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Push–Pull Chromophores

Solvent Effect on Color, Band Shape, and Charge-Density Distribution for Merocyanine Dyes Close to the Cyanine Limit**

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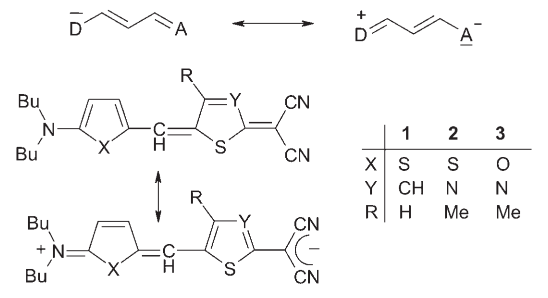
Donor–acceptor-substituted chromophores are the most important class of compounds for elucidating effects of solvent polarity.[1] Among the best-known dyes in this regard are Brooker's dye with positive solvatochromism (χ_R scale) and, in particular, Reichardt's dye with its pronounced negative solvatochromism ($E_T(30)$ scale).[2] Despite the broad application of these and other donor–acceptor chromophores[3] for the elucidation of solvent effects on reaction rates, chemical equilibria, nonlinear optical properties, and so on, accurately explaining their solvatochromic behavior remains the subject of controversial debate.[4] Thus, while it is nowadays well accepted that the magnitude of the energy difference between the ground and excited states of a dipolar dye is significantly influenced by intermolecular solute–solvent interactions,[1] there is no consensus on the extent to which the ground-state molecular structure of the dye is modified by polarization through a polar solvent. Notably, this effect was earlier erroneously considered to be the major contribution to solvatochromism (until the early 1950s; see reference [5]) due to the intuitively appealing notion that dipolar solvents should alter the molecular structure of the dye between two limiting mesomeric structures, a nonpolar and a zwitterionic one (Scheme 1).[6]



	1	2	3
X	S	S	O
Y	CH	N	N
R	H	Me	Me

$$\Psi_g = (1-c^2)^{1/2}\Psi(DA) + c\Psi(D^+A^-)$$

$$\Psi_a = c\Psi(DA) - (1-c^2)^{1/2}\Psi(D^+A^-)$$

Scheme 1. π-charge distribution in donor–acceptor-substituted polymethines according to a simple two-state model. The contribution of the two resonance structures strongly depends on the strength of the electron-donor and electron-acceptor groups. The c^2 parameter allows convenient classification of dyes: $c^2 = 0.5$ describes the resonance situation ("cyanine limit") in which the neutral and zwitterionic resonance forms have equal contributions. For $c^2 < 0.5$ the neutral resonance form dominates the ground state, and for $c^2 > 0.5$ the zwitterionic resonance form dominates the ground state. In the excited state the situation is reversed.

In recent years, this model with interdependent ground and excited states has been widely applied to evaluate donor–acceptor chromophores for nonlinear optics.[7] Although the donor and acceptor strengths and the influence of the π-conjugated bridge have been experimentally addressed in great detail, the impact of the solvent on the π charge-density distribution of dipolar dyes and its contribution to solvatochromism have only been elucidated by indirect experimental methods (e.g., IR frequencies, NMR chemical shifts, hyperpolarizability)[8] or by calculations[9] owing to the difficulty of determining dipole moments in polar media.[10] In this work we focused our attention on solvent-dependent electrooptical absorption (EOA) and UV/Vis measurements to determine the solvent-dependent dipole moments of dye **3** in the ground and excited states.[11]

According to our earlier observations, the series of dyes **1**–**3** (see Scheme 1) shows a remarkable change in optical and dipolar properties in weakly polar ether solvents like 1,4-dioxane[12a] and diethyl ether (thick black lines in Figure 1). Thus, while dye **1** has a polyene-like electronic structure ($c^2 \approx 0.3$[12a]) and a rather broad absorption band, by using a less aromatic and more electron-rich donor heterocycle and a more electron-poor acceptor heterocycle, an electron distribution at the so-called cyanine limit was realized for dye **3**, as indicated by a very sharp cyanine-type absorption band and a value of c^2 close to 0.5.[12a] Dye **2** falls in between the other two dyes in terms of its spectral and dipolar properties (Table 1).

