

Supporting Information for

Design, synthesis and structure of novel G-2 melamine-based dendrimers incorporating 4-(*n*-octyloxy)aniline as a peripheral unit

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Preparation of compounds 2a and 2b by Williamson etherification of compound 1 with 1-iodooctane

Under inert atmosphere and with vigorous stirring, into an anhyd. acetone (40 mL) solution containing compound **1** (1.000 g, 3.04 mmol), anhyd. K₂CO₃ (3.350 g, 24.32 mmol) was suspended. To this suspension, an anhyd. acetone (5 mL) solution containing 1-iodooctane (0.865 g, 0.65 mL, 3.60 mmol) was added dropwise (1 h) at -13 °C. The reaction mixture was stirred at -13 °C for 2 h then for 12 h at room temperature (TLC monitoring eluent ligroin/acetone 4:1). Furthermore, an anhyd. acetone (5 mL) solution containing 1-iodooctane (0.865 g, 0.65 mL, 3.60 mmol) was injected and the reaction mixture was stirred at room temperature for additional 72 h. Finally, the reaction mixture was heated at 50 °C for 8 h. After cooling at room temperature, chloroform (50 mL) and distilled water (50 mL) were added with stirring. The resulted two layers were separated and the organic phase was washed with distilled water (2 × 25 mL), dried over anhyd. Na₂SO₄, filtered off and evaporated to dryness under reduced pressure. The solid residue was separated by column chromatography to provide pure compound **2a** (0.688 g, 41% partial conversion of **1**) as the first fraction. Next elution afforded pure compound **2b** (0.143 g, 7% partial conversion of **1**).

Preparation of compound 2a by amination of cyanuric chloride with 4-(n-octyloxy)aniline

Under inert atmosphere and with vigorous stirring, to an anhyd. acetone (10 mL) solution containing cyanuric chloride (0.625 g, 3.39 mmol), an anhyd. acetone (26 mL) solution containing 4-(*n*-octyloxy)aniline (1.500 g, 6.78 mmol) was injected dropwise at 0–5 °C during 2 h. At the same temperature, a distilled water (8 mL) solution containing NaHCO₃ (0.569 g, 6.78 mmol) was then added. The resulted suspension was heated at 45 °C for 3 h then let to cool down to room temperature at which it was kept for additional 18 h with continuous stirring. After this period, TLC monitoring (eluent ligroin/acetone 4:1) indicated the complete consumption of the starting materials and formation of compound **2a** as a major spot. The reaction mixture was evaporated under reduced pressure to the complete removal of acetone. Distilled water (30 mL) was added and the resulted suspension was filtered off. After drying at room temperature, the crude product (1.85 g) was crystallised from boiling methanol (9 mL) to provide pure compound **2a** (1.760 g, 94% yield with respect to cyanuric chloride).

2-Chloro-4,6-bis[4-(*n*-octyloxy)phenylamino]-s-triazine (2a). White powder; m.p. 149–151 °C (MeOH). Yield 94%. *R*_f=0.58 (ligroin/acetone 4:1). Elemental analysis calcd (%) for C₃₁H₄₄ClN₅O₂: C 67.19, H 8.00, N 12.64; found: C 66.98, H 7.97, N 12.55. IR (KBr) ν_{max} 3347 (m), 3255 (m), 2958 (m), 2921 (s), 2852 (m), 1628 (m), 1573 (s), 1544 (s), 1525 (s), 1502 (s), 1419 (m), 1384 (m), 1212 (s), 1015 (m), 829 (m), 793 (m) cm⁻¹. ¹H and 2D-¹H, ¹H-COSY NMR (500 MHz, 5.0 mM in DMSO-*d*₆, 298 K): δ_{H} =0.86 (6H, t, ³*J*_{H,H}=6.8 Hz; CH₃), 1.26–1.35 (16H, m; CH₂, *n*-octyl), 1.40 (4H, tt app. qi, ³*J*_{H,H}=7.5 Hz; CH₂, *n*-octyl), 1.69 (4H, tt app. qi, ³*J*_{H,H}=6.8 Hz; OCH₂CH₂, *n*-octyl), 3.93 (4H, t, ³*J*_{H,H}=6.5 Hz; OCH₂, *n*-octyl), 6.87 (4H, d, ³*J*_{H,H}=8.0 Hz; H-3, -5, Ph), 7.46, 7.65 (4H, d, br s, ³*J*_{H,H}=8.0 Hz; H-2, -6, Ph), 9.85, 9.96, 10.03 (2H, br s, br s, s; NH) ppm. ¹H and 2D-¹H, ¹H-COSY NMR (500 MHz, 5.0 mM in DMSO-*d*₆, 363 K): δ_{H} =0.88 (6H, t, ³*J*_{H,H}=7.0 Hz; CH₃), 1.27–1.38 (16H, m; CH₂, *n*-octyl), 1.44 (4H, tt app. qi, ³*J*_{H,H}=7.0 Hz; CH₂, *n*-octyl), 1.72 (4H, tt app. qi, ³*J*_{H,H}=6.9 Hz; OCH₂CH₂, *n*-octyl), 3.97 (4H, t, ³*J*_{H,H}=6.8 Hz; OCH₂, *n*-octyl), 6.87 (4H, d, ³*J*_{H,H}=9.0 Hz; H-3, -5, Ph), 7.49 (4H, d, ³*J*_{H,H}=9.0 Hz; H-2, -6, Ph), 9.63 (2H, br s; NH) ppm. 2D-¹H-DOSY NMR (500 MHz, 5.0 mM in DMSO-*d*₆, 298 K): *D*=198 μm² s⁻¹. DEPT ¹³C NMR (125 MHz, 5.0 mM in DMSO-*d*₆, 298 K): δ_{C} =14.4 (CH₃), 22.6 (CH₂CH₃), 26.0, 29.16, 29.19, 29.3, 31.7 (CH₂; *n*-octyl), 68.1 (OCH₂; *n*-octyl), 114.7, 114.8 (C-3, -5; Ph), 122.5, 123.3 (C-2, -6; Ph), 131.6, 132.0 (C-1; Ph), 155.3, 155.5 (C-4; Ph), 163.7, 164.2, 164.4 (C-4, -6; s-triazine), 168.2, 168.7 (C-2; s-triazine) ppm. HRMS-APCI (rel. int.): *m/z* (%) 554.3246 (100) [M+H]⁺; [M+H]⁺ calcd. for C₃₁H₄₅ClN₅O₂, 554.3262.

2-Chloro-4-{N-(*n*-octyl)-N-[4-(*n*-octyloxy)phenyl]}amino-6-[4-(*n*-octyloxy)phenylamino]-s-triazine (2b).

White powder; m.p. 74-75 °C (column chromatography, eluent ligroin/acetone 4:1; cryst. from MeOH). R_f =0.76. Partial conversion of **1**, 7%. Elemental analysis calcd (%) for $C_{39}H_{60}ClN_5O_2$: C 70.29, H 9.08, N 10.51; found: C 69.98, H 9.27, N 10.55. IR (KBr) ν_{max} 3258 (m), 2960 (s), 2921 (s), 2853 (s), 1575 (s), 1530 (s), 1505 (s), 1484 (s), 1390 (m), 1375 (m), 1248 (s), 1230 (s), 983 (m), 830 (m), 796 (m) cm^{-1} . 1H and 2D- 1H , 1H -COSY NMR (500 MHz, 5 mM in DMSO- d_6 , 298 K): δ_H =0.80-0.86 (9H, m; CH₃), 1.19-1.78 (36H, m; CH₂, *n*-octyl), 3.80 (2H, t, $^3J_{H,H}$ =6.0 Hz; NCH₂, *n*-octyl), 3.85, 3.92, 3.97, 4.02 (4H, t, $^3J_{H,H}$ =7.0, 6.5, 6.3, 6.3 Hz; OCH₂, *n*-octyl), 6.50, 6.87, 6.95, 7.03 (4H, d, $^3J_{H,H}$ =8.5, 8.5, 9.0, 8.5 Hz; Ph), 7.16, 7.20, 7.35, 7.44, 7.61 (4H, d, $^3J_{H,H}$ =8.0, 8.5 Hz, br s, br s, d, $^3J_{H,H}$ =8.5 Hz; Ph), 9.43, 9.76, 9.89, 10.02 (1H, br s, br s, s, s; NH) ppm. 1H and 2D- 1H , 1H -COSY NMR (500 MHz, 5.0 mM in DMSO- d_6 , 403 K): δ_H =0.87-0.90 (9H, br m; CH₃), 1.27-1.50 (30H, br m; CH₂, *n*-octyl), 1.60 (2H, br t; CH₂, *n*-octyl), 1.71 (2H, br t, $^3J_{H,H}$ =6.0 Hz; CH₂, *n*-octyl), 1.78 (2H, br t, $^3J_{H,H}$ =5.8 Hz; CH₂, *n*-octyl), 3.87 (2H, t, $^3J_{H,H}$ =6.5 Hz; NCH₂, *n*-octyl), 3.93 (2H, t, $^3J_{H,H}$ =4.5 Hz; OCH₂, *n*-octyl), 4.05 (2H, t, $^3J_{H,H}$ =5.0 Hz; OCH₂, *n*-octyl), 6.72 (2H, d, $^3J_{H,H}$ =5.8 Hz; H-2, -6, Ph at C-4 *s*-triazine), 6.98 (2H, d, $^3J_{H,H}$ =7.0 Hz; H-3, -5, Ph at C-6 *s*-triazine), 7.16 (2H, d, $^3J_{H,H}$ =7.3 Hz; H-3, -5, Ph at C-4 *s*-triazine), 7.36 (2H, dd, $^3J_{H,H}$ =7.0 Hz; H-2, -6, Ph at C-6 *s*-triazine), 9.25 (1H, br s; NH) ppm. 2D- 1H -DOSY NMR (500 MHz, 5.0 mM in DMSO- d_6 , 298 K): D =197 $\mu m^2 s^{-1}$. DEPT ^{13}C NMR (125 MHz, 5.0 mM in DMSO- d_6 , 298 K): δ_C =14.35, 14.41 (CH₃), 22.5, 22.6 (CH₂CH₃), 26.02, 26.05, 26.1, 26.4, 26.8, 27.2, 27.3, 27.6 (CH₂; *n*-octyl), 29.0, 29.1, 29.19, 29.2, 29.3, 29.4 (CH₂; *n*-octyl), 49.3, 49.34, 49.36, 51.4 (NCH₂; *n*-octyl), 67.8, 67.97, 68.02, 68.06, 68.1, 68.3, 68.4 (OCH₂; *n*-octyl), 114.1, 114.2, 114.7, 114.8 (C-3, -5; Ph at C-6 *s*-triazine), 115.2, 115.3, 115.4 (C-3, -5; Ph at C-4, *s*-triazine), 121.21, 122.17, 122.3 (C-2, -6; Ph at C-6 *s*-triazine), 129.2, 129.6 (C-2, -6; Ph at C-4 *s*-triazine), 132.2, 132.3 (C-1; Ph at C-6 *s*-triazine), 135.0, 135.1, 135.2 (C-1; Ph at C-4 *s*-triazine), 154.5, 154.6, 155.2, 155.3 (C-4; Ph at C-6 *s*-triazine), 157.8, 158.0 (C-4; Ph at C-4 *s*-triazine), 162.6, 162.7, 163.7, 163.8 (C-6; *s*-triazine), 165.4, 165.5, 165.9 (C-4; *s*-triazine), 168.4, 168.6 (C-2; *s*-triazine) ppm. HRMS-APCI (rel. int.) m/z : 666.4500 (100) [$M+H$]⁺; [$M+H$]⁺ calcd. for $C_{39}H_{61}ClN_5O_2$, 666.4514.

Preparation of compound **3**

At room temperature, into an anhyd. THF (62 mL) solution containing anhyd. piperazine (1.057 g, 12.28 mmol), anhyd. K₂CO₃ (0.424 g, 3.07 mmol) was suspended with vigorous stirring. Compound **2a** (1.700 g, 3.07 mmol) was then added gradually as five equal portions, every 2 h. After each portion (0.340 g), TLC monitoring (eluent EtOH/aq. NH₃ 25% 9:0.3) indicated the complete consumption of the starting material **2a** and formation of compound **3** as a major spot. After that, the reaction mixture was stirred at room temperature for additional 24 h, and then evaporated under reduced pressure to dryness. Distilled water (35 mL) was added to the solid residue and the resulted suspension was filtered off and well washed with distilled water for the complete removal of piperazine. After drying, the crude product (1.800 g) was crystallised from boiling ethanol (5 mL) to provide pure compound **3** (1.760 g, 95% yield with respect to **2a**). **2-(Piperazin-1-yl)-4,6-bis[4-(*n*-octyloxy)phenylamino]-*s*-triazine (**3**)**. White powder; m.p. 137-139 °C (EtOH). Yield 95%. R_f =0.66 (EtOH/aq. NH₃ 25% 9:0.3). Elemental analysis calcd (%) for $C_{35}H_{53}N_7O_2$: C 69.62, H 8.85, N 16.24; found: C 69.48, H 9.02, N 16.35. IR (KBr) ν_{max} 3314 (m), 2932 (m), 2853 (m), 1573 (s), 1561 (s), 1519 (s), 1496 (s), 1419 (s), 1307 (m), 1290 (m), 1264 (m), 1048 (w), 1022 (w), 828 (m), 804 (m) cm^{-1} . 1H and 2D- 1H , 1H -COSY NMR (500 MHz, 5.0 mM in DMSO- d_6 , 298 K): δ_H =0.81 (6H, t, $^3J_{H,H}$ =6.8 Hz; CH₃), 1.26-1.35 (16H, m; CH₂, *n*-octyl), 1.40 (4H, tt app. qi, $^3J_{H,H}$ =7.1 Hz; CH₂, *n*-octyl), 1.68 (4H, tt app. qi, $^3J_{H,H}$ =7.3 Hz; OCH₂CH₂, *n*-octyl), 2.70 (4H, t, $^3J_{H,H}$ =4.8 Hz; H-3, -5, piperazine), 3.66 (4H, t, $^3J_{H,H}$ =4.8 Hz; H-2, -6, piperazine), 3.90 (4H, t, $^3J_{H,H}$ =6.5 Hz; OCH₂, *n*-octyl), 6.82 (4H, d, $^3J_{H,H}$ =9.0 Hz; H-3, -5, Ph), 7.56 (4H, br s; H-2, -6, Ph), 8.87 (2H, br s; NH) ppm. 1H and 2D- 1H , 1H -COSY NMR (500 MHz, 5.0 mM in DMSO- d_6 , 363 K): δ_H =0.88 (6H, t, $^3J_{H,H}$ =7.0 Hz; CH₃), 1.30-1.38 (16H, m; CH₂, *n*-octyl), 1.43 (4H, tt

app. qi, $^3J_{\text{H,H}}=7.4$ Hz; CH_2 , *n*-octyl), 1.71 (4H, tt app. qi, $^3J_{\text{H,H}}=6.9$ Hz; OCH_2CH_2 , *n*-octyl), 2.74 (4H, t, $^3J_{\text{H,H}}=5.0$ Hz; H-3, -5, piperazine), 3.67 (4H, t, $^3J_{\text{H,H}}=5.0$ Hz; H-2, -6, piperazine), 3.94 (4H, t, $^3J_{\text{H,H}}=6.5$ Hz; OCH_2 , *n*-octyl), 6.82 (4H, d, $^3J_{\text{H,H}}=9.0$ Hz; H-3, -5, Ph), 7.55 (4H, d, $^3J_{\text{H,H}}=9.0$ Hz; H-2, -6, Ph), 8.50 (2H, s; NH) ppm. 2D- ^1H -DOSY NMR (500 MHz, 5.0 mM in $\text{DMSO}-d_6$, 298 K): $D=191 \mu\text{m}^2 \text{s}^{-1}$. DEPT ^{13}C NMR (125 MHz, 5.0 mM in $\text{DMSO}-d_6$, 298 K): $\delta_{\text{C}}=14.4$ (CH_3), 22.6 (CH_2CH_3), 26.1, 29.2, 29.3, 31.7 (CH_2 ; *n*-octyl), 44.6 (C-2, -6; piperazine), 46.0 (C-3, -5; piperazine), 68.0 (OCH_2 ; *n*-octyl), 114.6 (C-3, -5; Ph), 122.0 (C-2, -6; Ph), 133.7 (C-1; Ph), 154.2 (C-4; Ph), 164.5 (C-2; s-triazine), 165.0 (C-4, -6; s-triazine) ppm. HRMS-APCI (rel. int.) m/z : 604.4298 (100) $[\text{M}+\text{H}]^+$; $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{35}\text{H}_{54}\text{N}_7\text{O}_2$, 604.4339.

Preparation of G-1 dendron **D-Cl**

Into a cooled (-10°C) and anhyd. THF (82 mL) solution containing cyanuric chloride (0.305 g, 1.66 mmol), anhyd. K_2CO_3 (0.458 g, 3.32 mmol) was suspended with vigorous stirring. An anhyd. THF (15 mL) solution containing compound **3** (2.000 g, 3.32 mmol) was then added during 2 h. The reaction mixture was stirred at -10°C for 3 h then let to reach the room temperature where it was kept for additional 36 h. In order to ensure completion of the reaction, the mixture was refluxed for 24 h with TLC monitoring (consumption of the starting material **3**, eluent EtOH/aq. NH_3 25% 9:0.3; formation of compound **D-Cl**, eluent hexane/ CH_2Cl_2 /acetone 5:3:1). After that, THF was removed by evaporation under reduced pressure to dryness and the resulted solid was taken up with distilled water (50 mL) and then filtered off. After three successive crystallisations from boiling ethanol (15 mL), the crude product (2.150 g) afforded pure compound **D-Cl** (2.080 g, 95% yield with respect to cyanuric chloride).

2-Chloro-4,6-bis{4-{4,6-bis[4-(*n*-octyloxy)phenylamino]-*s*-triazin-2-yl}-piperazin-1-yl}-*s*-triazine **D-Cl**

White powder; m.p. $184\text{--}186^\circ\text{C}$ (EtOH). Yield 95%. $R_f=0.50$ (hexane/ CH_2Cl_2 /acetone 5:3:1). Elemental analysis calcd (%) for $\text{C}_{73}\text{H}_{104}\text{ClN}_{17}\text{O}_4$: C 66.46, H 7.95, N 18.05; found: C 66.69, H 8.11, N 18.18. IR (KBr) ν_{max} 3408 (w), 3290 (w), 2924 (m), 2853 (m), 1650 (m), 1569 (s), 1515 (s), 1490 (s), 1420 (s), 1302 (m), 1286 (m), 1171 (s), 999 (m), 974 (m), 825 (m), 799 (m) cm^{-1} . ^1H and 2D- ^1H , ^1H -COSY NMR (500 MHz, 5.0 mM in $\text{DMSO}-d_6$, 298 K): $\delta_{\text{H}}=0.86$ (12H, t, $^3J_{\text{H,H}}=6.8$ Hz; CH_3), 1.26-1.31 (32H, m; CH_2 , *n*-octyl), 1.41 (8H, tt app. qi, $^3J_{\text{H,H}}=7.0$ Hz; CH_2 , *n*-octyl), 1.69 (8H, tt app. qi, $^3J_{\text{H,H}}=6.9$ Hz; OCH_2CH_2 , *n*-octyl), 3.82 (16H, tt app. q, $^3J_{\text{H,H}}=7.5$ Hz; piperazine), 3.92 (8H, t, $^3J_{\text{H,H}}=6.5$ Hz; OCH_2 , *n*-octyl), 6.85 (8H, d, $^3J_{\text{H,H}}=7.5$ Hz; H-3, -5, Ph), 7.57 (8H, br s; H-2, -6, Ph), 9.08 (4H, br s; NH) ppm. ^1H and 2D- ^1H , ^1H -COSY NMR (500 MHz, 5.0 mM in $\text{DMSO}-d_6$, 363 K): $\delta_{\text{H}}=0.88$ (12H, t, $^3J_{\text{H,H}}=7.0$ Hz; CH_3), 1.29-1.37 (32H, m; CH_2 , *n*-octyl), 1.45 (8H, tt app. qi, $^3J_{\text{H,H}}=7.1$ Hz; CH_2 , *n*-octyl), 1.72 (8H, tt app. qi, $^3J_{\text{H,H}}=7.0$ Hz; OCH_2CH_2 , *n*-octyl), 3.84 (16H, s; piperazine), 3.98 (8H, t, $^3J_{\text{H,H}}=6.5$ Hz; OCH_2 , *n*-octyl), 6.85 (8H, d, $^3J_{\text{H,H}}=9.0$ Hz; H-3, -5, Ph), 7.56 (8H, d, $^3J_{\text{H,H}}=9.0$ Hz; H-2, -6, Ph), 8.70 (4H, s; NH) ppm. 2D- ^1H -DOSY NMR (500 MHz, 5.0 mM in $\text{DMSO}-d_6$, 298 K): $D=129 \mu\text{m}^2 \text{s}^{-1}$. DEPT ^{13}C NMR (125 MHz, 5.0 mM in $\text{DMSO}-d_6$, 298 K): $\delta_{\text{C}}=14.4$ (CH_3), 22.6 (CH_2CH_3), 26.1, 29.2, 29.3, 31.7 (CH_2 ; *n*-octyl), 42.9, 43.0, 43.4 (piperazine), 68.0 (OCH_2 ; *n*-octyl), 114.7 (C-3, -5; Ph), 122.3 (C-2, -6; Ph), 133.2 (C-1; Ph), 154.5 (C-4; Ph), 164.4 (C-2, T-0; C-4, -6, T-1), 164.8 (C-4, -6; T-0), 169.3 (C-2; T-1) ppm. HRMS-ESI (rel. int.) m/z : 1318.8237 (10) $[\text{M}+\text{H}]^+$; $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{73}\text{H}_{105}\text{ClN}_{17}\text{O}_4$, 1318.8224.

Preparation of G-1 dendron **D-N<P>NH**

Into an anhyd. THF (45 mL) solution containing anhyd. piperazine (0.418 g, 4.84 mmol), anhyd. K_2CO_3 (0.168 g, 1.21 mmol) was suspended with vigorous stirring. The resulted suspension was heated at reflux when compound **D-Cl** (1.600 g, 1.21 mmol) was added gradually as five equal portions, every 8 h. After each portion (0.320 g), TLC monitoring (eluent CH_2Cl_2 /acetone/EtOH 8:2:1.5) indicated the presence of the starting material **D-Cl** in small traces only and formation of compound **D-N<P>NH** as a major spot. The

reaction reached completion after additional 15 h of reflux (TLC monitoring). The reaction mixture was then evaporated under reduced pressure to dryness. Distilled water (45 mL) was added to the solid residue and the resulted suspension was filtered off and well washed with distilled water for the complete removal of piperazine. After drying, the crude product (1.630 g) was two times crystallised from boiling ethanol (7 mL) to provide pure compound **D-N<P>NH** (1.540 g, 93% yield with respect to **D-Cl**).

2-(Piperazin-1-yl)-4,6-bis{4-[4,6-bis[4-(*n*-octyloxy)phenylamino]-*s*-triazin-2-yl]-piperazin-1-yl}-*s*-triazine **D-N<P>NH.** White powder; m.p. 161-163 °C (EtOH). Yield 93%. R_f =0.54 (CH₂Cl₂/acetone/EtOH 8:2:1.5). Elemental analysis calcd (%) for C₇₇H₁₁₃N₁₉O₄: C 67.56, H 8.32, N 19.44; found: C 67.81, H 7.99, N 19.55. IR (KBr) $\nu_{\max}$ 3413 (m), 3271 (m), 3200 (w), 2924 (m), 2853 (m), 1630 (m), 1557 (s), 1542 (s), 1515 (s), 1418 (s), 1241 (m), 1219 (m), 1000 (m), 826 (m), 802 (m) cm⁻¹. ¹H and 2D-¹H,¹H-COSY NMR (500 MHz, 5.0 mM in DMSO-*d*₆, 298 K): δ_H =0.86 (12H, t, ³ $J_{H,H}$ =6.5 Hz; CH₃), 1.26-1.31 (32H, m; CH₂, *n*-octyl), 1.41 (8H, tt app. qi, ³ $J_{H,H}$ =6.8 Hz; CH₂, *n*-octyl), 1.69 (8H, tt app. qi, ³ $J_{H,H}$ =6.9 Hz; OCH₂CH₂, *n*-octyl), 3.13 (2H, br s; H-3, -5, P-1), 3.67 (1H, br s; NH, P-1), 3.78 (16H, s; P-0), 3.92 (10H, t, ³ $J_{H,H}$ =6.3 Hz; 8H, OCH₂, *n*-octyl; 2H, H-2, -6, P-1), 6.84 (8H, d, ³ $J_{H,H}$ =8.5 Hz; H-3, -5, Ph), 7.58 (8H, br s; H-2, -6, Ph), 8.69, 8.93 (4H, br s, br s; NH) ppm. ¹H and 2D-¹H,¹H-COSY NMR (500 MHz, 5.0 mM in DMSO-*d*₆, 363 K): δ_H =0.90 (12H, t, ³ $J_{H,H}$ =7.0 Hz; CH₃), 1.30-1.37 (32H, m; CH₂, *n*-octyl), 1.44 (8H, tt app. qi, ³ $J_{H,H}$ =7.1 Hz; CH₂, *n*-octyl), 1.72 (8H, tt app. sx, ³ $J_{H,H}$ =6.8 Hz; OCH₂CH₂, *n*-octyl), 3.12 (2H, t, ³ $J_{H,H}$ =5.0 Hz; H-3, -5, P-1), 3.74 (1H, br s; NH, P-1), 3.81 (16H, s; P-0), 3.91 (2H, t, ³ $J_{H,H}$ =4.9 Hz; H-2, -6, P-1), 3.96 (8H, t, ³ $J_{H,H}$ =6.5 Hz; OCH₂, *n*-octyl), 6.85 (8H, d, ³ $J_{H,H}$ =9.0 Hz; H-3, -5, Ph), 7.57 (8H, d, ³ $J_{H,H}$ =9.0 Hz; H-2, -6, Ph), 8.57 (4H, s; NH) ppm. 2D-¹H-DOSY NMR (500 MHz, 5.0 mM in DMSO-*d*₆, 298 K): D =110 μm² s⁻¹. DEPT ¹³C NMR (125 MHz, 5.0 mM in DMSO-*d*₆, 298 K): δ_C =14.4 (CH₃), 22.6 (CH₂CH₃), 26.1, 29.2, 29.3, 31.7 (CH₂; *n*-octyl), 43.1, 43.2 (P-0, -1), 68.0 (OCH₂; *n*-octyl), 114.6 (C-3, -5; Ph), 122.1 (C-2, -6; Ph), 133.6 (C-1; Ph), 154.3 (C-4; Ph), 164.5 (C-2; T-1), 165.1 (C-2, T-0; C-4, -6, T-1), 165.20, 165.25 (C-4, -6; T-0) ppm. HRMS-APCI (rel. int.) m/z : 1368.8956 (30) [$M+H$]⁺; [$M+H$]⁺ calcd. for C₇₇H₁₁₄ClN₁₉O₄, 1368.9301.

Preparation of G-2 dendrimer **4**

Under inert atmosphere, to an anhyd. 1,4-dioxane (15 mL) solution containing cyanuric chloride (0.018 g, 0.10 mmol), G-1 dendron **D-N<P>NH** (0.493 g, 0.36 mmol) and anhyd. K₂CO₃ (0.050 g, 0.36 mmol) were added with vigorous stirring, at room temperature. The reaction mixture was refluxed for 48 h, i.e., until no more evolution of the reaction was observed (TLC monitoring: for the consumption of the starting material **D-N<P>NH**, eluent acetone/CH₂Cl₂/EtOH 2:8:1.5; formation of product **4**, eluent hexane/acetone 2:1.4). Next, since the HRMS monitoring still indicated an incomplete amination, i.e., the presence of G-2 monomeric and dimeric precursor of **4**, the reaction mixture was evaporated to dryness and 1,4-dioxane was replaced by anhyd. DMF (10 mL). After additional heating at 100 °C for 48 h of the reaction mixture, this was lyophilised and submitted to column chromatography (eluent hexane/acetone 2:1.4) to provide pure compound **4** (0.260 g, 62% yield with respect to cyanuric chloride).

2,4,6-Tris{4-[4,6-bis{4-[4,6-bis[4-(*n*-octyloxy)phenylamino]-*s*-triazin-2-yl]-piperazin-1-yl}-*s*-triazin-2-yl]-piperazin-1-yl}-*s*-triazine (4**).** Pale beige powder; m.p. 112-113 °C. Yield 62%. R_f =0.69 (hexane/acetone 2:1.4). Elemental analysis calcd (%) for C₂₃₄H₃₃₆N₆₀O₁₂: C 67.21, H 8.10, N 20.10; found: C 66.94, H 7.87, N 20.46. IR (KBr) $\nu_{\max}$ 3433 (w), 3260 (w), 2958 (m), 2925 (m), 2851 (m), 1549 (s), 1535 (s), 1511 (s), 1494 (s), 1472 (s), 1417 (s), 1354 (m), 1297 (w), 1255 (m), 1218 (m), 1172 (w), 997 (m), 826 (m), 803 (m) cm⁻¹. ¹H and 2D-¹H,¹H-COSY NMR (500 MHz, 2.5 mM in DMSO-*d*₆, 298 K): δ_H =0.85 (36H, m; CH₃), 1.23-1.26 (96H, m; CH₂, *n*-octyl), 1.41 (24H, br s; CH₂, *n*-octyl), 1.70 (24H, br s; OCH₂CH₂, *n*-octyl), 3.80 (72 H, br s; P-0, -1), 3.95 (24H, br s; OCH₂, *n*-octyl), 6.95 (24H, br s; H-3, -5, Ph), 7.49 (24H, br s; H-2, -6, Ph), 9.58, 9.84 (12H, 2×br s; NH) ppm. ¹H and 2D-¹H,¹H-COSY NMR (500 MHz, 2.5 mM in DMSO-*d*₆,

363 K): $\delta_{\text{H}}=0.86$ (36H, br t, $^3J_{\text{H,H}}=6.3$ Hz; CH_3), 1.27-1.33 (96H, m, CH_2 ; *n*-octyl), 1.43 (24H, tt app. qi, $^3J_{\text{H,H}}=7.0$ Hz; CH_2 , *n*-octyl), 1.71 (24H, tt ap. qi, $^3J_{\text{H,H}}=7.0$ Hz; OCH_2CH_2 , *n*-octyl), 3.81 (24H, br s; P-1), 3.84 (48H, br s; P-0), 3.96 (24H, br m; OCH_2 , *n*-octyl), 6.88 (24H, d, $^3J_{\text{H,H}}=8.5$ Hz; H-3, -5, Ph), 7.53 (24H, d, $^3J_{\text{H,H}}=9.0$ Hz; H-2, -6, Ph), 8.93 (12H, br s; NH) ppm. 2D- ^1H -DOSY NMR (500 MHz, 2.5 mM in $\text{DMSO}-d_6$, 298 K): $D=89 \mu\text{m}^2 \text{s}^{-1}$. ^{13}C NMR (125 MHz, 2.5 mM in $\text{DMSO}-d_6$, 363 K): $\delta_{\text{C}}=13.7$ (12C; CH_3), 21.9 (12C; CH_2CH_3), 25.5 (12C; CH_2 , *n*-octyl), 28.5, 28.7, 28.8 (36C; CH_2 , *n*-octyl), 31.1 (12C; OCH_2CH_2 , *n*-octyl), 42.5, 42.6, 42.8, 42.9, 43.1, 43.3 (36C; P-0, -1), 68.1 (12C; OCH_2 , *n*-octyl), 114.8 (24C; C-3, -5, Ph), 123.0 (24C; C-2, -6, Ph), 131.7 (12C; C-1, Ph), 155.1 (12C; C-4, Ph), 165.1 (30C; T-0, -1, -2) ppm. HRMS (ESI+, ACN+TFA) (rel. int.) m/z : 2091.3960 (1000) $[0.5(\text{M}+4\text{H})]^+$. Anal. calcd. for $[0.5(\text{M}+4\text{H})]^+$ 2091.3919.

Preparation of G-2 dendrimer 5

Under inert atmosphere and with vigorous stirring, to an anhyd. DMF (4.5 mL) solution containing G-0 dendron **D-Cl** (0.160 g, 0.12 mmol) and 1,3,5-tris(piperazinomethyl)benzene **A** (0.015 g, 0.040 mmol), anhyd. K_2CO_3 (0.017 g, 0.12 mmol) was added at room temperature. The resulted suspension was heated at 90–95 °C for 96 h (TLC monitoring: consumption of **D-Cl**, eluent hexane/ CH_2Cl_2 /acetone 5:3:1; consumption of **A** and formation of product **5**, eluent hexane/ CH_2Cl_2 /acetone 1:4:0.5). DMF was distilled under reduced pressure and the solid residue was taken up with distilled water (12 mL) then filtered off. The dried crude product (0.155 g) was purified by column chromatography (eluent hexane/ CH_2Cl_2 /acetone 1:4:0.5) to provide pure product **5** (0.110 g, 65% yield).

