

## Self-Organization of Polymethine Dyes in Thin Solid Layers

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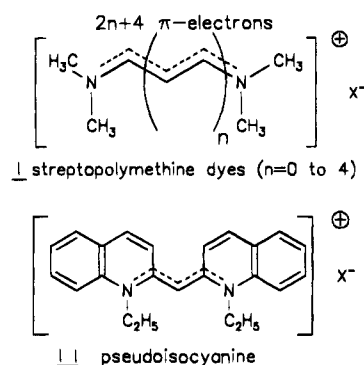
**Abstract:** Thin layers of polymethine dye salts were prepared by a fast spin coating process. Depending on the aggregation tendency of the dye molecules four different layer types were obtained, consisting respectively of polycrystallines, randomly distributed molecules, randomly distributed J-aggregates, and large-scale oriented J-aggregates. The latter are formed by a hitherto unknown self-organization (Thin Layer Crystallization, TLC) process in the solid state. The layers were investigated by dichroic optical spectroscopy. The spectra were compared with spectroscopic and structural data obtained for single crystals of the same compounds. Conclusions were drawn concerning the layer structure and the self-organization process. The layer structure could be influenced by the aggregation parameters temperature and air humidity.

## Introduction

Polymethine dyes are important as spectral sensitizers for semiconductors in photography<sup>1</sup> and in photovoltaic<sup>2</sup> and xerographic technology.<sup>3</sup> These processes require thin layers of the sensitizing dyes or their aggregates. In order to use the additional information of the light polarization for organic electrooptical devices related to light recording and amplification and for sensor materials it is necessary to orient the molecules in large-scale supramolecular assemblies.<sup>4</sup> Several techniques have been developed for this purpose. One possible method is the mechanical orientation of rod-like dyes or aggregates in polymer films which is realized by stretching<sup>5</sup> or by vertical spin coating.<sup>6</sup> Another way is to use the ability of specially designed molecules to organize themselves by intermolecular interactions. The Langmuir-Blodgett technique, for example, exploits the hydrophilic/hydrophobic interactions between amphiphilic molecules.<sup>7</sup> Other methods are physisorption using Coulomb interactions between polycations and polyanions,<sup>8</sup> the combination of dyes with liquid crystals by chemical bonding or by guest–host systems,<sup>9</sup> and the epitaxy of organic compounds, which, however, requires especially designed substrates.

We have developed a new technique which allows the homogeneous orientation of simple polymethine dye molecules in thin layers of the pure dye by exploiting their well-known propensity for forming aggregates<sup>10</sup> in solution and in the solid state. It is generally assumed that dispersion and hydrophobic forces cause the aggregation process.<sup>11</sup> Thus, the aggregation

Chart 1

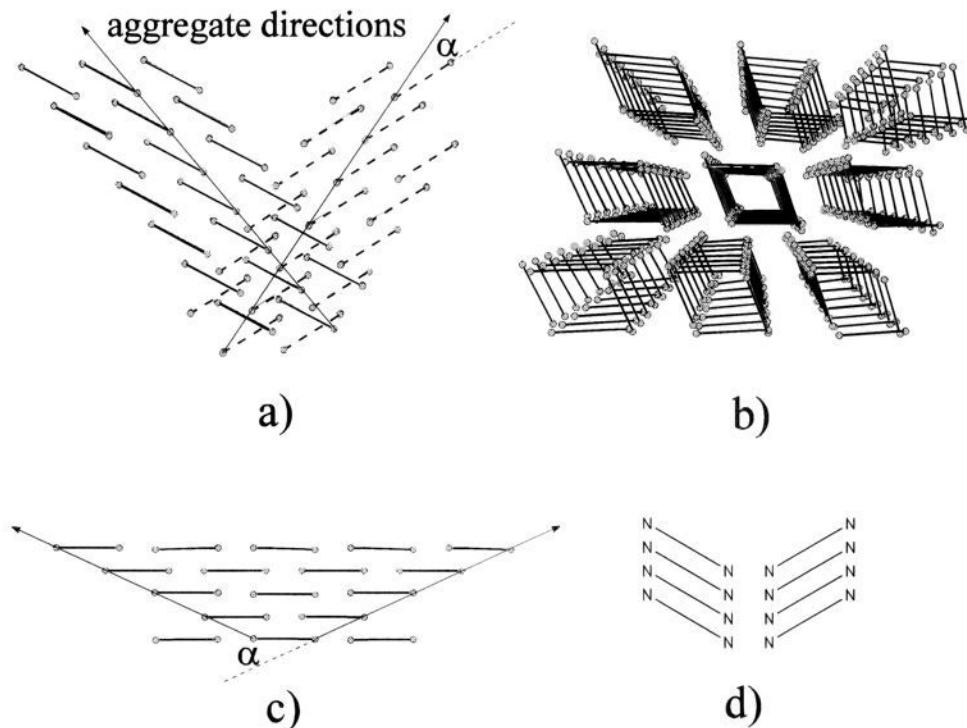


tendency of polymethines increases with their polarizability<sup>13</sup> which depends on methine chain lengths  $n$  (Chart 1)<sup>12</sup> and with the hydrophobic character of the end groups.<sup>13</sup> Because of the hydrophobic forces aggregates form preferably in aqueous solution.

