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Synthesis, Optical Properties, and LFER Analysis of Solvent-Dependent Binding Constants of Hamilton-Receptor-Connected Merocyanine Chromophores

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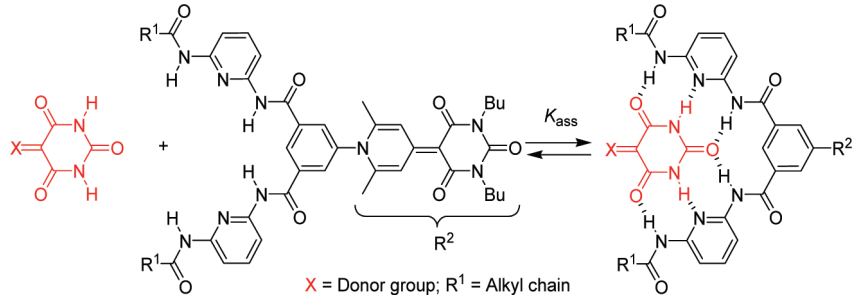
Received May 19, 2008



A merocyanine dye equipped with a Hamilton-receptor unit has been synthesized that enables strong noncovalent binding of other merocyanine dyes bearing barbituric acid acceptor groups by six hydrogen bonds. NMR and UV/vis titration experiments in toluene, chloroform, dichloromethane, dioxane, and THF provide evidence for the formation of 1:1 complexes even in the dipolar solvents. An enhanced binding strength is observed for the more dipolar merocyanine dyes in the head-to-tail assembly structure with binding constants up to $>10^8$ M^{-1} in toluene. In the present bimolecular complexes two merocyanine chromophores are assembled in a head-to-tail fashion that affords increased dipole moments as demanded for efficient electric field induced poling processes in nonlinear optical and photorefractive polymeric hosts. The solvent dependency of the binding constants for various barbituric acid dye−Hamilton receptor complexes as well as a perylene imide−melamine complex reveals linear free energy relationships (LFER) that allow for an estimation of binding constants larger than 10^{12} M^{-1} for Hamilton receptor organized head-to-tail merocyanine bimolecular complexes in aliphatic solvents. It is suggested that such LFER are valuable tools for the estimation of binding constants in solvents where experimental binding constants cannot be determined because of solubility or spectroscopic problems.

Introduction

The strength and directionality of hydrogen bonding is of paramount importance for the folding and assembly of natural macromolecules. Hydrogen bonding has also been amply applied in numerous supramolecular systems to achieve desirable structures with outstanding properties including molecular recognition,[1] supramolecular polymerization,[2] and self-replication.[3] One of the most useful synthetic receptor units was introduced by Chang and Hamilton in 1988,[4] which contains two properly preorganized diacylaminopyridine units for the efficient complexation of barbituric acids by six hydrogen bonds with binding constants of 2×10^4 M^{-1} in chloroform at room temperature. More recently, this receptor unit has been applied as a noncovalent contact between electron-donor and electron-

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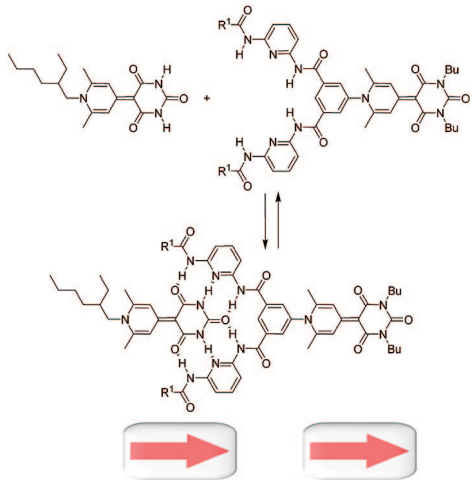
10.1021/jo801083b CCC: $40.75 © 2008 American Chemical Society
Published on Web 07/22/2008

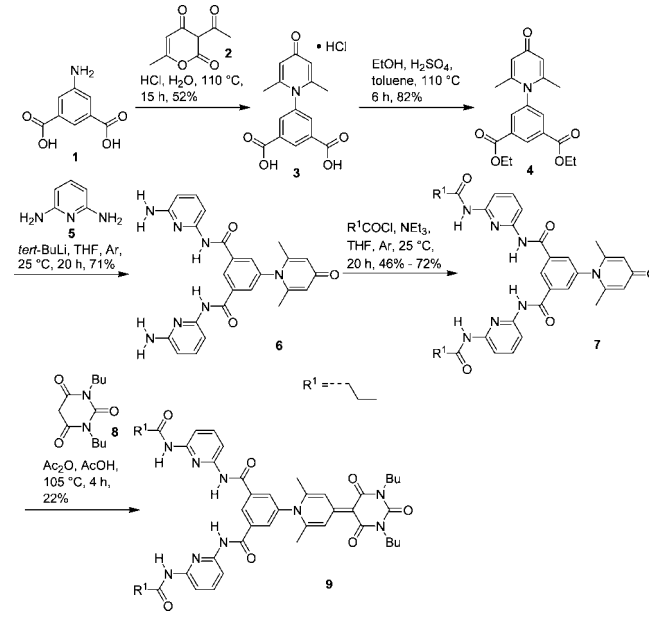
SCHEME 1. Concept for the Hydrogen Bond Directed Formation of Head-to-Tail Bismerocyanine Complexes with Enhanced Dipole Moments[a]



[a] The red arrows represent the orientation of ground state dipole moments of the merocyanine dyes.

acceptor dyes for photoinduced electron-transfer studies,[5] for the design of gelators for organic solvents,[6] for the formation of supramolecular polymers,[7] for the synthesis of supramolecular dendrimers,[8] and for the binding of barbituric acids to surfaces.[9] Furthermore, related systems based on melamines afforded [2 × 2] grids[10] as well as liquid crystals, rosette-type cyclic assemblies, and fluorescent gels bearing merocyanine dyes.[11,12] We became interested in this versatile receptor unit due to its intriguing orientation of two dipolar merocyanines in a bimolecular complex as depicted in Scheme 1. In such a supramolecular arrangement strong 6-fold hydrogen bonding is expected to overcome the otherwise preferred formation of antiparallel dimer aggregates of merocyanine dyes[13] that can hardly be oriented by electric fields owing to vanished dipole moments.[14] In contrast, a bimolecular complex as shown in Scheme 1 provides an increased dipole moment as demonstrated by electrooptical absorption spectroscopy in a recent communication.[15] Such orientation of merocyanine dyes by external electric fields is a highly desirable property for nonlinear optical and photorefractive polymeric composite materials.[16,17] In this paper, we describe the synthesis of this Hamilton-receptor-functionalized merocyanine dye and investigate its complexation properties in detail. In particular, we show that linear free energy relationships (LFER) are given for the solvent-dependent binding constants of these hydrogen-bonded complexes from which valuable information can be deduced.