1,3,5-Tris[4-{4,6-bis[4-{4,6-bis[4-(*n*-octyloxy)phenylamino]-*s*-triazin-2-yl]-piperazin-1-yl]-*s*-triazin-2-yl]-piperazin-1-yl)methyl]benzene (**5**). Beige powder; m.p. 210-211 °C. Yield 65%. $R_f=0.92$ (hexane/ CH_2Cl_2 /acetone 1:4:0.5). Elemental analysis calcd (%) for $\text{C}_{240}\text{H}_{345}\text{N}_{57}\text{O}_{12}$: C 68.30, H 8.24, 18.92; found: C 67.98, H 8.57, N 18.86. IR (KBr) ν_{max} . 3412 (w), 2926 (m), 2853 (m), 1600 (m), 1547 (s), 1512 (s), 1493 (s), 1476 (s), 1419 (s), 1260 (m), 1242 (m), 1219 (m), 1001 (m), 827 (w), 804 (w) cm^{-1} . ^1H and 2D- ^1H , ^1H -COSY NMR (500 MHz, 5.0 mM in $\text{DMSO}-d_6$, 298 K): $\delta_{\text{H}}=0.84$, 0.86 (36H, 2xt, $^3J_{\text{H,H}}=4.6$ Hz, $^3J_{\text{H,H}}=5.3$ Hz; CH_3), 1.25-1.28 (96H, br m; CH_2 , *n*-octyl), 1.41 (24H, tt app. h, $^3J_{\text{H,H}}=7.3$ Hz; CH_2 , *n*-octyl), 1.69 (24H, tt app. sp, $^3J_{\text{H,H}}=7.1$ Hz; OCH_2CH_2 , *n*-octyl), 3.78 (72 H, br s; P-0, -1; 6H, CH_2 -inner), 3.92, 3.91 (24H, 2xt, $^3J_{\text{H,H}}=6.8$ Hz, $^3J_{\text{H,H}}=6.5$ Hz; OCH_2 , *n*-octyl), 6.83-6.85 (24H, br s; H-3, -5, Ph-peripheral), 7.57 (27H: 24H, br s; H-2, -6, Ph-peripheral; 3H, benzene-core), 8.91, 8.93 (12H, 2xbr s; NH) ppm. ^1H and 2D- ^1H , ^1H -COSY NMR (500 MHz, 5.0 mM in $\text{DMSO}-d_6$, 363 K): $\delta_{\text{H}}=0.87$ (36H, t, $^3J_{\text{H,H}}=6.5$ Hz; CH_3), 1.29-1.35 (96H, m; CH_2 , *n*-octyl), 1.43 (24H, tt app. qi, $^3J_{\text{H,H}}=7.0$ Hz; CH_2 , *n*-octyl), 1.71 (24H, tt app. sp, $^3J_{\text{H,H}}=7.4$ Hz; OCH_2CH_2 , *n*-octyl), 3.79, 3.80 (78H: 72H, br s; P-0, P-1; 6H, br s; CH_2 -inner), 3.94, 3.96 (24H, 2xt, $^3J_{\text{H,H}}=6.3$ Hz, $^3J_{\text{H,H}}=6.0$ Hz; OCH_2 , *n*-octyl), 6.82, 6.85 (24H, d, dd, $^3J_{\text{H,H}}=8.5$ Hz, $^3J_{\text{H,H}}=6.5$ Hz, $^4J_{\text{H,H}}=2.5$ Hz; H-3, -5, Ph-peripheral), 7.55, 7.57 (27H: 24H, 2xdd, $^3J_{\text{H,H}}=7.5$ Hz, $^4J_{\text{H,H}}=1.8$ Hz, $^3J_{\text{H,H}}=8.0$ Hz, $^4J_{\text{H,H}}=3.0$ Hz; H-2, -6, Ph-peripheral; 3H, benzene-core), 8.51, 8.53, 8.55, 8.60 (12H, br s; NH) ppm. 2D- ^1H -DOSY NMR (500 MHz, 5.0 mM in $\text{DMSO}-d_6$, 298 K): $D=88 \mu\text{m}^2 \text{s}^{-1}$. 2D- ^1H , ^{13}C -HSQC, DEPT and ^{13}C NMR (125 MHz, 5.0 mM in $\text{DMSO}-d_6$, 298 K): $\delta_{\text{C}}=14.4$ (12C; CH_3), 22.9 (12C; CH_2CH_3), 26.1 (12C; CH_2 , *n*-octyl), 29.2, 29.3 (36C; CH_2 , *n*-octyl), 31.7 (12C; OCH_2CH_2 , *n*-octyl), 43.0, 43.2 (39C: 36C, P-0, -1; 3C, CH_2 -inner), 68.0 (12C; OCH_2 , *n*-octyl), 114.6 (24C; C-3, -5, Ph-peripheral), 122.1 (27C: 24C, C-2, -6, Ph-peripheral; 3C, C-2, -4, -6, benzene-core), 133.6 (15C: 12C, C-1, Ph-peripheral; 3C, C-1, -3, -5, benzene-core), 154.3 (12C; C-4, Ph-peripheral), 164.5 (12C; C-4, -6, T-0), 165.06, 165.10, 165.18, 165.22, 165.3 (6C, C-2, T-0; 9C, T-1) ppm. HRMS (ESI+, ACN+TFA) (rel. int.) m/z : 2110.9146 (32) $[0.5(\text{M}+4\text{H})]^+$. Anal. calcd. for $[0.5(\text{M}+4\text{H})]^+$ 2110.9225.

Preparation of G -2 dendrimer 6

Under inert atmosphere and vigorous stirring, into an anhyd. DMF (8 mL) solution containing G-1 dendron **D-Cl** (0.680 g, 0.516 mmol) and 2,4,6-tris(4-hydroxyphenylamino)-s-triazine **B** (65.8 mg, 0.16 mmol), anhyd. K₂CO₃ (0.265 g, 1.92 mmol) was suspended. The reaction mixture was heated at 100 °C for 56 h until no progress of the reaction was observed (TLC monitoring: consumption of **D-Cl**, eluent hexane/CH₂Cl₂/acetone 5:3:1; consumption of **B**, eluent ligroin/acetone 1:1; formation of **6**, eluent CHCl₃/hexane/acetone 4:1:0.3). In order to remove the unreacted **D-Cl**, the reaction mixture was evaporated to dryness under reduced pressure and the solid residue was dissolved in THF (25 mL) to which a solution obtained by dissolving KOH (0.210 g) in distilled water (20 mL) was added. Under inert atmosphere, the alkaline solution (pH ~ 13) was stirred for 24 h at room temperature then THF was removed under reduced pressure. The resulted suspension was filtered off and well washed with hot distilled water to neutrality. The dried crude product was purified by column chromatography (eluent CHCl₃/hexane/acetone 4:1:0.3) to provide pure compound **6** [0.240 g, 35% yield with respect to 2,4,6-tris(4-hydroxyphenylamino)-s-triazine **B**].

2,4,6-Tris{4-{4,6-bis{4-{4,6-bis[4-(*n*-octyloxy)phenylamino]-s-triazin-2-yl}-piperazin-1-yl}-s-triazin-2-oxy}-phenylamino}-s-triazine (**6**). Beige powder; m.p. 110-111 °C (column chromatography, eluent CHCl₃/hexane/acetone 4:1:0.3); *R*_f=0.64. Yield 35%. Elemental analysis calcd (%) for C₂₄₀H₃₂₇N₅₇O₁₅: C 67.82, H 7.75, N 18.78; found: C 67.93, H 7.65, N 18.63. IR (KBr) ν_{max} . 3411 (w), 2959 (m), 2924 (m), 2852 (m), 1736 (w), 1651 (w), 1577 (s), 1559 (s), 1515 (s), 1491 (s), 1438 (m), 1419 (m), 1380 (w), 1358 (m), 1287 (w), 1260 (w), 1243 (m), 1204 (w), 1110 (w), 1003 (w), 973 (m), 836 (w), 802 (w) cm⁻¹. ¹H and 2D-¹H,¹H-COSY NMR (500 MHz, 5.0 mM in DMSO-*d*₆, 363 K): δ_{H} =0.87 (36H, t, ³*J*_{H,H}=6.5 Hz; CH₃), 1.27-1.32 (96H, m; CH₂, *n*-octyl), 1.41 (24H, tt ap. qi, ³*J*_{H,H}=7.1 Hz; CH₂, *n*-octyl), 1.69 (24H, tt ap. qi, ³*J*_{H,H}=6.9 Hz; OCH₂CH₂, *n*-octyl), 3.77 (48H, br s; piperazine), 3.92 (24H, t, ³*J*_{H,H}=6.3 Hz; OCH₂, *n*-octyl), 6.80 (24H, d, ³*J*_{H,H}=9.0 Hz; H-3, -5, Ph-*peripheral*), 7.13 (6H, d, ³*J*_{H,H}=9.0 Hz; H-3, -5, Ph-*linker*), 7.53 (24H, d, ³*J*_{H,H}=9.0 Hz; H-4, -6, Ph-*peripheral*), 7.84 (6H, d, ³*J*_{H,H}=9 Hz; H-4, -6, Ph-*linker*), 8.55 (12H, s; NH-*peripheral*), 9.02 (3H, br s; NH-*core*) ppm. DEPT and ¹³QC NMR (125 MHz, 2.5 mM in DMSO-*d*₆, 363 K): δ_{C} =13.7 (12C; CH₃), 21.9 (12C; CH₂CH₃), 25.5 (12C; CH₂, *n*-octyl), 28.5 (12C; CH₂, *n*-octyl), 28.7 (12C; CH₂, *n*-octyl), 28.9 (12C; CH₂, *n*-octyl), 31.2 (12C; OCH₂CH₂, *n*-octyl), 42.6, 42.9 (24C; piperazine), 68.1 (12C; OCH₂, *n*-octyl), 114.5 (24C; C-3, -5, Ph-*peripheral*), 121.15 (6C; C-3, -5, Ph-*linker*), 121.22 (6C; C-2, -6, Ph-*linker*) 122.1 (24C; C-2, -6, Ph-*peripheral*), 133.1 (12C; C-1, Ph-*peripheral*), 136.8 (3C; C-1, Ph-*linker*), 147.4 (3C; C-4, Ph-*linker*), 154.3 (12C; C-4, Ph-*peripheral*), 164.2 (12C; C-4, -6, T-0), 164.4 (3C; T-2), 164.9 (6C; C-2, T-0), 166.1 (6C; C-4, -6, T-1), 170.6 (3C; C-2, T-1) ppm. HRMS (ESI+, ACN+TFA) (rel. int.) *m/z*: 2125.8369 (100) [0.5(*M*+4H)]⁺. Anal. calcd. for [0.5(*M*+4H)]⁺ 2125.8445.

Preparation of G-2 dendrimer **7a**

Under inert atmosphere, into an anhyd. THF (14 mL) solution containing G-1 dendron **D-N<P>NH** (0.4000 g, 0.29 mmol), anhyd. K₂CO₃ (0.0400 g, 0.29 mmol) was suspended with vigorous stirring. The suspension was cooled at 0 °C when trimesic acid trichloride (0.0254 g (0.095 mmol) as anhyd. THF (1.5 mL) solution was injected dropwise. The reaction mixture was stirred at room temperature for 72 h then heated at reflux (48 h) until no more evolution was observed (TLC monitoring, eluent acetone/CH₂Cl₂/EtOH 2:8:0.5). The reaction mixture was then evaporated under reduced pressure to dryness. Distilled water (10 mL) was added to the solid residue and the suspension was filtered off and well washed with distilled water. The crude and dried product was dissolved in CHCl₃ (25 mL) and the solution was washed four times with 1% NaOH aq. soln. (25 mL), then with distilled water (25 mL) to neutrality. The organic layer was dried over anhyd. Na₂SO₄, filtered off and evaporated under reduced pressure. The solid residue was purified by column chromatography (eluent acetone/CH₂Cl₂/EtOH 2:8:0.5) to provide pure compound **7a** (0.2000 g, 50% yield

with respect to trimesic acid trichloride).

*1,3,5-Tris[4-{4,6-bis[4-{4,6-bis[4-(*n*-octyloxy)phenylamino]-*s*-triazin-2-yl]-piperazin-1-yl]-*s*-triazin-2-yl]-piperazin-1-ylcarbonyl]benzene* **7a**. White-yellowish powder; m.p. 140-141 °C (column chromatography, eluent acetone/CH₂Cl₂/EtOH 2:8:0.5); *R*_f=0.95. Yield 50%. Elemental analysis calcd (%) for C₂₄₀H₃₃₉N₅₇O₁₅: C 67.62, H 8.02, N 18.73; found: C 67.31, H 7.85, N 19.02. IR (KBr) $\nu_{\max}$ 2958 (m), 2925 (m), 2852 (m), 1633 (m), 1582 (m), 1543 (s), 1512 (s), 1493 (s), 1474 (s), 1418 (s), 1261 (s), 1242 (s), 1220 (s), 998 (m), 826 (m), 805 (m) cm⁻¹. ¹H and 2D-¹H,¹H-COSY NMR (500 MHz, 2.5 mM in DMSO-*d*₆, 298 K): δ_{H} =0.85 (36H, br s; CH₃), 1.27 (96H, br s; CH₂, *n*-octyl), 1.40 (24H, br s; CH₂, *n*-octyl), 1.69 (24H, tt app. q, ³*J*_{H,H}=7.0 Hz; OCH₂CH₂, *n*-octyl), 3.78 (72H, br s; P-0, -1), 3.92 (24H, t, ³*J*_{H,H}=6.3 Hz; OCH₂, *n*-octyl), 6.84 (24H, br s; H-3, -5, Ph-*peripheral*), 7.58 (27H, br s: 24H, H-2, -6, Ph-*peripheral*; 3H, benzene-*core*), 8.94 (12H, br s, br s; NH) ppm. ¹H and 2D-¹H,¹H-COSY NMR (500 MHz, 2.5 mM in DMSO-*d*₆, 363 K): δ_{H} =0.87 (36H, br s; CH₃), 1.28 (96H, br s; CH₂, *n*-octyl), 1.42 (24H, br s; CH₂, *n*-octyl), 1.70 (24H, br s; OCH₂CH₂, *n*-octyl), 3.60 (12H, br s; H-2, -6, P-1), 3.80 (60H: 48H, br s, P-0; 12H, H-3, -5, P-1), 3.94 (24H, t, ³*J*_{H,H}=5.3 Hz; OCH₂, *n*-octyl), 6.83 (24H, d, ³*J*_{H,H}=7.0 Hz; H-3, -5, Ph-*peripheral*), 7.55 (24H, d, ³*J*_{H,H}=6.0 Hz; H-2, -6, Ph-*peripheral*), 7.60 (3H, s; benzene-*core*), 8.55 (12H, s; NH) ppm. 2D-¹H-DOSY NMR (500 MHz, 2.5 mM in DMSO-*d*₆, 298 K): *D*=107 μm² s⁻¹. DEPT and ¹³QC NMR (125 MHz, 5.0 mM in DMSO-*d*₆, 298 K): δ_{C} =14.4 (12C; CH₃), 22.6 (12C; CH₂CH₃), 26.1 (12C; CH₂, *n*-octyl), 29.2, 29.3 (36C; CH₂, *n*-octyl), 31.7 (12C; OCH₂CH₂, *n*-octyl), 43.06, 43.14, 43.20, 43.24 (36C; P-0, -1), 68.0 (12C; OCH₂, *n*-octyl), 114.7 (24C; C-3, -5, Ph-*peripheral*), 122.1, 122.2 (27C: 24C, C-2, -6, Ph-*peripheral*; 3C, C-2, -4, -6, benzene-*core*), 133.5 (15C: 12C, C-1, Ph-*peripheral*; 3C, C-1, -3, -5, benzene-*core*), 154.3 (12C; C-4, Ph-*peripheral*), 164.36, 164.39, 164.41, 164.46, 164.51 (12C; C-4, -6, T-0), 165.1 (6C: 3C, C=O; 3C, C-2, T-1), 165.3 (12C: 6C, C-2, T-0; 6C, C-4, -6, T-1) ppm. HRMS (ESI+, ACN+TFA) *m/z*: 2131.9060 (63) [0.5(*M*+4*H*)]⁺, 1421.6078 (100) [0.33(*M*+5*H*)]⁺; calcd. for [0.5(*M*+4*H*)]⁺ 2131.8915; calcd. for [0.33(*M*+5*H*)]⁺ 1421.5969.

Preparation of G-2 dendrimer **7b**

At room temperature and with vigorous stirring, compound **D-N<P>NH** (0.0860 g, 0.0628 mmol) and trimesic acid (0.0044 g, 0.0209 mmol) were dissolved in anhyd. THF (2 mL) and heated at 60 °C for 15 min. The resulted clear solution was evaporated under reduced pressure to dryness and the solid residue was dried under vacuum for additional 48 h to provide compound **7b** with quantitative yield (0.0904 g).

*Tris[4-{4,6-bis[4-{4,6-bis[4-(*n*-octyloxyphenyl)amino]-*s*-triazin-2-yl]-piperazin-1-yl]-*s*-triazin-2-yl]-piperazin-1-ium}-1,3,5-benzene tricarboxylate* **7b**. White powder; m.p. 140-141 °C. Yield 100%. Elemental analysis calcd (%) for C₂₄₀H₃₄₅N₅₇O₁₈: C 66.78, H 8.06, N 18.50; found: C 66.55, H 8.43, N 18.24. IR (KBr) $\nu_{\max}$ 3413 (w), 3273 (w), 2957 (m), 2926 (m), 2853 (m), 1702 (w), 1556 (s), 1542 (s), 1513 (s), 1475 (s), 1438 (m), 1419 (s), 1354 (w), 1258 (m), 1220 (m), 1172 (m), 999 (m), 826 (w) cm⁻¹. ¹H and 2D-¹H,¹H-COSY NMR (500 MHz, 2.5 mM in DMSO-*d*₆, 298 K): δ_{H} =0.86 (36H, t, ³*J*_{H,H}=6.8 Hz; CH₃), 1.26-1.31 (96H, m; CH₂, *n*-octyl), 1.41 (24H, tt ap. qi, ³*J*_{H,H}=7.0 Hz; CH₂, *n*-octyl), 1.69 (24H, tt ap. qi, ³*J*_{H,H}=6.9 Hz; OCH₂CH₂, *n*-octyl), 3.09 (12H, br s; H-2, -6, P-1), 3.78 (60H, br s: 48H, P-0; 12H, H-3, -5, P-1), 3.92 (24H, t, ³*J*_{H,H}=6.5 Hz; OCH₂, *n*-octyl), 6.84 (24H, d, ³*J*_{H,H}=8.5 Hz; H-3, -5, Ph-*peripheral*), 7.58 (24H, br s; H-2, -6, Ph-*peripheral*), 8.63 (3H, s; benzene-*core*), 8.93 (12H, br s; NH) ppm. ¹H and 2D-¹H,¹H-COSY NMR (500 MHz, 2.5 mM in DMSO-*d*₆, 363 K): δ_{H} =0.88 (36H, t, ³*J*_{H,H}=6.8 Hz; CH₃), 1.30-1.39 (96H, m; CH₂, *n*-octyl), 1.44 (24H, tt ap. qi, ³*J*_{H,H}=7.0 Hz; CH₂, *n*-octyl), 1.72 (24H, tt ap. qi, ³*J*_{H,H}=6.9 Hz; OCH₂CH₂, *n*-octyl), 2.90 (12H, br t, ³*J*_{H,H}=5.3 Hz; H-2, -6, P-1), 3.80 (60H, br s: 48H, P-0; 12H, H-3, -5, P-1), 3.96 (24H, t, ³*J*_{H,H}=6.5 Hz; OCH₂, *n*-octyl), 6.85 (24H, d, ³*J*_{H,H}=9.0 Hz; H-3, -5, Ph-*peripheral*), 7.57 (24H, d, ³*J*_{H,H}=9.0 Hz; H-2, -6, Ph-*peripheral*), 8.53 (12H, s; NH) 8.64 (3H, s; benzene-*core*) ppm. 2D-¹H-DOSY NMR (500 MHz, 2.5 mM in DMSO-*d*₆, 298 K): *D*=105 and 225 μm² s⁻¹. ¹³QC, DEPT and 2D-¹H, ¹³C-HSQC, -HMBC NMR (125 MHz,

2.5 mM in DMSO-*d*₆, 298 K): δ_C =13.7 (12C; CH₃), 21.9 (12C; CH₂CH₃), 25.5 (12C; CH₂, *n*-octyl), 28.5, 28.7, 28.9 (36C; CH₂, *n*-octyl), 31.1 (12C; OCH₂CH₂, *n*-octyl), 42.7, 42.8 (36C; P-0, -1), 68.1 (12C; OCH₂, *n*-octyl), 114.6 (24C; C-3, -5, *Ph-peripheral*), 122.1 (27C: 24C, C-2, -6, *Ph-peripheral*; 3C, C-2, -4, -6, *benzene-core*), 132.31, 132.34, 132.37 (3C; C-1, -3, -5, *benzene-core*), 133.3, 133.4 (12C; C-1, *Ph-peripheral*), 154.2 (12C; C-4, *Ph-peripheral*), 164.4 (12C; C-4, -6, T-0), 165.0, 165.1, 165.2 (15C: 6C, C-2, T-0; 6C, C-4, -6, T-1; 3C, C-2, T-1), 165.9 (3C, C=O) ppm.

Preparation of G-2 dendrimer **8**

An anhyd. DMSO (2 mL) solution containing compounds **D-N<P>NH** (0.0812 g, 0.0593 mmol) and **C1** (0.0114 g, 0.0198 mmol) was heated at 95 °C for 15 min. After cooling to room temperature, the solution was lyophilised to provide compound **8** in quantitative yield (0.0926 g).

*Tris{4-[4,6-bis{4-[4,6-bis[4-(*n*-octyloxy)phenylamino]-*s*-triazin-2-yl]-piperazin-1-yl]-*s*-triazin-2-yl]-piperazin-1-ium} 2,4,6-tris[4-(methoxyl)phenylamino]-*s*-triazine tricarboxylate **8***. White powder; m.p. 169-170 °C. Elemental analysis calcd (%) for C₂₅₈H₃₆₃N₆₃O₂₁: C 66.17, H 7.81, N 18.84; found: C 66.03, H 7.94, N 19.07. IR (KBr) $\nu_{\max}$. 3412 (w), 3260 (w), 2957 (w), 2925 (m), 2852 (w), 1651 (w), 1555 (s), 1541 (s), 1512 (s), 1491 (s), 1475 (s), 1418 (s), 1357 (w), 1256 (m), 1244 (m), 1218 (m), 1171 (w), 1000 (m), 827 (w), 803 (w), 633 (w) cm⁻¹. ¹H and 2D-¹H,¹H-COSY NMR (500 MHz, 5.0 mM in DMSO-*d*₆, 298 K): δ_H =0.86 (36H, t, ³*J*_{H,H}=6.8 Hz; CH₃), 1.27-1.34 (96H, m; CH₂, *n*-octyl), 1.41 (24H, tt ap. qi, ³*J*_{H,H}=7.1 Hz; CH₂, *n*-octyl), 1.69 (24H, tt ap. qi, ³*J*_{H,H}=6.9 Hz; OCH₂CH₂, *n*-octyl), 2.97 (12H, br s; H-2, -6, P-1), 3.78, 3.82 (60H, 2×br s: 48H, P-0; 12H, H-3, -5, P-1), 3.92 (24H, t, ³*J*_{H,H}=6.3 Hz; OCH₂, *n*-octyl), 6.73 (6H, br s; H-3, -5, *Ph-inner*), 6.85 (24H, d, ³*J*_{H,H}=8.0 Hz; H-3, -5, *Ph-peripheral*), 7.43 (6H, br s; H-2, -6, *Ph-inner*), 7.59 (24H, br s; H-2, -6, *Ph-peripheral*), 8.93 (15H, br s: 12H, *NH-peripheral*; 3H, *NH-inner*) ppm. ¹H, 2D-¹H,¹H-COSY NMR (500 MHz, 5.0 mM in DMSO-*d*₆, 363 K): δ_H =0.86 (36H, t, ³*J*_{H,H}=6.8 Hz; CH₃), 1.30-1.37 (96H, m; CH₂, *n*-octyl), 1.44 (24H, tt ap. qi, ³*J*_{H,H}=7.0 Hz; CH₂, *n*-octyl), 1.72 (24H, tt ap. qi, ³*J*_{H,H}=6.9 Hz; OCH₂CH₂, *n*-octyl), 2.92 (12H, br t, ³*J*_{H,H}=4.5 Hz; H-2, -6, P-1), 3.80 (66H, br s: 48H, P-0; 12H, H-3, -5, P-1; 6H, CH₂-*inner*), 3.96 (24H, t, ³*J*_{H,H}=6.3 Hz; OCH₂, *n*-octyl), 6.83 (6H, d, ³*J*_{H,H}=9.0 Hz; H-3, -5, *Ph-inner*), 6.85 (24H, d, ³*J*_{H,H}=8.5 Hz; H-3, -5, *Ph-peripheral*), 7.57 (30H, d, ³*J*_{H,H}=9.0 Hz: 24H, H-2, -6, *Ph-peripheral*; 6H, H-2, -6, *Ph-inner*), 8.54 (12H, s; *NH-peripheral*), 8.60 (3H, br s; *NH-inner*) ppm. 2D-¹H-DOSY NMR (500 MHz, 5.0 mM in DMSO-*d*₆, 298 K): *D*=113 μm² s⁻¹. ¹³CQ, DEPT and 2D-¹H,¹³C-HSQC, -HMBC NMR (125 MHz, 5.0 mM in DMSO-*d*₆, 298 K): δ_C =14.4 (12C; CH₃), 22.6 (12C; CH₂CH₃), 26.1 (12C; CH₂, *n*-octyl), 29.2, 29.3 (36C; CH₂, *n*-octyl), 31.7 (12C; OCH₂CH₂, *n*-octyl), 43.1, 43.2 (30C; P-0, -1), 68.0 (12C; OCH₂, *n*-octyl), 114.6 (30C: 24C, C-3, -5, *Ph-peripheral*; 6C, C-3, -5, *Ph-inner*), 122.1 (30C: 24C, C-2, -6, *Ph-peripheral*; 6C, C-2, -6, *Ph-inner*), 133.6 (15C: 12C, C-1, *Ph-peripheral*; 3C, C-1, *Ph-inner*), 154.3 (15C: 12C, C-4, *Ph-peripheral*; 3C, C-4, *Ph-inner*), 164.5 (15C: 6C, C-2, T-0; 9C, T-1), 165.0-165.3 (15C: 12C, C-4, -6, T-0; 3C, T-2) ppm.

Preparation of G-2 dendrimer **9**

An anhyd. DMSO (2 mL) solution containing compounds **D-N<P>NH** (0.0802 g, 0.0586 mmol) and **C3** (0.0129 g, 0.0195 mmol) was heated at 95 °C for 15 min. After cooling to room temperature, the solution was lyophilised to provide compound **9** with quantitative yield (0.0931 g).

*Tris{4-[4,6-bis{4-[4,6-bis[4-(*n*-octyloxy)phenylamino]-*s*-triazin-2-yl]-piperazin-1-yl]-*s*-triazin-2-yl]-piperazin-1-ium} 2,4,6-tris[4-(*prop*-1-yloxy)]phenylamino-*s*-triazine tricarboxylate **9***. White powder, m.p. 169-170 °C. Yield 100%. Elemental analysis calcd (%) for C₂₆₄H₃₇₅N₆₃O₂₁: C 66.51, H 7.93, N, 18.51; found: C 66.82, H 7.64, N 18.21. IR (KBr) $\nu_{\max}$. 3412 (w), 3274 (w), 2957 (m), 2926 (w), 2852 (m), 1542 (s), 1512 (s), 1492 (s), 1475 (s), 1418 (s), 1356 (w), 1243 (m), 1218 (m), 1171 (w), 1001 (m), 827 (w), 803 (w), 593

(w) cm^{-1} . ^1H and $2\text{D-}^1\text{H},^1\text{H-COSY}$ NMR (500 MHz, 5.0 mM in $\text{DMSO-}d_6$, 298 K): $\delta_{\text{H}}=0.86$ (36H, t, $^3J_{\text{H,H}}=6.5$ Hz; CH_3), 1.27-1.34 (96H, m; CH_2 , *n*-octyl), 1.41 (24H, tt ap. qi, $^3J_{\text{H,H}}=7.0$ Hz; CH_2 , *n*-octyl), 1.69 (24H, tt ap. qi, $^3J_{\text{H,H}}=6.9$ Hz; OCH_2CH_2 , *n*-octyl), 1.94 (6H, tt ap. q, $^3J_{\text{H,H}}=6.5$ Hz; $\beta\text{-CH}_2\text{-inner}$), 2.39 (6H, t, $^3J_{\text{H,H}}=7.3$ Hz; $\alpha\text{-CH}_2\text{-inner}$), 3.15 (12H, br s; H-2, -6, P-1), 3.78 (48H, s; P-0), 3.92 (36H, t, $^3J_{\text{H,H}}=6.5$ Hz; 24H, OCH_2 , *n*-octyl; 12H, H-3, -5, P-1), 3.93 (6H, t, $^3J_{\text{H,H}}=6.0$ Hz; $\gamma\text{-CH}_2\text{-inner}$), 6.85 (30H, d, $^3J_{\text{H,H}}=9.0$ Hz: 24H, H-3, -5, *Ph-peripheral*; 6H, H-3, -5, *Ph-inner*), 7.58 (30H: 24H, br s, H-2, -6, *Ph-peripheral*; 6H, H-2, -6, *Ph-inner*), 8.70 (3H, br s; *NH-inner*), 8.94 (12H, br s; *NH-peripheral*) ppm. ^1H and $2\text{D-}^1\text{H},^1\text{H-COSY}$ NMR (500 MHz, 5.0 mM in $\text{DMSO-}d_6$, 363 K): $\delta_{\text{H}}=0.86$ (36H, t, $^3J_{\text{H,H}}=6.8$ Hz; CH_3), 1.29-1.39 (96H, m; CH_2 , *n*-octyl), 1.44 (24H, tt ap. qi, $^3J_{\text{H,H}}=7.0$ Hz; CH_2 , *n*-octyl), 1.72 (24H, tt ap. qi, $^3J_{\text{H,H}}=6.9$ Hz; OCH_2CH_2 , *n*-octyl), 1.97 (6H, tt app. qi., $^3J_{\text{H,H}}=7.0$ Hz; $\beta\text{-CH}_2\text{-inner}$), 2.39 (6H, t, $^3J_{\text{H,H}}=7.3$ Hz; $\alpha\text{-CH}_2\text{-inner}$), 3.17 (12H, br s; H-2, -6, P-1), 3.81 (48H, s; P-0), 3.96 (36H, t, $^3J_{\text{H,H}}=6.5$ Hz: 24H, OCH_2 , *n*-octyl; 12H, H-3, -5, P-1), 4.00 (6H, t, $^3J_{\text{H,H}}=6.5$ Hz; $\gamma\text{-CH}_2\text{-inner}$), 6.85 (30H, d, $^3J_{\text{H,H}}=8.5$ Hz: 24H, H-3, -5, *Ph-peripheral*; 6H, H-3, -5, *Ph-inner*), 7.56 (24H, d, $^3J_{\text{H,H}}=9.0$ Hz; H-2, -6, *Ph-peripheral*), 7.59 (6H, d, $^3J_{\text{H,H}}=8.0$ Hz; H-2, -6, *Ph-inner*), 8.54 (12H, s; *NH-peripheral*), 8.57 (3H, br s; *NH-inner*) ppm. $2\text{D-}^1\text{H-DOSY}$ NMR (500 MHz, 5.0 mM in $\text{DMSO-}d_6$, 298 K): $D=115\text{ }\mu\text{m}^2\text{ s}^{-1}$. ^{13}CQ , DEPT and $2\text{D-}^1\text{H},^{13}\text{C-HSQC}$, -HMBC NMR (125 MHz, 5.0 mM in $\text{DMSO-}d_6$, 298 K): $\delta_{\text{C}}=14.4$ (12C; CH_3), 22.6 (12C; CH_2CH_3 , *n*-octyl), 24.8 (3C; $\beta\text{-CH}_2\text{-inner}$), 26.1 (12C; CH_2 , *n*-octyl), 29.2, 29.3 (36C; CH_2 , *n*-octyl), 30.6 (3C; $\alpha\text{-CH}_2\text{-inner}$), 31.7 (12C; OCH_2CH_2 , *n*-octyl), 43.1, 43.2 (30C: 24C, P-0; 6C, C-3, -5, P-1), 67.2 (3C; $\gamma\text{-CH}_2\text{-inner}$), 68.0 (12C; OCH_2 , *n*-octyl), 114.7 (30C: 24C, C-3, -5, *Ph-peripheral*; 6C, C-3, -5, *Ph-core*), 122.1 (24C; C-2, -6, *Ph-peripheral*), 122.5 (6C; C-2, -6, *Ph-inner*), 133.5 (15C: 12C, C-1, *Ph-peripheral*; 3C, C-1, *Ph-inner*), 154.3 (15C: 12C, C-4, *Ph-peripheral*; 3C, C-4, *Ph-inner*), 164.4 (15C: 6C, C-2, T-0; 9C, T-1), 165.1, (12C; C-4, -6, T-0), 165.3 (3C; T-2), 174.6 (3C; COO) ppm.

