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Syntheses and UV–visible spectroscopic properties of new 'fluorophilic' fluorine- and perfluoroalkyl-substituted solvatochromic pyridinium *N*-phenolate betaine dyes[†‡]

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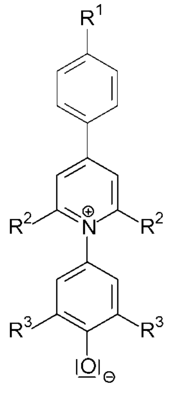
ABSTRACT: Syntheses and negative solvatochromism of three new 'fluorophilic' fluorine- and perfluoroalkyl-substituted pyridinium *N*-phenolate betaine dyes **3–5** are described in order to obtain new zwitterionic dyes which should be less basic and better soluble in perfluorinated solvents than the solvatochromic standard betaine dyes **1** and **2**, used to establish an empirical scale of solvent polarity, called the E_T (**30**) or E_T^N scale. The new betaine dyes **3–5** were designed to allow an extension of the existing E_T (**30**) scale to new solvents. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: betaine dyes; E_T (**30**) values; solvatochromism; solvent effects; UV–visible spectroscopy

INTRODUCTION

Solutions of the pyridinium *N*-phenolate betaine dye **1** (Scheme 1) are solvatochromic, thermochromic, piezochromic and halochromic.[3,4] That is, the longest wavelength intramolecular charge-transfer (CT) absorption band in the UV–visible (Vis) spectrum of dye **1** depends on solvent polarity,[3–5] solution temperature,[6] external pressure[7] (see also Ref. 14) and the nature and concentration of added salts[8] (for a review on chromogenic reagents, see Ref. 8k). Solutions of a chirally modified betaine dye **1** with four stereogenic centers show even the phenomenon of chiro-solvatochromism.[9] The unusual large negative solvatochromism of the standard betaine dye **1** was used by us to establish a UV–Vis spectroscopically derived empirical scale of solvent polarity, called the E_T (**30**) scale[3,4] (for definitions of the term 'solvent polarity,' see Ref. 5). E_T (**30**) values are simply defined as the molar *t*ransition *e*nergies (in kcal mol^{-1}; 1 kcal = 4.184 kJ) of the standard betaine dye **1**, measured in solvents of different polarity at room temperature (25 °C) and normal pressure (1 bar), according to the equation

$$\begin{aligned} E_T(\mathbf{30})(\text{kcal mol}^{-1}) &= hc\tilde{\nu}_{\max}N_{\mathrm{A}} \\ &= (2.8591 \times 10^{-3})\tilde{\nu}_{\max}(\text{cm}^{-1}) \\ &= 28591/\lambda_{\max}(\text{nm}) \end{aligned} \qquad (1)$$



1 - 5

	R^1	R^2	R^3
1	H	H_5C_6-	H_5C_6-
2	Me_3C-	4-Me_3C-C_6H_4-	4-Me_3C-C_6H_4-
3	H	F_5C_6-	F_5C_6-
4	F_3C-	4-F_3C-C_6H_4-	4-F_3C-C_6H_4-
5	$F_{13}C_6$-	4-$F_{13}C_6$-C_6H_4-	H_5C_6-

Scheme 1. Molecular structure of the betaine dyes **1–5**

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[§] Based on the PhD Thesis of M. Eschner.[2]

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where $\tilde{\nu}_{\max}$ is the wavenumber and $\lambda_{\max}$ the wavelength of the maximum of the long-wavelength solvatochromic CT absorption band of betaine dye **1**, and h, c, and N_A are Planck's constant, the speed of light, and Avogadro's constant, respectively. High solvent polarity, here defined as the overall solvation capability of a solvent,[5] corresponds to high E_T (**30**) values. As in the first publication[3a] the betaine dye **1** had accidentally the formula number 30, the number 30 was added later in order to avoid confusion with E_T, used as abbreviation for *t*riplet excitation *e*nergy in photochemistry. The E_T (**30**) solvent polarity scale ranges from 63.1 kcal mol^{-1} for water, the most polar solvent, to 30.7 kcal mol^{-1} for tetramethylsilane (TMS), as least polar solvent for which an E_T (**30**) value could be experimentally determined. In order to avoid the non-SI unit kcal mol^{-1}, in 1983 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 non-polar reference solvents, respectively, to fix the scale according to the equation[3b]

$$\begin{aligned} E_T^N &= [E_T(\text{solvent}) - E_T(\text{TMS})]/[E_T(\text{water}) \\ &\quad - E_T(\text{TMS})] \\ &= [E_T(\text{solvent}) - 30.7]/32.4 \end{aligned} \tag{2}$$

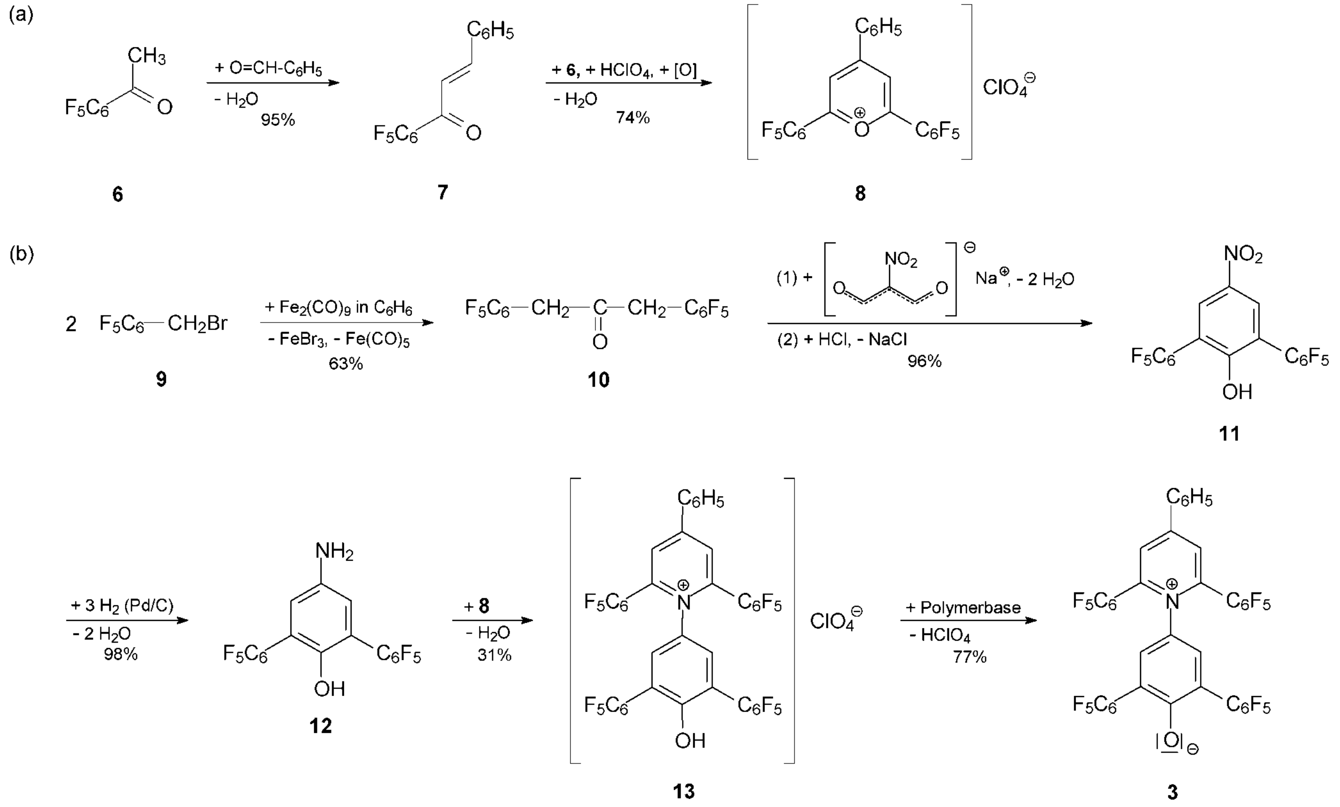
E_T (**30**) and E_T^N values are known for more than 360 solvents and for many binary solvent mixtures and also for other media (e.g. ionic liquids, microheterogeneous solutions, polymers, surfaces)[3,4] (for reviews on empirical solvent polarity parameters, see Refs. 4b and 10). These and other empirical parameters of solvent polarity have been successfully used in the correlation analysis of solvent influences on chemical equilibria, reaction rates, and spectral absorptions[10,11] within the framework of so-called linear free energy relationships.[12]

For UV–Vis spectroscopic solvatochromic measurements, the primary indicator dye **1** is sufficiently soluble in most organic solvents. However, betaine dye **1** is not or only sparingly soluble in non-polar solvents such as aliphatic hydrocarbons, perfluorohydrocarbons, and TMS and also in water as a very polar solvent. In order to obtain betaine dyes with better solubility in water, pyridyl-substituted pyridinium *N*-phenolates have recently been synthesized, in which some of the five peripheral hydrophobic phenyl groups, surrounding the zwitterionic chromophore of dye **1**, are replaced by hydrophilic pyridyl groups, thus allowing the study of the polarity of aqueous electrolyte solutions.[1] In order to obtain pyridinium *N*-phenolates which are soluble in non-polar solvents, the lipophilic penta-*tert*-butyl-substituted betaine dye **2** (see Scheme 1) was introduced as a secondary solvatochromic indicator dye.[3b] The excellent linear correlation between the E_T values of dyes **1** and **2** for those solvents in which both dyes are soluble allows the calculation of E_T (**30**) values [= E_T (**1**) values] for such non-polar solvents in which the primary probe dye **1** is not soluble enough for UV–Vis spectroscopic measurements. By means of correlation Eqn. (3),[13] it was possible to extend the E_T (**30**) scale to non-polar solvents such as aliphatic hydrocarbons[13] and supercritical-fluid carbon dioxide:[14]

$$\begin{aligned} E_T(\mathbf{2})(\text{kcal mol}^{-1}) &= 0.9424 E_T(\mathbf{30})(\text{kcal mol}^{-1}) \\ &\quad + 1.808 (n = 57;\ r = 0.999;\ = 0.17\,\text{kcal mol}^{-1}) \end{aligned} \tag{3}$$

However, even the lipophilic penta-*tert*-butyl-substituted betaine dye **2**[3b] and also a hepta-*tert*-butyl-substituted and a tris-*tert*-butyl-bis(adamantan-1-yl)-substituted pyridinium *N*-phenolate betaine dye[15] were not soluble in perfluorohydrocarbons such as perfluorooctane, perfluoro(methylcyclohexane) and perfluorodecalin. For perfluorohydrocarbons, which should be less polar than the corresponding hydrocarbons, E_T (**30**) values are still lacking. This is unfortunate because perfluorinated solvents have recently gained in importance as reaction media for organic syntheses.[16] Following the old alchemist's rule 'similia similibus solvuntur' (like dissolves like), we thought that the introduction of fluorine and perfluoroalkyl substituents into the peripheral phenyl groups of standard betaine dye **1** should lead to new 'fluorophilic' dyes with better solubility in perfluorohydrocarbons. For this reason, we have synthesized and studied UV–Vis spectroscopically three new pyridinium *N*-phenolate betaine dyes **3**–**5** (Scheme 1) with 20 fluorine substituents (**3**), five trifluoromethyl groups (**4**) and three perfluoro-1-hexyl residues (**5**).[2]

