Supporting Information

Examination of Structure-Activity Relationship of Viologen-Based Dendrimers as CXCR4 Antagonists and Gene Carriers

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Experimental details corresponding to the synthesis and analytical data of compounds VGD1 to VGD13. The synthesis of compounds: VGD1 to VGD13 are known described in literature.¹⁻¹⁰
**Figure S1.** Agarose gel electrophoresis of VGD/DNA polyplexes prepared at N/P 20.

**Figure S2.** PDI of hydrodynamic size of VGD/DNA polyplexes prepared at N/P 4.
Experimental details for the synthesis and analytical data of compounds VGD1 to VGD13

Unless otherwise mentioned, the chemicals were analytical grade from Aldrich, Merck or Fluka and used as received. Ethyl acetate, diethyl ether, THF, methanol and petrol ether were distilled before use. Organic solutions were dried over anhydrous Na₂SO₄ or MgSO₄ · 2H₂O and concentrated with a Heidolph rotary evaporator at reduced pressure. Yields are of purified products and were not optimized. All reactions were routinely monitored by thin-layer chromatography (TLC) on silica gel 60F₂₅₄ (Merck) plated and visualized by using UV erasing. Flash column chromatographic separations were carried out on silica gel Baker 60 (mesh 30-60) or Sephadex LH-20, Fluka (25-100 μm).¹H-NMR and ¹³C-NMR spectra were recorded in CD₃CN (δ = 1.93), Me₂SO-d₆ (δ = 2.50), CD₃OD-d₆ (δ = 4.87) with Me₄Si as internal standard. ¹H-NMR at 500.13 MHz and 250 MHz; ¹³C-NMR at 125.7 MHz and 63 MHz (Bruker Avance DPX-250 and Bruker AMX-500). Chemical shifts are given in ppm (δ) and the spectral data are consistent with the assigned structures. IR spectra were recorded with a Bruker Vector 22 FTIR Spektralphotometer. Elemental analyses were performed on a vario Micro cube analyzer and the maximum deviation data for C, H, and N is 4.75% of the theoretical values. This is according to requested purity of the compounds.
**Synthesis of Dendrons:**

*Synthesis of 1-(3-Bromopropyl)-5-methylpyrimidine-2,4(1H,3H)-dione* was performed according to the method by Baret et al.\(^1,2\)

To a solution of thymine (2.24 g, 17.6 mmol) in hexamethyldisilazane (HMDS, 11.4 ml, 54 mmol) under argon was added a catalytic amount of trimethylchlorosilane (1.08 ml, 8.54 mmol), and the mixture was stirred for 21 h under reflux. Excess HMDS was then removed under reduced pressure to afford crude O-silylated thymine. The crude material was taken up in DMF (10 ml), 1,3-dibromopropane (4.6 ml) was added, and the mixture was stirred at 80 °C for 24 h. Water (150 ml) was then added and, after stirring for 10 min, the mixture was filtered, and the aqueous filtrate was extracted with CH\(_2\)Cl\(_2\). The combined extracts were dried over MgSO\(_4\), filtered, and concentrated under reduced pressure. After crystallization of the residue from abs. EtOH and dried in vacuum (r.t., 24h), gave white crystals of 1-(3-bromopropyl)-5-methylpyrimidine-2,4(1H,3H)-dione; 1.5 g (6.07 mmol, 34.4%). M.p. 140 °C. \(^1\)H-NMR (500 MHz, DMSO – d\(_6\), \(\delta\)): 11.17 (s, 1H), 7.48 (s, 1H), 3.73 (t, \(^3J(\text{H, H}) = 7.0\), 2H), 3.51 (t, \(^3J(\text{H, H}) = 6.5\), 2H), 2.13 (qu, \(^3J(\text{H, H}) = 6.7\), 2H), 1.74 (s, 3H); \(^13\)C-NMR (125 MHz, DMSO - d\(_6\), \(\delta\)): 164, 151.1, 140.3, 110.4, 47.2, 31.2, 29.7, 12.6. Anal. calc. for C\(_8\)H\(_{11}\)BrN\(_2\)O\(_2\) (247.09): C 38.89, H 4.49, N 11.34; found: C 39.32, H 4.73, N 11.47.
Synthesis of 9-(2-bromoethyl)-9H-purin-6-amine. To a solution of 9 H-purin-6-amine (2.21 g, 16.35 mmol) dissolved in 110 ml of DMF, 15 g (6.8 ml) of 1,2-Dibromoethane and 6 g of \( \text{K}_2\text{CO}_3 \) was added. The reaction mixture was stirred at room temperature for 48 h under nitrogen. After 48 h the reaction mixture was filtered and the mother liquor was evaporated to dryness. The crude orange material was washed with water and filtered. The filter cake was dried and then recrystallized from EtOH. After dried in vacuum (r.t., 24h) 2 g (8.26 mmol, 50% yield) of 9-(2-bromoethyl)-9H-purin-6-amine was obtained. \( \text{^1H-NMR (500 MHz, CD}_3\text{CN,} \delta)\): 8.15 (s, 1H), 8.14 (s, 1H) 7.19 (s, 2H), 4.56 (t, 2H, \text{J}[\text{H-H}] = 6.2 \text{ Hz}), 3.93 (t, 2H, \text{J}[\text{H-H}] = 6.0 \text{ Hz}). \) \( \text{^13C-NMR (125 MHz, CD}_3\text{CN,} \delta)\): 155.8, 152.3, 149.4, 140.9, 118.6, 44.6, 31.4. Analy. calc. for \( \text{C}_7\text{H}_8\text{BrN}_5 \) (242): C 34.73, H 3.33, N 28.93; found: C 34.99, H 3.40, N 28.87.

