

Syntheses and UV/Vis-Spectroscopic Properties of Hydrophilic 2-, 3-, and 4-Pyridyl-Substituted Solvatochromic and Halochromic Pyridinium *N*-Phenolate Betaine Dyes as New Empirical Solvent Polarity Indicators^[‡]

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Syntheses and negative solvatochromism of nine new hydrophilic 2-, 3-, and 4-pyridyl-substituted pyridinium *N*-phenolate betaine dyes **3–11** are described. These were produced in order to obtain zwitterionic dyes better soluble in water and other aqueous media (such as binary water/solvent mixtures, aqueous ionophore solutions) than the rather

hydrophobic standard betaine dyes **1** and **2**, which have been used to establish an empirical scale of solvent polarity, called the $E_T(30)$ scale. Betaine dye **8**, in which three of the peripheral phenyl groups of **1** are replaced by two 3-pyridyl rings and one 4-pyridyl ring, proved to be particularly suitable for the determination of $E_T(30)$ values in aqueous media.

Introduction

Solutions of the pyridinium *N*-phenolate betaine dye **1** (Scheme 1) are solvatochromic, thermochromic, piezochromic, and halochromic.^[4–6] This means that the longest-wavelength intramolecular charge-transfer absorption band of the UV/Vis spectrum of **1** depends on solvent polarity,^[7–10] solution temperature,^[11–15] external pressure,^[16,17] and on the nature and concentration of added salts.^[18–28] By definition, negative (positive) solvatochromism means that solvent-dependent UV/Vis absorption bands of the solute are shifted hypsochromically (bathochromically) with increasing solvent polarity.^[5,31] Solutions of a chirally modified betaine dye **1** with four stereogenic centers even exhibit the phenomenon of chiro-solvatochromism.^[29] The extraordinarily large negative solvatochromism of the standard betaine dye **1** has been used to establish UV/Vis-spectroscopically derived empirical parameters of solvent polarity, known as $E_T(30)$ values.^[5,7,30,31] These $E_T(30)$ values are simply defined as the molar electronic

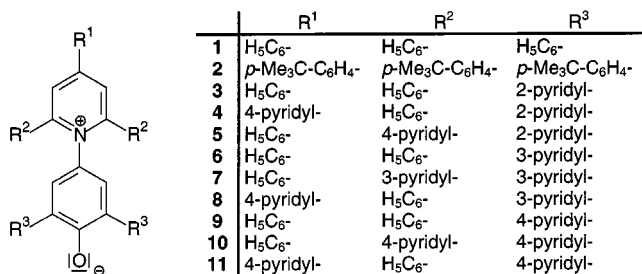
transition energies (in kcal/mol) of the standard betaine dye **1**, measured in solvents of different polarity at room temperature (25 °C) and normal pressure (1 bar), according to Equation (1), where $\tilde{\nu}_{\max}$ is the wavenumber and $\lambda_{\max}$ the wavelength of the maximum of the long-wavelength solvatochromic absorption band of betaine dye **1**.

$$E_T(30) [\text{kcal/mol}] = h \cdot c \cdot \tilde{\nu}_{\max} \cdot N_A = (2.8591 \cdot 10^{-3}) \cdot \tilde{\nu}_{\max} [\text{cm}^{-1}] = 28591/\lambda_{\max} [\text{nm}] \quad (1)$$

High $E_T(30)$ values correspond to high solvent polarity, here defined as the overall solvation capability of a solvent (for definitions of the term *solvent polarity* see refs.^[8–10,31]). Since, in the first publication,^[7] the betaine dye **1** had happened to have the formula number **30**, the number (**30**) was later added in order to avoid confusion with E_T , used in photochemistry as an abbreviation for triplet excitation energy. $E_T(30)$ values for more than 360 solvents and numerous binary solvent mixtures are known.^[4–6,30,31,34] These and other empirical parameters of solvent polarity have successfully been used in the correlation analysis of solvent effects on chemical equilibria, reaction rates, and spectral absorptions.^[31–35]

The $E_T(30)$ solvent polarity scale ranges from 63.1 kcal/mol for water, as the most polar solvent, to 30.7 kcal/mol for tetramethylsilane (TMS) as the least polar solvent. In 1983, in order to avoid use of the non-SI unit kcal/mol, the dimensionless, normalized E_T^N scale was introduced, using water ($E_T^N = 1.000$) and TMS ($E_T^N = 0.000$) as extreme polar and nonpolar reference solvents, respectively, by which to fix this scale.^[30]

The primary indicator dye **1** is sufficiently soluble in most solvents, although insoluble or only sparingly soluble in nonpolar solvents such as aliphatic hydrocarbons, perfluorohydrocarbons, and TMS, as well as in water. In order to obtain betaine dyes that were soluble in nonpolar solvents, the lipophilic penta-*tert*-butyl-substituted betaine dye **2** was introduced as a secondary probe.^[30] Even hepta-*tert*-butyl-substituted and tri-*tert*-butyl-bis(adamantan-1-yl)-



Scheme 1

[‡] Pyridinium *N*-Phenoxide Betaines and Their Application to the Determination of Solvent Polarities, XXV. – Part XXIV: Ref.^[1]

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substituted pyridinium *N*-phenolate betaine dyes were synthesized in order to increase solubility in nonpolar solvents.^[1] The excellent linear correlation between the E_T values of **1** and **2** for those solvents in which both dyes are soluble allows $E_T(\mathbf{30})$ values to be calculated for such nonpolar solvents in which the primary probe dye **1** is not soluble enough for UV/Vis-spectroscopic measurements.^[5,30,37] The quantitative link between the E_T values of the primary indicator dye **1** [i.e., $E_T(\mathbf{30})$] and the secondary indicator dye **2** [i.e., $E_T(\mathbf{2})$] is given by Equation (2), with $n = 57$, $r = 0.999$, and $s = 0.17$ kcal/mol.^[37]

$$E_T(\mathbf{2}) [\text{kcal/mol}] = 0.9424 \cdot E_T(\mathbf{30}) [\text{kcal/mol}] + 1.808 \quad (2)$$

In this way, it was easily possible to extend the $E_T(\mathbf{30})$ scale to nonpolar solvents such as aliphatic hydrocarbons and the supercritical fluid carbon dioxide.^[36] Unfortunately, it was not possible previously to find a solvatochromic betaine dye that is soluble in perfluorohydrocarbons.^[1]

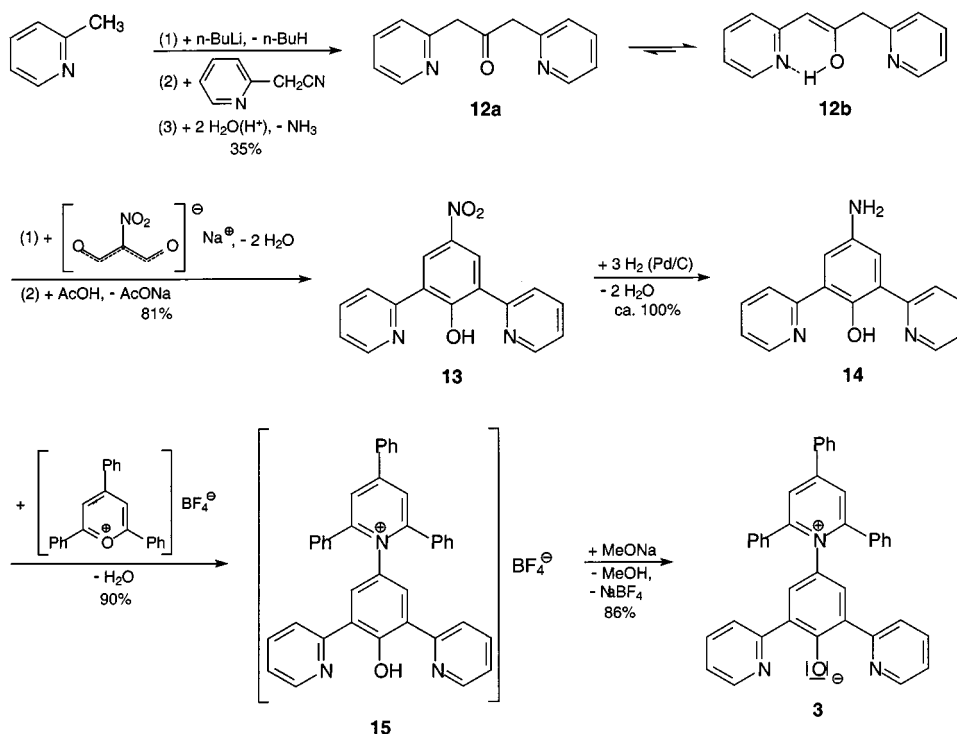
The primary indicator dye **1** is only sparingly soluble in water (its solubility in water is only about $2 \cdot 10^{-6}$ mol/L), just enough to determine its $E_T(\mathbf{30})$ value directly.^[38] This low solubility of **1** in water is clearly due to the core of five hydrophobic phenyl groups around the betaine chromophore. The low water solubility of **1** does not allow direct UV/Vis-spectroscopic determination of the polarity of highly aqueous binary solvent mixtures and of aqueous ionophore solutions.^[39] In order to obtain solvatochromic betaine dyes with better water solubilities, we synthesized pyridinium *N*-phenolates with one or more hydrophilic substituents, such as the carboxylate ($-\text{CO}_2^- \text{Na}^+$)^[40] and methanesulfonyl ($-\text{SO}_2\text{CH}_3$)^[41] groups, in the peripheral phenyl rings, but with limited success.^[40,41]

On the basis of the simple observation that benzene is practically insoluble in water, whereas pyridine is completely miscible with water, the replacement of some of the five peripheral phenyl rings in **1** with pyridyl rings should result in betaine dyes with better water solubilities. Without changing the basic zwitterionic chromophore of these solvatochromic betaine dyes, the additional peripheral nitrogen atoms should be prone to forming intermolecular hydrogen bonds with surrounding water molecules, thus pulling the whole dye into the aqueous solution. Here, we report on the synthesis, solvatochromism, and halochromism of such 2-, 3-, and 4-pyridyl-substituted betaine dyes (**3–11**; see Scheme 1), which did indeed prove to be much more water-soluble than **1**, thus allowing the empirical study of the polarities^[8–10] of aqueous ionophore^[39] solutions.^[42]

Results and Discussion

1. Syntheses

The key step in the synthesis of pyridinium *N*-phenolate betaine dyes is the condensation reaction between 2,4,6-triaryl-substituted pyrylium salts and 2,6-disubstituted 4-aminophenols, producing *N*-(4-hydroxyphenyl)pyridinium salts, which are eventually deprotonated to give the corresponding betaine dyes.^[7,30,43–48] In order to obtain the desired pyridyl-substituted betaine dyes **3–11**, it was first necessary to synthesize pyridyl-substituted pyrylium salts and 2,6-dipyridyl-substituted 4-aminophenols. None of these compounds were known previously, with the exception of an inseparable mixture of 4-phenyl-2,6-bis(pyridin-2-yl)pyryl-



Scheme 2. Synthesis of betaine dye **3** with two 2-pyridyl rings in the phenolate part

ium tetrafluoroborate and 4,6-diphenyl-2-(pyridin-2-yl)pyrylium tetrafluoroborate, obtained by Katritzky et al.^[49] from 3-phenyl-1-(pyridin-2-yl)prop-2-en-1-one,^[50] acetophenone, and tetrafluoroboric acid. Our attempts to obtain the former pyrylium salt in pure form by various classical methods for the synthesis of substituted pyrylium salts^[51,52] were unsuccessful.^[3]

The synthesis of betaine dye **3**, with two 2-pyridyl rings in the phenolate part, is outlined in Scheme 2. Lithiation of 2-methylpyridine with *n*-butyllithium in THF, according to Beumel et al.,^[53] and subsequent addition to (pyridin-2-yl)-acetonitrile resulted, after hydrolysis, in a sufficient yield of 1,3-bis(pyridin-2-yl)acetone (**12a**),^[54,55] which is partly enolized to **12b** in solution (ca. 60% enol form in CDCl₃). Base-catalyzed double aldol condensation of **12** with sodium nitromalonate^[56] gave the 4-nitrophenol **13** in good yield, and this was subsequently reduced to the 4-aminophenol **14** with dihydrogen and palladium as catalyst. Condensation of **14** with 2,4,6-triphenylpyrylium tetrafluoroborate^[7,57] yielded the *N*-(4-hydroxyphenyl)pyridinium salt **15**, which, on deprotonation with sodium methoxide in methanol, gave the desired betaine dye **3** as red-violet crystals, containing some water of crystallization (dihydrate).

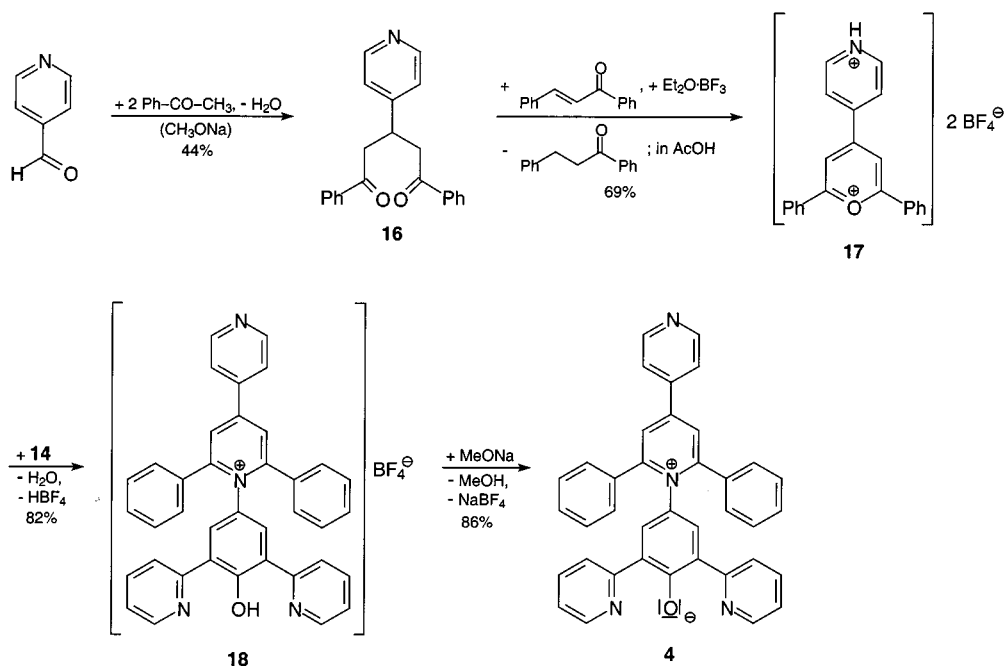
The synthesis of betaine dye **4** with three pyridyl rings (Scheme 3) began with the preparation of 2,6-diphenyl-4-(pyridin-4-yl)pyrylium salt **17**. Using a method of Katritzky et al.,^[58] base-catalyzed condensation of pyridin-4-carbaldehyde with acetophenone first gave the 1,5-diketone **16**, which on treatment with boron trifluoride–diethyl ether in acetic acid, in the presence of benzalacetophenone as hydride acceptor, underwent ring closure to give the pyrylium salt **17**.^[58] Subsequent condensation of **17** with the 4-aminophenol **14** yielded the pyridinium salt **18**, which was then

deprotonated to the betaine dye **4**, obtained as dark green crystals.