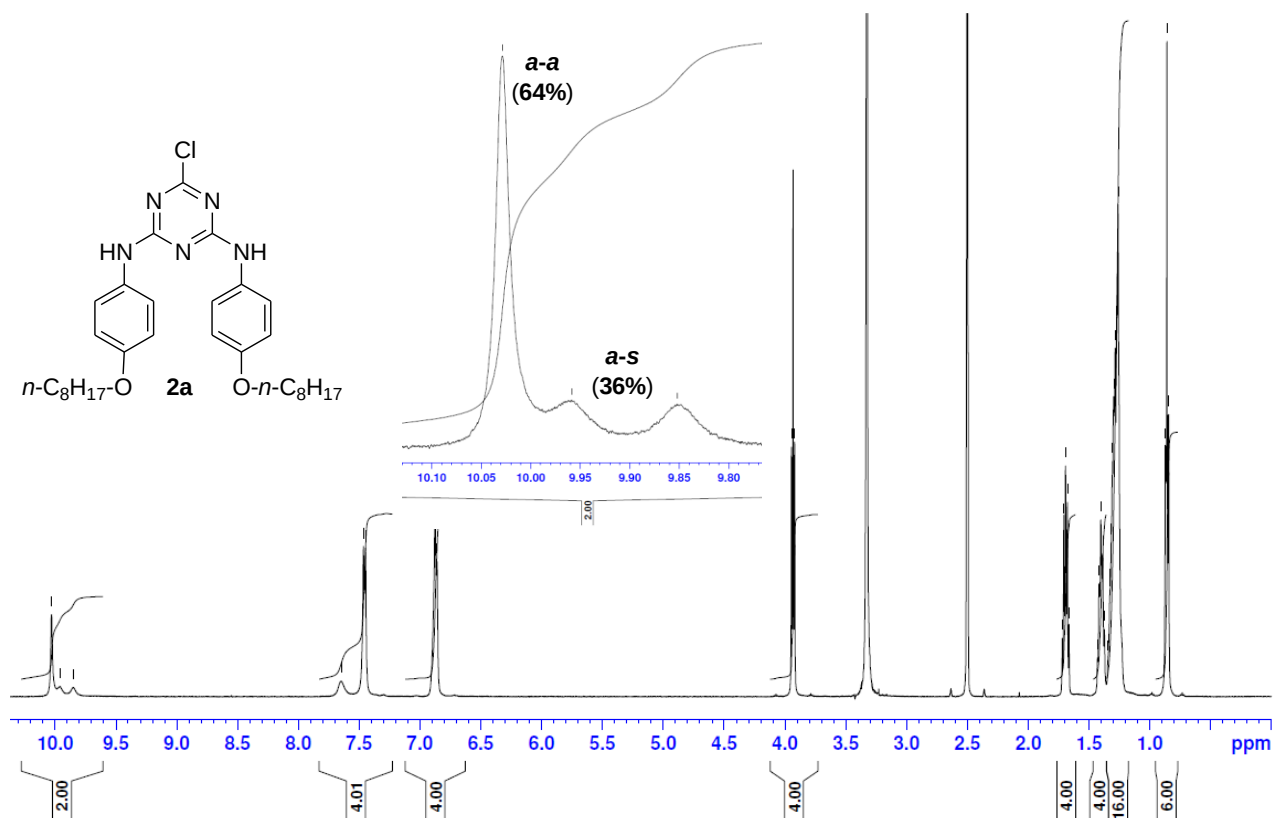


Figure S1: ^1H NMR spectrum of compound **2a** (500 MHz, 5.0 mM in $\text{DMSO-}d_6$, 298 K).

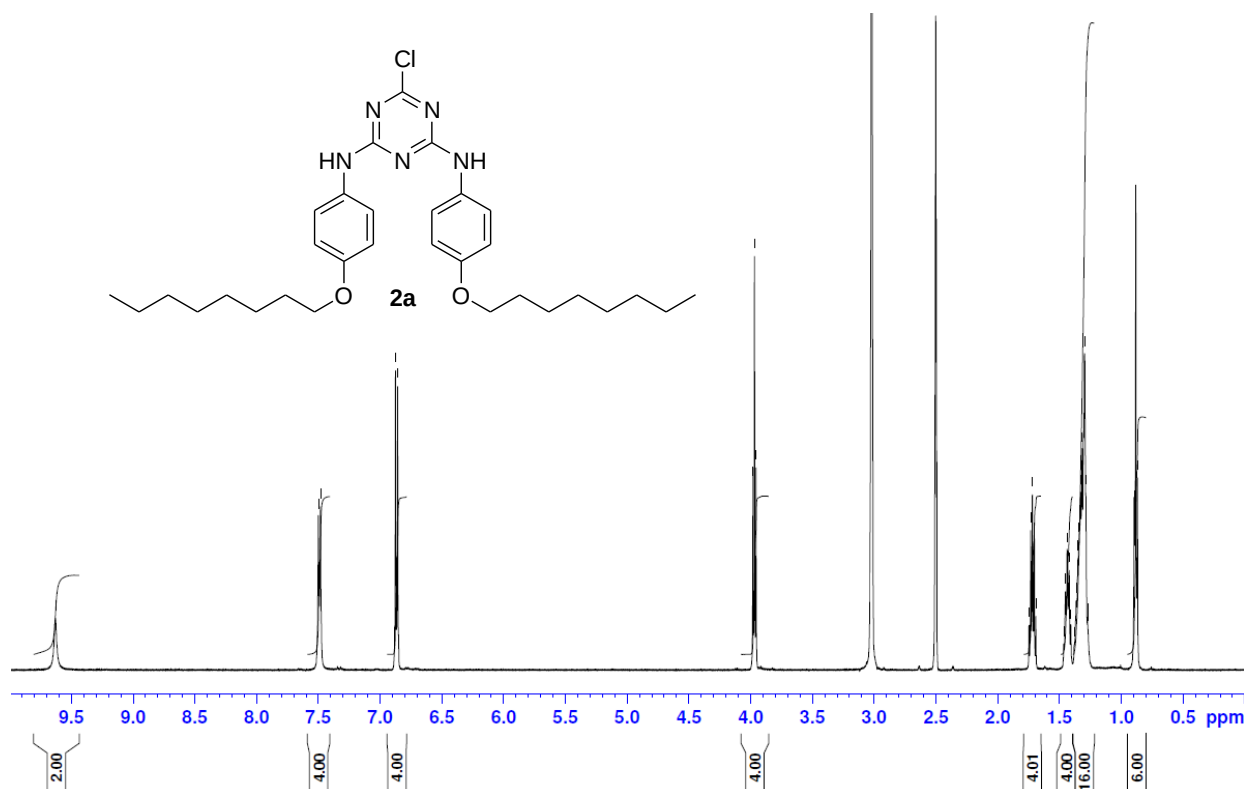


Figure S2: ^1H NMR spectrum of compound **2a** (500 MHz, 5.0 mM in $\text{DMSO-}d_6$, 363 K).

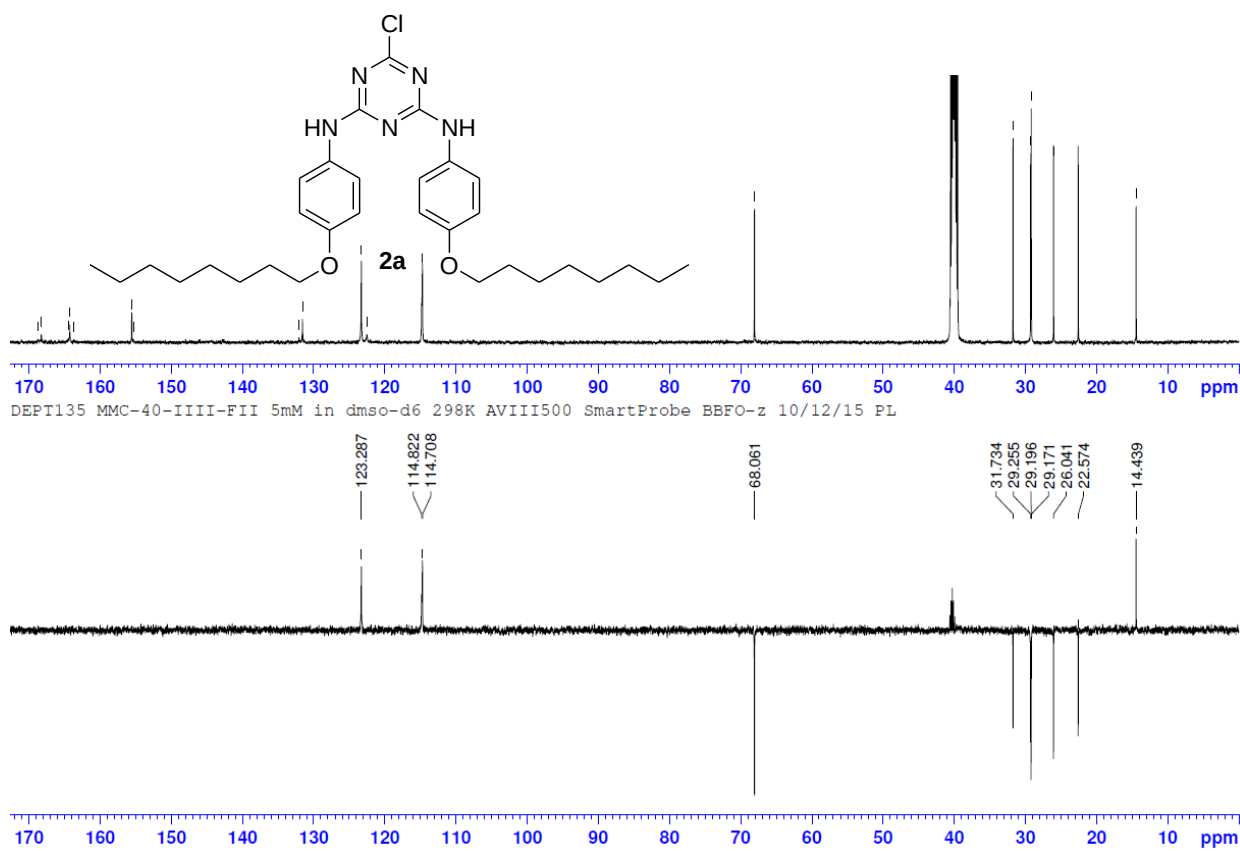


Figure S3: DEPT ^{13}C NMR spectrum of compound **2a** (125 MHz, 5.0 mM in DMSO- d_6 , 298 K).

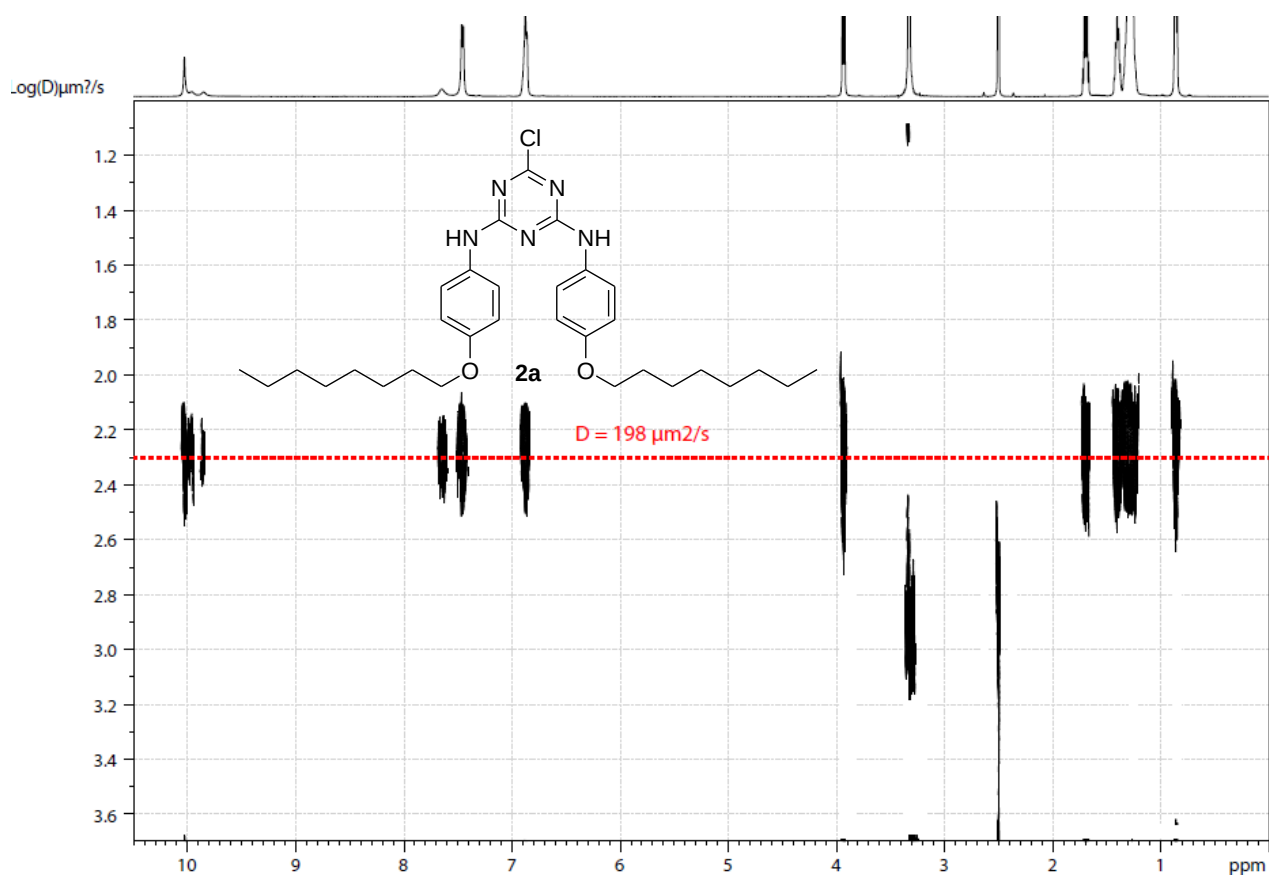


Figure S4: 2D- ^1H -DOSY NMR chart of compound **2a** (500 MHz, 5.0 mM in DMSO- d_6 , 298 K).

MMC_40_III_FII_150203121952 #1 RT: 0.01 AV: 1 NL: 2.10E9
T: FTMS + p APCI corona Full ms [150.00-2000.00]

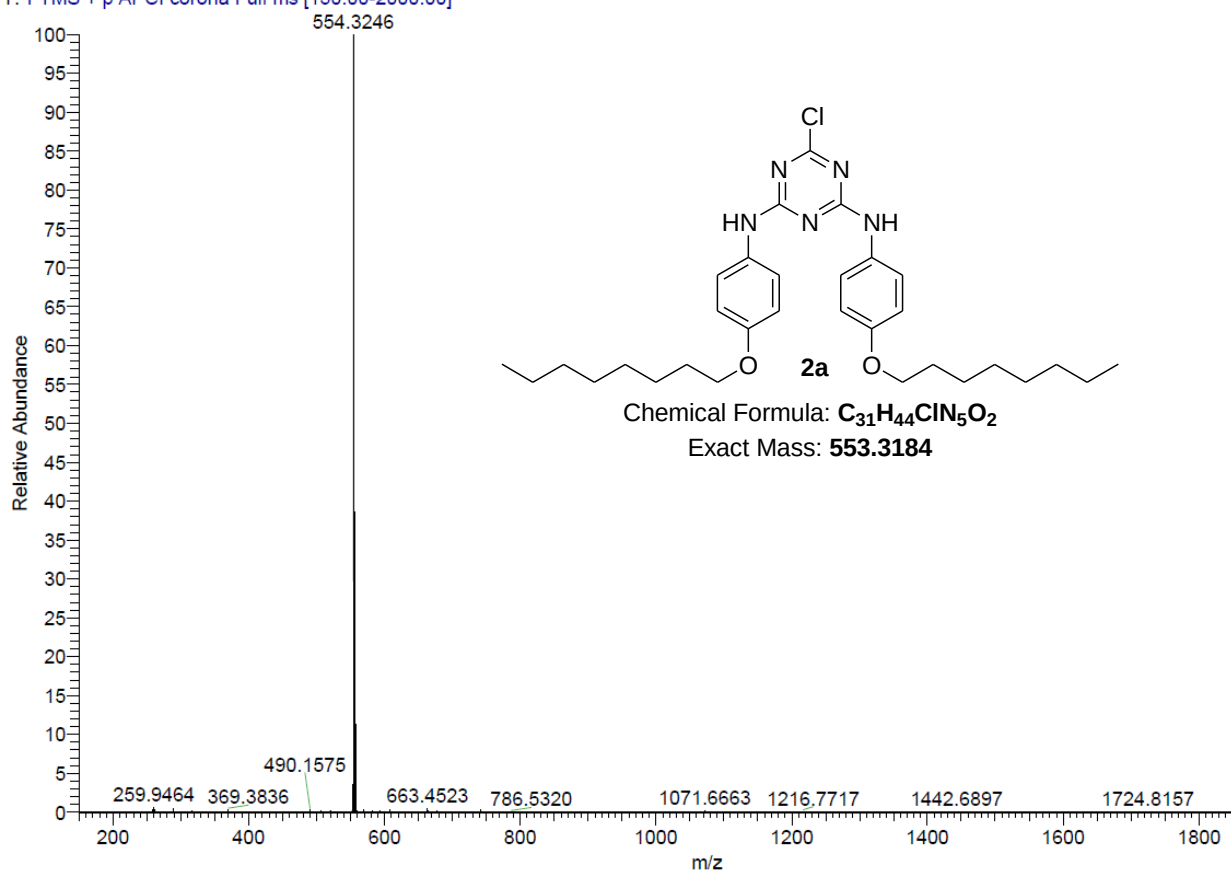


Figure S5: Mass spectrum of compound **2a** [HRMS (APCI+)].

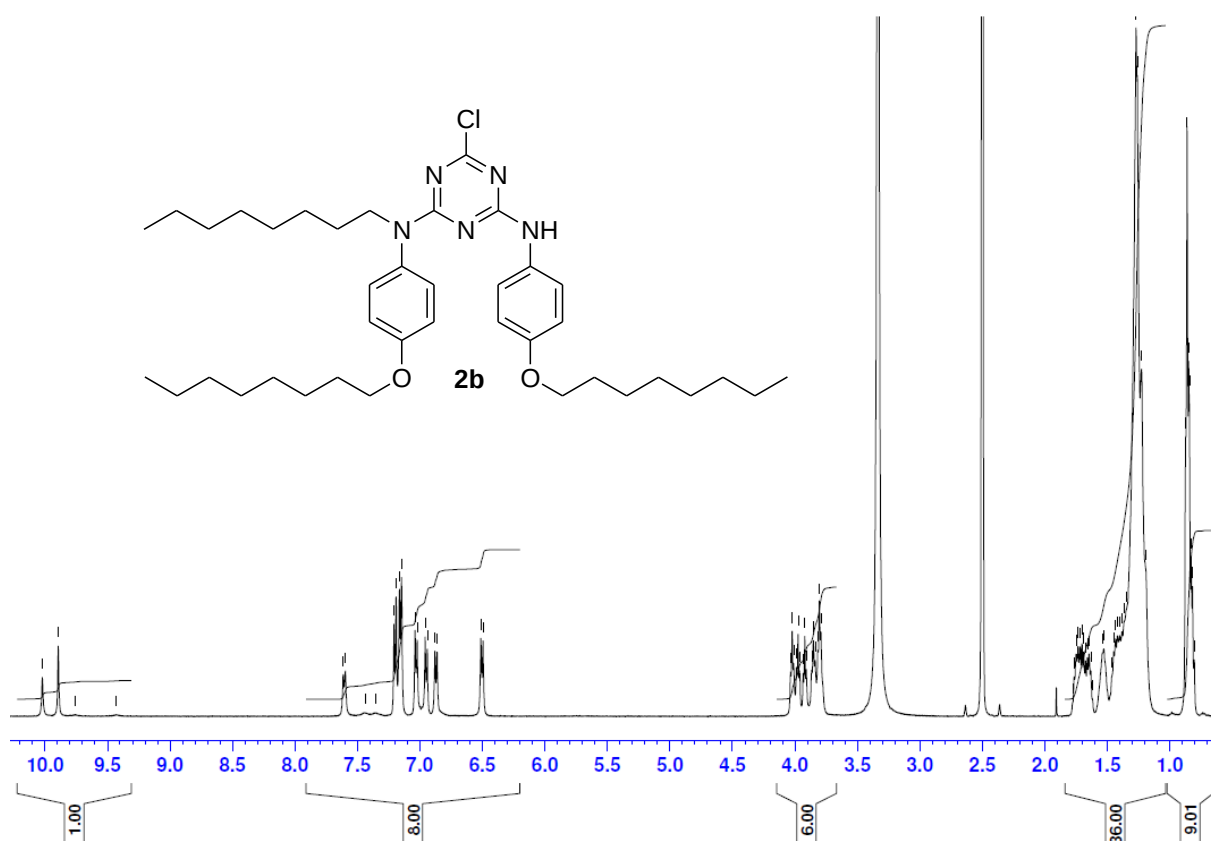


Figure S6: 1H NMR spectrum of compound **2b** (500 MHz, 5.0 mM in $DMSO-d_6$, 298 K).

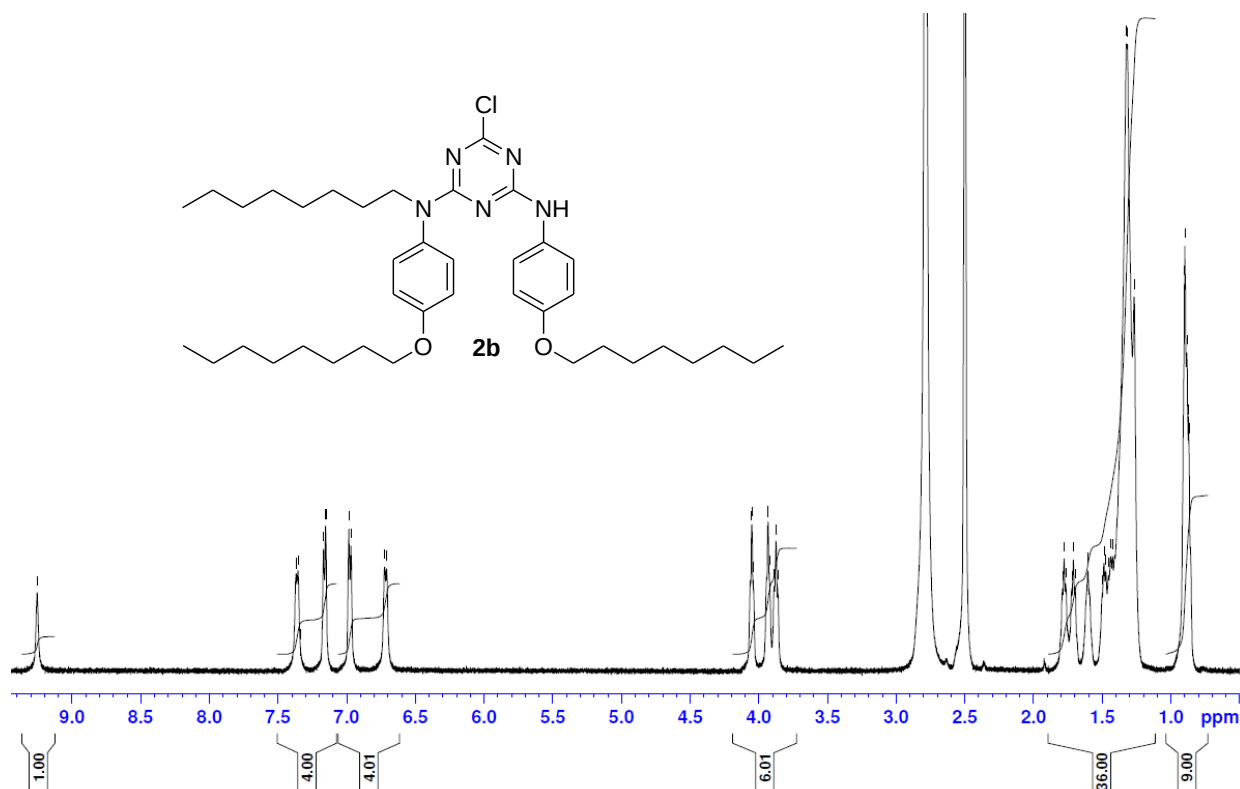


Figure S7: ¹H NMR spectrum of compound **2b** (500 MHz, 5.0 mM in DMSO-*d*₆, 403 K).

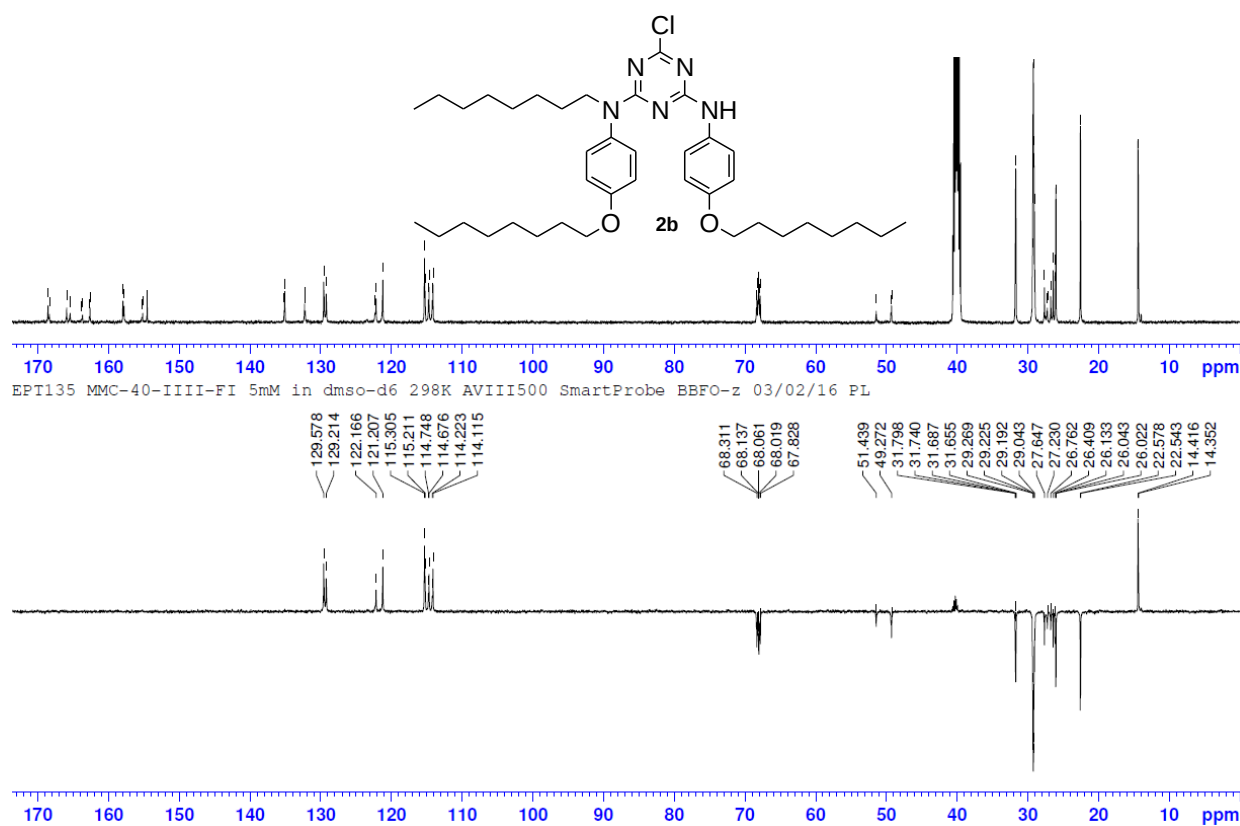


Figure S8: DEPT ¹³C NMR spectrum of compound **2b** (125 MHz, 5.0 mM in DMSO-*d*₆, 298 K).

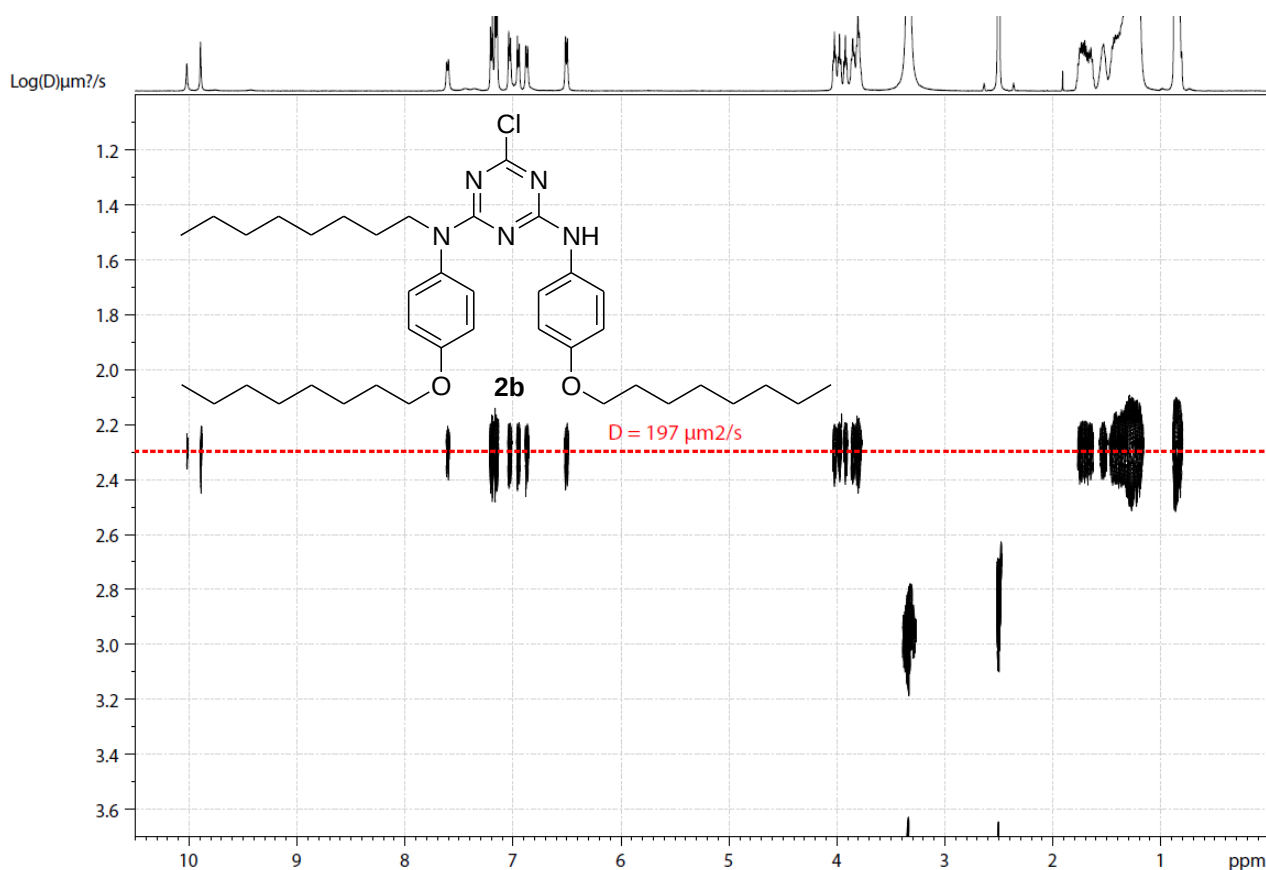


Figure S9: 2D- ^1H -DOSY NMR chart of compound **2b** (500 MHz, 5.0 mM in $\text{DMSO-}d_6$, 298 K).

MMC_40_III_FI_150130155007 #1 RT: 0.01 AV: 1 NL: 2.91E9
T: FTMS + p APCI corona Full ms [150.00-2000.00]

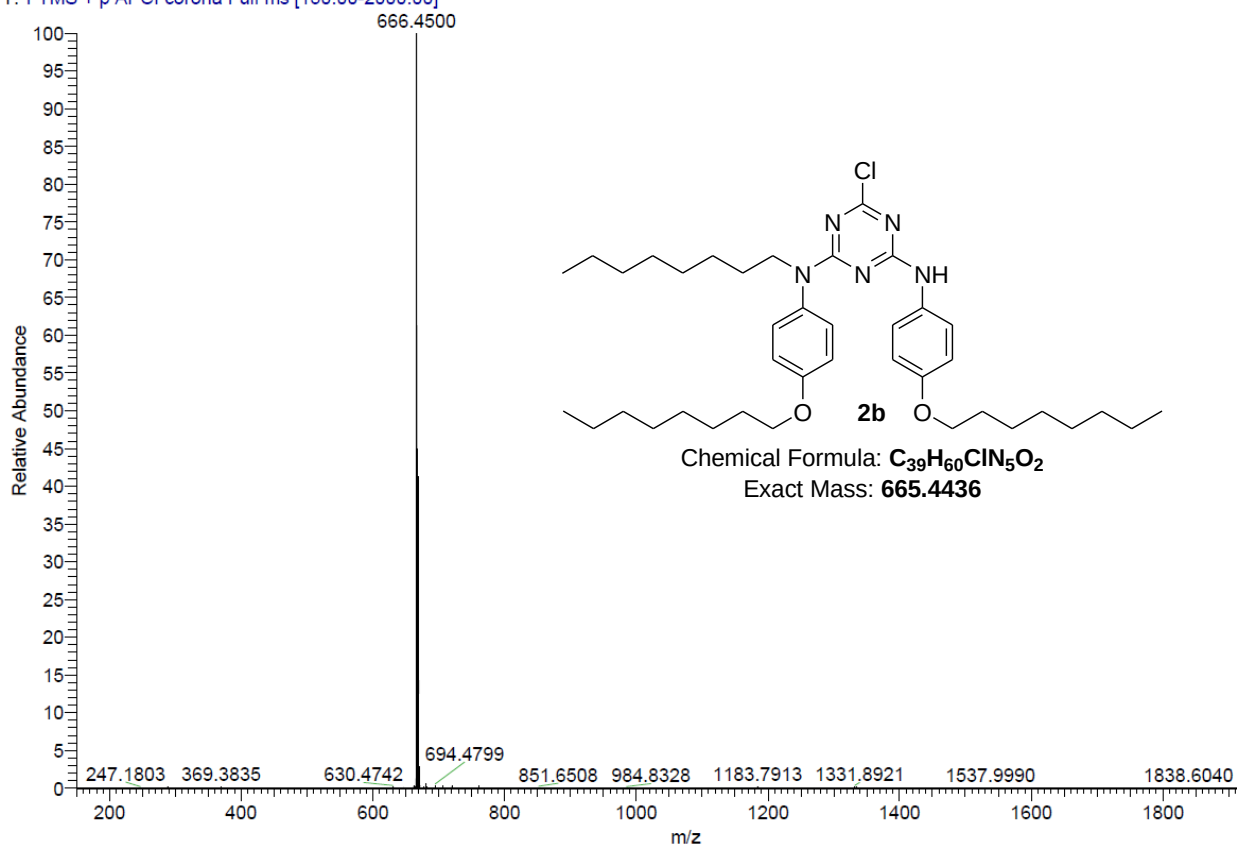


Figure S10: Mass spectrum of compound **2b** [HRMS (APCI $^+$)].

