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Depending on electronically or kinetically stabilizing effects determined by the substitution pattern or the reaction conditions, 6-amino substituted (5-chloropyrimidine-2,4-diyl)bis(hetarenium) salts or 5-chloro-2,6-bis-(pyridinio)-pyrimidin-4-aminides are formed on nucleophilic substitution of 4-(dimethylamino)pyridine, 4-(pyrrolidin-1-yl)pyridine, or 1-methylimidazole on 4-amino substituted 2,5,6-trichloropyrimidines.

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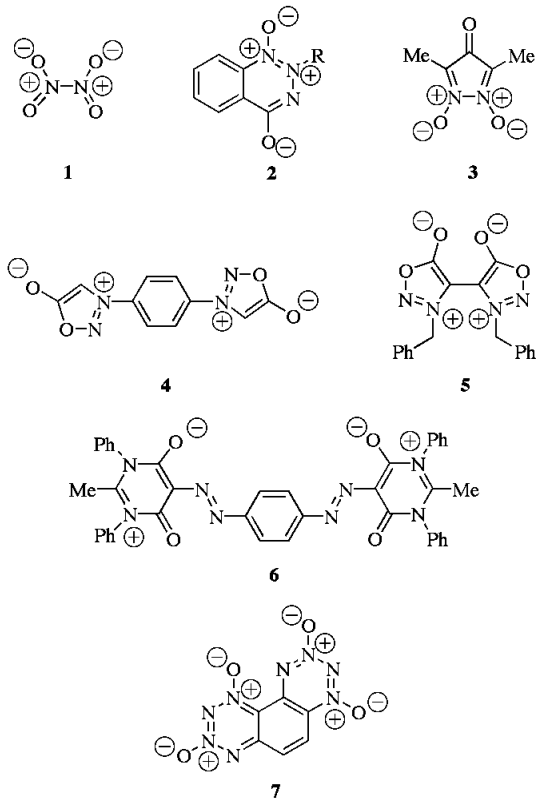
Introduction.

Mesomeric betaines are defined as neutral conjugated molecules which can be represented only by canonical formulae in which both the positive and negative charges are delocalized within the π-electron system [1]. This definition includes all types of synthetic and naturally occurring mesomeric betaines, *e.g.* ylids [2,3], *N*-oxides [4,5] as well as mesoions [6] and their subclasses sydnones [7] or münchnones [8]. Recently, multipolar substances such as dinitrogentetroxide **1** and the *N*,*N*-dioxides **2** [9] and **3** [10,11] have attracted considerable attention both from a synthetic and a theoretical point of view [12] (Scheme 1). Additional examples of tetrapolar substances are the conjugated disydnones **4** [13] and **5** [14], and the cross-conjugated bisbetaine **6** [15]. Very recently, the synthesis and characterization of the conjugated octapole **7** was described [16].

Scheme 1



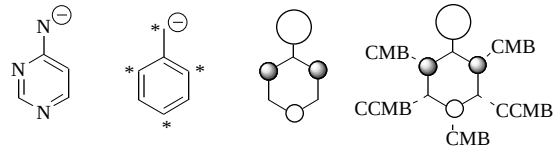
Taking the aforementioned definition into consideration, the tetrapoles **1** - **6** and the octapole **7** unambigously belong to the class of mesomeric betaines. They contain non-overlapped structure elements of one of the four major classes of mesomeric betaines, respectively, *i.e.* conjugated (CMB), cross-conjugated (CCMB), pseudo-cross-conjugated (PCCMB) mesomeric betaines and conjugated heterocyclic *N*-ylids [1]. They are neutral compounds as they possess an *even* number of positive and negative charges in conjugation or cross-conjugation. In contrast to that, molecules with an *odd* number of positive and negative charges form a distinct class of compounds, hybrids between mesomeric betaines and heteroarenium salts [17]. In continuation of our previous work on novel mesomeric betaines [18], heteroaromatic tripoles [19-21], and betainic nucleobases [22-24], we report here the synthesis and characterization of this class of betaines.

We focussed our interest on the unstable pyrimidinaminide moiety **I** as the anionic structure element and aimed at a stabilization of this system by two adjacent positive charges in cross-conjugation (Chart 1). 4-(Dimethylamino)pyridinium, 4-(pyrrolidin-1-yl)pyridinium and 3-methylimidazolium groups are known to stabilize highly reactive anions such as the ally anion [25]. As the target increment **I** is isoconjugate with the benzyl anion **II**, joining the cationic substituents to the two un-starred positions of **II** leads to cross-conjugation between the two charges [17,26]. These atoms are "inactive" nodal positions of the highest occupied molecular orbital (HOMO) **III** which prevent electron shifts to the lowest unoccupied molecular orbital (LUMO) in the ground state. Thus, for the case of cross-conjugation the positive and negatives charges are delocalized in separate parts of the common π-electron system. In contrast, substitution at one of the starred positions in the isoconjugate benzyl anion **II** would result in mesomeric betaines in which the charges are in mutual conjugation (CMB).

Results and Discussion.

Nucleophilic substitution of 4-(dimethylamino)pyridine and 4-(pyrrolidin-1-yl)pyridine on 4-amino-2,5,6-

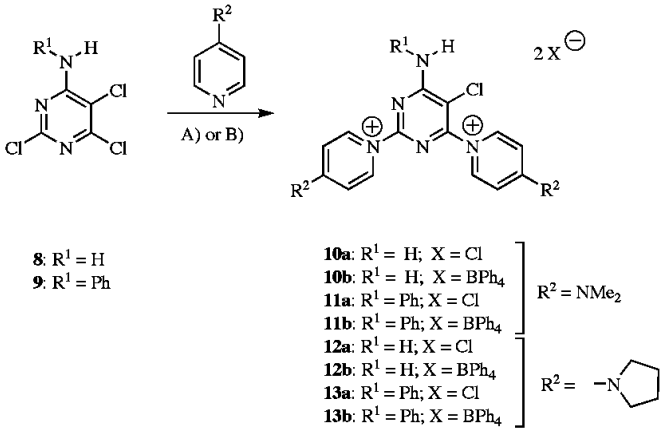
Chart 1



I **II** **III** **IV**

trichloropyrimidine (**8**) and 4-anilino-2,5,6-trichloropyrimidine (**9**) [27-30], respectively, in chlorobenzene resulted in the formation of the dichlorides **10a** – **13a** as colorless to slightly yellow solids (Scheme 2). Reaction of **8** and **9** with 4-(dimethylamino)pyridine and 4-(pyrrolidin-1-yl)pyridine in anhydrous ethyl acetate in the presence of stoichiometric amounts of sodium tetraphenylborate gave smoothly the 6-amino substituted (pyrimidine-2,4-diyl)dipyridinium bis(tetraphenylborates) **10b** – **13b**. No monosubstitution products were isolated. This is on the one hand due to the strong nucleophilicity of the heteroaromatics used, and on the other hand due to the disubstitution facilitating enhanced leaving group tendency of chlorine atoms in the presence of strongly electron-withdrawing groups attached to the pyrimidine rings [31]. The tetraphenylborate anion, known to be non-nucleophilic, non-hygroscopic, and kinetically stabilizing due to its steric bulkiness [32], proved to be valuable for our further investigations. One reason is the unambigous elucidation of the cation/anion ratio by integration of the ^{1}H NMR resonance frequencies.

