Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Aggregation Enhanced Excimer Emission (AEEE) with Efficient Blue Emission Based on Pyrene Dendrimers

Alaa S. Abd-El-Aziz,* Amani A. Abdelghani, Brian D. Wagner, and
Elsayed. M. Abdelrehim

*Department of Chemistry, University of Prince Edward Island, 550 University Avenue,
Charlottetown, PE, C1A 4P3, Canada*

Experimental

1. Materials

All chemicals and reagents were obtained from Sigma-Aldrich and were used without any further purification. All solvents were dried and stored over 3 Å molecular sieves before being used. The synthesis of the organoiron complexes **5, 7,** and **9** followed previously reported procedures.[1-3]

2. Instrumentation

A Bruker Avance NMR spectrometer (^{1}H, 300 MHz and ^{13}C, 75 MHz) was used to characterize all synthesized complexes in DMSO-d_6 or Acetone-d_6 with the chemical signals referenced to solvent residual signal in ppm. Attenuated total reflection Fourier transform IR (ATR-FTIR) absorption spectroscopic measurements were acquired on a Bruker Alpha FTIR spectrometer Alpha-P. Cyclic voltammetric experiments were carried out on a Princeton Applied Research/EG&G Model 263 potentiostat/ galvanostat using glassy carbon working electrode, Pt counter electrode, and Ag reference electrode. The experiments, which were carried out at a scan rate between 0.1 and 1.5Vs^{-1} and at a temperature between 25^{o}C and -25°C under nitrogen atmosphere in degassed propylene carbonate as solvent and tetrabutylammonium hexafluorophosphate as supporting electrolyte, were externally referenced to a DMF solution of ferrocene. The scanning electron micrographs (SEM) of the complexes were obtained on a Hitachi TM3000 SEM. Transmission electron microscope (TEM) Hitachi Bio

TEM 7500 electron microscope was operated at 80 kV. Images were captured with a side mounted digital camera AMT XR40, bought from Advance Microscopy Techniques, Danvers, MA, USA. Grids used in the experiment were 200 mesh copper grids carbon coated acquired from SPI Supplies Canada, London Ont. Elemental analyses were performed on CE-440 Elemental Analyser, Exeter Analytical, Inc. Thermogravimetric analysis (TGA) was conducted in platinum pans under nitrogen at a heating rate of 10°C on a TA Instruments TGA Q500. Fluorescence data were acquired on Photon Technology International Quantum Master 400 spectrofluorimeter. UV-vis absorption measurements were performed using a HP8543 UV-vis spectrophotometer.

3. Synthesis and characterization

3.1 Synthesis of compound (3a) 1-Pyrene with terminated aliphatic alcohol (8 carbons)

Steglich esterification[4] was used to convert the carboxylic group in 1-pyrenebutyric acid to a hydroxyl group. A 50 mL round-bottom flask was charged with **1** (0.58 g, 2 mmol), **2a** (0.29 g, 2 mmol), DMAP (0.25 g, 2 mmol), and 5 mL of DMF. The solution was stirred at 0°C under nitrogen atmosphere while DCC (0.41 g, 2 mmol) was added over a 15 minute period. The reaction mixture was then stirred under nitrogen for 24 hours at room temperature. The reaction mixture was cooled to -25^0C in a freezer for two hours, filtered to remove dicyclohexylurea (DCU) and then poured into 100 mL of 10% HCl solution. The product was extracted with three times 50 mL DCM, washed with 100 mL portions of water five times, then dried over $MgSO_4$, filtered, and the solvent removed with a rotary evaporator. The product was dissolved in acetone, cooled to −25°C in a freezer for 2 hours, filtered to remove remaining DCU and after solvent removal, the product was the resulting yellow solid (molecular weight 417 g/mol). Yield: (0.79 g, 94%). ^1H NMR data δ_H (300 MHz; Acetone-d_6): 8.47 (1H, m, Py-H), 8.22 (4H, m, Py-H), 8.09 (2H, s, Py-H), 8.00 (1H, m, Py-H), 7.91 (1H, m, Py-H), 4.09 (2H, m, CH_2), 3.52 (2H, m, CH_2), 3.41 (2H, m, CH_2), 2.49 (2H, m, CH_2), 2.15 (2H, m, CH_2), 1.84 (1H, m, OH), 1.53 (2H, m, CH_2), 1.49 (2H, m, CH_2), 1.30 (8H, m, CH_2). ^{13}C NMR δ_c (75 MHz; Acetone-$d_{6,}$): 173.14 (CO), 136.73, 132.00, 131.45, 130.42, and 129.00 (quat-C), 127.89, 127.02, 126.37, 125.18, and 123.86 (Ar-C), 64.35, 61.95, 33.81, 33.38, 32.76, 31.09, 27.36, 26.16, and 25.63 (C-CH_2). ATR-FTIR; ν_{max}/cm^{-1}: 3339 (OH), 2939 (Ar-C), 1726 (CO). Elemental analysis for $C_{28}H_{32}O_3$: calc (C: 80.73; H: 7.74), found (C: 81.01; H: 7.91).

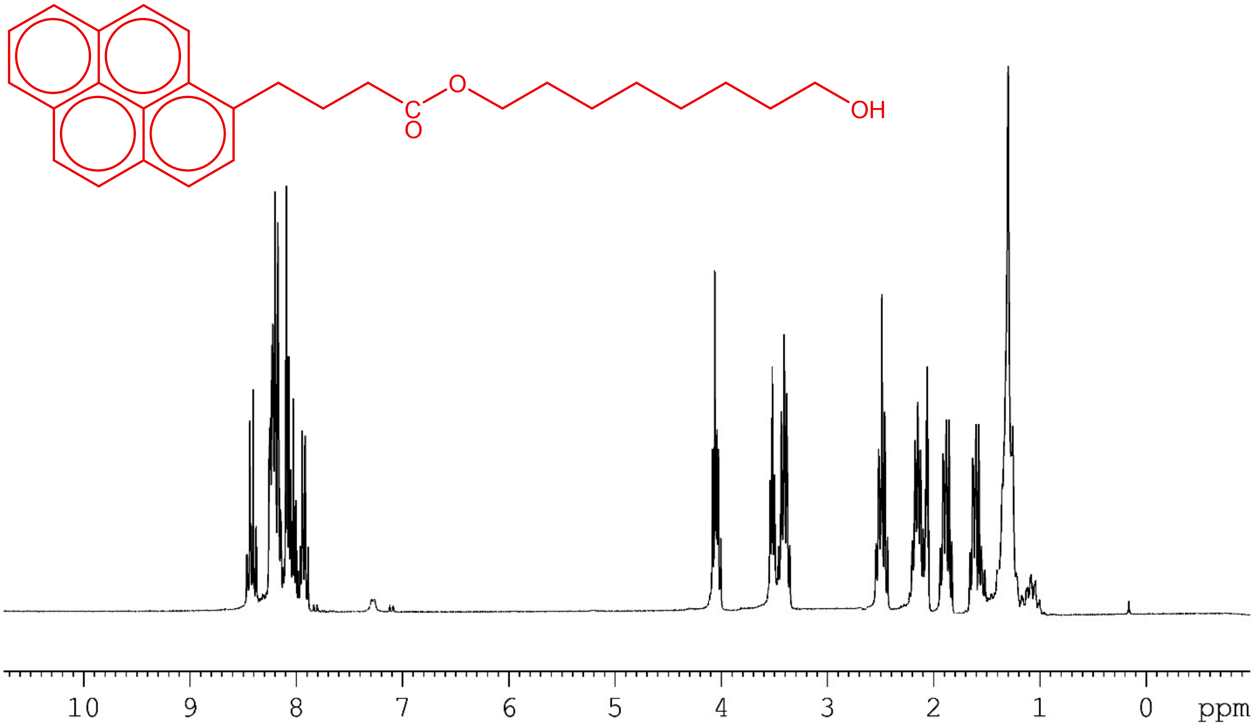


Figure 1. ^{1}H NMR spectra of compound **3a** in Acetone-d_6

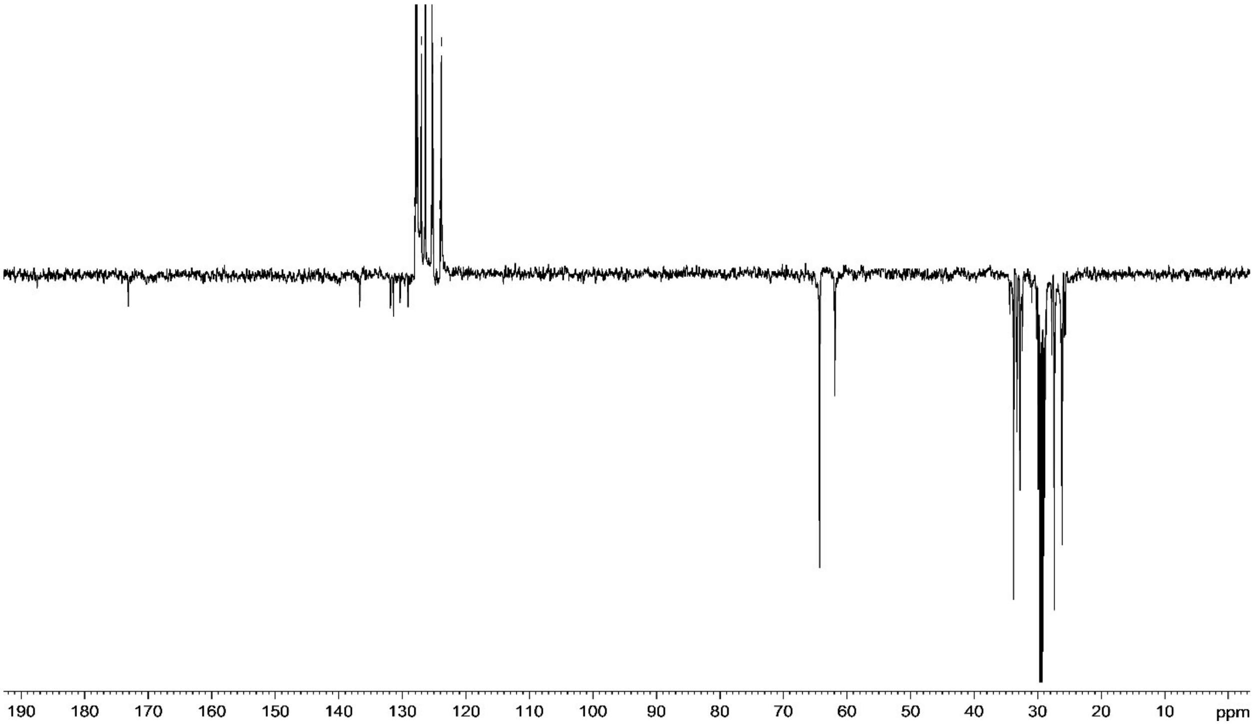


Figure 2. ^{13}C spectra of compound **3a** in Acetone-d_6

3.2 Synthesis of compound (3b) 1-Pyrenebyteric acid with terminated aliphatic alcohol (12 carbons)

In a procedure analogous to the synthesis of **3a**, **3b** was synthesized from **1** (0.58 g, 2 mmol), **2b** (0.41 g, 2 mmol), DMAP (0.25 g, 2 mmol), DCC (0.41 g, 2 mmol), and 5 mL of DMF. The product was the resulting light yellow solid (molecular weight 473 g/mol). Yield: (0.87 g, 91%). ^{1}H NMR data δ_{H} (300 MHz; Acetone-d$_{6}$): 8.46 (1H, m, Py-H), 8.23 (4H, m, Py-H), 8.12 (2H, s, Py-H), 8.05 (1H, m, Py-H), 7.96 (1H, m, Py-H), 4.08 (2H, m, CH$_{2}$), 3.53 (2H, m, CH$_{2}$), 3.42 (4H, m, CH$_{2}$), 2.51 (2H, m, CH$_{2}$), 2.17 (2H, m, CH$_{2}$), 1.84 (1H, m, OH), 1.59 (4H, m, CH$_{2}$), 1.49 (4H, m, CH$_{2}$), 1.29 (10H, m, CH$_{2}$). ^{13}C NMR δ_{c} (75 MHz; Acetone-d$_{6}$,): 173.12 (CO), 136.77, 131.95, 131.45, 130.08, and 129.16 (quat-C), 127.89, 127.01, 126.37, 125.18, and 123.86 (Ar-C), 64.30, 62.07, 34.37, 33.87, 33.33, 32.83, 27.79, 27.40, 26.21, 25.86, and 24.98 (C-CH$_{2}$). ATR-FTIR; ν_{max}/cm^{-1}: 3343 (OH), 2919 (Ar-C), 1730 (CO). Elemental analysis for $C_{32}H_{40}O_{3}$: calc (C: 81.32; H: 8.53), found (C: 81.64; H: 8.77).

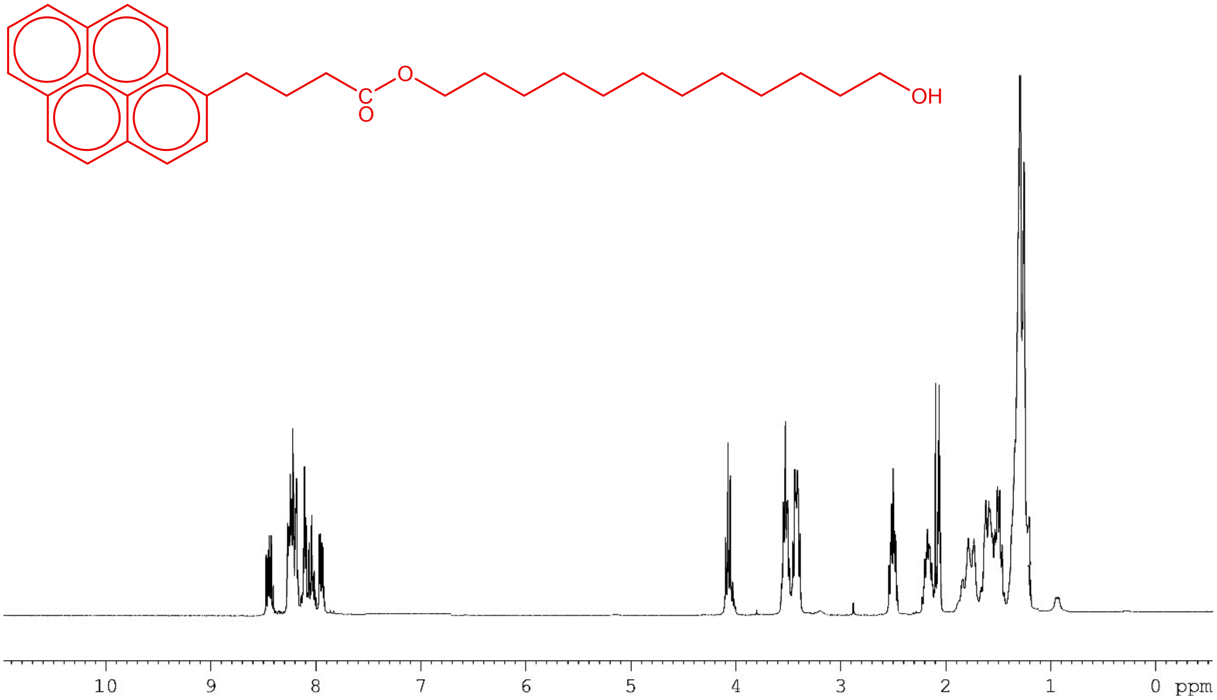


Figure 3. ^{1}H NMR spectra of compound **3b** in Acetone-d$_6$

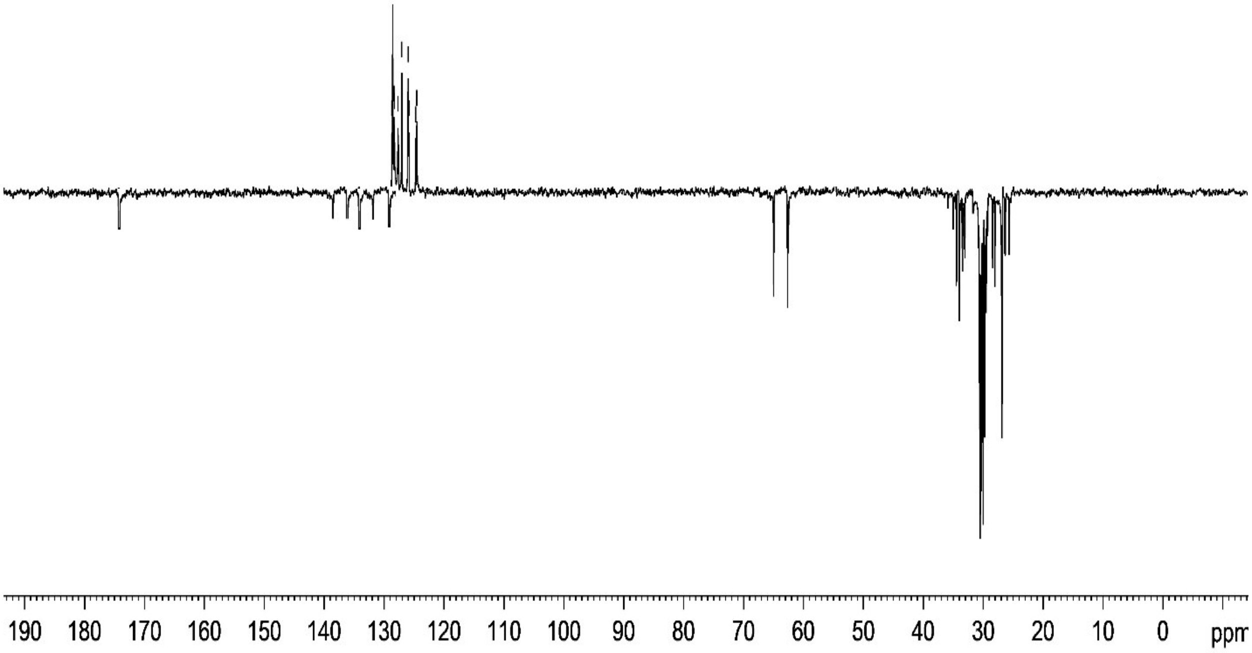


Figure 4. ^{13}C spectra of compound **3b** in Acetone-d$_6$

3.3 Carboxylic acid-terminated G_0 dendrimer (D1)

Nucleophilic substitution reaction was used to synthesize dendrimer **D1**. A 50 mL round-bottom flask was charged with **4** (0.25 g, 0.5 mmol), **5** (1.05 g, 2 mmol), K_2CO_3 (1.41 g, 10.23 mmol), and 10 mL of DMF. The reaction mixture was stirred at room temperature for two days after flushing with nitrogen for 1/2 hour. Subsequently, the reaction mixture was poured into 100 mL of 10% HCl solution, and NH_4PF_6 (0.33 g, 2 mmol) was added to precipitate the product. The product, a reddish yellow solid, was collected by suction filtration and dried under vacuum at room temperature. (Molecular weight 2401 g/mol). Yield: (0.98g, 80%). ^{1}H NMR data δ_H (300 MHz; DMSO-d_6): 13.16 (4H, br s, COOH), 8.10 (8H, d, *J= 8.7 Hz*, uncompleted Ar-H), 7.41 (8H, d, *J= 8.7 Hz*, uncompleted Ar-H), 6.49 (16H, s, complexed Ar-H), 5.18 (20H, s, Cp-H), 4.22 (8H, s, CH_2), 3.51 (8H, s, CH_2), 2.94 (8H, d, *J= 8.1 Hz*, CH_2). ^{13}C NMR δ_c (75 MHz; DMSO-d_6): 171.51 and 167.35 (CO), 157.86, 131.15, 129.07, 105.93, and 63.2 (quat-C), 132.93 and 120.77 (uncomplexed Ar-C), 84.27 and 77.74 (complexed Ar-C), 80.11 (Cp-C), 33.83 and 28.19 (**C**H_2). ATR-FTIR; ν_{max}/cm^{-1}: 3315 (COOH), 2926 (Ar-CH), 2853 (Cp-C), 1700 (CO), 1231 (C-O-C). Elemental analysis for $C_{89}H_{80}O_{20}S_4Fe_4P_4F_{24}$: calc (C: 44.52; H: 3.36), found (C: 44.83; H: 3.47).

