Polariton-Induced Color Tuning of Thin Dye Layers**

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The control of light absorption of supramolecular dye systems[1] is important for their technical application in photography,[2] xerography,[3] and electrooptical devices.[1, 3] The absorption energy of organic dyes depends on molecular parameters such as extension and delocalization of the conjugated π-electron system[4] as well as on intermolecular interactions between the dye and the surrounding medium.[1, 5] Since dyes are mostly applied in the solid state, the investigation and exploitation of such interactions are necessary. Up to now, three intermolecular interactions are widely known:

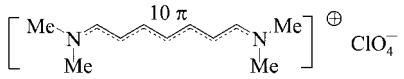
1. Polar dyes exhibit solvatochromism due to the influence of the solvent on the delocalization of the π-electron system.[5]
2. Charge-transfer transitions occur between dye molecules having unequal electron density. These are characterized by weak and broad absorption bands.[5]
3. Transition dipole interactions between dye molecules in aggregates and crystals yield intensive and often narrow absorption bands, shifted either to the red (J-aggregates) or to the blue (H-aggregates) relative to the monomer.[6, 7]

Furthermore, the absorption wavelength of anisotropic dye crystals can vary depending on the directional dispersion of polaritons;[8, 9] this phenomenon was rather unfamiliar until now. In contrast to the well-known excitons (electronic excitations in solids), polaritons include the interaction of excitons with the polarization of the crystal induced by optical excitation.[8] For weakly absorbing materials the difference is small, but for densely packed dye molecules unusual optical properties appear, which cannot be described by excitons alone. The interaction between excitons and polarization leads to different energies of the transverse (E_T) and longitudinal excitons (E_L). The energy difference $\Delta E = E_L - E_T$ depends on the strength of the transition dipole moment M and on the dye density N following the Lyddane–Teller–Sachs Equation (a).[8]

$$(E_L^2 - E_T^2)/E_T^2 \sim |M|^2 N \qquad \text{(a)}$$

Within the energy region ΔE light waves cannot propagate in the dye crystal, but are strongly reflected; broad reflection bands and a metallic luster result. Due to the small penetration depth of light, transmission spectra cannot be measured directly. Hence, the absorption can only be calculated from the reflection spectra, with the Kramers–Kronig relation.[9] In this way a further peculiarity of polaritons was shown, which arises from the anisotropic distribution of dipole moments in the crystal. The absorption maximum does not exhibit the excitation energy of the excitons (E_T), but depends on the angle β between the wave vector of the light and the transition dipole moment (see Figure 4). The absorption maximum lies at E_T only if $\beta = 90°$, that is, for normal incidence of light the dipole moment must be parallel to the crystal face. Otherwise, for decreasing β the absorption maximum shifts to higher energy till the energy of the longitudinal exciton is reached. Simultaneously, the absorption intensity decreases, as the transition dipole moment is projected onto the crystal face under consideration. This extraordinary behavior can be explained by excitation of an electromagnetic wave, the polariton, having mixed longitudinal–transverse polarization.

The direct observation of polariton absorption requires a layer thickness of about 80 nm (which depends on the penetration depth of the light), a single crystallike arrangement of the molecules over a large area, and the option to change the molecule inclination relative to the layer plane. Such layers could not be prepared by common techniques such as spin-coating, evaporation, Langmuir–Blodgett (LB) techniques, or epitaxy,[14] but were achieved by a new method (thin layer aggregation, TLA)[11] for salts of the dye 1,7-bis(dimethylamino)heptamethine cation BDH^+ (Scheme 1).



Scheme 1. The streptopolymethine dye 1,7-bis(dimethylamino)heptamethine perchlorate ($BDH^+ClO_4^-$).

In different crystals of this dye the values of both M and N are especially high, resulting in extraordinarily strong splittings with ΔE up to 14000 cm^{-1}.[10] The TLA method is based on the aggregation/crystallization of dye molecules in thin amorphous layers of an undercooled melt of $BDH^+ClO_4^-$. The originally prepared BDH^+ layers showed a high microscopical disorder, which prevented the observation of color variation by polaritons.[11] By using higher temperatures for the aggregation process, homogeneous molecule orientation and a variation of molecule inclination was achieved.