Synthesis of 1-[3-(5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)propyl]-4-(pyridin-4-yl)pyridinium hexafluorophosphate

1.5 g (6.07 mmol) of 1-(3-bromopropyl)-5-methylpyrimidine-2,4(1H,3H)-dione and 1 g (6.41 mmol) of 4,4’-Bipyridine were dissolved in 20 ml of nitrobenzene and stirred at 110 °C for 1 hour. At the beginning the solution was clear yellow and after few minutes a yellowish precipitate was obtained. The yellow suspension was filtered, washed four times with MeCN (80 ml) and dried in HV for 12 h to obtain 1.475 g (3.64 mmol, 60%
yield as bromide salt). The bromide salt (1.400 mg, 3.46 mmol) was dissolved in 25 ml of warm water and precipitated with 10% aq. NH₄PF₆ solution. The white precipitate was filtered, washed with water and dried in vacuum for 12 h to obtain 1.117 mg (2.38 mmol, 68% yields). \(^1\)H-NMR (500 MHz, CD₃CN, \(\delta\)): 9.17 (s, 1H), 8.87-8.83 (m, 4H), 8.33 (d, 2H, \(^3\)J[H-H] = 6.5 Hz), 7.80 (d, 2H, \(^3\)J[H-H] = 6.0 Hz), 7.23 (s, 1H), 4.61 (t, 2H, \(^3\)J[H-H] = 7.2 Hz), 3.80 (t, 2H, \(^3\)J[H-H] = 6.2 Hz), 2.39 (t, 2H, \(^3\)J[H-H] = 6.5 Hz), 1.85 (s, 3H). \(^13\)C-NMR (125 MHz, CD₃CN, \(\delta\)): 165.19, 155.47, 152.29, 146.22, 142.28, 141.72, 127.12, 122.89, 111.49, 59.79, 45.36, 31.39, 12.41. Anal. calc. for C\(_{17}\)H\(_{16}\)F\(_6\)N\(_7\)P (468.3): C 46.16, H 4.09, N 11.96; found: C 45.88, H 4.68, N 12.34.

**Synthesis of 1-[2-(6-amino-9H-purin-9-yl)ethyl]-4-(pyridin-4-yl)pyridinium hexafluorophosphate**

400 mg (1.65 mmol) of 9-(2-bromoethyl)-9H-purin-6-amine was dissolved in 30 ml of nitrobenzene and 330 mg (6.4 mmol) of 4,4'-bipyridine was added. The mixture was stirred at 100 °C for 24h. After reaction the cold mixture was filtered, washed 4 times with nitrobenzene and MeCN. After dried in vacuum (r.t., 12h), 362 mg (0.9 mmol, 55% yield) product was obtain as bromide salt. The bromide salt (362 mg, 0.9 mmol) was dissolved in 10 ml of warm water and precipitated with 10% aq. NH₄PF₆ solution. The white precipitate was filtered, washed with water and dried in vacuum (r.t., 12h) to obtain 327 mg (0.70 mmol, 78 % yields). \(^1\)H-NMR (500 MHz, CD₃CN, \(\delta\)): 8.83 (d, 2H, \(^3\)J[H-H] = 6.0 Hz, 8.53 (d, 2H, \(^3\)J[H-H] = 7.0 Hz), 8.16 (d, 2H, \(^3\)J[H-H] = 6.5 Hz), 7.90 (s, 1H), 7.85 (s, 1H), 7.71 (d, 2H, \(^3\)J[H-H] = 6.0 Hz), 5.99 (s, 1H), 5.00 (t, 2H, \(^3\)J[H-H] = 5.2 Hz), 4.77 (t, 2H, \(^3\)J[H-H] = 5.2 Hz); \(^13\)C-NMR (125 MHz, CD₃CN, \(\delta\)): 157.1, 156.3,
Synthesis of 1-ethyl-4-pyridin-4-ylpyridinium hexafluorophosphate

The synthesis was performed according to a literature procedure. A suspension of 6 g (73.4 mmol) of 4, 4'-bipyridyl with 50 g (459 mmol) of ethyl bromide was stirred at 34°C for 50 h under reflux. After 30 min a brown precipitate was obtained. After 7 hours a further portion of 5 g ethyl bromide in diethyl ether (30 ml) was added dropwise. The resulting precipitate was filtered and thoroughly washed with dry diethyl ether and toluene. The crystallization of the product proceeded slowly (48 h at 4°C) from ethanol-ether-toluene. The resulting yellowish powder was dried for 24 h in HV (22 mmol, 30% yield). 1-Ethyl-4-pyridin-4-yl-pyridinium salt (4 g, 15 mmol) was dissolved in 80 ml of water, and 10 ml of a 10 % aq. NH₄PF₆ solution was added dropwise. The resulting solid was filtered off, washed with cold water and dried for 24 h in HV (3.9 g 12.1 mmol, 80% yield). ¹H-NMR: (500 MHz, DMSO-d₆, δ): 9.25 (d, ³J[H,H] = 12.5 Hz, 2H), 8.92 (d, ³J[H,H] = 4.8 Hz, 2H), 8.64 (d, ³J[H,H] = 6.5 Hz, 2H), 8.12 (d, ³J[H,H] = 4.1 Hz, 2H), 4.68 (q, ³J[H,H] = 7.3 Hz, 1H), 1.60 (t, ²J[H,H] = 7.3 Hz, 3H). ¹³C-NMR (125 MHz, DMSO-d₆, δ): 150.6, 147.2, 138.8, 134.9, 132., 115.2, 55.6, 13.8. Anal. calc. for C₁₂H₁₃F₆N₂P (330): C 43.65, H 3.97, N 8.48; found: C 41.27, H 4.34, N 8.02.
Synthesis of N-(3,5-di(hydroxymethyl)-benzyl)-4,4'-bipyridinium-hexafluoro-phosphate

