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Supporting Information to

Halogen-Bonding for Visual Chloride Ion Sensing: A Case Study Using Supramolecular Poly(aryl ether) Dendritic Organogel System

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Table of Contents

1. General Information

Unless otherwise noted, all experiments were carried out under an inert atmosphere of dry nitrogen by using standard Schlenk-type techniques. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on Bruker AMX 300 Spectrometer (^{1}H: 300 MHz; ^{13}C: 75 MHz); Bruker AMX-600 spectrometers (^{1}H: 600 MHz; ^{13}C: 150 MHz) or Bruker AMX-500 spectrometers (^{1}H: 500 MHz; ^{13}C: 125 MHz) at 298 K. Chemical shifts are reported in parts per million (ppm) relative to the internal standards, partially deuterated solvents or tetramethylsilane (TMS). Coupling constants (*J*) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, m = multiplet, br = broad. High resolution MS (P-ESI HRMS) were obtained on Bruker Apex IV FTMS spectrometer. Elemental analysis was performed on a Flash EA 1112 Elemental Analyzer.

All chemicals were obtained from Aldrich, Alfa or Acros and used as received unless otherwise mentioned. The organic solvents used were dried according to published methods.

2. Description on Experimental Techniques

Scanning Electron Microscopy (SEM). The morphologies and sizes of the dendritic xerogels were characterized by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) at an accelerating voltage of 15 kV. Samples were prepared by dropping the diluted gels on silicon slices and dried by air for 2 days. To minimize sample charging, a thin layer of Au was deposited onto the samples before SEM examination.

Transmission Electron Microscopy (TEM). TEM was performed on a JEOL JEM-1011 microscope. Samples were prepared by dropping the diluted gels on carbon coated copper grids and the TEM pictures were obtained without staining.

Rheological Measurements. Rheological measurements were carried out with a stress-controlled rheometer (TA Instruments, AR-G2) equipped with steel parallel-plate geometry (40 mm diameter). The gap distance was fixed at 750μm. A solvent-trapping device was placed above the plate to avoid evaporation. All measurements were made at 10 °C.

The frequency sweep was obtained from 0.1 rad/s to 100 rad/s at a constant strain of 0.1%, well within the linear regime determined by the strain sweep.

Powder X-Ray Diffraction (PXRD). The dendritic organogel **1** in mixed solvent of DCM-n-Hexane (1:3, v/v) was coated on a glass plate and the solvent was slowly evaporated. Then the glass plates with dry gels were fixed on a sample holder and subjected to XRD analysis at room temperature on a Japan Rigaku D/MAX-2500/PC diffractometer. XRD patterns were recorded at a scanning rate of 2° min^{-1} in the 2θ range of 0.5 to 30 with Cu- $K\alpha$ radiation (λ = 1.54178 Å).

Small-angle X-ray scattering (SAXS). SAXS measurements were performed on equipment with a SAXSess camera (Anton-Paar, Graz, Austria), which is connected with an X-ray generator (Philips) operating at 40 kV and 50 mA employing Cu K_a radiation (γ = 0.154 nm). The 1D scattering function (log$I$(q)) was obtained by integrating the 2D scattering pattern, which was recorded on an imaging-plate detector (Perkin–Elmer) using SAXS Quant software (Anton-Paar, Graz, Austria). The gel samples were xerogels with the solvents being taken out in vacuo at room temperature. It was sealed in a solid sample holder and the blank scattering was subtracted from the sample scattering to obtain the xerogel exact diffraction pattern.

High-resolution mass spectrometry (HRMS-ESI). Mass spectra of **1**-Cl^- complex was measured on a Fourier transform ion cyclotron resonance mass (spectrometer Bruker Daltronic APEX-Qe 7.0), equipped with a nanospray ionization source. Solutions of **1** and tetrabutylammonium chloride in acetonitrile were used for nanospray ionization.

Thermal Behaviors of the Dendritic Gels: The thermally reversible gel–sol transition temperatures (T_{gel}) were determined by using a tube-inversion methodology.[S1] A sealed vial containing a gel was immersed upside-down in a thermostated water bath. The temperature of the bath was raised at a rate of approximately 2 ºC/min. The T_{gel} was defined as the temperature at which the gel moved on tilting of the vial. The experimental error of T_{gel} in repreated independent measurements was less than 1 ºC.

3. Additional Experimental Data and Figures

3.1 Gelation Tests

Gelation test: A weighed sample of dendritic gelator was mixed with a solvent (0.2 mL) in a septum-capped vial and heated in an oil bath until the solid was dissolved. If the compound was unable to dissolve, it was noted as insoluble (I). A stable turbid organogel was obtained when the prepared sample was treated with ultrasound (0.40 W/cm^2, 40 KHz,) for 1-10 minutes at the beginning of the cooling process in a certain solvent at ambient condition. The aggregation state was then assessed. If no flow was observed when inverting the vial, a stable gel was formed and noted as gelation (G). If part of the mixture formed a gel but flow was still observed, the phenomenon was recorded as partial gelation (PG). If precipitation occurred, P was noted, and if the clear solution (> 60 mg/mL) was retained, it was marked as soluble (S). Repeated heating and cooling under ultrasound treatment (0.40 W/cm^2, 40 KHz, 1~10 minutes) confirmed the thermo-reversibility of the gelation process. The critical gelation concentration (CGC) of the organogelator was determined by measuring the minimum amount of gelator required for the formation of a stable gel at room temperature.

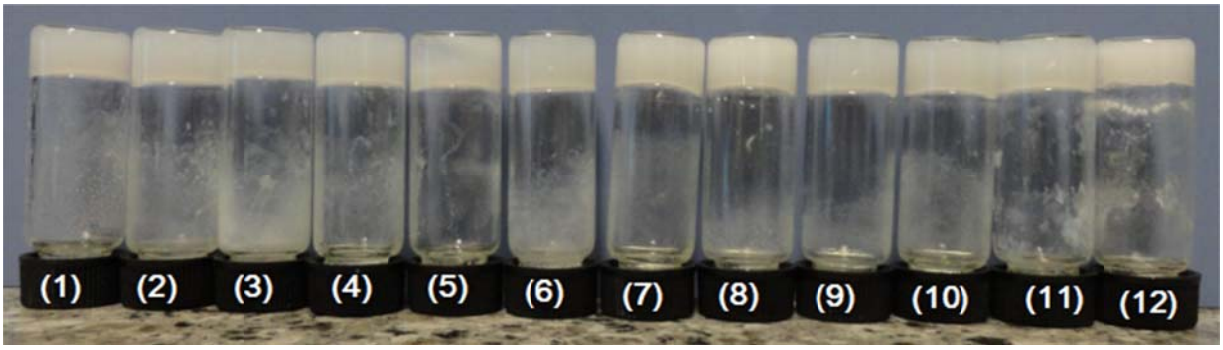


Figure S1. Photograph of dendron **1** showing gel formation which remained stable upon vial inversion in various organic solvents and mixed solvents (from left to right): (1) methanol, (2) ethanol, (3) isopropanol, (4) 1-butanol, (5) toluene/n-hexane = 1/3 (*v/v*), (6) anisole/n-hexane = 1/3 (*v/v*), (7) acetone/n-hexane = 1/8 (*v/v*), (8) 2-hexanone/n-hexane = 1/3 (*v/v*), (9) dichloromethane/n-hexane = 1/3 (*v/v*), (10) dichloroethane/n-hexane = 1/3 (*v/v*), (11) ethyl acetate /n-hexane = 1/3 (*v/v*), (12) THF/n-hexane = 1/8 (*v/v*).

Table S1. Critical gelation concentrations (CGCs) of dendrons **1** and **2** in various organic solvents and mixed solvents.[a]

Slovents	CGCs[b]	
	1	2
Toluene	S	S
Anisole	S	S
Pyridine	S	S
Ethyl acetate	S	S
Acetone	S	S
Cyclohexane	S	S
Acetonitrile	S	S
1,2-Dichloromethane	S	S
Methanol	G(3.3)	P
Ethanol	G(4.4)	P
Isopropanol	G(6.5)	P
1-Butanol	G(9.3)	P
Toluene:n-Hexane (1:3, v/v)	G(6.9)	I
Anisole:n-Hexane (1:3, v/v)	G(7.5)	S
Acetone:n-Hexane (1:8, v/v)	G(9.4)	S
2-Hexanone:n-Hexane (1:3, v/v)	G(7.5)	S
Dichloromethane:n-Hexane (1:3, v/v)	G(7.3)	I
1,2-Dichloroethane:n-Hexane (1:3, v/v)	G(5.7)	I
Ethyl acetate:n-Hexane (1:3, v/v)	G(6.6)	S
THF:n-Hexane (1:8, v/v)	G(8.7)	S

[a] G = stable gel, I = insoluble, P = precipitation, S = soluble (> 60 mg/mL). [b] CGC is the critical gelator concentration at which gelation was observed to restrict the flow of the medium at 25 °C.

The Dendritic Gelation Induced by Ultrasound

Ultrasound was also used as an external stimulus to trigger the phase transition of the gel.[S2] In our studies, it was found that the sonication exhibited an intriguing effect on the gelation efficiency. For example, when the heated solution of dendron **1** in ethanol was cooled to room temperature, suspension instead of stable gel was observed. But if the suspension or its hot solution was submitted to sonication irradiation for minutes (0.4 w/cm^2, 40 KHz), a translucent gel was formed rapidly.

To understand the effect of sonication on gelation process, the aggregates morphologies before and after sonication were studied by means of scanning electron microscopy (SEM). As shown in Figure S2, at the beginning, without ultrasound a morphology of microsphere aggregates with diameter about 2~5 μm emerged; short sonication (30 s) favored even smaller microspheres of diameter about 1~2 μm; prolonged sonication (60 s), the microsphere aggregates tended to interconnect and further evolve into extended superstructures; longer exposures (90 s) leaded to a “fur-like” network morphology; finally (180 s) it gave rise to a final architecture of a dense 3D network composed of much thinner, micrometer long fibers. The results above suggested that ultrasound induced not only rapid gel formation but also morphological changes from microspheres to nanofibers responsible for gelation.

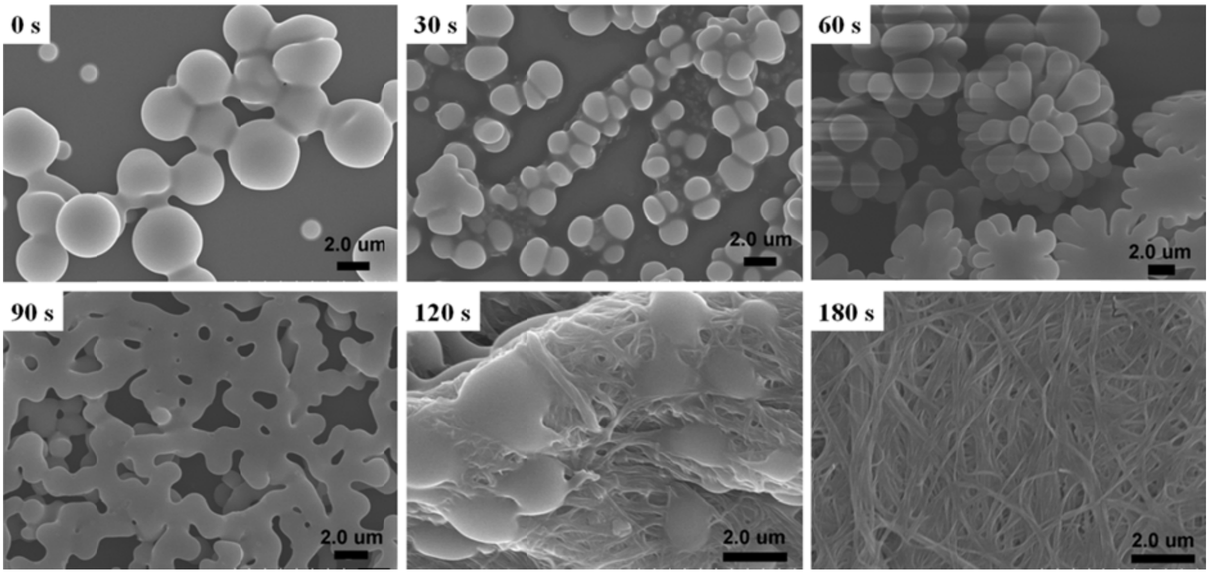


Figure S2. SEM observations of the conversion process from spheroidal aggregates into nanofibers. A homogeneous solution of dendron **1** in ethanol after heating above 100 ^{o}C was subjected to ultrasound for different time (0.40 W/cm^2, 40 KHz, 1~3 minutes).

3.2 Thermal Behaviors of the Dendritic Gels

The gel-sol phase transition temperatures (T_{gel}) of the dendritic gels were determined by the tube-inversion method. In general, the stability of the gels increased with increasing concentration, as established for the series of **1**/dichloroethane-n-hexane and **1**/toluene-n-hexane gels formed with the gelator concentrations varying from 7-24 mg/mL (Figure S3).

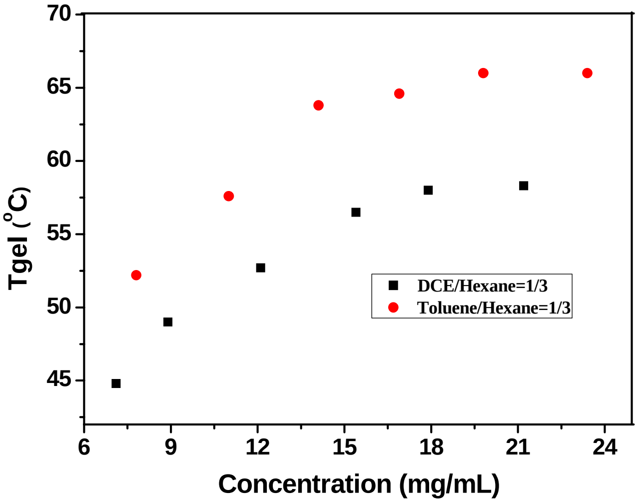


Figure S3. Plots of T_{gel} versus concentration of dendritic gelator **1** in mixed solvents.

3.3 The Elastic Properties of Dendritic Gels 1 by Rheological Measurements

The elastic property of dendritic gel **1** was also estimated using rheological measurements. As shown in Figure S4, the storage modulus G′ is larger than the loss modulus G″, and a pronounced plateau region of these moduli plotted against the frequency in range of 0.1-100 rad/s, which is a characteristic feature of gels.

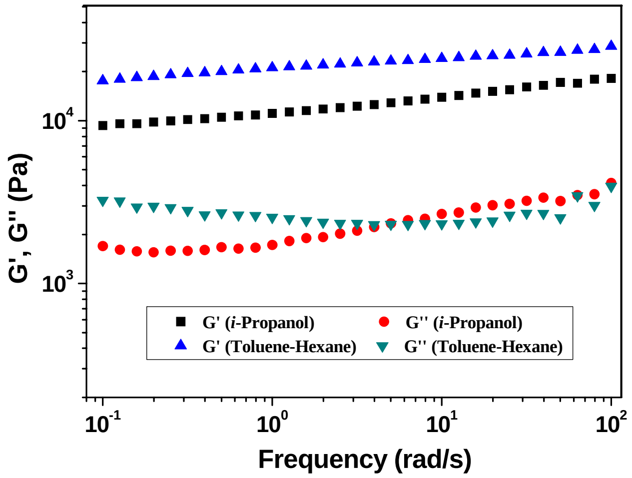


Figure S4. Evolution of storage modulus G' and loss modulus G″ as a function of frequency of the organogel **1** (20 mg/mL).

3.4 The Thixotropic Properties of Dendritic Gels 1 by Rheological Technique

To verify the thixotropic behaviors of the dendritic organogels, rheological experiments were carried out. As shown in Figure S5a, the storage modulus (G') and loss modulus (G") as a function of angular frequency (ω) of gel **1**/isopropanol at 20 mg/mL were determined, showing that the gels behaved as a true gel. Strain amplitude sweeps were also proceeded to reveal the elastic response of **1**/isopropanol. As shown in Figure S5b, the value of G' rapidly decreased in the region above the critical strain value ($\gamma > 1\%$), known as the upper of the linear viscoelastic regime, representing a partial collapse of the gel to a quasi-liquid state. Interestingly, this gel exhibited a very quick recovery of mechanical strength after the large amplitude oscillatory breakdown (Figure S5c). For example, the initial value of G' was ca. 9×10^3 Pa, it dropped to 78 Pa under a large amplitude oscillatory force (γ = 100%; ω = 6.28 rad s^{-1} (1.0 Hz)), indicating the transformation to a quasi-liquid state. However, when the amplitude oscillation was decreased ($\gamma = 0.1\%$) at the same frequency (1.0 Hz), G' immediately recovered to about 90% of its initial value (8100 Pa) within 10 s, representing the recovery of a quasi-solid state. However, with prolonged time of more than one hour, G′ and G" could reach their initial values (Figure S5d). Furthermore, this thixotropic process could be repeated several times. The thixotropic properties of dendritic organogels of **1** in mixed solvent (toluene/n-hexane) had also been investigated (Figure S6), affording conformable conclusions. All these results of rheological experiments indicated that **1** was promising candidates for thixotropic soft materials with both large mechanical strength and fast-recovery ability.