SCHEME 2. Synthesis of Hamilton-Receptor-Functionalized Merocyanine 9



Results and Discussion

Synthesis. The Hamilton-receptor-functionalized merocyanine dye **9** was synthesized according to the synthetic route outlined in Scheme 2. The key step of this sequence was the synthesis of pyridine hydrochloride **3**. This compound was obtained by the reaction of 5-aminoisophthalic acid **1** with dehydroacetic acid **2** in aqueous hydrochloric acid according to Hünig and Köbrich.[18] It is noteworthy that the initially attempted condensation with 2,6-dimethyl-4-pyrone failed owing to the insufficient nucleophilicity of the aromatic amine. Subsequently, compound **3** was transformed into its diethyl ester derivative **4** by conventional esterification. Amidation of diester **4** with monolithiated 2,6-diaminopyridine afforded diamide **6**, which was acylated with butanoyl chloride or 3,3-dimethylbutanoyl chloride to give the Hamilton-receptor-functionalized pyridone **7** as precursor for the target compound **9**. The Knoevenagel condensation reaction of the CH-acidic barbiturate **8** with pyridone **7** afforded the desired receptor-functionalized merocyanine dye **9**.

The reference receptor **13**, which lacks a merocyanine moiety, was synthesized by acylation of compound **12** with 3,3-

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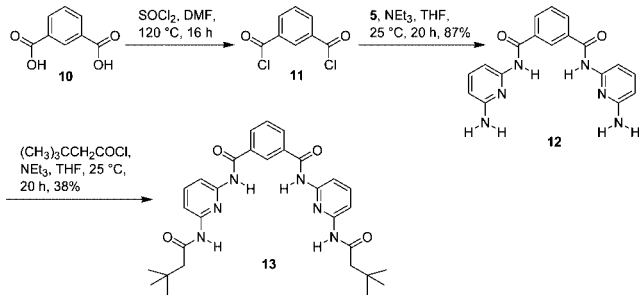
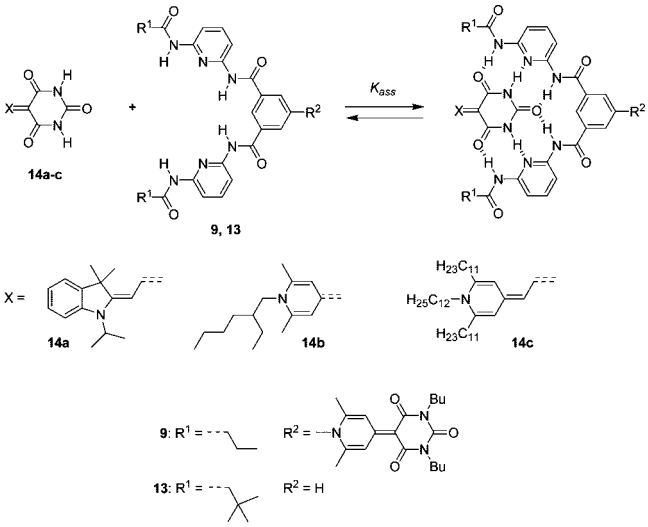
SCHEME 3. Synthesis of the Reference Hamilton Receptor 13



SCHEME 4. Complex Formation between the Hamilton Receptors 9 and 13 and Barbituric Acid Merocyanines 14a−c[a]



[a] X denotes the electron-donor unit.

dimethylbutanoyl chloride, while **12** was prepared according to literature procedures (Scheme 3).[4] Merocyanine dyes with barbituric acid acceptor groups **14a−c** (Scheme 4) applied in this work for the complexation with receptor **9** were prepared by known literature methods.[19] The synthetic details and characterization data for all unknown compounds are given in the Experimental Section.

Solvent-Dependent Properties of Merocyanines 14a−c. Three merocyanine dyes **14a−c** (see Scheme 4) bearing barbituric acid acceptor groups were chosen for the investigation of the hydrogen-bonding strength of the Hamilton receptor equipped with a merocyanine dye in the solvents toluene, chloroform, dichloromethane, dioxane, and THF. The three merocyanines are distinguished, on the one hand, by their color and position of their absorption maxima, i.e., at about 380 (pale yellow, **14b**), 460 (yellow, **14a**), and 510 nm (orange, **14c**) in 1,4-dioxane (Figure 1) and, on the other hand, by the magnitude of their dipole moments μ_g and their dipole moment changes $\Delta\mu$ upon optical excitation (Table 1).[20] As expected for such strongly dipolar dyes, the wavelengths of the absorption maxima vary in solvents of different polarity (Table 1). This solvatochromism can be related primarily to the magnitude of the dipole moment change $\Delta\mu$ upon optical excitation, i.e., a different energetic stabilization of the ground and the excited states of

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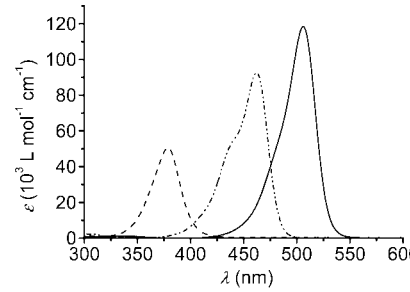

FIGURE 1. UV/vis absorption spectra of the barbituric acid merocyanine dyes **14b** (dashed line), **14a** (dash-dotted line), and **14c** (solid line) in 1,4-dioxane at 298 K.

TABLE 1. Dipole Moments and UV/vis Absorption Data of Merocyanine Dyes 14a−c

dye	μ (D)[a]	$\Delta\mu$ (D)[a]	solvent (ϵ_r)	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})
14a	6.2	+2.4	1,4-dioxane (2.21)	462	92 700
			THF (7.39)	462	80 600
			$CHCl_3$ (4.81)	469	81 800
			CH_2Cl_2 (8.93)	467	81 700
14b	10.1	−3.9	toluene (2.38)	380	50 600
			1,4-dioxane (2.21)	379	50 600
			THF (7.39)	377	49 900
			$CHCl_3$ (4.81)	372	45 900
			CH_2Cl_2 (8.93)	371	46 400
14c	13.5	−4.2	toluene (2.38)	510	110 800
			1,4-dioxane (2.21)	506	109 700
			THF (7.39)	500	103 200
			$CHCl_3$ (4.81)	487	89 000
			CH_2Cl_2 (8.93)	483	87 400

[a] Determined by electrooptical absorption spectroscopy (EOAM) at room temperature in 1,4-dioxane. [See the Experimental Section and ref 20.] "Gas phase" dipole moments have been calculated by a solvent correction within the approximation of Onsager's continuums model.