The synthesis was performed according to a literature procedure. 1g (6.40 mmol) 4, 4'-bipyridine and 1 g (4.32 mmol) 3, 5-di (hydroxymethyl)-benzylbromide were dissolved in 40 mL of anhydrous THF. The reaction mixture was then refluxed for 24 hours under nitrogen. During that time the product precipitated as a pale yellow solid which was filtered, washed with CH₂Cl₂ and dried under vacuum to yield 1.5 g (3.8 mmol, 60%) of N-(3,5-di(hydroxymethyl)-benzyl)-4,4'-bipyridinium as bromide salt. The bromide salt (1.5 g, 3.8 mmol) was dissolved in 25 mL of water, and 6 mL of a 10 % aq. NH₄PF₆ solution was added dropwise. The resulting solid was filtered off, washed with cold water, and dried for 24 h in HV (yield: 1.6 g, 3.53 mmol, 92%). ¹H-NMR (250 MHz, CD₃CN, δ): 8.86-8.82 (m, 4H), 8.31 (d, J[H,H] = 6.7 Hz, 2H), 7.77 (d, J[H,H] = 6.2 Hz, 2H), 7.39 (s, 1H), 7.35 (s, 2H), 5.47 (s, 2H), 4.59 (d, J[H,H] = 4.4 Hz, 4H), 3.36 (b, 2H). ¹³C-NMR (125 MHz, CD₃CN, δ): 155.1, 152.3, 144.6, 134.2, 126.7, 126.5, 122.1, 64.3, 63.8.

Synthesis of VGD precursors: VGD1, VGD2, and VGD3

Synthesis of 1,1'-bis[2-(6-amino-9H-purin-9-yl)ethyl]-4-(pyridin-4-yl) pyridinium dihexafluorophosphate (VGD1). 200 mg (0.43 mmol) of 1-[2-(6-amino-9H-purin-9-yl)
ethyl]-4-(pyridin-4-yl) pyridinium hexafluorophosphate and 1g (4.01 mmol) of 9-(2-bromoethyl)-9H-purin-6-amine was dissolved in 15 ml of DMF. The mixture was stirred at 90 °C for 10 days. The mixture was filtered, the solid washed with DMF and MeCN several times to remove the excesses of 9-(2-bromoethyl)-9H-purin-6-amine. After drying in vacuum (r.t., 24h), 25 mg (0.04 mmol, 9.3%) 1,1'-bis[2-(6-amino-9H-purin-9-yl)ethyl]-4,4'-bipyridinium dibromide was obtained as yellow powder. The product as a bromide salt was dissolved in water and precipitated with 10% aq.NH₄PF₆ solution. The precipitate was filtered, washed with water and dried in HV for 12 h to obtain 30 mg of 1,1'-bis[2-(6-amino-9H-purin-9-yl)ethyl]-4,4'-bipyridinium dihexafluorophosphate (0.038 mmol, 95% yields). ¹H NMR (250 MHz, DMSO-d₆, δ): 9.19 (d, J=6.91 Hz, 4H), 8.63 (d, J=6.91 Hz, 4H), 8.11 (s, 2H), 7.78 (s, 2H), 7.26 (br. s., 4H), 5.14 (t, J=5.30 Hz, 4H), 4.85 (t, J=4.10 Hz, 4H); ¹³C-NMR (125 MHz, D₂O, δ): 155.82, 152.75, 150.69, 149.19, 146.21, 142.02, 127.34, 118.19, 61.52, 44.09. Anal. calc. for VGD1 as PF₆⁻ salt C₂₄H₂₄F₁₂N₁₂P₂ + 0.8 H₂O (770.46 + 14.4): C 37.41, H 3.14, N 21.82; found: C 36.73, H 3.29, N 21.41.

Synthesis of 1-[2-(6-amino-9H-purin-9-yl)ethyl]-1'-[3-(5-methyl-2,4-dioxo-3,4-dihydropyrimidin -1(2H)-yl)propyl]-4-(pyridin-4-yl) pyridinium dihexafluoro-phosphate (VGD2). 200 mg (0.44 mmol) of 1-[2-(6-amino-9H-purin-9-yl)ethyl]-4-(pyridin-4-yl)pyridinium hexafluorophosphate and 180 mg (0.72 mmol) of 1-(3-bromopropyl)-5-methylpyrimidine-2,4(1H,3H)-dione were dissolved in 30 ml of warm MeCN and stirred under reflux for 4 days. The resulting precipitate was filtered, washed four times with MeCN (40 ml) and one time with ether (10 ml). After drying in vacuum (r.t., 12h) 1-[2-(6-amino-9H-purin-9-yl)ethyl]-1'-[3-(5-methyl-2,4-dioxo-3,4dihydropyrimidin - 1(2H)-
yl)propyl]-4-(pyridin-4-yl) pyridinium dibromide 104 mg (0.16 mmol, 36% yield) was obtained. The bromide salt (100 mg, 0.15 mmol) was dissolved in 10 ml of warm water and precipitated with 10% aq.NH$_4$PF$_6$ solution. The precipitate was filtered, washed with water and dried in vacuum (r.t., 12h) (93 mg, 0.12 mmol, 80% yield). $^1$H NMR (250 MHz, CD$_3$CN, $\delta$): 9.78 (br. s, 1H), 8.94 (d, J=6.91 Hz, 2H), 8.67 (d, J=6.91 Hz, 2H), 8.34 (d, J=6.91 Hz, 2H), 8.23 (d, J=6.59 Hz, 2H), 7.94 (s, 1H), 7.79 (s, 1H), 7.23 (s, 1H), 6.22 (br. s., 2H), 5.07 (t, J=5.70 Hz, 2H), 4.80 (t, J=5.00 Hz, 2H), 4.67 (t, J=7.06 Hz, 2H), 3.79 (t, J=6.12 Hz, 2H), 2.40 (quin, J=1.00 Hz, 2H), 1.85 (s, 3H); $^{13}$C-NMR (125 MHz, CD$_3$CN, $\delta$): 165.78, 157.43, 154.05, 152.90, 151.96(s), 151.70, 151.20, 147.69, 147.37, 142.32(d), 142.08, 128.65, 128.54, 120.26, 111.93, 63.02, 60.93, 45.43, 45.40, 31.86, 12.73. Anal. calc. for VGD2 as PF$_6^-$ salt C$_{25}$H$_{27}$F$_{12}$N$_9$O$_2$P$_2$ + 0.1 H$_2$O (775.48 + 1.8): C 38.72, H 3.51, N 16.26; found: C 38.63, H 3.53, N 16.22.