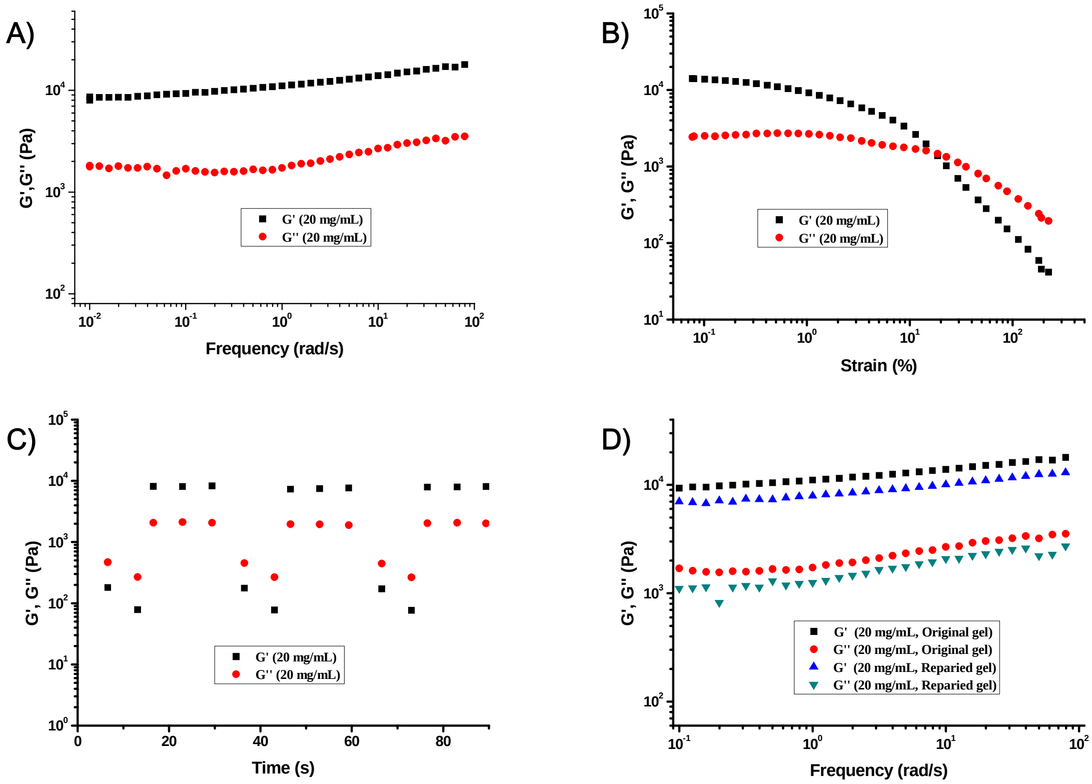


Figure S5. Rheological data of **1** gel from isopropanol (c = 20 mg/mL, 15 ^{o}C): (A) frequency sweep (ω = 0.1-100 rad/s), (B) strain amplitude sweeps, (C) step strain and (D) frequency sweep measurement. Step strain was a continuous measurement for three cycles.

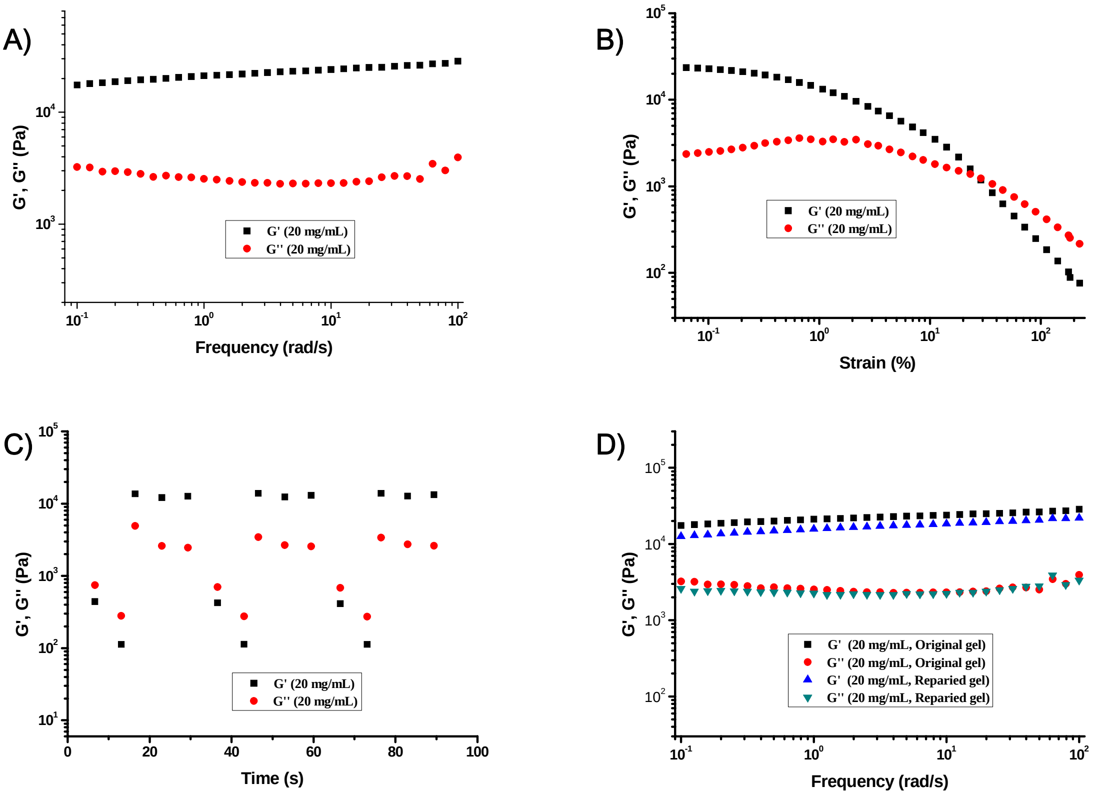


Figure S6. Rheological data of **1** gel from toluene/n-hexane (1/3, *v/v*, 20 mg/mL, 15 °C): (A) frequency sweep (ω = 0.1-100 rad/s), (B) strain amplitude sweeps, (C) step strain and (D) frequency sweep measurement (c = 6 mM). Step strain was a continuous measurement for three cycles.

3.5 Additional SEM and TEM Images

3.5.1 SEM images of the dendritic xerogels of 1 in different solvents

It is should be noted that the different morphologies of the xerogels might depend on the properties of the gelling solvents. For example, as for alcoholic solvents, the morphologies show networks interweaved by fine flexible fibers with diameters smaller than 150 nm and lengths of several micrometers. However, the xerogels from mixed solvents exhibited a bigger and straight ribbon structures with the width from 200-500 nm.

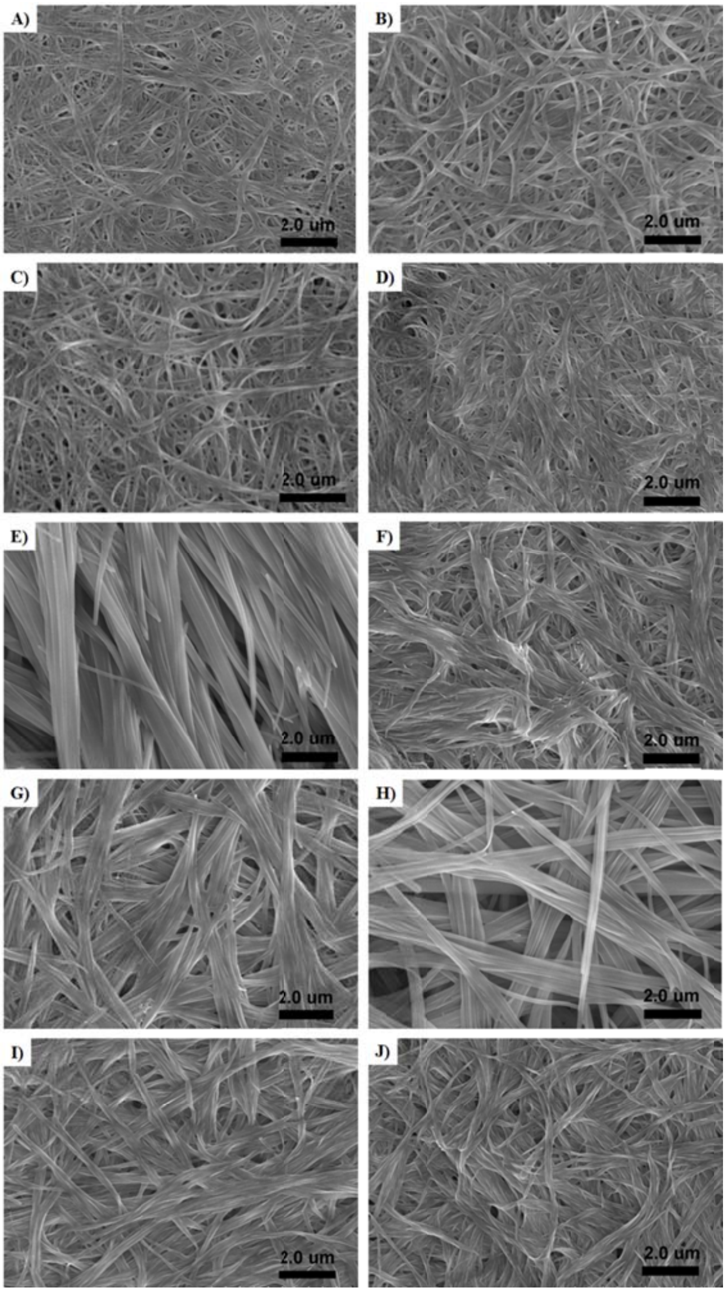


Figure S7. Selected SEM images of the xerogels of **1** in different solvents: (A) methanol, (B) ethanol, (C) isopropanol, (D) 1-butanol, (E) toluene/n-hexane = 1/3 (*v/v*), (F) acetone/n-hexane = 1/8 (*v/v*), (G) 2-hexanone/n-hexane = 1/3 (*v/v*), (H) dichloromethane/n-hexane = 1/3 (*v/v*), (I) 1,2-dichloroethane /n-hexane = 1/3 (*v/v*), (J) ethyl acetate/n-hexane = 1/3 (*v/v*).

3.5.2 TEM images of the dendritic xerogels of 1 in different solvents

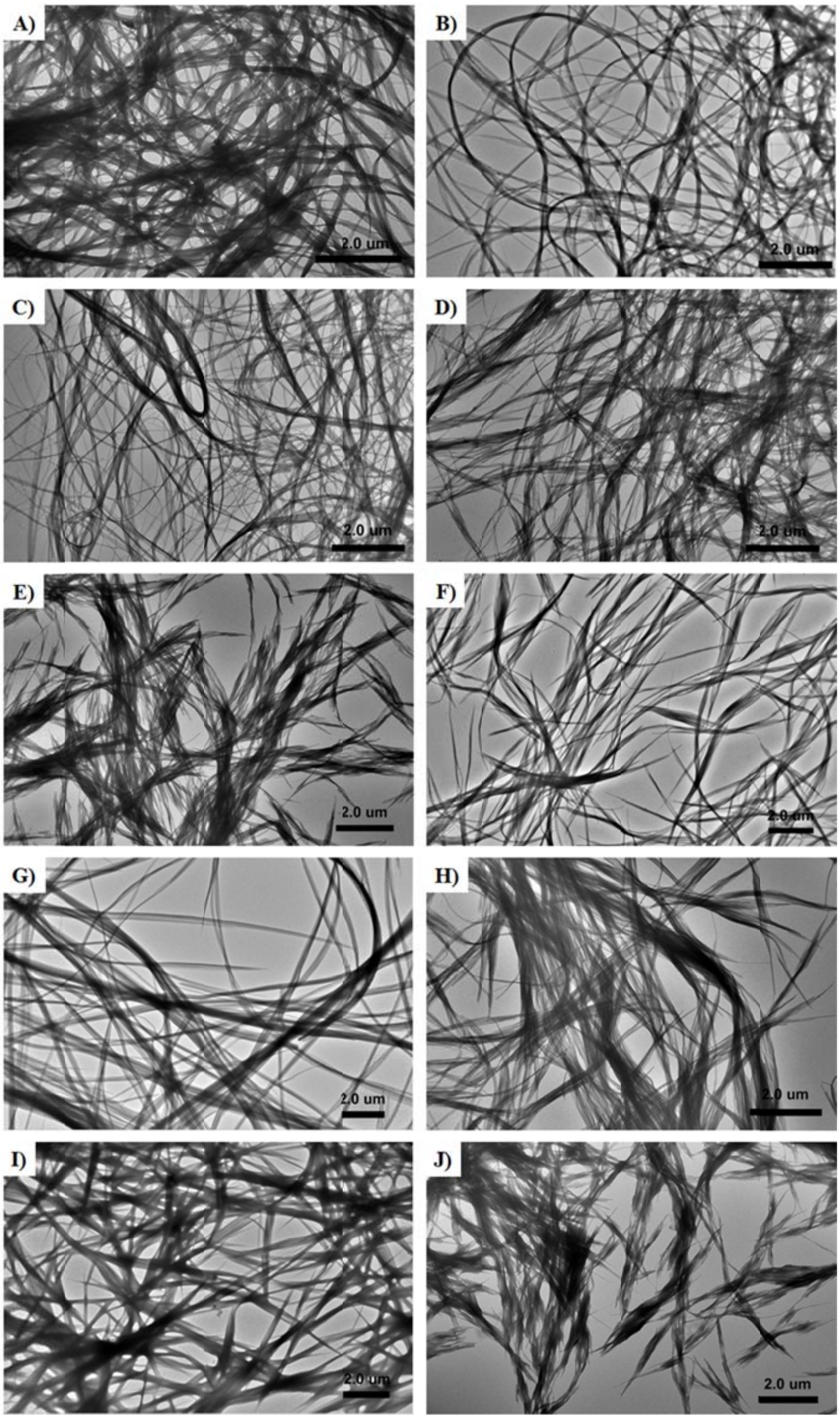


Figure S8. Selected TEM images of the xerogels of **1** in different solvents: (A) methanol, (B) ethanol, (C) isopropanol, (D) 1-butanol, (E) acetone/n-hexane = 1/8 (*v/v*), (F, G) 1,2-dichloroethane/n-hexane = 1/3 (*v/v*), (H) ethyl acetate/n-hexane = 1/3 (*v/v*), (I) 2-hexanone/n-hexane = 1/3 (*v/v*), (J) THF /n-hexane = 1/8 (*v/v*).

3.6 small-angle χ-ray scattering (SAXS) experiment of dendritic xerogel 1

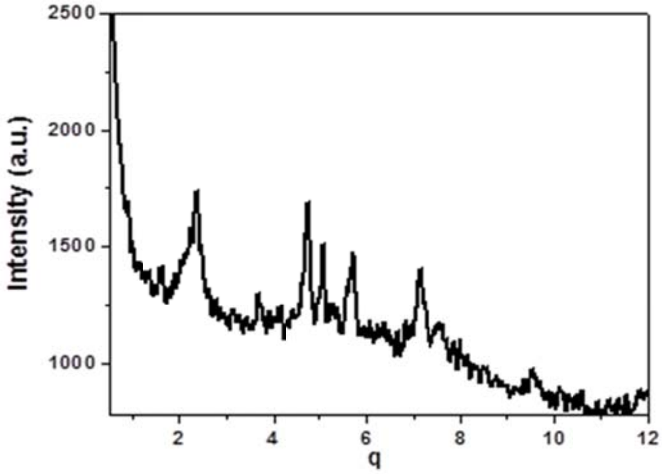


Figure S9. SAXS diagram of **1** xerogel from toluene/n-hexane (1:3, *v/v*) mixed solvents.

	q	$d_{obs.}$ (nm)	$d_{cal.}$ (nm)	hkl
1	1.15	5.46	5.43	010
2	1.63	3.85	3.84	011
3	2.26	2.78	2.72	020
4	2.53	2.48	2.43	021
5	3.67	1.71	1.72	031
6	4.76	1.32	1.36	040
7	5.10	1.23	1.21	042
8	5.73	1.10	1.09	050
9	6.84	0.92	0.91	060
10	7.16	0.88	0.89	061

This pattern is reasonably assigned to a columnar square structure whose diameter of the column is a = b = 5.43 nm, c = 0.37 nm

Number of monodendrons per column stratum:

$$\mu = (N_A ab t\rho)/M$$

Avogadro's number $N_A = 6.0220455 \times 10^{23}$ mol^{-1},

The average height of the column stratum $t = 3.7$ Å,

M is the molecular weight of monodendron.

ρ is the density of dendron **1** (assumed to be 1.6 g/cm^3). Powder of dendron **1** was immersed in several calibrating organic solvents. We decided that the approximate density of **1** was the point at which the powder neither floated nor sank.

So, we can calculate the average number of dendritic molecules in a single slice of the cylinders is approximately six.

