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Large Electric-Field Effects on the Dipolar Aggregation of Merocyanine Dyes**

Rüdiger Wortmann, Ulrich Rösch, Mesfin Redi-Abshiro, and Frank Würthner**

Dedicated to Professor Wolfgang Liptay on the occasion of his 75th birthday

The effects of external electric fields on macroscopic systems, including phases with chemical equilibria, is of fundamental interest in chemical thermodynamics.[1] General thermodynamic equations for dielectrics of variable composition in external electric fields have been developed by Koenig[2] based on the work by Guggenheim.[3] In addition, the dynamic effects of pulsed electric fields were investigated and applied in studies of fast reaction kinetics and dielectric relaxation phenomena related to chemical rate processes.[4–6] The influence of biological membrane potentials on the dimerization of a fluorescent dye was studied by Webb and Dragsten.[7] Liptay et al. investigated electric-field effects on the formation of charge transfer (CT) complexes.[8] Herein, we report the observation of an unusually strong electric-field effect on the dimerization equilibrium of the strongly dipolar merocyanine dye **1**.
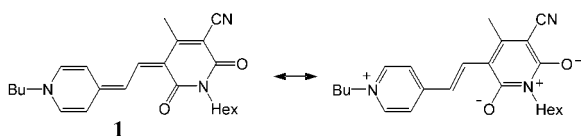
The electronic structure of merocyanine dyes, such as **1**, with electron-donating and electron-accepting groups is often described in terms of a two-state valence-bond model. This simple model assumes resonance of neutral and zwitterionic structures and provides a useful qualitative interpretation of phenomena, such as solvatochromism and bond-length alternation.[9] The electronic structure of the dyes may vary

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between the "neutral" form **1** (left) and the "zwitterionic" form (right). Dyes with equal contributions of the neutral and zwitterionic forms are in the "cyanine-limit". The two-level valence-bond model has been discussed critically at a higher level of theory.[10]

Merocyanine dyes have been intensely studied in the quest for promising chromophores for electrooptically active materials, such as electrooptical and photorefractive polymers.[11] It has been demonstrated that the photorefractive figure-of-merit of the dyes is maximized close to the cyanine limit and chromophores optimized according to this principle have been presented.[12] As a result of the zwitterionic character of the dyes near to and beyond the cyanine limit their dipole moments are very large which may lead to dimer formation by dipolar aggregation in the polymer and in liquid solution.[13]

Dimer formation is especially pronounced for dye **1** and can be observed even in dilute dioxane solution. The absorption spectrum, Figure 1, shows two concentration-dependent bands with a clear isobestic point over a broad
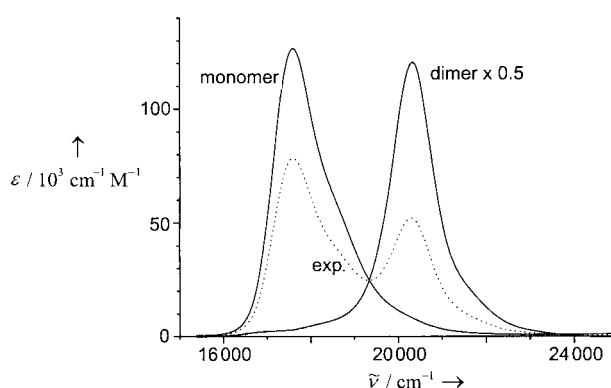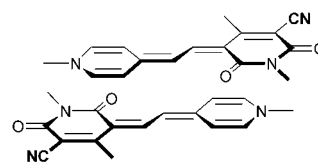

Figure 1. Optical absorption spectrum (·····, "exp") of a solution of **1** in dioxane ($c_{0M} = 5.16 \times 10^{-6}$ M, $T = 298$ K) and derived spectra of pure monomer and dimer (——).

concentration range. The concentration dependence of the bands indicates an equilibrium $2\,M \rightleftharpoons D$ between the only two species, monomeric (M) and dimeric (D) dye units. The intensity of the monomer band decreases with increasing concentration while that of the dimer increases. The dimer band is hypsochromically shifted with respect to the monomer band as is typical for H-type aggregates. This effect is attributed to an (almost) antiparallel ordering of the dipolar dye molecules (Scheme 1).[13]

A quantitative analysis of the concentration dependence by nonlinear regression allows deconvolution of the optical

Scheme 1.

absorption into the pure monomer and dimer spectra (Figure 1). This analysis is based on a dimerization model[13,14] according to Equations (1) and (2), where K_c is the dimerization constant, c_M and c_D the concentrations of monomer and dimer, respectively, and c_{0M} the initial concentration of the monomer.

