. 2. As in [2], for $c = 0.006$ (≈ 1 wt. %), $I_c \sim 0.01$ of its value for the pure 5CB.

The light-induced DR for different angles θ_e between \mathbf{E} and \mathbf{n}_0 was studied using a planar cell (\mathbf{n}_0 being fixed in the substrate plane by obliquely deposited SiO_2 layers) where θ_e could vary from 0 to 90° by changing the linear polarization of the beam ($\lambda = 633 \mu\text{m}$) normal to the cell. It is known that in an azo-dye-doped NLC, depending on the angle θ_e , the DR caused by a Gaussian beam may result either in self-focusing of the beam (the refraction index at the axis is larger than at the periphery) or in its defocusing (the refraction index at the axis is lower), depending on how the director is reoriented, towards \mathbf{E} or away from \mathbf{E} , respectively [8]. We observed such inversion from focusing for $50^\circ < \theta_e \leq 90^\circ$ to defocusing for $0 \leq \theta_e < 50^\circ$ in 5CB doped with D4 which is not an azo dye. For $\theta_e = 90^\circ$ ($\mathbf{E} \perp \mathbf{n}_0$), the DR threshold I_\perp was very close to that for the homeotropic cells. For $\theta_e = 0$ (this case with $\mathbf{E} \parallel \mathbf{n}_0$ seems

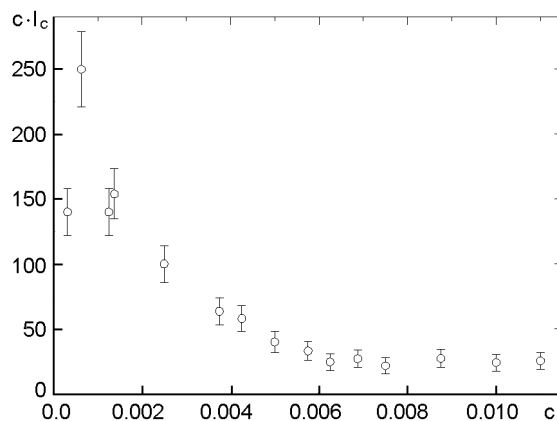


Fig. 2. Product $I_c(c) \cdot c$ vs c ; homeotropic 10 μm cell.

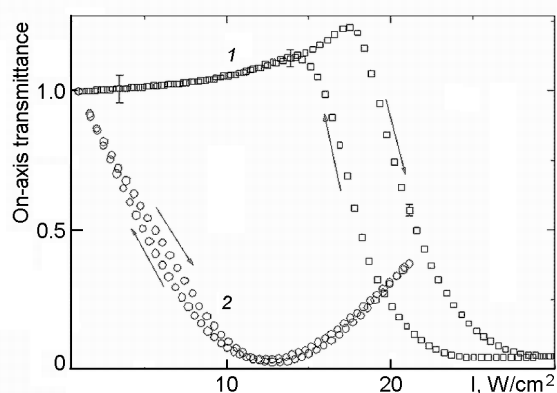


Fig. 3. Normalized on-axis transmittance of a planar 10 μm cell vs increasing (\rightarrow) and decreasing (\leftarrow) intensity I of light polarized either normally (1, $\theta_e = 90^\circ$) or parallel (2, $\theta_e = 0$) to the initial director, $c = 0.0084$. The ramping speed is 3 s per data point; a slower speed 120 s per point does not change the data.

to be not studied before), we found a remarkable DR effect with a very low threshold $I_\parallel \sim 0.17I_\perp$. The difference between $\theta_e = 90^\circ$ and $\theta_e = 0$ is not only quantitative but also qualitative, Fig. 3. For $\theta_e = 0$, smooth reversible changes are observed typical of the second order transition, Fig. 3. In contrast, when $\theta_e = 90^\circ$, DR features a strong hysteresis as in the first order transition.

The main experimental findings, i.e., nonlinear $\alpha(c)$, non-constant $cI_c(c)$ and hysteresis, do not fit in an obvious manner the models of non-interacting dye molecules, but can be qualitatively explained by the dye aggregation.