3.7 Concentration-Dependent ^{1}H NMR Spectra of dendron 1

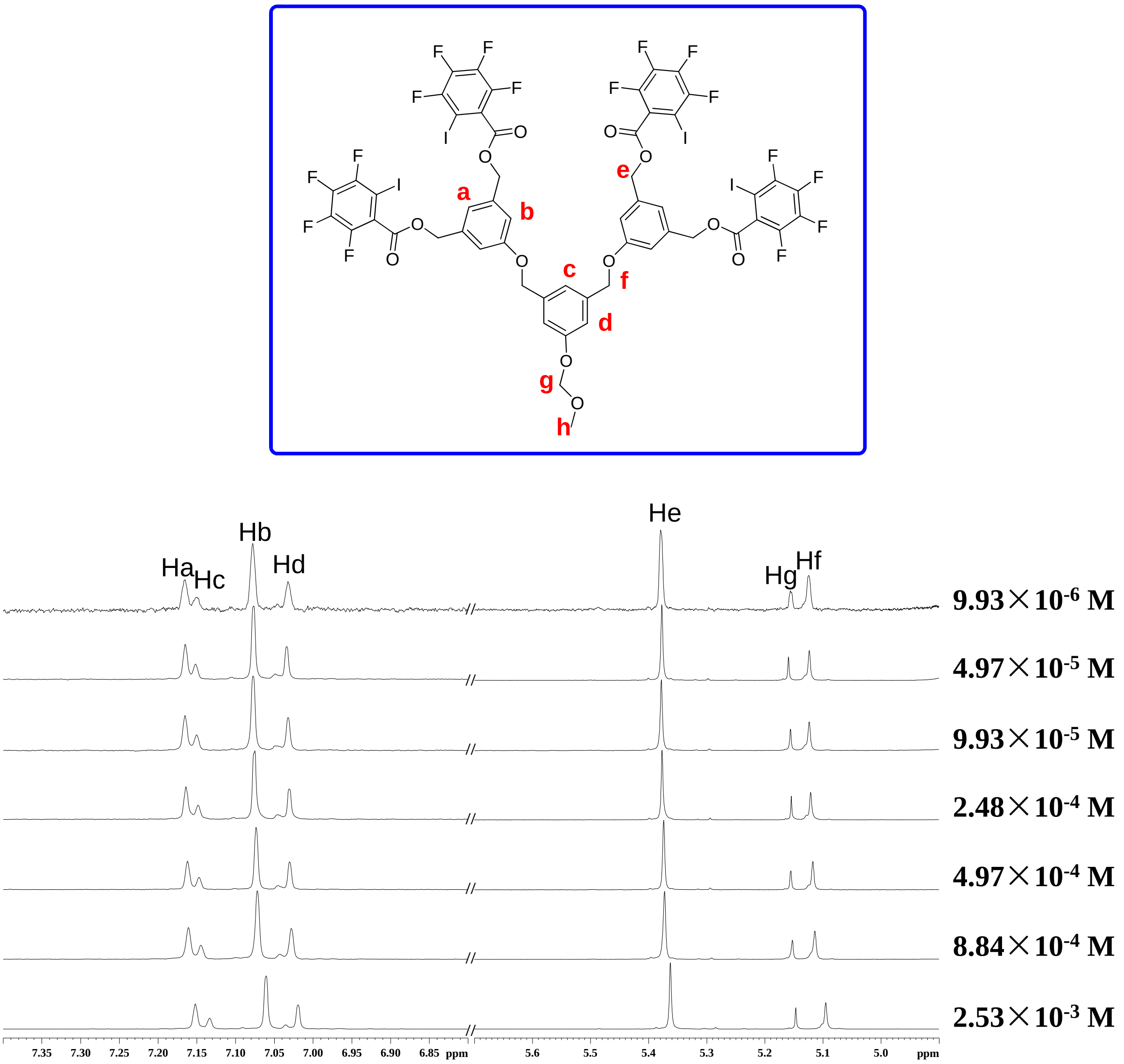
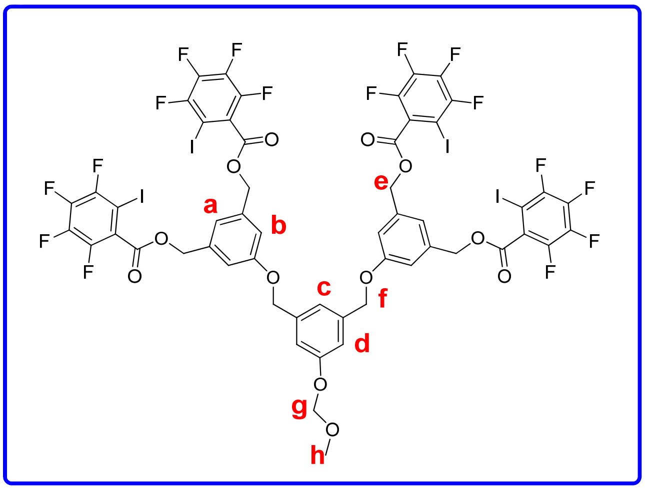


Figure S10. Partial ^{1}H NMR spectra (600 MHz, d_4-methanol) of dendron **1** at different concentrations (298 K) showing the aromatic region (using TMS as internal standard).

3.8 Temperature-Dependent ^1H NMR Spectra of dendron 1



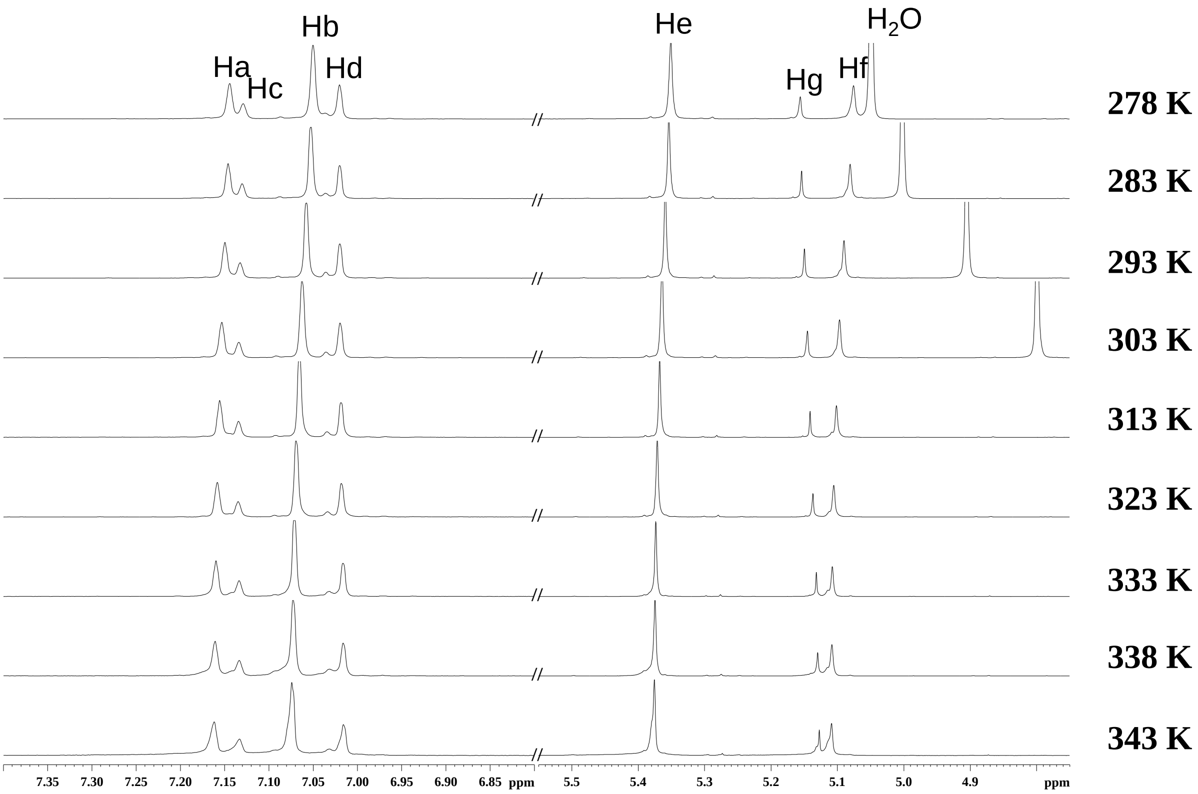
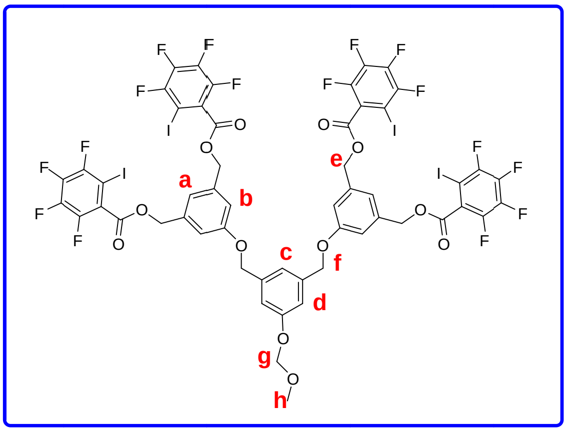


Figure S11. Partial ^{1}H NMR spectra of dendritic gel **1** at different temperatures showing the aromatic region. The gel sample turned into solution at about 333 K (600 MHz, d_4-methanol, 4.0 mg/mL, using TMS as internal standard).

3.9 Solvent Titration Experiment

It has been reported that the solvophobic interaction can effectively enhance supramolecular organizations involving π–π stacked structures.[S3] In our study, dendron **1** was chosen for solvent titration experiment to explore the aggregation behavior. The measurement of ^{1}H NMR spectra was carried out in the $CDCl_3$-CCl_4 binary solvent at a concentration of 24 mg/mL.

The signal-shift trend in the ^{1}H NMR spectra also supported the solvophobically driven π–π stacking. Increasing the volume ratio of $CDCl_3$-CCl_4 resulted in slight upfield shift of the resonance signals for the aromatic protons on the peripheral benzyl rings and the internal benzyl rings, consistent with the results of CD- and TD-^{1}H NMR experiments as shown in Figure S14 and S15. This result indicated that strong solvophobic interactions can enhance aromatic π–π stacking interactions.



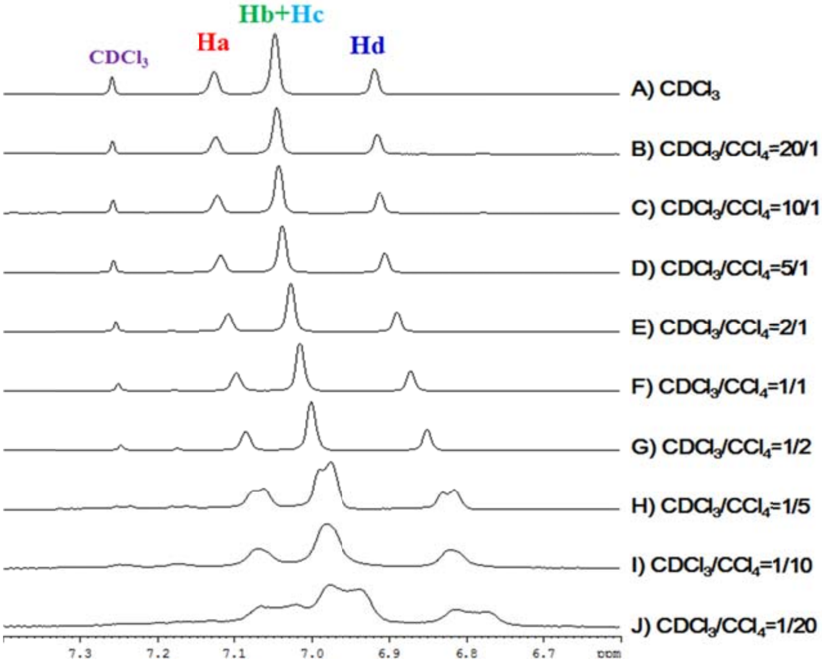


Figure S12. ^{1}H NMR spectra of **1** in the $CDCl_3$-CCl_4 mixed solvent with different CCl_4 volume ratios at 25 °C (300 MHz, 24 mg/mL, using TMS as internal standards). In the cases of (I) and (J), complete gel formation were observed.

3.10 Powder X-Ray Diffraction (PXRD)

From the wide-angle X-ray diffraction of the xerogel of dendron **1** obtained from the mixed solvent (DCM/n-Hexane = 1/3, *v/v*), a *d*-spacing of ca. 3.6 Å similar to the typical π–π stacking distance was observed, suggesting the key role of π–π stacking in the formation of the gel.[S4]

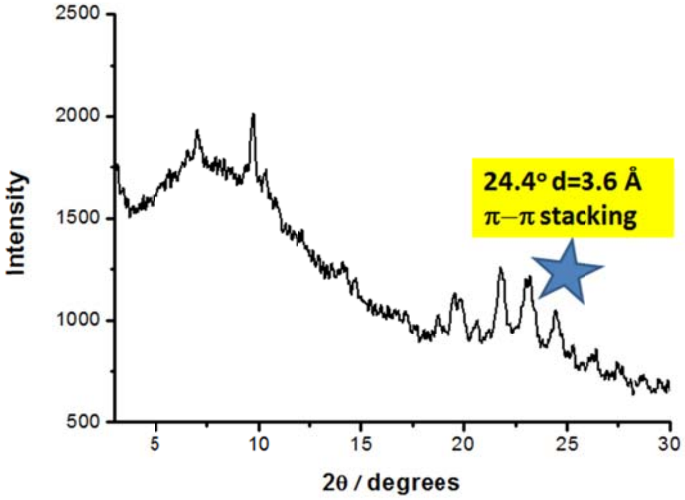


Figure S13. Wide-angle X-ray diffraction of the xerogel of dendron **1** obtained from a mixed solvent (DCM/n-hexane = 1/3, *v/v*).

3.11 Visual discrimination of Chloride anion by Dendritic Gel 1.

Aiming at developing a simple approach to visual discrimination of halogen anions, the anion recognition experiment was first conducted by adding 0.8 equivalent selected target anions (Cl^-, Br^-, I^-, HSO_4^-, NO_3^-, and CN^- as tetrabutylammonium slats, 50 μL in acetone) added onto the stable turbid dendritic gels (12.0 mg/mL, acetone:n-hexane = 1:8, *v/v*). After ten minutes, the vial was inversed and gel-to-sol transition was monitored.

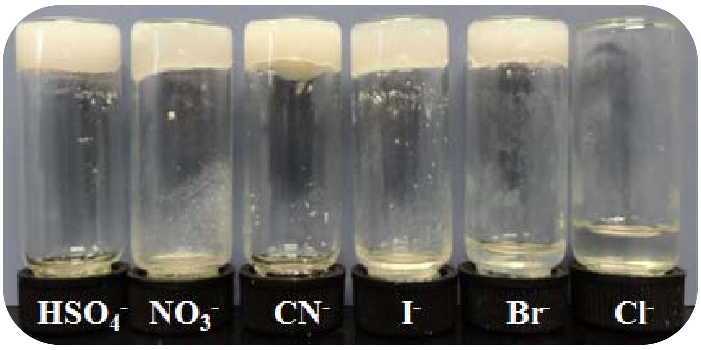
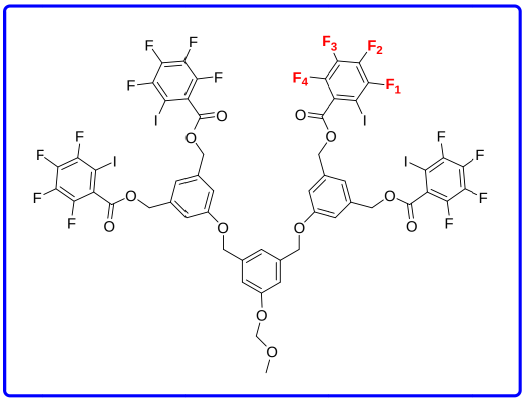


Figure S14. Photographs of the dendritic organogel **1** from mixed solvents (12.0 mg/mL, acetone/ n-hexane = 1/8, *v/v*) after the addition of different anions.

3.12 Determination of Binding Constants by ^{19}F-NMR



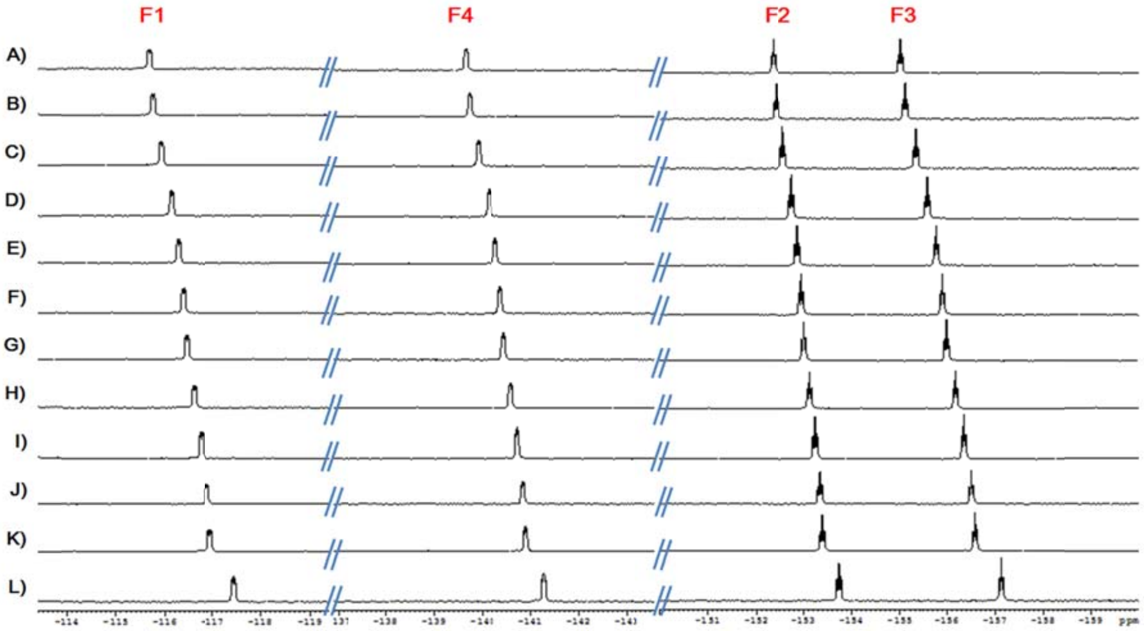


Figure S15. ^{19}F NMR spectra (500 MHz, d_6-acetone, 6.72×10^{-4} M) of dendron **1** at 298 K with different equivalent tetrabutylammonium chloride**.** From the top to the bottom: (A) 0 equiv, (B) 0.2 equiv, (C) 0.4 equiv, (D) 1.0 equiv, (E) 1.4 equiv, (F) 1.8 equiv, (G) 2.0 equiv, (H) 3.0 equiv, (I) 4.0 equiv, (J) 5.0 equiv, (K) 6.0 equiv, (L) 20.0 equiv.

◆ **1-[n-$Bu_4N^+Cl^-$] (298 K, d_6-acetone): $K_a = (6.5\pm0.4)\times10^2\ M^{-1}$**

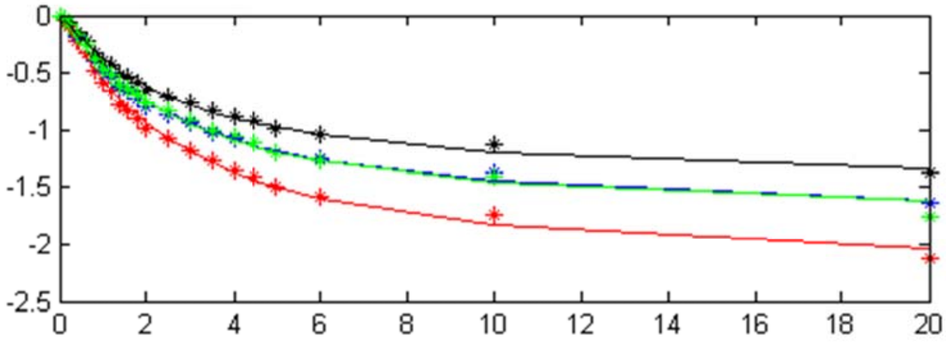


Figure S16. Binding constants K_a was determined by curve-fitting 1:1 binding isotherms to ^{19}F NMR titration data and was found to be $(6.5\pm0.4)\times10^2\ M^{-1}$ at 298K in anhydrous d_6-acetone.