The aggregates of polymethine dyes are subdivided into H-aggregates exhibiting a blue shift of the absorption band and J-aggregates<sup>10,14</sup> where dipole–dipole interactions lead to a strong red shift of up to  $4000\text{ cm}^{-1}$ .<sup>15</sup> Extraordinary properties have been found for the most frequently investigated J-aggregates of pseudoisocyanine dye II such as coherent energy propagation,<sup>16</sup> structure-enhanced nonlinear optical properties,<sup>17</sup> and the phenomenon of superfluorescence.<sup>18</sup> Several possible structures of J-aggregates are shown in Figure 1. Pseudoisocyanine II and the homologue series of streptocyanine dyes I ( $n = 1-4$ ) were chosen for the experiments. The latter served as model compounds for the class of polymethine dyes because they consist only of the basic structural element which is responsible for the deep color. The 1,7-bis(dimethylamino)-heptamethinium I ( $n = 3$ , BDH<sup>+</sup>) forms several aggregate

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**Figure 1.** Aggregate structures of polymethine dyes **I** in crystals (only the nitrogen atoms are shown): (a) two alternately distorted layers of one-dimensional ladder aggregates of  $\text{BDH}^+\text{ClO}_4^-$ ;<sup>20</sup> (b) tube structure of  $\text{BDH}^+\text{BF}_4^-$ ;<sup>21</sup> (c) two-dimensional brickwork structure of  $\text{BDH}^+\text{Cl}^-$ ;<sup>19</sup> (d) model of herring-bone structure.<sup>10</sup>

structures in crystals, depending on the inorganic counterion (Figure 1).<sup>19–21</sup>

### Experimental Section

**Synthesis.** The dye salts were synthesized by known methods<sup>22</sup> and extensively purified by recrystallization and reprecipitation from methanol–diethyl ether. Traces of solvent and water were removed in high vacuum. The substances were characterized by NMR, UV/vis, mass spectroscopy, and elemental analysis.

**Layer Preparation.** Thin layers of polymethine dyes were prepared by the spin-coating process. In contrast to the usual spin coating of polymers, the time for solvent removal must be very short to prevent the crystallization of salts into polycrystalline layers. This was realized by using a high acceleration of the spinning rate (1.6 s to 3000 rpm) and by using concentrated solutions in solvents with high vapor pressure. Additionally, the spin table was heated and a dry air stream was directed onto the layer during the coating process. Solutions of dye salts,  $1 \times 10^{-2}$  to  $5 \times 10^{-2}$  M in dry acetone or dichloromethane, were coated on quartz substrates ( $22 \times 22 \text{ mm}^2$ ). Small dust particles in the solution were removed before deposition by filtering with regenerated cellulose ultrafilters of  $0.2 \mu\text{m}$  pore size (Schleicher & Schüll). The quartz glass substrate was purified with  $\text{KOH}/\text{H}_2\text{O}_2$ , washed with distilled water, and strongly dried. The film thickness can be varied over a wide range according to dye concentration, spin table temperature, and spinning rate. A layer thickness between 5 and 100 nm was chosen in the experiments. Within an 85 nm thick sample the layer thickness differs by less than 3%. The layer thickness was determined by dissolving the complete film in a defined volume of acetone followed by a spectroscopic measurement of the dye quantity. The thickness was calculated from this value by assuming that the layer density corresponds to the known density of single crystals.<sup>20,21</sup> A well-defined air humidity was maintained during the aggregation process in closed glass vessels, the bottoms of which were covered with saturated salt solutions ( $\text{MgCl}_2$ , 33% relative humidity;  $\text{K}_2\text{CO}_3$ , 43%;  $\text{Mg}(\text{NO}_3)_2$ , 53%).

**Measurements.** The optical spectra of the layers were recorded using a Universal Microscope Spectral Photometer USMP 80 (Carl Zeiss, Oberkochen) with quartz optics. The maximal spatial resolution is 500 nm. The light source was a 75-W xenon lamp dispersed by a grating monochromator and polarized by a calcite polarizer. The polarizer was positioned between the light source and the sample in order to reduce the decomposition of the dye by the focused light beam to less than 2% per measurement. For measurements of high resolved spectra silicone oil was used as the immersion liquid because of the insolubility of the salts in it. The solution spectra were recorded in methanol solution by a Lambda 2 spectrometer (Perkin Elmer). The low-temperature spectrum of J-aggregates of **II** was obtained at 10 K with a  $10^{-3}$  molar solution in a water–ethylene glycol matrix.

