

Supporting Information for JO049142S

CONTENTS	Page No.
1. 1,4-Bis(1,2,6-triphenylpyridinium-4-yl)benzene (1[1]) Triflate	S4
2. 1,4-Bis[1-(4-aminophenyl)-2,6-diphenylpyridinium-4-yl]benzene (2[1]) Triflate	S4
3. 1,4-Bis[1-(4-acetamidophenyl)-2,6-diphenylpyridinium-4-yl]benzene (3[1]) Triflate	S6
4. General Procedure for the Hydrolysis of Diacetamido Oligomers 3[n] to 2[n]	S7
5. 1,4-Bis[1-(4-acetamidophenyl)-2,6-diphenylpyridinium-4-yl]benzene (3[1]) Perchlorate	S8
6. 3[1] <i>p</i> -Toluenesulfonate	S9
7. 2[1] <i>p</i> -Toluenesulfonate	S10
8. 3[1] Trifluoroacetate	S11
9. 1,4-Bis[1-(4-acetamidophenyl)-2,6-diphenylpyridinium-4-yl]benzene (3[1]) Chloride	S11
10. 1,4-Bis[1-(4-acetamidophenyl)-2,6-diphenylpyridinium-4-yl]benzene (3[1]) Dodecamethylcarba- <i>closo</i> -dodecaborate	S12
11. General Procedure for the Exchange of Anions for Dodecamethylcarborate (CB ₁₁ Me ₁₂ ⁻) Anion	S12
12. 3-{4-[1-(4-Acetamidophenyl)-2,6-diphenylpyridinium-4-yl]-phenyl}-1,5-diphenylpent-2-ene-1,5- dione (7) Trifluoromethanesulfonate	S13
13. 1-([4-acetamidophenyl]-2,6-diphenylpyridinium-4-yl)-4-(2,6-diphenylpyrylium-4-yl)benzene (8) Trifluoromethanesulfonate	S14
14. α -(4-Acetamidophenyl)- ω -aminomono[(2,6-diphenylpyridinium-1,4-diyl)-1,4-phenylene(2,6- diphenylpyridinium-4,1-diyl)-1,4-phenylene] (4[1]) Trifluoromethanesulfonate	S15
15. Partial Hydrolysis of Diacetamide 3[1]	S16
16. α -(4-Acetamidophenyl)- ω -acetamidodi[(2,6-diphenylpyridinium-1,4-diyl)-1,4-phenylene(2,6- diphenylpyridinium-4,1-diyl)-1,4-phenylene] (3[2]) Trifluoromethanesulfonate	S16
17. α -(4-Acetamidophenyl)- ω -aminodi[(2,6-diphenylpyridinium-1,4-diyl)-1,4-phenylene(2,6-	

diphenylpyridinium-4,1-diyl)-1,4-phenylene] (4[2]) Perchlorate	S17
18. α -(4-Aminophenyl)- ω -aminodi[(2,6-diphenylpyridinium-1,4-diyl)-1,4-phenylene(2,6-diphenylpyridinium-4,1-diyl)-1,4-phenylene] (2[2]) Perchlorate	S18
19. α -(4-Aminophenyl)- ω -aminotri[(2,6-diphenylpyridinium-1,4-diyl)-1,4-phenylene(2,6-diphenylpyridinium-4,1-diyl)-1,4-phenylene] (2[3]) Trifluoromethanesulfonate	S19
20. α -(4-Acetamidophenyl)- ω -acetamidotri[(2,6-diphenylpyridinium-1,4-diyl)-1,4-phenylene(2,6-diphenylpyridinium-4,1-diyl)-1,4-phenylene] (3[3]) Trifluoromethanesulfonate	S20
21. α -(4-Acetamidophenyl)- ω -acetamidotetra[(2,6-diphenylpyridinium-1,4-diyl)-1,4-phenylene(2,6-diphenylpyridinium-4,1-diyl)-1,4-phenylene] (3[4]) Trifluoromethanesulfonate	S21
22. α -(4-Acetamidophenyl)- ω -acetamidopenta[(2,6-diphenylpyridinium-1,4-diyl)-1,4-phenylene(2,6-diphenylpyridinium-4,1-diyl)-1,4-phenylene] (3[5]) Trifluoromethanesulfonate	S22
23. References	S24

Oligomers of “Extended Viologen”, *p*-Phenylene-bis-4,4'-(1-aryl-2,6-diphenylpyridinium), as Candidates for Electron-Dopable Molecular Wires

Michal Valášek^{†‡}, Jaroslav Pecka^{†*}, Jindřich Jindřich^{†‡}, Gérard Calleja[†], Peter R. Craig[†], and

Josef Michl^{*‡}

Department of Organic Chemistry, Charles University, Albertov 2030, Prague 2, Czech Republic, and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215

michl@eefus.colorado.edu *Experimental Part*

Experimental Part

All chemicals were of standard commercial quality. Some $\text{Me}_3\text{NH}^+ \text{CB}_{11}\text{H}_{12}^-$ was synthesized¹ and some was purchased from Katchem, Elišky Krásnohorské 6, 11 000 Prague, Czech Republic. Permethylation followed published procedures.^{2,3} Solvents were dried and distilled before use. Commercial *p*-phenylenediamine (**6**) was sublimed before use. Samples were dried at 100-120 °C under reduced pressure (1.4 Pa) and stored in a dessicator over P_2O_5 . NMR spectra were recorded at 400 MHz (^1H) at 25 °C in $\text{DMSO}-d_6$. ^1H NMR spectra were referenced to TMS. ^{13}C -NMR with total decoupling of protons was referenced against the solvent (DMSO, δ 31.5 ppm). Signal multiplicity was determined by DEPT, and the assignment of some protons was done by HSQC and HMBC experiments. For ^{19}F -NMR spectra CF_2Cl_2 was used as external standard. Samples for ESI MS spectra were dissolved in MeCN. IR spectra were measured in KBr matrix by

[†] Charles University

[‡] University of Colorado

diffuse reflectance. UV-Vis spectra were measured in acetonitrile, THF and DMF in a 1 cm quartz cell at 20 °C (extinction coefficients measured in acetonitrile are given below in units of L.mol⁻¹cm⁻¹).

1,4-Bis(1,2,6-triphenylpyridinium-4-yl)benzene (1[1]) Triflate. To the solution of **5** triflate (0.4 g, 0.48 mmol) in dry dimethylformamide (12 mL) freshly distilled aniline (0.098 g, 1.05 mmol) was added and the mixture was stirred and heated at 60 °C. After 2 h dry benzene (4 mL) was added and water was distilled off using a Dean-Stark trap at 130 °C. Then the solution was stirred and heated to 120 °C for 8 h. After cooling the solvents were evaporated (1.4 Pa, 40 °C) and the crude product was stirred with toluene (5 mL). The solid was filtered and washed with chloroform (2×20 mL) and diethyl ether (20 mL). The yield of the light brown product was 0.42 g (89%). ¹H NMR δ 7.19-7.22 (m, 6H), 7.34-7.51 (m, 24H), 8.67 (s, 4H), 8.87(s, 4H); ¹³C NMR δ 125.61, 128.09, 128.58, 129.73, 129.93, 129.99, 132.99, 136.67, 138.99, 153.88; IR (KBr) ν cm⁻¹ 3061 (bw, ν(CH), pyridinium and arom.), 1620 (s, ν(C-C), pyridinium and arom.), 1510 (s, ν(C-C), arom.), 1264 (vs, ν_{as}(SO₃⁻)), 1156 (bm, ν(CF₃)), 1030 (s, ν_s(SO₃⁻)), 764 (w, γ(CH), phenylene), 697 and 638 (m, γ(CH), Ph); UV (λ_{max}/nm, ε): 332 (54 000), 248 (18 000); ESI MS *m/z* (%) 839.9 (35.6, [M-A]⁺), 345.3 (100, [M-2A]²⁺); Anal. Calcd for C₅₄H₃₈F₆N₂O₆S₂ (989.01) C, 65.58, H, 3.87, N, 2.83; Found : C, 65.83, H, 3.94, N, 2.91.

1,4-Bis[1-(4-aminophenyl)-2,6-diphenylpyridinium-4-yl]benzene (2[1]) Triflate.

Method A. To the solution of **5** (24 g, 29 mmol) in dry dimethylformamide (200 mL), **6** (10.9 g, 101 mmol) was added and the mixture was stirred and heated at 60 °C. After 5 h dry benzene (20 mL) was added and water was distilled off using Dean-Stark trap at 110 °C. Then the solution was stirred and heated to 110 °C for next 4 h. After cooling the solvents were evaporated (1.4 Pa, 40 °C)

and the solid was heated under reflux in toluene (300 mL) for 30 min, filtered and washed with chloroform (300 mL). The crude product was heated under reflux in ethanol (300 mL) for about 3 h and after cooling washed with water (300 mL), ethanol (200 mL), chloroform (200 mL), diethyl ether (100 mL) and dried. The yield of reddish brown product was 27.2 g (92%).