**Synthesis of 1,1'-bis[3-(5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)propyl]-4-(pyridin-4-yl) pyridinium dihexafluorophosphate (VGD3).** 1.756 g (7.1 mmol, 2.3 eqv.) of 1-(3-Bromopropyl)-5-methylpyrimidine-2,4(1H,3H)-dione and 0.240 g (1.54 mmol) of 4,4'-bipyridine were dissolved in 60 ml dry DMF and stirred at 80°C for 4 days. Resulted light-yellow precipitate was filtered, washed with 20 ml DMF, 20 ml Et$_2$O and dry in ultra high vacuum at 45°C to afford 760 mg of VGD-3 as bromide salt (1.16 mmol, 76%). $^1$H NMR (500 MHz, D$_2$O, $\delta$): 9.26 (d, J=6.62 Hz, 4H), 8.66 (d, J=6.30 Hz, 4H), 7.60 (s, 2H), 4.93 (t, J=7.25 Hz, 4H), 4.05 (t, J=6.62 Hz, 4H), 2.65 (quin, J=6.70 Hz, 4H), 1.96 (s, 6H); $^{13}$C NMR (125 MHz, D$_2$O, $\delta$): 166.87, 152.31, 150.31, 145.76, 142.49, 127.16, 111.47, 59.43, 45.25, 29.53, 11.33. Anal. calc. for VGD3 as PF$_6^-$ salt C$_{26}$H$_{36}$F$_{12}$N$_6$O$_4$P$_2$ (780.48): C 40.0, H: 3.87, N 10.77; found C 39.69, H 3.60, N 10.71.
**Synthesis of comb-branched VGD: VGD4, VGD5, and VGD6**

Synthese of 1,1’-Bis[3,5-bis(bromomethyl)phenyl]-4,4’bipyridinium dihexafluoro-phosphate (4-fold nucleophilic core)

1,1’-Bis(2,4-dinitrophenyl)-4,4’-bipyridinium dichloride: the synthesis follows a known procedure.5 4 g (25.6 mmol) of 4,4’ bipyridine and 26 g (89.6 mmol) of 2,4-dinitrochlorobenzene in MeCN (150 ml) was stirred at 90°C for 24 h under reflux. At the beginning, the solution was clear brown, after 4 h first yellow crystals were obtained. The yellow suspension was filtered. The filtrate was washed once with MeCN (50 ml) and four times with diethyl ether (40 ml). After drying in vacuum for 16 h, 10.6 g as chloride (yield 18.9 mmol, 74%) of 1,1’-Bis(2,4-dinitrophenyl)-4,4’-bipyridinium dichloride was obtained.

1H-NMR (250 MHz, CD3OH, δ): 9.67 (d, J[H,H] = 7.0 Hz, 4H), 8.99 (d, J[H,H] = 7.0 Hz, 4H), 8.44 (d, J[H,H] = 7.5 Hz, 4H), 8.07 (d, J[H,H] = 7.5 Hz, 4H).

3,5-Bis-(hydroxymethyl)aniline was synthesized in two steps from 5- aminoisophthalic acid according to previously reported procedures.6-7 LiAlH4 2 g (52.7 mmol) was suspended in 300 mL of diethylether. 5-amino-isophtalsäuredimethylester 5 g (23.9 mmol) was extracted with refluxing ether for 1 week at 50°C. During that time there was a hydrogen evolution, and the color of the reaction mixture turned to orange. After cooling to 0°C, the reaction mixture was quenched by addition of 200 mL of water and neutralized with 10% of H2SO4. The ether phase was evaporated, and the aqueous phase was extracted in a Ludwig-extractor with ethyl acetate for 3 days. After this period ethyl acetate was removed in vacuum, and the residue was crystallized from MeOH/Et2O to
yield 1.20 g (7.65 mmol, 32%) of yellow crystals. $^1$H-NMR (250 MHz, DMSO-d$_6$, $\delta$): 6.50 (s, 1H), 6.45 (8s, 2H), 4.93 (t, $J_{H,H} = 5.8$Hz, 4H), 4.32 (d, $J_{H,H} = 5.3$ Hz, 4H).

$1,1'$-bis[3,5-bis(hydroxymethyl)phenyl]4,4'$'$-bipyridinium dihexafluorophosphate

A mixture of 1 g (1.28 mmol) of 1,1'-Bis(2,4-dinitrophenyl)-4,4'-bipyridinium dichloride and 460 mg (3.1 mmol) of 2,4-Bis-(hydroxymethyl)aniline in 50 ml MeOH was stirred at 70°C for 23 h under reflux. The cold mixture was poured into 100 ml of brined diethyl ether. The brown precipitate was filtered off and washed three times with ether and dried in HV. The resulted brown powder was dissolved in 80 ml H$_2$O and 10 ml of a 10% NH$_4$PF$_6$ solution was added dropwise. After drying in vacuum for 6 h, 813 mg (1.14 mmol, 89 % yield) of 1,1'-bis[3,5-bis(hydroxymethyl)phenyl]4,4'-bipyridinium dihexafluorophosphate was obtained. $^1$H-NMR: (250 MHz, DMSO-d$_6$, $\delta$): 9.68 (d, $J_{H,H} = 6.1$ Hz, 4H), 9.03 (d, $J_{H,H} = 6.2$ Hz, 4H), 7.74 (s, 4H), 7.68 (s, 2H), 5.58 (b, 4H), 4.70 (s, 8H).

