Supporting Information

Trimethylenedipyridinium Dendrimers: Synthesis and Sequential Complexation of Anthraquinone disulfonate in Molecular Shells

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1. Experimental Section

General:

The synthetic procedure of the benzylicbromide precursors V₁, W₁ and the end group E”·PF₆⁻ have been reported elsewhere.¹ All starting materials and solvents were purchased from Sigma-Aldrich and used without further purification. All reactions were performed under dry conditions. HPLC grade or ACS Spectrophotometric grade solvents were used for Electrochemical measurements. Elemental analyses were performed on Elementar Vario Micro cube instrument. For the host-guest interaction studies, commercially available anthraquinone-2,6-disulfonic acid disodium salt was ion-exchanged using TBA.Br in DCM/H₂O and the obtained (TBA)₂.AQDS was NMR pure [slight excess of TBA.Br was noticed].

NMR spectra were recorded on Bruker 250 Avance spectrometer at 25°C, ¹H NMR spectra were measured at 250 MHz; ¹³C NMR spectra were measured at 63 MHz using CD₃CN or DMSO-d₆ as a solvent and internal reference. All chemical shifts are reported in parts per million (δ, ppm) with respect to internal standard. ¹H NMR titrations were recorded on Bruker Avance 250 spectrometer. DOSY and NOESY spectra were recorded on a Bruker Avance III 500 MHz spectrometer. Diffusion measurements were performed at different guest concentrations using a ¹H NMR pulsed-gradient experiment: the simulated spin-echo sequence which leads to the measurement of the diffusion coefficient D, where D is the slope of the straight line obtained when ln(I) is displayed against the gradient-pulse power’s square according to the following equation: ln(I) = -γ²G²Dδ²(Δ-δ/3), where I is the relative intensity of a chosen resonance, γ is the proton gyromagnetic ratio, Δ is the intergradient delay (60 ms), δ is the gradient pulse duration (varied between 1.5 ms to 5 ms), and G is the gradient intensity.
Electrochemistry:

Cyclic voltammograms were measured under Ar with a PGSTAT 20 potentiostat from AUTOLAB controlled by a PC running under GPES for Windows, Version 4.2 (ECO Chemie 1995); a glassy carbon electrode (GCE) from Metrohm (6.0804.010) with an active electrode surface of 0.07 cm$^2$ at $v = 0.1$ V/s was used at RT. The electrode surface was polished with Al$_2$O$_3$ prior to each scan. The reference electrode was Ag / AgCl / KCl(sat.), separated by a salt bridge (DMF + 0.1 M TBA.PF$_6$) from the cell; the counter electrode was a Pt-wire.
2. Detailed synthetic procedures

The procedures are organized according to the following sequence

a) Synthesis of benzylic TMDPy dendrimers using the divergent strategy

\[ \text{V}_2.\text{PF}_6^-: \]
\[ \text{E}.\text{PF}_6^-: \]
\[ \text{E}'.\text{PF}_6^-: \]
\[ \text{P}_0.3\text{PF}_6^-: \]
\[ \text{G}_0.6\text{PF}_6^-: \]
\[ \text{G}_0'.6\text{PF}_6^-: \text{ (not mentioned in main paper)} \]
\[ \text{G}_0' '.6\text{PF}_6^-: \text{ (not mentioned in main paper)} \]
\[ \text{P}_1.6\text{PF}_6^-: \]
\[ \text{G}_1.18\text{PF}_6^- \]
\[ \text{P}_2.18\text{PF}_6^-: \]
\[ \text{G}_2.42\text{PF}_6^-: \]

b) Synthesis of benzylic TMDPy dendrimer subunits for the divergent synthetic strategy

\[ \text{W}_2.2\text{PF}_6^-: \]
\[ \text{W}_3.4\text{PF}_6^-: \]
a) Synthesis of benzylic TMDPy dendrimers using divergent strategy

\[ \text{V}_2\text{PF}_6: \quad 1-(3,5\text{-bis(hydroxymethyl)benzyl})-4-(3\text{-(pyridin-4-yl)propyl})\text{pyridinium hexafluorophosphate (V):} \]