### Results

**(I) Types of Layers.** Solutions of the dyes **I** and **II** were coated on a quartz substrate and investigated by polarization microscopy and by optical spectroscopy. Four layer types were obtained which show distinct optical and spectroscopic properties:

**Case 1:** For the  $\text{BDH}^+$  chloride, bromide, and azide salt it was impossible to remove the solvent fast enough before the crystallization starts. Consequently, polycrystalline layers were obtained. Because of the strong reflection<sup>15</sup> and light scattering on the microcrystals no meaningful absorption spectra could be obtained.

**Case 2:** The bis(dimethylamino)mono- ( $n = 0$ ), bis(dimethylamino)tri- ( $n = 1$ ), and bis(dimethylamino)pentamethinium ( $n = 2$ ) perchlorate salts **I** formed transparent glass-like layers. The maximum of their absorption band was almost at the same wavelength as in solution. Because of the strong interactions of the randomized oriented transition dipoles the band was inhomogeneously broadened (Figure 2). Although the glassy state does not correspond to the thermodynamic equilibrium, a reorganization of the molecules was not observed.

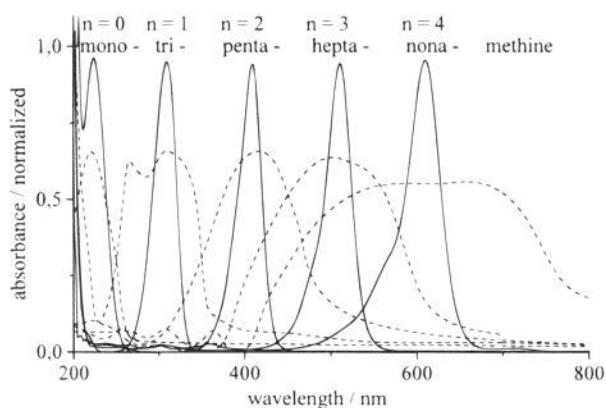
**Case 3:** The bis(dimethylamino)nonamethine **I** ( $n = 4$ ) and the pseudoisocyanine chloride **II** also formed glass-like layers.

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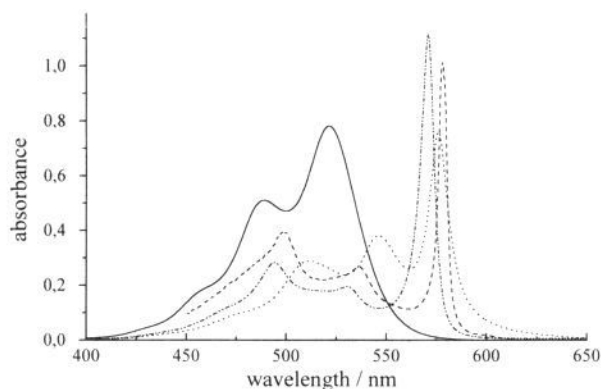
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**Figure 2.** Absorption spectra of the streptopolymethine dyes **I** ( $n = 1-4$ ): (—) in methanolic solution; (---) in thin layer.

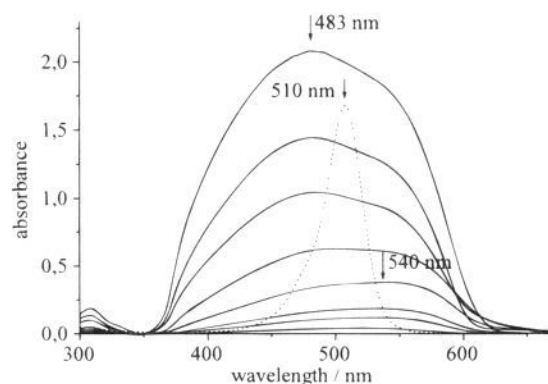


**Figure 3.** Absorption spectra of dye **II**: (—) monomers in solution; (- -) J-aggregates in solution, 10 K; (---) J-aggregates in the layer; (···) J-aggregates in the layer after intercalation of water.