Method B. Aqueous solution of trifluoromethanesulfonic acid (60 mL, 2.5 M) was added to the solution of **3[1]** triflate (3 g, 3 mmol) in methanol (150 mL) and the mixture was boiled under reflux for 5 h. After cooling, the solution was neutralized with aqueous ammonia to the neutral pH and the precipitated **2[1]** triflate was filtered off and washed with water (200 mL) and diethyl ether (50 mL). The filtrate was evaporated and the residue washed with water (100 mL) and diethyl ether (40 mL). The combined yield was 2.75 g (99 %). ^1H NMR δ 5.42 (s, 4H, NH_2), 6.21 (d, $J=8.8$ Hz, 4H, *o*-aniline), 6.94 (d, $J=8.8$ Hz, 4H, *m*-aniline), 7.40-7.45 (m, 20H, Ph), 8.60 (s, 4H, phenylene), 8.76 (s, 4H, pyridinium); ^{13}C NMR δ 112.23 (*o*-CH, aniline), 125.44 (CH, pyridinium), 127.01 (C, aniline), 127.80 (*m*-CH, Ph), 128.72 (*m*-CH, aniline), 129.45 (*o*-CH, Ph), 129.51 (*p*-CH, Ph), 129.51 (CH, phenylene), 133.24 (C, Ph), 136.49 (C, phenylene), 149.21 (*p*-C, aniline), 153.23 (*p*-C, pyridinium), 156.96 (*o*-C, pyridinium); IR (KBr) ν cm^{-1} 3480 (bw, $\nu_{\text{as}}(\text{NH})$), 3373 (bw, $\nu_{\text{s}}(\text{NH})$), 3073 (bw, $\nu(\text{CH})$, pyridinium and arom.), 1617 (s, $\nu(\text{C}-\text{C})$, pyridinium and arom.), 1510 (s, $\nu(\text{C}-\text{C})$, arom.), 1277 (vs, $\nu_{\text{as}}(\text{SO}_3^-)$), 1172 (bm, $\nu(\text{CF}_3)$), 1032 (s, $\nu_{\text{s}}(\text{SO}_3^-)$), 839 (w, $\gamma(\text{CH})$, phenylene), 768 and 701 (m, $\gamma(\text{CH})$, Ph); UV ($\lambda_{\text{max}}/\text{nm}$, ϵ): 330 (50 000), 246 (29 000); ESI MS m/z (%) 869.7 (23.3, $[\text{M} - \text{A}]$), 720.6 (5.5, $[\text{M} - 2\text{A}]$), 628.5 (8.8, $[\text{M} - 2\text{A} - \text{PhNH}_2]$), 360.4 (100, $[\text{M}-2\text{A}]/2$) FAB MS m/z (%) 869 (3.2, $[\text{M} - \text{A}]$), 720 (3.7 $[\text{M} - 2\text{A}]$), 628 (4.4, $[\text{M} - 2\text{A} - \text{PhNH}_2]^+$), 437; (2.0), 231 (100, $[\text{CF}_3\text{SO}_3^- + \text{PhNH}_2]^+$); Anal. Calcd. for $\text{C}_{54}\text{H}_{40}\text{F}_6\text{N}_4\text{O}_6\text{S}_2$ (1019.05) C, 63.65, H, 3.96, N, 5.50; Found : C, 63.28, H, 3.94, N, 5.43.

1,4-Bis[1-(4-acetamidophenyl)-2,6-diphenylpyridinium-4-yl]benzene (3[1]) Triflate.

Method A. The triflate salt of **5** (600 mg, 715 μmol) and **9** (227 mg, 1.51 μmol) in dry dimethylformamide (10 mL) were heated to 60 °C for 2 h with stirring. Toluene (~2 mL) was added, the temperature was increased to 120 °C and water was distilled off azeotropically (Dean-Stark trap). The reddish brown solution was then stirred at this temperature for 6 h. The solvents were evaporated at 40 °C and pressure 1.4 Pa. The residue was heated under reflux in sequence with toluene (20 mL), ethanol (15 mL) and diethyl ether (30 mL), and filtered each time. The solid was washed with water (10 mL), diethyl ether (2×20 mL) and dried to yield 733 mg (93%) of yellow product.

Method B. Acetyl chloride (28 mL, 0.49 mmol) was added to a solution of **2[1]** triflate (200 mg, 0.196 mmol) in dry pyridine (10 mL) with stirring and cooling in a water bath, under argon atmosphere. The reaction mixture was stirred and heated to 60 °C for 6 h. The solvent was distilled off under reduced pressure, toluene added and again distilled off. The residue was refluxed in sequence with toluene (20 mL), ethanol (15 mL) and diethyl ether (30 mL) and filtered each time. Finally, it was recrystallized from acetonitrile to yield **3[1]** triflate (182 mg, 84%). ^1H NMR δ 1.97 (s, 6H, CH_3), 7.35 (d, $J=5.2$ Hz), 4H, *o*-acetanilide), 7.40-7.48 (m, 24H, *m*-acetanilide, Ph), 8.64 (s, 4H, phenylene), 8.83 (s, 4H, pyridinium), 10.01 (s, 2H, NH); ^{13}C NMR δ 24.01 (CH_3), 117.78 (*o*-CH, acetanilide), 125.60 (CH, pyridinium), 128.13 (*m*-CH, Ph), 129.03 (*m*-CH, acetanilide), 129.71 (*o*-CH, Ph), 129.90 (CH, phenylene), 129.98 (*p*-CH, Ph), 133.06 (C, Ph), 133.39 (C, phenylene), 133.66 (C, acetanilide), 140.14 (*p*-C, acetanilide), 153.77 (*o*-C, pyridinium), 156.73 (*p*-C, pyridinium), 168.77 (CO); ^{19}F NMR δ -77.29 (s); IR (KBr) ν cm^{-1} 3497 (bw, $\nu(\text{N-H})$), 3066 (bw, $\nu(\text{CH})$, pyridinium and arom.), 1691 (m, amide I), 1619 (s, $\nu(\text{C-C})$, pyridinium and arom.), 1541

(bm, amide II), 1511 (s, $\nu(\text{C-C})$, arom.), 1250 (bs, $\nu_{\text{as}}(\text{SO}_3^-)$), 1177 (bm, $\nu(\text{CF}_3)$), 1031 (s, $\nu_{\text{s}}(\text{SO}_3^-)$), 848 (m, $\gamma(\text{CH})$, phenylene), 763 and 694 (m, $\gamma(\text{CH})$, Ph); UV ($\lambda_{\text{max}}/\text{nm}$, ϵ): 331 (53 000), 248 (42 000); ESI MS m/z (%) 953.8 (36.8, [M-A]), 805.6 (6.6, [M-2A]), 670.6 (2.4, [M-2A-PhNHAc]), 402.5 (100, [M-A]/2); Anal. Calcd for $\text{C}_{58}\text{H}_{44}\text{F}_6\text{N}_4\text{O}_8\text{S}_2$ (1103.12) C, 63.15, H, 4.02, N, 5.08; Found : C, 63.41, H, 4.10, N, 4.98.

For examination of the validity of the Lambert-Beer law, ultraviolet absorption spectra were measured in DMSO solutions in 1 - 100 mm quartz cells at concentrations 1.0×10^{-4} , 1.0×10^{-5} , 1.0×10^{-6} , 1.0×10^{-7} , and 1.0×10^{-8} M ($\pm 3\%$), and the observed decadic molar extinction coefficients at the first first peak maximum were 52000, 52500, 50300, 51400, and ~ 50000 .

The temperature dependence of the ^1H NMR spectrum of a 0.9×10^{-3} M solution in $\text{DMSO}-d_6$ was measured between 20 and 100 °C in 10 °C increments. Upon going from 20 to 100 °C, all peaks shifted to lower values of δ : 10.01 to 9.75, 8.83 to 8.74, 8.64 to 8.56; the shifts of the other proton signals were 0.03 ppm or less.

