Electronic Supplementary Information (ESI) for:

Synthesis and Properties of Aromatic Polyamide Dendrimers with Polyhedral Oligomeric Silsesquioxane Cores

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EXPERIMENTAL SECTION

Materials. DMAc was purchased from Wako Pure Chemical Industries Ltd. and distilled from calcium hydride before use. Thionyl chloride was purchased from Kanto Chemical Co., Inc., and used as received.

Synthesis of the G3 dendrimer. The compound 3,5-bis(trifluoroacetamido)benzoic acid (3.58 g, 10.4 mmol) was refluxed in thionyl chloride (35 mL) for 3 h. After the removal of thionyl chloride by distillation, chloroform was added and then distilled off to ensure complete removal of thionyl chloride. The resulting product was dried under vacuum and then dissolved in DMAc (10 mL). To a solution of G2 dendrimer (1.03 g, 0.25 mmol) in DMAc (4.5 mL) was added the former solution, and the resulting mixture was stirred at room temperature for 12 h under nitrogen. After stirring at 50 °C for further 1 h, water (1.5 mL) was added to the mixture, and it was stirred at 50 °C for another 3 h. Hydrazine monohydrate (12 mL) was then added, and the mixture was stirred at 50 °C for 4 h. This mixture was then poured into 5% $NaHCO_{3aq}$. The resulting precipitate was collected by filtration and washed with methanol, and then dried at 80 °C for 12 h in vacuo. The yield was 1.95 g (93%). ^{1}H NMR (DMSO-d_6, δ, ppm): 0.46–0.80 (m, 16 H), 1.54–1.80 (m, 16 H), 3.14–3.38 (m, 16 H), 4.96 (s, 128 H), 5.99 (s, 32 H), 6.33 (s, 64 H), 7.75-8.02 (m, 48 H), 8.32–8.65 (m, 32 H), 10.16 (s, 32 H), 10.51 (s, 16H). Anal. Calcd. for ($C_{416}H_{400}N_{120}O_{68}Si_8$ 21.3H_2O): C, 56.93; H, 5.08; N, 19.15; Found: C, 57.22; H, 5.06; N, 18.85.

Synthesis of the G4 dendrimer. The compound 3,5-bis(trifluoroacetamido)benzoic acid (0.70 g, 2.03 mmol) was refluxed in thionyl chloride (6 mL) for 3 h. After the removal of thionyl chloride by distillation, chloroform was added and then distilled off to ensure complete removal of thionyl chloride. The resulting product was dried under vacuum and then dissolved in DMAc (1.2 mL). To a solution of G3 dendrimer (0.20 g, 0.024 mmol) in DMAc (1.8 mL) was added the former solution, and the resulting mixture was stirred at room temperature for 12 h under nitrogen. After stirring at 50 °C for further 3 h, water (0.2 mL) was added to the mixture, and it was stirred at 50 °C for another 2 h. Hydrazine monohydrate (2.3 mL) was then added, and the mixture was stirred at 50 °C for 4 h. This mixture was then poured into 5% $NaHCO_{3aq}$. The resulting precipitate was collected by filtration and washed with methanol, and then dried at 80 °C for 12 h in vacuo. The yield was 0.38 g (93%). ^{1}H NMR (DMSO-d_6, δ, ppm): 0.41–0.80 (m, 16 H), 1.54–1.80 (m, 16 H), 3.14–3.38 (m, 16 H), 4.93 (s, 256 H), 6.00 (s, 64 H), 6.35 (s, 128 H), 7.84-8.09 (m, 112 H), 8.32–8.59 (m, 64 H), 10.14 (s, 64 H), 10.57 (s, 48H). Anal. Calcd. for ($C_{864}H_{784}N_{248}O_{132}Si_8$ 29.2H_2O): C, 59.29; H, 4.85; N, 19.84; Found: C, 59.50; H, 5.07; N, 19.66.