For merocyanine **1**, a continuous shift of the absorption maximum to longer wavelength is observed with increasing solvent polarity for a series of dipolar aprotic solvents (Figure 1, top). Although such positive solvatochromism could be explained by the increasing reaction-field strength of the solvent,[13] the significant alteration of the spectral shape[14] and the saturation behavior (Figure 2) for the more polar solvents are quite unusual.[15] Thus, in the most-polar solvents, acetone and acetonitrile, sharp and intense cyanine-

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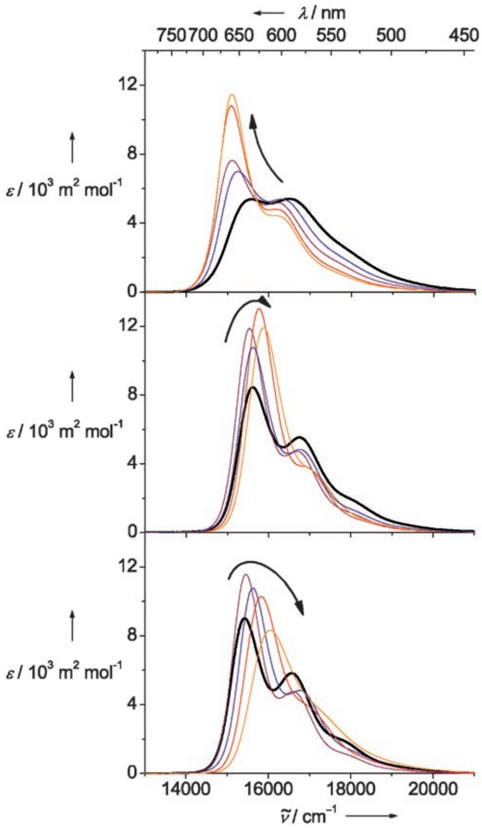

Figure 1. UV/Vis absorption spectra of dyes **1** (top), **2** (middle), and **3** (bottom) in solvents of different polarity at 298 K ($c = 10^{-5}$ M). The thick black line is for the least polar solvent diethyl ether (in 1,4-dioxane the spectra are almost identical), blue line: ethyl acetate, purple line: tetrahydrofuran, red line: acetone, and orange line: acetonitrile. The arrows indicate the spectral shift with increasing solvent polarity.

Table 1: Optical and electrical properties[a] of merocyanine dyes **1**–**3** from UV/Vis and electrooptical absorption spectroscopy.[b]

Dye	Solvent	λ_{max}	ε_{max}	μ_{ag}	μ_g	$\Delta\mu$	c^2[c]
1	DX	647 (606)	5.69	9.8	14.0	5.0 (7.7)	0.307 (0.228)
2	DX	642 (599)	7.83	9.4	17.1	0.7 (2.1)	0.474 (0.409)
3	MCH	649 (603)	4.73	9.3	12.8	1.8 (4.3)	0.414 (0.336)
3	DX	650 (606)	9.62	9.8	16.5	−1.1 (−0.8)	0.541 (0.536)
3	TO	657 (612)	7.60	9.2	15.5	0.3 (0.5)	0.488 (0.478)
3	DEM	648 (604)	7.17	9.5	14.9	0.1 (1.0)	0.494 (0.459)
3	DMM	647 (603)	8.46	9.8	15.5	−0.2 (0.5)	0.507 (0.479)
3	*n*BuE	651 (607)	6.45	9.3	15.2	1.0 (2.0)	0.457 (0.415)
3	$CHCl_3$	652 (608)	12.30	9.8	18.8	−1.8 (1.3)	0.559 (0.559)
3	2MTHF	649 (605)	10.81	9.7	17.7	−1.4 (−1.0)	0.550 (0.540)
3	THF	647 (604)	11.42	9.7	18.6	−2.7 (−2.1)	0.590 (0.593)
3	CH_2Cl_2	646 (604)	12.30	9.8	18.8	−2.6 (−1.7)	0.583 (0.578)