General Procedure for the Hydrolysis of Diacetamido Oligomers 3[n] to 2[n]: An aqueous solution of trifluoromethanesulfonic acid (1:3 v/v) was added to a solution of 3[n] in methanol. The mixture was refluxed for 6 h and after cooling, it was neutralized with aqueous ammonia. During neutralization the color changed from yellow to reddish brown. The precipitated material was filtered off, washed twice with excess water and then diethyl ether and dried under reduced pressure overnight. The yield was quantitative. The solid product was checked by ^1H NMR for the absence of diacetamido signals at δ 1.97 (s, 6H, CH_3), and 10.02 (s, 2H, NH) and for the presence of diaminophenyl signals at 5.42 (s, 4H, NH_2), 6.19-6.22 (d, 4H, *o*- PhNH_2) and 6.91-6.95 (d, 4H, *m*- PhNH_2).

1,4-Bis[1-(4-acetamidophenyl)-2,6-diphenylpyridinium-4-yl]benzene (3[1]) Perchlorate.

The solution of **5** perchlorate (2 g, 2.7 mmol), sodium acetate (0.2 g, 2.4 mmol) and **9** (1 g, 6.7 mmol) in dry ethanol (20 mL) was stirred and heated to 50 °C for 48 h. The brown precipitate was filtered, washed with ethanol (10 mL), water (10 mL) and diethyl ether (2×10 mL), and recrystallized from ethanol. The yield was 2.4 g (89%). ¹H NMR δ 1.97 (s, 6H, CH₃), 7.35 (d, J=6 Hz), 4H, *o*-acetanilide), 7.40-7.48 (m, 24H, *m*-acetanilide, Ph), 8.64 (s, 4H, phenylene), 8.83 (s, 4H, pyridinium), 10.02 (s, 2H, NH); ¹³C NMR δ 24.01 (CH₃), 117.78 (*o*-CH, acetanilide), 125.60 (CH, pyridinium), 128.14 (*m*-CH, Ph), 129.02 (*m*-CH, acetanilide), 129.71 (*o*-CH, Ph), 129.89 (CH, phenylene), 129.98 (*p*-CH, Ph), 133.06 (C, Ph), 133.39 (C, phenylene), 136.66 (C, acetanilide), 140.14 (*p*-C, acetanilide), 153.77 (*o*-C, pyridinium), 156.73 (*p*-C, pyridinium), 168.77 (CO); IR (KBr) ν cm⁻¹ 3335 (bw, ν(N-H), 3064 (bw, ν(CH), pyridinium and arom.), 1691 (wm, amide I), 1620 (s, ν(C-C), pyridinium and arom.), 1535 (bm, amide II), 1510 (s, ν(C-C), arom.), 1097 (bs, ν(ClO₄⁻)), 845 (w, γ(CH), phenylene), 763 and 699 (wm, γ(CH), Ph), 623 (m, γ(ClO₄⁻)); ESI MS *m/z* (%) 807.0 (3.0, [M-2A]), 402.5 (100, [M-2A]/2); Anal. Calcd for C₅₆H₄₄Cl₂N₄O₁₀ (1003.89) C, 67.00, H, 4.42, N, 5.88; Found : C, 66.80, H, 4.46, N, 5.45.

1,4-Bis[1-(4-aminophenyl)-2,6-diphenylpyridinium-4-yl]benzene (2[1]) Perchlorate. The solution of **5** perchlorate (300 mg, 0.406 mmol) and **6** (154 mg, 1.43 mmol) in dry dimethylformamide (4 mL) was stirred and heated at 60 °C for 5 h in argon atmosphere. Benzene (1 mL) was added, the temperature was increased to 110 °C, and a small portion of the solvents was distilled off. Then the solvents were evaporated under reduced pressure (1.4 Pa), the brown residue was refluxed in toluene (50 mL), filtered, and washed with chloroform (80 mL). The solid was refluxed in ethanol (40 mL) and then in diethyl ether (30 mL). Next it was filtered and washed with

water (30 mL), ethanol (10 mL) and diethyl ether (50 mL) and dried. The yield of the yellow product was 350 mg (94%). ^1H NMR δ 5.41 (s, 4H, NH_2), 6.22 (d, $J=8.8$ Hz, 4H, *o*-aniline), 6.95 (d, $J=8.8$ Hz, 4H, *m*-aniline), 7.42-7.46 (m, 20H, Ph), 8.60 (s, 4H, phenylene), 8.76 (s, 4H, pyridinium); ^{13}C NMR δ 112.33 (*o*-CH, aniline), 125.53 (CH, pyridinium), 127.11 (C, aniline), 127.96 (*m*-CH, Ph), 128.85 (*m*-CH, aniline), 129.59 (*o*-CH, Ph), 129.65 (*p*-CH, Ph), 129.65 (CH, phenylene), 133.41 (C, Ph), 136.58 (C, phenylene), 149.58 (*p*-C, aniline), 153.25 (*p*-C, pyridinium), 157.03 (*o*-C, pyridinium); IR (KBr) ν cm^{-1} 3476 (bw, $\nu_a(\text{NH})$), 3384 (w, $\nu_s(\text{NH})$), 3061 (bw, $\nu(\text{CH})$, pyridinium and arom.), 1624 (s, $\nu(\text{C-C})$, pyridinium and arom.), 1559 and 1513 (m, $\nu(\text{C-C})$, arom.), 1096 (vs, $\nu(\text{ClO}_4^-)$), 840 (w, $\gamma(\text{CH})$, phenylene), 760 and 700 (m, $\gamma(\text{CH})$, Ph), 622 (m, $\gamma(\text{ClO}_4^-)$).

p-Toluenesulfonates, tetrafluoroborates and trifluoroacetates of **2[1]** and **3[1]** were prepared similarly as trifluoromethanesulfonates and perchlorates.

3[1]*p*-Toluenesulfonate. ^1H NMR δ 1.97 (s, 6H, CH_3), 2.28 (s, 6H, CH_3 -toluenesulfonyl), 7.09 (d, $J=7.6$ Hz, 4H, *m*-toluenesulfonyl), 7.35 (d, $J=4$ Hz, 4H, *o*-acetanilide), 7.40-7.48 (m, 28H, *m*-acetanilide, toluenesulfonyl, Ph), 8.64 (s, 4H, phenylene), 8.82 (s, 4H, pyridinium), 10.02 (s, 2H, NH); ^{13}C NMR δ 20.74 (CH_3 , toluenesulfonyl), 24.00 (CH_3), 117.75 (*o*-CH, acetanilide), 125.44 (*m*-CH, tosyl), 125.57 (CH, pyridinium), 127.98 (*o*-CH, toluenesulfonyl), 128.11 (*m*-CH, Ph), 129.03 (*m*-CH, acetanilide), 129.72 (*o*-CH, Ph), 129.89 (CH, phenylene), 129.95 (*p*-CH, Ph), 133.06 (C, Ph), 133.39 (C, phenylene), 136.64 (C, acetanilide), 137.48 (*p*-C, tosyl), 140.13 (*p*-C, acetanilide), 145.81 (C, toluenesulfonyl), 153.72 (*o*-C, pyridinium), 156.72 (*p*-C, pyridinium), 168.77 (CO); IR (KBr) ν cm^{-1} 3486 (bw, $\nu(\text{N-H})$), 3046 (bw, $\nu(\text{CH})$, pyridinium and arom.), 2952 (w, $\nu_{\text{as}}(\text{CH}_3)$), 2872 (w, $\nu_s(\text{CH}_3)$), 1689 (m, amide I), 1628 (s, $\nu(\text{C-C})$, pyridinium and arom.), 1551 (bm, amide II), 1513 (s, $\nu(\text{C-C})$, arom.), 1188 (vs, $\nu_a(\text{SO}_3^-)$), 1033 (m, $\nu_s(\text{SO}_3^-)$), 850 (vm, $\gamma(\text{CH})$, phenylene), 765 and 700

(wm, γ (CH), Ph); ESI MS m/z (%) 975.7 (42.6, [M-A]), 804.5 (3.2, [M-2A]), 671.0 (2.6, [M-2A-PhNHAc]), 564.8 (3.3), 402.4 (100, [M-2A]/2), 300.5 (4.7).