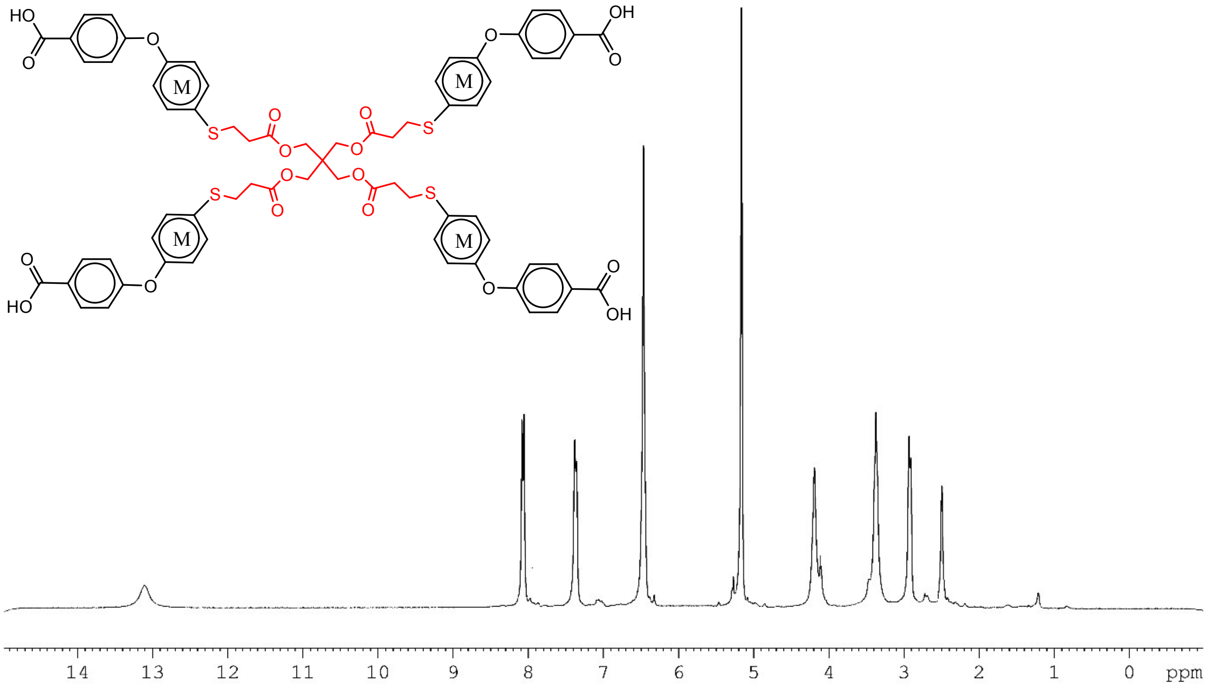


Figure 5. ^{1}H NMR spectra of dendrimer **D1** in DMSO-d_6

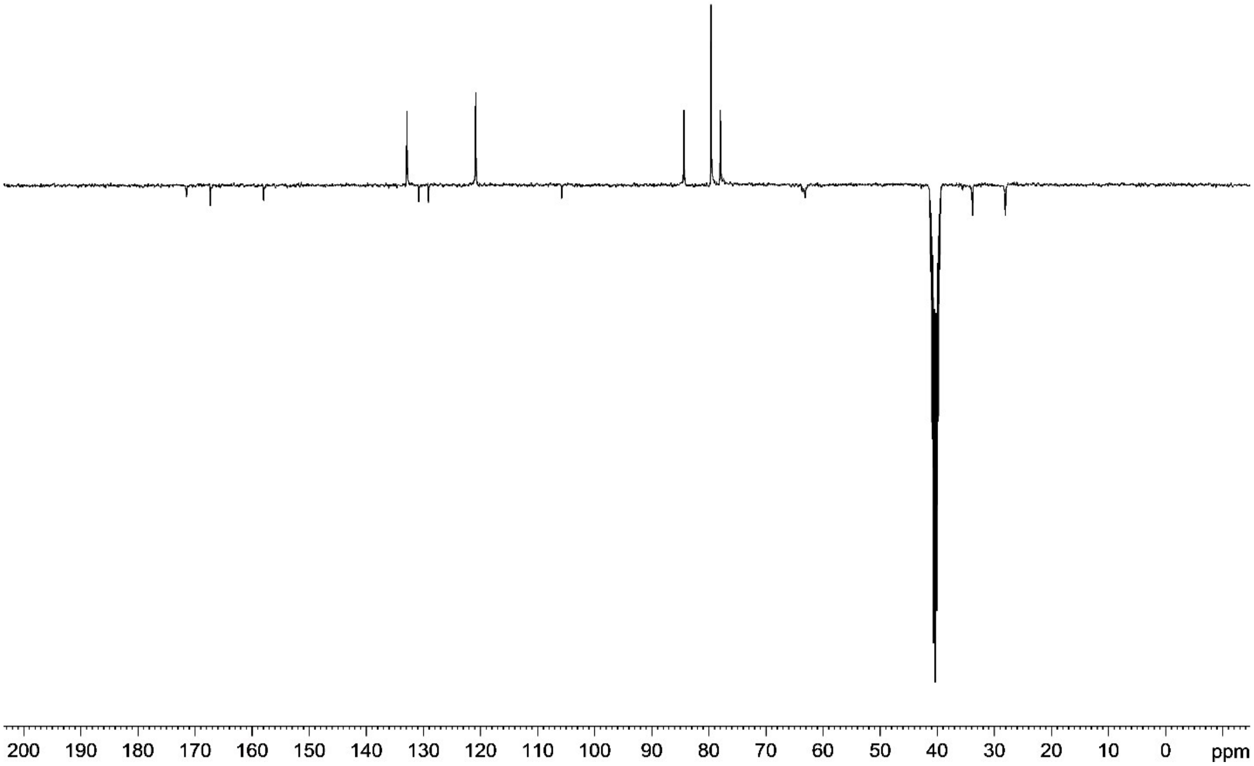
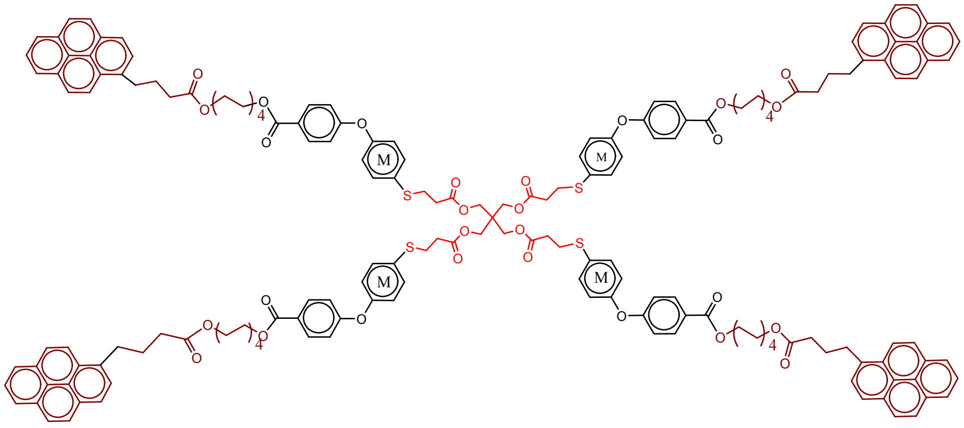


Figure 6. ^{13}C spectra of dendrimer **D1** in DMSO-d_6

3.4 Pyrene-terminated G_0 dendrimer (D2a)

The synthesis of dendrimer **D2a** followed a procedure analogous to the synthesis of compound **3**. In 50-mL round-bottom flask was charged with dendrimer **D1** (0.5 g, 0.21 mmol), compound **3a** (0.35 g, 0.83 mmol), DMAP (0.1 g, 0.83 mmol), DCC (0.17 g, 0.83 mmol), and 5 mL of DMF. (Molecular weight 3995 g/mol). Yield: (0.69 g, 83%). ^{1}H NMR data δ_H (300 MHz; DMSO-d$_6$): 8.40 (4H, m, Py-H), 8.26 (16H, m, Py-H), 8.12 (8H, s, Py-H), 8.10 (4H, m, Py-H), 8.05 (4H, m, Py-H), 7.93 (8H, d, *J= 7.2 Hz*, uncompleted Ar-H), 7.35 (8H, br s, uncompleted Ar-H), 6.46 (16H, s, complexed Ar-H), 5.15 (20H, s, Cp-H), 4.20 (16H, s, CH_2), 3.98 (8H, m, CH_2), 2.82 (8H, s, CH_2), 2.36 (8H, m, CH_2), 2.03 (8H, m, CH_2), 1.71 (32H, s, CH_2), 1.49 (32H, m, CH_2). ^{13}C NMR δ_c (75 MHz; DMSO-d$_6$): 173.69, 171.54, and 167.35 (CO), 165.9, 157.91, 153.85, 131.78, 131.28, 130.22, 125.11, and 65.81 (quat-C), 128.56, 128,29, 128.16, 127.44, 127.01, 127.43, 124.44, 124.21, 121.00, and 120.84 (uncomplexed Ar-C), 84.37 and 78.12 (complexed Ar-C), 79.67 (Cp-C), 64.69, 63.15, 34.08, 33.82, 32.78, 31.21, 29.34, and 28.04 (**C**H_2). ATR-FTIR; ν_{max}/cm^{-1}: 2925 (Ar-CH), 2852 (Cp-C), 1717 (CO), 1232 (C-O-C). Elemental analysis for $C_{201}H_{200}O_{28}S_4Fe_4P_4F_{24}$: calc (C: 60.43; H: 5.05), found (C: 60.74; H: 5.22).



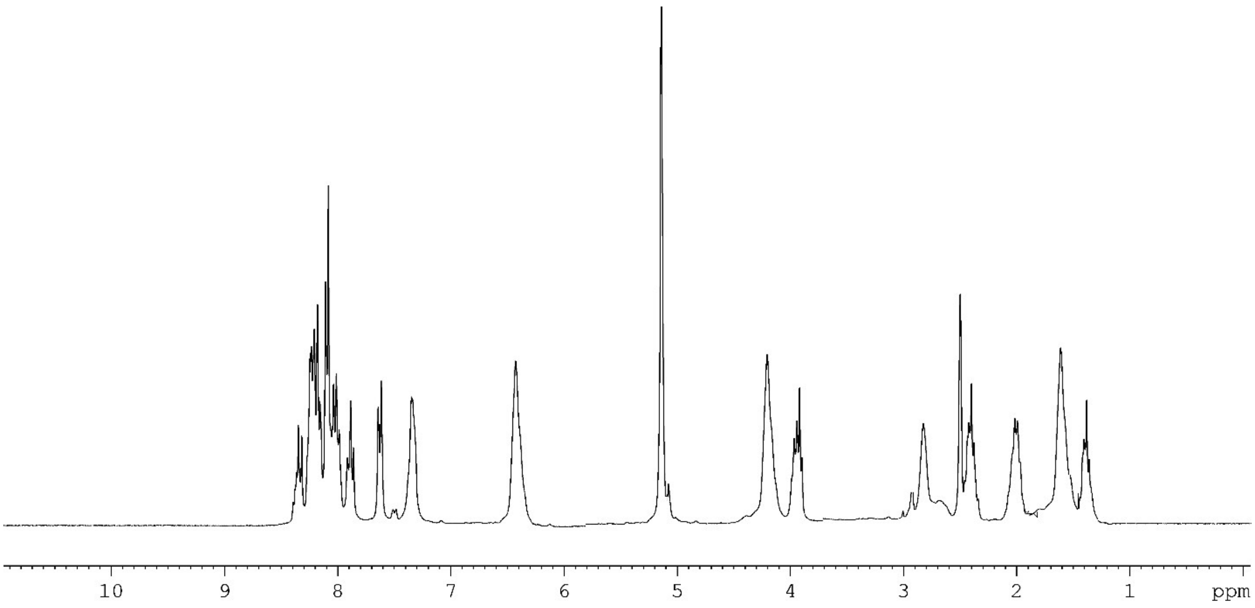


Figure 7. ^{1}H NMR spectra of dendrimer **D2a** in DMSO-d$_6$

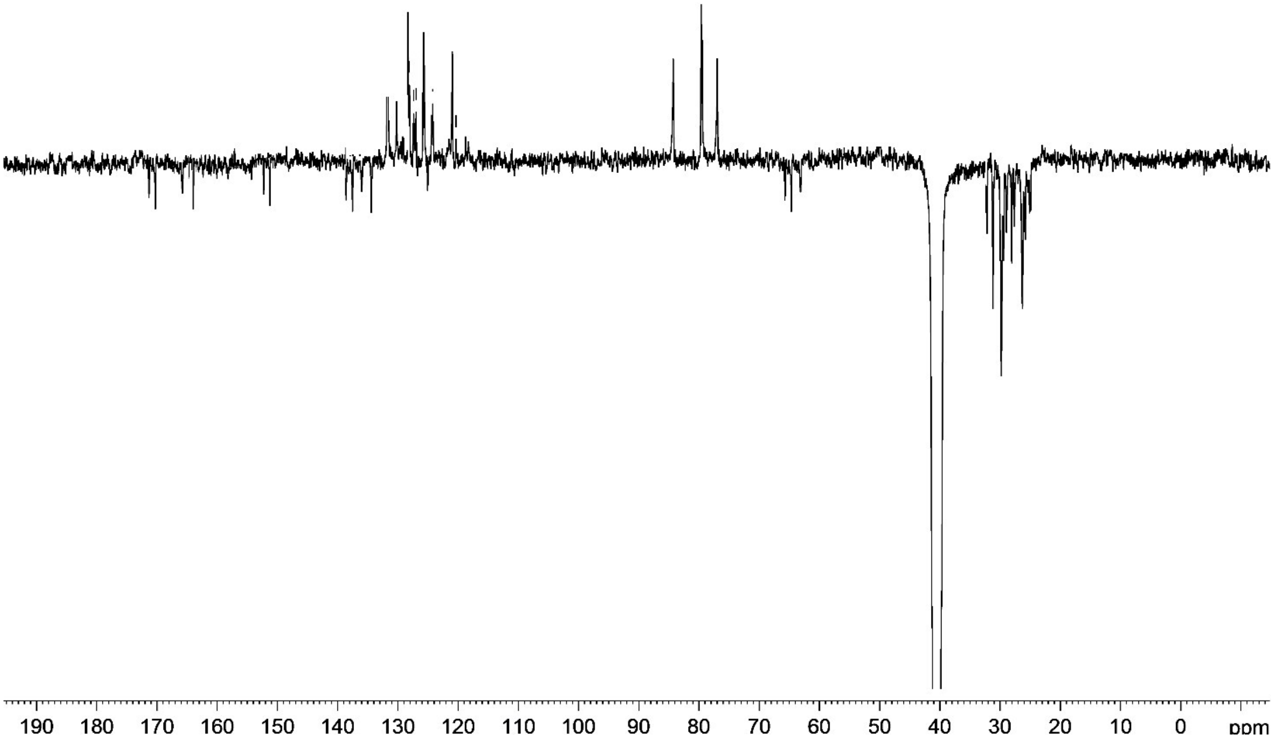
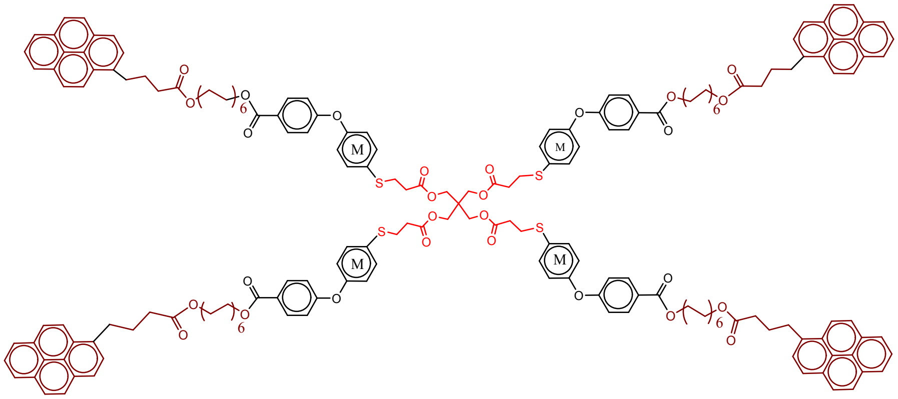


Figure 8. ^{13}C spectra of dendrimer **D2a** in DMSO-d$_6$

3.5 Pyrene-terminated G_0 dendrimer (D2b)

The synthesis of dendrimer **D2b** followed a procedure analogous to the synthesis of dendrimer **D2a**. In 50-mL round-bottom flask was charged with dendrimer **D1** (0.5 g, 0.21 mmol), compound **3b** (0.39 g, 0.83 mmol), DMAP (0.1 g, 0.83 mmol), DCC (0.17 g, 0.83 mmol), and 5 mL of DMF. (Molecular weight 4220 g/mol). Yield: (0.66 g, 75%). ^{1}H NMR data δ_H (300 MHz; DMSO-d_6): 8.45 (4H, m, Py-H), 8.23 (16H, m, Py-H), 8.12 (8H, s, Py-H), 8.06 (4H, m, Py-H), 7.97 (4H, m, Py-H), 7.40 (8H, d, *J= 6.6 Hz*, uncompleted Ar-H), 7.07 (8H, m, uncompleted Ar-H), 6.55 (16H, s, complexed Ar-H), 5.28 (20H, s, Cp-H), 4.32 (16H, s, CH_2), 4.08 (8H, m, CH_2), 3.43 (16H, s, CH_2), 2.73 (8H, m, CH_2), 2.51 (8H, m, CH_2), 2.17 (8H, m, CH_2), 2.03 (16H, s, CH_2), 1.71 (32H, m, CH_2), 1.49 (32H, m, CH_2). ^{13}C NMR δ_c (75 MHz; DMSO-d_6): 173.67, 171.44, and 168.04 (CO), 154.73, 154.35, 137.15, 136.89, 136.18, 131.81, 131.42, 128.99, 125.04, and 65.78 (quat-C), 130.55, 128.52, 127.34, 126.96, 125.75, 124.37, and 120.98 (uncomplexed Ar-C), 84.36 and 77.95 (complexed Ar-C), 79.55 (Cp-C), 64.69, 63.01, 61.56, 33.45, 32.21, 31.25, 29.83, 29.54, and 28.94 (**C**H_2). ATR-FTIR; ν_{max}/cm^{-1}: 2925 (Ar-CH), 2852 (Cp-C), 1700 (CO), 1232 (C-O-C). Elemental analysis for $C_{217}H_{232}O_{28}S_4Fe_4P_4F_{24}$: calc (C: 61.77; H: 5.54), found (C: 61.35; H: 5.82).