There is an additional reason for the preparation of pyridinium *N*-phenolate dyes bearing such strongly electron-withdrawing substituents. In acidic solvents, betaine dyes **1** and **2** are easily and reversibly protonated at the phenolic oxygen atom and the long-wavelength solvatochromic CT absorption band disappears. That is, E_T (**30**) values are not directly available for more acidic solvents. The border between acidic and less acidic solvents, for which E_T (**30**) values are available, is determined by the acidity constant of the corresponding acid of **1**: the pK_a of protonated **1** is 8.65 ± 0.05[17] and 8.63 ± 0.03[18] in water. Replacing the two 2,6-phenyl groups in the phenolate moiety of **1** by two chlorine substituents reduces the phenolate basicity by nearly three orders of magnitude [pK_a = 4.78 for protonated 2,6-dichloro-4-(2,4,6-triphenylpyridinium-1-yl)phenolate!], thus allowing the determination of E_T values for more acidic solvents.[17] Introduction of fluorine and fluorine-containing substituents into the betaine chromophore of **1** should also reduce its phenolate basicity, to give possibly suitable additional solvatochromic indicator dyes for the direct determination of E_T (**30**) values for more acidic solvents.[2]



Scheme 2. Synthesis of the eicosanfluoro (F_{20})-substituted betaine dye **3**

RESULTS AND DISCUSSION

Syntheses of betaine dyes 3–5

In the synthesis of pyridinium *N*-phenolate betaine dyes, the key step is the condensation reaction between 2,4,6-triaryl-substituted pyrylium salts and 2,6-disubstituted 4-aminophenols, leading to *N*-(4-hydroxyphenyl)pyridinium salts, which are eventually deprotonated to afford the corresponding betaine dyes.[3,19] In order to obtain the desired fluorine-substituted betaine dyes **3**–**5**, the correspondingly substituted pyrylium salts and 4-aminophenols had to be synthesized first, most of which were not known before.

The eicosanefluoro (F_{20})-substituted betaine dye **3** was prepared according to Scheme 2. Base-catalyzed condensation of pentafluoroacetophenone (**6**) with benzaldehyde gives the corresponding chalcone **7**,[20] which on treatment with **6** and perchloric acid leads to the decafluoro-substituted pyrylium salt **8**[21] (for reviews on the synthesis of substituted pyrylium salts, see Ref. 22). Attempts to obtain analogously the 2,4,6-tris(pentafluorophenyl)pyrylium salt with 15 fluorine atoms were unsuccessful.[2]

Reaction of (bromomethyl)pentafluorobenzene (**9**) with diiron nonacarbonyl affords the decafluoro-substituted dibenzyl ketone **10**,[23] which, by a twofold aldol condensation reaction with sodium nitromalonaldehyde,[24] is converted into the 4-nitrophenol **11**.[2] Reduction of **11** to **12** and its condensation with pyrylium salt **8** affords *N*-(4-hydroxyphenyl)pyridinium salt **13**, which is deprotonated with a suspension of (diethylaminomethyl)polystyrene in dichloromethane to give the F_{20}-betaine dye **3** as fine violet crystals.

The penta(trifluoromethyl)-substituted betaine dye **4** is synthesized as outlined in Scheme 3. Condensation of 4-(trifluoromethyl)acetophenone (**14**) with 4-(trifluoromethyl)benzaldehyde gives chalcone **15**. This reacts with ketone **14** in a base-catalyzed Michael addition to the 1,5-diketone **16**, which, on treatment with triphenylcarbenium perchlorate (as hydride acceptor), undergoes ring closure to the new tris(4-trifluoromethylphenyl)-substituted pyrylium salt **17**.

4-(Bromomethyl)-(trifluoromethyl)benzene (**18**) reacts with diiron nonacarbonyl to afford 4,4′-bis(trifluoromethyl)-substituted dibenzyl ketone **19**, which is converted into the 4-nitrophenol **20** by condensation with sodium nitromalonaldehyde.[24] Reduction of **20** to **21**, its condensation with pyrylium salt **17** and deprotonation of the intermediate pyridinium salt **22** with a suspension of (diethylaminomethyl)polystyrene in dichloromethane afford eventually the penta(trifluoromethyl)-substituted betaine dye **4** as fine green crystals.

Finally, the tris(perfluorohex-1-yl)-substituted betaine

Table 1. Long-wavelength solvent-dependent CT absorption maxima, $\lambda_{\max}$ (nm), and the corresponding E_T (**X**) values (kcal mol^{-1}; in parentheses) of betaine dyes **X** = **3**–**5**, measured in up to 40 solvents of different polarity at 25 °C and normal pressure, ordered according to decreasing E_T (**30**) values[4b]

Solvent	E_T (**30**)[a]	$\lambda_{\max}$(**3**) [E_T (**3**)][b]	$\lambda_{\max}$(**4**) [E_T (**4**)][b]	$\lambda_{\max}$(**5**) [E_T (**5**)][b]
HFIP[c]	(65.3)[c]	443 (64.5)	–	–
2,2,2-Trifluoroethanol	59.8	467 (61.2)	–	–
2-Cyanoethanol	59.6	471 (60.7)	–	–
Ethane-1,2-diol	56.3	483 (59.2)	–	–
3-Chlorophenol	–	484 (59.1)[d]	–	–
Formamide	55.8	492 (58.1)	533 (53.6)	–[e]
Methanol	55.4	489 (58.5)	521 (54.9)	562 (50.9)
2,2,2-Trichloroethanol	54.1	515 (55.5)	559 (51.1)	597 (47.9)
N-Methylformamide	54.1	503 (56.8)	–	–
Acetic anhydride	(43.9)	506 (56.5)	–	–
N-Methylacetamide	52.0[f]	509 (56.2)[d]	–	–
Ethanol	51.9	512 (55.8)	–	–
1-Propanol	50.7	524 (54.6)	563 (50.8)	620 (46.1)
1-Butanol	49.7	533 (53.6)	574 (49.8)	632 (45.2)
1-Pentanol	49.1	539 (53.0)	–	–
3-Methyl-1-butanol	49.0	543 (52.7)	–	–
1-Hexanol	48.8	542 (52.7)	582 (49.1)	642 (44.5)
2-Methyl-1-propanol	48.6	537 (53.2)	–	–
1-Heptanol	48.5	546 (52.4)	582 (49.1)	643 (44.5)
2-Propanol	48.4	542 (52.7)	589 (48.5)	651 (43.9)
1-Octanol	48.1	549 (52.1)	–	–
2-Butanol	47.1	566 (50.5)	609 (46.9)	674 (42.4)
Nitromethane	46.3	–	632 (45.2)	687 (41.6)
Acetonitrile	45.6	579 (49.4)	632 (45.2)	691 (41.4)
Dimethyl sulfoxide	45.1	581 (49.2)	628 (45.5)	692 (41.3)
2-Methyl-2-propanol	43.3[f]	610 (46.9)[f]	–	–
N,*N*-Dimethylformamide	43.2	589 (48.5)	–	–
N,*N*-Dimethylacetamide	42.9	600 (47.6)	654 (43.7)	731 (39.1)
Acetone	42.2	603 (47.4)	673 (42.5)	753 (38.0)
1,2-Dichloroethane	41.3	660 (43.3)	–	–
Morpholine	41.0	638 (44.8)	719 (39.8)	780 (36.7)
HMPT	40.9	610 (46.9)	–	–
Dichloromethane	40.7	660 (43.3)	–	–
1-Chloro-3,3,3-trifluoropropane	40.7	671 (42.6)	–	–
Pyridine	40.5	638 (44.8)	–	–
Trichloromethane	39.1	680 (42.0)	–	–
1,2-Dimethoxybenzene	38.4	655 (43.7)	754 (37.9)	832 (34.4)
Ethyl acetate	38.1	669 (42.7)	735 (38.9)	826 (34.6)
1,2-Dichlorobenzene	38.0	–	775 (36.9)	847 (33.8)
Tetrahydrofuran	37.4	–	749 (38.2)	839 (34.1)
Methoxybenzene	37.1	711 (40.2)	792 (36.1)	861 (33.2)
Ethoxybenzene	36.6	724 (39.5)	797 (35.9)	867 (33.0)
1,1,1-Trichloroethane	36.2	711 (40.2)	801 (35.7)	871 (32.8)
1,4-Dioxane	36.0	–[e]	808 (35.4)	870 (32.9)
Diethyl ether	34.5	–[e]	820 (34.9)	915 (31.2)
Benzene	34.3	–[e]	843 (33.9)	–[e]
Hexafluorobenzene	34.2	–[e]	839 (34.1)	912 (31.3)
Toluene	33.9	–[e]	848 (33.7)	925 (30.9)
Ethylbenzene	33.2	–[e]	845 (33.8)	918 (31.1)

[a] Taken from Refs 2 and 4b.

[b] The E_T(**X**) values given in parentheses are calculated from the visible absorption maxima of **X** = **3**–**5** according to Eqn. (1).

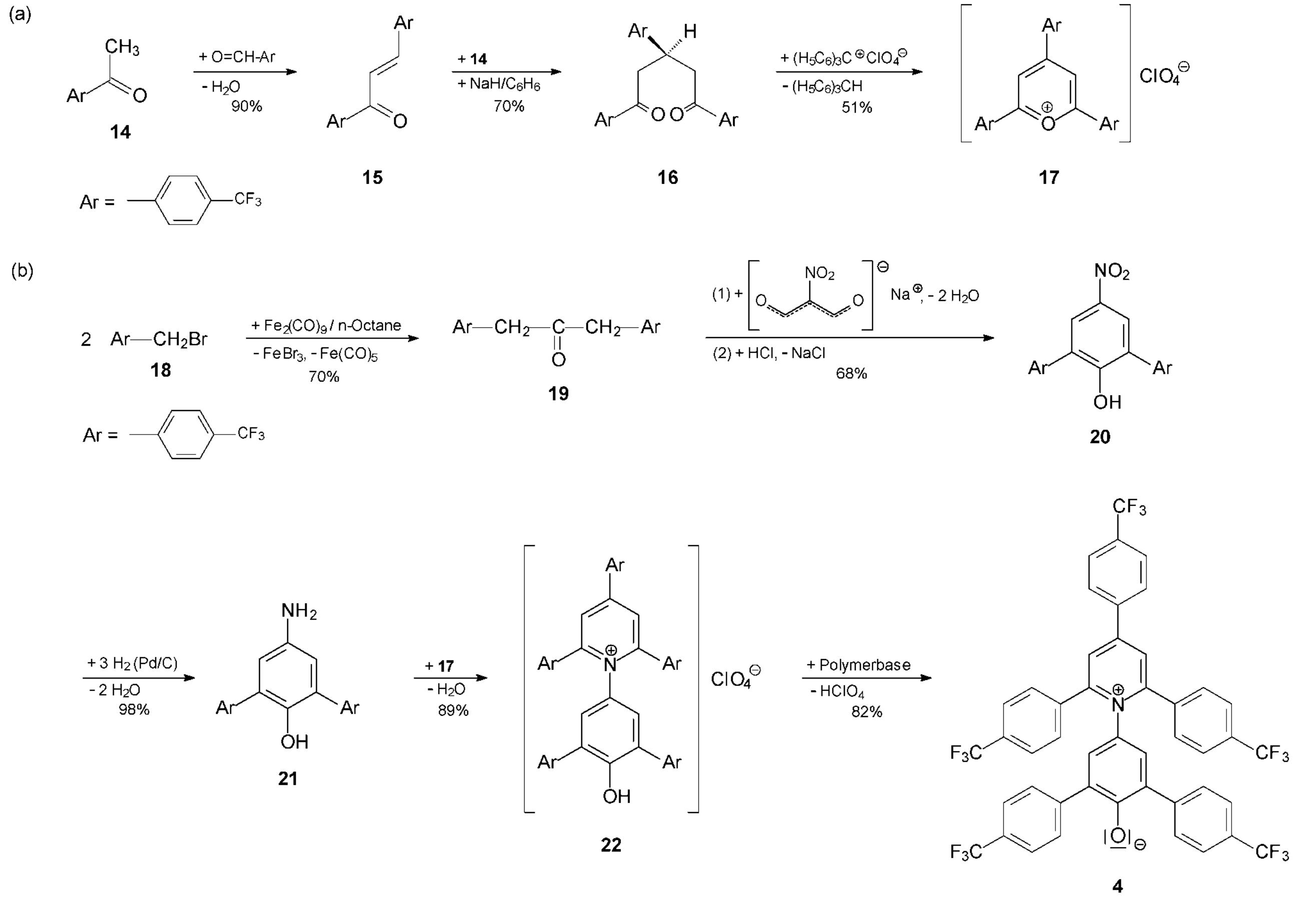
[c] HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol; the E_T (**30**) value for HFIP is taken from Ref. 13.