◆ **1-[n-$Bu_4N^+Br^-$] (298 K, d_6-acetone): $K_a = (3.9\pm0.3)\times10^2\ M^{-1}$**

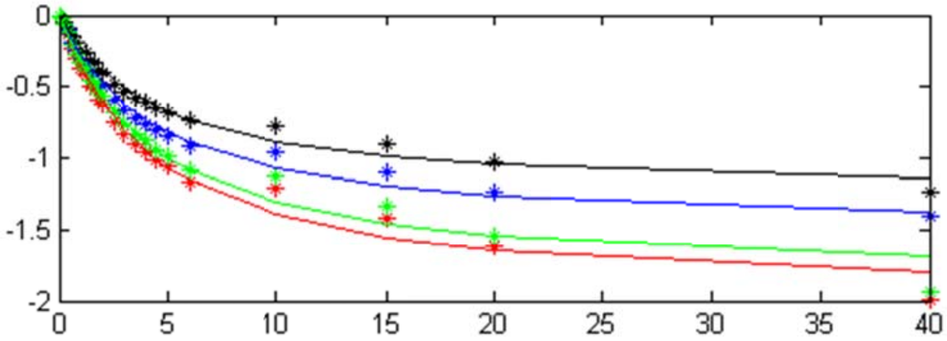


Figure S17. Binding constants K_a was determined by curve-fitting 1:1 binding isotherms to ^{19}F NMR titration data and was found to be $(3.9\pm0.3)\times10^2\ M^{-1}$ at 298K in anhydrous d_6-acetone.

◆ **1-[n-$Bu_4N^+I^-$] (298 K, d_6-acetone): $K_a = (1.4\pm0.1)\times10^2\ M^{-1}$**

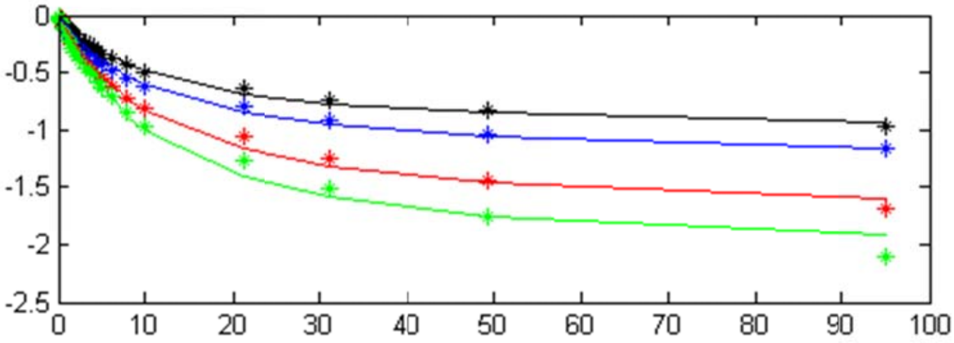


Figure S18. Binding constants K_a was determined by curve-fitting 1:1 binding isotherms to ^{19}F NMR titration data and was found to be $(1.4\pm0.1)\times10^2\ M^{-1}$ at 298 K in anhydrous d_6-acetone.

3.13 Studies of 1-chloride ion complexes by HRMS-ESI.

The mass spectra of **1**-chloride ion complex was measured on a Fourier transform ion cyclotron resonance mass spectrometer, equipped with a nanospray ionization source. Solution of dendritic gelator **1** and tetrabutylammonium chloride (5 equiv) in acetonitrile was used for nanospray ionization.

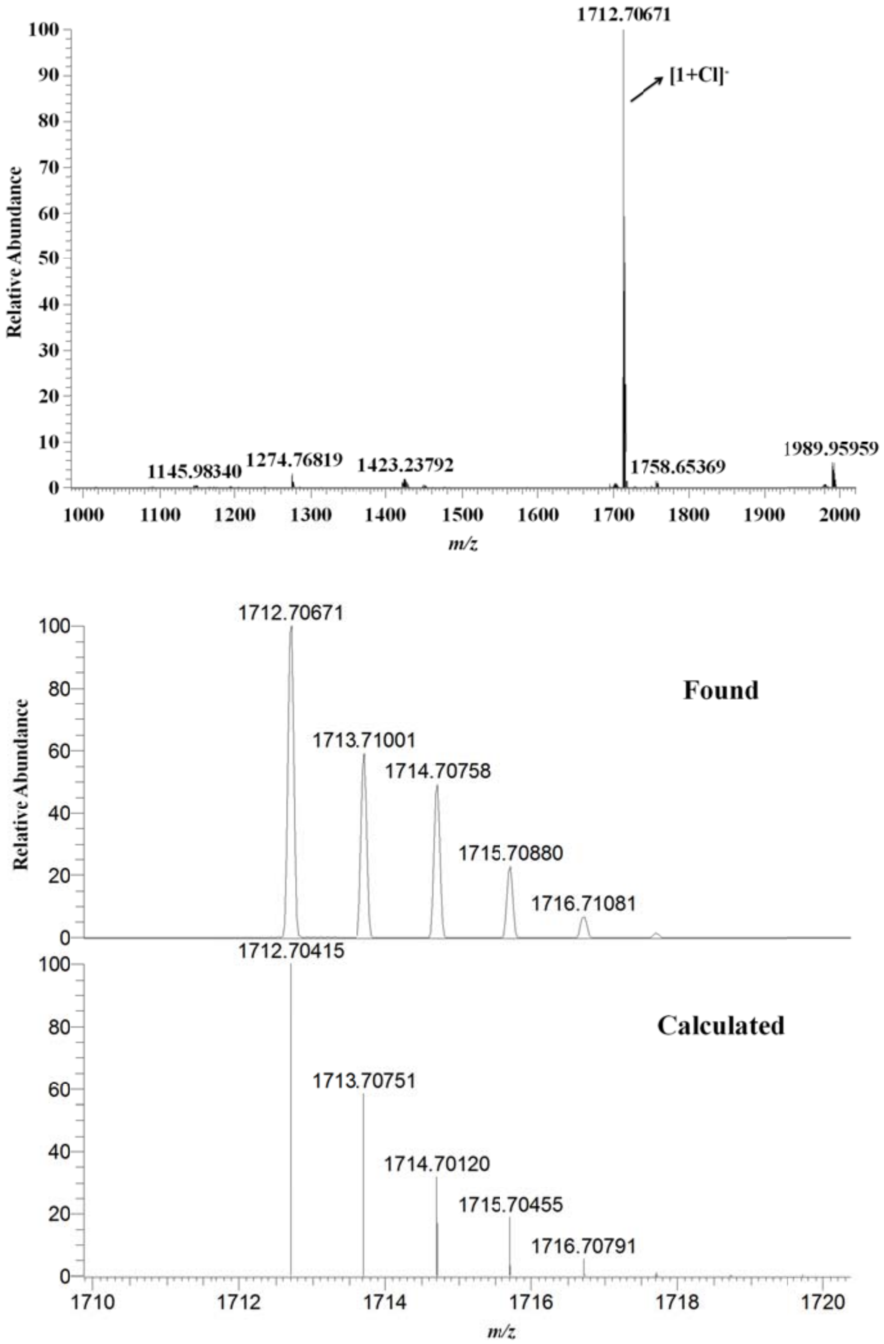


Figure S19. HRMS spectra of the complex of dendritic gelator **1** and chloride ion.

3.13 Details of Computational Study

The geometry was optimized in gas phase using Gaussian 09 program[S5] with PBE0 hybrid density functional[S6] and double-ζ quality def2-SVP basis set[S7], with Grimme's DFT-D3[S8] empirical dispersion correction (with zero short range damping) included. To consider the scalar relativistic effect of iodine, the MCDHF small-core relativistic pseudopotential (ECP) was employed.[S9]

Cartesian Coordinates of DFT Optimized Geometry

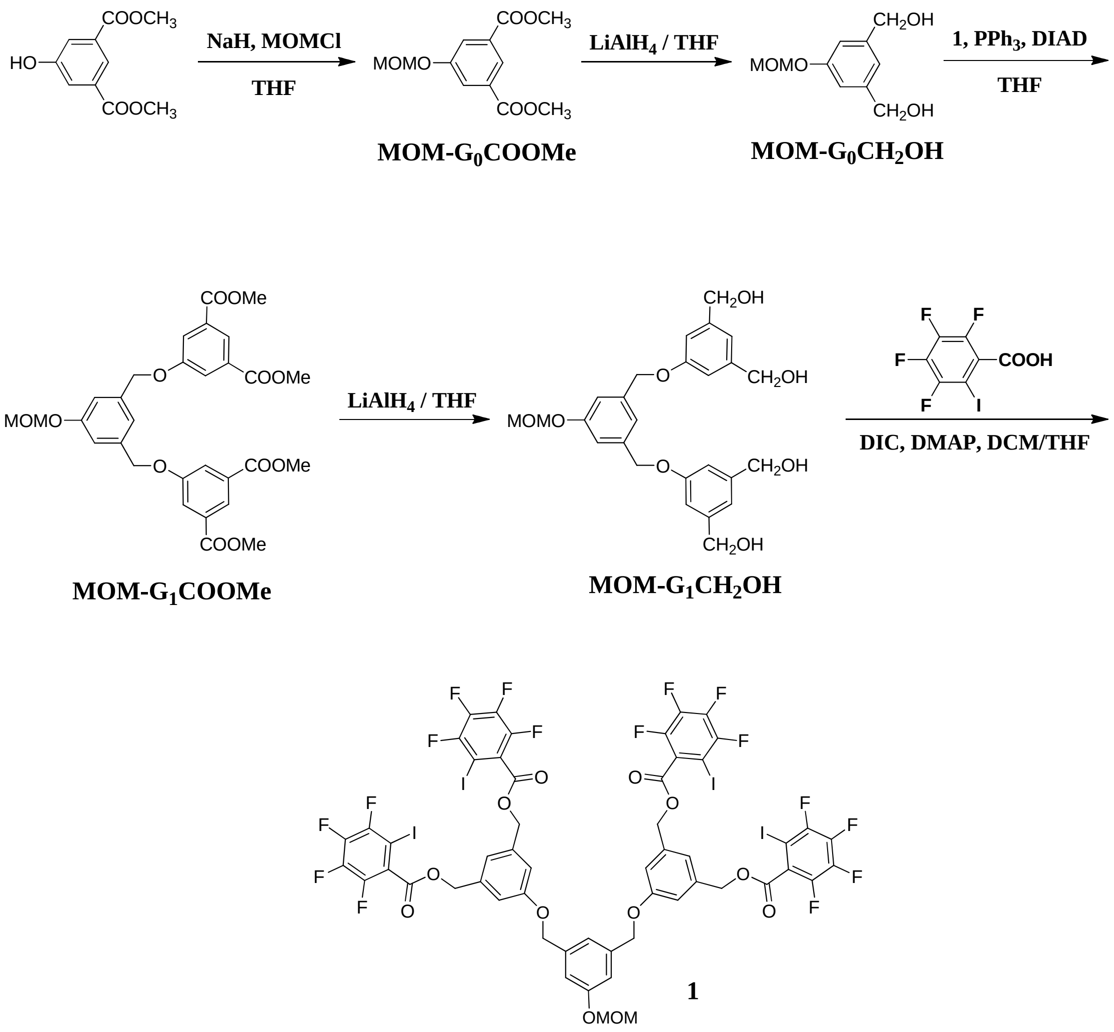
1-Cl$^-$

C	0.51884400	-2.36539100	-2.67694600
C	0.84572600	-1.75148800	-1.46170200
C	1.39095500	-0.47242400	-1.45112700
C	1.63146800	0.20476100	-2.65304500
C	1.30986300	-0.40347600	-3.85821700
C	0.74292400	-1.68744300	-3.88021200
H	0.12202000	-3.37984900	-2.65844200
H	1.67942700	-0.00356300	-0.50679900
H	1.51590600	0.08309500	-4.81458900
C	2.31956600	1.54606200	-2.61492400
H	1.64872700	2.32201200	-2.21404500
H	2.60432600	1.86053200	-3.63523900
C	0.58205400	-2.45575700	-0.15052700
H	1.30286900	-2.09834200	0.60652800
H	-0.42473900	-2.19187400	0.21385000
O	3.43189300	1.54407900	-1.73903800
O	0.59153200	-3.85956000	-0.24575500
C	4.34793300	0.54990500	-1.92571300
C	4.76487700	-0.16173700	-0.80513500
C	4.84291300	0.20682100	-3.18564900
C	5.66116700	-1.22392600	-0.93525000
H	4.34537700	0.10395400	0.16789400
C	5.74627700	-0.84731800	-3.32287200
H	4.51127700	0.75072400	-4.07262600
C	6.15988200	-1.56028600	-2.19328900
H	6.86138500	-2.39273300	-2.29521100
C	1.80277700	-4.49407000	-0.26197400
C	2.09114100	-5.31828500	-1.34587300
C	2.69058200	-4.41539000	0.81281200
C	3.28540500	-6.03905200	-1.37946200
H	1.37793100	-5.39589200	-2.16492200
C	3.88191100	-5.14755600	0.79735800
H	2.42217300	-3.82222300	1.69173800
C	4.18687400	-5.93209700	-0.31621300
H	5.12324500	-6.49341200	-0.34232100
O	0.46992900	-2.18431700	-5.09918300
C	-0.16844900	-3.44269000	-5.22601600
H	-1.05485500	-3.45769800	-4.55172900
H	0.53363500	-4.24860100	-4.96445200
C	6.03232600	-2.02140300	0.27423200
H	5.15180800	-2.20540200	0.90698300
H	6.47666800	-2.99019600	-0.00716500
C	6.25731200	-1.22050800	-4.67892400
H	6.31315900	-2.31320100	-4.79148900
H	5.61339300	-0.82929800	-5.48111900
C	4.77192900	-5.09625900	2.01561900
H	5.34727600	-4.16215100	2.07042400
H	4.14218100	-5.16113600	2.91705700
C	3.57645000	-6.96230400	-2.53302400
H	4.27864100	-7.74729000	-2.22633300
H	2.64599600	-7.42424100	-2.89546000
O	7.01370800	-1.29977100	1.02800300
O	7.57862900	-0.69171700	-4.83776800
O	5.75494400	-6.12254900	2.06450900
O	4.23021900	-6.32801400	-3.63799900
C	8.14979500	-0.90879600	-6.01524300
O	7.59462400	-1.38502000	-6.96946600
C	7.22960500	-1.69118200	2.27528000
O	6.49925200	-2.39760200	2.92074100
C	3.49452600	-5.60287700	-4.46692200
O	2.29912800	-5.46917500	-4.34695900
C	5.32004600	-7.35061900	2.33804100

O	4.16522500	-7.62259400	2.53547500
C	9.58044800	-0.45132000	-6.01799300
C	9.93619100	0.51544400	-6.95662600
C	10.55826600	-0.97624900	-5.15253200
C	11.24441300	0.98208500	-7.05092200
C	11.86721800	-0.50983600	-5.26115200
C	12.21235600	0.46438300	-6.19757300
C	8.53821500	-1.16014800	2.78337800
C	9.75155400	-1.56689000	2.20023300
C	8.54328700	-0.30947700	3.88354800
C	10.94431200	-1.09649600	2.74126500
C	9.74110300	0.16500900	4.41272700
C	10.94398900	-0.23268500	3.83740100
C	4.29596200	-5.01965500	-5.58644100
C	5.70687900	-4.87424800	-5.58230400
C	3.58464200	-4.62610700	-6.73371700
C	6.33815800	-4.38147600	-6.72545400
C	4.23415200	-4.10671200	-7.85137200
C	5.61658000	-3.98634600	-7.85096400
C	6.42928500	-8.35836000	2.41023300
C	7.59184300	-8.36041700	1.60429600
C	6.24984600	-9.38994900	3.34456900
C	8.50085800	-9.41013700	1.74756000
C	7.17607200	-10.41939700	3.48189400
C	8.30538400	-10.43094000	2.67536900
I	9.77649300	-2.92214400	0.57148300
I	8.14950900	-6.90290200	0.15419000
I	10.15369800	-2.50435500	-3.74996400
I	7.03234700	-5.12600100	-3.93373600
Cl	9.18755000	-4.79487400	-1.79435700
F	2.27435700	-4.75127000	-6.83587000
F	3.53692200	-3.75097400	-8.91803600
F	6.23593100	-3.51295700	-8.91097400
F	7.64998100	-4.24074400	-6.78513800
F	9.60064900	-9.48354200	1.01303100
F	9.18972100	-11.40625200	2.79333000
F	6.98841800	-11.37397200	4.37974700
F	5.21126500	-9.42246800	4.16150900
F	7.40655800	0.08885300	4.43949600
F	9.74118500	0.98973500	5.44868700
F	12.08571000	0.21044100	4.33866100
F	12.11830500	-1.45309500	2.24423400
F	9.02900900	1.03983700	-7.76899300
F	11.56621700	1.91388600	-7.93480000
F	13.45967700	0.89771300	-6.28124300
F	12.83470200	-0.97462800	-4.48645000
O	-0.53410600	-3.61605700	-6.53298800
C	-1.51266300	-2.72332600	-6.98708000
H	-1.14973400	-1.68128200	-6.99013600
H	-1.77239300	-3.01358900	-8.01435000
H	-2.42777300	-2.77013600	-6.36283900

4. Synthetic Procedures and Characterizations

Dendrons were prepared according to previously reported synthetic procedures[S10]



Scheme S1. The synthetic route to dendritic gelator **1**.

Synthesis of MOM-G$_0$COOMe: To an ice cooled solution of dimethyl 5-hydroxyisophthalate (5.685 g, 27.046 mmol) in anhydrous THF (50 mL) was added NaH (1.623 g, 40.568 mmol, as 60% dispersion in oil). The mixture was stirred for 30 min and chloromethylether (MOMCl, 3.266 g, 3.08 mL, 40.568 mmol) was added dropwise. After warming to room temperature the mixture was stirred for a further 3 h then poured into water (100 mL), and the product was extracted with dichloromethane. The combined extract was dried over anhydrous Na_2SO_4 and concentrated to afford the product. Drying *in vacuo* for 3 h at 50 °C afforded **MOM-G$_0$COOMe** (6.807 g, 99% yield) as an off-white solid. ^{1}H NMR

(300 MHz, $CDCl_3$): δ = 3.49 (s, CH_3OCH_2, 3H), 3.94 (s, $COOCH_3$, 6H), 5.25 (s, CH_3OCH_2, 2H), 7.88 (d, *J* = 1.4 Hz, Ar*H*, 2H), 8.34 (t, *J* = 1.4 Hz, Ar*H*, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ =166.4, 157.6, 132.2, 124.5, 121.9, 94.8, 56.7, 52.8. HRMS-FAB (*m/z*): $[M+H]^+$ calcd. for $C_{12}H_{15}O_6$, 255.0863; found, 255.0863.