Amorphous layers of $BDH^+ClO_4^-$ were obtained by fast spin-coating of $BDH^+ClO_4^-$ solutions in acetone on quartz substrates.[11] We chose a layer thickness of approximately 80 nm, which yielded a maximal optical density of 2.5 in the absorption bands. After an incubation time of some minutes a few nuclei were formed in the layer. These grew radially to large spherulites with diameters up to 20 mm. The assembled structures exhibit strong dichroism. All microphotographs and spectroscopic investigations were therefore performed with linearly polarized light (Figure 1), which avoids the superposition of the two transition moments, excludes pleochroism effects,[12] and gives the genuine dichroic colors due to light absorption. In contrast, similar pictures of liquid crystals, taken between crossed polarizers, only shows apparent colors due to birefringence. Interference effects could be excluded as origin of the observed colors. Variation of layer thickness changed only the intensity and not the position of the absorption band. Furthermore, interference at layers of 80 nm can appear only in case of very high refractive indices

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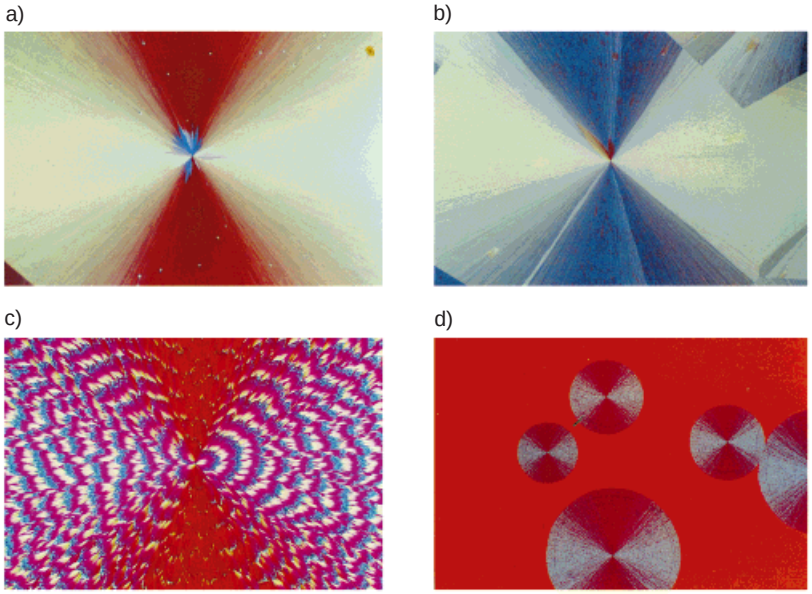

Figure 1. Microphotographs of $BDH^+ClO_4^-$ layers, aggregated at different temperatures (picture size $600 \times 900\ \mu m^2$, horizontally polarized light in transmission). a) Aggregation at 110°C, red/colorless region; b) aggregation at 110°C, blue/colorless region; c) aggregation at 88°C; d) aggregation at 20°C; the red layer is the amorphous phase.

n, which could be reached at most in the absorption maximum.

The growth process was performed at different temperatures between 20 and 155°C and at constant absolute air moisture of $12\ g\,m^{-3}$, because moisture also influenced the aggregation process. For that purpose, freshly prepared amorphous layers were transferred to a heating plate having electronically controlled temperature. The growth velocity depends on the temperature and increases from $0.35\ \mu m\,s^{-1}$ at 25°C to about $400\ \mu m\,s^{-1}$ at 140°C. The melting point (155–157°C) of the formed layers is independent of the aggregation temperature, which points to an identical aggregate structure. Four different layer types were obtained within following temperature regions:

1. Thin-layer aggregation at 90–155°C: Aggregation in this temperature interval yields spherulites that exhibit two differently colored layer regions. In light polarized in tangential (T) direction with respect to the aggregate circle (T polarization), one region is red (Figure 1a) and the other one blue (Figure 1b), whereas both are colorless in light polarized in radial (R) direction (R polarization). The polarized UV/Vis spectra were taken with a microspectralphotometer on $4 \times 4\ \mu m^2$ points of the spherulites (Figure 2a). Only for T polarization do they show an absorption band at 574 nm for the red/colorless and at 628 nm for the blue/colorless region. The layer spectra agree well with the dichroic absorption spectra of the $BDH^+ClO_4^-$ single crystal (Figure 2a), calculated from reflection spectra of crystal faces, where $\beta = 90°$.[13] The two absorption bands arise from two molecular directions in the unit cell of the $BDH^+ClO_4^-$ crystal[15]. Interactions between the molecular transition dipole moments lead to two perpendicularly oriented excitonic components m_+ (639 nm, blue) and m_- (591 nm, red; Figure 3).[7, 13] The total transition moment M of the crystal is distributed in the m_+ and m_- component in the ratio 1:2. Thus, the components show a fairly large splitting of $\Delta E_+ = 5400\ cm^{-1}$ and $\Delta E_- = 11\,400\ cm^{-1}$. Because the sensitivity of the solid-state spectra to the molecule arrangement is high,[10] two conclusions could be drawn from the good

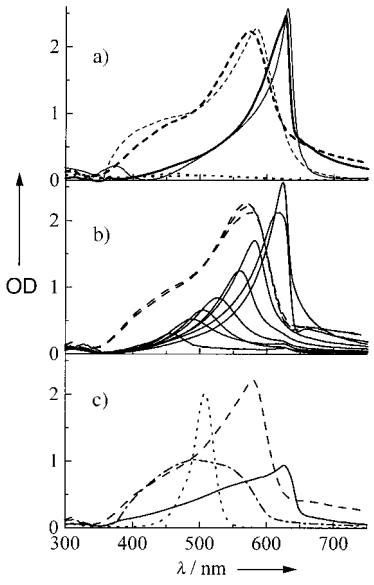

Figure 2. Spectra of optical density OD of $BDH^+ClO_4^-$: a) samples aggregated at 110°C: blue/colorless region (T polarization; bold —); m_+ component of the single crystal[13] (—); red/colorless region (T polarization; bold – – –); m_- component of the single crystal (– – –); both layer regions (R polarization; ···); b) sample aggregated at 88°C: spectra from eight successive points within one color period: R polarization (—), T polarization (– – –; due to the similarity of the spectra only three are shown); c) BDH^+ monomer in methanol (···); amorphous layer (–·–·–); sample aggregated at 20°C: R polarization (—), T polarization (– – –).

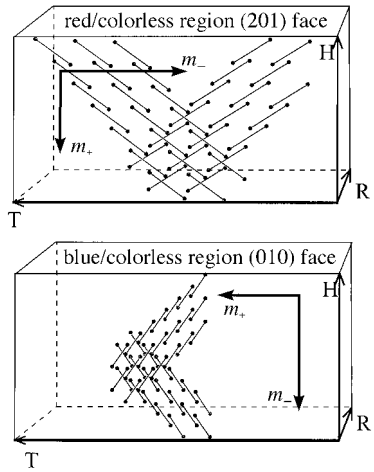

Figure 3. Orientation of BDH^+ cations (sketched as dumbbells) and the transition moments of the m_+ and m_- component in the red/colorless and blue/colorless region of the layer aggregated at 110°C; H: layer height, T: tangential direction, R: radial and growth direction (derived by spectroscopic data and X-ray structure analysis).[15]

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Table 1. Spectroscopic data of the transition dipole components m_+ and m_- of $BDH^+ClO_4^-$ in single crystals[10] and in the ordered layer.