$$K_c = \frac{c_D}{c_M^2} \tag{1}$$

$$c_M = \frac{\sqrt{8\,K_c\,c_{0M}+1}-1}{4\,K_c} \tag{2}$$

The extinction coefficient a of the dye solutions may be expressed as a sum over the monomer and dimer contributions (K = M, D) [Eq. (3)] where ε_M and ε_D are the molar decadic absorption coefficients of monomer and dimer, respectively. The regression yields the spectra of the pure monomer and dimer as well as the value of $K_c = 112\,000\,\text{M}^{-1}$ for the aggregation constant in dioxane at 298 K (Figure 1).

$$a = \sum_K \varepsilon_K\,c_K \tag{3}$$

An interesting question is now whether and to which extend such an aggregation can be influenced by internal or external electric fields. Proof of such an influence would be important for the optimization of photorefractive polymers. Such materials operate at very high external electric fields and dimer formation in them has already been demonstrated.[12] To directly demonstrate the influence of electric fields on the aggregation equilibrium of **1** we employed the very sensitive method of electrooptical absorption measurements (EOAM).[15]

In EOAM one detects the influence of an external electric field on the decadic extinction coefficient $a = \varepsilon c$ of a dilute solution of the dye with a molar decadic extinction coefficient ε and concentration c. The measurements are carried out for two polarizations of the incident light (parallel ($\phi = 0°$) and perpendicular ($\phi = 90°$) to the applied field) and for several wavenumbers $\tilde{\nu}$ within the absorption band. The effect of the electric field on the extinction coefficient may be described to second order in the field E by Equation (4) which represents essentially the relative change of the optical absorption induced by the field.[15]

$$L(\phi,\tilde{\nu}) = \frac{1}{a}\frac{\partial a}{\partial E^2} \tag{4}$$

Applying external electric fields to dilute solutions of **1** indeed revealed a remarkable effect on the optical absorption. Figure 2 shows the result of an EOAM experiment for parallel polarization ($\phi = 0°$). The extinction coefficient a of the solution is clearly reduced in the region of the dimer band while it is increased in the monomer region.

To quantitatively analyze this result both the field dependence of the molar extinction coefficient ε_K and the field dependence of the equilibrium concentrations c_K of monomer and dimer (K = M, D) must be taken into account [Eq. (5)].
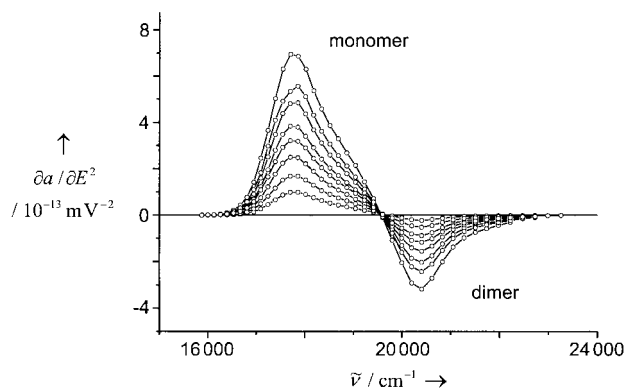

Figure 2. Electric-field effect on the extinction coefficient of solutions of **1** in dioxane at various concentrations ($c_{0M} = 1.05, 1.88, 2.93, 3.69, 4.70, 6.11, 7.62, 9.42 \times 10^{-6}\,\text{M}$; $T = 298$ K; $\phi = 0°$).

$$\frac{\partial a}{\partial E^2} = \sum_K \left(c_K \frac{\partial \varepsilon_K}{\partial E^2} + \varepsilon_K \frac{\partial c_K}{\partial E^2} \right) \tag{5}$$

The field derivative of ε_K in Equation (5) may be described by the theory of electrochromism developed by Liptay.[15] For dipolar molecules the main contributions result from the orientation effect caused by partial alignment of dipolar dye molecules and the band-shift effect caused by charge redistribution (dipole moment change)[16] upon excitation. Large electrochromic signals are expected only for the strongly dipolar monomer while those of the dimer should be weak because of the small dipole moment of the (nearly) antiparallel arrangement of the monomer subunits. Multilinear regression of the EOAM spectrum $L\varepsilon/\tilde{\nu}$ based on the optical absorption spectrum $\varepsilon/\tilde{\nu}$ and its first and second derivative yields a set of six coefficients[15] of which usually only three (E, F, and G) are significant in case of dipolar molecules. These coefficients may be approximated here as Equations (6) and (7)[11] where μ_g is the dipole of the electronic ground state, $\Delta\mu$ the change of the dipole upon excitation to the Franck–Condon (FC) excited state, α the angle between the transition dipole moment and the ground state dipole moment, k_B the Boltzmann constant, f_0 a static local field factor and T the temperature.

$$E = f_0^2\mu_g^2(3\cos^2\alpha-1)/(k_B\,T)^2 \tag{6}$$

$$F = G = f_0^2\mu_g\,\Delta\mu\cos\alpha/(k_B\,T) \tag{7}$$

In Equations (6) and (7) the transition dipole moment and the dipole change are assumed to be parallel, which is usually valid for intense CT bands in elongated donor–acceptor-substituted π systems.[11] Coefficients F and G are equal in this approximation; f_0 is approximated by the Lorentz factor in this case.