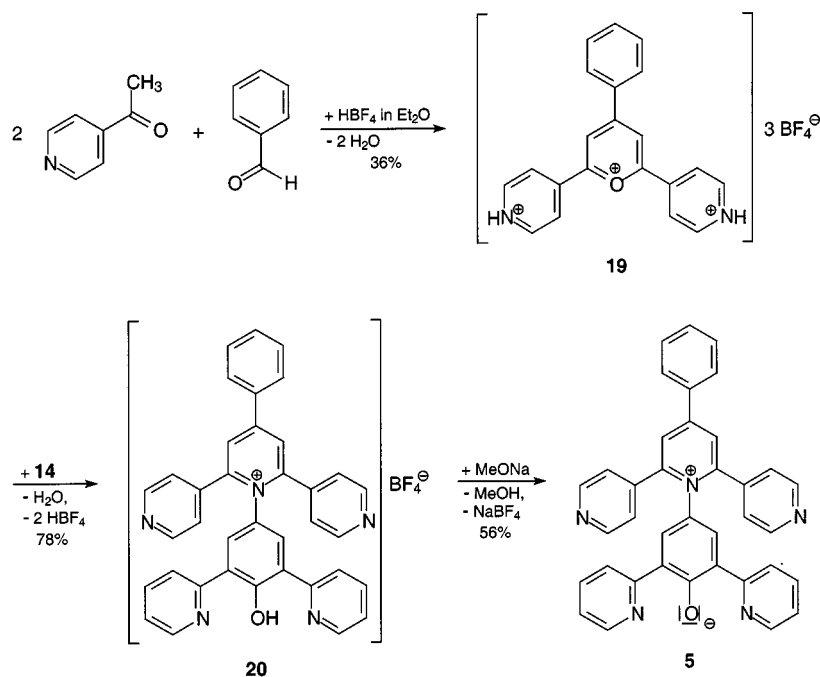
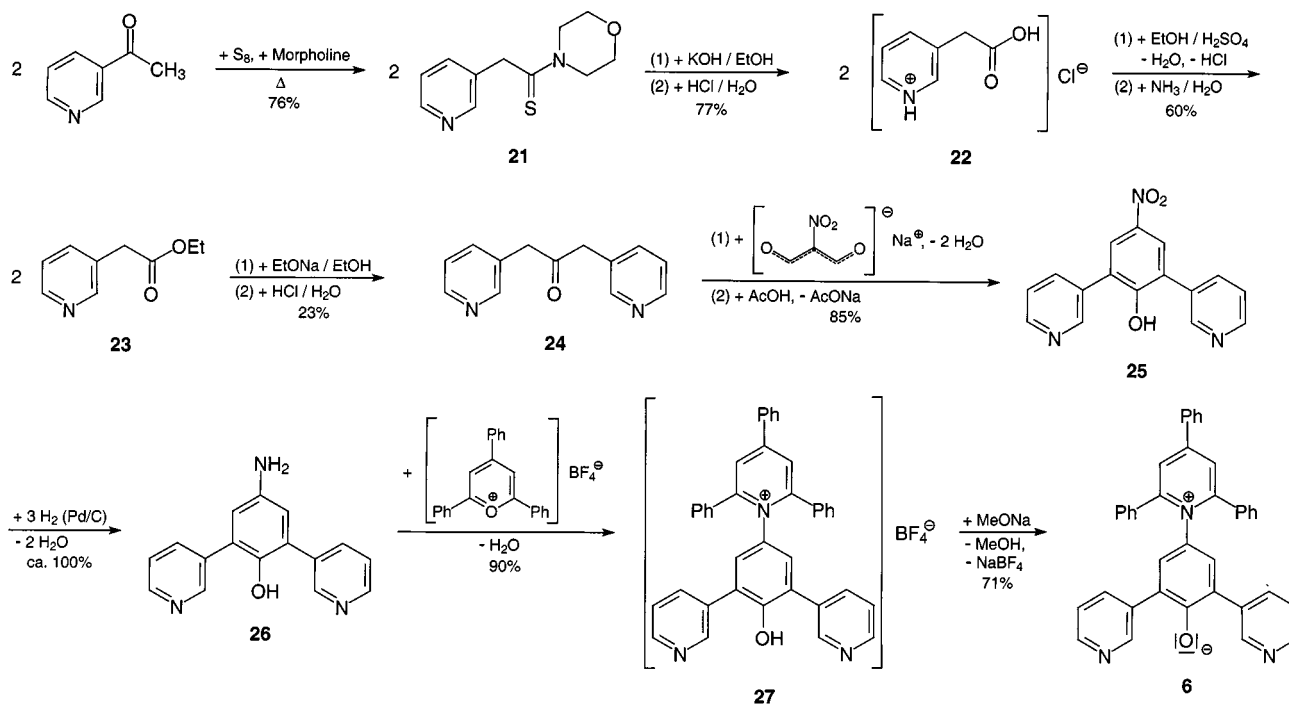
Betaine dye **5**, with four pyridyl rings, was prepared correspondingly, through the pyridinium salt **20**, from 4-phenyl-2,6-bis(pyridin-4-yl)pyrylium salt **19** and the 4-aminophenol **14**, as black-violet crystals (Scheme 4). The pyrylium salt **19** was synthesized directly from 4-acetylpyridine, benzaldehyde, and tetrafluoroboric acid (54%) in diethyl ether in moderate yield, analogously to the procedure in ref.^[57,59] but with a slight modification.^[2]

For the synthesis of betaine dye **6** (Scheme 5), with two 3-pyridyl rings in the phenolate part, it was first necessary to prepare the intermediate 1,3-bis(pyridin-3-yl)acetone (**24**). Willgerodt–Kindler redox amidation of 3-acetylpyridine with sulfur and morpholine gave the thiomorpholide **21**, which was hydrolyzed to (pyridin-3-yl)acetic acid hydrochloride (**22**).^[60] Acid-catalyzed esterification of **22** with ethanol produced the ester **23**,^[61] which on treatment with sodium ethoxide in ethanol yielded the desired ketone **24**, though in rather low yield. Ketone **24** had previously been obtained by Novelli et al. as an undesired side product, in 6% yield.^[62] Condensation of ketone **24** with sodium nitromalonate^[56] yielded the 4-nitrophenol **25**, which was easily reduced to the 4-aminophenol **26**. Condensation of **26** with 2,4,6-triphenylpyrylium tetrafluoroborate^[7,57] eventually gave (via **27**) the desired betaine dye **6** as a violet, amorphous powder.

Betaine dye **7** (Scheme 6), with four 3-pyridyl rings altogether, was prepared analogously, from 4-aminophenol **26** and 4-phenyl-2,6-bis(pyridin-3-yl)pyrylium salt **28**, via **29**, as violet powder. The pyrylium salt **28** was obtained by treatment of 3-acetylpyridine, benzaldehyde, and tetrafluoroboric acid (54%), dissolved in diethyl ether, in



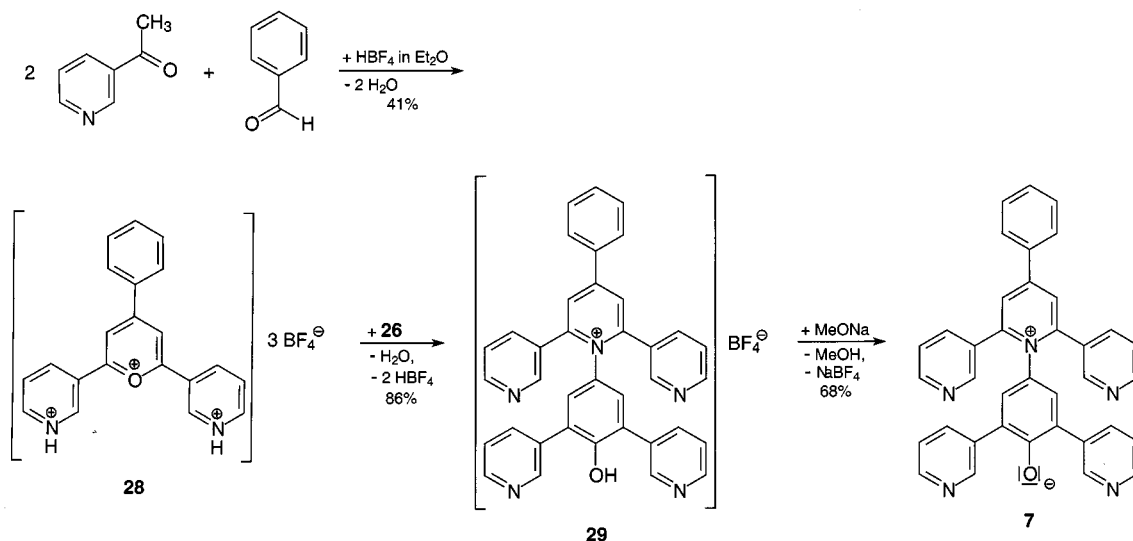
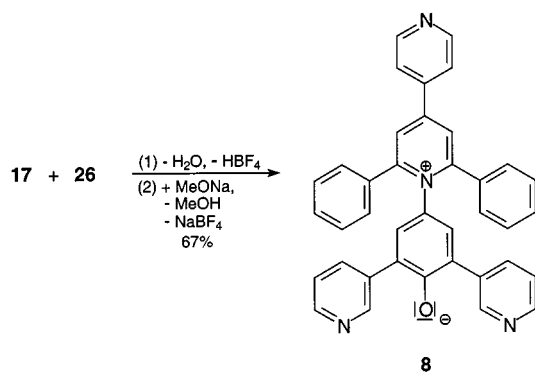
Scheme 3. Synthesis of betaine dye **4** with two 2-pyridyl rings in the phenolate part and one 4-pyridyl ring in the pyridinium part

Scheme 4. Synthesis of betaine dye **5** with two 2-pyridyl rings in the phenolate part and two 4-pyridyl rings in the pyridinium partScheme 5. Synthesis of betaine dye **6** with two 3-pyridyl rings in the phenolate part

analogy to the preparation of pyrylium salt **19** (Scheme 4).^[2,57,59]

Betaine dye **8** (Scheme 7) was similarly obtained as a violet powder by treatment of pyrylium salt **17** (see Scheme 3) with the 4-aminophenol **26** (see Scheme 5), but without isolation of the corresponding intermediary *N*-(4-hydroxyphenyl)pyridinium salt. It was not possible to isolate this pyridinium salt in pure form.^[3]

The synthesis of betaine dye **9**, with two 4-pyridyl rings in the phenolate part, was more difficult (Scheme 8). The necessary intermediate, 1,3-bis(pyridin-4-yl)acetone (**30**), was unknown. It was first attempted to produce **30** by oxidation of 1,3-bis(pyridin-4-yl)-2-propanol with various oxidizing agents (such as KMnO₄, DMSO/Ac₂O, DCC, Dess–Martin periodinane), but without success.^[3] 1,3-Bis(pyridin-4-yl)-2-propanol was prepared from 4-(sodiome-

Scheme 6. Synthesis of betaine dye **7** with four 3-pyridyl ringsScheme 7. Synthesis of betaine dye **8** with two 3-pyridyl rings in the phenolate part and one 4-pyridyl ring in the pyridinium part

thyl)pyridine (obtained from 4-methylpyridine with sodium amide in liquid ammonia) and ethyl formate, analogously to a procedure given by Bekun and Levine for the synthesis of 1,3-bis(pyrazin-2-yl)-2-propanol.^[63] The preparation of 1,3-bis(pyridin-4-yl)-2-propanol as described in a patent^[64] could not be reproduced in our hands.^[3] Therefore, a different procedure for the preparation of **30** had to be found. In analogy to the synthesis of ketone **24** (Scheme 5),^[62] ethyl (pyridin-4-yl)acetate was treated with sodium ethoxide in ethanol to give the desired, not very stable, ketone **30**, but only in a very low yield (ca. 2%). In order to obtain sufficient quantities of **30**, this reaction step was repeated several times. Finally, double aldol condensation of **30** with sodium nitromalonate monohydrate^[56] to give the 4-nitrophenol **31**, reduction of this to the 4-aminophenol **32**, and condensation with 2,4,6-triphenylpyrylium tetrafluoroborate^[7,57] yielded the desired betaine dye **9** as a red-violet powder, without isolation of the intermediate *N*-(4-hydroxyphenyl)pyridinium salt.

The symmetrical betaine dye **10** (Scheme 9) with four 4-pyridyl rings altogether, two in the phenolate and two in the pyridinium moiety, was prepared directly by condensation of pyrylium salt **19** (see Scheme 4) with 4-aminophenol

32 (see Scheme 8), again without isolation of the intermediate *N*-(4-hydroxyphenyl)pyridinium salt. Betaine **10** exists as an amorphous violet powder containing ca. 3.5 mol of water of recrystallization.

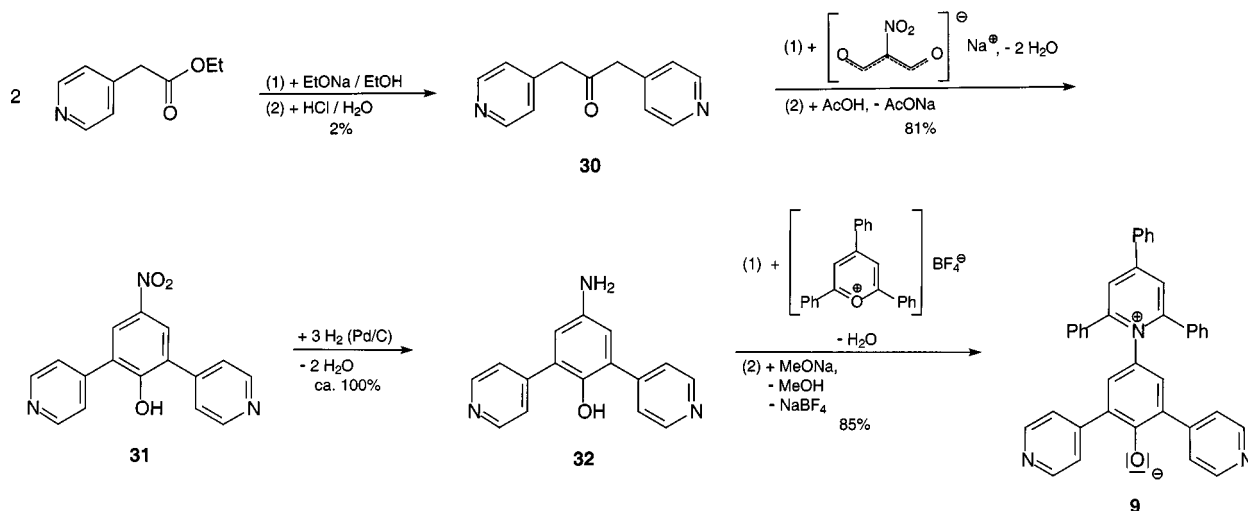
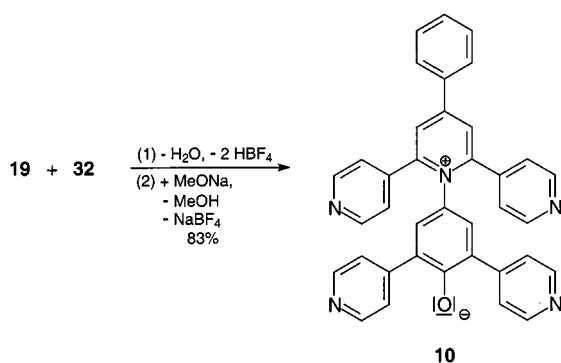
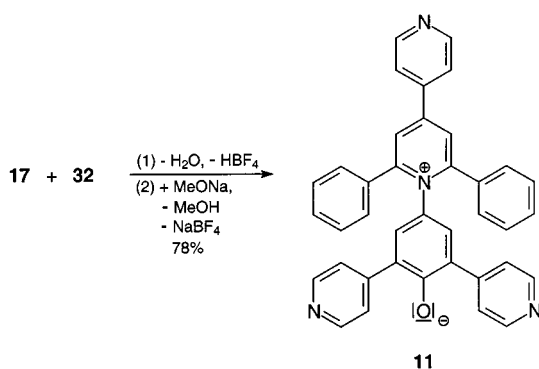
The last betaine dye in this series, compound **11** with three 4-phenyl rings (Scheme 10), was synthesized analogously from the pyrylium salt **17** (see Scheme 3) and the 4-aminophenol **32** (see Scheme 8) and isolated as violet crystals with 3 mol of water of recrystallization.

The molecular structures of all the new compounds were confirmed by elemental analysis, UV/Vis, IR, mass spectrometry, ¹H NMR, and ¹³C NMR (see Exp. Sect.).

2. UV/Vis Spectra and Solvatochromism of Betaine Dyes 3–11

All pyridyl-substituted betaine dyes **3–11** are suitably soluble in water and sufficiently soluble in most organic solvents, including benzene as a nonpolar solvent (except **10** and **11**), but insoluble in tetrachloromethane and cyclohexane. Obviously, together with the phenolate oxygen atom, the peripheral pyridyl nitrogen atoms are capable of forming further intermolecular hydrogen bonds to the surrounding water molecules, pulling the whole dye molecule into aqueous solution. The betaine dyes **3–11** exhibit extreme negative solvatochromism, comparable to that of the standard betaine dye **1** used to establish the $E_T(30)$ scale: On going from benzene to water as solvent, the long-wavelength Vis absorption band of **3–11** is hypsochromically shifted by $\Delta\lambda \approx 340$ nm (!), corresponding to a solvent-induced increase in the molar excitation energy of $\Delta E_T \approx 26$ kcal/mol. Hence, the new dyes meet the requirements for new solvatochromic probe molecules,^[5] particularly for the determination of polarity in all kinds of aqueous media. The solvent-dependent long-wavelength absorption maxima of **3–11**, measured in 27 solvents of different polarity, are collected in Table 1.

