Supporting Information

Control of Intramolecular Excimer Emission in the Luminophores-Integrated Ionic POSS Possessing Flexible Side-Chains

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General

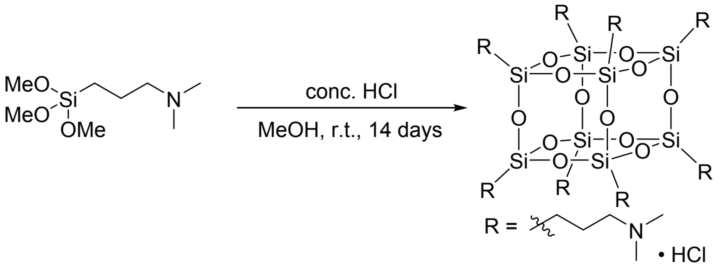
^{1}H, ^{13}C and ^{29}Si NMR spectra were measured with a JEOL AL-400 (400 MHz for ^{1}H, 100 MHz for ^{13}C, 80 MHz for ^{29}Si NMR) spectrometer. The chemical shifts are expressed in ppm downfield from tetramethylsilane as an internal standard. Sodium 3-(trimethylsilyl)-1-propanesulfonate was used as an internal standard in D_2O. Coupling constants (J value) are reported in Hertz. UV−vis absorption spectra were measured with SHIMADZU UV-vis-NIR Spectrometer UV-3600 at 25 °C. PL spectra were measured with HORIBA JOBIN YVON FluoroMax-4P at 25 °C using a 1 cm path length quartz cell. Fluorescence lifetime was measured with Horiba FluoreCube spectrofluorometer system. Absolute PL quantum yield was measured with Hamamatsu Photonics Quantaurus-QY Plus. Thermogravimetric analysis (TGA) was performed using a DTA-60 (Shimadzu, Kyoto, Japan) at a heating rate of 10 °C/min in N_2.

Materials

[3-(*N*,*N*-Dimethylamino)propyl]trimethoxysilane, 1-(bromomethyl)naphthalene, 9-(chloromethyl)anthracene, 1-(chloromethyl)pyrene, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), $NaBF_4$, $NaBPh_4$, sodium dodecyl sulfate (SDS), lithium heptadecafluoro-1-octanesulfonate (LiPFOS), sodium 3-(trimethylsilyl)-1-propanesulfonate, dodecyltrimethylammonium chloride (DTMA), monolaurin (ML), sodium dodecylbenzenesulfonate (hard type) (SDBS), sodium laurate (SL), bis(2-ethylhexyl) sulfosuccinate sodium salt (BSSS) and 3-(dodecyldimethylammonio)propane-1-sulfonate (DSB) were purchased from Tokyo Chemical Industry Co., Ltd. and used without further purification. Hydrochloric acid, K_2CO_3, Na_2SO_4, $MgSO_4$, NaCl, $Na_4P_2O_7$, trimethylamine, MeOH, DMF, acetone, Et_2O, hexane, dodecane, CH_2Cl_2, $CHCl_3$ and DMSO were obtained from Wako Pure Chemical Industries, Ltd. $CDCl_3$ and DMSO-d_6 were purchased from Nacalai Tesque, Inc. Sodium polystyrene sulfonate (PSSNa) and sodium polyacrylate (PANa) were obtained from Sigma-Aldrich Co. LLC. D_2O was obtained from Kanto Chemical Co., Inc. Deionized water was purified using an Autopure WEX3 system from Yamato Scientific Co., Ltd.

Synthetic Procedures and Characterization

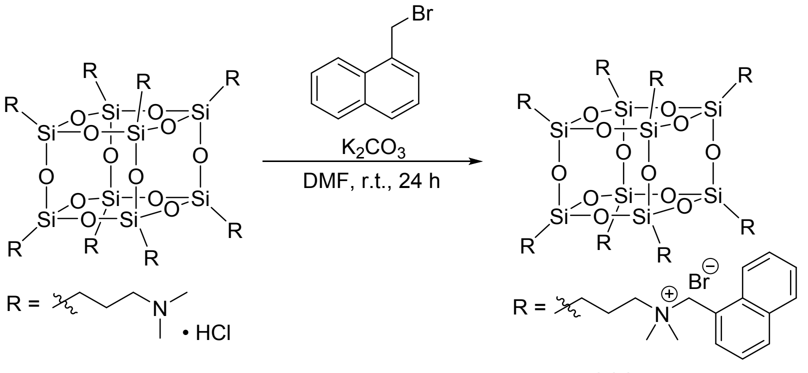
Synthesis of DMA-POSS.



DMA-POSS (17% yield)

Concentrated HCl*aq*. (36%, 38.3 mL) was slowly added to the solution of [3-(*N*,*N*-dimethylamino)propyl]trimethoxysilane (25 mL, 0.115 mol) in MeOH (153 mL) with a dropping funnel for 30 min and then stirred at room temperature for 14 d. White precipitation was collected via filtration and washed with MeOH. The obtained powder was dried in vacuum at room temperature to give the **DMA-POSS** (3.45 g, 17%) as a white solid. ^{1}H NMR (Chart 1, 400 MHz, D_2O, 25 °C): δ 3.15 (t, J = 7.9 Hz, 16H), 2.86 (s, 48H), 1.80 (m, 16H), 0.80 (t, J = 8.4 Hz, 16H) ppm; ^{13}C NMR (Chart 2, 100 MHz, D_2O, 25 °C): δ 62.0, 45.1, 20.4, 10.7 ppm; ^{29}Si NMR (Chart 3, 80 MHz, D_2O, 25 °C): δ –69.1 ppm. HRMS (APCI): calcd. for $[C_{40}H_{96}N_8O_{12}Si_8+H]^+$: m/z 1105.5375; found: m/z 1105.5363. Elemental analysis calcd. for $C_{40}H_{104}Cl_8N_8O_{12}Si_8$: C 34.38 H 7.50 N 8.02, found: C 29.55 H 7.34 N 7.23.

Synthesis of NPOSS.

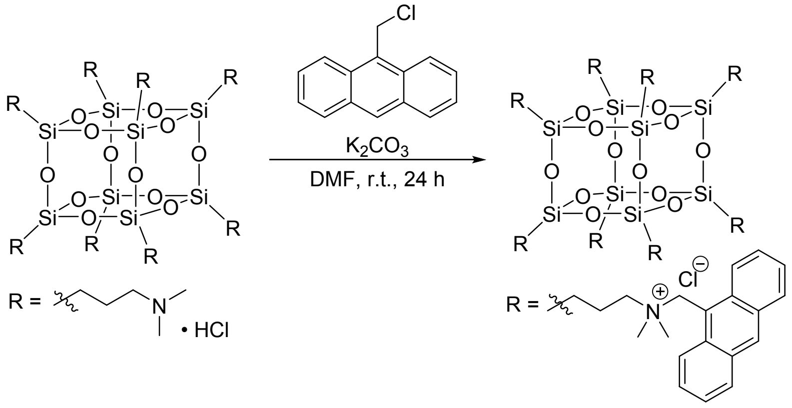


NPOSS (40% yield)

DMA-POSS (100 mg, 0.072 mmol), 1-(bromomethyl)naphthalene (254 mg, 1.15 mmol) and K_2CO_3 (80 mg, 0.072 mmol) were added to a Schlenk flask and purged with Ar. DMF (7.2 mL) was poured into the mixture via syringe and the white suspension was stirred under Ar atmosphere at room temperature for 24 h. After the reaction, the suspension was filtrated to remove white precipitation and the filtrate was poured into Et_2O. Precipitation was collected via filtration and washed with Et_2O. The product was re-dissolved in

CH_2Cl_2 and dried over Na_2SO_4. After filtration, the filtrate was poured into hexane. The precipitation was obtained via filtration and dried at 110 °C in vacuum to give the **NPOSS** (83 mg, 40%) as a white solid. ^1H NMR (Chart 4, 400 MHz, $CDCl_3$): δ 8.47 (d, J = 8.7 Hz, 8H), 7.90 (d, J = 7.1 Hz, 8H), 7.76 (d, J = 7.6 Hz, 8H) 7.74 (d, J = 7.3 Hz, 8H), 7.54 (dd, J = 7.9, 7.5 Hz, 8H), 7.42 (dd, J = 7.6, 7.5 Hz, 8H), 7.30 (dd, J = 7.8, 7.7 Hz, 8H), 5.40 (s, 16H), 4.22 (br, 16H), 3.13 (s, 48H), 2.34 (br, 16H), 1.11 (br, 16H) ppm; ^{13}C NMR (Chart 5, 100 MHz, $CDCl_3$): δ 133.9, 133.7, 133.0, 131.5, 128.9, 127.9, 126.3, 124.9, 124.2, 123.4, 68.8, 63.6, 50.1, 17.5, 9.5 ppm; ^{29}Si NMR (Chart 6, 80 MHz, $CDCl_3$): δ –68.9 ppm. Elemental analysis calcd. for $C_{128}H_{168}Br_8N_8O_{12}Si_8$: C 53.48 H 5.89 N 3.90, found: C 43.87 H 5.11 N 3.35.

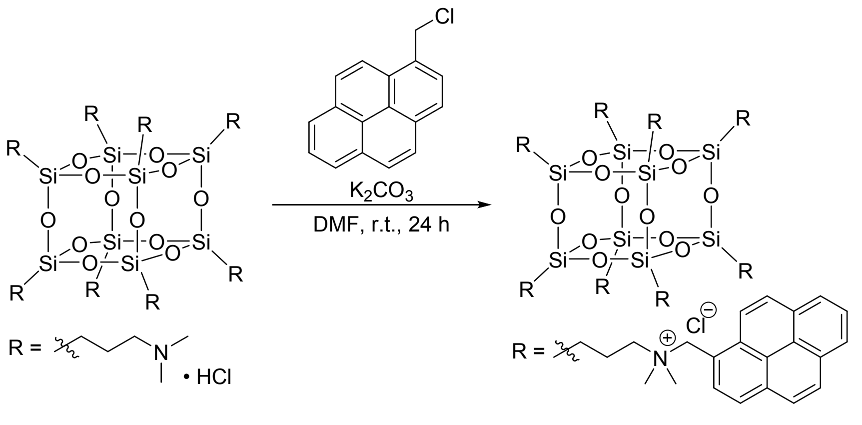
Synthesis of APOSS.



APOSS (48% yield)

DMA-POSS (100 mg, 0.072 mmol), 9-(chloromethyl)anthracene (261 mg, 1.15 mmol) and K_2CO_3 (40 mg, 0.036 mmol) were added to a Schlenk flask and purged with Ar. DMF (1.8 mL) was poured into the mixture via syringe and the white suspension was stirred under Ar atmosphere at room temperature for 24 h. After the reaction, the suspension was filtrated to remove white precipitation and the filtrate was poured into acetone. Precipitation was collected via filtration and washed with acetone. The product was re-dissolved in $CHCl_3$ and dried over Na_2SO_4. After filtration, the filtrate was poured into hexane. The precipitation was obtained via filtration and dried at 110 °C in vacuum to give the **APOSS** (101 mg, 48%) as a pale yellow solid. ^1H NMR (Chart 7, 400 MHz, $CDCl_3$): δ 8.66 (d, J = 8.8 Hz, 16H), 8.43 (s, 8H), 7.89 (d, J = 8.3 Hz, 16H), 7.55 (dd, J = 8.0, 7.6 Hz, 16H), 7.36 (dd, J = 7.8, 7.2 Hz, 16H), 5.91 (s, 16H), 4.47 (br, 16H), 3.11 (s, 48H), 2.41 (br, 16H), 1.17 (br, 16H) ppm; ^{13}C NMR (Chart 8, 100 MHz, $CDCl_3$): δ 133.0, 131.7, 131.0, 129.2, 128.2, 125.3, 124.6, 118.2, 69.1, 59.7, 50.3, 17.5, 9.6 ppm; ^{29}Si NMR (Chart 9, 80 MHz, $CDCl_3$): δ –68.4 ppm. Elemental analysis calcd. for $C_{160}H_{184}C_{l8}N_8O_{12}Si_8$: C 65.82 H 6.35 N 3.84, found: C 58.94 H 6.40 N 3.91.

