Well-defined poly(vinylidene fluoride) (PVDF) based-dendrimers synthesized by click chemistry: enhanced crystallinity of PVDF and increased hydrophobicity of PVDF films

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Supporting Information

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S1. Materials and Methods

● Chemicals and purification methods.

Chemicals were purchased from Aldrich, Acros, Fluka, Alfa Aesar and Strem, and were used without further purification, except for $P_3N_3Cl_6$ which was recrystallized from hexane, 4-hydroxybenzaldehyde which was recrystallized from diethyl ether. Organic solvents were dried and distilled according to usual procedures.[1] Phosphorhydrazone dendrimers (PPH) dendrimers were synthesized according to published procedures.[2]

Purifications by column chromatography were performed on silica gel (60 Å, 53-250 μm) or on an automatic Flash chromatography system, SPOT™ II Ultimate. TLCs were performed on silica gel 60 F254 plates and detection was carried out under UV light or using appropriate dyeing reagent.

● NMR

Most of **NMR** spectra were recorded with Bruker AV 300 and AV 400. All spectra were measured at 25 °C in the indicated deuterated solvents. References for NMR chemical shifts were H_3PO_4 (85%) for ^{31}P NMR, and $SiMe_4$ for ^{1}H and ^{13}C NMR spectroscopy.^{1}H, ^{13}C and ^{31}P chemical shifts (δ) are reported in ppm and coupling constants (J) are reported in Hertz (Hz). The signals in the spectra are described as s (singlet), d (doublet), t (triplet), m (multiplet) and br (broad resonances).

Some experiments (DOSY, ROESY, HSBC and HMBC) were recorded on a Bruker Avance 500 spectrometer equipped with a 5 mm triple resonance inverse Z-gradient probe (TBI 1H, 31P, BB). All chemical shifts for 1H were relative to TMS using 1H (residual) chemical shifts of the solvent as a secondary standard.

- Diffusion ordered spectroscopy (DOSY) NMR was used to measure the translational diffusion coefficient D. The DOSY spectra were acquired at 291K with the stebpgp1s pulse program from Bruker topspin software. All spectra were recorded with 16K time domain data point in the t2 dimension and 16 t1 increments. The gradients strength was linearly incremented in 16 steps from 2% up to 95% of the maximum gradient strength. All measurements were performed with a compromise diffusion delay Δ of 220ms and a gradient pulse length δ of 3,2ms (error on the diffusion coefficient: below 5%). For these experiments, the cycloaddition reaction was performed in deuterated THF and the crude was directly analyzed.

- For ROESY experiment, spectra were acquired at 293K using a mixing time of 200 ms, 16 averages for each *t*1 value after 4 dummy scans, a datum set of 2048 time domain data point in the t2 dimension with 256 *t*1 increments, and the States-TPPI method for quadrature detection in the *t*1 dimension.

- 1H spectra were recorded at 293K, using the following parameters: spectral width, 13 ppm; 30° nutation angle duration, 6.7μs; recycling delay, 3-s (2-s acquisition time and 1-s relaxation delay).

- Two-dimensional experiments including heteronuclear single quantum coherence (HSQC), and heteronuclear multiple bond correlation (HMBC) were acquired with a data point of 2 K × 256 (t2× t1).
The long-range coupling time for HMBC was 63 ms.

● Fourier Transform Infrared

FTIR analyses were performed using a PerkinElmer Spectrum 1000 in ATR mode, with an accuracy of ±2 cm^{-1}.

● Mass spectrometry

Mass spectroscopy was carried out on a Thermo Fisher DS QII (DCI/NH_3), GTC Premier Waters (DCI/CH_4) or with Maldi Micro MX Waters (Maldi/DCTB).

● Dynamic Light scattering

Dynamic Light Scattering (DLS) experiments were performed at 25 °C on a Malvern instrument Nano-ZS (ZEN3600, UK) equipped with a He-Ne laser as the light source (λ = 633 nm). The scattered light was detected at the scattering angle of ν = 173°. Samples of THF solutions of dendrimers (10 mg mL^{-1})[3] were introduced into cells (pathway, 10 mm) after filtration through 0.45 lm PTFE microfilters.

The apparent equivalent hydrodynamic radius (Rh) was determined using the Stokes–Einstein equation ($Rh=k_BT/6\pi\eta D$), where η is the diluent viscosity (0.48 for THF). Hydrodynamic radius values were obtained from three different runs. Standard deviations were evaluated from radius distribution and were equal to 1.3 nm as a maximum for dendrimer **5** and to 0.2 nm as a maximum for dendrimer **3**.

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[1] D. D. Perrin et W. L. F. Almerego, *Purification of Laboratory Chemicals 3rd Ed.*, Pergamon Press. Oxford, **1998**.
[2] N. Launay, A.-M. Caminade, J.-P. Majoral, *J. Organomet. Chem.* **1997**, *529*, 51.
[3] For these experiments, the crude reaction medium was directly analyzed, re-solubilization of dry star polymer **5** being difficult in THF.

● Size exclusion chromatography

Size exclusion chromatograms (SEC) were recorded using a triple detection GPC from Agilent Technologies with its corresponding Agilent software, dedicated to multi-detector GPC calculation. The system used two PL1113-6300 ResiPore 300 x 7.5 mm columns with DMF (containing 0.1 wt % of LiCl) as the eluent with a flow rate of 0.8 mL.min-1 and toluene as flow rate marker (compounds **3**, **4** and **5** were also analyzed by using THF as the eluent). The detector suite comprised a PL0390-0605390 LC light scattering detector with 2 diffusion angles (15° and 90°), a PL0390-06034 capillary viscosimeter, and a 390-LC PL0390-0601 refractive index detector. The entire SEC-HPLC system was thermostated at 35°C. PMMA standards were used for the calibration. The typical sample concentration was 10 mg/mL.

● HR Transmission electron microscopy

High resolution transmission electron microscopy **(HRTEM)**, scanning transmission electron spectroscopy (**STEM**) and energy dispersive X-ray (**EDX**) were performed at the "Service Commun de Microscopie Electronique de l'Université Paul Sabatier" (UPS-TEMSCAN) and recorded on a JEOL JEM 2100 F electron microscope working at 200 kV with a resolution point of 2.5 Å and equipped with X-ray analysis PGT (light elements detection, resolution 135 eV). Samples for **HRTEM** analyses were prepared by slow evaporation of a drop of crude colloidal solution deposited onto holey carbon-covered copper grids. On the EDX spectra, Cu signals are due to the grids on which the samples were deposited and Si signals were found to come from the preparation of samples.

● Thermogravimetric Analyses

TGA analyses were carried out on 10-15 mg samples on a TGA Q50 apparatus from TA Instruments from 20 °C to 580 °C, in platinum pans, at a heating rate of 10 °C min^{-1}, under air. *A thermal degradation temperature at 5% weight loss (T_d 5%) was arbitrarily chosen.*

● Differential Scanning Calorimetry

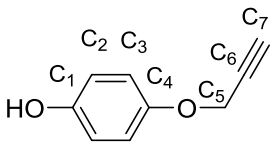
DSC measurements were performed on 10-15 mg samples on a Netzsch DSC 200 F3 instrument using the following heating/cooling cycle: cooling from room temperature (ca. 20 °C) to -50 °C at 20 °C/min, isotherm plateau at -50 °C for 5 min, first heating ramp from -50 to 200 °C at 10 °C/min, cooling stage from 200 to -50 °C at 10 °C/min, isotherm plateau at -50 °C for 3 min, second heating ramp from -50 °C to 200 °C at 10 °C/min and last cooling stage from 200 °C to room temperature (ca. 20 °C). The instrument was calibrated with noble metals and checked before analysis with an indium sample. Glass transition temperatures were assessed as the inflexion point in the heat capacity jump while melting points were determined at the maximum of the enthalpy peaks.

● Water Contact Angle and Spin Coating

WCA measurements were carried on the polymer thin film prepared by spin-coating (acceleration time: 10 s, rpm = 3000, time = 1.30 min) from THF crude product on glass slides followed by drying at room temperature for 1 h. WCA measurements were carried out on Contact Angle System OCA-Data Physics using the water sessile drop method at ambient temperature. The probe liquid was water (θ_{H2O}) and the average CA value was determined from five different drops per sample of 5.0 µL deposited on the same sample. The experiments were repeated on two samples for each compound.

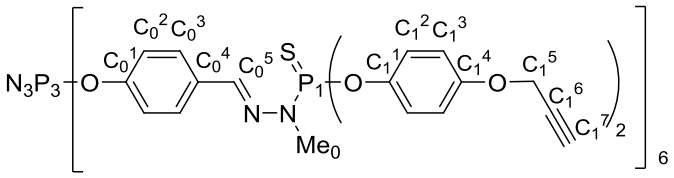
S2. Procedures for preparation and characterization of compounds 2-5.

Synthesis of propargyloxyphenol 2 (procedure adapted from reference 4) (M = 148.05)



To a solution of hydroquinone (25.00 g, 227.0 mmol) in dry acetone (125 mL) refluxed for 30 min at 65°C, was added anhydrous K_2CO_3 (31.38 g, 227,0 mmol) and the mixture was refluxed for 45 min. To this mixture, propargyl bromide (7.02 g, 59.0 mmol) was added dropwise over a period of 5 h. The resulting mixture was refluxed for an additional period of 24 h and then cooled, filtered and the filtrate was evaporated. The brown oily residue was dissolved in CH_2Cl_2 (125 mL) and the solution was washed with water (2 x 50 mL) followed by saturated brine solution (50 mL). The organic layers were dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product consisted in a mixture of unreacted hydroquinone, propargyloxyphenol and bispropargyloxybenzene which were separated by column chromatography on silica gel using hexane/ethyl acetates (8:2). Propargyloxyphenol was obtained as a yellow oil (5.25 g, 60% yield).
IR-ATR (cm^{-1}): 3285 (νC≡C), 2121 (ν C≡C-H).
^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ **(ppm)** 6.88 and 6.99 (m, 4H), 4.61 (d, 2H, J = 2.44 Hz, C^5-H), 2.48 (t, 1H, J = 2.44 Hz, C^7-H).

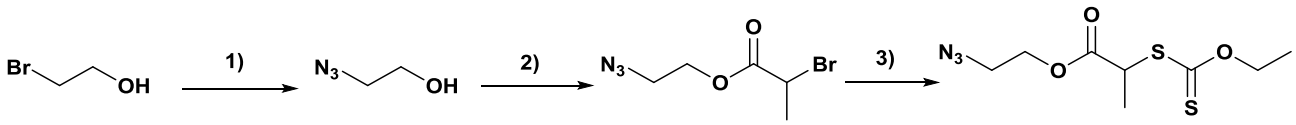
Synthesis of PPH dendrimer bearing propargylic surface functions 3:[5] (M = 3167.97)



Cs_2CO_3 (1,28 g, 3.936 mmol) was added to a THF (20 mL) solution of the dendrimer **1** (300 mg, 0.164 mmol) and propargyloxyphenol (320 mg, 2,167 mmol). The reaction mixture was stirred at 40°C until the reaction was complete (24 h, monitored by 31P{1H} NMR). Inorganic salts were filtered through a Celite® pad and the residual solvent was evaporated under reduced pressure. The crude product was purified by silica gel flash chromatography eluting with 7:3 to 5:5 pentane/ethyl acetate. Dendrimer **3** was obtained as a white foam (390 mg, 75 %).

^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ **(ppm)** 7.63 (d, , 12 H, C_0^3), 7.58 (s, 6 H, C_0^5-H), 7.11 (d, 24 H, C_1^2-H), 7.02 (d, 12 H, C_0^2-H), 6.86 (d, 24 H, C_0^2-H), 4.60 (d, J = 2.4 Hz, 24 H, C_1^5-H), 3.24 (d, J = 10.2 Hz, 18 H, Me_0), 2.50 (t, J = 2.4Hz, 12 H, C_1^7-H) ppm.
^{31}P{1H} NMR (121.5 MHz, $CDCl_3$, 25°C): δ **(ppm)** 63.94 (P_1), 8.41 (P_0).
MALDI TOF-MS (matrice): m/z: 3168 $[M+H]^+$ (spectrum below).
GPC (in THF) using light scattering detector: Mw = 2598, Mn=2547, Đ = 1.02

Synthesis of PVDF-N_3 4:



(i) Synthesis of 2-azidoethanol

2-bromoethanol (10.0 g, 77.3 mmol) and sodium azide (7.66 g, 118 mmol) were disssolved in a mixture of acetone (120 mL) and DI water (30 mL) and the resulting solution was left under stirring and reflux for 16 h. Acetone was then removed under vacuum, 100 mL of DI water was added and the expected 2-azidoethanol was extracted with 3 x 100 mL of diethyl ether. The organic layers collected were then dried over $MgSO_4$ and, after removal of solvent under reduced pressure, 2-azidoethanol was isolated as a colourless oil. (5.0g, 74 %).
^{1}H NMR (400 MHz, $(CD_3)_2CO$, 25°C): δ **(ppm)** 3.32 (2H, t, J = 5.1 Hz, N_3-**CH_2**-CH_2-OH), 3.72 (2H, q, J = 4.9 Hz, N_3-CH_2-**CH_2**-OH), 4.21 (2H, t, J = 5.4 Hz, N_3-CH_2-CH_2-**OH**).

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[4] M. Srinivasan, S. Sankararaman, H. Hopf, I. Dix, P. G. Jones. *J. Org. Chem.* **2001,** 66, 4299-4303.
[5] E. Cavero, M. Zablocka, A.-M. Caminade, J.-P. Majoral. *Eur. J. Org. Chem*. **2010**, 2759–2767.