4,4’-Trimethylenedipyridine (2.14 g, 10.8 mmol) was dissolved in 30 mL CH\textsubscript{3}CN and heated to 80°C under stirring. To this solution 3,5-bis(hydroxymethyl)benzyl bromide \text{V}_1 (0.5 g, 2.16 mmol) dissolved in CH\textsubscript{3}CN (20 mL) was added slowly over 6 h. The solution was stirred for another 10 h, cooled to RT and the solvent was removed under reduced pressure. The residue was partitioned between water (100 mL) and CH\textsubscript{2}Cl\textsubscript{2} (100 mL), washed with CH\textsubscript{2}Cl\textsubscript{2} to remove excess 4,4’-trimethylenedipyridine. The aqueous solution was then concentrated to 50 mL, 3 mL of 3M NH\textsubscript{4}PF\textsubscript{6} solution was added and a viscous liquid settled down, the aqueous layer was decanted, washed with water and dried to yield \text{V}_2\text{PF}_6 as brown viscous liquid, 0.96 g (89%); \text{1H-NMR (250 MHz, (CD}_3\textsubscript{2}CO) 8 ppm 8.98 (d, 2H), 8.34 (dd, 2H), 8.05 (d, 2H), 7.36 (s, 3H), 7.20 (dd, 2H), 5.85 (s, 2H), 4.56 (s, 4H), 3.02 (t, 2H), 2.73 (t, 2H), 2.16-2.04 (m, 2H). \text{13C NMR (63 MHz, (CD}_3\textsubscript{2}CO) 8 ppm 163.4, 151.4, 148.7, 143.9, 133.3, 128.3, 125.7, 125.3, 124.1, 63.9, 63.1, 34.7, 34.1, 29.6.}

\[ \text{E’PF}_6: \quad \text{1-benzyl-4-(3-(pyridin-4-yl)propyl)pyridinium hexafluorophosphate(V)} \]

The above mentioned procedure is followed. Brown viscous liquid, 1.02 g (80%); \text{1H-NMR (250 MHz, CD}_3\text{CN) 8 ppm 8.64 (d, 2H), 8.49 (d, 2H), 7.88 (d, 2H), 7.49 (s, 5H), 7.26 (d, 2H), 7.09 (m, 1H), 6.83 (d, 2H), 6.50 (s, 1H), 2.43 (s, 3H), 1.89 (s, 3H), 1.64 (s, 3H), 1.53 (s, 3H).}
5.68 (s, 2H), 2.96 (t, 2H), 2.74 (t, 2H), 1.97 (s, 2H). $^{13}$C-NMR (63 MHz, $CD_3CN$) δ ppm 163.6, 151.2, 149.1, 143.7, 133.2, 129.8, 129.5, 129.0, 128.3, 124.1, 63.7, 34.6, 33.9, 29.7.

**E.PF$_6$:** 1-(4-tert-butylbenzyl)-4-(3-(pyridin-4-yl)propyl)pyridinium hexafluorophosphate(V)

![Chemical Structure](image)