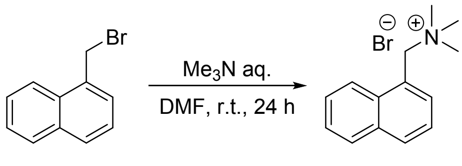
Synthesis of PPOSS.



PPOSS (65% yield)

DMA-POSS (100 mg, 0.072 mmol), 1-(chloromethyl)pyrene (288 mg, 1.15 mmol) and K_2CO_3 (40 mg, 0.28 mmol) were added to a Schlenk flask and purged with Ar. DMF (1.8 mL) was poured into the mixture via syringe and the white suspension was stirred under Ar atmosphere at room temperature for 24 h. After the reaction, the suspension was filtrated to remove white precipitation and the filtrate was poured into Et_2O. Precipitation was collected via filtration and washed with Et_2O. The product was re-dissolved in $CHCl_3$ and dried with Na_2SO_4. After filtration, the filtrate was poured into hexane. The precipitation was obtained via filtration and dried at 110 °C in vacuum to give the **PPOSS** (145 mg, 65%) as a pale yellow solid. ^{1}H NMR (Chart 10, 400 MHz, $CDCl_3$): δ 8.65 (d, J = 9.5 Hz, 8H), 8.25 (d, J = 7.8 Hz, 8H), 7.99 (d, J = 7.3 Hz, 8H), 7.95 (d, J = 9.5 Hz, 8H), 7.84 (m, 8H), 7.76 (d, J = 9.0 Hz, 8H), 7.67 (d, J = 8.1 Hz, 8H), 7.51 (d, J = 9.0 Hz, 8H), 5.79 (s, 16H), 4.38 (br, 16H), 3.18 (s, 48H), 2.57 (br, 16H), 1.27 (br, 16H) ppm; ^{13}C NMR (Chart 11, 100 MHz, $CDCl_3$): δ 132.3, 132.0, 131.6, 130.6, 129.9, 129.4, 128.5, 126.5, 126.1, 125.9, 125.7, 124.3, 124.1, 123.6, 123.2, 120.2, 69.0, 63.6, 49.9, 17.7, 9.7 ppm; ^{29}Si NMR (Chart 12, 80 MHz, $CDCl_3$): δ –68.2 ppm. Elemental analysis calcd. for $C_{176}H_{184}Cl_8N_8O_{12}Si_8$: C 67.93 H 5.96 N 3.60, found: C 59.16 H 6.19 N 3.08.

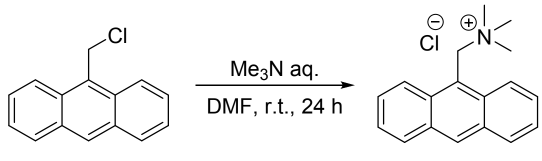
Synthesis of NTMA.



NTMA (87% yield)

Trimethylamine (30% in water, 267 μL, 1.35 mmol) was added to the solution of 1-(bromomethyl)naphthalene (100 mg, 0.45 mmol) in DMF (4.5 mL) and stirred at room temperature for 24 h. After the reaction, the solution was poured into Et_2O. Precipitation was collected via filtration and washed with Et_2O, and the product was dried at 80 °C in vacuum to give the **NTMA** (110 mg, 87%) as a white solid. ^{1}H NMR (Chart 13, 400 MHz, DMSO-d_6): δ 8.52 (d, J = 8.5 Hz, 1H), 8.14 (d, J = 8.2 Hz, 1H), 8.05 (d, J = 7.9 Hz, 1H), 7.80 (d, J = 6.9 Hz, 1H), 7.7–7.5 (m, 3H), 5.08 (s, 2H), 3.10 (s, 9H) ppm; ^{13}C NMR (Chart 14, 100 MHz, DMSO-d_6): δ 133.6, 132.8, 131.4, 129.0, 127.3, 126.3, 125.3, 124.6, 124.1, 63.8, 52.2 ppm; HRMS (ESI): calcd for $[C_{14}H_{18}N]^+$: m/z 200.1434; found: m/z 200.1430.

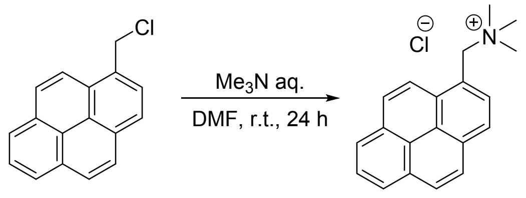
Synthesis of ATMA.



ATMA (92% yield)

Trimethylamine (30% in water, 260 μL, 1.32 mmol) was added to the solution of 9-(chloromethyl)anthracene (100 mg, 0.44 mmol) in DMF (4.4 mL) and stirred at room temperature for 24 h. After the reaction, the solution was poured into Et_2O. Precipitation was collected via filtration and washed with Et_2O, and the product was dried at 80 °C in vacuum to give the **ATMA** (116 mg, 92%) as a pale yellow solid. ^{1}H NMR (Chart 15, 400 MHz, DMSO-d_6): δ 8.91 (s, 1H), 8.73 (d, J = 9.0 Hz, 2H), 8.22 (d, J = 8.3 Hz, 2H), 7.70 (m, 2H), 7.61 (dd, J = 8.3, 6.6 Hz, 2H), 5.69 (s, 2H), 3.09 (s, 9H) ppm; ^{13}C NMR (Chart 16, 100 MHz, DMSO-d_6): δ 132.8, 131.8, 131.0, 129.4, 127.4, 125.3, 124.8, 119.7, 58.8, 52.7 ppm; HRMS (ESI): calcd for $[C_{18}H_{20}N]^+$: m/z 250.1590; found: m/z 250.1586.

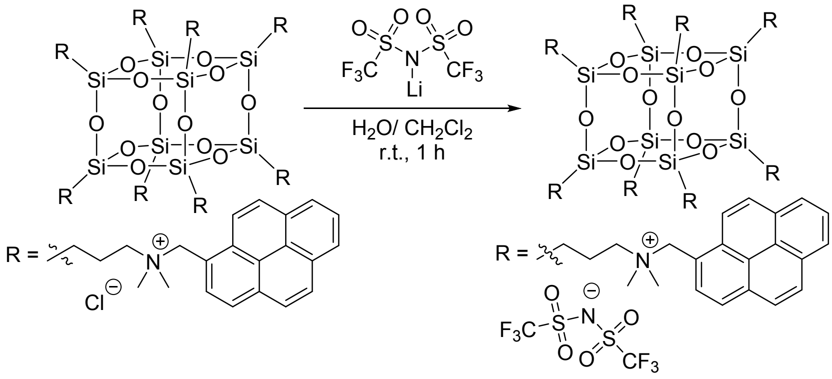
Synthesis of PTMA.



PTMA (80% yield)

Trimethylamine (30% in water, 237 µL, 1.20 mmol) was added to the solution of 1-(chloromethyl)pyrene (100 mg, 0.40 mmol) in DMF (4.0 mL) and stirred at room temperature for 24 h. After the reaction, the solution was poured into acetone. Precipitation was collected via filtration and washed with acetone, and the product was dried at 80 °C in vacuum to give the **PTMA** (100 mg, 80%) as a white solid. ^{1}H NMR (Chart 17, 400 MHz, DMSO-d_6): δ 8.82 (d, J = 9.3 Hz, 1H) , 8.5–8.2 (m, 7H), 8.16 (dd, J = 7.6, 7.6 Hz, 1H), 5.39 (s, 2H), 3.18 (s, 9H) ppm; ^{13}C NMR (Chart 18, 100 MHz, DMSO-d_6): δ 132.4, 132.3, 131.5, 130.6, 129.9, 127.2, 126.2, 125.9, 124.7, 124.1, 123.5, 121.9, 64.2, 52.0 ppm; HRMS (ESI): calcd for $[C_{20}H_{20}N]^+$: m/z 274.1590; found: m/z 274.1585.

Preparation of PPOSS-TFSI.



PPOSS-TFSI (51% yield)

Solution of lithium bis(trifluoromethanesulfonyl)imide (147 mg, 0.51 mmol) in H_2O (10 mL) was poured into the solution of **PPOSS** (20 mg, 6.4 μmol) in CH_2Cl_2 (10 mL) and stirred at room temperature for 1 h. After the reaction, CH_2Cl_2 layer was extracted and washed with water two times. The solution was dried with $MgSO_4$ and filtrated. Following concentration of the filtrate by evaporation, the solution was poured into hexane. Precipitation was collected via filtration and washed with hexane, and the product was dried in vacuum to give the **PPOSS-TFSI** (16.4 mg, 51%) as a white solid. ^{1}H NMR (Chart 19, 400 MHz, $CDCl_3$): δ 7.9–7.8 (m, 24H), 7.8–7.7 (m, 24H), 7.6–7.5 (m, , 16H), 7.37 (d, J = 9.0 Hz, 8H), 5.04 (s, 16H), 3.80 (br, 16H), 2.77 (s, 48H), 2.31 (br, 16H), 1.13 (br, 16H) ppm; ^{13}C NMR (Chart 20, 100 MHz, $CDCl_3$): δ 132.5, 130.9, 130.3, 129.6 129.3, 128.6, 126.2, 126.1, 125.8, 124.2, 123.8, 123.2, 121.1, 120.1 (q, J = 321 Hz), 118.3, 70.0, 64.1, 49.0, 29.7, 16.7, 9.1 ppm; ^{29}Si NMR (Chart 21, 80 MHz, $CDCl_3$): δ –68.9 ppm. Elemental analysis calcd. for $C_{192}H_{184}F_{48}N_{16}O_{28}S_{16}Si_8$: C 47.91 H 3.85 N 4.66, found: C 45.31 H 3.88 N 4.31.

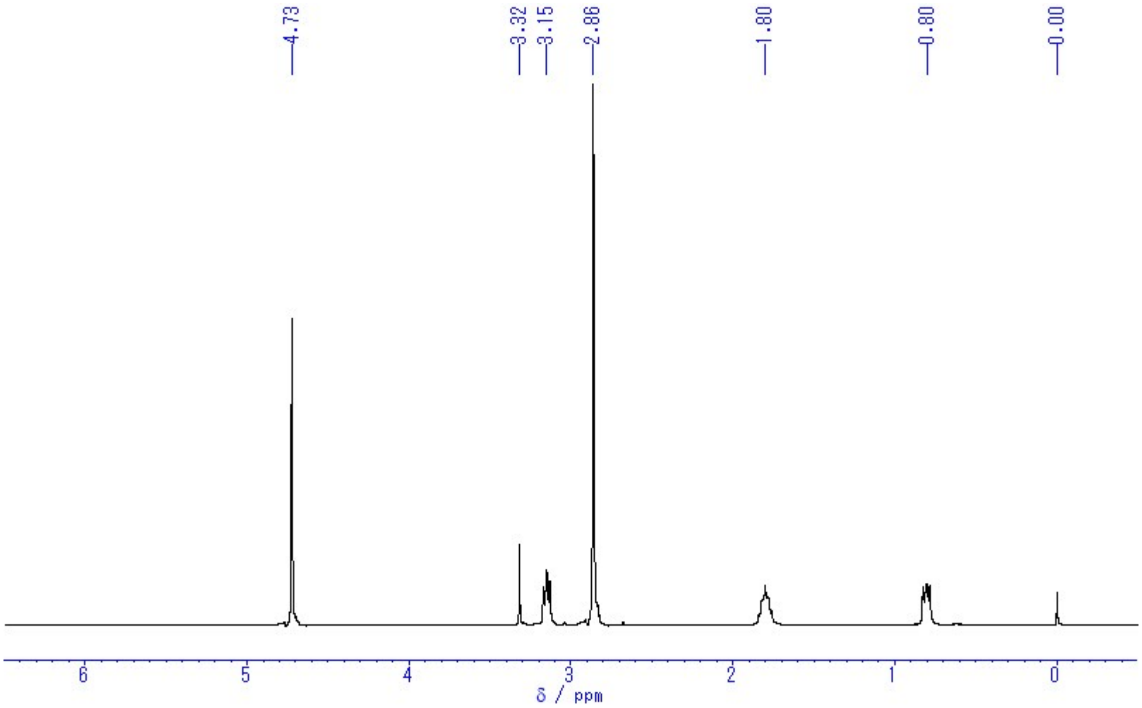


Chart 1. ^{1}H NMR spectrum of the **DMA-POSS** in D_2O at 25 °C (400 MHz).