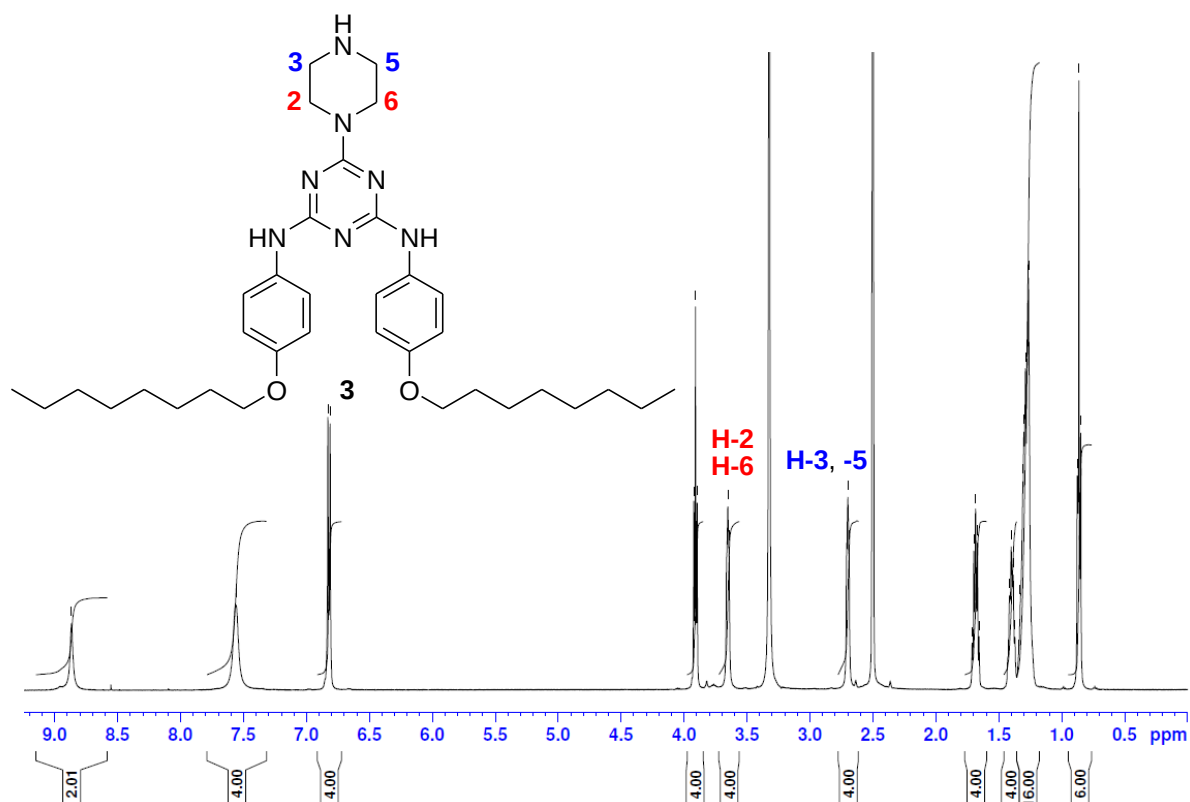


Figure S11: ^1H NMR spectrum of compound **3** (500 MHz, 5.0 mM in $\text{DMSO}-d_6$, 298 K).

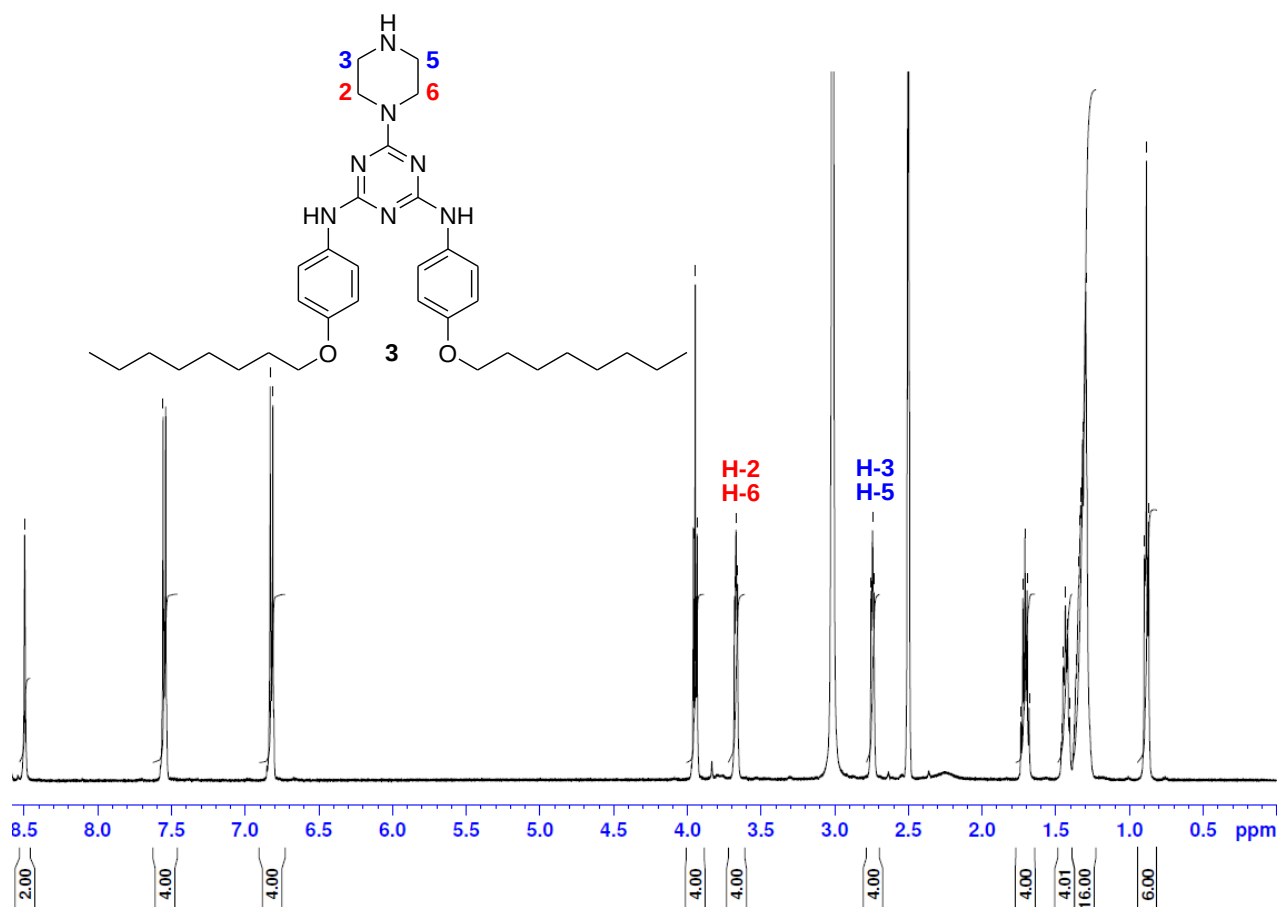


Figure S12: ^1H NMR spectrum of compound **3** (500 MHz, 5.0 mM in $\text{DMSO}-d_6$, 363 K).

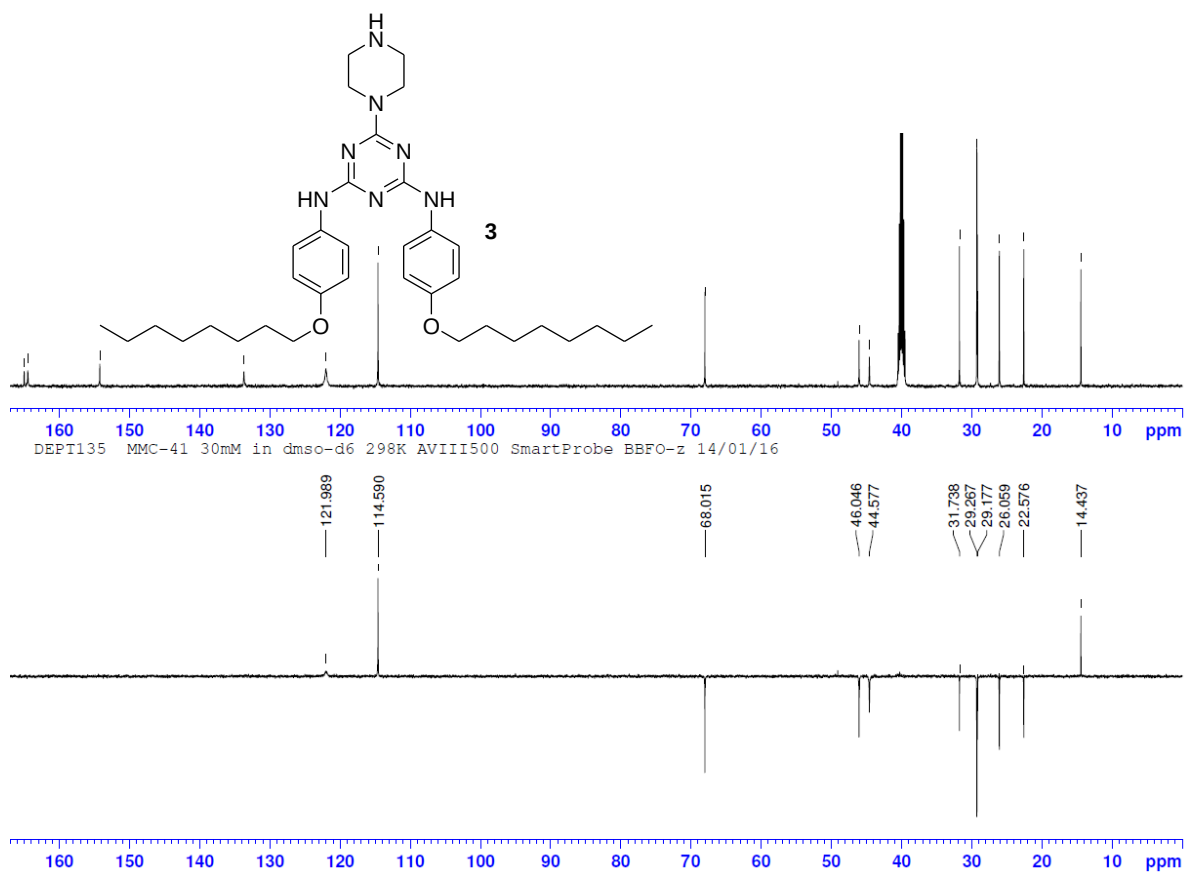


Figure S13: DEPT ^{13}C NMR spectrum of compound 3 (125 MHz, 5.0 mM in DMSO- d_6 , 298 K).

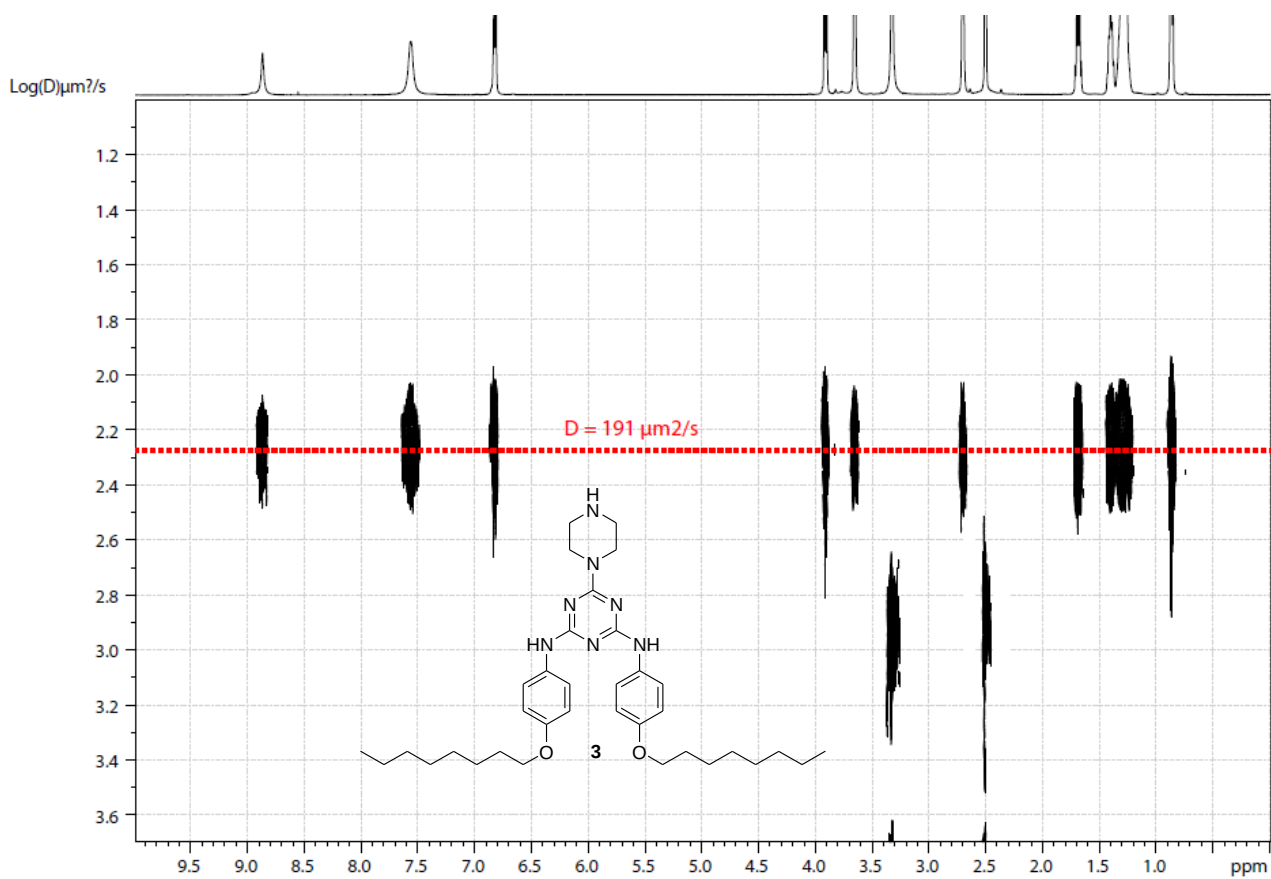


Figure S14: 2D- ^1H -DOSY NMR chart of compound 3 (500 MHz, 5.0 mM in DMSO- d_6 , 298 K).

MMC_41_150217123105 #1 RT: 0.02 AV: 1 NL: 3.47E6
T: FTMS + p APCI corona Full ms [100.00-2000.00]

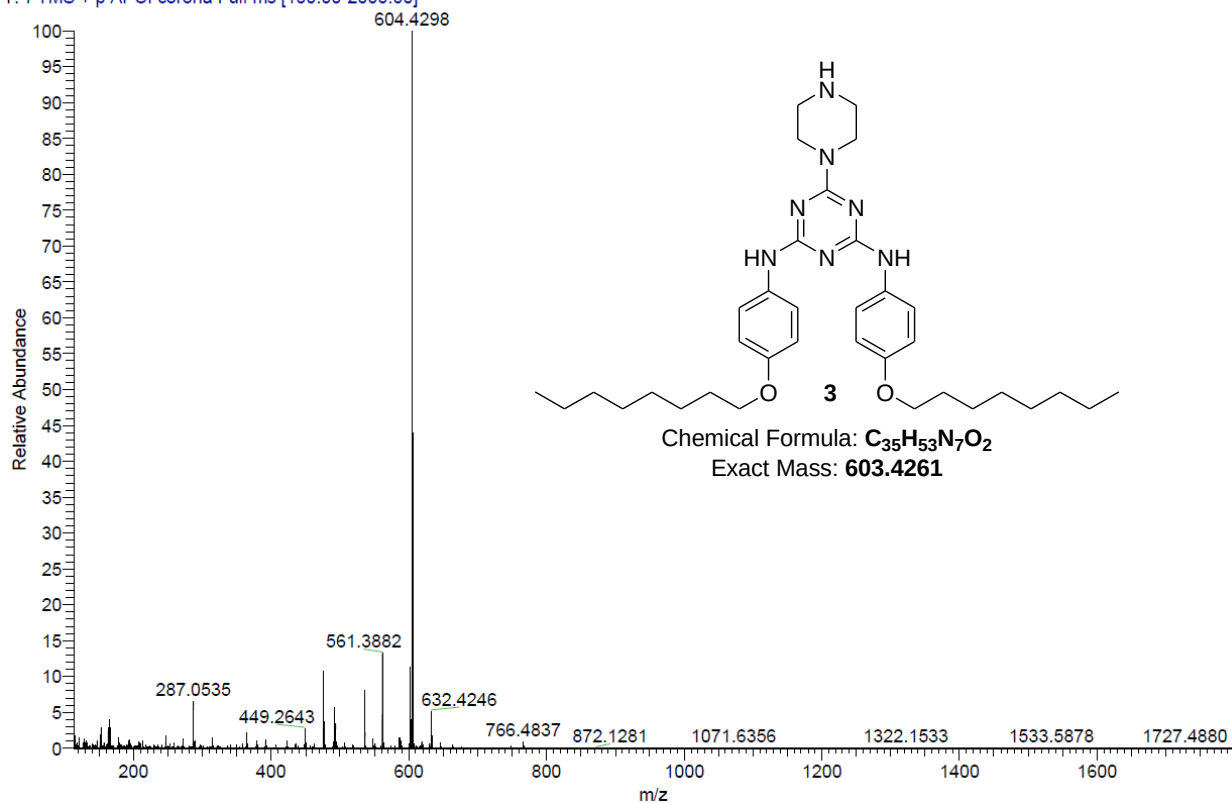


Figure S15: Mass spectrum of compound **3** [HRMS (APCI+)].

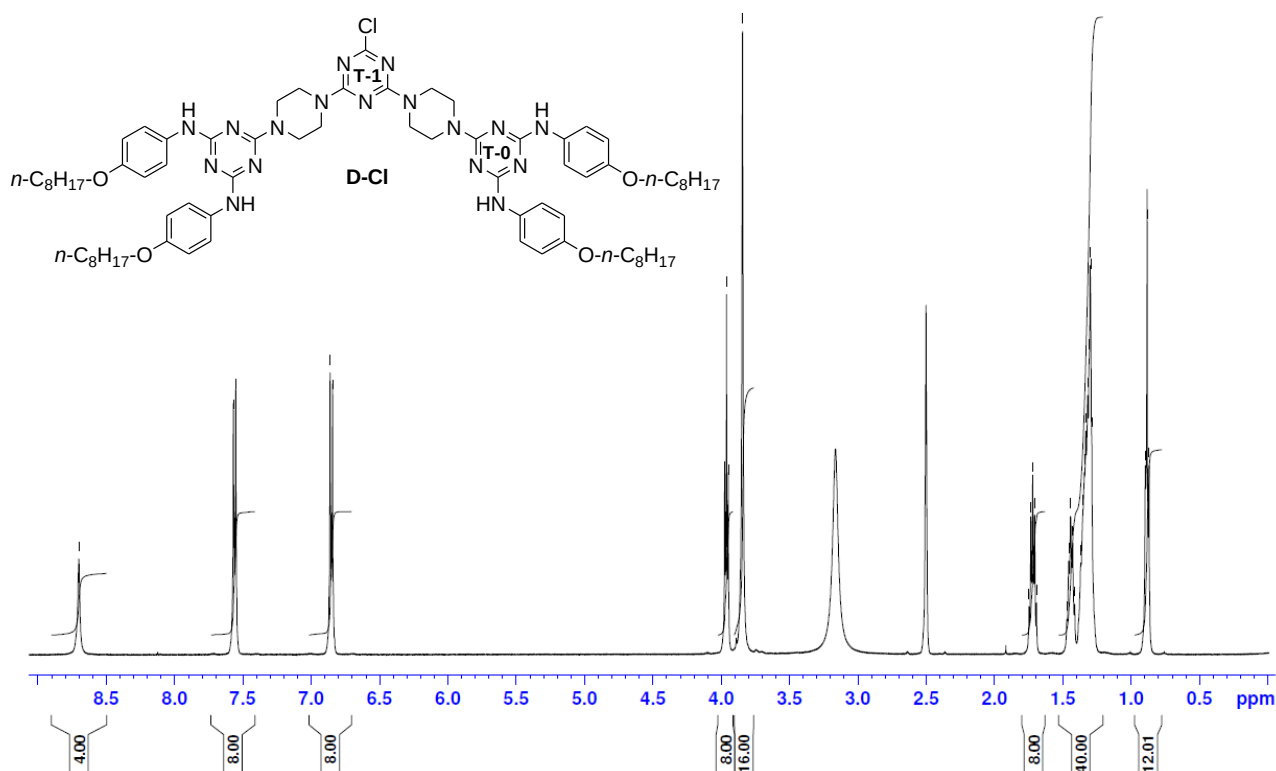


Figure S16: 1H NMR spectrum of compound **D-Cl** (500 MHz, 5.0 mM in $DMSO-d_6$, 363 K).

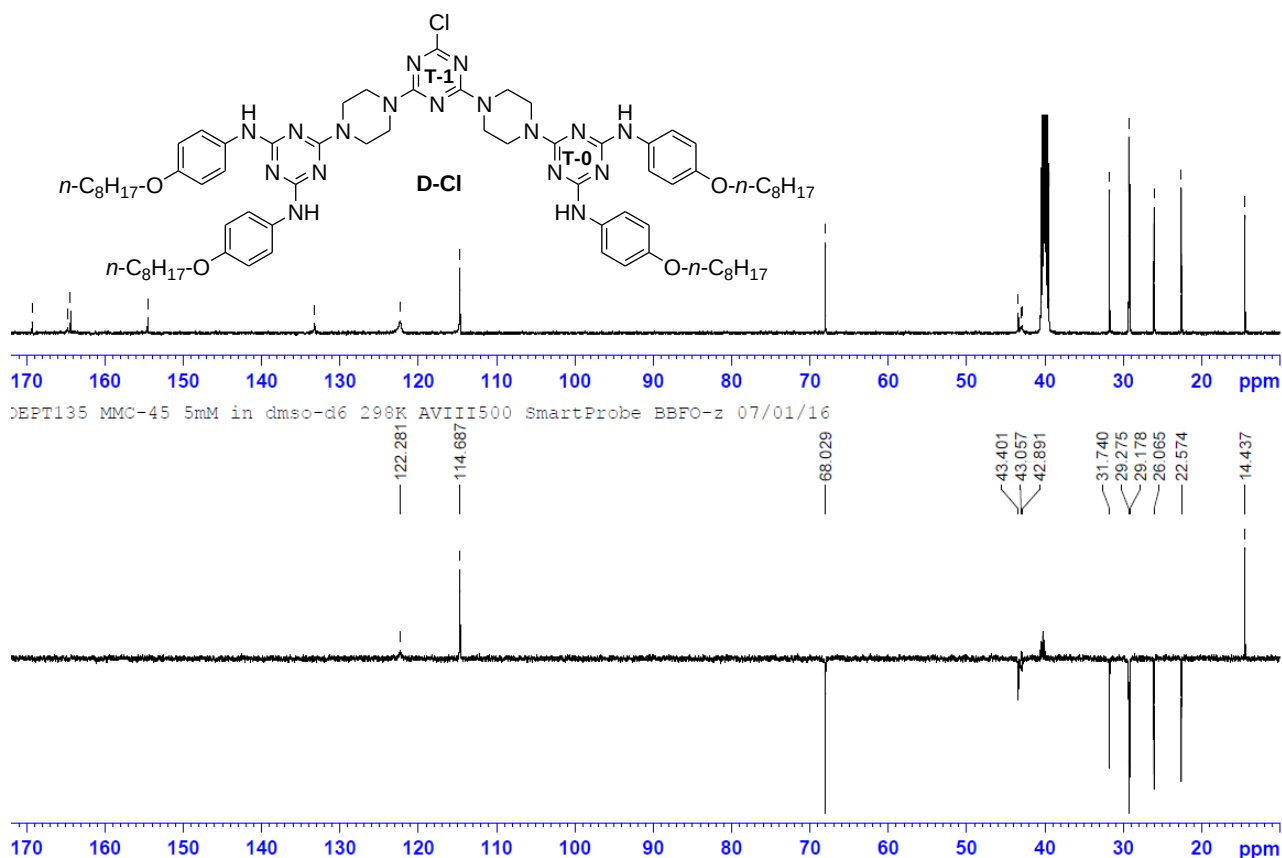


Figure S17: DEPT ^{13}C NMR spectrum of compound **D-Cl** (125 MHz, 5.0 mM in DMSO- d_6 , 298 K).

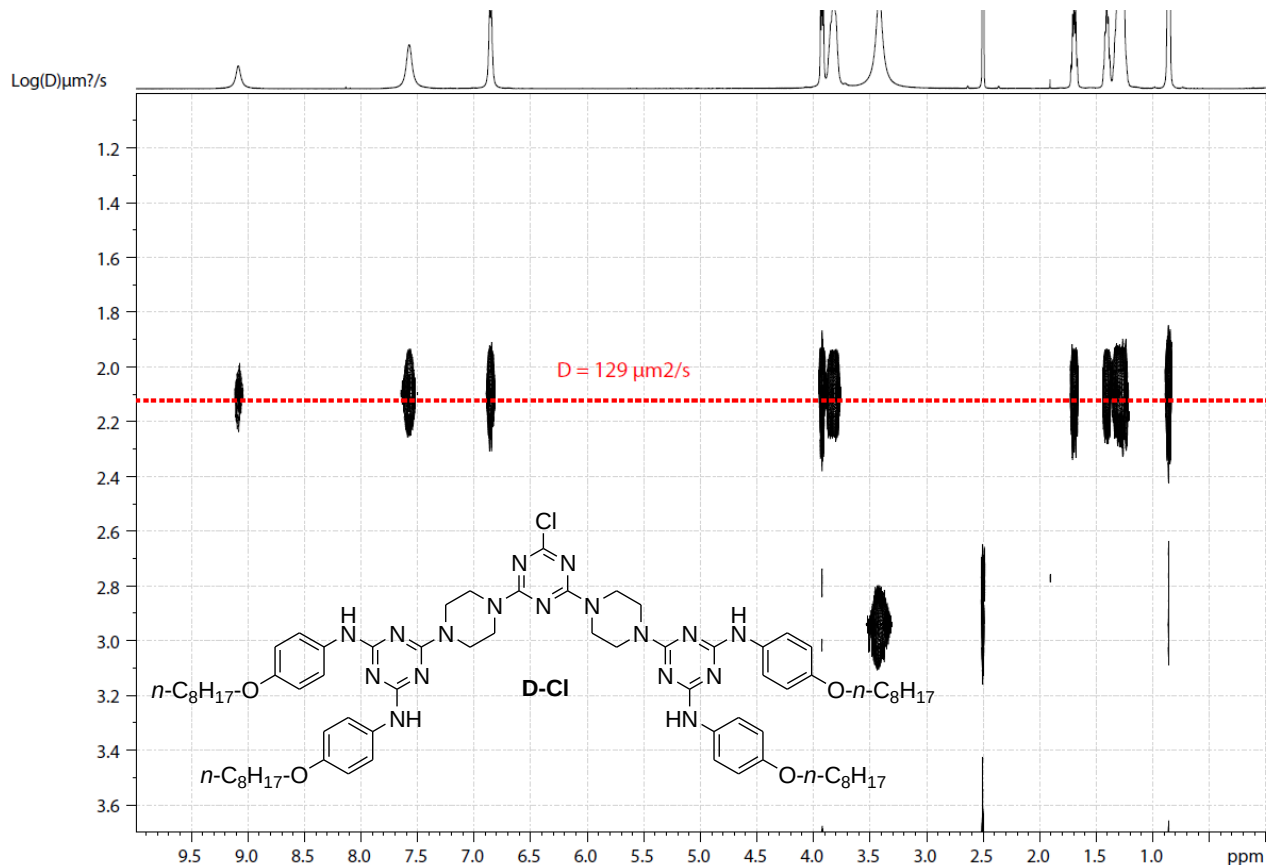


Figure S18: 2D- ^1H -DOSY NMR chart of compound **D-Cl** (500 MHz, 5.0 mM in DMSO- d_6 , 298 K).

MMC_45_150404111237 #1 RT: 0.02 AV: 1 NL: 2.79E7
T: FTMS + c ESI Full ms [250.00-2000.00]

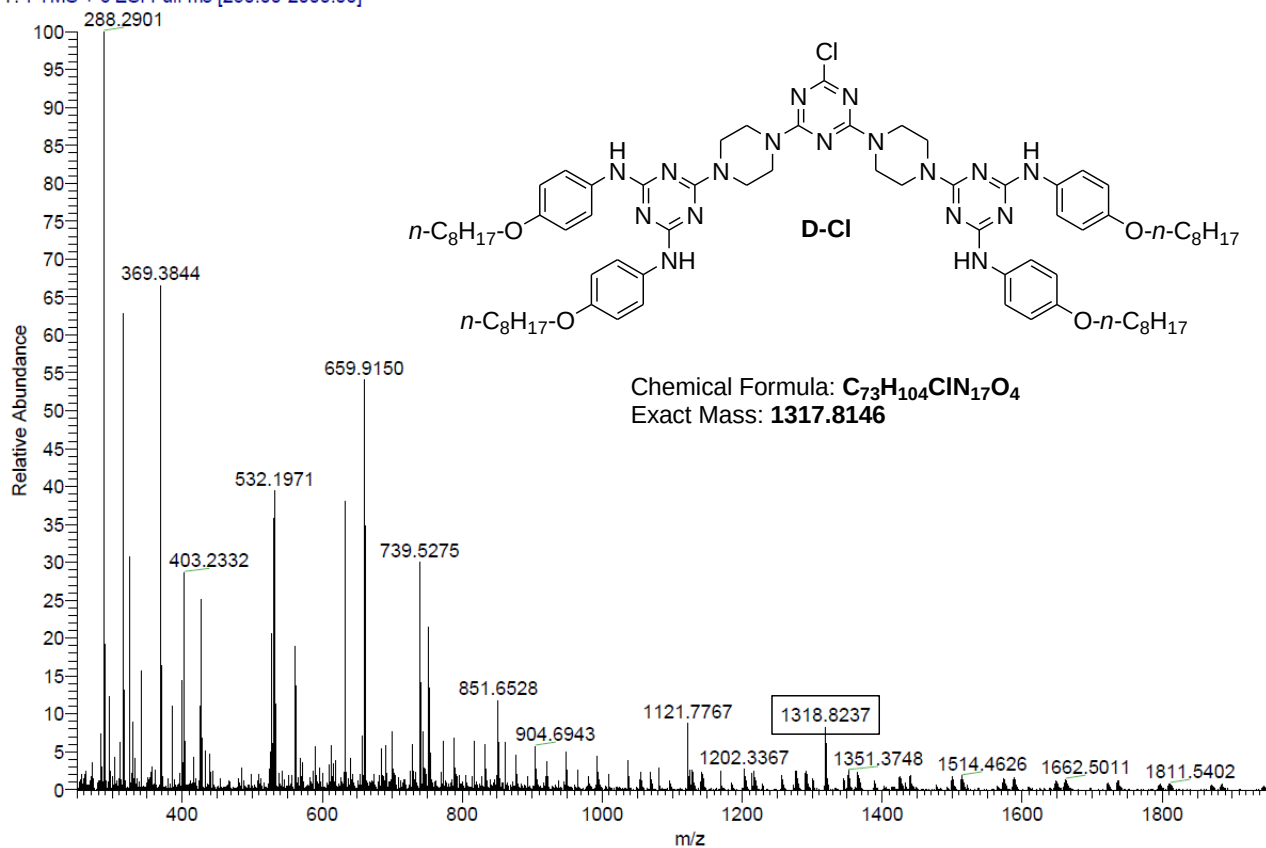


Figure S19: Mass spectrum of compound **D-Cl** [HRMS (ESI+), ACN+TFA].

