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Hydrogen-Bond-Directed Head-to-Tail Orientation of Dipolar Merocyanine Dyes: A Strategy for the Design of Electrooptical Materials**

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Merocyanine dyes are undoubtedly among the best chromophores for nonlinear optical (NLO)^[1] and photorefractive (PR) applications.^[2] For no other π -conjugated systems can the dipole moment μ , polarizability α and hyperpolarizabilities β and γ be better optimized by proper donor–acceptor substitution according to established structure–property relationships.^[1–3] Nevertheless, exploitation of optimized molecular properties at the macroscopic level remains a challenge. For technologically promising polymer composite materials, optimized molecular properties μ , α , β , and γ must be transformed into optimized macroscopic susceptibilities by appropriate orientation of the dipolar dyes by an external electric field.^[4] However, the efficiency of this field-induced poling approach is hampered by the thermodynamically favored antiparallel aggregation of dipolar dyes to give dimers with extinguished dipole moments (Figure 1a).^[5,6] This kind of H-aggregated dimer has been established as the predominant supramolecular species arising from push–pull chromophores^[6] in NLO and PR materials at the required high concentrations (> 20 wt %), while the desirable parallel orientation (Figure 1b) has not been realized to date in a thermodynamically equilibrated system.^[7,8]

Here we introduce a supramolecular approach in which a receptor is employed to orient two merocyanine dyes in the desirable head-to-tail parallel fashion through multiple hydrogen bonding. As we show by electrooptical absorption (EOA) spectroscopy,^[9] collective alignment of such a hydrogen-bonded complex in an electric field affords a markedly improved degree of dye orientation.

To demonstrate the feasibility of the concept outlined in Figure 1c, two merocyanine dyes are required that contain complementary receptor units of sufficient strength to

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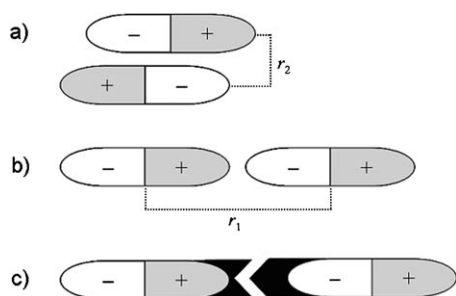
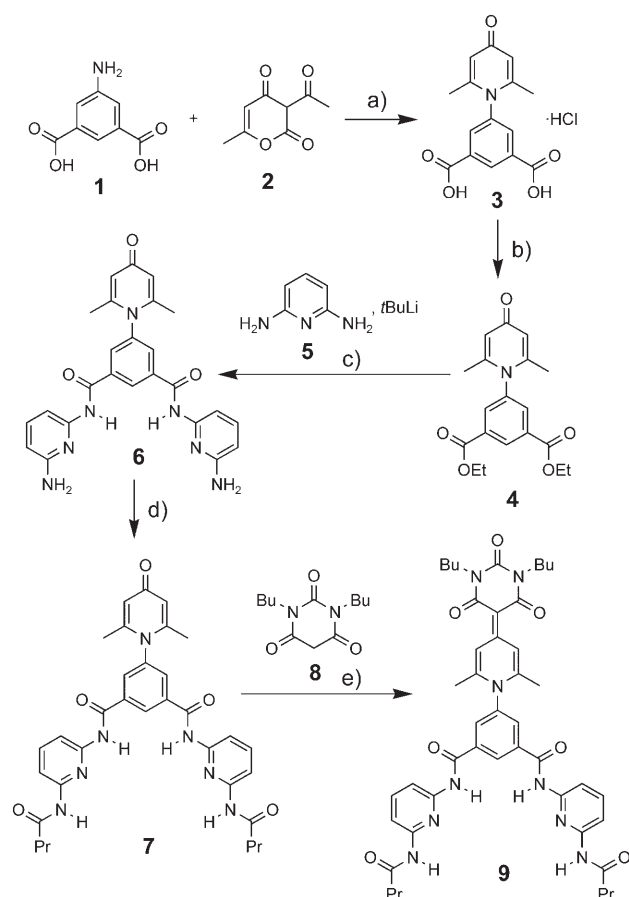