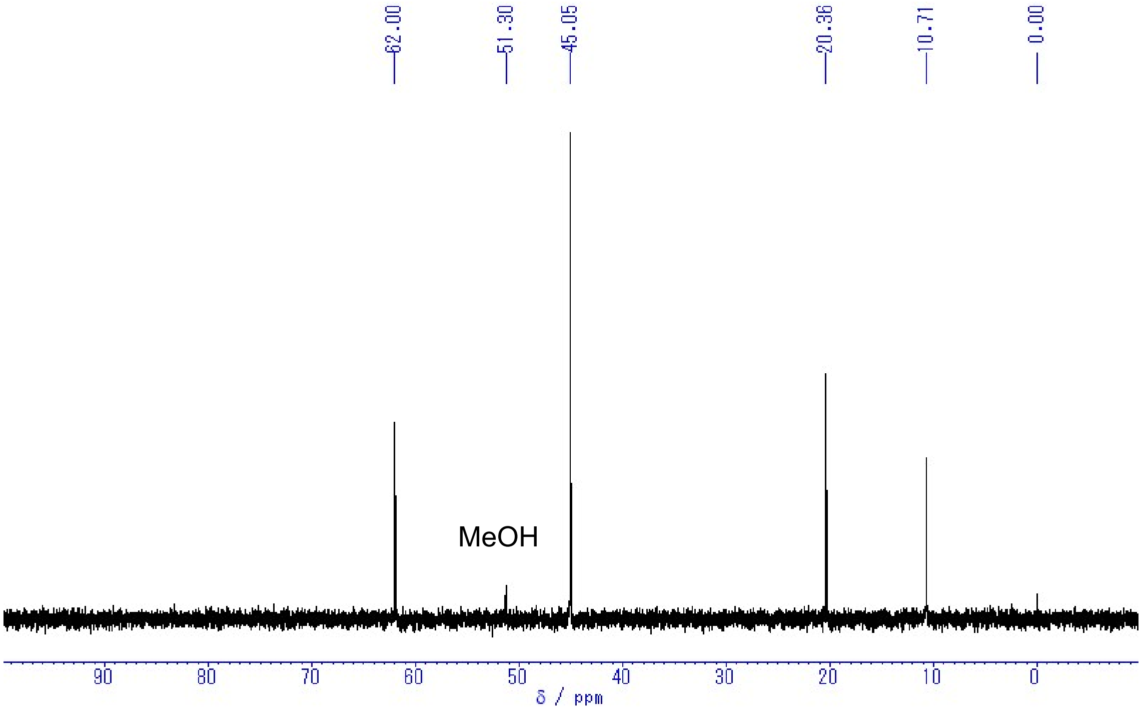


Chart 2. ^{13}C NMR spectrum of the **DMA-POSS** in D_2O at 25 °C (100 MHz).

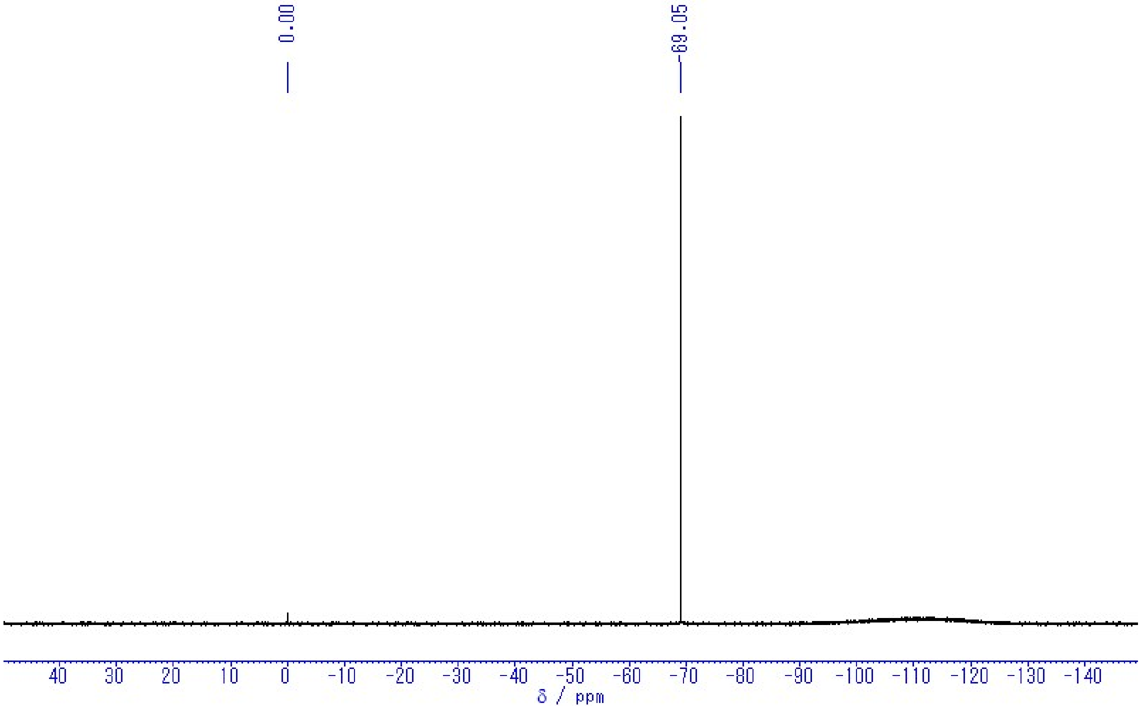


Chart 3. ^{29}Si NMR spectrum of the **DMA-POSS** in D_2O at 25 °C (80 MHz).

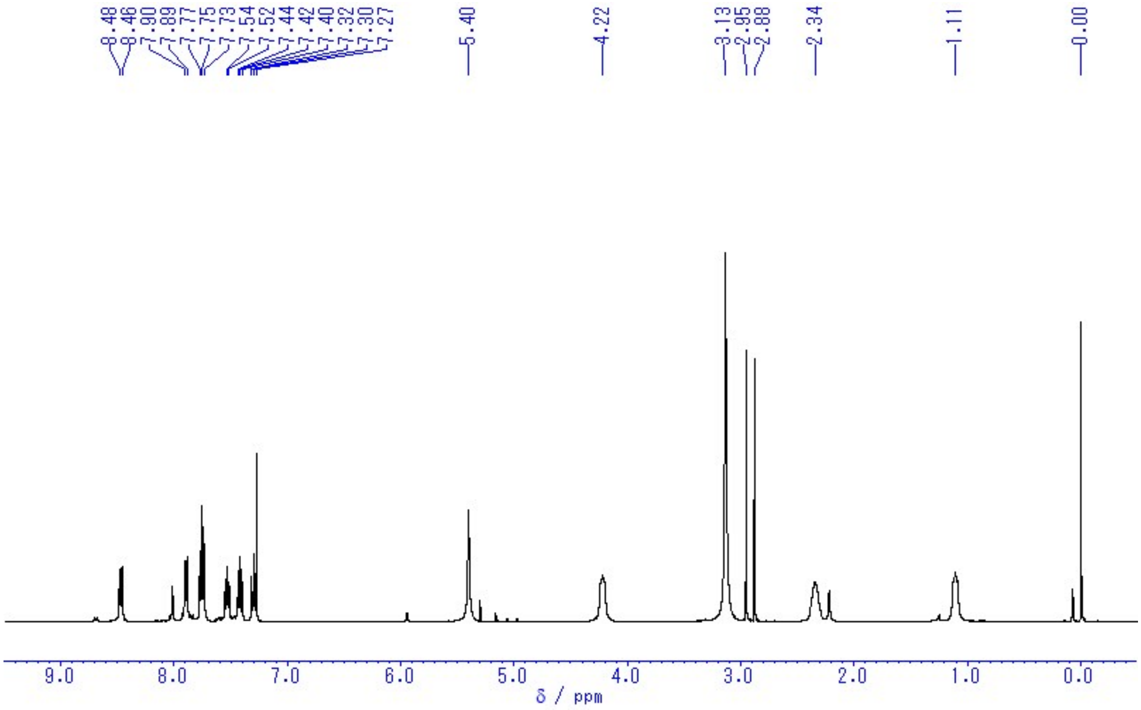


Chart 4. ^{1}H NMR spectrum of the **NPOSS** in $CDCl_3$ at 25 °C (400 MHz).

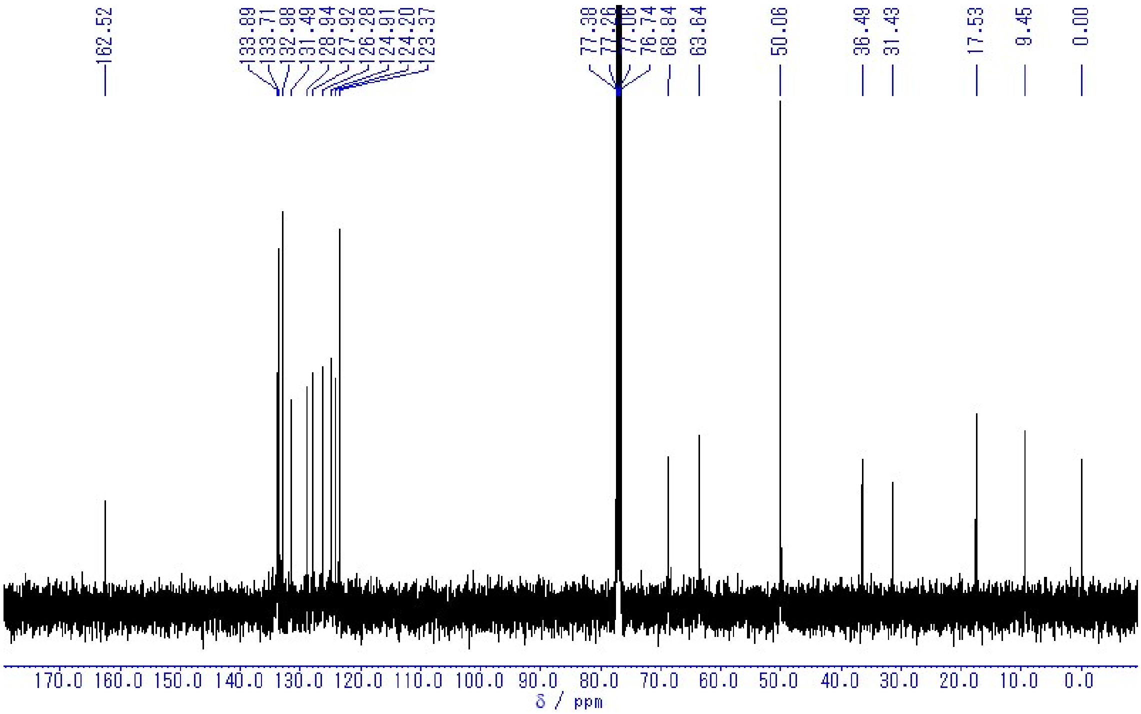


Chart 5. ^{13}C NMR spectrum of the **NPOSS** in $CDCl_3$ at 25 °C (100 MHz).