the solute by the solvent environment.[21] The solvatochromism of dye **14a** with its almost cyanine-like electronic structure (i.e., $\Delta\mu$ close to zero) is rather small, whereas for the more dipolar dyes **14b** and **14c** with $\Delta\mu < 0$ a negative solvatochromism is noted. For merocyanine **14c**, the most pronounced color shift from orange (in the little polar solvent toluene) to yellow (in the polar solvent dichloromethane) is observed. For all dyes, we observe a significant decrease of the absorption coefficient ϵ (Table 1) upon increasing the solvent polarity and a concomitant broadening of the absorption band. This indicates a change of the dyes' electronic structure from a more cyanine-like to a betaine-like chromophore evoked by the polarizing effect of the dipolar and polarizing solvent environment.[22]

Solvent-Dependent Complexation Properties. A significant color change is observed for merocyanine dyes **14a−c** not only upon changing the solvent but also upon complexation with a Hamilton receptor (Figure 2). In the least polar solvent toluene a shift of the absorption maximum from 510 to 498 nm is observed for dye **14c** during the titration with receptor **13**. Thus, the partial exchange of the toluene solvation shell by a 6-fold hydrogen-bonding Hamilton receptor affords the same blue-

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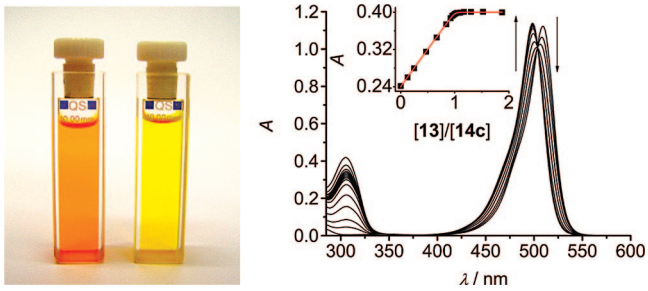


FIGURE 2. Left: Solutions of merocyanine dye **14c** (orange) and a 1:1 mixture of merocyanine dye **14c** and Hamilton receptor **13** (yellow) in 1,4-dioxane at identical concentrations. Right: UV/vis titration of merocyanine dye **14c** at a constant concentration of 1×10^{-5} M with increasing amounts of Hamilton receptor **13** in toluene at 298 K. The inset shows the titration isotherm at a wavelength of 470 nm.

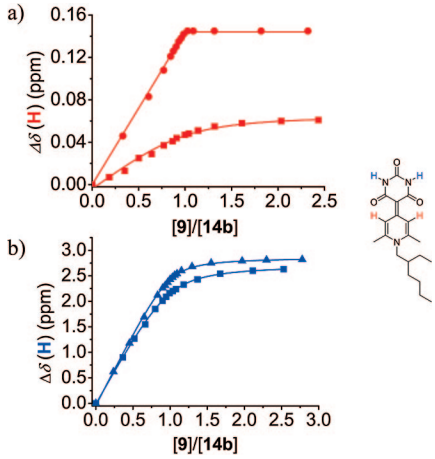


FIGURE 3. ^{1}H NMR titration experiments for the host−guest system **9**:**14b**. Part a shows the change of the chemical shifts for the dihydropyridine protons 3,5 (red) in $CDCl_3$ (circles) and dioxane-d_8 (squares) and part b shows the change of the imide protons (blue) in THF-d_8 (triangles) and dioxane-d_8 (squares) upon addition of increasing amounts of Hamilton-receptor-functionalized merocyanine **9** at 298 K and binding isotherms calculated by nonlinear regression analysis.

shifted absorption band as found for dye **14c** if completely solvated by the polar solvent THF (Table 1). Accordingly, the concomitant shift of the absorption bands upon complexation offers a convenient tool for the determination of the binding constant by UV/vis titration experiments (Scheme 4). In addition, ^{1}H NMR titration is applicable to follow the 1:1 complex formation. Here, the most significant shift was found consistently for the imide protons of the barbituric acid subunit (see Figure S1 in the Supporting Information). However, owing to strong broadening of these proton signals in some solvents (particularly in $CDCl_3$) during the titration, other protons afforded often higher quality binding isotherms despite a less pronounced change of the chemical shift (Figure 3). A reversal of host and guest molecules is possible as well due to notable signal shifts of the amide protons of the Hamilton receptor in ^{1}H NMR titration experiments (Figure S2 in the Supporting Information).

In Table 2 the binding constants for the 1:1 complexes between the Hamilton receptors **9** (with appended merocyanine) and **13** (reference without additional substituent) and the barbituric acid dyes **14a**−**c** in dioxane and in THF are collected. This data set allows us to analyze the substituent effects on the binding strength in three directions: (1) the impact of the electron-donor subunit of the three merocyanine

TABLE 2. Binding Constants K_{ass} (M^{-1}) for the Complexes 13:14a−c and 9:14a−c from ^{1}H NMR Titration Experiments in Dioxane-d_8 and THF-d_8 at 298 K[a]

	13:14		9:14	
	dioxane-d_8	THF-d_8	dioxane-d_8	THF-d_8
14a	310	n.d.	1800	1500
14b	5000[b]	2.2×10^4[b]	1.8×10^4[b]	3.6×10^4[b]
14c	3.1×10^4	1.5×10^5	8.2×10^4	1.3×10^5

[a] From constant host titration experiments in which the Hamilton receptors were the host molecules. The binding constants are the average value from the two amide NH group data sets that were independently analyzed by nonlinear regression analysis. The experimental errors are ca. ±20% for K values <5000 but increase significantly for higher K values where only the order of magnitude can be correctly assigned. [b] From a constant host titration in which **14b** was the host and the shift of the imide and/or 3,5 protons of the dihydropyridine units were analyzed by the nonlinear regression method.

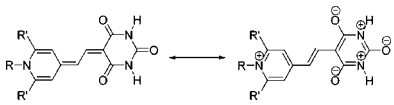
dyes, (2) the impact of a dipolar merocyanine substituent at the Hamilton receptor, and (3) the impact of the solvent. For the latter two aspects, the effects are rather small and hardly above the error range of the experiment. In general, the values in dioxane are a bit smaller than those in THF. On the basis of the significantly higher permittivity value of THF (ϵ_r = 7.39) compared to dioxane (ϵ_r = 2.21) a much larger effect, i.e., much higher binding constants, in dioxane was expected.

Obviously, it is not the dipolarity but the hydrogen-bond acceptor capability of the solvent that counts. Here both solvents are of similar nature and dioxane has even two ether oxygen atoms as hydrogen bond acceptors and THF has only one which may compensate for the smaller dipolarity of this solvent. It is tempting to consider a specific hydrogen-bonding mode for dioxane in which one solvent molecule is chelated between two amide hydrogen bond donating units of the two diacylaminopyridine arms of the Hamilton receptor. But this idea is discarded based on our data analysis by linear free energy relationships (vide infra).