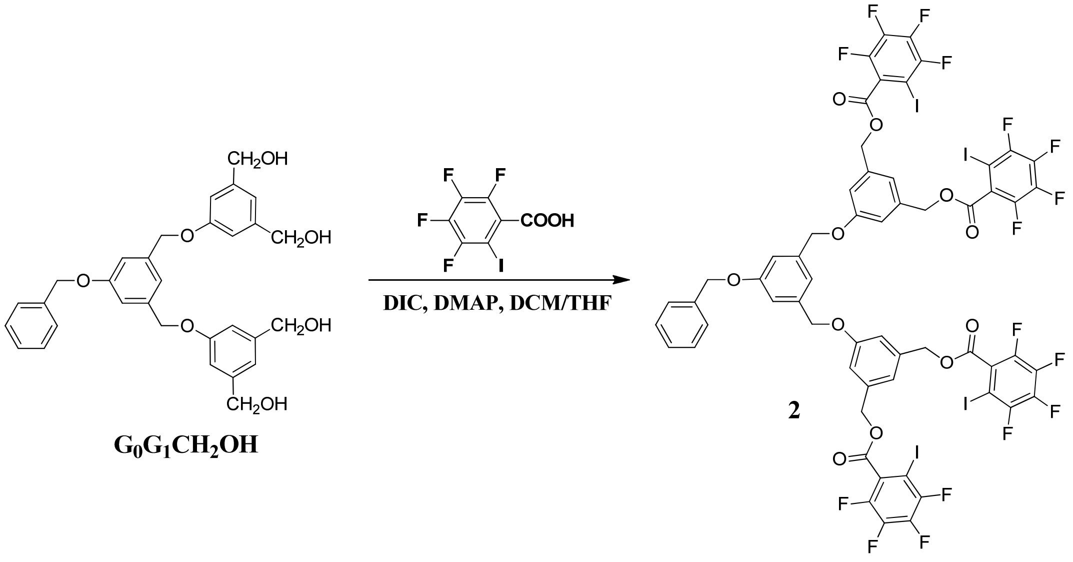
General Procedure for the Reduction Reactions. Synthesis of MOM-G$_0$CH$_2$OH

To a suspension of lithium aluminum hydride (LAH, 1.632 g, 43.016 mmol) in THF was added dropwise a solution of **MOM-G$_0$COOMe** (4.971 g, 19.552 mmol) in dry THF (300 mL) at 0 °C. The reaction mixture was then stirred and refluxed for 1 h. The reaction was quenched successively by dropwise addition of 0.7 mL of H_2O, 0.7 mL of 15% NaOH solution, and 2.1 mL of H_2O. At this point, H_2 evolution ceased. The granular salts were filtered and washed with THF (3 × 50 mL). The combined filtrate was concentrated under reduced pressure. To the resultant solid was added 100 mL of water. The aqueous layer was extracted with EtOAc (3 × 150 mL). The organic layer was combined and dried over sodium sulfate, filtered, and evaporated to give **MOM-G$_0$CH$_2$OH** (3.134 g, 81%) as an off-white solid. ^{1}H NMR (300 MHz, d^6-acetone): δ = 3.42 (s, CH_3OCH_2O), 4.18 (t, *J* = 5.8 Hz, $ArCH_2OH$, 2H), 4.59 (d, *J* = 5.8 Hz, $ArCH_2OH$, 4H), 5.17 (s, CH_3OCH_2, 2H), 6.92 (s, Ar*H*, 2H), 6.97 (s, Ar*H*, 1H). ^{13}C NMR (75 MHz, d^6-acetone): δ = 158.5, 144.9, 118.9, 113.7, 95.1, 64.6, 64.5, 56.0. HRMS-FAB (*m/z*): $[M+H]^+$ calcd. for $C_{10}H_{15}O_4$: 199.0965; found,199.0967.

Synthesis of MOM-G$_1$COOMe: To an ice-bath cooled solution of **MOM-G$_0$CH$_2$OH** (3.992 g, 20.139 mmol), dimethyl 5-hydroxyisophthalate (10.583 g, 50.348 mmol), triphenylphosphine (PPh_3, 13.206 g, 50.348 mmol) in dry THF (60 mL) was added diisopropylazodicarboxylate (DIAD, 10.180 g, 50.348 mmol, 10.08 mL) dropwise via syringe. The reaction mixture was then stirred for 10 min at 0 °C and then 12-24 h at 25-50 °C under a nitrogen atmosphere. The reaction was monitored by TLC upon the completion. The crude product was purified as follows: a) The reaction mixture (about 36 mL) was added to diethyl ether (420 mL) under vigorous stirring, and the precipitate was isolated by filtration; b) The resulting precipitate was redissolved in THF (36 mL), and precipitated into methanol (360 mL). After filtration, an off-white solid of **MOM-G$_1$COOMe** was obtained (10.559 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.50 (s, CH_3OCH_2, 3H), 3.94 (s, $COOCH_3$, 12H), 5.13 (s, ArC*H*$_2$O, 4H), 5.22 (s, CH$_3$OC*H*$_2$O, 2H), 7.12 (s, Ar*H*, 2H), 7.18 (s, Ar*H*, 1H), 7.83 (s, Ar*H*, 4H), 8.29 (s, Ar*H*, 2H). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 166.0, 158.6, 157.9, 138.2, 131.9, 123.3, 120.1, 119.7, 115.0, 94.5, 70.1, 56.1, 52.4. HRMS-FAB (*m/z*): [M+Na]$^+$ calcd. for $C_{30}H_{30}O_{12}Na$, 605.1629; found, 605.1627.

MOM-G$_1$CH$_2$OH: Following the procedure for **MOM-G$_0$CH$_2$OH**. LAH (1.163 g, 30.635 mmol) in THF (50 mL) and **MOM-G$_1$COOMe** (4.056 g, 6.962 mmol) in THF (300 mL) yielded **MOM-G$_1$CH$_2$OH** (3.145 g, 96%) as an off-white solid. ^{1}H NMR (300 MHz, d_6-Acetone) δ = 3.43 (s, C*H*$_3$OCH$_2$O, 3H), 4.24 (t, *J* = 5.8 Hz, ArCH$_2$O*H*, 4H), 4.58 (d, *J* = 5.8 Hz, ArC*H*$_2$OH, 8H), 5.07 (s, ArC*H*$_2$O, 4H), 5.21 (s, CH$_3$OC*H*$_2$, 2H), 6.92 (s, Ar*H*, 6H), 7.11 (s, Ar*H*, 2H), 7.22 (s, Ar*H*, 1H). ^{13}C NMR (75 MHz, d^6-acetone) δ = 159.9, 158.6, 144.9, 140.3, 120.5, 118.0, 115.4, 112.3, 95.2, 70.1, 64.7, 56.1. HRMS-FAB (*m/z*): [M+H]$^+$ calcd. for $C_{26}H_{31}O_8$, 471.2013; found, 471.1998.

Synthesis of 1: To an oven-dried, 100 mL round-bottomed flask equipped with a stir bar and cooled under an atmosphere of argon were added 2,3,4,5-tetrafluoro-6-iodobenzoic acid[S11] (1.701 g, 5.316 mmol), **MOM-G$_1$CH$_2$OH** (0.610 g, 1.296 mmol), 4-dimethylaminopyridine (DMAP, 0.065 g, 0.532 mmol) and N,N′-diisopropylcarbodiimide (DIC, 0.718 g, 0.9 mL, 5.704 mmol) in the mixed solvent of dichloromethane/tetrahydrofuran (2:1, *v/v*) (60 mL). The reaction mixture was then stirred overnight. The resulting solution was quenched with saturated aqueous NH$_4$Cl, and was extracted with dichloromethane (50 mL×3). The combined organic extracts were washed with brine, dried over Na$_2$SO$_4$ and concentrated in vacuo. The crude mixture was purified by flash column chromatography affording the product as a white solid (1.268 g, 58%). ^{1}H NMR (600 MHz, CDCl$_3$) δ = 3.48 (s, C*H*$_3$OCH$_2$O, 3H), 5.06 (s, ArC*H*$_2$O, 4H), 5.18 (s, CH$_3$OC*H*$_2$O, 2H), 5.39 (s, ArC*H*$_2$O, 8H), 7.05 (s, Ar*H*, 4H), 7.06 (s, Ar*H*, 2H), 7.13 (s, Ar*H*, 3H). ^{13}C NMR (150 MHz, CDCl$_3$, Proton-Decoupled): δ = 162.4, 159.1, 157.9, 148.8, 148.7, 147.1, 147.1, 146.1, 146.0, 144.4, 144.3, 141.9, 141.8, 141.7, 141.7, 141.5, 141.4, 140.1, 140.0, 140.0, 139.9, 139.8, 139.7, 138.6, 136.5, 123.7, 123.6, 121.2, 119.6, 115.3, 114.9, 94.5, 74.8, 74.6, 69.9, 68.2, 56.2. ^{13}C NMR (150 MHz, CDCl$_3$, Proton and Fluorine-Decoupled): δ = 162.4, 159.1, 157.9, 147.9, 145.2, 140.9, 140.9, 140.7, 140.7, 138.6, 136.5, 123.6, 121.2, 119.6, 115.3, 114.9, 94.5, 74.7, 69.9, 68.2, 56.2. ^{19}F NMR (470 MHz, d^6-acetone): δ = –115.6 (m, 1F), –139.6 (m, 1F), –152.3 (m, 1F), –155.0 (m, 1F). HRMS-ESI (*m/z*): [M+Na]$^+$ calcd. for $C_{54}H_{26}O_{12}F_{16}I_4Na$, 1700.72397; found, 1700.72304. Anal. Calcd. for $C_{54}H_{26}F_{16}I_4O_{12}$: C, 38.64; H, 1.56. Found: C, 38.75; H, 1.52.



Synthesis of 2: Following the procedure for **1**. 2,3,4,5-tetrafluoro-6-iodobenzoic acid (2.843 g, 8.885 mmol), **$G_0G_1CH_2OH$** (1.020 g, 1.974 mmol), 4-dimethylaminopyridine (DMAP, 0.109 g, 0.889 mmol) and N,N′-diisopropylcarbodiimide (DIC, 1.118 g, 1.41 mL, 8.885 mmol) in the mixed solvent of dichloromethane/tetrahydrofuran (2:1, *v/v*) (60 mL) yielded **2** as a white solid after purified by flash column chromatography (2.077 g, 61%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.06 (s, ArCH_2O, 2H), 5.07 (s, ArCH_2O, 4H), 5.38 (s, ArCH_2O, 8H), 7.01(s, Ar*H*, 2H), 7.04 (s, Ar*H*, 4H), 7.06 (s, Ar*H*, 1H), 7.13 (s, Ar*H*, 2H), 7.32-7.41 (m, Ph*H*, 5H). ^{13}C NMR (150 MHz, $CDCl_3$, Proton-Decoupled): δ = 159.5, 159.2, 148.8, 148.7, 147.2, 147.1, 146.2, 146.1, 144.5, 144.4, 141.9, 141.8, 141.7, 141.6, 141.5, 140.2, 140.1, 140.0, 139.9, 139.8, 138.7, 136.6, 128.7, 128.2, 127.6, 123.7, 123.7, 123.6, 123.6, 121.3, 118.6, 115.4, 113.5, 74.8, 74.6,70.2, 69.9, 68.2. ^{13}C NMR (150 MHz, $CDCl_3$, Proton and Fluorine-Decoupled): δ = 162.4, 159.5, 159.1, 147.9, 145.2, 140.9, 140.7, 138.6, 136.5, 128.6, 128.1, 127.5, 123.6, 121.2, 118.5, 115.4, 113.5, 74.7, 70.2, 69.9, 68.2. ^{19}F NMR (150 MHz, $CDCl_3$): δ = –112.7 (m, 1F), –136.5 (m, 1F), –149.1 (m, 1F), –152.0 (m, 1F). HRMS-ESI (m/z): [M+Na]$^+$ calcd. for $C_{59}H_{28}O_{11}F_{16}I_4Na$, 1746.74471; found, 1746.74225. Anal. Calcd. for $C_{59}H_{28}F_{16}I_4O_{11}$: C, 41.09; H, 1.64. Found: C, 41.34; H, 1.69.

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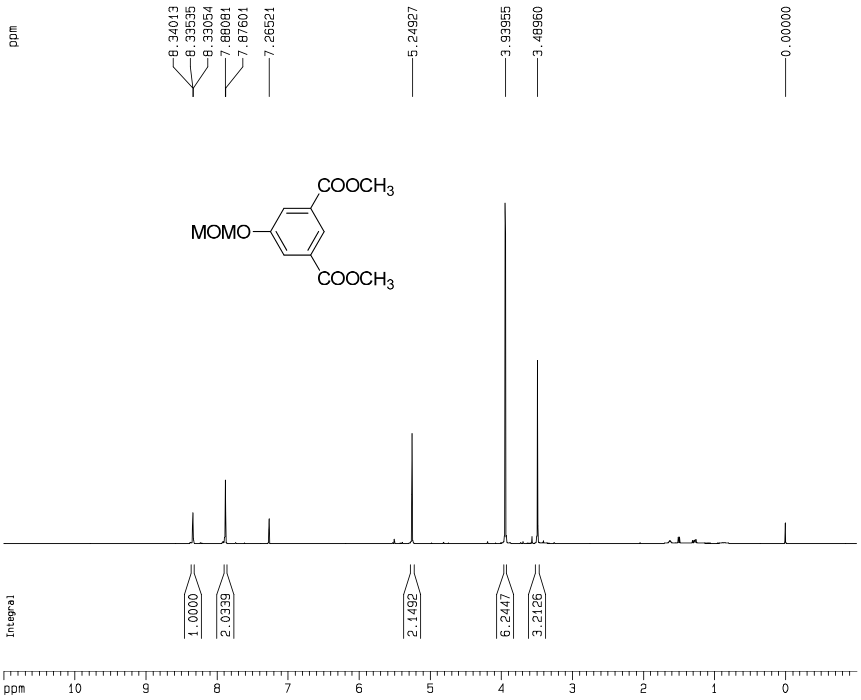
6. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and Mass Spectra of New Compounds

Figure S20. ^{1}H NMR, ^{13}C NMR and HRMS-FAB mass spectra of **MOM-G$_0$COOMe**



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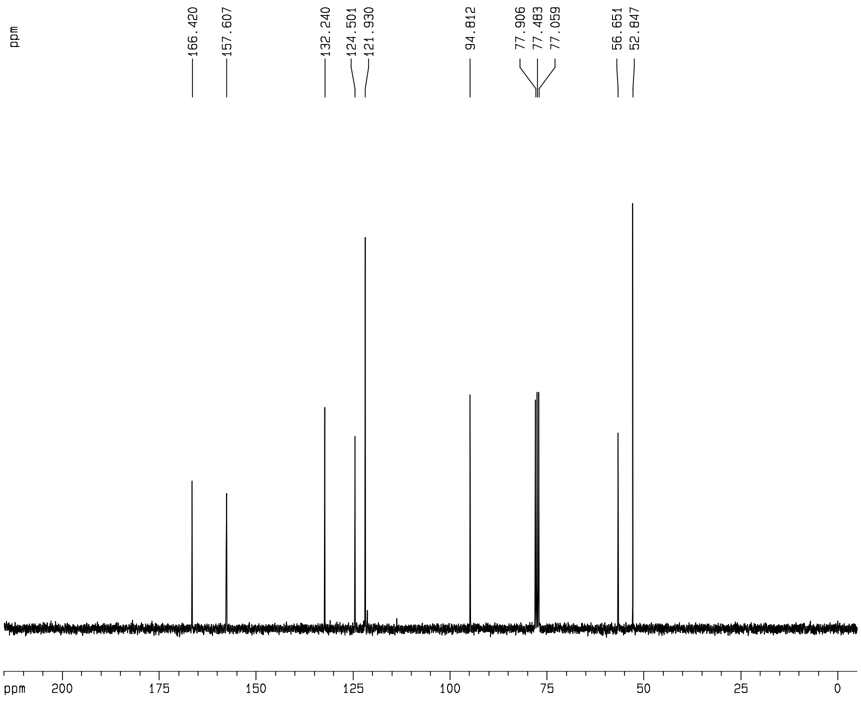
Current Data Parameters
NAME     Fy-MOM-protecte
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060711
Time               20.06
INSTRUM            av300
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ             5.3084660 sec
RG                 322.5
DW                81.000 usec
DE                  6.00 usec
TE                 301.4 K
D1            2.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.30 usec
PL1                -1.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300047 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                  8.00 cm
F1P               11.000 ppm
F1               3301.43 Hz
F2P               -1.000 ppm
F2               -300.13 Hz
PPMCM            0.60000 ppm/cm
HZCM           180.07800 Hz/cm
```



