J|A|C|S
ARTICLES
Published on Web 12/29/2006

# Electrostatics and Color: Massive Electrostatic Perturbation of Chromophores by Ion Cluster Ligands

Robert Weiss* and Frank G. Pühlhofer

*Contribution from the Institut für Organische Chemie, Universität Erlangen-Nürnberg, Henkestrasse 42, D-91054 Erlangen, Germany*

Received July 11, 2006; E-mail: robert.weiss@chemie.uni-erlangen.de

***Abstract:*** The SASAPOS protocol, a general reaction sequence allowing complete exchange of various neutral ligands X in organic, elementorganic, and inorganic systems by cationic ligands $L^+$, has been applied to a variety of pentafluorophenyl-substituted dyes of the general formula $C_6F_5-X{=}Y-D$ (X, Y = N, CH; D = donor substituted arene), yielding the corresponding polycationically substituted dyes. The perturbation of the chromophores by the massive electrostatic effects introduced via the SASAPOS method led to bathochromic shifts of the absorption maxima of up 140 nm, 7600 $cm^{-1}$, respectively. A strong dependency of the specific shifts on the nature of the connecting $\pi$ linker $-X{=}Y-$ (N vs CH) has been detected by UV−vis absorption spectroscopy. Additionally, the effects of resubstitution of cationic ligands $L^+$ by OH and $O^-$ have been studied.

## Introduction

In recent work we have presented evidence that the pentakisonio-substituted phenyl anion derivative **2** can act as a potent leaving group in heteropolar C−X disconnections (X = C, P, and H) according to Scheme 1.[1,2]

We figured that systems of type **2** should be representatives of a new class of sterically highly demanding and electronically, strongly accepting ligands. As they are composed of a polycation in close association with a neutralizing sphere of anions, we have termed systems of type **2** *ion cluster ligands* (IC ligands). We have introduced a variety of IC ligand precursors and IC ligand-substituted templates in previous work.[1−5]

As a first elaboration of this concept we subsequently describe syntheses of classical azo dyes and related aldimines and stilbenes whose chromophore is massively modified due to the specific electronic and steric qualities of an incorporated IC ligand.

## Results and Discussion

Experiments to introduce an IC ligand via direct nucleophilic substitution are not very promising due to its electrostatically, strongly reduced nucleophilicity (cf. the leaving group character of **2**)[1,2] and its steric congestion. However, the desired result can be achieved indirectly by subjecting appropriate pentafluorophenyl derivatives of a substrate to the SASAPOS protocol (**s**elf-**a**ctivated **s**ilyl-**a**ssisted **p**oly-**o**nio-**s**ubstitution),[1−5] shown in generalized form in Scheme 2.

Following this strategy, several known and hitherto unknown pentafluoro azo arenes **8a**−**f** were synthesized[6] and "sasaposed" to yield the novel polycationic dye salts **9a**−**f** and **10** according to Scheme 3.

All compounds (cf. Scheme 3) were fully characterized by $^1H$ and $^{13}C$ NMR spectroscopy, FAB-MS, elemental analysis, and UV−vis absorption spectroscopy.

The complete exchange of fluorine substituents against $DMAP^+$ ligands during the SASAPOS cascade (cf. Scheme 3) leads to strong bathochromic shifts of the absorption maxima of the azo dyes; e.g., shifts from yellow/orange (**8**) to red/violet (**9, 10**) (cf. Table 1 and Figure 1 below).

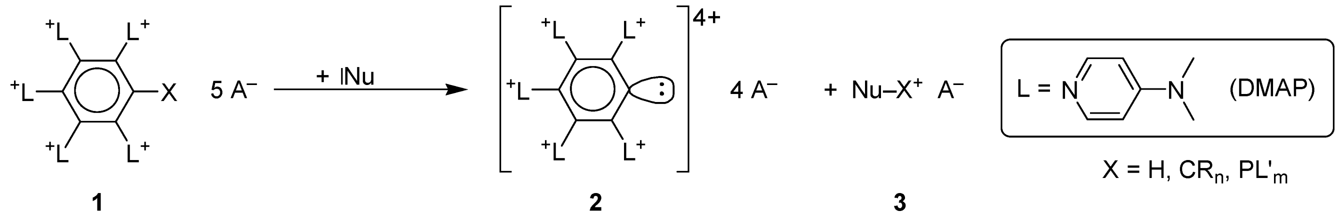
What are the reasons for the dramatic red shifts (up to 140 nm, 7600 $cm^{-1}$ respectively, for **9a**) in the longest-wavelength UV−vis absorptions in going from the pentafluoro phenyl precursors **8** to the corresponding peronio substituted[9] dyes **9** and **10** (cf. Table 1)?

Simple PM3 model calculations suggest that both the pentafluoro phenyl as well as the pentakisonio substituents of compounds **8** and **9**, **10** respectively are completely rotated out of conjugation with the azo chromophore. Thus, *mesomeric* effects are not operative between those two $\pi$-subsystems in both types of dyes. In particular, although highly electron-deficient, the pentakisonio-substituted phenyl moiety in **9**(**10**) cannot act as an M acceptor due to this orthogonality. The latter is a consequence of the steric requirements of the rigid ion cluster contained in **9**(**10**), in which all five pyridinio substituents

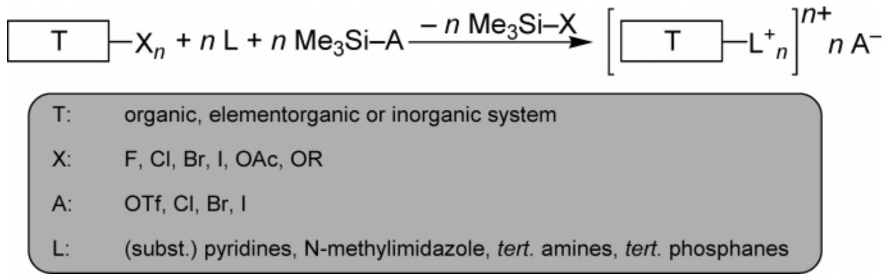
(1) Pühlhofer, F. G.; Weiss, R. *Eur. J. Org. Chem.* **2004**, *5*, 1002−1007.
(2) Huber, S. M.; Pühlhofer, F. G.; Weiss, R. *Eur. J. Org. Chem.* **2005**, *16*, 3530−3535.
(3) Weiss, R.; Pomrehn, B.; Hampel, F.; Bauer, W. *Angew. Chem.* **1995**, *107*, 1446−1448; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1319−1321.
(4) Weiss, R.; May, R.; Pomrehn, B. *Angew. Chem.* **1996**, *108*, 1319−1321; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1232−1234.
(5) Weiss, R.; Pühlhofer, F. G.; Jux, N.; Merz, K. *Angew. Chem.* **2002**, *114*, 3969−3971; *Angew. Chem. Int. Ed.* **2002**, *41*, 3815−3817.

(6) The synthesis of pentafluoro azo arenes shown in Scheme 3 was previously described for the syntheses of compounds **8b** and **8c**.[7] Compound **8a** was previously known, but synthesized via a different method.[8]
(7) Kosynkin, D.; Bockman, T. M.; J. Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2003−2012.
(8) Matsui, M.; Funabiki, K.; Shibata, K. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 531−536.
(9) As is characteristic for the SASAPOS protocol, no partially onio-substituted derivatives were formed.