Likewise, only a small difference is found in the comparison of the binding strengths of the two Hamilton receptors **9** and **13**. With one exception (**13**:**14c** in THF; but here the values are prone to significant experimental errors due to their large magnitude leading to very steep binding isotherms in NMR titrations in the millimolar concentration regime), it is always the merocyanine-functionalized Hamilton receptor **9** that exhibits the larger binding strength. Two possible reasons might account for this effect. One is a conformational effect, i.e., the bulky merocyanine substituent at the phenyl group might contribute to a better preorganization of the two arms of the Hamilton receptor (for a discussion of the different conformations of this receptor, see ref 7). The other possibility is an attractive dipole−dipole interaction between the bound barbituric acid dye and the Hamilton-receptor-appended merocyanine dye. Obviously, these effects are, however, not very significant.

On the other hand, a very significant effect is observed for the series of three different barbituric acid dyes **14a**−**c**. For both Hamilton receptors **9** and **13**, a strong increase of the binding constants by about 2 orders of magnitude is observed in the series **14a** → **14b** → **14c**. In the same direction an increased dipolarity of the dyes is given (Table 1) as well as an increased contribution of the zwitterionic resonance structures. Scheme 5 shows the two most extreme resonance structures, i.e., a nonpolar polyene-type structure (the left one) and a strongly dipolar zwitterionic structure with two aromatic heterocycles (the right one). The amazingly high acidity of

SCHEME 5. Two Resonance Structures for Merocyanine 14c



barbituric acids is explained by a considerable contribution of polar bonds as shown in the right structure, and the large dipole moment of dye **14c** provides further evidence for the important zwitterionic contribution to the electronic structure of these dyes. Thus, the observed increase in the binding strength in the series **14a** → **14b** → **14c** can be related to an increasing contribution of zwitterionic resonance structures in the given series. As more charge density is accumulated at the barbituric acid acceptor unit (i.e., at the carbonyl oxygen atoms) the higher is the complexation constant for hydrogen bond directed bimolecular association with the Hamilton receptors **9** and **13**.

To further elucidate the solvent effect on the binding constant between barbituric acid dyes and Hamilton receptors, another series of titration experiments was performed in the solvents dichloromethane, chloroform, and toluene. For these solvents, much higher binding constants are expected because they lack the competing hydrogen bond acceptor capability of dioxane and THF. For higher binding strength than given above (Table 2), lower concentrations of about 10^{-5} M are needed for an accurate determination of the binding constants. Because of the critical signal-to-noise ratio at such low concentrations in NMR spectroscopy, these titration experiments were now carried out by UV/vis spectroscopy. In the case of the reference Hamilton receptor **13**, these experiments were rather straightforward because the absorption bands of this colorless receptor do not interfere with those of guest merocyanines (see Figure 2). Therefore, a comprehensive series of UV/vis titrations was carried out for the two complexes **13**:**14a** and **13**:**14b**. For complex **9**:**14a**, the same experiments were carried out but data analysis here was restricted to that part of the absorption band of host **14a** (λ > 480 nm) that is free from the absorbance of guest **9** as confirmed by the saturation of the signal in the binding isotherm (Figure 4, inset).

The combined data sets in Tables 2 and 3 allow now for a more meaningful comparison of the solvent effects on the binding strength between the Hamilton receptors and the barbituric acid dyes. Thus, while the values in THF and dioxane (dipolar and hydrogen bond acceptor solvents) are pretty similar as well as those in chloroform (weakly dipolar and weak

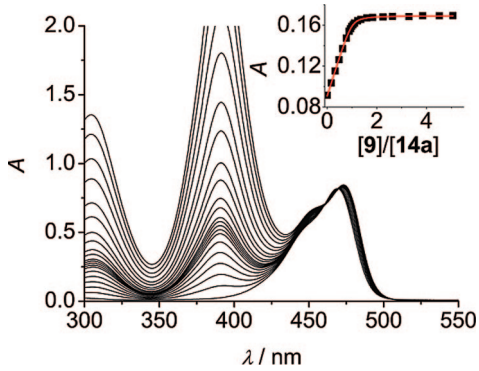


FIGURE 4. UV/vis titration of merocyanine dye **14a** at a constant concentration of 1×10^{-5} M with increasing amounts of receptor-functionalized merocyanine **9** in $CHCl_3$ at 298 K. The inset shows the titration isotherm at a wavelength of 492 nm.

TABLE 3. Binding Constants K_{ass} (M^{-1}) for the Complexes 13:14a,b and 9:14a Determined by UV/Vis Titration Experiments in Chloroform, Dichloromethane, and Toluene at 298 K and Estimated by Linear Free Energy Relationships (LFER) for Methylcyclohexane (MCH) and *n*-Hexane[a]

	$CHCl_3$	CH_2Cl_2	toluene	MCH	*n*-hexane
13:**14a**	8.4×10^5	1.5×10^6	3.8×10^8	1.1×10^{12}	4.0×10^{12}
13:**14b**	1.3×10^6	6.2×10^6	4.7×10^8	1.2×10^{13}	4.9×10^{13}
9:**14a**	5.2×10^6	5.8×10^6	$>2 \times 10^{7b}$	1.2×10^{13c}	4.9×10^{13c}

[a] The experimental errors are ca. ±15% for K values $<1 \times 10^7$ but increase significantly for higher K values where only the order of magnitude can be correctly assigned. [b] This experimental value could only be estimated due to the problems arising from overlapping absorption bands of guest and host molecules and the difficulties encountered by working under very high dilution conditions. [c] In this LFER analysis the estimated value in toluene was not included.

hydrogen bond donor solvent) and dichloromethane (dipolar solvent), we note a more than 2 orders of magnitude higher binding constant in the chlorinated solvents that lack the hydrogen bond acceptor capabilities of the ether solvents. A further increase by about 2 orders of magnitude is observed in toluene that lacks hydrogen-bond donor/acceptor capabilities and dipolarity as well. Thus, specific hydrogen bond based solvation as well as unspecific solvation effects contribute to the measured binding constants. These results are in accordance with the well-known fact that the specific solvation by hydrogen-bond donor and hydrogen-bond acceptor solvents cannot be properly described by macroscopic permittivity functions and has led to the development of empirical multiparameter analyses that include hydrogen-bond donor and hydrogen-bond acceptor strength parameters of the respective solvents.[23] In the field of medicinal chemistry Abraham and co-workers have widely applied such parameters to quantify the binding strength of drugs to biological receptors in QSAR (quantitative structure−activity relationship, Abraham model).[24]

With our available data set it is interesting to analyze the solvent-dependent binding constants for the three available complexes by means of a linear free energy relationship (LFER). As shown in Figure 5a, the solvent-dependent Gibbs free complexation energies $\Delta G^0 = -RT \ln(K_{ass}/M^{-1})$ reveal a quite good LFER ΔG^0(**13**:**14b**) = 1.06 × ΔG^0(**13**:**14a**) with a correlation coefficient of 0.891. The slope of almost unity is in accordance with the nearly identical binding units based on 6-fold hydrogen bonding between two different barbituric acids with the same Hamilton receptor. On the logarithmic energy scale only a small impact of the respective barbituric acid units is found leading to slightly higher ΔG^0 values for **13**:**14b** than for **13**:**14a**, i.e., a slope of slightly larger than unity. Likewise ΔG^0(**9**:**14a**) = 1.13 × ΔG^0(**13**:**14a**) is obtained if the Hamilton receptor unit is exchanged.