$1,1'$-bis[3,5-bis(halomethyl)phenyl]-4,4'$'$-bipyridinium hexafluorophosphate

The synthesis was performed according to a literature procedure.$^4$ 1,1'-Bis[3,5-bis(hydroxymethyl)phenyl]-4,4'-bipyridinium salt (630 mg, 0.875 mmol) was dissolved in 150 ml of HBr/acetic acid under argon and stirred for 4 d. at r.t. The reaction mixture...
was evaporated, and the residue was dissolved in 2 ml of water and 3 ml of a 10% aq. \( \text{NH}_4\text{PF}_6 \) solution was added. The brown precipitate was filtered, washed with water and dried in HV. The resulting brown powder was dissolved in MeNO\(_2\) and 5 ml of 10% aq. \( \text{NH}_4\text{PF}_6 \) was added dropwise. The organic phase was filtered, and the light brown precipitate was washed with CHCl\(_3\), ether and water. A light brown powder was isolated and dried for 24 h in HV (0.501 mmol, 57% yields). \(^1\text{H}-\text{NMR}:\) (250 MHz, CD\(_3\)CN, \( \delta \)): 9.21 (d, \(^3\text{J}[\text{H,H}] = 7.1 \text{ Hz}, \ 4\text{H})\), 8.64 (d, \(^3\text{J}[\text{H,H}] = 7.1\text{ Hz}, \ 4\text{H})\), 7.93 (s, 2H), 7.80 (s, 2H), 4.71 (s, 8H), 4.69 (s, 8H). \(^{13}\text{C}-\text{NMR}\) (63 MHz, CD\(_3\)CN, \( \delta \)) : 150.7, 146.3, 143.0, 142.5, 133.6, 128.0, 125.6, 31.5. Anal. calc. for C\(_{26}\)H\(_{22}\)Br\(_4\)F\(_6\)N\(_2\)P\(_2\) (972): C 32.13, H 2.28, N 2.88; found: C 31.54, H 2.44, N 2.83.

Synthesis of VGD5

80 mg (0.082 mmol) tetrabromide precursor and 230 mg (0.49 mmol) of 1-[3-(5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)propyl]-4-(pyridin-4-yl)pyridinium hexafluorophosphate were dissolved in 20 mL of MeCN. The mixture was refluxed at 70 °C for 5 days. The cooled reaction mixture was filtered, washed with MeCN (10 mL) and ether, respectively, and dried. The mother liquor was evaporated, and the residue was dried. The residue was dissolved in 7 mL of nitromethane and extracted with 3 mL of a NH\(_4\)PF\(_6\) solution (10 % in water). The organic phase was washed one more time with water and evaporated to dryness. The residue was put in water, filtered, washed several times with water and dried in a vacuum for 12 h. The product was purified by chromatography (Sephadex LH-20, column 2.5 × 25 cm, MeCN : MeOH,1:1 as eluent) the product 160 mg dendrimer VGD-5 (0.051 mmol, 62% yields), after dried in a vacuum at 40°C for 24
$^1$H-NMR (500 MHz, CD$_3$CN, δ): 9.10 (d, 4H, $^3$J[H-H] = 6.5 Hz), 8.98 (d, 8H, $^3$J[H-H] = 5.5 Hz), 8.94 (d, 8H, $^3$J[H-H] = 6.0 Hz), 8.63 (d, 4H, $^3$J[H-H] = 4.0 Hz), 8.41 (d, 8H, $^3$J[H-H] = 5.5 Hz, 8.37 (d, 8H, $^3$J[H-H] = 5.5 Hz), 7.97 (s, 2H), 7.90 (s, 4H), 7.20 (s, 4H), 5.98 (s, 8H). 4.65 (t, 6H, $^3$J[H-H] = 7.2 Hz), 3.77 (t, 8H, $^3$J[H-H] = 6.2 Hz), 2.36 (t, 8H, $^3$J[H-H] = 6.7 Hz), 1.82 (s, 12H). $^{13}$C-NMR (125 MHz, CD$_3$CN, δ): 165.2, 152.6, 152.0, 151.0, 147.1, 147.0, 146.8, 144.5, 141.7, 137.3, 135.0, 128.7, 128.3, 128.1, 111.6, 64.2, 60.4, 45.3, 31.4, 12.4. IR (cm$^{-1}$): 3650.5, 3073.0, 2977.6, 1674.8, 1637.4, 1452.4, 1366.1, 1223.2, 820.1, 552.9. UV-Vis (MeCN, partial reduced): $V^{++}$ $\lambda_{max}$: 264 (64465), 422 (4352); $V^+$ at -0.5 V $\lambda_{max}$: 402 (70253), 608 (27740). Anal. calc. for C$_{98}$H$_{98}$F$_{60}$N$_{18}$O$_{8}$P$_{10}$ (3105.5): C 37.90, H 3.18, N 8.12; found: C 37.10, H 4.71, N 7.87.

**Synthesis of dendrimer VGD6**

100 mg (0.028 mmol) octabromide precursor and 150 mg (0.31 mmol) of 1-[3-(5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)propyl]-4-(pyridin-4-yl)pyridinium hexafluorophosphate were dissolved in 20 ml of MeCN. The mixture, protected from light was refluxed at 75 °C for 1 week. The cooled reaction mixture was filtered and washed with ether, respectively, and dried. The mother liquor was evaporated, and the residue was dried. The residue was dissolved in 7 mL of nitromethane and extracted with 3 mL of a NH$_4$PF$_6$ solution (10 % in water). The organic phase was washed one more time with water and evaporated to dryness. The residue was put in water, filtered, washed several times with water and dried in a vacuum for 12 h. The product was purified by chromatography (Sephadex LH-20, column 2.5 × 25 cm, MeCN : MeOH,1:1 as eluent) the product 140 mg VGD-6 (0.017 mmol, 60% yields) after dried in vacuum at 40°C for
24 h. $^1$H-NMR (500 MHz, CD$_3$CN, $\delta$): 9.16 (s, 4H), 8.97-8.92 (m, 48H), 8.68 (s, 4H), 8.44-8.37 (m, 48H), 8.01 (s, 4H), 7.68 (s, 12H), 7.66 (s, 2H), 7.23 (s, 8H), 5.98 (s, 8H), 5.84 (s, 24H), 4.67 (t, 16H, $^3$J[H-H] = 7.2 Hz), 3.79 (t, 16H, $^3$J[H-H] = 6.0 Hz), 2.38 (qu, 16H, $^3$J[H-H] = 6.6 Hz), 1.83 (s, 24H). $^{13}$C-NMR (125 MHz, CD$_3$CN, $\delta$): 165.3, 152.7, 151.7, 151.1, 147.1, 146.9, 146.8, 141.8, 137.4, 137.2, 128.6, 128.5, 128.3, 111.6, 64.8, 64.2, 45.3, 31.4, 12.4. IR (cm$^{-1}$): 3650.0, 3071.9, 2977.7, 1674.0, 1636.9, 1451.6, 1367.3, 1223.1, 1172.2, 851.3. UV-Vis (MeCN, partial reduced): $V^{\text{+}}$, $\lambda_{\text{max}}$: 269 (250850), 424 (16487); $V^{\text{+}}$ at -0.5 V $\lambda_{\text{max}}$: 402 (206665), 608 (78825). Anal. calc. for C$_{246}$H$_{242}$F$_{156}$N$_{42}$O$_{16}$P$_2$ (7811.8): C 37.82, H 3.12, N 7.53; found: C 36.66, H 4.71, N 7.30.