Synthesis of the G5 dendrimer. The compound 3,5-bis(trifluoroacetamido)benzoic acid (1.40 g, 4.07 mmol) was refluxed in thionyl chloride (14 mL) for 3 h. After the removal of thionyl chloride by distillation, chloroform was added and then distilled off to ensure complete removal of thionyl chloride. The resulting product was dried under vacuum and then dissolved in DMAc (3.9 mL). To a solution of G4 dendrimer (0.4 g, 0.024 mmol) in DMAc (1.8 mL) was added the former solution, and the resulting mixture was stirred at room temperature for 12 h under nitrogen. After stirring at 50 °C for further 3 h, water (0.6 mL) was added to the mixture, and it was stirred at 50 °C for another 2 h. Hydrazine monohydrate (4.7 mL) was then added, and the mixture was stirred at 50 °C for 4 h. This mixture was then poured into 5% $NaHCO_{3aq}$. The resulting precipitate was collected by filtration and washed with methanol, and then dried at 80 °C for 12 h in vacuo. The yield was 0.74 g (91%). ^{1}H NMR (DMSO-d_6, δ, ppm): 0.38–0.72 (m, 16 H), 1.53–1.75 (m, 16 H), 3.13–3.35 (m, 16 H), 4.93 (s, 512 H), 6.00 (s, 128 H), 6.35 (s, 256 H), 7.84-8.12 (m, 240 H), 8.31–8.60 (m, 128 H), 10.15 (s, 128 H), 10.50-10.76 (m, 112 H). Anal. Calcd. for ($C_{1760}H_{1552}N_{504}O_{260}Si_8$ 57.2H_2O): C, 60.09; H, 4.77; N, 20.07; Found: C, 60.36; H, 4.86; N, 19.80.

Synthesis of the G6 dendrimer. The compound 3,5-bis(trifluoroacetamido)benzoic acid (1.05 g, 3.05 mmol) was refluxed in thionyl chloride (10 mL) for 3 h. After the removal of thionyl chloride by distillation, chloroform was added and then distilled off to ensure complete removal of thionyl chloride. The resulting product was dried under vacuum and then dissolved in DMAc (3.0 mL). To a solution of G5 dendrimer (0.3 g, 0.0088 mmol) in DMAc (1.3 mL) was added the former solution, and the resulting mixture was stirred at room temperature for 12 h under nitrogen. After stirring at 50 °C for further 3 h, water (0.4 mL) was added to the mixture, and it was stirred at 50 °C for another 2 h. Hydrazine monohydrate (3.5 mL) was then added, and the mixture was stirred at 50 °C for 4 h. This mixture was then poured into 5% $NaHCO_{3aq}$. The resulting precipitate was collected by filtration and washed with methanol, and then dried at 80 °C for 12 h in vacuo. The yield was 0.51 g (91%). ^{1}H NMR (DMSO-d_6, δ, ppm): 0.23–0.56 (m, 16 H), 1.44–1.70 (m, 16 H), 3.07–3.29 (m, 16 H), 4.92 (s, 1024 H), 5.97 (s, 256 H), 6.32 (s, 512 H), 7.83-8.16 (m, 496 H), 8.30–8.64 (m, 256 H), 10.15 (s, 256 H), 10.50-10.85 (m, 240 H). Anal. Calcd. for ($C_{3552}H_{3088}N_{1016}O_{516}Si_8$ 150.4H_2O): C, 59.92; H, 4.80; N, 19.99; Found: C, 60.13; H, 4.75; N, 19.78.

Relaxation measurement. The T_1 and T_2 relaxation times were determined for the terminal phenyl protons of the amine-terminated dendrimers (protons ***b*** and ***c*** in Fig. 1 and S2-4) and the fluorines of the TFAA-terminated dendrimers. The T_1 values were determined using inversion recovery pulse sequence with 30 values of the delay time (τ) from 10 ms to 5 s for ^{1}H, and from 100 ms to 7 s for ^{19}F at 25 ^{o}C. The T_2 values were determined using Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence with 30 values of τ from 0.4 ms to 1.5 s for both ^{1}H and ^{19}F at 25 ^{o}C.

FIG.S S1-S7

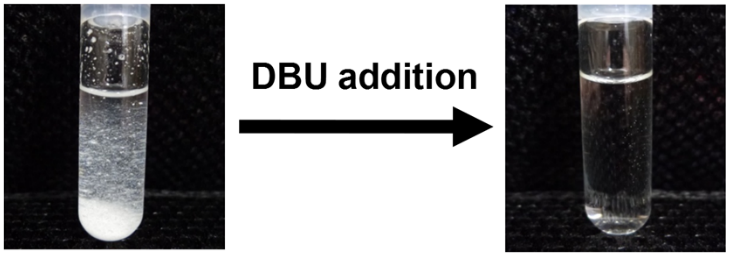


Fig. S1. Photographs of the solubility tests of octa(n-propylamine)-POSS in DMAc before and after addition of DBU.