```
Current Data Parameters
NAME         MOM-G1COOMe
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080129
Time               11.30
INSTRUM            av300
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   125
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                1824.6
DW                27.800 usec
DE                  6.00 usec
TE                 295.6 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 12.50 usec
PL1                 2.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -1.00 dB
PL12               16.98 dB
PL13               18.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF            75.4677169 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
CY                 10.00 cm
F1P              215.000 ppm
F1              16225.56 Hz
F2P               -5.000 ppm
F2               -377.34 Hz
PPMCM           11.00000 ppm/cm
HZCM           830.14490 Hz/cm
```

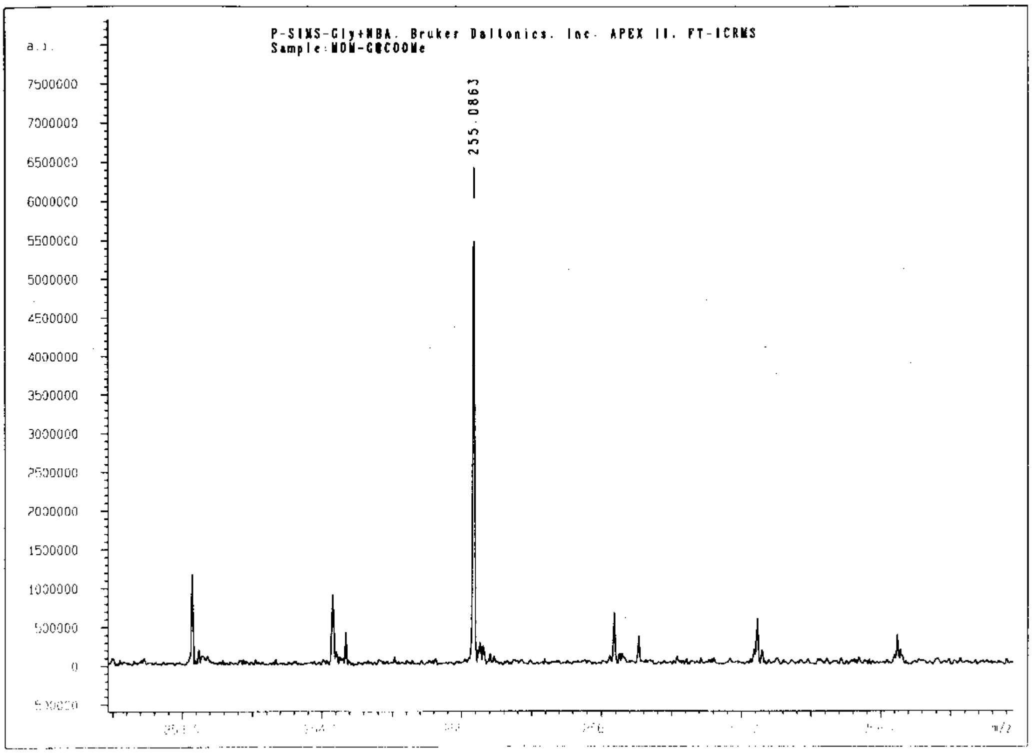
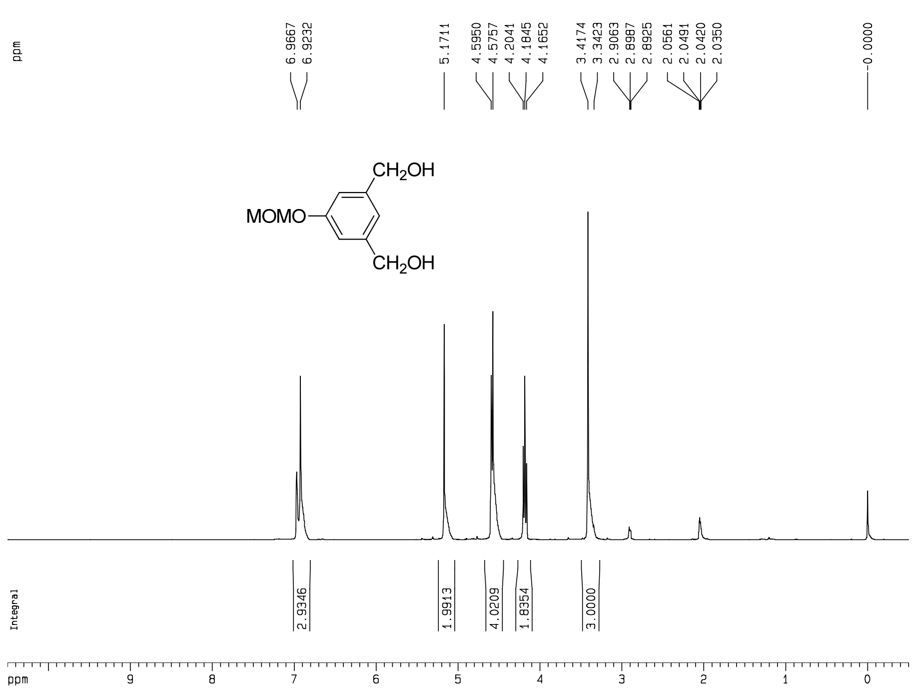


Figure S21. ^{1}H NMR, ^{13}C NMR and HRMS-FAB mass spectra of **MOM-G$_0$CH$_2$OH**



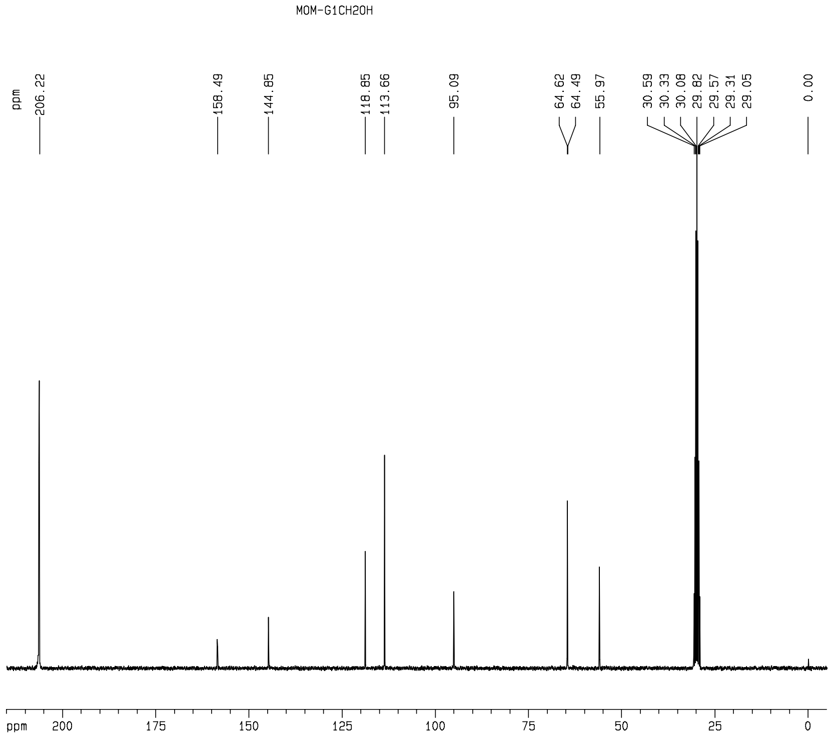
```
Current Data Parameters
NAME     Fy-MOM-G1CH2OH
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20071023
Time              11.38
INSTRUM           av300
PROBHD   5 mm DUL 13C-1
PULPROG            zg30
TD                65536
SOLVENT         Acetone
NS                   16
DS                    0
SWH            8992.806 Hz
FIDRES         0.137219 Hz
AQ            3.6438515 sec
RG                  114
DW               55.600 usec
DE                 6.00 usec
TE                298.8 K
D1           5.00000000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                10.60 usec
PL1               -1.00 dB
SFO1        300.1318534 MHz

F2 - Processing parameters
SI                32768
SF          300.1300050 MHz
WDW                  EM
SSB                   0
LB                 0.35 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.00 cm
CY                 8.00 cm
F1P              10.500 ppm
F1              3151.36 Hz
F2P              -0.500 ppm
F2              -150.07 Hz
PPMCM           0.50000 ppm/cm
HZCM          150.06500 Hz/cm
```



```
Current Data Parameters
NAME     Fy-MOM-G1CH2OH
EXPNO               3
PROCNO              1

F2 - Acquisition Parameters
Date_          20071023
Time              11.42
INSTRUM           av300
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT         Acetone
NS                  673
DS                    4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ            1.8219508 sec
RG                322.5
DW               27.800 usec
DE                 6.00 usec
TE                299.0 K
D1           2.00000000 sec
d11          0.03000000 sec
d12          0.00002000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                12.20 usec
PL1               -0.32 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -1.00 dB
PL12              16.56 dB
PL13              18.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
SF           75.4676811 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
CY                12.50 cm
F1P             215.000 ppm
F1             16225.55 Hz
F2P              -5.000 ppm
F2              -377.34 Hz
PPMCM          11.00000 ppm/cm
HZCM          830.14447 Hz/cm
```

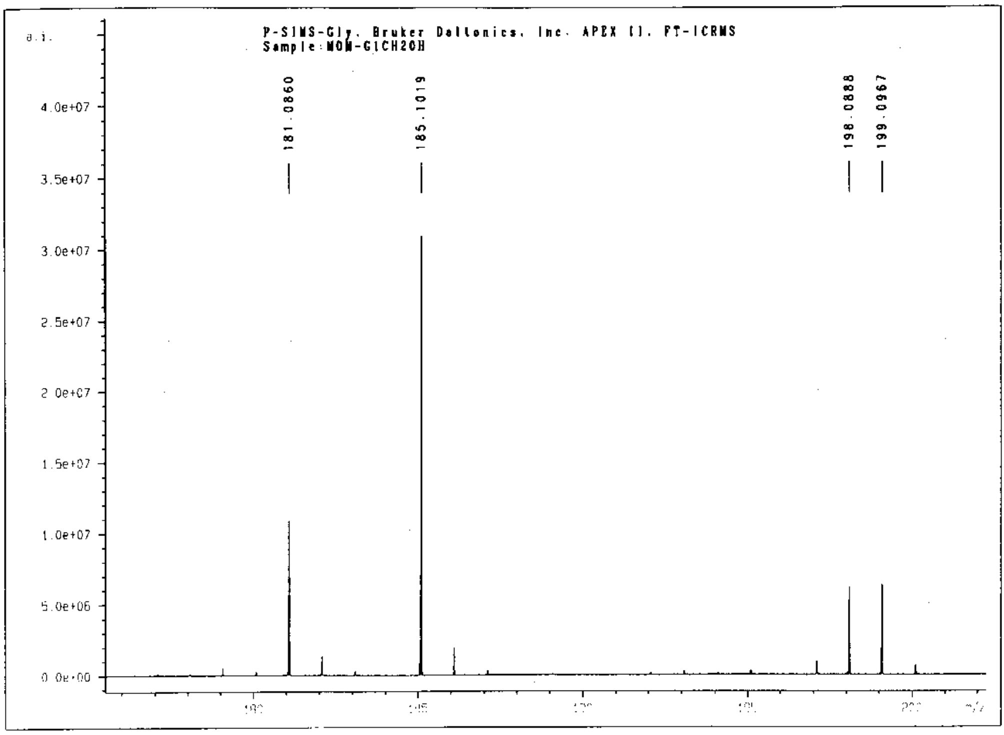
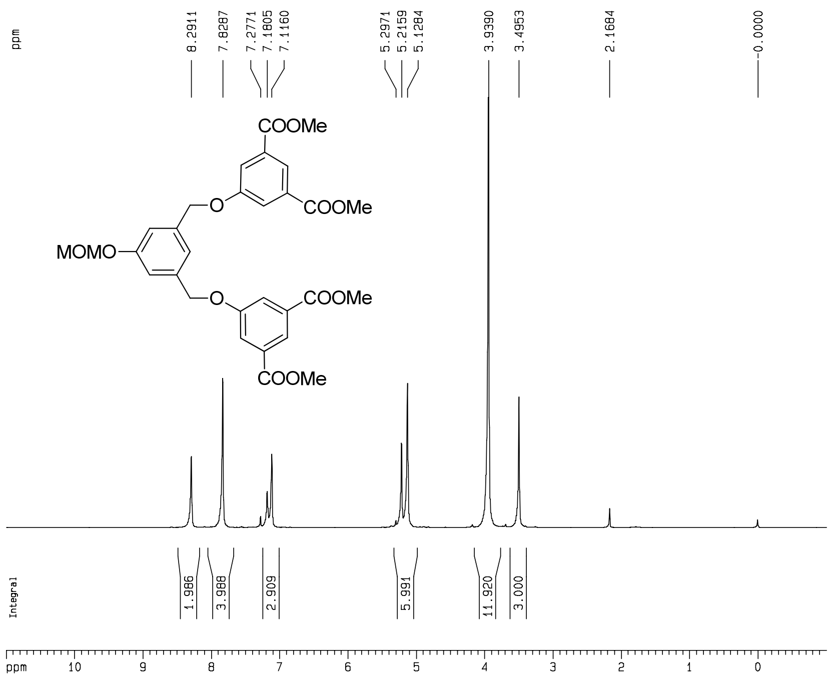


Figure S22.^{1}H NMR, ^{13}C NMR and HRMS-FAB mass spectra of **MOM-G$_1$COOMe**



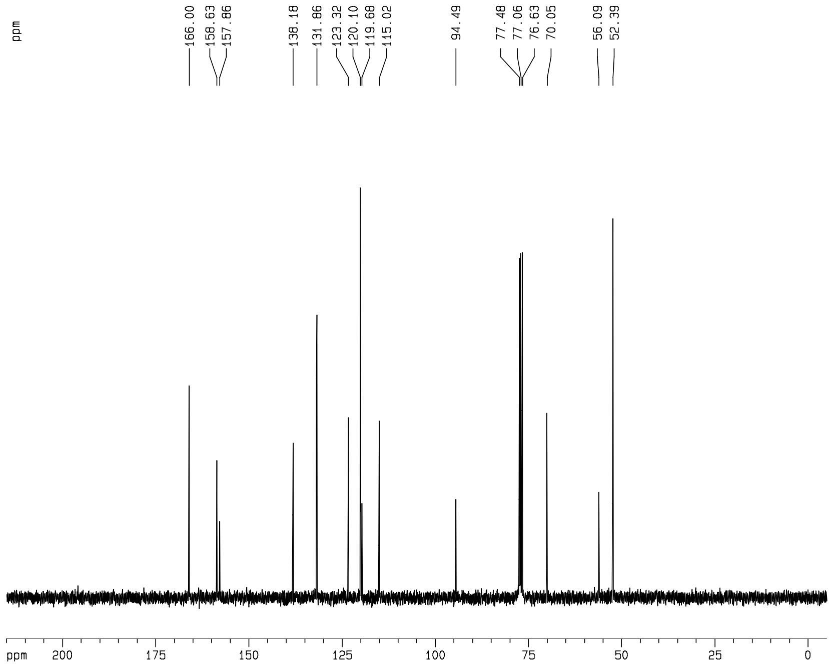
```
Current Data Parameters
NAME      Fy-MOM-G2COOMe
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070125
Time               14.15
INSTRUM            av300
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ             5.3084660 sec
RG                   128
DW                81.000 usec
DE                  6.00 usec
TE                 296.4 K
D1            2.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.30 usec
PL1                -1.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300005 MHz
WDW                   EM
SSB                    0
LB                  0.35 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                 12.00 cm
F1P               11.000 ppm
F1               3301.43 Hz
F2P               -1.000 ppm
F2               -300.13 Hz
PPMCM            0.60000 ppm/cm
HZCM           180.07800 Hz/cm
```