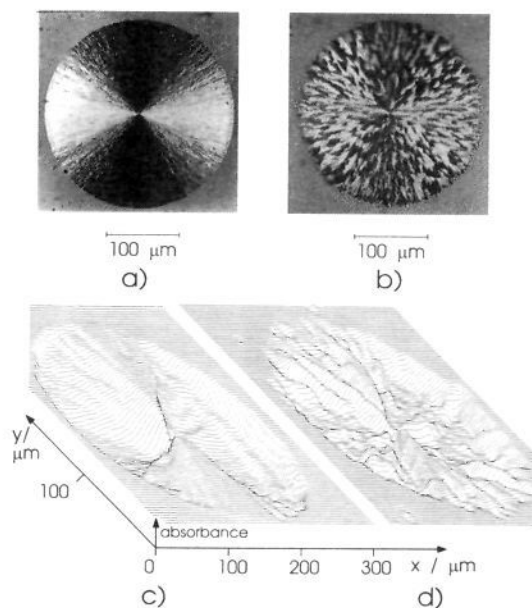
However, in contrast to Case 2, the absorption band was red-shifted with respect to the monomer absorption in solution (Figures 2 and 3). The new absorption band of **II** resembled the spectra of the J-aggregates of **II** in solution (Figure 3). The color of this dye layer changed on treatment with humid air. The absorption band was narrowed and shifted to the blue (Figure 3). This process was reversible; after the layer was dried the initial spectrum appeared. The spectra of these layers did not depend on the light polarization at least within the spatial resolution of 500 nm. First attempts failed to achieve a macroscopic orientation of the aggregates by the technique of vertical spin coating, which is realized for J-aggregates of **II** in polymeric matrices.<sup>6</sup> In our experiments the time between the aggregate formation and the solvent removal may be too short for this orientation process.

**Case 4:** For  $\text{BDH}^+ \text{I}$  ( $n = 3$ ) perchlorate and tetrafluoroborate salts the coating process yielded at first glassy layers as in Case 2, but their absorption band is broader (Figure 2). In order to determine the origin of this band, the spectra of the layers were measured depending on the layer thickness of 3 to 120 nm. Between 3 and 30 nm the spectrum was dominated by an absorption with a maximum at 540 nm (Figure 4). At larger layer thickness the intensity of this band remained constant, but a second absorption band grew at 483 nm, whose intensity was determined by the Lambert–Beer law at layer thickness larger than 60 nm. The  $\text{BDH}^+ \text{ClO}_4^-$  salt behaved similarly but both transitions were red-shifted by 6 nm to 490 and 546 nm, respectively.

In contrast to Case 2 the amorphous state was not stable. After a few minutes the color of the red layer changed to blue. With the microscope it was observed that colored circles grew in the layer presumably starting at some critical nuclei (Figure



**Figure 4.** Absorption of the non-aggregated  $\text{BDH}^+ \text{BF}_4^-$  layer at different layer thicknesses (5 to 100 nm): (---) absorption in solution.

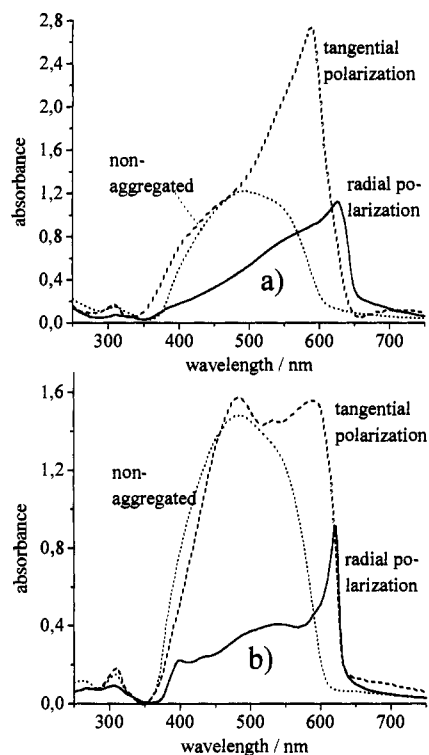


**Figure 5.** Photographs of self-organized  $\text{BDH}^+ \text{BF}_4^-$  layers (horizontal light polarization): (a) aggregation at 25 °C and 33% air humidity; (b) aggregation at 25 °C and 43% air humidity; (c) relief picture of absorption ( $\lambda = 470$  nm) of a circle (aggregated as in part a); (d) relief picture of absorption of a circle (aggregated as in part b).

5). After the circles joined each other, the amorphous state was completely converted into a highly organized state. With simple polarized light sectors of the circles appear red and blue-white, respectively. Between crossed polarizers the sectors of the circle were dark and bright. Hence, a wavelength-dependent rotation of the light polarization in the dye layer did not occur. The self-organization process of Case 4 was studied in more depth because it represents a new method for orienting large-scale areas of sensitizing dyes on solid surfaces.

**(II) Spectroscopic Investigation of Case 4.** The dichroic absorption spectra of the aggregated layers show two different transitions which were polarized radially ( $\mathbf{m}_+$ ) and tangentially ( $\mathbf{m}_-$ ) with respect to the circle (Figure 6a,b). The spectra were independent of the distance from the center of the circles, which indicates uniform structure and orientation in the entire circle. The oscillator strength of the transitions was estimated by integration of the spectra over the energy. An exact calculation was not possible because the refractive index functions of the layer are unknown. The spectroscopic data are listed in Table 1.