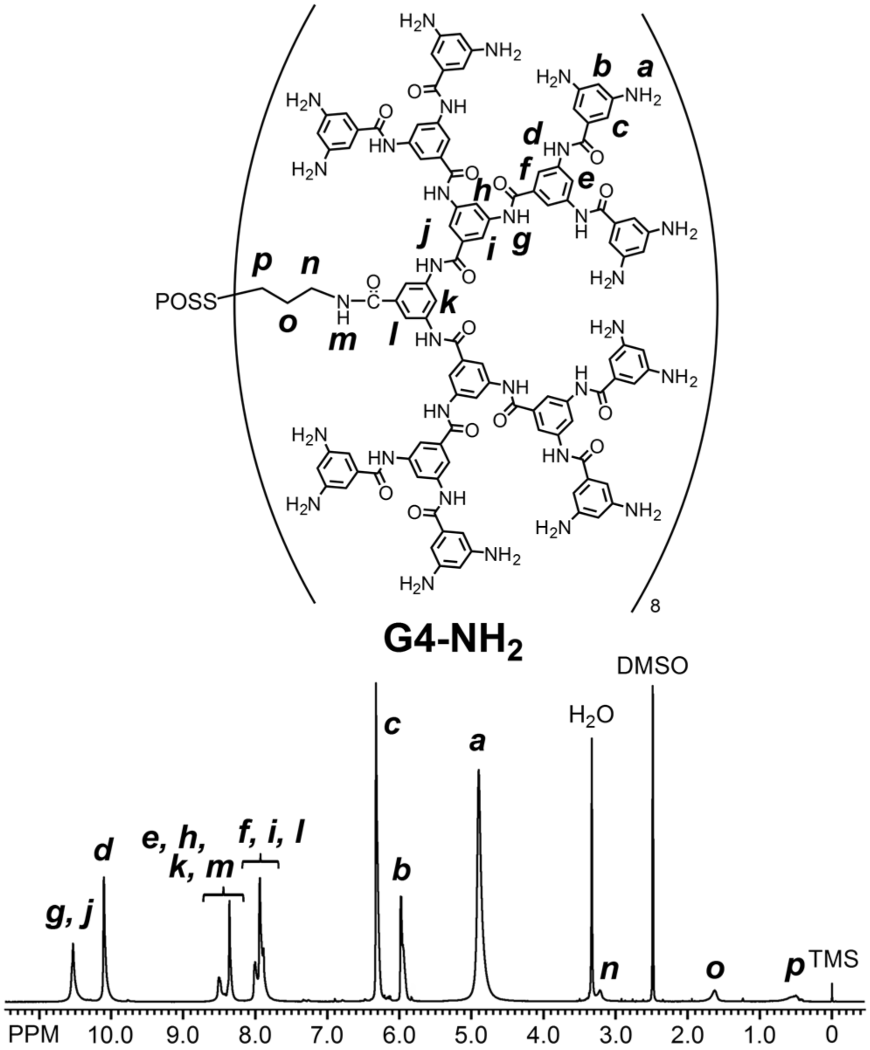


Fig. S2. ^{1}H NMR spectrum of G4-NH$_2$ in DMSO-d_6 at room temperature.