2[1] *p*-Toluenesulfonate. ^1H NMR δ 2.27 (s, 6H, CH_3), 5.42 (s, 4H, NH_2), 6.22 (d, $J=8.8$ Hz, 4H, *o*-aniline), 6.95 (d, $J=8.8$ Hz, 4H, *m*-aniline), 7.09 (d, $J=8$ Hz, 4H, *m*-toluenesulfonyl), 7.40-7.48 (m, 24H, toluenesulfonyl, phenyl), 8.60 (s, 4H, phenylene), 8.75 (s, 4H, pyridinium); ^{13}C NMR δ 20.75 (CH_3) 112.36 (*o*-CH, aniline), 125.45 (*m*-CH, toluenesulfonyl), 125.55 (CH, pyridinium), 127.16 (C, aniline), 128.00 (*m*-CH, Ph), 128.03 (*o*-CH, toluenesulfonyl), 128.94 (*m*-CH, aniline), 129.68 (*o*-CH, Ph), 129.71 (CH, phenylene), 129.76 (*p*-CH, Ph), 133.50 (C, Ph), 136.62 (C, phenylene), 137.49 (*p*-C, toluenesulfonyl), 145.81 (C, toluenesulfonyl), 149.42 (*p*-C, aniline), 153.21 (*p*-C, pyridinium), 157.09 (*o*-C, pyridinium); IR (KBr) ν cm^{-1} 3440 (bw, $\nu_{\text{as}}(\text{NH})$), 3390 (bw, $\nu_{\text{s}}(\text{NH})$), 3059 (bw, $\nu(\text{CH})$, pyridinium and arom.), 1621 (s, $\nu(\text{C-C})$, pyridinium and arom.), 1515 (s, $\nu(\text{C-C})$, arom.), 1197 (vs, $\nu_{\text{as}}(\text{SO}_3^-)$), 1034 (s, $\nu_{\text{s}}(\text{SO}_3^-)$), 840 (w, $\gamma(\text{CH})$, phenylene), 761 and 702 (m, $\gamma(\text{CH})$, Ph); ESI MS m/z (%) 531.7 (6.4, [M]/2), 360.47 (100, [M - 2A]/2), 92.0 (3.3).

3[1] Tetrafluoroborate. ^1H NMR δ 1.97 (s, 6H, CH_3), 7.35 (d, $J=6.0$ Hz), 4H, *o*-acetanilide), 7.40-7.48 (m, 24H, *m*-acetanilide, Ph), 8.64 (s, 4H, phenylene), 8.83 (s, 4H, pyridinium), 10.01 (s, 2H, NH); ^{13}C NMR δ 24.01 (CH_3), 117.78 (*o*-CH, acetanilide), 125.59 (CH, pyridinium), 128.14 (*m*-CH, Ph), 129.03 (*m*-CH, acetanilide), 129.71 (*o*-CH, Ph), 129.89 (CH, phenylene), 129.98 (*p*-CH, Ph), 133.05 (C, Ph), 133.39 (C, phenylene), 136.66 (C, acetanilide), 140.14 (*p*-C, acetanilide), 153.75 (*o*-C, pyridinium), 156.73 (*p*-C, pyridinium), 168.78 (CO); IR (KBr) ν cm^{-1} 3363 (bw, $\nu(\text{NH})$), 3063 (bw, $\nu(\text{CH})$, pyridinium and arom.), 1691 (bm, amide I), 1620 (s, $\nu(\text{C-C})$, pyridinium and arom.), 1536 (bs, amide II), 1510 (s, $\nu(\text{C-C})$, arom.), 1061 (bs, $\nu(\text{BF}_4^-)$), 846 (wm, $\gamma(\text{CH})$, phenylene), 763 and 699 (m, $\gamma(\text{CH})$, Ph), 521 (m, $\gamma(\text{BF}_4^-)$); ESI MS m/z (%) 402.4

(100, [M-A]/2).

3[1] Trifluoroacetate. ^1H NMR δ 1.97 (s, 6H, CH_3), 7.36 (d, $J=5.6$ Hz), 4H, *o*-acetanilide), 7.39-7.48 (m, 24H, *m*-acetanilide, Ph), 8.64 (s, 4H, phenylene), 8.83 (s, 4H, pyridinium), 10.07 (s, 2H, NH); ^{13}C NMR δ 24.02 (CH_3), 113.83 (CF_3), 117.78 (*o*-CH, acetanilide), 125.60 (CH, pyridinium), 128.16 (*m*-CH, Ph), 129.05 (*m*-CH, acetanilide), 129.74 (*o*-CH, Ph), 129.92 (CH, phenylene), 129.99 (*p*-CH, Ph), 133.09 (C, Ph), 133.41 (C, phenylene), 136.67 (C, acetanilide), 140.17 (*p*-C, acetanilide), 153.75 (*o*-C, pyridinium), 156.75 (*p*-C, pyridinium), 157.48 (OCO), 168.82 (CO); ^{19}F NMR (376 MHz, d^6 -DMSO) δ -69.15 (s); IR (KBr) ν cm^{-1} 3450 (bw, $\nu(\text{NH})$), 3051 (bw, $\nu(\text{CH})$, pyridinium and arom.), 1686 (bs, amide I), 1679 (s, $\nu_a(\text{OCO})$), 1619 (vs, $\nu(\text{C-C})$, pyridinium and arom.), 1547 (bm, amide II), 1508 (s, $\nu(\text{C-C})$, arom.), 1457 (w, $\nu(\text{C-C})$, arom.), 1412 (wm, $\nu_s(\text{OCO})$), 1198 (bs, $\nu(\text{CF}_3^-)$), 851 and 828 (m, $\gamma(\text{CH})$, phenylene), 763 and 701 (wm, $\gamma(\text{CH})$, Ph), 719 (w, $\gamma(\text{OCO})$); ESI MS m/z (%) 402.5 (100, [M-2A]/2).

1,4-Bis[1-(4-acetamidophenyl)-2,6-diphenylpyridinium-4-yl]benzene (3[1]) Chloride. **3[1]** perchlorate, (98 mg, 0.1 mmol) was dissolved in methanol (20 mL) and slowly (~2 h) filtered through the column of an ion exchange column in Cl^- cycle (Amberlite-IRA 410, rinsed with methanol). The column was rinsed with another portion of methanol (20 mL, over ~2 h). After evaporation of methanol 84 mg (a quantitative yield) of **3[1]** chloride was obtained.

1,4-Bis[1-(4-acetamidophenyl)-2,6-diphenylpyridinium-4-yl]benzene (3[1]) Dodecamethylcarba-*closo*-dodecaborate. To the stirred solution of **3[1]** chloride (84 mg, 0.1 mmol) in methanol (7 mL) the solution of thallium dodecamethylcarba-*closo*-dodecaborate^{3,7} (103 mg, 0.2 mmol) in methanol (2 mL) was slowly added dropwise. The precipitated TlCl was filtered off, the solution was evaporated under reduced pressure, and the residue was washed with diethyl

ether (2×3 mL). The crude material was dissolved in tetrahydrofuran (2 mL) and the solution was filtered and concentrated to about 0.5 mL. Dry diethyl ether (1 mL) was added and the precipitated material was filtered off, washed with a mixture of tetrahydrofuran and diethyl ether (1:5), and dried under reduced pressure overnight. The yield was 121 mg (86%). The product is well soluble in methanol, ethanol and tetrahydrofuran. It is poorly soluble in diethyl ether. ¹H NMR δ -0.62 (6H, ws, CH₃B-), -0.51 (30H, ws, CH₃B-), -0.42 (30H, ws, CH₃B-), 0.74 (6H, s, CH₃C-), 2.06 (6H, s, CH₃CO), 7.20 (4H, d, J=9 Hz), 7.38-7.47 (24H, complex multiplet), 8.44 (4H, s), 8.64(4H, s).

For examination of the validity of the Lambert-Beer law, ultraviolet absorption spectra were measured for THF solutions in 1 mm - 100 mm quartz cells at concentrations 1.0×10⁻⁴, 1.0×10⁻⁵, 1.0×10⁻⁶, 1.0×10⁻⁷, and 1.0×10⁻⁸ M (± 3%), and the observed decadic molar extinction coefficients at the first peak maximum were 51600, 52000, 50000, 49000, and ~49400.

The temperature dependence of the ¹H NMR spectrum of 7×10⁻⁴ and 3×10⁻⁵ M solutions in THF-*d*₈ was measured between 20 and 60 °C in 10 °C increments, with identical results at the two concentrations. Upon going from 20 to 60 °C, all peaks shifted to lower values of δ: 9.23 to 9.02, 8.76 to 8.71, 8.52 to 8.46; the shifts of the other proton signals were smaller than 0.18 ppm.

General Procedure for the Exchange of Anions for Dodecamethylcarborate (CB₁₁Me₁₂⁻)

Anion. The lithium salt of dodecamethylcarba-*closo*-dodecaboranate (1.5 equiv. of Li⁺CB₁₁Me₁₂⁻ per starting anion) was added to a solution of **m[n]** in acetonitrile. This solution was stirred for 0.5 h and then an excess of water was added. The precipitate was filtered off, washed twice with water, benzene, diethyl ether (only for the higher oligomers, *n* = 3 - 5) and dried under reduced pressure overnight. The yield was quantitative. The resulting solid was checked by ESI MS for the presence of CB₁₁Me₁₂⁻ anion (*m/z*= 311.5) and absence of others (*m/z*=149.0 for TfO⁻, *m/z*=145.0 for PF₆⁻)

or by ^{19}F NMR (CD_3CN) for the absence of fluorine signals and by ^1H NMR (CD_3CN) for the presence of methyl signals of the carborate anion: 0.787 (s, 3H, $\text{CH}_3(1)$), -0.370 (s, 15H, $\text{CH}_3(2-6)$), -0.465 (s, 15H, $\text{CH}_3(7-11)$), and -0.568 (s, 3H, $\text{CH}_3(12)$).