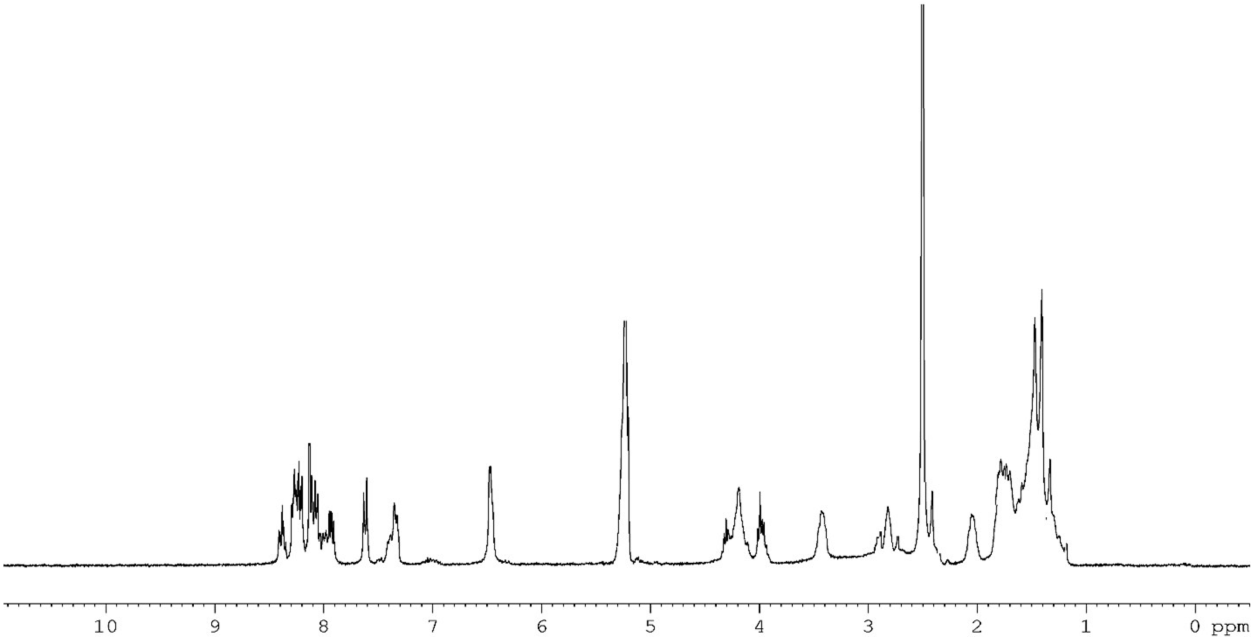


Figure 9. ^{1} H NMR spectra of dendrimer **D2b** in DMSO-d_6

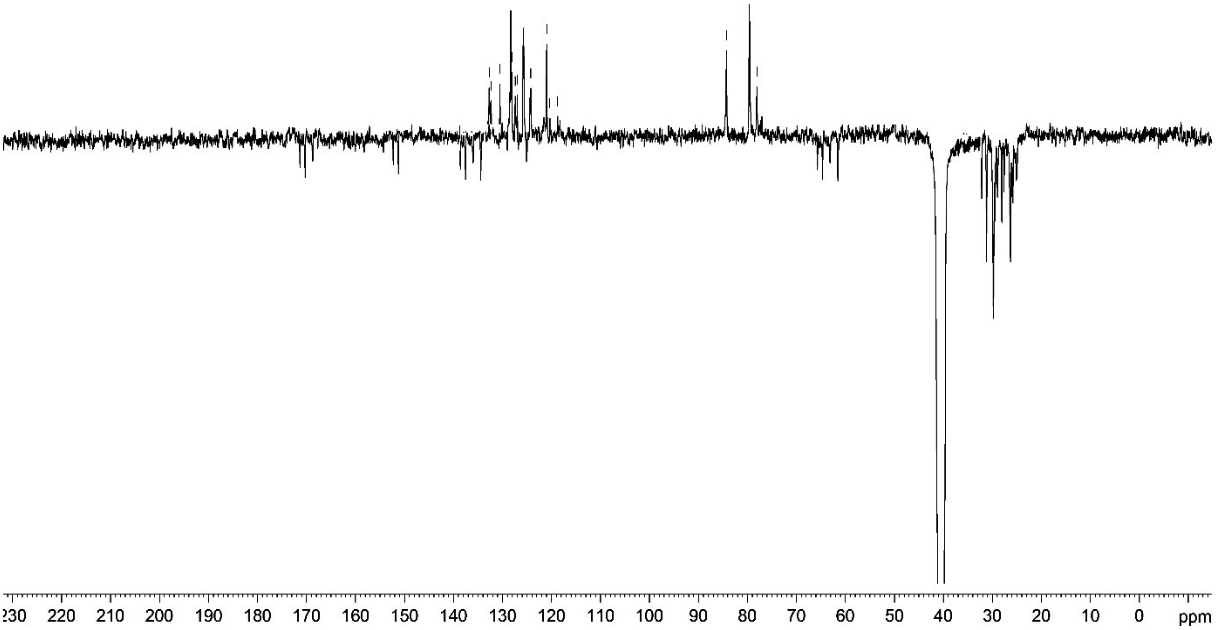


Figure 10. ^{13}C spectra of dendrimer **D2b** in DMSO-d_6

3.6 Demetallated pyrene-terminated G_0 dendrimer (D3a)

Dendrimer **D3a** was demetallated following a previously reported procedure.[5, 6] Dendrimer **D2a** (0.6 g, 0.15 mmol) was dissolved in 30 mL of acetonitrile in a Pyrex test tube and then flushed with nitrogen for 10 minutes. The mixture was irradiated with UV radiation for 24 hours in a Rayonett photochemical reactor equipped with 300 nm lamps. The mixture was then filtered through a small silica gel column and the solvent was evaporated. The residue was extracted with 50 mL chloroform and after that washed with three times 100 mL water. The extract was dried over $MgSO_4$, followed by evaporation of the chloroform. (Molecular weight 2932 g/mol). Yield: (0.3 g, 68%). ^1H NMR data δ_H (300 MHz; Acetone-d_6): 8.41 (20H, br s, Py-H), 8.02 (8H, s, Py-H), 8.07 (4H, m, Py-H), 8.00 (4H, m, Py-H), 7.55 (8H, d, *J= 6.3 Hz*, Ar-H), 7.43 (8H, br s, Ar-H), 7.09 (16H, s, Ar-H), 4.23 (8H, s, CH_2), 4.03 (8H, s, CH_2), 3.39 (8H, s, CH_2), 3.16 (8H, s, CH_2), 2.66 (8H, s, CH_2), 2.45 (8H, s, CH_2), 2.13 (8H, s, CH_2), 1.71 (24H, s, CH_2), 1.49 (32H, br s, CH_2). ^{13}C NMR δ_c (75 MHz; Acetone-d_6): 173.06, 171.14, and 168.27 (CO), 159.26, 156.26, 154.87, 154.39, 136.74, 131.48, 130.39, 128.99, and 64.35 (quat-C), 132.91, 132.00, 129.83, 127.93, 127.68, 126.46, 125.37, 125.18, 124.06, 120.17, and 118.27 (Ar-C), 64.35, 64.21, 62.81, 34.36, 33.81, 32.77, 32.30, 30.95, 27.71, 26.42 (**C**H_2). ATR-FTIR; ν_{max}/cm^{-1}: 2925 (Ar-CH), 1717 (CO), 1232 (C-O-C). Elemental analysis for $C_{181}H_{180}O_{28}S_4$: calc (C: 74.16; H: 6.19), found (C: 74.77; H: 6.35).

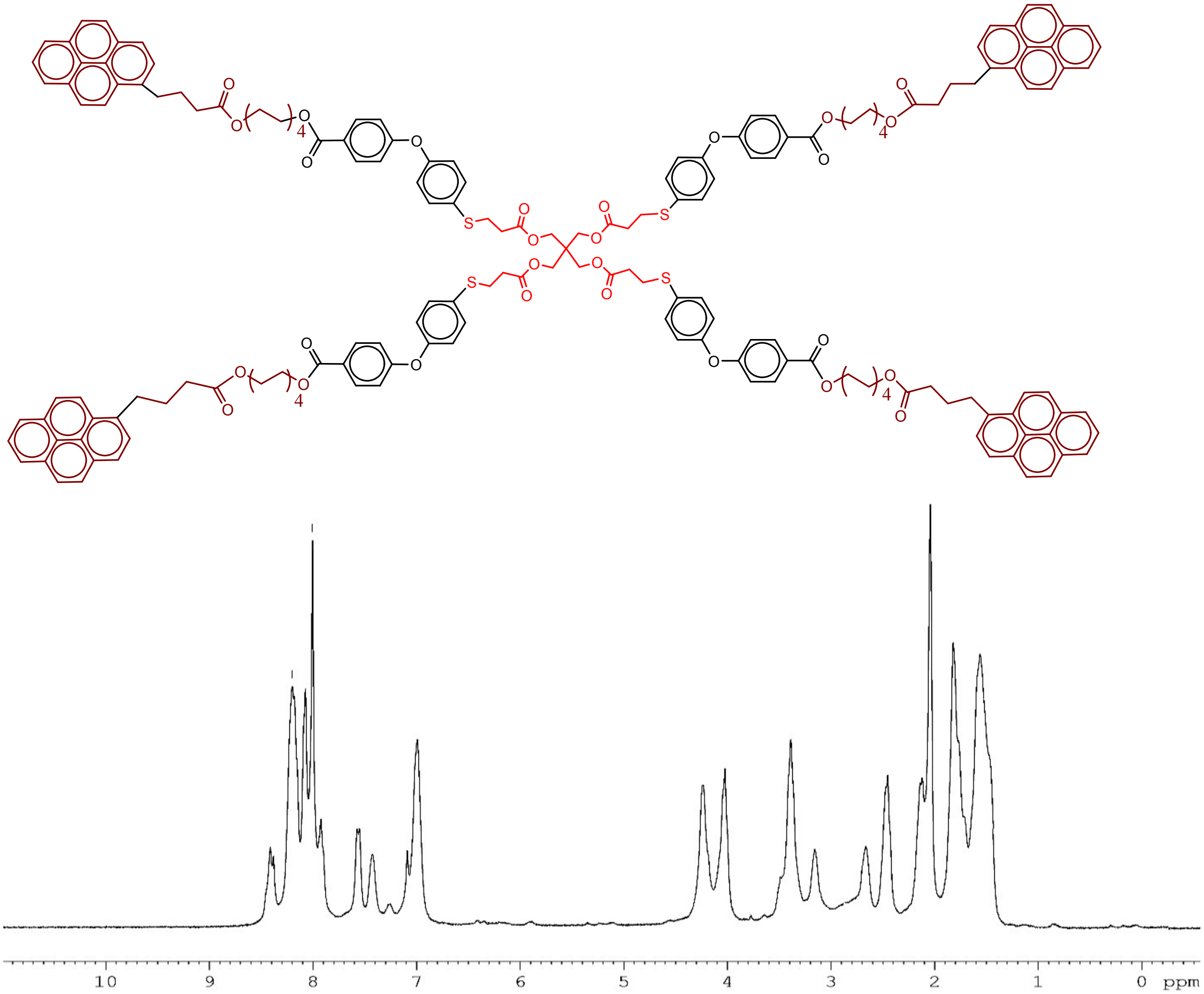


Figure 11. ^{1}H NMR spectra of dendrimer **D3a** in Acetone-d_6

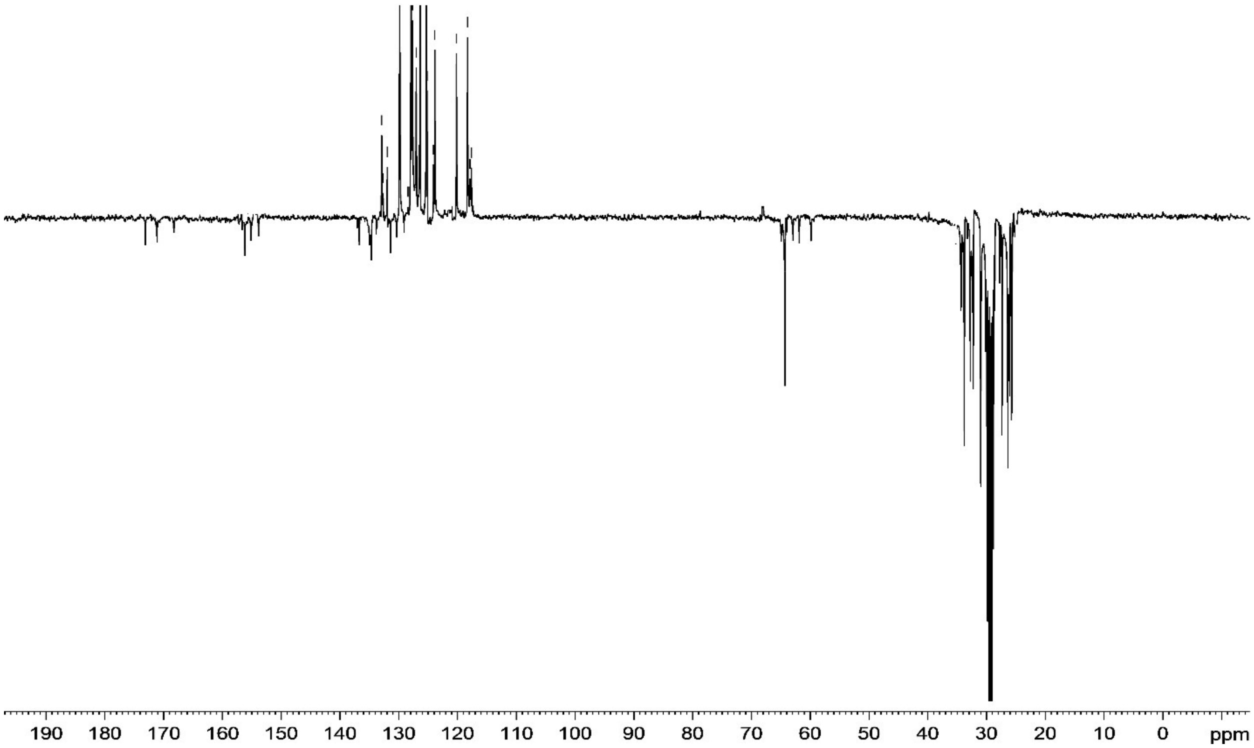
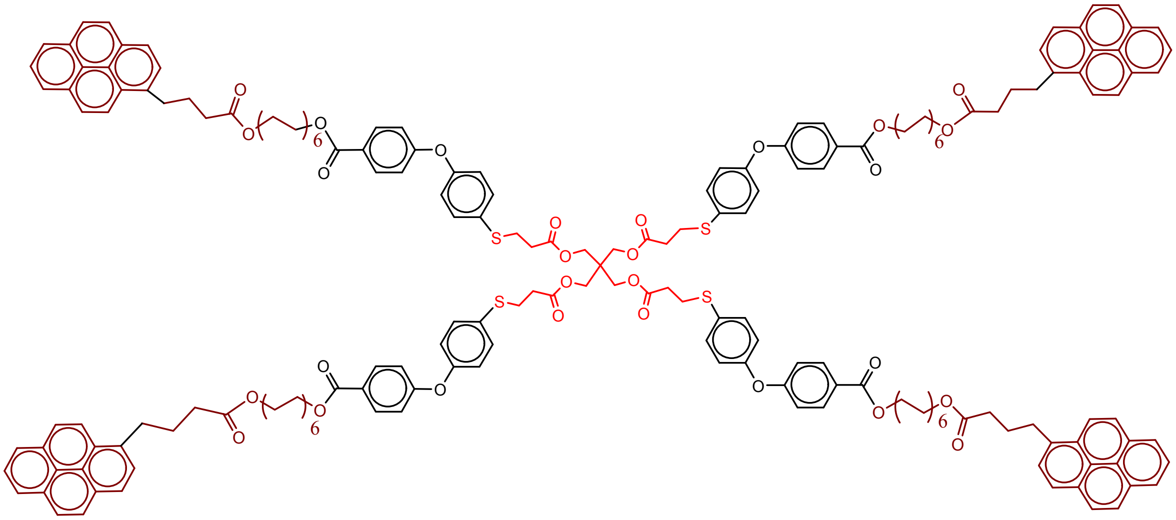


Figure 12. ^{13}C spectra of dendrimer **D3a** in Acetone-d$_6$

3.7 Demetallated pyrene-terminated G$_0$ dendrimer (D3b)

The demetallation of dendrimer **D3b** followed a procedure analogous to the demetallation of dendrimer **D3a** using dendrimer **D2b** (0.5 g, 0.12 mmol). (Molecular weight 3156 g/mol). Yield: (0.22 g, 59%). ^{1}H NMR data δ_H (300 MHz; Acetone-d$_6$): 8.47 (4H, m, Py-H), 8.25 (16H, m, Py-H), 8.21 (8H, s, Py-H), 8.12 (4H, m, Py-H), 7.98 (4H, m, Py-H), 7.59 (8H, br s, Ar-H), 7.47 (8H, br s, Ar-H), 7.04 (16H, s, Ar-H), 4.27 (8H, s, CH$_2$), 4.08 (8H, m, CH$_2$), 3.51 (8H, s, CH$_2$), 3.42 (16H, m, CH$_2$), 2.71 (8H, s, CH$_2$), 2.51 (8H, m, CH$_2$), 2.17 (8H, m, CH$_2$), 1.85 (16H, s, CH$_2$), 1.78 (16H, m, CH$_2$), 1.74 (16H, s, CH$_2$), 1.62 (32H, m, CH$_2$). ^{13}C NMR δ_c (75 MHz; Acetone-d$_6$): 173.15, 171.16 and 170.64 (CO), 159.31, 156.23, 154.82, 154.40, 137.15, 131.95, 131.42, and 64.23 (quat-C), 133.44, 132.86, 129.81, 128.08, 126.43, 124.12, 120.20, and 118.35 (Ar-C), 62.77, 61.78, 34.39, 33.81, 32.85, 32.44, 32.28, 27.40, 26.39, 28.23, 25.77, and 25.66 (**C**H_2). ATR-FTIR; ν_{max}/cm^{-1}: 2925 (Ar-CH), 1700 (CO), 1232 (C-O-C). Elemental analysis for $C_{197}H_{212}O_{28}S_4$: calc (C: 74.97; H: 6.77), found (C: 75.46; H: 6.93).



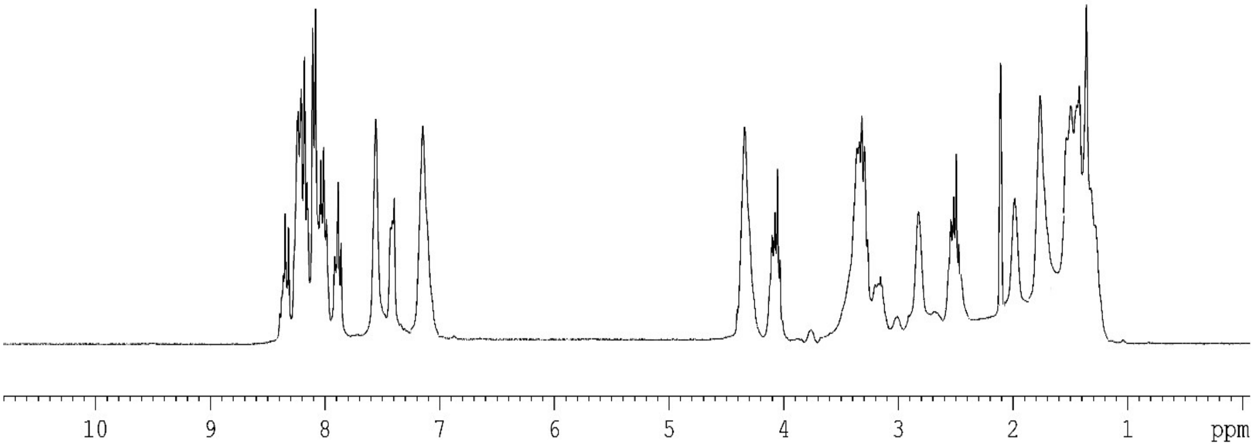


Figure 13. ^{1}H NMR spectra of dendrimer **D3b** in Acetone-d_6

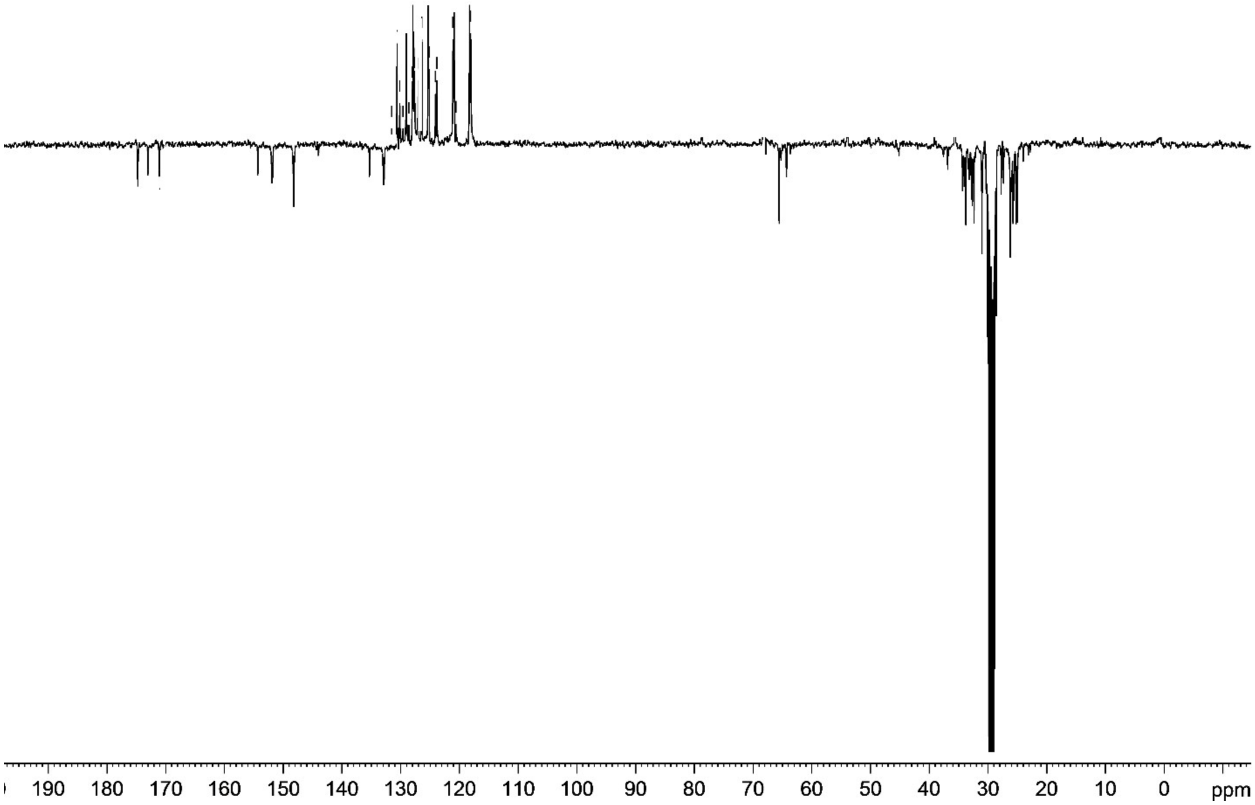
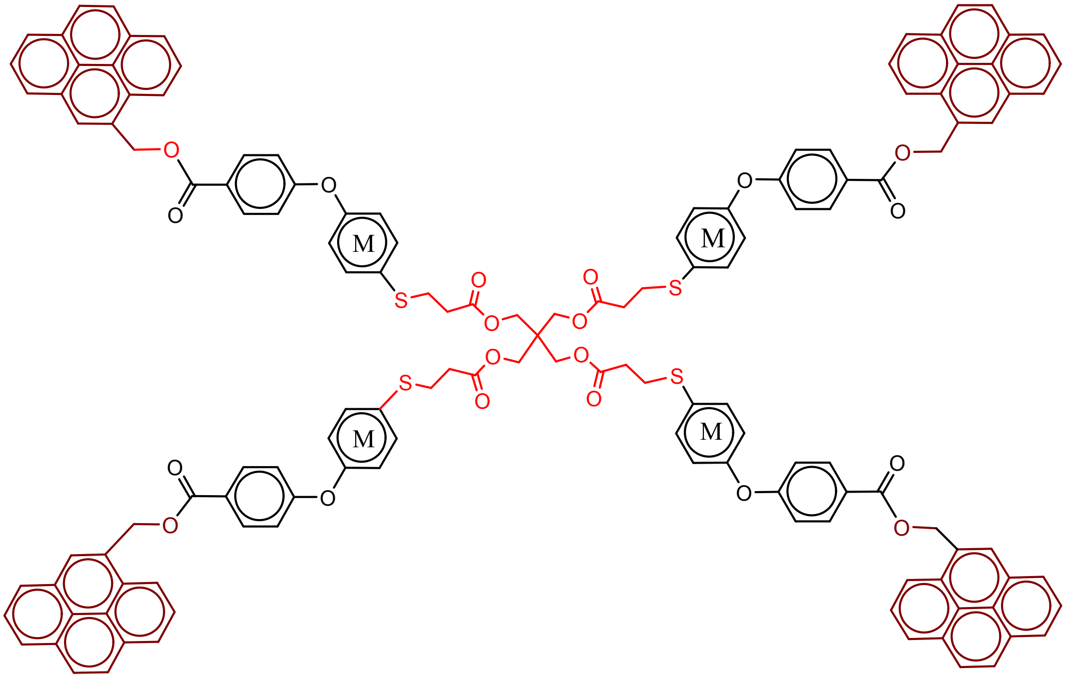