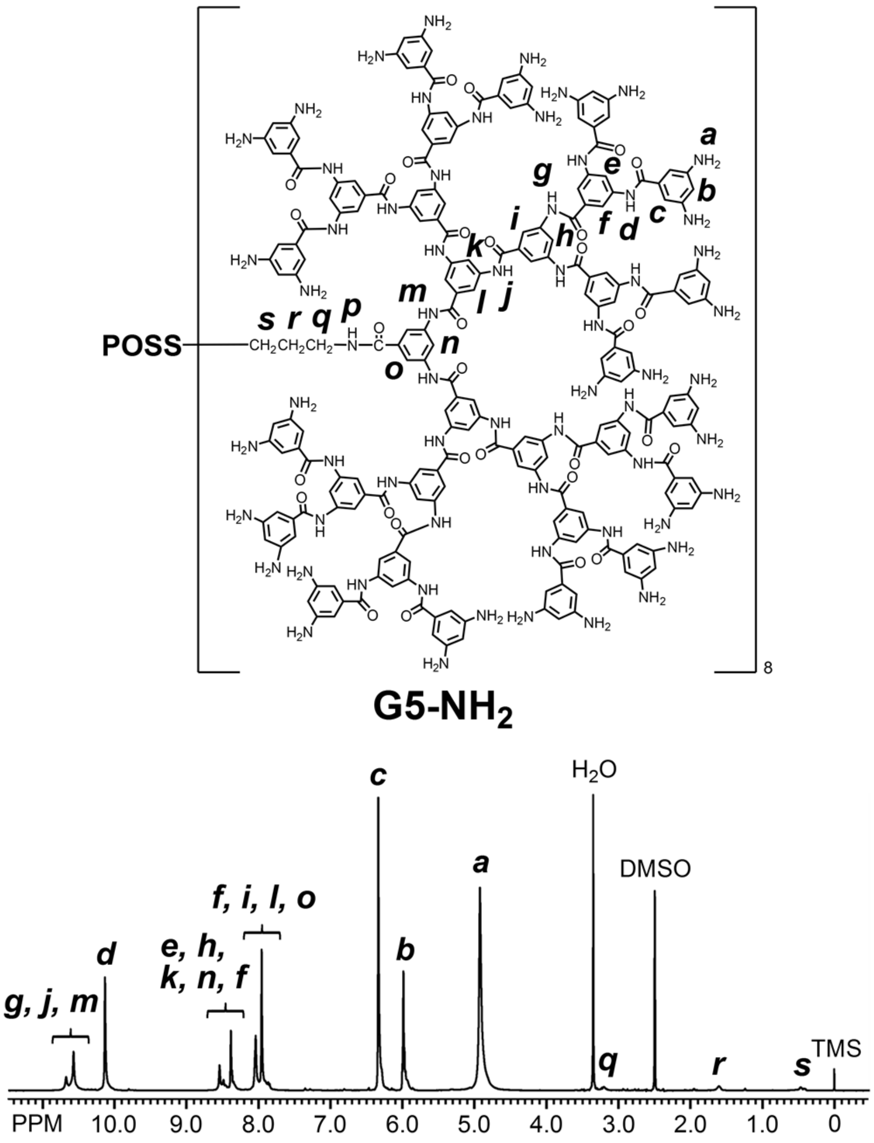
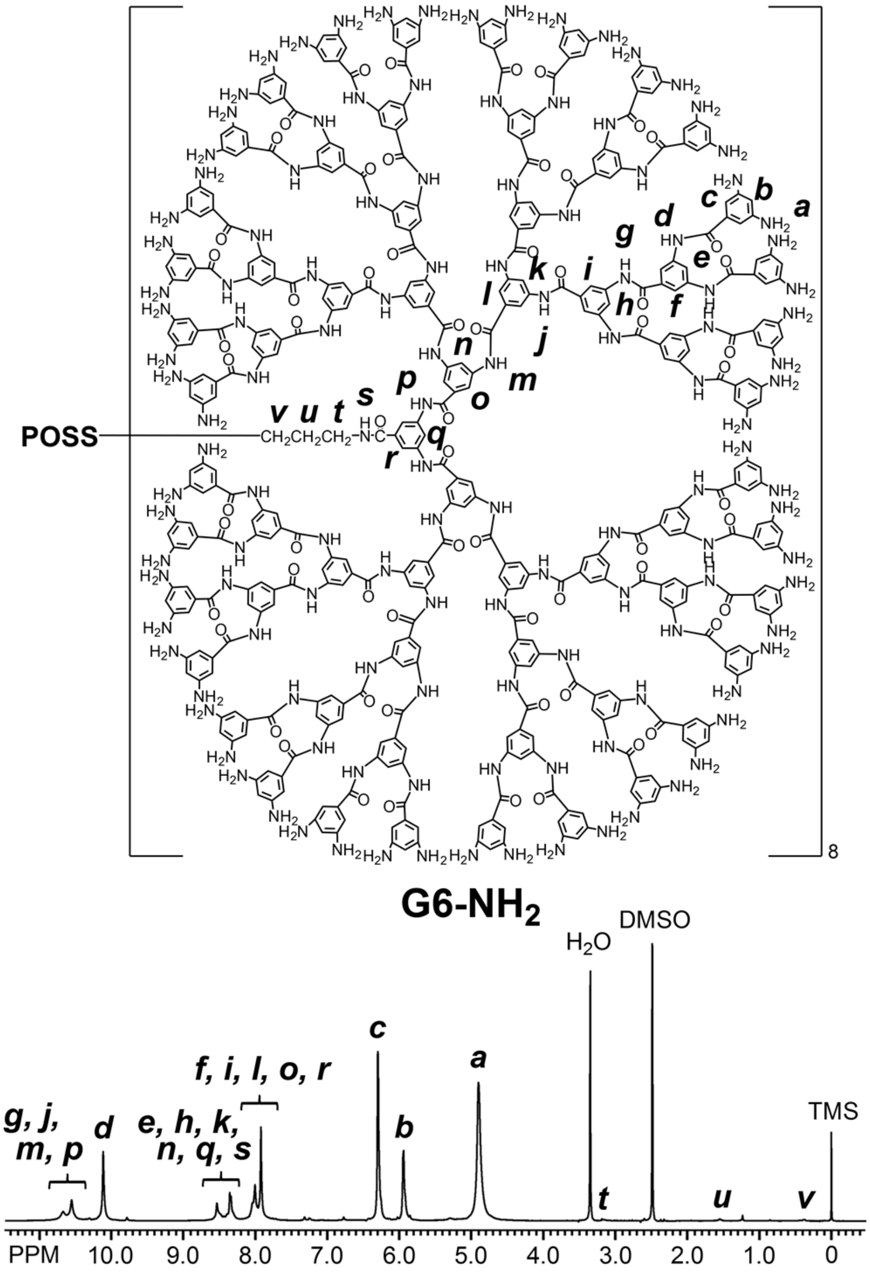