3-{4-[1-(4-Acetamidophenyl)-2,6-diphenylpyridinium-4-yl]-phenyl}-1,5-diphenylpent-2-ene-1,5-dione (7) Trifluoromethanesulfonate. A solution of **5** triflate (15 g, 17.88 mmol) and **9** (2.55 g, 17.00 mmol) in dry dimethylformamide (140 mL) was heated to 50 °C for 12 h. The solvent was evaporated at 40 °C under reduced pressure (1.4 Pa). The crude mixture (17.1 g), containing the triflates of **5**, **8**, and **3[1]** was dissolved in acetonitrile (300 mL) and a solution of sodium acetate (8.1 g, 98.7 mmol) in water (100 mL) was added with stirring. During 2 h of stirring, the mixture darkened and then turned lighter again and a precipitate of the tetraketone, *p*-phenylene-bis-3,3'-(1,5-diphenylpent-2-ene-1,5-dione), formed. It was filtered off (2.8 g) and acetonitrile evaporated from the solution. The resulting aqueous suspension was extracted with chloroform (3×80 mL), the combined chloroform extracts were dried with MgSO_4 , and the solvent was removed under reduced pressure. The residual solid (13.8 g) was dissolved in acetonitrile and adsorbed on silica gel (20 g). The material was placed on a silica gel column (320 g) and eluted with gradient $\text{CHCl}_3/\text{MeOH}$: 600 mL, 50:1 (the tetraketone), 800 mL, 30:1 (pure **8** triflate), and 500 mL, 20:1 (**8** triflate and then **3[1]** triflate). The yield of yellow solid was 4.9 g (32.7% from both steps). ^1H NMR δ 1.98 (s, 3H, CH_3), 4.97 (bs, 2H, CH_2), 7.38 (m, 4H, acetanilide), 7.41 (m, 6H, *m,p*-Ph), 7.47 (m, 4H, *o*-Ph), 7.56 (t, 2H, $J=2\times 8$ Hz, *m*-Ph), 7.59 (t, 2H, $J=2\times 8$ Hz, *m*-Ph), 7.66 (t, 1H, $J=2\times 8$ Hz, *p*-Ph), 7.67 (t, 1H, $J=2\times 8$ Hz, *p*-Ph), 7.79 (s, 1H, CH), 8.02 (d, 4H, $J=8.5$ Hz, phenylene), 8.09 (d, 2H, $J=8$ Hz, *o*-Ph), 8.10 (d, 2H, $J=8$ Hz, *o*-Ph), 8.44 (d, 4H, $J=8.5$ Hz, phenylene), 8.71 (s, 2H, pyridinium), 9.98 (s, 1H, NH); ^{13}C NMR δ 23.92 (CH_3), 41.8 (CH_2), 117.7 (*o*-CH, acetanilide), 124.6 ($=\text{CH}-$), 125.1 (CH,

pyridinium), 128.0 (CH, phenylen), 128.1 (*m*-CH, Ph), 128.3 (*p*-CH, Ph), 128.7 (2CH, phenylen, *o*-Ph), 129.0 (3CH, *m*-acetanilide, *m*-Ph, *o*-Ph), 129.6 (*o*-CH, Ph), 129.8 (*p*-CH, Ph), 133.1 (C, Ph; *p*-CH, Ph), 133.3 (*p*-CH, Ph), 133.4 (*p*-C, acetanilide), 133.9 (C, phenylene), 136.6 (C, Ph), 138.2 (C, Ph), 140.0 (C, acetanilide), 144.6 (C, phenylene), 150.5 (=C-), 154.5 (*p*-C, pyridinium), 156.5 (*o*-C, pyridinium), 168.7 (CO-NH), 190.3 ($\underline{\text{C}}\text{O-CH=}$), 196.0 ($\underline{\text{C}}\text{O-CH}_2$); ^{19}F NMR δ -77.29 (s); IR (KBr) ν cm^{-1} 3313 (bw, $\nu(\text{N-H})$), 3064 (bw, $\nu(\text{CH})$, pyridinium and arom.), 1687 (m, amide I, CO), 1621 (s, $\nu(\text{C-C})$, pyridinium and arom.), 1597 (s, $\nu(\text{C=C})$), 1543 (bm, amide II), 1511 (s, $\nu(\text{C-C})$, arom.), 1258 (bs, $\nu_a(\text{SO}_3^-)$), 1221 (s, arylketone), 1156 (bm, $\nu(\text{CF}_3)$), 1033 (s, $\nu_s(\text{SO}_3^-)$), 845 (m, $\gamma(\text{CH})$, phenylene), 764 and 702 (m, $\gamma(\text{CH})$, Ph); UV ($\lambda_{\text{max}}/\text{nm}$, ϵ): 337 (33 000), 245 (31 000); ESI MS m/z (%) 689.6 (100, $[\text{M-A}]^+$); Anal. Calcd. for $\text{C}_{49}\text{H}_{37}\text{F}_3\text{N}_2\text{O}_6\text{S}$ (838.89) C, 70.16, H, 4.45, N, 3.34; Found: C, 69.97, H, 4.51, N, 3.39.

1-([4-acetamidophenyl]-2,6-diphenylpyridinium-4-yl)-4-(2,6-diphenylpyrylium-4-yl)benzene (8) Trifluoromethanesulfonate. To the stirred solution of **7** (1g, 1.19 mmol) in chloroform (100 mL) was dropwise added freshly prepared solution of TfOH in acetic anhydride (5% v/v, 0.2 mL TfOH in 4 mL anhydride). Almost immediately an oily precipitate started to form. The mixture was then stirred at room temperature for 2 h and the precipitate became crystalline. The yellow product was filtered off, washed with chloroform (2×20mL), diethyl ether (2×10mL) and then dried (100 °C, 1.4 Pa). The yield of the yellow product was 1.04 g (90%). ^1H NMR δ 1.98 (s, 3H, CH_3), 7.37 (m, 4H, acetanilide), 7.42 (m, 6H, *m,p*-Ph), 7.49 (m, 4H, *o*-Ph), 7.83 (m, 4H, *m*-Ph), 7.89 (m, 2H, *p*-Ph), 8.65 (d, 4H, $J=8$ Hz), 8.75 (d, 2H, $J=8$), 8.85 (d, 2H, $J=8$ Hz), 8.89 (s, 2H, pyrylium), 9.32 (s, 2H, pyridinium), 10.02 (s, 1H, NH); ^{13}C NMR δ 24.04 (CH_3), 115.89, 117.80, 119.07, 122.27, 125.92, 128.20, 129.02, 129.14, 129.76, 129.94, 130.03, 131.03, 133.12, 133.49,

135.26, 135.60, 138.91, 140.17, 153.51, 156.90, 163.71, 168.81, 170.47 (CO); ^{19}F NMR δ -73.46 (s); IR (KBr) ν cm^{-1} 3320 (bw, $\nu(\text{N-H})$), 3069 and 3028 (bw, $\nu(\text{CH})$, pyridinium, pyrylium and arom.), 1687 (m, amide I), 1621 (bs, $\nu(\text{C-C})$, pyrid., pyryl. and arom.), 1595 (bs, $\nu(\text{C=C})$), 1540 (bm, amide II), 1510 (s, $\nu(\text{C-C})$, arom.), 1463 (m, $\nu(\text{C-C})$, pyryl.), 1261 (bs, $\nu_{\text{as}}(\text{SO}_3^-)$), 1164 (bm, $\nu(\text{CF}_3)$), 1030 (s, $\nu_{\text{s}}(\text{SO}_3^-)$), 998 (w, $\nu(\text{C-C})$, pyryl.), 847 (m, $\gamma(\text{CH})$, phenylene), 764 and 702 (m, $\gamma(\text{CH})$, Ph); UV ($\lambda_{\text{max}}/\text{nm}$, ϵ): 337 (33 000), 245 (31 000); ESI MS m/z (%) 689.6 (100, $[\text{M-2A}]^{2+}$), 703.4 (13.3); Anal. Calcd. for $\text{C}_{50}\text{H}_{36}\text{F}_6\text{N}_2\text{O}_8\text{S}_2$ (970.94) C, 61.85, H, 3.74, N, 2.89, S, 6.60; Found: C, 62.06, H, 3.63, N, 2.94, S, 6.70.