Figure 14. ^{13}C spectra of dendrimer **D3b** in Acetone-d_6

3.8 Pyrene-terminated G0 dendrimer (D4)

The synthesis of dendrimer **D4** followed a procedure analogous to the synthesis of dendrimer **D2**. In 50-mL round-bottom flask was charged with dendrimer **D1** (0.5 g, 0.21 mmol), compound **6** (0.19 g, 0.83 mmol), DMAP (0.1 g, 0.83 mmol), DCC (0.17 g, 0.83 mmol), and 5 mL of DMF. (Molecular weight 3258 g/mol). Yield: (0.55 g, 81%). ^{1}H NMR data δ_H (300 MHz; DMSO-d_6): 8.36 (4H, m, Py-H), 8.21 (16H, m, Py-H), 8.16 (8H, s, Py-H), 8.13 (4H, m, Py-H), 8.05 (4H, m, Py-H), 7.65 (8H, d, *J= 8.1 Hz*, uncompleted Ar-H), 7.34 (8H, br s, uncompleted Ar-H), 6.43 (16H, s, complexed Ar-H), 5.23 (8H, s, CH_2), 5.12 (20H, s, Cp-H), 4.18 (8H, s,

CH_2), 3.84 (8H, s, CH_2), 2.80 (8H, m, CH_2). ^{13}C NMR δ_c (75 MHz; DMSO-d_6): 171.52 and 167.93 (CO), 165.69, 158.41, 154.54, 132.08, 131.59, 131.05, 128.66, 125.93, 125.54, and 65.99 (quat-C), 132.65, 130.51, 129.05, 128.16, 126,39, 124.31, and 121.04 (uncomplexed Ar-C), 84.27 and 78.05 (complexed Ar-C), 79.55 (Cp-C), 63.22, 62.24, 34.08, 33.82, and 32.18 (**C**H_2). ATR-FTIR; ν_{max}/cm^{-1}: 2926 (Ar-CH), 2851 (Cp-C), 1696 (CO), 1230 (C-O-C). Elemental analysis for $C_{157}H_{120}O_{20}S_4Fe_4P_4F_{24}$: calc (C: 57.88; H: 3.71), found (C: 58.31; H: 3.97).



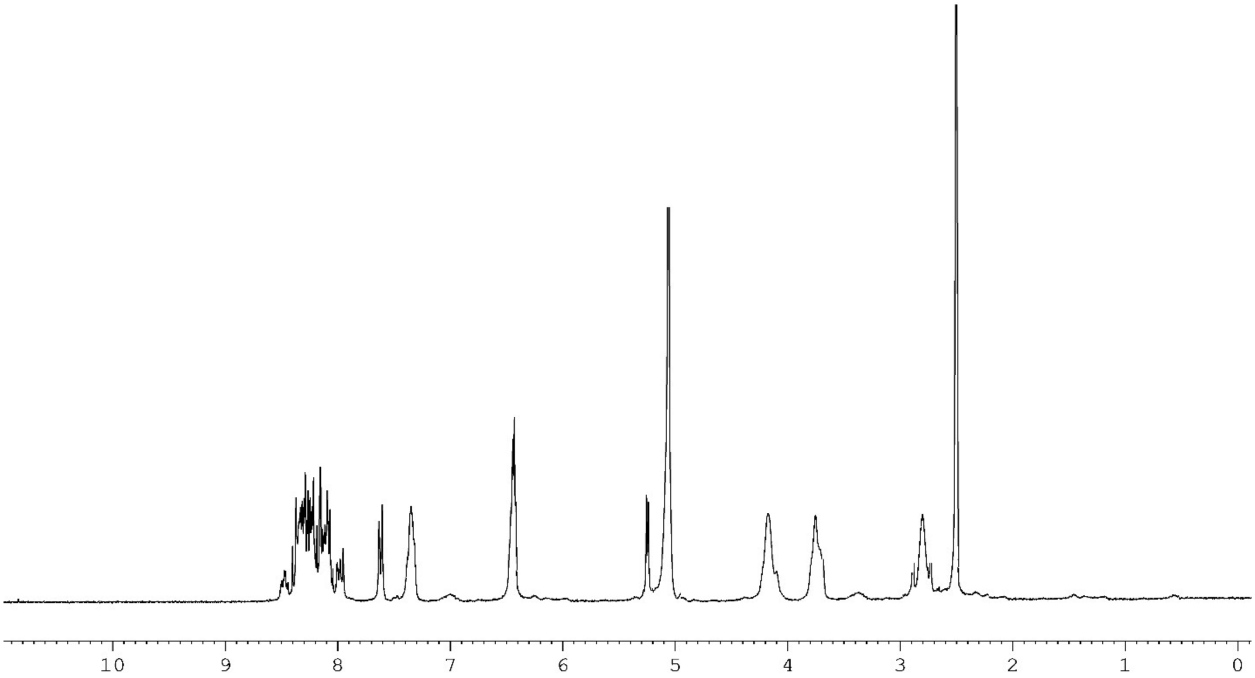


Figure 15. ^{1}H NMR spectra of dendrimer **D4** in DMSO-d_6

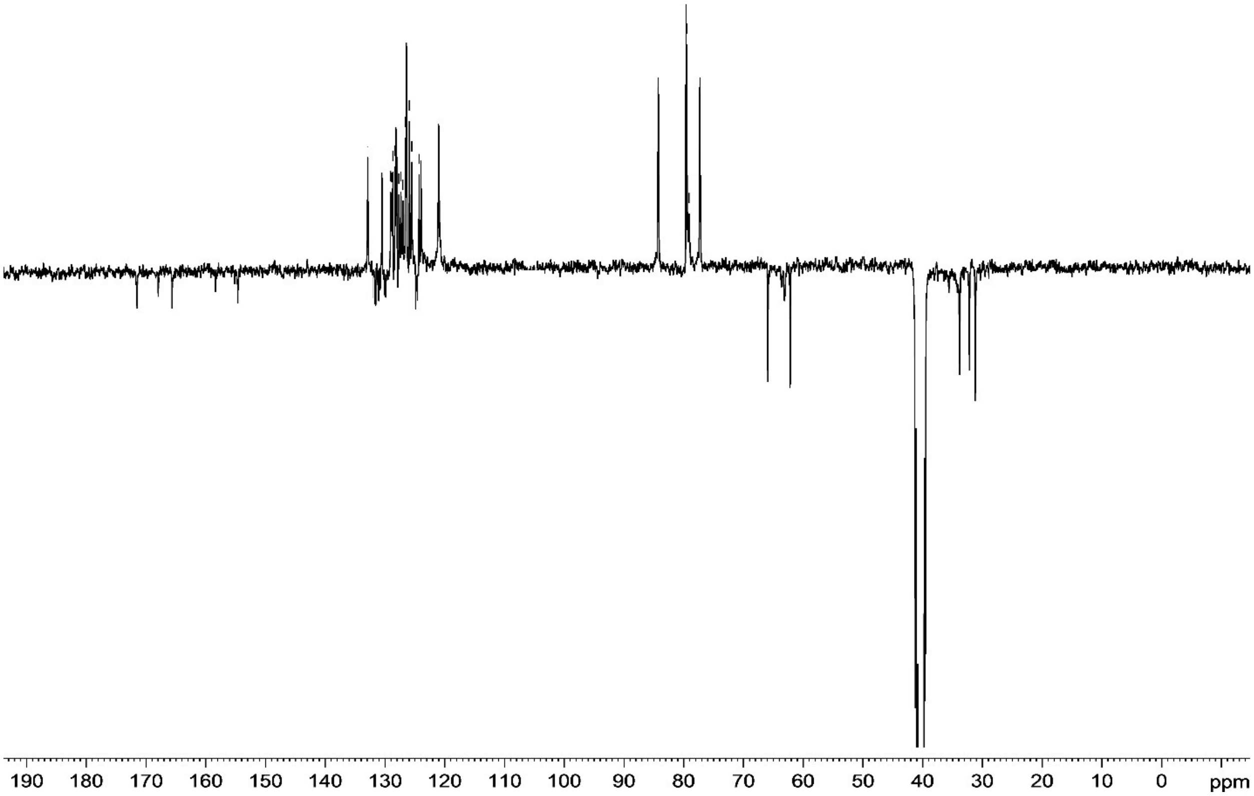
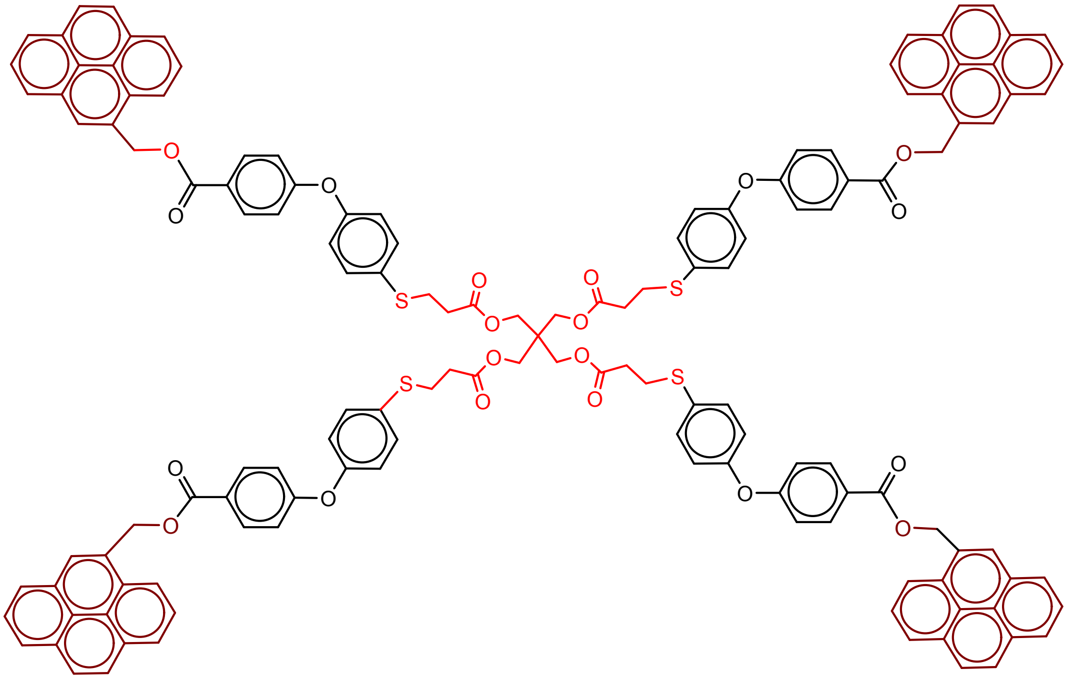


Figure 16. ^{13}C spectra of dendrimer **D4** in DMSO-d_6

3.9 Demetallated pyrene-terminated G_0 dendrimer (D5)

The demetallation of dendrimer **D5** followed a procedure analogous to the demetallation of dendrimer **D3** using dendrimer **D4** (0.5 g, 0.15 mmol). (Molecular weight 2195 g/mol). Yield: (0.21 g, 62%). ^{1}H NMR data δ_H (300 MHz; Acetone-d$_6$): 8.47 (4H, m, Py-H), 8.30 (16H, m, Py-H), 8.26 (8H, s, Py-H), 8.18 (4H, m, Py-H), 8.03 (4H, m, Py-H), 7.59 (8H, d, *J= 8.1 Hz*, Ar-H), 7.44 (8H, br s, Ar-H), 7.01 (16H, s, Ar-H), 5.40 (8H, s, CH_2), 4.25 (8H, s, CH_2), 3.18 (8H, s, CH_2), 2.66 (8H, br s, CH_2). ^{13}C NMR δ_c (75 MHz; Acetone-d$_6$): 171.08, 168.53, and 165.67 (CO), 165.69, 158.41, 154.54, 132.08, 131.59, 131.05, 128.66, 125.93, 125.54, and 65.17 (quat-C), 132.75, 131.18, 129.84, 128.16, 127.32, 126,32, 125.84, 121.04, and 1218.36 (Ar-C), 64.09, 35.14, 34.37, and 30.95 ($\mathbf{C}H_2$). ATR-FTIR; ν_{max}/cm^{-1}: 2926 (Ar-CH), 1696 (CO), 1230 (C-O-C). Elemental analysis for $C_{137}H_{100}O_{20}S_4$: calc (C: 74.98; H: 4.59), found (C: 75.62; H: 4.83).



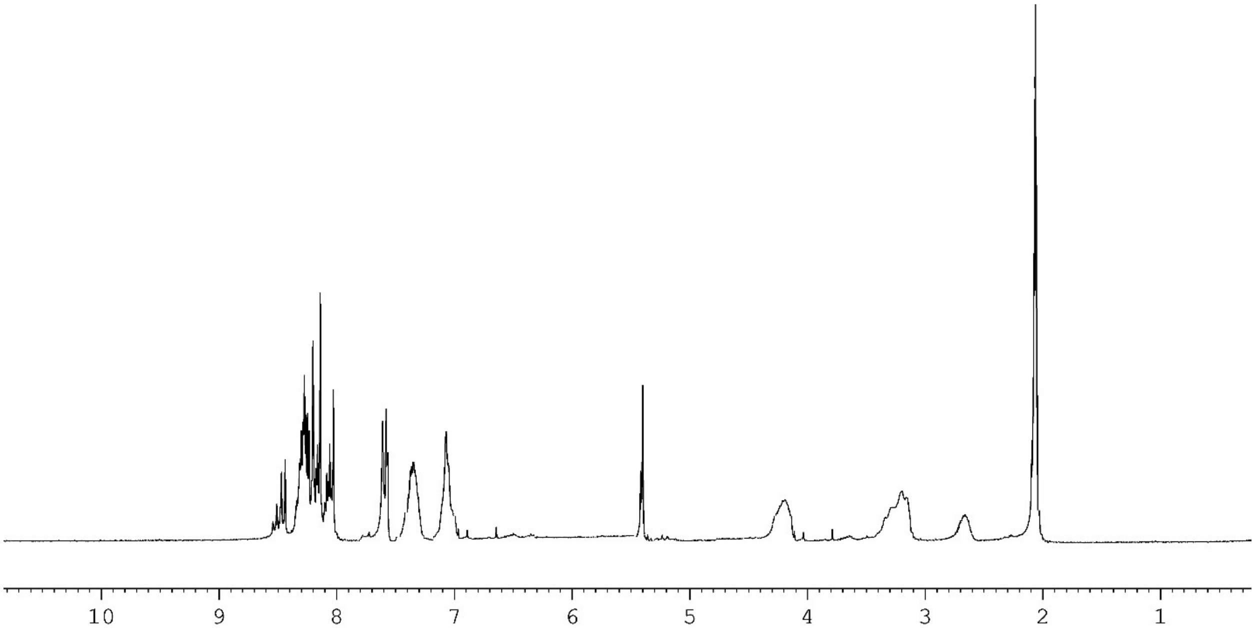


Figure 17. ^{1}H NMR spectra of dendrimer **D5** in Acetone-d_6

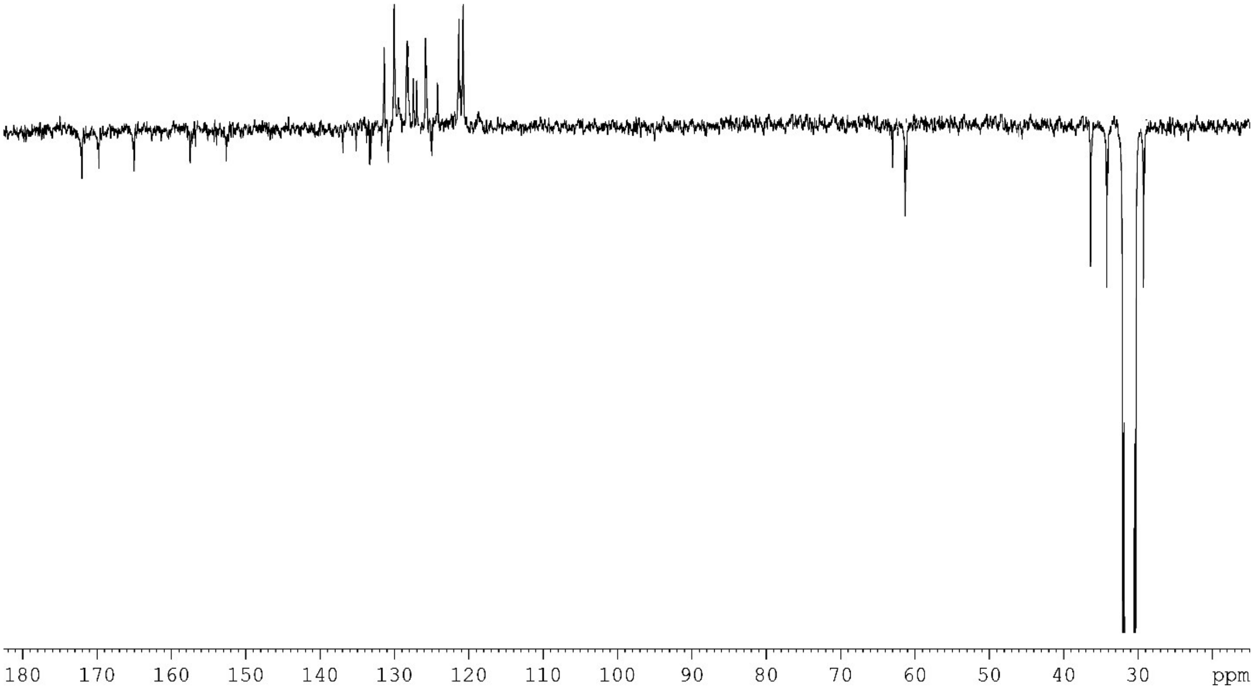
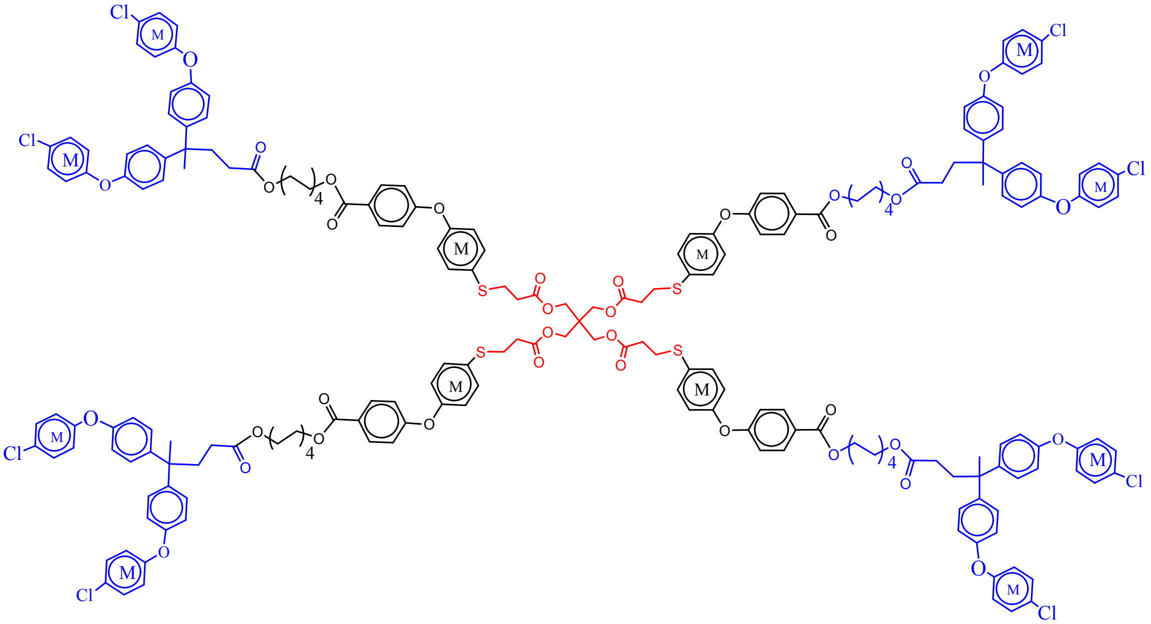