(ii) Synthesis of 2-azidoethyl-2-bromopropanoate

A solution of 2-bromopropionate bromide (18.6g, 86.3 mmol) in 25 mL of dry THF was added drop wise to a solution of 2-azidoethanol (5.0 g, 57 mmol) and (8.7 g, 86 mmol) in 90 mL of dry THF at 0°C. After complete addition, the reaction mixture was allowed to stir for 1 hour at 25 °C. The excess of 2-bromopropionate bromide was quenched with 17 mL of methanol. The precipitated salt of triethylammonium bromide was filtered on Celite® and the solvents (MeOH and THF) were remove under vacuum. The crude product was dissolved in 100 mL of dichloromethane, washed twice with a solution of saturated ammonium chloride, and twice with a saturated solution of potassium carbonate. The DCM solution was dried on $MgSO_4$ and the solvent was removed under vacuum until constant weight yielding a yellow oil (8.68 g, 68 %).
δ_H (400 MHz, $(CD_3)_2CO$): 1.81 (3H, d, J = 6.8 Hz, N_3-CH_2-CH_2-O(C=O)-CH(**CH_3**)-Br), 3.61 (2H, d, J = 5.1 Hz, N_3-**CH_2**-CH_2-O(C=O)-CH(CH_3)-Br), 4.34 (2H, t, J = 4.8 Hz, N_3-CH_2-**CH_2**-O(C=O)-CH(CH_3)-Br), 4.6 (1H, q, J = 6.9 Hz, N_3-CH_2-CH_2-O(C=O)-**CH**(CH_3)-Br).

(iii) Synthesis of 2-azidoethyl-(carbonothioyl)thio)propanoate

2-azidoethyl-2-bromopropanoate (8.7g, 39 mmol) and potassium ethyl xanthogenate (30.0g, 187 mmol) were dissolved in 180 mL of $CHCl_3$ and the heterogenous mixture was left under vigorous stirring 3 days at 30 °C. The excess xanthogenate salt was removed by filtration on Celite® and the organic solution was washed twice with 100 mL of DI water The solution was dried on $MgSO_4$ and the solvent was removed under vacuum. The crude product was then purified using flash chromatography (SiO_2, Cyclohexane/ Ethyl Acetate (90 :10)). The product was isolated as an odorless yellowish oil (6.6 g, 64 %).
δ_H (400 MHz, $(CD_3)_2CO$): 1.41 (3H, t, J = 7.0 Hz, N_3-CH_2-CH_2-O(C=O)-CH(CH_3)-S(C=S)-OCH_2-**CH_3**), 1.57 (3H, t, J = 7.4 Hz, N_3-CH_2-CH_2-O(C=O)-CH(**CH_3**)-S(C=S)-OCH_2-CH_3), 3.61 (2H, t, J = 5.3 Hz, N_3-**CH_2**-CH_2-O(C=O)-CH(CH_3)-S(C=S)-OCH_2-CH_3), 4.33 (2H, t, J = 5.0 Hz, N_3-CH_2-**CH_2**-O(C=O)-CH(CH_3)-S(C=S)-OCH_2-CH_3), 4.45 (1H, q, J = 7.6 Hz, N_3-CH_2-CH_2-O(C=O)-**CH**(CH_3)-S(C=S)-OCH_2-CH_3), 4.66 (2H, q, J = 7.1 Hz, N_3-CH_2-CH_2-O(C=O)-CH(CH_3)-S(C=S)-O**CH_2**-CH_3).

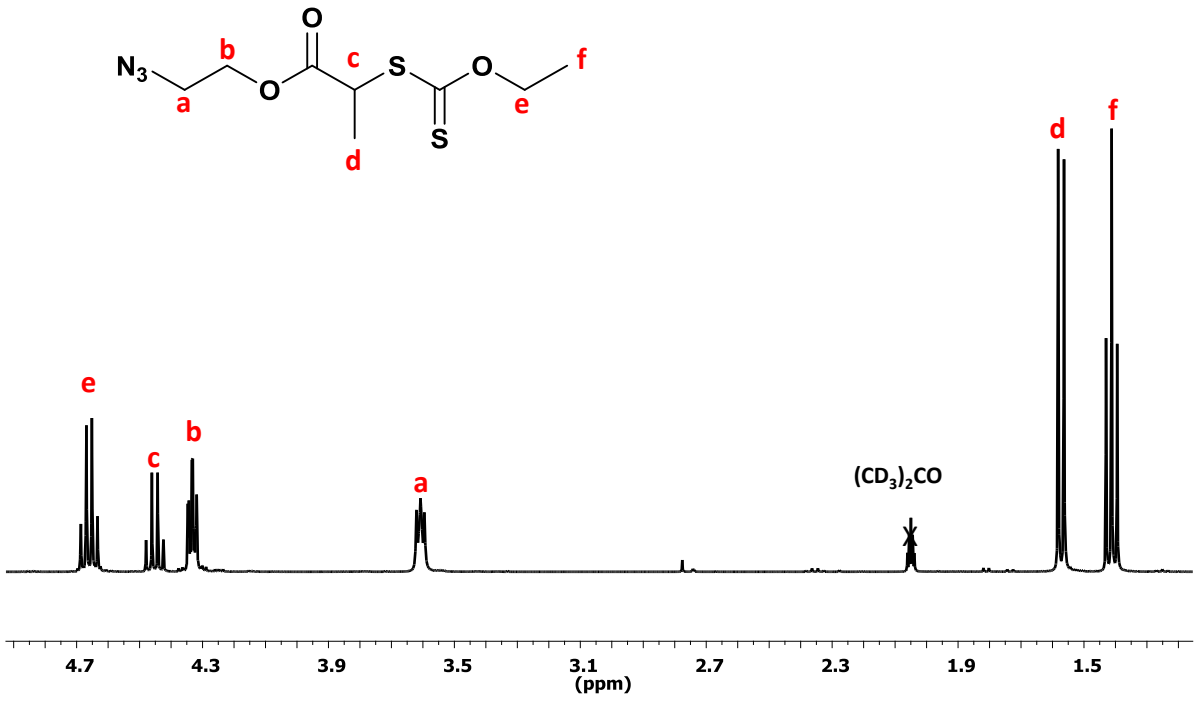
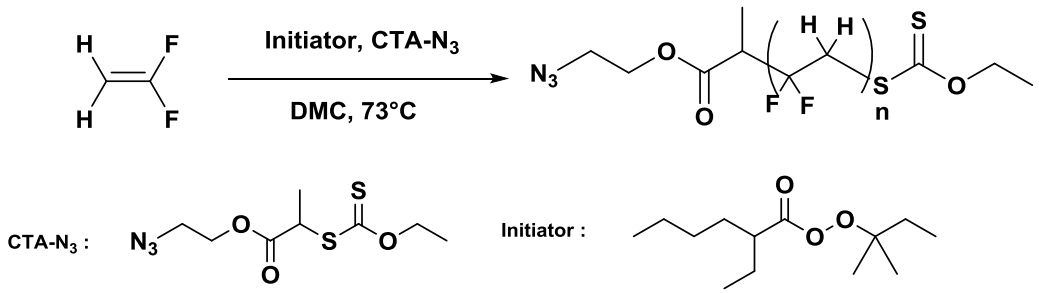


Figure S1. ^{1}H NMR spectrum of 2-azidoethyl-(carbonothioyl)thio)propanoate RAFT agent recorded in $(CD_3)_2CO$



Autoclave

The polymerization of VDF was performed in a 100 mL Hastelloy Parr autoclave systems (HC 276), equipped with a mechanical Hastelloy stirring system, a rupture disk (3000 PSI), inlet and outlet valves, and a Parr electronic controller to regulate the stirring speed and the heating. Prior to reaction, the autoclave was pressurized with 30 bars of nitrogen to check for leaks. The autoclave was then put under vacuum (20 10^{-3} bar) for 30 minutes to remove any trace of oxygen. A degassed solution of solvent, initiator and the chain transfer agent was introduced via a funnel under vacuum. The reactor was then cooled down using a liquid nitrogen bath, and VDF was transferred by double weighing (i.e. the mass difference before and after filling the autoclave with VDF). After warming up to ambient temperature, the autoclave was heated to the targeted temperature under mechanical stirring.

(iv) Synthesis of 4.

RAFT Homopolymerization of Vinylidene Fluoride (VDF) using azide RAFT agent

Using the experimental setup described above, a typical polymerization of VDF was performed as follows: A solution of *tert*-amyl peroxy-2-ethylhexanoate (Trigonox 121, 144 mg, 6.25 10^{-4} mol) and 2-azidoethyl-(carbonothioyl)thio)propanoate (CTA-N_3, 1.64 g, 6.25 10^{-3} mol) in dimethylcarbonate DMC (60 mL), was degassed by N_2 bubbling during 30 min. This homogenous solution was introduced into the autoclave using a funnel, VDF gas (20.0 g, 3.12 10^{-1} mol) was transferred in the autoclave at low temperature, and the reactor was gradually heated to 73 °C. The reaction was stopped after 20 h. During the reaction, the pressure increased to a maximum of 25 bars and then decreased to 10 bars after 24 h. The autoclave was cooled down to room temperature (ca. 20 °C), purged from the residual monomers and dimethylcarbonate was removed under vacuum. The crude product was dissolved in 30 mL of warm THF (ca. 40 °C), and left under vigorous stirring for 30 minutes. This polymer solution was then precipitated from 400 mL of chilled hexane. The precipitated polymer (white powder) was filtered through a filter funnel and dried under vacuum (15 10^{-3} bar) for two hours at 50°C. The polymerization yield was determined by gravimetry. (yield = 35%).

δ_H (400 MHz, $(CD_3)_2CO$): 1.23-1.29 (d, -CH(**CH_3**)(C=O)-, $^3J_{HH}$= 7.3 Hz), 1.40-1.46 (t, -S(C=S)O-CH_2-**CH_3**, $^3J_{HH}$= 7.2 Hz), 2.25-2.44 (m,-CF_2-**CH_2**-**CH_2**-CF_2-, VDF-VDF TT reverse addition), 2.71-3.20 (t, -CF_2-**CH_2**-CF_2-, VDF-VDF HT regular addition), 3.30-3.50 (quintet, -CF_2-**CH_2**-CF_2-S(C=S)OEt, $^3J_{FH}$= 16.2 Hz), 3.52-3.63 (t, -CH(CH_3)(C=O)-O-CH_2-**CH_2**-N_3, $^3J_{HH}$= 5.1 Hz), 4.02-4.17 (t, -CF_2-**CH_2**-S(C=S)OEt, $^3J_{HF}$= 18 Hz), 4.21-4.35 (t, -CH(CH_3)(C=O)-O-**CH_2**-CH_2-N_3, $^3J_{HH}$= 5.6 Hz), 4.66-4.82 (q, (-S(C=S)O-**CH_2**-CH_3, $^3J_{HH}$= 7.2 Hz), 6.05-6.45 (tt, $^2J_{HF}$= 55 Hz , $^3J_{HH}$= 4.6 Hz -CH_2-CF_2-**H**)

δ_F (376 MHz, $(CD_3)_2CO$): -115.63 (-CH_2-CF_2-**CF_2**-CH_2-CH_2-, VDF-VDF HH reverse addition), -114.29 ($^2J_{HF}$= 55 Hz, -CH_2-**CF_2**-H), -113.34 (-CH_2-**CF_2**-CF_2-CH_2-CH_2-, HH reverse addition), -113.09 (CH_2-CF_2-**CF_2**-CH_2-S-), -112.69 (-CH_2-**CF_2**-CF_2-CH_2-S-), -94.79 (-CH_2-CH_2-**CF_2**-CH_2-), -93.50 (-CH_2-**CF_2**-CH_2-CH(CH_3)(C=O)-), -92.12 (-CH_2-**CF_2**-CH_2-CF_2H), 91.95 (-CH_2-**CF_2**-CH_2-CF_2-S-), -91.44 (-CH_2-CH_2-CF_2-CH_2-**CF_2**-CH_2-CF_2-, regular VDF-VDF HT addition), -91.00 (-CH_2-**CF_2**-CH_2-, regular VDF-VDF HT addition).