1-(4-tert-butylbenzyl)-4-(3-(pyridin-4-yl)propyl)pyridinium hexafluorophosphate(V) was synthesized by reacting 4,4′-trimethylenedipyridine (1.74 g, 8.8 mmol) and 4-( tert-butyl)benzyl bromide (4-tert-BuBnBr) (1 g, 4.4 mmol) in 50 mL EtOAc under refluxing conditions. The solution was stirred for 6 h, cooled to RT and the precipitate was filtered, washed with excess EtOAc. The residue was dissolved in water, 3 mL of 3M NH$_4$PF$_6$ solution was added, the product settled down as a viscous liquid, the aqueous layer was decanted, washed with water and dried to yield E.PF$_6$ as white solid, 2.05 g (95%); $^1$H-NMR (250 MHz, $CD_3CN$) δ ppm 8.61 (d, 2H), 8.49 (s, 2H), 7.86 (d, 2H), 7.54 (d, 2H), 7.38 (d, 2H), 7.24 (d, 2H), 5.63 (s, 2H), 2.95 (t, 2H), 2.73 (t, 2H), 2.12-2.01 (m, 2H), 1.33 (s, 9H); $^{13}$C-NMR (63 MHz, $CD_3CN$) δ ppm 163.6, 153.1, 150.9, 149.3, 143.5, 130.3, 128.7, 128.3, 126.4, 124.1, 63.4, 34.6, 34.4, 30.4, 29.7; Anal. Calcd for C$_{24}$H$_{29}$N$_2$PF$_6$.H$_2$O: C, 56.69; H, 6.14; N, 5.51. Found C, 56.56; H, 6.04; N, 5.53.
$P_{0.3}PF_6$: 1,1’,1''-(benzene-1,3,5-triyl)tris(methylene)tris(4-(3-(pyridin-4-yl)propyl)pyridinium) hexafluorophosphate(V)

4,4’-Trimethylenedipyridine (6.25 g, 31.5 mmol) was dissolved in 50 mL CH$_3$CN and heated to 80°C under stirring. To this solution 1,3,5-tris(bromomethyl)benzene (0.75 g, 2.1 mmol) dissolved in CH$_3$CN (20 mL) was added slowly over 8 h. The solution was stirred overnight, cooled to RT and the solvent was removed under reduced pressure. The residue was partitioned between water (100 mL) and CH$_2$Cl$_2$ (100 mL), washed with CH$_2$Cl$_2$ to remove excess 4,4’-trimethylenedipyridine. The aqueous layer was then concentrated to 50 mL, 3 mL of 3M NH$_4$PF$_6$ solution was added, viscous liquid settled down, the aqueous layer was decanted, washed with water and the sample was dried to yield $P_{0.3}PF_6$ as a brown solid, 1.92 g (80%); $^1$H-NMR (250 MHz, CD$_3$CN) $\delta$ ppm 8.51 (dd, 12H), 7.85 (d, 6H), 7.49 (s, 3H), 7.29 (d, 6H), 5.65 (d, 6H), 2.96 (t, 6H), 2.76 (t, 6H), 2.07 (m, 6H); $^{13}$C-NMR (63 MHz, CD$_3$CN) $\delta$ ppm 163.9, 152.2, 148.5, 143.8, 135.4, 130.9, 128.3, 124.4, 62.6, 34.6, 34.0, 29.6; Anal. Caled for C$_{48}H_{51}N_6P_{3}F_{18}$.4.5H$_2$O: C, 46.95; H, 4.92; N, 6.84. Found C, 47.06; H, 4.98; N, 7.01.
$G_{0.6}\text{PF}_6$:

![Chemical structure image](image)

$P_{0.3}\text{PF}_6$ (0.2 g, 0.17 mmol) and 4-$t$-BuBnBr (0.19 mL, 1.04 mmol) were dissolved in 20mL CH$_3$CN, refluxed for 1 d. The solution was cooled, solvent was removed under reduced pressure and the residue was washed with EtOAc to remove excess 4-$t$-BuBnBr. The residue was then dissolved in MeOH/H$_2$O, precipitated with 3M NH$_4$PF$_6$, filtered, washed with H$_2$O and dried to yield $G_{0.6}\text{PF}_6$ as a brown solid, 0.32 g (91%); $^1$H-NMR (250 MHz, CD$_3$CN) $\delta$ ppm 8.61 (dd, 12H), 7.89 (s, 12H), 7.54 (d, 9H), 7.38 (s, 6H), 5.64 (s, 12H), 2.98 (t, 12H), 2.09 (m, 6H), 1.33 (s, 27H); $^{13}$C-NMR (63 MHz, CD$_3$CN) $\delta$ ppm 163.2, 162.8, 153.1, 143.9, 143.7, 135.3, 131.0, 128.8, 128.3, 126.4, 63.5, 62.6, 34.3, 30.4, 28.8; Anal. Calcd for C$_{81}$H$_{96}$N$_6$P$_6$F$_{36}$.3H$_2$O: C, 46.83; H, 4.95; N, 4.05. Found C, 46.87; H, 5.27; N, 4.15.