Figure 18. ^{13}C spectra of dendrimer **D5** in Acetone-d_6

3.10 Chloro-terminated G_1 dendrimer (D6)

Compound **7** was used to synthesize dendrimer **D6**, following the Steglich esterification procedure. A 50 mL round-bottom flask was charged with dendrimer **D1** (1 g, 0.42 mmol), **7** (1.94 g, 1.67 mmol), DMAP (0.2 g, 1.67 mmol), and 10 mL of DMF. The solution was stirred at 0°C under nitrogen atmosphere while DCC (0.34 g, 1.67 mmol) was added over a 5 minute period. The reaction mixture was stirred under nitrogen for 24 hours at room temperature. The reaction mixture was cooled to -25°C in a freezer for two hours then filtered to remove dicyclohexylurea (DCU) and then poured in to 100 mL of 10% HCl solution, and NH_4PF_6 (0.27 g, 1.67 mmol) was added to precipitate the product. The remaining DCU was removed by dissolving the product in acetone, cooling to -25°C in a freezer for two hour, filtering to remove more DCU and pouring into 100 mL of 10% HCl solution, into which NH_4PF_6 (0.27 g, 1.67 mmol) was added to precipitate the product. The product was a resulting yellow solid collected by suction filtration and dried under vacuum at room temperature. (Molecular weight 6999 g/mol). Yield: (2.40 g, 82%). ^{1}H NMR data δ_H (300 MHz; Acetone-d$_6$): 7.37 (24H, s, uncompleted Ar-H), 7.29 (24H, s, uncompleted Ar-H), 6.82 (16H, s, complexed Ar-H), 6.44 (32H, d, s, complexed Ar-H), 5.28 (40H, s, Cp-H), 5.15 (20H, s, Cp-H), 4.22 (16H, s, CH_2), 3.98 (8H, br s, CH_2), 3.48 (16H, s, CH_2), 2.43 (8H, s, CH_2), 2.12 (8H, s, CH_2), 1.78 (24H, m, CH_2), 1.67 (12H, s, CH_3), 1.52 (24H, s, CH_2). ^{13}C NMR δ_c (75 MHz; DMSO-d$_6$,): 173.72 and 171.53 (CO), 167.96, 165.79, 155.19, 152.03, 147.12, 104.57, and 65.70 (quat-C), 132.83, 130.59, 130.14, and 121.09 (uncomplexed Ar-C), 87.69 and 77.32 (complexed Ar-

C), 80.23 and 79.67 (Cp-C), 64.89, 63.18, 45.88, 36.89, 33.82, 32.17, 30.60, 29.49, and 28.07 (CH_2), 27.82 (CH_3). ATR-FTIR; ν_{max}/cm^{-1}: 2930 (Ar-CH), 2856 (Cp-CH), 1729 (CO), 1241 (C-O-C). Elemental analysis for $C_{277}H_{272}O_{36}S_4Cl_8Fe_{12}P_{12}F_{72}$: calc (C: 47.54; H: 3.92), found (C: 47.98; H: 4.09).



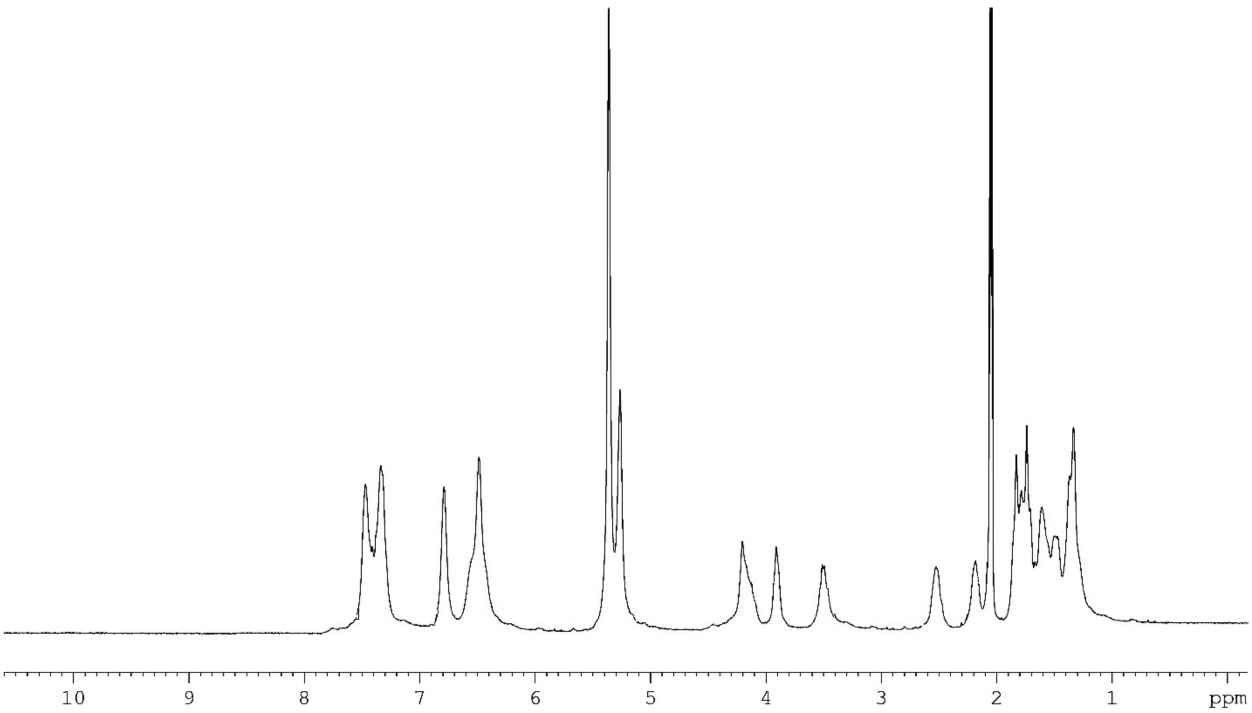


Figure 19. ^{1}H NMR spectra of dendrimer **D6** in Acetone-d$_6$

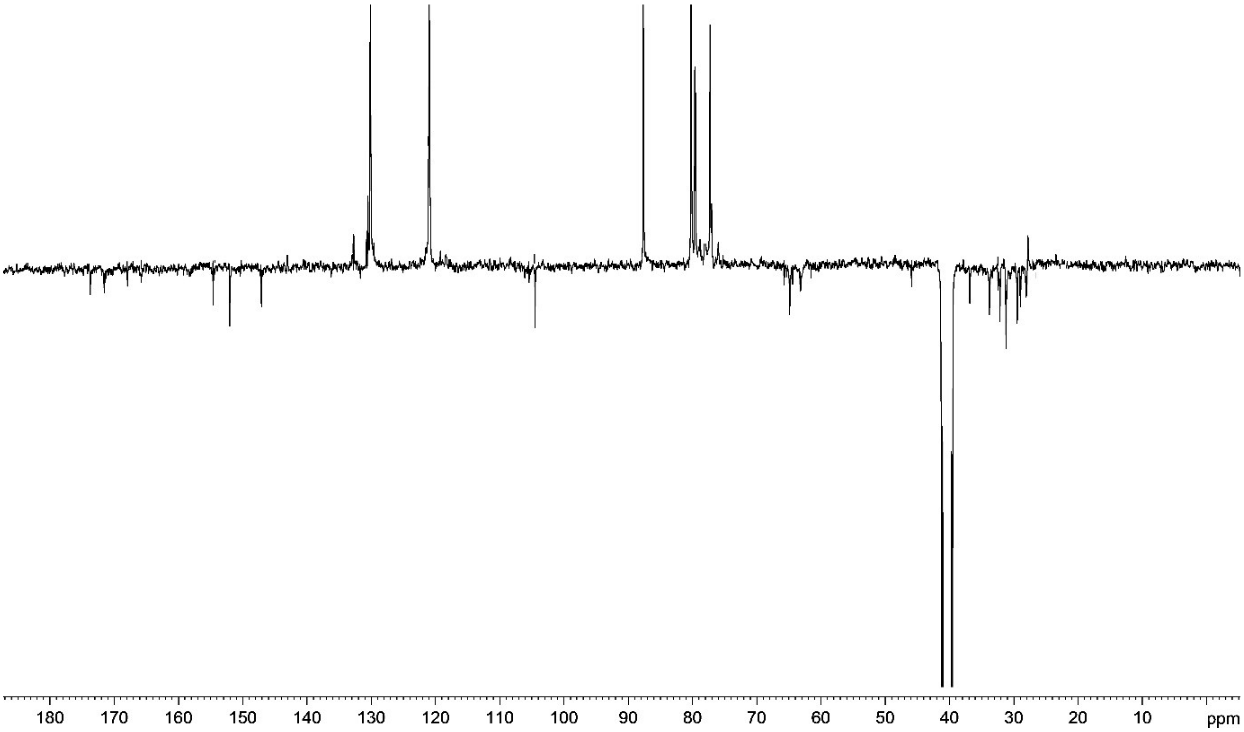


Figure 20. ^{13}C spectra of dendrimer **D6** in DMSO-d$_6$

3.11 Hydroxybenzyl alcohol-terminated G_1 dendrimer (D7)

The synthesis of dendrimer **D7** followed a procedure analogous to the synthesis of dendrimer **D1**. A 50 mL round-bottom flask was charged with dendrimer **D6** (1 g, 0.14 mmol), **8** (0.14 g, 1.14 mmol), K_2CO_3 (0.79 g, 5.71 mmol), and 10 mL of DMF. (Molecular weight 7700 g/mol). Yield: (0.86 g, 78%). ^{1}H NMR data δ_H (300 MHz; DMSO-d$_6$): 7.50 (16H, d, J= 8.4 Hz, uncompleted Ar-H), 7.37 (16H, m, uncompleted Ar-H), 7.25 (48H, m, uncomplexed Ar-H), 6.26 (48H, m, completed Ar-H), 5.22 (60H, s, Cp-H), 5.09 (16H, s, CH_2), 4.37 (8H, s, OH), 4.11 (16H, s, CH_2), 3.97 (8H, s, CH_2), 3.48 (16H, s, CH_2), 2.43 (8H, s, CH_2), 2.13 (8H, s, CH_2), 1.78 (24H, m, CH_2), 1.65 (12H, m, CH_3), 1.52 (24H, m, CH_2). ^{13}C NMR δ_c (75 MHz; DMSO-d$_6$,): 174.00 and 173.80 (CO), 166.02, 152.84, 146.75, 141.68, 133.04, 132.74, 131.39, and 65.66 (quat-C), 130.68, 129.51, 121.13, and 120.77 (uncomplexed Ar-C), 78.78 (Cp-C), 76.05 and 75.43 (complexed Ar-C), 64.89, 63.08, 36.88, 33.52, 33.34, 30.62, 29.39, and 28.85 (CH_2), 27.89 (CH_3). ATR-FTIR; ν_{max}/cm^{-1}: 3311 (OH), 2925 (Ar-CH), 2852 (Cp-CH), 1720 (CO), 1229 (C-O-C). Elemental analysis for $C_{333}H_{328}O_{52}S_4Fe_{12}P_{12}F_{72}$: calc (C: 51.94; H: 4.29), found (C: 52.46; H: 4.48).

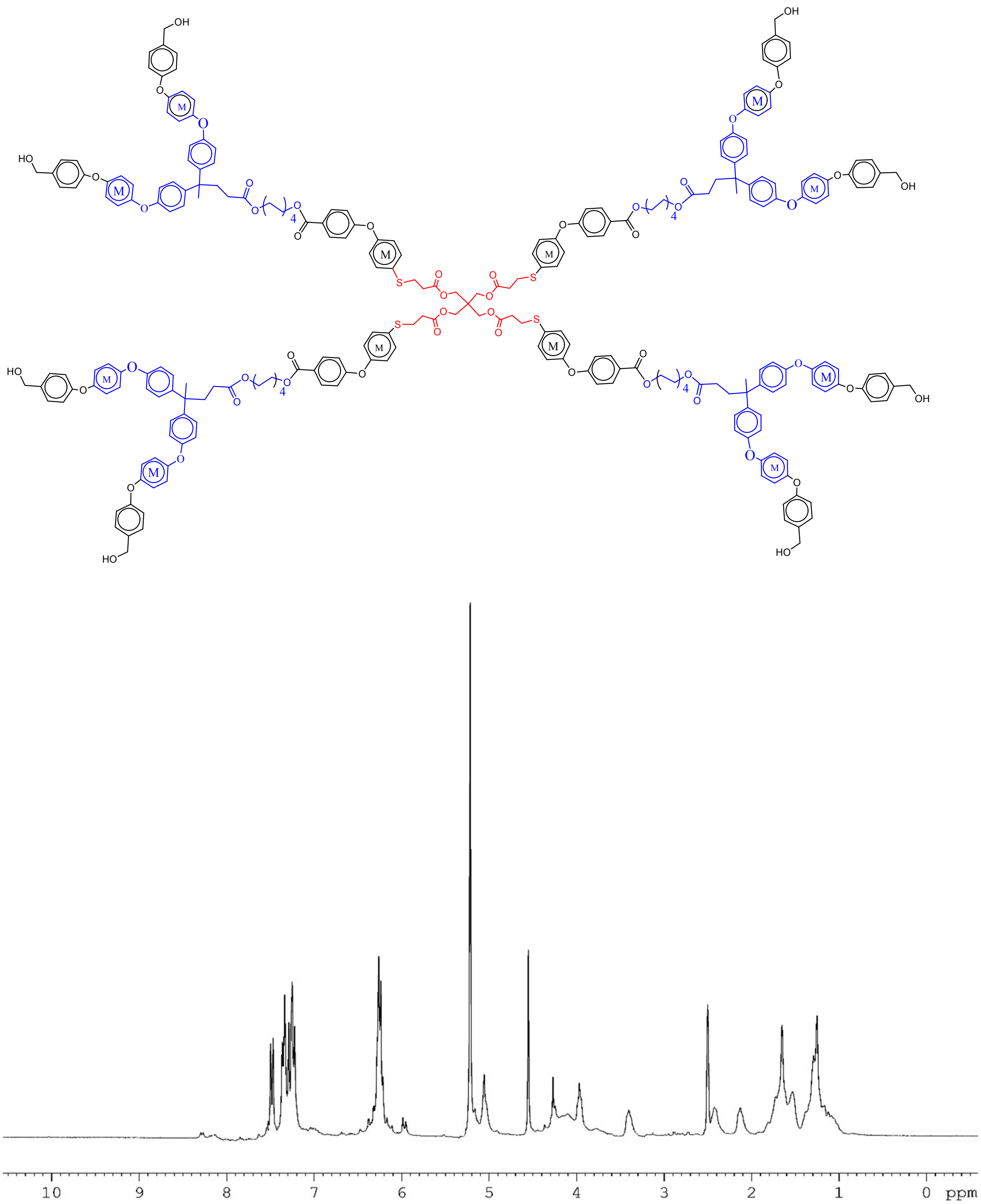


Figure 21. ^{1}H NMR spectra of dendrimer **D7** in DMSO-d_6

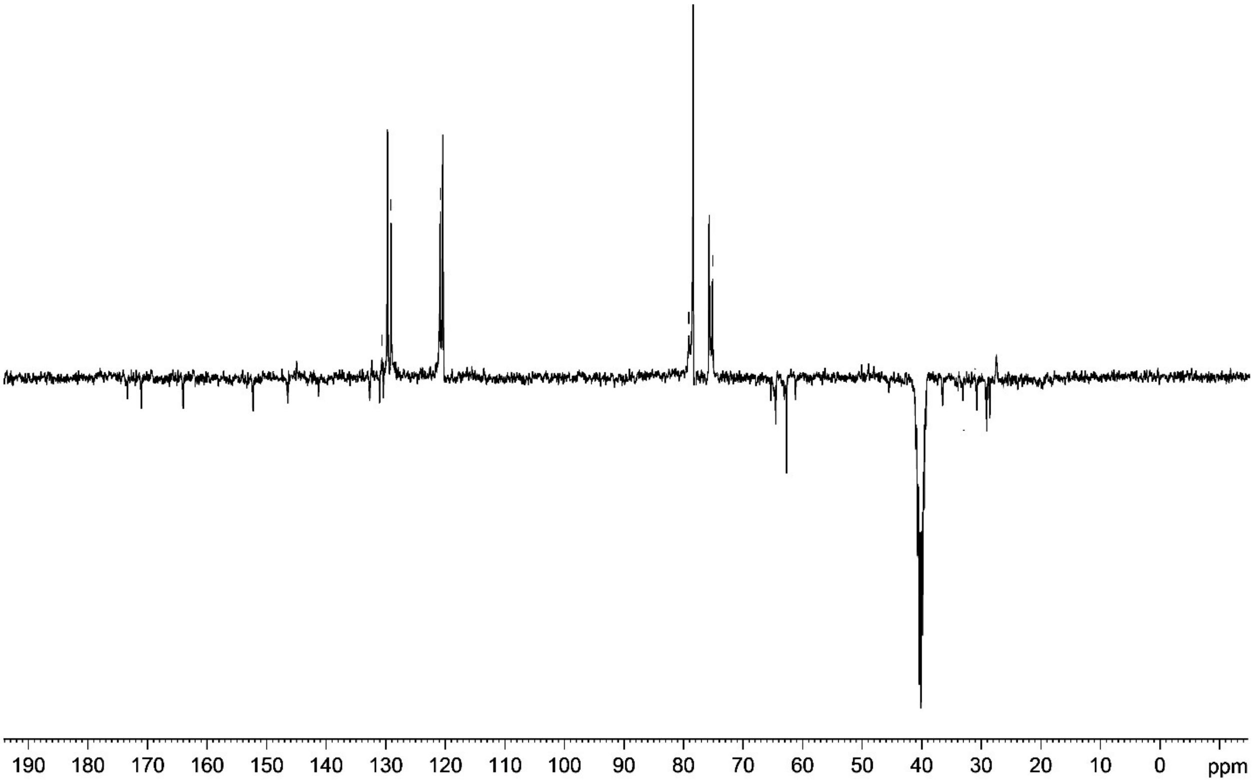
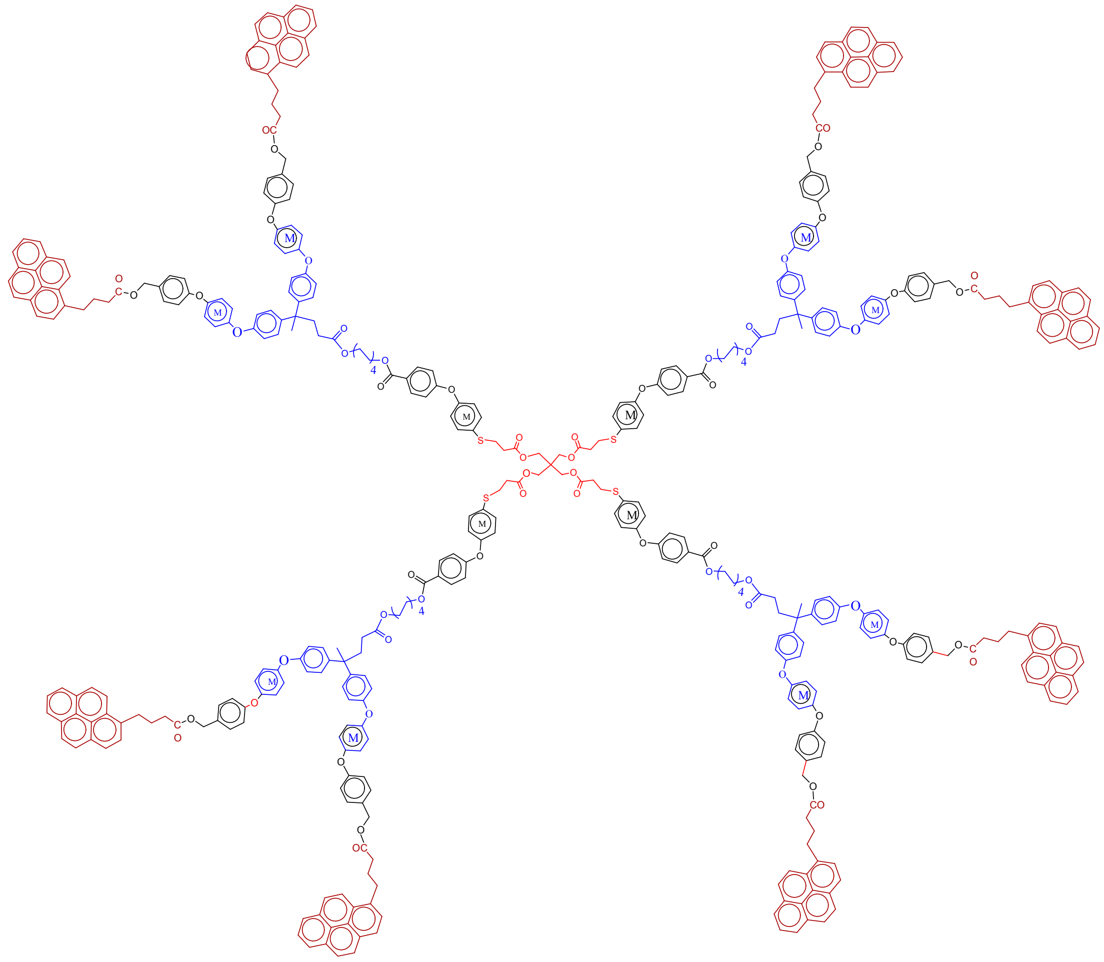