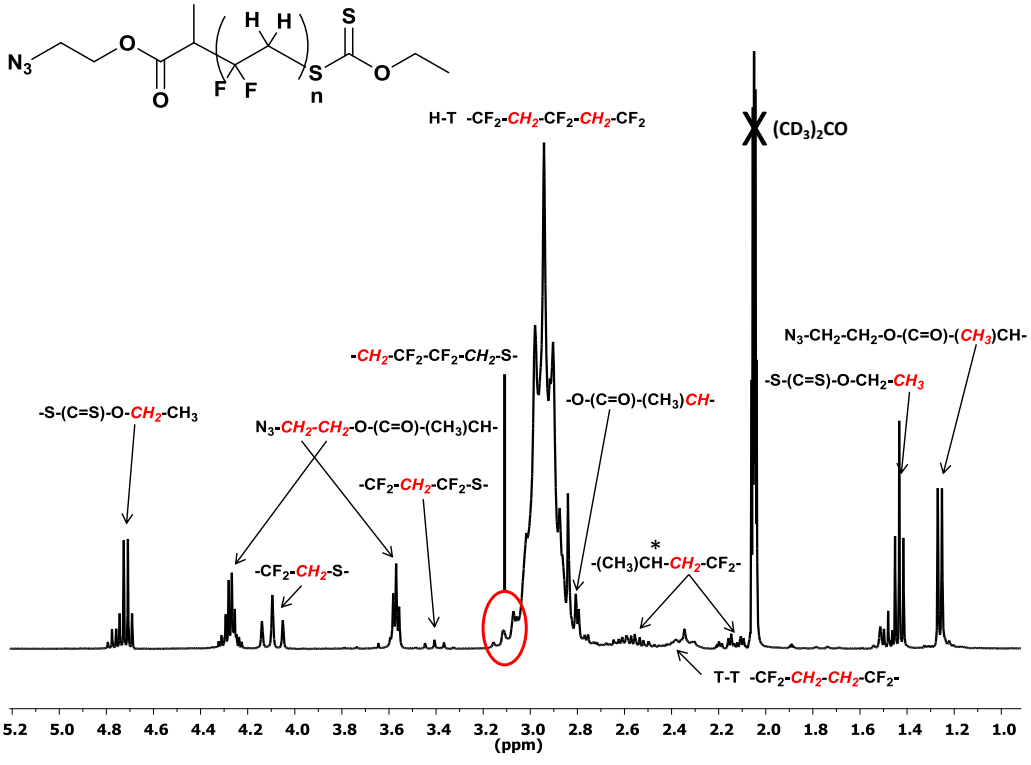


Figure S2. Expansion of the 0.9-5.2 ppm region of the ^{1}H NMR spectrum in $(CD_3)_2CO$ of PVDF-N_3 homopolymer (**4**) synthesized by RAFT polymerization. Protons were assigned according to our previous study.[6]

$$(1)\quad DP = \frac{\int_{2.71}^{3.21} CH_2\,(HT) + \int_{2.25}^{2.44} CH_2(TT) + \int_{4.02}^{4.17} CH_2(\text{End}-\text{group})}{2/3 \times \int_{1.19}^{1.24} CH_3\,(R-CTA)}$$

$$(1)\quad DP = \frac{62.75 + 1.91 + 1.72}{2/3 \times 3} = 33$$

$$(2)\quad M_{n,NMR}(R) = M_{n,CTA} + (DP \times M_{n,VDF})$$

$$(2)\quad M_{n,NMR}(R) = 208.3 + (33 \times 64.04) = 2400\ g.mol^{-1}$$

Where $M_{n\,CTA}$ = 208.3 g.mol^{-1} and $M_{n\,VDF}$= 64.04 g.mol^{-1}

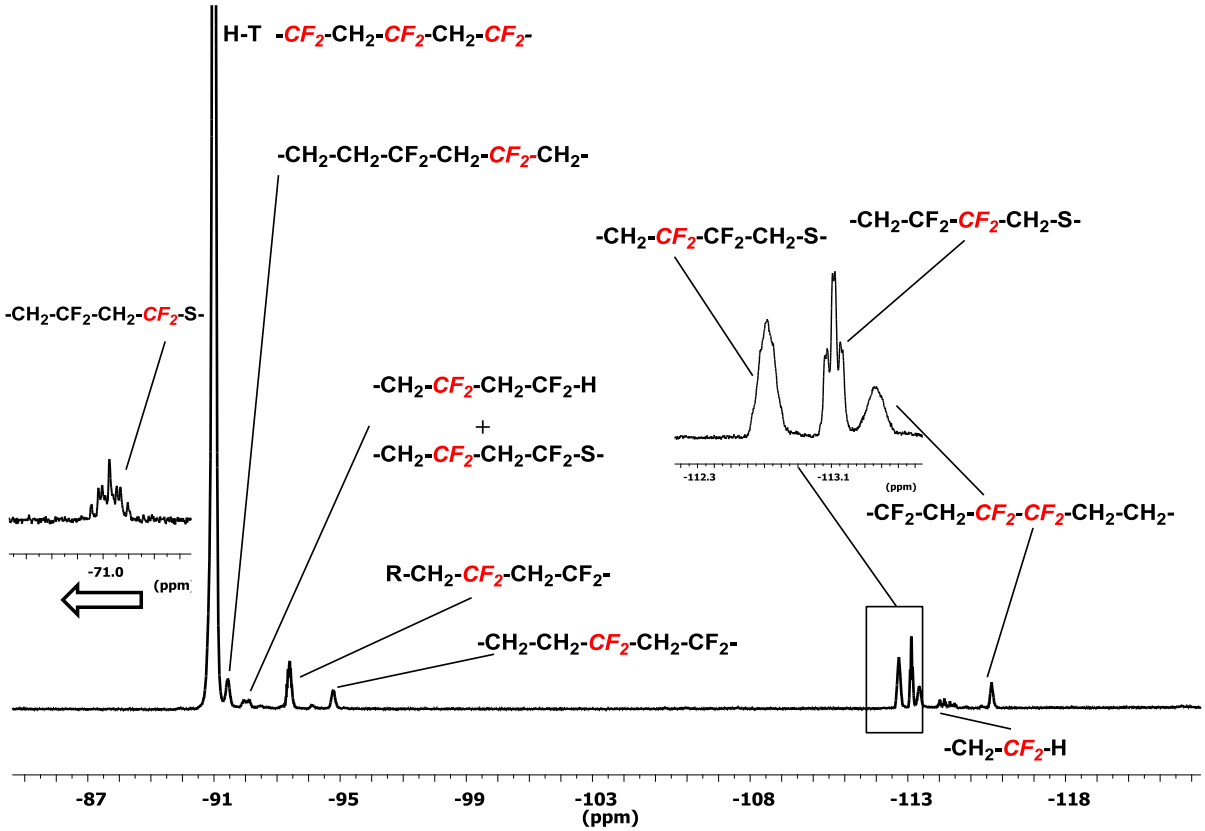


Figure S3. Expansion of the -84.5 to -122 ppm region of the ^{19}F NMR spectrum of PVDF-N_3 homopolymer (**4**) synthesized via RAFT polymerization (recorded in $(CD_3)_2CO$ at room temperature).

[6] (a) M. Guerre, G. Lopez, T. Soulestin, C. Totée, B. Améduri, G. Silly, V. Ladmiral, *Macromol. Chem. Phys.*, DOI: 10.1002/macp.201600109.

GPC data of 4	IR spectrum of 4

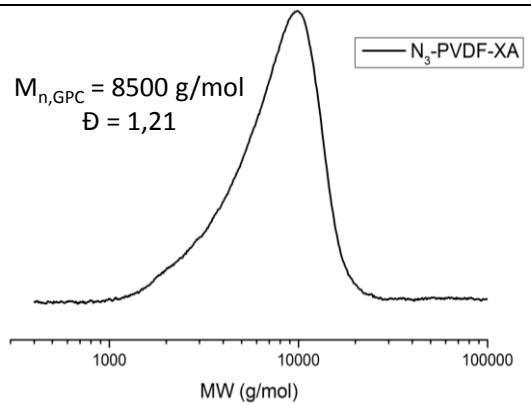
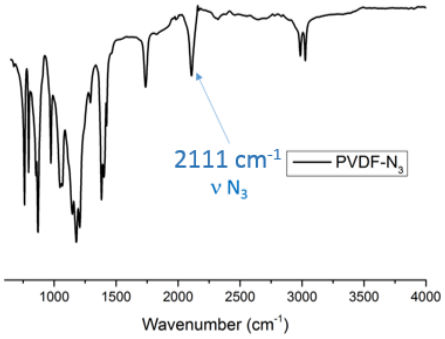
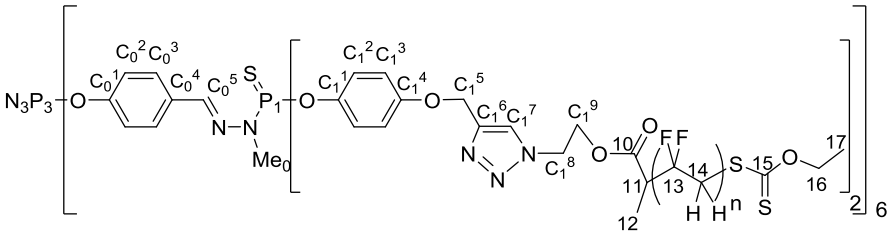

	

Figure S4. SEC data of **4** based on PMMA narrow standard calibration (solvent : DMF)	**Figure S5.** IR spectrum of PVDF-N_3 **4** The click reaction between **3** and **4** was monitored: by the disappearance of the characteristic band of the azido group at 2111 cm^{-1} of **4** (monitoring by IR spectroscopy, figure above).

Synthesis of dendritic PVDF 5:

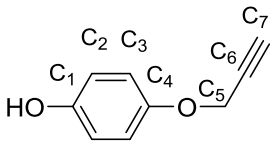


To a suspension of CuI (0.7 mg, 3.8 µmol) and *N*,*N*-diisopropylethylamine (26 µl, 151.2 µmol) in THF (0.5 mL) was added a solution of dendrimer **3** (20 mg, 6.3 µmol) in THF (0.5 mL). PVDF-N_3 **4** (170 mg, 77.2 µmol) was added and the mixture was diluted in THF (3.5 mL). The reaction mixture was stirred at 40°C for 24 h, and the progress of the reaction was monitored by ^{31}P {1H} and ^{1}H NMR. Inorganic salts were hot filtered through a Celite® pad and the residual solvent was evaporated under reduced pressure. The crude product was washed several times with cold THF to remove the excess of **4**.
5 was obtained as a brown powder (177 mg, 95% yield).

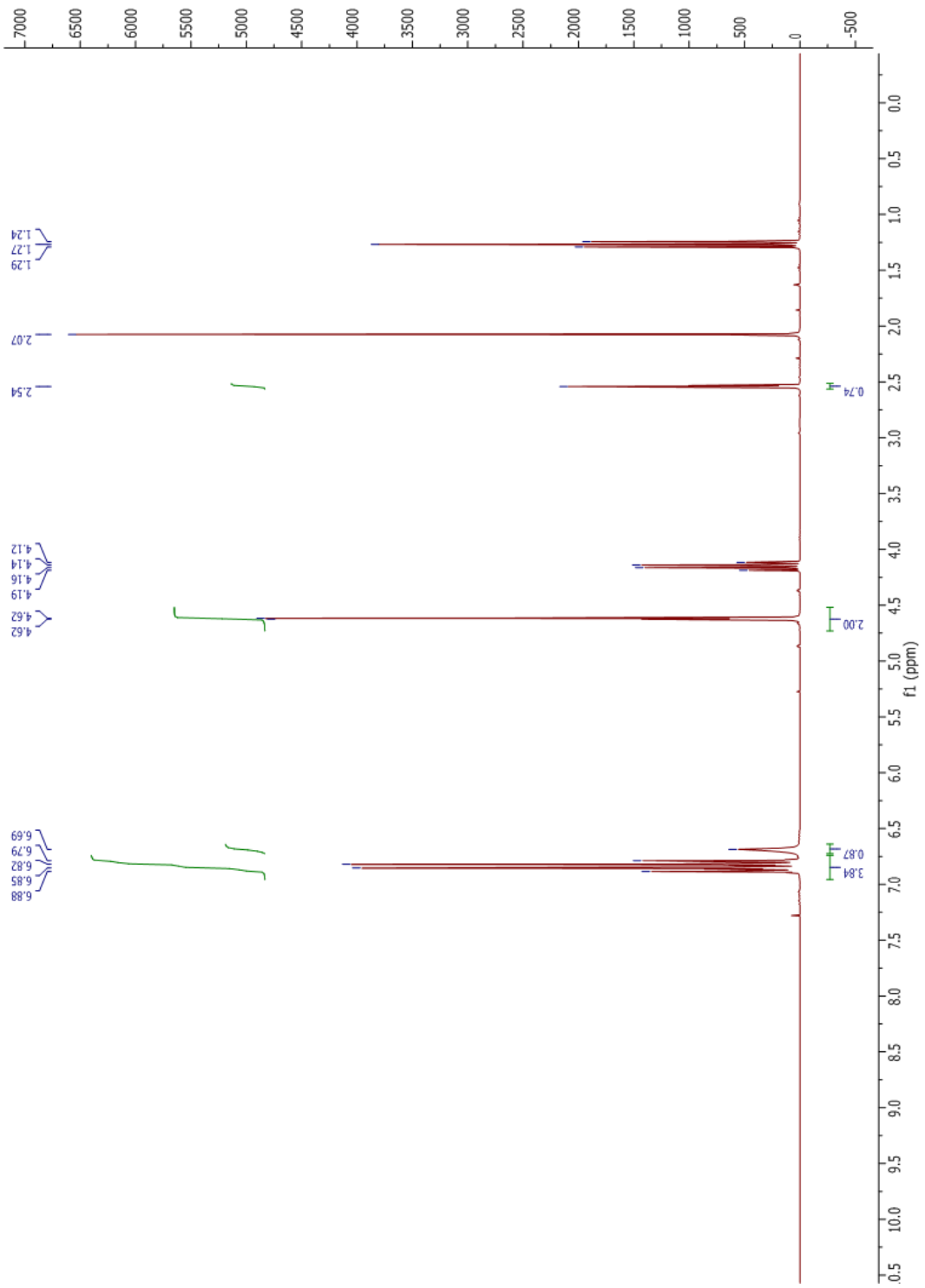
The molar mass and molar mass distribution of this dendrictic PVDF could not be assessed by GPC.
Indeed, the determination of the molar mass and molar mass distribution using GPC requires a concentration detector such as a RI detector. PVDF gives a negative signal using a RI detector in DMF (or THF) while PPH gives a positive signal in the same conditions. In consequence, the RI GPC trace of the dendritic PVDF **5** cannot be used to give a correct assessment of the molar mass or molar distribution. However, the monomodal shape of the GPC trace and the shift toward high molecular weight of the dendritic PVDF suggests a good addition of the PVDF chains onto the acetylenic dendrimer.