Why did we synthesize such a variety of nine pyridyl-substituted betaine dyes, and which of them is the most

Scheme 8. Synthesis of betaine dye **9** with two 4-pyridyl rings in the phenolate partScheme 9. Synthesis of betaine dye **10** with four 4-pyridyl ringsScheme 10. Synthesis of betaine dye **11** with three 4-pyridyl rings

suitable for our purpose? In acetonitrile, a solvent of intermediate polarity, the UV/Vis spectra of **3–11** exhibit four main absorption bands of different intensities: at $\lambda_{\max} = 570\text{--}630\text{ nm}$ ($\epsilon = 2600\text{--}5300$), $415\text{--}440\text{ nm}$ ($\epsilon = 8000\text{--}14000$), $300\text{--}390\text{ nm}$ ($\epsilon = 9000\text{--}42000$), and $230\text{--}250\text{ nm}$ ($\epsilon = 25000\text{--}42000\text{ L/mol}\cdot\text{cm}$). Only the position of the long-wavelength absorption band is strongly solvent-dependent; the others are not. This absorption band is the product of an intramolecular charge transfer (CT) from the HOMO of the phenolate to the LUMO of

Table 1. Long-wavelength, solvent-dependent CT absorption maxima, $\lambda_{\max}$ in nm, of betaine dyes **3–11**, measured in 27 solvents of decreasing polarity at 25 °C and at normal pressure (1 bar)

Solvents	3	4	5	6	7	8	9	10	11
Water	— ^[a]	464	461	447	460	473	— ^[a]	451	462
2,2,2-Trifluoroethanol	— ^[a]	— ^[a]	— ^[a]	451	475	491	440	476	478
Formamide	489	522	516	497	511	529	488	511	519
Methanol	474	507	499	482	495	514	473	493	503
<i>N</i> -Methylformamide	500	532	522	506	516	536	496	513	525
Ethanol	497	529	521	505	516	538	494	514	525
1-Propanol	503	539	530	516	530	550	504	529	536
1-Butanol	507	543	535	523	538	557	511	536	544
1-Pentanol	514	548	541	526	541	562	516	543	550
1-Hexanol	511	546	541	532	546	568	523	550	556
1-Heptanol	515	550	545	535	548	570	528	554	561
2-Propanol	524	562	551	534	551	569	523	550	558
1-Octanol	519	552	549	538	551	570	531	556	564
1-Nonanol	520	553	550	—	—	—	—	—	—
1-Decanol	519	551	552	539	552	578	538	562	571
Acetonitrile	575	612	607	590	605	629	571	597	603
Dimethyl sulfoxide	583	619	605	594	603	632	573	588	605
Dimethylformamide	599	637	624	614	624	653	589	605	623
Acetone	618	658	647	634	646	675	608	638	643
1,2-Dichloroethane	631	682	685	650	684	703	627	678	676
Dichloromethane	637	691	692	657	691	709	637	685	686
Pyridine	637	685	675	657	676	703	631	662	672
Trichloromethane	652	713	717	671	711	731	655	709	711
Ethyl acetate	673	723	707	695	709	738	666	— ^[b]	703
Tetrahydrofuran	684	731	719	705	723	750	675	703	715
1,4-Dioxane	697	757	757	735	761	787	710	— ^[c]	— ^[c]
<i>tert</i> -Butyl methyl ether	742	— ^[c]	787	762	— ^[c]	— ^[c]	731	— ^[c]	— ^[c]
Benzene	736	809	804	769	795	824	748	— ^[c]	— ^[c]

^[a] Not measurable because of overlap with the intensive UV/Vis absorption band at shorter wavelength, leading to a shoulder only.

— ^[b] Decomposition. — ^[c] Not soluble in this solvent.

the pyridinium moiety (for various quantum chemical calculations of the UV/Vis spectrum of betaine dye **1**, see refs.^[65–73]). Therefore, the position of the CT band should depend on the ionization energy of the electron donor (i.e., the phenolate part) and on the electron affinity of the electron acceptor (i.e., the pyridinium part). On protonation of

the phenolate parts of **3–11**, the solvent-dependent CT bands disappear and the corresponding *N*-(4-hydroxyphenyl)pyridinium salts formed (i.e., **15**, **18**, **20**, **27**, and **29**) absorb at $\lambda_{\text{max}} = 300\text{--}310$ nm, corresponding to a $\pi\text{--}\pi^*$ absorption in the 2,4,6-triarylpyridinium chromophore. For this reason, betaine dyes **3–11**, as well as **1** and **2**, cannot be used as polarity indicators in acidic solvents.

Replacement of the two 2,6-phenyl groups in the phenolate part of the standard betaine dye **1** ($\lambda_{\text{max}} = 627$ nm in acetonitrile) by two pyridyl rings results in all three cases (**3**, **6**, and **9**) in a hypsochromic shift of the long-wavelength CT band, amounting to $\Delta\lambda = 575\text{--}627 = -52$ nm for **3** (with two 2-pyridyl rings), $\Delta\lambda = -37$ nm for **6** (with two 3-pyridyl rings), and $\Delta\lambda = -56$ nm for **9** (with two 4-pyridyl rings). Introduction of electron-withdrawing pyridyl substituents in the phenolate part of the zwitterionic chromophore increases the ionization energy of the phenolate moiety, with the experimentally observed hypsochromic CT band shift as a consequence. According to the $\Delta\lambda$ values of **3**, **6**, and **9**, the electron-withdrawing effect of the pyridyl rings increases in the order 3-pyridyl ($\sigma_a = +0.72$) < 2-pyridyl ($\sigma_a = +0.81$) < 4-pyridyl ($\sigma_a = +0.95$); that is, in the same sequence as given by the Hammett substituent constants σ_a of the 2-, 3-, and 4-pyridyl groups (given in parentheses).^[74,75] These σ_a values (taken from ref.^[75]) are interpreted as due to the substitution of pyridyl for phenyl ($\sigma_a = 0$).^[74]

Replacement of the three 2-, 4-, and 6-phenyl groups in the pyridinium part of betaine dye **1** by pyridyl rings should increase the electron affinity of the pyridinium moiety, with a bathochromic CT band shift as the result. This is indeed the case: Replacement of the 4-phenyl or the 2-phenyl ring of **1** by one 4-pyridyl group results in bathochromic CT band shifts of $\Delta\lambda = +43$ and $+41$ nm, respectively.^[2] However, the corresponding new betaine dyes with only one peripheral pyridyl substituent are not included in this paper and in Scheme 1, because they are insufficiently water-soluble.^[2]

For the other betaine dyes (**4**, **5**, **7**, **8**, and **10**) in Scheme 1, with pyridyl rings in both parts of the zwitterionic chromophore, a hypsochromic CT band shift is always – with one exception (**8**) – obtained as result of a phenyl $\rightarrow$ pyridyl replacement in **1**: $\Delta\lambda$ (measured in acetonitrile) = -15 nm (for **4**), -20 nm (for **5**), -22 nm (for **7**), and -30 nm (for **10**), demonstrating the dominating electron-withdrawing influence of the pyridyl groups in the phenolate part of the betaine chromophore.

Only betaine dye **8**, with $\Delta\lambda = 629 - 627 = +2$ nm (in acetonitrile), shows a small bathochromic CT band shift, due to dominance of the electron-withdrawing effect of the 4-(4-pyridyl) ring in the pyridinium part over that of the two 2,6-bis(3-pyridyl) rings in the phenolate part of **8**. Clearly, the positions of the long-wavelength CT absorption band of dyes **3–11** depend on subtle mutual interplay between the pyridyl substituents in the electron donor and electron acceptor parts of the zwitterionic chromophore. In addition, it should be mentioned that the molecules of dyes **3–11** are certainly not planar: Not only the pyridinium and

phenolate moiety should be strongly twisted, but also the peripheral phenyl and pyridyl rings. This assumption is made by analogy with a peripheral 4-bromo-substituted derivative of betaine dye **1**, for which an X-ray molecular structure analysis is known.^[76] The extent of the electron-withdrawing effect of the pyridyl rings also depends on the twist angle, and is therefore difficult to estimate any more quantitatively.

A solvent-induced and/or substituent-induced hypsochromic shift of the solvent-dependent long-wavelength CT band means that this band comes closer to the more intensive solvent-independent absorption band at shorter wavelengths. In water as solvent, this can lead to some overlap, and the solvatochromic CT band degenerates to a shoulder. This is the case for betaine dyes **3** and **9** (see Table 1). For betaine dyes **10** and **11**, when they are dissolved in water, the CT band is also only poorly separated from the strong bands at shorter wavelengths. Therefore, these dyes are less well suited for the study of the polarity of aqueous media. From the remaining betaine dyes, **4–8**, dye **8** is obviously the most suitable for this purpose, because its CT band, with $\lambda_{\text{max}} = 473$ nm, is located at the longest wavelength position, which leaves a margin for further hypsochromic band shifts without overlap, which might be induced by media more polar than water. For this reason, and because of its relatively easy availability (see Scheme 7), we have chosen

Table 2. $E_T(\mathbf{8})$ values of the new tertiary standard betaine dye **8** and the $E_T(\mathbf{30})$ values of the primary standard betaine dye **1** for 26 solvents, in kcal/mol

No.	Solvents	$E_T(\mathbf{30})^{[a]}$	$E_T(\mathbf{8})^{[b]}$
1	Water	63.1	60.4
2	2,2,2-Trifluoroethanol	59.8	58.2
3	Formamide	55.8	54.0
4	Methanol	55.4	55.6
5	<i>N</i> -Methylformamide	54.1	53.3
6	Ethanol	51.9	53.1
7	1-Propanol	50.7	52.0
8	1-Butanol	49.7	51.3
9	1-Pentanol	49.1	50.9
10	1-Hexanol	48.8	50.3
11	1-Heptanol	48.5	50.2
12	2-Propanol	48.4	50.2
13	1-Octanol	48.2	50.2
14	1-Decanol	47.7	49.5
15	Acetonitrile	45.6	45.5
16	Dimethyl sulfoxide	45.1	45.2
17	Dimethylformamide	43.2	43.8
18	Acetone	42.2	42.4
19	1,2-Dichloroethane	41.3	40.7
20	Dichloromethane	40.7	40.3
21	Pyridine	40.5	40.7
22	Trichloromethane	39.1	39.1
23	Ethyl acetate	38.1	38.7
24	Tetrahydrofuran	37.4	38.1
25	1,4-Dioxane	36.0	36.3
26	Benzene	34.3	34.7
	ΔE_T [kcal/mol] =	28.8 ^[c]	25.7 ^[c]

[a] Taken from ref.^[5] – [b] Calculated according to Equation (1) from the Vis absorption maxima of **8** given in Table 1. – [c] $\Delta E_T = E_T(\text{H}_2\text{O}) - E_T(\text{C}_6\text{H}_6)$.

betaine dye **8** (in addition to dyes **1** and **2**) as a new ternary, suitably water-soluble standard betaine dye for the study of aqueous media.

Table 2 shows the molar transition energies $E_T(\mathbf{8})$ of betaine dye **8** in 26 hydrogen-bond donor (HBD) and non-HBD solvents, together with the corresponding $E_T(\mathbf{30})$ values of the primary indicator dye **1**. As regression Equation (3) and Figure 1 show, there is a good linear correlation between the E_T values of the two solvatochromic dyes, with a correlation coefficient of $r = 0.987$ and a standard deviation of $\sigma[E_T(\mathbf{8})] = 1.172$ kcal/mol for $n = 26$ solvents.

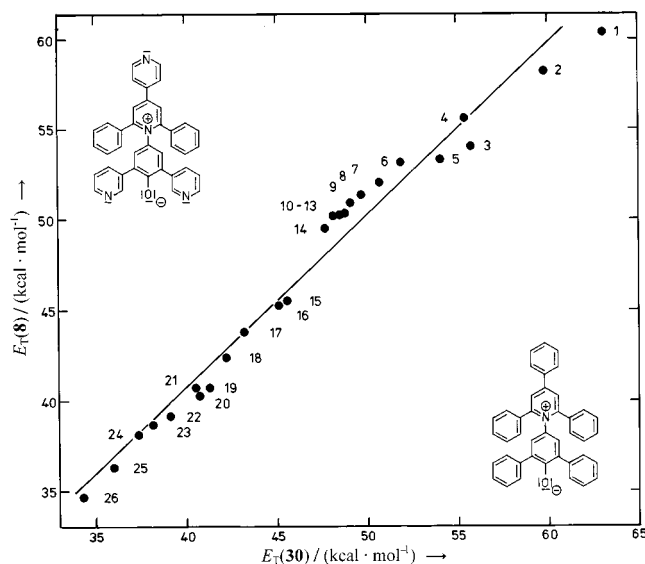


Figure 1. Linear correlation between the $E_T(\mathbf{30})$ values of standard betaine dye **1** and the $E_T(\mathbf{8})$ values of the tripyridyl-substituted betaine dye **8**, measured in 26 solvents (numbering as in Table 2), according to Equation (3)

$$E_T(\mathbf{8}) [\text{kcal/mol}] = 0.948 \cdot E_T(\mathbf{30}) [\text{kcal/mol}] + 2.799 \quad (3)$$

Equation (3) allows the calculation of $E_T(\mathbf{30})$ values for aqueous media in which the hydrophobic standard dye **1** is insufficiently soluble, in the same way that the secondary lipophilic probe dye **2** has permitted the indirect determination of $E_T(\mathbf{30})$ values for nonpolar solvents by means of Equation (2).^[30] The slope of the regression line, at 0.948, is slightly less than unity, indicating that betaine dye **8** is somewhat less sensitive to changes in solvent polarity than dye **1** is. The corresponding regression coefficients for the linear correlations between the E_T values of all new hydrophilic betaine dyes **3–11** and the $E_T(\mathbf{30})$ values of **1** are collected in Table 3. It can be seen that the E_T values of all new betaine dyes **3–11** exhibit good linear correlations with $E_T(\mathbf{30})$, with correlation coefficients of $r = 0.98–0.99$. The slopes of the regression lines vary between $a \approx 0.91$ (for **11**) and 1.06 (for **3**), indicating that dyes **3–11** exhibit susceptibilities to changes in solvent polarity similar to that of the standard dye **1**.

Table 3. Regression parameters for the linear correlations between the $E_T(X)$ values of betaine dyes $X = \mathbf{3–11}$ and the $E_T(\mathbf{30})$ values of the standard betaine dye **1**,^[5] according to the correlation equation: $E_T(X) [\text{kcal/mol}] = a \cdot E_T(\mathbf{30}) [\text{kcal/mol}] + b$

X	a	b	$n^{[a]}$	$r^{[b]}$	$\sigma[E_T(X)]^{[c]}$
3	1.058	2.535	26	0.981	1.348
4	0.970	3.086	26	0.977	1.473
5	0.996	2.424	27	0.980	1.475
6	1.010	3.078	27	0.989	1.189
7	0.981	3.049	26	0.984	1.342
8	0.948	2.799	26	0.987	1.172
9	1.031	3.555	26	0.993	0.882
10	0.940	5.388	23	0.982	1.210
11	0.909	6.148	24	0.987	1.021

[a] Number of solvents. — [b] Correlation coefficient. — [c] Standard deviation of the estimate in kcal/mol.

A closer look at the correlation given by Equation (3) and illustrated in Figure 1 reveals some family-dependent behavior; the HBD solvents (i.e., alcohols and water) follow a regression line with a slope somewhat smaller than that of the regression line for the non-HBD solvents. This line dispersion is illustrated in Figure 2 and can be quantitatively described by Equation (4) (HBD solvents) and Equation (5) (non-HBD solvents).