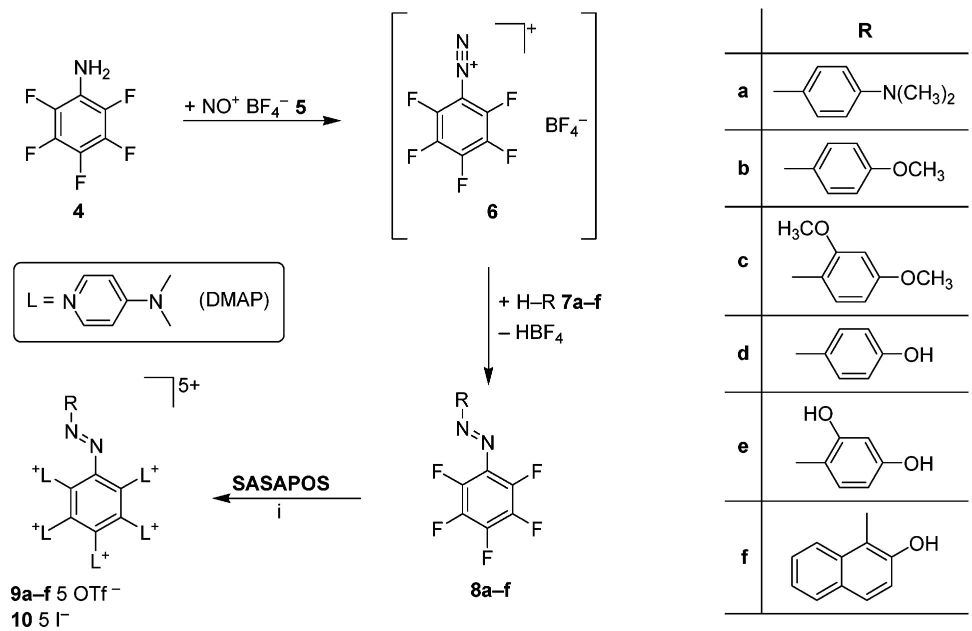
***Scheme 1.*** Formation of **2** by Heteropolar C−X Disconnections



***Scheme 2.*** General Form of the SASAPOS Protocol



***Scheme 3.*** Syntheses of Pentafluorophenylazo Dyes **8a**−**f** and Subsequent SASAPOS Cascades[a]



[a] (i) +5 DMAP, +5 TMSOTf (**9a**−**f**)/TMSI (**10**); −5 TMSF; PhCl, Δ; 24 h; >95%.

***Table 1.*** UV−vis Absorption Data of Azo Dye Solutions in Acetonitrile

| | 8 | | 9 | | |
|---|---|---|---|---|---|
| | $\lambda_{max}$ [nm] (E [cm$^{-1}$]) | $\epsilon_{max}$ | $\lambda_{max}$ [nm] (E [cm$^{-1}$]) | $\epsilon_{max}$ | "SASAPOS-shift" [nm] ([cm$^{-1}$]) |
| **a** | 433 (23100) | 25000 | 573 (17500) | 50000 | 140 (5600) |
| **b** | 317 (31500) | 12000 | 419 (23900) | 28000 | 102 (7600) |
| **c** | 358 (27900) | 11500 | 429 (23300) | 20000 | 71 (4600) |
| **d** | 327 (30600) | 14000 | 413 (24200) | 22500 | 86 (6400) |
| **e** | 389 (25700) | 12500 | 477 (21000) | 30500 | 88 (4700) |
| **f** | 455 (22000) | 9500 | 545 (18300) | 22500 | 90 (3700) |
| compound **10** | | | 574 (17400) | 60000 | |
| compound **11** | | | 503 (19900) | 35000 | |

are in their turn perpendicular to the phenyl system as the central carrier, this whole arrangement being further rigidified by five closely associated counteranions in defined positions.[3−5,10,11]

As for **8**, lone pair repulsion between the *o*-fluorines and the azo function are responsible for the calculated deconjugation. The principal difference between dyes of type **8** and the corresponding "sasaposed"[1,2] modifications of type **9**(**10**) is the pentacationic charge of the peronio-substituted phenyl substituent, whose positive electrostatic potential (somewhat attenuated by the negative potential of the counterions) is primarily felt by the adjacent orthogonal azo chromophore. By virtue of this massive electrostatic effect, the longest-wavelength UV−vis transitions in dyes **9**(**10**) is strongly red-shifted, as this particular UV−vis transition is connected with significant charge-transfer from the donor substituent(s) into the azo chromophore. This is well-known from traditional push−pull substituted azo compounds and is also qualitatively reproduced by our model calculations.

We have previously shown[3] that ion clusters structurally similar to **9** undergo a selective monohydrolysis under weakly

(10) Pühlhofer, F. G. Dissertation, Universität Erlangen-Nürnberg, 2001.
(11) These effects are also adequately modeled by PM3 calculations.

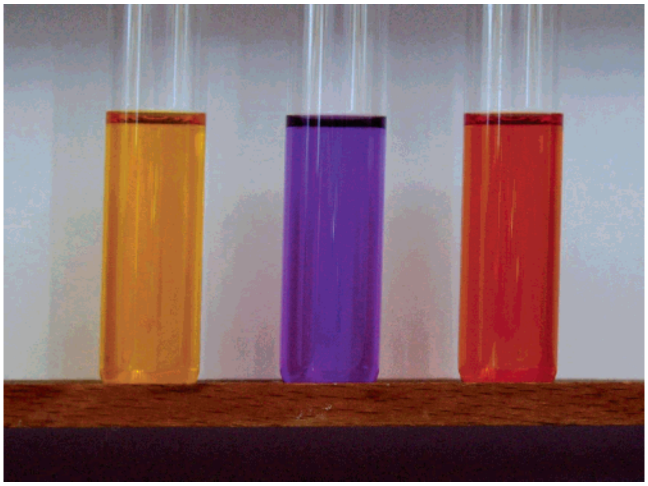


***Figure 1.*** Solutions (acetonitrile) of **8a**, **9a**, and **11** (from left to right).

basic conditions. In the present case the isolated product resulted from exchange of one $DMAP^+$ ligand against a hydroxyl group, followed by deprotonation of the latter to yield the corresponding phenoxide compound. In a representative experiment, **9a** was refluxed in wet acetonitrile in the presence of DMAP as base to yield the new, fully characterized dye **11** (Scheme 4). Colors in Scheme 4 indicate the hypsochromic shift of the absorption maximum observed in the process (cf. Table 1 and Figure 1 below).

In principle, substitution of an acceptor ligand ($DMAP^+$) by a donor substituent ($O^-$) strongly decreases the electrostatic potential of the polyonio-substituted moiety. Hence, for the example in Scheme 4 one expects a hypsochromic shift of the absorption maxima from **9a** to **11**; for detailed data, see Table 1 and Figure 1 below.

The effect of F/$DMAP^+$ exchange on the UV−vis absorption spectra ("SASAPOS-shift") varies with the donor character of the electron rich arene in the azo dye without obvious dependency (Table 1). The "SASAPOS-shift" varies between 71 and 140 nm in terms of wavelength, 3700 $cm^{-1}$ and 7600 $cm^{-1}$ in terms of energy, respectively. To further confirm this, DMAP was added to a solution of **9d** in acetonitrile during an UV−vis absorption experiment. The aim was to increase the donor character of the OH group (in **9d**) by deprotonation. In the resulting spectrum the band of **9d** at 413 nm ($\epsilon$ = 22500, 24200 $cm^{-1}$) disappeared and a stronger new band was found at 535 nm ($\epsilon$ = 26500, 18700 $cm^{-1}$). Overall this modification led to a further red-shift of 122 nm (5500 $cm^{-1}$).

The $\lambda_{max}$ (503 nm; 19900 $cm^{-1}$) for **11** shows that the decrease of electrostatic potential reduces the "SASAPOS-shift". Instead of 140 nm (5600 $cm^{-1}$) between **8a** and **9a**, the "SASAPOS-shift" (70 nm; 3200 $cm^{-1}$) is exactly half of this (in nm; 60% in $cm^{-1}$) (cf. Figure 1).

In addition to the variations of the electron rich arene (cf. Scheme 2) and the electron poor ion cluster arene (cf. compounds **10** and **11**) variations (substitution of N by CH groups) of the connecting $\pi$-linker were made (Scheme 5). Starting materials **12**−**14** for the corresponding SASAPOS cascades were previously described (**13**/**14**)[12] or synthesized in accordance to literature procedures (see exp. section) (**12**).[13] Application of the SASAPOS protocol (cf. Scheme 1) to **12**−**14** yielded the corresponding ion cluster aldimines **15** and **16** and stilbene **17** (Scheme 5).

All new compounds were fully characterized by $^{1}H$ and $^{13}C$ NMR spectroscopy, FAB-MS, elemental analysis, and UV−vis absorption spectrsocopy.

Analysis of the UV−vis absorption spectra of **8a**, **9a**, and **12**−**14** (Schemes 3 and 5, Table 2) indicated a strong dependence between "SASAPOS-shift" and the nature of atoms forming the $\pi$-linker between donor arene and IC ligand.