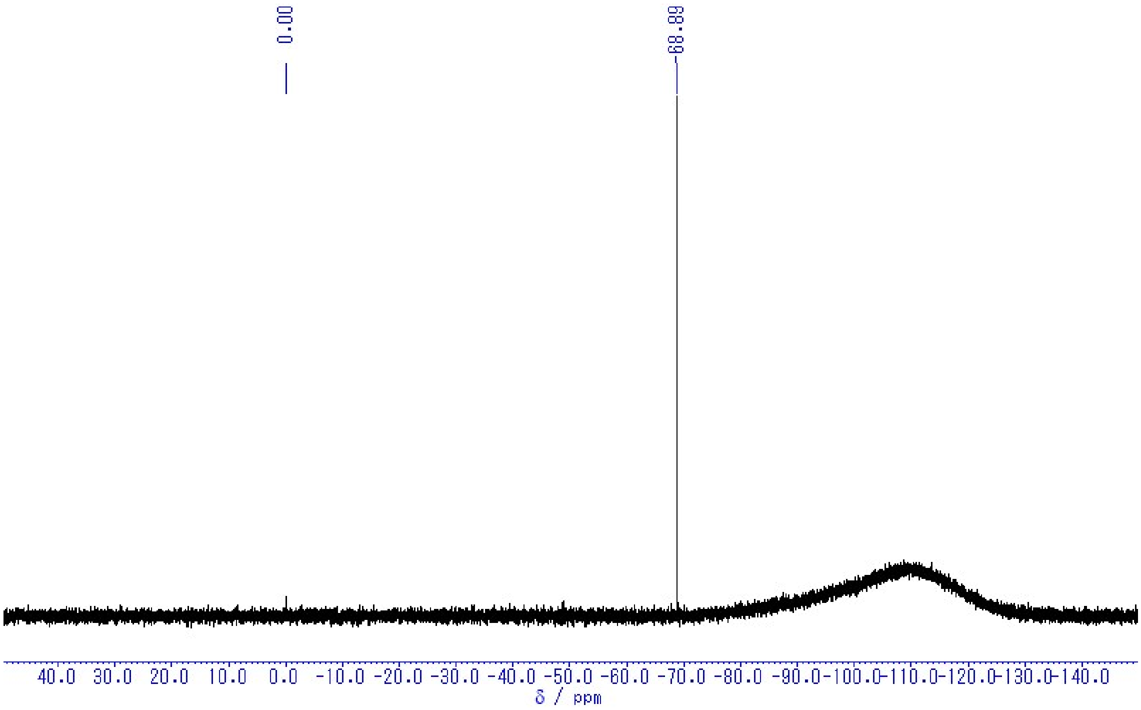


Chart 6. ^{29}Si NMR spectrum of the **NPOSS** in $CDCl_3$ at 25 °C (80 MHz).

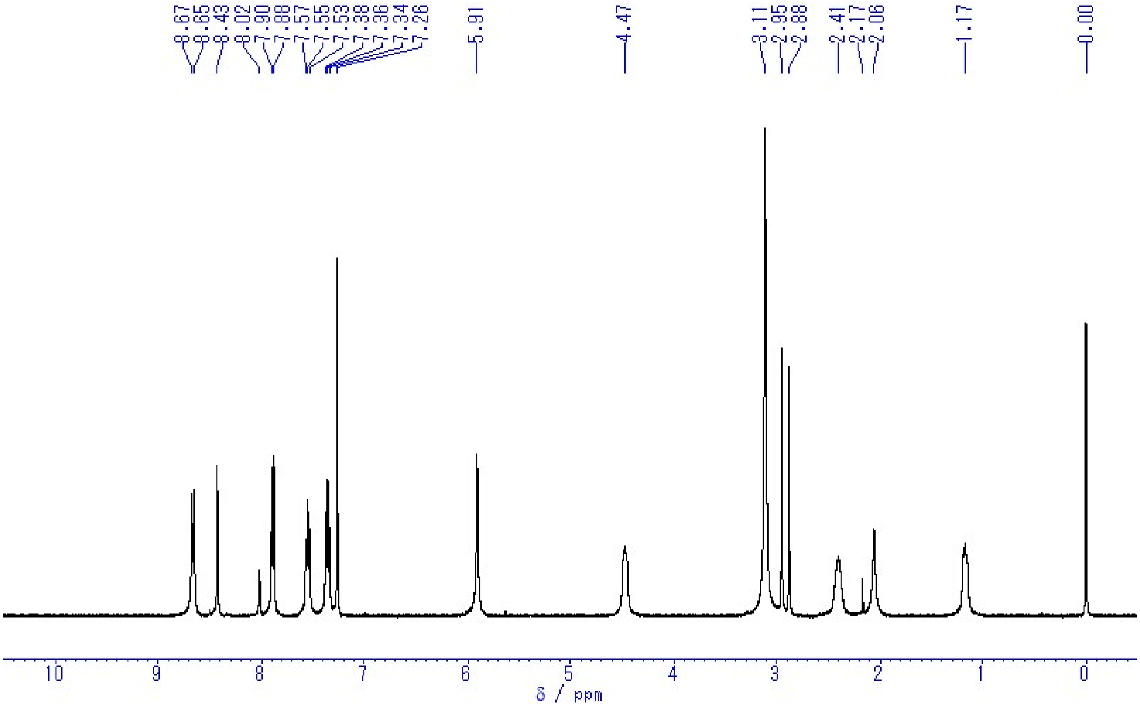


Chart 7. ^{1}H NMR spectrum of the **APOSS** in $CDCl_3$ at 25 °C (400 MHz).

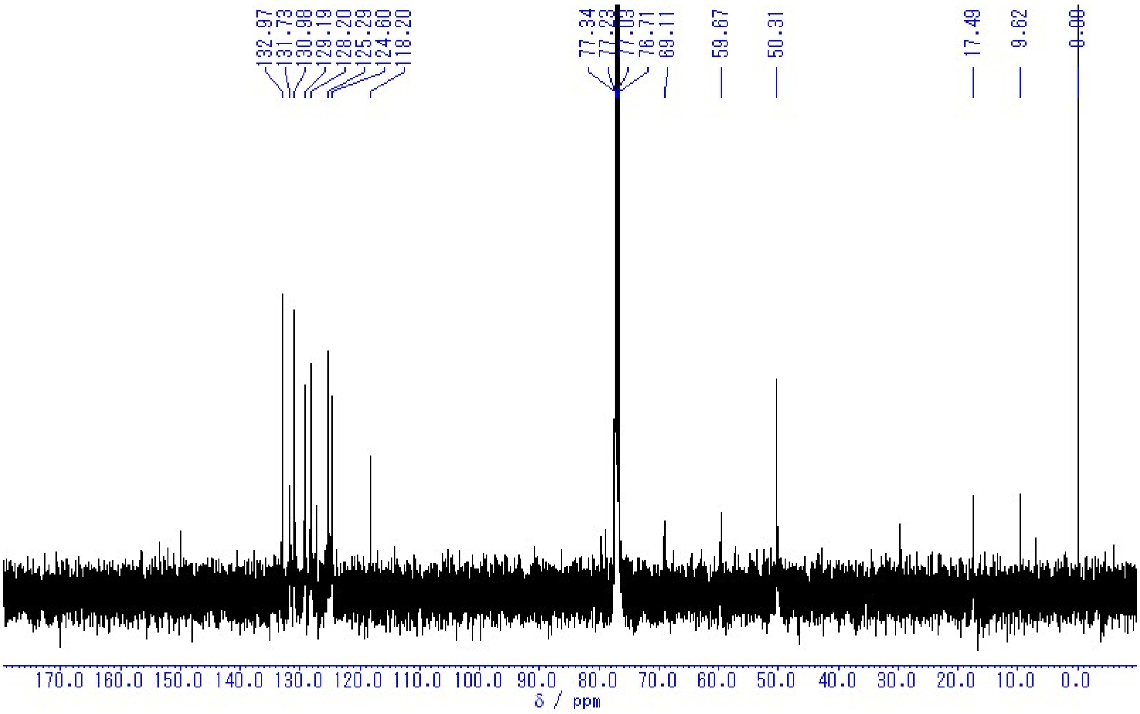


Chart 8. ^{13}C NMR spectrum of the **APOSS** in $CDCl_3$ at 25 °C (100 MHz).

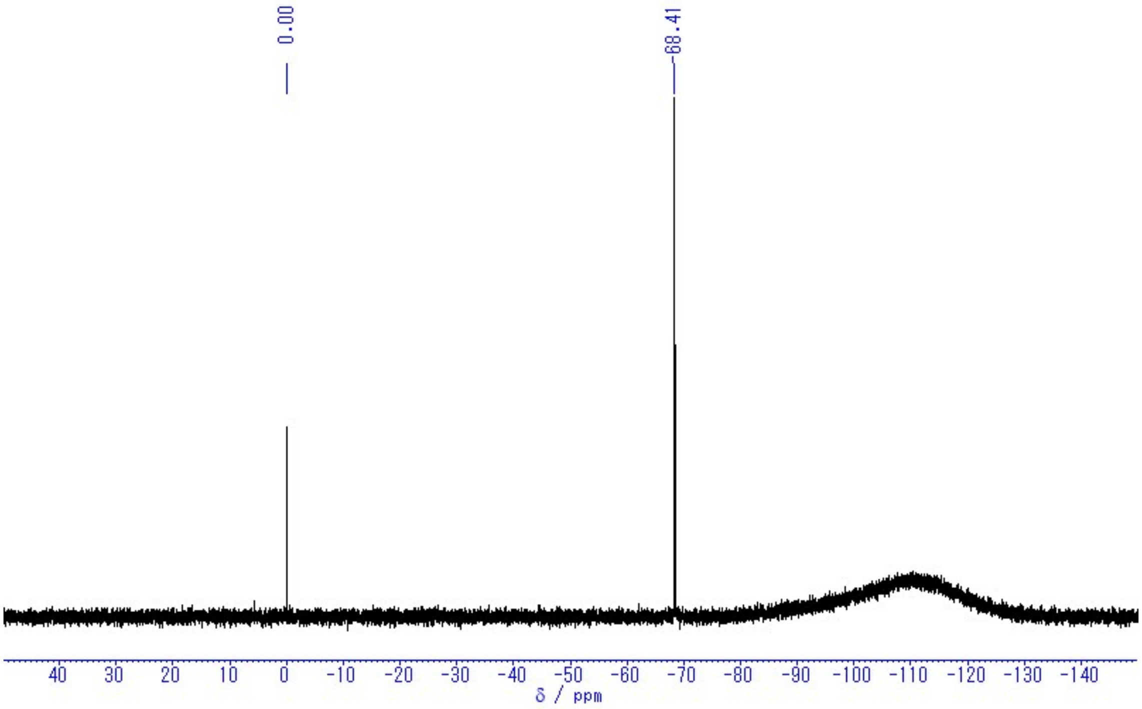


Chart 9. ^{29}Si NMR spectrum of the **APOSS** in $CDCl_3$ at 25 °C (80 MHz).

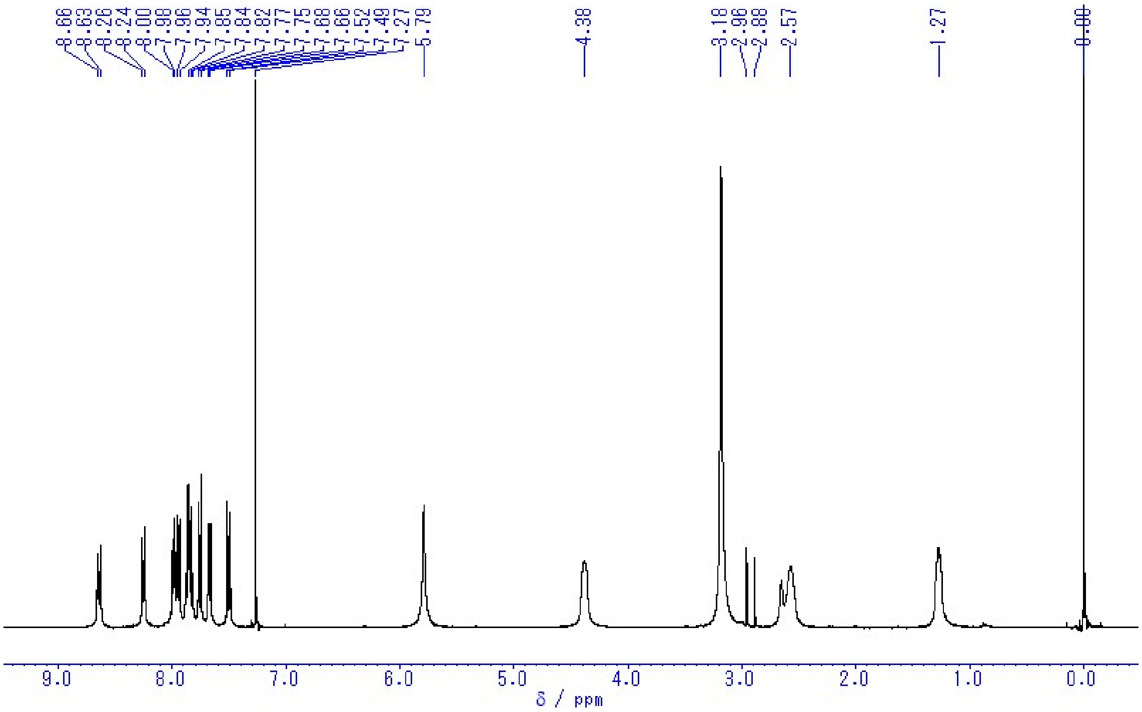


Chart 10. ^{1}H NMR spectrum of the **PPOSS** in $CDCl_3$ at 25 °C (400 MHz).