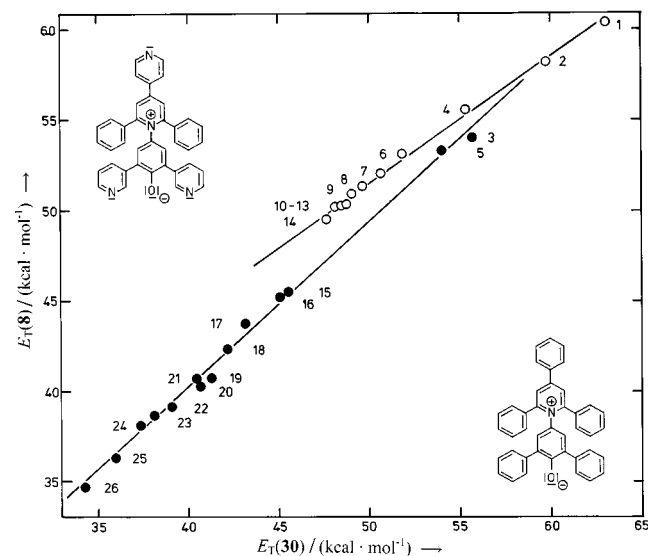


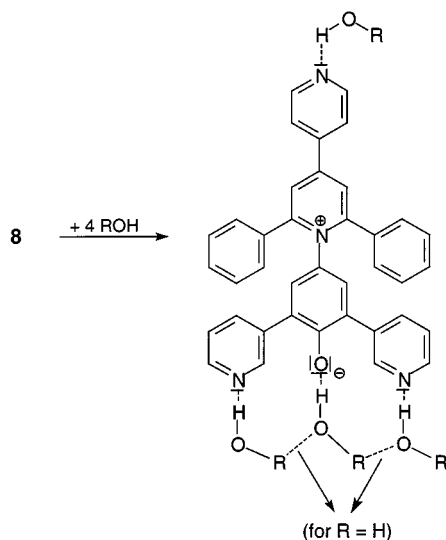
Figure 2. Linear correlations between the $E_T(\mathbf{30})$ values of standard betaine dye **1** and the $E_T(\mathbf{8})$ values of betaine dye **8** with separate lines for 12 HBD (open circles) and 14 non-HBD solvents (full circles) (numbering as in Table 2), according to Equations (4) and (5), respectively

$$E_T(\mathbf{8}) (\text{HBD}) = 0.704 \cdot E_T(\mathbf{30}) + 16.236 \quad (n = 12; r = 0.998; \sigma = 0.238) \quad (4)$$

$$E_T(\mathbf{8}) (\text{non-HBD}) = 0.914 \cdot E_T(\mathbf{30}) + 3.610 \quad (n = 14; r = 0.997; \sigma = 0.428) \quad (5)$$

According to r and σ , the linear correlations are now excellent. Analogous HBD/non-HBD dispersions of the linear correlations compiled in Table 3 are also found for the other pyridyl-substituted betaine dyes. Obviously, the spe-

cific solvation of dye **8** with four hydrogen-bond-accepting sites by HBD solvents according to Scheme 11 results in an enhanced stabilization of the electronic ground state and somewhat reduces its susceptibility to changes in the surrounding HBD solvent (i.e., changes of R in ROH). Nevertheless, Equation (3) can be used for the calculation of $E_T(\mathbf{30})$ values for aqueous media, with the aid of $E_T(\mathbf{8})$ values of the hydrophilic betaine dye **8**, without making a larger mistake.



Scheme 11. Specific solvation of betaine dye **8** by HBD solvents ROH (with R = H, alkyl)

3. Solvatochromism of Betaine Dye **8** in a Binary Solvent Mixture

Investigation, with standard dye **1**, of polarities^[8–10] of binary solvent mixtures containing water as one of the two components often suffers from the low solubility of **1** in the highly aqueous region. Addition of water to an organic stock solution of **1** can result in the precipitation of **1**, forming a cloudy solution not suitable for UV/Vis measurements. In order to demonstrate the usefulness of the new hydrophilic betaine dye **8** for the study of aqueous binaries, the $E_T(\mathbf{8})$ values of a water/1,4-dioxane mixture were determined and are collected in Table 4.

The graphical illustration in Figure 3 shows that the addition of small amounts of water to a solution of **8** in 1,4-dioxane, and also the addition of a little 1,4-dioxane to an aqueous solution of **8**, produces a disproportionately large hypsochromic/bathochromic CT band shift.

This S-shape deviation from linearity is typical of preferential solvation of the solute by one of the two solvent components and has been widely studied with various solvatochromic probes, particularly with betaine dye **1** (for some leading work on preferential solvation of solvatochromic probes in binary solvent mixtures, see refs.^[77–85]). The dashed line in Figure 3 represents the expected behavior for an ideal binary solvent mixture without preferential solvation. The non-ideal behavior of solutions of dye **8** in water/1,4-dioxane mixtures corresponds precisely to the analog-

Table 4. Long-wavelength CT absorption maxima, $\lambda_{\max}$ in nm, of betaine dye **8**, measured in binary water/1,4-dioxane mixtures at 25 °C, and the corresponding $E_T(\mathbf{8})$ values in kcal/mol, calculated according to Equation (1)

$x(1,4\text{-dioxane})^{[a]}$	$\lambda_{\max}$	$E_T(\mathbf{8})$
0.0	473	60.4
0.1	520	55.0
0.2	541	52.8
0.3	559	51.1
0.4	573	49.9
0.5	589	48.5
0.6	605	47.3
0.7	627	45.6
0.8	657	43.5
0.9	707	40.4
1.0	787	36.3

[a] Mol fraction of 1,4-dioxane. $\Delta\lambda = -314$ nm; $\Delta E_T = 24.1$ kcal/mol.

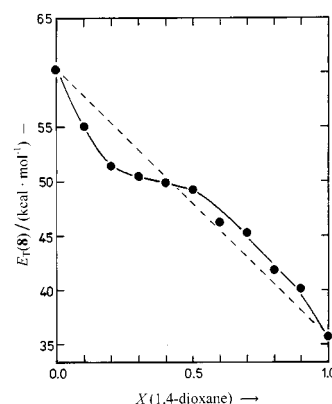


Figure 3. Nonlinear correlation between the $E_T(\mathbf{8})$ values of betaine dye **8** and the mol fraction x of 1,4-dioxane for binary water/1,4-dioxane mixtures

ous non-ideal behavior of standard dye **1** observed in the same binary solvent mixture.^[86–92] The deviations found on addition of polar water to a solution of dye **8** (or **1**) in less polar 1,4-dioxane can easily be explained by preferential solvation of the dye molecule by water molecules, producing the observed disproportional hypsochromic CT band shift. The deviations from linearity found for solutions of dye **8** in water on addition of 1,4-dioxane are the result of specific solute/solvent and solvent/solvent interactions. Presumably, the addition of 1,4-dioxane as a double hydrogen-bond acceptor changes the structure of the water through its HBD and HBA abilities, resulting in a new kind of solvent with a different solvation capability for solutes.^[82,91] Using a two-step solvent exchange model, an excellent quantitative description of the $E_T(\mathbf{30})$ behavior of such binary solvent mixtures has been found.^[79,91] With the new hydrophilic betaine dye **8**, the study of such aqueous binaries should now be much easier to perform, particularly in water-rich regions.

4. Halochromism of Betaine Dye **8** in Aqueous Ionophore Solutions

Are aqueous solutions of ionophores^[39] (electrolytes, salts) more polar than pure water? Is it possible to measure their polarity empirically by means of solvatochromic probe dyes? It is well known that not only solvent change, but also addition of chemically inert ionophores to reaction media, can influence the course (e.g., rate, yield, stereochemistry, regioselectivity) and equilibrium position of chemical reactions; this is normally called a *salt effect*.^[93–95] The change in $E_T(\mathbf{30})$ values after addition of ionophores to solutions of probe dye **1** in organic solvents has been investigated,^[4,5,18–28] and termed *genuine halochromism*.^[40] The term negative (positive) halochromism was suggested for a hypsochromic (bathochromic) shift of the UV/Vis absorption band of a dissolved light-absorbing probe dye on increasing ionophore concentration, provided that this band shift is not caused by a drastic change in the molecular structure of the chromophore.^[40] This definition is in contrast to the *trivial halochromism* first described by Bayer et al.,^[96] when studying salt formation during the reaction between colorless triphenylcarbinol and sulfuric acid, which produced a yellow solution of a triphenylcarbenium salt. During this treatment, the molecular structure of the chromophore is completely changed, whereas the chromophore of a genuine halochromic compound maintains its molecular structure on addition of ionophores. Furthermore, the genuine halochromism of a solvatochromic probe dye can be preferentially anion- or cation-dependent.^[97]

In some exploratory measurements, we have studied the Vis-spectral behavior of aqueous solutions of the new hydrophilic betaine dye **8** on addition of alkali metal halides, urea, and tetramethylammonium chloride (see Table 5). According to Entries 1–5 in Table 5, addition of alkali metal chlorides to aqueous solutions of dye **8** always results, with increasing salt concentration, in small hypsochromic band shifts. These can be up to $\Delta\lambda = -2$ to -8 nm for a 3 M salt solution, depending on the charge density (= charge/volume) of the alkali cation: The larger the cation, the

smaller its charge density and the band shift $\Delta\lambda$. These hypsochromic band shifts correspond to an increase in the molar transition energies of **8** by $\Delta E_T = 0.4$ to 1.1 kcal/mol for 3 M salt solutions. Entries 6–8 in Table 5 show that the observed genuine halochromism of **8** depends not only on the charge density of the cation, but also on that of the anion: Addition of various sodium halides also results in a hypsochromic band shift of $\Delta\lambda = -4$ to -7 nm, corresponding to ΔE_T values of 0.6 to 1.0 kcal/mol, depending on the charge density of the anion. Because of the low solubility of sodium fluoride in water [$c(\text{NaF})$ only ca. 0.95 mol/L for a saturated solution], this salt was excluded from these measurements.

These results demonstrate that aqueous ionophore solutions behave as media slightly more polar than pure water towards the solvatochromic probe dye **8**. This polarity increase is graphically illustrated by the block diagram given

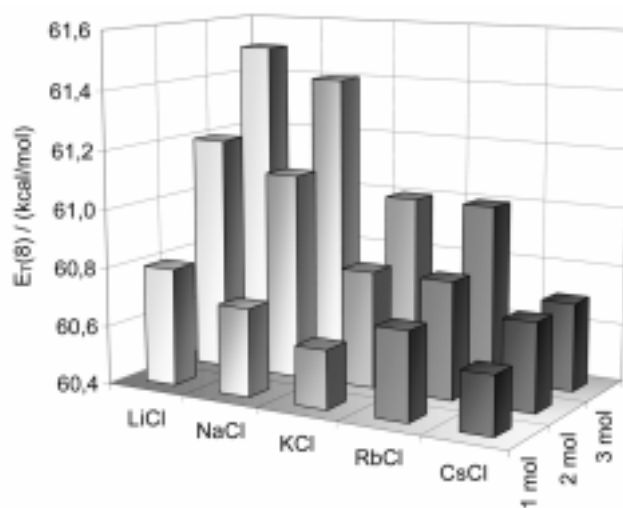


Figure 4. Graphical representation of the increase in $E_T(\mathbf{8})$ values on addition of alkali metal chlorides to aqueous solutions of dye **8**, depending on the concentration and the charge density of the alkali cation, with a base plane corresponding to the $E_T(\mathbf{8})$ value of pure water (60.4 kcal/mol; cf. Table 5)

Table 5. Long-wavelength CT absorption maxima, $\lambda_{\max}$ in nm, of betaine dye **8**, measured in nine ionophore/water solutions at 25 °C with four salt concentrations, together with the corresponding $E_T(\mathbf{8})$ values in kcal/mol (in parentheses), calculated according to Equation (1)

Entry	Ionophore	1 mol	2 mol	$\lambda_{\max}$ [$E_T(\mathbf{8})$] 3 mol	Sat. sol. ^[a]	$\Delta\lambda$ (ΔE_T) ^[b]
1	LiCl	470 (60.8)	467 (61.2)	465 (61.5)	— ^[c]	−8 (+1.1)
2	NaCl	471 (60.7)	468 (61.1)	466 (61.4)	463 (61.8)	−7 (+1.0)
3	KCl	472 (60.6)	470 (60.8)	469 (61.0)	465 (61.5)	−4 (+0.6)
4	RbCl	471 (60.7)	470 (60.8)	469 (61.0)	468 (61.1)	−4 (+0.6)
5	CsCl	472 (60.6)	471 (60.7)	471 (60.7)	— ^[c]	−2 (+0.4)
6	NaCl	471 (60.7)	468 (61.1)	466 (61.4)	463 (61.8)	−7 (+1.0)
7	NaBr	470 (60.8)	468 (61.1)	467 (61.2)	— ^[c]	−6 (+0.8)
8	NaI	470 (60.8)	469 (61.0)	469 (61.0)	— ^[d]	−4 (+0.6)
9	Urea	477 (59.9)	479 (59.7)	481 (59.4)	491 (58.3)	+8 (−1.0)
10	$\text{Me}_4\text{N}^+\text{Cl}^-$	476 (60.1)	481 (59.4)	486 (58.8)	505 (56.6)	+13 (−1.6)

^[a] Saturated aqueous solutions: $c(\text{LiCl}) \approx 19.3$; $c(\text{NaCl}) \approx 6.2$; $c(\text{KCl}) \approx 4.6$; $c(\text{RbCl}) \approx 7.5$; $c(\text{CsCl}) \approx 10.7$; $c(\text{NaBr}) \approx 7.7$; $c(\text{NaI}) \approx 11.9$; $c(\text{urea}) \approx 18.2$; and $c(\text{Me}_4\text{N}^+\text{Cl}^-) \approx 6.0$ mol/L. — ^[b] $\Delta\lambda = \lambda_{\max}(3 \text{ M salt}) - \lambda_{\max}(\text{H}_2\text{O}) = \lambda_{\max}(3 \text{ M salt}) - 473$; $\Delta E_T = E_T(3 \text{ M salt}) - E_T(\text{H}_2\text{O}) = E_T(3 \text{ M salt}) - 60.4$. — ^[c] Dye not soluble. — ^[d] Not measurable.

in Figure 4, the basal plane of which corresponds to the $E_T(8)$ value of 60.4 kcal/mol for plain water. The increase in $E_T(8)$ with increasing salt concentration and increasing charge density of the alkali cation can be seen nicely in Figure 4, despite some small irregularities (e.g. RbCl).

In contrast to Entries 1–8, Entries 9,10 in Table 5 display a small bathochromic band shift of $\Delta\lambda = 8\text{--}13\text{ nm}$, corresponding to a decrease of $\Delta E_T = -1.0\text{ to }-1.6\text{ kcal/mol}$ in the molar transition energy, on addition of urea or tetramethylammonium chloride to aqueous solutions of dye **8**. Such aqueous solutions, as determined by the probe dye **8**, seem to be less polar than water. Analogous results have been obtained by Spange et al. for aqueous urea solutions, with the standard betaine **1**:^[98] Addition of urea or *N,N'*-dimethylurea to aqueous solutions of **1** not only resulted in a similar bathochromic band shift, but also substantially increased the solubility of dye **1** in water! Addition of urea (up to 75 cg/g) to an aqueous solution of dye **1** reduced the polarity of water [$E_T(30) = 63.1\text{ kcal/mol}$] to $E_T(30) = 60.6\text{ kcal/mol}$.^[98]

What is the reason for this *genuine halochromism*, with no substantial change of the molecular structure of the betaine chromophore on ionophore addition in water? Because of the high relative permittivity of water ($\epsilon_r = 78.3$), a loose association or a stronger complex formation between the betaine dye and the cations (at the phenolate part) or anions (at the pyridinium part) of the added salt, as has been found for some organic solvents,^[18–27] cannot be the reason for the ionophore-induced band shifts in the Vis spectrum of dye **8**. All these results can be better explained at least qualitatively by the assumption that some of the added species are *structure breakers* or *structure makers* with respect to the intermolecular long-range order characteristic of pure bulk water.^[99–102]

According to Frank and Wen,^[103,104] the solvation of ions (cations and anions) in highly ordered solvents such as water gives rise to three different regions in the solvent surrounding the solute ion: a primary hydration shell **A**, with profoundly immobilized water molecules, interacting directly with the ions through ion–dipole forces and, at a sufficient distance from the ion, a region **C** with the normal, tetrahedrally ordered structure of undisturbed bulk water; because of the incompatibility of regions **A** and **C**, an intermediate region **B**, with disoriented, more mobile water molecules, must exist. The difference in the development of regions **A** and **B** determines whether an ion is structure-making or structure-breaking. Small ions with high charge density, such as Li^+ or F^- , cause enhanced development of **A** at the expense of **B** and are considered as structure-making ions. Large ions with small charge density, such as Cs^+ or I^- , are considered as structure-breaking, because in this case the first hydration shell is less well developed.^[99–102] At high salt concentrations ($c > 5\text{ mol/L}$), region **C** can be abolished and only regions **A** and **B** survive, resulting in an aqueous solvent called “dihydrogen ether”.^[105,106]

The decrease in $\Delta\lambda$ on going from Entry 1 to Entry 5 in Table 5 (with decreasing *cation* charge density) and on going from Entry 6 to Entry 8 (with decreasing *anion* charge

density) corresponds to the decreasing capability of the added salts to act as structure-breakers, which in turn corresponds to an increasing activity as structure-makers.^[99] The better the structure-breaking ability of the ionophore added, the more disoriented mobile water molecules are available for the hydration of betaine dye **8**, with an increase in its $E_T(8)$ values and thus of the polarity of the aqueous ionophore solution as the result.