The field derivative of the equilibrium concentrations c_K in Equation (5) may be described by the theory of Koenig.[2] Taking local field factors into account gives Equation (8) where ν_K are the stoichiometric coefficients (for the dimerization reaction: $\nu_M = -2$ and $\nu_D = 1$).

$$\left(\frac{\partial \ln K_c}{\partial E}\right)_{p,T} = \frac{f_0^2 E}{3 k_B^2 T^2} \sum_K \nu_K \mu_{gK}^2 \tag{8}$$

According to Equation (8) the driving force for the shift of chemical equilibria by external electric fields is the stabilization of dipolar species in the field. Neglecting the small dipole μ_{gD} of the dimer gives with Equations (1) and (2) for the relative field dependencies of the concentrations of monomer and dimer to second order in the applied field, Equations (9) and (10).

$$\frac{1}{c_M}\frac{\partial c_M^E}{\partial E^2} = \frac{c_{0M}-c_M}{(2c_{0M}-c_M)}\frac{f_0^2 \mu_{gM}^2}{3 k_B^2 T^2} \tag{9}$$

$$\frac{1}{c_D}\frac{\partial c_D^E}{\partial E^2} = -\frac{c_M}{(2c_{0M}-c_M)}\frac{f_0^2 \mu_{gM}^2}{3 k_B^2 T^2} \tag{10}$$

These equations suggest that the external field increases the monomer concentration at the expense of the dimer concentration.

Figure 3 shows the result of the band-shape analysis of the EOAM spectrum taking the effects on the absorption coefficient ε_K (Equations (6) and (7)) and the equilibrium concentrations c_K (Equations (9) and (10)) into account. The regression was based on the precisely derived spectra of the pure monomer and dimer (Figure 1) and their first deriva-
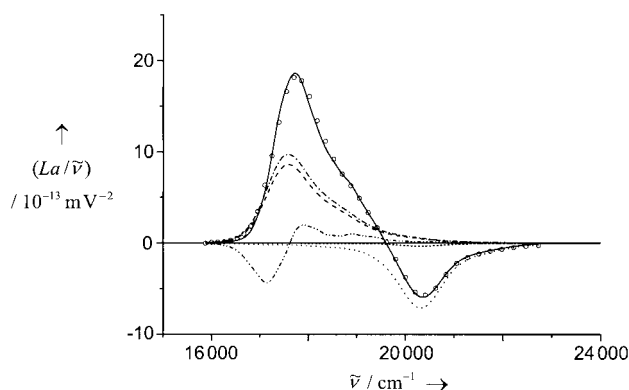

Figure 3. Band-shape analysis of the electrooptical absorption spectrum of a solution of **1** in dioxane ($c_{0M} = 3.69 \times 10^{-6}$ M; $T = 298$ K; $\phi = 0°$). The Figure shows experimental data points (○) and a multilinear regression curve (——). The spectrum results from superposition of partial contributions arising from electrodichroism of the monomer (–·–·) and dimer (-----), the band shift of the monomer (····), and the field-induced concentration changes of monomer (– – –) and dimer (•••••).

tives. The EOAM experiments were carried out for eight different initial concentrations (see legend of Figure 2). The regression results are listed in Table 1.

The EOAM spectrum of the monomer/dimer band system of **1** in Figure 3 may be interpreted as follows: The strong increase of the optical absorption in the region of the monomer band is mainly a result of the positive electrodichroism [Eq. (6)] caused by alignment of the dipolar

Table 1: Results of concentration-dependent electrooptical absorption measurements on merocyanine dye **1** in dioxane solution ($T = 298$ K).