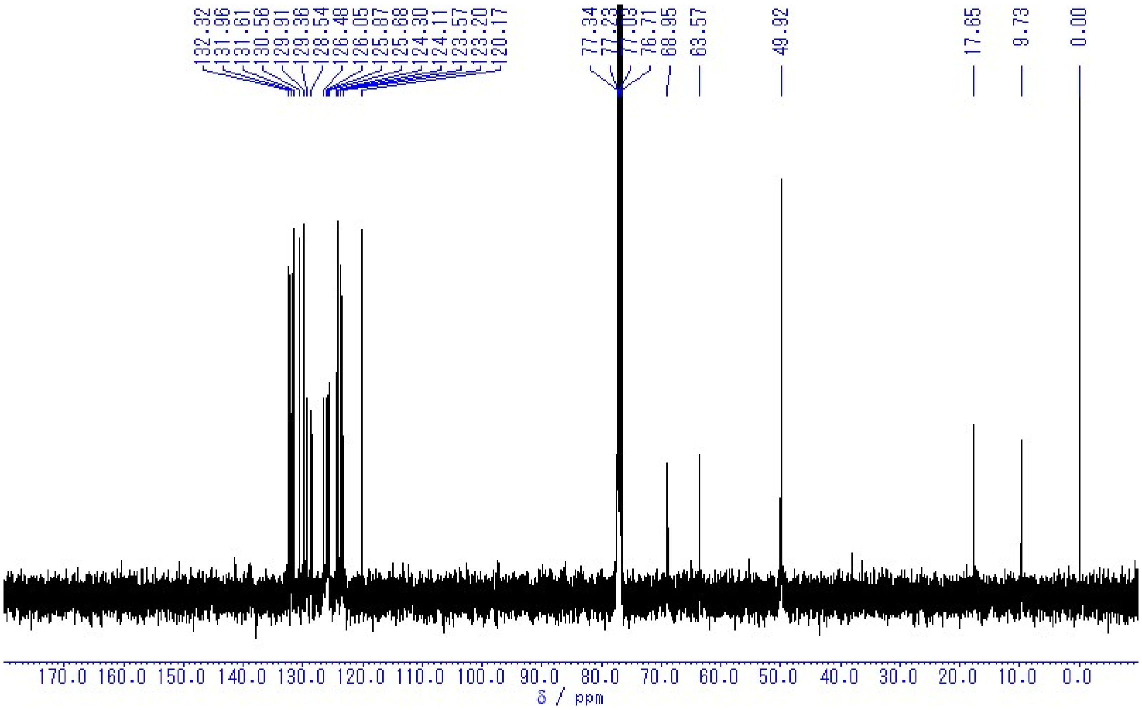


Chart 11. ^{13}C NMR spectrum of the **PPOSS** in $CDCl_3$ at 25 °C (100 MHz).

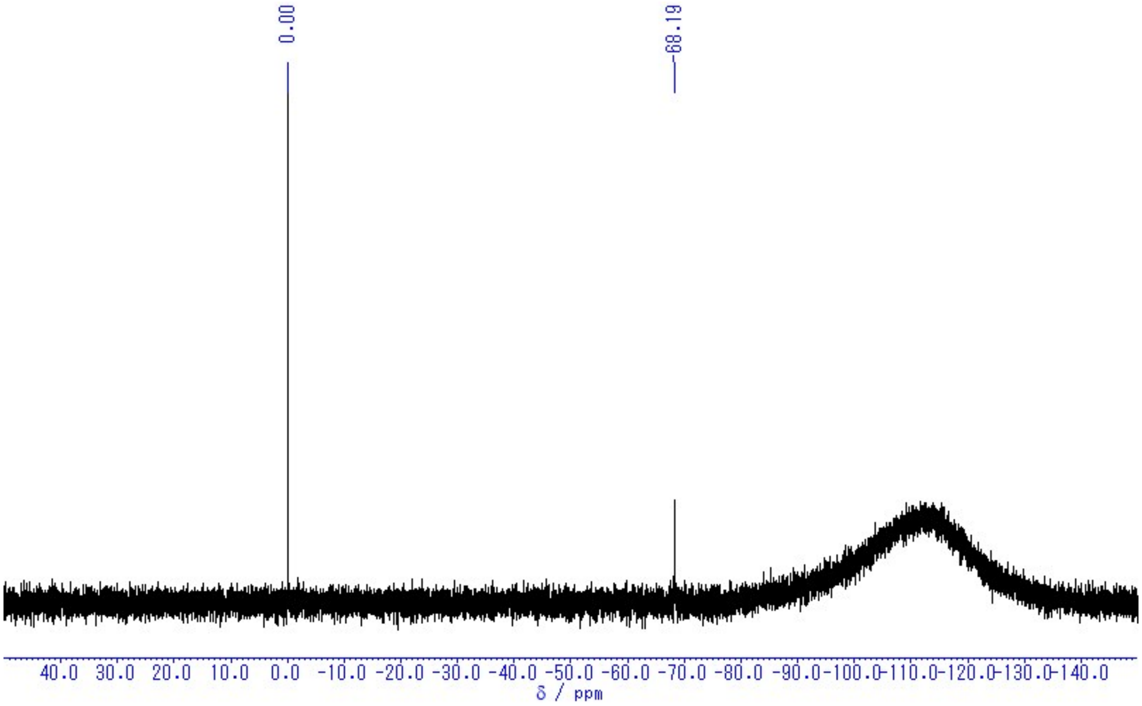


Chart 12. ^{29}Si NMR spectrum of the **PPOSS** in $CDCl_3$ at 25 °C (80 MHz).

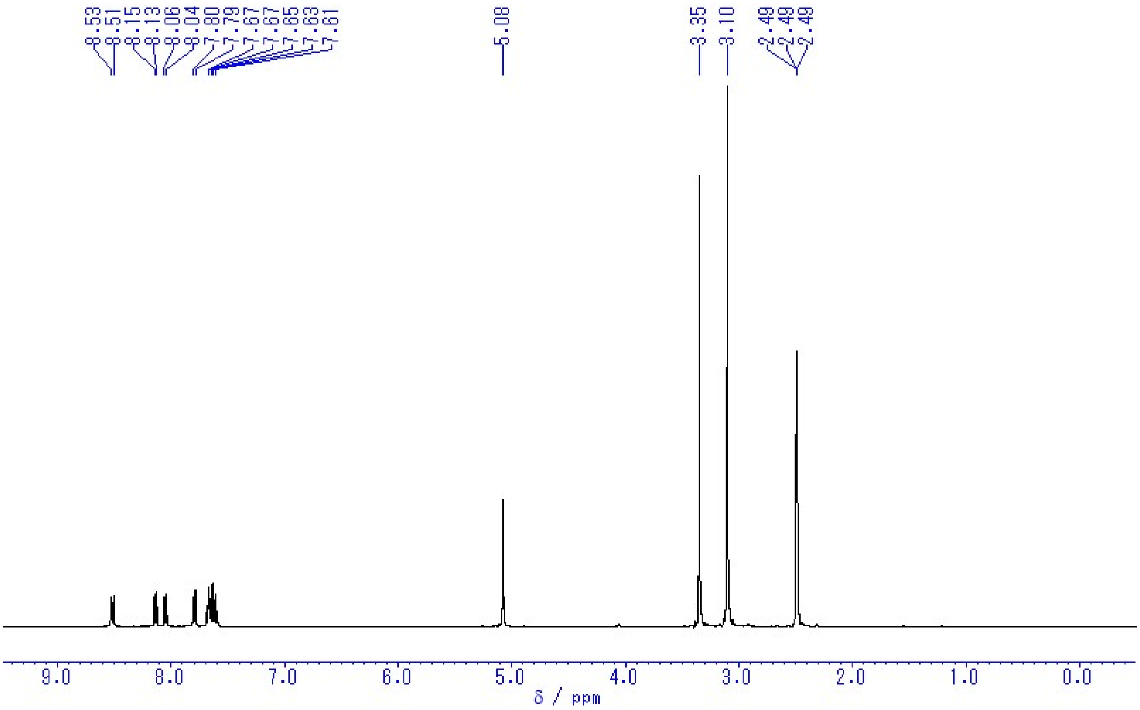


Chart 13. ^{1}H NMR spectrum of the **NTMA** in DMSO-d_6 at 25 °C (400 MHz).

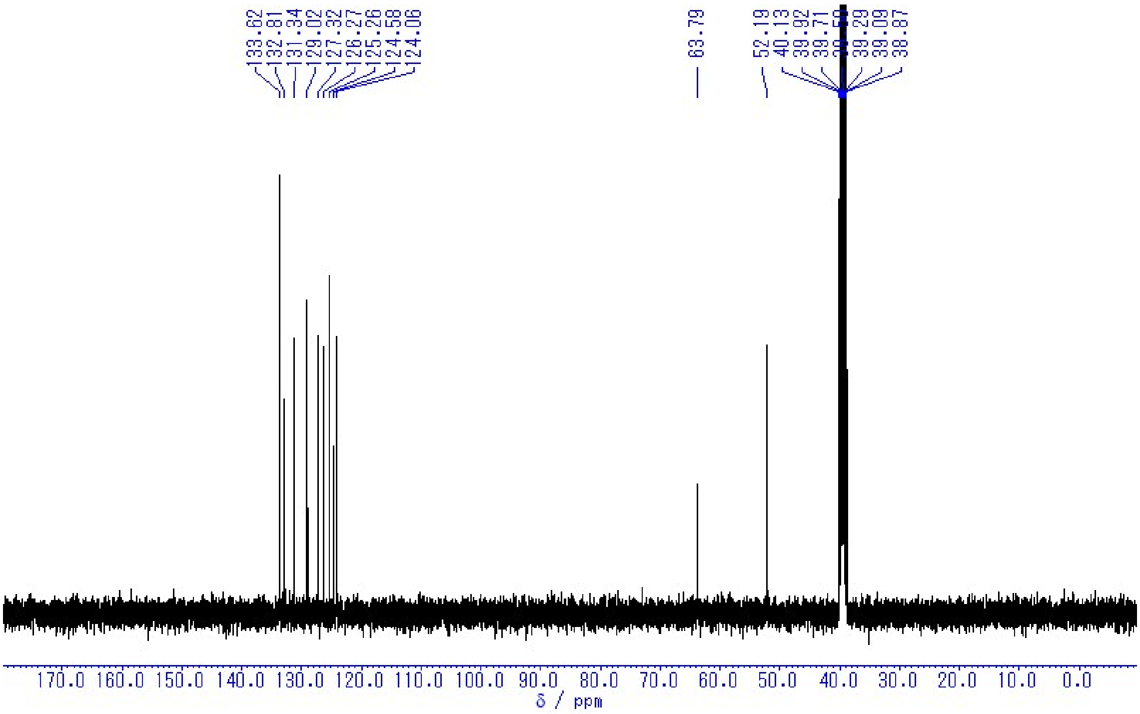


Chart 14. ^{13}C NMR spectrum of the **NTMA** in DMSO-d_6 at 25 °C (100 MHz).