The adverse influence of tetramethylammonium chloride and urea on $\Delta\lambda$ (Entries 9,10 in Table 5) is more difficult to explain. Tetraalkylammonium salts are usually regarded as possessing structure-making properties; however, for a somewhat different reason.^[99–102,107,108] Large tetraalkylammonium ions with hydrophobic alkyl groups and low charge densities enhance the tetrahedral structure of water with its three-dimensional hydrogen-bonded network in the same way that other hydrophobic solutes do. The increasing degree of water–water hydrogen bonding in the cybotactic region around the nonpolar solute has been termed *hydrophobic hydration*.^[109] This hydrophobic hydration can be somewhat reduced by the corresponding anions, depending on its size and charge density.^[110] A strengthening of the three-dimensional water structure by hydrophobic solutes diminishes the quantity of disordered, more mobile water molecules necessary for the hydration of dye **8**, with the observed small bathochromic band shift as its consequence (Entry 10 in Table 5).

Urea changes the water structure so that it suppresses hydrophobic interactions, which results in an increase of the water solubility of hydrocarbons such as benzene; in other words, urea “salts in” nonpolar compounds.^[107,108] Even the solubility of standard betaine dye **1** increases substantially on addition of urea to its aqueous solution.^[98] This urea-induced solubility increase may be due to a change in the water structure,^[107,108] but may also be due to a specific hydrogen-bond formation between urea as hydrogen-bond donor/acceptor and the solute.^[111] According to Franks et al.,^[107,108] urea displaces the water equilibrium by destroying the long-range order of bulk water towards a liquid with a short-range order, by resembling water in its ability to form hydrogen bonds, but by having the wrong geometry to take part in the three-dimensional hydrogen-bonded network of water. More recent results show, however, that urea seems to fit very comfortably into the normal tetrahedral structure of water, not being the strong water structure-breaker that is usually supposed.^[112] According to Dempsey et al.,^[111] the increase in the water solubility of suitable solutes (e.g., 4-hydroxybenzoic acid and its alkyl esters) arising from addition of urea as cosolute can alternatively be explained by a 1:1 association between solute and urea, due mainly to mutual hydrogen bonding with urea as hydrogen-bond donor and acceptor.

In any case, addition of urea to aqueous solutions of dye **8** seems to reduce the amount of disordered, more mobile water molecules necessary for the specific hydration of the dye molecule, with the observed small bathochromic band shift as its result (Entry 9 in Table 5).

This qualitative discussion of the genuine halochromism of betaine dyes such as **8** is certainly oversimplified. For a sounder, more quantitative discussion, additional systematic UV/Vis-spectroscopic measurements are necessary, to augment the more exploratory data in Table 5. Water-soluble pyridyl-substituted pyridinium *N*-phenolate betaine dyes such as **3–11** should be ideal candidates for such studies of the polarity of aqueous solutions of ionophores, ionogens, and nonelectrolytes, because their chemical structures combine features of (zwitter)ionic and nonelectrolyte species.

Conclusion

Replacement of some of the peripheral hydrophobic phenyl groups in the standard betaine dye **1**, used as a primary probe dye for the $E_T(\mathbf{30})$ solvent polarity scale, by more hydrophilic pyridyl rings results in betaine dyes **3–11**, with better water solubilities. Thanks to the good linear correlation between the $E_T(\mathbf{30})$ values of **1** and the corresponding E_T values of dyes **3–11**, particularly with $E_T(\mathbf{8})$ [see Equation (3)], the new water-soluble probe dyes can be used to extend the $E_T(\mathbf{30})$ scale to all kinds of aqueous media; for example, to binary water/solvent mixtures and to aqueous ionophore solutions as preliminarily shown in this paper, but also, presumably, to microheterogeneous media such as aqueous solutions of surfactants, micelles, vesicles, and bilayers.

Experimental Section

General Methods: Melting points (not corrected): Kofler–Mikroheiztisch (Reichert). – Elemental analyses: performed with a CHN-Automat Vario EL (Heraeus) at the Analytik-ServiceLabor of the Department of Chemistry, Marburg. – UV/Vis spectra: Double-beam UV/Vis/NIR U-3410 spectrophotometer (Hitachi) with thermostatted 1.00-cm quartz cells SUPRASIL (Hellma). – IR spectra: IFS 88 spectrophotometer (Bruker) with KBr discs. – ^1H and ^{13}C NMR spectra: ARX 200 and AM 300 spectrometers (Bruker), in CDCl_3 or CD_3SOCD_3 with tetramethylsilane as internal standard. Because of low solubility and signal overlap, not all expected signals can be seen in some ^{13}C NMR spectra. – Mass spectra: MAT CH-7A spectrometer (Varian) with electron impact (EI, 70 eV), MAT 711 (Varian) with field desorption (FD), and HP 5989-B (Hewlett–Packard) with atmospheric pressure chemical ionization (APCI) technique. – Analytical TLC: 60F-245 plates with silica gel and fluorescence indicator on aluminium foil (Merck). – Flash chromatography: Silica gel 60 (Merck), particle size 0.040–0.063 mm; carried out according to Still et al.^[113] – Solvents: Solvents for the solvatochromic measurements were used as commercially available in the highest available quality (analytical or spectroscopic grade) and were additionally dried and purified by means of molecular sieves and, if necessary, by filtration through a column of basic alumina, activity grade I, in order to remove traces of acids. For these measurements the solvents must be acid-free. Otherwise, the betaine dyes are (reversibly) protonated at the phenolate oxygen atom and the long-wavelength CT absorption band disappears. Solvents for synthetic work were purified according to the usual standard methods.^[31,114–116]

Preparation of Betaine Dye 3: See Scheme 2.

1,3-Bis(pyridin-2-yl)propan-2-one (12): *n*BuLi (250 mL of a 1.5 M solution in *n*-hexane, 0.38 mol) was added at -30°C under nitrogen to a stirred solution of 2-methylpyridine (37.3 g, 40 mL, 0.40 mol) in dry THF (200 mL), over a period of 30 min. The dark red solution was allowed to warm up to room temp. and stirring was continued for 1 h. It was cooled to 0°C , and a solution of (pyridin-2-yl)acetonitrile (23.6 g, 22 mL, 0.20 mol) in dry THF (50 mL) was added, with stirring, over 30 min. The reaction mixture was then heated under reflux for 1.5 h. It was then cooled to 0°C , and aqueous HCl (300 mL of 2 N HCl) was added dropwise. The two phases thus formed were separated. The aqueous phase was neutralized by addition of aqueous ammonia (15%) and then extracted three times, each time with 200 mL of dichloromethane. The four organic phases were combined and the solvent was distilled off in a rotary evaporator. The remaining liquid was purified by fractional distillation in vacuo (b.p. $149^\circ\text{C}/0.1$ Torr) to afford 15.4 g (35%; ref.^[54,55] 38%) of **12** as a yellow liquid, which crystallized after cooling to 4°C to give yellow crystals with m.p. 80°C (ref.^[54,55] 81°C). – ^1H NMR (CDCl_3): $\delta = 3.55$ (s, 2 H, CH_2 of enol form), 3.93 (s, 4 H, CH_2 of keto form), 5.30 (s, 1 H, $\text{CH} =$ of enol form), 6.7–8.5 (m, pyridyl-H), 15.04 (s, 1 H, OH of enol form). – ^{13}C NMR (CDCl_3): $\delta = 45.7$ (CH_2 of keto form), 51.9 (CH_2 of enol form), 95.9 ($\text{CH} =$ of enol form), 117.8, 120.6, 121.4, 121.8, 123.5, 124.2, 136.3, 136.4, 136.9, 143.2, 149.2, 149.4, 154.5, 157.9, and 158.0 (pyridyl-C), 168.5 ($=\text{COH}$ of enol form), 203.7 ($\text{C}=\text{O}$ of keto form).

4-Nitro-2,6-bis(pyridin-2-yl)phenol (13): A solution of NaOH (1.60 g, 40.0 mmol) in water (40 mL) was added to a solution of **12** (4.40 g, 20.7 mmol) and sodium nitromalonate monohydrate (3.40 g, 21.7 mmol)^[56] in ethanol (30 mL), and the mixture was stirred at room temp. over a period of 3 d. The red solution was transferred in a rotary evaporator and about half of the solvent was distilled off. The remaining solution was neutralized with aqueous acetic acid (30%, w/w), and the precipitate formed was filtered off, washed several times with water, and recrystallized from ethanol (300 mL) to afford 5.10 g (81%) of **13** as yellow needles with m.p. 205°C . – ^1H NMR (CD_3SOCD_3): $\delta = 7.49$ (m, 2 H, pyridyl-5/5'-H), 8.02 (m, 2 H, pyridyl-3/3'-H), 8.42 (d, $^3J = 8.1$ Hz, 2 H, pyridyl-4/4'-H), 8.71 (dd, 2 H, $^3J = 4.1$ and $^4J = 1.8$ Hz, pyridyl-6/6'-H), 8.88 (s, 2 H, aromatic phenol-H), 14.31 (s, 1 H, OH). – ^{13}C NMR (CD_3SOCD_3): 122.9, 123.4, 125.2, 138.1, 147.3, and 154.0 (phenol and pyridyl-C). – IR (KBr): $\tilde{\nu} = 3438$ (OH) cm^{-1} , 1339 (NO_2). – MS (EI): m/z (%) = 293 (100) [M^+]. – $\text{C}_{16}\text{H}_{11}\text{N}_3\text{O}_3 \cdot 0.5 \text{C}_2\text{H}_5\text{OH}$ (293.3 + 23.0 = 316.2): calcd. C 64.55, H 4.46, N 13.26; found C 64.13, H 4.16, N 13.69.

4-Amino-2,6-bis(pyridin-2-yl)phenol (14): A suspension of a palladium catalyst (10% Pd on charcoal; ca. 200 mg) in a solution of **13** (1.47 g, 5.00 mmol) in methanol (150 mL) was reduced with dihydrogen (ca. 380 mL of H_2) at room temp. and normal pressure over a period of 2 d. The catalyst was filtered off under nitrogen, and the solvent was distilled off in vacuo to give **14** (1.34 g, ca. 100%) as a pale brown solid, which turned dark on contact with air. Because of its sensitivity to oxygen, **14** was immediately transformed into the pyridinium salt **15** without further characterization.

1-[4-Hydroxy-3,5-bis(pyridin-2-yl)phenyl]-2,4,6-triphenylpyridinium Tetrafluoroborate (15): Anhydrous sodium acetate (1.65 g, 20.0 mmol) and 2,4,6-triphenylpyridium tetrafluoroborate (1.98 g, 5.00 mmol)^[57] were added to a stirred solution of freshly prepared **14** (1.34 g, 5.00 mmol) in dry methanol (40 mL) and the mixture was heated at reflux with a water bath for 3 h. Water (30 mL) was added to the hot, dark red solution, resulting in a yellow precipit-

ate. After the reaction mixture had been stirred for ca. 12 h at room temp., the yellow precipitate formed was filtered off and dried in vacuo to give **15** (2.89 g, 90%) as light yellow, fine crystals with m.p. 171 °C. – ¹H NMR (CD₃SOCD₃): δ = 7.30–7.46 (m, 8 H, 6 phenyl-H and 2 pyridyl-5/5'-H), 7.54–7.60 (m, 4 H, phenyl-H), 7.64–7.74 (m, 3 H, phenyl-H), 7.88–7.99 (m, 4 H, 2 phenyl-H and 2 phenol-3/3'-H), 8.19 (s, 2 H, pyridyl-3/3'-H), 8.37 (d, ³J = 8.2 Hz, 2 H, pyridyl-4/4'-H), 8.60 (d, ³J = 4.1 Hz, 2 H, pyridyl-6/6'-H), 8.71 (s, 2 H pyridinium-3/3'-H), 15.89 (s, 1 H, OH). – ¹³C NMR (CD₃SOCD₃): δ = 122.3, 123.2, 125.3, 128.4, 129.0, 130.0, 130.2, 130.4, 132.8, 133.5, 133.7, 138.1, 147.7, 154.4, 155.8, 157.0, and 158.2 (aromatic and heteroaromatic C); because of poor resolution, only 17 signals were observed instead of the expected 20. – IR (KBr): $\tilde{\nu}$ = 3446 (OH) cm⁻¹, 1083 (BF₄). – UV (CH₃CN): λ_{max} (lg ε) = 303 nm (4.62), 233 (4.57). – MS (FD): *m/z* (%) = 554 (100) [M⁺ – BF₄]. – C₃₉H₂₈BF₄N₃O·2H₂O (641.5 + 36.0 = 677.5): calcd. C 69.14, H 4.76, N 6.20; found C 69.29, H 4.52, N 6.14.

2,6-Bis(pyridin-2-yl)-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (3): Sodium methoxide (0.22 g, 4.00 mmol) was added at room temp. to a solution of **15** (0.68 g, 1.00 mmol) in dry methanol (30 mL), during which the color of the solution changed from yellow to dark. After having been heated under reflux for 5 min, the hot solution was poured into aqueous NaOH (10% w/w, 100 mL). After standing for ca. 24 h at room temp., the violet precipitate formed was filtered off and washed several times with water and three times with diethyl ether (3 × 50 mL). Purification by twofold hot extraction, first with 80 mL of boiling water/methanol (1:1) and then with 80 mL of boiling water/methanol (1:2) gave, after drying with P₄O₁₀ in vacuo, betaine dye **3** (0.51 g, 86%) as red-violet crystals with m.p. 260 °C, still containing ca. 2 mol of water of crystallization. – ¹H NMR (CD₃SOCD₃): δ = 7.08 (m, 2 H, pyridyl-5/5'-H), 7.36–7.78 (m, 15 H, phenyl-H), 7.90 (s, 2 H, phenolate-3/3'-H), 8.10 (m, 2 H, pyridyl-3/3'-H), 8.48 (m, 2 H, pyridyl-4/4'-H), 8.57 (s, 2 H, pyridinium-3/3'-H), 9.06 (m, 2 H, pyridyl-6/6'-H). – ¹³C NMR (CD₃SOCD₃): δ = 128.2, 128.9, 130.1, and 148.1 (aromatic and heteroaromatic C); because of low solubility, only 4 signals were observed instead of the expected 20. – IR (KBr): $\tilde{\nu}$ = 3371 (OH) cm⁻¹. – UV/Vis (CH₃CN): λ_{max} (lg ε) = 574.5 nm (3.41), 437.5 (4.10), 301 (4.54), 242 (4.52). – MS (FD): *m/z* (%) = 554 (100) [M⁺ + 1], 553 (94) [M⁺]. – C₃₉H₂₇N₃O·2H₂O (553.7 + 36.0 = 589.7): calcd. C 79.44, H 5.30, N 7.13; found C 79.38, H 5.18, N 7.11.

Preparation of Betaine Dye 4: See Scheme 3.