α -(4-Acetamidophenyl)- ω -aminomono[(2,6-diphenylpyridinium-1,4-diyl)-1,4-phenylene(2,6-diphenylpyridinium-4,1-diyl)-1,4-phenylene] (4[1]) Trifluoromethanesulfonate.

To the solution of **8** triflate (1 g, 1.03 mmol) in dry dimethylformamide (30 mL), **6** (245 mg, 2.27 mmol) was added and the mixture was stirred and heated at 45 °C. After 6 h dry benzene (10 mL) was added and water was distilled off using at 130 °C (Dean-Stark trap). The solution was stirred and heated to 120 °C for 3 h. After cooling the solvents were evaporated (1.4 Pa, 40 °C) and the solid was refluxed in toluene (20 mL), filtered and washed with chloroform (3×50 mL), water (20 mL), ethanol (20 mL), diethyl ether (30 mL) and then dried under reduced pressure. The yield of brown product was 972 mg (89%). ^1H NMR δ 1.97 (s, 3H, CH_3), 5.42 (s, 2H, NH_2), 6.21 (d, $J=7$ Hz, 2H, *o*-aniline), 6.94 (d, $J=7$ Hz, 2H, *m*-aniline), 7.35 (d, $J=7$ Hz, 2H, *o*-anilide), 7.35-7.48 (m, 22H, *m*-acetanilide, Ph), 8.62 (s, 4H, phenylene), 8.77 (s, 2H), 8.83 (s, 2H), 10.00 (s, 1H, NH); ^{13}C NMR (100 MHz, d^6 -DMSO) δ 24.04 (CH_3), 117.78, 125.58, 127.14, 128.07, 128.15, 128.94, 129.05, 129.72, 133.08, 133.50, 136.80, 140.14, 149.45, 153.20, 153.80, 156.74, 157.11, 168.79 (CO); IR (KBr) ν cm^{-1} 3457, 3366 (bw, $\nu(\text{N-H})$), 3063 (bw, $\nu(\text{CH})$, pyridinium and arom.), 1693 (m,

amide I), 1619 (s, $\nu(\text{C-C})$, pyridinium and arom.), 1549 (bm, amide II), 1512 (s, $\nu(\text{C-C})$, arom.), 1260 (bs, $\nu_{\text{as}}(\text{SO}_3^-)$), 1162 (bm, $\nu(\text{CF}_3)$), 1031 (s, $\nu_{\text{s}}(\text{SO}_3^-)$), 845 (m, $\gamma(\text{CH})$, phenylene), 764 and 702 (m, $\gamma(\text{CH})$, Ph); UV ($\lambda_{\text{max}}/\text{nm}$, ϵ): 337 (33 000), 245 (31 000); ESI MS m/z (%) 689.6 (100, $[\text{M}-2\text{A}]^{2+}$); Anal. Calcd. for $\text{C}_{56}\text{H}_{42}\text{F}_6\text{N}_4\text{O}_7\text{S}_2$ (1061.08) C, 63.39, H, 3.99, N, 5.28; Found; C, 63.65, H, 3.87, N, 5.22.

Partial Hydrolysis of Diacetamide 3[1]. Diacetamide **3[1]** chloride (84 mg, 0.1 mmol) was dissolved in boiling ethanol (15 mL) and aqueous hydrochloric acid (6 mL, 1 M) was added. The mixture was refluxed at 80-81 °C and in regular time intervals, samples (1 mL) of the mixture were taken. Each sample was neutralized with aqueous ammonia (0.3 mL, 1 M) and water was evaporated in vacuum. The residue was washed with water (about 1 mL) and after drying, the ^1H -NMR spectrum was recorded. It revealed the presence of diacetate **3[1]**, diamine **2[1]** and monoacetate **4[1]**. Under these conditions the maximum concentration of **4[1]** is reached in about 30 min. The constituents were separated and purified by HPLC chromatography.

α -(4-Acetamidophenyl)- ω -acetamidodi[(2,6-diphenylpyridinium-1,4-diyl)-1,4-phenylene(2,6-diphenylpyridinium-4,1-diyl)-1,4-phenylene] (3[2]) Trifluoromethanesulfonate.

Method A. A solution of **8** triflate (1 g, 1.03 mmol) and **6** (55.1 mg, 0.510 mmol) in dry DMF (20 mL) was stirred and heated under argon for 2 h at 80 °C. Dry benzene (6 mL) was added, the temperature was increased to 120 °C and water was azeotropically removed using a Dean-Stark trap. The solvents were evaporated under reduced pressure (1.4 Pa, 45 °C, and remaining DMF was eliminated by adding toluene and distilling it off. The residue was stirred with methanol (10 mL), filtered off and washed with chloroform (2×20 mL). The crude material (1.01 g) was purified by crystallization from acetonitrile. The yield of **3[2]** triflate was 890 mg (86 %).

Method B. A solution of **8** triflate (0.5 g, 0.515 mmol) and **4[1]** triflate (536 mg, 0.505 mmol) in dry DMF (8 mL) was stirred and heated under argon for 1 h at 60 °C. Dry benzene (6 mL) was added, the temperature was increased to 130 °C and water was azeotropically removed using a Dean-Stark trap. The solvents were evaporated under reduced pressure (1.4 Pa, 45 °C), and remaining DMF was eliminated by addition of toluene and distillation. The residue was stirred with toluene (6 mL), filtered off, washed with chloroform (3×30 mL), diethyl ether (10 mL), and dried under reduced pressure. The yield of **3[2]** triflate was 941 mg (92 %). ¹H NMR δ 1.97 (s, 6H, CH₃), 7.25-7.32 (m, 24H, inner *o*-Ph, *p*-Ph, phenylene, acetanilide), 7.35-7.47 (m, 20H, outer Ph), 7.50-7.63 (m, 8H, inner *m*-Ph), 8.50-8.67 (m, 12H), 8.72 (s, 2H, *m*-pyridinium-phenylene-NH₂), 8.80 (s, 4H, *m*-pyridinium-phenylene-NHAc), 10.00 (s, 2H, NHAc); IR (KBr) ν cm⁻¹ 3644 (bw, ν_a(NH₂)), 3394 (bw, ν(NH), ν_s(NH₂)), 3059 (bw, ν(CH), pyridinium and arom.), 1690 (bw, amide I), 1617 (s, ν(C-C), pyridinium and arom.), 1531 (bm, amide II), 1510 (m, ν(C-C), arom.), 1263 (bs, ν_{as}(SO₃⁻)), 1162 (bm, ν(CF₃)), 1035 (s, ν_s(SO₃⁻)), 840 (m, γ(CH), phenylene), 762 and 702 (s, γ(CH), Ph); UV (λ_{max}/nm, ε): 334 (99 000), 247 (63 000); ESI MS *m/z* (%) 354.4 (12.3, [M-4A]⁴⁺), 381.4 (100), 395.3 (28.1); Anal. Calcd. for C₁₀₆H₇₆F₁₂N₆O₁₄S₄ (2014.01) C, 63.21, H, 3.80, N, 4.17; Found: C, 63.50, H, 3.96, N, 4.09.

α-(4-Acetamidophenyl)-ω-aminodi[(2,6-diphenylpyridinium-1,4-diyl)-1,4-phenylene(2,6-diphenylpyridinium-4,1-diyl)-1,4-phenylene] (4[2]) Perchlorate. The solution of **5** (500 mg, 0.676 mmol) and **9** (102 mg, 0.676 mmol) in dry DMF was stirred and heated under argon for 2 h at 60 °C. The perchlorate salt of **2[1]** (622 mg, 0.676 mmol) was added and the mixture was stirred and heated to 70 °C for about 70 h. Dry toluene (5 mL) was added, the temperature was increased to 120 °C and water was azeotropically removed using a Dean-Stark trap.