The homogeneity of the molecular alignment was investigated by a spatial scanning of the circles with polarized light at 470 nm. The different light absorption yields relief pictures of the



**Figure 6.** Dichroic spectra of non-organized (···) and organized layers: (a)  $\text{BDH}^+\text{ClO}_4^-$ ; (b)  $\text{BDH}^+\text{BF}_4^-$ .

circles (Figure 5c,d). The mountains in the relief pictures were caused by different directions of the aggregates with respect to the light polarization and not by the formation of large microcrystals or by different aggregate structures. This was proved by rotation of the polarization direction of the light, which afforded an inverse relief picture. From these reliefs the area of a homogeneous molecule orientation was deduced.

**(III) Influences on the Aggregation Process.** The rate of the self-organization process, the homogeneity, and the size of the circles as well as the dichroic spectra were influenced by the following effects:

**(a) Nucleation.** The nucleation of the dye self-organization could be induced by small dust particles (no filtering), by water molecules (treatment with humid air), or by mechanical means (scratching on the surface). Thus, in order to produce large assemblies of equal orientation these factors must be avoided. This way the circles reach diameters up to 12 mm.

**(b) Layer Thickness.** The layer thickness was varied between 3 and 120 nm. Below approximately 30 nm thickness the growth rate lowered rapidly and the absorption bands became broader and shifted to shorter wavelengths (Table 1).

**(c) Humidity.** The influence of humidity was investigated in the region from 15% to 75% relative air humidity. The temperature and layer thickness were kept constant at 23 °C and 85 nm. Three different effects were found: First, increasing humidity shortened the time of the self-organization process from hours to seconds. Below a relative air humidity of 15% the nonaggregated layers were stable for some hours. Second, in the case of  $\text{BDH}^+\text{BF}_4^-$  the aggregation at 50% humidity and above resulted in circles with a crumpled structure and macroscopic disorder in orientation (Figure 5b,d). The regions with almost the same molecule orientation reach only  $30 \times 100 \mu\text{m}^2$ . A high degree of order was obtained, however, if the aggregation was performed below 43% humidity (Figure 5a,c). With the optical scanning of the circle it was found that the regions with equal orientation can reach up to  $300 \times 500 \mu\text{m}^2$  under these aggregation conditions. Third, in the case of the

perchlorate salt high humidity shifted the absorption maxima to the red (Table 1).

**(d) Temperature.** The aggregation process was investigated at temperatures between  $-5$  and  $30$  °C and a constant humidity of 43%. The growth time of the circles decreased rapidly with decreasing temperature from minutes at  $30$  °C to several hours at  $5$  °C. Below  $0$  °C no organization of molecules was observed. Because of the long aggregation time at low temperature, many more nuclei were formed, resulting in very small circles.

**(e) Counterion.** The described self-organization process was found for  $\text{BDH}^+$  only in the case of the counterions perchlorate and tetrafluoroborate. The spectra of the aggregate circles strongly depend on the counterion (Figure 6a,b), whereas the absorption maxima of the non-organized layers differ only by 6 nm, as was already mentioned.

## Discussion

**(I) Types of Layers.** The spin coating process is generally used for preparing layers of polymers. If this method is applied for salts or small organic molecules polycrystalline layers almost always were obtained.

Case 1 represents the expected behavior and corresponds to the thermodynamic equilibrium of the layer, which is the crystalline state. These layers were formed exclusively by  $\text{BDH}^+$  salts, which crystallize in a two-dimensional brickwork structure (Figure 1c) with parallel arrangement of molecules.<sup>15</sup> This simple structure and the content of four-crystal water per dye molecule may cause the fast crystallization.

Case 2 was observed for polymethine dyes, which have a low tendency to aggregate. The same absorption maximum of the layer and the solution points to an isotropic distribution of molecules in the layer (Figure 2). The broadening of the absorption band arises from random dipole-dipole interactions between the dye molecules. The additional absorption at shorter wavelength of the trimethine dye may arise from dimer formation<sup>10</sup> or from interactions with the substrate surface.

Case 3 is found for dyes which possess a high aggregation tendency. The similarity between the J-aggregate spectra in solution and the layer spectra of **II** shows that the layers consist of J-aggregates, which are randomly distributed like the molecule chains in Case 2 (Figure 3). Obviously, the aggregation process starts before the solvent is completely removed. The broader J-band in the layer arises from additional dipole interactions between the aggregates. The intercalation of water reduces these interactions and results in the narrowing of the J-band. A narrowing due to a reorganization of the molecules can be excluded because of the reversibility of this process. The red shift of the J-aggregate absorption is smaller in the layer than in solution and is further diminished by the intercalation process (Figure 3). Possibly the aggregates in the layer do not have the ideal orientation and lengths, which reduce the red shift of absorption.

