How Many Molecular Layers of Polar Solvent Molecules Control Chemistry? The Concept of Compensating Dipoles

Heinz Langhals,* Patricia Braun, Christian Dietl, and Peter Mayer^[a]

Dedicated to Professor Wolfgang Beck on the occasion of his 80th birthday

Abstract: The extension of the solvent influence of the shell into the volume of a polar medium was examined by means of *anti*-collinear dipoles on the basis of the $E_{\rm T}(30)$ solvent polarity scale (i.e., the molar energy of excitation of a pyridinium-*N*-phenolate-

betaine dye; generally: $E_{\rm T} = 28591 \text{ nm kcal mol}^{-1}/\lambda_{\rm max}$) where no compensation effects were found. As a

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consequence, solvent polarity effects are concentrated to a very thin layer of a few thousand picometres around the solute where extensions into the bulk solvent become unimportant. A parallelism to the thin surface layer of water to the gas phase is discussed.

Introduction

Both the majority of technical syntheses and biological processes proceed in liquids where solvent effects play a predominant role. Polar interactions between dissolved material and the solvent are of special importance where the knowledge of such interactions is essentially based on the fundamental works of Debye, Onsager, Clausius-Mossotti and Hückel about the interaction of spherical, charged particles or dipoles in solvents as dielectric media. However, such Coulomb interactions are comparably long reaching and hardly represent the majority of chemically important cases. Weaker fluctuating dipole-dipole interactions dominate mostly where a faster damping with increasing distance can be expected. There are many concepts for the description of such solvent effects,^[1] however, a final solution for this problem is still lacking; this may be complicated by varying influences of both the bulk solvent and the contact layer between the solvent and the solute. One may ask how many molecular layers of solvent molecules are important for the polar control of chemical reactions.

Results and Discussion

We applied the pyridinium-*N*-phenolatebetaine dye **1** (betaine No. 30) of Dimroth and Reichardt^[2,3] as a molecular probe for the interaction of dipolar substrates with polar sol-

 [a] Prof. Dr. H. Langhals, Dr. P. Braun, C. Dietl, Dr. P. Mayer Department of Chemistry, LMU University of Munich Butenandtstrasse 13, 81377 Munich (Germany)
 Fax: (+49)89-2180-77640
 E-mail: Langhals@lrz.uni-muenchen.de

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vents because its strong negative solvatochromism allows the detection of even small medium effects with high sensitivity (see Figure 1). The solvent-induced spectral band



Figure 1. Left) Molecular structure of the betaine dye **1** as the basis of the $E_{\rm T}(30)$ solvent polarity scale, the direction of the ground-state dipole moment and its molecular dimensions. Right) Electronic highest occupied molecular orbital (HOMO, bottom) and lowest unoccupied molecular orbital (LUMO, top) of **1**, as obtained by DFT calculations (B3-LYP).^[4]

shifts of **1**, which are observed in solvents of different polarity, are caused by the differential solvation of the highly dipolar zwitterionic electronic ground state of **1** (S_0) and its much less dipolar first excited state (S_1); in polar solvents, the ground state is much more stabilised by solvation than the excited state (see Figure 2). As a consequence, the colour of a solution of **1** shifts from yellow (absorbing at short wavelengths) in highly polar media through the visible until the near-infrared (NIR) region for media with low sol-

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Figure 2. Solvent influences causing the solvatochromism of 1; the large dipole in the ground state (S_0) of 1 is strongly solvated in polar media and appreciably lowered in energy, whereas the small dipole in the electronically excited state (S_1) is only slightly solvated (vertical transitions $h\nu$ and $h\nu'$, respectively).

vent polarity such as 1,4-dioxane. The molar energy of excitation of **1** is applied as the solvent polarity scale $E_{\rm T}(30)^{[3]}$ (generally: $E_{\rm T}=28591$ nm kcal mol⁻¹/ $\lambda_{\rm max}$).

We constructed *anti*-collinear dyads where the dipole of **1** compensates in order to test the extension of the solvent shell. Very thin solvent shells would be able to solvate the individual dipoles with individual solvatochromism, whereas compensation would be expected to become more and more important with the extension of the solvent shell and finally extinguish solvatochromism for very large shells; compare also reference [5]. There is some relation of this question to

the recently studied question^[6] about the extension of the interfacial layer between water and the gas phase.

We started the synthesis of a dyad with two *anti*-collinearly arranged chromophores of **1** with 4-bromobenzaldehyde (**2**) and allowed a condensation with acetophenone to form the pyrylium salt^[7] **3** as a key intermediate for the new dyads **8** and **10** (see Scheme 1). 2,6-Diphenylphenol (**4**) was nitrated^[8] to give intermediate **5**, which was reduced to form 4-amino-2,6-diphenylphenol (**6**). The latter was allowed to react in a convergent synthesis with the pyrylium salt **3** to give product **7**, which was coupled in a Heck reaction to form the dyad **8** with *anti*-collinear dipoles; the solvent polarity scale derived from **8** will be consequently named $E_{\rm T}(30 {\rm dyad})$.

The application of **1** is limited to non-acidic solvents because the strongly basic phenolate anion is easily protonated. Wolfbeis et al. have synthesised^[9] the betaine derivative **11** (see Scheme 2), which is less basic because of the electron-withdrawing effect of the two chlorine atoms and they named it pyridinium-*N*-phenolate 33 as a continuation of the initially published series of betaine dyes; as a consequence, the solvent polarity scale on the basis of **11** was named $E_{\rm T}(33)$. We prepared the dyad **10** of the chromophore of **11** analogously to **8** by the condensation of 4amino-2,6-dichlorophenol with **3** to give **9**, which was coupled to form **10** as the analogue of **8**. The corresponding sol-



Scheme 1. Synthesis of *anti*-collinear dyads 8 and 10 of the betaine dyes used for the extension of the $E_T(30)$ and the $E_T(33)$ solvent polarity scales. i) Acetophenone. ii) HNO₃. iii) Na₂S₂O₄. iv) Pd(OAc)₂, Ac = acyl.

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Scheme 2. The pyridinium-*N*-phenolate betaine dyes **11** and **24** as the basis of the solvent polarity scales $E_{\rm T}(33)^{[9]}$ and $E_{\rm T}(30t{\rm Bu})$, respectively. $t{\rm Bu} = tert$ -butyl.

vent polarity scales were designated as $E_{\rm T}(33 \, {\rm dyad})$ and $E_{\rm T}(30 \, {\rm dyad})$, respectively.

We further wanted to diminish any π interactions between the components of dyads with compensating dipoles and introduced a bicyclo[2.2.2]octane unit as a stiff, purely aliphatic spacer. The synthesis started with the diphenyl^[10] derivative 12, where iodation with hypervalent iodine compounds^[11] gave the iodide 13 and a reaction^[12] with CuCN in NMP gave the dinitrile 14 (Scheme 3).^[13] A reduction with DIBAL-H^[12] allowed the preparation of the dialdehyde 15^[14] and a base-induced condensation with acetophenone analogously to reference [15] yielded the tetraketone 16. The latter was cyclized with acetic anhydride analogously to reference [16] and crystallised as the naphthalene sulphonate 17. A final condensation with diphenylaminophenol gave the bicyclo[2.2.2]octane derivative 18 analogously to reference [8]. Finally, 4-(4-tert-butylphenyl)-2,6-diphenylpyrylium tetrafluoroborat was prepared in analogy to reference [17] and condensed with diphenylaminophenol in analogy to reference [8] to obtain compound 24 for comparison, where the central C-C-bonds in 18 are formally cut and replaced by hydrogen atoms. As a consequence, compound 24 represents one functional chromophore of the dyad 18.