Fig. S3. ^{1}H NMR spectrum of G5-NH$_2$ in DMSO-d_6 at room temperature.



$G6\text{-}NH_2$

Fig. S4. ^1H NMR spectrum of $G6\text{-}NH_2$ in DMSO-d_6 at room temperature.

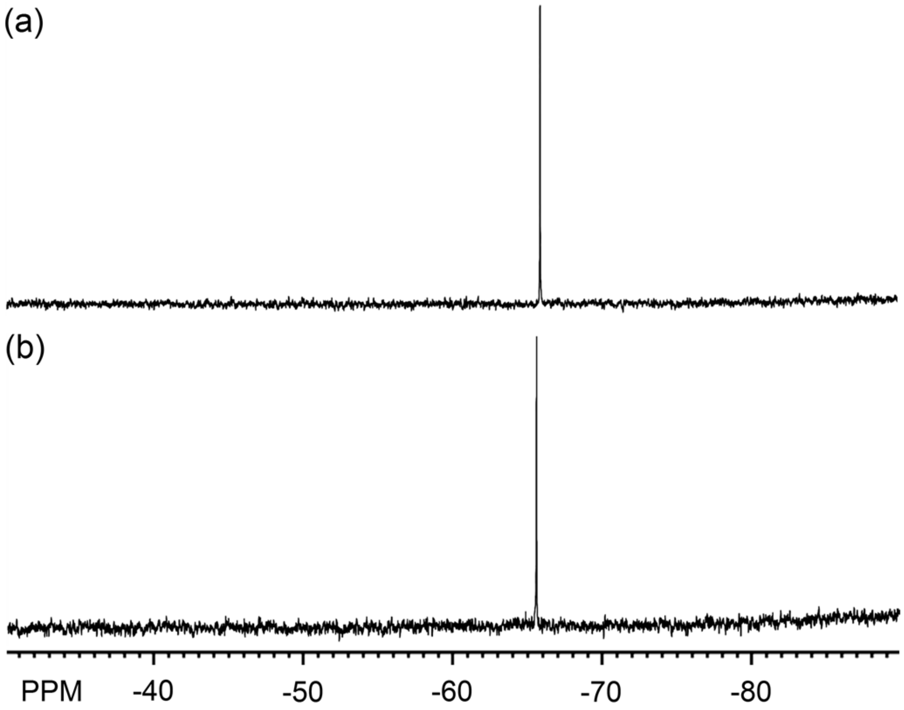


Fig. S5. ^{29}Si NMR spectra of (a) octa(n-propylamine)-POSS and (b) G1-NH$_2$ measured in DMSO-d_6 at room temperature.