Scheme 2



8: R^1 = H
9: R^1 = Ph

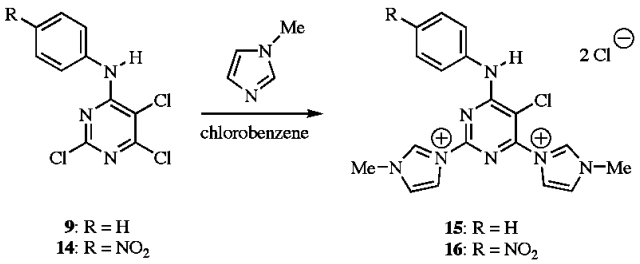
10a: R^1 = H; X = Cl
10b: R^1 = H; X = BPh_4
11a: R^1 = Ph; X = Cl
11b: R^1 = Ph; X = BPh_4
R^2 = NMe_2

12a: R^1 = H; X = Cl
12b: R^1 = H; X = BPh_4
13a: R^1 = Ph; X = Cl
13b: R^1 = Ph; X = BPh_4
R^2 = –N

Reaction conditions: A) chlorobenzene, reflux; B) sodium tetraphenylborate, ethyl acetate, reflux

Application of these reaction conditions to 1-methylimidazole as the heteroaromatic nucleophile proved to be less successful. 4-Amino-2,5,6-trichloropyrimidine (**8**) in chlorobenzene gave a glassy material, from which no characterizable compound was isolated. However, the 4-anilino substituted pyrimidine **9** and the 2,5,6-trichloro-4-(4-nitrophenylamino)-pyrimidine (**14**), respectively, gave the desired dicationic dichlorides **15** and **16** in good yields (Scheme 3). Treatment of **8** and **9**, respectively, with 1-methylimidazole in anhydrous ethyl acetate in the presence of sodium tetraphenylborate gave decomposition products.

Scheme 3



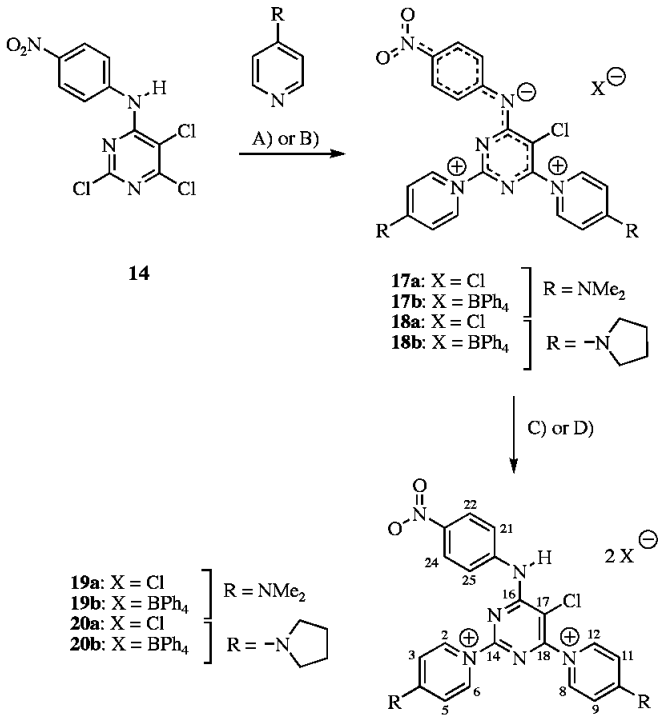
9: R = H
14: R = NO_2

15: R = H
16: R = NO_2

Surprisingly, reaction of 2,5,6-trichloro-4-(4-nitrophenylamino)pyrimidine (**14**) with an excess of 4-(dimethylamino)pyridine or 4-(pyrrolidin-1-yl)pyridine resulted in the formation of the target tripolar bispyridiniopyrimidinaminides **17a,b** and **18a,b** as intensely orange colored solids in one single step (Scheme 4). Two positive and one negative charge are delocalized in the cross-conjugated π-electron systems forming monocationic species which have one external anion, respectively. The monochlorides **17a** and **18a** were converted into the slightly yellow colored dicationic dichlorides **19a** and **20a** by treatment with dilute hydrochloric acid in ethanol, careful concentration *in vacuo* without heating, and slow crystallization on cooling. Similarly, the mono(tetraphenylborates) **17b** and **18b** were converted into the dicationic bis(tetraphenylborates) **19b** and **20b** by dilute hydrochloric acid followed by anion exchange of the resulting mixed salts with excess sodium tetraphenylborate in ethyl acetate.

Encouraged by these results, deprotonations of the dicationic species **10** - **13** to tripoles were attempted. The anion exchange resin Amberlite IRA-400 in its hydroxy form, however, was not able to deprotonate the solutions of the almost colorless dications **10a**-**13a** in aqueous ethanol into the corresponding intensily orange tripoles. Instead, anion exchange of the chlorides to the corresponding hydroxides presumably occurred which proved to be very unstable. Thus, ^{1}H nmr spectra of freshly prepared samples, which were solved under Argon in DMSO-d_6, essentially displayed no changes of the heterocyclic ring system. After a short period of time at room temperature, the nearly colorless solids turned to brown and decomposition products could be detected spectroscopically. Tripole formation starting from the 4-anilino derivatives was finally accomplished by treatment of the tetraphenylborates **11b** and **13b** in a mixture of acetonitrile and ethanol with the non-nucleophilic

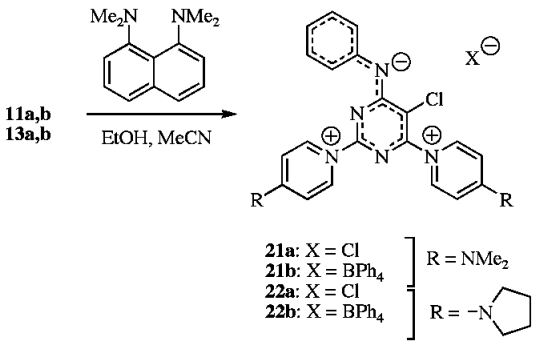
Scheme 4



Reaction conditions: A) chlorobenzene, reflux; B) sodium tetraphenylborate, ethyl acetate, reflux; C) for **19a**, **20a**: HCl, ethanol; D) for **19b**, **20b**: 1. HCl, ethanol, 2. $NaBPh_4$, ethyl acetate

1,8-dimethylaminonaphthalene (DMAN, proton sponge) which is known to be one the strongest organic bases (pK_a 12.34 [33]; proton affinity in the gas phase: 242 Kcal/mol [34]). The tripolar tetraphenyborates **21b** and **22b** were isolated after careful crystallization as intensely orange colored compounds (Scheme 5). The orange chlorides **21a** and **22a** and the 2,6-bisimidazolio-pyrimidine-4-(4-nitrophenyl)aminides prepared analogously starting from **15** and **16** decomposed rapidly and could therefore not be characterized. The color of solutions of the *N*-unsubstituted salts **10** and **12** remained unchanged on addition of proton sponge and no changes in the nmr spectra were detectable.

Scheme 5



In accord with the cross-conjugation between the pyridinium rings and the anionic moiety of the molecules, the ^1H nmr resonance frequencies of the pyridinium rings of the dicationic salts are relatively unaffected on conversion into the corresponding tripoles, whereas all signals of the phenyl rings shift upfield due to the diminished overall charge of the betaines. Correspondingly, the NH resonance frequencies at 10.48 – 10.91 ppm disappear on betaine formation. Table 1 summarizes the characteristic chemical shift changes. Unambigous structure elucidation is moreover possible by determining the cation:anion ratio of the tetraphenylborates. Thus, the ^1H nmr spectra of **17b**, **18b**, **21b**, and **22b** clearly show the presence of one tetraphenylborate anion despite the presence of two pyridinium rings in the molecules, respectively. In the ^{13}C nmr spectra, a characteristic upfield shift of C(5) of the pyrimidine ring is observable on betaine formation (spectroscopic numbering: C(17), *cf.* Scheme 4).