Even more interesting, a pretty good LFER is also found with the Gibbs free binding energies for the triple hydrogen bond based bimolecular complex between perylene imide **15** and melamine **16** (Scheme 6) that was investigated by our group a couple of years ago[25] (Figure 5b):

$$\Delta G^0(\mathbf{13}{:}\mathbf{14a}) = 2.54 \times \Delta G^0(\mathbf{15}{:}\mathbf{16}) \quad r^2 = 0.953$$

$$\Delta G^0(\mathbf{13}{:}\mathbf{14b}) = 2.76 \times \Delta G^0(\mathbf{15}{:}\mathbf{16}) \quad r^2 = 0.893$$

(23) (a) Taft, R. W.; Abboud, J.-L. M.; Kamlet, M. J.; Abraham, M. H. *J. Solution Chem.* **1985**, *14*, 153–186. (b) Kamlet, M. J.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877–2887.
(24) Abraham, M. H. *Chem. Soc. Rev.* **1993**, *22*, 73–83.

$$\Delta G^0(\mathbf{9}{:}\mathbf{14a}) = 2.76 \times \Delta G^0(\mathbf{15}{:}\mathbf{16}) \quad r^2 = 0.990$$

The values for the slopes of 2.54−2.76 pinpoint the increased binding strength of 6-fold versus 3-fold hydrogen bonding in the respective bimolecular complexes while the high correlation coefficient reveals an equal ratio of unspecific and specific solvent effects on the binding enthalpies of these complexes. In particular, this analysis does not reveal any special chelate-type binding features between the solvent dioxane and the Hamilton receptor as assumed at first glance based only on the data sets for barbituric acid−Hamilton receptor complexes (see above).

Such solvent-dependent LFER have been widely applied for absorption energies and reaction rates,[21,23] but rarely for binding constants. This is rather surprising since LFER relationships are quite a useful tool not only for revealing specific interactions with a particular solvent as demonstrated above for 1,4-dioxane, but they can also be applied for the estimation of binding constants of systems where an accurate determination is hampered by spectroscopic problems, as in our UV/vis studies of **9**:**14a**−**c** due to spectral overlap of host and guest absorption bands or in some of our ^{1}H NMR studies due to signal broadening caused by dynamic exchange phenomena. Likewise, they are applicable for those instances where trivial problems, such as solubility limitations or just the existence of too large or too small binding constants that require concentrations out of the sensitivity range of the available spectroscopic technique, prevent an accurate determination of the binding constant. To give an example, the determination of binding constants for complexes **13**:**14a**−**c** and **9**:**14a**−**c** in solvents of even lower polarity than toluene is hard to achieve without having performed more difficult competitive titration experiments where one weakly bound guest molecule is replaced by a more strongly binding one. However, with the values given in the literature[25] for **15**:**16** in methylcyclohexane (21 000 M^{-1}) and in *n*-hexane (90 000 M^{-1}) and the above LFER equations a proper estimation is possible (Table 3). According to this analysis, we can safely claim that complexes between barbituric acid dyes **14a**−**c** and Hamilton receptors **9** or **13** will even prevail in the low nanomolar down to the picomolar concentration regime in aliphatic solvents. Such high binding constants can be very useful, e.g., they should enable the formation of electrooptically active long-chain supramolecular polymer fibers[26] even under highly dilute conditions, which is one of the current goals of our research.

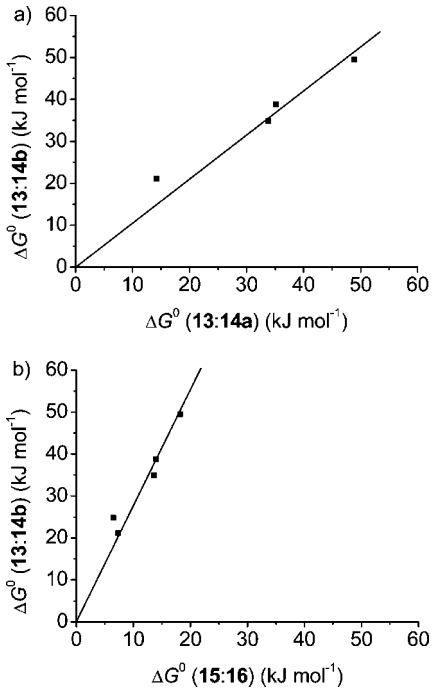
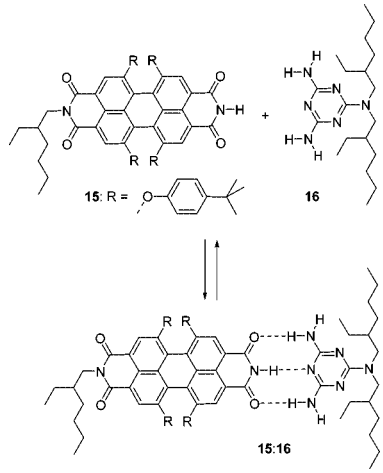


FIGURE 5. Linear free energy relationships for the solvent-dependent Gibbs free binding enthalpies for the bimolecular complexes: (a) **13**:**14a** and **13**:**14b** and (b) **13**:**14b** and **15**:**16**. The data are shown in Tables 2 and 3 and in Table S2 in the Supporting Information.

SCHEME 6. Complex Formation between Perylene Imide 15 and Melamine 16 by Three Hydrogen Bonds



Conclusion

Our work has shown that 6-fold hydrogen bonding between merocyanine dyes equipped with a Hamilton receptor and merocyanine dyes bearing a barbituric acid acceptor moiety is a powerful approach to direct the assembly of these dipolar dyes into a desirable NLO-active head-to-tail orientation of two dyes in a bimolecular complex. Pronounced spectral shifts and color changes upon complexation reveal a polarization of the barbituric acid merocyanine dye by 6-fold hydrogen bonding. On a qualitative level, this effect was discussed as a kind of specific solvation because similar spectral shifts could be observed upon variation of the solvent polarity. In a future paper these effects will be elucidated in a quantitative manner based on data from electrooptical absorption spectroscopy.[20] Additionally, we have shown that linear free energy relationships (LFER) are given for the solvent-dependent Gibbs binding enthalpies between various series of hydrogen-bonded complexes. It is suggested that such LFER are a valuable tool for the estimation of binding constants in solvents where experimental binding constants cannot be determined because of solubility or spectroscopic problems.