1,5-Diphenyl-3-(pyridin-4-yl)pentane-1,5-dione (16): Acetophenone (5.00 g, 41.6 mmol) was added at 0 °C to a well-stirred solution of sodium hydride (0.15 g, 6.25 mmol) in dry methanol (15 mL), followed, slowly at 0 to 10 °C, by pyridin-4-carbaldehyde (2.00 g, 21.0 mmol). Water was then added dropwise until a milky suspension was formed. After further stirring for 4 h at room temp., a brown viscous oil was beginning to separate from the reaction mixture. After standing for ca. 24 h at 0 °C, the oil had crystallized. The solid was filtered off and recrystallized from ethanol/water (9:1) to afford **16** (3.02 g, 44%) as fine, colorless needles with m.p. 124–126 °C (ref.^[58] 125–126 °C).

2,6-Diphenyl-4-[(1*H*)-pyridinium-4-yl]pyrylium Bis(tetrafluoroborate) (17): Boron trifluoride–diethyl ether (20 mL) was added dropwise to a stirred solution of **16** (5.00 g, 15.2 mmol) and benzalacetophenone (3.30 g, 15.8 mmol) in hot, anhydrous acetic acid (8 mL) and the red solution was heated at reflux for 6 h. After cooling to room temp. and addition of diethyl ether (50 mL), the precipitate

formed was filtered off and recrystallized from acetic acid to give **17** (4.30 g, 69%) as orange crystals with m.p. 275–277 °C (ref.^[58] 275–277 °C).

1-[4-Hydroxy-3,5-bis(pyridin-2-yl)phenyl]-2,6-diphenyl-4-(pyridin-4-yl)pyridinium Tetrafluoroborate (18): According to the procedure described for **15**, freshly prepared 4-aminophenol **14** (1.34 g, 5.00 mmol), the pyrylium salt **17** (2.05 g, 5.00 mmol), and sodium acetate (1.65 g, 20.00 mmol) in methanol (40 mL) were transformed into **18**, which was recrystallized from water/methanol (1:3) and dried with P₄O₁₀ in vacuo to afford **18** (2.78 g, 82%) as yellow crystals, containing ca. 2 mol of water of crystallization, with m.p. 191 °C. – ¹H NMR (CD₃SOCD₃): δ = 7.38–7.52 (m, 8 H, 6 phenyl-H and 2 2-pyridyl-5/5'-H), 7.62 (m, 4 H, 2 phenyl-H and 2 2-pyridyl-3/3'-H), 7.92–8.06 (m, 4 H, 2 phenyl-H and 2 2-pyridyl-4/4'-H), 8.23 (s, 2 H, phenol-3/3'-H), 8.38 (d, ³J = 4.5 Hz, 2 H, 4-pyridyl-3/3'-H), 8.64 (d, ³J = 4.5 Hz, 2 H, 2-pyridyl-6/6'-H), 8.89 (s, 2 H, pyridinium-3/3'-H), 8.97 (d, ³J = 4.5 Hz, 2 H, 4-pyridyl-2/2'-H), 16.80 (s, 1 H, OH). – ¹³C NMR (CD₃SOCD₃): δ = 122.0, 122.3, 122.9, 123.0, 126.0, 128.1, 129.6, 129.7, 130.0, 130.1, 133.0, 137.8, 140.7, 147.4, 151.0, 153.1, 154.1, 157.3, and 158.1 (aromatic and heteroaromatic C). – IR (KBr): $\tilde{\nu}$ = 3429 (OH) cm⁻¹, 1093 (BF₄). – UV (CH₃CN): λ_{max} (lg ε) = 267 nm (4.62), 240 (4.60). – MS (FD): *m/z* (%) = 555 (100) [M⁺ – BF₄]. – C₃₈H₂₇BF₄N₄O·2H₂O (642.5 + 36.0 = 678.5): calcd. C 67.27, H 4.61, N 8.26; found C 67.59, H 4.43, N 8.20.

4-[2,6-Diphenyl-4-(pyridin-4-yl)pyridinium-1-yl]-2,6-bis(pyridin-2-yl)phenolate (4): According to the procedure described for betaine dye **3**, the pyridinium salt **18** (0.68 g, 1.00 mmol), dissolved in methanol (30 mL), was transformed into **4** using sodium methoxide (0.22 g, 4.00 mmol). The product was purified analogously, by twofold hot extraction, filtered off, and dried with P₄O₁₀ in vacuo to afford **4** (0.50 g, 86%) as dark green crystals, containing ca. 1.5 mol of water of crystallization, with m.p. 292 °C. – ¹H NMR (CD₃SOCD₃): δ = 7.00 (m, 2 H, 2-pyridyl-5/5'-H), 7.32–7.58 (m, 12 H, 10 phenyl-H and 2 2-pyridyl-3/3'-H), 7.83 (s, 2 H, phenolate-3/3'-H), 8.27 (d, ³J = 4.8 Hz, 2 H, 2-pyridyl-4/4'-H), 8.39 (d, ³J = 4.5 Hz, 2 H, 4-pyridyl-3/3'-H), 8.62 (s, 2 H, pyridinium-3/3'-H), 8.86 (d, ³J = 4.5 Hz, 2 H, 4-pyridyl-2/2'-H), 9.00 (d, ³J = 8.1 Hz, 2 H, 2-pyridyl-6/6'-H). – ¹³C NMR (CDCl₃): δ = 121.7, 123.9, 127.9, 128.2, 129.0, 129.2, 131.2, 136.8, 137.4, 149.1, and 151.5 (aromatic and heteroaromatic C); because of poor resolution, only 11 signals were observed instead of the expected 19. – IR (KBr): $\tilde{\nu}$ = 3368 (OH) cm⁻¹. – UV/Vis (CH₃CN): λ_{max} (lg ε) = 612 nm (3.47), 438 (4.12), 249 (4.63). – MS (FD): *m/z* (%) = 555 (100) [M⁺ + 1], 554 (73) [M⁺]. – C₃₈H₂₆N₄O·1.5 H₂O (554.6 + 27.0 = 581.6): calcd. C 78.47, H 5.03, N 9.63; found C 78.30, H 4.94, N 9.51.

Preparation of Betaine Dye 5: See Scheme 4.

4-Phenyl-2,6-bis[(1*H*)-pyridinium-4-yl]pyrylium Tris(tetrafluoroborate) (19): A one-necked, round-bottomed 50-mL flask was equipped with dropping funnel (with pressure equalizer), reflux condenser (on top of the dropping funnel), and magnetic stirrer. 4-Acetylpyridine (7.50 g, 62.0 mmol) and freshly distilled benzaldehyde (3.30 g, 31.1 mmol) were placed inside, and tetrafluoroboric acid in diethyl ether (54% w/w, 20 mL, 146 mmol) was added dropwise at room temp. to the stirred mixture. The yellow precipitate formed was dissolved by heating the reaction mixture, during which the diethyl ether was distilled off and collected in the dropping funnel. The remaining stirred mixture was heated to ca. 150 °C for 10 min. After cooling to room temp., the mixture was thoroughly digested with diethyl ether. Acetone (15 mL) was then added to the

remaining solid, and the suspension was stirred for 2 h at room temp. The solid was filtered off and washed several times with acetone. For further purification, a suspension of this solid in hot acetone (15 mL) was stirred for 15 min. After cooling to room temp., the solid was filtered off and this procedure was repeated to afford, after drying with P_4O_{10} in vacuo, the pyrylium salt **19** (6.40 g, 36%) as yellow, fluorescent crystals with m.p. 236–247 °C (dec.). – 1H NMR (CF_3CO_2D): δ = 8.17–8.85 (m, 5 H, phenyl-H), 9.48 (d, 3J = 5.5 Hz, 4 H, 2 pairs of 4-pyridyl-3/3'-H), 9.67 (d, 3J = 5.5 Hz, 4 H, 2 pairs of 4-pyridyl-2/2'-H), 9.80 (s, 2 H, pyrylium-3/3'-H). – ^{13}C NMR (CF_3CO_2D): δ = 111.3 (pyrylium-C-3/3'), 115.1 (4-pyridyl-C-3/3'), 118.8 (4-phenyl-C-2/2'), 122.6 (4-phenyl-C-3/3'), 129.1 (4-pyridyl-C-4/4'), 143.1 (4-phenyl-C-4), 146.2 (4-pyridyl-C-2/2'), 147.8 (4-phenyl-C-1), 168.5 (pyrylium-C-4), 174.8 (pyrylium-C-2/2'). – IR (KBr): $\tilde{\nu}$ = 1053 cm^{-1} (BF_4). – MS (FD): m/z (%) = 312 (100) [$M^+ - 3 BF_4^- - 2 H^+$]. – $C_{21}H_{17}B_3F_{12}N_2O$ (573.8): calcd. C 43.96, H 2.99, N 4.88; found C 43.59, H 3.11, N 4.84.

1-[4-Hydroxy-3,5-bis(pyridin-2-yl)phenyl]-4-phenyl-2,6-bis(pyridin-4-yl)pyridinium Tetrafluoroborate (20): Anhydrous sodium acetate (1.65 g, 20.0 mmol) and the pyrylium salt **19** (2.87 g, 5.00 mmol) were added to a stirred solution of freshly prepared 4-aminophenol **14** (1.34 g, 5.00 mmol) in dry methanol (40 mL). The mixture was heated with a water bath at reflux for 3 h, and a yellow precipitate formed. After the mixture had stood for ca. 12 h at room temp., water (40 mL) was added. The precipitate formed was filtered off and thoroughly washed with water and three times with diethyl ether (3×80 mL), and dried with P_4O_{10} in vacuo to afford **20** (2.58 g, 78%) as yellow crystals with m.p. 218 °C, containing ca. 1 mol of water of crystallization. – 1H NMR (CD_3SOCD_3): δ = 7.36 (m, 2 H, 2-pyridyl-5/5'-H), 7.49 (d, 3J = 4.5 Hz, 4 H, 2 pairs of 4-pyridyl-3/3'-H), 7.58–7.94 (m, 7 H, phenyl-H and 2 2-pyridyl-3/3'-H), 8.17 (s, 2 H, phenol-3/3'-H), 8.32 (d, 3J = 8.2 Hz, 2 H, 2-pyridyl-4/4'-H), 8.53–8.57 (m, 6 H, 2 2-pyridyl-6/6'-H and 2 pairs of 4-pyridyl-2/2'-H), 8.80 (s, 2 H, pyridinium-3/3'-H), 15.83 (s, 1 H, OH). – ^{13}C NMR (CD_3SOCD_3): δ = 122.0, 123.2, 123.8, 123.9, 125.4, 128.8, 129.1, 129.4, 129.7, 132.8, 133.0, 137.8, 140.4, 147.4, 149.5, 153.8, 154.2, 156.2, and 158.5 (aromatic and heteroaromatic C). – IR (KBr): $\tilde{\nu}$ = 3410 (OH) cm^{-1} , 1070 (BF_4). – UV (CH_3CN): λ_{max} (lg ϵ) = 303 nm (4.68), 234 (4.70). – MS (FD): m/z (%) = 556 (100) [$M^+ - BF_4$]. – $C_{37}H_{26}BF_4N_5O \cdot H_2O$ (643.4 + 18.0 = 661.4): calcd. C 67.19, H 4.27, N 10.59; found C 67.17, H 4.68, N 10.36.

4-[4-Phenyl-2,6-bis(pyridin-4-yl)pyridinium-1-yl]-2,6-bis(pyridin-2-yl)phenolate (5): In analogy with the procedure described for betaine dye **3**, the pyridinium salt **20** (0.66 g, 1.00 mmol), dissolved in methanol (30 mL), was transformed into **5** using sodium methoxide (0.22 g, 4.00 mmol). The product was purified by hot extraction with water/methanol (4:1, 50 mL), filtered off, and dried with P_4O_{10} in vacuo to give **5** (0.33 g, 56%) as black-violet crystals, containing ca. 2 mol of water of crystallization, with m.p. 237 °C. – 1H NMR (CD_3SOCD_3): δ = 7.00 (m, 2 H, 2-pyridyl-5/5'-H), 7.51–7.72 (m, 9 H, phenyl-H and 2 pairs of 4-pyridyl-3/3'-H), 7.85 (s, 2 H, phenolate-3/3'-H), 8.31 (m, 2 H, 2-pyridyl-3/3'-H), 8.39 (m, 2 H, 2-pyridyl-4/4'-H), 8.57 (m, 4 H, 2 pairs of 4-pyridyl-2/2'-H), 8.65 (s, 2 H, pyridinium-3/3'-H), 8.98 (d, 3J = 8.1 Hz, 2 H, 2-pyridyl-6/6'-H). – ^{13}C NMR (CD_3SOCD_3): δ = 118.8, 119.7, 123.0, 123.8, 125.8, 126.8, 128.5, 129.2, 129.5, 132.2, 133.4, 134.7, 141.3, 147.8, 149.2, 154.1, 154.2, 157.2, and 171.6 (aromatic and heteroaromatic C). – IR (KBr): $\tilde{\nu}$ = 3377 (OH) cm^{-1} . – UV/Vis (CH_3CN): λ_{max} (lg ϵ) = 607 nm (3.73), 438.5 (4.14), 302 (4.62), 240 (4.65). – MS (FD): m/z (%) = 556 (80) [$M^+ + 1$], 555 (100) [M^+]. – $C_{37}H_{25}N_5O \cdot 2H_2O$ (555.6 + 36.0 = 591.6): calcd. C 75.11, H 4.94, N 11.84; found C 74.99, H 5.18, N 11.43.

Preparation of Betaine Dye 6: See Scheme 5.

(Pyridin-3-yl)thioacetmorpholide (21):^[60] A mixture of 3-acetylpyridine (228 g, 1.88 mol), morpholine (164 g, 1.88 mol), and sulfur powder (60 g, 1.88 mol) was heated under reflux for 12 h in a round-bottomed 1-L flask equipped with reflux condenser. The warm solution was then poured onto an ice/water slush (ca. 500 mL). The yellow precipitate formed was filtered off and dried with P_4O_{10} in vacuo to afford **21** (318 g, 76%) as a yellow solid of m.p. 78 °C (ref.^[60] 78–80 °C), which was used without further purification in the next reaction step.

(Pyridin-3-yl)acetic Acid Hydrochloride (22):^[60] A solution of **21** (44.5 g, 200 mmol) and KOH (12.0 g, 214 mmol) in ethanol (95%, 200 mL) was heated at reflux for 72 h in a round-bottomed 500-mL flask equipped with reflux condenser. The mixture was then poured into water (400 mL). The volume of the solution was reduced to ca. 200 mL by distilling off the solvents in a rotary evaporator (hood!). After further addition of water (200 mL), the solvents were distilled off nearly to dryness in a rotary evaporator. Aqueous HCl (6 N, 200 mL) was then added, and the solvents were completely distilled off in the rotary evaporator. The remaining solid was thoroughly digested three times with ethanol (3×200 mL), the ethanolic solution was transferred into a rotary evaporator, and the solvent was distilled off to yield the hydrochloride **22** (26.70 g, 77%) as yellow crystals. It was used without further purification in the next reaction step.

Ethyl (Pyridin-3-yl)acetate (23):^[60,61] A solution of hydrochloride **22** (26.0 g, 150 mmol) in a mixture of concd. sulfuric acid (30 mL) and anhydrous ethanol (70 mL) was heated at reflux for 4 h in a round-bottomed 250-mL flask equipped with a reflux condenser. After cooling to room temp., the reaction mixture was poured onto ice (ca. 300 g). Concd. aqueous ammonia was then added, until a pH value of > 7 was reached. The aqueous solution was extracted four times with diethyl ether (4×300 mL), the collected ethereal phases were dried with $MgSO_4$, and the solvent was distilled off in a rotary evaporator. The remaining liquid was fractionally distilled to afford **23** (14.9 g, 60%) as a colorless liquid with b.p. 120–122 °C/10 Torr (ref.^[60] 121–122 °C/10 Torr). The compound partially crystallized on standing at +4 °C. – 1H NMR ($CDCl_3$): δ = 1.14 (t, 3J = 7.1 Hz, 3 H, CH_3), 3.50 (s, 2 H, CH_2CO), 4.05 (q, 3J = 7.1 Hz, 2 H, OCH_2), 7.14 (dd, 1 H, pyridyl-5-H), 7.53 (m, 1 H, pyridyl-4-H), 8.40 (m, 2 H, pyridyl-2-H and 6-H). – ^{13}C NMR ($CDCl_3$): δ = 13.8 (CH_3), 38.2 ($O-CH_2$), 60.9 (CH_2-CO), 123.1, 129.7, 136.5, 148.3, and 150.2 (pyridyl-C), 170.4 ($C=O$).