Case 4 was obtained with dyes whose aggregation tendency lies between the borderline Cases 2 and 3.<sup>13</sup> Thus, at first layers of isotropically distributed molecules were formed. In contrast to Case 2 the absorption band is broader and consists of two none-polarized transitions (Figure 4). The different dependence on layer thickness leads to the conclusion that the transition at 540 nm arises from a preorientation of molecules on the quartz surface, whereas the 483-nm transition reflects the bulk absorption of the randomly distributed molecules. The medium aggregation tendency of the  $\text{BDH}^+$  molecules leads to the subsequent self-organization process, starting with some critical nuclei. The thermodynamically unstable glassy state breaks down in favor of the formation of dye aggregates or nearly two-

**Table 1.** Spectroscopic Data for Single Crystals and Thin Layers of  $\text{BDH}^+\text{ClO}_4^-$  and  $\text{BDH}^+\text{BF}_4^-$ 

substance:preparation; humidity; temp; layer thickness	tangential direction $\lambda_{\text{max}}$ of $\mathbf{m}_-$ ( $f_{\text{osc}}$ )	radial direction $\lambda_{\text{max}}$ of $\mathbf{m}_+$ ( $f_{\text{osc}}$ )	splitting energy, $\text{cm}^{-1}$
$\text{BDH}^+\text{ClO}_4^-$			
single crystal <sup>25</sup>	592 nm (3.7)	639 nm (1.8)	1242
layer; agg 33%; 30 °C; 85 nm	588 nm (3.1)	626 nm (1.25)	1032
layer; agg 33%; 23 °C; 85 nm	574 nm (2.7)	610 nm (1.25)	1028
layer; agg 95%; 23 °C; 85 nm	609 nm	629 nm	522
layer; agg 33%; 23 °C; 9 nm	578 nm	594 nm	466
$\text{BDH}^+\text{BF}_4^-$			
single crystal <sup>24</sup>	566 nm (0.7)	599 nm (4.8)	948
layer; agg 33%; 23 °C; 85 nm	586 nm (2.0)	622 nm (0.6)	987
smooth layer structure			
layer; agg 43%; 23 °C; 85 nm	598 nm (1.9)	620 nm (0.6)	593
crumpled layer structure			

dimensional crystals, respectively. This process proceeds slowly and depends strongly on the environmental conditions.

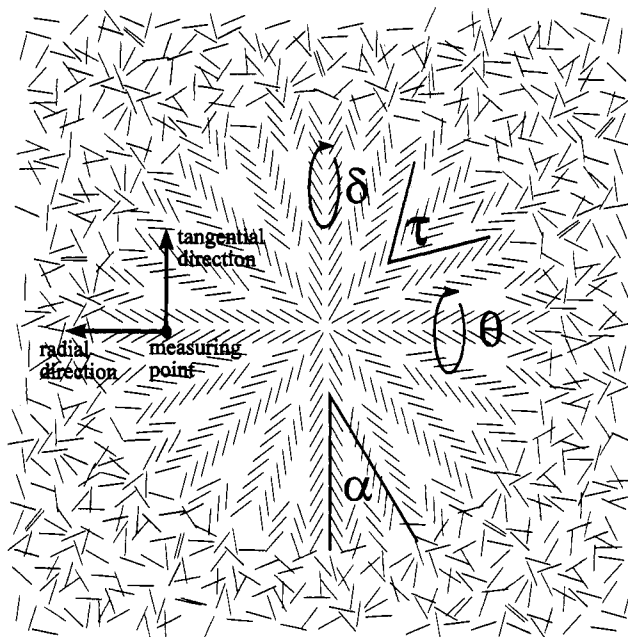
**(II) Spectroscopy.** Conclusions concerning the structure and orientation of the dye aggregates were drawn based on the evaluation of the optical layer spectra. The monomeric  $\text{BDH}^+$  molecule has only one strong absorption band at 510 nm with an absorption coefficient of  $190\,000\text{ L mol}^{-1}\text{ cm}^{-1}$  (Figure 2). The absorption in the solid state can be quite different from that of the single molecule, because of the very dense packing of the molecular transition dipoles. Small differences in the stacking structure influence the spectrum strongly. As is known from the spectroscopy of  $\text{BDH}^+$  single crystals, the absorption in the solid state is determined by three factors:<sup>15,24,25</sup>

1. In dependence on the dislocation angle  $\alpha$  (Figures 1 and 7) between the molecular axis and the stacking direction the absorption energy in the solid state shifts to red ( $\alpha < 54^\circ$ ) or to blue ( $\alpha > 54^\circ$ ) with respect to the monomer. This correlation is roughly described by the KASHA theory.<sup>14,19</sup>

2. If the molecular transition dipoles are non-parallelly aligned in the unit cell of the crystal, the one absorption band splits up into two Davydov components  $\mathbf{m}_+$  and  $\mathbf{m}_-$ .<sup>23-25</sup> The angle  $\tau$  (Figure 7) between the two molecule directions in the unit cell determines the splitting energy and the intensity ratio between the Davydov components  $\mathbf{m}_+$  and  $\mathbf{m}_-$ .<sup>23</sup> The absorptions of the two components are always polarized perpendicularly to each other.