Experimental Section

1-(3,5-Dicarboxy)phenyl-2,6-dimethyl-4-pyridone Hydrochloride (3). To a suspension of 5-aminoisophthalic acid **1** (27.4 g,

(25) Würthner, F.; Thalacker, C.; Sautter, A.; Schärtl, W.; Ibach, W.; Hollricher, O. *Chem. Eur. J.* **2000**, *6*, 3871–3886. Notably, in this study no values for toluene were given. However, due to the similarity of benzene and toluene with regard to dipolarity and hydrogen-bonding properties it appeared reasonable to combine values measured for **13**:**14a**,**b** in toluene with values measured for **15**:**16** in benzene.

(26) Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Hirschberg, J. H. K. K.; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W. *Science* **1997**, *278*, 1601–1604.

151 mmol) and dehydroacetic acid **2** (27.4 g, 151 mmol) in H_2O (160 mL) was added an aqueous solution of HCl (37%, 97 mL) and the resultant mixture was heated to 110 °C for 15 h. After cooling to 0 °C, the precipitated gray solid was separated by filtration and recrystallized from methanol to give pure **3** as a white crystalline solid (30.5 g, 0.106 mol, 70%): mp 250 °C dec. ^{1}H NMR (400 MHz, MeOH-d_4) δ 8.68 (t, ^4J = 1.5 Hz, 1H), 8.18 (d, ^4J = 1.5 Hz, 2H), 7.04 (s, 2H), 2.10 (s, 6H). Anal. Calcd for $C_{15}H_{13}NO_5$: C, 55.65; H, 4.36; N, 4.33. Found: C, 55.56; H, 4.46; N, 4.31.

1-(3,5-Dicarbethoxy)phenyl-2,6-dimethyl-4-pyridone (4). To a suspension of pyridone hydrochloride **3** (30.5 g, 0.106 mol) in toluene (470 mL) were added ethanol (190 mL) and concentrated H_2SO_4 (5.5 mL) and the mixture was heated to reflux at 110 °C by using a water separator. After 1.5 h of heating hydrochloride **3** was dissolved, and ethanol/toluene 1:2 (20 mL) was added to replace the separated amount of toluene/H_2O. While heating for a further 20 h, the reaction volume was kept constant by replacing the separated amount of toluene/H_2O with a ethanol/toluene 1:2 mixture. After being cooled to room temperature, the solution was poured into water (140 mL). The resultant solid was separated by filtration and dissolved in chloroform (100 mL), then made basic (pH 9−10) by adding saturated aqueous Na_2CO_3 solution. After separation of the organic layer, the aqueous layer was extracted with chloroform (3 × 40 mL). The combined organic layers were washed with water (3 × 70 mL) and dried over Na_2SO_4, and the solvent was evaporated. The residue was recrystallized from cyclohexane/ethyl acetate to give pure **4** as a white crystalline solid (24.2 g, 70.5 mmol, 82%): mp 218−219 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (t, ^4J = 1.5 Hz, 1H), 8.08 (d, ^4J = 1.5 Hz, 2H), 6.38 (s, 2H), 4.47 (q, ^3J = 7.1 Hz, 4H), 1.92 (s, 6H), 1.45 (t, ^3J = 7.1 Hz, 6H). MS (EI) *m/z* (%) 343 (57) $[M]^+$, 315 (100) $[M - CO]^+$. Anal. Calcd for $C_{19}H_{21}NO_5$: C, 66.46; H, 6.16; N, 4.08. Found: C, 66.27; H, 6.25; N, 4.05.

1-[3,5-Bis(6-aminopyridine-2-yl)carbamoyl]phenyl-2,6-dimethyl-4-pyridone (6). 2,6-Diaminopyridine **5** (9.56 g, 87.6 mmol) was dissolved in dry THF (150 mL) under an argon atomosphere and the mixture was cooled to −78 °C. At this temperature *tert*-buthyllithium (1.7 M in *n*-pentane, 51.5 mL, 87.6 mmol) was added dropwise. Afterward a solution of pyridone **4** (6.00 g, 17.5 mmol) in dry THF (200 mL) was added dropwise and the reaction mixture was stirred for 4 h at −78 °C and an additional 16 h at room temperature. The resulting suspension was poured into a saturated aqueous solution of $NaHCO_3$ (200 mL, pH 8−10). After extracting the aqueous layer with $CHCl_3$ (3 × 150 mL) the combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was recrystallized from methanol to give pure **6** (5.80 g, 12.3 mmol, 71%): mp 317 °C dec. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.55 (br s, 2H), 8.57 (t, ^4J = 1.6 Hz, 1H), 8.13 (d, ^4J = 1.6 Hz, 2H), 7.45 (t, ^3J = 7.8 Hz, 2H), 7.38 (dd, ^3J = 7.8 Hz, ^4J = 0.8 Hz, 2H), 6.28 (dd, ^3J = 7.8 Hz, ^4J = 0.8 Hz, 2H), 6.12 (s, 2H), 5.77 (s, 4H), 1.93 (s, 6H). MS (FAB, 3-nitrobenzyl alcohol) *m/z* 470 $[M + H]^+$ (calcd 469.5). Anal. Calcd for $C_{25}H_{23}N_7O_3$: C, 63.96; H, 4.94; N, 20.88. Found: C, 63.78; H, 5.11; N, 20.74.

1-{3,5-Bis[(6-butyrylamino)pyridine-2-yl]carbamoyl}phenyl-2,6-dimethyl-4-pyridone (7). To a suspension of pyridone **6** (2.26 g, 4.81 mmol) in dry THF (140 mL) under an argon atmosphere was added NEt_3 (1.5 mL, 1.12 g, 11.1 mmol) and afterward a solution of butanoyl chloride (1.16 mL, 1.18 g, 11.1 mmol) in dry THF (40 mL) was added dropwise at 0 °C. The mixture was stirred for 3 h at 0 °C and for an additional 20 h at room temperature. The resulting suspension was poured into a saturated aqueous solution of $NaHCO_3$ (200 mL, pH 8−10). The aqueous layer was extracted with $CHCl_3$ (4 × 50 mL) and the combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure and the obtained solid crude product was recrystallized from EtOAc/MeOH 1:4 to give pure **7** (2.10 g, 3.44 mmol, 72%): mp 293−295 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.76 (br s, 2H), 10.04 (br s, 2H), 8.60 (t, ^4J = 1.6 Hz, 1H), 8.21 (d, ^4J = 1.6 Hz, 2 H), 7.79−7.85 (m, 6H), 6.15 (s, 2H), 2.38 (t, ^3J = 7.4 Hz, 4H), 1.94 (s, 6H), 1.62 (m, 4H), 0.91 (t, ^3J = 7.4 Hz, 6H). HRMS (ESI) *m/z* calcd for $C_{33}H_{36}N_7O_5$ $[M + H]^+$ 610.2772, found 610.2775.