Let the unit vectors \mathbf{a} and \mathbf{d} making the angle θ_d be the aggregate axis and long axis of D4 molecule, respectively, Fig. 4. The

two phenyl groups sticking out of the D4 molecular plane suggest that full face-to-face contact of the adjacent molecules is hindered, so that $\theta_d \neq \pi/2$. At the reorientation, the initial director \mathbf{n}_0 changes to \mathbf{n} which is its perturbed state. \mathbf{a} makes a nonzero angle θ_a with \mathbf{n} : the tilted stack of the plane-like molecules is anchored to the director \mathbf{n} , but neither \mathbf{a} nor \mathbf{d} is parallel to \mathbf{n} . The aggregate can rotate about the director n , but not about its own axis a as this would change the orientation of NLC molecules at the aggregate surface. The aggregate orientations are randomly distributed over a cone with the apex angle θ_a and axis \mathbf{n} . In the absence of field, the cone axis is \mathbf{n}_0 . The electric field of light $\mathbf{E} = E\mathbf{e}$ polarizes the aggregate thus creating a torque Γ_a that reorients it. This reorientation causes director distortions, mostly twist about the axis of aggregate reorientation. The distortions result in the elastic pair interaction between aggregates that depends on their orientations relative to each other and to \mathbf{E} . The effect of all pair interactions depends obviously on the axis n_0 of the orientational distribution cone relative to \mathbf{E} . As a result, the free energy (FE) depends both on \mathbf{n}_0 and \mathbf{E} . For a fixed \mathbf{E} , to minimize the FE, the director might rotate by some angle θ from the initial state \mathbf{n}_0 to the new state \mathbf{n} , which is the DR effect. To find θ and thus to describe the DR, we shall explain first how the idea of aggregation is substantiated by the data on light absorption and polarizability. Then we shall estimate the field-induced polarization and torque Γ_a , and finally, a simple Onsager-type model will be introduced, where the aggregate interaction is modeled by the excluded volume effect. The field-induced director distortions increase the excluded volume and thus lower the entropy; both the excluded volume and entropy depend on n relative to \mathbf{E} . To avoid the entropy loss, the system relaxes by reorienting \mathbf{n} to the maximum entropy state.

For simplicity sake, let all the aggregates have the same aggregation number $N \sim 10$ and length Nl and their density be $\rho = c\rho_0/N$. First, we explain why the polarizability α' of D4 aggregates is highly nonlinear whereas the absorption is linear in c . On light absorption, the ground state (g) of the dye molecule transforms into the excited (e) state. The absorption and polarizability of dye monomers are proportional to c , regardless of whether they are in the g or e state. However, the energy band structure of a

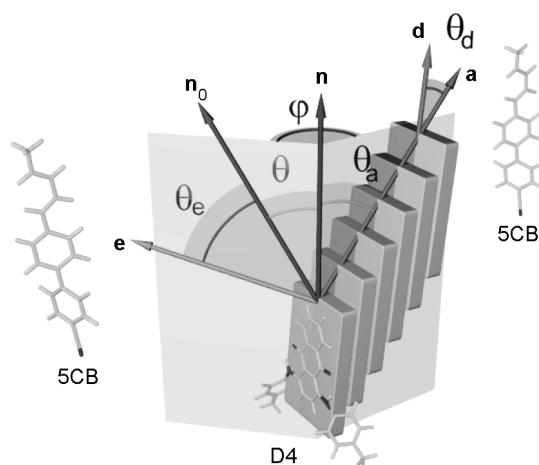


Fig. 4. Geometry of the columnar aggregate.