**Synthesis of spheroidal VGD: VGD7-13**

$1,1'$-1''-[benzene-1,3,5-triyl-tris(methylene)]-tris-[1'-1-(3-propyl)-5-methyl-pyrimidine-2,4(1H,3H)-dione]-4,4'-bipyridinium hexafluorophosphate – VGD$_8$

A solution of 214 mg (0.20 mmol) of 1,1',1''-[benzene-1,3,5-triyl-tris(methylene)tris(4-pyridin-4-ylpyrimidin trihexafluorophosphate in 10 ml of MeCN were added to a stirred solution of 1,570 g (6.33 mmol) of 1-(3-bromopropyl)-5-methyl -1H- pyrimidine -2,4-dione in 45 ml of MeCN. The whole mixture was refluxed for four days at 85 °C. The cooled reaction mixture was added dropwise to 30 ml of a stirred tetrabutylammonium chloride solution (5 % in MeCN). The yellowish precipitate was filtered off and washed three times with 10 ml of MeCN and three times with 10 ml of CH$_2$Cl$_2$. After drying for 24 hours in vacuum the powder was dissolved in 20 ml of water and precipitated with NH$_4$PF$_6$ solution(10 % in water).The residue was washed several times with water and
dried in vacuum for 24 hours to obtain 285 mg (0.14 mmol, 70 %) of VGD-8 thymine.

$^1$H-NMR (500 MHz, CD$_3$CN, $\delta$): 9.34 (s, 3H), 8.98 (d, $^3$J [H,H] = 6.5 Hz, 6H), 8.93 (d, $^3$J [H,H] = 7.0 Hz, 6H), 8.43-8.34 (m, 12H), 7.68 (s, 3H), 7.24 (s, 3H), 5.86 (s, 6H), 4.68 (t, $^3$J [H,H] = 7.2 Hz, 6H), 3.80 (t, $^3$J [H,H] = 6.2 Hz, 6H), 2.39 (qu, $^3$J [H,H] = 6.7 Hz, 6H), 1.85 (s, 9H). $^{13}$C-NMR (125 MHz, CD$_3$CN, $\delta$): 165.4, 152.7, 151.7, 151.1, 146.8, 141.7, 136.1, 132.8, 128.5, 111.6, 64.8, 60.4, 45.3, 31.4, 12.4. Anal. calc. for C$_6$H$_{66}$F$_{36}$N$_{12}$O$_6$P$_6$ (1957): C 38.66, H 3.39, N 8.58; found: C 38.37, H 3.65, N 7.60.

**Synthesis of 1,1',1''-[benzene-1,3,5-triyltris(methylene) tris(3,5-di(bromomethyl) benzene- (4,4'-bipyridinium)] hexafluorophosphate**

1,1',1''-[benzene-1,3,5-triyltris(methylene)tris(4-pyridin-4-ylpyridinium trihexafluorophosphate]

The synthesis was performed according to a literature procedure. 4,4'-Bipyridine (14 g, 89 mmol) was dissolved in warm MeCN (80 ml), and 2.1 g (5.8 mmol) of 1,3,5 tris (bromomethyl) benzene was added in 50 ml MeCN within 7 h (1 ml/8.5 minute). The mixture was stirred at 70°C for 30 h under reflux. The cold mixture was filtered and
washed three times with CH$_2$Cl$_2$. The filter cake was dissolved in water and extracted four times with CH$_2$Cl$_2$. Methanol was added dropwise to initiate the precipitation. A yellow powder was obtained and dried in HV (4.4 mmol, 74% yields as bromide salt). The bromide-salt (3.2 g, 3.88 mmol) was dissolved in 80 ml of water, and 15 ml of a NH$_4$PF$_6$ 10% was added dropwise. The precipitate was filtered and washed with cold water; a white powder was obtained and dried for 24 h in HV (2.7 mmol, 78% yields).

$^1$H-NMR: (250 MHz, CD$_3$CN, δ): 8.87 (d, $^3$J[H,H] = 6.3 Hz, 6H), 8.82 (d, $^3$J[H,H] = 7.0 Hz, 6H), 8.38 (d, $^3$J[H,H] = 7.0 Hz, 6H), 7.83 (d, $^3$J[H,H] = 6.3 Hz, 6H), 7.59 (s, 3H), 5.81 (s, 6H).