[d] Measured at 36 °C.

[e] Not soluble in this solvent.

[f] Measured at 30 °C.

dye **5** was synthesized as shown in Scheme 4. Alkylation of 4-iodoacetophenone (**23**) with perfluoro-1-iodohexane in the presence of copper bronze in DMSO yields 4-(perfluorohex-1-yl)acetophenone **24**.[25,26] Analogous alkylation of ethyl 4-bromobenzoate (**26**), prepared from acid **25** with triethyloxonium tetrafluoroborate,[27] with perfluoro-1-iodohexane affords the (perfluorohex-1-yl)-substituted ester **27**.[25,26] Reduction of this ester with



Scheme 3. Synthesis of the penta(trifluoromethyl)-substituted betaine dye **4**

lithium aluminum hydride to the benzyl alcohol **28**, followed by its oxidation with pyridinium fluorochromate,[28] affords the substituted benzaldehyde **29**.

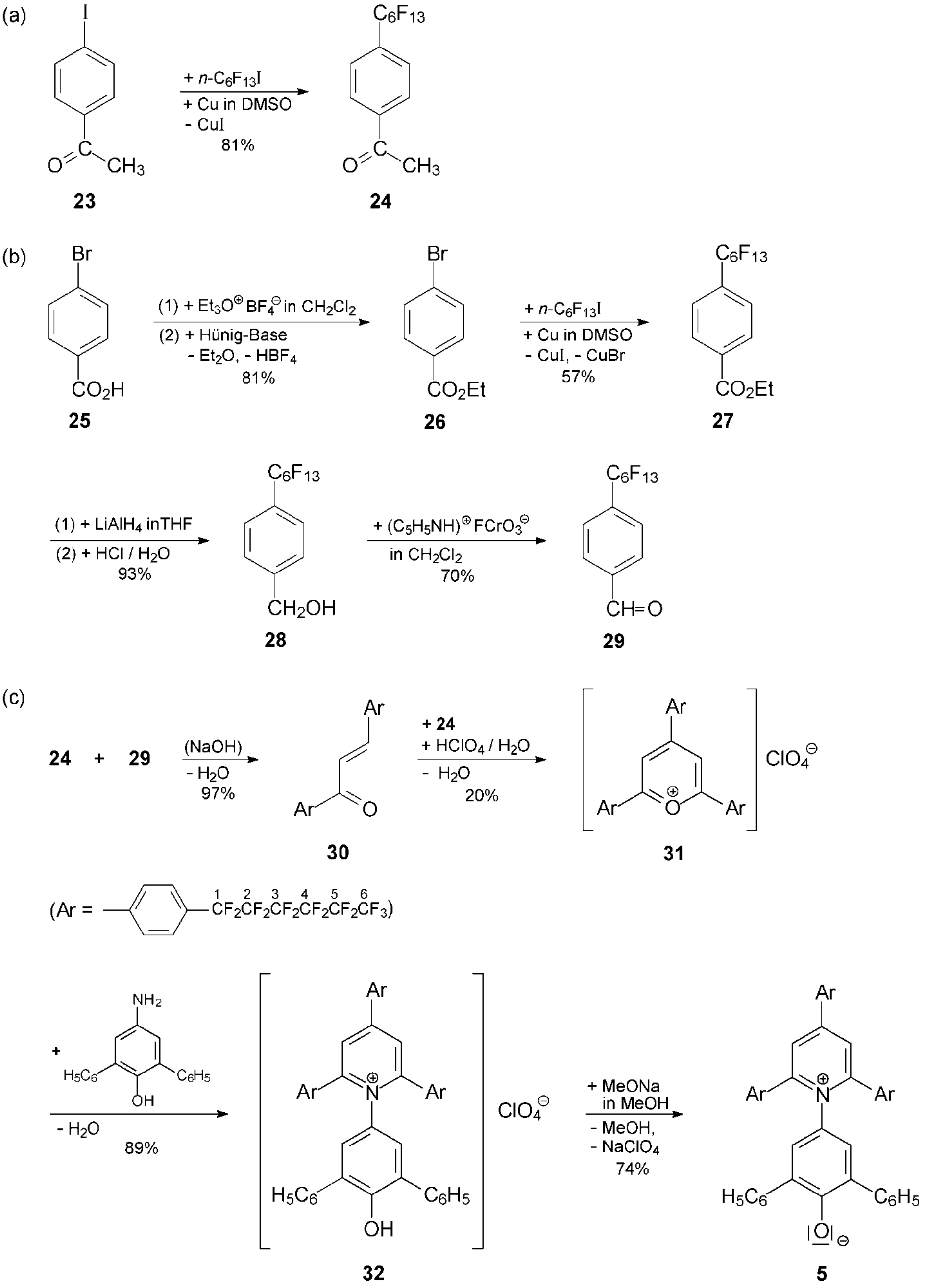
Condensation of ketone **24** with aldehyde **29** leads to chalcone **30**, which on reaction with **24** in the presence of perchloric acid[22] gives the new pyrylium salt **31**. Eventually, condensation of pyrylium salt **31** with 4-amino-2,6-diphenylphenol[3a,19] to the pyridinium salt **32** and its deprotonation with sodium methanolate in methanol afford the desired tris(perfluorohexyl)-substituted betaine dye **5** as fine dark-green crystals.

The molecular structures of all new compounds were confirmed by elemental analysis and UV–Vis, IR, mass, and NMR spectra (see Experimental section).

UV–Vis spectra and solvatochromism of betaine dyes 3–5

In acetonitrile, a solvent of intermediate polarity, the UV–Vis spectra of the new betaine dyes **3**–**5** exhibit three main absorption bands of different intensity: at $\lambda_{max} \approx 580$–$690$ nm ($\varepsilon \approx 1200$–$7400\,l\,mol^{-1}\,cm^{-1}$), 325–380 nm ($\varepsilon \approx 12\,000$–$30\,000\,l\,mol^{-1}\,cm^{-1}$) and 230–295 nm ($\varepsilon \approx 26\,000$–$37\,000\,l\,mol^{-1}\,cm^{-1}$); see Table 1 and Experimental section. Only the position of the long-wavelength absorption band is strongly solvent- (and substituent-) dependent; the others are not. Quantum chemical calculations show that this absorption band is related to an intramolecular charge-transfer (CT) from the HOMO of the phenolate to the LUMO of the pyridinium moiety (for various quantum chemical calculations on the standard betaine dye 1, see Ref. 29). For this reason, the position of the long-wavelength 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 part of dyes **3**–**5**, the solvent-dependent CT band disappears and the corresponding *N*-(hydroxyphenyl)pyridinium salts formed (e.g. **13**, **22**, and **32**) absorb at $\lambda_{max} \approx 295$–$330$ nm ($\epsilon = 30\,000$–$40\,000$ $1\,mol^{-1}\,cm^{-1}$), corresponding to a local π–π^* absorption of the 2,4,6-triarylpyridinium chromophore. Therefore, betaine dyes **3**–**5** and also **1** and **2** cannot be used as polarity indicators in acidic solvents such as carboxylic acids.

Introduction of three strongly electron-withdrawing perfluoro-1-hexyl substituents into the three 2,4,6-triphenyl rings of the pyridinium part of betaine dye **1** to give **5** should increase the electron affinity of the



Scheme 4. Synthesis of the tris(tridecafluoro-1-hexyl)-substituted betaine dye **5**

pyridinium moiety, with a significant bathochromic CT band shift as consequence. This is indeed the case: on going from betaine dye **1** to dye **5**, a bathochromic CT band shift of $\Delta\lambda = +64$ nm ($\Delta E_T = -4.2$ kcal mol^{-1}) is observed in acetonitrile as solvent (cf. Table 1). In contrast, a large hypsochromic CT band shift of $\Delta\lambda = -48$ nm ($\Delta E_T = +3.8$ kcal mol^{-1}) is observed in acetonitrile on going from betaine dye **1** to dye **3** with altogether 20 electron-withdrawing fluorine substituents, half of them in the pyridinium and half in the phenolate part. This means that the 10 electron-withdrawing fluorine substituents located in the phenolate part of dye **3**, causing an increase in its ionization energy, exceed the influence of the other 10 fluorine atoms in the pyridinium moiety of **3** on the electron affinity of that part of the dye molecule. On going from betaine dye **1** to dye **4** with five peripheral trifluoromethyl substituents, there is only a very small bathochromic CT band shift of $\Delta\lambda = +5$ nm ($\Delta E_T = -0.4$ kcal mol^{-1}) observed in acetonitrile. Obviously, in this case the electron-withdrawing influence of the three CF_3 groups in the pyridinium part and that of the two CF_3 groups in the phenolate part are practically equal and an electronically balanced situation results.

Table 2. Regression parameters for the linear correlations between the E_T (**X**) values of betaine dyes **X** = **3**–**5** and the E_T (**30**) values of the standard betaine dye **1**[4b] according to the correlation equation E_T (**X**) (kcal mol^{-1}) = aE_T (**30**) (kcal mol^{-1}) + b

X	a	b	n[a]	r[b]	$\sigma[E_T(\mathbf{X})]$[c]
3	0.926	7.04	37	0.986	1.04
4	0.961	1.38	28	0.992	0.86
5	0.902	0.22	26	0.997	0.45

[a] Number of solvents.
[b] Correlation coefficient.
[c] Standard deviation of the estimate in kcal mol^{-1}.