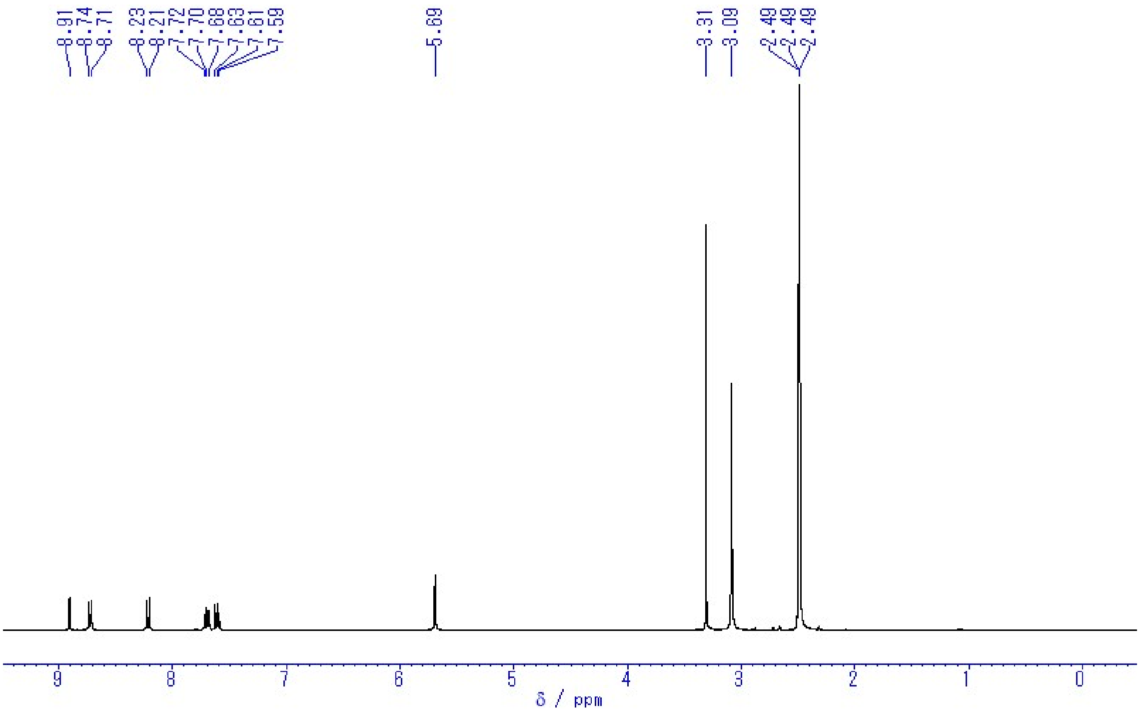


Chart 15. ^{1}H NMR spectrum of the **ATMA** in DMSO-d_6 at 25 °C (400 MHz).

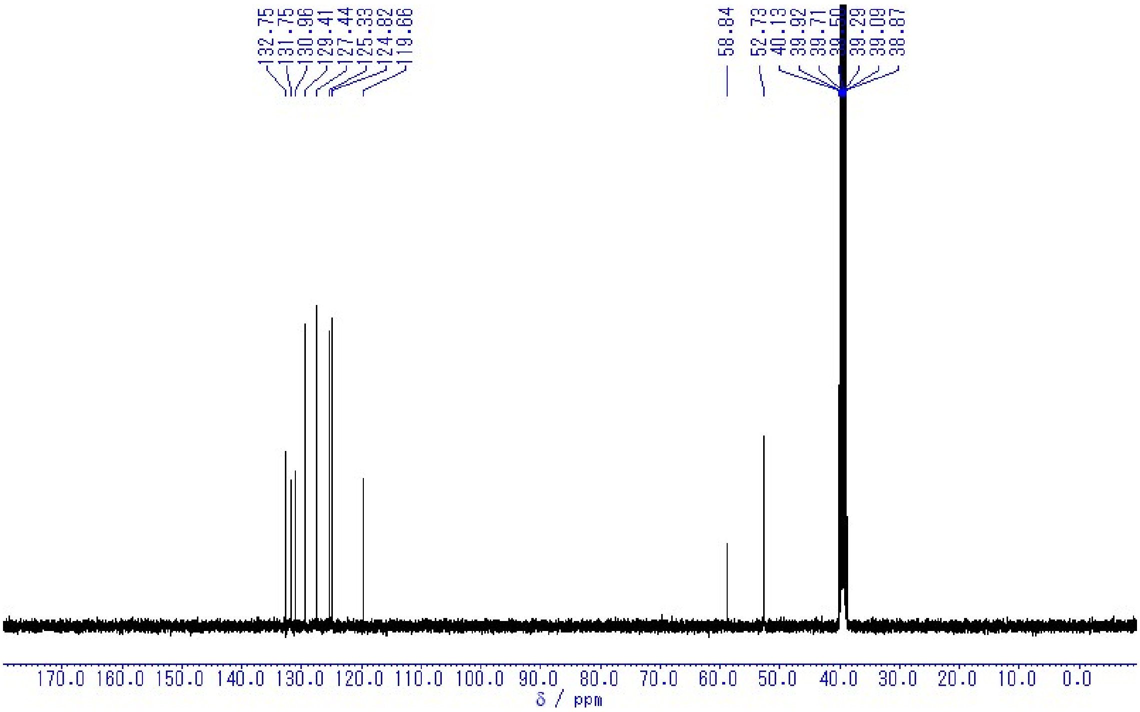


Chart 16. ^{13}C NMR spectrum of the **ATMA** in DMSO-d_6 at 25 °C (100 MHz).

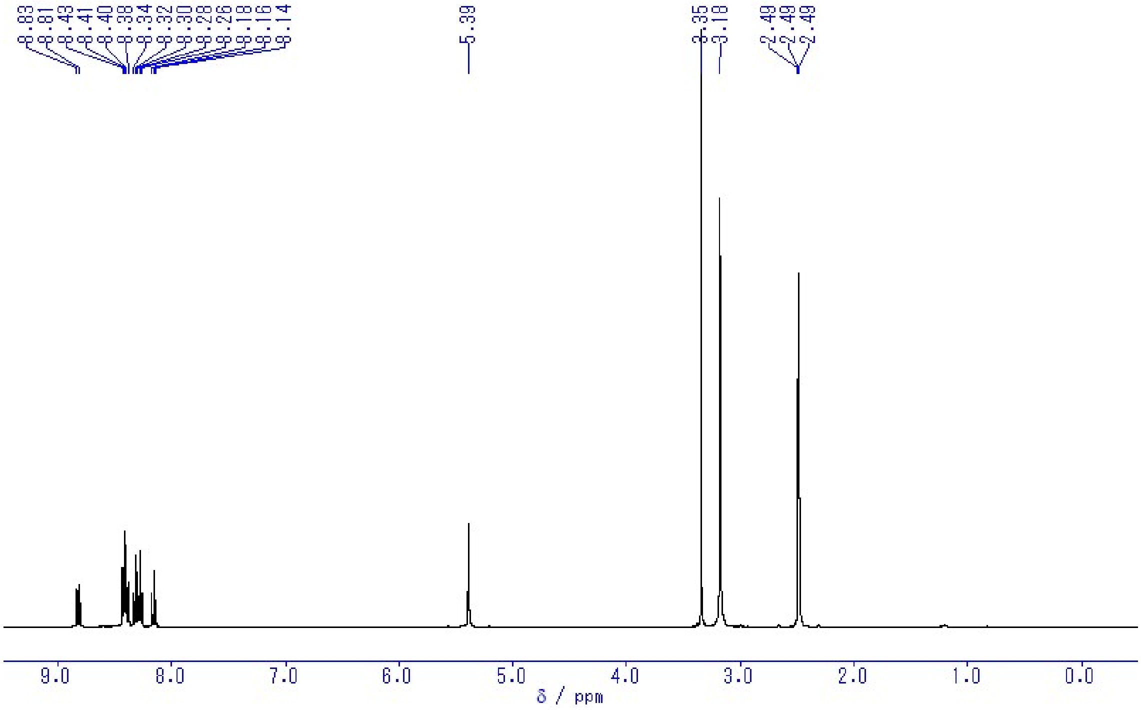


Chart 16. ^{1}H NMR spectrum of the **PTMA** in DMSO-d_6 at 25 °C (400 MHz).

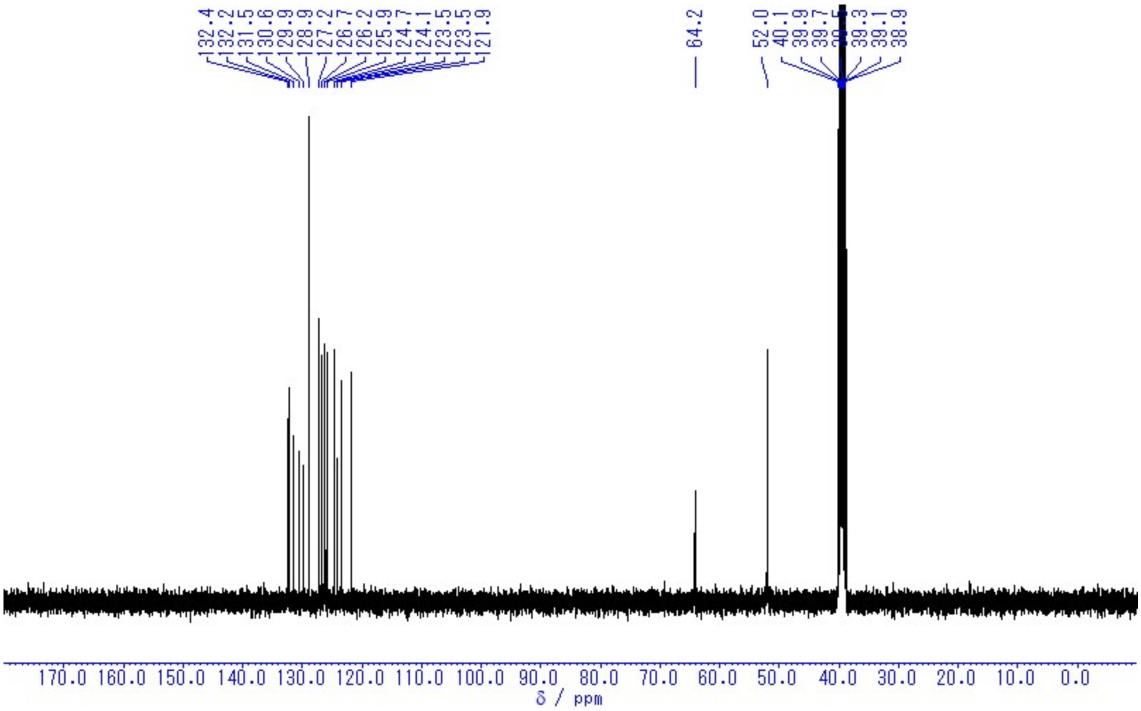


Chart 18. ^{13}C NMR spectrum of the **PTMA** in DMSO-d_6 at 25 °C (100 MHz).

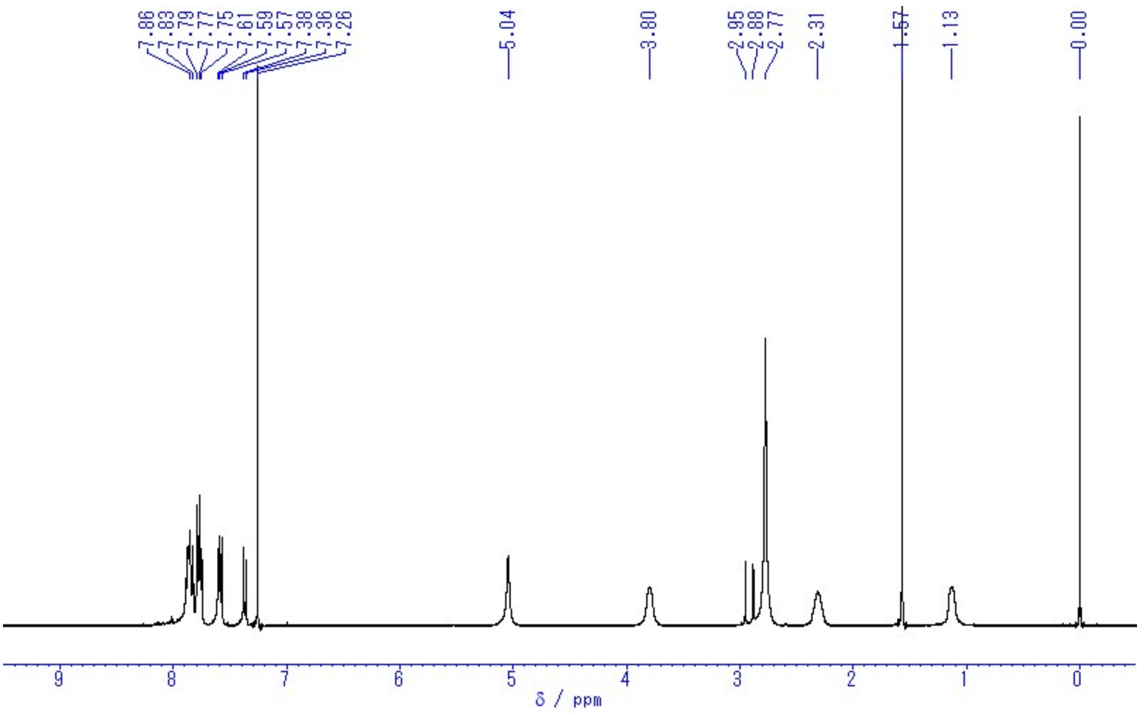


Chart 19. ^{1}H NMR spectrum of the **PPOSS-TFSI** in $CDCl_3$ at 25 °C (400 MHz).