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A spacer with a diamantane structure was introduced for the arrangement of two laterally displaced chromophores of **1** still keeping their long axes parallel. Thus, the diiodo diamantane^[11] **19** was allowed to react with CuCN to form the dinitile **20**, where the dialdehyde **21** was prepared by reduction with DIBAL-H. A further condensation with acetophenone formed the bispyrylium perchlorate **22** (Caution! Compound **22** may be explosive!) applied without further purification for the subsequent condensation with diphenylaminophenol to form **23** (Scheme 4).

The electronic transition of the longest-wavelength light absorption of **1** (more than $\lambda = 450$ nm) proceeds essentially between the HOMO and the LUMO for which we report the quantum-chemically calculated orbitals (DFT method B3-LYP)^[4] in Figure 1. For the corresponding HOMO/ LUMO calculations of 1 (ZINDO, DFT and COSMO methods) see also reference [18]. The π -electron density of the HOMO is concentrated at the phenolate ion, whereas in the LUMO the electron density is more located around the nitrogen atom of the pyridinium ring. As a consequence, the electronic excitation causes an appreciable shift of the charge along the long molecular axis according to the experimentally observed reduction of the dipole moment. A direct experimental evidence for the light-induced intramolecular charge-transfer was found by Schmuttenmaer et al.^[19] by means of terahertz spectroscopy. We calculated a dipole moment of 12 D for the ground state; this value is in the same order as the experimental result for similar compounds.[2,20]

Compound **1** exhibits only very weakly fluorescence,^[21] preferment at low temperature; for fast photo physical processes see reference [22]. The spectrum of **1** in the typical solvent acetone is recorded in Figure 3 (solid line). An energy-linear Gaussian analysis^[23] with the parameters E_i , λ_i and σ_i of the spectrum according to Equation (1) was successful and the positions and intensities of the Gaussian bands are



Scheme 3. Synthesis of *anti*-collinear dyad **18** of the betaine dyes used for the extension of the $E_T(30)$ and the $E_T(33)$ solvent polarity scales. i) (Bis(tri-fluoroacetoxy)iodo)benzene, I₂. ii) CuCN, *N*-methyl-2-pyrrolidine (NMP). iii) Diisobutylaluminium hydride (DIBAL-H). iv) Acetophenone, base. v) Acetic anhydride, naphthalsulfonic acid. vi) 4-Amino-2,6-diphenylphenol.

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Scheme 4. Synthesis of *anti*-collinear dyad **23** of the betaine dyes used for the extension of the $E_{\rm T}(30)$ and the $E_{\rm T}(33)$ solvent polarity scales. i) CuCN, DMF. ii) Diisobutylaluminium hydride (DIBAL-H). iii) Acetophenone, HClO₄. iv) 1. 4-Amino-2,6-diphenylphenol, 2. NaOH.



Figure 3. UV/Vis spectrum of $1 [E_T(30) \text{ scale}]$ in acetone (thick, solid line) and Gaussian analysis of the spectrum. Dotted line (mostly covered by the solid line): simulated spectrum on the basis of the Gaussian analysis. Bars: Positions and intensities of the Gaussian bands. Dashed line: UV/Vis spectrum of the dyad **18** [$E_T(30\text{bic})$]. Bic=bicyclo[2.2.2]octane.

shown in Figure 3 as bars; compare reference [24]. The simulated spectrum on the basis of this analysis is very close to the experimental spectrum (dotted line in Figure 3 nearly completely covered by the solid line of the experimental spectrum). Two Gaussian functions were found for the most bathochromic absorption with the absorption maximum in between; the whole spectrum in the visible can be split into n=6 Gaussian functions; compare reference [25] for the simulation of the bathochromic absorption maximum.

$$E_{(\lambda)} = \sum_{i=0}^{n} E_i \cdot e^{-\frac{\left(\frac{1}{\lambda} \cdot L\right)^2}{2\sigma_i^2}}$$
(1)

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Figure 4. Bottom) Molecular structure of the ground state of the dyad **8**, showing the *anti*-collinear orientation of the internal ground-state dipole moments, and its molecular dimensions. Top) Electronic HOMO (bottom) and LUMO (top) of **8** obtained by DFT calculations (B3-LYP).^[4]

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Compound **8** formally represents a donor–acceptor–acceptor–donor system; for more structures of polar components forming centrosymmetric or quadrupolar dyes and their solvent influences see reference [26].

We tested the extension of the solvent shells experimentally by means of the anti-collinear arrangement of the individual two chromophores of 1 in dyad 8 where the dipole moments compensate in the whole molecule (see Figure 4 bottom). Indeed, an insignificantly small dipole moment was calculated for 8 by the DFT method^[4] ($\mu < 0.001 \text{ D}$). Dyad 8 is still strongly negasolvatochromic tively (see Figure 5 for the solvent polarity-induced shift of the band at longest wavelengths). The absorption of 8 resembles 1 (see

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Figure 5. UV/Vis spectra of 8 in selected solvents with its long-wavelength absorption band around $\lambda = 500-800$ nm, measured in thirteen solvents at room temperature. From right to left: chlorobenzene (solid), diglyme (dashed), dichloromethane (dotted), butanone (solid), acetone (dashed), DMF (dotted), DMSO (solid), acetonitrile (dashed), 1-butanol (dotted), 1-propanol (solid), ethanol (dashed), ethanol/water 80:20 (dotted), methanol (solid).

Figure 4 for comparison) and a Gaussian analysis results in similar parameters. The molar energy of the excitation of 8, that is, $E_{\rm T}$ (30dyad), was compared with that of the non-compensating monochromophoric 1, that is, $E_{\rm T}(30)$, for twenty pure solvents of different solvent polarity (see Figure 6). A



Figure 6. Solvatochromism of 8 $[E_T(30dyad)]$ for twenty pure solvents compared with the solvatochromism of $\mathbf{1}$ [$E_{\mathrm{T}}(30)$] and their mutual linear correlation calculated by the least square method. Slope: 1.02. Intercept: -2.43. Correlation number r: 0.993, for n=20. Standard deviation in $E_{\rm T}$ (30dyad): 0.7. Ionic liquid: The ionic liquid used was 1-butyl-3-methylimidazolium tetrafluoroborate.

linear relationship war found between the $E_{\rm T}(30 \, {\rm dyad})$ of 8 and the $E_{\rm T}(30)$ scale, based on 1, with an unusually good correlation number of r=0.993 (n=20), including solvents such as benzyl alcohol with complex solvent interactions, an ionic liquid, and highly polar alcohols, as compared with other linear-free energy relationships between empirical solvent polarity scales.^[1] The exclusion of hydrogen-bond-forming solvents would not alter the result.