Table 1

^1H nmr Chemical Shift Changes $\Delta\delta$[ppm] of the Protons of the Phenyl Substituents on Protonation of the Tripoles to the Bispyridinium Salts

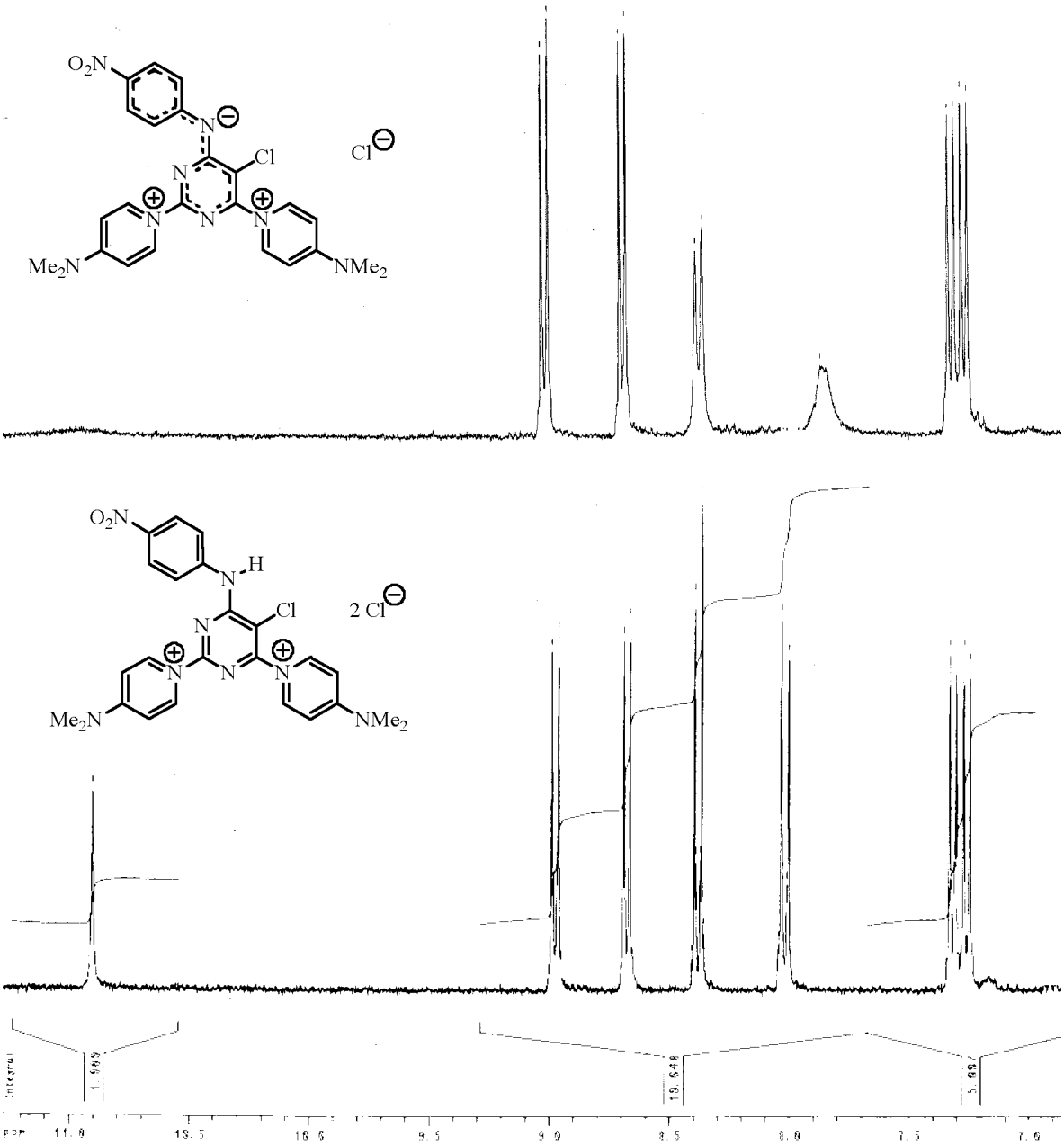
	o-H	*m*-H	β-H
17a → **19a**	+0.23	+0.08	+0.07
18a → **20a**	+0.12	+0.02	+0.01
17b → **19b**	+0.69	+0.25	+0.12
18b → **20b**	+0.70	+0.27	+0.19

Our findings concerning the stability of the pyrimidinaminide **I** (Chart 1) are in well accord to *Kröhnke´*s rule which originally predicted increasing stabilization of *N*-ylids and related betaines with increasing number of atoms involved in the negative charge delocalization [3,35]. Thus, the pyrimidinaminide must be stabilized by at least two strongly electron-withdrawing substituents, the pyridinium rings at C(2) and C(4) of pyrimidine, and an additional phenyl ring at the aminide nitrogen atom for the negative charge delocalization. In addition, either kinetic stabilization by the bulky tetraphenylborate anion, or electronic stabilization by a nitro group at the phenyl ring is necessary. As a consequence, the stabilizing phenyl ring at the aminide nitrogen atom must adopt the *Z*-configuration, because *E*-configuration caused a considerable steric hindrance to the chlorine atom at C(5) of the pyrimidine ring and reduced *p*-overlap due to the resulting nonplanarity of the anionic part of the tripoles. The *Z*-configuration is confirmed by ^1H nmr spectroscopy. As shown in Chart 2, due to the magnetic non-equivalency of the *o*-protons of the phenyl rings, their signals are considerably broadened.

EXPERIMENTAL

The ^1H nmr and ^{13}C nmr spectra were recorded on a Bruker ARX 300 (300 MHz) in dimethylsulfoxide-d_6 referenced to

Chart 2



TMS. The ir spectra were taken on a Nicolet 205 in the range of 400 – 4000 cm^{-1} (2.5% pellets in KBr). The fast atom bombardement mass spectra (fabms) were performed on an AMD-40/AMD Intectra GmbH Harpstedt spectrometer. The elemental analyses were performed on a CHNS-932 analyzer (LECO) and in the laboratory for elemental analyses of the Institute of Chemistry and Biochemistry of the University of Greifswald, Germany. In accordance with known hetarenium compounds [17-25] and X-ray crystallographic results of related systems [18-20, 23], all substances crystallized with considerable amounts of water. Dried compounds (80 °C *in vacuo*) rapidely picked up water during weighing. The melting points were determined on a Boëtius melting point apparatus and are not corrected.

General Procedure for the Preparation of the 6-Amino Substituted 1,1'-(5-Chloropyrimidine-2,4-diyl)-bishetarenium dichlorides (**10a**), (**11a**), (**12a**), and (**13a**).

A suspension of 4-amino-2,5,6-trichloropyrimidine (**8**) (0.50 g, 2.5 mmol) and 4-anilino-2,5,6-trichloropyrimidine (**9**) (0.69 g, 2.5 mmol), respectively, in 100 mL of chlorobenzene was treated with 4-(dimethylamino)pyridine (0.73 g, 6.0 mmol) or 4-(pyrrolidin-1-yl)pyridine (0.89 g, 6.0 mmol) and heated at reflux temperature over the period of 1 hour. After cooling, the precipitates were collected by filtration, washed with ethyl acetate and recrystallized.