```
Current Data Parameters
NAME      Fy-MOM-G2COOMe
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070125
Time               14.31
INSTRUM            av300
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   268
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                 287.4
DW                27.800 usec
DE                  6.00 usec
TE                 296.8 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.40 usec
PL1                -1.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -1.00 dB
PL12               18.00 dB
PL13               18.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF            75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
CY                 10.00 cm
F1P              215.000 ppm
F1              16225.57 Hz
F2P               -5.000 ppm
F2               -377.34 Hz
PPMCM           11.00000 ppm/cm
HZCM           830.14520 Hz/cm
```

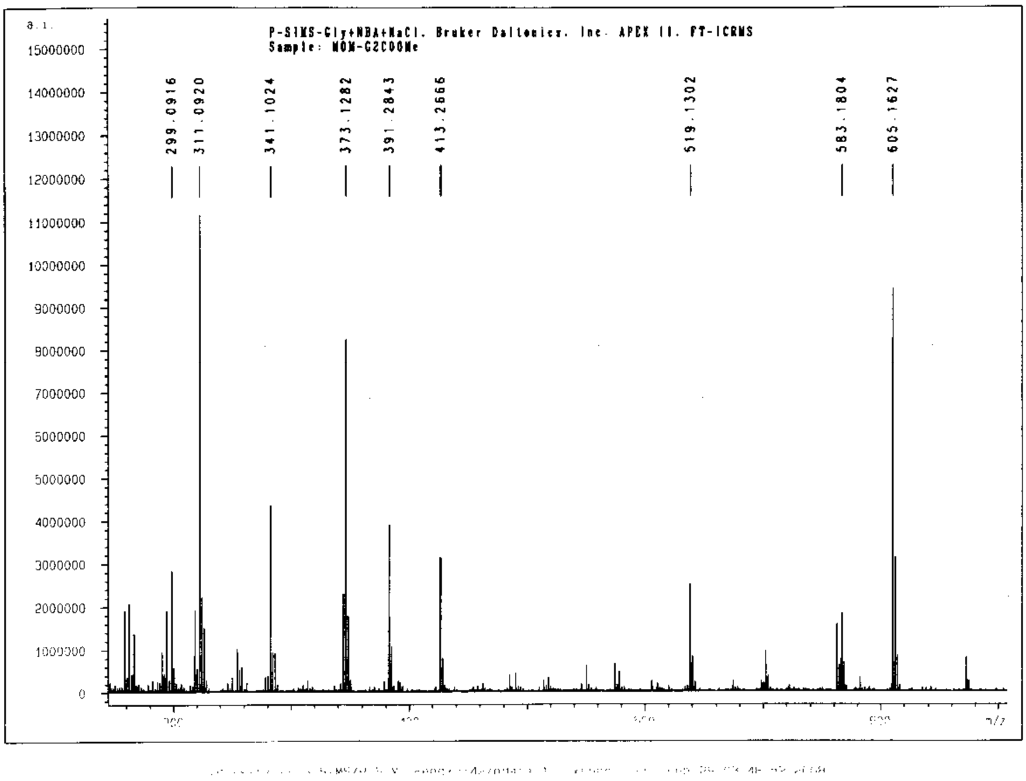
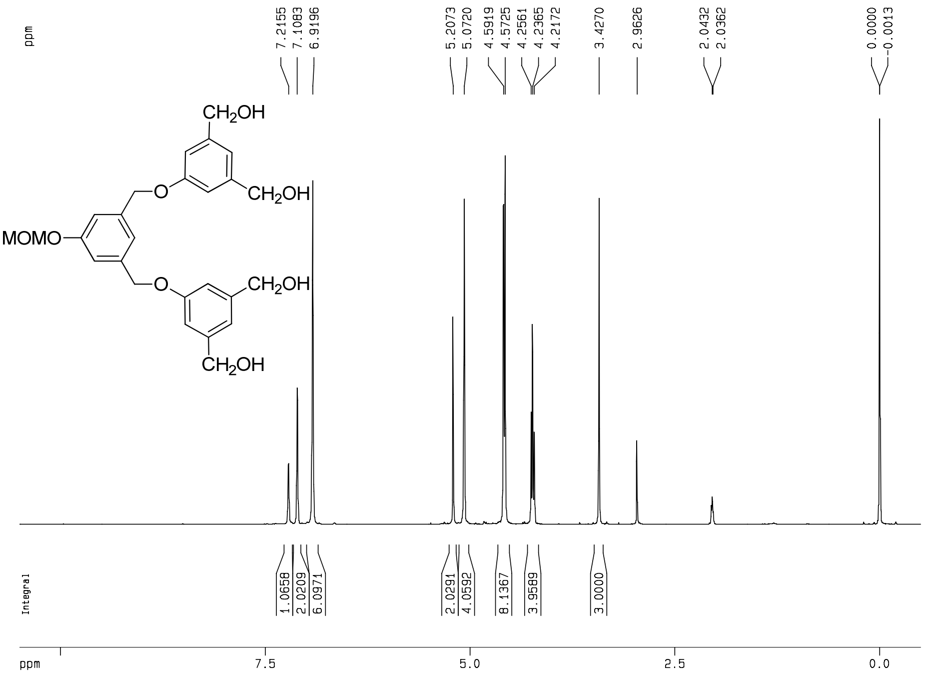


Figure S23. ^{1}H NMR, ^{13}C NMRand HRMS-FAB mass spectra of **MOM-G$_1$CH$_2$OH**



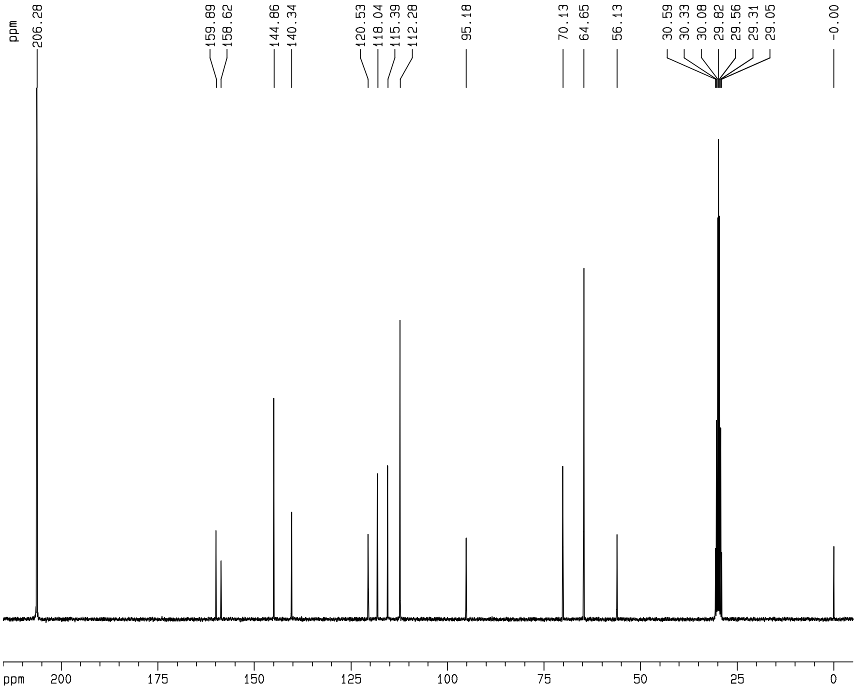
```
Current Data Parameters
NAME      Fy-MOM-G2CH2OH
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20071027
Time               12.39
INSTRUM            av300
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT          Acetone
NS                     8
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ             3.6438515 sec
RG                  90.5
DW                55.600 usec
DE                  6.00 usec
TE                 298.9 K
D1            5.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.60 usec
PL1                -1.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300064 MHz
WDW                   EM
SSB                    0
LB                  0.35 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.00 cm
CY                 10.00 cm
F1P               10.500 ppm
F1               3151.36 Hz
F2P               -0.500 ppm
F2               -150.06 Hz
PPMCM            0.50000 ppm/cm
HZCM           150.06497 Hz/cm
```



```
Current Data Parameters
NAME     Fy-MOM-G2CH2OH
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20071027
Time              12.43
INSTRUM           av300
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT         Acetone
NS                  776
DS                    4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ            1.8219508 sec
RG                  256
DW               27.800 usec
DE                 6.00 usec
TE                299.4 K
D1           2.00000000 sec
d11          0.03000000 sec
d12          0.00002000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                12.20 usec
PL1               -0.32 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -1.00 dB
PL12              16.56 dB
PL13              18.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
SF           75.4676834 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
CY                12.50 cm
F1P             215.000 ppm
F1             16225.55 Hz
F2P              -5.000 ppm
F2              -377.34 Hz
PPMCM          11.00000 ppm/cm
HZCM          830.14447 Hz/cm
```

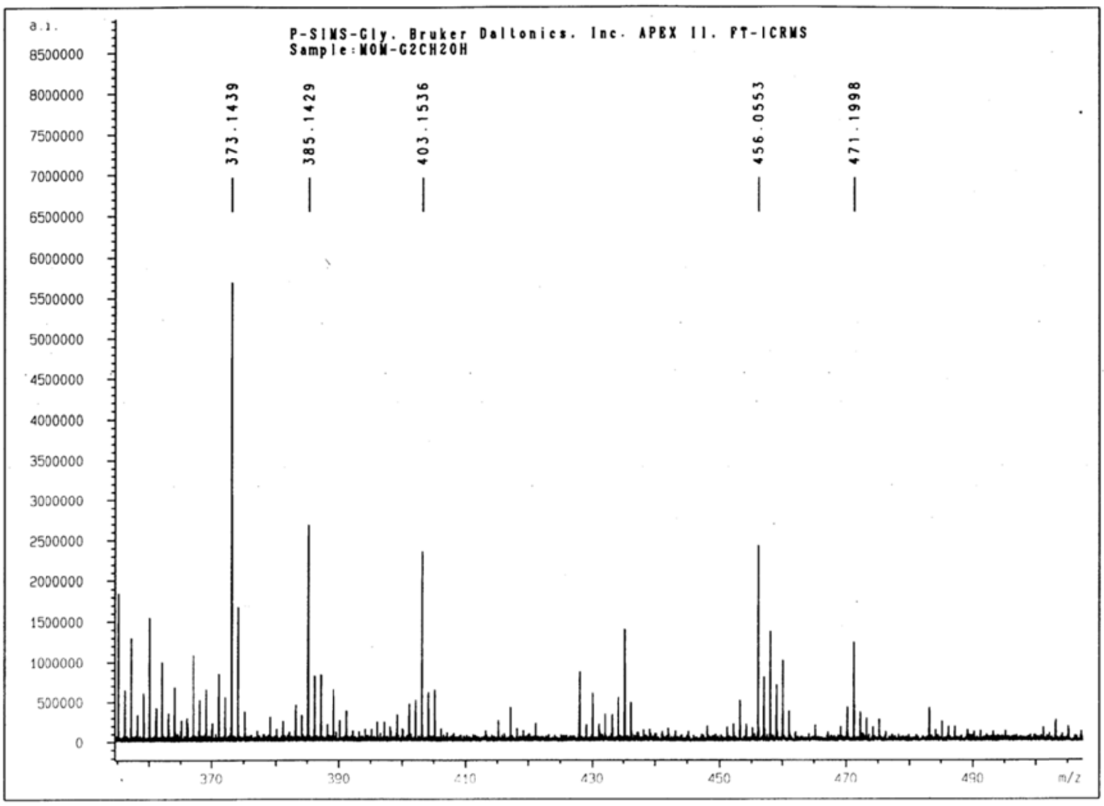


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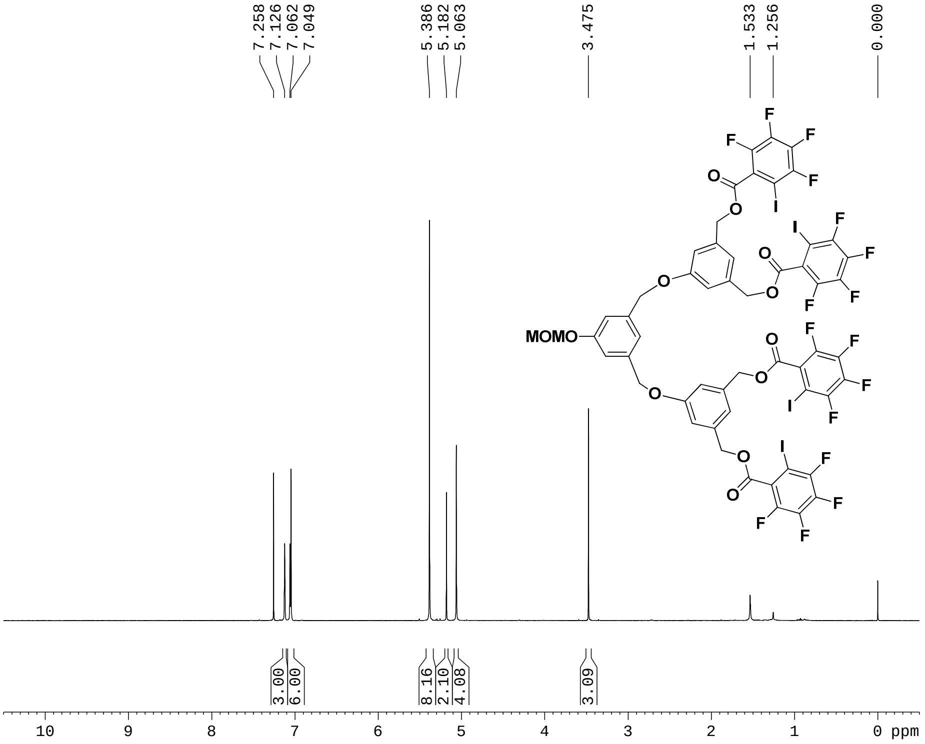
Figure S24. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and HRMS-ESI mass spectra of dendron **1**

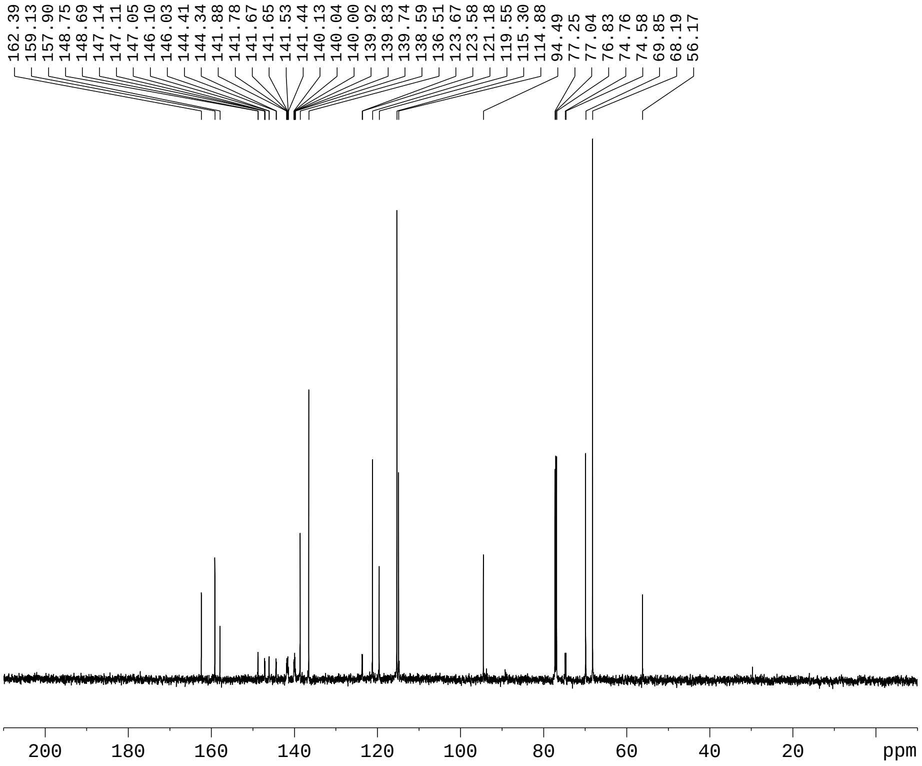


```
Current Data Parameters
NAME            G2-TFIB
EXPNO               428
PROCNO                1

F2 - Acquisition Parameters
Date_          20151210
Time              16.56
INSTRUM           spect
PROBHD   5 mm PATBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                    8
DS                    0
SWH          17985.611 Hz
FIDRES        0.548877 Hz
AQ           0.9110004 sec
RG                  256
DW              27.800 usec
DE                6.50 usec
TE               301.2 K
D1          2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1               12.00 usec
PL1              -0.60 dB
SFO1       600.1324005 MHz

F2 - Processing parameters
SI                65536
SF         600.1300235 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



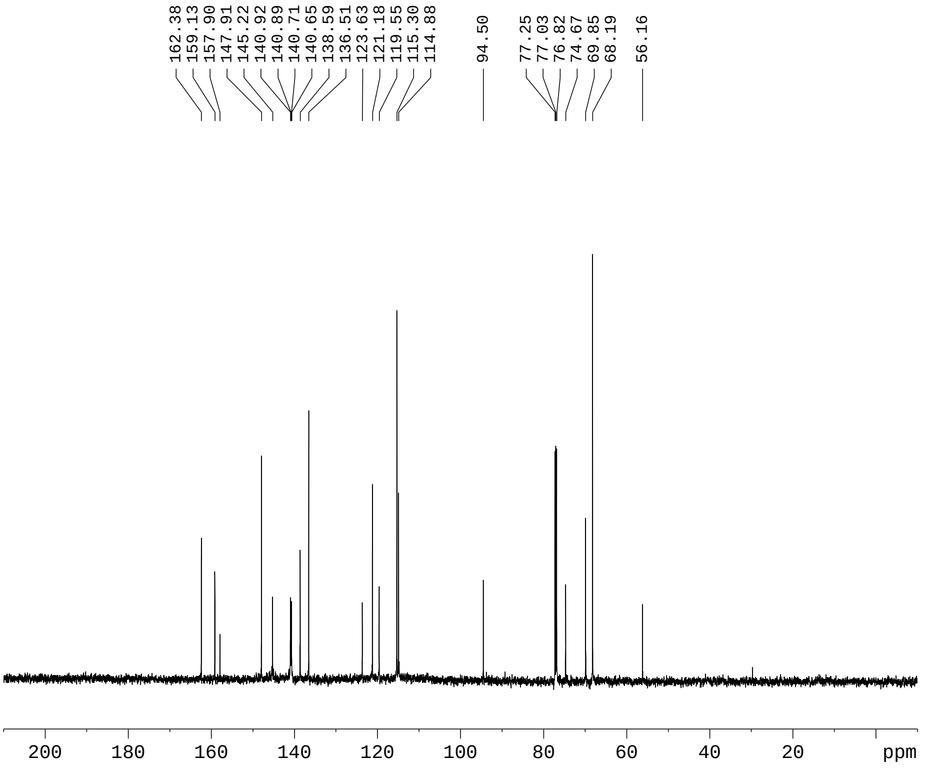
```
Current Data Parameters
NAME            G2-TFIB
EXPNO               120
PROCNO                1

F2 - Acquisition Parameters
Date_          20151209
Time              23.26
INSTRUM           spect
PROBHD   5 mm PATBO BB-
PULPROG            zgpg
TD                32768
SOLVENT           CDCl3
NS                  205
DS                    4
SWH          37593.984 Hz
FIDRES        1.147277 Hz
AQ           0.4358644 sec
RG                32768
DW              13.300 usec
DE                6.50 usec
TE               300.5 K
D1          1.50000000 sec
D11         0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1               12.00 usec
PL1               3.00 dB
SFO1       150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            70.00 usec
PL2              -0.60 dB
PL12             14.72 dB
PL13            120.00 dB
SFO2       600.1324005 MHz

F2 - Processing parameters
SI                32768
```