Figure 22. ^{13}C spectra of dendrimer **D7** in DMSO-d$_6$

3.12 Pyrene-terminated G$_1$ dendrimer (D8)

The synthesis of dendrimer **D8** followed a procedure analogous to the synthesis of dendrimer **D4**. A 50 mL round-bottom flask was charged with dendrimer **D7** (0.5 g, 0.06 mmol), **1** (0.15 g, 0.52 mmol), DMAP (0.06 g, 0.52 mmol), DCC (0.11 g, 0.52 mmol), and 5 mL of DMF. (Molecular weight 9863 g/mol). Yield: (0.43 g, 67%). ^{1}H NMR data δ_H (300 MHz; DMSO-d$_6$): 8.37 (8H, m, Py-H), 8.25 (32H, m, Py-H), 8.11 (16H, s, Py-H), 8.07 (8H, m, Py-H), 8.04 (8H, m, Py-H), 7.52 (16H, s, uncompleted Ar-H), 7.33 (32H, br s, uncompleted Ar-H), 7.23 (32H, s, uncomplexed Ar-H), 6.22 (48H, s, completed Ar), 5.21 (20H, s, Cp-H), 5.17 (40H, s, Cp-H), 5.03 (24H, s, CH$_2$), 4.26 (8H, s, CH$_2$), 3.95 (16H, s, CH$_2$), 3.46 (8H, s, CH$_2$), 3.17 (16H, s, CH$_2$), 2.40 (24H, s, CH$_2$), 2.08 (24H, s,

CH_2), 1.78 (24H, s, CH_2), 1.69 (12H, s, CH_3), 1.52 (24H, br s, CH_2). ^{13}C NMR δ_c (75 MHz; DMSO-d_6,): 173.71 and 173.49 (C=O), 156.09, 154.30, 153.98, 146.68, 136.94, 131.39, 130.91, 129.55, 128.13, 124.26, and 65.66 (quat-C), 143.06, 135.15, 130.29, 128.96, 128.33, 127.08, 124.26, 125.86, 121.38, and 120.80 (complexed Ar-C), 78.70 (Cp-C), 76.08, and 75.91 (complexed Ar-C), 64.89, 63.08, 36.88, 33.52, 33.34, 30.62, 29.39, and 28.85 (CH_2), 27.89 (CH_3). ATR-FTIR: ν_{max}/cm^{-1} 2933 (Ar-CH), 2854 (Cp-CH), 1717 (CO), 1227 (C-O-C). Elemental analysis for $C_{493}H_{440}O_{60}S_4Fe_{12}P_{12}F_{72}$: calc (C: 60.04; H: 4.50), found (C: 60.66; H: 4.94).



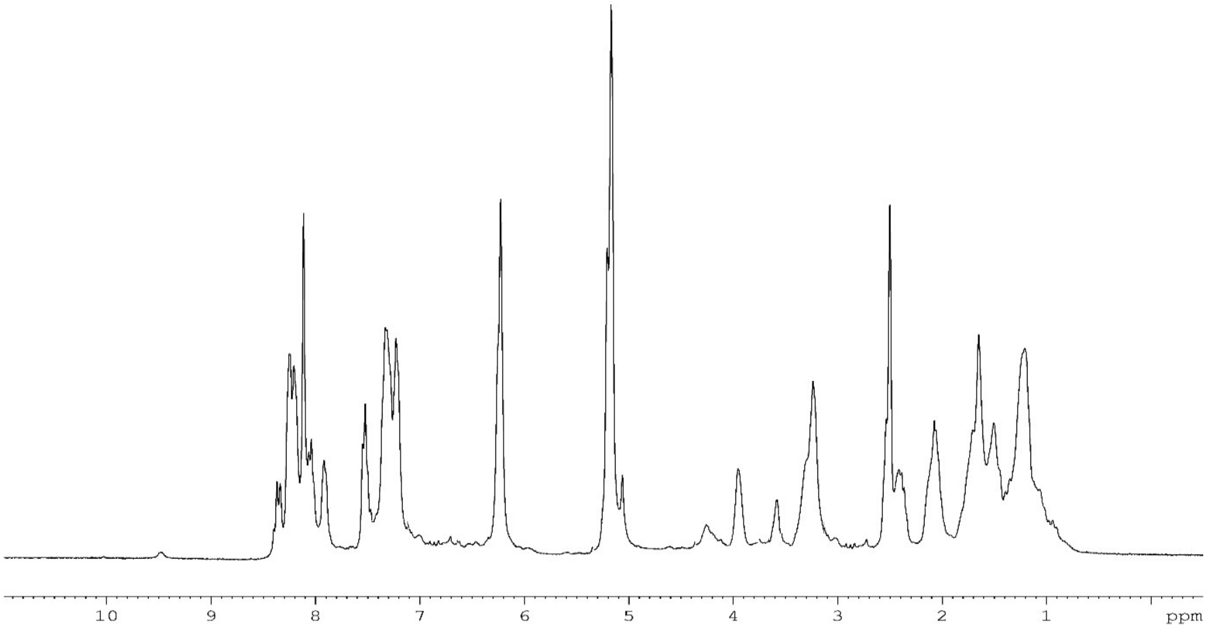


Figure 23. ^{1}H NMR spectra of dendrimer **D8** in DMSO-d$_6$

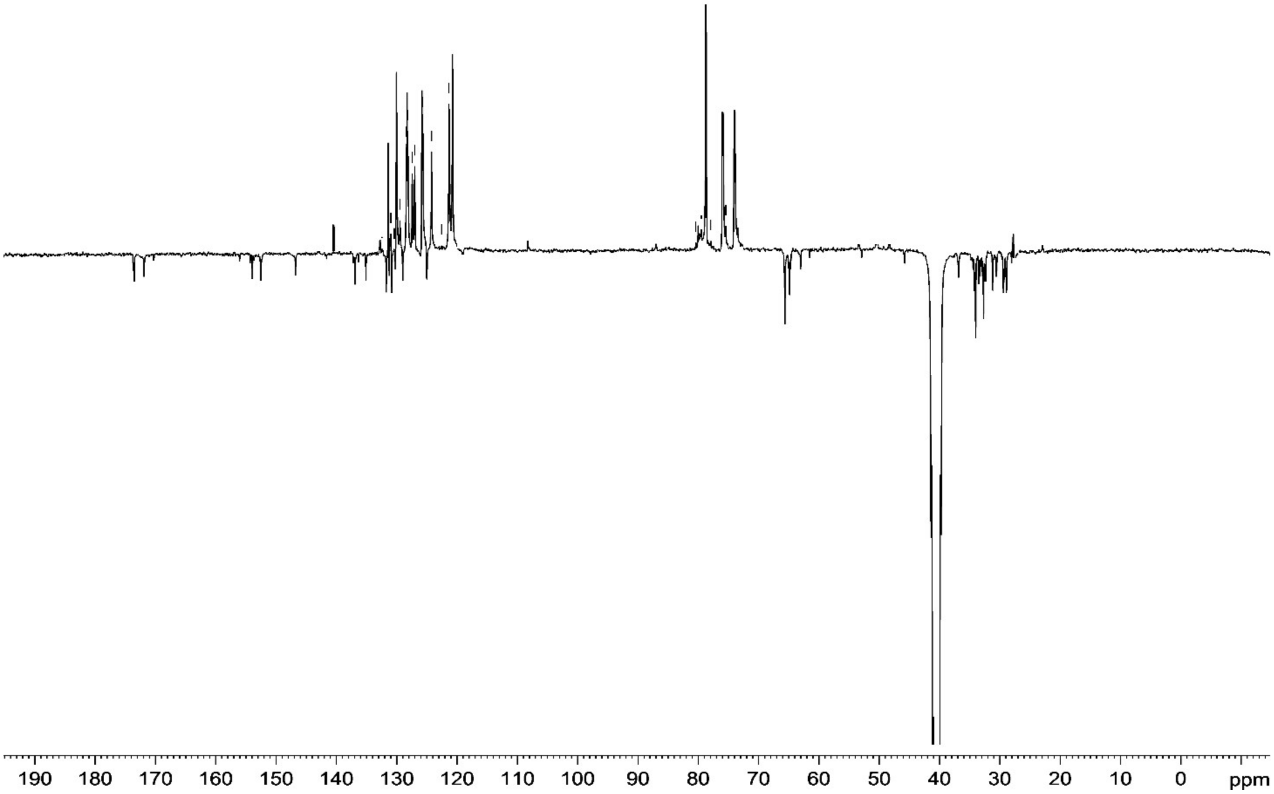


Figure 24. ^{13}C spectra of dendrimer **D8** in DMSO-d$_6$

3.13 Demetallated pyrene-terminated G_1 dendrimer (D9)

The demetallation of dendrimer **D9** followed a procedure analogous to the demetallation of dendrimer **D3** using dendrimer **D8** (0.3 g, 30.42 μM). (Molecular weight 6672 g/mol). Yield: (0.14 g, 69%). ^{1}H NMR data δ_H (300 MHz; Acetone-d_6): 8.36 (8H, m, Py-H), 8.26 (32H, m, Py-H), 8.17 (16H, s, Py-H), 8.12 (8H, m, Py-H), 8.05 (8H, m, Py-H), 7.52 (16H, m, Ar-H), 7.33 (32H, s, Ar-H), 7.23 (32H, s, Ar-H), 6.98 (48H, m, Ar-H), 5.14 (24H, s, CH_2), 4.18 (8H, s, CH_2), 3.88 (16H, s, CH_2), 3.43 (8H, m, CH_2), 3.23 (16H, m, CH_2), 2.51 (24H, s, CH_2), 2.17 (24H, s, CH_2), 1.83 (24H, m, CH_2), 1.78 (12H, s, CH_3), 1.65 (24H, s, CH_2). ^{13}C NMR δ_c (75 MHz; Acetone-d_6,): 173.24 and 172.95 (CO), 158.34, 156.25, 152.87, 143.97, 137.22, 136.61, 130.51, 13015, 124.13, 123.89, and 65.71 (quat-C), 130.71, 130.16, 129.05, 127.95, 126.41, 125.37, 123.90, 121.19, 120.95, and 118.25 (Ar-C), 64.38, 45.11, 36.94, 34.33, 33.84, 32.82, 32.44, 31.09, 27.74, and 26.22 (CH_2), 27.74 (CH_3). ATR-FTIR; ν_{max}/cm^{-1}: 2933 (Ar-CH), 1717 (CO), 1227 (C-O-C). Elemental analysis for $C_{433}H_{380}O_{60}S_4$: calc (C: 77.95; H: 5.74), found (C: 78.44; H: 6.02).

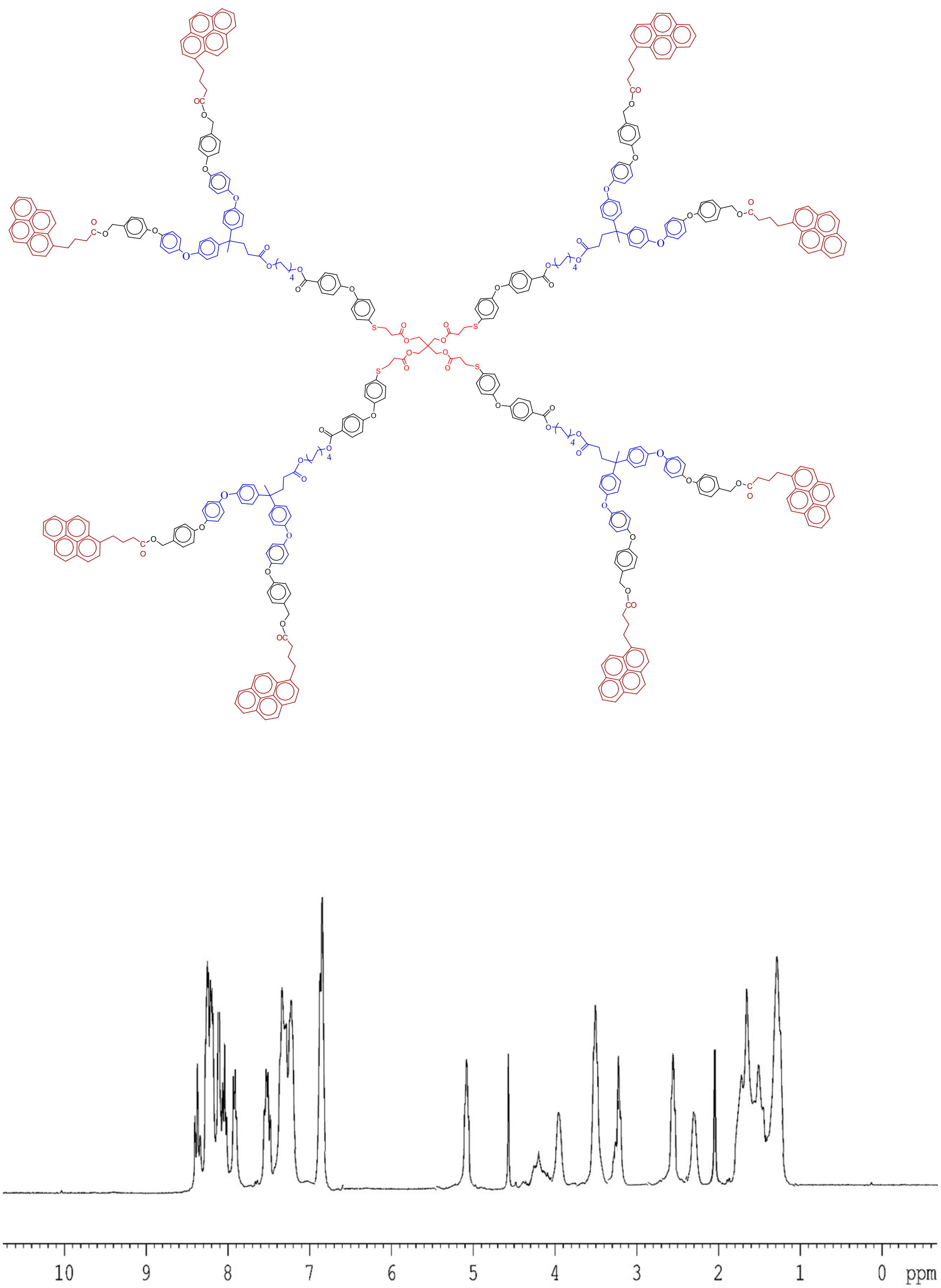


Figure 25. ^{1}H NMR spectra of dendrimer **D9** in Acetone-d_6

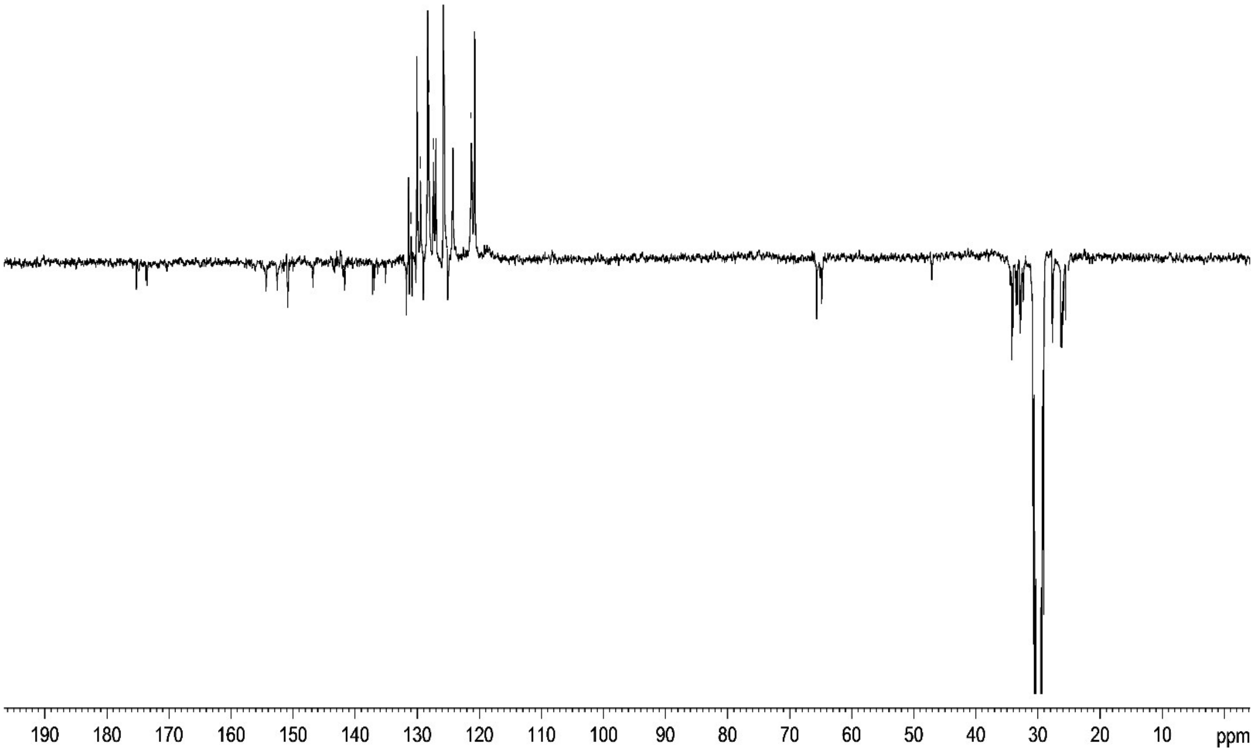
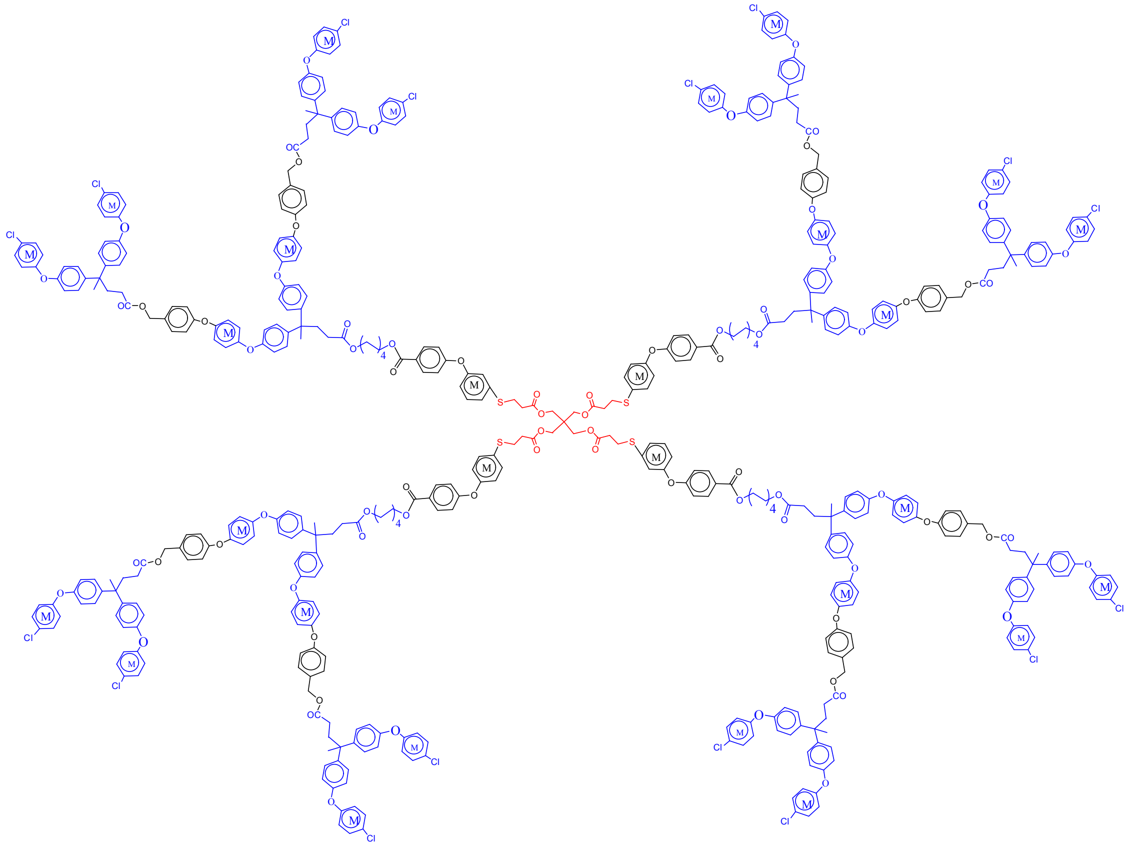