Figure 1. Supramolecular structures formed by self-assembly of dipolar dyes. For typical dyes with $(r_1/r_2) > 2^{1/3}$ the antiparallel arrangement (a) is preferred over the more desirable parallel orientation (b) according to predictions based on electrostatic interactions in the dipole approximation.^[8] A concept for the realization of a parallel arrangement by taking advantage of a supramolecular receptor unit is depicted in (c).

facilitate hydrogen bond directed self-assembly at micromolar concentrations. It appeared to us that an ideal choice might be a combination of the Hamilton receptor^[10] and barbituric acids, because the latter units are present as electron acceptors in many merocyanine dyes. Scheme 1

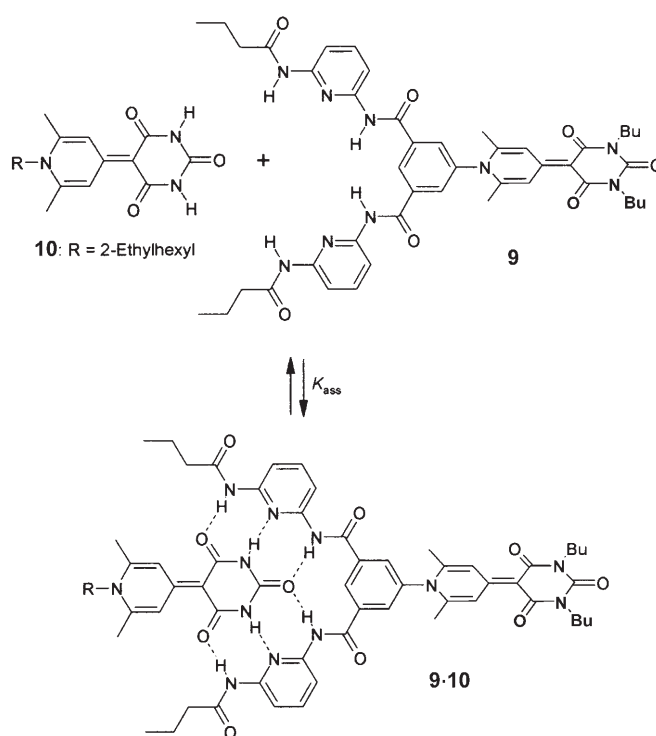


Scheme 1. Synthesis of merocyanine dyes bearing a Hamilton receptor. a) HCl/H₂O, 110 °C, 15 h, 53 %; b) EtOH, H₂SO₄, toluene, reflux, 6 h, 82 %; c) THF, RT, 20 h, 55 %; d) C₃H₇COCl, Et₃N, THF, RT, 20 h, 78 %; e) Ac₂O, AcOH, 105 °C, 4 h, 22 %.

outlines our strategy to connect merocyanine dyes in a rigid fashion to the Hamilton receptor.

In the first step, 5-aminoisophthalic acid (**1**) was treated with dehydroacetic acid **2** to give pyridone hydrochloride **3**,^[11] which was subsequently transformed into its diethyl ester derivative **4**. Reaction of diester **4** with lithiated 2,6-diaminopyridine (**5**) afforded diamide **6**, which can be easily acylated with butanoyl chloride to give pyridone-bearing Hamilton receptor **7**. This pyridone is only moderately reactive towards nucleophiles, but it did react with barbituric acid **8** to provide the desired receptor-functionalized merocyanine **9** in moderate yield.^[12]

Two design features make this dye-appended receptor **9** particularly promising for the realization of a thermodynamically favored parallel arrangement of two dipolar dyes (Scheme 2): 1) The Hamilton receptor is well-positioned at