$G_{0'}\text{.6PF}_6$:

![Chemical structure image](image)

Brown solid; Yield: 75%; $^1$H-NMR (250 MHz, CD$_3$CN) $\delta$ ppm 8.61 (dd, 12H), 7.89 (d, 12H), 7.40 (m, 18H), 5.69 (d, 12H), 3.00 (s, 12H), 2.12 (m, 6H); $^{13}$C-NMR (63 MHz, CD$_3$CN) $\delta$
ppm 163.3, 162.9, 143.9, 143.8, 135.3, 133.1, 131.0, 129.8, 129.5, 129.0, 128.8, 128.4, 128.3, 63.8, 62.7, 34.3, 28.7; Anal. Calcd for C_{69}H_{72}N_{6}P_{6}F_{36}H_{2}O: C, 44.24; H, 3.98; N, 4.48. Found C, 44.36; H, 4.02; N, 4.45.

G_{0.6}PF_{6}:

Pale brown solid, Yield: 73%; \textsuperscript{1}H-NMR (250 MHz, CD_{3}CN) \delta ppm 8.55 (dd, 12H), 7.49 (s, 3H), 5.66 (s, 6H), 4.28 (s, 9H), 3.00 (s, 12H), 2.15-2.03 (m, 6H); \textsuperscript{13}C-NMR (63 MHz, CD_{3}CN) \delta ppm 163.3, 161.9, 144.7, 143.9, 135.3, 131.0, 128.4, 127.8, 47.6, 47.6, 34.3, 34.3, 28.8; Anal. Calcd for C_{51}H_{60}N_{6}P_{6}F_{36}: C, 37.65; H, 3.72; N, 5.16. Found C, 37.71; H, 4.18; N, 5.15.

P_{1.6}PF_{6}:
\( \mathbf{P}_{0.3} \mathbf{PF}_6 \) (0.75 g, 0.65 mmol) and 3,5-bis(hydroxymethyl)benzyl bromide \( \mathbf{V}_1 \) (0.56 g, 2.42 mmol) were dissolved in 20mL \( \text{CH}_3\text{CN} \), refluxed for 1 d. (Note: After alkylation, the product is insoluble, hence bromination was carried out with the insoluble residue which became soluble in 5.6M \( \text{HBr/HOAc} \) upon refluxing at RT. The resulting brominated product was soluble in either \( \text{H}_2\text{O} \) or \( \text{MeOH/H}_2\text{O} \) with a little residue left behind; hence the solution was filtered before converting it into the \( \mathbf{PF}_6 \) salt. As prolonged exposure to air causes decomposition of the hexabromide and insolubility, the product is stored at 4°C under argon). The aqueous solution was cooled; the solvent was removed under reduced pressure, brominated using 200 mL 5.6M \( \text{HBr/HOAc} \) for 2 d. The acid was removed under reduced pressure, the residue was dissolved in \( \text{H}_2\text{O} \) or \( \text{MeOH/H}_2\text{O} \), precipitated with 3M \( \text{NH}_4\mathbf{PF}_6 \), filtered, washed with excess water and dried to yield \( \mathbf{P}_{1.6} \mathbf{PF}_6 \) as a pale brown powder, 1.05 g (66%); \(^1\text{H}-\text{NMR} \) (250 MHz, \( \text{CD}_3\text{CN} \)) \( \delta \) ppm 8.66-8.57 (m, 12H), 7.91 (d, 12H), 7.6-7.45 (m, 12H), 5.66 (d, 12H), 4.59 (s, 12H), 2.99 (t, 12H), 2.10 (m, 6H); \(^{13}\text{C}-\text{NMR} \) (63 MHz, \( \text{CD}_3\text{CN} \)) \( \delta \) ppm 163.2, 144.0, 140.4, 135.3, 134.4, 131.0, 129.4, 128.4, 63.0, 62.6, 34.4, 32.1, 28.8; Anal. Calcd for \( \text{C}_{75}\text{H}_{78}\text{N}_6\text{Br}_6\mathbf{PF}_6\cdot2\text{H}_2\text{O} \): C, 36.79; H, 3.37; N, 3.43. Found C, 37.06; H, 3.38; N, 3.43.
P1.6PF6 (0.15 g, 62 µmol) and E.PF6 (0.228 g, 466 µmol) were dissolved in 30 mL CH3CN, refluxed for 4 d. The solvent was removed under reduced pressure, the residue was dissolved in MeOH/H2O, precipitated with 3M NH4PF6, filtered, washed with H2O and dried to yield G1.18PF6 as a dark brown solid, 0.348 g (97%); 1H-NMR (250 MHz, DMSO-d6) δ ppm 8.98 (dd, 36H), 8.04 (bs, 36H), 7.60-7.57 (m, 12H), 7.45 (s, 24H), 5.74 (s, 36H), 2.95 (bs, 36H), 2.08 (m, 18H), 1.25 (s, 54H); 13C-NMR (63 MHz, DMSO-d6) δ ppm 162.8, 162.2, 152.4, 144.6, 136.3, 131.9, 128.9, 128.4, 126.5, 62.9, 62.3, 34.9, 34.5, 31.4, 31.1, 28.6; Anal. Calcd for C219H252N18P18F108·18H2O: C, 43.33; H, 4.78; N, 4.15. Found C, 43.04; H, 4.96; N, 3.70.
**P$_2$.18PF$_6$:**