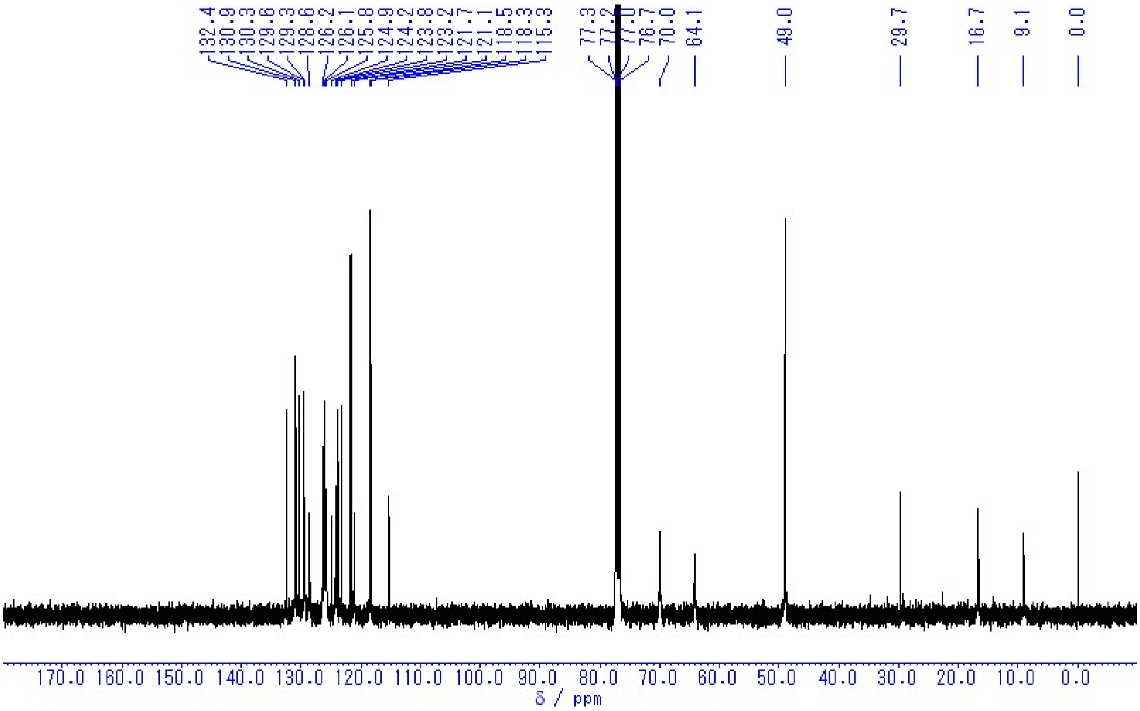


Chart 20. ^{13}C NMR spectrum of the **PPOSS-TFSI** in $CDCl_3$ at 25 °C (100 MHz).

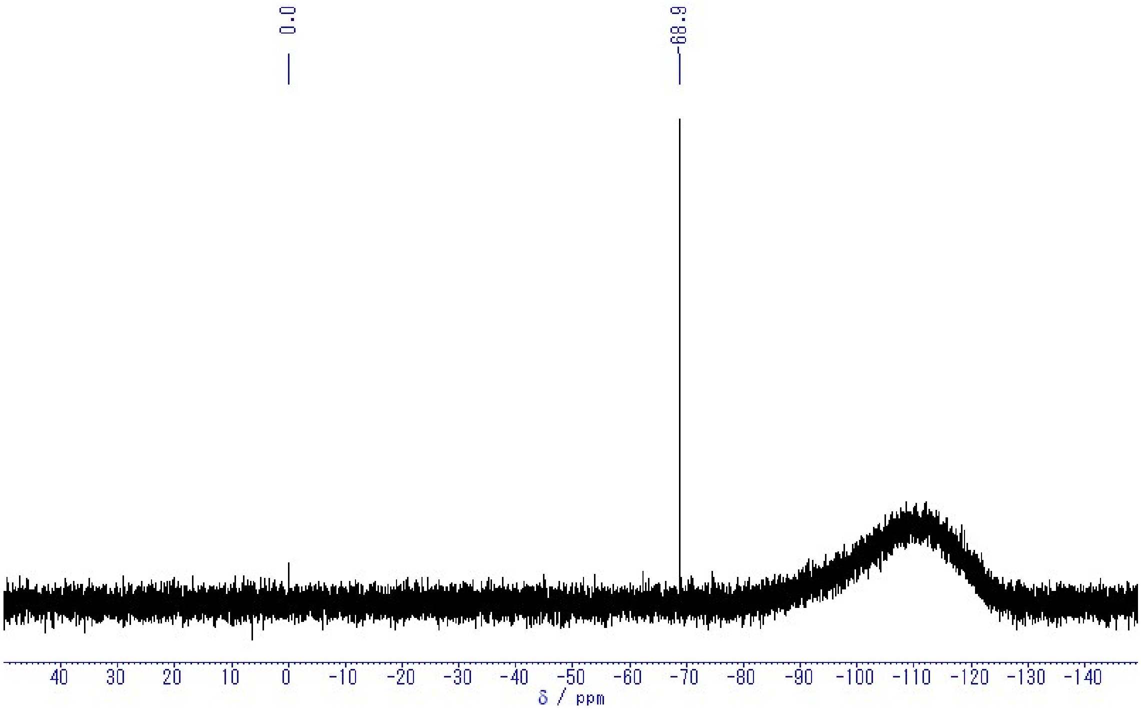


Chart 21. ^{29}Si NMR spectrum of the **PPOSS-TFSI** in $CDCl_3$ at 25 °C (80 MHz).

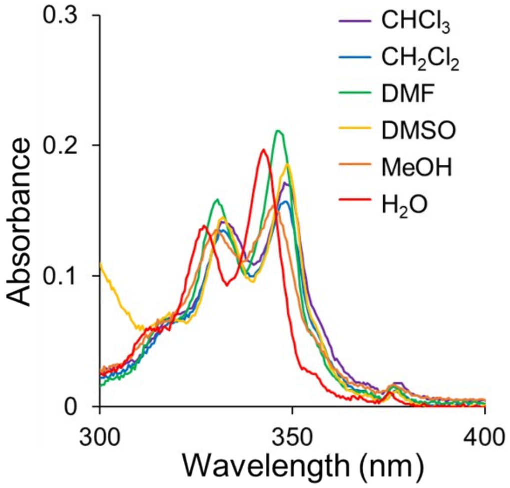


Figure S1. Absorption spectra of **PPOSS** in various solvents (1.0×10^{-6} M, including 1 v/v% of DMSO).

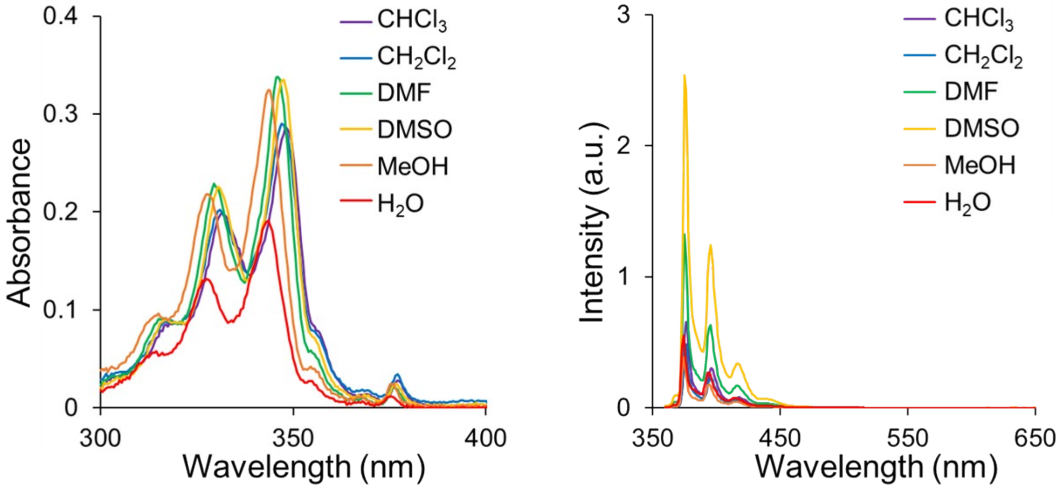


Figure S2. UV–vis absorption and PL spectra of **PTMA** in various solvents (1.0×10^{-6} M, including 1 v/v% of DMSO) excited at 349 nm.

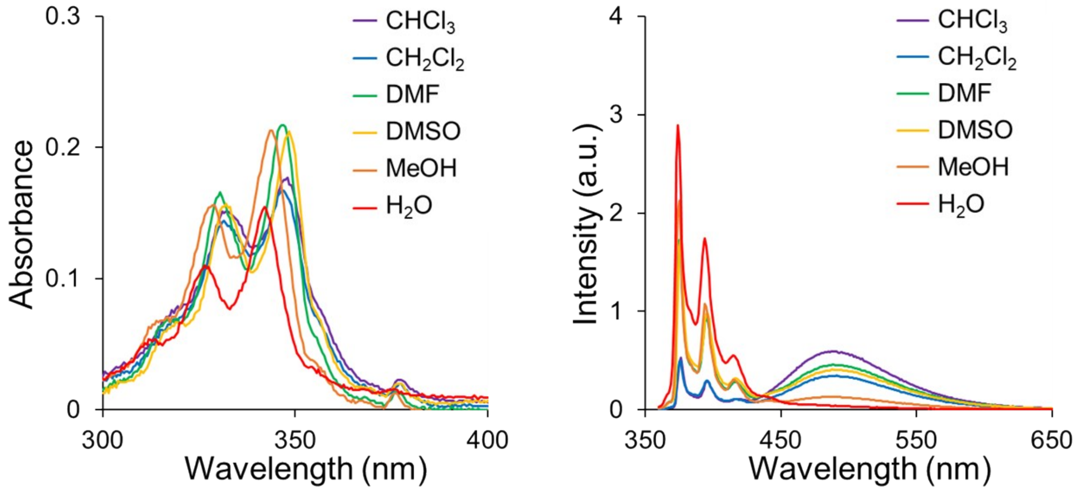


Figure S3. UV–vis absorption and PL spectra of **PPOSS-TFSI** in various solvents (1.0×10^{-6} M, including 1 v/v% of DMSO) excited at 349 nm.

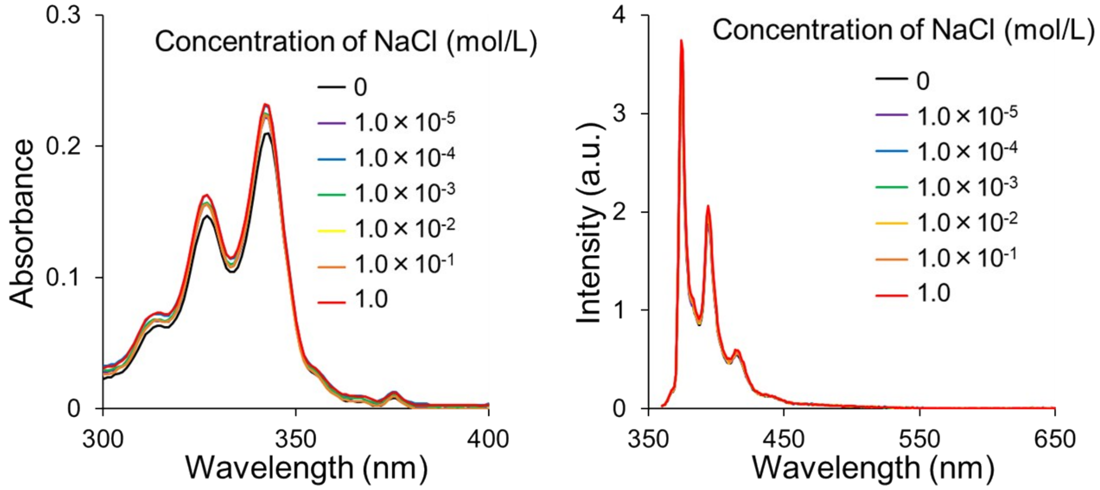


Figure S4. UV–vis absorption and PL spectra of **PPOSS** in H_2O (1.0×10^{-6} M, including 1 v/v% of DMSO) with various concentration of NaCl excited at 349 nm.