3. The factors 1 and 2 determine the *absolute* (transverse) absorption of the crystal, which could only be measured, however, if the angle between incident light and the Davydov component is  $90^\circ$ . For other angles the *measured* absorption energy shifts to shorter wavelengths with respect to the *absolute* absorption energy. This is caused by polaritons with strong directional dispersion,<sup>26,27</sup> which exist in the solid state of  $\text{BDH}^+$ .<sup>15,24</sup> For the evaluation of the spectra it is therefore necessary to know the angles  $\theta$  and  $\delta$  (Figure 7), which mark the angles between the Davydov components and the layer surface.

The two radially and tangentially polarized absorptions in the organized layers of  $\text{BDH}^+\text{BF}_4^-$  and  $\text{BDH}^+\text{ClO}_4^-$  arise from the Davydov splitting into the components  $\mathbf{m}_+$  and  $\mathbf{m}_-$ . Hence it follows that the dye molecules are stacked in two different directions. Such molecular arrangements are also known from the single crystals of these salts (Figure 1),<sup>20,21</sup> but the dichroic



**Figure 7.** Model of the self-organization process of  $\text{BDH}^+$  in layers: lines represent the axes of the molecules,  $\tau$  is the angle between the molecules,  $\alpha$  is the angle between the molecule axis and the aggregate axis,  $\delta$  is the angle between the layer plane and the aggregate axis (respectively the radial Davydov component), and  $\theta$  is the angle between the layer plane and the normal of the aggregate axis (respectively the tangential Davydov component).

absorption spectra of layers and crystals show remarkable differences (Table 1).

In order to determine the *absolute* absorption energies from the measured spectra the inclination of the Davydov components with respect to the substrate surface was estimated. Because of the angle of  $90^\circ$ , which was measured between the projections of the components on the layer, at least one of the Davydov components is parallel to the surface. The direction of the other Davydov component can be estimated from the ratio of measured to total oscillator strength. The latter is independent of the crystal structure and amounts to 5.5.<sup>25</sup> If both Davydov components are parallel to the surface, the oscillator strength should reach this value. The oscillator strength sum of 4.35 for the  $\text{BDH}^+\text{ClO}_4^-$  layer points to a small angle between the surface and the other Davydov component, whereas the low value of 2.6 for the  $\text{BDH}^+\text{BF}_4^-$  layer indicates a remarkably larger angle. If the corresponding Davydov component is a polariton, this angle results in a blue shift of the absorption band. Therefore, by means of the measured spectra it is not possible to separate the polariton effect and the shift of the absolute absorption energy of the layers, which prevents detailed conclusions with regard to the aggregate structure.

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It must be pointed out that the absorption bands are almost too broad for electronic transitions in the crystalline state, especially the tangential absorption of  $\text{BDH}^+\text{BF}_4^-$  (Figure 6b). The broadness of the bands could have two reasons: First, the aggregates rotate or oscillate in regions below the resolution of the spectrometer around the angles  $\theta$  in the case of a broad tangential absorption band or  $\delta$  for a broad radial absorption, respectively (Figure 7). Second, the preorientation of molecules in the initial state of the layer formation remains during the aggregation process and results in a superposition of the absorption bands of the preoriented molecules around 540 nm and the later formed aggregates.

**Structure of the  $\text{BDH}^+\text{ClO}_4^-$  Layer.** The absorption maxima, the splitting energy, and the oscillator strength of the dry aggregated  $\text{BDH}^+\text{ClO}_4^-$  (Figure 6a) correspond roughly to that of the single crystal (Table 1), which points to a similar structure in the layer and the crystal. It could not be decided, however, based on the spectra whether the aggregates have the proposed herring-bone structure (Figures 1d and 7) or an alternating distorted layer structure as in crystals of  $\text{BDH}^+\text{ClO}_4^-$  (Figure 1a). The latter structure makes a regular growth of the aggregates impossible and could lead to a crumpled appearance of the layer as observed in the case of the tetrafluoroborate layer at wet aggregation (Figure 5b).

The variation of the aggregation conditions results in strong changes of absorption energies and of the splitting energy (Table 1), which points to a change of the aggregate structure and/or to a different inclination of the aggregates with respect to the surface. Therefore, a control of the layer structure should be achievable if the aggregation process was done by particularly defined conditions.