![Chemical structure of P$_2$.18PF$_6$]

P$_1$.6PF$_6$ (0.4 g, 0.174 mmol) and V$_2$.PF$_6$ (0.576 g, 1.27 mmol) were dissolved in 40mL CH$_3$CN, refluxed for 4 d. The solution was cooled; the solvent was removed under reduced pressure, brominated using 200 mL 5.6M HBr/HOAc for 2 d. The acid was removed under reduced pressure, the residue was dissolved in MeOH/H$_2$O, precipitated with 3M NH$_4$PF$_6$, filtered, washed with excess water and dried to yield P$_2$.18PF$_6$ as a pale brown powder, 0.65 g (60%); $^1$H-NMR (250 MHz, CD$_3$CN) δ ppm 8.61 (m, 36H), 7.91 (m, 36H), 7.52 (m, 30H), 5.65 (s, 36H), 4.59 (s, 24H), 3.01 (t, 36H), 2.06 (m, 18H); $^{13}$C-NMR (63 MHz, CD$_3$CN) δ ppm 163.2, 144.0, 140.4, 135.3, 134.4, 131.0, 129.4, 128.3, 63.0, 62.7, 34.4, 32.2, 28.8; Anal. Calcd for C$_{207}$H$_{216}$N$_{18}$Br$_{12}$P$_{18}$F$_{108}$: C, 38.11; H, 3.34; N, 3.86. Found C, 38.07; H, 3.31; N, 3.84.
$G_{2.42PF_6}$:

$P_{2.18PF_6}$ (0.15 g, 23 µmol) and $E.PF_6$ (0.158 g, 322 µmol) were dissolved in 50 mL CH$_3$CN, refluxed for 7 d. The solvent was removed under reduced pressure, the residue was dissolved in MeOH/H$_2$O, precipitated with 3M NH$_4$PF$_6$, filtered, washed with H$_2$O and dried to yield $G_{2.42PF_6}$ as a dark brown solid, 0.292 g (96%);  $^1$H-NMR (250 MHz, DMSO-$d_6$) δ ppm 8.97 (m, 84H), 8.04 (m, 84H), 7.61 (m, 30H), 7.45 (s, 48H), 5.74 (s, 84H), 2.95 (m, 84H), 2.08 (m, 42H), 1.24 (s, 108H); $^{13}$C-NMR (63 MHz, DMSO-$d_6$) δ ppm 162.8, 162.2, 152.4, 144.7, 144.5, 136.4, 131.9, 128.9, 128.5, 126.5, 62.8, 62.3, 34.9, 34.6, 31.4, 28.6; Anal. Calcd for C$_{495}$H$_{564}$N$_{42}$P$_{42}$F$_{252}$H$_2$O: C, 42.63; H, 4.68; N, 4.22. Found C, 41.87; H, 4.76; N, 3.83.
b) Synthesis of the convergent dendrons