Figure 26. ^{13}C spectra of dendrimer **D9** in Acetone-d$_6$

3.14 Chloro-terminated G_2 dendrimer (D10)

The Steglich esterification procedure was used to synthesize dendrimer **D10**, from **D7** (0.5 g, 0.06 mmol), **9** (0.54 g, 0.52 mmol), DMAP (0.06 g, 0.52 mmol), DCC (0.11 g, 0.52 mmol), and 5 mL of DMF. (Molecular weight 15870 g/mol). Yield: (0.82 g, 80%). ^{1}H NMR δ_H (300 MHz; DMSO-d$_6$): 7.42 (72H, m, uncomplexed Ar-H), 7.33 (72H, d, *J= 8.7 Hz*, uncomplexed Ar-H), 6.81 (32H, d, *J= 6.3 Hz*, complexed Ar-H), 6.44 (32H, d, *J= 6.6 Hz*, complexed Ar-H), 6.27 (48H, s, complexed Ar-H), 5.28 (80H, br s, Cp-H), 5.22 (60H, s, Cp-H), 5.16 (16H, s, CH$_2$), 4.39 (8H, s, CH$_2$), 3.98 (16H, s, CH$_2$), 3.60 (16H, s, CH$_2$), 3.17 (8H, s, CH$_2$), 2.44 (16H, s, CH$_2$), 2.25 (16H, s, CH$_2$), 2.11 (16H, s, CH$_2$), 1.69 (36H, s, CH$_3$), 1.55 (40H, s, CH_2). ^{13}C NMR δ_c (75 MHz; DMSO-d_6,): 175.27, 173.76, and 173.60 (CO), 153.93, 152.44, 152.00, 147.26, 134.99, 132.84, 130.779, 104.53, and 65.90 (quat-C), 132.84, 130.13, 121.33, 121.06, 120.8, and 108.16 (uncomplexed Ar-C), 87.62, 77.19, and 75.93 (complexed Ar-C), 80.20 and 78.79 (Cp-C), 65.13, 63.15, 45.93, 36.81, 33.35, 31.25, 29.44, 28.94, and 26.23 (CH_2), 27.85 (CH_3). ATR-FTIR; ν_{max}/cm^{-1}: 2931 (Ar-CH), 2856 (Cp-CH), 1729 (CO), 1227 (C-O-C). Elemental analysis for $C_{645}H_{584}O_{76}S_4Cl_{16}Fe_{28}P_{28}F_{168}$: calc (C: 48.82; H: 3.71), found (C: 49.48; H: 3.98).



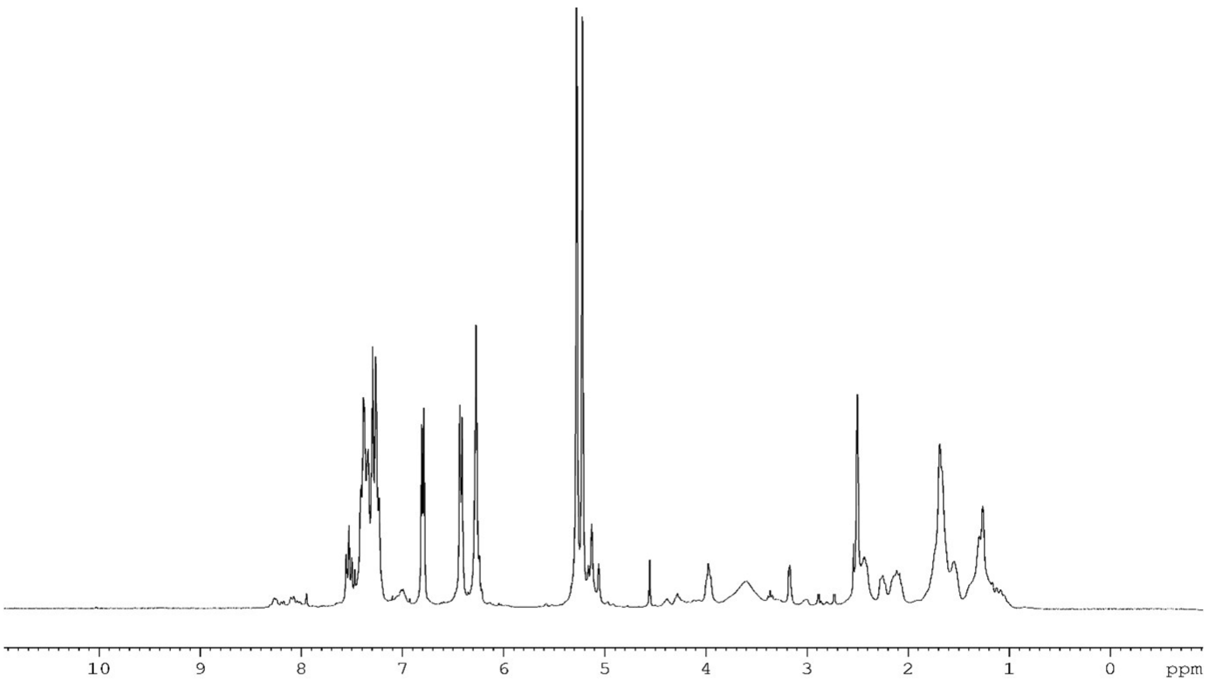


Figure 27. ^{1}H NMR spectra of dendrimer **D10** in DMSO-d$_6$

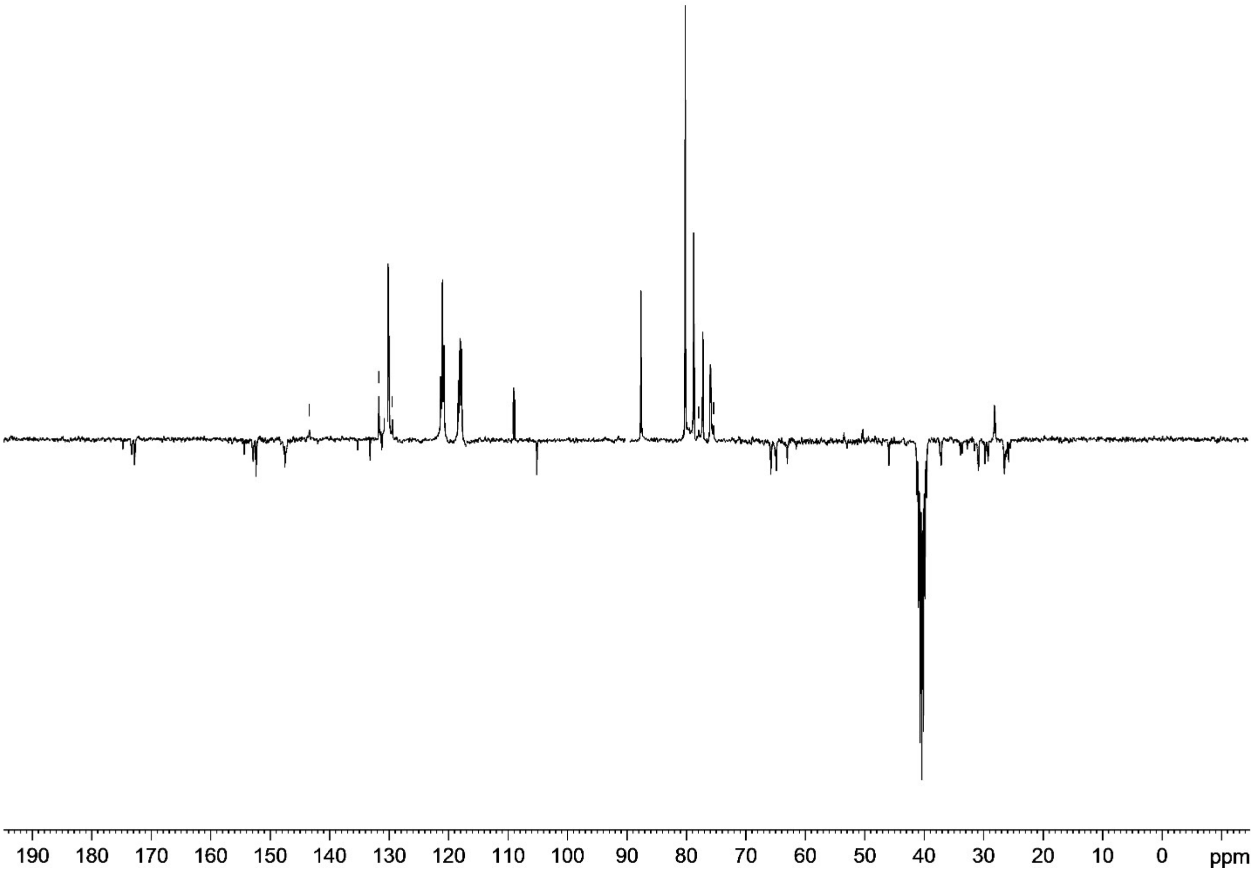


Figure 28. ^{13}C spectra of dendrimer **D10** in DMSO-d$_6$

3.15 Hydroxybenzyl alcohol -terminated G_2 dendrimer (D11)

In a procedure analogous to the synthesis of **D7**, dendrimer **D11** was synthesized from **D10** (0.5 g, 31.51μM), **8** (0.06 g, 0.50 mmol), K_2CO_3 (0.35 g, 2.52 mmol), and 5 mL DMF. (Molecular weight 17272 g/mol). Yield: (0.44 g, 81%). ^{1}H NMR δ_H (300 MHz; DMSO-d$_6$): 7.50 (48H, d, J= 8.4 Hz, uncomplexed Ar-H), 7.35 (80H, br s, uncomplexed Ar-H), 7.29 (80H, m, uncomplexed Ar-H), 6.24 (112H, m, complexed Ar-H), 5.22 (140H, br s, Cp-H), 5.06 (16H, s, CH_2), 5.12 (16H, s, OH), 4.55 (32H, s, CH_2), 4.27 (16H, s, CH_2), 3.97 (24H, s, CH_2), 3.36 (16H, s, CH_2), 2.44 (16H, s, CH_2), 2.23 (16H, s, CH_2), 2.14 (16H, s, CH_2), 1.66 (36H, s, CH_3), 1.55 (32H s, CH_2). ^{13}C NMR δ_C (75 MHz; DMSO-d$_6$): 175.27, 173.72, and 173.61 (C=O), 154.05, 152.71, 152.49, 147.25, 146.77, 141.63, 136.31, 134.94, 131.43, 131.43, 65.81 and 64.79 (quat-C), 130.73, 130.04, 129.48, 121.30, 121.13, and 120.71 (uncomplexed Ar-C), 78.75 (Cp-C), 76.02 and 75.46 (complexed Ar-C), 61.58, 45.84, 36.88, 33.55, 33.32, 30.60, 29.44, and 26.20 (CH_2), 27.84 (CH_3). ATR-FIIR; ν_{max}/cm^{-1}: 3313 (OH), 3092 (Ar-CH), 2939 (Cp-CH), 1720 (CO), 1226 (C-O-C). Elemental analysis for $C_{757}H_{696}O_{108}S_4Fe_{28}P_{28}F_{168}$: calc (C: 52.64; H: 4.06), found (C: 53.12; H: 4.24).