The slope of this correlation with 1.01, close to unity, is even more surprising than the good linear correlation because it indicates the independent operation of both chromophores in dyad 8 and excludes significant compensating effects concerning the solvatochromism; as a consequence, the solvent shell around the dipole of 1 must be extremely thin and concentrates essentially to one molecular layer; compare reference [21]. Otherwise, the slope should be less than unity because the dipoles compensate for far-reaching interactions. The sensitivity of the system to dipole-dipole interactions is indicated by the non-zero intercept caused by static arrangement of the two intramolecular dipoles in 8. We could support this results with an analogous investigation by means of the dyad 10, that is, $E_{\rm T}$ (33dyad), and the betaine dye 11 as the basis of the $E_{\rm T}(33)$ solvent polarity scale, and obtained completely analogous results with a slope of 1.08 for the linear $E_{\rm T}(33 \, {\rm dyad})/E_{\rm T}(33)$ correlation, even with respect to the reported special solvent interactions^[29] of chlorine atoms. This must be unimportant in 10 for the extension of the very small solvent shell (see Figure 7). The verification of the results obtained with 8 by means of 10 can be taken as an indication for a more general effect.



Figure 7. Solvatochromism of 10 $[E_T(33dyad)]$ for thirteen pure solvents compared with the solvatochromism of **11** $[E_T(33)]$ and linear correlation according to the least squares. Slope: 1.08. Intercept: -6.42. Correlation number r: 0.996 for n = 13. Standard deviation in $E_T(33 dyad)$: 1.5.

Finally, we wanted to definitely exclude any influence by the residual conjugation between the chromophores in the dyads. To this end, we introduced the purely aliphatic, stiff bicyclo[2.2.2]octane spacer in the dyad 18 as a barrier. A slightly increased size to 3100 pm was calculated for 18 with still 1270 pm for each pyridiniumphenolate betaine (see Figure 8). $E_{\rm T}(30 {\rm bic})$ was defined for **18** as a solvent polarity scale analogously to dyad 1. A linear correlation between $E_{\rm T}(30 {\rm bic})$ and $E_{\rm T}(30 t {\rm bu})$ (i.e., 24) was again found for pure solvents according to Figure 9, analogously to Figure 6. The slope is 1.00 with r = 0.998 (n = 24) and excludes compensating effects even for completely decoupled chromophores in dyads.

Extending the concept of compensating dipoles, we laterally displaced two chromophores of 1 keeping the long axes still parallel by means of the introduction of a diamantane (diam) spacer to obtain 23 (solvent polarity scale $E_T(30 \text{diam})$; this special arrangement can be seen in the Xray crystal structure analysis of 20 in Figure 10. The linear correlation between the solvent polarity scales derived from 23 and 24 is shown in Figure 11. A slope close to unity was again obtained for the dipoles arranged slightly out of complete compensation; as a consequence solvation is expected

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Figure 8. Bottom) Dyad **18**, the *anti*-collinear orientation of the dipole moments and molecular dimensions. Top) Calculated electronic HOMO (bottom) and LUMO (top) of **18** as obtained by DFT calculations (B3-LYP).^[4]



Figure 9. Solvatochromism of **18** $[E_T(30\text{bic})]$ for 24 pure solvents compared with the solvatochromism of **24** $[E_T(30t\text{bu})]$ and linear correlation according to the least squares. Slope: 1.00. Intercept: -0.27. Correlation number *r*: 0.998 for *n*=24. Standard deviation in $E_T(30\text{bic})$: 0.3.

to proceed very close to the dipoles and remains unaffected by slight intramolecular displacements.

The experimentally shown independent operation of the two betaine chromophores in the dyads **8**, **10**, **18** and **23**, indicates that dipolar compensating effects are unimportant. As a consequence, the significant solvation shell around the two molecular dipoles must be very small and can be roughly estimated to extend no more than half the dimension of **1**, and this is in the order below 500 pm. The distance be-



Figure 10. Molecular structure of crystalline **20** as determined by X-ray analysis. Ellipsoids are drawn at the 50% probability level. The lateral displacement of the peripheral substituents still keeping their long axes parallel can be seen.^[30]



Figure 11. Solvatochromism of **23** $[E_T(30\text{diam})]$ for twelve pure solvents compared with the solvatochromism of **24** $[E_T(30t\text{bu})]$ and linear correlation according to the least squares. Slope: 1.03. Intercept: -1.34. Correlation number *r*: 0.999 for *n*=12. Standard deviation in $E_T(30\text{diam})$: 0.2.

tween the heteroatoms in **1** is 560 pm. These results are further supported by former measurements of a nested (shortened by one 1,4-phenylene unit) *anti*-collinear bisbetaine^[28] described by Dimroth and Reichardt, however, this chromophoric system was not a real dyad of **1** such as **8**, **18** and **23**, but nevertheless can be taken as a further, independent indicator. The interaction of dipoles can be simulated with magnetic dipoles (see Figure 12).

The surprisingly thin solvation shell of 8 of roughly less than 500 pm finds its counterpart in the surface layer of liquid water to the gas phase, which amounts only to about 300 pm and where the unperturbated bulk structure of water exists already for slightly larger distances. One may find a parallelism between both effects because a dissolved molecule in a liquid forms a local disruption of the solvent structure and generates a novel internal surface around the dissolved molecule; this analogously resembles the formation of a surface to the gas phase as a disruption of the bulk solvent structure.

On the other hand, the experimental evidence for a very thin solvation shell may help in understanding some discrepancies in solvent influences for high polarity. Generally, functions of the relative permittivity of the solvent (dielectric constant) such as the equation of Onsager or the function of Kirkwood, $(\varepsilon_r-1)/(2\varepsilon_r+1)$, are popular measures for the solvent polarity and are successfully applied for solvents with low polarity. However, the very high ε_r of *N*-methylacetamide of 191 (at 35 °C), for example, would imply a much more higher solvent polarity than water ($\varepsilon_r=81$),

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Figure 12. Dipole interactions simulated with magnetic dipoles; corresponding to a molecular size of the dipole of 1300 pm. a) Isolated dipole. Streamlines of the field are visualized by means of iron filings. b) Two compensating dipoles with independent action. Distance: 700 pm. c) Interaction of the left dipole with a third, close one with a size of 700 pm and a distance of 700 pm from the connecting line. The right dipole remains essentially unaffected. d) Interaction with a third dipole with a size of 1300 pm at a distance of 700 pm from the connecting line and a lateral shift of 700 pm. The third dipole interacts with both dipoles. e) Interaction of compensating dipoles with a third distant dipole with a size of 1300 pm and a distance of 1300 pm from the connecting line. All dipoles are interacting.

whereas both chemical experience and, for example, the $E_{\rm T}(30)$ solvent polarity scale $[E_{\rm T}(30) = 52.0]$ indicate a lower solvent polarity than water $[E_T(30)=63.1]$ where the solvent refractive index and the ability of donating hydrogen bonds may be of further influence.^[29] The relative permittivity ε_r of a solvent concerns the solvent properties in the unaffected volume of a solvent, whereas both the chemical solvent polarity and the empirical solvent polarity scale reflect more inner surface effects of solvents. Polar properties of solvents may be of similar influence on both the effects in the bulk and the effects at surfaces and this makes the application of ε_r useful, however, a strict parallelism is not given and there are exceptions for some cases such as for N-methylacetamide. The strong thermal motions in liquids at room temperature may be responsible for whipping-out arrangements of larger distance in liquids so that the direct contact of the solute with the solvent remains dominating.