\[ \text{W}_2 \text{2PF}_6: \quad \text{1,1'}-(5\text{-hydroxymethyl}-1,3\text{-phenylene})\text{bis(methylene)bis}(4\text{-}(3\text{-}(\text{pyridin}-4\text{-yl})\text{propyl})\text{pyridinium})\text{hexafluorophosphate(V)}: } \]

4,4’-Trimethylenedipyridine (5.06 g, 25 mmol) was dissolved in 30 mL CH\textsubscript{3}CN, heated to 80°C under stirring. To this solution 5-hydroxymethyl-1,3-bis(bromomethyl)benzene, \text{W}_1 (0.75 g, 2.5 mmol) dissolved in CH\textsubscript{3}CN (20 mL) was added slowly over 8 h. The solution was stirred for another 12 h, cooled to RT and the solvent was removed under reduced pressure. The residue was partitioned between water (100 mL) and CH\textsubscript{2}Cl\textsubscript{2} (100 mL), washed with CH\textsubscript{2}Cl\textsubscript{2} to remove excess 4,4’-trimethylenedipyridine. The aqueous solution was then concentrated to 50 mL, 3 mL of 3M NH\textsubscript{4}PF\textsubscript{6} solution was added, viscous liquid settled down, the aqueous layer was decanted, washed with water and dried to yield \text{W}_2 \text{2PF}_6 as a brown solid, 1.6 g (76%); \textsuperscript{1}H-NMR (250 MHz, CD\textsubscript{3}CN) \(\delta\) ppm 8.6-8.4 (unresolved coupling, 8H), 7.83 (s, 4H), 7.34 (m, 3H), 7.21 (d, 4H), 5.65 (s, 4H), 4.64 (s, 2H), 2.98 (t, 4H), 2.73-2.70 (m, 4H), 2.17-2.02 (m, 4H); \textsuperscript{13}C-NMR (63 MHz, CD\textsubscript{3}CN) \(\delta\) ppm 164.0, 152.0, 150.8, 149.3, 148.9, 145.3, 143.6, 134.3, 128.2, 124.2, 63.1, 62.6, 34.7, 34.0, 30.5, 29.6; Anal. Calcd for C\textsubscript{35}H\textsubscript{38}N\textsubscript{4}P\textsubscript{2}F\textsubscript{12}O: C, 51.23; H, 4.66; N, 6.82. Found C, 51.60; H, 4.77; N, 7.04.
**W₃.₄PF₆:**

![Image of molecular structure]

W₂.₂PF₆ (0.2 g, 243 µmol) and 4-t-bubnbr (0.13 mL, 731 µmol) were dissolved in 20mL CH₃CN, refluxed for 1 d. The solution was cooled, solvent was removed under reduced pressure and the residue was washed with EtOAc to remove excess 4-t-BuBnBr. The residue was then dissolved in MeOH/H₂O, precipitated with 3M NH₄PF₆, filtered, washed with H₂O and dried to yield W₃.₄PF₆ as a brown solid, 0.23 g (68%); ¹H-NMR (250 MHz, CD₃CN) δ ppm 8.63 (s, 8H), 7.89 (s, 8H), 7.56 (d, 4H), 7.47 (s, 2H), 7.40 (d, 5H), 5.66 (s, 8H), 4.61 (s, 2H), 3.00 (t, 8H), 2.11 (m, 4H), 1.34 (s, 18H); ¹³C-NMR (63 MHz, CD₃CN) δ ppm 163.1, 162.8, 153.1, 143.9, 143.7, 134.2, 130.2, 128.8, 128.3, 128.1, 126.4, 63.5, 63.2, 62.6, 34.4, 30.4, 28.7; Anal. Calcd for C₅₇H₆₈N₄P₄F₂₄O·H₂O: C, 48.11; H, 4.96; N, 3.94. Found C, 47.85; H, 4.84; N, 4.23.
\( \textbf{W}_3'.4\text{PF}_6: \)