[a] Note that in this table the dipole moments of the dyes in the respective solvent are given, whilst in our earlier work (e.g., reference [12]) pure molecular, that is, "gas-phase", dipole moments were calculated by solvent correction within the approximation of the Onsager continuum model. DX = 1,4-dioxane; MCH = methylcyclohexane; TO = toluene; DEM = diethoxymethane; DMM = dimethoxymethane; *n*BuE = di-*n*-butyl ether; 2MTHF = 2-methyltetrahydrofuran; THF = tetrahydrofuran. 1st and (2nd) absorption maxima: λ_{max}/nm; molar extinction coefficient: $\varepsilon_{max}/10^3\ m^2\,mol^{-1}$; transition dipole moment of the whole CT band: μ_{ag}/D; ground- and excited-state dipole moment: μ_g and μ_a/D; dipole difference: $\Delta\mu = \mu_a - \mu_g$. [b] $T = 298$ K. Multilinear fittings were performed separately for the long- (1st band) and the short-wavelength peaks (in parentheses, 2nd band). [c] For the calculation of c^2 [Eq. (1)] from the vibronic transitions, a Gaussian fitting of the CT band was done in order to obtain μ_{ag} of each single vibronic band.

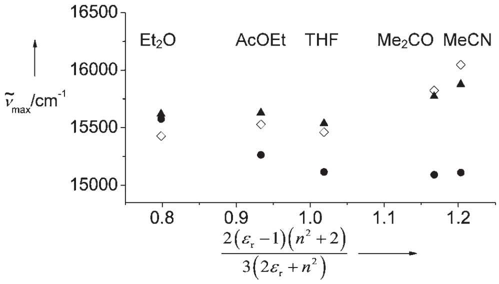

Figure 2. Position of the UV/Vis absorption maxima for dyes **1** (●), **2** (▲), and **3** (◇) against the solvent-dependent term of the Onsager reaction-field factor for polarizable dipoles.

type absorption bands are observed that indicate the absence of bond-length alternation on excitation from the ground to the electronically excited state and, accordingly, a c^2 value close to 0.5.

If such pronounced polarization effects are exerted on the polyene-type dye **1** ($c^2 = 0.3$ in 1,4-dioxane) by polar solvents, it is to be expected that the more dipolar dyes **2** and **3** can be polarized significantly beyond the cyanine limit into the zwitterionic regime ($c^2 > 0.5$).[16] Such behavior is indeed evident from the solvent-dependent spectra (Figure 1) and wavenumber maxima (Figure 2) of these two dyes. Thus, with increasing solvent polarity both dyes show first a bathochromic shift of their absorption maxima that is inverted to a hypsochromic shift for the most-polar solvents. As a common feature for all three dyes the most-bathochromically shifted spectra always exhibit the characteristic band shape of a cyanine dye, a situation that is reached in acetonitrile ($\varepsilon_r = 35.9$) for dye **1**, in acetone ($\varepsilon_r = 20.56$) for dye **2**, and in THF ($\varepsilon_r = 7.58$) for dye **3**.

Notably, similar solvent-dependent changes of UV/Vis spectra were found for other merocyanine dyes,[5] and such unusual changes in the vibronic progressions were explained by Scheibe, Daltrozzo, and co-workers in terms of a sensitive change of the potential curves for the ground and excited states by structural variations.[14] However, an unequivocal assignment of the solvent-dependent spectral properties to the respective electron-density distribution requires determination of the dipolar properties in a whole series of solvents of different polarity, which has not been achieved so far. Toward this goal, we selected dye **3** owing to its ideally positioned resonance limit in 1,4-dioxane and carried out an EOA study in a series of ten solvents with polarity ranging from $\varepsilon_r = 2.02$ (methylcyclohexane) to $\varepsilon_r = 8.93$ (dichloromethane).