Scheme 2. Hydrogen bond directed complexation of merocyanine **10** with the Hamilton receptor of merocyanine **9**.

the “head” of one merocyanine dye. Strong and directional intermolecular forces provided by six hydrogen bonds to the “tail” of another merocyanine dye should make the parallel head-to-tail assembly thermodynamically preferable to electrostatically driven antiparallel aggregation; 2) two methyl groups at the *ortho* positions of the dihydropyridine ring result in an almost orthogonal orientation of the two planes of the merocyanine dye and its Hamilton receptor (and to the dye complexed with the Hamilton receptor as well). This geometry is expected to be important in diminishing the propensity towards antiparallel aggregation for the even more dipolar hydrogen-bonded complex **9-10**.

At an equimolar stoichiometry of the Hamilton receptor functionalized merocyanine **9** and complementary barbituric acid merocyanine **10**,^[13] clear evidence for the formation of a 1:1 complex **9·10** (Scheme 2) was obtained by ¹H NMR spectroscopy. Formation of hydrogen bonds became evident from pronounced downfield shifts of all hydrogen-bonded protons, that is, the NH protons of barbituric acid **10** shift from $\delta = 7.30$ to $\delta = 11.93$ ppm in **9·10** (all values in CDCl₃), and the two NH protons of the diacylpyridine units of Hamilton receptor **9** shift from $\delta = 7.55$ and 8.38 ppm to $\delta = 10.52$ and 10.63 ppm, respectively. Owing to the high binding strength provided by six hydrogen bonds, complexation could even be realized in hydrogen-bond acceptor solvents such as dioxane at a millimolar concentration. Notably, saturation of all hydrogen-bond donor and acceptor sites within complex **9·10** resulted in a twisted geometry and remarkable solubility of this highly dipolar complex even in weakly polar solvents such as toluene, in which individual dyes **9** and **10** are poorly soluble.^[14]

To obtain more profound information on the binding strength in solvents that are suitable for EOA measurements (chloroform, dioxane, toluene), titration experiments were performed. Due to dynamic broadening of all signals for hydrogen-bonded NH protons during titration of **10** with **9** (or vice versa), the extent of complexation was assessed from the downfield shift of the protons at the 3,5-positions of the dihydropyridine unit of **10** (Figure 2). Well-defined binding

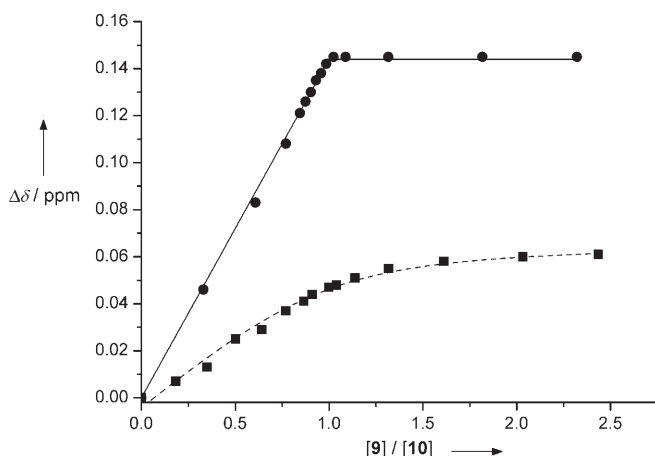


Figure 2. ¹H NMR titration data for protons H-3,5 of merocyanine **10** (1×10^{-3} M) on addition of merocyanine **9** in [D₈]dioxane (■) and CDCl₃ (●) at 298 K, and binding isotherms calculated by nonlinear regression analysis.

isotherms in [D₈]dioxane and CDCl₃ are indicative of 1:1 complex stoichiometry and significantly higher binding strength for the complex in CDCl₃. Nonlinear least-square regression analysis afforded values for the binding constant of $K = (9 \pm 3) \times 10^3 \text{ M}^{-1}$ in [D₈]dioxane and $K > 10^6 \text{ M}^{-1}$ in CDCl₃. Even higher binding constants can be expected in less polar aromatic and aliphatic solvents,^[15] but binding isotherms could not be determined in such solvents by ¹H NMR titration due to insufficient solubility of free dyes **9** and **10**.^[16]