\( \textbf{W}_2.2\text{PF}_6 \) (0.2 g, 243 \( \mu \)mol) and CH\(_3\)I (0.15 mL, 2.43 mmol) were dissolved in 20mL CH\(_3\)CN, stirred at 50° C for 1 d. The solution was cooled, solvent was removed under reduced pressure, the residue was dissolved in MeOH/H\(_2\)O, precipitated with 3M NH\(_4\)PF\(_6\), filtered, washed with H\(_2\)O and dried to yield \( \textbf{W}_3'.4\text{PF}_6 \) as a brown solid, 0.17 g (61%); \(^1\)H-NMR (250 MHz, CD\(_3\)CN) \( \delta \) ppm 8.57 (s, 8H), 7.89 (s, 8H), 7.49 (s, 2H), 7.41 (s, 1H), 5.68 (s, 4H), 4.62 (s, 2H), 4.27 (s, 6H), 3.00 (s, 8H), 2.12 (m, 4H); \(^{13}\)C-NMR (63 MHz, CD\(_3\)CN) \( \delta \) ppm 163.1, 161.9, 145.1, 144.6, 143.9, 134.2, 128.4, 128.1, 127.8, 63.2, 62.6, 47.6, 34.3, 34.2, 28.8.
3. Estimation of association constant of the first AQDS complexation with an empty G_2-dendrimer:

DOSY experiment: c(G_2)_{initial} = c(AQDS)_{initial} = 0.97 \text{ mM} = 1 \times 10^{-3} \text{ M}

at 8 equ. addition of AQDS there is no free AQDS observed leading to the assumption, that more than 90 % of AQDS is complexed at the first addition.

first association equilibrium:

\[ G_2 + AQDS \rightleftharpoons G_2\text{-AQDS} \quad K \]

\[ K = \frac{c(G_2\text{-AQDS})_{eq}}{c(AQDS)_{eq} \times c(G_2)} \]

\[ = \frac{1 \times 10^{-3}}{(1 \times 10^{-4} \times 1 \times 10^{-4})} = 10^5 \text{ M}^{-1} \]

Thus the real K is expected $> 10^5 \text{ M}^{-1}$.
4. NOESY

NOESY spectra were done on mixtures of $G_1$ and AQDS. Interestingly we do not observe any cross-peaks between the protons of the dendrimer and AQDS. However, there are well defined cross peaks corresponding to intramolecular interaction of protons $H_1$, $H_3$ and $H_5$ on the dendrimer (Figure S1).

*Figure S1:* NOESY spectrum of $G_1$ dendrimer + 8eq. AQDS
5. MM+ simulation

The MM+ force field implemented in HyperChem 8.0.8\textsuperscript{2} was used for the geometry optimization of G\textsubscript{0}, G\textsubscript{1} and G\textsubscript{2}. The charge was +1 on all pyridinium N and -0.33 on all oxygens of the sulfonate groups. All other atoms were at 0 charge. Atomic charges and cut-off: none was selected in the options. In most sets of optimizations the guest molecule(s) was/were name selected: fixed atom in order to let the dendrimer wrap them and to omit distortions on the AQDS. All hyperchem hin files of the structures shown in Fig. 9 and in the suppl. mat. are available upon request from the authors.