Conclusion

We resume that no compensating effects were found for the solvation of two *anti*-collinear molecular dipoles, analysed

by means of the strong solvatochromism of pyridinium-*N*-phenolate betaine dyes. The molecular dimensions of the investigated *anti*-collinear dipoles indicate a small solvent shell of only a few hundred picometres where the polar solvent properties seem to concentrate to a molecular layer. This resembles the very thin layer of about 300 pm found for the interface between water and the gas phase. A possible reason is the strong thermal movement of the solvent molecules causing a scrambling of the interaction and a very rapid damping with an increasing distance.

Experimental Section

General methods: Column chromatography was performed by using SiO₂ (0.040–0.063 mm, 230–400 mesh ASTM) from Merck. IR spectra: Perkin Elmer 1420 Ratio Recording Infrared Spectrometer, FT 1000 and Perkin Elmer BXII FT-IR with ATR-unit; UV/Vis spectra: Varian Cary 5000 and Bruins Omega 20; fluorescence spectra: Varian Cary Eclispe; NMR spectroscopy: Varian Vnmrs 600 (600 MHz); mass spectroscopy: Finnigan MAT 95.

Compound 8: 4-(4-Bromophenyl)-2,6-diphenyl-N-(3,5-diphenylphenyl-4phenolate)pyridinium betaine (7) (500 mg, 793 µmol), tetrabutylammonium bromide (70.4 mg, 218 µmol) and Pd(OAc)₂ (2.0 mg, 5.5 µmol) in anhydrous toluene (20 mL) under argon atmosphere were treated with triethylamine (1 mL), and heated at 120 °C for 20 h. The reaction mixture was quenched by the addition of 2M aqueous HCl (100 mL), extracted with CHCl3 (3×100 mL), washed with 2M aqueous NaOH (100 mL) and distilled water (100 mL), dried with Na₂SO₄ and purified by column separation (Al₂O₃, dichloromethane/ethanol 40:1). Yield: 89.0 mg (80.8 µmol, 20%) of a light green solid. M.p. > 250 °C; $R_{\rm f}$ (Al₂O₃, dichloromethane/ ethanol 20:1)=0.71; ¹H NMR (600 MHz, CDCl₃, 25 °C, trimethylsilane (TMS)): $\delta = 5.58$ (s, 2H; OH), 7.10 (d, ${}^{3}J(H,H) = 7.1$ Hz, 8H; H_{aron}), 7.32–7.41 (m, 28H; $H_{arom.}$), 7.74 (d, ${}^{3}J(H,H) = 4.1$ Hz, 8H; $H_{arom.}$), 7.82 (d, ${}^{3}J(H,H) = 7.9 \text{ Hz}, 4H; H_{arom.}), 8.12 (d, {}^{3}J(H,H) = 7.9 \text{ Hz}, 4H; H_{arom.}),$ 8.24 ppm (s, 4H; H_{pyridinium}); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): $\delta\!=\!125.9,\,128.4,\,128.5,\,128.9,\,129.0,\,129.1,\,129.3,\,129.6,\,130.1,\,130.2,\,131.8,$ 133.4, 133.8, 135.1, 135.9, 136.7, 143.0, 149.9, 155.8, 157.0 ppm; IR (ATR): $\tilde{\nu} = 3050.0$ (w), 1619.4 (m), 1595.6 (m), 1575.6 (w), 1562.3 (w), 1543.1 (w), 1493.5 (m), 1464.9 (m), 1420.8 (m), 1358.3 (w), 1241.1 (m), 1123.5 (w), 1063.2 (w), 1048.2 (w), 1029.2 (w), 1001.6 (w), 889.1 (w), 823.6 (w), 759.5 (m), 730.6 (m), 698.0 (s), 673.7 (m), 673.7 cm⁻¹ (w); UV/Vis (CH₂Cl₂/1,5diazabicyclo[5.4.0]undec-5-ene (DBU)): λ_{max} (E_{rel})=358.6 (1.00), 735.2 nm (0.22); MS (FAB⁺): m/z (%): 1150.6 (0.15), 1137.4 (0.08), 1117.7 (0.18) $[M^++OH]$, 1102.6 (0.85) $[M^++H]$, 873.5 (0.15), 857.6 (0.85), 779.5 (0.07), 652.5 (0.09), 627.5 (0.11), 576.0 (0.14), 559.4 (0.10), 551.4 (0.62), 500.4 (0.09); HRMS: m/z calcd for C₈₂H₅₈N₂O₂: 1102.4487; found: 1102.4489, $\Delta = -0.0002$.

Compound 10: 4-(4-Bromophenyl)-1-(3.5-dichloro-4-phenolate)-2.6-diphenylpyridinium betaine (9) (500 mg, 913 µmol), tetrabutylammonium bromide (81.0 mg, 251 µmol) and Pd(OAc)₂ (25.0 mg, 110 µmol) in anhydrous toluene (20 mL) under argon atmosphere were treated with triethylamine (1 mL), and stirred at 120 °C for 16 h. The reaction mixture was quenched by the addition of 2M aqueous HCl (100 mL), extracted with CHCl₃ (3×100 mL), washed with 2M aqueous NaOH (100 mL) and distilled water (100 mL), dried with magnesium sulphate, purified by column separation (silica gel, CHCl₃/EtOH 2:1), dissolved in a small amount of ethanol, precipitated with 2M aqueous NaOH and washed with distilled water (50 mL). Yield: 166 mg (36%) of a reddish violet solid. M.p. > 250 °C; $R_{\rm f}$ (silica gel, CHCl₃/EtOH 2:1)=0.66; ¹H NMR (400 MHz, CD₃OD, 25°C, TMS): $\delta = 7.05$ (s, 4H; H_{phenol}), 7.47–7.75 (m, 20H; H_{phenyl}), 8.10 (d, ³*J*(H,H)=8.7 Hz, 4H; $H_{arom.}$), 8.38 (d, ³*J*(H,H)=8.7 Hz, 4H; $H_{arom.}$), 8.57 ppm (s, 4H; $H_{pyridinium}$); ¹³C NMR (100 MHz, CD₃OD, 25°C, TMS): δ=123.1, 125.3, 127.6, 128.2, 128.3, 129.3, 129.6, 130.1, 133.7, 142.9, 155.2, 157.7, 160.6 ppm; IR (ATR): $\tilde{v} = 3186.5$ (w), 3051.4 (w), 2362.1 (w), 2338.8 (w), 1616.4 (m), 1590.4 (m), 1573.6 (m),

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1558.7 (m), 1531.0 (m), 1504.7 (s), 1489.7 (s), 1449.2 (w), 1443.8 (w), 1391.3 (w), 1350.9 (w), 1259.5 (m), 1240.5 (m), 1183.4 (w), 1158.1 (w), 1122.2 (w), 1062.2 (w), 1039.5 (m), 1000.0 (w), 983.6 (w), 925.6 (w), 894.7 (w), 886.9 (w), 872.1 (w), 834.5 (w), 819.9 (m), 792.0 (w), 781.8 (m), 771.1 (s), 744.0 (w), 697.7 (s), 667.9 cm⁻¹ (w); UV/Vis (CH₂Cl₂): λ_{max} (E_{rel}) = 362.8 (1.00), 555.2 nm (0.10); MS (ESI⁺): m/z (%): 935.2 (0.1) [M^+ +H], 479.6 (0.3), 468.1 (1.0) [M^2 +H]; elemental analysis calcd (%) for C₅₈H₃₆Cl₄N₂O₂·4H₂O (1006.8): C 69.19, H 4.41, N 2.78; found: C 69.58, H 4.30, N 2.78.