Parameter	Monomer	Dimer
$E (10^{-20}$ V^{-2} m^2)	81400 ± 1600	-5972 ± 1400
$F (10^{-40}$ C V^{-1} m^2)	-5780 ± 240	–
$G (10^{-40}$ C V^{-1} m^2)	-5056 ± 240	–
$\mu_g (10^{-30}$ C m)	59 ± 1[a]	22 ± 3[b]
μ_g[c] $(10^{-30}$ C m)	69 ± 2	–
μ_g[d] $(10^{-30}$ C m)	69 ± 1	–
$\Delta\mu (10^{-30}$ C m)	-27 ± 2	–

[a] from Equation (6) assuming $\alpha = 0°$. [b] From Equation (6) assuming $\alpha = 90°$. [c] From Equation (9). [d] From Equation (10).

monomer molecules in the applied field and of the increase of the monomer concentration [Eq. (9)] caused by field-induced dissociation of the dimer. Remarkably, the latter effect is nearly as large as the electrodichroic one. A smaller contribution in the region of the monomer band is because of the band-shift effect [Eq (7)] caused by the dipole change of the monomer upon electronic excitation. Evaluation of the regression coefficients E, F, and G of the monomer yields its ground-state dipole moment and dipole-moment change. It was assumed in the calculations that the angle in Equations (6) and (7) may be approximated by $\alpha = 0°$ for the monomer. A very large ground-state dipole moment is found for the monomer. The dipole-moment change of the monomer is negative, that is, the absorption band is shifted hypsochromically in the external field. The negative dipole-moment change is consistent with the observed negative solvatochromism[16] of this compound.

The negative electrooptical signal in the spectral region of the dimer band (Figure 3) is almost entirely a result of the field-induced reduction of the dimer concentration. Since the monomer dipole moments tend to cancel each other out in the dimer the dipole moment of the dimer is expected to be small. Indeed the regression yields a only small negative electrodichroic contribution in the dimer band (Figure 3). A dipole moment of only 22×10^{-30} C m may be estimated from the coefficient E of the dimer assuming that the dipole moment is orthogonal to the transition dipole moment, $\alpha = 90°$ in Equation (6). Within experimental error no significant band shift and accordingly no change of the dipole moment of the dimer upon excitation was observed. This result is in accordance with the notion of a strongly coupled exciton state and complete delocalization of the excitation energy.[13]

Figure 4 illustrates the results of the relative field-induced changes of the concentrations c_M and c_D. The experimental data points were fitted by the functional dependencies of Equations (9) and (10). Excellent agreement with the theoretical predictions was found. However, the obtained monomer dipole moment is larger than the one obtained from electrodichroism with Equation (6) (see Table 1). This discrepancy is probably because of a nonvanishing angle α between the transition dipole moment and the ground state dipole moment.

The electric-field strength in EOAM experiments is typically of the order $E = 10^6$ V m^{-1}. According to Equations (9) and (10) such a field shifts the dimerization
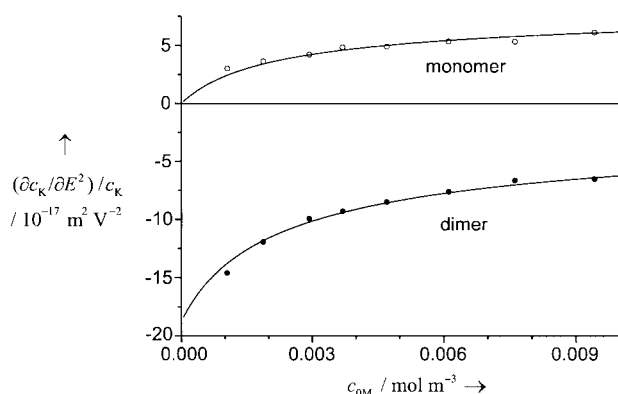
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Figure 4. Relative field dependencies of the monomer and dimer concentrations obtained by electrooptical absorption measurements at various concentrations (see legend of Figure 2, $T = 298$ K). The curves were calculated from Equations (9) and (10) with $\mu_{gM} = 69 \times 10^{-30}$ C m.

Experimental Section

The synthesis of merocyanine dye **1** has been reported elsewhere.[13] Electrooptical absorption measurements were performed as described in ref. [17] The measurements were carried out in the solvent dioxane which was purified and carefully dried by distillation from Na/K under Argon prior to use. Absorbance spectra of the solutions were recorded with a spectrophotometer (Perkin-Elmer Lambda 900).

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equilibrium of **1** by about 0.01% at an equilibrium concentration of $c_M = c_{0M}/2$. This small concentration change requires the use of the lock-in technique (EOAM) for it to be detected. On the other hand, the electric-field strength applied to organic photorefractive or electrooptical polymer materials may reach values of $E = 10^8$ V m^{-1}. The dimerization equilibrium may be shifted by several 10% in such materials leading to substantial effects on the refractive index modulation.

In summary, we investigated the effect of an external electric field on the dipolar aggregation equilibrium of a merocyanine dye by electrooptical absorption measurements. It could be experimentally confirmed that the external field stabilizes the highly dipolar monomeric form relative to the weakly dipolar dimeric form. To our knowledge this is the first quantitative demonstration of an electric-field effect on the dimerization of a merocyanine dye by concentration-dependent electrooptical absorption experiments. Implications of the observed findings on the design of photonic materials containing excitonically coupled dimers have been discussed.

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