The variations of the "SASAPOS-shifts" reported in Table 2 can be explained by analyzing the effects of substitution of nitrogen atoms by CH groups. Comparison of compound pairs **8a**/**9a** and **14**/**17** indicates an increase of the "SASAPOS-shift" from 5600 $cm^{-1}$ to 6600 $cm^{-1}$. Substitution of the −N=N− bridge by the less electronegative CHCH bridge leads to decreased coefficients of $\pi$ orbitals and increased coefficients of $\pi^*$ orbitals on the bridging centers. Hence, the "SASAPOS-shift" is increased by 1000 $cm^{-1}$. Data of compound pair **13**/**16** show that nearly the same increase of "SASAPOS-shift" (900 $cm^{-1}$) is produced, if only the nitrogen atom adjacent to the pentakisonio-substituted phenyl moiety is exchanged by a CH group. In contrast, substitution of the other center (**12**/**15**) even leads to a decreased "SASAPOS-shift" (3400 $cm^{-1}$). The latter two cases demonstrate the electrostatic effects induced by SASAPOS on orbital energies. In principle, F/$DMAP^+$ exchange leads to electrostatically induced energetic stabilization of both occupied and virtual orbitals. Due to Coulomb's law, orbitals having large coefficients close to the origin of the electrostatic effects are much more affected than orbitals having only small coefficients in these regions. Since coefficients of $\pi$ orbitals are larger on N atoms and coefficients of $\pi^*$ orbitals are larger on CH groups, in **12**/**15** electrostatic effects stabilize occupied orbitals stronger than unoccupied ones resulting in a decreased "SASAPOS shift" (3400 $cm^{-1}$) compared to **8a**/**9a** (5600 $cm^{-1}$). In **13**/**16** electrostatic effects stabilize the virtual orbitals stronger than occupied resulting in an increased "SASAPOS shift" (6500 $cm^{-1}$) compared to **8a**/**9a** (5600 $cm^{-1}$).

Finally, the data in Table 1 also indicate that changing the counteranion from triflate (**9a**) to iodide (**10**) has no measurable effect on the absorption maximum and only a minor effect on the molar absorption coefficient. We further tested solutions of **9a** and **10** by addition of an excess of different anions ($I^-$, $BPh_4^-$, $[Fe(CN)_6]^{3-}$), and again no effect could be detected. To analyze the solvatochromic effects of the ion cluster dyes, we performed UV−vis absorption spectra of **9a** in different solvents.[14] The $\lambda_{max}$ values range around 573 nm (acetonitrile) within less than 10 nm and without any correlation between shift and the solvent characteristics (e.g., $\epsilon$ and $E_T(30)$). Hence, even if the IC ligands in **9a** and **10** are affected by the above modifications, UV−vis absorption spectra are not sufficiently sensitive to detect these effects.

## Conclusion

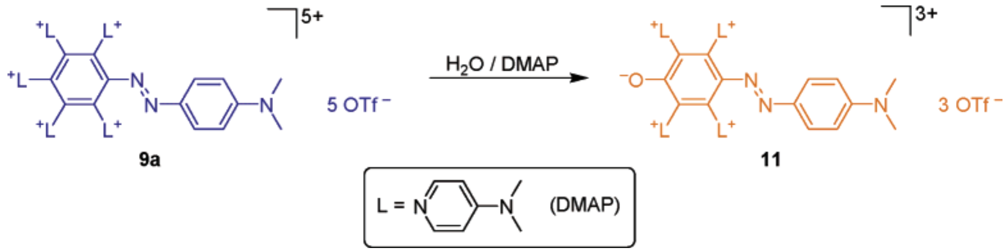
A pentakisonio-substituted phenyl unit, generated in the first synthesis of dyes **9**−**11** and **15**−**17**, turned out to function as a

(12) Pagagni, A.; Maiorana, S.; Del Buttero, P.; Perdicchia, D.; Cariati, F.; Cariati, E.; Marcolli, W. *Eur. J. Org. Chem.* **2002**, 1380−1384.

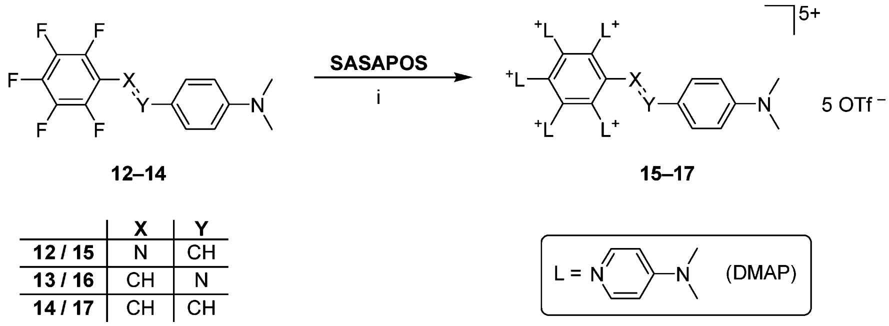
(13) Synthesis of **12** according to: Li, A.; Bin, X.; Zhu, S. *J. Fluorine Chem.* **1994**, 145−148.

(14) Solvents used: water, methanol, ethanol, acetonitrile, acetone, and dichloromethane. $E_T(30)$ [kcal/mol] values range (in that order) from 63.1 to 41.1; $\epsilon$ ranges from 78.39 to 8.93. Data taken from: Reichardt, C. *Solvent effects in organic chemistry*; VCH: New York, 1978; Vol. 3, appendix, pp 270−272.

***Scheme 4.*** Hydrolysis of **9a** in the Presence of DMAP




***Scheme 5.*** SASAPOS Cascades of Aldimines **12** and **13** and Stilbene **14**[a]




| | X | Y |
|---|---|---|
| **12 / 15** | N | CH |
| **13 / 16** | CH | N |
| **14 / 17** | CH | CH |

[a] (i) +5 DMAP, +5 TMSOTf; −5 TMSF; PhCl, Δ; 2 d; >85%.

***Table 2.*** UV−vis Absorption Data of Azo, Aldimine, and Stilbene Dye Solutions in Acetonitrile

| | pentafluoro precursor | | pentakis onio compound | | |
|---|---|---|---|---|---|
| | $\lambda_{max}$ [nm] (E [cm$^{-1}$]) | $\epsilon_{max}$ | $\lambda_{max}$ [nm] (E [cm$^{-1}$]) | $\epsilon_{max}$ | "SASAPOS-shift" |
| **8a/9a** | 433 (23100) | 25000 | 573 (17500) | 50000 | 140 (5600) |
| **12/15** | 363 (27500) | 37000 | 415 (24100) | 29000 | 52 (3400) |
| **13/16** | 397 (25200) | 21000 | 534 (18700) | 28000 | 137 (6500) |
| **14/17** | 359 (27900) | 15000 | 470 (21300) | 24000 | 111 (6600) |

highly effective auxochrome. Together with its counter anions this unit may be regarded as a first representative of ion cluster ligands. Bathochromic shifts of up to 140 nm were achieved by transforming a pentafluorophenyl substituent into the ion cluster ligand via the SASAPOS protocol[1−5] (cf. Scheme 2) in a one-pot synthesis in excellent yields. Due to the structural rigidity of the pentacationically substituted phenyl moiety in the above examples, orbital energies were massively disturbed by the electrostatic potential of the IC ligand predominantly via through space interactions. Due to the variable choice of the counteranion in the SASAPOS protocol, the IC ligand modified dyes can be synthesized as polyhalide salts (cf. compound **10**) which will show excellent solubility in water (especially the polychloride and -bromide salts). Besides the effect on optical characteristics, we also expect strong influences of ion cluster ligands on a variety of properties of any template connected to such ligands. In general those effects are increased ionization potentials and electron affinities as well as modifications of reactivity toward nucleophiles (increased) and electrophiles (decreased). Furthermore, this concept for the introduction of strong electrostatic potentials is not limited to organic templates and will be transferable to elementorganic and inorganic templates. For the latter in particular, we expect a distinct electrostatic stabilization of unusual (especially low) oxidation states.

## Experimental Section

If not indicated otherwise, all reactions were carried out under an $N_2$ atmosphere in dry solvents.

**General Procedure for the Syntheses of Azo Dyes 8a−f.** In a typical procedure, a solution of pentafluoroaniline (1.83 g, 10.0 mmol) in acetonitrile (15 mL) was added dropwise to a solution of nitrosonium tetrafluoroborate (1.17 g, 10.0 mmol) in acetonitrile (15 mL) at −30 °C over 30 min. After 1 h of additional stirring at −30 °C, the coupling compound (40.0 mmol) was added dropwise. The resulting dye solution was allowed to warm to room temperature. Water (50 mL) was added after 12 h followed by extraction with dichloromethane (3 × 50 mL). The collected organic phases were dried ($MgSO_4$) and evaporated to dryness. Recrystallization from methanol (**8a−c**) or ethanol/water (50:50, v:v; **8d−f**) yielded the pentafluoro azo dyes. Isolated yields (not optimized, after recrystallization) ranged from 40% (**8a**) to 72% (**8e**).