1,1'-(6-Amino-5-chloro-pyrimidine-2,4-diyl)-bis-[4-(dimethylamino)pyridinium] dichloride (**10a**).

Recrystallization from ethanol yielded 0.99 g (77%) of this colorless solid, mp 265 – 269 °C; ir 3349.1, 3068.2, 1648.0 cm^{-1}; ^1H nmr: δ 3.37 (s, 12H, 19-H, 20-H, 21-H, 22-H), 7.29 (dd, 4H, J = 8.0/7.8 Hz, 3-H, 5-H, 9-H, 11-H), 8.63 (d, 2H, J = 7.8 Hz, 8-H, 12-H), 9.01 (d, 2H, J = 8.0 Hz, 2-H, 6-H); fabms: *m/z* 373.1 (M^+ + 2H), 372.1 (M^+ +H), 371.1 (M^+), 355.0 (M^+ - NH_2), 249.7 (M^+ - DMAP).

Anal. Calcd. for $C_{18}H_{22}Cl_3N_7 \cdot 4H_2O$: C, 41.99; H, 5.87; N, 19.04. Found: C, 42.12; H, 5.90; N, 19.30.

1,1'-(6-Anilino-5-chloropyrimidine-2,4-diyl)-bis-[4-(dimethylamino)pyridinium] dichloride (**11a**).

Recrystallization from ethanol furnished 0.88 g (54%) of this colorless solid, decomposition > 224 °C; ir: 3068.1, 1651.1 cm^{-1}; ^1H nmr: δ 3.32 (s, 6H, 28-H, 29-H), 3.35 (s, 6H, 26-H, 27-H), 7.41 (m, 9H, 3-H, 5-H, 9-H, 11-H, 21-H, 25-H), 8.63 (d, 2H, J = 8.1 Hz, 8-H, 12-H), 8.87 (d, 2H, J = 8.1 Hz, 2-H, 6-H), 10.48 (s, 1H, NH); fabms: *m/z* 447.1 (M^+), 123.3.

Anal. Calcd. for $C_{24}H_{26}Cl_3N_7 \cdot 3H_2O$: C, 50.31; H, 5.63; N, 17.11. Found: C, 50.01; H, 5.86; N, 16.02.

1,1'-(6-Amino-5-chloropyrimidine-2,4-diyl)-bis-[4-(pyrrolidin-1-yl)pyridinium] dichloride (**12a**).

Recrystallization from ethanol furnished 0.63 g (53%) of this colorless solid, decomposition > 240 °C; ir: 3081.4, 3080.4, 2981.9, 1650.6, 1591.6, 1573.8 cm^{-1}; ^1H nmr: δ 2.05 (m, 8H, 21-H, 22-H, 26-H, 27-H), 3.68 (m, 8H, 20-H, 23-H, 25-H, 28-H), 7.11 (m, 4H, 3-H, 5-H, 9-H, 11-H), 8.61 (d, J = 7.8 Hz, 2H, 8-H, 12-H), 9.01 (d, J = 8.1 Hz, 2H, 2-H, 6-H); fabms: *m/z* 424.1 (M^+), 149.6.

Anal. Calcd. for $C_{22}H_{26}Cl_3N_7 \cdot 6H_2O$: C, 43.83; H, 6.35; N, 16.26. Found: C, 43.76; H, 6.22; N, 16.32.

1,1'-(6-Anilino-5-chloropyrimidine-2,4-diyl)-bis-[4-(pyrrolidin-1-yl)pyridinium] dichloride (**13a**).

Recrystallization from ethanol yielded 1.34 g (77%) of a slightly yellow solid, mp > 300 °C; ir: 1650.3, 1609.3, 1575.3, 1408.4, 1386.7, 1212.0, 1162.8 cm^{-1}; ^1H nmr: δ 2.08 (m, 8H, 33-H, 34-H), 3.68 (m, 8H, 28-H, 29-H), 7.09 (d, J = 8.1 Hz, 2H, 3-H, 5-H), 7.15 (d, J = 7.9 Hz, 2H, 9-H, 11-H), 7.34 (tt, J = 8.3/1.1 Hz, 1H, 23-H), 7.52 (t, J = 8.3 Hz, 2H, 22-H, 24-H), 7.63 (dd, J = 8.3/1.3 Hz, 2H, 21-H, 25-H), 8.65 (d, J = 7.9 Hz, 2H, 8-H, 12-H), 8.89 (d, J = 8.1 Hz, 2H, 2-H, 6-H), 10.49 (s, 1H, NH); ^{13}C nmr: δ 24.55 (C-33, C-34), 24.60 (C-28, C-29), 49.26 (C-32, C-35), 49.42 (C-27, C-30), 105.92 (C-17), 108.29 (C-9, C-11), 108.73 (C-3, C-5), 124.21 (C-21, C-25), 126.13 (C-23), 128.94 (C-22, C-24), 136.42 (C-8, C-12), 136.96 (C-20), 140.40 (C-2, C-6), 151.42 (C-10), 153.81 (C-14), 154.48 (C-18), 159.26 (C-16); fabms: *m/z* 499.3 (M^+), 149.4.

Anal. Calcd. for $C_{28}H_{30}Cl_3N_7 \cdot 7H_2O$: C, 48.24; H, 6.36; N, 14.07. Found: C, 48.44; H, 6.13; N, 14.39.

General Procedure for the Preparation of the 6-Amino Substituted 1,1'-(5-Chloropyrimidine-2,4-diyl)-bishetarenium bis(tetraphenylborates) (**10b**), (**11b**), (**12b**), and (**13b**).

A suspension of 4-amino-2,5,6-trichloropyrimidine (**8**) (0.50 g, 2.5 mmol) and 4-anilino-2,5,6-trichloropyrimidine (**9**) (0.69 g, 2.5 mmol), respectively, in 150 mL of anhydrous ethyl acetate was treated with 4-(dimethylamino)pyridine (0.63 g, 5.2 mmol) or 4-(pyrrolidin-1-yl)pyridine (0.77 g, 5.2 mmol) and 1.77 g (5.2 mmol) of sodium tetraphenylborate, and then heated at reflux temperature over the period of 1 hour. After cooling, the precipitates were collected by filtration, washed with 50 mL of ethyl acetate and recrystallized.

1,1'-(6-Amino-5-chloropyrimidine-2,4-diyl)-bis-[4-(dimethylamino)pyridinium] Bis(tetraphenylborate) (**10b**).

Recrystallization from ethanol yielded 1.60 g (63%) of this colorless solid, decomposition > 171 °C; ir: 3331.0, 3054.7, 1651.1, 1620.4, 1579.5, 1553.3, 1426.5, 1369.7, 1165.2, 735.5, 707.7 cm^{-1}; ^1H nmr: δ 3.34 (12H, 19-H, 20-H, 21-H, 22-H), 6.78 (t, J = 7.2 Hz, 8H, BPh_4), 6.91 (t, J = 7.2 Hz, 16H, BPh_4), 7.16 (m, 18H, 9-H, 11-H, BPh_4), 7.24 (d, J = 7.9 Hz, 2H, 3-H, 5-H), 8.58 (d, J = 7.8 Hz, 2H, 8-H, 12-H), 8.90 (d, J = 7.9 Hz, 2H, 2-H, 6-H); fabms: *m/z* 371.0 (M^+), 42.1.