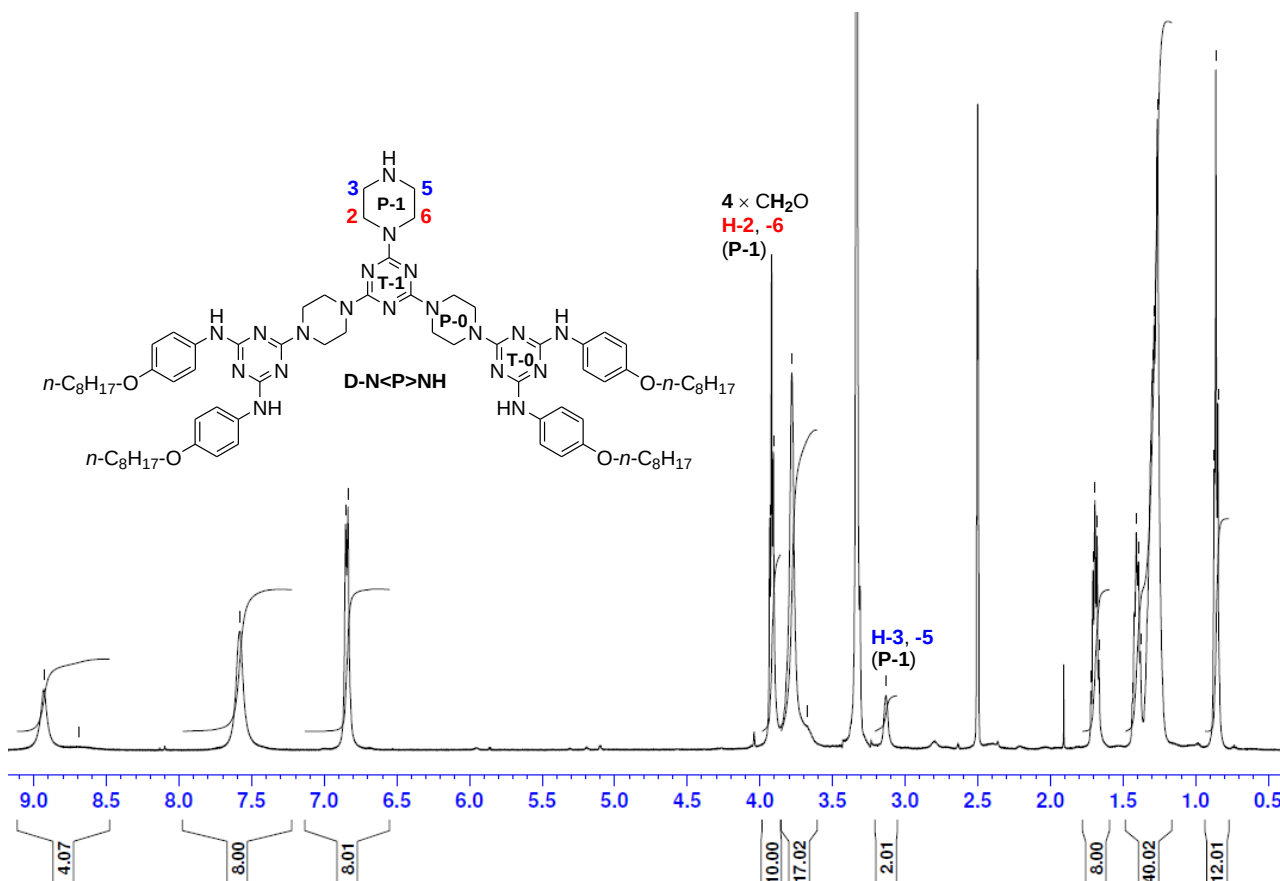


Figure S20: ^1H NMR spectrum of compound **D-N<P>NH** (500 MHz, 5.0 mM in DMSO- d_6 , 298 K).

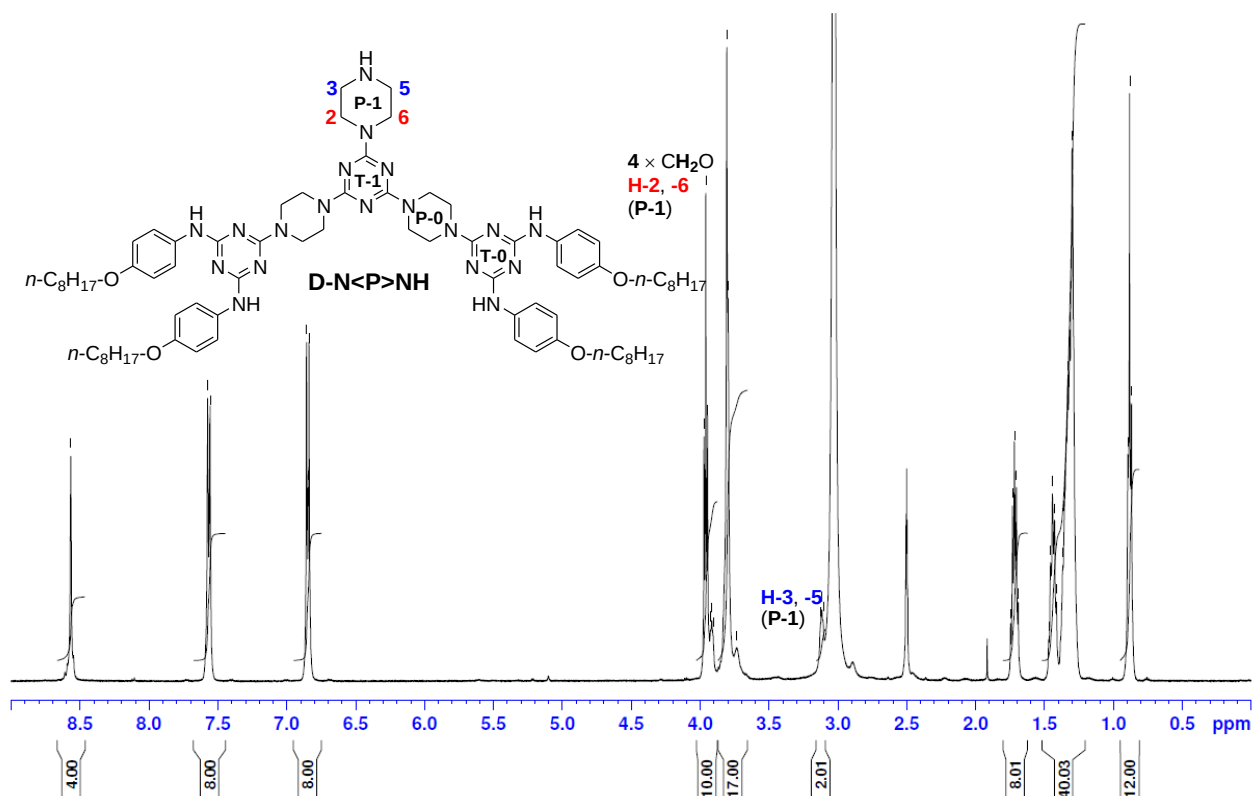


Figure S21: ¹H NMR spectrum of compound **D-N<P>NH** (500 MHz, 5.0 mM in DMSO-d₆, 363 K).

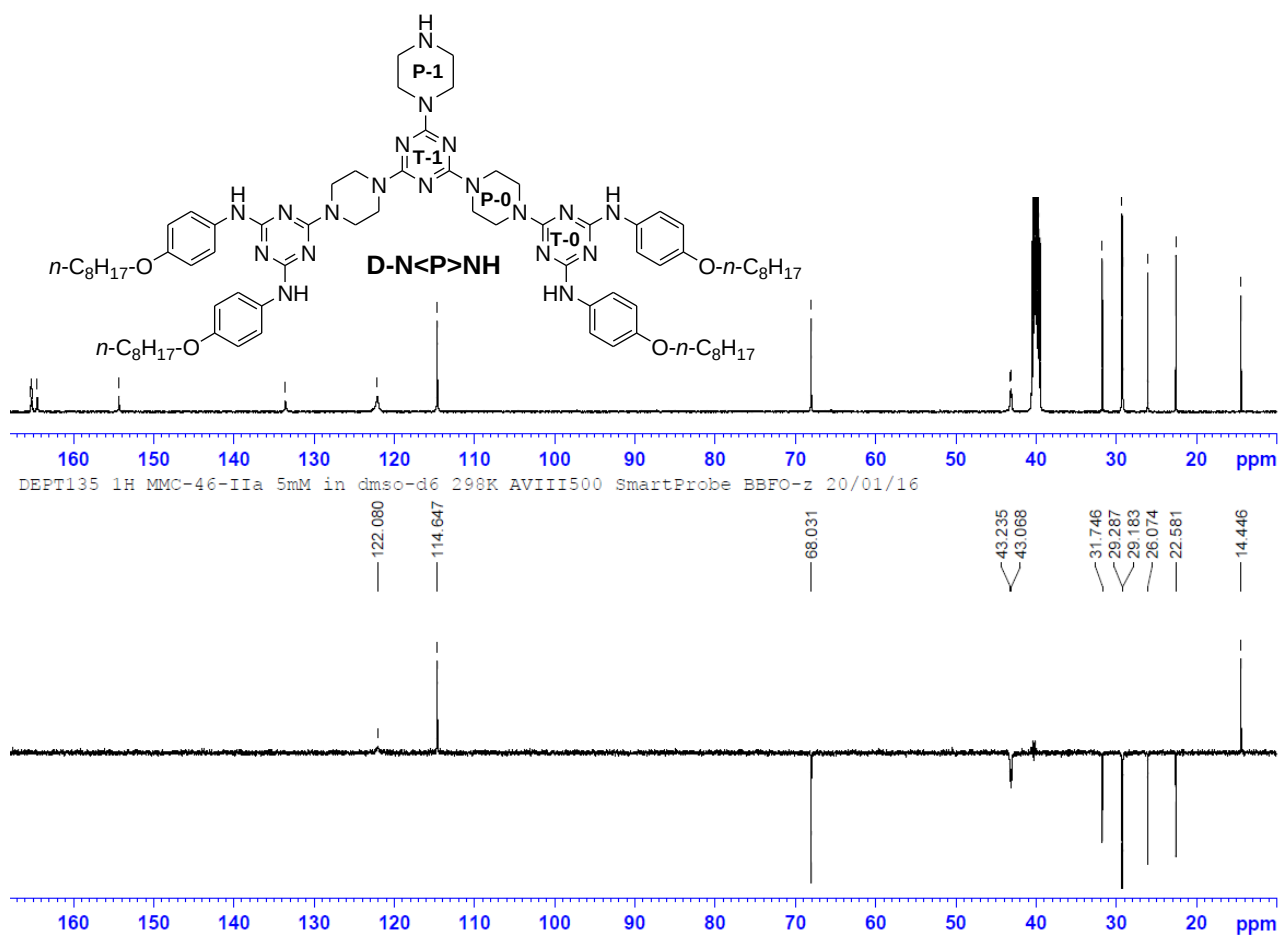


Figure S22: DEPT ¹³C NMR spectrum of compound **D-N<P>NH** (125 MHz, 5.0 mM in DMSO-d₆, 298 K).

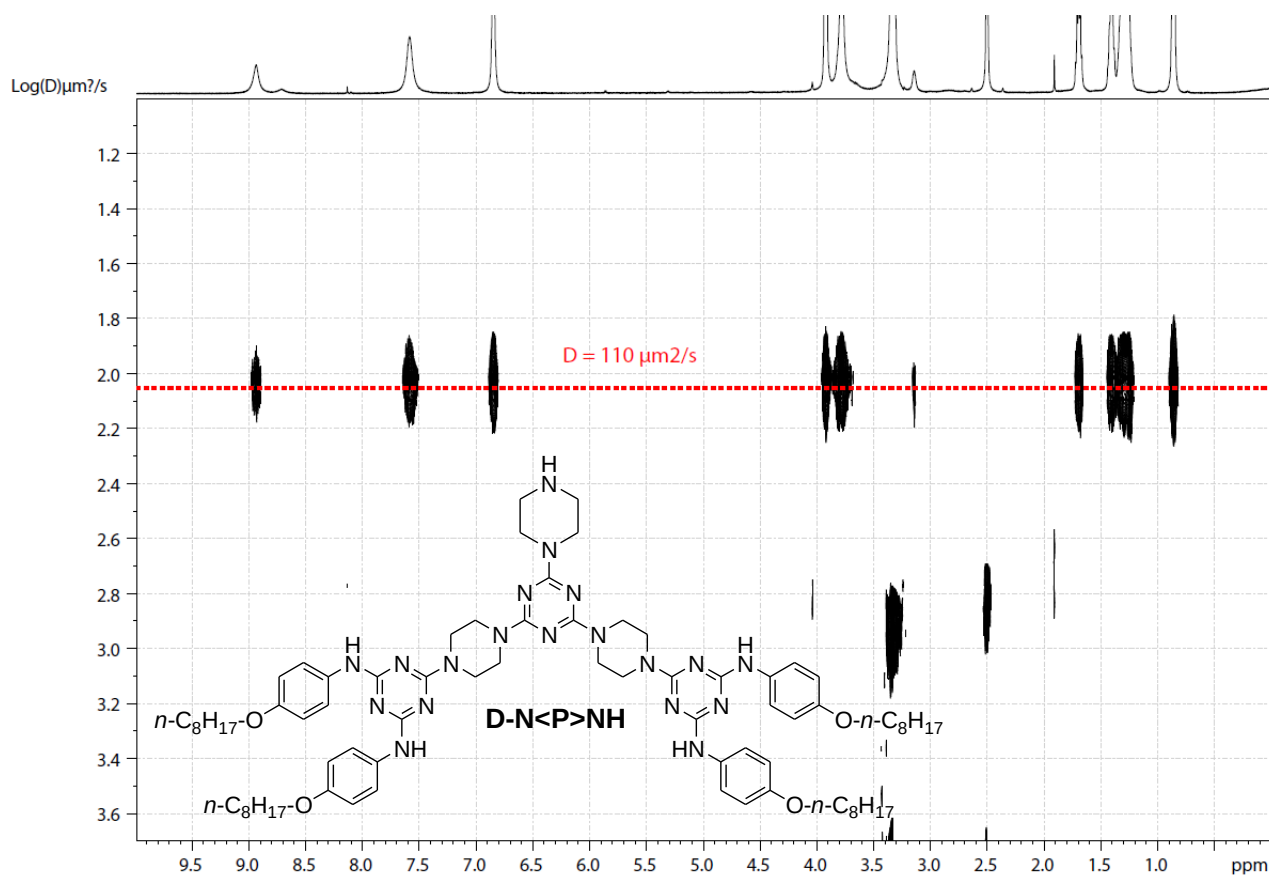


Figure S23: 2D- ^1H -DOSY NMR chart of compound **D-N<P>NH** (500 MHz, 5.0 mM in $\text{DMSO-}d_6$, 298 K).

MMC_46_IL_150703101740 #1 RT: 0.00 AV: 1 NL: 2.91E6
T: FTMS + p APCI corona Full ms [250.00-2000.00]

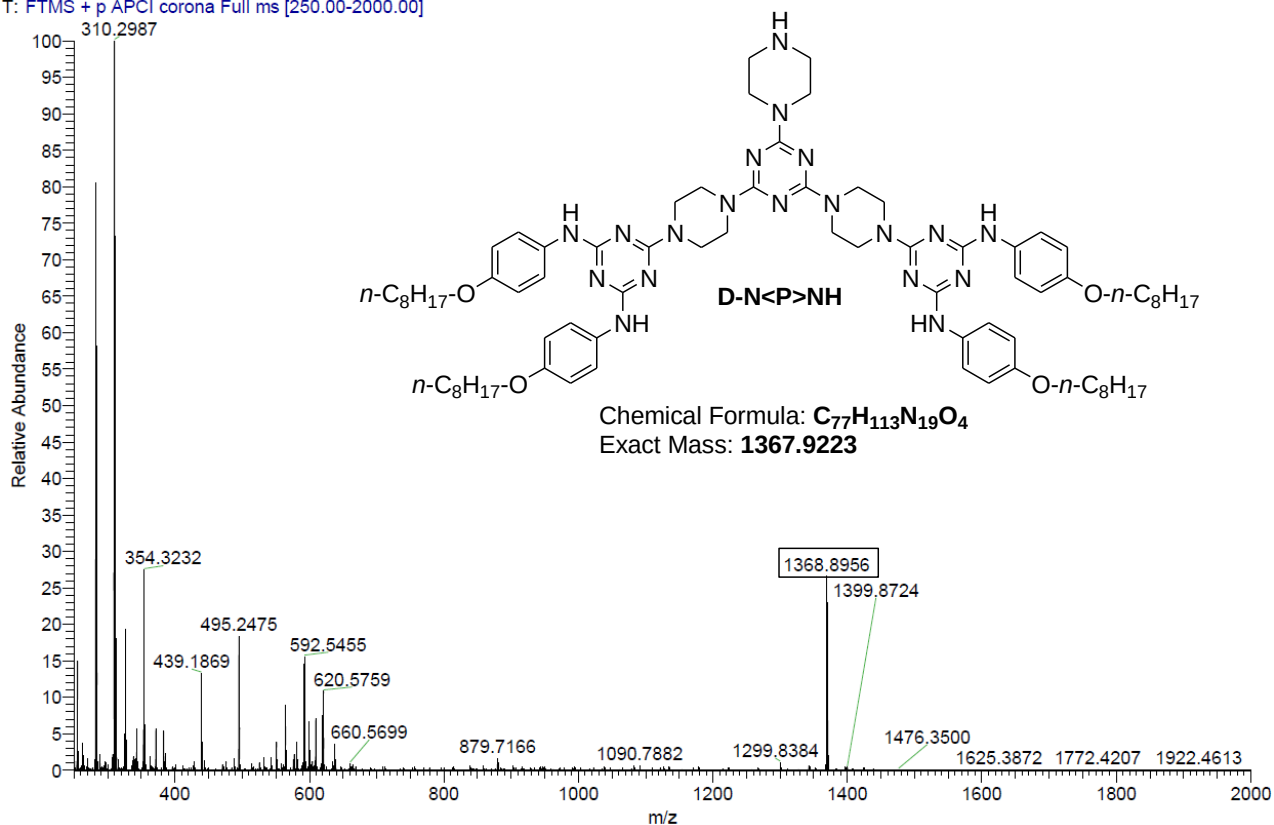


Figure S24: Mass spectrum of compound **D-N<P>NH** [HRMS (APCI+)].

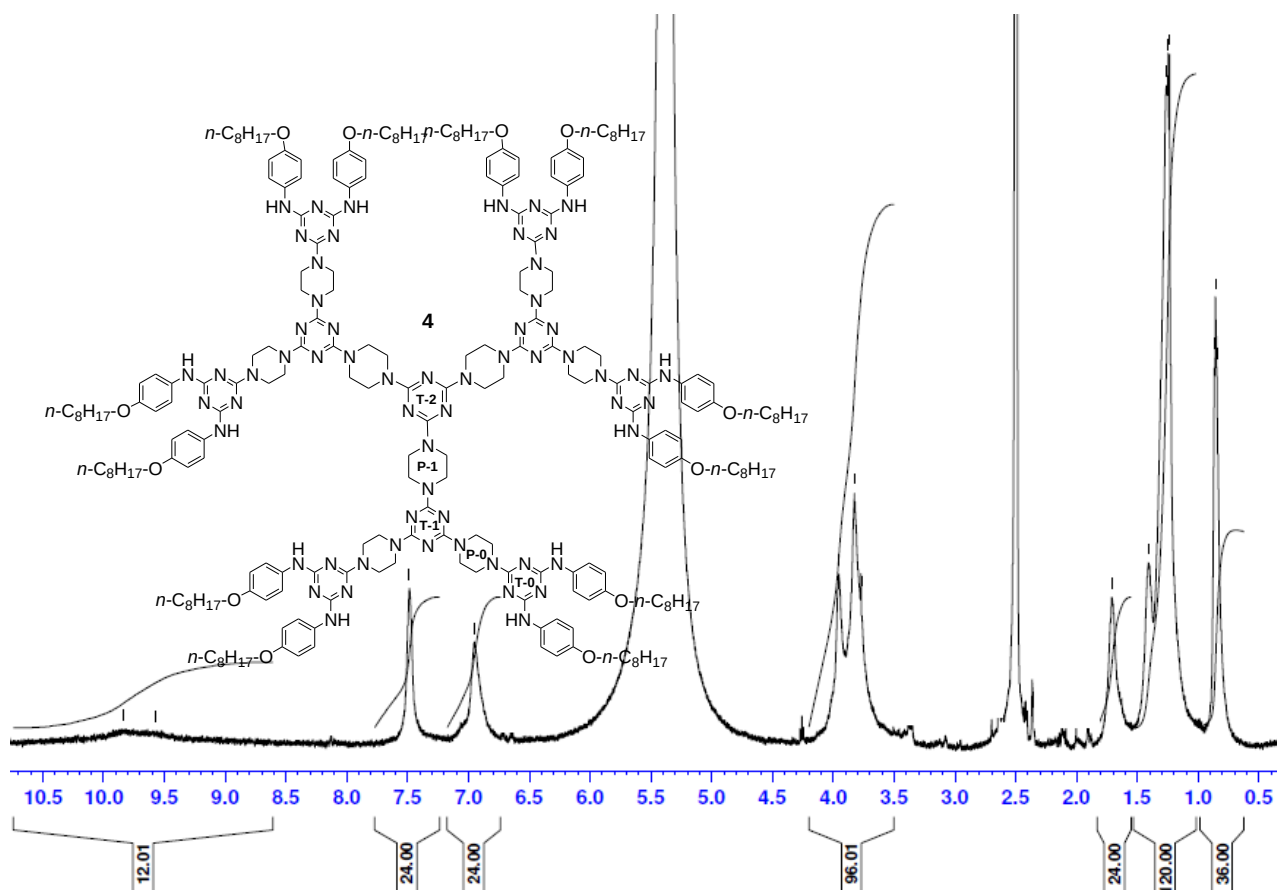


Figure S25: ^1H NMR spectrum of compound 4 (500 MHz, 2.5 mM in $\text{DMSO-}d_6$, 298 K).

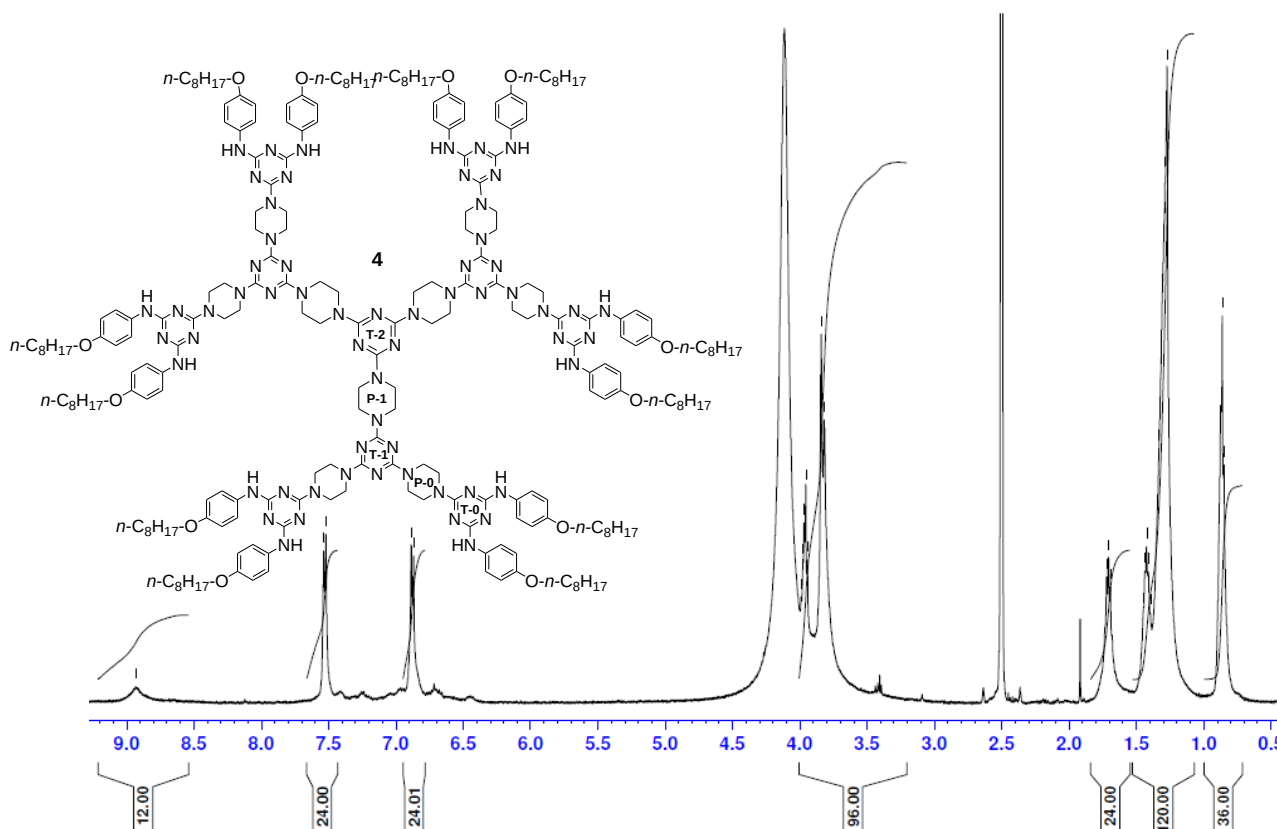


Figure S26: ^1H NMR spectrum of compound 4 (500 MHz, 2.5 mM in $\text{DMSO-}d_6$, 363 K).

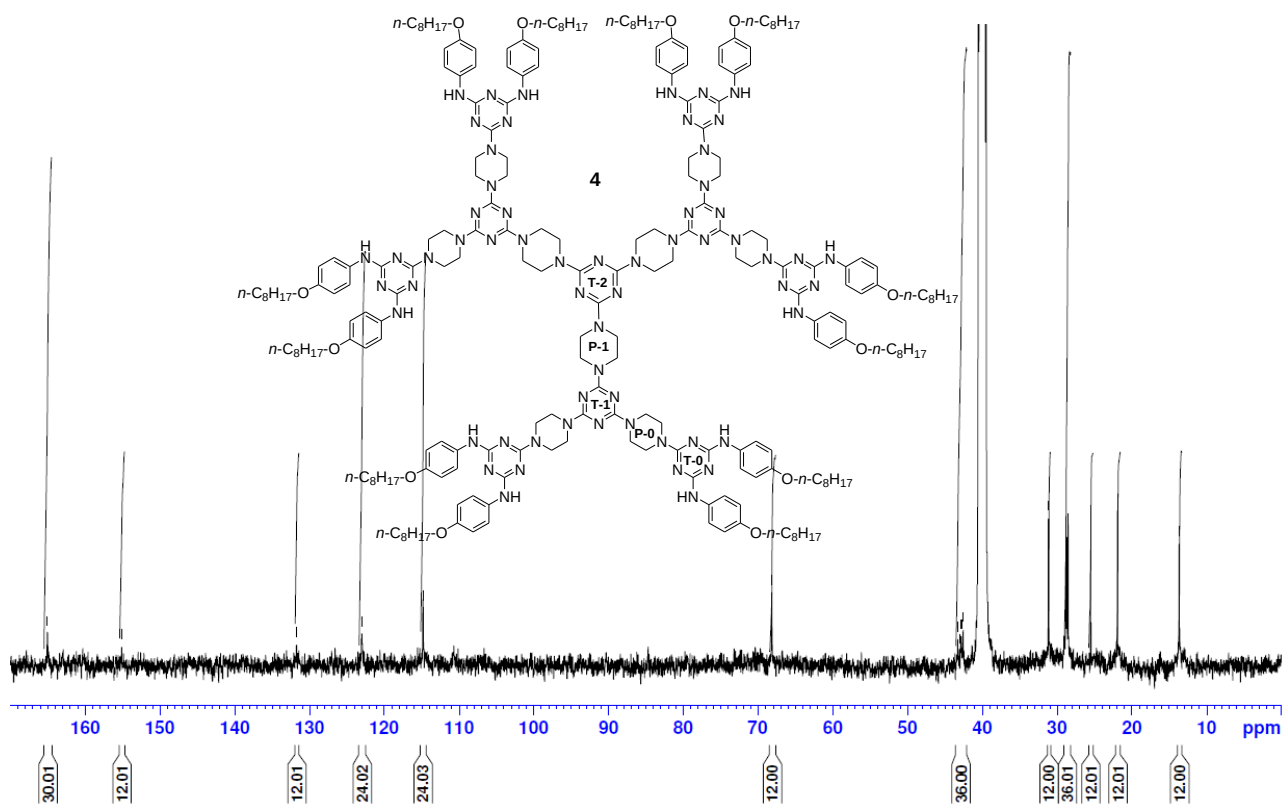


Figure S27: ^{13}C NMR of compound **4** (125 MHz, 2.5 mM in $\text{DMSO-}d_6$, 363 K).

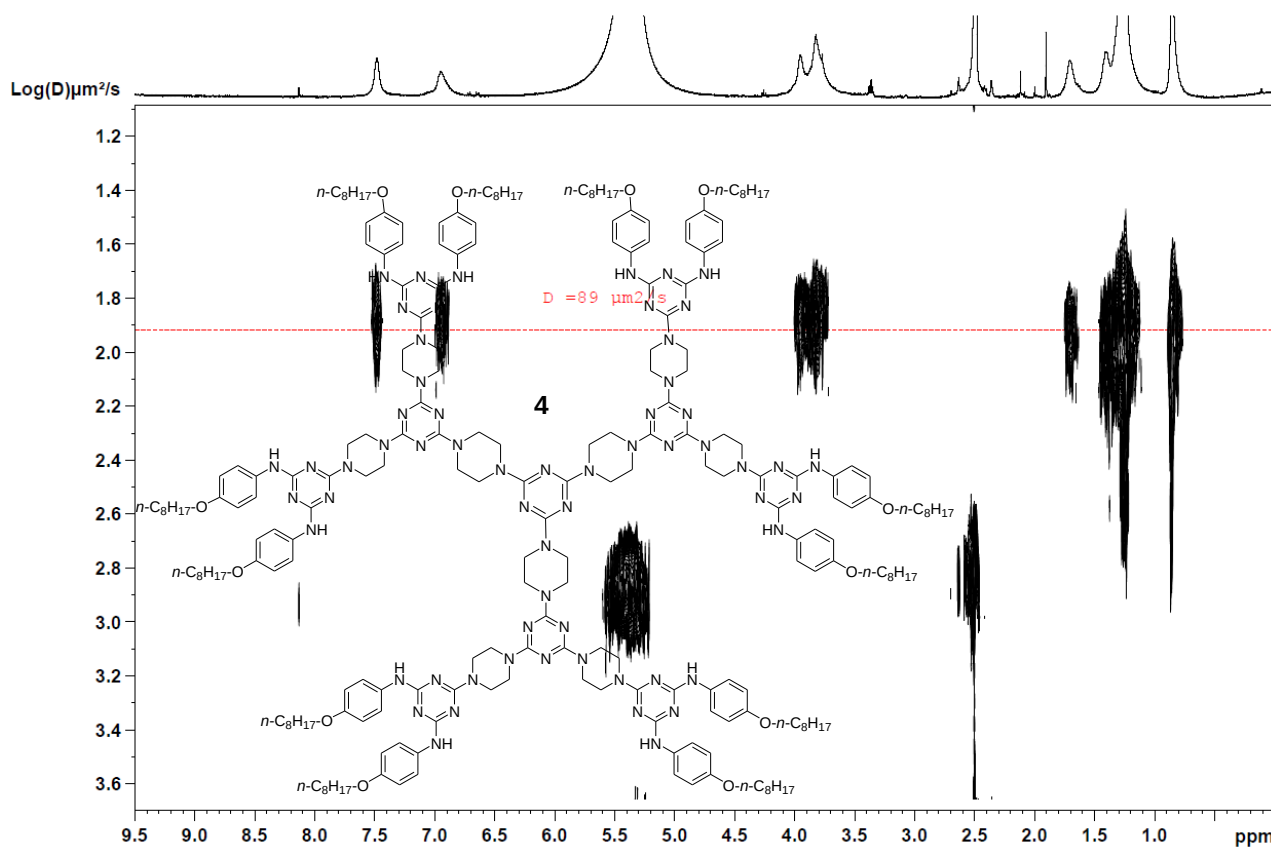


Figure S28: 2D- ^1H -DOSY NMR chart of compound **4** (500 MHz, 2.5 mM in $\text{DMSO-}d_6$, 298 K).