Figure 3 shows the EOA spectra of dye **3** in di-*n*-butyl ether and THF, and Table 1 collects all data derived from measurements in these and the other solvents.[17] The most obvious feature in both solvents is the pronounced positive electrodichroism (enhanced absorption for light polarized parallel to the electric field ($L\varepsilon\tilde{\nu}^{-1} > 0$) and reduced absorption for light polarized perpendicular to the electric field ($L\varepsilon\tilde{\nu}^{-1} < 0$)) with a nearly solvent-independent distance between the first and second band/shoulder ($\Delta\tilde{\nu} \approx 1100$–$1200\ \mathrm{cm}^{-1}$, see the Supporting Information).

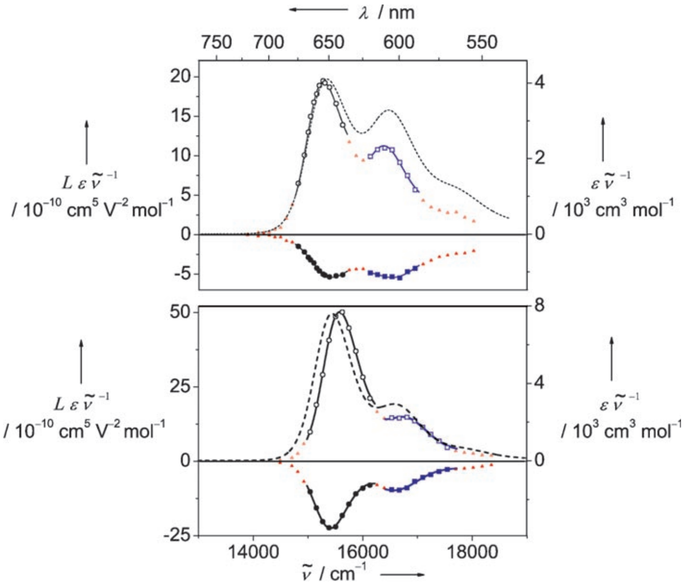

Figure 3. Fitted EOA spectra (solid lines, left scale) at 298 K for merocyanine **3** in di-*n*-butyl ether (top) and THF (bottom). Open symbols show the measured change of absorption for light polarized parallel to the electrical field, filled symbols for light polarized perpendicular to the electrical field. Data marked with black circles and blue squares define the 1st band and 2nd band, respectively. For comparison, the UV/Vis absorption spectra are also shown (dashed lines, right scale).

The most important difference between the spectra in di-*n*-butyl ether and THF is the position of the EOA band for parallel polarized light (open symbols) relative to the UV/Vis absorption band (Figure 3). In di-*n*-butyl ether both bands are almost perfectly superimposed (circles). This absence of a Stark effect is characteristic for a vanishing change of the dipole moment on optical excitation ($c^2 \approx 0.5$). In contrast, in the more polar solvent THF a pronounced negative Stark effect occurs with a shift of the EOA band to higher energy relative to the UV/Vis absorption band, indicative of a less dipolar excited state relative to the ground state($c^2 > 0.5$). For solvents of lower polarity than di-*n*-butyl ether (*n*BuE), such as methylcyclohexane (MCH), the situation is just reversed ($c^2 < 0.5$). Thus, the absorption band is shifted to lower energy in the presence of an electric field as consequence of a sign change of $\Delta\mu$ (see also Supporting Information).

The band-shape analysis of the EOA spectra affords exact values for the dipole moment in the ground state and the dipole-moment change on electronic excitation (Table 1).[10] Quantitative analysis of two vibronic bands constituting the CT transition confirms that the polarization of their transition dipole moments is approximately parallel to the ground-state dipole moment, that is directed along the long axis of the molecule. Whereas the independent fittings of these two bands in the EOA spectra (Figure 3) yielded expectedly an equal ground-state dipole moment, for the corresponding two excited vibronic states different excited state dipole moments are obtained. This is the first time that the variation of the excited-state charge distribution in different vibronic states of merocyanines could be proven by EOA measurements (for details, see the Supporting Information). Due to this difference, the solvent-dependent change of the band structure (Figure 1) can now be traced back to a solvent-dependent change of $\Delta\mu$ and, in turn, to different solvatochromic behavior of the two major vibronic bands (Figure 3 and Supporting Information). From the $\Delta\mu$ values and the transition dipole moments of the single bands, the c^2 value can be calculated for each vibronic band, as well as for the total CT band, according to Equation (1).