Anal. Calcd. for $C_{66}H_{62}B_2ClN_7 \cdot 0.5\ H_2O$: C, 77.77; H, 6.23; N, 9.62. Found: C, 77.49; H, 6.44; N, 8.95.

1,1'-(6-Anilino-5-chloropyrimidine-2,4-diyl)-bis-[4-(dimethylamino)pyridinium] Bis(tetraphenylborate) (**11b**).

Recrystallization from ethanol yielded 1.68 g (61%) of this colorless solid, mp 138 °C; ir (KBr) 3054.6, 1651.6, 1608.9, 1579.0, 1425.1, 1397.5, 1366.7, 1217.6, 1161.3, 734.5, 706.9 cm^{-1}; ^1H nmr: δ 3.32 (s, 6H, 28-H, 29-H), 3.35 (s, 6H, 26-H, 27-H), 6.78 (t, J = 7.2 Hz, 8H, BPh_4), 6.92 (t, J = 7.2 Hz, 16H, BPh_4), 7.16 (m, 16H, BPh_4), 7.19 (t, overlapped, 23-H), 7.24 (d, J = 7.9 Hz, 2H, 9-H, 11-H), 7.34 (d, overlapped, 3-H, 5-H), 7.51 (t, J = 7.6 Hz, 2H, 22-H, 24-H), 7.63 (d, J = 7.6 Hz, 2H, 21-H, 25-H), 8.65 (d, J = 7.9 Hz, 2H, 8-H, 12-H), 8.86 (d, J = 8.1 Hz, 2H, 2-H, 6-H), 10.52 (s, 1H, NH); ^{13}C nmr: 40.36 (C-28, C-29), 40.44 (C-26, C-27), 106.32 (C-17), 107.41 (C-9, C-11), 107.75 (C-3, C-5), 121.42 (BPh_4), 123.97 (C-21, C-25), 125.22 (BPh_4), 125.43 (C-23), 128.71 (C-22, C-24), 135.43 (BPh_4), 136.23 (C-8, C-12), 138.44 (C-20), 140.36 (C-2, C-6), 151.14 (C-10), 153.88 (C-4), 156.57 (C-14), 157.23 (C-18), 158.70 (C-16), 163.28 (q, J_{CB} = 49.8 Hz, BPh_4);fabms: *m/z* = 447.4 (M^+), 325.8 (M^+ - DMAP), 41.3.

Anal. Calcd. for $C_{72}H_{66}B_2ClN_7 \cdot H_2O$: C, 78.30; H, 6.21; N, 8.87. Found: C, 77.98; H, 6.40; N, 9.05.

1,1'-(6-Amino-5-chloropyrimidine-2,4-diyl)-bis-[4-(pyrrolidin-1-yl)pyridinium] Bis(tetraphenylborate) (**12b**).

Recrystallization from ethanol gave 1.82 g (59%) of this colorless solid, mp 239 – 241 °C; ir: 3359.3, 3054.7, 1651.0, 1620.7, 1576.2, 1414.7, 1371.1, 1341.7, 1169.8, 735.7 cm^{-1}; ^1H nmr: δ 2.04 (m, 8H, 21-H, 22-H, 26-H, 27-H), 3.65 (m, 8H, 20-H, 23-H, 26-H, 27-H), 6.78 (t, J = 7.2 Hz, 8H, BPh_4), 6.92 (t, J = 7.2 Hz, 16H, BPh_4), 7.16 (m, 20H, BPh_4, 3-H, 5-H, 9-H, 11-H), 8.58 (d, J = 7.6 Hz, 2H, 8-H, 12-H), 9.00 (d, J = 7.9 Hz, 2H, 2-H, 6-H); fabms: *m/z* 423.9 (M^+), 55.2.

Anal. Calcd. for $C_{70}H_{66}B_2ClN_7 \cdot 9.5H_2O$: C, 68.15; H, 6.17; N, 7.94. Found: C, 68.33; H, 5.83; N, 7.98.

1,1'-(6-Anilino-5-chloropyrimidine-2,4-diyl)-bis-[4-(pyrrolidin-1-yl)pyridinium] dichloride (**13b**).

Recrystallization from ethanol yielded 0.77 g (54%) of this colorless solid, mp 239 – 243 °C; ir: 3054.1, 2983.3, 1652.2, 1606.5, 1576.8, 1427.2, 1411.7, 1368.5, 1212.5, 1166.2, 734.7, 706.1 cm^{-1}; ^1H nmr: δ 2.03 (m, 8H, 33-H, 34-H), 3.64 (m, 8H, 28-H, 29-H), 6.78 (t, J = 7.2 Hz, 8H, BPh_4), 6.92 (t, J = 7.2 Hz,

16H, BPh_4), 7.05 (d, J = 7.8 Hz, 2H, 9-H, 11-H), 7.11 (d, J = 8.1 Hz, 2H, 3-H, 5-H), 7.16 (m, 16H, BPh_4), 7.33 (t, J = 7.5 Hz, 1H, 23-H), 7.50 (t, J = 7.5 Hz, 2H, 22-H, 24-H), 7.61 (d, J = 7.5 Hz, 2H, 21-H, 25-H), 8.59 (d, J = 7.8 Hz, 2H, 8-H, 12-H), 8.86 (d, J = 8.1 Hz, 2H, 2-H, 6-H), 10.44 (s, 1H; NH); fabms: *m/z* 499.3 (M^++1), 149.4.

Anal. Calcd for $C_{76}H_{70}B_2ClN_7 \cdot 10H_2O$: C, 69.22; H, 6.88; N, 7.46. Found: C, 69.16; H, 5.35; N, 6.41.

General Procedure for the Preparation of the 6-Amino Substituted 1,1'-(5-Chloropyrimidine-2,4-diyl)-bis-(3-methylimidazolium) Dichlorides (**15**) and (**16**).

A suspension of 4-anilino-2,5,6-trichloropyrimidine (**9**) (0.69 g, 2.5 mmol) and 0.80 g (2.5 mmol) of 2,5,6-trichloro-4-(4-nitranilino)pyrimidine (**14**), respectively, and 0.49 g of 1-methylimidazole in 100 mL of chlorobenzene was heated at reflux temperature over the period of 1 hour. After cooling, the precipitate was collected by filtration and washed with ethyl acetate.

1,1'-(6-Anilino-5-chloropyrimidine-2,4-diyl)-bis-(3-methylimidazolium) Dichloride (**15**).

Recrystallization from ethanol yielded 0.67 g (56%) of compound (**15**), mp 254 °C; ir: 3075.4, 1621.3, 1578.9, 1538.4, 1518.9, 1442.9, 1064.4, 767.7, 761.0, 616.4 cm^{-1}; ^{1}H nmr: δ 4.01 (s, 3H, 25-H), 4.10 (s, 3H, 24-H), 7.32 (t, J = 7.5 Hz, 1H, 21-H), 7.51 (t, J = 8.1 Hz, 2H, 20-H, 22-H), 7.69 (d, J = 7.5 Hz, 2H, 19-H, 23-H), 7.98 (m, 1H, 9-H), 8.11 (m, 4-H), 8.28 (m, 1H, 10-H), 8.62 (m, 1H, 5-H), 10.23 (s, 1H, 7-H), 10.48 (s, 1H, 2-H), 10.53 (s, 1H, NH); ^{13}C nmr: δ 36.66 (C-24, C-25), 104.25 (C-15), 118.92 (C-9), 121.76 (C-4), 123.76 (C-19, C-23), 124.13 (C-10)*, 125.11 (C-21)*, 125.86 (C-4)*, 128.81 (C-20, C-22), 136.73 (C-2, C-7), 138.42 (C-18), 148.55 (C-12), 148.71 (C-16), 159.58 (C-14), *: peak assignments exchangeable.