In Table 1, the molar transition energies E_T (**3**), E_T (**4**), and E_T (**5**) of the new betaine dyes **3**–**5**, measured for up to 40 hydrogen-bond donor (HBD) and non-HBD solvents, are also given, together with the corresponding E_T (**30**) values of the primary indicator dye **1**. In all three cases there is a good linear correlation between the E_T values of the new dyes **3**–**5** and the E_T (**30**) values of dye **1** with correlation coefficients $r \approx 0.99$, as shown by the regression parameters compiled in Table 2. The slope of all three regression lines, $a \approx 0.9$, is slightly smaller than unity, indicating that the new solvatochromic betaine dyes **3**–**5** are less sensitive to a change in solvent polarity than standard dye **1**. The good quality of the correlation equations in Table 2 should allow the calculation of E_T (**30**) values for such media, for which a direct experimental determination is not possible for reasons of limited solubility or strong acidity, in this way using the new dyes **3**–**5** as tertiary standard dyes in addition to the secondary standard dye **2**.

The introduction of the electron-withdrawing fluorine and perfluoroalkyl substituents into the peripheral phenyl groups of dye **1** leads to a reduced basicity of the pyridinium *N*-phenolate and betaine dyes **3**–**5** are less prone to protonation in more acidic solvents. This can be well seen from solutions of their protonated precursors **13**, **22**, and **32** (Schemes 2 and 3) in methanol: even in the absence of bases, these solutions are already reddish because partial ionization of the *N*-(4-hydroxyphenyl)-pyridinium salts produces small amounts of the corresponding betaine dyes **3**–**5**, the solutions of which in methanol are red (λ_{max} = 489, 521, and 562 nm, respectively; Table 1). The phenolic OH group in **13**, **22**, and **32** is more acidic than in protonated **1** because of the strong $-I$ effect of the fluorine and perfluoroalkyl substituents.

The E_T (**30**) value of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) is not directly measurable with dye **1** because of the high acidity of this solvent (pK_a = 9.3[30a]). However, the F_{20} betaine dye **3** is not protonated in this solvent and the CT absorption band at λ_{max} = 443 nm can be observed (Table 1). With the corresponding E_T (**3**) value of 64.5 kcal mol^{-1} and the first correlation equation given in Table 2, an E_T (**30**) value of 62.1 kcal mol^{-1} can be calculated for HFIP. This value is surprisingly smaller than the already published value of 65.3 kcal mol^{-1}.[4b,13] The latter value is, however, not the result of a direct measurement; it was obtained by extrapolation of the λ_{max} (**1**) values of 2-propanol–HFIP and (n-Bu)$_4$N$^+$HO$^-$–HFIP mixtures.[13] The E_T (**30**) value of 62.1 kcal mol^{-1} for HFIP, which is smaller than that of water (63.1 kcal mol^{-1}), seems to be the more reliable one, based directly on the solvatochromism of betaine dye **3**. As a control, the E_T (**30**) value of 2,2,2-trifluoroethanol (TFE) analogously calculated from E_T (**3**) amounts to 58.5 kcal mol^{-1}, which is in satisfactory agreement with the directly measured value of 59.8 kcal mol^{-1} (Table 1).

Using the E_T (**3**) value of 3-chlorophenol (pK_a = 9.1[30b]) given in Table 1, in the same way an E_T (**30**) value for this solvent can be calculated. The E_T (**30**) value of 56.2 kcal mol^{-1} found for 3-chlorophenol fits fairly well into the values of a whole series of other substituted phenols, determined in a different manner;[31] however, it is in disagreement with another published value[32] for this solvent (60.8 kcal mol^{-1}).

With the E_T (**3**) value of acetic anhydride given in Table 1, an E_T (**30**) value for this problematic solvent can be analogously calculated. The E_T (**30**) value found for acetic anhydride in this way, 53.4 kcal mol^{-1}, is higher than the published value of 43.9 kcal mol^{-1}.[3b,4b] Again, the already published much lower value was not directly measured, but was calculated from Kosower's Z values[33] by means of a correlation equation established by Griffiths and Pugh [E_T (**30**) = 0.752 Z −7.87] with 15 carefully selected solvents.[34] In more acidic solvents, in which even the new betaine dyes **3**–**5** are protonated, the correlation equation introduced by Griffiths and Pugh is still the only means to obtain calculated E_T (**30**) values for such solvents (e.g. carboxylic acids[3b,4b]), since Z values are directly measurable in acids.

Solvatochromic dyes such as **1** and **2** can also be used as probe molecules for the determination of the polarity of solid surfaces[35,37] and of solid materials such as various polymers.[36,37] In addition to standard dyes **1** and **2**, the F_{20} betaine dye **3** has also stood its 'acid test' as a surface polarity indicator: adsorbed on the solid material, dye **3** has already been used for the determination of the surface polarity of various solid acids such as bare and functionalized silicas, aluminas, alumosilicates, titanium dioxides[37a] and polysaccharides[37b] and, dissolved in thin, transparent polymer films, for measurements of the polarity of different synthetic polymers and copolymers.[37c] For example, the E_T (**30**) values of the surfaces of Al_2O_3 (Condea) and TiO_2 (Anatas; Condea) are 57.3 and 59.7 kcal mol^{-1}, respectively.[37a] That is, the surface polarity of these oxides corresponds to the polarity of alcohols such as glycerol (57.0) and 2,2,2-trifluoroethanol (59.8).

To our disappointment, it was not possible to determine indirectly by means of the 'fluorophilic' new betaine dyes **3**–**5** the E_T (**30**) values of perfluoroalkanes, using the correlation equations given in Table 2. As least polar solvents, they should have E_T (**30**) values of less than ca 30–31 kcal mol^{-1} as found for alkanes and TMS. All three dyes **3**–**5** are surprisingly not soluble in solvents such as perfluorohexane, perfluorooctane, perfluoro(methylcyclohexane) and perfluorodecalin. Because of the high electronegativity of fluorine atoms and their very small polarizability, the dispersion interactions between perfluoroalkanes and the zwitterionic dyes are not sufficient to break down the crystal lattice of the highly dipolar betaine dyes. Even common organic solvents are not miscible with perfluoroalkane solvents. Maybe the additional introduction of sterically demanding substituents such *tert*-butyl or 1-adamantyl into betaine dyes **3**–**5**, thus weakening the strong dye–dye interactions in the crystal lattice, can lead to solvatochromic dyes capable of measuring empirically the polarity of perfluoroalkanes.

CONCLUSION

The new betaine dyes **3**–**5**, synthesized according to Schemes 2–4, enlarge the supply of highly solvatochromic indicator dyes which can be used, in addition to the known standard betaine dyes **1** and **2**, to extend the E_T (**30**) scale of solvent polarity by new solvents of interest. Dyes **3**–**5** are particularly useful for the indirect determination of E_T (**30**) values of more acidic solvents, polymers and solid surfaces, with which **1** and **2** are protonated. Disappointingly, in spite of the introduction of fluorine and perfluoroalkyl substituents, they are still not sufficiently soluble for UV–Vis spectroscopic measurements in perfluoroalkanes, for which E_T (**30**) values are still lacking.

EXPERIMENTAL

General methods. Melting-points (not corrected): Kofler-Mikroheiztisch (Reichert). Elemental analyses: Analytik-Servicelabor of the Department of Chemistry, Marburg, and Mikroanalytisches Laboratorium Malissa-Reuter, Engelskirchen-Elbach. UV–Vis spectra: U-3410 double-beam UV–Vis–NIR spectrophotometer (Hitachi) with thermostated 1.00 cm quartz cells. IR spectra: IFS-88 spectrophotometer (Bruker) with KBr discs. NMR spectra: AM-300 and WM-400 spectrometers (Bruker), with TMS and trichlorofluoromethane as internal standards. Mass spectra: MAT CH-7A spectrometer (Varian) with electron ionization (EI, 70 eV) and MAT 711 spectrometer (Varian) with field desorption (FD). Column chromatography: silica gel 60 (Merck), particle size 0.063–0.200 mm, and N-Super I and B-Super I aluminum oxide (ICN Biomedicals). Solvents: solvents for the solvatochromic measurements were used as supplied commercially in the highest quality available (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 aluminum oxide (B-Super I), in order to remove traces of acids. For these measurements the solvents must be water free and absolutely acid free. Solvents for the synthetic work were purified according to the usual standard methods.[38]

Synthesis of betaine dye 3 (Scheme 2). *1-Pentafluorophenyl-3-phenylprop-2-en-1-one (**7**).* To an ice-cold solution of NaOH (0.25 g, 8.25 mmol) in water (11 ml) and ethanol (9 ml; 96%, v/v) were added acetylpentafluorobenzene (**6**) (5.00 g, 23.8 mmol) and freshly distilled benzaldehyde (2.78 g, 25.2 mmol). After stirring at room temperature for 1 h, the precipitate formed was filtered off, washed with water, dried *in vacuo* with P_4O_{10}, and recrystallized from a small amount of ethanol (96%), to give the chalcone **7** (6.50 g, 95%) as colorless needles with m.p. 101 °C (lit.[20] 102–103 °C).

*2,6-Di(pentafluorophenyl)-4-phenylpyrylium perchlorate (**8**).* To a stirred mixture of ketone **6** (4.21 g, 20.0 mmol) and chalcone **7** (5.73 g, 20.0 mmol) was added at 80 °C dropwise and carefully aqueous perchloric acid (70%, w/w; 6.32 g, 44.0 mmol) and then the mixture was kept at 100 °C for 2 h. After cooling to room temperature, diethyl ether (ca 100 ml) was added, the precipitate formed was filtered off, washed with diethyl ether, and recrystallized from acetic acid, to give, after drying *in vacuo* with KOH, the pyrylium salt **8** (7.69 g, 74%) as yellow crystals with m.p. 250 °C (lit.[21] 249–251 °C).

*1,3-Di(pentafluorophenyl)propan-2-one (**10**).* A solution of (bromomethyl)pentafluorobenzene **9** (13.64 g, 52.3 mmol; Aldrich; **caution**: lachrymator!) and diiron nonacarbonyl (19.00 g, 52.3 mmol) in dry benzene (200 ml) was heated under reflux under nitrogen for 3 h. After cooling to room temperature, the precipitate formed ($FeBr_3$) was filtered off and extracted four times with boiling benzene. The filtrate and the four extracts were combined and the benzene was distilled off [**caution**: the benzene contains toxic Fe $(CO)_5$!]. The solid residue was purified by column chromatography with neutral alumina (activity grade III) and benzene–light petroleum (b.p. 40–60 °C) (1:9) as eluent ($R_f = 0.16$) and then recrystallized from *n*-hexane to afford the ketone **10** (6.00 g, 63%) as fine colorless needles with m.p. 100 °C (lit.[23a,b] 104 °C). ^{13}C NMR ($CDCl_3$): δ (ppm) = 35.7 (CH_2), 107.4 (quaternary phenyl-C), 136.0–147.0 (phenyl-C), 197.0 (C=O).

*4-Nitro-2,6-di(pentafluorophenyl)phenol (**11**).* To a stirred solution of NaOH (1.28 g, 32.0 mmol) in water (48 ml) and ethanol (112 ml; 96%, v/v) was added ketone **10** (12.08 g, 32.0 mmol) and sodium nitromalonaldehyde monohydrate (4.56 g, 32.0 mmol)[24] and the mixture was stirred at room temperature over a period of 15 days.