$$c^2 = \frac{1}{2}[1 - \Delta\mu(4\mu_{\mathrm{ag}}^2 + \Delta\mu^2)^{-1/2}] \qquad (1)$$

These c^2 values (Table 1) now quantify the above analysis and reveal a significant change of the electronic structure of dye **3** in solvents of different polarity. In the least polar solvent MCH the ground-state dipole moment of 12.8 D increases to give a Franck–Condon (FC) excited state with a dipole moment of 14.6 D (for simplicity, our discussion is now focused on the 0–0 vibronic transition). In contrast, for the more polar solvent THF the dipole moment in the ground state is already 18.6 D, and on optical excitation a decrease of the dipole moment is observed to give an FC excited state with $\mu = 15.9$ D. The respective c^2 values for dye **3** of 0.41 in the aliphatic solvent MCH and 0.59 in THF corroborate the conclusions drawn before from the UV/Vis absorption spectra: In the gas phase and in weakly polar solvents (MCH, *n*BuE, TO) dye **3** is more polyene-like with a higher contribution of the neutral resonance form (Scheme 1), but under the influence of more-polarizing solvents the situation changes to afford a cyanine-type π system (DMM, DEM, etc.), and eventually a more zwitterionic π system (2MTHF, $CHCl_3$, CH_2Cl_2, etc.; Figure 4).

It is gratifying that this solvent-dependent EOA analysis affords a quantitative understanding in terms of the charge-density distribution for the ground and excited states of dye **3** that corroborates the intuitive conclusions drawn from the band shape and solvatochromism of its UV/Vis spectra. In more detail, the pronounced variation of the band shape can be explained by different solvatochromic behavior of the respective vibronic states. Furthermore, it was possible for the first time to unambiguously relate the phenomenon of inverted solvatochromism with increasing solvent polarity (first bathochromic and then hypsochromic shift) to a change

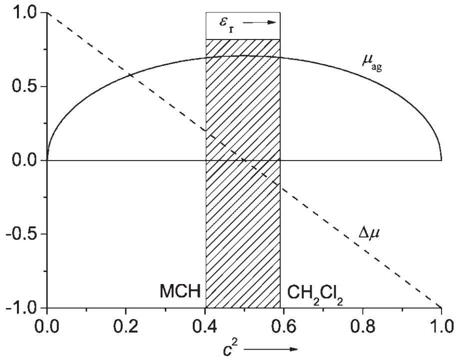

Figure 4. Normalized solvent-dependent variation of μ_{ag} and $\Delta\mu$ of **3** is shown by the hatched box. Curves of μ_{ag} and $\Delta\mu$ were calculated according to a two-center model.[7c]

of the ground-state electronic character of the merocyanine dye from polyene to betaine type, as already suggested a long time ago.[5] Any merocyanine dye with a c^2 value slightly below 0.5 in weakly polar solvents is expected to show inverted solvatochromism. The extent of this effect, however, will strongly depend on the polarizability of the merocyanine dye. For extended polymethine chains, more significant effects are expected. These results not only resolve a long-standing puzzle in the understanding of solvatochromism, but are also of paramount importance for the proper design of merocyanine dyes for electrooptic, photorefractive, and photovoltaic materials, in which strong polarization effects originate in the condensed state.

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[15] There is also a good linear correlation with the empirical π* solvent polarity scale (see reference [1]) for dye **1**.

[16] Based on a single-crystal X-ray analysis for dye **1** (to be published elsewhere) and NMR and molecular modeling studies for dyes **1–3**, a planar X–S *cis* configuration is reasonable for these dyes.

[17] Owing to the very high field strength, such experiments must be carried out with caution and in carefully dried solvents, in particular for the more polar solvents.