MMC-48-II-purificat_BUN_160419184004 #1 RT: 0.02 AV: 1 NL: 9.52E6
T: FTMS + c ESI Full ms [200.00-4000.00]

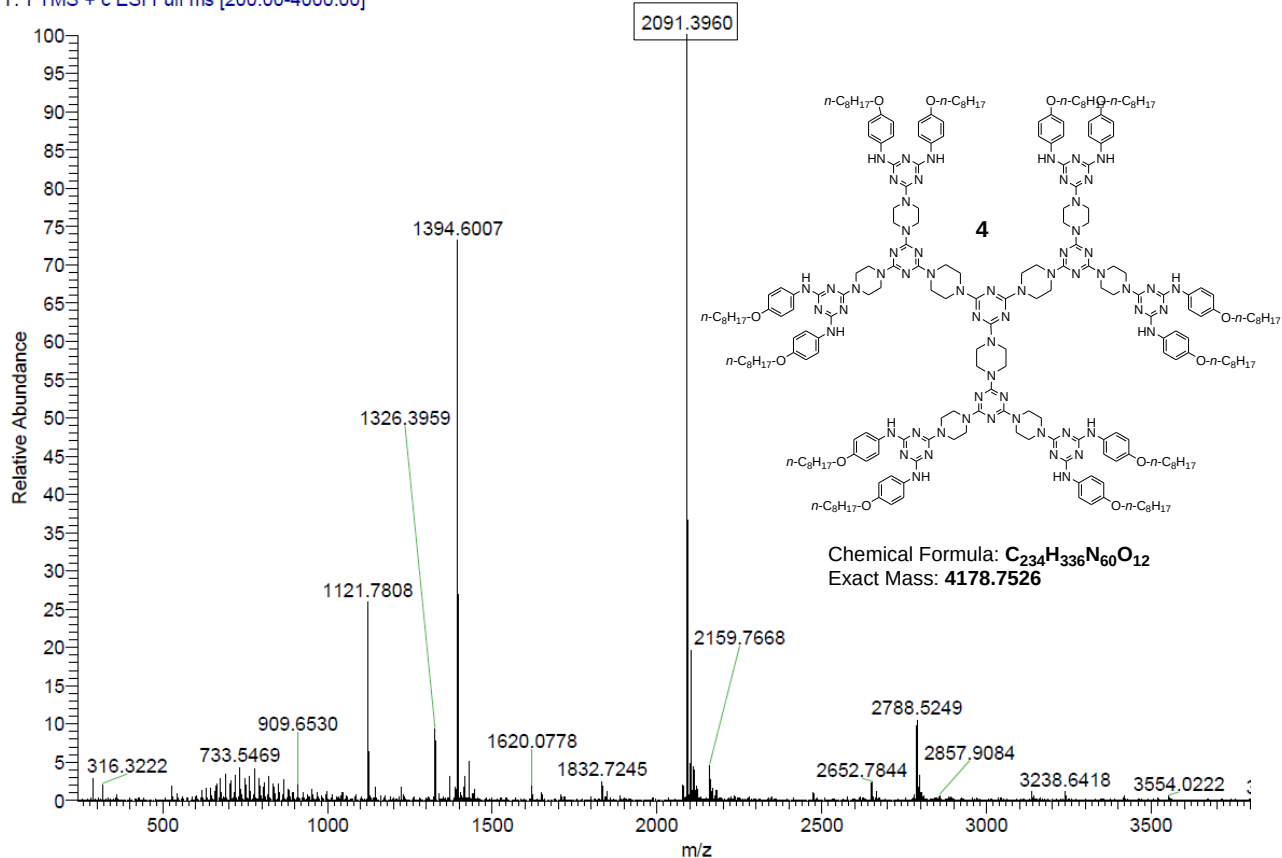


Figure S29: Mass spectrum of compound 4 [HRMS (ESI+) ACN+TFA].

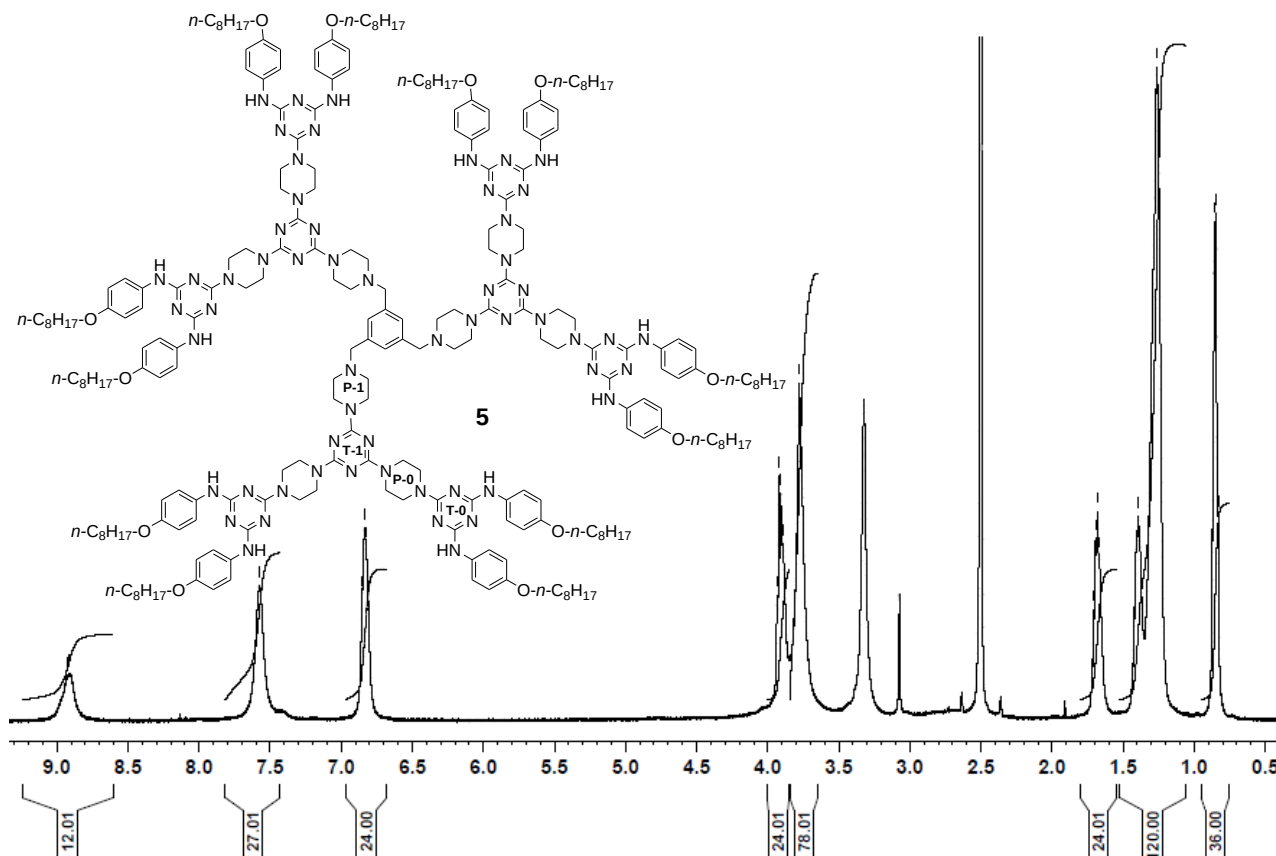


Figure S30: 1H NMR spectrum of compound 5 (500 MHz, 5.0 mM in $DMSO-d_6$, 298 K).

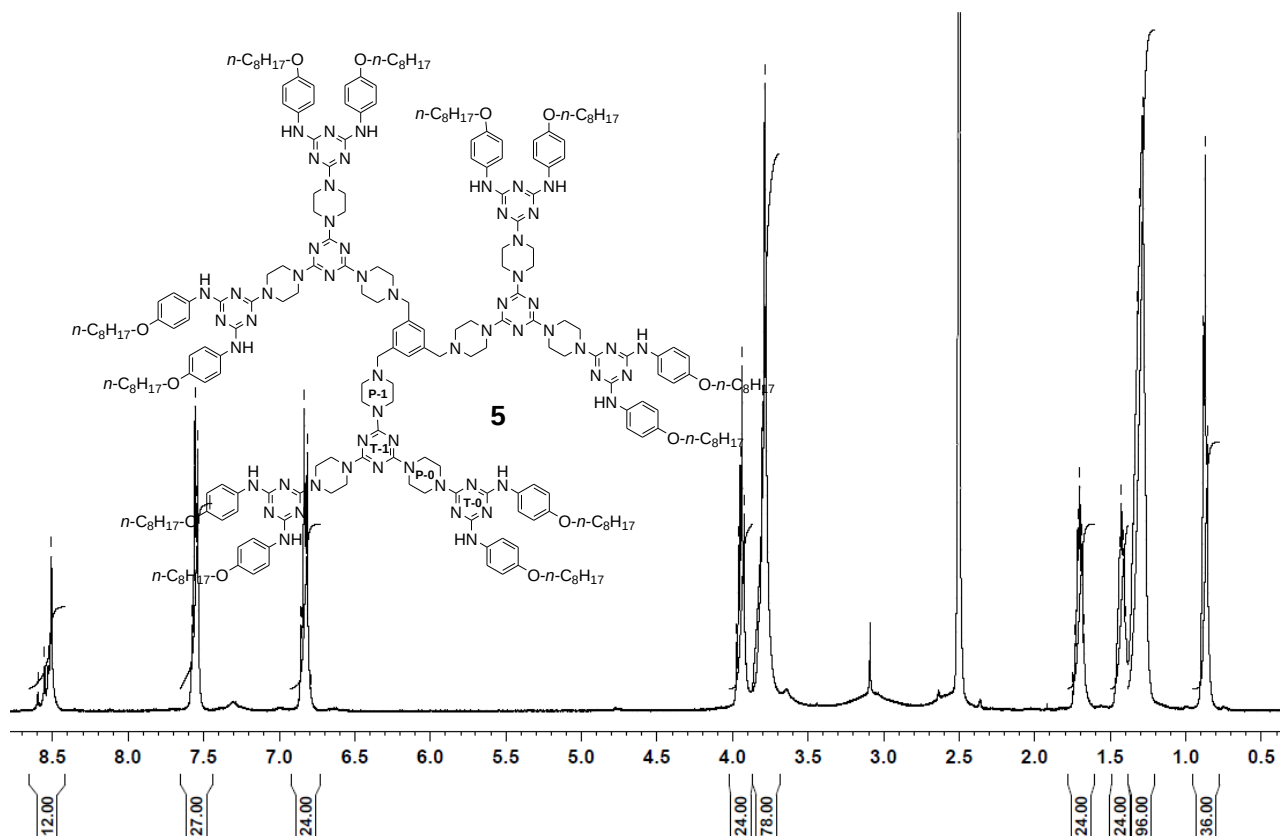


Figure S31: ¹H NMR spectrum of compound 5 (500 MHz, 5.0 mM in DMSO-*d*₆, 363 K)

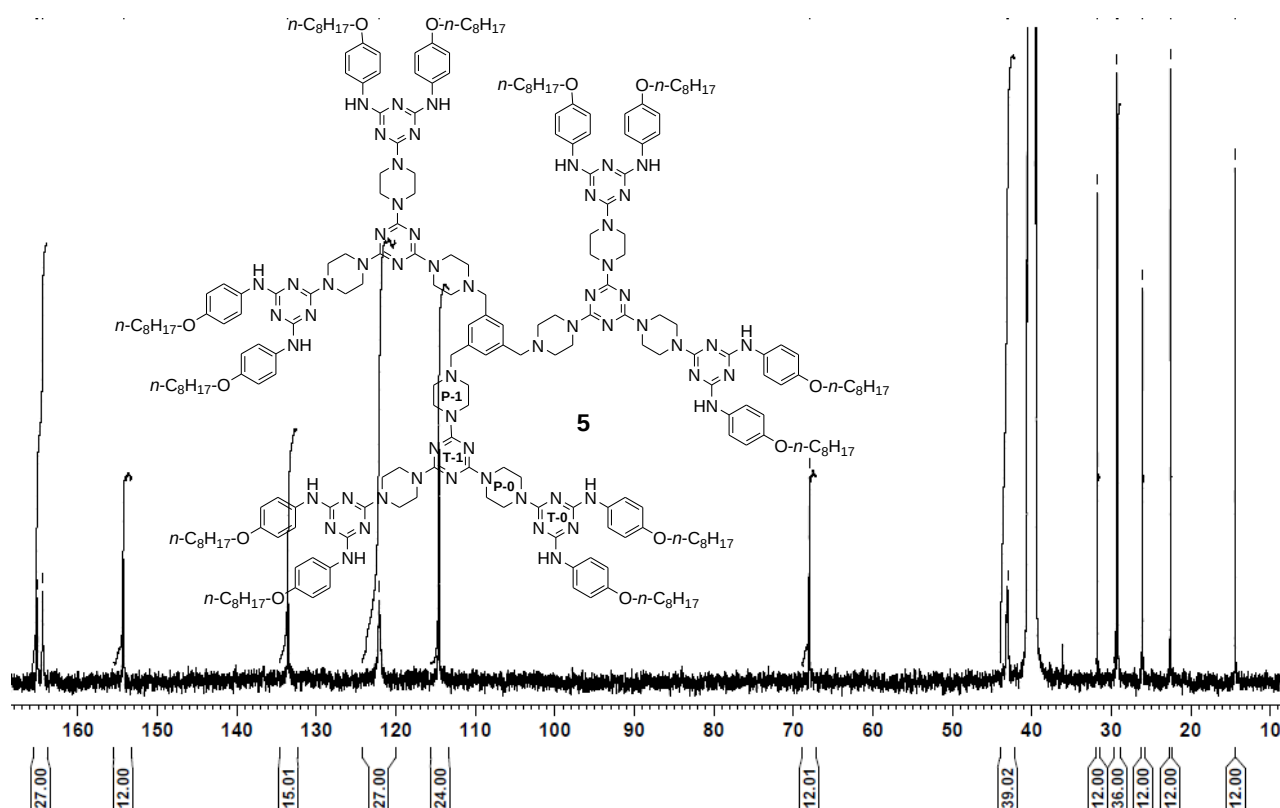


Figure S32: ¹³C NMR of compound 5 (125 MHz, 5.0 mM in DMSO-*d*₆, 298 K).

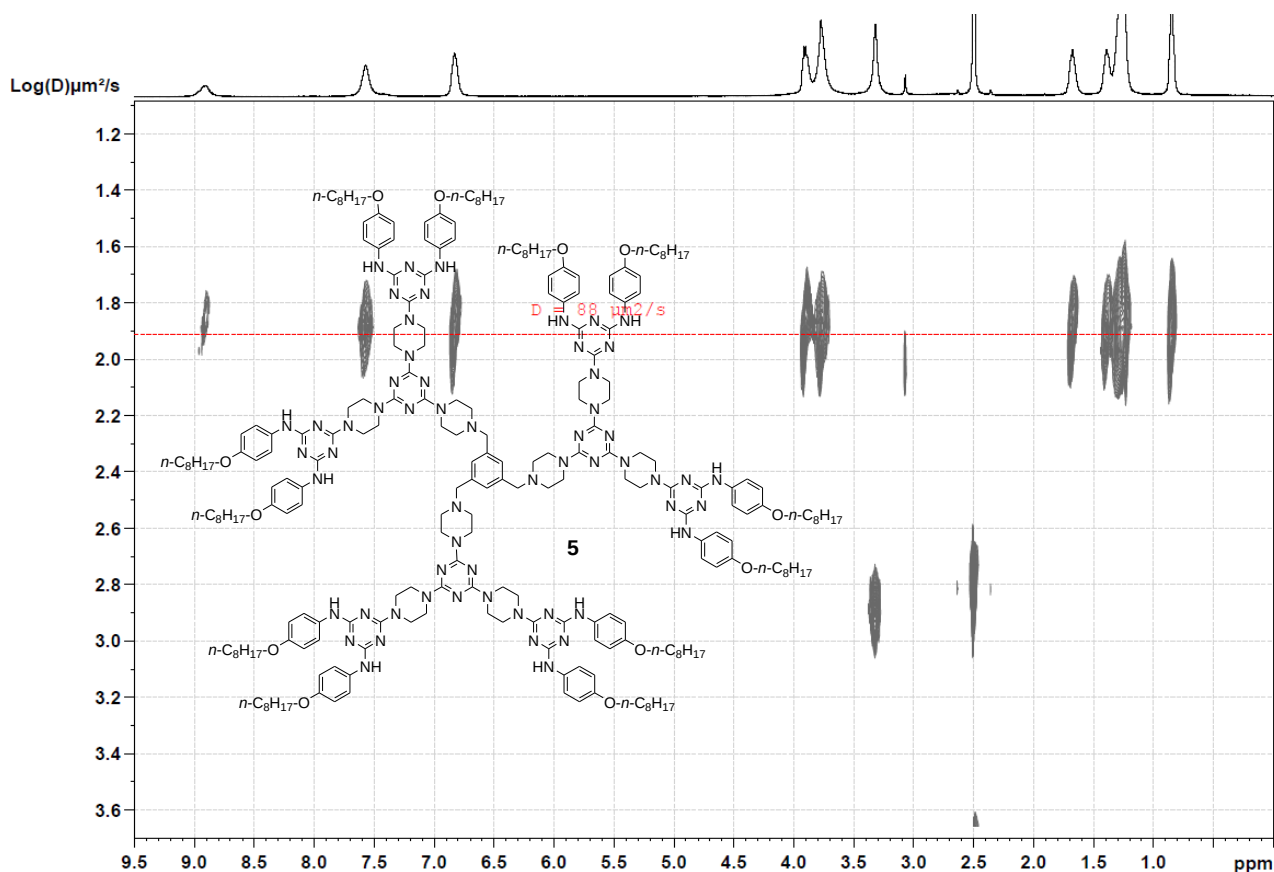


Figure S33: 2D-¹H-DOSY NMR chart of compound **5** (500 MHz, 5.0 mM in DMSO-*d*₆, 298 K).

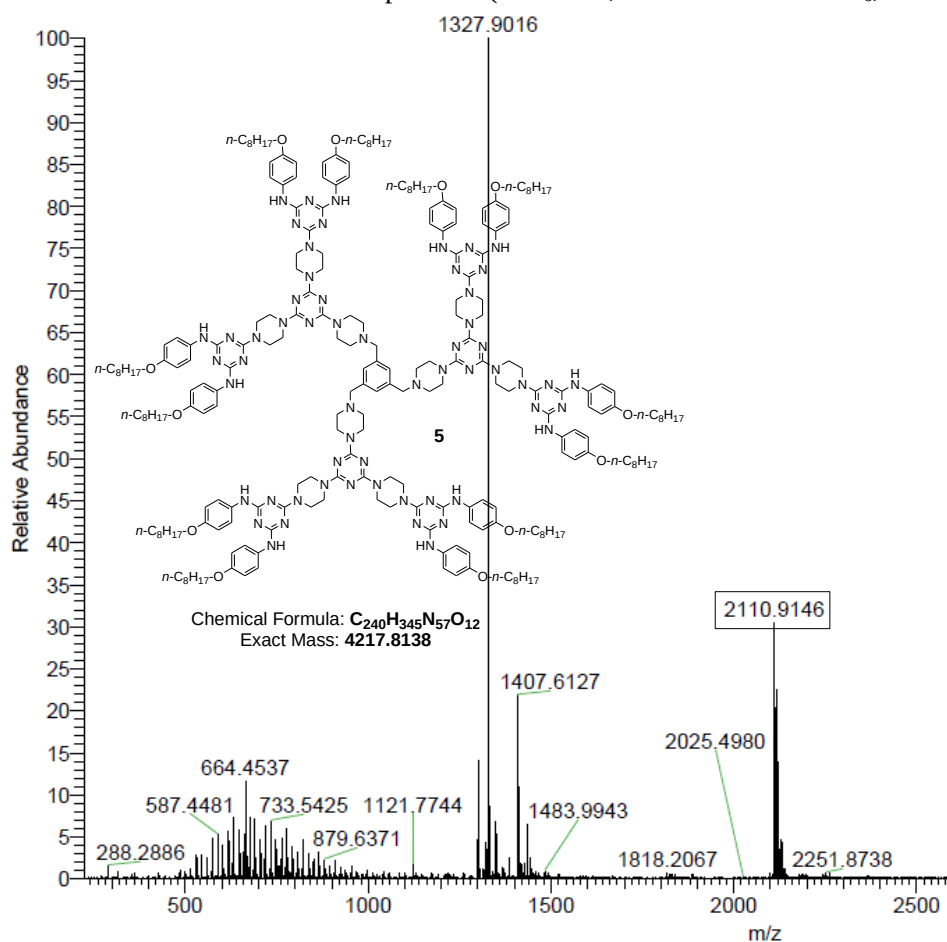


Figure S34: Mass spectrum of compound **5** [HRMS (ESI⁺), ACN+TFA].

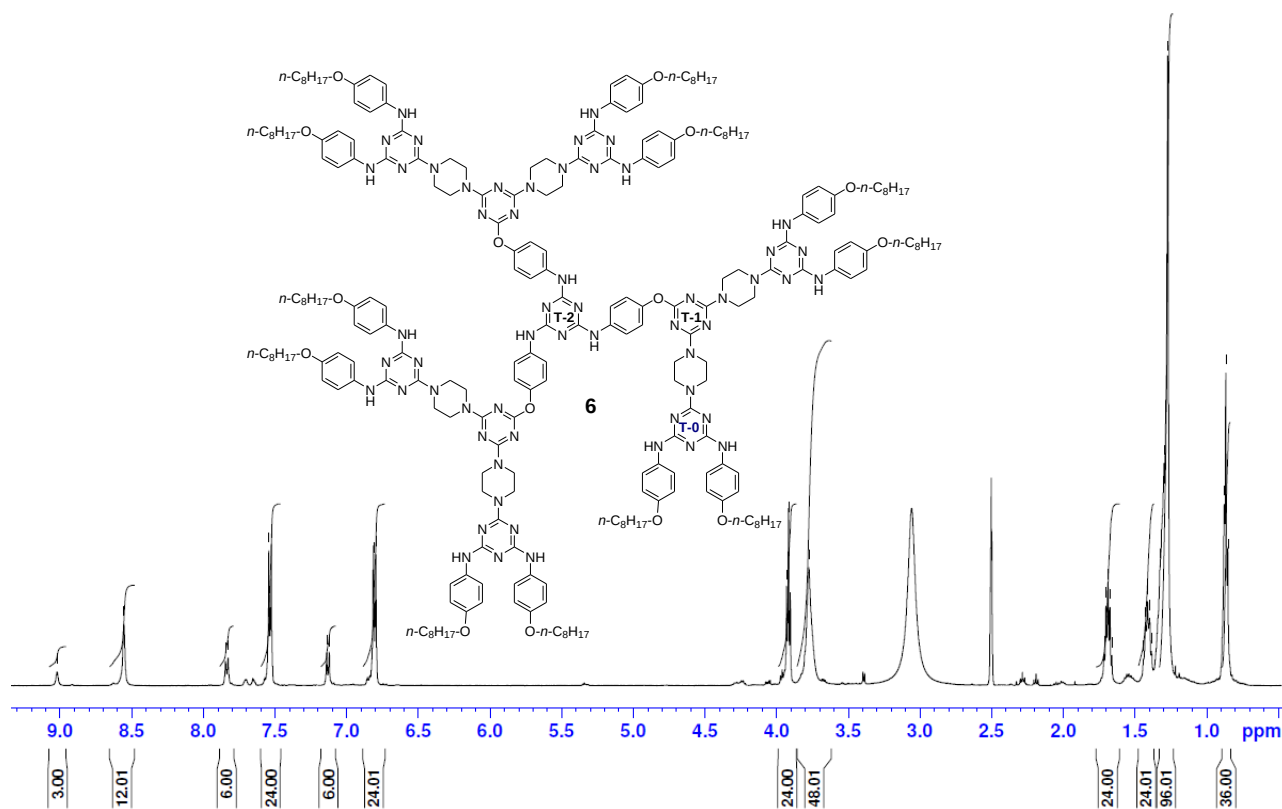


Figure S35: ^1H NMR spectrum of compound **6** (500 MHz, 2.5 mM in $\text{DMSO}-d_6$, 363 K).

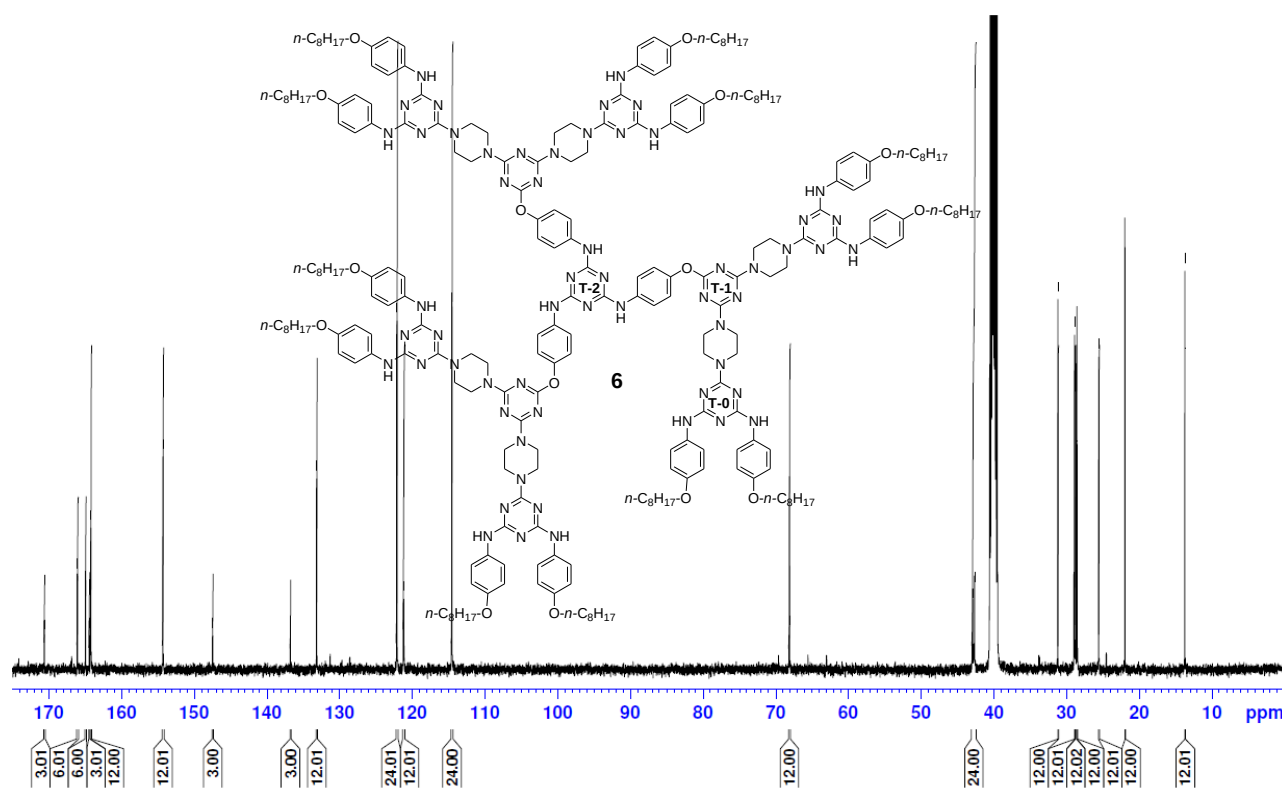


Figure S36: ^{13}C NMR of compound **6** (125 MHz, 2.5 mM in $\text{DMSO}-d_6$, 363 K).

MMC-49a-F-IV_160119170127 #1 RT: 0.02 AV: 1 NL: 8.29E6
T: FTMS + c ESI Full ms [350.00-4000.00]

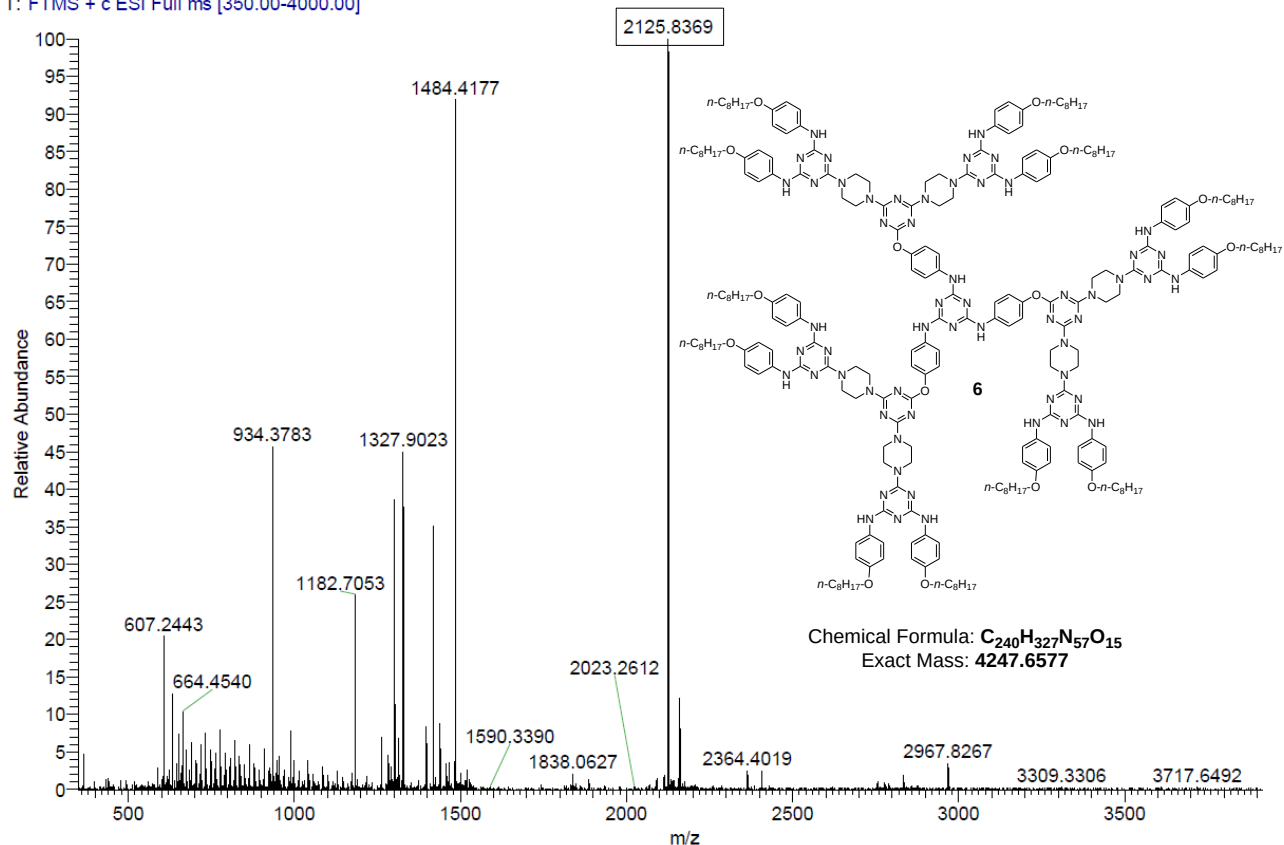


Figure S37: Mass spectrum of compound **6** [HRMS (ESI+), ACN+TFA].

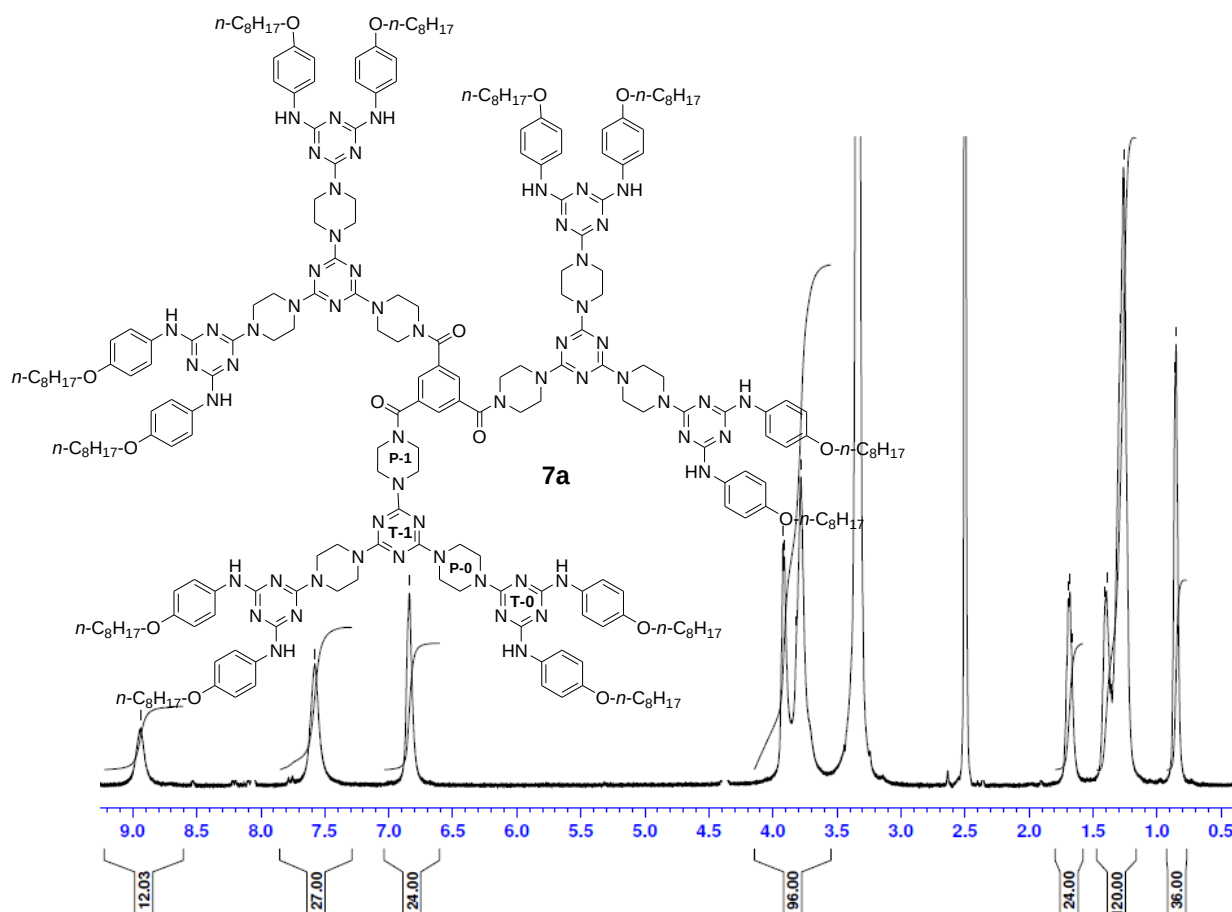


Figure S38: 1H NMR spectrum of compound **7a** (500 MHz, 2.5 mM in $DMSO-d_6$, 298 K).