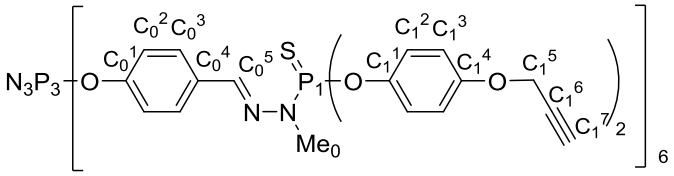
^{1}H NMR (400 MHz, DMSO, 20°C): δ **(ppm)** 8.19 (s, 12 H, C_1^7, protons of the triazolic ring), 7.84 (s br, 6 H, C_0^5-H), 7.67 (s br, 12 H, C_0^3-H), 7.05 (d br, 36 H, C_0^2-H, C_1^2-H), 6.95 (d br, 24 H, C_1^3-H), 5.04 (s br, 24 H, C_1^5-H), 4.67 (q, 24 H, C^{16}-H), 4.62 (m, 24 H, C_1^8-H), 4.32-4.51 (m, 24 H, C_1^9-H), 4.08 (t br, S-$C^{14}H_2$-CF_2), 3.23 (m, Me_0), 2.70-3.05 (m, C^{14}-H PVDF chain), 2.67 (s br, C^{11}-H), 1.37 (t br, 36 H, C^{17}-H), 1.04 (d br, 36 H, C^{12}-H).
^{13}C NMR (125 MHz, DMSO, 20°C): δ **(ppm)** 211.00 (C=S), 174.85 (C=O), 155.94 (C_1^4), 151.20 (C_0^1), 144.35 (C_1^1), 143.10 (C_1^6), 140.20 (C_0^5), 132.30 (C_0^4), 128.65 (C_0^3), 125.20 (C_1^7), 122.37 (m, C^{13}), 121.33 (C_0^2), 121.31 (C_1^2), 115.99 (C_1^3), 71.92 (C^{16}), 62.89 (C_1^9), 62.04 (C_1^5), 48.97 (C_1^8), 40.20 (C^{14}), 33.57 (C^{11}), 33.28 (Me_0)18.31 (C^{12}), 13.75 (C^{17}).
^{31}P{1H} NMR (121.5 MHz, DMSO, 20 °C): δ **(ppm)** 64.3 (P_1), 8.3 (P_0).
^{19}F{1H} NMR (376 MHz, DMSO, 20 °C): δ **(ppm)** see pages 7 and 22.

S3. Selected ^{1}H, ^{13}C, ^{31}P, ^{19}F NMR and MALDI-TOF mass spectra

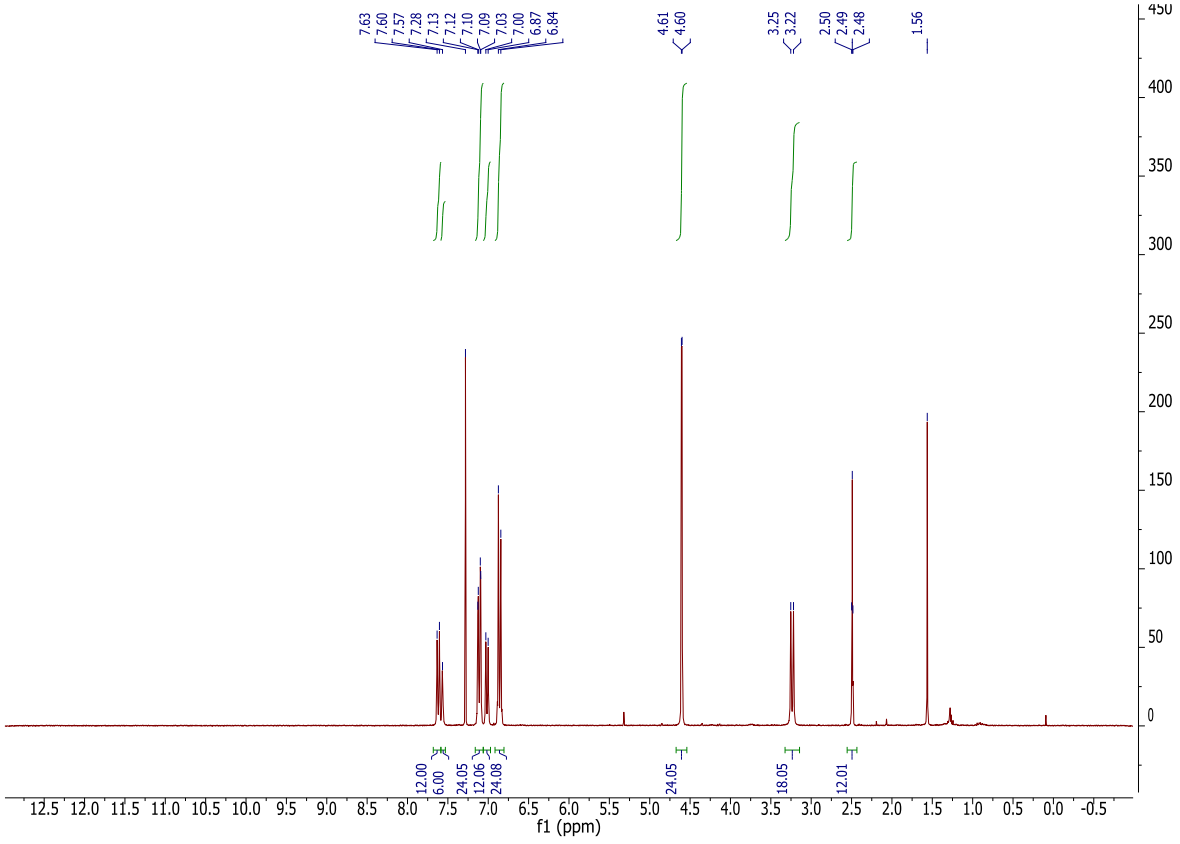


^{1}H NMR spectrum of 2 ($CDCl_3$)

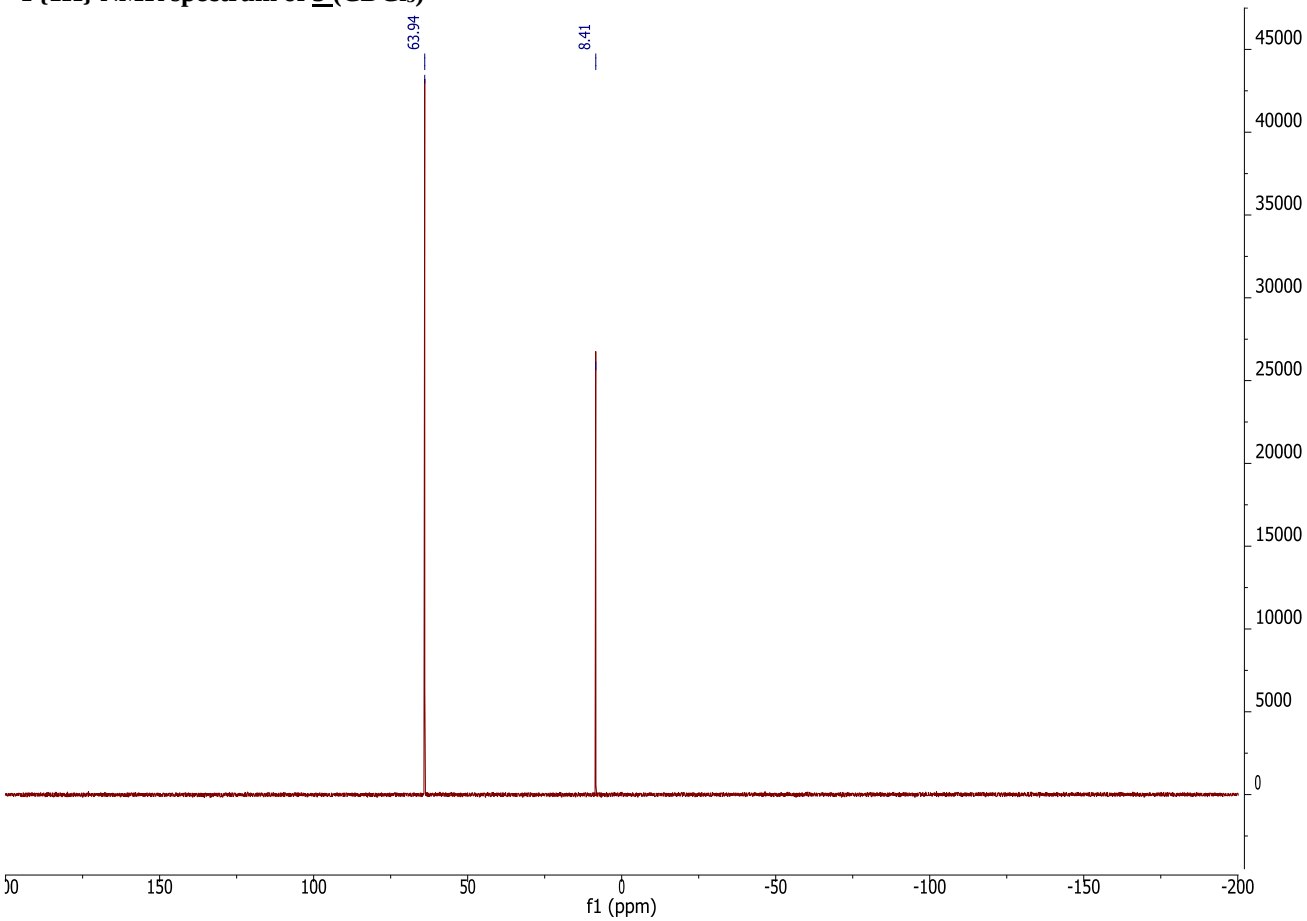




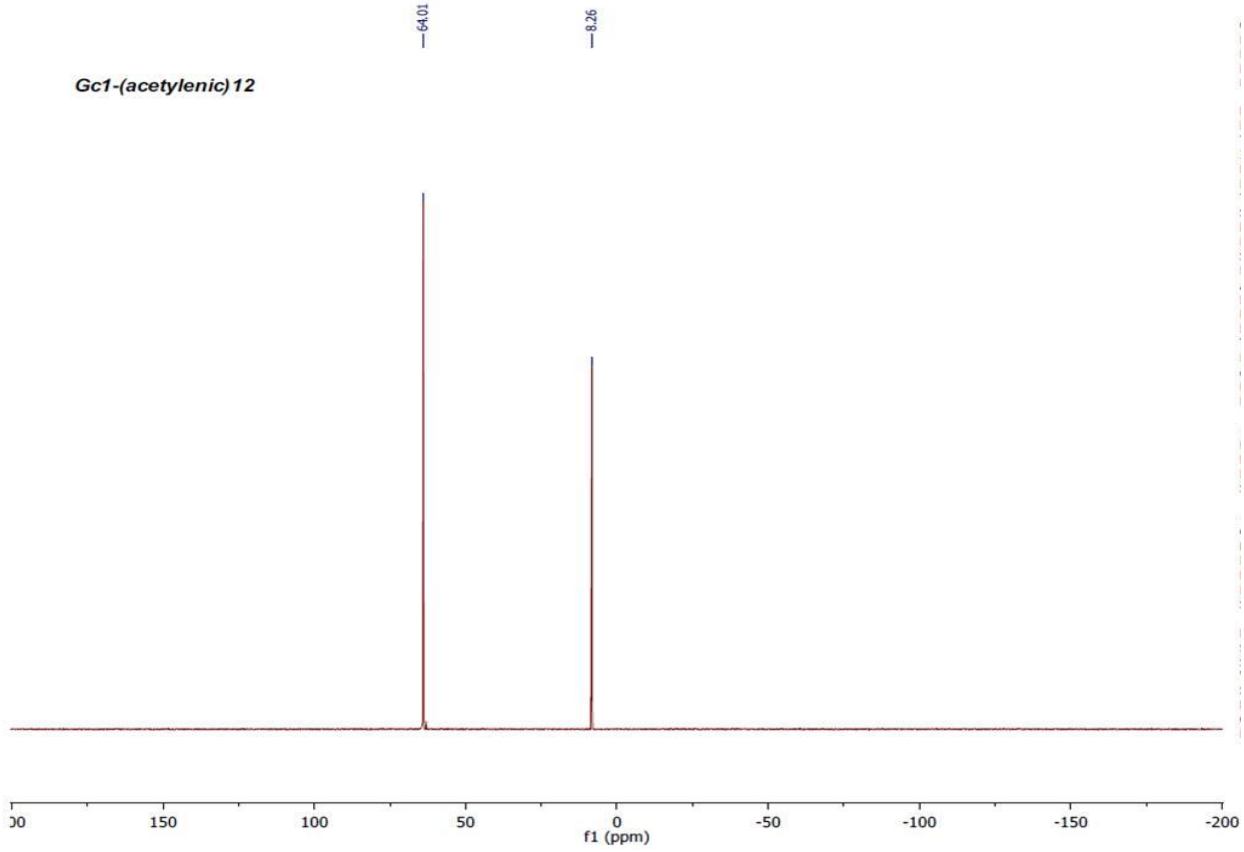
^{1}H NMR spectrum of 3 ($CDCl_3$)