1,4-Bis-(4-iodophenyl)bicyclo[2.2.2]octane (13): 1,4-Bisphenylbicyclo-[2.2.2]octane (1.32 g, 4.98 mmol) in CHCl₃ (27 mL) was added to (bis(trifluoroacetoxy)iodo)benzene (4.45 g, 9.42 mmol) and iodine (2.02 g, 4.76 mmol) under an argon atmosphere, stirred at room temperature for 160 min, poured into distilled water (40 mL) and treated with Na₂SO₃ until becoming colourless. The organic phase was separated, dried with Na₂SO₄, evaporated and the residue was purified by crystallisation from chlorobenzene. Yield: 1.12 g (44%) of a colourless solid. M.p. > 250°C; ¹H NMR (400 MHz, CD₂Cl₂, 25 °C, TMS): $\delta = 1.92$ (s, 12 H; $CH_{2bicyclo[2.2.2]octane}$), 7.13 (d, ${}^{3}J(H,H) = 8.4$ Hz, 4H; CH_{phenyl}), 7.63 ppm (d, $^{3}J(H,H) = 8.4$ Hz, 4H; CH_{phenyl}); ^{13}C NMR (100 MHz, CD₂Cl₂, 25 °C, TMS): $\delta = 32.4$, 34.8, 90.6, 127.8, 137.0, 149.6 ppm; IR (ATR): $\tilde{\nu} = 2935.1$ (w), 2857.6 (w), 2360.7 (s), 2341.1 (s), 1558.9 (w), 1540.3 (w), 1485.2 (w), 1456.4 (w), 1389.5 (w), 1056.3 (w), 1004.1 (w), 989.3 (m), 810.0 (m), 757.8 (w), 709.8 (w), 689.6 (w), 668.0 cm⁻¹ (m); HRMS; m/z calcd for C₂₀H₂₀I₂: 513.9654; found 513.9656, $\Delta = -0.0002$; elemental analysis calcd (%) for C₂₀H₂₀I₂ (513.9): C 46.72, H 3.92; found: C 47.42, H 4.09.

1,4-Bis-(4-cyanophenyl)bicyclo[2.2.2]octane (14): CuCN (798 mg, 8.91 mmol) and 1,4-bis(4-iodophenyl)-bicyclo[2.2.2]octane (13) (1.10 g, 2.14 mmol) were dissolved in *N*-methylpyrrolidone (NMP) (14.5 mL) and heated at 200 °C (bath) for 7 h. Toluene (300 mL) was added and the mixture was washed with 7.5% aqueous ethylenediamine solution (250 mL) and distilled water (20 mL), dried with Na₂SO₄ and evaporated. The residue was purified by column separation (silica gel, CHCl₃/isohexane 4:1). Yield: 210 mg (31%) of a colourless solid. $R_{\rm f}$ (silica gel, CHCl₃/isohexane 4:1)=0.56; ¹H NMR (200 MHz, CDCl₃, 25°C, TMS): δ =1.98 (s, 12 H; CH₂), 7.46 (td, ³J(H,H)=8.9, ⁴J(H,H)=1.8 Hz, 4H; CH_{phenyl}), 7.61 ppm (td, ³J(H,H)=8.9, ⁴J(H,H)=1.8 Hz, 4H; CH_{phenyl}); MS (EI⁺): m/z (%): 312.2 (100) [M^+], 283.2 (8), 155.1 (65), 116.1 (24); HRMS: m/z calcd for C₂₂H₂₀N₂: 312.1626; found: 312.1629, Δ =0.0003.

1,4-Bis(4-formylphenyl)bicyclo[2.2.2]octane (15): 1.4-Bis(4-cvanophenyl)bicyclo[2.2.2]octane (14) (223 mg, 716 µmol) was dissolved in CH₂Cl₂ (3.6 mL), cooled to 0 °C, treated slowly dropwise with DIBAL-H (1 M in n-hexane, 1.62 mL, 1.62 mmol) and the reaction was allowed to proceed at room temperature for 3 h. The reaction mixture was poured into 6M aqueous HCl solution (10 mL) and some ice and stirred for 1 h. The organic phase was separated and the aqueous phase was extracted with CH₂Cl₂ (3×50 mL). The combined organic phases were washed with saturated aqueous NaHCO3 solution (100 mL) and distilled water (100 mL), dried with Na₂SO₄, evaporated and purified by column separation (silica gel, CHCl₃/isohexane 4:1). Yield: 228 mg (716 μ mol, \approx 100 %) of a colourless solid. $R_{\rm f}$ (silica gel, CHCl₃/isohexane 4:1)=0.29; ¹H NMR (200 MHz, CDCl₃, 25°C, TMS): $\delta = 2.03$ (s, 12H; CH₂), 7.54 (d, ³J- $(H,H) = 8.4 \text{ Hz}, 4 \text{ H}; CH_{\text{phenvl}}), 7.84 (d, {}^{3}J(H,H) = 8.4 \text{ Hz}, 4 \text{ H}; CH_{\text{phenvl}}),$ 9.99 ppm (s, 2H; CHO); MS (EI⁺): *m/z* (%): 318.2 (100) [*M*⁺], 289.2 (5), 160.2 (45), 130.1 (25), 91.1 (12); HRMS: m/z calcd for $C_{22}H_{22}O_2$: 318.1620; found: 318.1609, $\Delta = -0.0011$.