conjugated one-dimensional chain of N molecules (such as, e.g., J-aggregates) is similar to that of a semiconductor [3]. The g electrons are localized at the individual molecules, the g state polarizability $\propto l$ and the total polarizability of aggregates scales as $\rho Nl \propto cl$. However, the e -electrons are delocalized and can move along the aggregate axis, so that the polarizability of an aggregate with N_e excited molecules is $\propto N_e(Nl) \propto N^2l$. Then the total polarizability $\propto \rho N^2l \propto cNl$ which, indeed, may be nonlinear since N strongly depends on c [3, 9]. A similar dependence on the aggregation number N was observed for resonance light scattering in isotropic solutions [11]. We emphasize that if the excitations were localized at the individual molecules, the polarizability would be linear in c , and thus both the dye aggregation and delocalization of the excited electrons are necessary for the nonlinearity [10]. Therefore, both α'_{532} and α'_{633} in Fig. 1 have to be attributed to the excited molecules in aggregates. Then $\alpha'E^2$ is the linear polarizability of the e -molecules in the aggregates which $\propto E^2$ since $N_e \propto E^2$. Thus, the aggregates absorb light in the g state whereas the induced polarization comes from the e state. This explains in a unique way why the light absorption is necessary and why it is linear whereas the polarizability is highly nonlinear in c .

The transition dipole moment of the D4 g molecule is along its long axis \mathbf{d} . Because of delocalization, the dominating component of the field-induced polarization \mathbf{P} of an aggregate is along \mathbf{a} . The light-aggregate interaction energy can be expressed as $-(\mathbf{P} \cdot \mathbf{E}) = -\gamma g(\varphi, \mathbf{n}, \mathbf{e})$, where $g(\varphi, \theta, \theta_e) = (\mathbf{d}(\varphi, \theta) \cdot \mathbf{e})^2 (\mathbf{a}(\varphi, \theta) \cdot \mathbf{e})^2$ and

$\gamma \propto N^2 l E^4$; φ is the azimuthal angle made by the planes $(\mathbf{e}, \mathbf{n}_0, \mathbf{n})$ and $(\mathbf{n}, \mathbf{d}, \mathbf{a})$. This interaction gives rise to a torque on the aggregate. Here we only need its component Γ_a along the vector $\mathbf{n} \times \mathbf{a}$ which obtains as minus the θ_a -derivative of the energy, i.e.,

$$\Gamma(\varphi, \theta, \theta_e, E) = \gamma(E) \partial g / \partial \theta_a. \quad (1)$$

Let us estimate $\gamma \sim PE$. Delocalization of the excited electrons implies $P \sim$ (elementary charge) $\times l$ where $l \sim 10^{-9}$ m. For $c = 0.01$, the Janossy critical field $E \sim 0.1$ of the Frederiks threshold $\pi(K/h^2 \epsilon_0 \Delta \epsilon)^{1/2}$ where $K \sim 8 \cdot 10^{-12}$ N is the elastic constant, $\Delta \epsilon \approx 0.6$ is the dielectric anisotropy for $\lambda = 633$ nm, ϵ_0 is the vacuum permittivity. For $h = 10$ μ m this gives $P \sim 50$ D, $E \sim 3 \cdot 10^4$ V/m, and $\gamma \sim 5 \cdot 10^{-24}$ J.

The experiment shows that the dielectric permittivity of 5CB+D4, which determines the dielectric torque, changes very little as compared to that of pure 5CB. Thus, the induced P is compensated by the depolarizing coat of the LC molecules. Nonetheless, as the balancing torque $-\Gamma$ is distributed over the coat, the director therein is distorted. This distortion is mainly a twist about the axis $\mathbf{n} \times \mathbf{a}$ around which the aggregate is reoriented by the field. The twist amplitude $\delta\theta$ in the coat, defined as the angle between the director at the aggregate surface and \mathbf{n}_0 , can be estimated from the boundary condition describing the balance of the dielectric and elastic torque on the aggregate surface: $\Gamma \sim K(\delta\theta/\bar{r}^2)V$ where $V \sim NS\bar{r}$ is the domain volume and S is the aggregate lateral area per constituent molecule. The twist produced by rods $\mathbf{a}(\varphi_1)$ and $\mathbf{a}(\varphi_2)$ come separated by some distance r_x , is $|\Delta\theta/r_x|$, where $\Delta\theta = \delta\theta(\varphi_1) - \delta\theta(\varphi_2)\cos\Delta\varphi$, $\delta\theta(\varphi_1)$ and $\delta\theta(\varphi_2)$ are the twist amplitudes, and $\Delta\varphi = \varphi_1 - \varphi_2$. When the two rods are parallel, $\varphi_1 = \varphi_2$, then the two twists cancel out, and the aggregates do not interact; whereas when $\Delta\varphi = \pi$ they repel each other with the maximum strength. When the distance r_x is small and the distortions are large, the gradient $|\Delta\theta/r_x|$ might exceed the inverse nematic correlation length $1/\xi$; $\xi \sim 10$ nm [13] and the aggregates should repel each other as hard rods with effectively infinite potential as at $r_x < \xi|\Delta\theta|$ the director distortions would be accompanied by the highly energetic change of the scalar order parameter.