Then, the solution was acidified (pH $\approx$ 1) and some water was added in order to complete the precipitate formation. The precipitate formed was filtered off, washed acid free with water, and dried with P_4O_{10} *in vacuo* to afford the nitrophenol **11** (14.40 g, 96%), which is sufficiently pure for the next step. Analytically pure **11** was obtained by recrystallization of a small sample from 1,2-dichlorobenzene to give light-yellow crystals with m.p. 210 °C. IR (KBr): $\tilde{\nu}(\mathrm{cm}^{-1}) = 3459$ (OH), 1519 and 1349 (NO_2). UV–Vis (CH_3OH): $\lambda_{\max}$ (log ϵ) = 388 (4.29), 316 (3.96), 221 (4.27), 181 nm (3.70). ^{1}H NMR (CD_3CN): δ (ppm) = 8.09 (broad s, OH), 8.39 (s, 2 H. aromatic H). ^{13}C NMR (CD_3SOCD_3): δ (ppm) = 110.3 (quat. C_6F_5-C), 115.3 (quat. phenol-C-2), 129.1 (phenol-C-3), 137.1–144.3 (C_6F_5-C and phenol-C-4), 159.3 (C–OH). ^{19}F NMR (CD_3COCD_3): δ (ppm) = −139.9 (*ortho*-F), −155.0 (*para*-F), −163.2 (*meta*-F). MS (FD): *m/z* (%) = 471 (100) [M^+]. $C_{18}H_3F_{10}NO_3$ (471.2): calcd C 45.88, H 0.64, N 2.97; found C 46.08, H 0.61, N 3.03%.

*4-Amino-2,6-di(pentafluorophenyl)phenol (**12**).* A suspension of a palladium catalyst (10% Pd on charcoal, ca 100 mg) in a solution of nitrophenol **11** (4.70 g, 10.0 mmol) in ethanol (100 ml, 96%, v/v) was reduced with dihydrogen at room temperature and normal pressure until the necessary amount of H_2 was absorbed. Under nitrogen, the catalyst was filtered off and the solvent was distilled off *in vacuo* to give **12** (4.30 g, 98%) as a beige powder with m.p. 160–165 °C, which turned dark on air. Because of its sensitivity to oxygen, **12** was immediately converted into the pyridinium salt **13** without detailed further characterization. ^{1}H NMR (CD_3COCD_3): δ (ppm) = 3.42 (s, 2 H, NH_2), 6.71 (s, 2 H, aromatic H); the OH signal was not detected.

*2,6-Di(pentafluorophenyl)-4-phenyl-1-[4-hydroxy-3,5-di(pentafluorophenyl)phenyl]pyridinium perchlorate (**13**).* A solution of freshly prepared aminophenol **12** (4.42 g, 10.0 mmol), pyrylium salt **8** (4.31 g, 8.33 mmol) and water-free sodium acetate (1.71 g, 20.8 mmol) in dry ethanol (100 ml) was heated under reflux for 2.5 h. Then, at room temperature, the solution was acidified (pH $\approx$ 1) by addition of a few drops of aqueous $HClO_4$ (70%, w/w) and the product was precipitated by addition of water. The precipitate formed was filtered off, washed acid free with water, and dried with P_4O_{10} *in vacuo*. The product was dissolved in ethanol (96%) and precipitated by addition of *n*-hexane. This procedure was repeated to afford **13** (3.19 g, 31%) as fine brownish crystals with m.p. 194–196 °C. IR (KBr): $\tilde{\nu}\,(\mathrm{cm}^{-1}) = 3307$ (OH), 1119 (ClO_4). UV–Vis (CH_3CN): $\lambda_{\max}$ (log ϵ) = 332 (4.47), 218 nm (4.70). ^{1}H NMR (CD_3COCD_3): δ (ppm) = 7.68–7.82 and 8.34 (m, 5 H, 4-phenyl-H), 7.93 (s, 2 H, phenol-3-H), 9.38 (s, 2 H, pyridinium-3-H), 9.79 (broad s, 1 H, OH). ^{13}C NMR (CD_3COCD_3): δ (ppm) = 108.3 (quat. C_6F_5-C), 110.5 (quat. C_6F_5-C), 117.3 (quat. phenol-C-2), 130.3 (quat, phenyl-C-1), 130.6 (phenyl-C-2), 131.0 (phenyl-C-3), 131.1 (phenol-C-3), 131.8 (pyridinium-C-3), 133.3 (pyridinium-C-4), 135.3 (phenyl-C-4), 140.5 (d, $^1J_{CF} = 248$ Hz), 146.0 (phenol-C-4), 146.7 (d, $^1J_{CF} = 255$ Hz), 147.4 (d, $^1J_{CF} = 240$ Hz), 157.2 (pyridinium-C-2), 161.1 (C-OH). ^{19}F NMR (CD_3COCD_3): δ (ppm) = −134.6 (2 F), −141.8 (2 F), −148.3 (1 F), −154.5 (1 F), −161.0 (2 F), −163.2 (2 F). MS (FD): *m/z* (%) = 911 (14) [M^+ $-HClO_4$], 891 (100) [M^+ $-HClO_4$ $-HF$]. $C_{41}H_{10}ClF_{20}NO_5 \cdot 0.5H_2O$ (1012.0 + 9.0 = 1021.0): calcd C 48.23, H. 1.09, N 1.37; found C 48.31, H 1.19, N 1.48%.

*4-[2,6-Di(pentafluorophenyl)-4-phenylpyridinium-1-yl]-2,6-di(pentafluorophenyl)phenolate (**3**) ('F_{20}-betaine').* To a stirred solution of perchlorate **13** (1.00 g, 0.98 mmol) in dry dichloromethane (30 ml) was added the granulated polymer base (diethylaminomethyl) polystyrene (Fluka; 0.84 g, base equivalent 2.52 mmol) and the suspension was stirred for 30 min at room temperature. Then, the polymer base was filtered off, washed with dichloromethane and discarded. The solvent of the combined filtrates was distilled off *in vacuo* to afford betaine dye **3** (0.70 g, 77%) as fine hygroscopic violet crystals, which on heating melted at ca 186 °C and decomposed at ca 190 °C. UV–Vis (CH_3CN): $\lambda_{\max}$ (log ϵ) = 579 (3.50), 325 nm (4.49). ^{1}H NMR (CD_3COCD_3): δ (ppm) = 7.28 (s, 2 H, phenolate-3-H), 7.69–8.32 (m, 5 H, phenyl-H), 9.31 (s, 2 H, pyridinium-3-H). ^{13}C NMR (CD_3COCD_3): δ (ppm) = 108.4, 110.2, 117.2, 130.3, 130.5, 131.0, 131.1, 131.8, 133.3, 135.3, 137–146 (six broad m of low intensity; pentafluorophenyl-C), 146.9, 157.2, 161.1 (C—O$^-$). ^{19}F NMR (CD_3COCD_3): δ (ppm) = −136.6 (2 F), −142.8 (2 F), −149.8 (1 F), −158.4 (1 F), −161.9 (2 F), −165.4 (2 F). MS (FD): *m/z* (%) = 911 (100) [M^+]. $C_{41}H_9F_{20}NO \cdot H_2O$ (911.5 + 18.0 = 929.5): calcd C 52.98, H 1.19, N 1.51, F 40.88; found C 52.87, H 1.18, N 1.55, F 41.04%.

Synthesis of betaine dye 4 (Scheme 3). *1,3-Di[4-(trifluoromethyl)phenyl]-prop-2-en-1-one (**15**).* To a stirred solution of NaOH (5.12 g, 128 mmol) in water (20 ml) and ethanol (20 ml; 96%, v/v) were added 4-(trifluoromethyl)acetophenone **14** (18.82 g, 100 mmol) and 4-(trifluoromethyl)benzaldehyde (17.42 g, 100 mmol). After stirring at room temperature for 2 h, the precipitate formed was filtered off, washed with water, and dried with P_4O_{10} *in vacuo*, to give ketone **15** (30.97 g, 90%) as crude product, sufficiently pure for the next reaction step. Analytically pure **15** was obtained by sublimation at 130 °C/10^{-3} Torr (1 Torr = 133.3 Pa) as yellow crystals with m.p. 98–100 °C. IR (KBr): $\tilde{\nu}(\mathrm{cm}^{-1}) = 1670$ (C=O). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.56 (d, $^3J = 15.8$ Hz, 1 H, CO–C*H*=CH), 7.51–7.81 (m, 4 H, aromatic H), 7.84 (d, $^3J = 15.8$ Hz, 1 H, CO–CH=C*H*), 8.05 and 8.12 (m, 4 H, aromatic H). ^{13}C NMR ($CDCl_3$): δ (ppm) = 123.6 (q, $^1J_{CF} = 270$ Hz, CF_3), 123.8 (q, $^1J_{CF} = 270$ Hz, CF_3), 125.7, 126.0, 128.6, 128.8, 132.2 (q, $^2J_{\mathrm{CF}} = 30.0$ Hz, *C*–CF$_3$), 134.3 (q, $^2J_{\mathrm{CF}} = 30.0$ Hz, *C*–CF$_3$), 137.8, 140.6, 143.7 (CO–CH=*C*H), 189.1 (C=O). ^{19}F NMR (CDCl$_3$): δ (ppm) = −63.4 (s, CF$_3$), −63.6 (s, CF$_3$). MS (FD): *m/z* (%) = 344 (100) [M$^+$]. $C_{17}H_{10}F_6O$ (344.3): calcd C 59.31, H 2.93; found C 59.22, H 2.34%.

*1,3,5-Tris[4-(trifluoromethyl)phenyl]pentan-1,5-dione (**16**).* To a refluxing suspension of sodium hydride (6.48 g, 216 mmol; from an 80% suspension of NaH in light petroleum) in dry benzene (100 ml) was added a solution of chalcone **15** (29.98 g, 87.0 mmol) and 4-(trifluoromethyl)acetophenone **14** (16.29 g, 87.0 mmol) in dry benzene (300 ml) and the mixture was heated under reflux for 3 h. After cooling to room temperature, crushed ice was carefully added to the reddish brown solution and the solution was acidified (pH ≈ 1) with aqueous 2 M HCl. The organic phase was separated and the aqueous phase was extracted four times with diethyl ether. The combined organic extracts were washed acid free with water and dried with MgSO$_4$. After filtration, the solvents were distilled off *in vacuo* and the solid residue was recrystallized from light petroleum (b.p. 40–60 °C) to afford **16** (32.60 g, 70%) as brownish crystals, which were sufficiently pure for the next reaction step. Analytically pure, colorless **16** was obtained after further recrystallization from cyclohexane with m.p. 120–121 °C. IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 1697 (C=O). ^{1}H NMR (CDCl$_3$): δ (ppm) = 3.47 and 3.60 (AB part of ABX system, $^3J_{\mathrm{AB}} = 17.3$ Hz, 4 H, CH$_2$), 4.20 (X part of ABX system, $^3J_{\mathrm{AX}} = 12.3$ Hz, $^3J_{\mathrm{BX}} = 1.4$ Hz, 1 H, CH), 7.47 and 7.59 (AA BB, 4 H, aromatic H), 7.76 and 8.08 (AA BB, 8 H, aromatic H). ^{13}C NMR (CDCl$_3$): δ (ppm) = 36.5 (CH), 44.6 (CH$_2$), 123.5 (q, $^1J_{\mathrm{CF}} = 272$ Hz, CF$_3$), 123.8 (q, $^1J_{\mathrm{CF}} = 273$ Hz, CF$_3$), 125.8, 127.9, 128.4, 129.3 (q, $^2J_{\mathrm{CF}} = 32.5$ Hz, *C*–CF$_3$), 134.7 (q, $^2J_{\mathrm{CF}} = 32.5$ Hz, *C*–CF$_3$), 139.2, 147.3, 196.9 (C=O). ^{19}F NMR (CDCl$_3$): δ (ppm) = −62.7 (s, 3 F, CF$_3$), −63.3 (s, 6 F, CF$_3$). MS (FD): *m/z* (%) = 532 (100) [M$^+$]. $C_{26}H_{17}F_9O_2$ (532.4): calcd C 58.66, H 3.22; found C 58.80, H 3.44%.