3-[4-(4-{4-[3-Oxo-1-(2-oxo-2-phenylethyl)-3-phenylpropyl]phenyl}bicyclo-[2.2.2]oct-1-yl)phenyl]-1,5-diphenylpentan-1,5-dione (16): 1,4-Bis(4-formylphenyl)bicyclo[2.2.2]octane (15) (176 mg, 553 µmol) and acetophenone (1.32 g, 11.0 mmol) were dissolved in 95% aqueous ethanol, heated to 65 °C, treated with aqueous KOH (194 mg 85% KOH, 2.94 mmol, in 1.76 mL distilled water), heated to reflux for 5 h, allowed to cool down and poured into CHCl₃ (200 mL). The organic phase was washed with distilled water (3×150 mL), dried with Na₂SO₄, evaporated and purified by column separation (silica gel, CHCl₃/toluene 1:1). Yield: 188 mg (246 µmol, 44%) of a yellowish solid. R_f (silica gel, CHCl₃/toluene 1:1)= 0.09; ¹H NMR (600 MHz, CDCl₃, 25°C, TMS): δ =1.89 (s, 12H; CH_{2(bicveloctane)}), 3.41 (ddd, ³J(H,H)=43.1, ⁴J(H,H)=6.9, ⁴J(H,H)=6.9 Hz,



8H; CH₂C=O), 4.05 (quin., ${}^{3}J(H,H) = 6.9$ Hz, 2H; CH), 7.23 (q. ${}^{3}J(H,H) = 11$ Hz, 8H; CH_{arom}), 7.44 (t, ${}^{3}J(H,H) = 8.0$ Hz, 8H; CH_{arom}), 7.54 (t, ${}^{3}J(H,H) = 7.6$ Hz, 4H; CH_{arom}), 7.94 ppm (d, ${}^{3}J(H,H) = 7.0$ Hz, 8H; CH_{arom}), 1 ${}^{3}C$ NMR (150 MHz, CDCl₃, 25 °C, TMS): $\delta = 32.7$, 34.7, 36.6, 44.9, 125.7, 127.1, 128.1, 128.5, 133.0, 136.9, 140.9, 148.1, 198.7 ppm; MS (EI⁺): m/z: 762.37.



Bispyrylium salt 17: Triphenylmethanol (308 mg, 1.18 mmol), naphthalenesulphonic acid monohydrate (264 mg, 1.18 mmol) and acetanhydride (3.7 mL) were stirred for 3 h at room temperature. The obtained solution was added to compound 16 (188 mg, 246 µmol) in acetanhydride (2 mL), stirred at 100 °C for 1 h and allowed to cool down for crystallisation. The solid was collected by vacuum filtration, thoroughly washed with cold acetic anhydride and ethanol and dried in medium vacuum. Yield: 245 mg (87%) of a yellow solid. M.p. > 250 °C; ¹H NMR (400 MHz, $[D_6]$ DMSO, 25°C, TMS): $\delta = 2.04$ (s, 12H; CH₂), 7.47–7.50 (m, 4H; CH_{naphthyl}), 7.67–7.70 (m, 2H; CH_{naphthyl}), 7.75–7.79 (m, 12H; CH_{phenyl}, CH_{phenvl-bicyclooctane}), 7.81–7.92 (m, 10H; CH_{naphthyl}, CH_{phenyl-bicyclooctane}), 8.11 (s, 2H; $CH_{naphthyl}$), 8.55–8.57 (m, 12H; CH_{phenyl}), 9.11 ppm (s, 4H; CH_{pyrylium}); IR (ATR): v=3424 (w), 3053 (w), 2942 (w), 2861 (w), 1715 (w), 1623 (m), 1593 (s), 1577 (m), 1511 (m), 1491 (s), 1466 (m), 1437 (m), 1404 (w), 1362 (w), 1344 (w), 1256 (m), 1222 (m), 1194 (s), 1134 (m), 1088 (m), 1029 (s), 995 (m), 953 (w), 901 (w), 862 (w), 840 (w), 818 (m), 778 (m), 749 (w), 718 (w), 672 cm⁻¹ (s); HRMS: m/z calcd for C₅₄H₄₄O₂⁺: 724.3341; found: 724.3307, $\Delta = -0.0034$.



Compound 18 [E_T (30bic)]: Compound 17 (240 mg, 211 µmol) and 4amino-2,6-diphenylphenol (480 mg, 420 µmol) were dispersed in anhydrous ethanol (4.8 mL), heated to reflux, treated with anhydrous sodium acetate (240 mg, 1.34 mmol), heated to reflux for 3 h, allowed to cool down, poured into 2 M aqueous NaOH solution (100 mL) and extracted with CH₂Cl₂ (3×150 mL). The combined organic phases were washed with distilled water until becoming neutral, dried with MgSO₄, evaporated in vacuo and purified by column separation (Al₂O₃ neutral, toluene/ methanol 10:1). Yield: 119 mg (47%) of a green solid. M.p. > 250°C; R_f (Al₂O₃, neutral, toluene/methanol 10:1)=0.10; ¹H NMR (600 MHz, CDCl₃, 25°C, TMS): δ =2.06 (s, 12H; 6 × CH₂), 6.57 (s, 4H; CH_{phenol}), 7.11 (t, ³*J*(H,H)=7.6 Hz, 4H; 4 CH_{phenyl}), 7.18 (t, ³*J*(H,H)=7.7 Hz, 8H; 3,3'-CH_{phenyl}), 7.29 (d, ³*J*(H,H)=8.5 Hz, 4H; CH_{phenyl}), 7.39–7.41 (m, 20H; CH_{phenyl}), 7.61 (d, ³*J*(H,H)=8.5 Hz, 4H; CH_{phenyl}), 7.85 (d,

³*J*(H,H) = 8.5 Hz, 4 H; CH_{phenyt-bicyclocetane}), 8.06 ppm (s, 4 H; CH_{pyridinium}); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): δ =32.4, 35.6, 125.2, 125.5, 127.2, 127.4, 127.6, 128.0, 128.9, 129.0, 129.1, 130.2, 130.5, 131.4, 133.9, 140.3, 153.9, 154.5, 156.8 ppm; IR (ATR): $\tilde{\nu}$ =3054.4 (w), 2936.3 (w), 2857.8 (w), 1620.7 (m), 1607.9 (m), 1573.7 (w), 1544.4 (w), 1494.1 (w), 1465.8 (w), 1451.5 (w), 1419.8 (w), 1360.2 (w), 1313.0 (w), 1236.4 (w), 1159.9 (w), 1123.7 (w), 1077.5 (w), 1064.3 (w), 1047.0 (w), 1029.6 (w), 996.0 (w), 921.3 (w), 893.0 (w), 836.1 (w), 821.7 (w), 785.3 (w), 767.8 (m), 750.0 (m), 729.3 (w), 697.6 (s), 675.2 (w), 658.1 cm⁻¹ (w); UV/Vis (CHCl₃): λ_{max} (*E*_{rel})=327.8 (1.00), 384.0 (0.25), 736.0 nm (0.18); HRMS: *m*/*z* calcd for C₉₀H₆₉O₂N₂: 1209.5359; found: 1209.5298, Δ = -0.0061; elemental analysis calcd (%) for C₉₀H₆₉O₂N₂·3H₂O (1262.6): C 85.55, H 5.90, N 2.22; found: C 85.82, H 5.80, N 2.17.