**Structure of the  $\text{BDH}^+\text{BF}_4^-$  Layer.** The aggregate structure and the inclination of the  $\text{BDH}^+$  molecules in the tetrafluoroborate layer clearly deviate from that of the perchlorate layer. This was derived from the different dichroic absorption spectra (Figure 6), the different ratios of oscillator strengths (Table 1), as well as the different changes of the spectra and of the layer homogeneity at alteration of the aggregation conditions (Figure 5). The radial absorption band (Figure 6b) of the  $\text{BDH}^+\text{BF}_4^-$  layer at 622 nm is nearly independent of the aggregation process. Compared to the crystal the absorption maximum is red-shifted by 23 nm (Table 1), which cannot be caused by the directional dispersion of the polaritons. Therefore, the layer structure is different from the crystal structure. Obviously, the tube structure in crystals of  $\text{BDH}^+\text{BF}_4^-$  (Figure 1b) is not a preferred aggregate structure of this dye because of the small overlap between the dye molecules. In thin layers, however, the steric requirements of the anion play a subordinate role and the dye can form more appropriate structures.

Until now, no reasonable explanation could be given for the disorderly growth of the tetrafluoroborate aggregates at high humidity (Figure 5d). It may be caused by different interactions between layer and wet surface above a threshold humidity. Because either the smooth or the crumpled structure and not an intermediate one was found. A quite different aggregate structure can be excluded, because the spectra only slightly differ (Table 1).

**(III) Model of the Self-Organization Process.** A model for the orientation process of Case 4 was inferred from the spectroscopic data (Figure 7). The spin coating of  $\text{BDH}^+$  solutions yields layers with isotropically oriented  $\text{BDH}^+$  molecules. Only on the substrate surface does a preorientation of the molecules exist. After a certain time self-organization starts at some critical nuclei. A constant molecule arrangement grows in the radial direction whereby the structural information is replicated from the nucleus about the whole circle. If the layer

thickness is reduced below 30 nm the self-organization process becomes faulty. The number of molecules in the layer is too small for forming ideal aggregates and for an exact transfer of the structure information. The preorientation of the molecules on the quartz layer surface perturbs the orientation process, as well.

The structure and the orientation of the aggregates, the layer homogeneity, the size, and the growth rate of the circles depend sensitively on the temperature, the air humidity, and the nucleation process. The radial Davydov component in the  $\text{BDH}^+\text{BF}_4^-$  layer exhibits a narrow absorption band width and a lower transition energy than the tangential absorption. Thus, it could be assigned to the absorption of J-aggregates. The radial absorption of the  $\text{BDH}^+\text{ClO}_4^-$  layer is broader than common J-bands. Probably, the aggregate direction changes by the angle  $\delta$  in regions below the spatial resolution of the microscope and the resulting spectrum is the superposition of different polariton absorptions.

Up to now the described orientation method of *Thin Layer Crystallization (TLC)* has been restricted to streptopolymethine dyes with medium aggregation tendency. Perhaps, the rod-like shape of the molecules (similarly to liquid crystals) and the preferred orientation of the molecules in two different directions in the unit cell of crystals are also necessary requirements for the self-organization process. An extension of the experiments to differently shaped polymethine dyes will clarify this point.

## Summary

A modified spin-coating process was developed in order to produce thin layers of large-scale oriented polymethine dyes for organic electrooptical devices. In dependence on the aggregation tendency of the investigated dyes 4 different layer types were obtained by this process, namely polycrystalline layers, layers of isotropically distributed molecules, layers of randomly oriented J-aggregates, and layers of highly oriented J-aggregates. The latter most important one was formed with  $\text{BDH}^+$  dye, which has a medium aggregation tendency. The spin coating of these dyes yields layers with randomly distributed molecules, which later organize themselves in the *TLC* process into large-scale assemblies of J-aggregates. Thereby the spectroscopic properties of the layer changed dramatically because of the formation of aggregates with three-dimensional orientation. From the spectroscopy with polarized light a model was deduced for the orientation process and the structure of the layer. The self-organization process is strongly dependent on the temperature, the humidity, and the counterion. By specific variation of these factors it should be possible to produce well-defined structures of J-aggregates.

The *TLC* method allows, for the first time, the investigation of both single dye molecules and oriented J-aggregates under identical conditions of medium, concentration, temperature, and layer thickness. Thus, it will be a powerful tool for further investigation of the cooperative phenomena<sup>16,17</sup> and the size-dependent optical properties of J-aggregates.<sup>18</sup> Furthermore, a technical application of this method is conceivable for obtaining light polarization dependent recording or sensor materials and specifically designed electrooptical devices.

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