1,3-Bis(pyridin-3-yl)propan-2-one (24):^[62] The ester **23** (16.5 g, 100 mmol) was added dropwise at room temp., over a period of 30 min, to a stirred solution of sodium ethoxide in ethanol, prepared from sodium (2.3 g, 100 mmol) and anhydrous ethanol (100 mL). The mixture was then stirred for 12 h at 60–70 °C. After it had cooled to room temp., concd. aqueous HCl (80 mL) was added and the solution was heated under reflux for 3 h. After it had cooled to room temp., water (100 mL) was added and the solution was extracted twice with trichloromethane (2×100 mL). Aqueous NaOH (10% w/w) was added to the aqueous phase until the pH value had reached a value of > 7 and this solution was extracted three times with trichloromethane (3×100 mL). The organic phases were collected and dried with $MgSO_4$, and the solvent was distilled off in a rotary evaporator to afford ketone **24** (2.5 g, 23%) as colorless crystals with m.p. 104 °C (ref.^[62] 103–104 °C). – 1H NMR ($CDCl_3$): δ = 3.82 (s, 4 H, CH_2), 7.25–7.32 (m, 2 H, pyridyl-5/5'-H), 7.50–7.55 (m, 2 H, pyridyl-4/4'-H), 8.45 (s, 2 H, pyridyl-2/2'-H), 8.55 (d, 3J = 3.8 Hz, 2 H, pyridyl-6/6'-H). – ^{13}C

NMR (CDCl₃): δ = 46.2 (CH₂), 123.5, 129.1, 137.0, 148.7, and 150.4 (pyridyl-C), 203.1 (C=O).

4-Nitro-2,6-bis(pyridin-3-yl)phenol (25): A solution of NaOH (1.60 g, 40.0 mmol) in water (40 mL) was added to a stirred solution of ketone **24** (4.40 g, 20.7 mmol) and sodium nitromalonate monohydrate (3.40 g, 21.7 mmol)^[56] in ethanol (30 mL), and the mixture was stirred at room temp. over a period of 3 d. The red solution was transferred into a rotary evaporator, the ethanol was distilled off, and the remaining solution was neutralized by addition of aqueous acetic acid (30%, w/w). The yellow precipitate formed was filtered off, washed several times with water, and purified by hot extraction with ethanol (70 mL), to afford the nitrophenol **25** (5.18 g, 85%) as yellow needles with m.p. 238–239 °C. – ¹H NMR (CD₃SOCD₃): δ = 7.51–7.57 (dd, 2 H, pyridyl-5/5'-H), 8.04 (m, 2 H, pyridyl-4/4'-H), 8.18 (s, 2 H, phenol-3/3'-H), 8.61 (dd, 2 H, ³J = 4.8 Hz and ⁴J = 1.5 Hz, pyridyl-6/6'-H), 8.82 (d, ⁴J = 2.2 Hz, 2 H, pyridyl-2/2'-H); the broad OH signal was not detectable. – ¹³C NMR (CD₃SOCD₃): δ = 122.8, 125.2, and 136.4 (phenol and pyridyl-C); because of the low solubility, only 3 signals were observed instead of the expected 9. – IR (KBr): $\tilde{\nu}$ = 3450 (OH) cm⁻¹, 1327 (NO₂). – MS (FD): *m/z* (%) = 293 (100) [M⁺]. – C₁₆H₁₁N₃O₃ (293.3): calcd. C 65.53, H 3.78, N 14.33; found C 65.24, H 3.70, N 14.35.

4-Amino-2,6-bis(pyridin-3-yl)phenol (26): A suspension of a palladium catalyst (10% Pd on charcoal, ca. 200 mg) in a solution of **25** (1.47 g, 5.00 mmol) in ethanol (75 mL) and trichloromethane (75 mL) was reduced with dihydrogen (ca. 380 mL H₂) at room temp. and normal pressure over a period of 2 d. The catalyst was filtered off under nitrogen, and the solvents were distilled off in vacuo to give, after drying in vacuo, the aminophenol **26** (1.34 g, ca. 100%) as a pale brown solid, which turned dark on exposure to air. Because of its sensitivity to oxygen, **26** was immediately converted into the pyridinium salt **27** without further characterization.

1-[4-Hydroxy-3,5-bis(pyridin-3-yl)phenyl]-2,4,6-triphenylpyridinium Tetrafluoroborate (27): Anhydrous sodium acetate (1.65 g, 20.0 mmol) and 2,4,6-triphenylpyrylium tetrafluoroborate (1.98 g, 5.00 mmol)^[57] were added to a stirred solution of freshly prepared 4-aminophenol **26** (1.34 g, 5.00 mmol) in dry methanol (40 mL), and the mixture was heated with a water bath under reflux for 3 h. Water (30 mL) was added to the hot, dark red solution, resulting in a light green precipitate. After the mixture had been stirred for ca. 12 h at room temp., the precipitate formed was filtered off, washed once with water and several times with diethyl ether, and dried with P₄O₁₀ in vacuo, to afford **27** monohydrate (2.89 g, 90%) as light green crystals with m.p. 237–239 °C. – ¹H NMR (CD₃SOCD₃): δ = 7.42–7.68 (m, 19 H, 15 phenyl-H, 2 phenol-3/3'-H, and 2 3-pyridyl-5/5'-H), 8.27 (d, ⁴J = 2.1 Hz, 2 H, 3-pyridyl-2/2'-H), 8.37 (m, 2 H, 3-pyridyl-4/4'-H), 8.52 (dd, 2 H, ³J = 4.8 Hz and ⁴J = 1.6 Hz, 3-pyridyl-6/6'-H), 8.73 (s, 2 H, pyridinium-3/3'-H); the broad OH signal was not detectable. – ¹³C NMR (CD₃SOCD₃): δ = 123.5, 125.1, 127.5, 128.4, 129.0, 129.9, 130.0, 130.2, 130.7, 132.7, 133.5, 136.6, 148.7, 149.4, 156.8, and 177.9 (aromatic and heteroaromatic C); because of low solubility and insufficient resolution, only 16 signals were observed instead of the expected 20. – IR (KBr): $\tilde{\nu}$ = 3430 (OH) cm⁻¹, 1090 (BF₄). – UV (CH₃CN): λ_{max} (lg ϵ) = 307 nm (4.58), 226 (4.63). – MS (APCI, positive): *m/z* = 554 [M⁺]. – C₃₉H₂₈BF₄N₃O · H₂O (641.5 + 18.0 = 659.5): calcd. C 71.03, H 4.58, N 6.37; found C 71.23, H 4.79, N 6.40.

2,6-Bis(pyridin-3-yl)-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (6): Sodium methoxide (0.22 g, 4.00 mmol) was added at room temp.

to a solution of pyridinium salt **27** (0.66 g, 1.00 mmol) in dry methanol (30 mL). After heating at reflux for 5 min, the hot solution was poured into aqueous NaOH (10% w/w, 100 mL). The violet solution was then extracted three times with trichloromethane (3 × 100 mL). The collected organic phases were washed with water (100 mL) and dried with MgSO₄, and the solvent was distilled off in a rotary evaporator, to yield, after drying with P₄O₁₀ in vacuo, betaine dye **6** (0.39 g, 71%) as a violet amorphous powder, still containing some water and trichloromethane, with m.p. 197–198 °C. – ¹H NMR (CD₃SOCD₃): δ = 6.93 (s, 2 H, phenolate-3/3'-H), 7.17 (dd, 2 H, 3-pyridyl-5/5'-H), 7.39–7.65 (m, 15 H, phenyl-H), 7.88 (m, 2 H, 3-pyridyl-4/4'-H), 8.23 (dd, 2 H, ³J = 4.7 Hz and ⁴J = 1.5 Hz, 3-pyridyl-6/6'-H), 8.37 (d, ⁴J = 1.9 Hz, 2 H, 3-pyridyl-2/2'-H), 8.55 (s, 2 H, pyridinium-3/3'-H). – ¹³C NMR (CD₃SOCD₃): δ = 122.3, 124.7, 125.3, 128.3, 128.7, 128.9, 129.6, 129.8, 134.6, 135.2, 136.8, 145.7, 149.0, 153.8, 156.9, and 177.9 (aromatic and heteroaromatic C); because of low solubility and insufficient resolution, only 16 signals were observed instead of the expected 20. – IR (KBr): $\tilde{\nu}$ = 3440 (OH) cm⁻¹. – UV/Vis (CH₃CN): λ_{max} (lg ϵ) = 590 nm (3.56), 416 (3.89), 302 (4.53), 232 (4.52). – MS (APCI, positive): *m/z* = 554 [M⁺ + 1]. – C₃₉H₂₇N₃O · 0.5 H₂O · 0.5 CHCl₃ (553.7 + 45.0 + 59.7 = 658.4): calcd. C 72.06, H 4.98, N 6.38; found C 71.92, H 4.71, N 6.18.

Preparation of Betaine Dye 7: See Scheme 6.

4-Phenyl-2,6-bis[1*H*-pyridinium-3-yl]pyrylium Tris(tetrafluoroborate) (28): A one-necked, round-bottomed 50-mL flask was equipped with dropping funnel (with pressure equalizer), reflux condenser (on top of the dropping funnel), and magnetic stirrer. Freshly distilled 3-acetylpyridine (7.50 g, 62.0 mmol) and freshly distilled benzaldehyde (3.30 g, 31.1 mmol) were placed inside, and tetrafluoroboric acid in diethyl ether (54% w/w, 20 mL, 146 mmol) was added dropwise at room temp. to the stirred mixture, giving rise to a yellow precipitate. The reaction mixture was heated until the whole of the diethyl ether had distilled off and condensed in the dropping funnel. The remaining stirred mixture was then heated to ca. 150 °C for 10 min. After cooling to room temp., the brown mixture was thoroughly digested several times with diethyl ether. Acetone (20 mL) was added to the remaining, rubber-like solid and the suspension was stirred at room temp. for 2 d. The solid was filtered off and washed several times with acetone. For further purification, a suspension of this solid in hot acetone (15 mL) was stirred for 15 min. After cooling to room temp., the solid was filtered off and the procedure with hot acetone was repeated, to afford, after drying with P₄O₁₀ in vacuo, pyrylium salt **28** (7.29 g, 41%) as yellow fluorescent crystals, still containing some water, with m.p. 167 °C. – ¹H NMR (CF₃CO₂D): δ = 7.97 (m, 2 H, 4-phenyl-*m*-H), 8.17 (m, 1 H, 4-phenyl-*p*-H), 8.58 (m, 2 H, 3-pyridyl-5/5'-H), 8.67 (m, 2 H, 4-phenyl-*o*-H), 9.35 (m, 2 H, 3-pyridyl-6/6'-H), 9.43 (m, 2 H, 3-pyridyl-2/2'-H), 9.80 (m, 2 H, 3-pyridyl-4/4'-H), 10.15 (s, 2 H, pyrylium-3/3'-H). – ¹³C NMR (CD₃CO₂D): δ = 120.5, 130.3, 132.3, 132.4, 143.7, 146.6, 148.1, and 167.1 (phenyl and pyridyl-C), 188.4 (pyrylium-C-2); because of low solubility and insufficient resolution, only 9 signals were observed instead of the expected 12. – IR (KBr): $\tilde{\nu}$ = 3396 (OH) cm⁻¹, 1059 (BF₄). – MS (FD): *m/z* (%) = 311 (100) [M⁺ – BF₄ – 2 HBF₄]. – C₂₁H₁₇B₃F₁₂N₂O · 1.5 H₂O (573.8 + 27.0 = 600.8): calcd. C 42.25, H 3.75, N 4.33; found C 41.98, H 3.36, N 4.66.

1-[4-Hydroxy-3,5-bis(pyridin-3-yl)phenyl]-4-phenyl-2,6-bis(pyridin-3-yl)pyridinium Tetrafluoroborate (29): Anhydrous sodium acetate (1.65 g, 20.0 mmol) and the pyrylium salt **28** (3.00 g, 5.00 mmol) were added to a stirred solution of freshly prepared 4-aminophenol **26** (1.34 g, 5.00 mmol) in dry methanol (40 mL). The mixture was

heated with a water bath under reflux for 3 h. Water (30 mL) was added to the hot solution, producing a precipitate. After the mixture had been stirred for ca. 12 h at room temp., the precipitate formed was filtered off, washed once with water and several times with diethyl ether, and dried with P_4O_{10} in vacuo, to afford **29** (2.76 g, 86%) as colorless crystals, still containing some water, with m.p. 192–194 °C. – 1H NMR (CD_3SOCD_3): δ = 7.43–7.74 (m, 11 H, 5 4-phenyl-H, 2 phenol-3/3'-H, and 2 pairs of 3-pyridyl-5/5'-H), 7.95 (m, 2 H, 3-pyridyl-4/4'-H), 8.32 (d, 4J = 1.9 Hz, 2 H, 3-pyridyl-2/2'-H), 8.40 (m, 2 H, 3-pyridyl-4/4'-H), 8.55 (dd, 2 H, 3J = 4.8 and 4J = 1.5 Hz, 3-pyridyl-6/6'-H), 8.66 (dd, 2 H, 3J = 4.8 and 4J = 1.5 Hz, 3-pyridyl-6/6'-H), 8.78 (d, 4J = 2.0 Hz, 2 H, 3-pyridyl-2/2'-H), 8.91 (s, 2 H, pyridinium-3/3'-H); the broad OH signal was not detectable. – ^{13}C NMR (CD_3SOCD_3): δ = 123.3, 123.6, 126.0, 128.1, 129.1, 129.6, 132.4, 136.6, 137.5, 148.9, 149.3, 149.7, 151.1, 154.3, and 177.9 (aromatic and heteroaromatic C); because of low solubility and insufficient resolution, only 15 of the expected 21 signals were observed. – IR (KBr): $\tilde{\nu}$ = 3430 (OH) cm^{-1} , 1059 (BF_4). – UV (CH_3CN): λ_{max} (lg ϵ) = 309 nm (4.56), 228 (4.60). – MS (APCI, positive): m/z = 556 [M^+]. – $C_{37}H_{26}BF_4N_5O_2 \cdot H_2O$ (643.4 + 18.0 = 661.5): calcd. C 67.19, H 4.27, N 10.59; found C 66.88, H 4.70, N 10.31.

4-[4-Phenyl-2,6-bis(pyridin-3-yl)pyridinium-1-yl]-2,6-bis(pyridin-3-yl)phenolate (7): Sodium methoxide (0.22 g, 4.00 mmol) was added at room temp. to a solution of pyridinium salt **29** (0.66 g, 1.00 mmol) in dry methanol (30 mL). After heating under reflux for 5 min, the hot solution was poured into aqueous NaOH (10% w/w, 100 mL). The violet solution was then extracted three times with trichloromethane (3 $\times$ 100 mL). The collected organic phases were washed with water (100 mL), dried with $MgSO_4$, and the solvent was distilled off in a rotary evaporator, to afford, after drying the remaining solid with P_4O_{10} in vacuo, betaine dye **7** (0.38 g, 68%) as a violet amorphous powder, still containing some water, with m.p. 198–200 °C. – 1H NMR ($CDCl_3$): δ = 6.62 (s, 2 H, phenolate-3/3'-H), 7.11 (dd, 2 H, 3-pyridyl-5/5'-H), 7.32 (dd, 2 H, 3-pyridyl-5/5'-H), 7.60–7.70 (m, 5 H, phenyl-H), 7.90 (dd, 2 H, 3-pyridyl-4/4'-H), 8.06–8.10 (m, 4 H, 3-pyridyl-2/2'-H or 4/4'-H), 8.20 (s, 2 H, pyridinium-3/3'-H), 8.27 (dd, 2 H, 3J = 4.6 and 4J = 1.2 Hz, 3-pyridyl-6/6'-H), 8.66 (dd, 2 H, 3J = 4.9 and 4J = 1.6 Hz, 3-pyridyl-6/6'-H), 8.78 (d, 4J = 2.2 Hz, 2 H, 3-pyridyl-2/2'-H); assignment of the 12 3-pyridyl-H signals to the 2 3-pyridyl rings either at the pyridinium or at the phenolate ring was not possible. – ^{13}C NMR ($CDCl_3$): δ = 122.4, 123.5, 126.2, 127.7, 127.9, 128.0, 129.8, 130.3, 133.1, 135.7, 136.2, 136.8, 146.7, 148.7, 148.9, and 151.7 (aromatic and heteroaromatic C); because of low solubility and insufficient resolution, only 16 signals were observed instead of the expected 21. – IR (KBr): $\tilde{\nu}$ = 3430 (OH) cm^{-1} . – UV/Vis (CH_3CN): λ_{max} (lg ϵ) = 605 nm (3.66), 419 (3.89), 381 (3.93), 305 (4.60), 229 (4.59). – MS (APCI, positive): m/z = 556 [M^+ + 1]. – $C_{37}H_{25}N_5O \cdot 2.5 H_2O$ (555.6 + 45.0 = 600.7): calcd. C 73.98, H 5.03, N 11.66; found C 73.87, H 5.51, N 11.24.