**General procedure for the Syntheses of Azo Dyes 9a−f, and 10.** In a typical procedure, the corresponding pentafluorophenyl azo dye **8a−f** (1.5 mmol) was added to a solution of DMAP (12 mmol) and TMSOTf (TMSI respectively for the synthesis of **10**) (9 mmol) in chlorobenzene (25 mL). The deeply colored solution was stirred under reflux for 24 h, whereby the product started to precipitate after 1 h. The precipitate was filtered, washed with dichloromethane (3 × 10 mL), and dried in high vacuum. Isolated yields ranged from 95% to quantitative.

**Hydrolysis of Compound 9a.** DMAP (122 mg, 1.0 mmol) was added to a solution of **9a** (321 mg, 0.2 mmol) in wet acetonitrile (25 mL). The reaction solution was stirred under reflux, whereby the color changed from deep purple to deep red. After 12 h the solvent was fully removed in high vacuum and dichloromethane (100 mL) was added. The resulting suspension was stirred for 12 h to remove the formed protonated DMAP. The precipitate was filtered, washed with dichloromethane (3 × 10 mL), and dried in high vacuum to yield 74% of **11** as red-orange powder.

**Synthesis of 12.** Pentafluoroaniline (1.00 g, 5.47 mmol) was stirred under reflux in $SOCl_2$ (20 mL). The resulting yellow solution was cooled to room temperature after gas evolution stopped. The remaining solvent was fully removed in vacuum. Toluene (20 mL) and 4-dimethylaminobenzaldehyde (816 mg, 5.47 mmol) were added and stirred under reflux for 12 h. The solvent was removed in vacuum, and the resulting solid was recrystallized from hot acetone. Yield 65%; yellow-orange needles.

**General Procedure for the Syntheses of Aldimines 15 and 16 and Stilbene 17.** In a typical procedure, the corresponding pentafluorophenyl precursor **12**−**14** (1.0 mmol) was added to a solution of DMAP (7 mmol) and TMSOTf (6 mmol) in chlorobenzene (25 mL). The deeply colored solution was stirred under reflux for 2 d, whereby the product started to precipitate after 2 h. The precipitate was filtered, washed with dichloromethane (3 × 10 mL), and dried in high vacuum. Isolated yields ranged from 85% to quantitative.

**4-Dimethylaminophenylazopentafluorobenzene, 8a.** Yield = 40%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.11 (s, 6H, CH$_3$), 6.71 (d, $^3J_{HH}$ = 9.2 Hz, 2H, H3/5 phenyl), 7.84 (d, $^3J_{HH}$ = 9.2 Hz, 2H, H2/6 phenyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 40.24 (s, CH$_3$), 111.27 (s, C3/5 phenyl), 125.86 (s, C2/6 phenyl), 144.19 (s, C1 phenyl), 153.61 (s, C4 phenyl) ppm. $^{19}$F NMR (282 MHz, CDCl$_3$): −151.50 (m, 2F), −156.41 (t, $|^3J_{FF}|$ = 21 Hz, 1F), −162.92 (m, 2F) ppm. FAB MS (NBA): $m/z$ = 315 [M]$^+$, 120 [M − N$_2$ − C$_6$F$_5$]$^+$. $C_{14}H_{10}F_5N_3$ (315.25): calcd C 53.34 H 3.20 N 13.33; found C 53.78 H 3.31 N 13.05. UV−vis absorption (CH$_3$CN): 433 nm (25000).

**4-Methoxyphenylazopentafluorobenzene, 8b.** Yield = 43%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.89 (s, 3H, CH$_3$), 7.00 (d, $^3J_{HH}$ = 9.0 Hz, 2H, H3/5 phenyl), 7.91 (d, $^3J_{HH}$ = 9.2 Hz, 2H, H2/6 phenyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 55.68 (s, CH$_3$), 114.39 (s, C3/5 phenyl), 125.51 (s, C2/6 phenyl), 147.48 (s, C1 phenyl), 163.66 (s, C4 phenyl) ppm. $^{19}$F NMR (282 MHz, CDCl$_3$): −150.59 (m, 2F), −153.99 (t, $|^3J_{FF}|$ = 21 Hz, 1F), −162.31 (m, 2F) ppm. FAB MS (NBA): $m/z$ = 303 [M + H]$^+$, 302 [M]$^+$. $C_{13}H_7F_5N_2O$ (302.20): calcd C 51.67 H 2.33 N 9.27; found C 51.59 H 2.39 N 9.30. UV−vis absorption (CH$_3$CN): 317 nm (12000).

**2,4-Dimethoxyphenylazopentafluorobenzene, 8c.** Yield = 57%. $^1$H NMR (400 MHz, acetone-$d_6$): $\delta$ = 3.94 (s, 3H, CH$_3$), 4.01 (s, 3H, CH$_3$), 6.64 (dd, $^3J_{HH}$ = 9.1 Hz, $^4J_H$−H = 2.5 Hz, 1H, H5 phenyl), 6.79 (d, $^4J_{HH}$ = 2.5 Hz, 1H, H3 phenyl), 7.69 (d, $^3J_{HH}$ = 9.2 Hz, 1H, H6 phenyl) ppm. $^{13}$C NMR (100 MHz, acetone-$d_6$): $\delta$ = 56.32 (s, CH$_3$), 56.76 (s, CH$_3$), 99.66 (s, C3 phenyl), 107.75 (s, C5 phenyl), 118.17 (s, C6 phenyl), 138.12 (s, C1 phenyl), 161.44 (s, C4 phenyl), 167.08 (s, C2 phenyl) ppm. $^{19}$F NMR (282 MHz, acetone-$d_6$): −153.32 (m, 2F), −157.62 (t, $|^3J_{FF}|$ = 21 Hz, 1F), −164.92 (m, 2F) ppm. FAB MS (NBA): $m/z$ = 333 [M + H]$^+$, 332 [M]$^+$. $C_{14}H_9F_5N_2O_2$ (332.23): calcd C 50.61 H 2.73 N 8.43; found C 50.68 H 2.80 N 8.40. UV−vis absorption (CH$_3$CN): 358 nm (11500).

**4-Hydroxyphenylazopentafluorobenzene, 8d.** Yield = 44%. $^1$H NMR (400 MHz, acetone-$d_6$): $\delta$ = 7.04 (d, $^3J_{HH}$ = 8.9 Hz, 2H, H3/5 phenyl), 7.86 (d, $^3J_{HH}$ = 8.9 Hz, 2H, H2/6 phenyl), 9.64 (s, 1H, OH) ppm. $^{13}$C NMR (100 MHz, acetone-$d_6$): $\delta$ = 116.95 (s, C3/5 phenyl), 126.50 (s, C2/6 phenyl), 147.69 (s, C1 phenyl), 163.44 (s, C4 phenyl) ppm. $^{19}$F NMR (282 MHz, acetone-$d_6$): −152.84 (m, 2F), −156.78 (t, $|^3J_{FF}|$ = 21 Hz, 1F), −164.73 (m, 2F) ppm. FAB MS (NBA): $m/z$ = 289 [M + H]$^+$, 288 [M]$^+$. $C_{12}H_5F_5N_2O$ (288.18) + 0.5 H$_2$O: calcd C 48.50 H 2.03 N 9.43; found C 48.87 H 2.34 N 9.31. UV−vis absorption (CH$_3$CN): 327 nm (14000).

**2,4-Dihydroxyphenylazopentafluorobenzene, 8e.** Yield = 72%. $^1$H NMR (400 MHz, acetone-$d_6$): $\delta$ = 6.42 (dd, $^4J_{HH}$ = 2.5 Hz, $J$ = 2 Hz, 1H, H3 phenyl), 6.67 (dd, $^3J_{HH}$ = 8.9 Hz, $^4J_H$−H = 2.5 Hz, 1H, H5 phenyl), 7.75 (d, $^3J_{HH}$ = 8.9 Hz, $J$ = 2 Hz, 1H, H6 phenyl), 10.04 (s, 1H, $p$-OH), 12.33 (s, 1H, $o$-OH) ppm. $^{13}$C NMR (100 MHz, acetone-$d_6$): $\delta$ = 103.85 (s, C3 phenyl), 103.90 (s, C3 phenyl), 110.96 (s, C5 phenyl), 134.92 (s, C1 phenyl), 134.99 (s, C1 phenyl), 135.78 (s, C6 phenyl), 135.87 (s, C6 phenyl), 156.72 (s, C2 phenyl), 157.12 (s, C2 phenyl), 165.79 (s, C4 phenyl) ppm. $^{19}$F NMR (282 MHz, acetone-$d_6$): −152.43 (m, 2F), −156.72 (m, 1F), −164.52 (m, 2F) ppm. FAB MS (NBA): $m/z$ = 305 [M + H]$^+$, 304 [M]$^+$. $C_{12}H_5F_5N_2O_2$ (304.18) + 0.5 H$_2$O: calcd C 46.02 H 1.93 N 8.94; found C 46.33 H 2.29 N 8.78. UV−vis absorption (CH$_3$CN): 389 nm (12500).