4-(4-tert-Butylphenyl)-2,6-diphenylpyrylium tetrafluoroborate: 4-tert-Butylbenzaldehyde (1.00 g, 6.16 mmol) and acetophenone (1.60 g, 13.6 mmol) under an argon atmosphere were heated at $56 \,^{\circ}$ C, treated slowly dropwise with POCl₃ (1.50 g, 0.91 mL) and stirred at $65 \,^{\circ}$ C for 2 h. The still warm, highly vis-

cous mixture was dissolved in acetone (20 mL) and poured into ethanol (50 mL), which was heated to reflux. The solution was concentrated to about 35 mL by distillation, treated with 50% aqueous HBF₄ (3 mL) and allowed to cool down. The precipitate was collected by vacuum filtration, washed with ethanol (80 mL) and distilled water (100 mL) and dried in air at 100°C. Yield: 644 mg (23%) of a sun yellow solid. M.p. 264°C; IR (ATR): $\tilde{\nu} = 1630.1$ (m), 1600.4 (m), 1509.9 (m), 1495.6 (s), 1438.1 (w), 1273.6 (w), 1250.2 (w), 1188.6 (w), 1028.9 (s), 998.0 (w), 957.7 (w), 884.6 (w), 834.4 (m), 777.0 (m), 744.1 (w), 721.0 (m), 685.4 cm⁻¹ (s); ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): $\delta = 1.24$ (s, 9 H; CH₃), 7.60 (d, ³*J*(H,H) = 8.7 Hz, 2H; CH_{aron}), 7.72–7.77 (m, 6H; CH_{phenvl}), 8.32 (d, ${}^{3}J(H,H) =$ 8.7 Hz, 2H; CH_{arom}), 8.35-8.38 (m, 4H; CH_{phenvl}), 8.63 ppm (s, 2H; CH_{pyrvlium}); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): $\delta = 30.7$, 35.6, 114.0, 127.6, 128.5, 130.1, 130.4, 135.4, 160.9, 165.7, 170.1 ppm; UV/Vis (CHCl₃): λ_{max} (E_{rel}) = 400.6 nm (1.00); MS (FAB⁺): m/z (%): 817.3 (6) [2 M^+ -BF₄], 730.3 (5), [2M⁺], 365.2 (100) [M⁺]; HRMS: m/z calcd for $C_{27}H_{25}O^+$: 365.1905; found: 365.1915, $\Delta = 0.0010$.



4-(4-tert-Butylphenyl)-2,6-diphenyl-N-(3,5-diphenyl-4-phenolate)pyridinium betaine (24): 4-(4-tert-Butylphenyl)-2,6-diphenylpyrylium tetrafluoroborate (500 mg, 1.10 mmol) and 4-amino-2,6-diphenylphenol (522 mg, 1.20 mmol) were dissolved in anhydrous ethanol (10 mL), which was heated to reflux, treated with anhydrous sodium acetate (288 mg, 3.5 mmol), heated to reflux for 3 h (colour change from red to dark blue), still hot, the solution was treated with 5% aqueous NaOH solution (2.8 mL) and allowed to cool down. The precipitate was collected by vacuum filtration, washed with 1% aqueous NaOH solution (50 mL) and distilled water (50 mL), dried at 100 °C and purified by column separation (silica gel, ethanol). Yield: 60 mg (10%) of a fir green solid. M.p. > 300 °C; $R_{\rm f}$ (silica gel, ethanol) = 0.20; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): $\delta = 1.38$ (s, 9H; CH₃), 6.44 (s, 2H; CH_{phenol}), 7.07 (tt, ${}^{3}J(H,H) =$ 7.4, ${}^{4}J(H,H) = 1.4 \text{ Hz}$, 2H; CH_{phenyl}), 7.14 (t, ${}^{3}J(H,H) = 7.4 \text{ Hz}$, 4H; CH_{phenyl}), 7.33 (d, ${}^{3}J(H,H) = 7.1$ Hz, 4H; CH_{phenyl}), 7.35–7.38 (m, 10H; CH_{phenyl}), 7.62 (d, ${}^{3}J(H,H) = 8.6 \text{ Hz}$, 2H; $CH_{tert-butylphenyl}$), 7.80 (d, ${}^{3}J$ - $(H,H) = 8.6 \text{ Hz}, 2 \text{ H}; CH_{tert-butylphenyl}), 8.02 \text{ ppm}$ (s, 2 H; CH_{pyridinium}); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): $\delta = 31.1$, 35.2, 124.1, 125.2,

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125.3, 127.0, 127.2, 127.5, 127.9, 129.0, 129.1, 130.2, 130.6, 131.1, 134.1, 140.8, 156.3, 156.4, 156.7 ppm; IR (ATR): $\tilde{\nu}$ =3051.4 (w), 2961.4 (w), 1618.2 (m), 1597.0 (m), 1533.5 (w), 1491.9 (m), 1466.8 (m), 1436.9 (m), 1359.1 (w), 1286.5 (w), 1246.3 (w), 1182.0 (w), 1114.1 (w), 1074.5 (w), 1028.1 (w), 1008.2 (w), 993.4 (w), 893.4 (w), 842.6 (w), 799.7 (w), 776.1 (w), 756.7 (m), 733.9 (w), 694.1 (s), 659.9 (w), 628.9 (w), 613.9 cm⁻¹ (w); UV/Vis (CHCl₃): λ_{max} (ε)=374 (9900), 714 nm (6800); MS (FAB⁺): *m/z* (%): 1215 (1) [2*M*⁺+H], 624 (5) [*M*⁺+OH], 608 (100) [*M*⁺+H], 592 (5) [*M*⁺-CH₃]; HRMS: *m/z* calcd for C₄₅H₃₈NO: 608.2953; found: 608.2957; Δ=0.0004; elemental analysis calcd (%) for C₄₅H₃₇NO-H₂O (625.8): C 86.37, H 6.28, N 2.24; found: C 86.96, H 6.13, N 2.26.



4,9-Bis(4-cyanophenyl)diamantane (20): 4,9-Di(4-iodophenyl)diamantane (730 mg, 1.23 mmol) and CuCN (34 mg, 3.54 mmol) in DMF (14 mL) were heated to reflux with stirring for 3 h, allowed to cool down, poured into ice water/concentrated ammonia (60 mL, 10:1), stirred for 20 min, and extracted with dichloromethane (3×100 mL). The combined organic phases were washed with 2M aqueous HCl solution (100 mL), dried with Na₂SO₄, evaporated and purified by column separation (silica gel, CHCl₃/ isohexane 5:1). Yield: 367 mg (76%) of a colourless crystalline solid. M.p. > 300 °C; $R_{\rm f}$ (silica gel, CHCl₃) = 0.67; ¹H NMR (600 MHz, CDCl₃, 25°C, TMS): $\delta = 1.98-2.03$ (m, 18H; CH_{2diamantane}), 7.51 (d, ³*J*(H,H) = 8.7 Hz, 4H; CH_{arom}), 7.64 ppm (d, ${}^{3}J(H,H) = 8.7$ Hz, 4H; CH_{arom}); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): $\delta = 34.8$, 37.0, 42.9, 109.5, 119.1, 126.0, 132.0, 155.6 ppm; IR (ATR): v2917.3 (m), 2897.6 (m), 2878.4 (m), 2868.3 (m), 2847.7 (m), 2231.8 (m), 1605.5 (m), 1504.4 (m), 1461.5 (w), 1440.1 (w), 1398.4 (w), 1398.4 (w), 1376.0 (w), 1352.0 (w), 1294.4 (w), 1269.8 (w), 1179.5 (m), 1112.1 (w), 1075.1 (m), 1049.8 (m), 1020.5 (w), 985.8 (m), 954.0 (m), 836.1 (s), 797.2 cm⁻¹ (s); MS (EI⁺): m/z (%): 390.2 (100) [M⁺], 288.2 (10), 194.2 (12), 116.1 (10); HRMS: m/z calcd for $C_{28}H_{26}N_2$: 390.2096; found: 390.2087; $\Delta = -0.0009$; elemental analysis calcd (%) for C₂₈H₂₆N₂ (390.2): C 86.12, H 6.71, N 7.17; found: C 85.73, H 6.72, N 7.14.