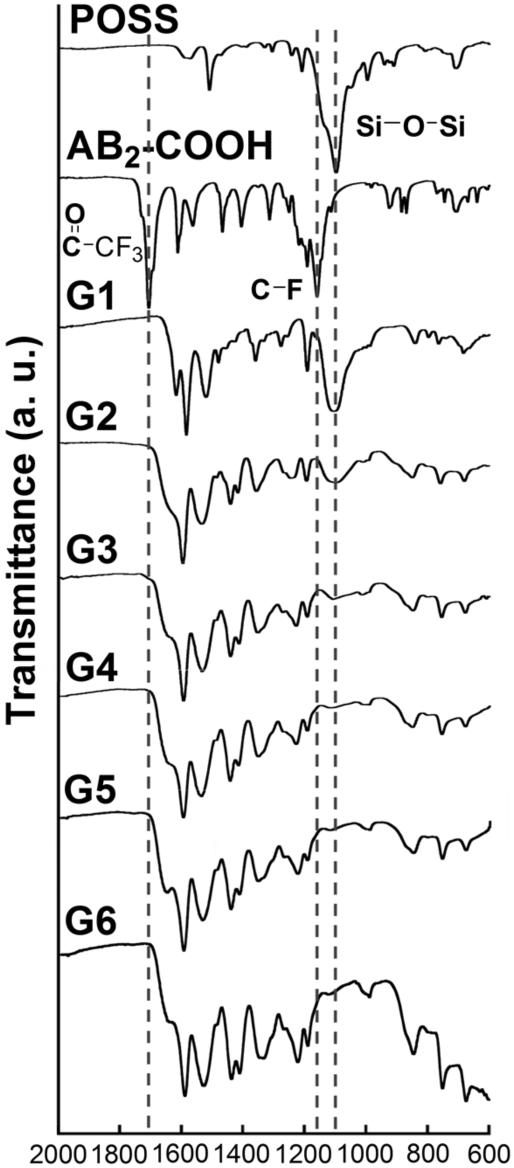


Fig. S6. FT-IR spectra of core molecule, AB_2 building block, and amine-terminated dendrimers.

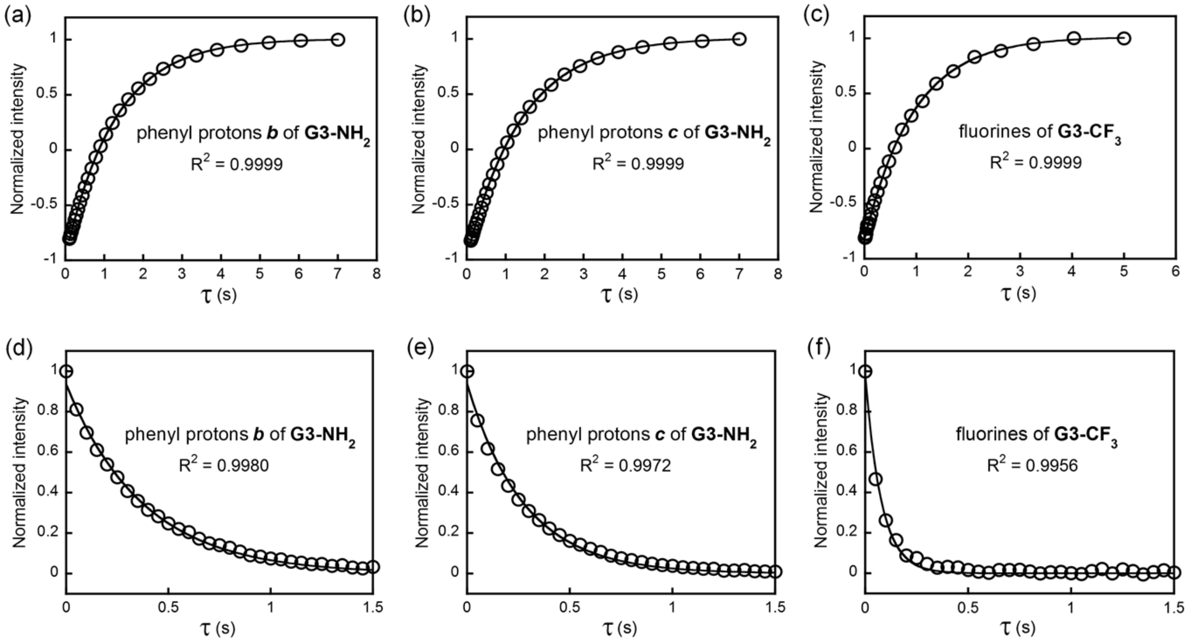


Fig. S7. Magnetization recovery and decay in inversion recovery and CPMG experiments for terminal protons and fluorines of G3-NH$_2$ and G3-CF$_3$.