**2-Hydroxynaphthylazopentafluorobenzene, 8f.** Yield = 47%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 6.69 (d, $^3J_{HH}$ = 9.3 Hz, 1H, H3/4), 7.45 (t, $^3J_{HH}$ = 8.2 Hz, 1H, H6/7), 7.59 (t, $^3J_{HH}$ = 8.4 Hz, 1H, H6/7), 7.66 (d, $^3J_{HH}$ = 7.8 Hz, 1H, H5/8), 7.82 (d, $^3J_{HH}$ = 9.3 Hz, 1H, H3/4), 8.50 (d, $^3J_{HH}$ = 8.3 Hz, 1H, H5/8), 14.99 (s, 1H, OH) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 122.15 (s), 122.82 (s), 126.40 (s), 128.41 (s), 128.63 (s), 129.49 (s), 132.32 (s), 132.96 (s), 140.89 (s, C1 naphthyl), 166.14 (s, C2 naphthyl) ppm. $^{19}$F NMR (282 MHz, CDCl$_3$): −150.84 (m, 2F), −156.09 (t, $|^3J_{FF}|$ = 21 Hz, 1F), −161.42 (m, 2F) ppm. EI MS (70 °C): $m/z$ = 338(75) [M]$^+$, 171(18) [M − C$_6$F$_5$]$^+$, 143(100) [M − N$_2$ − C$_6$F$_5$]$^+$. $C_{16}H_7F_5N_2O$ (338.24) + 0.5 H$_2$O: calcd C 55.34 H 2.32 N 8.07; found C 55.87 H 2.42 N 7.95. UV−vis absorption (CH$_3$CN): 455 nm (9500).

**4-Dimethylaminophenylazopentakis[4-(dimethylamino)-1-pyridinio]-benzene Pentakis(triflate), 9a.** Yield = quant. $^1$H NMR (400 MHz, CD$_3$CN): $\delta$ = 3.16 (s, 6H, CH$_3$), 3.17 (s, 6H, CH$_3$), 3.18 (s, 12H, CH$_3$), 3.23 (s, 12H, CH$_3$), 6.72 (d, $^3J_{HH}$ = 9.5 Hz, 2H, H3/5 phenyl), 6.85 (d, $^3J_{HH}$ = 8.1 Hz, 2H, H3/5 $p$-DMAP), 6.87 (d, $^3J_{HH}$ = 8.1 Hz, 4H, H3/5 DMAP), 6.92 (d, $^3J_{HH}$ = 8.1 Hz, 4H, H3/5 DMAP), 7.20 (d, $^3J_{HH}$ = 9.4 Hz, 2H, H2/6 phenyl), 8.16 (d, $^3J_{HH}$ = 8.1 Hz, 6H, H2/6 DMAP), 8.17 (d, $^3J_{HH}$ = 8.1 Hz, 4H, H2/ 6 DMAP) ppm. $^{13}$C NMR (100 MHz, CD$_3$CN): $\delta$ = 41.12 (s, CH$_3$), 41.23 (s, CH$_3$), 41.37 (s, CH$_3$), 109.09 (s, C3/5 DMAP), 110.28 (s, C3/5 DMAP), 110.38 (s, C3/5 $p$-DMAP), 113.95 (s, C3/5 phenyl), 121.84 (q, $|^1J_{CF}|$ = 320 Hz, CF$_3$), 132.81 (s, C4 onio-phenyl), 134.70 (s, C2/3/5/6 onio-phenyl), 139.58 (s, C2/3/5/6 onio-phenyl), 141.17 (s, C2/6 DMAP), 141.53 (s, C2/6 $p$-DMAP), 143.00 (s, C2/6 DMAP), 143.85 (s, C2/6 phenyl), 144.24 (s, C1/4 phenyl/C1 onio-phenyl), 145.78 (s, C1/4 phenyl/C1 onio-phenyl), 148.74 (s, C1/4 phenyl/C1 onio-phenyl), 157.42 (s, C4 DMAP), 157.62 (s, C4 $p$-DMAP), 157.71 (s, C4 DMAP) ppm. FAB MS (NBA): $m/z$ = 1426 [M − OTf]$^+$, 1277 [M − 2OTf]$^+$, 1144 [M + H − NC$_6$H$_4$N(CH$_3$)$_2$ − 2OTf]$^+$, 1022 [M + H − DMAP − NC$_6$H$_4$N-(CH$_3$)$_2$ − 2OTf]$^+$. $C_{54}H_{60}F_{15}N_{13}O_{15}S_5$ (1576.42) + 2 H$_2$O: calcd C 40.22 H 4.00 N 11.29 S 9.94; found C 40.10 H 4.04 N 11.14 S 9.44. UV−vis absorption (CH$_3$CN): 573 nm (50000).

**4-Methoxyphenylazopentakis[4-(dimethylamino)-1-pyridinio]-benzene Pentakis(triflate), 9b.** Yield = 97%. $^1$H NMR (400 MHz, CD$_3$NO$_2$): $\delta$ = 3.28 (s, 6H, CH$_3$), 3.29 (s, 12H, CH$_3$), 3.34 (s, 12H, CH$_3$), 3.91 (s, 3H, OCH$_3$), 6.99 (d, $^3J_{HH}$ = 9.3 Hz, 2H, H3/5 phenyl), 7.01 (d, $^3J_{HH}$ = 7.9 Hz, 2H, H3/5 $p$-DMAP), 7.02 (d, $^3J_{HH}$ = 8.1 Hz, 4H, H3/5 DMAP), 7.06 (d, $^3J_{HH}$ = 8.1 Hz, 4H, H3/5 DMAP), 7.50 (d, $^3J_{HH}$ = 9.2 Hz, 2H, H2/6 phenyl), 8.26 (d, $^3J_{HH}$ = 8.1 Hz, 2H, H2/6 $p$-DMAP), 8.31 (d, $^3J_{HH}$ = 7.9 Hz, 4H, H2/6 DMAP), 8.33 (d, $^3J_{HH}$ = 7.9 Hz, 4H, H2/6 DMAP) ppm. $^{13}$C NMR (100 MHz, CD$_3$NO$_2$): $\delta$ = 41.31 (s, CH$_3$), 41.42 (s, CH$_3$), 57.12 (s, OCH$_3$), 109.36 (s, C3/5 DMAP), 110.53 (s, C3/5 DMAP), 110.63 (s, C3/5 $p$-DMAP), 116.52 (s, C3/5 phenyl), 122.11 (q, $|^1J_{CF}|$ = 320 Hz, CF$_3$), 128.34 (s, C2/6 phenyl), 136.07 (s, C2/3/5/6 onio-phenyl), 136.81 (s, C4 onio-phenyl), 140.40 (s, C2/3/5/6 onio-phenyl), 141.73 (s, C2/6 DMAP), 141.77 (s, C2/6 $p$-DMAP), 143.22 (s, C2/6 DMAP), 148.66 (s, C1 phenyl/onio-phenyl), 148.95 (s, C1 phenyl/onio-phenyl), 157.71 (s, C4 $p$-DMAP), 157.75 (s, C4 DMAP), 158.09 (s, C4 DMAP), 167.99 (s, C4 phenyl) ppm. FAB MS (NBA): $m/z$ = 1413 [M − OTf]$^+$, 1265 [M + H − 2OTf]$^+$, 1116 [M + H − 3OTf]$^+$. $C_{53}H_{57}F_{15}N_{12}O_{16}S_5$ (1563.38): calcd C 40.72 H 3.67 N 10.75 S 10.25; found C 40.41 H 3.74 N 10.59 S 10.03. UV−vis absorption (CH$_3$CN): 419 nm (28000).