Anal. Calcd. for $C_{18}H_{18}Cl_3N_7 \cdot 2.5H_2O$: C, 44.68; H, 4.79; N, 20.26. Found: C, 44.79; H, 4.79; N, 20.41.

1,1'-[5-Chloro-6-(4-nitrophenylamino)pyrimidin-2,4-diyl]-bis-(3-methylimidazolium) Dichloride (**16**).

Recrystallization from ethanol furnished 0.59 (49%) of this slightly yellow solid, mp 278 – 280 °C; ir 1621.5; 1594.2, 1575.2, 1510.0, 1420.2, 1444.6, 1420.2, 1340.8, 1241.6, 1064.8, 930.7, 855.6, 770.7, 749.9, 610.5 cm^{-1}; ^{1}H nmr: δ 4.05 (s, 3H, 25-H), 4.10 (s, 3H, 24-H), 8.02 (s, 1H, 9-H), 8.05 (d, J = 9.0 Hz, 2H, 19-H, 23-H), 8.12 (s, 1H, 4-H), 8.38 (d, J = 9.0 Hz, 2H, 20-H, 22-H), 8.47 (s, 1H, 10-H), 8.64 (s, 1H, 5-H) 10.31 (s, 1H, 7-H), 10.53 (s, 1H, 2-H), 10.88 (s, 1H, NH); ^{13}C nmr: δ 36.63 (C-24, C-25), 105.63 (C-15), 119.18 (C-9), 121.82 (C-4), 123.31 (C-19, C-23), 124.20 (C-10), 124.59 (C-20, C-22), 125.16 (C-4), 136.82 (C-7), 138.40 (C-2), 143.57 (C-18), 148.43 (C-12), 149.12 (C-16), 159.29 (C-14).

Anal. Calcd. for $C_{18}H_{17}Cl_3N_8O_2$: C, 40.20; H, 4.31; N, 20.84. Found: C, 39.92; H, 4.17; N, 20.67.

5-Chloro-2,6-bis-[(4-dimethylamino)pyridinio)]-pyrimidine-4-(4-nitrophenyl)aminide Chloride (**17a**).

A suspension of 4-(nitrophenylamino)-2,5,6-trichloropyrimidine (**14**) (0.80 g, 2.5 mmol) and 4-(dimethylamino)pyridine (0.73, 6.0 mmol) in 100 mL of chlorobenzene was heated at reflux temperature over the period of 1 hour. After cooling, the precipitate was collected by filtration, washed with ethyl acetate and recrystallized from ethanol to furnish 0.69 g (45%) of the tripole (**17a**), mp > 300 °C; ir: 1650.8, 1582.4, 1509.2, 1398.3, 1351.0, 1330.4, 1225.9, 1159.7 cm^{-1}; ^{1}H nmr: δ 3.29 (s, 6H, 28-H, 29-H), 3.32 (s, 6H, 26-H, 27-H), 7.19 (d, J = 8.2 Hz, 2H, 3-H, 5-H), 7.25 (d, J = 8.0 Hz, 2H, 9-H, 11-H), 7.79 (br d, 2H, 21-H, 25-H), 8.29 (d, J = 8.8 Hz, 2H, 22-H, 24-H), 8.61 (d, J = 8.0 Hz, 2H, 8-H, 12-H), 8.93 (d, J = 8.2 Hz, 2H, 2-H, 6-H); ^{13}C nmr: δ 40.65 (C-28, C-29), 40.73 (C-26, C-27), 107.67 (C-9, C-11), 108.04 (C-3, C-5), 123.69 (C-21, C-25), 124.79 (C-22, C-24), 136.79 (C-8, C-12), 140.55 (C-2, C-6), 151.43 (C-10), 156.88 (C-14), 157.55 (C-18), 159.00 (C-16); fabms: *m/z* 494.6 (M^++2H), 493.6 (M^++H), 492.6 (M^+), 371.0 (M^+-DMAP).

Anal. Calcd. for $C_{24}H_{24}Cl_2N_8 \cdot 5H_2O$: C, 46.68; H, 5.55; N, 18.14. Found: C, 46.29; H, 5.58; N, 17.58.

5-Chloro-2,6-bis-[(4-dimethylamino)pyridinio]-pyrimidine-4-(4-nitrophenyl)aminide Tetraphenylborate (**17b**).

A suspension of 4-(4-nitrophenylamino)-2,5,6-trichloropyrimidine (**14**) (0.80 g, 2.5 mmol), 4-(dimethylamino)pyridine (0.73 g, 6.0 mmol) and 1.77 g (5.2 mmol) of sodium tetraphenylborate in 150 mL of anhydrous ethyl acetate was heated at reflux temperature over the period of 1 hour. After cooling, the precipitate was collected by filtration, washed with ethyl acetate and recrystallized from ethanol to yield 1.05 g (52%) of an intensely orange colored solid, mp 127 °C; ir: 1650.6, 1609.2, 1578.3, 1479.5, 1426.6, 1392.3, 1216.0, 1152.8, 743.6, 707.9 cm^{-1}; ^{1}H nmr: δ 3.25 (s, 6H, 28-H, 29-H), 3.28 (s, 6H, 26-H, 27-H), 6.78 (t, J = 7.2 Hz, 4H, BPh_4), 6.92 (t, J = 7.2 Hz, 8H, BPh_4), 7.17 (m, 12H, BPh_4, 3-H, 5-H, 9-H, 11-H), 7.33 (d, J = 9.0 Hz, 2H, 21-H, 25-H), 8.13 (d, J = 9.0 Hz, 2H, 22-H, 24-H), 8.57 (d, J = 8.0 Hz, 2H, 8-H, 12-H), 8.89 (d, J = 8.3 Hz, 2H, 2-H, 6-H); fabms: *m/z* 447.5 (M^++1), 41.2.

Anal. Calcd. for $C_{48}H_{44}BClN_8O_2 \cdot 5H_2O$: C, 63.96; H, 6.04; N, 12.43. Found: C, 63.53; H, 5.32; N, 12.30.

5-Chloro-2,6-bis-[4-(pyrrolidin-1-yl)pyridinio)]-pyrimidine-4-(4-nitrophenyl)aminide Chloride (**18a**).

A suspension of 4-(4-nitrophenylamino)-2,5,6-trichloropyrimidine (**14**) (0.80 g, 2.5 mmol) and 4-(pyrrolidin-1-yl)pyridine (0.89 g, 6.0 mmol) in 100 mL of chlorobenzene was heated at reflux temperature over the period of 1 hour. After cooling, the precipitate was collected by filtration, washed with ethyl acetate and recrystallized from ethanol to furnish 1.13 g (78%), mp > 220 °C; ir: 3085.3, 2975.6, 1651.7, 1618.6, 1579.8, 1504.0, 1406.4, 1337.0, 1214.7, 1163.1, 855.9, 829.5 cm^{-1}; ^{1}H nmr: δ 2.06 (m, 8H, 33-H, 34-H), 3.67 (m, 8H, 28-H, 29-H), 7.07 (d, J = 8.1 Hz, 2H, 3-H, 5-H), 7.12 (d, J = 7.9 Hz, 2H, 9-H, 11-H), 7.93 (br d, 2H, 21-H, 25-H), 8.33 (d, J = 9.0 Hz, 2H, 22-H, 24-H), 8.63 (d, J = 7.9 Hz, 2H, 8-H, 12-H), 8.97 (d, J = 8.1 Hz, 2H, 2-H, 6-H).