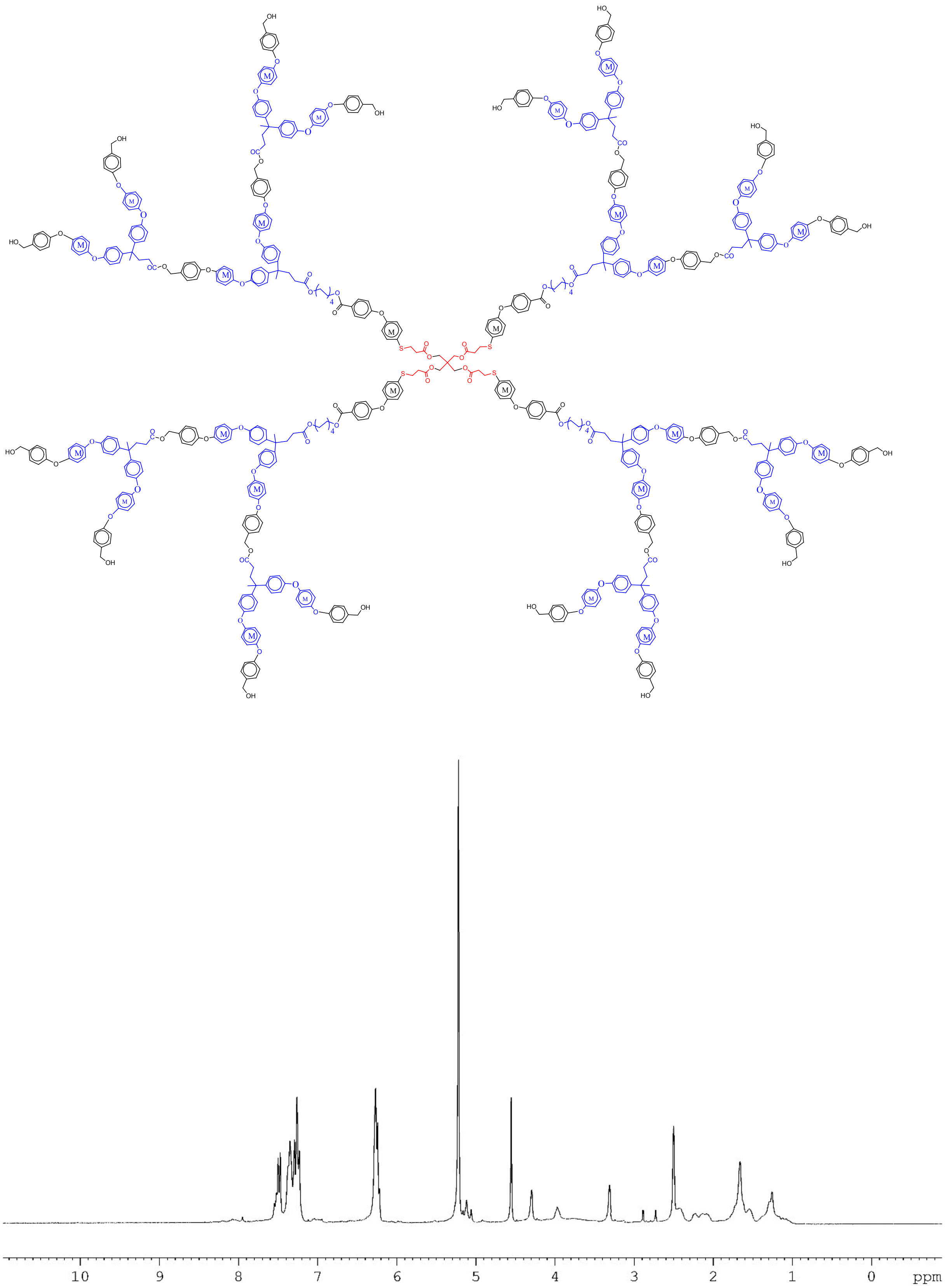


Figure 29. ^{1}H NMR spectra of dendrimer **D11** in DMSO-d$_6$

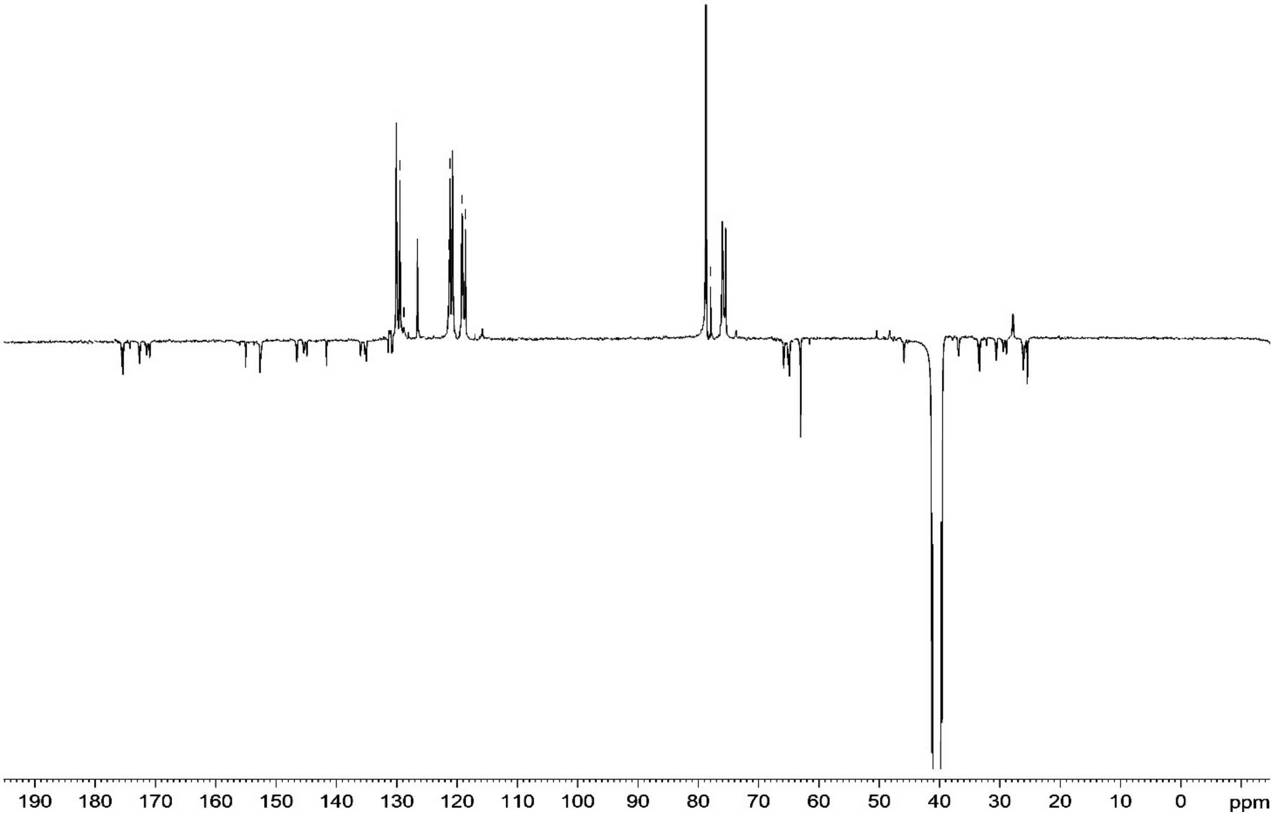
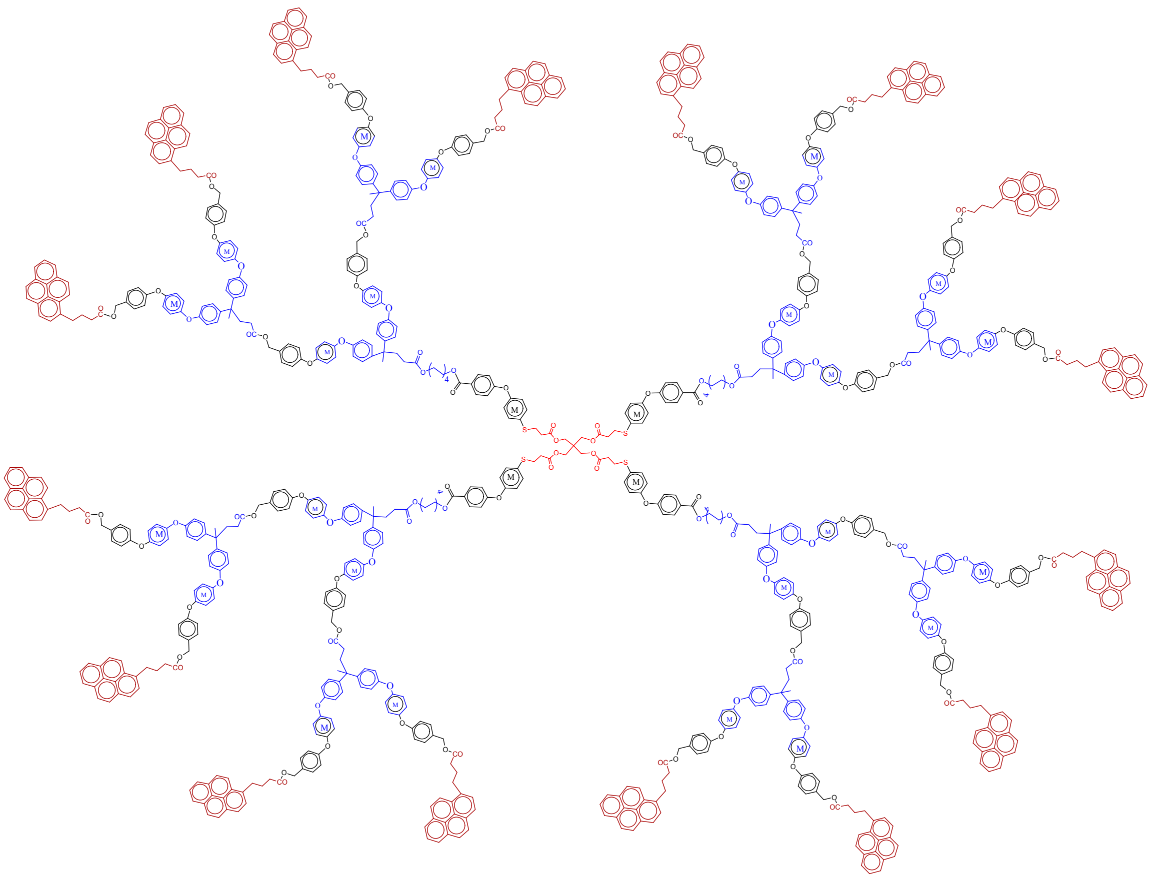


Figure 30. ^{13}C spectra of dendrimer **D11** in DMSO-d_6

3.16 Pyrene-terminated G_2 dendrimer (D12)

The synthesis of dendrimer **D12** followed a procedure analogous to the synthesis of dendrimer **D8**. A 50 mL round-bottom flask was charged with dendrimer **D11** (0.25 g, 14.47 μM) and **1** (0.07 g, 0.23 mmol), DMAP (0.03 g, 0.23 mmol), DCC (0.05 g, 0.23 mmol), and 5 mL of DMF. (Molecular weight 21598 g/mol). Yield: (0.23 g, 73%). ^{1}H NMR data δ_H (300 MHz; DMSO-d_6): 8.39 (16H, m, Py-H), 8.28 (64H, m, Py-H), 8.17 (32H, s, Py-H), 8.14 (16H, m, Py-H), 8.09 (16H, m, Py-H), 7.55 (48H, m, uncomplexed Ar-H), 7.35 (80H, br s, uncomplexed Ar-H), 7.24 (80H, m, uncomplexed Ar-H), 6.26 (112H, s, complexed Ar-H), 5.21 (140H, m, Cp-H), 5.12 (16H, s, CH_2), 4.55 (32H, s, CH_2), 4.26 (24H, s, CH_2), 3.96 (48H, s, CH$_2$), 3.36 (48H, s, CH$_2$), 2.44 (48H, s, CH$_2$), 2.23 (16H, s, CH$_2$), 2.14 (16H, s, CH$_2$), 1.66 (36H, s, CH$_3$), 1.55 (32H, s, CH$_2$). ^{13}C NMR δ_C (75 MHz; DMSO-d$_6$): 173.59, 173.52, and 173.11 (CO), 153.91, 152.56, 152.49, 146.75, 146.77, 141.63, 136.89, 134.90, 131.40, 129.46, and 65.72 (quat-C), 130.73, 130.04, 129.48, 121.30, 121.13, and 120.71 (uncomplexed Ar-C), 78.80 (Cp-C), 76.01 (complexed Ar-C), 63.04, 45.88, 36.811, 34.03, 32.94, 32.72, 30.52, and 26.29 (CH$_2$), 27.80 (CH$_3$). ATR-FIIR; ν_{max}/cm^{-1}: 3092 (Ar-CH), 2939 (Cp-CH), 1720 (CO), 1226 (C-O-C). Elemental analysis for $C_{1077}H_{920}O_{124}S_4Fe_{28}P_{28}F_{168}$: calc (C: 59.89; H: 4.29), found (C: 60.42; H: 4.61).



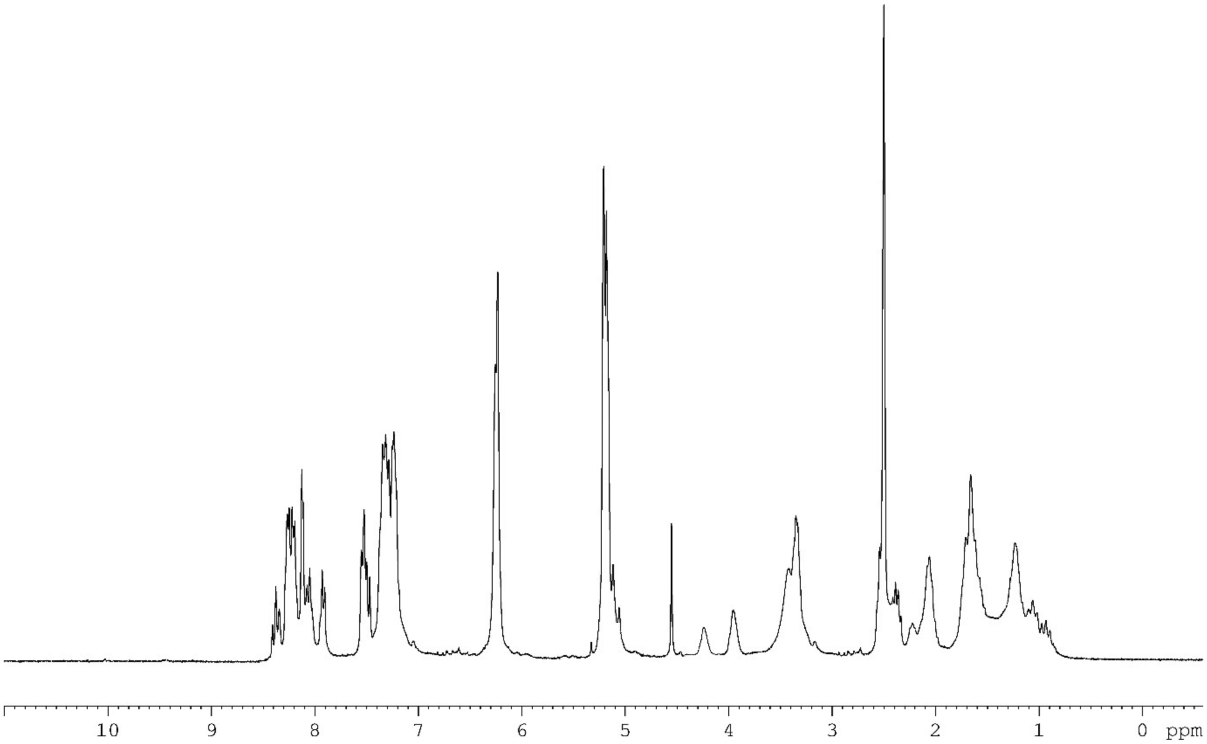


Figure 31. ^{1}H NMR spectra of dendrimer **D12** in DMSO-d_6

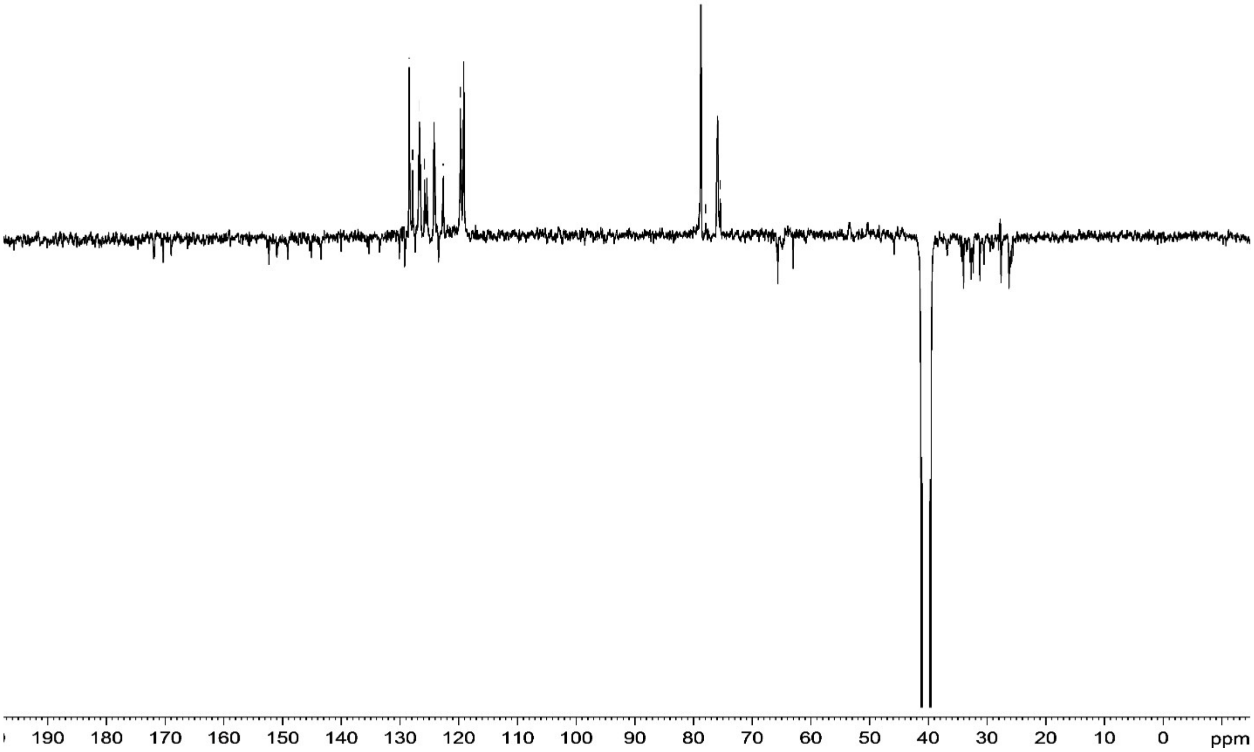


Figure 32. ^{13}C spectra of dendrimer **D12** in DMSO-d_6

3.17 Demetallated pyrene-terminated G_2 dendrimer (D13)

The demetallation of dendrimer **D13** followed a procedure analogous to the demetallation of dendrimer **D3** using dendrimer **D12** (0.2 g, 9.26 μM). (Molecular weight 14152 g/mol). Yield: (0.1 g, 76%). ^{1}H NMR data δ_H (300 MHz; Acetone-d_6): 8.39 (16H, m, Py-H), 8.28 (64H, m, Py-H), 8.20 (32H, s, Py-H), 8.05 (16H, m, Py-H), 8.04 (16H, m, Py-H), 7.54 (48H, m, Ar-H), 7.39 (80H, br s, Ar-H), 7.29 (80H, m, Ar-H), 7.03 (112H, m, Ar-H), 5.12 (16H, s, CH_2), 4.62 (40H, s, CH_2), 4.39 (16H, m, CH_2), 4.02 (48H, s, CH_2), 3.39 (48H, m, CH_2), 2.52 (48H, s, CH_2), 2.28 (16H, s, CH_2), 2.18 (16H, s, CH_2), 1.71 (36H, m, CH_3), 1.59 (32H s, CH_2). ^{13}C NMR δ_C (75 MHz; Acetone-d_6): 174.37, 173.88, and 171.73 (CO), 154.35, 152.98, 152.63, 147.52, 146.47, 141.34, 135.22, 133.94, 135.43, 131.43, 64.61, and 63.22 (quat-C), 131.32, 131.14, 130.88, 121.30, 120.13, and 118.79 (Ar-C), 61.58, 45.84, 36.88, 33.55, 33.32, 30.60, 29.44, and 26.20 (CH_2), 27.84 (CH_3). ATR-FIIR; ν_{max}/cm^{-1}: 3092 (Ar CH), 1720 (CO), 1226 (C-O-C). Elemental analysis for $C_{937}H_{780}O_{124}S_4$: calc. (C: 79.52; H: 5.56), found (C: 80.01; H: 5.94).

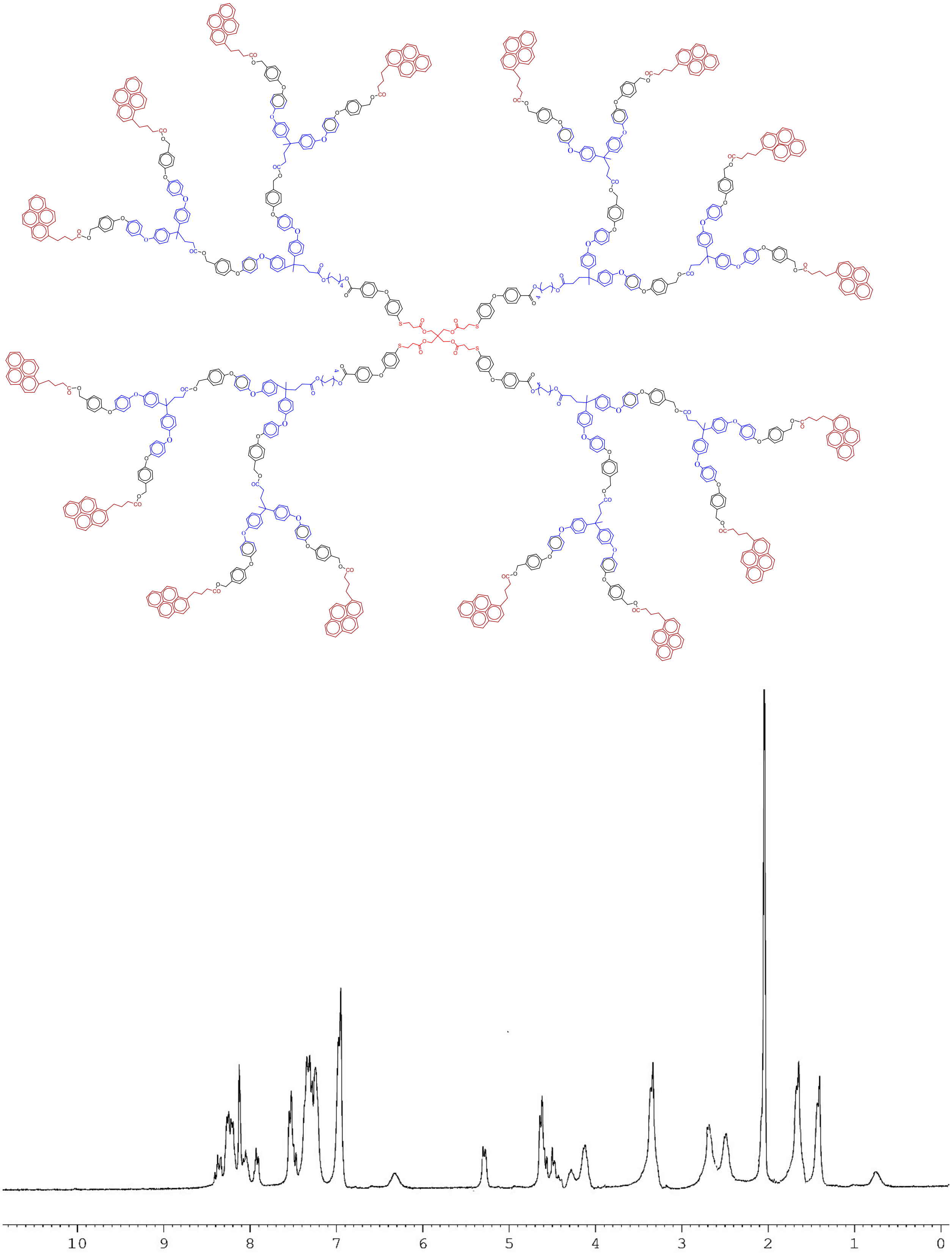


Figure 33. ^{1}H NMR spectra of dendrimer **D13** in Acetone-d$_6$

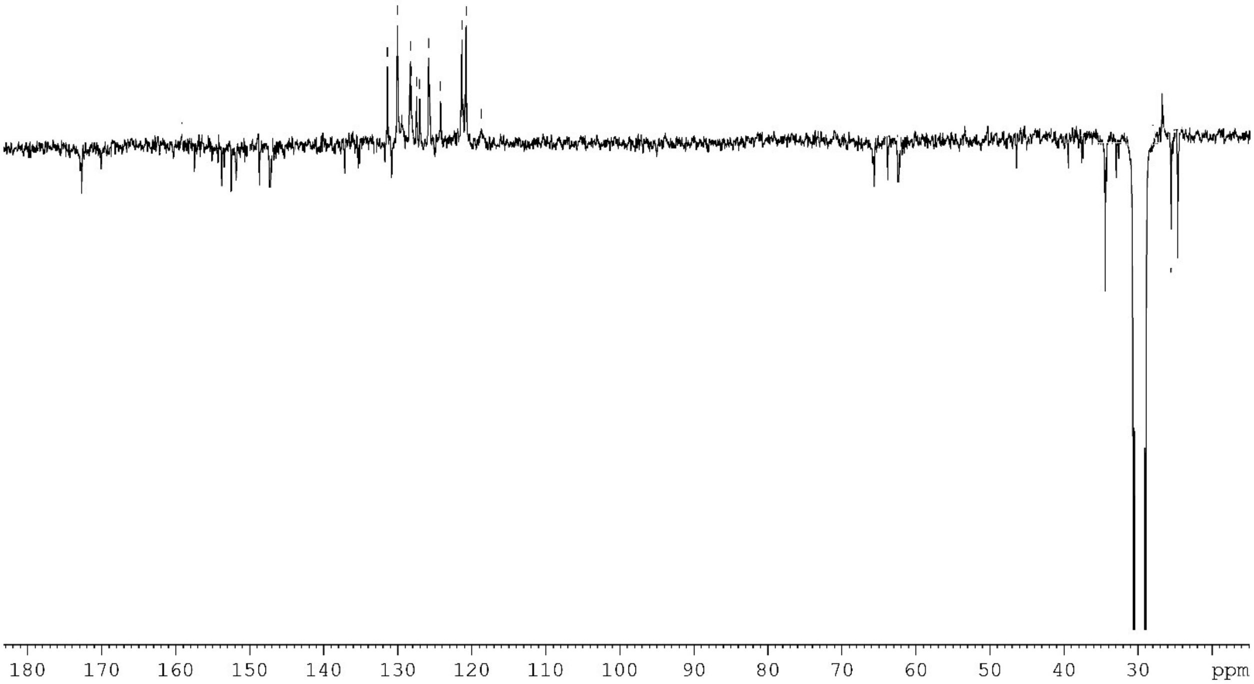


Figure 34. ^{13}C spectra of dendrimer **D13** in Acetone-d_6

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