**2,4-Dimethoxyphenylazopentakis[4-(dimethylamino)-1-pyridinio]-benzene Pentakis(triflate), 9c.** Yield = 98%. $^1$H NMR (400 MHz, CD$_3$NO$_2$): $\delta$ = 3.28 (s, 6H, CH$_3$), 3.28 (s, 12H, CH$_3$), 3.34 (s, 12H, CH$_3$), 3.86 (s, 3H, OCH$_3$), 3.93 (s, 3H, OCH$_3$), 6.47 (dd, $^3J_{HH}$ = 9.6 Hz, $^4J_H$−H = 2.5 Hz, 1H, H5 phenyl), 6.59 (d, $^4J_{HH}$ = 2.8 Hz, 1H, H3 phenyl), 6.98 (d, $^3J_{HH}$ = 7.7 Hz, 2H, H3/5 $p$-DMAP), 7.00 (d, $^3J_{HH}$ = 7.7 Hz, 4H, H3/5 DMAP), 7.04 (d, $^3J_{HH}$ = 7.7 Hz, 4H, H3/5 DMAP), 7.29 (d, $^3J_{HH}$ = 9.4 Hz, 1H, H6 phenyl), 8.27 (d, $^3J_{HH}$ = 8.2 Hz, 4H, H2/6 DMAP), 8.30 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H2/6 $p$-DMAP), 8.32 (d, $^3J_{HH}$ = 8.3 Hz, 4H, H2/6 DMAP) ppm. $^{13}$C NMR (100 MHz, CD$_3$-

$NO_2$): $\delta$ = 41.25 (s, $CH_3$), 41.42 (s, $CH_3$), 56.79 (s, $OCH_3$), 57.32 (s, $OCH_3$), 99.28 (s, C3 phenyl), 109.42 (s, C3/5 DMAP), 110.10 (s, C5 phenyl), 110.46 (s, C3/5 DMAP), 110.54 (s, C3/5 *p*-DMAP), 119.84 (s, C6 phenyl), 122.16 (q, $|^1J_{CF}|$ = 320 Hz, $CF_3$), 135.78 (s, C4 onio-phenyl), 135.88 (s, C2/3/5/6 onio-phenyl), 139.36 (s, C1 phenyl), 140.24 (s, C2/3/5/6 onio-phenyl), 141.85 (s, C2/6 DMAP), 142.00 (s, C2/6 *p*-DMAP), 143.22 (s, C2/6 DMAP), 148.93 (s, C1 onio-phenyl), 157.75 (s, C4 DMAP), 158.20 (s, C4 DMAP), 164.20 (s, C4 phenyl), 170.99 (s, C2 phenyl) ppm. FAB MS (NBA): $m/z$ = 1443 [M − OTf]$^+$, 1294 [M − 2OTf]$^+$, 1144 [M + H − $NC_6H_4(OCH_3)_2$ − 2OTf]$^+$. $C_{54}H_{59}F_{15}N_{12}O_{17}S_5$ (1593.41): calcd C 40.70 H 3.73 N 10.55 S 10.06; found C 40.60 H 4.00 N 10.61 S 10.00. UV−vis absorption ($CH_3CN$): 429 nm (20000).

**4-Hydroxyphenylazopentakis[4-(dimethylamino)-1-pyridinio]-benzene Pentakis(triflate), 9d.** Yield = 95%. $^1$H NMR (400 MHz, $CD_3NO_2$): $\delta$ = 3.28 (s, 6H, $CH_3$), 3.29 (s, 12H, $CH_3$), 3.33 (s, 12H, $CH_3$), 6.90 (d, $^3J_{HH}$ = 9.1 Hz, 2H, H3/ 5 phenyl), 7.00 (d, $^3J_{HH}$ = 7.7 Hz, 2H, H3/5 *p*-DMAP), 7.01 (d, $^3J_{HH}$ = 8.0 Hz, 4H, H3/5 DMAP), 7.04 (d, $^3J_{HH}$ = 8.0 Hz, 4H, H3/5 DMAP), 7.43 (d, $^3J_{HH}$ = 9.1 Hz, 2H, H2/6 phenyl), 8.29 (d, $^3J_{HH}$ = 7.7 Hz, 6H, H2/6 DMAP), 8.34 (d, $^3J_{HH}$ = 8.0 Hz, 4H, H2/6 DMAP) ppm. $^{13}$C NMR (100 MHz, $CD_3NO_2$): $\delta$ = 41.30 (s, $CH_3$), 41.43 (s, $CH_3$), 109.34 (s, C3/5 DMAP), 110.49 (s, C3/5 DMAP), 110.58 (s, C3/5 *p*-DMAP), 118.13 (s, C3/5 phenyl), 122.08 (q, $|^1J_{CF}|$ = 319 Hz, $CF_3$), 128.75 (s, C2/ 6 phenyl), 136.02 (s, C2/3/5/6 onio-phenyl), 136.49 (s, C4 onio-phenyl), 140.35 (s, C2/3/ 5/6 onio-phenyl), 141.79 (s, C2/6 DMAP), 141.87 (s, C2/6 *p*-DMAP), 143.25 (s, C2/6 DMAP), 148.64 (s, C1 phenyl/onio-phenyl), 148.83 (s, C1 phenyl/ onio-phenyl), 157.71 (s, C4 *p*-DMAP), 157.74 (s, C4 DMAP), 158.09 (s, C4 DMAP), 166.59 (s, C4 phenyl) ppm. FAB MS (NBA): $m/z$ = 1399 [M − OTf]$^+$, 1250 [M − 2OTf]$^+$, 1144 [M + H − $NC_6H_4OH$ − 2OTf]$^+$. $C_{52}H_{55}F_{15}N_{12}O_{16}S_5$ (1549.36) + 4 $H_2O$: calcd C 38.52 H 3.92 N 10.37 S 9.89; found C 38.61 H 3.83 N 9.95 S 9.71. UV−vis absorption: 413 nm (22500) ($CH_3CN$); 535 (26500) ($CH_3CN$ + excess DMAP).

**2,4-Dihydroxyphenylazopentakis[4-(dimethylamino)-1-pyridinio]-benzene Pentakis(triflate), 9e.** Yield = quant. $^1$H NMR (400 MHz, $CD_3NO_2$): $\delta$ = 3.26 (s, 6H, $CH_3$), 3.27 (s, 12H, $CH_3$), 3.32 (s, 12H, $CH_3$), 6.13 (sb, 1H, H3 phenyl), 6.48 (d, $^3J_{HH}$ = 9.4 Hz, 1H, H5 phenyl), 6.96 (d, $^3J_{HH}$ = 7.7 Hz, 2H, H3/5 *p*-DMAP), 6.97 (mb, 1H, H6 phenyl), 6.98 (d, $^3J_{HH}$ = 8.0 Hz, 4H, H3/5 DMAP), 7.04 (d, $^3J_{HH}$ = 8.3 Hz, 4H, H3/5 DMAP), 8.28 (d, $^3J_{HH}$ = 8.0 Hz, 2H, H2/6 *p*-DMAP), 8.32 (d, $^3J_{HH}$ = 8.0 Hz, 4H, H2/6 DMAP), 8.34 (d, $^3J_{HH}$ = 7.7 Hz, 4H, H2/6 DMAP), 12.17 (sb, OH) ppm. $^{13}$C NMR (100 MHz, $CD_3NO_2$): $\delta$ = 41.29 (s, $CH_3$), 41.38 (s, $CH_3$), 104.55 (s, C5 phenyl), 109.73 (s, C3/5 DMAP), 110.36 (s, C3/5 DMAP), 110.45 (s, C3/5 *p*-DMAP), 116.11 (sb, C3 phenyl), 122.10 (q, $|^1J_{CF}|$ = 319 Hz, $CF_3$), 134.85 (s, C6 phenyl), 137.36 (s), 140.51 (s), 141.55 (s), 141.88 (s, C2/6 DMAP), 142.32 (s, C2/6 *p*-DMAP), 142.53 (s), 143.23 (s, C2/6 DMAP), 149.15 (s, C1 onio-phenyl), 157.74 (s, C4 DMAP), 158.06 (s, C4 DMAP) ppm. FAB MS (NBA): $m/z$ = 1415 [M − OTf]$^+$, 1266 [M − 2OTf]$^+$, 1144 [M + H − $NC_6H_3(OH)_2$ − 2OTf]$^+$. $C_{52}H_{55}F_{15}N_{12}O_{17}S_5$ (1565.35) + $H_2O$: calcd C 39.45 H 3.63 N 10.62 S 10.12; found C 39.38 H 3.64 N 10.49 S 10.19. UV−vis absorption ($CH_3CN$): 477 nm (30500).