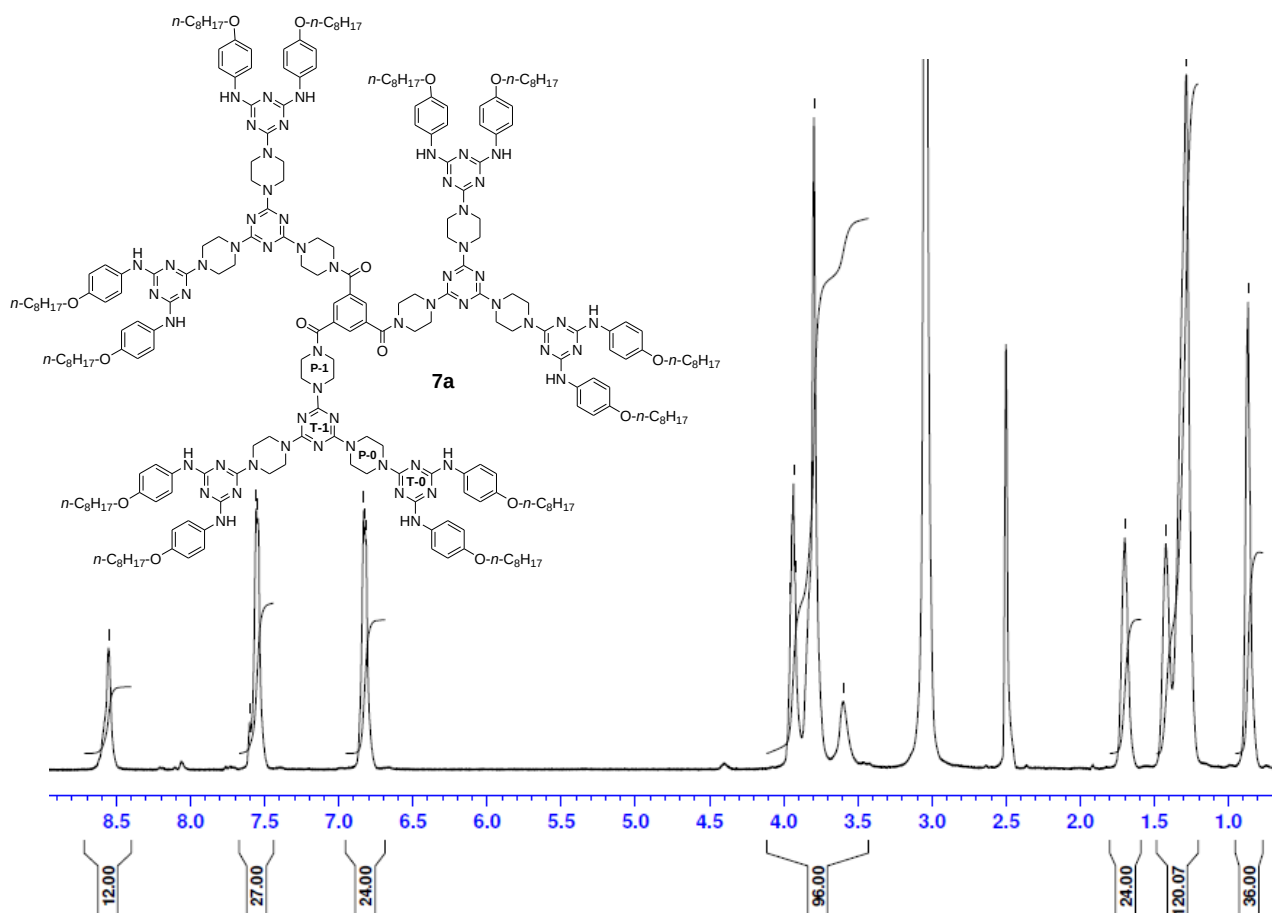


Figure S39: ^1H NMR spectrum of compound **7a** (500 MHz, 2.5 mM in $\text{DMSO}-d_6$, 363 K).

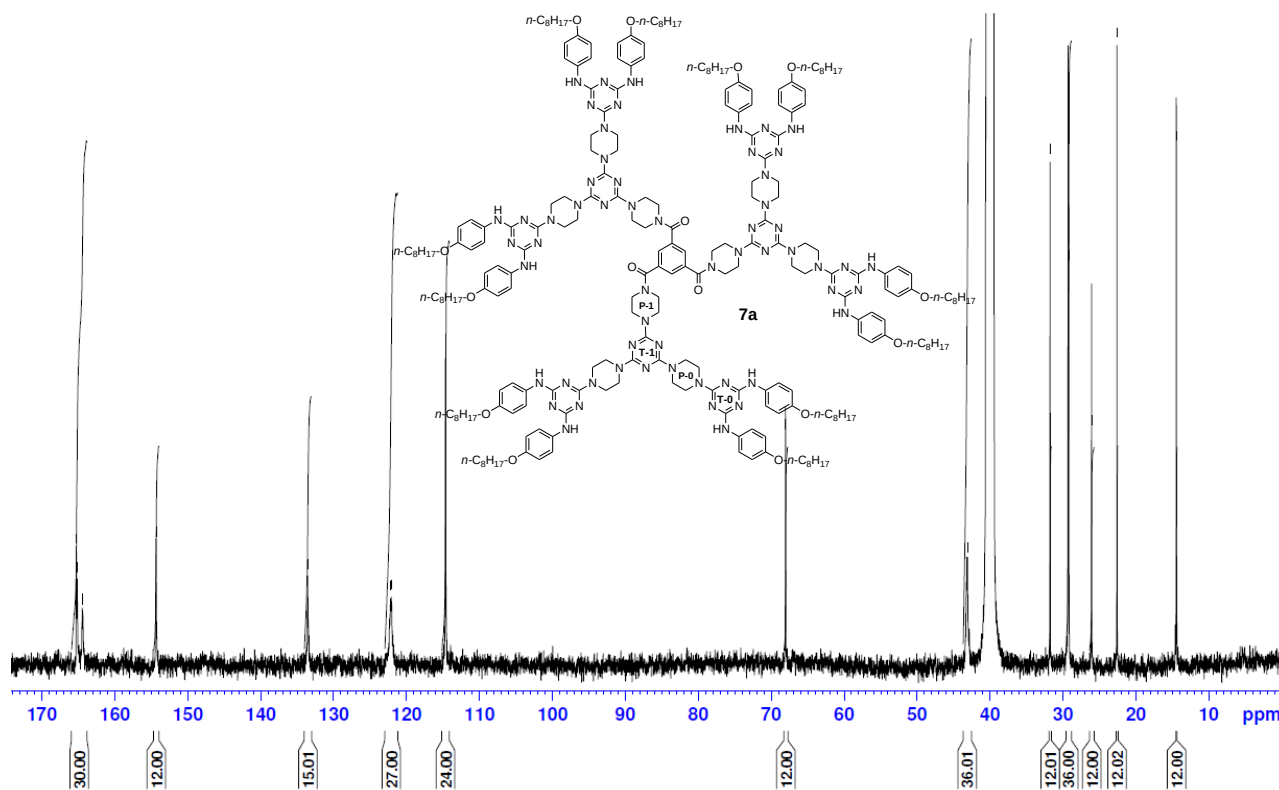


Figure S40: ^{13}C NMR spectrum of compound **7a** (125 MHz, 5.0 mM in $\text{DMSO}-d_6$, 298 K).

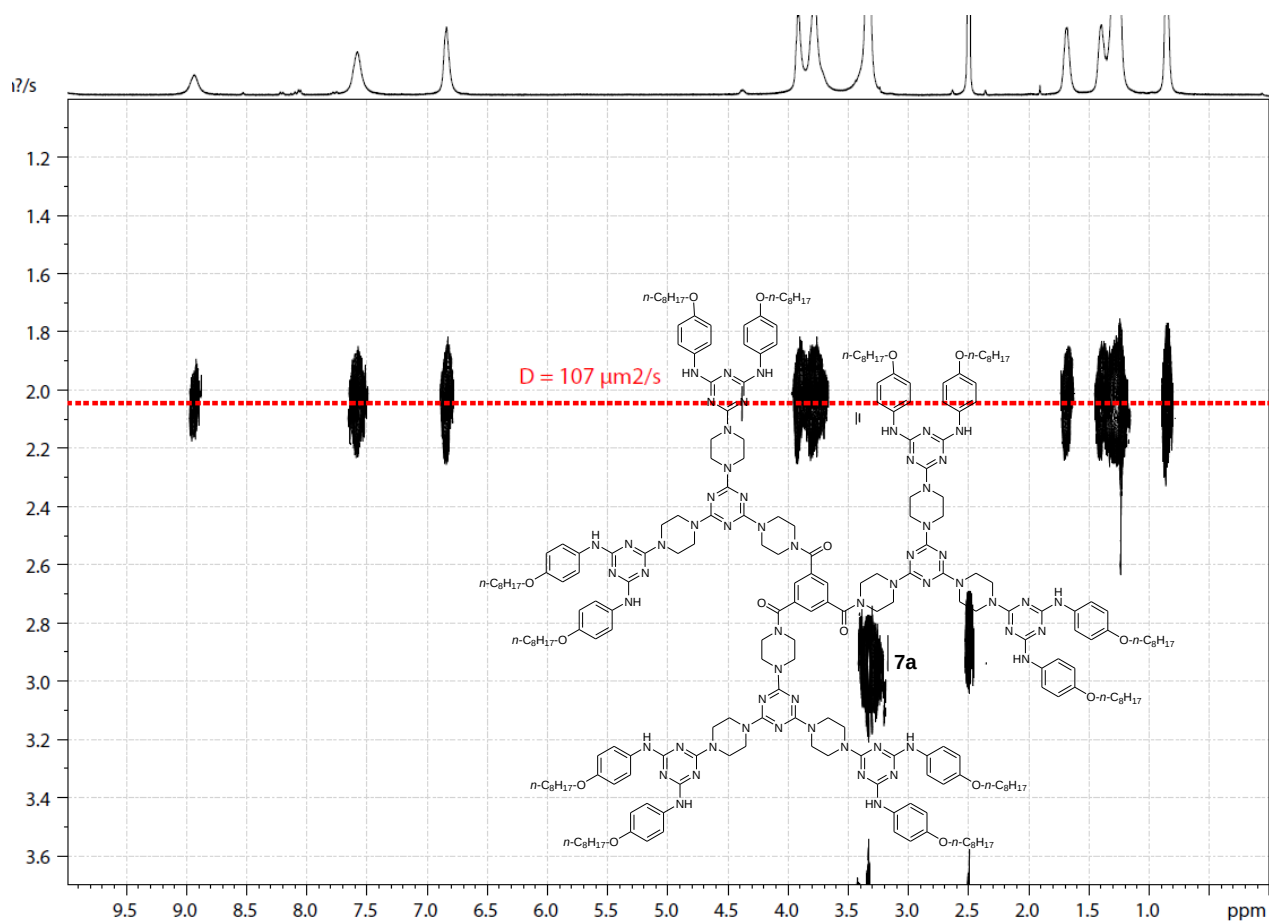


Figure S41: 2D-¹H-DOSY NMR chart of compound **7a** (500 MHz, 2.5 mM in DMSO-*d*₆, 298 K).

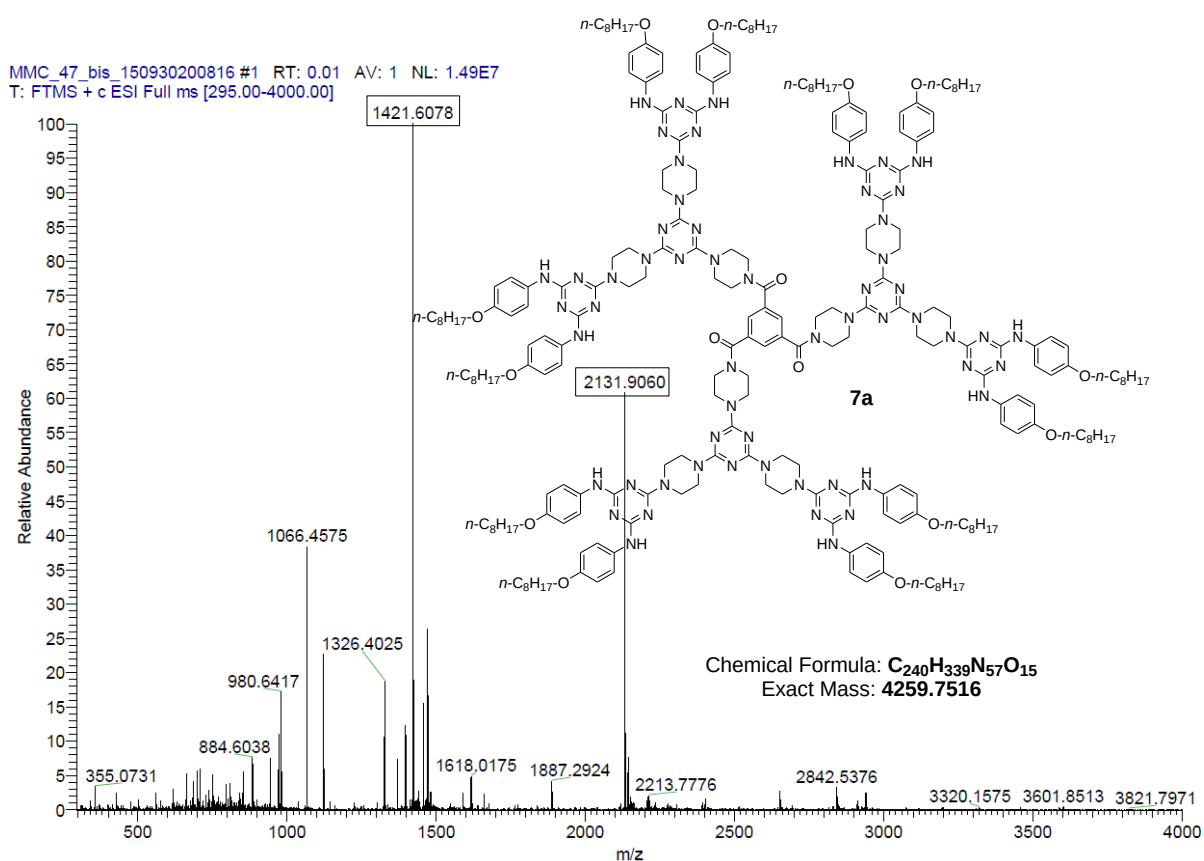


Figure S42: Mass spectrum of compound **7a** [HRMS (ESI+), ACN+TFA].

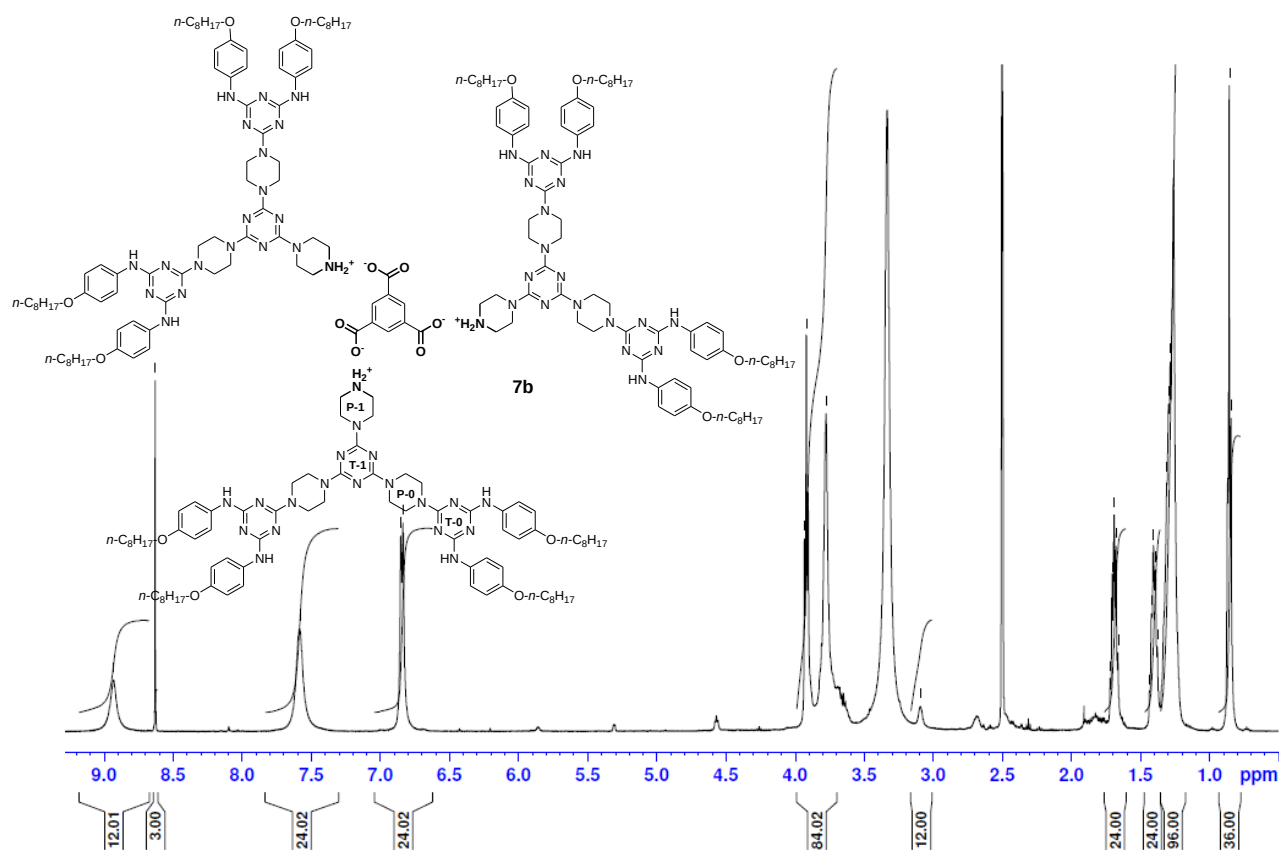


Figure S43: ¹H NMR spectrum of compound **7b** (500 MHz, 2.5 mM in DMSO-*d*₆, 298 K).

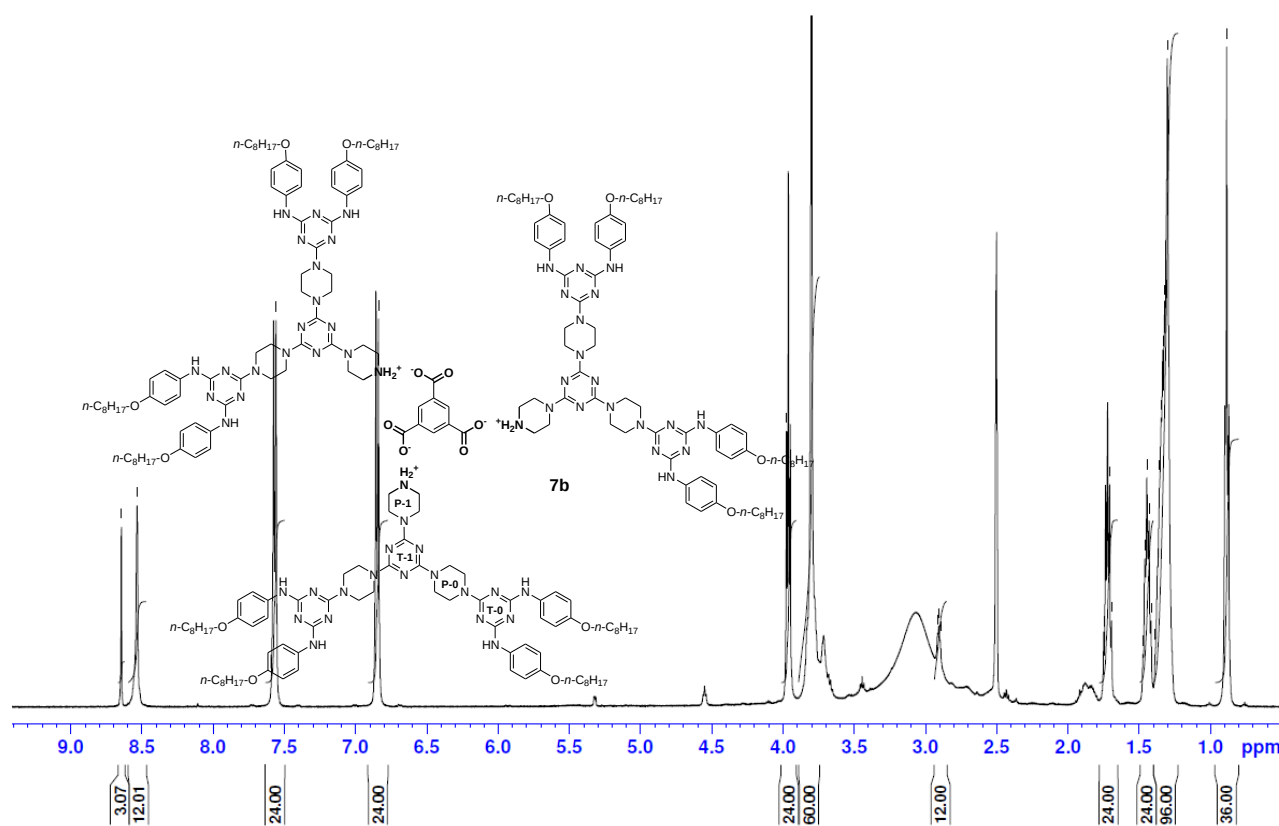


Figure S44: ¹H NMR spectrum of compound **7b** (500 MHz, 2.5 mM in DMSO-*d*₆, 363 K).

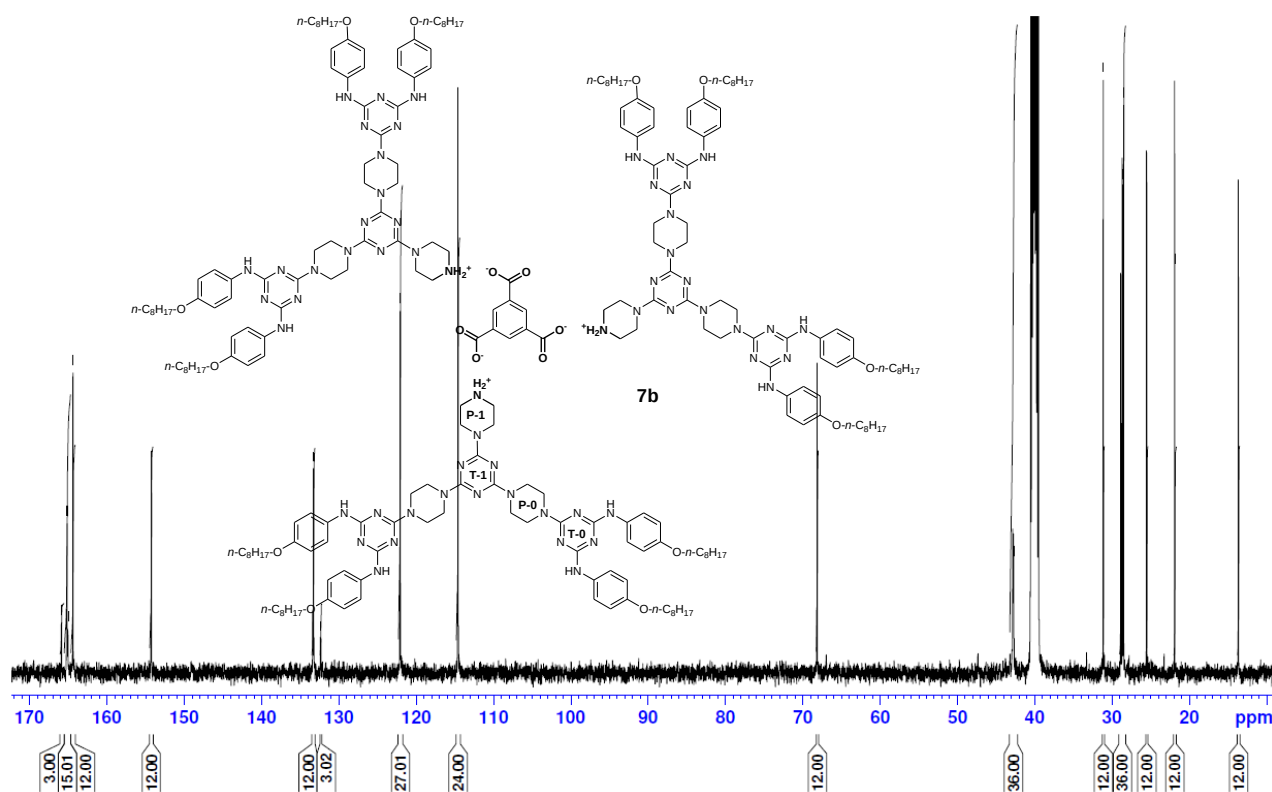


Figure S45: ¹³C QM NMR spectrum of compound **7b** (125 MHz, 2.5 mM in DMSO-*d*₆, 298 K).

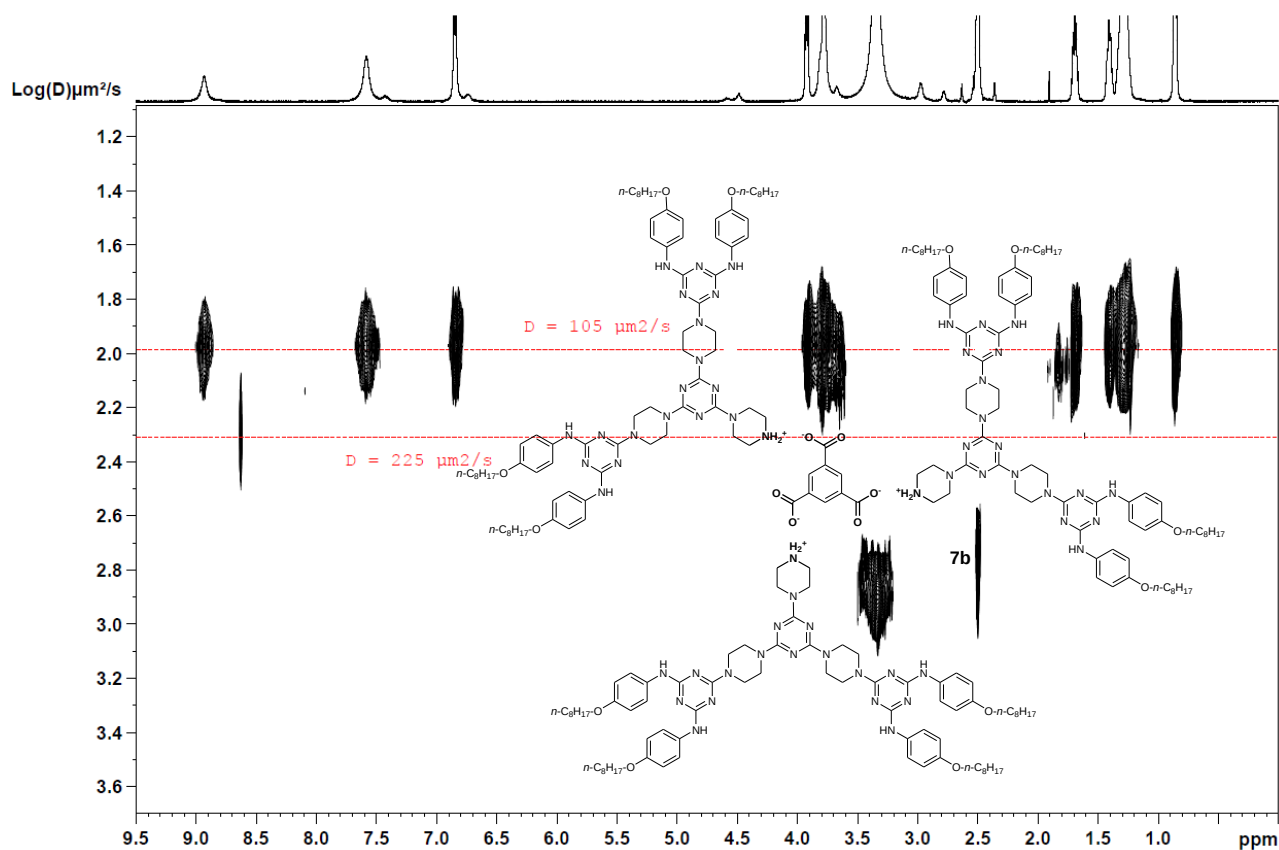


Figure S46: 2D-¹H-DOSY NMR chart of compound **7b** (500 MHz, 2.5 mM in DMSO-*d*₆, 298 K).

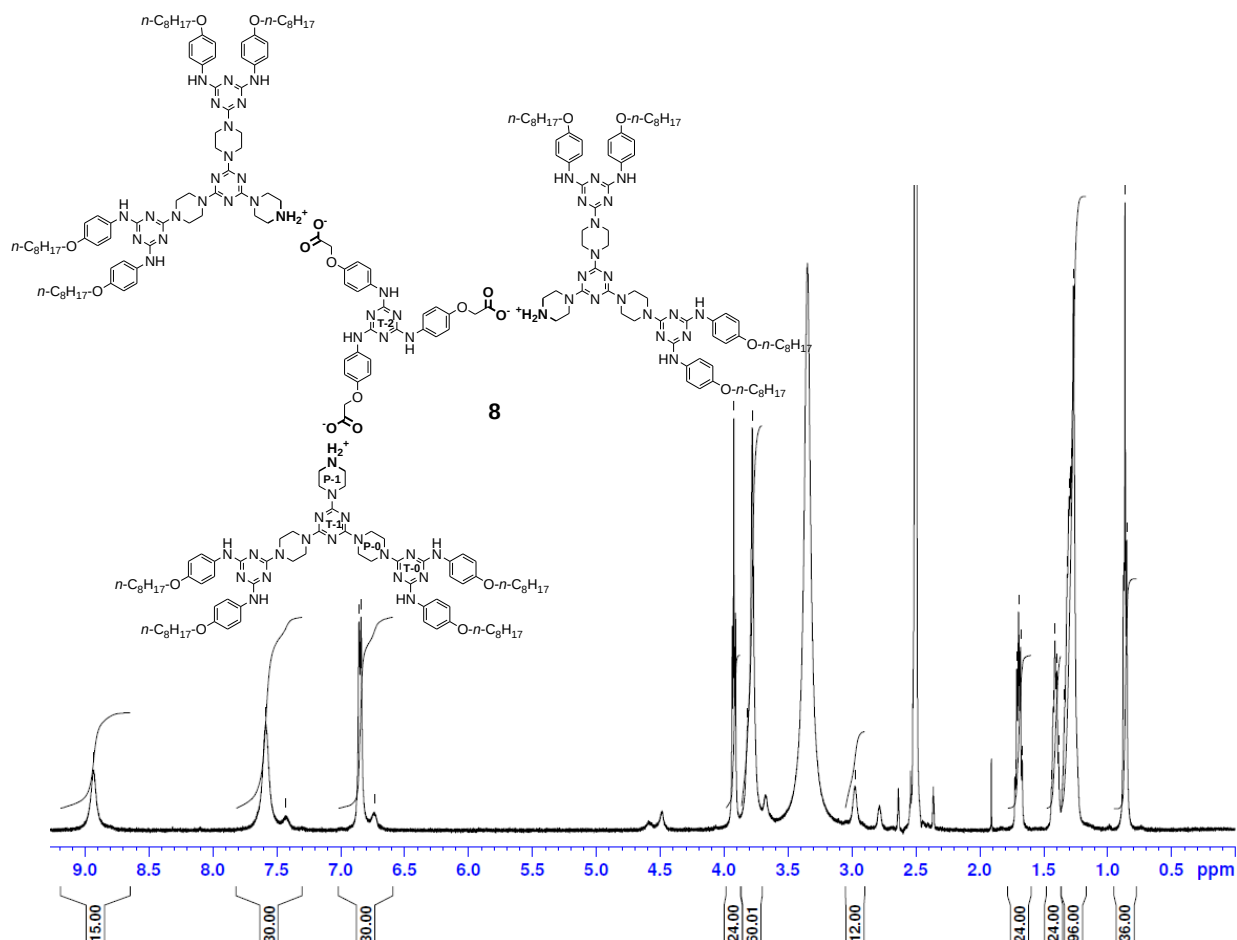


Figure S47: ¹H NMR spectrum of compound **8** (500 MHz, 5.0 mM in DMSO-*d*₆, 298 K).