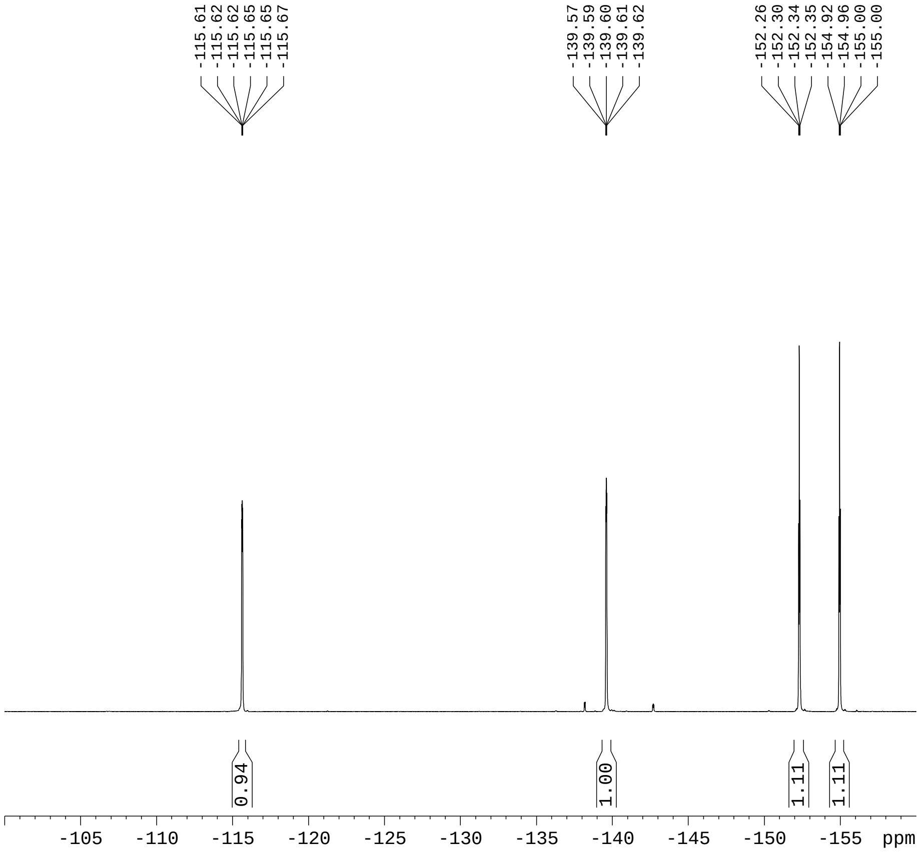
```
Current Data Parameters
NAME            G2-TFIB
EXPNO               126
PROCNO                1

F2 - Acquisition Parameters
Date_          20151210
Time               0.15
INSTRUM           spect
PROBHD   5 mm PATBO BB-
PULPROG     zgigf2igf3
TD                32768
SOLVENT           CDCl3
NS                  212
DS                    0
SWH           37593.984 Hz
FIDRES         1.147277 Hz
AQ            0.4358644 sec
RG                13004
DW               13.300 usec
DE                 6.50 usec
TE                300.8 K
D1           1.50000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                12.00 usec
PL1                3.00 dB
SFO1        150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2           garp4
NUC2                19F
PCPD2             31.30 usec
PL2                0.00 dB
PL12               2.50 dB
PL2W        25.11886406 W
PL12W       14.12537575 W
SFO2        564.6118494 MHz

======== CHANNEL f3 ========
```



```
Current Data Parameters
NAME         氯离子络合比
EXPNO                79
PROCNO                1

F2 - Acquisition Parameters
Date_          20131224
Time               9.40
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG     zgfhigqn.2
TD               131072
SOLVENT         Acetone
NS                   32
DS                    0
SWH          138888.891 Hz
FIDRES         1.059638 Hz
AQ            0.4719092 sec
RG                71.67
DW                3.600 usec
DE                 6.50 usec
TE                298.2 K
D1           1.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        470.6488054 MHz
NUC1                19F
P1                12.50 usec

F2 - Processing parameters
SI                65536
SF          470.7052900 MHz
WDW                  EM
SSB                   0
LB                 5.00 Hz
GB                    0
PC                 1.00
```

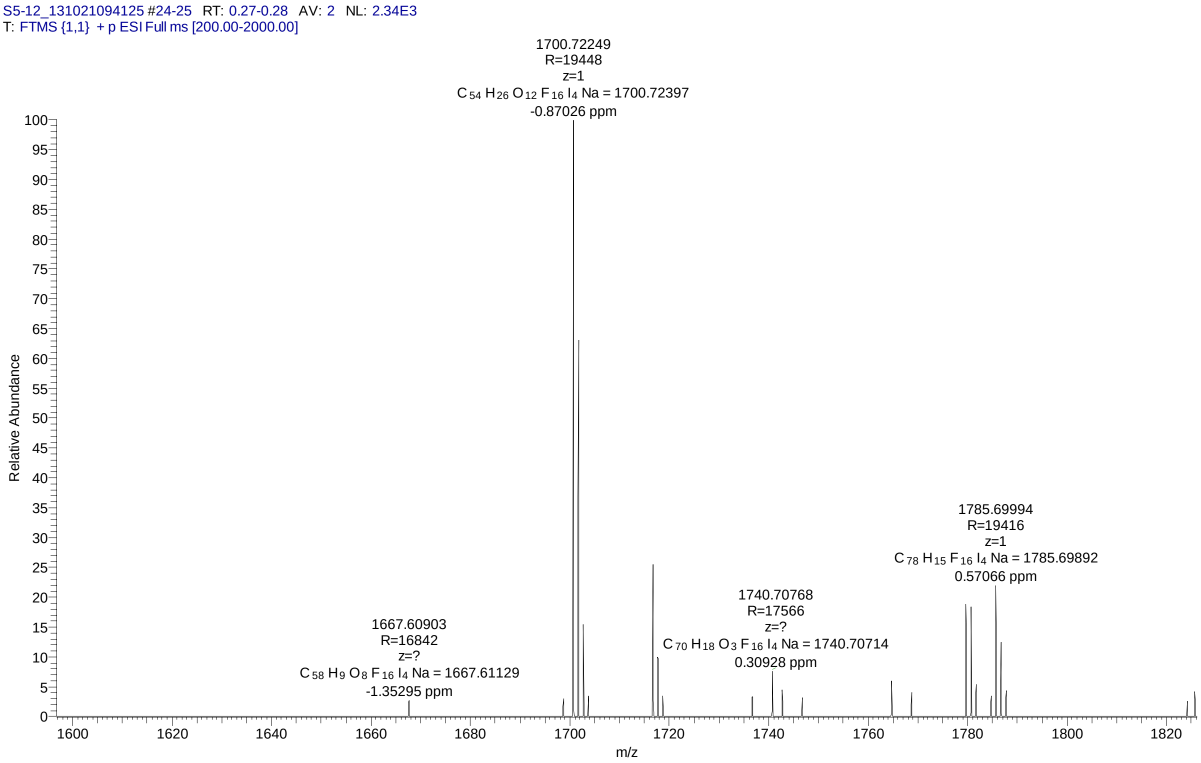
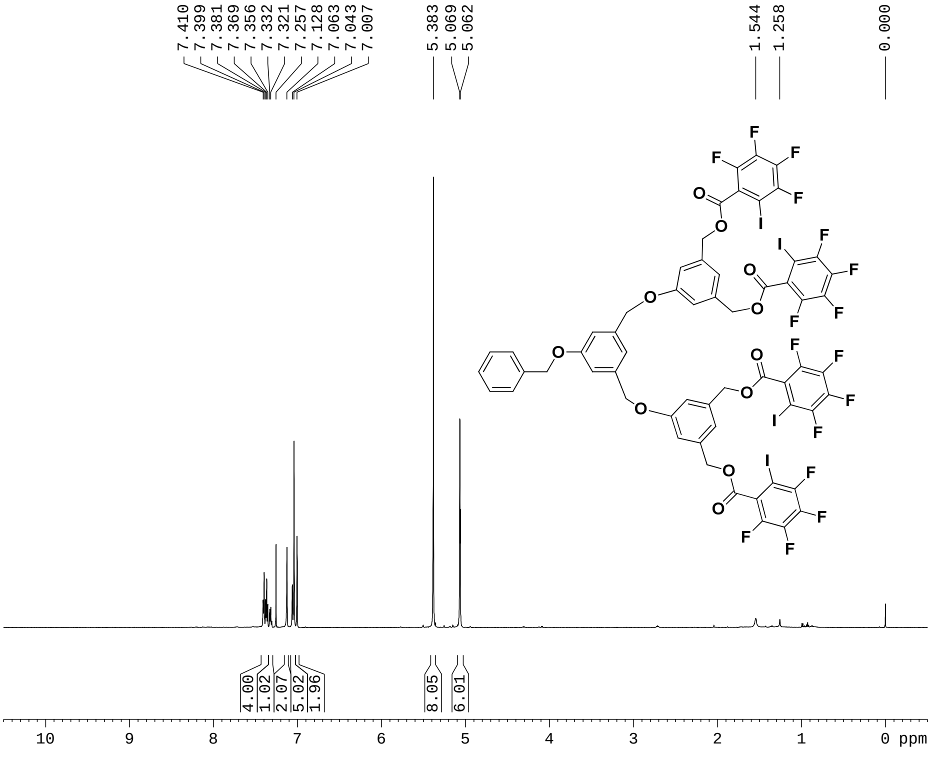


Figure S25. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and HRMS-ESI mass spectra of dendron **2**

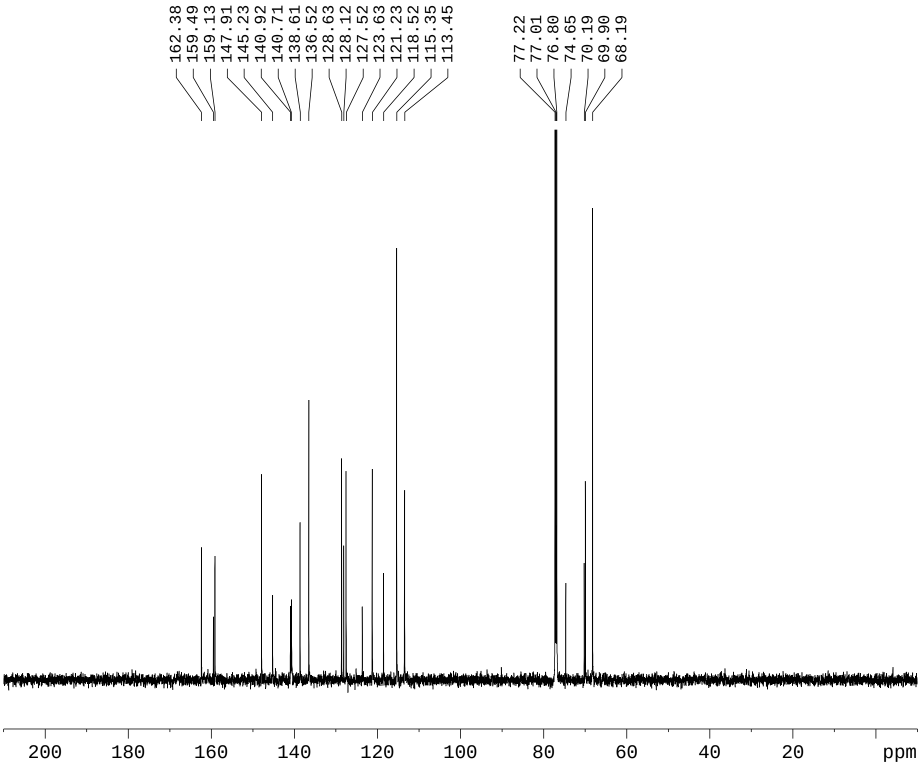


```
Current Data Parameters
NAME             G2-TFIB
EXPNO                427
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151210
Time                0.29
INSTRUM            spect
PROBHD   5 mm PATBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     8
DS                     0
SWH            17985.611 Hz
FIDRES          0.548877 Hz
AQ             0.9110004 sec
RG                   256
DW                27.800 usec
DE                  6.50 usec
TE                 299.9 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -0.60 dB
SFO1         600.1324005 MHz

F2 - Processing parameters
SI                 65536
SF           600.1300237 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



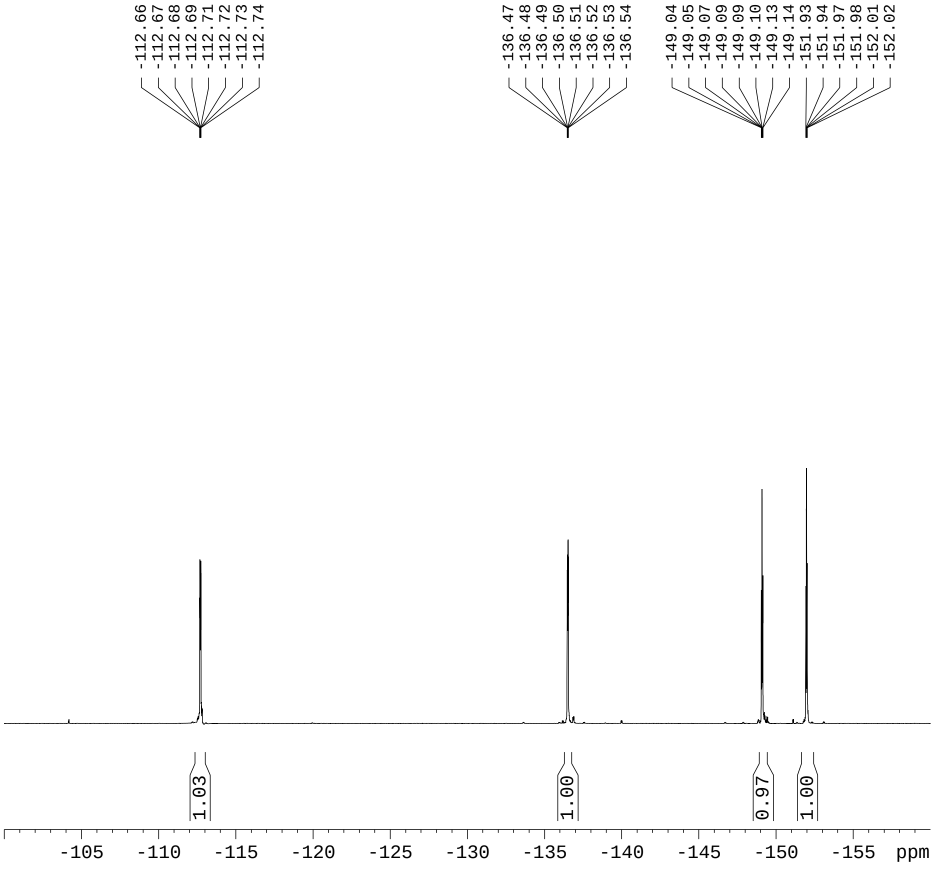
```
Current Data Parameters
NAME            G2-TFIB
EXPNO               127
PROCNO                1

F2 - Acquisition Parameters
Date_          20151210
Time               0.30
INSTRUM           spect
PROBHD   5 mm PATBO BB-
PULPROG      zgigf2igf3
TD                32768
SOLVENT           CDCl3
NS                 1659
DS                    0
SWH           37593.984 Hz
FIDRES         1.147277 Hz
AQ            0.4358644 sec
RG                13004
DW               13.300 usec
DE                 6.50 usec
TE                300.9 K
D1           1.50000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                12.00 usec
PL1                3.00 dB
SFO1        150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2           garp4
NUC2                19F
PCPD2             31.30 usec
PL2                0.00 dB
PL12               2.50 dB
PL2W        25.11886406 W
PL12W       14.12537575 W
SFO2        564.6118494 MHz

======== CHANNEL f3 ========
```

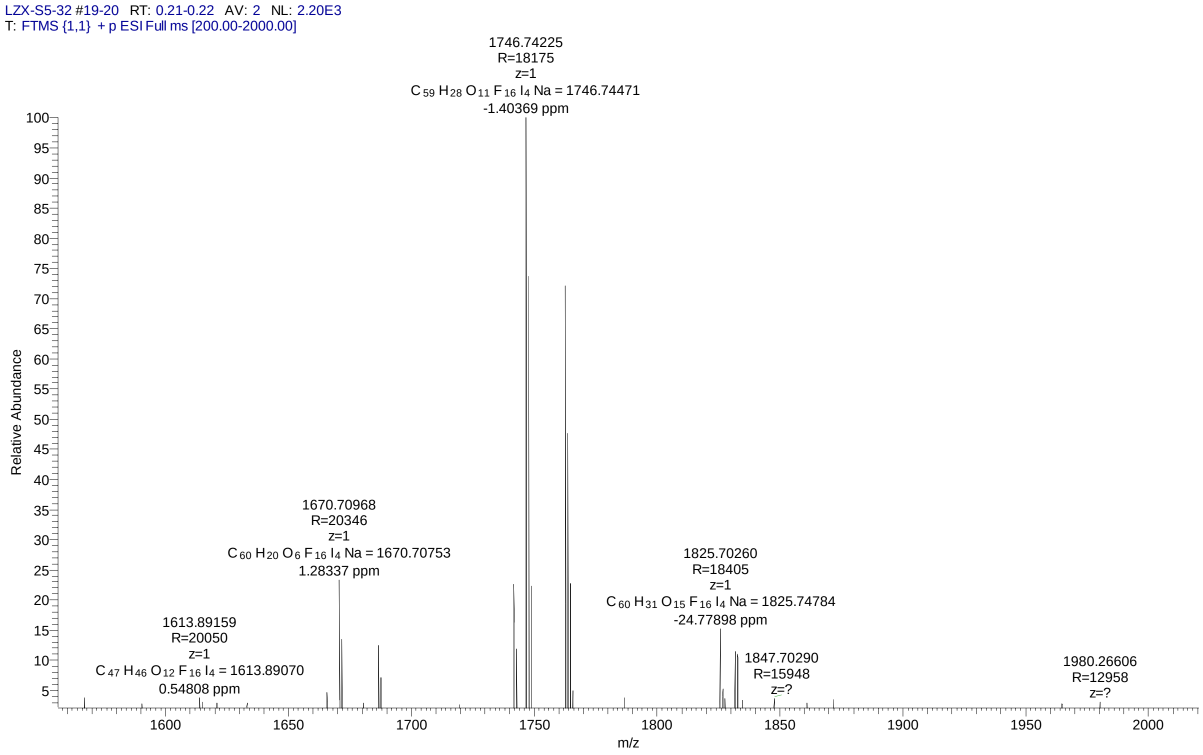


```
Current Data Parameters
NAME     19F-NMR 20140304
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140304
Time               11.17
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG       zgfhigqn.2
TD                131072
SOLVENT            CDCl3
NS                    16
DS                     0
SWH           113636.367 Hz
FIDRES          0.866977 Hz
AQ             0.5767668 sec
RG                 71.67
DW                 4.400 usec
DE                  6.50 usec
TE                 298.2 K
D1            3.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         470.6111772 MHz
NUC1                 19F
P1                 12.50 usec

F2 - Processing parameters
SI                 65536
SF           470.6582430 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```


LZX-S5-32 #19-20 RT: 0.21-0.22 AV: 2 NL: 2.20E3
T: FTMS {1,1} + p ESI Full ms [200.00-2000.00]
1746.74225
R=18175
z=1
$C_{59}H_{28}O_{11}F_{16}I_4Na$ = 1746.74471
-1.40369 ppm
1670.70968
R=20346
z=1
$C_{60}H_{20}O_6F_{16}I_4Na$ = 1670.70753
1.28337 ppm
1613.89159
R=20050
z=1
$C_{47}H_{46}O_{12}F_{16}I_4$ = 1613.89070
0.54808 ppm
1825.70260
R=18405
z=1
$C_{60}H_{31}O_{15}F_{16}I_4Na$ = 1825.74784
-24.77898 ppm
1847.70290
R=15948
z=?
1980.26606
R=12958
z=?
Relative Abundance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
1600
1650
1700
1750
1800
1850
1900
1950
2000
m/z