The latter feature reminds one of the Onsager model [12], in which repulsion of the

hard rods of length L and diameter $d \ll L$ through the "excluded volume" effect results in the entropy drop $\propto \rho^2 T L^2 d$ (compared to the ideal gas of sizeless particles) where ρ is the rod density and T is the temperature. In our case, the director deformations at $\mathbf{E} \neq 0$ make the rods thicker than the bare rods at $\mathbf{E} = 0$ by some length D , $d \rightarrow d + D$, which can be estimated from the conditions $\Delta\theta/D \approx 1/\xi$ and Eq.(1):

$$D(\varphi_1, \varphi_2, \mathbf{n}, \mathbf{E}) = D_E \left| \frac{\partial g(\varphi_1)}{\partial \theta_a} - \cos\Delta\varphi \frac{\partial g(\varphi_2)}{\partial \theta_a} \right|, \quad (2)$$

where $D_E = \gamma(E)\xi / (KN\Delta S\rho^{1/3}) \propto I^2$ and $g = g(\varphi, \mathbf{n}, \mathbf{e})$. The effective increase of hard core diameter (2) of two rods depends on their orientation relative to \mathbf{E} and \mathbf{n} ; it grows as E^4 , reaches a maximum when the columns are crossed, $\Delta\varphi = \pi$, and vanishes for $\Delta\varphi = 0$.

The angular dependence of D allows us to estimate the DR threshold by considering the FE of our system as in the Onsager model [13], replacing the rod length and diameter by Nl and D , respectively, and assuming homogeneous φ -distribution of the rod orientation around the director. This FE density is the sum

$$f = \frac{K}{2} \left(\frac{d\theta}{dz} \right)^2 + \rho_0 k_B T \kappa X(\mathbf{e}, \mathbf{n}) \quad (3)$$

of the elastic term (z is the coordinate across the sample) and the entropy drop $\propto \kappa X$. Here $\kappa(E) = c\rho(Nl)^2 D_E = \rho_0 c^2 l^2 D_E \propto E^4$ characterizes the excluded volume and

$$X = \int_0^{2\pi} \frac{d\varphi_1 d\varphi_2}{4\pi^2} \beta \left| \frac{\partial g(\varphi_1)}{\partial \theta_a} - \cos\Delta\varphi \frac{\partial g(\varphi_2)}{\partial \theta_a} \right|, \quad (4)$$

where

$\beta = 2\sin\theta_a \sin(\Delta\varphi/2) [1 - \sin^2\theta_a \sin^2(\Delta\varphi/2)]^{1/2}$ is sine of the angle made by the two crossing columns [13]. Now we can derive the c dependence of the critical intensity $I_c(c)$. At the DR threshold, the dye-induced torque originated from the term $\propto T\kappa$ is equal to the elastic torque $\propto K/h^2$ which gives $T\kappa(I_c) \propto K/h^2$. In the context of the above estimates $\gamma \propto N^2$, $\alpha' \propto cN$ and the experimental trend $\alpha'_{633} \sim c^{2.75}$ we find $I_c \propto K/(hD_E c^2/T)^{1/2} \sim c^{-2}$ using $\alpha'_{532} \sim c^2$ instead of α'_{633} gives $I_c \sim c^{-1.5}$. This explains qualitatively the deviation from $cI_c \sim \text{const}$ in Fig. 2. To