The UV/Vis absorption spectrum of complex **9·10** exhibits two absorption maxima at 380.4 and 389.7 nm which can be attributed to its two components, that is, chromophores **10** ($\lambda = 379.8 \text{ nm}$) and **9** ($\lambda = 396.4 \text{ nm}$) (Figure 3). Another

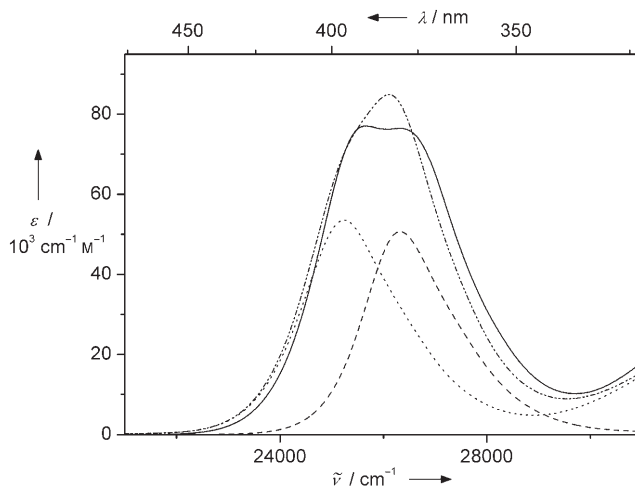


Figure 3. UV/Vis absorption spectra of merocyanines **10** (----) and **9** (.....), and their complex **9·10** (—), as well as the calculated sum of the spectra of **9** and **10** (— · —) in toluene at 298 K (ca. 10^{-6} M).

indication for simple additive behavior of the two dye building blocks is given by the integral absorption I_A , which is proportional to the square of the electric transition dipole moment μ_{ag} . Thus, I_A for complex **9·10** is equal to the sum of the individual parts $I_A(\mathbf{9})$ and $I_A(\mathbf{10})$ (Table 1). Nevertheless, a

Table 1: Dipole moments of the ground (μ_g) and excited states (μ_a) derived from UV/Vis and EOA measurements on **9**, **10**, and **9·10** and integral absorption I_A of their CT transitions in toluene at $T = 298 \text{ K}$.

	9	10	9·10
μ_g [D]	8.5 ± 0.1	10.4 ± 0.1	18.3 ± 0.1
μ_a [D]	4.5 ± 0.4	7.0 ± 0.2	13.6 ± 0.2
I_A [$\text{m}^2 \text{mol}^{-1}$]	552	435	984

closer look at the molar decadic absorption coefficients ϵ reveals a small mutual interaction between the two building blocks. Thus, the maximum of the calculated sum of the spectra of **9** and **10** is higher and the band width is smaller in comparison to the experimental spectrum of the complex (Figure 3). This variation of the band structure can be attributed to hydrogen bond directed polarization of merocyanine **10** and weak exciton coupling between the two chromophores in the complex.

The most sophisticated technique for obtaining reliable information on dipole moments of the ground and excited states is the determination of $L(\varphi, \tilde{\nu})$ [Eq. (1)] of a dilute

$$L(\varphi, \tilde{\nu}) = \frac{\epsilon^E(\varphi, \tilde{\nu}) - \epsilon(\tilde{\nu})}{\epsilon(\tilde{\nu})} \frac{1}{E^2} \quad (1)$$

solution of compounds in an electric field E by EOA

spectroscopy.^[9] The direct measurement of the very small absorption difference $\varepsilon^E(\varphi, \tilde{\nu}) - \varepsilon(\tilde{\nu})$ is carried out with linearly polarized light that is polarized parallel ($\varphi = 0^\circ$) and perpendicular ($\varphi = 90^\circ$) to the applied electric field E (Figure 4);