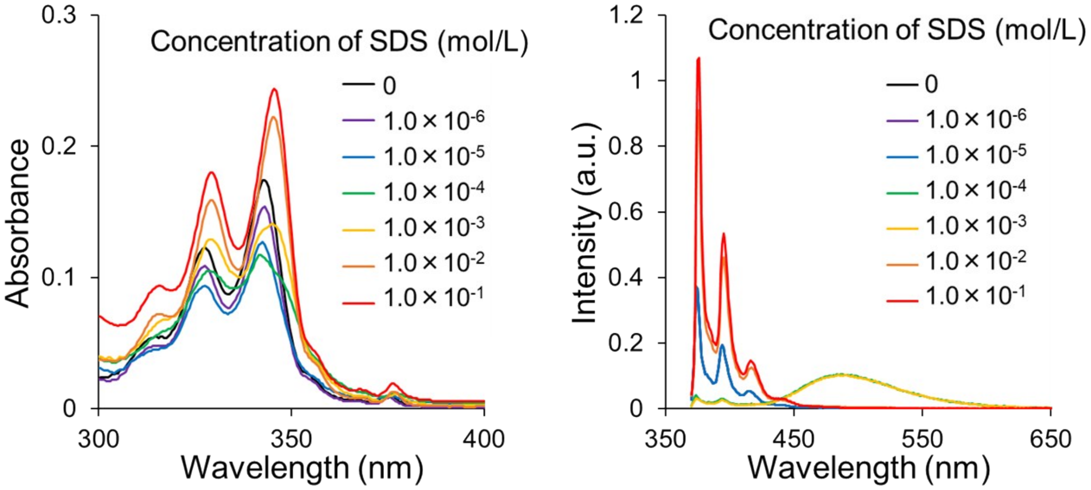


Figure S5. UV−vis absorption and PL spectra of **PPOSS** in H_2O (1.0×10^{-6} M, including 1 v/v% of DMSO) with various concentration of SDS excited at 349 nm.

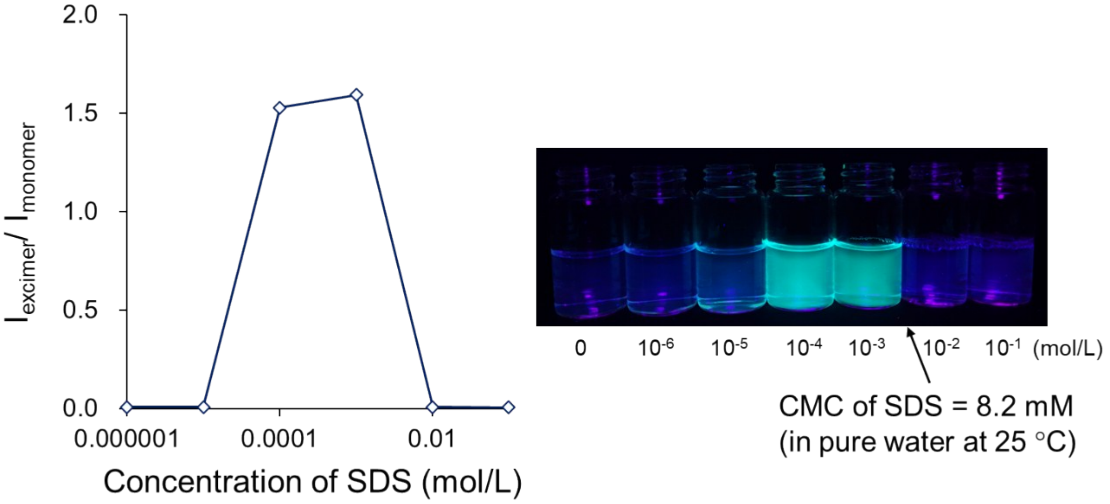


Figure S6. Intensity of excimer to monomer emission of **PPOSS** aqueous solution (1.0×10^{-6} M, including 1 v/v% of DMSO) with various concentration of SDS excited at 349 nm.

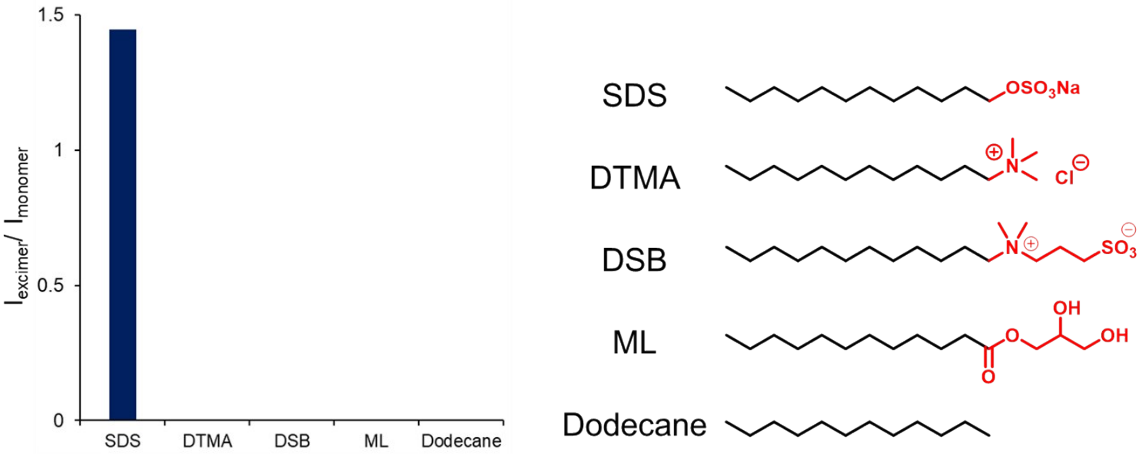


Figure S7. Intensity of excimer to monomer emission of **PPOSS** aqueous solution (1.0×10^{-6} M, including 1 v/v% of DMSO) with various amphiphilic molecules (1.0×10^{-4} M) excited at 349 nm.

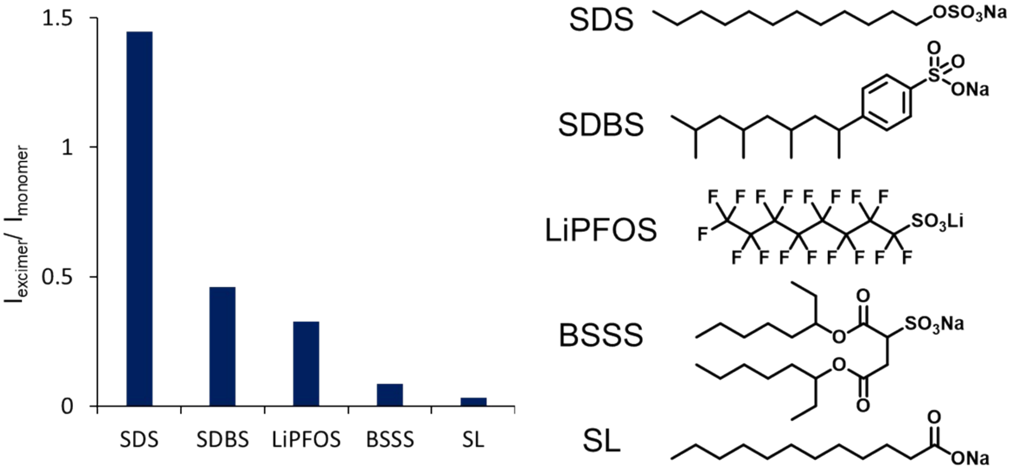


Figure S8. Intensity of excimer to monomer emission of **PPOSS** aqueous solution (1.0×10^{-6} M, including 1 v/v% of DMSO) with various anionic surfactants (1.0×10^{-4} M) excited at 349 nm.

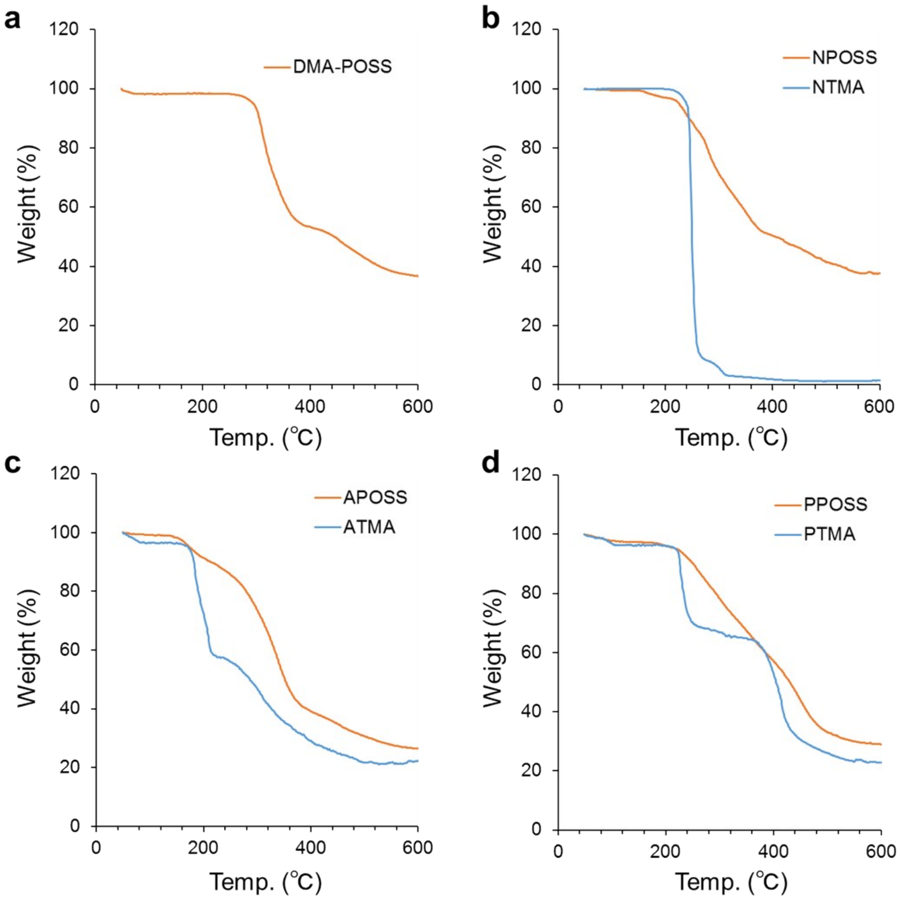


Figure S9. TGA thermograms of the compounds.

Table S1. The results of TGA

	DMA-POSS	NPOSS	NTMA	APOSS	ATMA	PPOSS	PTMA
T_{d10}^{a} [°C]	305	245	242	213	181	251	226

[a] Thermal decomposition temperature with a 10% mass loss.

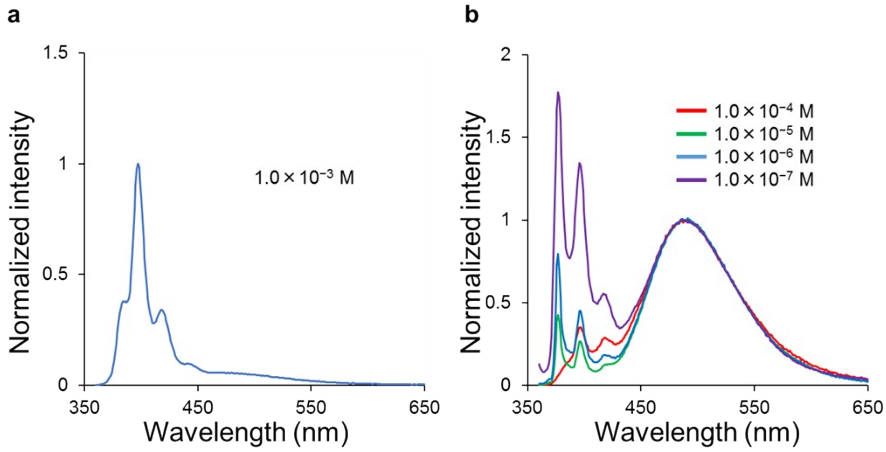


Figure S10. PL spectra with variable concentrations in chloroform containing (a) PTMA and (b) PPOSS (λ_{ex} = 349 nm, 25 °C).