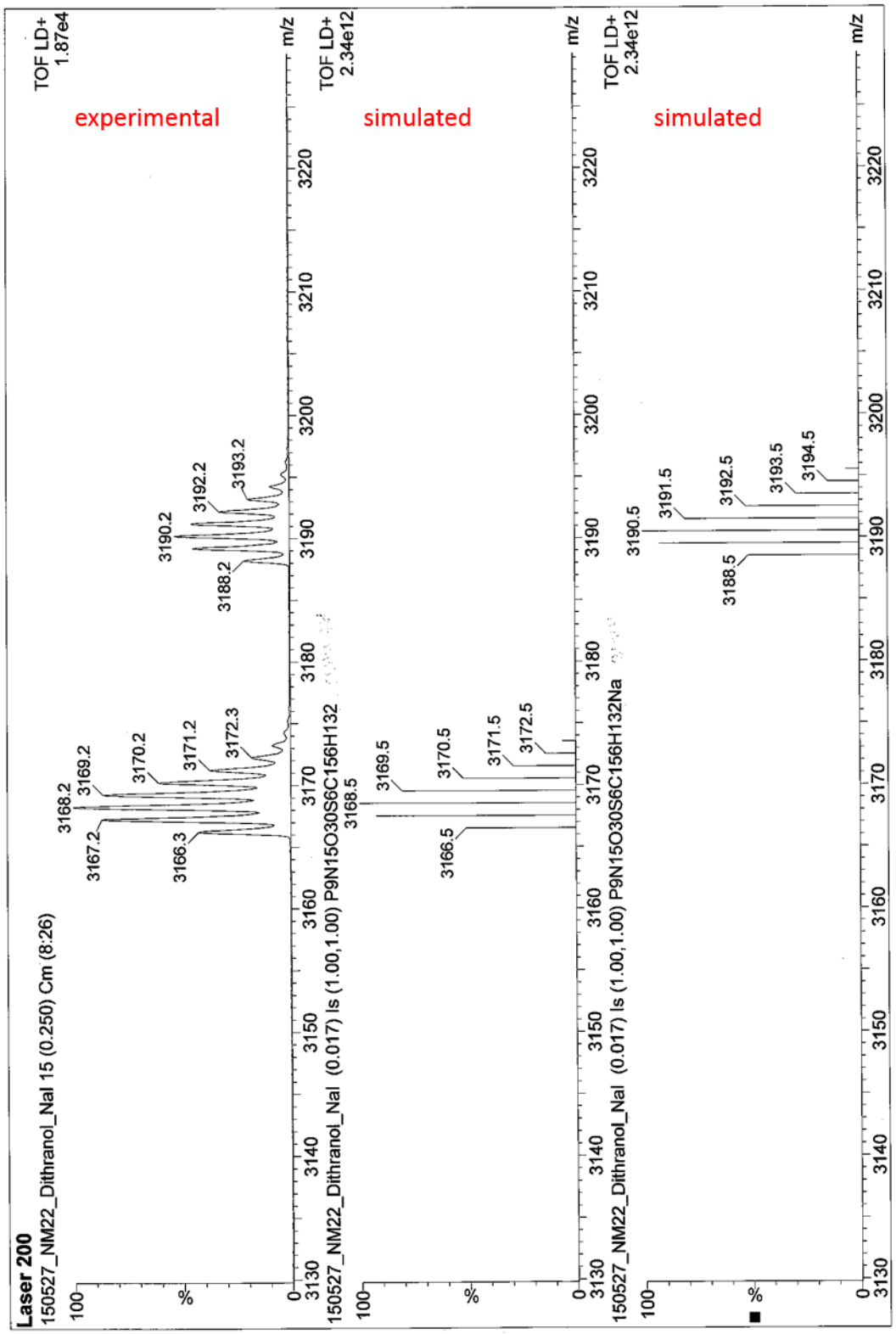
$^{31}P\{1H\}$ NMR spectrum of 3 ($CDCl_3$)



$^{31}P\{1H\}$ NMR spectrum of 3 (DMSO d6)

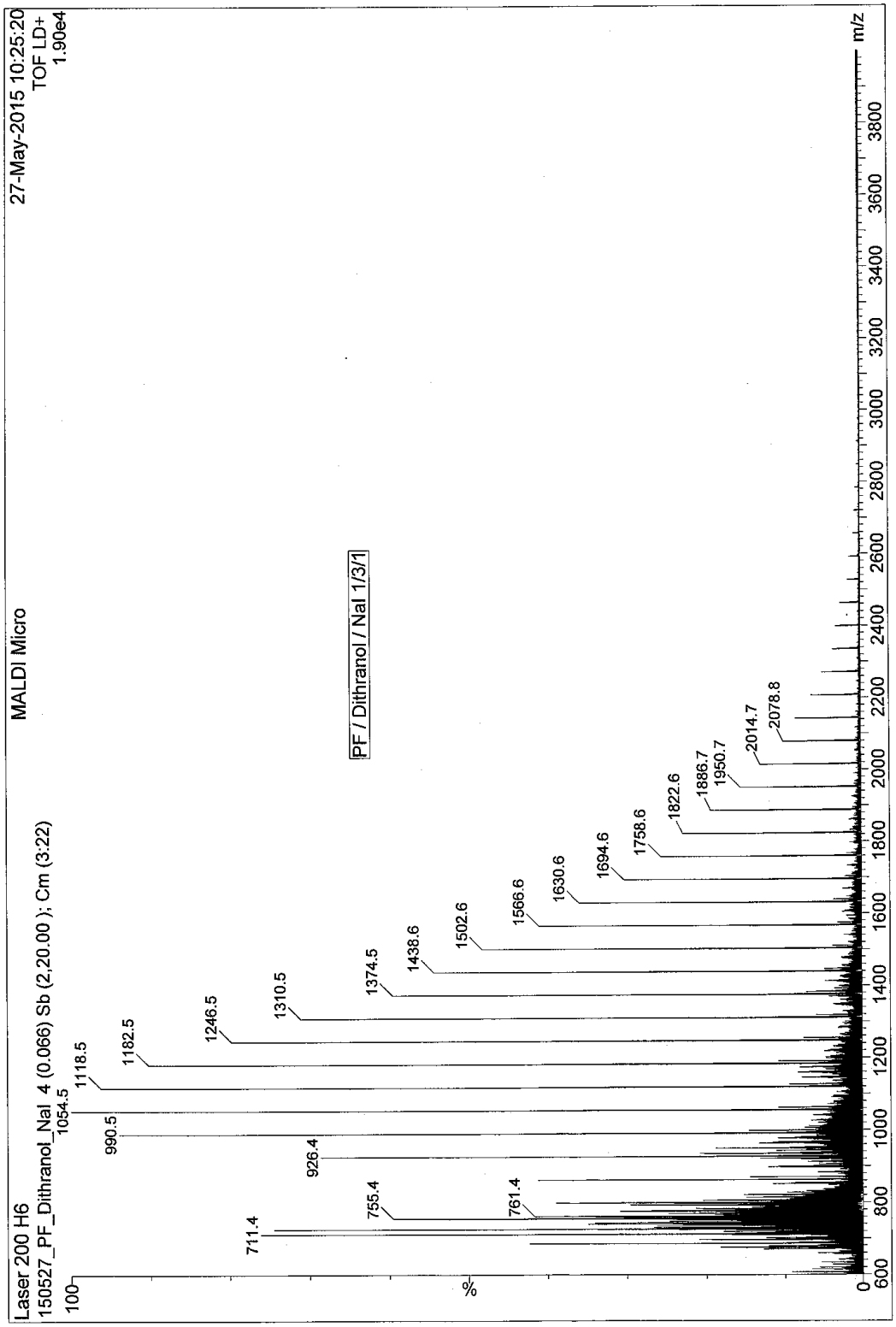


Experimental and simulated MS spectra (MALDI-TOF-MS) for dendrimer 3

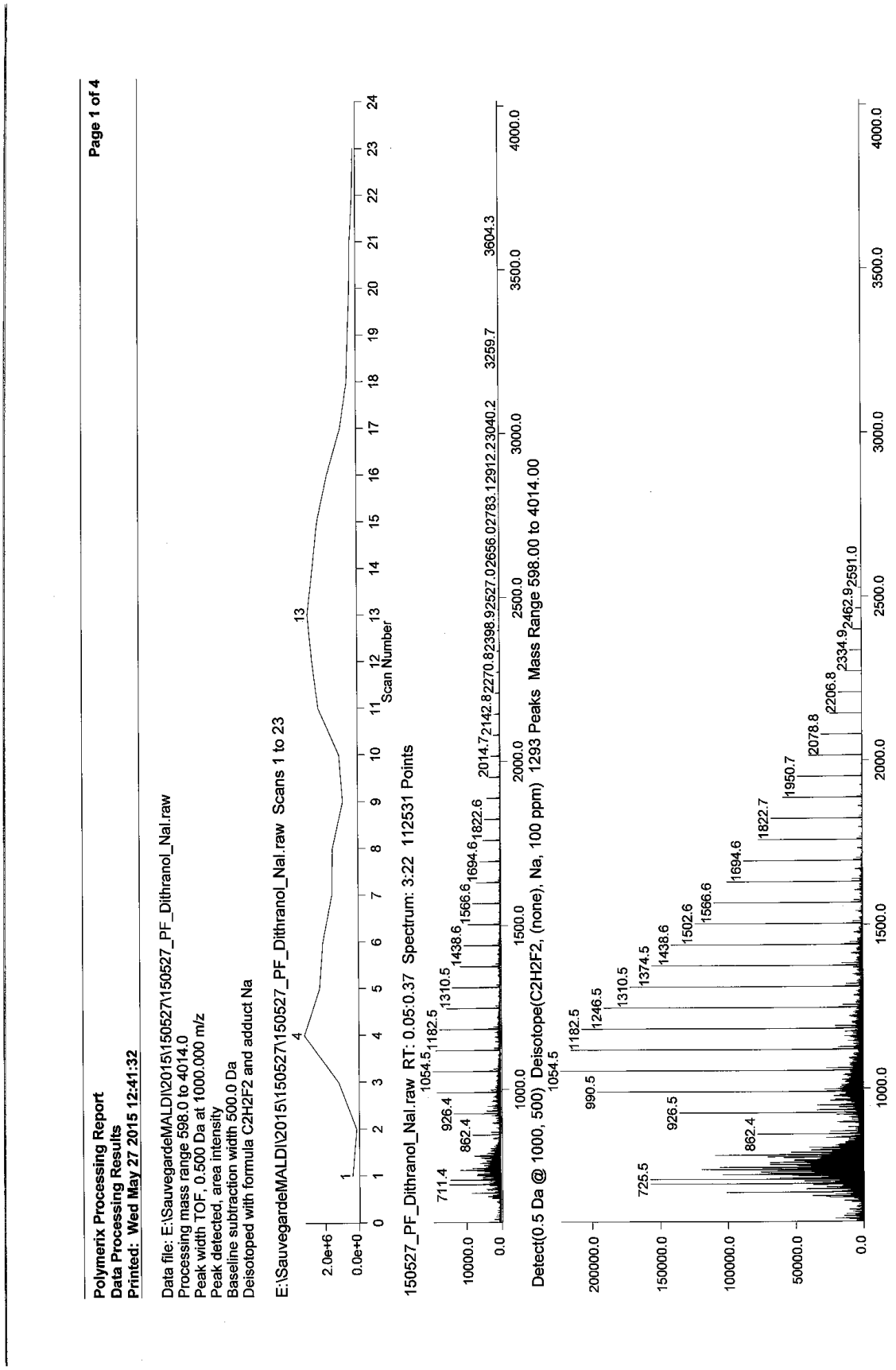


MS spectrum (MALDI-TOF-MS) for PVDF-N_3 (compound 4)

Experimental spectrum:

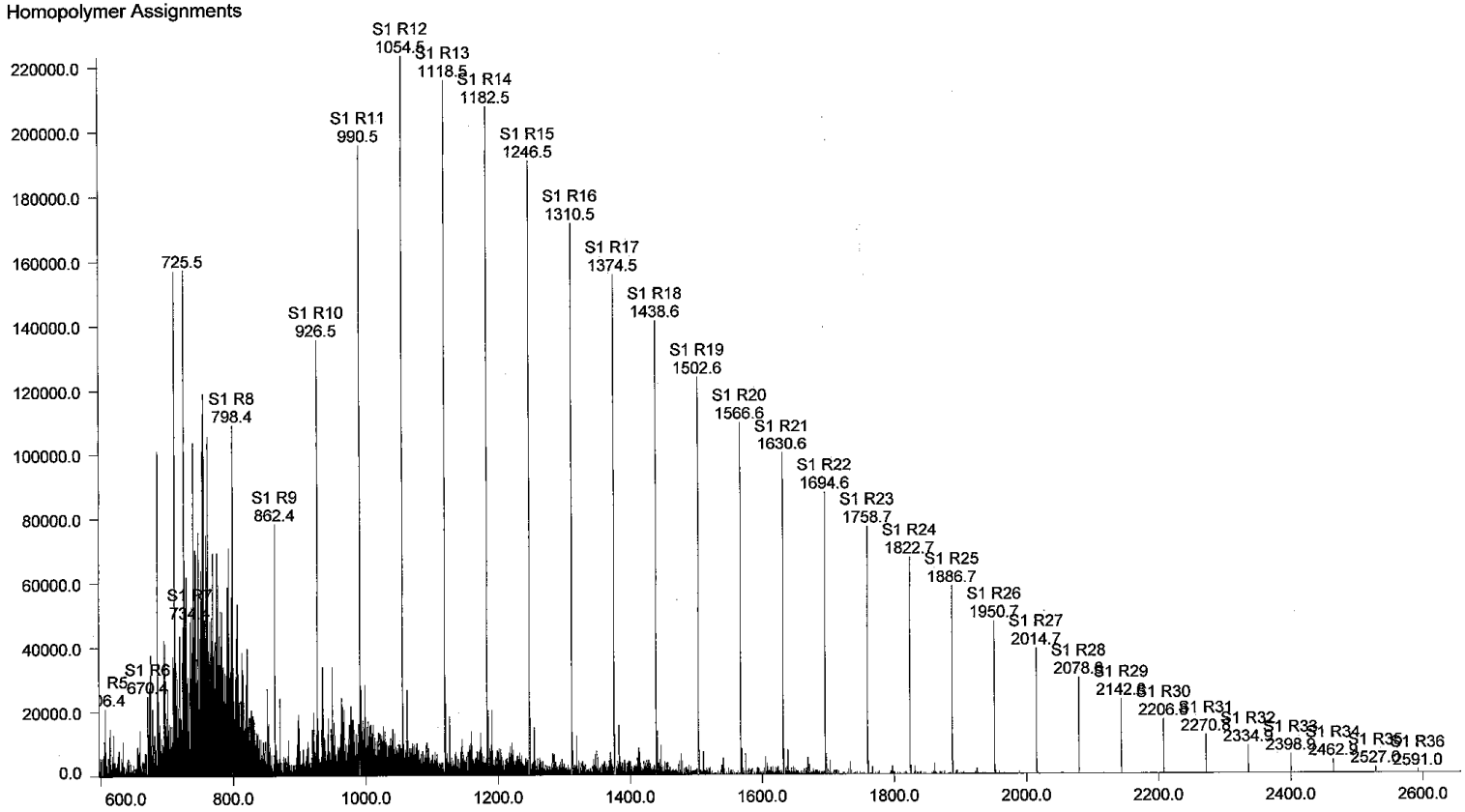


Simulation with Polymerix: The experimental and theoretical spectra are found to be in very good agreement.



Data file: E:\SauvegardeMALDI\2015\150527\150527_PF_Dithranol_NaI.raw
Monoisotopic mass mode
Match tolerance TOF mode +/- 0.400 Da at 1000.0 m/z

Homopolymer Assignments



Data file: E:\SauvegardeMALDI\2015\150527\150527_PF_Dithranol_NaI.raw
Monoisotopic mass mode
Match tolerance TOF mode +/- 0.400 Da at 1000.0 m/z

Homopolymer Results Summary

Series Label	Mn	Mw	Mz	PD	DPn	DPw	DPz	Percent Series	Percent Spectrum
Total/Average	1286.285	1389.080	1492.960	1.080	15.985	17.591	19.214	100.00	20.23
S1	1286.285	1389.080	1492.960	1.080	15.985	17.591	19.214	100.00	20.23

Series Label	Alpha End Group	Repeat	Omega End Group	Charge State	Adduct	Loss
Total/Average	N3C5H8O2	C2H2F2	S2OC3H5	1	Na	
S1	N3C5H8O2	C2H2F2	S2OC3H5	1	Na	

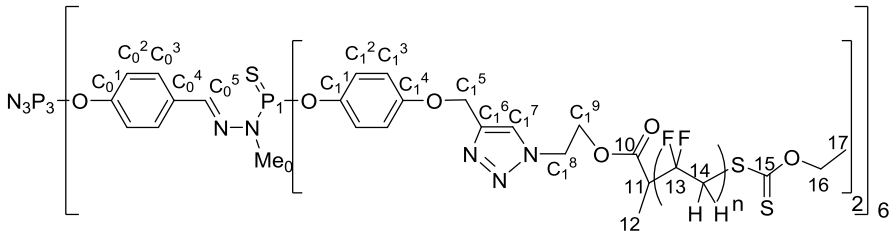
Series Label	Series Formula
Total/Average	N3C5H8O2 [C2H2F2]n S2OC3H5 + Na
S1	N3C5H8O2 [C2H2F2]n S2OC3H5 + Na

Homopolymer Analysis Details

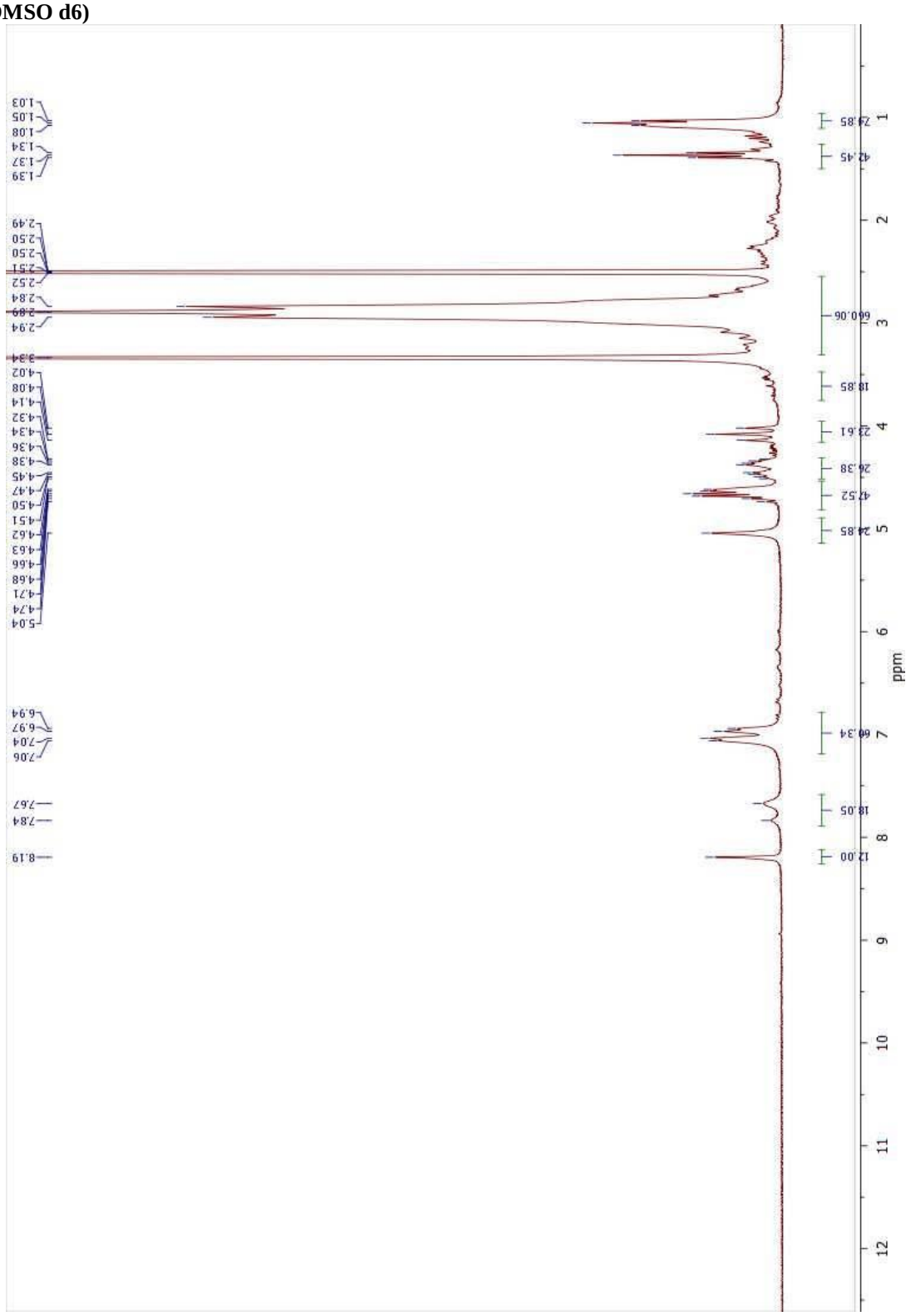
Series Label: S1

Repeat Count	Percent Series	Percent Spectrum	Computed m/z	Found m/z	Weighted m/z	Found Intensity
5	0.7700	0.1557	606.092	606.373	606.373	21004.20
6	0.9129	0.1847	670.104	670.393	670.393	24905.05
7	1.7595	0.3559	734.117	734.403	734.403	47997.99
8	3.9985	0.8088	798.129	798.376	798.376	109077.56
9	2.8660	0.5797	862.142	862.439	862.439	78184.03
10	4.9654	1.0043	926.154	926.457	926.457	135456.34
11	7.1697	1.4502	990.167	990.466	990.466	195587.70
12	8.1750	1.6535	1054.179	1054.478	1054.478	223012.41
13	7.9009	1.5981	1118.192	1118.491	1118.491	215535.49
14	7.6018	1.5376	1182.204	1182.506	1182.506	207375.66
15	6.9826	1.4123	1246.216	1246.517	1246.517	190483.20
16	6.2763	1.2695	1310.229	1310.529	1310.529	171215.04
17	5.6938	1.1517	1374.241	1374.549	1374.549	155325.21
18	5.1659	1.0449	1438.254	1438.562	1438.562	140923.83
19	4.5251	0.9153	1502.266	1502.577	1502.577	123443.60
20	4.0099	0.8111	1566.279	1566.594	1566.594	109388.63
21	3.6552	0.7393	1630.291	1630.611	1630.611	99712.70
22	3.2047	0.6482	1694.304	1694.627	1694.627	87424.13
23	2.8139	0.5692	1758.316	1758.652	1758.652	76761.73

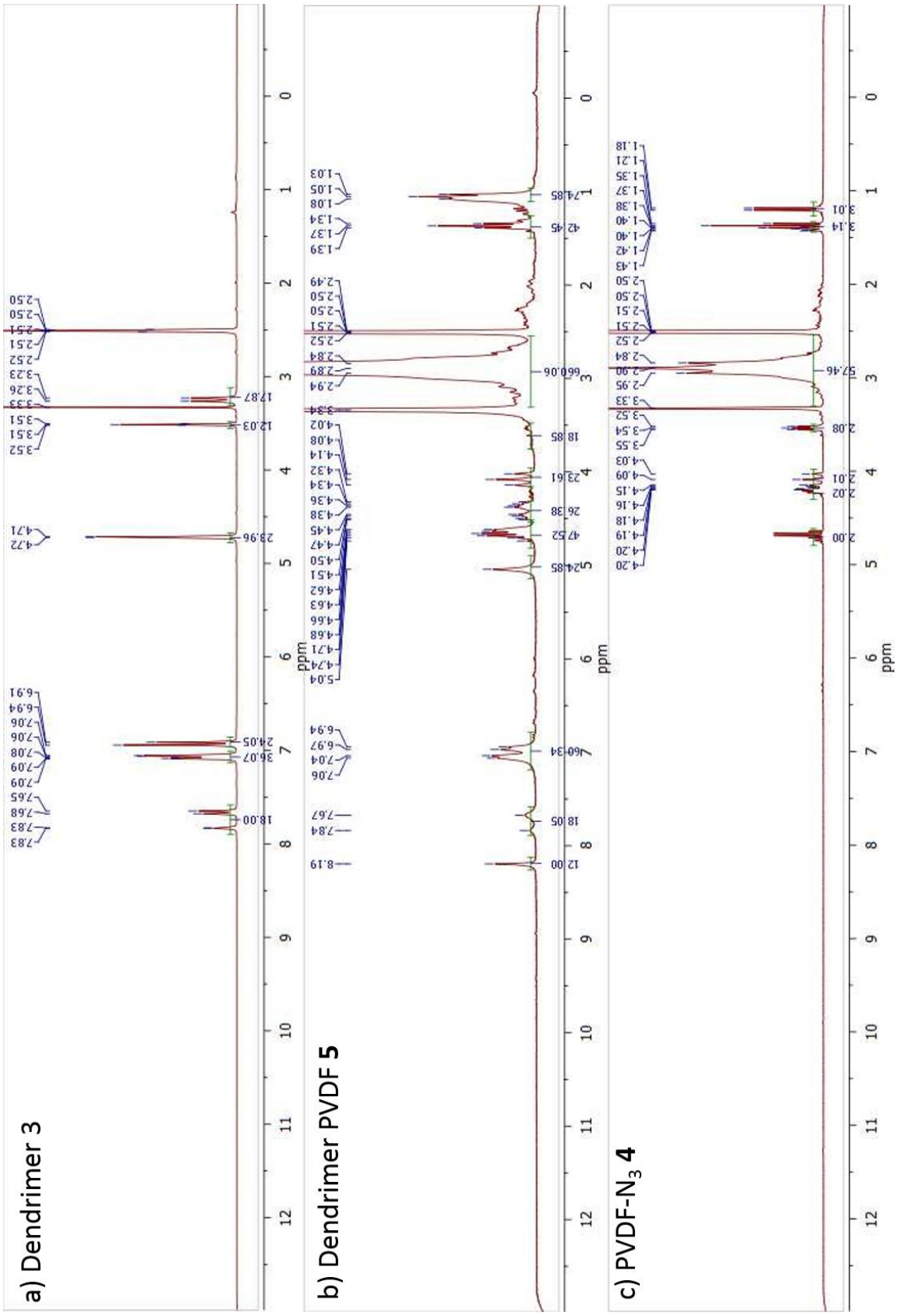
24	2.4631	0.4982	1822.329	1822.672	1822.672	67192.58
25	2.1345	0.4317	1886.341	1886.696	1886.696	58227.92
26	1.7365	0.3512	1950.353	1950.712	1950.712	47372.49
27	1.4284	0.2889	2014.366	2014.740	2014.740	38966.06
28	1.0928	0.2210	2078.378	2078.765	2078.765	29810.69
29	0.8520	0.1723	2142.391	2142.789	2142.789	23243.44
30	0.6194	0.1253	2206.403	2206.813	2206.813	16897.39
31	0.4408	0.0892	2270.416	2270.847	2270.847	12025.62
32	0.3136	0.0634	2334.428	2334.868	2334.868	8554.70
33	0.2161	0.0437	2398.441	2398.890	2398.890	5894.93
34	0.1515	0.0306	2462.453	2462.920	2462.920	4132.61
35	0.0666	0.0135	2526.466	2526.956	2526.956	1816.49
36	0.0378	0.0077	2590.478	2590.955	2590.955	1032.48