The solvents were evaporated under reduced pressure (1.4 Pa, 45 °C), and remaining DMF was eliminated by addition of toluene and distillation. The residue was washed with methanol twice (80 and 100 mL). The crude product (600 mg) was purified by repeated crystallization from methanol. The yield of the singly acetylated **4[2]** perchlorate was 240 mg (35%). ¹H NMR δ 1.97 (s, 3H, CH₃), 5.42 (s, 2H, NH₂), 6.20 (bs, 2H, *o*-aniline), 6.93 (bs, 2H, *m*-aniline), 7.20-7.33 (bs, 20H, inner *o*-Ph, *p*-Ph, phenylene, acetanilide), 7.34-7.48 (bs, 20H, outer Ph), 7.49-7.64 (m, 8H, inner *m*-Ph), 8.45-8.67 (m, 12H), 8.73 (s, 2H, *m*-pyridinium-phenylene-NH₂), 8.79 (s, 2H, *m*-pyridinium-phenylene-NHAc), 10.01 (s, 1H, NHAc); ¹³C NMR δ 30.67, 112.40, 117.78, 125.62, 126.09, 128.13, 128.43, 128.91, 129.18, 129.70, 129.91, 130.92, 132.16, 133.05, 133.46, 140.14, 153.75, 156.53, 157.07, 206.55; IR (KBr) ν cm⁻¹ 3507 (bw, ν_a(NH₂)), 3471 (bw, ν(NH)), 3375 (bw, ν_s(NH₂)), 3066 (bw, ν(CH), pyridinium and arom.), 1686 (bw, amide I), 1618 (s, ν(C-C), pyridinium and arom.), 1551 (bm, amide II), 1497 (m, ν(C-C), arom.), 1092 (bs, ν(ClO₄⁻)), 841 (m, γ(CH), phenylene), 759 and 699 (s, γ(CH), Ph), 623 (s, γ(ClO₄⁻)); UV (λ_{max}/nm, ε): 335 (96 000), 248 (55 000).

α-(4-Aminophenyl)-ω-aminodi[(2,6-diphenylpyridinium-1,4-diyl)-1,4-phenylene(2,6-diphenylpyridinium-4,1-diyl)-1,4-phenylene] (2[2]) Perchlorate. Hydrochloric acid (3 mL, 2 M) was added to the solution of **4[2]** perchlorate (20 mg, 11.3 mmol) in methanol (6 mL) and the mixture was refluxed for 5 h. After neutralization with aqueous ammonia, the solvent was evaporated and the residue washed with water (60 mL) in several portions and with diethyl ether (5 mL) and recrystallized from a methanol/chloroform (1:2) mixture. The yield was 16 mg (82%). ¹H NMR δ 5.32 (s, 4H, NH₂), 6.24 (d, J=8.4 Hz, 4H, *o*-aniline), 6.92 (d, J=8.0 Hz, 4H, *m*-aniline), 7.28 (bs, 16H, inner *o*-Ph, *p*-Ph, phenylene), 7.34-7.50 (m, 20H, outer Ph), 7.51-7.64 (m, 8H, inner *m*-Ph), 8.46-8.65 (m, 12H), 8.71 (s, 4H, *m*-pyridinium-phenylene-NH₂); ¹³C NMR (100 MHz, d⁶-DMSO)

δ 128.42, 128.92, 129.64, 156.58; IR (KBr) ν cm^{-1} 3451 (bw, $\nu_{\text{a}}(\text{NH}_2)$), 3358 (bw, $\nu_{\text{s}}(\text{NH}_2)$), 3064 (bw, $\nu(\text{CH})$, pyridinium and arom.), 1620 (s, $\nu(\text{C-C})$, pyridinium and arom.), 1499 (m, $\nu(\text{C-C})$, arom.), 1090 (bs, $\nu(\text{ClO}_4^-)$), 844 (m, $\gamma(\text{CH})$, phenylene), 754 and 698 (s, $\gamma(\text{CH})$, Ph), 625 (s, $\gamma(\text{ClO}_4^-)$); UV ($\lambda_{\text{max}}/\text{nm}$, ϵ): 333 (95 000), 245 (51 000).

α -(4-Aminophenyl)- ω -aminotri[(2,6-diphenylpyridinium-1,4-diyl)-1,4-phenylene(2,6-diphenylpyridinium-4,1-diyl)-1,4-phenylene] (2[3]) Trifluoromethanesulfonate. The triflate salt of **2[1]** (15.3 g, 15 mmol) was dissolved in DMF (200 mL) and benzene (100 mL) was added. About 80 mL of a solvent mixture was distilled off under argon to remove traces of water. A solution of **5** triflate (126 mg, 0.15 mmol) in dry DMF (7 mL) was added and the reaction mixture was heated to reflux for 4 h under argon while water was removed with a Dean-Stark adapter. Additional **5** triflate (126 mg, 0.15 mmol in 7 mL DMF) was added and the mixture was heated and stirred overnight (bath temperature, 140 - 150 °C). The solvents were distilled off (1.4 Pa, 50 °C), the solid was stirred with toluene (100 mL) for ~1 h, filtered and added to methanol (300 mL). The mixture was stirred and refluxed for 1 h and then allowed to cool to room temperature. Filtration yielded a mixture of ~2% of **2[3]** with unreacted **2[1]**. The latter was separated repeated extraction with a methanol/chloroform (1:2) mixture, in which it dissolves while **2[3]** is practically insoluble. After the content of **2[3]** exceeded 50%, the purification was finished by crystallization from acetonitrile. The yield of pure compound was 610 mg (71%). ^1H NMR δ 5.41 (s, 4H, NH_2), 6.21 (d, $J=8.8$ Hz, 4H, *o*-aniline), 6.93 (d, $J=8.8$ Hz, 4H, *m*-aniline), 7.27-7.31 (m, 32H, inner *o*-Ph, *p*-Ph, phenylene), 7.39-7.45 (m, 20H, outer Ph), 7.52-7.59 (m, 16H, inner *m*-Ph), 8.50 (s, 4H), 8.54 (s, 8H), 8.57 (s, 4H), 8.60 (s, 4H), 8.72 (s, 4H, *m*-pyridinium-phenylene- NH_2); ^{13}C NMR δ 112.38, 119.05, 122.26, 125.64, 126.08, 127.16, 128.07, 128.44, 128.94, 129.23, 129.67, 129.77, 129.94,

130.96, 132.18, 133.48, 136.00, 136.36, 137.02, 140.17, 149.44, 153.19, 153.69, 153.78, 156.56, 157.11; ESI MS m/z (%) 2689.8 (16.5, [M-A]), 1271.1 (18.6, [M-2A]/2), 795.7 (5.6, [M-3A]/3), 561.2 (60.6, [M-4A]/4), 419.2 (72.4, [M-5A]/5), 324.5 (100, [M-6A]/6); IR (KBr) ν cm⁻¹ 3471 (bw, ν_a (NH)), 3368 (bw, ν_s (NH₂)), 3044 (w, ν (CH), pyridinium and arom.), 1619 (s, ν (C-C), pyridinium and arom.), 1555 (m, ν (C-C), pyridinium), 1497 (m, ν (C-C), arom.), 1261 (bs, ν_{as} (SO₃⁻)), 1158 (bm, ν (CF₃)), 1031 (s, ν_s (SO₃⁻)), 848 (w, γ (CH), phenylene), 758 and 700 (m, γ (CH), Ph); UV (λ_{max} /nm, ϵ): 338 (147 000), 248 (54 000); FAB MS m/z (%) 2692 (55.0, [M-A]), 2573 (70.0), 2541 (65.0, [M-2A]), 2497 (54.0), 2392 (63.0, [M-3A]), 2243 (62.0, [M-4A]), 2107 (100, [M-5A]), 2069 (87.0).

α -(4-Acetamidophenyl)- ω -acetamidotri[(2,6-diphenylpyridinium-1,4-diyl)-1,4-phenylene(2,6-diphenylpyridinium-4,1-diyl)-1,4-phenylene] (3[3]) Trifluoromethanesulfonate.

The solution of **2[1]** triflate (0.5 g, 0.491 mmol) and **8** triflate (1.0 g, 1.030 mmol) in dry DMF (30 mL) was stirred and heated under argon for 2 h at 80 °C. Then dry benzene (12 mL) was added, the temperature was increased to 120 °C, water was azeotropically removed using a Dean-Stark trap and the mixture was stirred for 13 h. The solvents were evaporated under reduced pressure (1.4 Pa, 45 °C), and remaining DMF was eliminated by addition of toluene and distillation. The residue was stirred with methanol (20 mL), filtered off, washed with chloroform (2×30 mL) and dried under reduced pressure. The crude product (1.34 g) was purified by crystallization from acetonitrile. The yield of pure **3[3]** triflate was 1.19 g (83%). ¹H NMR δ 1.98 (s, 6H, CH₃), 7.20-7.33 (m, 40H, inner *o*-Ph, *p*-Ph, phenylene, acetanilide), 7.34-7.46 (m, 20H, outer Ph), 7.50-7.62 (m, 16H, inner *m*-Ph), 8.48-8.64 (m, 20H), 8.79 (s, 4H, *m*-pyridinium-NHAc), 10.00 (s, 2H, NH-Ac); ¹³C NMR δ 117.77, 125.61, 126.07, 128.15, 128.42, 128.92, 129.21, 129.69, 129.99, 130.94, 132.14, 133.02, 140.14, 153.44, 153.67, 156.55, 156.73, 168.78; IR (KBr) ν cm⁻¹ 3620 (bw, ν_a (NH₂)), 3065 (bw, ν (CH),