**2-Hydroxynaphthylazopentakis[4-(dimethylamino)-1-pyridinio]-benzene Pentakis(triflate), 9f.** Yield = 97%. $^1$H NMR (400 MHz, $CD_3NO_2$): $\delta$ = 3.25 (s, 6H, $CH_3$), 3.27 (s, 12H, $CH_3$), 3.31 (s, 12H, $CH_3$), 6.42 (d, $^3J_{HH}$ = 9.4 Hz, 1H, naphthyl), 6.92 (d, $^3J_{HH}$ = 8.2 Hz, 1H, naphthyl), 6.95 (d, $^3J_{HH}$ = 8.2 Hz, 2H, H3/5 *p*-DMAP), 6.98 (d, $^3J_{HH}$ = 8.1 Hz, 4H, H3/5 DMAP), 7.08 (d, $^3J_{HH}$ = 7.7 Hz, 4H, H3/5 DMAP), 7.30 (m, 1H, naphthyl), 7.53 (d, $^3J_{HH}$ = 7.2 Hz, 1H, naphthyl), 7.68 (m, 1H, naphthyl), 8.05 (d, $^3J_{HH}$ = 7.8 Hz, 1H, naphthyl), 8.27 (d, $^3J_{HH}$ = 7.9 Hz, 2H, H2/6 *p*-DMAP), 8.32 (d, $^3J_{HH}$ = 7.9 Hz, 4H, H2/6 DMAP), 8.37 (d, $^3J_{HH}$ = 7.7 Hz, 4H, H2/6 DMAP) ppm. $^{13}$C NMR (100 MHz, $CD_3NO_2$): $\delta$ = 41.30 (s, $CH_3$), 41.35 (s, $CH_3$), 110.06 (s, naphthyl), 109.32 (s, C3/5 DMAP), 110.39 (s, C3/5 DMAP), 110.46 (s, C3/5 DMAP), 111.12 (s, naphthyl), 122.16 (q, $|^1J_{CF}|$ = 320 Hz, $CF_3$), 127.46 (s), 130.34 (s), 130.59 (s), 130.94 (s), 131.04 (s), 132.25 (s), 140.63 (s), 141.88 (s, C2/6 DMAP), 142.36 (s), 142.57 (s, C2/6 *p*-DMAP), 143.05 (s, C2/6 DMAP), 143.85 (s), 157.71 (s, C4 DMAP), 158.31 (s, C4 DMAP) ppm. FAB MS (NBA): $m/z$ = 1449 [M − OTf]$^+$, 1299 [M − 2OTf]$^+$, 1144 [M + H − $NC_{10}H_6OH$ − 2OTf]$^+$. $C_{56}H_{57}F_{15}N_{12}O_{16}S_5$ (1599.42) + 3 $H_2O$: calcd C 40.68 H 3.84 N 10.17 S 9.69; found C 41.42 H 3.86 N 10.27 S 9.10. UV−vis absorption ($CH_3CN$): 545 nm (22500).

**4-Dimethylaminophenylazopentakis[4-(dimethylamino)-1-pyridinio]-benzene Pentakis(iodide), 10.** Yield = quant. $^1$H NMR (400 MHz, $D_2O/CF_3COOD$, low concentration → low resolution): $\delta$ = 2.09 (s, $CH_3$), 2.10 (s, $CH_3$), 2.11 (s, $CH_3$), 2.13 (s, $CH_3$), 5.80 (d, 6H, H3/5 DMAP), 5.82 (d, 4H, H3/5 DMAP), 5.95 (d, $^3J_{HH}$ = 9.5 Hz, 2H, phenyl), 6.24 (d, $^3J_{HH}$ = 9.3 Hz, 2H, phenyl), 6.98 (d, $^3J_{HH}$ = 8.0 Hz, 4H, H2/6 DMAP), 7.24 (d, $^3J_{HH}$ = 7.8 Hz, 6H, H2/6 DMAP) ppm. $^{13}$C NMR (concentration too low). FAB MS (NBA): $m/z$ = 1338 [M − I]$^+$, 1211 [M − 2I]$^+$, 1084 [M − 3I]$^+$. $C_{49}H_{60}I_5N_{13}$ (1465.63) + 3 $H_2O$: calcd C 38.73 H 4.38 N 11.98; found C 38.82 H 4.31 N 11.89. UV−vis absorption ($CH_3CN$): 574 nm (60000).

**4-(4-Dimethylaminophenylazo)tetrakis[4-(dimethylamino)-1-pyridinio]phenolate Tris(triflate), 11.** Yield = 74%. $^1$H NMR (400 MHz, $CD_3CN$): $\delta$ = 3.00 (s, 6H, $CH_3$), 3.28 (s, 12H, $CH_3$), 3.33 (s, 12H, $CH_3$), 6.57 (d, $^3J_{HH}$ = 9.3 Hz, 2H, H3/5 phenyl), 6.96 (d, $^3J_{HH}$ = 7.7 Hz, 4H, H3/5 DMAP), 6.99 (d, $^3J_{HH}$ = 7.7 Hz, 4H, H3/5 DMAP), 7.01 (d, $^3J_{HH}$ = 9.2 Hz, 2H, H2/6 phenyl), 8.06 (d, $^3J_{HH}$ = 7.7 Hz, 4H, H2/6 DMAP), 8.18 (d, $^3J_{HH}$ = 7.8 Hz, 4H, H2/6 DMAP) ppm. $^{13}$C NMR (100 MHz, $CD_3CN$): $\delta$ = 40.86 (s, $CH_3$), 41.00 (s, $CH_3$), 108.63 (s, C3/5 DMAP), 108.89 (s, C3/5 DMAP), 112.72 (s, C3/5 phenyl), 122.39 (q, $|^1J_{CF}|$ = 320 Hz, $CF_3$), 125.39 (s, C2/6 phenyl), 125.68 (s, C1/4 phenyl/C1 onio-phenyl), 132.67 (s, C2/3/5/6 onio-phenyl), 135.94 (s,C2/3/5/6 onio-phenyl), 144.35 (s, C2/6 DMAP), 144.66 (s, C2/6 DMAP), 144.87 (s, C1/4 phenyl/C1 onio-phenyl), 154.09 (s, C1/4 phenyl/C1 onio-phenyl), 157.85 (s, C4 DMAP), 158.12 (s, C4 DMAP), 164.11 (s, C4 onio-phenyl) ppm. FAB MS (NBA): $m/z$ = 1022 [M − OTf]$^+$, 872 [M − HOTf − OTf]$^+$. $C_{45}H_{50}F_9N_{11}O_{10}S_3$ (1172.13) + 3 $H_2O$: calcd C 44.08 H 4.60 N 12.57 S 7.84; found C 43.92 H 4.37 N 12.37 S 7.68. UV−vis absorption ($CH_3CN$): 503 nm (35000).

**Pentafluorobenzaldehyde 4-Dimethylaminophenylimine, 12.** Yield = 65%. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.07 (s, 6H, $CH_3$), 6.73 (d, $^3J_{HH}$ = 9.1 Hz, 2H, H3/5 phenyl), 7.79 (d, $^3J_{HH}$ = 9.1 Hz, 2H, H2/6 phenyl), 8.35 (s, 1H, -C*H*=N-) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 40.25 (s, $CH_3$), 111.67 (s, C3/5 phenyl), 123.14 (s, C1 phenyl), 131.48 (s, C2/6 phenyl), 153.38 (s, C4 phenyl), 167.57 (s, *C*H=N) ppm. $^{19}$F NMR (282 MHz, $CDCl_3$): −161.71 (m, 2F), −164.37 (m, 2F), −172.68 (m, 1F) ppm. FAB MS (NBA): $m/z$ = 314 [M]$^+$. $C_{15}H_{11}F_5N_2$ (314.26): calcd C 57.33 H 3.53 N 8.91; found C 57.22 H 3.51 N 8.77. UV−vis absorption ($CH_3CN$): 363 nm (37000).