[1] H NMR (DMSO d6)

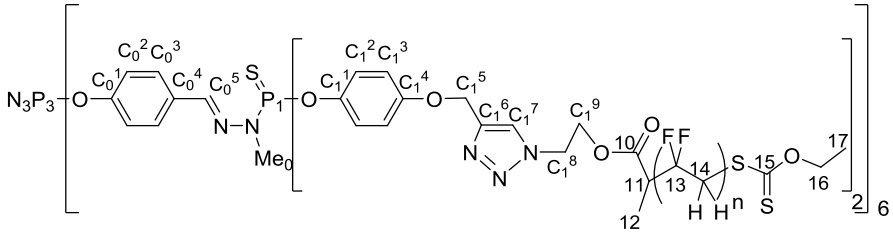


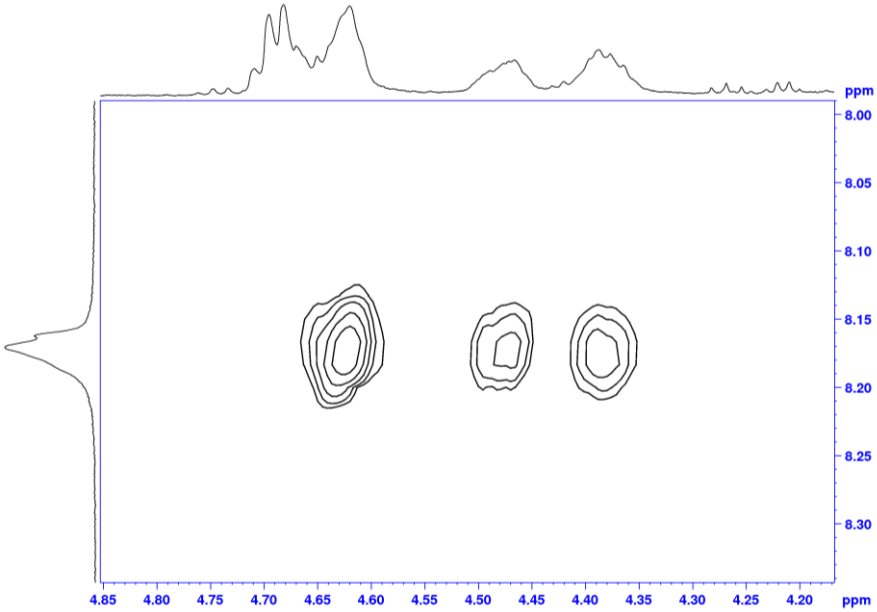
Comparison of ^{1}H spectra for dendrimers 3 and 5 and PVDF-N_3 4 (DMSO d6)



ROESY Experiment (compound 5)

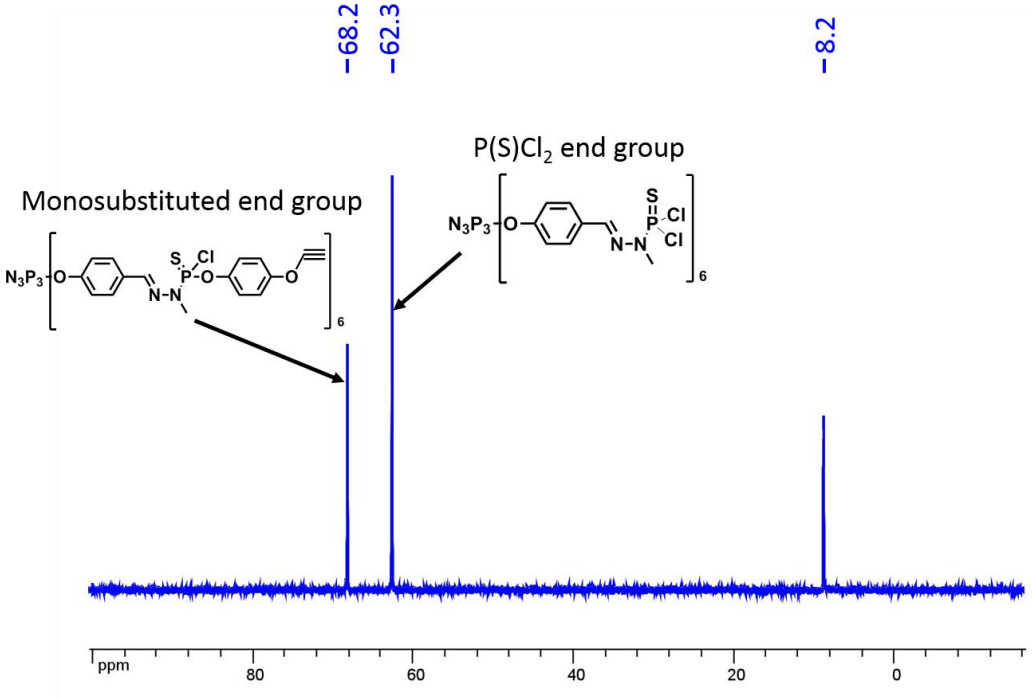
ROESY experiments highlighted spatial correlations between protons **7** (8.19 ppm) and protons **8** (4.62) and **9** (4.32-4.51) which constitutes a further element in favour of a successful cycloaddition.



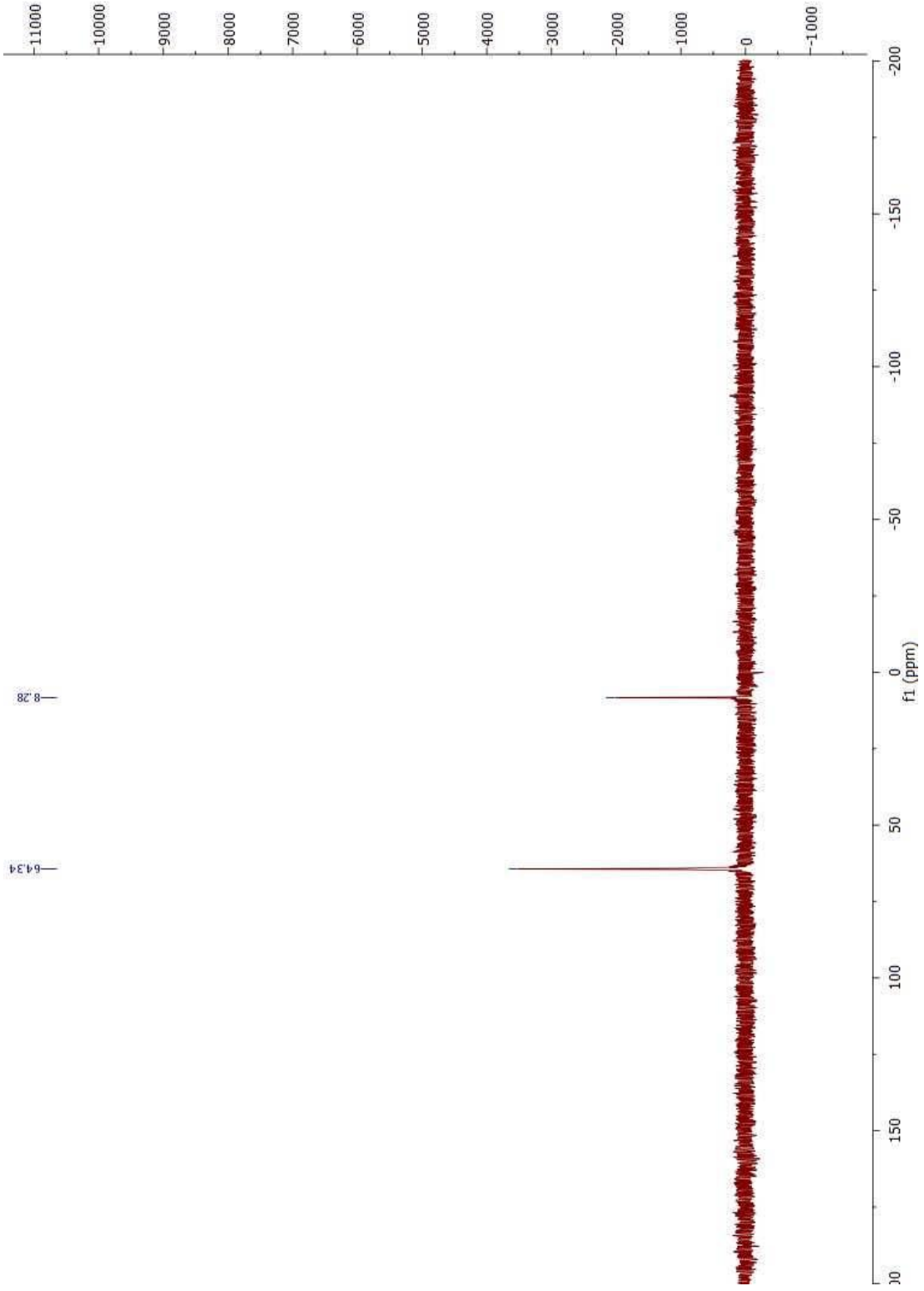


Monitoring of the nucleophilic substitution of P-Cl bonds of dendrimer 1 by phenol 2 by using ^{31}P NMR spectroscopy

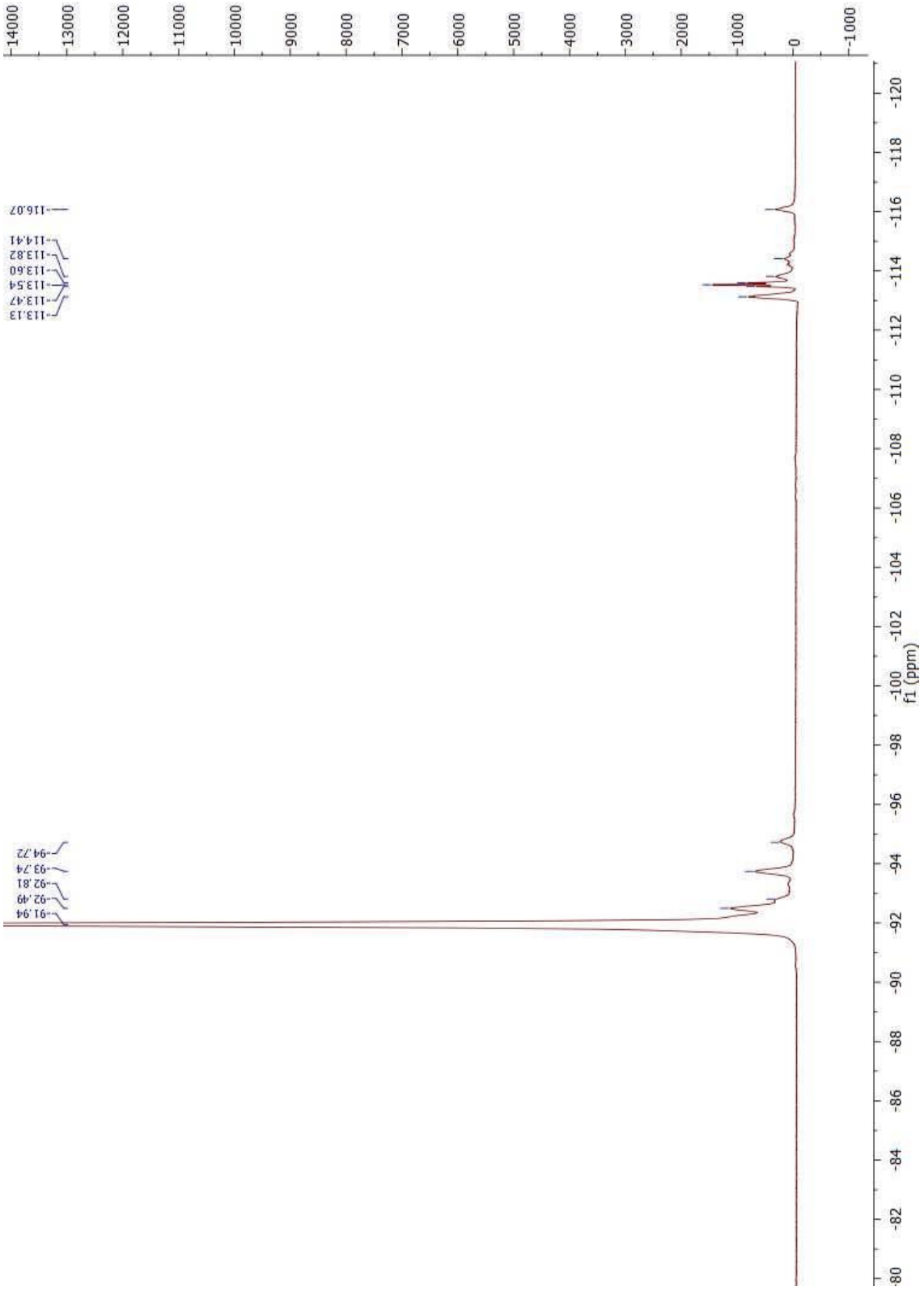
Substitution of the P-Cl bonds from the $P(S)Cl_2$ end groups by any phenol derivative ArOH (including **2** bearing acetylenic functions, see Figure 1, main text) can easily be monitored by ^{31}P NMR on the crude (THF as the solvent in that case). Indeed, intermediate monosubstituted end groups P(S)(Cl)-OAr give rise to a high-shifted singlet at about 68 ppm against about 62 ppm for the starting $P(S)Cl_2$ end groups (figure below). The vanishing of both of these signals and the appearance of a new singlet indicate the completion of the reaction and the disubstitution of all the $P(S)Cl_2$ end groups.