	$\lambda(m_+)$ transverse [nm]	$\lambda(m_+)$ longitudinal [nm]	$\lambda(m_-)$ transverse [nm]	$\lambda(m_-)$ longitudinal [nm]	Ratio of oscillator strengths f_+/f_-	M.p. [°C]
layer	628	430	574	345[a]	0.456	155–157
crystal	639	475	591	353	0.464	176–178

[a] Not exactly determinable.

agreement of layer and crystal spectra (Table 1). Firstly, layer and crystal structure are similar, although deviations in melting point (of 21 °) and absorption wavelength (of 11 and 17 nm) indicate small differences, which however, might be caused by the small layer thickness, too. Secondly, the layers virtually have the long- and short-range order of a single crystal within large regions. This is remarkable, because such high degree of order is hardly achievable by common layer preparation methods.[1, 14, 18] The apparently higher layer absorption in the long-wavelength region is caused by the layer reflection (Figure 2a). For both layer regions, the arrangement of BDH^+ was derived from the spectroscopic data and the known single-crystal structure.[15] As only one absorption band exists in each region, one excitonic component has to be perpendicular to the layer plane ($\beta = 0°$, Figure 3). Due to the orthogonality of m_+ and m_-, the other component is parallel to the surface ($\beta = 90°$). This is fulfilled for the blue/colorless region in the case of the (010) crystal face where only m_+ is observable and for the red/colorless region in the case of an approximate (201) face, where only m_- absorbs light. None of these crystal faces were formed by crystal growth of $BDH^+ClO_4^-$ in solution. It is not quite clear yet which factors in the TLA process influence the ratio between both regions.

2. TLA at temperatures between 40 and 90°C: Layers formed at these temperatures exhibit in growth direction for R polarization a periodical variation of color in the order colorless, yellow, orange, red, violet and blue (Figure 1c). For T polarization, the color always remains red. The period length increases from 2 μm at a growth temperature of 40°C to approximately 100 μm at 88°C and becomes infinite for the red/colorless region (Figure 1a) above 90°C. The polarized absorption spectra were taken step by step in growth direction within one period. While T polarization yielded almost the same absorption spectrum for every point with a maximum at 574 nm, for R polarization the absorption bands shifted from 435 nm to 628 nm (Figure 2b). Neither the aggregate structure nor the layer thickness changed remarkably within the period as indicated by the same melting point, the almost constant absorption spectrum for T polarization, and a nearly flat surface profile measured by atomic force microscopy.[16] Therefore, the observed color variation can only be caused by directional dispersion of polaritons. A successive widening of the angle β_+ between m_+ and the layer normal increases the absorption intensity and shifts the absorption maximum from $E_L = 430$ nm at $\beta_+ \approx 0°$ to $E_T = 628$ nm at $\beta_+ = 90°$ according to the polariton model (Figure 4).[8, 9] The m_- component always lies in T direction ($\beta_- = 90°$) yielding the unchanged absorption spectra at 574 nm (Figure 2b). The reason for the periodical change of orientation might be mechanical stress

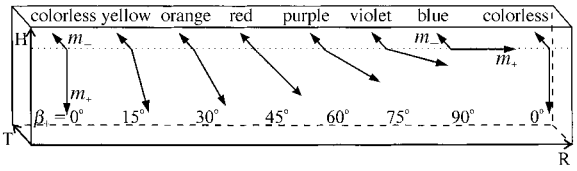

Figure 4. Orientation of the transition moments m_+ and m_- within one color period of a layer aggregated at 88°C; H: layer height, T: tangential direction, R: radial and growth direction; β_+: angle between m_+ component and face normal.

in the layer, possibly caused by different growth rates on the interfaces or by the deviation between growth and aggregate direction. Similar phenomena are known from self-organization processes, such as the crystal growth in undercooled melts of salol.[17]

3. TLA below 40°C: Aggregation at strong undercooling leads to period lengths below the spatial resolution of the microscope. Consequently, an unusually broad spectrum was measured for R polarization,[11] which arises from the superposition of all spectra within one period (Figure 2c). In contrast to spherulites prepared at higher temperatures the positions of both dichroic absorption bands depend sensitively on the humidity and other parameters and can vary by up to 15 nm.[11] Spectra of dyes are generally broader in thin layers than in solution. As possible molecular explanations for this phenomenon $\pi-\pi$ interactions, charge transfer transitions and light scattering are discussed.[1, 18] Our results show that polariton effects, especially at strong absorbing dyes, also have to be taken into account. Not only do different orientations of crystallites lead to the superposition of different spectra, but even in case of a single-crystal arrangement the absorption bands of dye J aggregates are broadened (Figure 2a) as a result of dramatic changes of the refractive index n within the energy region ΔE.[13] If the refractive index function is taken into account by calculation, the aggregate absorption in layers is as narrow as the J band in solution.[9, 10]