1-{3,5-Bis[(6-(3,3-dimethyl)butyrylamino)pyridine-2-yl]carbamoyl}phenyl-2,6-dimethyl-4-pyridone (7a). Derivative **7a** was prepared according to the procedure described above for the pyridine **7** by using 3,3-dimethylbutanoyl chloride (1.32 g, 9.81 mmol) instead of butanoyl chloride. The crude product was first purified by silica gel column chromatography with EtOAc/EtOH 2:1 as eluent and subsequently precipitated from highly saturated CH_2Cl_2 solution by adding *n*-hexane to give pure **7a** (1.30 g, 1.95 mmol, 46%): mp 287−290 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.78 (br s, 2H), 9.97 (br s, 2H), 8.61 (t, ^4J = 1.5 Hz, 1H), 8.20 (d, ^4J = 1.5 Hz, 2H), 7.79−7.85 (m, 6H), 6.15 (s, 2H), 2.30 (s, 4H), 1.94 (s, 6H) 1.02 (s, 18H). HRMS (ESI) *m/z* calcd for $C_{37}H_{44}N_7O_5$ $[M + H]^+$ 666.3398, found 666.3393.

5-{1-[3,5-Bis[(6-butyrylamino)pyridine-2-yl]carbamoyl]phenyl-2,6-dimethylpyridine-4-ylidene}-1,3-dibutylpyrdimidine-2,4,6-trione (9). A mixture of pyridone **7** (300 mg, 0.492 mmol) in Ac_2O (10 mL) and AcOH (1 mL) was heated to 95 °C. At this temperature a solution of *N*,*N*′-dibutylbarbituric acid (144 mg, 0.599 mmol) in Ac_2O (5 mL) and AcOH (1 mL) was added dropwise and the resulting mixture was heated to 105 °C for 4 h. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography with CH_2Cl_2/EtOH 40:1 → 10:1 as eluent. The product was then precipitated from highly saturated CH_2Cl_2 solution by adding *n*-hexane to give **9** in a pure form as a yellow solid (90 mg, 0.108 mmol, 22%): mp 321−322 °C. ^{1}H NMR (400 MHz, MeOH-d_4) δ 8.91 (s, 2H), 8.84 (t, ^4J = 1.6 Hz, 1H), 8.29 (d, ^4J = 1.6 Hz, 2H), 7.98 (dd, ^3J = 7.5 Hz, ^4J = 0.9 Hz, 2H), 7.81 (t, ^3J = 8.0 Hz, 2H), 7.74 (dd, ^3J = 7.5 Hz, ^4J = 0.9 Hz, 2H), 3.99 (t, ^3J = 7.5 Hz, 4H), 2.40 (t, ^3J = 7.5 Hz, 4H), 2.33 (s, 6H), 1.74 (m, 4H), 1.63 (m, 4H), 1.38 (m, 4H), 1.01 (t, ^3J = 7.4 Hz, 6H), 0.98 (t, ^3J = 7.3 Hz, 6H). HRMS (ESI) *m/z* calcd for $C_{45}H_{53}N_9NaO_7$ $[M + Na]^+$ 854.3960, found 854.3963. Anal. Calcd for $C_{45}H_{53}N_9O_7 \cdot CH_3OH$: C, 63.95; H, 6.65; N, 14.59. Found: C, 63.75; H, 6.33; N, 14.63.

5-{1-[3,5-Bis[(6-(3,3-dimethyl)butyrylamino)pyridine-2-yl]carbamoyl]phenyl-2,6-dimethylpyridine-4-ylidene}-1,3-dibutylpyrdimidine-2,4,6-trione (9a). Compound **9a** was prepared according to the procedure described above for compound **9** by using pyridine derivative **7a** (500 mg, 0.751 mmol) instead of pyridine **7**. The crude product was first purified by silica gel column chromatography with CH_2Cl_2/EtOH 40:1 → 10:1 as eluent and then precipitated from highly saturated CH_2Cl_2 solution by adding *n*-hexane to give **9a** in a pure form as a yellow solid (130 mg, 0.146 mmol, 19%): mp 360−361 °C. ^{1}H NMR (400 MHz, $CDCl_3$/MeOH-d_4 1:1) δ 8.97 (s, 2H), 8.91 (t, ^4J = 1.5 Hz, 1H), 8.20 (d, ^4J = 1.5 Hz, 2H), 7.98 (d, ^3J = 8.1 Hz, 2H), 7.79 (t, ^3J = 8.1 Hz, 2H), 7.69 (d, ^3J = 8.1 Hz, 2H), 3.98 (t, ^3J = 7.6 Hz, 4H), 2.32 (s, 6H), 2.29 (s, 4H), 1.66 (m, 4H), 1.42 (m, 4H), 1.12 (m, 18H), 0.98 (t, ^3J = 7.3 Hz, 6H). MS (FAB, 3-nitrobenzylalcohol) *m/z* 888 $[M]^+$ (calcd 888.08). Anal. Calcd for $C_{49}H_{61}N_9O_7$: C, 66.27; H, 6.92; N, 14.19. Found: C, 65.80; H, 6.99; N, 13.82.

1,3-Bis{[(6-(3,3-dimethyl)butyrylamino)pyridine-2-yl]carbamoyl}benzene (13). To a solution of diamine **12** (1.50 g, 4.31 mmol) and NEt_3 (1.57 mL, 1.13 g, 11.2 mmol) in dry THF (100 mL) was added 3,3-dimethylbutanoyl chloride (1.39 mL, 1.33 g, 9.88 mmol) in dry THF (50 mL) dropwise at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and then an additional 14 h at room temperature. Afterward, the mixture was poured into a saturated aqueous solution of $NaHCO_3$ (200 mL) and extracted with $CHCl_3$ (3 × 150 mL), and the united organic phases were dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by precipitation from CH_2Cl_2/*n*-hexane to give pure **13** as a white solid (880 mg, 1.62 mmol, 38%): mp 133−135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (t, ^4J = 1.7 Hz, 1H), 8.37 (s, 2H), 8.12 (dd, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 2H),

8.06 (dd, ^3J = 8.0 Hz, ^4J = 0.7 Hz, 2H), 7.99 (dd, ^3J = 8.1 Hz, ^4J = 0.8 Hz, 2H), 7.79 (t, ^3J = 8.1 Hz, 2H), 7.58 (t, ^3J = 7.6 Hz, 1H), 7.55 (s, 2H), 2.27 (s, 4H), 1.13 (s, 18H). HRMS (ESI) *m/z* calcd for $C_{30}H_{37}N_6O_4$ $[M + H]^+$ 545.2871, found 545.2871. Anal. Calcd for $C_{30}H_{36}N_6O_4 \cdot H_2O$: C, 64.04; H, 6.81; N, 14.94. Found: C, 64.12; H, 6.67; N, 15.00.