**Pentakis[4-(dimethylamino)-1-pyridinio]benzaldehyde 4-Dimethylaminophenylimine Pentakis(triflate), 15.** Yield = 85%. $^1$H NMR (400 MHz, $CD_3NO_2$): $\delta$ = 3.07 (s, 6H, $CH_3$), 3.22 (s, 12H, $CH_3$), 3.26 (s, 6H, $CH_3$), 3.26 (s, 12H, $CH_3$), 6.66 (d, $^3J_{HH}$ = 9.2 Hz, 2H, H2/3/5/6 phenyl), 6.96 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H3/5 *p*-DMAP), 6.97 (d, $^3J_{HH}$ = 7.9 Hz, 4H, H3/5 DMAP), 6.98 (d, $^3J_{HH}$ = 8.2 Hz, 4H, H3/5 DMAP), 7.48 (d, $^3J_{HH}$ = 9.2 Hz, 2H, H2/3/5/6 phenyl), 8.23 (s, 1H, -N=CH-), 8.30 (m, 10H, H2/6 DMAP) ppm. $^{13}$C NMR (100 MHz, $CD_3NO_2$): $\delta$ = 40.32 (s, $CH_3$), 41.17 (s, $CH_3$), 41.35 (s, $CH_3$), 109.72 (s, C3/5 DMAP), 110.35 (s, C3/5 DMAP), 110.39 (s, C3/5 *p*-DMAP), 112.49 (s, C3/5 phenyl), 122.18 (q, $|^1J_{CF}|$ = 320 Hz, $CF_3$), 122.75 (s, C1/4 (onio-)phenyl), 131.61 (s, C1/4 (onio-)phenyl), 133.65 (s, C2/6 phenyl), 134.39 (s, C2/3/5/6 onio-phenyl), 139.29 (s, C2/3/5/6 onio-phenyl), 141.86 (s, C2/6 DMAP), 142.49 (s, C2/6 *p*-DMAP), 142.92 (s, C2/6 DMAP), 154.32 (s, C1/4 (onio-)phenyl), 156.10 (s, C1/4 (onio-)phenyl), 157.73 (s, C4 *p*-DMAP), 157.76 (s, C4 DMAP), 157.96 (s, C4 DMAP), 168.87 (s, -N=CH-) ppm. FAB MS (NBA): $m/z$ = 1425 [M − OTf]$^+$, 1275 [M − HOTf-OTf]$^+$, 1155 [M−$C_6H_4N(CH_3)_2$-DMAP − 2OTf]$^+$, 1021 [M−$CHC_6H_4N(CH_3)_2$-DMAP − 2OTf]$^+$. $C_{55}H_{61}F_{15}$-

$N_{12}O_{15}S_5$ (1575.44) + 2 $H_2O$: calcd C 40.99 H 4.07 N 10.43 S 9.95; found C 40.82 H 3.96 N 10.44 S 9.88. UV−vis absorption ($CH_3CN$): 415 nm (29000).

**4-Dimethylaminobenzaldehyde Pentakis[4-(dimethylamino)-1-pyridinio]phenylimine Pentakis(triflate), 16.** Yield = quant. $^1$H NMR (400 MHz, $CD_3NO_2$): $\delta$ = 3.00 (s, 6H, $CH_3$), 3.27 (s, 6H, $CH_3$), 3.28 (s, 12H, $CH_3$), 3.37 (s, 12H, $CH_3$), 6.61 (d, $^3J_H$−H = 9.4 Hz, 2H, H2/3/5/6 phenyl), 6.91 (d, $^3J_{HH}$ = 9.4 Hz, 2H, H2/3/5/6 phenyl), 6.97 (d, $^3J_{HH}$ = 7.7 Hz, 2H, H3/5 *p*-DMAP), 6.99 (d, $^3J_{HH}$ = 7.7 Hz, 4H, H3/5 DMAP), 7.11 (d, $^3J_{HH}$ = 7.7 Hz, 4H, H3/5 DMAP), 8.12 (s, 1H, -CH═N-), 8.27 (d, $^3J_{HH}$ = 8.2 Hz, 2H, H2/6 *p*-DMAP), 8.31 (d, $^3J_{HH}$ = 7.7 Hz, 4H, H2/6 DMAP), 8.37 (d, $^3J_{HH}$ = 7.7 Hz, 4H, H2/6 DMAP) ppm. $^{13}$C NMR (100 MHz, $CD_3NO_2$): $\delta$ = 40.46 (s, $CH_3$), 41.35 (s, $CH_3$), 41.41 (s, $CH_3$), 109.89 (s, C3/ 5 DMAP), 110.43 (s, C3/5 DMAP), 110.52 (s, C3/5 *p*-DMAP), 113.13 (s, C3/5 phenyl), 122.17 (q, $|^1J_{CF}|$ = 320 Hz, $CF_3$), 125.60 (s, C2/6 phenyl), 137.04 (s, C1/4 (onio-)phenyl), 137.98 (s, C1/4 (onio-)phenyl), 138.95 (s, C1/4 (onio-)phenyl), 140.14 (s, -CH═N-), 140.47 (s, C2/3/5/6 onio-phenyl), 141.15 (s, C2/3/5/6 onio-phenyl), 141.88 (s, C2/6 DMAP), 143.17 (s, C2/6 DMAP), 153.72 (s, C1/4 (onio-)phenyl), 157.75 (s, C4 DMAP), 158.26 (s, C4 DMAP) ppm. FAB MS (NBA): *m*/*z* = 1425 [M − OTf]$^+$, 1155 [M − $C_6H_4N(CH_3)_2$ − DMAP − 2OTf]$^+$, 1021 [M −$CHC_6H_4N(CH_3)_2$ − DMAP − 2OTf]$^+$. $C_{55}H_{61}F_{15}N_{12}O_{15}S_5$ (1575.44) + $H_2O$: calcd C 41.46 H 3.99 N 10.55 S 10.06; found C 41.29 H 3.75 N 10.49 S 9.89. UV−vis absorption ($CH_3CN$): 534 nm (28000).

**Pentakis[4-(dimethylamino)-1-pyridinio]-4-dimethylaminophenylstilbene Pentakis(triflate), 17.** Yield = 92%. $^1$H NMR (400 MHz, $CD_3NO_2$): $\delta$ = 2.98 (s, 6H, $CH_3$), 3.26 (s, 6H, $CH_3$), 3.27 (s, 12H, $CH_3$), 3.31 (s, 12H, $CH_3$), 6.28 (d, $^3J_H$ = 16.6 Hz, 1H, -CH═CH-), 6.60 (d, $^3J_{HH}$ = 9.0 Hz, 2H, H2/3/5/6 phenyl), 6.52 (d, $^3J_{HH}$ = 16.5 Hz, 1H, -CH═CH-), 6.96 (d, $^3J_{HH}$ = 6.6 Hz, 2H, H3/5 *p*-DMAP), 6.98 (d, $^3J_{HH}$ = 7.9 Hz, 4H, H3/5 DMAP), 7.08 (d, $^3J_{HH}$ = 8.1 Hz, 4H, H3/5 DMAP), 7.11 (d, $^3J_{HH}$ = 8.9 Hz, 2H, H2/3/5/6 phenyl), 8.23 (d, $^3J_{HH}$ = 8.1 Hz, 2H, H2/6 *p*-DMAP), 8.26 (d, $^3J_{HH}$ = 7.9 Hz, 4H, H2/6 DMAP), 8.32 (d, $^3J_{HH}$ = 7.9 Hz, 4H, H2/6 DMAP) ppm. $^{13}$C NMR (100 MHz, $CD_3NO_2$): $\delta$ = 40.29 (s, $CH_3$), 41.31 (s, $CH_3$), 41.38 (s, $CH_3$), 109.63 (s, -CH═CH-), 110.17 (s, C3/5 DMAP), 110.43 (s, C3/5 DMAP), 110.46 (s, C3/5 *p*-DMAP), 112.97 (s, C3/5 phenyl), 122.17 (q, $|^1J_{CF}|$ = 321 Hz, $CF_3$), 123.58 (s, C1/4 (onio-)phenyl), 130.56 (s, C2/6 phenyl), 135.34 (s, C1/4 (onio-)phenyl), 139.50 (s, C/3/5/6 onio-phenyl), 140.55 (s, C2/3/5/6 onio-phenyl), 141.78 (s, C2/6 DMAP), 142.02 (s,C2/6 *p*-DMAP), 142.78 (s,C2/6 DMAP), 144.04 (s, C1/4 (onio-)phenyl), 144.58 (s, -CH═CH-), 153.62 (s, C1/4 (onio-)phenyl), 157.71 (s, C4 DMAP), 158.00 (s, C4 DMAP) ppm. FAB MS (NBA): *m*/*z* = 1424 [M − OTf]$^+$, 1274 [M − HOTf − OTf]$^+$, 1154 [M − $C_6H_4N(CH_3)_2$ − HOTf − OTf]$^+$, 1020 [M − $CHC_6H_4N(CH_3)_2$ − DMAP − 2OTf]$^+$. $C_{56}H_{62}F_{15}N_{11}O_{15}S_5$ (1574.45) + 2 $H_2O$: calcd C 41.76 H 4.13 N 9.57 S 9.95; found C 41.58 H 3.97 N 9.21 S 10.00. UV−vis absorption ($CH_3CN$): 470 nm (24000).

**Acknowledgment.** Support of this research by the Deutsche Forschungsgemeinschaft (grants WE 599/ 9-1 and 599/9-2) is gratefully acknowledged.

JA064907U