Anal. Calcd. for $C_{28}H_{28}Cl_2N_8O_2 \cdot 5.5H_2O$: C, 49.56; H, 5.79; N, 16.51. Found: C, 49.16; H, 5.41; N, 16.62.

5-Chloro-2,6-bis-[4-(pyrrolidin-1-yl)pyridinio]-pyrimidine-4-(4-nitrophenyl)aminide Tetraphenylborate (**18b**).

A suspension of 4-(4-nitrophenylamino)-2,5,6-trichloropyrimidine (**14**) (0.80 g, 2.5 mmol), 4-(pyrrolidin-1-yl)pyridine (0.89 g, 6.0 mmol) and 1.77 g (5.2 mmol) of sodium tetraphenylborate in 150 mL of anhydrous ethyl acetate was heated at reflux temperature over the period of 1 hour. After cooling, the precipitates were collected by filtration, washed with ethyl acetate and recrystallized from ethanol to furnish 1.38 g (64%) of a colorless solid,

mp 245 – 251 °C; ir: 1650.7, 1606.2, 1571.9, 1514.8, 1407.8, 1304.1, 1241.2, 1155.3, 1108.3 cm^{-1}; ^1H nmr: δ 2.03 (m, 8H, 33-H, 34-H), 3.61 (m, 8H, 28-H, 29-H), 6.77 (t, J = 7.2 Hz, 4H, BPh_4), 6.91 (t, J = 7.2 Hz, 8H, BPh_4), 6.98 (d, J = 8.0 Hz, 2H, 3-H, 5-H), 7.03 (d, J = 7.8 Hz, 2H, 9-H, 11-H), 7.16 (m, 8H, BPh_4), 7.33 (d, J = 9.1 Hz, 2H, 21-H, 25-H), 8.12 (d, J = 9.1 Hz, 2H, 22-H, 24-H), 8.55 (d, J = 7.8 Hz, 2H, 8-H, 12-H), 8.90 (d, J = 8.0 Hz, 2H, 2-H, 6-H); ^{13}C nmr: δ 24.75 (C-28, C-29, C-33, C-34), 49.06 (C-27, C-30, C-32, C-35), 108.03 (C-9, C-11), 108.24 (C-3, C-5), 110.13 (C-17), 121.69 (BPh_4), 123.16 (C-21, C-25), 124.70 (C-22, C-24), 125.47 (BPh_4), 135.64 (C-8, C-12), 136.61 (C-20), 140.12 (C-2, C-6), 140.94 (C-4), 151.57 (C-10), 152.43 (C-23), 153.79 (C-14), 154.54 (C-18), 157.83 (C-16), 163.47 (q, J_{CB} = 49.8 Hz); fabms: *m/z* 544.5 (M^+), 55.1.

Anal. Calcd. for $C_{52}H_{48}BClN_8O_2$: C, 72.35; H, 5.60; N, 12.98. Found: C, 71.89; H, 5.78; N, 12.96.

1,1'-[5-Chloro-6-(4-nitrophenylamino)pyrimidine-2,4-diyl]-bis-[4-(dimethylamino)pyridinium] Dichloride (**19a**).

A solution of the salt **17a** (0.31 g, 0.5 mmol) in 150 mL of ethanol was treated with 10 mL of 10% hydrochlorid acid. After concentrating the solution *in vacuo* and crystallization overnight at 8 °C, the resulting precipitate was recrystallized from ethanol to furnish the dichloride **19a** (95%) as slightly yellow crystals, decomposition > 240 °C; ir 1650.5, 1581.3, 1509.0, 1398.8, 1369.2, 1333.2, 1222.3, 1160.5 cm^{-1}; ^1H nmr: δ 3.37 (s, 6H, 28-H, 29-H), 3.41 (s, 6H, 26-H, 27-H), 7.26 (d, J = 8.1 Hz, 2H, 3-H, 5-H), 7.32 (d, J = 8.1 Hz, 2H, 9-H, 11-H), 8.02 (d, J = 9.3 Hz, 2H, 21-H, 25-H), 8.37 (d, J = 9.3 Hz, 2H, 22-H, 24-H), 8.67 (d, J = 8.1 Hz, 2H, 8-H, 12-H), 8.97 (d, J = 8.1 Hz, 2H, 2-H, 6-H), 10.91 (s, 1H, NH).

Anal. Calcd. for $C_{24}H_{25}Cl_3N_8O_2 \cdot 4H_2O$: C, 45.33; H, 5.23; N, 17.62. Found: C, 45.55; H, 5.48; N, 17.54.

1,1'-[5-Chloro-6-(4-nitrophenylamino)pyrimidine-2,4-diyl]-bis-[4-(dimethylamino)pyridinium] Bis(tetraphenylborate) (**19b**).

A solution of 0.40 g (0.5 mmol) of the betainium salt **17b** in 150 mL of ethanol was treated with 1 mL of 10% hydrochloric acid and then evaporated to dryness. The residue was dissolved in 500 mL of ethyl acetate, treated with 0.34 g (1.0 mmol) of sodium tetraphenylborate and concentrated *in vacuo*. After cooling overnight a slightly yellow precipitate crystallized which was collected by filtration and recrystallized from ethanol. Yield: 94%; mp 159 – 161 °C; ir: 3054.9, 1651.8, 1617.4, 1581.2, 1512.8, 1398.1, 1369.0, 1335.0, 1218.1, 1161.7, 743.0, 734.6, 707.1, 612.9 cm^{-1}; ^1H nmr: δ 3.35 (s, 12H, 28-H, 29-H), 6.78 (t, J = 7.2 Hz, 8H, BPh_4), 6.92 (t, J = 7.2 Hz, 16H, BPh_4), 7.16 (m, 16H, BPh_4), 7.23 (d, J = 8.1 Hz, 2H, 9-H, 11-H), 7.29 (d, J = 8.1 Hz, 2H, 3-H, 5-H), 8.02 (d, J = 9.3, 2H, 22-H, 24-H), 8.38 (d, J = 9.3 Hz, 2H, 21-H, 25-H), 8.67 (d, J = 8.1 Hz, 2H, 8-H, 12-H), 8.97 (d, J = 8.1 Hz, 2H, 2-H, 6-H), 10.91 (s, 1H, NH); fabms: *m/z* 492.4 $(M^{2+}+e^-)^+$, 371.0 (M^+-DMAP).

Anal. Calcd. for $C_{72}H_{65}B_2ClN_8O_2 \cdot 10H_2O$: C, 65.70; H, 6.51; N, 8.51. Found: C, 65.05; H, 5.53; N, 8.48.

1,1'-[5-Chloro-6-(4-nitrophenylamino)pyrimidine-2,4-diyl]-bis-[4-(pyrrolidin-1-yl)pyridinium] Dichloride (**20a**).