4,9-Bis(4-formylphenyl)diamantane (21): 4,9-Bis(4-cyanophenyl)diamantane (**20**) (340 mg, 871 µmol) under an argon atmosphere was dispersed in anhydrous dichloromethane (27 mL), cooled to 4 °C, treated dropwise within 10 min with 1 M DIBAL-H in hexane (5.44 mL), stirred at room temperature for three hours, slowly poured into a 1:1 mixture of ice water and 2 M aqueous HCl solution (100 mL), stirred for 20 min, extracted with chloroform (3×100 mL), dried with Na₂SO₄, evaporated and purified by column separation (silica gel, chloroform). Yield: 238 mg (95%) of a colourless crystalline solid. M.p. > 300°C. *R*_f (silica gel, CHCl₃) = 0.49; ¹H NMR (400 MHz, CDCl₃, 25°C, TMS): δ = 2.00 (m, 18H; CH_{2diamantane}), 7.57 (d, ³*J*(H,H) = 8.2 Hz, 4H; CH_{arom}), 7.85 (d, ³*J*(H,H) = 8.3 Hz, 4H; CH_{arom}), 9.99 ppm (s, 2H; CH_{aldehyde}); ¹³C NMR (100 MHz, CDCl₃, 25°C, TMS): δ = 35.0, 37.1, 43.0, 125.8, 129.8, 133.0, 134.2, 157.5,



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192.1 ppm; IR (ATR): $\tilde{\nu}$ =2920.6 (w), 2873.7 (w), 2850.9 (w), 1696.0 (m), 1685.5 (m), 1601.7 (m), 1568.8 (m), 1457.9 (w), 1441.9 (w), 1413.9 (w), 1395.5 (w), 1305.5 (w), 1266.3 (w), 1217.7 (m), 1190.4 (w), 1172.7 (m), 1113.0 (w), 1070.5 (m), 1051.4 (m), 981.7 (m), 827.8 (s), 797.2 (s), 730.1 (w), 714.8 (s), 664.5 cm⁻¹ (m); MS (EI⁺): *m/z* (%): 396.2 (100) [*M*⁺], 291.2 (9), 197.3 (42); HRMS: *m/z* calcd for C₂₈H₂₈O₂: 396.2089; found: 396.2083, Δ =-0.0006.

4,4'-(4,9-Diphenyldiamantyl)bis-(2,6-diphenyl)pyrylium perchlorate (22): Acetophenone (4.30 g, 4.48 mL) and 4,9-di(4-benzaldehydo)diamantane (**21**) (179 mg, 451 µmol) were dispersed in a mixture of acetic acid (1.8 mL) and acetic anhydride (0.9 mL), slowly dropwise treated with 60% aqueous HClO₄ (0.54 mL), heated to reflux with stirring for 90 min (turning to brown), allowed to cool, poured into diethyl ether (80 mL), collected by vacuum filtration, plenty washed with diethyl ether, dried in vacuo and stored under argon. The yellow solid was directly used for the subsequent reaction without further purification because of its possibly explosive properties (not further tested).



4,4'-(4,9-Diphenyldiamanty-1-yl)-bis-[1-(3,5-diphenyl-4-phenolate)-2,6-diphenylpyridinium betaine] (23): 4,4'-(4,9-Diphenyldiamantyl)bis-(2,6-diphenyl)pyrylium perchlorate (22) (180 mg, 223 µmol) and 2,6-diphenyl-4aminophenol (178 mg, 682 µmol) were dispersed in anhydrous ethanol (9 mL), treated with anhydrous sodium acetate (40 mg) heated to reflux for 3 h (dark green solution), allowed to cool down, poured into chloroform (100 mL), washed with 2M aqueous NaOH solution (100 mL) and with distilled water (2×100 mL), dried with Na₂SO₄ and purified by column separation (basic alumina, chloroform for removing byproducts and chloroform/ethanol 50:1 for collecting). Yield: 10 mg (7.8 µmol, 3% over two steps) of a green solid. R_f (Al₂O₃, CHCl₃/EtOH 50:1)=0.10; ¹H NMR (600 MHz, CDCl₃, 25 °C, TMS): $\delta = 2.00-2.03$ (m, 18H; $CH_{2diamantane}$), 7.14 (d, ${}^{3}J(H,H) = 7.3 Hz$, 8H; CH_{phenyl}), 7.25 (s, 4H; CH_{arom.}), 7.29 (t, ${}^{3}J(H,H) = 7.4$ Hz, 8H; CH_{phenyl}), 7.34 (t, ${}^{3}J(H,H) =$ 7.5 Hz, 8H; CH_{phenyl}), 7.40–7.42 (m, 12H; CH_{phenyl}), 7.60 (d, ${}^{3}J(H,H) =$ 8.8 Hz, 4H; CH_{arom}), 7.66–7.67 (m, 8H; CH_{phenyl}), 7.95 (d, ${}^{3}J(H,H) =$ 8.8 Hz, 4H; CH_{arom}), 8.18 ppm (s, 4H; CH_{pyridyl}); ¹³C NMR (150 MHz, CDCl₃, 25 °C, TMS): δ=34.8, 37.1, 43.0, 125.5, 126.6, 128.3, 128.5, 128.7, 129.0, 129.3, 129.4, 129.9, 130.1, 133.6, 155.5, 156.0, 156.8 ppm; IR (ATR): $\tilde{\nu} = 2880.9$ (w), 1619.0 (m), 1596.9 (m), 1493.9 (w), 1463.9 (w), 1421.0 (m), 1354.7 (w), 1243.3 (w), 1119.0 (w), 1074.4 (w), 1027.9 (w), 985.0 (w), 887.0 (w), 839.9 (w), 760.8 (m), 743.1 (w), 732.9 (w), 698.0 (s), 674.1 (w), 659.0 cm⁻¹ (w); MS (FAB⁺): m/z (%): 1304.6 (3) [M⁺+OH], 1288.8 (7) [M⁺+H], 1060.3 (2), 1043.7 (7), 644.5 (14), 552.5 (4); HRMS: m/z calcd for $C_{96}H_{74}N_2O_2$: 1288.5862; found: 1288.5869, $\Delta = +0.0007$.

Acknowledgements

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Solvent Shells

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Р.	Mayer								-	

How Many Molecular Layers of Polar Solvent Molecules Control Chemistry? The Concept of Compensating Dipoles



How thin can it be? The extension of the solvent influences was examined by means of *anti*-collinear dipoles on the basis of the solvent polarity scale of a pyridinium-*N*-phenolatebetaine dye (i.e., $E_{\rm T}(30)$), where no compensation effects were found (see figure). As a consequence, solvent polarity effects seem to be concentrated to a very thin layer of a few hundred picometres.