*Figure S2*: Contraction of G\textsubscript{2} without counter ions upon addition of 42 Iodide ions (red spheres) or 42 PF\textsubscript{6}\textsuperscript{-} ions (yellow octahedras).
Figure S3: Substructure from MM+ simulation showing magnetic non-equivalency of H₁ and equivalency of H₃ in the non-complexed (AQDS free) relaxed state.
6. Scheme of Squares

\[
\begin{align*}
\text{AQDS}^{2-} + \text{G}^{n+} & \rightleftharpoons K^{2-} \text{AQDS}^{2-} - \text{G}^{n+} \\
+e^{-} & \rightleftharpoons E^{\circ \prime}_{\text{(free)}} \\
\text{AQDS}^{3-} + \text{G}^{n+} & \rightleftharpoons K^{3-} \text{AQDS}^{3-} - \text{G}^{n+} \\
+e^{-} & \rightleftharpoons E^{\circ \prime}_{\text{(complexed)}} \\
E^{\circ \prime}_{\text{(free)}} - E^{\circ \prime}_{\text{(complexed)}} & = 0.06 \text{V} \log(K^{2-}/K^{3-})
\end{align*}
\]

Scheme of squares

Upon complexation of a redox active guest its standard reduction potential \(E^{\circ \prime}_{\text{(free)}}\) may shift to \(E^{\circ \prime}_{\text{(complexed)}}\) if one of the oxidation states has a higher affinity towards the dendrimer (larger \(K\) value) than the other oxidation state. As AQDS\(^{2-}\) becomes AQDS\(^{3-}\) after reduction, one might expect \(K^{3-} > K^{2-}\) and thus, \(E^{\circ \prime}_{\text{(complexed)}}\) to be more positive than \(E^{\circ \prime}_{\text{(complexed)}}\). This is experimentally observed but (i) it is hidden by the adsorption behavior and (ii) the potential shift is rather small.\(^3\)
7. $^1$H, $^{13}$C & DEPT spectras of the key intermediates and title compounds:

$V_2PF_6$: $^1$H NMR:

$V_2PF_6$: $^{13}$C NMR:
E.PF₆⁻¹H NMR:

TMDP dendron with 4-(t-bu)benzyl group
E.PF$_6$-$^{13}$C NMR:

![NMR Spectrum of E.PF$_6$-$^{13}$C NMR]

E.PF$_6$-$^{13}$C NMR parameters:
- Acquisition Parameters:
  - Data: 20503211
  - Time: 10.64 s
- Processing Parameters:
  - SF2: 62.965 MHz
  - SF1: 62.9412 MHz

E.PF$_6$-DEPT:

![DEPT Spectrum of E.PF$_6$]

E.PF$_6$-DEPT parameters:
- Acquisition Parameters:
  - Data: 20503211
  - Time: 10.64 s
- Processing Parameters:
  - SF2: 62.965 MHz
  - SF1: 62.9412 MHz

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$P_0.3PF_6^{-1}H$ NMR:

$P_0.3PF_6^{-13}C$ NMR:
$P_{0.3}PF_6$ - DEPT:

$G_{0.6}PF_6 - ^1H$ NMR:

G0 TMDP with 4-(t-butyl)benzyl end group
G₆PF₆₋₁³C NMR:

G₆PF₆₋DEPT:

G₀ TMDP with 4-(t-bu)benzyl end group
P$_{1.6}$PF$_6$ $^{1}$H NMR:

P$_{1.6}$PF$_6$ $^{13}$C NMR:
P1.6PF₆~DEPT:

G₁.18PF₆⁻¹H NMR:
$G_1.18PF_6^{-13}C$ NMR:

$P_2.18PF_6^{-1}H$ NMR:
P₂.₁₈PF₆⁻¹³C NMR:

G₂.₄₂PF₆⁻¹H NMR:
G$_2$42PF$_6$-$^{13}$C NMR:

C$_{17}$-H NMR:
$^{13}$C NMR:

C$_1$-DEPT:
C$_2$-H NMR:

C$_2$-^{13}C NMR:
Supporting References:


(2) HyperChem(TM) Professional 8.0.8, Hypercube, Inc., 1115 NW 4th Street, Gainesville, Florida 32601, USA