3,5-Di(hydroxymethyl)benzylbromide:

The synthesis follows a known procedure.$^4$ A solution of 4.4 g (26.2 mmol) 1,3,5-tris(hydroxymethyl)benzene and 6.86 g (26.2 mmol) triphenylphosphine in anhydrous THF 220 ml was stirred at room temperature. Dropwise solution of 8.6 g (25.9 mmol) tetrabromomethane in anhydrous THF was added. The reaction occurred for 2.5 hours. The white precipitate of triphenylphosinoxide was filtered and the mother liquor evaporated. The mixture of 3,5-di(hydroxymethyl)benzylbromide, 3,5-di(bromomethyl)hydroxymethyl benzene and 1,3,5-tris(bromomethyl) benzene was separated by column chromatography (silica gel and ethyl acetate as eluent). The first fraction was 1,3,5-tris(bromomethyl) benzene, the second fraction was 3,5-di(bromomethyl)hydroxymethyl benzene 279 mg (0.95 mmol, 8%) and the third fraction was 3,5-di(hydroxymethyl) benzylbromide 1150 mg (5.4 mmol, 45%). The second fraction was recrystallized from chloroform/petrolether and the third fraction was
recrystallized from dioxane/petrolether. \(^1\text{H}\)-NMR: (250 MHz, CD\(_3\)CN, \(\delta\)): 7.29 (s, 2H), 7.25 (s, 1H), 4.60 (s, 2H) 4.57 (d, \(3J_{\text{H-H}} = 5.9\) Hz, 4H), 3.30 (t, \(3J_{\text{H-H}} = 5.9\) Hz, 2H).

1 g (0.98 mmol) 1,3,5-tris(4,4’-bipyridinium)methyl)benzene-tris(hexafluorophosphate) was dissolved in MeCN (50 ml) and 0.9 g (3.9 mmol) of 1,3,5-di(hydroxymethyl)benzyl bromide in 5 ml MeCN was added. The mixture was stirred at 95°C for 44 h under reflux. The resulting precipitate was filtered and thoroughly washed with dry diethyl ether and dried in vacuum. The product was isolated as light yellow powder as bromide salt 1.46 g (0.96 mmol, 98% yield). The bromide salt (1.46 g, 0.96 mmol) was dissolved in 80 ml of water, and 15 ml of a NH\(_4\)PF\(_6\) 10% was added dropwise. The precipitate was filtered and washed with cold water; a white powder was obtained and dried for 24 h in vacuum, 1.6 g (0.84 mmol, 87% yields) of 1,1,’1,”’-[benzene-1,3,5-triyltris(methylene) tris(3,5-di(hydroxymethyl)benzene- (4,4’-bipyridinium)) hexafluorophosphate was obtained. \(^1\text{H}\)-NMR: (250 MHz, CD\(_3\)CN, \(\delta\)): 8.95 (d, \(3J_{\text{H-H}} = 6.5\) Hz, 6H), 8.92 (d, \(3J_{\text{H-H}} = 6.5\) Hz, 6H), 8.40-8.36 (m, 12H), 7.67 (s, 3H), 7.44 (s, 3H), 7.40 (s, 6H), 5.82 (s, 12H), 4.63 (d, \(3J_{\text{H-H}} = 5.0\) Hz, 12H), 3.42 (t, \(3J_{\text{H-H}} = 5.3\) Hz, 6H).

1,1,’1,”’-[benzene-1,3,5-triyltris(methylene) tris(3,5-di(brommethyl)benzene- (4,4’-bipyridinium)) hexafluorophosphate] The synthesis was performed according to a literature procedure.\(^3\) 1,1,’1,”’-[benzene-1,3,5-triyltris(methylene) tris(3,5-di(hydroxymethyl)benzene- (4,4’-bipyridinium)) hexafluorophosphate (1 g, 0.6 mmol) was dissolved in 200 ml of HBr/acetic acid under argon and stirred for 4 d. at r.t. The reaction mixture was evaporated, and the residue was dissolved in 2 ml of water and 3 ml of a 10% aq. NH\(_4\)PF\(_6\) solution was added. The brown precipitate was filtered, washed with water and dried in HV. A white powder was isolated
and dried for 24 h in HV (1.20 g, 0.52 mmol, 86 % yields). $^1$H-NMR: (250 MHz, CD$_3$CN, $\delta$ ): 8.95 (d, $^3$J[H,H] = 6.5 Hz, 6H), 8.64 (d, $^3$J[H,H] = 6.5Hz, 6H), 8.39 (d, $^3$J[H,H] = 6.5 Hz, 12H), 7.69 (s, 3H), 7.60 (s, 3H), 7.47 (s, 6H), 5.82 (s, 6H), 5.80 (s, 6H), 4.58 (s,12H). $^{13}$C-NMR (63 MHz, CD$_3$CN, $\delta$ ): 150.7, 146.3, 135.3, 134.0, 132.1, 131.5, 130.1, 128.2, 64.2, 32.5.

**Synthesis of VGD10**

106 mg (0.046 mmol) hexabromide precursor and 230 mg (0.49 mmol) of 1-[3-(5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)propyl]-4-(pyridin-4-yl)pyridinium hexafluoro-phosphate were suspended in 20 mL of MeCN. The mixture, protected from light was refluxed at 75 °C for 6 days. The cooled reaction mixture was filtered and washed with ether, respectively, and dried. The mother liquor was evaporated, and the residue was dried. The combined solids were dissolved in 10 mL of nitromethane and extracted with 4 mL of a NH$_4$PF$_6$ solution (10 % in water). The organic phase was washed one more time with water and evaporated to dryness. The residue was put in water, filtered, washed several times with water and dried in a vacuum for 12 h. For purification the product was further dissolved in MeNO$_2$ and extracted with water for one week in a Ludwig apparatus. The MeNO$_2$ phase was evaporated and dried in HV for 12 h. The residue was washed with water, filtered and dried in a vacuum to obtain 156 mg 7 (0.028 mmol, 61% yields). $^1$H-NMR (500 MHz, DMSO-$d_6$, $\delta$ ): $\delta$ = 9.29 (s, 6H), 8.98-8.92 (m, 36H ), 8.32-8.38 (m, 36H ), 7.69 (s, 9H ), 7.65 (s, 3H), 7.24 (s, 6H), 5.85 (s, 24H), 4.69 (t, 12H, $^3$J[H-H] = 7.5 Hz), 3.81 (t, 12H, $^3$J[H-H] = 8.7 Hz), 2.39 (t, 12H, $^3$J[H-H] = 6.7 Hz), 1.85 (s, 18H). $^{13}$C-NMR (125 MHz, CD$_3$CN, $\delta$ ): 165.6, 153.1, 152.3,
151.7, 147.4, 142.2, 136.5, 136.5, 133.5, 133.4, 129.1, 129.1, 128.8, 112.1, 65.3, 61.0, 45.8, 31.8, 12.0. IR (cm⁻¹): 3651.4, 3072.2, 2977.9, 1674.8, 1637.9, 1450.9, 1362.6, 1223.4, 1167.7, 813.0, 552.3. UV-Vis (MeCN): V⁺⁺ λmax: 268 (159365), 422 (20177); V⁺ at -0.5 V λmax: 402 (121785), 608 (37488). Anal. calc. for C₁₇₄H₁₇₄F₁₀₈N₃₀O₁₂P₁₈ (5486.8): C 38.09, H 3.20, N 7.66; found: C 37.20, H 3.35, N 7.39.