*2,4,6-Tris[4-(trifluoromethyl)phenyl]pyrylium perchlorate (**17**).* A solution of diketone **16** (5.82 g, 11.0 mmol) and triphenylcarbenium perchlorate (3.76 g, 11.0 mmol) in glacial acetic acid (25 ml) was heated under reflux for 15 min. After cooling to room temperature, the precipitate formed was filtered off, washed with diethyl ether, recrystallized from glacial acetic acid or acetonitrile, and dried with KOH *in vacuo*, to yield the pyrylium salt **17** (3.42 g, 51%) as shiny, yellow, plate-like crystals with m.p. 287 °C (decomp.). IR (KBr): $\tilde{\nu}$(cm^{-1}) = 1067 (ClO$_4$). ^{1}H NMR (CD$_3$COCD$_3$): δ (ppm) = 8.13 and 8.80 (AA BB, 4 H, 4-phenyl-H), 8.16 and 8.93 (AA BB, 8 H, 2,6-phenyl-H). ^{13}C NMR (CD$_3$COCD$_3$): δ (ppm) = 119.7 (pyrylium-C-3), 124.5 (q, $^1J_{\mathrm{CF}} = 272$ Hz, two CF$_3$), 124.6 (q, $^1J_{\mathrm{CF}} = 272$ Hz, one CF$_3$), 127.6, 131.4, 131.8, 133.6, 135.9 (q, $^2J_{\mathrm{CF}} = 32$ Hz, one *C*–CF$_3$), 136.1 (q, $^2J_{\mathrm{CF}} = 30$ Hz, two *C*–CF$_3$), 137.6, 167.4 (pyrylium-C-4), 171.8 (pyrylium-C-2). ^{19}F NMR (CD$_3$COCD$_3$): δ (ppm) = −62.9 (s, one CF$_3$), −63.0 (s, two CF$_3$). MS (FD): *m/z* (%) = 513 (67) [M$^+$ −ClO$_4$]. $C_{26}H_{14}ClF_9O_5$ (612.8): calcd C 50.96, H 2.30; found C 50.95, H 1.98%.

*1,3-Di[4-(trifluoromethyl)phenyl]propan-2-one (**19**).* A solution of 4-(bromomethyl)-(trifluoromethyl)benzene **18** (9.56 g, 40.0 mmol; Aldrich; **caution**: lachrymator!)[39] and diiron nonacarbonyl (21.84 g, 60.0 mmol) in dry *n*-octane (200 ml) was heated under reflux under nitrogen for 18 h. After cooling to room temperature, the precipitate formed (FeBr$_3$) was filtered off and extracted five times with boiling toluene. The filtrate and the five extracts were combined and the solvents were distilled off [**caution**: the solvents contain toxic Fe(CO)$_5$!]. The solid residue was purified by column chromatography with neutral alumina (activity grade III) and diethyl ether–light petroleum (b.p. 40–60 °C) (2:5) as eluent. From the second fraction the solvents were distilled off to afford ketone **19** (4.78 g, 70%) as colorless needles with m.p. 63–67 °C (lit.[40] 63–67 °C). ^{1}H NMR (CDCl$_3$): δ (ppm) = 3.82 (s, 4 H, CH$_2$), 7.26 and 7.58 (AA BB, 8 H, aromatic H). ^{13}C NMR (CDCl$_3$): δ (ppm) = 49.0 (CH$_2$), 124.1 (q, $^1J_{\mathrm{CF}} = 272$ Hz, CF$_3$), 125.7 (q, $^3J_{\mathrm{CF}} = 3.7$ Hz, *C*=C–CF$_3$), 129.7 (q, $^2J_{\mathrm{CF}} = 33$ Hz, *C*–CF$_3$), 129.9 (aromatic C), 137.5 (aromatic =*C*–CH$_2$), 203.4 (C=O).

*4-Nitro-2,6-di[4-(trifluoromethyl)phenyl]phenol (**20**).* To a stirred solution of NaOH (0.56 g, 14.1 mmol) in water (9 ml) and ethanol (45 ml; 96%, v/v) were added ketone **19** (4.87 g, 14.1 mmol) and sodium nitromalonaldehyde monohydrate (1.35 g, 14.2 mmol)[24] and the mixture was stirred at room temperature for 24 h. Then the solution was acidified with aqueous 2 M HCl (pH ≈ 1) and some water was added in order to complete the formation of a precipitate (which sometimes came as an oil). The suspension was extracted eight times with diethyl ether (8 × 50 ml). The combined ether extracts were washed acid free with water and dried with MgSO$_4$. The ether was distilled off and the residue was purified by column chromatography with silica gel and toluene as eluent ($R_f = 0.43$). Removal of the toluene from the eluate by distillation yielded a viscous yellow oil, still containing some toluene, which was removed by drying *in vacuo* at 80 °C/10^{-3} Torr, to afford nitrophenol **20** (4.04 g, 68%) as sand-colored microcrystals with m.p. 114–116 °C. IR (KBr): $\tilde{\nu}$(cm^{-1}) = 3450 (OH), 1514 and 1325 (NO$_2$). ^{1}H NMR (CDCl$_3$): δ (ppm) = 5.90 (s, 1 H, OH), 7.70 and 8.04 (AA BB, 4 H, phenyl-H), 8.32 (s, 2 H, phenol-3-H). ^{13}C NMR (CDCl$_3$): δ (ppm) = 123.7 (q, $^1J_{\mathrm{CF}} = 272$ Hz, CF$_3$), 125.9 (quat. phenol-C-2), 126.2 (q, $^3J_{\mathrm{CF}} = 3.6$ Hz, *C*=C–CF$_3$), 128.4 (phenyl-C), 129.6 (phenol-C-3), 131.0 (q, $^2J_{\mathrm{CF}} = 33$ Hz, *C*–CF$_3$), 138.5 (phenyl-C), 141.5 (C–NO$_2$), 154.2 (C–OH). ^{19}F NMR (CDCl$_3$): δ (ppm) = −62.9 (s, CF$_3$). MS (FD): *m/z* (%) = 427 (100)

[M$^+$]. $C_{20}H_{11}F_6NO_3$ (427.3): calcd C 56.22, H 2.59, N 3.28; found C 56.30, H 2.18, N 3.14%.

*4-Amino-2,6-di[4-(trifluoromethyl)phenyl]phenol (**21**).* A suspension of a palladium catalyst (10% Pd on charcoal; ca 200 mg) in a solution of nitrophenol **20** (4.04 g, 9.45 mmol) in ethanol (100 ml; 96%, v/v) was reduced with dihydrogen at room temperature and normal pressure until the necessary amount of H_2 was absorbed. Under nitrogen, the catalyst was filtered off and the solvent was distilled off *in vacuo*, to afford **21** (3.68 g, 98%) as yellow microcrystals with m.p. 158–162 °C, which turned reddish in air. Because of its sensitivity to oxygen, **21** was immediately converted into the pyridinium salt **22** without further detailed characterization. ^{1}H NMR (CD_3COCD_3): δ (ppm) = 2.13 (s, 2 H, NH_2), 6.74 (s, 2 H, phenol-3-H), 6.83 (s, 1 H, OH), 7.80 (AA BB, 4 H, phenyl-H).

*1-{3,5-Di[4-(trifluoromethyl)phenyl]-4-hydroxyphenyl}-2,4,6-tri[4-(trifluoromethyl)phenyl]pyridinium perchlorate (**22**).* A solution of freshly prepared aminophenol **21** (3.75 g, 9.44 mmol), pyrylium salt **17** (4.82 g, 7.87 mmol), and water-free sodium acetate (1.55 g, 18.9 mmol) in dry ethanol (95 ml) was heated under reflux for 2.5 h. Then, at room temperature, the blue solution was acidified (pH $\approx$ 1) by addition of a few drops of aqueous $HClO_4$ (70%, w/w) and the product was precipitated by addition of water. The precipitate formed was filtered off, washed acid free with water, and dried with P_4O_{10} *in vacuo*. The product was recrystallized from xylene, digested with diethyl ether at room temperature for 2 h, and again dried with P_4O_{10} *in vacuo*, to afford perchlorate **22** (6.91 g, 89%) as fine colorless needles which decomposed without melting at ca 300 °C. IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3559 (OH), 1067 (ClO_4). UV–Vis (CH_3CN): λ_{max} (*log* ϵ) = 295 (4.61), 231 nm (4.63). ^{1}H NMR (CD_3COCD_3): δ (ppm) = 7.67 (s, 2 H, phenol-3-H), 7.48 and 7.74 (AA BB, 8 H, phenyl-H), 7.90 and 7.97 (AA BB, 8 H, phenyl-H), 8.03 and 8.51 (AA BB, 4 H, phenyl-H), 8.87 (s, 2 H, pyridinium-3-H). ^{13}C NMR (CD_3COCD_3): δ (ppm) = 124.8 (q, $^1J_{CF}$ = 272 Hz, two CF_3), 124.9 (q, $^1J_{CF}$ = 272 Hz, one CF_3), 125.2 (q, $^1J_{CF}$ = 272 Hz, two CF_3), 126.2, 127.3 (q, $^3J_{CF}$ = 3.8 Hz, $C{=}C{-}CF_3$), 128.3 (phenol-C-3), 130.5, 130.6, 131.0, 132.0, 131.5 (pyridinium-C-3), 132.4 (q, $^2J_{CF}$ = 32 Hz, two $C{-}CF_3$), 132.5 (pyridinium-C-4), 133.7 (q, $^2J_{CF}$ = 32 Hz, one $C{-}CF_3$), 135.2, 139.2, 141.2, (phenol-C-2), 152.8 (phenol-C-4), 157.0 (pyridinium-C-2), 157.1 (C–OH). ^{19}F NMR (CD_3COCD_3): δ (ppm) = −62.2 (s, 6 F, two CF_3), −62.6 (s, 6 F, two CF_3), −62.7 (s, 3 F, CF_3). MS (FD): *m/z* (%) = 892 (33) [M$^+$ −ClO_4], 513 (100). $C_{46}H_{25}ClF_{15}NO_5$ (992.1): calcd. C 55.69, H 2.54, N 1.41, F 28.72; found C 55.56, H 2.57, N 1.38, F 28.54%.