A solution of 0.29 g (0.5 mmol) of the betaine **18a** in 150 mL of ethanol was treated with 10 mL of 10% hydrochloric acid. After concentrating the solution *in vacuo* the product was precipitated at 8 °C, collected by filtration and recrystallized from ethanol to yield the dichloride **20a** as colorless crystals (89%), decomposition > 243 °C; ir: 3108.0, 3085.3, 2975.6, 1651.7, 1618.6, 1579.8, 1504.0, 1406.4, 1337.0, 1214.7, 1163.1 cm^{-1};^1H nmr: δ 2.07 (m, 8H, 33-H, 34-H), 3.70 (m, 8H, 28-H, 29-H), 7.13 (d, J = 8.1 Hz, 2H, 3-H, 5-H), 7.17 (d, J = 7.8 Hz, 2H, 9-H, 11-H), 8.05 (d, J = 9.0 Hz, 2H, 21-H, 25-H), 8.38 (d, J = 9.0 Hz, 2H, 22-H, 24-H), 8.69 (d, J = 7.8 Hz, 2H, 8-H, 12-H), 9.00 (d, J = 8.1 Hz, 2H, 2-H, 6-H), 10.78 (s, 1H, NH).

Anal. Calcd. for $C_{28}H_{29}Cl_3N_8O_2 \cdot 3.5H_2O$: C, 49.53; H, 5.34; N, 16.50. Found: C, 49.60; H, 5.29; N, 16.48.

1,1'-[5-Chloro-6-(4-nitrophenylamino)pyrimidine-2,4-diyl]-bis-[4-(pyrrolidin-1-yl)pyridinium] Bis(tetraphenylborate) (**20b**).

A solution of 0.43 g (0.5 mmol) of the betaine **18b** in 150 mL of ethanol was treated with 1 mL of 10% hydrochloric acid. Evaporation of the solution to dryness *in vacuo* was followed by dissolving the residue in 500 mL of ethyl acetate and addition of 0.34 g (1.0 mmol) of sodium tetraphenylborate. After concentrating the solution *in vacuo* and cooling overnight, a precipitate formed, which was collected by filtration and recrystallized from ethanol. The bis(tetraphenylborate) **20b** was finally obtained as colorless crystals in 81% yield, mp 283 – 285 °C; ir: 1650.1, 1571.5, 1511.7, 1408.2, 1303.6, 1156.0, 1108.7, 705.60 cm^{-1}; ^1H nmr: δ 2.07 (m, 8H, 28-H, 29-H, 33-H, 34-H), 3.70 (m, 8H, 27-H, 30-H, 32-H, 35-H), 6.78 (t, J = 7.2 Hz, BPh_4), 6.92 (t, J = 7.2 Hz, BPh_4), 7.17 (m, 20H, 3-H, 5-H, 9-H, 11-H), 8.03 (d, J = 9.3 Hz, 2H, 21-H, 25-H), 8.39 (d, J = 9.3 Hz, 2H, 22-H, 24-H), 8.68 (d, J = 7.8 Hz, 2H, 8-H, 12-H), 8.99 (d, J = 8.1 Hz, 2H, 2-H, 6-H), 10.93 (s, 1H, NH); fabms: *m/z* 545.6 (M^+), 39.1.

Anal. Calcd. for $C_{76}H_{69}B_2ClN_8O_2 \cdot 4.5H_2O$: C, 72.18; H, 6.22. Found: C, 71.94; H, 5.94.

5-Chloro-2,6-bis-[4-(dimethylamino)pyridinio]-pyrimidine-4-phenylaminide Tetraphenylborate (**21a**).

To a solution of 0.20 g (0.18 mmol) of the dication **11a** in a mixture of 50 mL of ethanol and 25 mL of acetonitrile was added 39 mg (0.18 mmol) of proton sponge. The resulting orange-colored solution was carefully concentrated *in vacuo*. After cooling overnight, the precipitate was collected by filtration, washed with 50 mL of ethyl acetate and dried *in vacuo* to yield 58 mg (42%) of the betaine **21a**, mp 127 °C; ir 3056.3, 1650.6, 1609.2, 1578.3, 1479.5, 1426.6, 1392.3, 1216.0, 1152.8, 743.6, 707.9 cm^{-1}; ^1H nmr: δ 3.25 (s, 6H, 28-H, 29-H), 3.28 (s, 6H, 26-H, 27-H), 6.78 (t, J = 7.2 Hz, 8H, BPh_4), 6.92 (t, J = 7.2 Hz, 16H, BPh_4), 7.05 (d, J = 8.2 Hz, 2H, 22-H, 24-H), 7.09 (t, J = 8.2 Hz, 2H, 23-H), 7.17 (m, 19H, BPh_4, 9-H, 11-H, 3-H, 5-H), 7.23 (d, J = 8.2 Hz, 2H, 21-H, 25-H), 8.58 (d, J = 7.8 Hz, 2H, 8-H, 12-H), 8.85 (d, J = 8.4 Hz, 2H, 2-H, 6-H); fabms: *m/z* = 447.5 (M^++1), 41.2.

Anal.Calcd. for $C_{48}H_{45}BClN_7 \cdot 3H_2O$: C, 70.29; H, 6.27. Found: C, 69.61; H, 5.58.

5-Chloro-2,6-bis-[4-(pyrrolidin-1-yl)pyridinio]-pyrimidine-4-phenylaminide Tetraphenylborate (**21b**).

To a solution of 0.20 g (0.18 mmol) of the dication **11b** in a mixture of 50 mL of ethanol and 25 mL of acetonitrile were added 39 mg (0.18 mmol) of proton sponge. The orange-colored solution was concentrated *in vacuo* and cooled. The resulting precipitate was collected by filtration, washed with 50 mL of ethyl acetate and dried *in vacuo* to give 74 mg (51%) of the betaine **21b**, mp 238 – 241 °C; ir 3056.8, 1650.3, 1607.5, 1570.6, 1479.0, 1427.7, 1404.9, 1210.6, 1153.7, 743.6, 714.8 cm^{-1}; ^1H nmr: δ

2.01 (m, 8H, 33-H, 34-H), 3.57 (m, 8H, 28-H, 29-H), 6.78 (t, J = 7.2 Hz, 4H, BPh_4), 6.92 (t, J = 7.2 Hz, 8H, BPh_4), 7.02 (m, overlapped, 7H, 21-H, 23-H, 25-H, 3-H, 5-H, 9-H, 11-H), 7.16 (m, 8H, BPh_4), 7.20 (m, overlapped, 2H, 22-H, 24-H), 8.55 (d, J = 7.7 Hz, 2H, 8-H, 12-H), 8.86 (d, J = 8.0 Hz, 2H, 2-H, 6-H); ^{13}C nmr: δ 24.48 (C-33, C-34), 24.54 (C-28, C-29), 48.72 (C-32, C-35), 48.82 (C-27, C-30), 107.71 (C-9, C-11), 107.78 (C-3, C-5), 109.36 (C-17), 121.40 (BPh_4), 120.40 (C-23), 122.59 (C-21, C-25), 125.17 (q, J_{BC} = 3.0 Hz, BPh_4), 127.99 (C-22, C-24), 135.42 (BPh_4), 136.18 (C-8, C-12), 140.94 (C-2, C-6), 149.12 (C-10), 151.06 (C-4), 151.50 (C-14), 153.49 (C-18), 154.28 (C-16), 163.57 (q; J_{BC} = 49.8 Hz, BPh_4); fabms: *m/z* 505.4 (M+), 149.7.

Anal. Calcd. for $C_{52}H_{49}BClN_7 \cdot 5\ H_2O$: C, 68.76; H, 6.55. Found: C, 69.95; H, 5.51.

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