**Synthesis of dendrimer VGD11**

140 mg (0.022 mmol) dodecaboride precursor and 150 mg (0.32 mmol) of 11-[3-(5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)propyl]-4-(pyridin-4-yl)pyridinium hexafluorophosphate were suspended in 20 mL of MeCN. The mixture, protected from light was refluxed at 75 °C for 4 days. The cooled reaction mixture was filtered and washed with ether, respectively, and dried. The mother liquor was evaporated, and the residue was dried. The combined solids were dissolved in 10 mL of nitromethane and extracted with 4 mL of a NH₄PF₆ solution (10 % in water). The organic phase was washed one more time with water and evaporated to dryness. The residue was put in water, filtered, washed several times with water and dried in a vacuum for 12 h. For purification the product was further dissolved in MeNO₂ and extracted with water for one week in a Ludwig apparatus. The MeNO₂ phase was evaporated and dried in HV for 12 h. The residue was washed with water, filtered and dried in a vacuum at 40 °C for 24 h to obtain 140 mg **VGD11** (0.011 mmol, 50% yields). ¹H-NMR (500 MHz, CD₃CN, δ): 11.24 (s, 12H), 9.37 (s, 84H), 9.14 (m, 84H), 7.79 (b, 30H), 7.49 (s, 12H), 5.92 (s, 60H), 4.74 (s, 24H), 3.78 (s, 24H), 2.35 (s, 24H), 1.77 (s, 36H). ¹³C-NMR (125 MHz, CD₃CN, δ): 164.2, 151.1, 149.1, 148.3, 146.0, 140.8, 135.3, 130.0, 126.8, 126.3, 109.0, 62.7,
58.6, 43.9, 30.2, 11.9. IR (cm⁻¹): 3648.6, 3073.0, 2980.5, 1673.3, 1637.7, 1450.9, 1363.5, 1223.6, 1167.7, 817.0, 553.3. UV-Vis (MeCN): V⁺⁺ λmax: 267 (436080), 422 (20119); V⁺ at -0.5 V λmax: 402 (358640), 608 (145420). Anal. calc. for C₃₉₆H₃₉₀F₂₅₂N₆₆O₂₄P₄₂ (12546.3): C 37.91, H 3.13, N 7.37; found: C 36.59, H 3.39, N 6.81.

**Synthesis of dendrimer VGD13**

230 mg (0.016 mmol) tetraeicosaborimid precursor and 225 mg (0.48 mmol) of 1-[3-(6-hydroxy-5-methyl-2-oxo-1,2,3,6-tetrahydropyridin-3-yl)propyl]-4-(pyridin-4-yl)pyridinium were suspended in 15 mL of MeCN. The mixture was refluxed at 75 °C for one week. The cooled reaction mixture was filtered and washed with ether, respectively, and dried. The mother liquor was evaporated, and the residue was dried. The combined solids were dissolved in 10 mL of nitromethane and extracted with 4 mL of a NH₄PF₆ solution (10 % in water). The organic phase was washed one more time with water and evaporated to dryness. The residue was put in water, filtered, washed several times with water and dried in a vacuum for 12 h. For purification the product was further dissolved in MeNO₂ and extracted with water for one week in a Ludwig apparatus. The MeNO₂ phase was evaporated and dried in HV for 12 h. The residue was washed with water, filtered and dried in a vacuum at 40°C for 24 h to obtain 270 mg VGD13 (0.010 mmol, 63% yields). ¹H-NMR (500 MHz, CD₃CN, δ): 8.98-8.93 (m, 180H), 8.40-8.39 (m, 180H), 7.68 (b, 66H), 7.25 (s, 24H), 5.86 (s, 132H), 4.68 (t, 48H, ¹J[H-H] = 7.0 Hz), 3.80 (t, 48H, ¹J[H-H] = 5.5 Hz), 2.39 (t, 48H, ³J[H-H] = 6.0 Hz), 1.84 (s, 72H). ¹³C-NMR (125 MHz, CD₃CN, δ) 165.1, 152.4, 151.5, 150.8, 146.6, 135.7, 132.6, 128.4, 128.3, 128.3, 111.35, 64.5, 60.1, 45.0, 31.2, 12.1. IR (cm⁻¹): 3650.7, 3138.63, 2977.7, 1676.3, 1638.2,
1451.1, 1380.2, 1165.0, 820.7, 553.7. UV-Vis (MeCN): $V^{++}$ $\lambda_{\text{max}}$: 268 (517700), 416 (28088); $V^+$ at -0.5 V $\lambda_{\text{max}}$: 402 (418805), 608 (170175). Anal. calc. for C$_{841}$H$_{824}$F$_{540}$N$_{138}$O$_{48}$P$_{90}$ (26679.4): C 37.86, H 3.11, N 7.25; found: C 36.03, H 3.47, N 6.62.

The compound VGD-4, VGD-9, VGD-12, VGD-8 were performed according to a literature procedure.$^{10,11}$

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