*4-{2,4,6-Tri[4-(trifluoromethyl)phenyl]pyridinium-1-yl}-2,6-di[4-(trifluoromethyl)phenyl]phenolate (**4**) ('penta-CF_3-betaine').* To a stirred solution of perchlorate **22** (0.96 g, 0.97 mmol) in dry dichloromethane (40 ml) was added the granulated polymer base (diethylaminomethyl)polystyrene (Fluka, 1.00 g, base equivalent ca 3 mmol) and the suspension was stirred for 30 min at room temperature. Then, the polymer base was filtered off, washed with dichloromethane and discarded. The solvent from the combined filtrates was distilled off and the solid residue was dried with P_4O_{10} *in vacuo*, to yield betaine dye **4** (0.71 g, 82%) as fine green crystals which melted, after a phase transition at 180–195 °C, at 284 °C. UV–Vis (CH_3CN): λ_{max} (log ϵ) = 632 (3.09), 381 (3.48). ^{1}H NMR (CD_3COCD_3): δ (ppm) = 7.52 (s, 2H, phenolate-3-H), 7.45 and 7.64 (AA BB, 8 H, phenyl-H), 7.86 and 7.93 (AA BB, 8 H, phenyl-H), 8.01 and 8.50 (AA BB, 4 H, phenyl-H), 8.85 (s, 2 H, pyridinium-3-H). ^{13}C NMR (CD_3COCD_3): δ (ppm) = 124.8 (q, $^1J_{CF}$ = 272 Hz, two CF_3), 124.9 (q, $^1J_{CF}$ = 272 Hz, one CF_3), 125.3 (q, $^1J_{CF}$ = 272 Hz, two CF_3), 125.8 (q, $^3J_{CF}$ = 3.8 Hz, two $C{=}C{-}CF_3$), 126.2 (q, $^3J_{CF}$ = 3.8 Hz, two $C{=}C{-}CF_3$), 127.3 (q, $^3J_{CF}$ = 4.5 Hz, one $C{=}C{-}CF_3$), 128.2 (phenolate-C-3), 129.7 (q, $^2J_{CF}$ = 32 Hz, two $C{-}CF_3$), 130.3, 130.4, 130.6, 130.8, 131.3 (pyridinium-C-3), 131.9, 132.3 (q, $^2J_{CF}$ = 32 Hz, two $C{-}CF_3$), 133.7 (q, $^2J_{CF}$ = 32 Hz, one $C{-}CF_3$), 138.3, 139.1, 142.1 (phenolate-C-2), 155.8 (phenolate-C-4), 156.5 (pyridinium-C-2), 156.9 (C–O$^-$). ^{19}F NMR (CD_3COCD_3): δ (ppm) = −62.4 (s, 3 F, CF_3), −63.3 (s, 6 F, two CF_3), −63.8 (s, 6 F, two CF_3). MS (FD): *m/z* (%) = 891 (100) [M$^+$]. $C_{46}H_{24}F_{15}NO$ (891.7): calcd C 61.96, H 2.71, N 1.57, F 31.96; found C 56.79, H 2.30, N 1.51, F 29.44%. Because of the high fluorine content of **4**, the value found for carbon is too low.

Synthesis of betaine dye 5 (Scheme 4). *4-(Tridecafluorohex-1-yl)acetophenone (**24**).* In a 250 ml three-necked round-bottomed flask with a thermometer and reflux condenser, copper bronze (Aldrich, copper powder 99% for organic syntheses; 11.21 g, 1.76 mmol) was dried by heating it under nitrogen. At room temperature, a solution of 4-iodoacetophenone **23** (15.88 g, 64.5 mmol) in water-free dimethyl sulfoxide (110 ml) was added and the suspension was heated to 125–130 °C. At this temperature, iodine-free perfluoro-1-iodohexane (34.54 g, 77.4 mmol) was slowly added over a period of 1–1.5 h and heating was continued for 5 h. After cooling to room temperature, the precipitate formed (copper bronze and copper iodide) was filtered off and washed five times with diethyl ether. The combined filtrates were washed DMSO free with water and dried with $MgSO_4$. Then, the solvent was distilled off and the residue was purified by fractional distillation, to give ketone **24** (22.89 g, 81%) as a colourless liquid with b.p. 64–65 °C/0.008 Torr, which solidified on standing to colorless crystals with m.p. 47–49 °C (lit.[25,26] b.p. 68 °C/0.039 Torr; m.p. 47–49 °C). ^{1}H NMR ($CDCl_3$): δ (ppm) = 2.66 (s, 3 H, CH_3), 7.72 and 8.09 (AA BB, 4

H, phenyl-H). ^{13}C NMR ($CDCl_3$): δ (ppm) = 26.8 (CH_3), 127.4 (t, $^{3}J_{CF}$ = 6.5 Hz, phenyl-C-3), 128.5 (phenyl-C-2), 133.1 (t, $^{2}J_{CF}$ = 24 Hz, phenyl-C-4), 139.9 (phenyl-C-1 = *C*–CO–CH_3), 197.1 (C=O). ^{19}F NMR ($CDCl_3$): δ (ppm) = −81.3 (t, $^{4}J_{FF}$ = 10 Hz, 3 F, CF_3), −111.7 (t, $^{4}J_{FF}$ = 10 Hz, 2 F, CF_2-1), −121.9 (broad m, 2 F, CF_2-2 or CF_2-3), −122.3 (m, 2 F, CF_2-3 or CF_2-2), −123.3 (m, 2 F, CF_2-4), −126.6 (m, 2 F, CF_2-5). For the C numbering of the perfluorohexyl chain, see Scheme 4.

*Ethyl 4-bromobenzoate (**26**).* To a stirred suspension of 4-bromobenzoic acid **25** (50.00 g, 250 mmol) and triethyloxonium tetrafluoroborate (49.02 g, 270 mmol)[27] in dry dichloromethane (300 ml) was added dropwise at 0 °C ethyl diisopropylamine (32.15 g, 250 mmol) and then stirring was continued for 24 h at room temperature. In a separating funnel, the reaction mixture was extracted twice with aqueous $NaHCO_3$ solution (2 × 150 ml), and washed subsequently with water (150 ml), aqueous 2 M HCl and again with water. After drying with $MgSO_4$, the solvent was distilled off and the residue was purified by fractional distillation, to afford the ester **26** (46.62 g, 81%) as a colorless liquid with b.p. 136 °C/23 Torr (lit.[41] 136.8 °C/17 Torr). ^{1}H NMR ($CDCl_3$): δ (ppm) = 1.39 (q, ^{3}J = 7.2 Hz, 3 H, CH_3), 4.38 (q, ^{3}J = 7.2 Hz, 2 H, CH_2), 7.58 and 7.91 (AA BB, 4 H, phenyl-H).

*Ethyl 4-(Tridecafluorohex-1-yl)benzoate (**27**).* In a 250 ml three-necked round-bottomed flask with a thermometer and reflux condenser, copper bronze (Aldrich, copper powder 99% for organic syntheses; 5.21 g, 82.0 mmol) was dried by heating it under nitrogen. At room temperature, a solution of ester **26** (6.87 g, 30.0 mmol) in water-free dimethyl sulfoxide (50 ml) was added and the suspension was heated to 125–135 °C. At this temperature, iodine-free perfluoro-1-iodohexane (10.05 g, 36.0 mmol) was added dropwise over a period of ca 1 h and heating was continued for 18 h. After cooling to room temperature and addition of diethyl ether (50 ml), the precipitate formed (copper bronze and copper iodide) was filtered off and washed five times with diethyl ether. The combined filtrates were washed DMSO free with water and dried with $MgSO_4$. Then, the solvent was distilled off and the solid residue was purified by fractional distillation with a spinning band column (50 cm), to yield the ester **27** (8.02 g, 57%) as a colorless liquid with b.p. 92–100 °C/2 Torr, which solidified on standing to colorless crystals with m.p. 29–30 °C (lit.[26] b.p. 80–81 °C/0.13 Torr and m.p. 29–30 °C). According to its ^{1}H NMR spectrum, the purity of **27** was ca 94%, still containing some starting material and side products, which were removed during the subsequent reaction steps. ^{1}H NMR ($CDCl_3$): δ (ppm) = 1.42 (t, ^{3}J = 7.2 Hz, 3H, CH_3), 4.43 (q, ^{3}J = 7.2 Hz, 2 H, CH_2), 7.68 and 8.19 (AA BB, 4 H, phenyl-H).

*4-(Tridecafluorohex-1-yl)benzyl alcohol (**28**).* To a suspension of $LiAlH_4$ (4.55 g, 120 mmol) in dry tetrahydrofuran (100 ml), placed in a 500 ml three-necked round-bottomed flask with a stirrer, dropping funnel, and reflux condenser, a solution of ester **27** (23.41 g, 47.0 mmol) in tetrahydrofuran (60 ml) was slowly added at ca 0 °C with stirring. Stirring was continued for 30 min and then the mixture was heated under reflux for 2 h. After cooling to ca 0 °C, the mixture was hydrolyzed by addition of ice-cold water and then acidified (pH ≈ 1) by addition of dilute HCl. After addition of diethyl ether, the organic and aqueous phase were separated and the aqueous phase was extracted four times with diethyl ether in a separating funnel. The combined ethereal phases were washed with saturated aqueous NaCl solution and dried with $MgSO_4$. The solvent was distilled off, to afford crude **28** (19.62 g, ca 93%) as a yellow oil, which partly solidified on standing at room temperature. According to its ^{1}H NMR spectrum, the purity of **28** was ca 95%, which was sufficient for the next reaction step. ^{1}H NMR ($CDCl_3$): δ (ppm) = 2.06 (s, 1 H, OH), 4.78 (s, 2 H, CH_2), 7.50 and 7.58 (AA BB, 4 H, phenyl-H).

*4-(Tridecafluorohex-1-yl)benzaldehyde (**29**).* To a stirred suspension of pyridinium fluorochromate (12.83 g, 64.0 mmol)[28] in dry dichloromethane (70 ml), placed in a 250 ml three-necked round-bottomed flask with a stirrer and reflux condenser, a solution of alcohol **28** (19.62 g, 43.7 mmol) in dry dichloromethane (20 ml) was added at room temperature and stirring was continued for 6 h. Then, to the reaction mixture an equal volume of diethyl ether was added and the solution was percolated under vacuum through a silica gel bed placed on a sintered glass funnel. The silica gel bed was thoroughly extracted with diethyl ether. All filtrates were combined, the solvent was distilled off, and the residue was purified by fractional distillation with a packed column (30 cm), filled with Wilson spirals, to afford the aldehyde **29** (12.94 g, 70%) as a colorless liquid with b.p. 90 °C/0.1 Torr, which solidified to colorless crystals with m.p. 29–33 °C. IR (KBr): $\tilde{\nu}(\mathrm{cm}^{-1}) = 1711$ (C=O). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.79 and 8.04 (AA BB, 4 H, phenyl-H), 10.13 (s, 1 H, CHO). ^{13}C NMR ($CDCl_3$): δ (ppm) = 110–119 (several m of low intensity, perfluorohexyl-C), 127.6 (t, $^{3}J_{CF}$ = 6.4 Hz, *C*=C–CF_2–), 129.5 (*C*=C–CHO), 134.2 (t, $^{2}J_{CF}$ = 24 Hz, *C*–CF_2–), 138.7 (*C*–CHO), 190.9 (CHO). ^{19}F NMR ($CDCl_3$): δ (ppm) = −81.3 (t, $^{4}J_{FF}$ = 10 Hz, 3 F, CF_3), −111.8 (t, $^{4}J_{FF}$ = 14 Hz, 2 F, CF_2-1), −121.9 (m, 2 F, CF_2-2 or CF_2-3), −122.2 (m, 2 F, CF_2-3 or CF_2-2), −123.3 (m, 2 F, CF_2-4), −126.7 (m, 2 F, CF_2-5). For the C numbering of the perfluorohexyl chain, see Scheme 4. MS (EI; 70 eV): *m/z* (%) = 424 (75) [M^+], 423 (66) [M^+ −1], 405 (20) [M^+ −F], 357 (4) [M^+ −CF_3], 305 (1) [M^+ −C_2F_5], 238 (1) [M^+ −C_3F_7], 205 (3) [M^+ −C_4F_9], 155 (100) [M^+ −C_5F_{11}], 127 (75) [C_6H_5–CF_2^+], 105 (2) [M^+ −C_6F_{13}], 77 (19) [$C_6H_5^+$], 50 (8) [CF_2^+]. $C_{13}H_5F_{13}O$ (424.2): calcd C 36.81, H 1.19; found C 36.96, H 1.05%.