5-[2-(1,3-Dihydro-3,3-dimethyl-1-isopropyl-2*H*-indol-2-ylidene)ethylidene]pyrimidine-2,4,6-trione (14a). To a solution of barbituric acid (216 mg, 1.69 mmol), DMF (130 μL, 123 mg, 1.69 mmol), and 1-isopropyl-2,3,3-trimethylindoleniumiodide (500 mg, 1.52 mmol) in Ac_2O (2 mL) was added KOAc (170 mg, 1.74 mmol). The reaction mixture was heated to 120 °C for 3 h. Upon cooling to 0 °C a solid was precipitated, which was separated by filtration. Purification of the crude product by silica gel column chromatography with CH_2Cl_2/MeOH 9:1 as eluent gave pure **14a** as an orange solid (110 mg, 0.324 mmol, 21%): mp 360 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, ^3J = 14.5 Hz, 1H), 7.82 (d, ^3J = 14.1 Hz, 1H), 7.62 (s, 1H), 7.53 (s, 1H), 7.20−7.38 (m, 4H), 4.80 (sept, ^3J = 6.8 Hz, 1H), 1.71 (s, 6H), 1.66 (d, ^3J = 6.9 Hz, 6H). HRMS (ESI) *m/z* calcd for $C_{19}H_{21}N_3O_3$ $[M + H]^+$ 339.1577, found 339.1579.

5-[2,6-Dimethyl-1-(2-ethyl)hexylpyridine-4-ylidene]pyrimidine-2,4,6-trione (14b). To a solution of 5-(2,6-dimethylpyrane-4-ylidene)pyrimidine-2,4,6-trione (1.00 g, 4.27 mmol) and 2-ethyl-1-hexylamine (3.30 mL, 20.0 mmol) in EtOH (40 mL) was added NEt_3 (2.0 mL, 1.44 g, 14.2 mmol) then the solution was heated to reflux for 20 h. Upon cooling to 0 °C a solid was precipitated, which was filtered and recrystallized from EtOH to give **14b** as a light yellow solid (1.32 g, 3.82 mmol, 90%): mp 282 °C dec. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.90 (s, 2H), 7.71 (s, 2H), 4.05 (d, ^3J = 7.7 Hz, 2H), 2.54 (s, 6H), 1.79 (m, 1H), 1.34 (m, 2H), 1.15−1.26 (m, 6H), 0.82−0.88 (m, 6H). MS (EI) *m/z* (%) 345 (97) $[M]^+$. Anal. Calcd for $C_{19}H_{27}N_3O_3$: C, 66.06; H, 7.88; N, 12.16. Found: C, 65.81; H, 7.86; N, 11.95.

5-[2-(2,6-Diundecyl-1-dodecylpyridine-4-ylidene)ethylidene]pyrimidine-2,4,6-trione (14c). A mixture of barbituric acid (0.260 g, 2.03 mmol) and *N*,*N*-dibutylformamide (310 mg, 1.97 mmol) in Ac_2O (2 mL) was heated to 120 °C for 1 h. 1-Dodecyl-4-methyl-2,6-diundecylpyridinium perchlorate (1.20 g, 1.80 mmol) and KOAc (200 mg, 2.04 mmol) were added and the resulting solution was stirred for a further 2 h at 120 °C. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography with CH_2Cl_2/MeOH 93.5:6.5 as eluent. Recrystallization of the product from acetic acid afforded pure **14c** as a bright red solid (880 mg, 1.24 mmol, 63%): mp 168−169 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, ^3J = 15.3 Hz, 1H), 7.76 (br s, 2H), 7.39 (d, ^3J = 15.3 Hz, 1H), 7.16 (s, 2H), 3.97 (t, ^3J = 8.2 Hz, 2H), 2.71 (t, ^3J = 8.0 Hz, 4H), 1.70 (m, 6H), 1.36 (m, 50H), 0.88 (m, 9H). HRMS (ESI) *m/z* calcd for $C_{45}H_{78}N_3O_3$ $[M + H]^+$ 708.6038, found 708.6036. Anal. Calcd for $C_{45}H_{77}N_3O_3$: C, 76.32; H, 10.97; N, 5.94. Found: C, 76.33; H, 10.67; N, 5.91.

General Procedure for the ^{1}H NMR Titration Experiments. The ^{1}H NMR titration experiments were performed as constant host titrations. To solutions of the hosts (in most cases receptors **9a** or **13**, concentration 1 mM) aliquots of solution of a guest (in most cases merocyanine dyes **14a**−**c**, concentration 5 mM) in the same host solution were added and ^{1}H NMR spectra (400 MHz) were recorded after each addition. Analysis of the data was made by nonlinear regression analysis.

General Procedure for the UV/vis Titration Experiments. For practical reasons (detection of spectral changes in the vis region), the role of the host and guest reversed in these experiments compared to those of ^{1}H NMR measurements. To the solution of a host (merocyanine dyes **14a**−**c**, concentration 1 × 10^{-5} M) aliquots of a solution of a guest (receptor **9** or **13**, concentration 2 × 10^{-4} M) in the same host solution were added and UV/vis spectra at 25 °C were recorded after each addition. Analysis of the data was made by nonlinear regression analysis.

Dipole Moment Determination. The dipole moments μ_g in the ground state and the dipole moment changes upon optical excitation $\Delta\mu = \mu_a - \mu_g$ were determined for dyes **14a**−**c** by electrooptical absorption spectroscopy[27] in dilute ($c < 10^{-5}$ mol L^{-1}) solutions in 1,4-dioxane at room temperature at the Technical University of Kaiserslautern, Germany, in the group of Prof. H.-G. Kuball.[20]

Acknowledgment. Financial support for this work by the Volkswagen foundation within the priority programme "Complex Materials: Cooperative Projects of the Natural, Engineering and Biosciences" is gratefully acknowledged.

Supporting Information Available: ^{1}H NMR titration experiments and binding constants, and ^{1}H NMR spectra of key compounds **9**, **13**, and **14a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO801083B

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