describe the DR, in the director reference frame where $\mathbf{n} = (0,0,1)$, $\mathbf{e} = (0, \sin(\theta_e + \theta), \cos(\theta_e + \theta))$ and $\mathbf{a} = (\sin\theta_a \sin\varphi, \sin\theta_a \cos\varphi, \cos\theta_a)$ we fix $\theta_a, \theta_d, \theta_e$ and calculate the FE $\int_0^h f dz$ vs θ for different κ . The entropy drop X does offer a relevant mechanism of DR. X depends on the angle θ_e between \mathbf{E} and \mathbf{n} and has a minimum for some $\theta = \theta_{min}$, Fig. 5. For $\theta_e = 90^\circ$, $X(\theta)$ offers a possibility that for sufficiently large θ_a the transition from $\theta = 0$ to θ_m can be of the first order (curve 2) while for larger θ_a , it can be of the second order (curve 3). At the same time, the point $\theta = 0$ in the geometry with $\theta_e = 0$ is highly unstable. This picture is just that is necessary to describe the experiment. The elasticity resists the light-induced DR which, as a result, can occur only for sufficiently large $\kappa \propto I^2$, but the total FE behaves similarly to X . We have calculated the effect of elasticity ($\theta = 0$ at the cell substrates) for $\theta_a = 52^\circ$, $\theta_d = 27^\circ$, and the above values of N_a, c_d, K and h . The normal field, $\theta_e = 90^\circ$, causes the first order transition from $\theta = 0$ to $\theta \simeq 43^\circ$ at $\kappa_\perp \simeq 1.5 \cdot 10^{-6}$ and the reverse transition at $\kappa_\perp^{**} \simeq 0.49 \kappa_\perp$. At the same time, the field along the director, $\theta_e = 0$, causes the second order transition at $\kappa_0 \simeq 0.03 \kappa_\perp$ ($I_0/I_\perp \simeq 0.17$). In our model the focusing-defocusing crossover is not related to the sign change of the dielectric constant as its origin is thermodynamic rather than dielectric. For our parameters, it occurs at $\theta_{e,inv} \simeq 50^\circ$. This behavior is close to that observed in the experiment. With known κ_\perp , the light-induced torque γ on an aggregate for the experimental intensity I_c and $c = 0.01$ can be found from the definitions of κ and D_E . This gives 1/50 of the above estimate $\gamma \sim PE$ with $P \sim 50$ D. Thus, the induced aggregate dipole sufficient for the DR is small, $P \sim 1$ D, which shows high efficiency of the mechanism. Another property that makes this thermodynamic mechanism efficient is that the mean separation of aggregates $\bar{r} = \rho^{-1/3}$ is close to ξ and hence their elastic repulsion is appreciable.

To conclude, we have shown that the dye aggregation may be one of the fea-

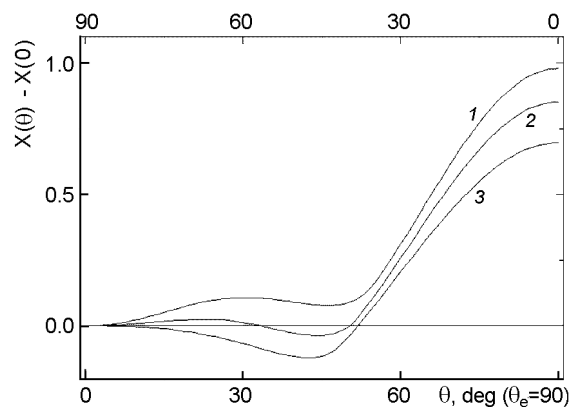


Fig. 5. Entropy reduction $X(\theta) - X(0)$ for $\theta_e = 90^\circ$ ($\mathbf{E} \perp \mathbf{n}_0$, lower abscissa) and $\theta_e = 0^\circ$ ($\mathbf{E} \parallel \mathbf{n}_0$ upper abscissa), $\theta_d = 30^\circ$: (1) $\theta_a = 45^\circ$; (2) $\theta_a = 51^\circ$; (3) $\theta_a = 55^\circ$.

tures of Janosy effect. To conclude, we have shown that the dye aggregation may be the reason for the Janssy effect.

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Збільшена фотоіндукована реорієнтація директора та агрегація барвника у нематичному рідкому кристалі

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Наші експериментальні та теоретичні дані показують, що сильне збільшення фотоіндукованої переорієнтації директора у нематичному кристалі, допованому барвником, може бути обумовлене агрегацією молекул барвника.