*1,3-Di[4-(tridecafluorohex-1-yl)phenyl]-prop-2-en-1-one (**30**).* To a stirred solution of NaOH (1.02 g, 25.6 mmol) in water (20 ml) and ethanol (60 ml, 96%, v/v) were added ketone **24** (8.76 g, 20.0 mmol) and aldehyde **29** (8.48 g, 20.0 mmol). After stirring at room temperature for 1 h, the precipitate formed was filtered off, washed with water, and dried with P_4O_{10} *in vacuo*, to give chalcone **30** (16.35 g, ca 97%) as light-yellow crystals, which were sufficiently pure for the next reaction step. Recrystallization from 2-propanol yielded analytically pure **30** as light-yellow crystals with m.p. 138–140 °C. IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 1688 (C=O). ^1H NMR ($CDCl_3$): δ (ppm) = 7.58 (B part of AB system, ^3J = 16 Hz, 1 H, C*H*–CO), 7.76 and 7.79 (AA BB, 4 H, phenyl-H), 7.86 (A part of AB system, ^3J = 16 Hz, 1 H, C*H*=CH–CO), 7.67 and 8.14 (AA BB, 4 H, phenyl-H). ^{13}C NMR ($CDCl_3$): δ (ppm) = 123.9 (*C*H–CO), 127.6, 128.5, 128.7, 130.8 (t, $^3J_{CF}$ = 49 Hz, *C*–C_6F_{13}), 132.9 (t, $^3J_{CF}$ = 49 Hz, *C*–C_6F_{13}), 138.1, 140.8, 143.9 (*C*H=CH–CO), 189.2 (C=O). Because of their low intensity, the ^{13}C signals of the two perfluorohexyl groups are not seen in the spectrum. ^{19}F NMR ($CDCl_3$): δ (ppm) = −81.2 (m, 6 F, two CF_3), −111.5 (m, 2 F), −111.6 (m, 2 F), −121.9 (m, 4 F), −122.3 (m, 4 F), −123.2 (m, 4 F), −126.6 (m, 4 F) for the CF_2 groups. MS (FD): *m/z* (%) = 844 (100) [M$^+$]. $C_{27}H_{10}F_{26}O$ (844.3): calcd C 38.41, H 1.19; found C 38.25, H 1.00%.

*2,4,6-Tri[4-(tridecafluorohex-1-yl)phenyl]pyrylium perchlorate (**31**).* In a 100 ml three-necked round-bottomed flask with a stirrer, dropping funnel, and reflux condenser, a mixture of chalcone **30** (4.22 g, 5.00 mmol) and ketone **24** (2.19 g, 5.00 mmol) was heated with stirring until a homogeneous melt was formed (bath temperature 95–100 °C). Then, aqueous $HClO_4$ (70%, w/w; 1.15 g, 8.00 mmol) was slowly added dropwise and the mixture was held at 100 °C for 1 h. After 5–10 min, the product already separated out from the hot, red reaction mixture. After cooling to room temperature, diethyl ether (50 ml) was added and the precipitate formed was filtered off, washed with diethyl ether, recrystallized from glacial acetic acid, and dried with KOH *in vacuo*, to yield the pyrylium salt **31** (1.36 g, 20%) as shiny orange crystals with m.p. 226–229 °C. IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 1100 (ClO_4). ^1H NMR (CD_3COCD_3): δ (ppm) = 8.17 and 8.87 (AA BB, 4 H, 4-phenyl-H), 8.21 and 9.01 (AA BB, 8 H, 2- and 6-phenyl-H), 9.61 (s, 2 H, pyrylium-2-H). ^{13}C NMR (CD_3COCD_3): δ (ppm) = 129.2, 131.7, 133.9, 134.6, and 137.9 (phenyl-C), 167.4 (pyrylium-C-4), 171.8 (pyrylium-C-2). Because of their low intensity, the ^{13}C signals of the three perfluorohexyl groups are not seen in the spectrum. ^{19}F NMR (CD_3COCD_3): δ (ppm) = −81.2 (t, $^4J_{FF}$ = 9 Hz, three CF_3), −111.1 (m, 6 F, CF_2-1), −121.4 (m, 6 F, CF_2-2 or CF_2-3), −121.6 (m, 6 F, CF_2-3 or CF_2-2), −122.9 (m, 6 F, CF_2-4), −126.3 (m, 6 F, CF_2-5). For the C numbering of the perfluorohexyl chain, see Scheme 4. MS (FD): *m/z* (%) = 1263 (100) [M$^+$ −ClO_4]. $C_{41}H_{14}ClF_{39}O_5$ (1362.9): calcd C 36.13, H 1.04; found C 35.95, H 1.02%.

*1-(3,5-Diphenyl-4-hydroxyphenyl)-2,4,6-tri[4-(tridecafluorohex-1-yl)phenyl]pyridinium perchlorate (**32**).* A solution of freshly prepared 4-amino-2,6-diphenylphenol (0.65 g, 2.49 mmol),[3a,19] pyrylium salt **31** (2.79 g, 2.05 mmol), and water-free sodium acetate (0.42 g, 5.12 mmol) in dry ethanol (25 ml) was heated under reflux for 2 h. At room temperature, the solution was acidified (pH ≈ 1) by addition of a few drops of $HClO_4$ (70%, w/w) and the product was precipitated by addition of water. After standing for ca 12 h at room temperature, the precipitate formed was filtered off, washed acid free with water, recrystallized from a small amount of 2-propanol and dried with P_4O_{10} *in vacuo*, to afford perchlorate **32** (2.94 g, 89%) as yellow needles with m.p. 138–140 °C. IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 1096 (ClO_4). UV–Vis (CH_3CN): λ_{max} (lg ϵ) = 295 nm (4.65). ^1H NMR ($CDCl_3$): δ (ppm) = 7.16 (s, 2 H, phenolate-3-H), 5.57 (s, 1 H, OH), 7.01, 7.67, 7.73, and 7.95 (four m, phenyl-H), 8.08 (s, 2 H, pyridinium-3-H). ^{13}C NMR (CD_3COCD_3): δ (ppm) = 127.7, 128.3 (phenolate-C-3), 128.7, 128.8, 129.2, 130.0, 130.4, 130.6, 131.4, 130.9 (t, $^2J_{CF}$ = 34 Hz, two *C*–C_6F_{13}), 131.8 (t, $^2J_{CF}$ not measurable, one C–C_6F_{13}), 137.8, 138.4, 139.5 (phenolate-C-2), 141.8 (phenolate-C-4), 152.6 (pyridinium-C-2), 156.8 (C–OH). Because of their low intensity, the ^{13}C signals of the three perfluorohexyl groups are not seen in the spectrum. ^{19}F NMR (CD_3COCD_3): δ (ppm) = −81.2 (9 F, three CF_3), −110.9 (6 F, CF_2-1), −121.6 (12 F, CF_2-2 and CF_2-3), −122.9 (6 F, CF_2-4), −126.3 (CF_2-5). For the C numbering of the perfluoroalkyl chain, see Scheme 4. MS (FD): *m/z* (%) = 1507 (100) [M$^+$ −ClO_4], 1499 (21). $C_{59}H_{27}ClF_{39}NO_5 \cdot 0.5H_2O$ (1606.2 + 9.0 = 1615.2): calcd C 43.87, H 1.75, N 0.86; found C 43.86, H 1.84, N 0.90%.

*2,6-Diphenyl-4-{2,4,6-[4-(tridecafluorohex-1-yl)phenyl]pyridinium-1-yl}phenolate (**5**) ('tris-C_6F_{13}-betaine').* To a solution of perchlorate **32** (2.85 g, 1.76 mmol) in dry methanol (45 ml) sodium methanolate (0.24 g, 4.44 mmol) was added and the dark solution was heated under reflux for 5 min. The cold solution was then poured into aqueous NaOH (10%, w/w; 150 ml). After standing for ca 12 h at room temperature, the precipitate formed was filtered off, washed with water, dried with P_4O_{10} *in vacuo*, recrystallized from 2-propanol, and dried again, to yield betaine dye **5** (2.00 g, 74%) as fine dark-green crystals with m.p. 237–240 °C (decomp.). UV–Vis (CH_3CN): λ_{max} (log ϵ) = 691 (3.87), 380 (4.06), 290 nm (4.42). ^1H NMR (CD_3COCD_3): δ (ppm) = 6.81 (s, 2 H, phenolate-3-H), 7.05 and 7.37 (AA BB, 10 H, 2,6-*diphenyl*phenolate-H), 7.87 and 7.96 (AA BB, 8 H, 2,6-*diphenyl*pyridinium-H), 7.99 and 8.59 (AA BB, 4 H, 4-*phenyl*pyridinium-H), 8.81 (s, 2 H, pyridinium-3-H). ^{13}C NMR (CD_3COCD_3): δ (ppm) = 125.4, 127.4, 127.8, 128.6 (phenolate-C-3), 128.7, 129.5, 129.7, 129.9, 130.1, 131.1, 131.3 (pyridinium-C-3), 139.4, 140.0, 142.8 (phenolate-C-2), 152.6 (phenolate-C-4), 155.5 (pyridinium-C-2), 171.2 (C–O$^-$). Because of their low intensity, the ^{13}C signals of the three perfluoroalkyl groups are not seen in the spectrum. ^{19}F NMR (CD_3COCD_3): δ (ppm) = −81.2 (9 F, three CF_3), −110.9 (6 F, CF_2-1), −121.6 (12 F, CF_2-2 and CF_2-3), −122.9 (6 F, CF_2-4), −126.3 (6 F, CF_2-5). For the C numbering of the perfluoroalkyl chain, see Scheme 4. MS (FD): *m/z* (%) = 1505 (100) [M$^+$]. $C_{59}H_{26}F_{39}NO \cdot H_2O$ (1505.8 + 18.0 = 1523.8): calcd C 46.50, H 1.85, N 0.92; found C 46.99, H 2.17, N 0.95%.

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