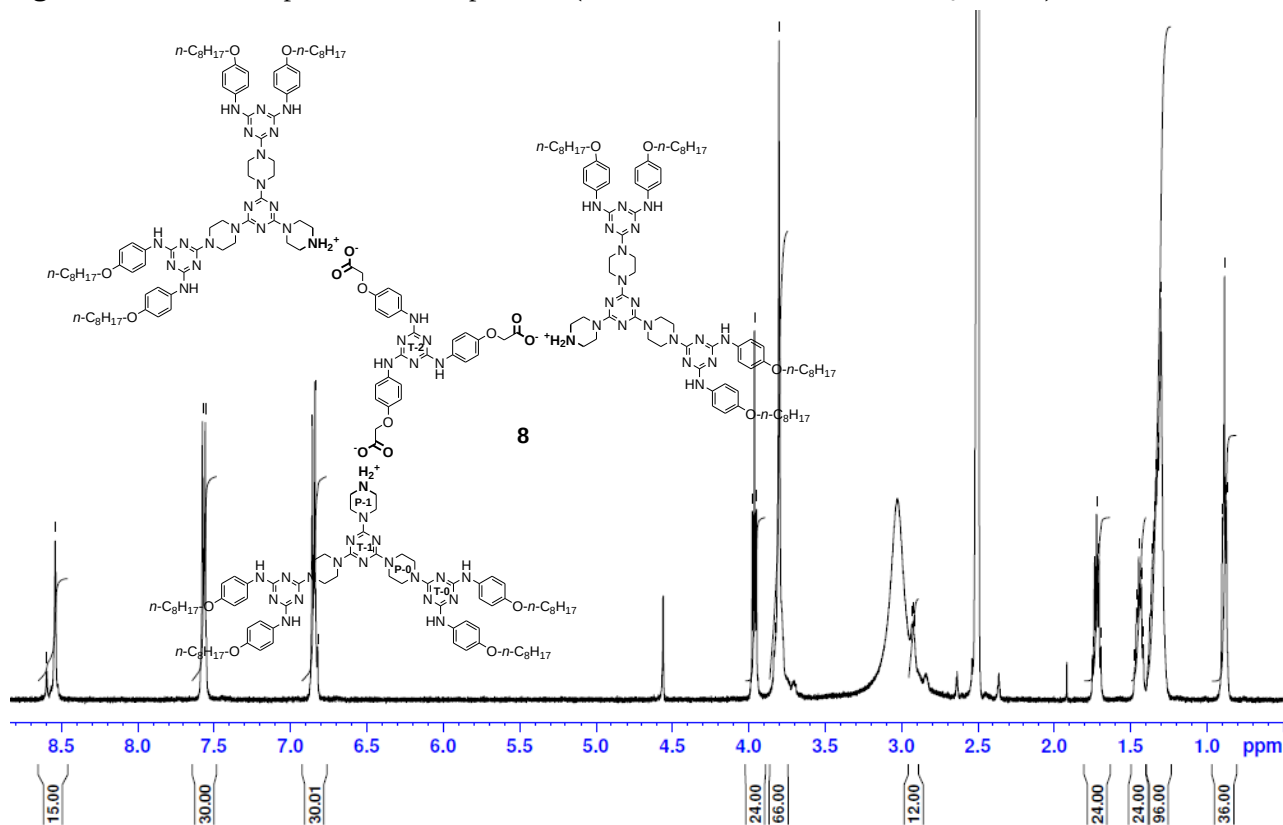


Figure S48: ¹H NMR spectrum of compound **8** (500 MHz, 5.0 mM in DMSO-*d*₆, 363 K).

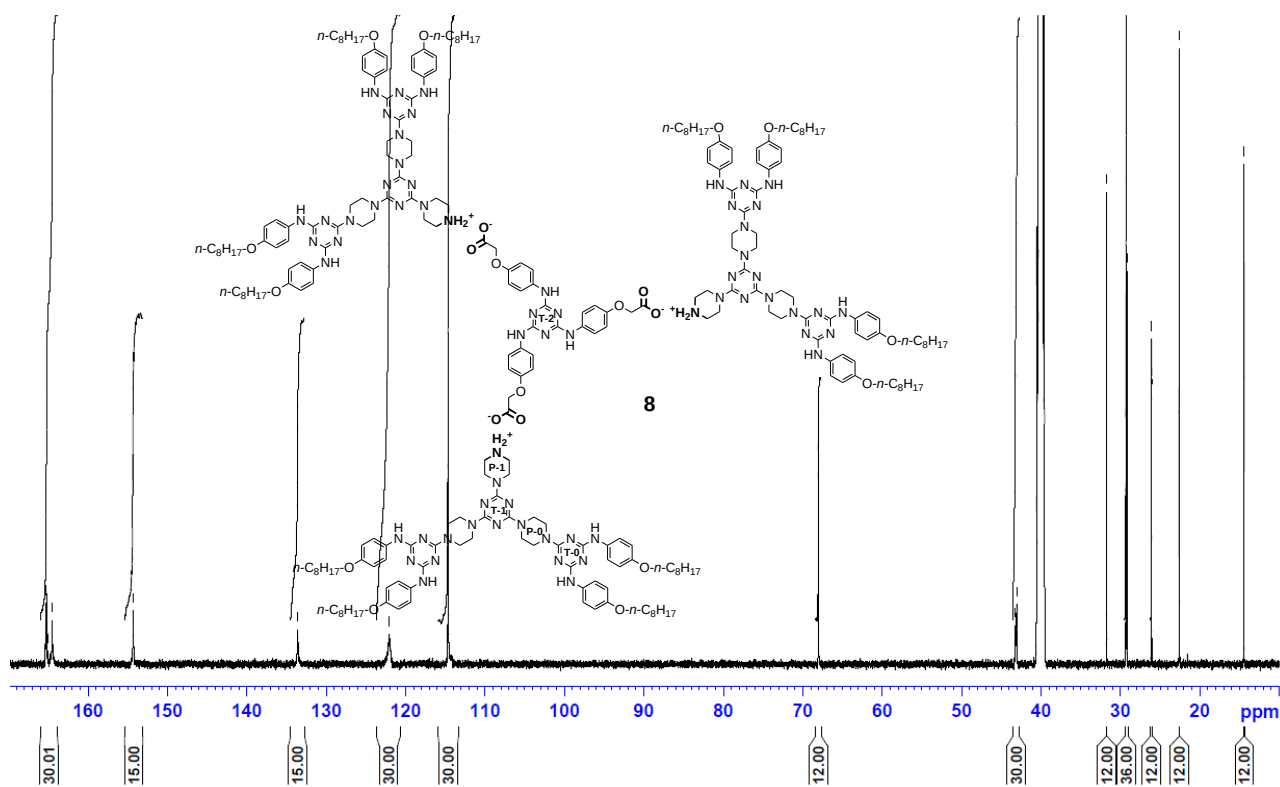


Figure S49: ^{13}C NMR spectrum of compound **8** (125 MHz, 5.0 mM in $\text{DMSO}-d_6$, 298 K).

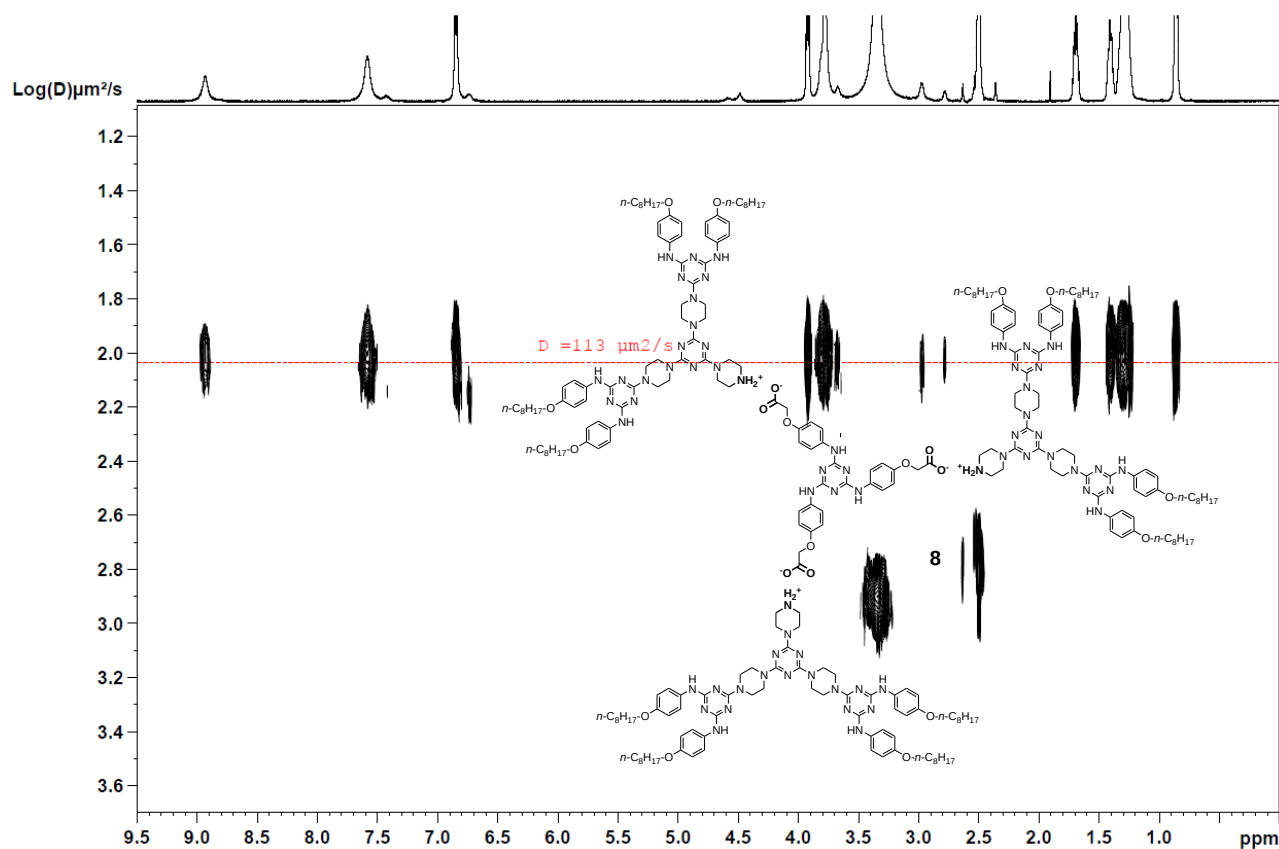
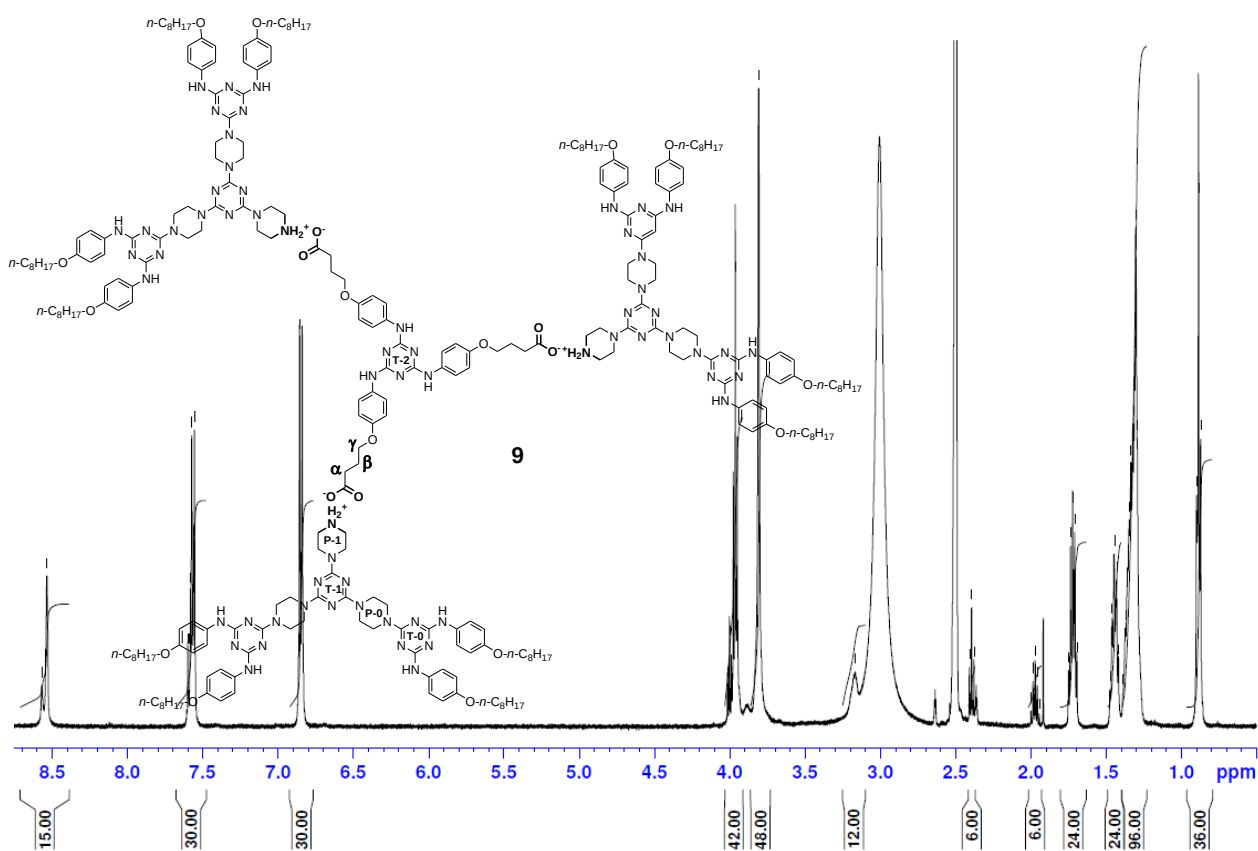
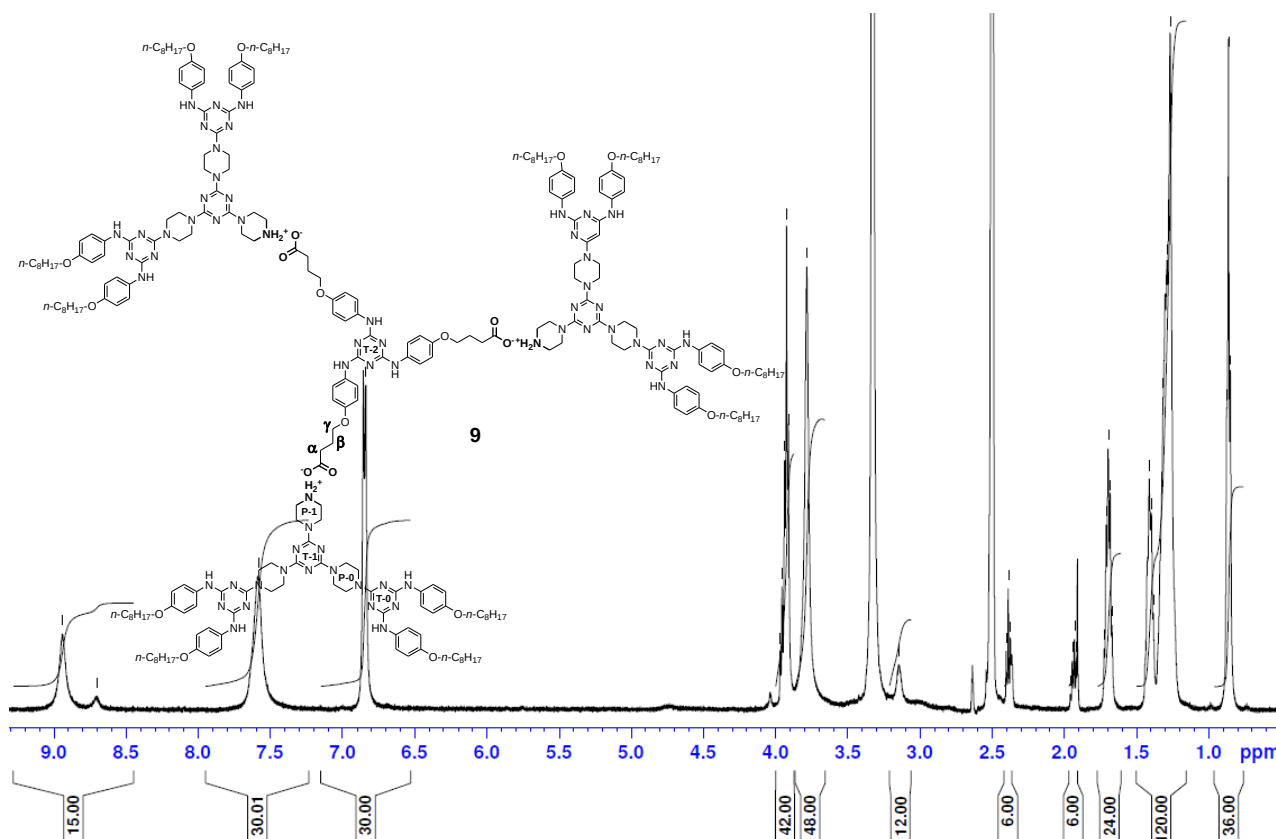


Figure S50: 2D- ^1H -DOSY NMR chart of compound **8** (500 MHz, 5.0 mM in $\text{DMSO}-d_6$, 298 K).



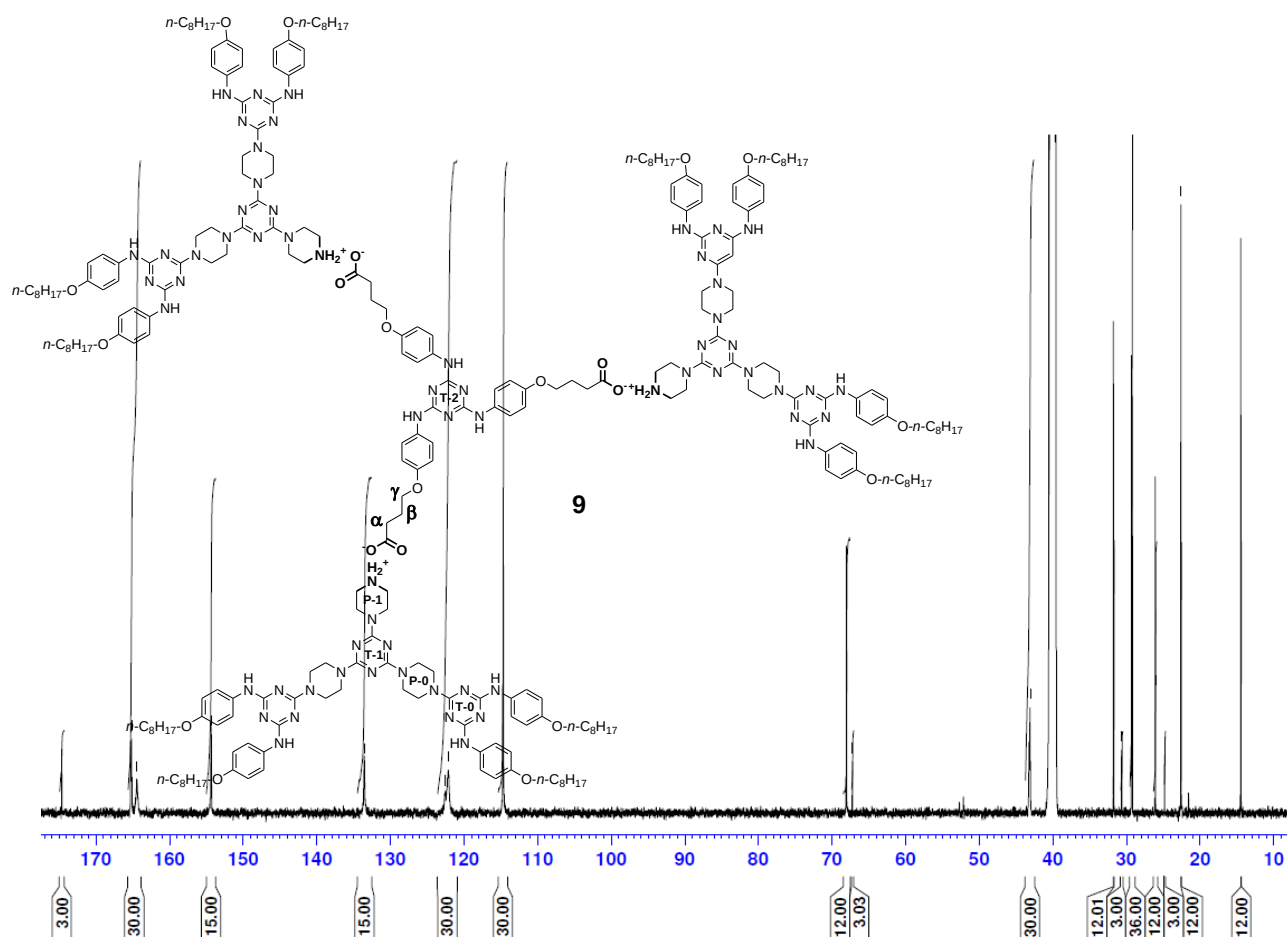


Figure S53: ^{13}C QM NMR spectrum of compound **9** (125 MHz, 5.0 mM in $\text{DMSO-}d_6$, 298 K).

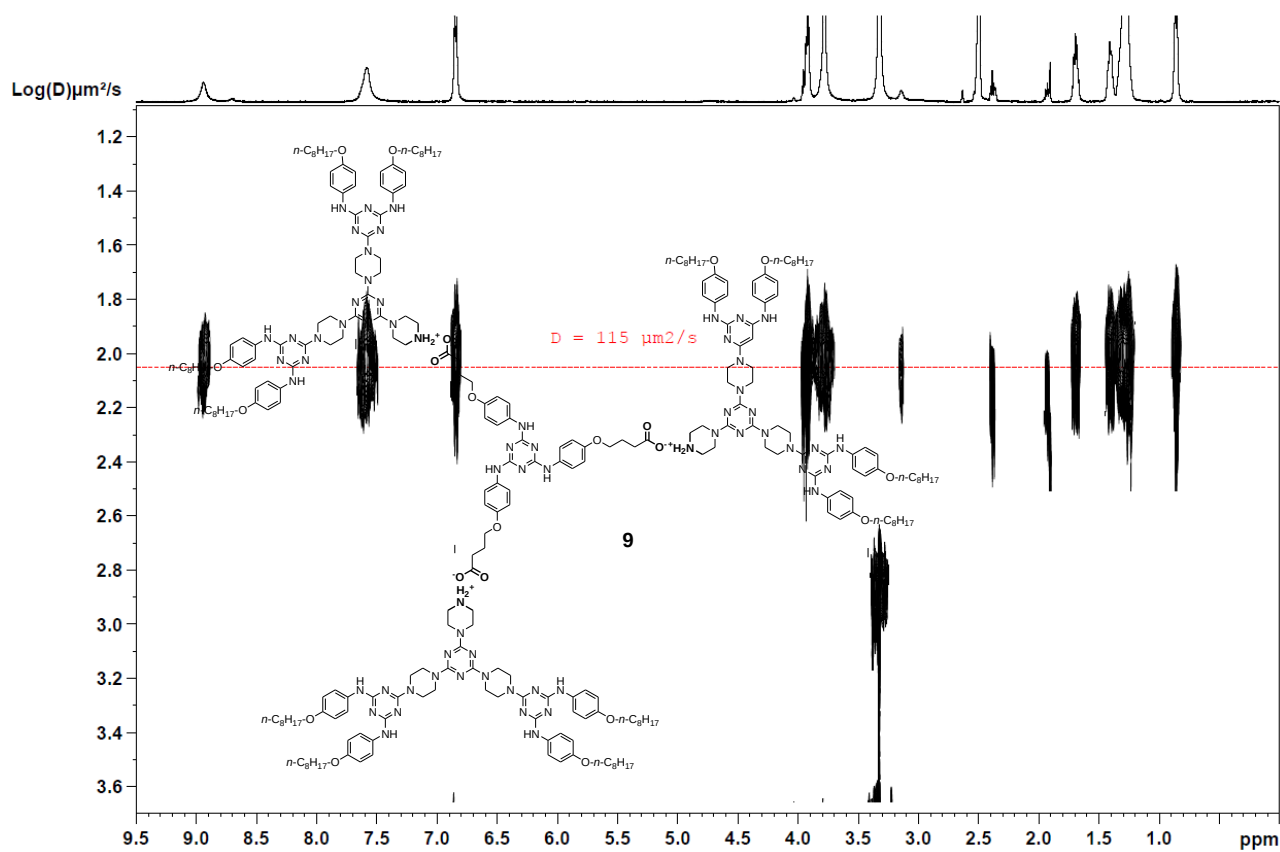


Figure S54: 2D- ^1H -DOSY NMR chart of compound **9** (500 MHz, 5.0 mM in $\text{DMSO-}d_6$, 298 K).

Extracted data from the output files of the ΔG of solvation calculation for compounds **2a**, **3**, **D-Cl** and **D-N<P>NH**

1. Compound **2a** in THF

 (Unpolarised solute)-Solvent (Kcal mol⁻¹) = -15.41
 (Polarised solute)-Solvent (Kcal mol⁻¹) = -19.73
 Solute polarisation (Kcal mol⁻¹) = +2.36
 Total electrostatic (Kcal mol⁻¹) = -17.38

 SMD-CDS (non-electrostatic) energy (Kcal mol⁻¹) = -17.60
 Total non electrostatic (Kcal mol⁻¹) = -17.60
 ΔG of solvation (Kcal mol⁻¹) = -34.97

2. Compound **2a** in 1,4 Dioxane

 (Unpolarised solute)-Solvent (Kcal mol⁻¹) = -9.43
 (Polarised solute)-Solvent (Kcal mol⁻¹) = -10.95
 Solute polarisation (Kcal mol⁻¹) = +0.80
 Total electrostatic (Kcal mol⁻¹) = -10.15

 SMD-CDS (non-electrostatic) energy (Kcal mol⁻¹) = -14.34
 Total non electrostatic (Kcal mol⁻¹) = -14.34
 ΔG of solvation (Kcal mol⁻¹) = -24.49

3. Compound **3** in THF

 (Unpolarised solute)-Solvent (Kcal mol⁻¹) = -17.48
 (Polarised solute)-Solvent (Kcal mol⁻¹) = -22.72
 Solute polarisation (Kcal mol⁻¹) = +2.89
 Total electrostatic (Kcal mol⁻¹) = -19.83

 SMD-CDS (non-electrostatic) energy (Kcal mol⁻¹) = -20.21
 Total non electrostatic (Kcal mol⁻¹) = -20.21
 ΔG of solvation (Kcal mol⁻¹) = -40.03

4. Compound **3** in 1,4 Dioxane

 (Unpolarised solute)-Solvent (Kcal mol⁻¹) = -10.78
 (Polarised solute)-Solvent (Kcal mol⁻¹) = -12.55
 Solute polarisation (Kcal mol⁻¹) = +0.94
 Total electrostatic (Kcal mol⁻¹) = -11.61

 SMD-CDS (non-electrostatic) energy (Kcal mol⁻¹) = -17.66
 Total non electrostatic (Kcal mol⁻¹) = -17.66
 ΔG of solvation (Kcal mol⁻¹) = -29.27

5. Compound **D-Cl** in THF

 (Unpolarised solute)-Solvent (Kcal mol⁻¹) = -36.81
 (Polarised solute)-Solvent (Kcal mol⁻¹) = -48.00
 Solute polarisation (Kcal mol⁻¹) = +6.19
 Total electrostatic (Kcal mol⁻¹) = -41.82

 SMD-CDS (non-electrostatic) energy (Kcal mol⁻¹) = -48.66
 Total non electrostatic (Kcal mol⁻¹) = -48.66
 ΔG of solvation (Kcal mol⁻¹) = -90.47

6. Compound **D-Cl** in 1,4-Dioxane

 (Unpolarised solute)-Solvent (Kcal mol⁻¹) = -22.56
 (Polarised solute)-Solvent (Kcal mol⁻¹) = -26.32
 Solute polarisation (Kcal mol⁻¹) = +1.99
 Total electrostatic (Kcal mol⁻¹) = -24.33

 SMD-CDS (non-electrostatic) energy (Kcal mol⁻¹) = -43.60
 Total non electrostatic (Kcal mol⁻¹) = -43.60
 ΔG of solvation (Kcal mol⁻¹) = -67.92

7. Compound **D-N<P>NH** in THF

 (Unpolarised solute)-Solvent (Kcal mol⁻¹) = -38.87
 (Polarised solute)-Solvent (Kcal mol⁻¹) = -50.43
 Solute polarisation (Kcal mol⁻¹) = +6.37
 Total electrostatic (Kcal mol⁻¹) = -44.07

 SMD-CDS (non-electrostatic) energy (Kcal mol⁻¹) = -51.93
 Total non electrostatic (Kcal mol⁻¹) = -51.93
 ΔG of solvation (Kcal mol⁻¹) = -96.00

8. Compound **D-N<P>NH** in 1,4-Dioxane

 (Unpolarised solute)-Solvent (Kcal mol⁻¹) = -23.84
 (Polarised solute)-Solvent (Kcal mol⁻¹) = -27.73
 Solute polarisation (Kcal mol⁻¹) = +2.06
 Total electrostatic (Kcal mol⁻¹) = -25.67

 SMD-CDS (non-electrostatic) energy (Kcal mol⁻¹) = -46.33
 Total non electrostatic (Kcal mol⁻¹) = -46.33
 ΔG of solvation (Kcal mol⁻¹) = -72.00

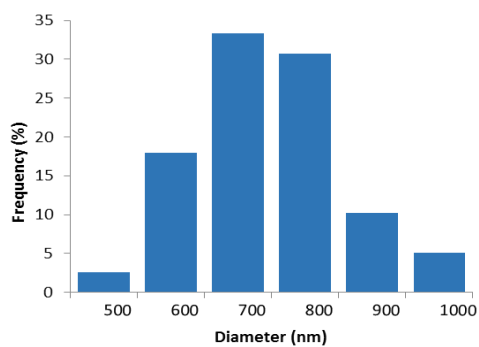
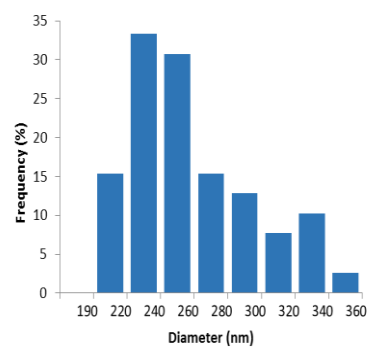
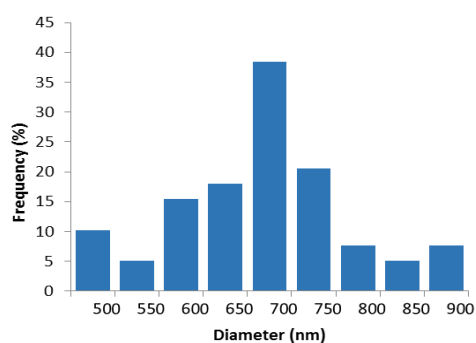
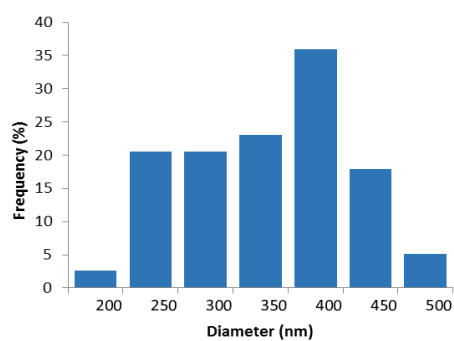
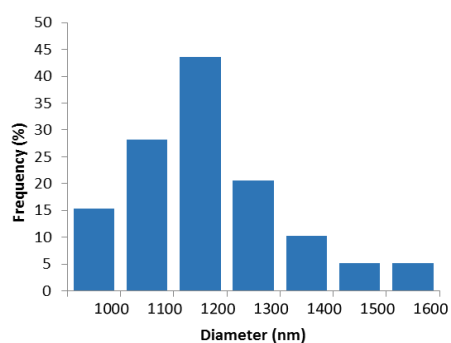
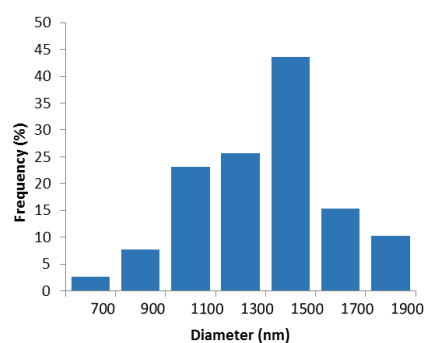
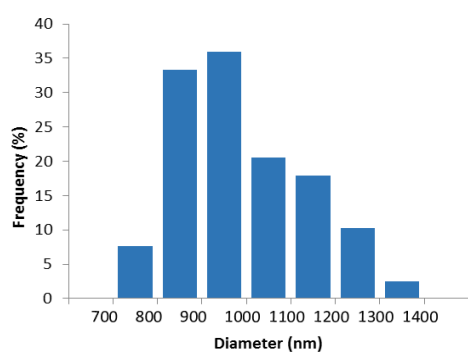
**D-N<P>NH****5****6****7a****7b****8****9**

Figure S55: Spherical nano-aggregates diameter distributions of compounds **D-N<P>NH** and **5-9** (from DMSO).

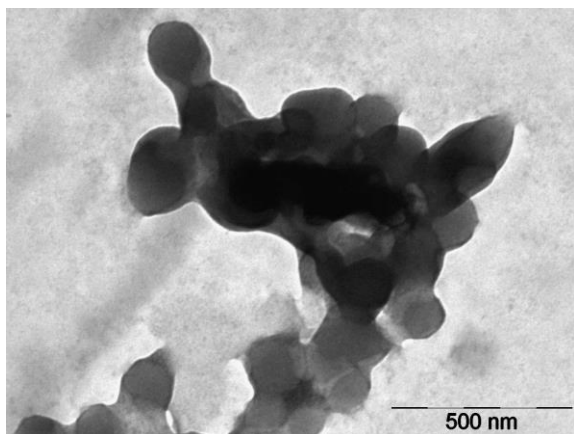


Figure S56: TEM image of compound **4** (from DMSO)