pyridinium and arom.), 1618 (s, $\nu(\text{C-C})$, pyridinium and arom.), 1553 (bm, amide II), 1259 (bs, $\nu_{\text{as}}(\text{SO}_3^-)$), 1158 (bm, $\nu(\text{CF}_3)$), 1030 (s, $\nu_s(\text{SO}_3^-)$), 846 (m, $\gamma(\text{CH})$, phenylene), 759 and 700 (s, $\gamma(\text{CH})$, Ph); UV ($\lambda_{\text{max}}/\text{nm}$, ϵ): 337 (152 000), 246 (91 000); ESI MS m/z (%) 338.5 (100, $[\text{M-6A}]6^+$), 435.9 (27.1, $[\text{M-5A}]5^+$), 582.1 (5.4, $[\text{M-4A}]4^+$); Anal. Calcd. for $\text{C}_{154}\text{H}_{108}\text{F}_{18}\text{N}_8\text{O}_{20}\text{S}_6$ (2924.91) C, 63.24, H, 3.72, N, 3.83, S, 6.58; Found: C, 63.38, H, 3.81, N, 3.78, S, 6.67.

α -(4-Acetamidophenyl)- ω -acetamidotetra[(2,6-diphenylpyridinium-1,4-diyl)-1,4-phenylene(2,6-diphenylpyridinium-4,1-diyl)-1,4-phenylene] (3[4]) Trifluoromethanesulfonate.

The solution of **2[2]** triflate (480 mg, 0.249 mmol) and **8** triflate (510 mg, 0.522 mmol) in dry DMF (15 mL) was stirred and heated under argon for 2 h at 80 °C. Then dry benzene (7 mL) was added, the temperature was increased to 120 °C and water was azeotropically removed using a Dean-Stark trap. After 14 h, the solvents were evaporated under reduced pressure (1.4 Pa, 45 °C), and remaining DMF was eliminated by addition of toluene and distillation. The residue was stirred with methanol (15 mL), filtered off, washed with chloroform (2×30 mL) and dried under reduced pressure. The crude product (921 mg) was purified by extraction with acetonitrile (50 mL). The yield of pure **3[4]** triflate was 746 mg (78 %). ^1H NMR δ 2.07 (s, 6H, CH_3), 7.20-7.33 (m, 56H, inner *o*-Ph, *p*-Ph, phenylene, acetanilide), 7.34-7.46 (m, 20H, outer Ph), 7.50-7.62 (m, 24H, inner *m*-Ph), 8.48-8.64 (m, 28H), 8.79 (s, 4H, *m*-pyridinium-NHAc), 10.00 (s, 2H, NH-Ac); ^{13}C NMR δ 117.80, 118.09, 125.65, 126.10, 128.15, 128.43, 128.94, 129.22, 129.72, 129.99, 130.95, 132.16, 133.06, 133.41, 136.35, 136.90, 140.17, 153.68, 156.56, 156.73, 168.82; IR (KBr) ν cm^{-1} 3501 (bw, $\nu(\text{N-H})$), 3064 (bw, $\nu(\text{CH})$, pyridinium and arom.), 1688 (m, amide I), 1617 (s, $\nu(\text{C-C})$, pyridinium and arom.), 1549 (bm, amide II), 1495 (s, $\nu(\text{C-C})$, arom.), 1261 (bs, $\nu_a(\text{SO}_3^-)$), 1157 (bm, $\nu(\text{CF}_3)$), 1030 (s, $\nu_s(\text{SO}_3^-)$), 847 (m, $\gamma(\text{CH})$, phenylene), 757 and 700 (m, $\gamma(\text{CH})$, Ph); UV ($\lambda_{\text{max}}/\text{nm}$, ϵ): 340

(206 000), 247 (118 000); ESI MS m/z (%) 330.5 (100, [M-8A]⁸⁺), 399.0 (59.6, [M-7A]⁷⁺), 490.2 (36.0, [M-6A]⁶⁺), 618.1 (5.7, [M-5A]⁵⁺); Anal. Calcd. for C₂₀₂H₁₄₀F₂₄N₁₀O₂₆S₈ (3835.81) C, 63.25, H, 3.68, N, 3.65, S, 6.69; Found: C, 63.38, H, 3.75, N, 3.58, S, 6.74.

α -(4-Acetamidophenyl)- ω -acetamidopenta[(2,6-diphenylpyridinium-1,4-diyl)-1,4-phenylene(2,6-diphenylpyridinium-4,1-diyl)-1,4-phenylene] (3[5]) Trifluoromethanesulfonate.

Method A. The solution of **2[3]** triflate (100 mg, 0.034 mmol) and **8** triflate (73 mg, 0.075 mmol) in dry DMF (8 mL) was stirred and heated under argon for 2 h at 80 °C. Then dry benzene (5 mL) was added, the temperature was increased to 120 °C and water was azeotropically removed using a Dean-Stark trap. After 18 h, the solvents were evaporated under reduced pressure (1.4 Pa, 45 °C), and remaining DMF was eliminated by addition of toluene and distillation. The residue was stirred with methanol (10 mL), filtered off, washed with chloroform (2×30 mL) and dried under the reduced pressure. The crude product (153 mg) was purified by extraction with acetonitrile (50 mL). The yield of pure **3[5]** triflate was 139 mg (86 %).

Method B. A solution of **2[3]** triflate (497 mg, 0.175 mmol) in DMF (10 mL) was added to a solution of **5**-triflate (17 g, 20.3 mmol) in DMF (270 mL) and benzene (50) mL. The mixture was stirred and boiled under argon atmosphere (bath temperature, 150 °C) under a Dean-Stark trap for 2 h. Additional **2[3]** (497 mg, 0.175 mmol) in DMF (10 mL) was added, the reaction mixture was diluted with benzene (30 mL) and the heating continued for 24 h. Then, **9** (10 g, 66.6 mmol) and benzene (100 mL) were added and the mixture was stirred and refluxed under a Dean-Stark trap overnight to remove water by azeotropic distillation. The solvent was distilled off under reduced pressure, toluene (300 mL) was added, and the heterogeneous mixture was heated under reflux for 2 h. Then the solid was filtered off on a frit and washed with chloroform. Monomeric **3[1]** was

removed by repeated extraction with a methanol/chloroform (1:1) mixture. The residue (150 mg) was recrystallized from acetonitrile. The yield of the yellow **3[5]** triflate was 98 mg (58%). ^1H NMR δ 1.96 (s, 6H, CH_3), 7.20-7.33 (m, 72H, inner *o*-Ph, *p*-Ph, phenylene, acetanilide), 7.34-7.48 (m, 20H, outer Ph), 7.49-7.62 (m, 32H, inner *m*-Ph), 8.45-8.67 (m, 36H), 8.79 (s, 4H, *m*-pyridinium-NHAc), 10.02 (s, 2H, NH-Ac); ^{13}C NMR δ 117.85, 126.10, 128.22, 128.48, 128.97, 129.26, 129.73, 129.98, 130.94, 132.18; IR (KBr) ν cm^{-1} 3548 and 3320 (bw, $\nu(\text{NH})$), 3066 (bw, $\nu(\text{CH})$, pyridinium and arom.), 1686 (wm, amide I), 1618 (s, $\nu(\text{C-C})$, pyridinium and arom.), 1555 (bm, amide II), 1498 (m, $\nu(\text{C-C})$, arom.), 1262 (bs, $\nu_{\text{a}}(\text{SO}_3^-)$), 1158 (bs, $\nu(\text{CF}_3)$), 1031 (s, $\nu_{\text{s}}(\text{SO}_3)$), 848 (wm, $\gamma(\text{CH})$, phenylene), 758 and 699 (m, $\gamma(\text{CH})$, Ph); UV ($\lambda_{\text{max}}/\text{nm}$, ϵ): 342 (252 000), 248 (145 000); ESI MS m/z (%) 325.4 (100, $[\text{M}-10\text{A}]^{10+}$), 378.4 (67.7, $[\text{M}-9\text{A}]^{9+}$), 444.3 (18.0, $[\text{M}-8\text{A}]^{8+}$), 529.0 (11.7, $[\text{M}-7\text{A}]^{7+}$); Anal. Calcd. for $\text{C}_{250}\text{H}_{172}\text{F}_{30}\text{N}_{12}\text{O}_{32}\text{S}_{10}$ (4746.70) C, 63.26, H, 3.65, N, 3.54; Found: C, 63.52, H, 3.73, N, 3.62.

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