Preparation of Betaine Dye 8: See Scheme 7.

4-[2,6-Diphenyl-4-(pyridin-4-yl)pyridinium-1-yl]-2,6-bis(pyridin-3-yl)phenolate (8): Anhydrous sodium acetate (0.66 g, 8.00 mmol) and the pyrylium salt **17** (0.97 g, 2.00 mmol) were added to a stirred solution of freshly prepared 4-aminophenol **26** (0.54 g, 2.00 mmol) in dry methanol (15 mL). The mixture was heated with a water bath under reflux for 3 h. Sodium methoxide (0.44 g, 8.00 mmol) was then added, and the dark solution was heated under reflux for 5 min and poured into aqueous NaOH (10% w/w, 100 mL). The violet solution was extracted three times with trichloromethane (3 $\times$ 100 mL). The collected organic phases were washed with water

(100 mL) and dried with $MgSO_4$, and the solvent was distilled off in a rotary evaporator, to afford, after drying the remaining solid with P_4O_{10} in vacuo, betaine dye **8** (0.74 g, 67%) as violet amorphous powder, containing ca. 2 mol of water, with m.p. 213–215°. – 1H NMR ($CDCl_3$): δ = 6.50 (s, 2 H, phenolate 3/3'-H), 7.06 (dd, 2 H, 3-pyridyl-5/5'-H), 7.30–7.46 (m, 10 H, phenyl-H), 7.72 (dd, 2 H, 3J = 4.5 and 4J = 1.6 Hz, 4-pyridyl-3/3'-H), 7.89 (d, 4J = 1.9 Hz, 2 H, 3-pyridyl-2/2'-H), 8.04–8.16 (m, 4 H, pyridinium-3/3'-H and 3-pyridyl-4/4'-H), 8.24 (dd, 2H, 3J = 4.8 and 4J = 1.7 Hz, 3-pyridyl-6/6'-H), 8.86 (dd, 2 H, 3J = 4.5 and 4J = 1.6 Hz, 4-pyridyl-2/2'-H). – ^{13}C NMR ($CDCl_3$): δ = 118.5, 121.2, 122.1, 126.3, 127.3, 127.8, 128.9, 129.3, 130.7, 133.3, 136.1, 136.7, 141.2, 146.3, 148.8, 151.5, 151.6, 157.4, and 170.2 (aromatic and heteroaromatic C). – IR (KBr): $\tilde{\nu}$ = 3414 (OH) cm^{-1} . – UV/Vis (CH_3CN): λ_{max} (lg ϵ) = 629 nm (3.67), 415 (3.93), 386 (3.95), 251 (4.61). – MS (APCI, positive): m/z = 555 [M^+ + 1]. – $C_{38}H_{26}N_4O \cdot 2H_2O$ (554.7 + 36.0 = 590.7): calcd. C 77.27, H 5.12, N 9.49; found C 77.65, H 4.71, N 9.54.

Preparation of Betaine 9: See Scheme 8.

1,3-Bis(pyridin-4-yl)propan-2-one (30): Ethyl (pyridin-4-yl)acetate (16.5 g, 100 mmol) was added dropwise at room temp. over a period of 30 min to a stirred sodium ethoxide solution, freshly prepared from sodium (2.3 g, 100 mmol) and anhydrous ethanol (100 mL). The mixture was stirred for 12 h at 60–70 °C. After the mixture had cooled to room temp., concd. aqueous HCl (80 mL) was added and the mixture was heated under reflux for 3 h. After the mixture had cooled to room temp., water (100 mL) was added and the solution was washed twice with trichloromethane (2 $\times$ 100 mL). Aqueous NaOH (10% w/w) was then added to the aqueous phase until a pH of > 7 was reached. This solution was now extracted three times with trichloromethane (3 $\times$ 100 mL). The collected organic phases were dried with $MgSO_4$ and the solvent was distilled off in a rotary evaporator. The remaining brown oil was purified by flash chromatography [13] (solvent: ethanol; R_f = 0.33), to afford the ketone **30** (0.2 g, 2%) as brown, waxy solid, still containing some water, with m.p. 65–67 °C. Ketone **30** was not very stable; after two weeks of storage under argon at –18 °C, decomposition had taken place and the color had changed to red. In order to obtain sufficient amounts of **30** for the next reaction step, this preparation procedure was repeated several times. – 1H NMR ($CDCl_3$): δ = 3.73 (s, 4 H, CH_2), 7.04 (d, 3J = 4.6 Hz, 4 H, 2 pairs of 4-pyridyl-3/3'-H), 8.49 (d, 3J = 4.6 Hz, 4 H, 2 pairs of 4-pyridyl-2/2'-H). – ^{13}C NMR ($CDCl_3$): δ = 48.4 (CH_2), 124.7, 142.0, and 150.1 (pyridyl-C), 201.7 (C=O). – IR (KBr): $\tilde{\nu}$ = 1712 (C=O) cm^{-1} . – MS (EI): m/z (%) = 212 (2) [M^+], 120 (28) [$C_5H_4N - CH_2 - CO$], 93 (100) [$C_5H_4N - CH_3$], 92 (52) [$C_5H_4N - CH_2$]. – $C_{13}H_{12}N_2O \cdot 0.25 H_2O$ (212.3 + 4.5 = 216.8): calcd. C 72.04, H 5.81, N 12.92; found C 72.30, H 5.70, N 12.92.

4-Nitro-2,6-bis(pyridin-4-yl)phenol (31): A solution of NaOH (1.60 g, 40.0 mmol) in water (40 mL) was added to a stirred solution of ketone **30** (4.40 g, 20.8 mmol) and sodium nitromalonate monohydrate (3.40 g, 21.7 mmol)^[56] in ethanol (30 mL), and the mixture was stirred at room temp. over a period of 3 d, during which time an orange precipitate formed. The ethanol was then distilled off in a rotary evaporator, and the remaining solution was neutralized by addition of aqueous acetic acid (30%, w/w). The orange precipitate was filtered off, washed several times with water, and purified by hot extraction with ethanol (70 mL) to afford the nitrophenol **31** (5.10 g, 81%) as orange needles, containing ca. 2 mol of water, with m.p. 310 °C. – 1H NMR (CD_3SOCD_3): δ = 3.44 (s, 1 H, OH), 7.86 (d, 3J = 6.3 Hz, 4 H, 2 pairs of 4-pyridyl-3/3'-H), 8.19 (s, 2 H, phenol-3/3'-H), 8.76 (d, 3J = 6.3 Hz, 4 H, 2

pairs of 4-pyridyl-2/2'-H). – ^{13}C NMR (CD_3SOCD_3): δ = 123.7, 127.1, 147.8, and 148.1 (aromatic and heteroaromatic C); because of low solubility and insufficient resolution, only 4 of the expected 7 signals were observed. – IR (KBr): $\tilde{\nu}$ = 3386 (OH) cm^{-1} , 1332 (NO_2). – MS (FD): m/z (%) = 293 (100) [M^+]. – $\text{C}_{16}\text{H}_{11}\text{N}_3\text{O}_3 \cdot 2\text{H}_2\text{O}$ (293.3 + 36.0 = 329.3): calcd. C 58.36, N 4.59, N 12.76; found C 58.79, H 4.66, N 12.64.

4-Amino-2,6-bis(pyridin-4-yl)phenol (32): A suspension of a palladium catalyst (10% Pd on charcoal, ca. 200 mg) in a solution of nitrophenol **31** (0.33 g, 1.00 mmol) in methanol (150 mL) was reduced with dihydrogen (ca. 80 mL) at room temp. and normal pressure over a period of 2 d. The catalyst was filtered off under nitrogen, and the solvent was distilled off in vacuo, to afford, after drying the remaining solid with P_4O_{10} in vacuo, aminophenol **32** (0.27 g, ca. 100%) as a pale brown solid. Because of its sensitivity to oxygen, **32** was immediately transformed into **9** without further characterization.

2,6-Bis(pyridin-4-yl)-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (9): Anhydrous sodium acetate (0.33 g, 4.00 mmol) and 2,4,6-triphenylpyrylium tetrafluoroborate (0.40 g, 1.00 mmol)^[57] were added to a stirred solution of freshly prepared 4-aminophenol **32** (0.27 g, 1.00 mmol) in dry methanol (40 mL) and the mixture was heated under reflux with a water bath for 3 h. Sodium methoxide (0.22 g, 4.00 mmol) was then added, the dark solution was heated under reflux for 5 min, and the hot solution was poured into aqueous NaOH (10%, w/w, 100 mL). After standing for ca. 24 h, the dark red precipitate was filtered off, and washed once with water and three times with diethyl ether (3 $\times$ 50 mL). Purification by hot extraction with water/methanol (3:1, 50 mL) and drying with P_4O_{10} in vacuo afforded betaine dye **9** (0.47 g, 85%) as red crystals, containing ca. 3 mol of water of crystallization, with m.p. 220 °C. – ^1H NMR (CDCl_3): δ = 6.42 (s, 2 H, phenolate-3/3'-H), 7.25–7.67 (m, 15 H, phenyl-H), 7.91 (d, 3J = 5.8 Hz, 4 H, 2 pairs of 4-pyridyl-3/3'-H), 8.13 (s, 2 H, pyridinium-3/3'-H), 8.32 (d, 3J = 5.8 Hz, 4 H, 2 pairs of 4-pyridyl-2/2'-H). – ^{13}C NMR (CDCl_3): δ = 123.1, 123.2, 128.7, 129.0, 129.2, 148.7, and 148.8 (aromatic and heteroaromatic C); because of low solubility and poor resolution, only 7 of the expected 18 signals were observed. – IR (KBr): $\tilde{\nu}$ = 3430 (OH) cm^{-1} . – UV/Vis (CH_3CN): λ_{max} (lg ϵ) = 571 nm (3.67), 432 (4.16), 301 (4.62), 239 (4.60). – MS (APCI, positive): m/z = 554 [M^+ + 1]. – $\text{C}_{39}\text{H}_{27}\text{N}_3\text{O} \cdot 3\text{H}_2\text{O}$ (553.7 + 54.0 = 607.7): calcd. C 75.96, H 5.56, N 6.81; found C 75.66, H 5.06, N 6.79.

Preparation of Betaine Dye 10: See Scheme 9.

4-[4-Phenyl-2,6-bis(pyridin-4-yl)pyridinium-1-yl]-2,6-bis(pyridin-4-yl)phenolate (10): Anhydrous sodium acetate (0.33 g, 4.00 mmol) and the pyrylium salt **19** (0.57 g, 1.00 mmol) were added to a stirred solution of freshly prepared 4-aminophenol **32** (0.27 g, 1.00 mmol) in dry methanol (40 mL) and the mixture was heated under reflux with a water bath for 3 h. Sodium methoxide (0.22 g, 4.00 mmol) was then added, the dark solution was heated under reflux for 5 min, and the hot solution was poured into aqueous NaOH (10% w/w, 100 mL). After the mixture had been stirred for ca. 24 h at room temp., the precipitate formed was filtered off, and washed once with water and three times with diethyl ether (3 $\times$ 50 mL). Purification by hot extraction with water/methanol (3:1, 50 mL) and drying with P_4O_{10} in vacuo afforded betaine dye **10** (0.46 g, 83%) as violet crystals still containing water of crystallization with m.p. 344 °C. – ^1H NMR (CD_3SOCD_3): δ = 7.15 (s, 2 H, phenolate-3/3'-H), 7.52–7.69 (m, 13 H, 5e phenyl-H and 4 pairs of 4-pyridyl-3/3'-H), 8.16 (d, 3J = 5.8 Hz, 4 H, 2 pairs of 4-pyridyl-2/2'-H), 8.68 (d, 3J = 5.8 Hz, 4 H, 2 pairs of 4-pyridyl-2/2'-H),

8.74 (s, 2 H, pyridinium-3/3'-H); assignment of the 16 4-pyridyl-H signals to the 2 pyridyl rings either at the pyridinium or the phenolate ring was not possible. – ^{13}C NMR (CD_3SOCD_3): δ = 122.4, 124.0, 148.7, and 149.8 (aromatic and heteroaromatic C); because of low solubility and insufficient resolution, only 4 of the expected 17 signals were observed. – IR (KBr): $\tilde{\nu}$ = 3415 (OH) cm^{-1} . – UV/Vis (CH_3CN): λ_{max} (lg ϵ) = 597 nm (3.57), 435 (3.89), 305 (4.35), 234 (4.40). – MS (APCI, positive): m/z = 555 [M^+], 556 [M^+ + 1]. – $\text{C}_{37}\text{H}_{25}\text{N}_5\text{O} \cdot 3.5 \text{H}_2\text{O}$ (555.6 + 63.1 = 618.7): calcd. C 71.83, H 5.21, N 11.32; found C 71.53, H 4.91, N 10.94.

Preparation of Betaine Dye 11: See Scheme 10.

4-[2,6-Diphenyl-4-(pyridin-4-yl)pyridinium-1-yl]-2,6-bis(pyridin-4-yl)phenolate (11): Anhydrous sodium acetate (0.33 g, 4.00 mmol) and the pyrylium salt **17** (0.48 g, 1.00 mmol) were added to a stirred solution of freshly prepared 4-aminophenol **32** (0.27 g, 1.00 mmol) in dry methanol (40 mL), and the mixture was heated under reflux with a water bath for 3 h. Sodium methoxide (0.22 g, 4.00 mmol) was then added, the dark solution was heated under reflux for 5 min, and the hot solution was poured into aqueous NaOH (10%, w/w, 100 mL). After the mixture had been left standing for ca. 24 h, the precipitate was filtered off, and washed once with water and three times with diethyl ether (3 $\times$ 50 mL). Purification by hot extraction with water/methanol (3:1, 50 mL) and drying with P_4O_{10} in vacuo afforded **11** (0.43 g, 78%) as violet crystals, still containing water of crystallization, with m.p. 350–352 °C. – ^1H NMR (CD_3SOCD_3): δ = 7.05 (s, 2 H, phenolate-3/3'-H), 7.40–7.58 (m, 14 H, 10 phenyl-H and 2 pairs of 4-pyridyl-3/3'-H, located at the phenolate ring), 8.30 (m, 6 H, 2 pairs of 4-pyridyl-2/2'-H, located at the phenolate ring), and 1 pair of 4-pyridyl-3/3'-H, located at the pyridinium ring), 8.70 (s, 2 H, pyridinium-3/3'-H), 8.86 (s, 2H, 3J = 6.2 Hz, 1 pair of 4-pyridyl-2/2'-H, located at the pyridinium ring). – ^{13}C NMR (CD_3SOCD_3): δ = 122.5, 128.4, 129.8, 134.4, 148.3, 148.6, and 151.1 (aromatic and heteroaromatic C); because of low solubility and insufficient resolution, only 7 of the expected 17 signals were observed. – IR (KBr): $\tilde{\nu}$ = 3432 (OH) cm^{-1} . – UV/Vis (CH_3CN): λ_{max} (lg ϵ): 603 nm (3.60), 433 (4.07), 250 (4.57). – MS (APCI, positive): m/z = 555 [M^+ + 1]. – $\text{C}_{38}\text{H}_{26}\text{N}_4\text{O} \cdot 3\text{H}_2\text{O}$ (554.7 + 54.0 = 608.7): calcd. C 74.98, H 5.30, N 9.20; found C 74.59, H 5.12, N 9.01.

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