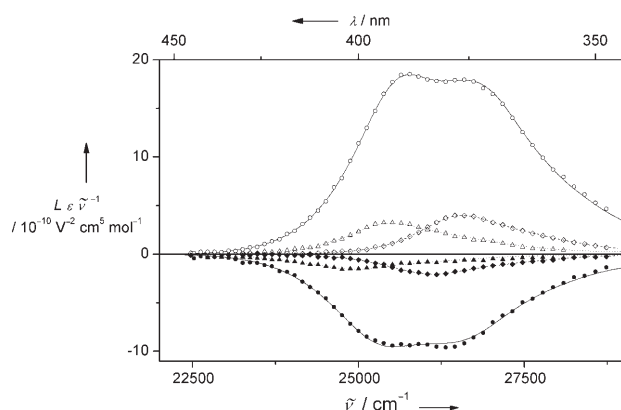


Figure 4. Measured data points of the EOA spectra $L(\varphi)\varepsilon\tilde{\nu}^{-1}$ for $\varphi = 0^\circ$ (Δ , \diamond , \circ) and $\varphi = 90^\circ$ (\blacktriangle , \blacklozenge , \bullet) as well as multilinear regression curves (\cdots , $---$, $—$) of merocyanines **9** (Δ , \blacktriangle , \cdots) and **10** (\diamond , \blacklozenge , $---$) and their complex **9·10** (\circ , \bullet , $---$) in toluene ($T = 298\text{ K}$, $E \approx 4 \times 10^6\text{ V m}^{-1}$, ca. 10^{-6} M).

$\varepsilon^E(\varphi, \tilde{\nu})$ is the molar decadic absorption coefficient of the solution in an externally applied field.

For dyes **9** and **10** as well as complex **9·10**, Figure 4 shows increased absorbance when the light beam is polarized parallel to the direction of the electric field (open symbols) and decreased absorbance when it is polarized perpendicular to the direction of the electric field (filled symbols). Significantly, for complex **9·10** the observed effect is far more pronounced than for the individual dyes. To explain this observation, it should be taken into account that for highly dipolar chromophores like **9** and **10** and the associate **9·10**, $L\varepsilon\tilde{\nu}^{-1}$ is mainly determined by the square of the ground-state dipole moment μ_g . Consequently, the fact that $L\varepsilon\tilde{\nu}^{-1}$ for complex **9·10** is more than four times larger than the sum of the $L\varepsilon\tilde{\nu}^{-1}$ of **9** and **10** (Figure 4) unequivocally confirms cooperative orientation of these dyes in the electric field.

The quantitative evaluation of the optical and electro-optical data provides ground-state dipole moments μ_g , excited-state dipole moments μ_a , and the integral absorption I_A for **9**, **10** and **9·10** (Table 1). These results corroborate the qualitative conclusion for the collective orientation and our predictions for a geometry of **9·10** in which all moments seem to be approximately parallel to each other and to the longest axis of the head-to-tail assembly of two chromophores as well. Also, the excited-state dipole moments μ_a , determined through $L\varepsilon\tilde{\nu}^{-1}$ due to the shift of the absorption band, gives a further hint for cooperative orientation of the two chromophores in complex **9·10**. This will be discussed in detail in a forthcoming paper.

In summary, this work introduces the first supramolecular architecture in which two dipolar dyes are assembled in a head-to-tail fashion by multiple hydrogen bonds with summation of their dipole moments. In this geometry a cooper-

ative alignment of the two dyes in the complex becomes possible in an external electric field with an unprecedented degree of dye alignment for this type of chromophore. We intend to apply this concept to optimized NLO and PR chromophores and to design self-complementary merocyanine dye building blocks that afford supramolecular polymers^[17] with improved nonlinear optical and photorefractive properties.

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