The results prove for the first time the strong directional dependence of absorption energy of excitonic polaritons in transparent dye layers. The observation of this phenomenon was possible because of the nearly single crystallike deposition of dye aggregates in thin layers and to the variation of the molecule's inclination relative to the substrate in the TLA process. The findings offer an important engineering opportunity for tuning the absorption behavior of thin dye layers without changing the thickness, the molecular structure, the crystal structure, or the substrate.

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A Chemosensor for Citrate in Beverages**

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The high specificity of antibodies and enzymes makes them the current tools of choice for sensing and quantitating structurally complex molecules in a mixture of analytes. However, the sophistication of rationally designed and synthetic receptors is now high enough that their use as sensors is realistic.[1] Neutral and cationic analytes such as sugars,[2] metal ions,[3] creatinine,[4] and arenes,[5] as well as a few anions,[6] have been targeted.[7] Until now, the vast majority of synthetic sensors have not demonstrated the sensitivity and selectivity necessary to analyze solutions in which contaminates are competitive. For example, almost all past studies focused upon the analysis of solutions of analyte alone. Herein, we demonstrate that a chemosensor, a synthetic receptor coupled with a signaling element,[8] can be used to analyze for a specific compound in a multicomponent aqueous solution in a manner similar to that of antibody-based biosensors in immunoassays.

Immunoassays are facile because a simple competition approach is most often employed.[9] When the solution to be analyzed, which contains an unlabeled antigen, is added to the receptor, a labeled antigen is released and hence a signal change results. Such competition assays have not been widely exploited with synthetic receptors. As long as the chemosensor has useful selectivity for its analyte within an application, results comparable to those obtained with antibodies would be expected. Further, immunoassays typically rely on fluorescence spectroscopy.[10] Fluorescence emission appears at longer wavelengths than excitation, and hence the background signal is typically low, resulting in very high sensitivity.[11]

Considering antibody analysis methods and the current state of the art using synthetic receptors, we had two goals in mind. The first was to demonstrate that synthetic receptors can be selective enough for their analytes to sense and quantitate them in competitive media. We defined competitive media as water that is relatively high in ionic strength and other contaminants. Our second goal was to show that a competition assay could be quite readily applied to any synthetic receptor. For accomplishing these goals, citrate seemed to be an ideal analyte.[12]

Since at neutral pH citrate has a charge of minus three, it is quite distinctive from other possible interfering species. Hence, a receptor complementary to citrate in both charge and hydrogen bonding ability would likely not suffer interference from many other competing analytes, such as salts, mono- and dicarboxylic acids, and sugars.

We recently reported that receptor **1** is selective for the recognition of citrate in water over di- and monocarboxylates, phosphates, sugars, and simple salts.[13a] The receptor binds citrate better than simple dicarboxylic acids and monocarboxylic acids by factors of approximately 35 and 700, respectively.[13b] The receptor consists of three guanidinium groups for hydrogen bonding and charge pairing[14] with citrate.[13c] The steric gearing imparted by ethyl groups on the 2-, 4-, and 6-positions[15] ensures that the guanidinium moieties are preorganized on the same face of the benzene ring. This conformation yields several hydrogen bonds and three sets of ionic interactions in the host – guest complex (as shown in Scheme 1), leading to good binding in water ($K_a = 6.8 \times 10^3\,\text{M}^{-1}$).

Our assay for citrate employed an ensemble of 5-carboxyfluorescein (**2**, a fluorescent probe) and **1**. Carboxyfluorescein **2** was chosen since it is commercially available, it has two carboxylates for binding with host **1**, and only very small quantities proved to be necessary (typically 5 to 18 μM). The absorbance/fluorescence of probe **2** is very sensitive to pH changes, and therefore a buffer to maintain constant pH was necessary in the sensing experiments.[16] It is well known that any charged buffer will act as a competitor for the binding

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