$^{31}P\{1H\}$ NMR spectrum of 5 (DMSO d6)

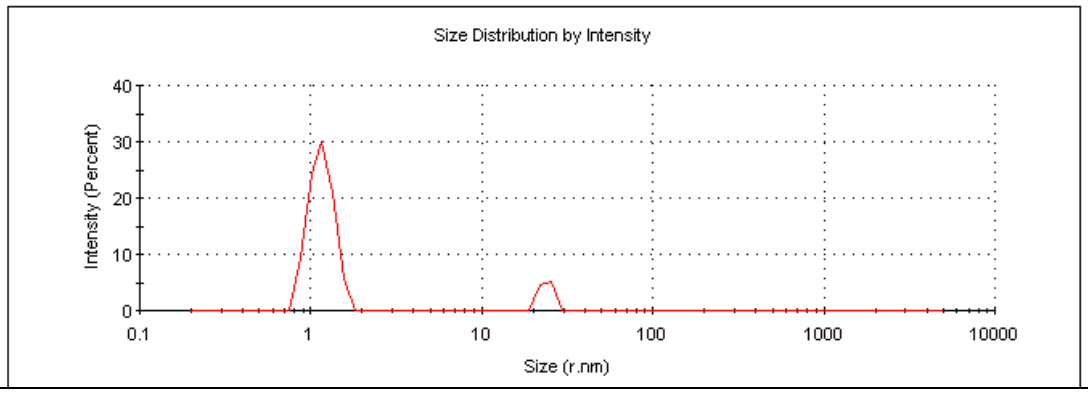


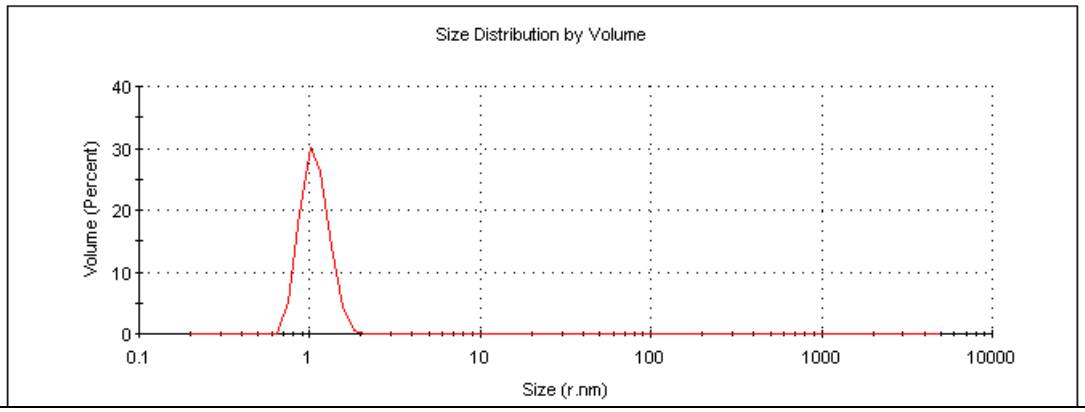
^{19}F NMR spectrum of 5 (DMSO d6)

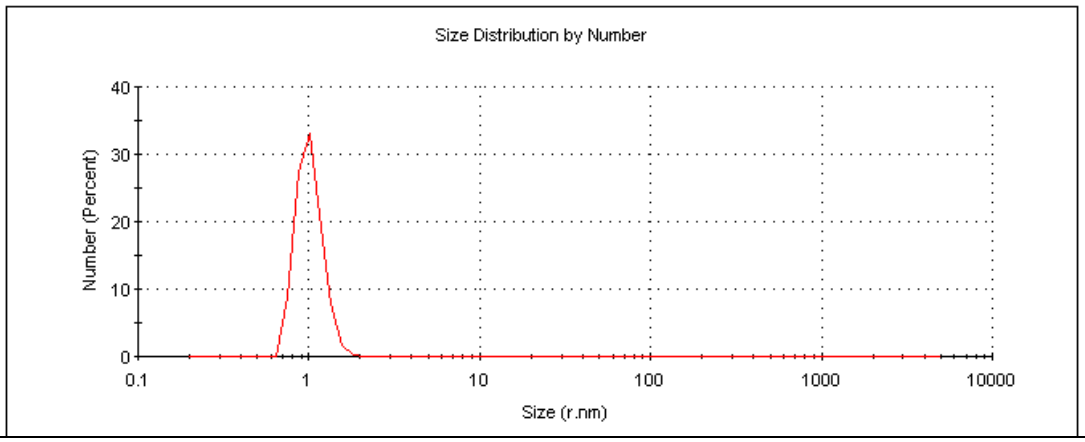


S4. Dynamic Light Scattering

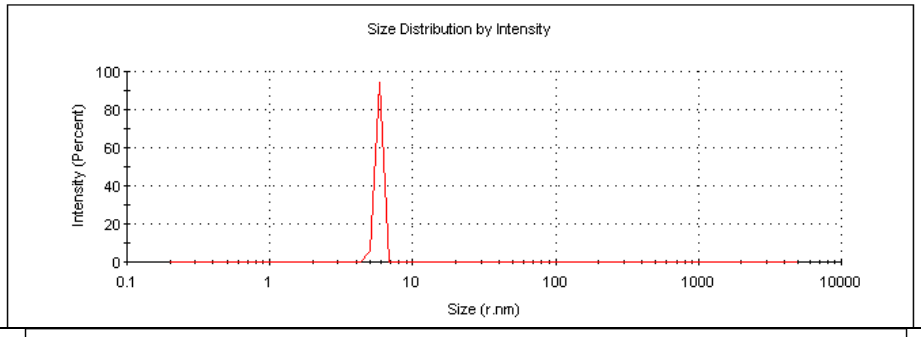
For dendrimer 3

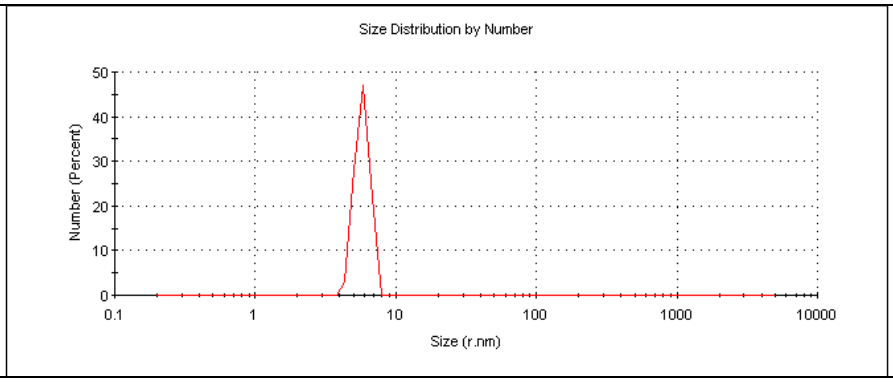


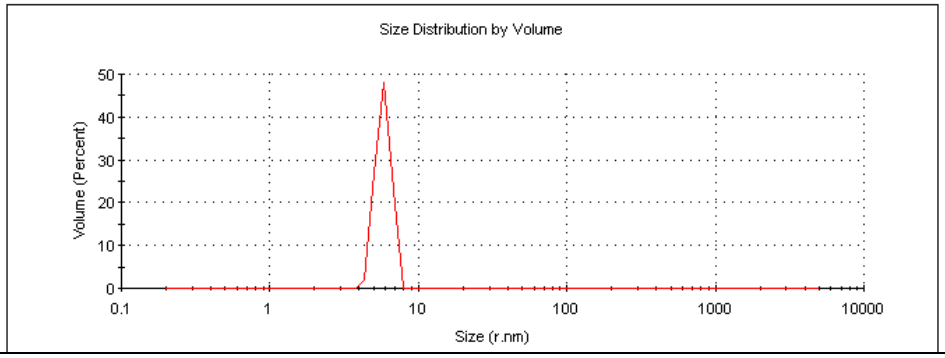




For dendrimer 5

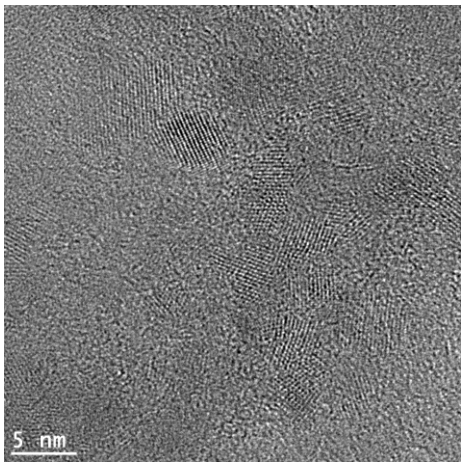


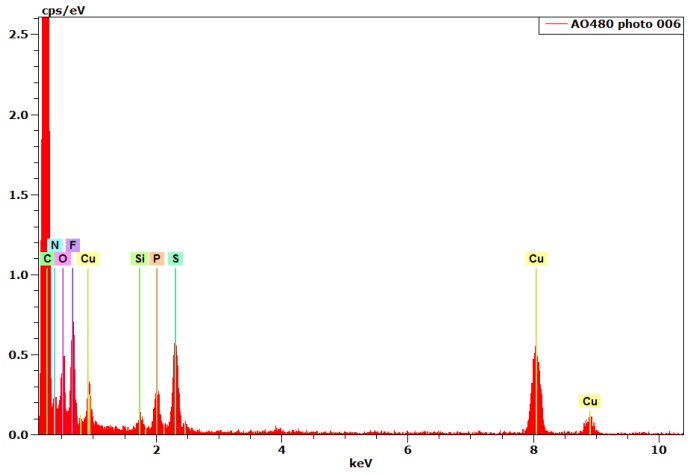




S5. High Resolution Transmission Electron Microscopy (HRTEM), Scanning Transmission Electron Microscopy and Energy Dispersive X-ray

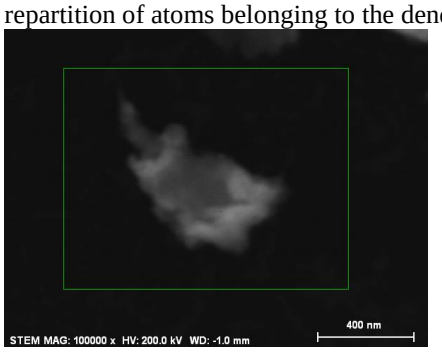
On the **EDX spectrum**, Cu signals are due to the grids on which the samples were deposited.

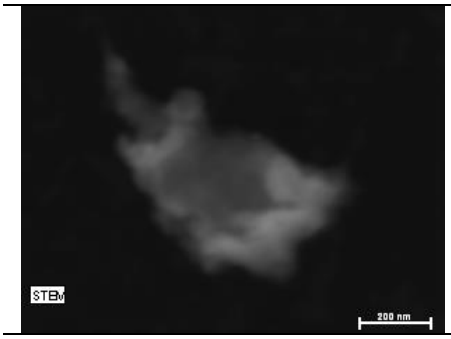




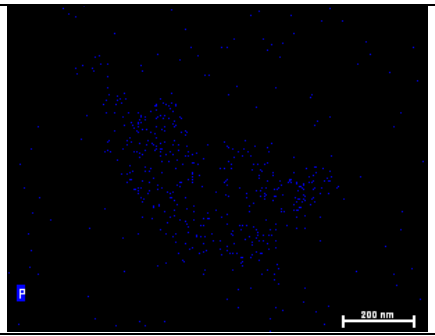
STEM analyses

Composition **mapping** was performed using high resolution STEM images. These analyses revealed an homogeneous repartition of atoms belonging to the dendritic PPH skeleton (P, S) and those belonging to the PVDF branches (F, S).

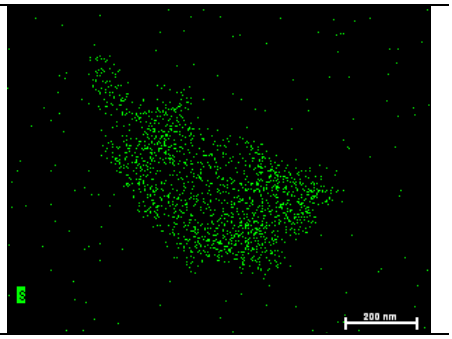




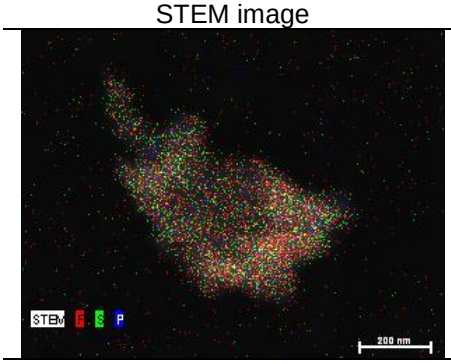
STEM image

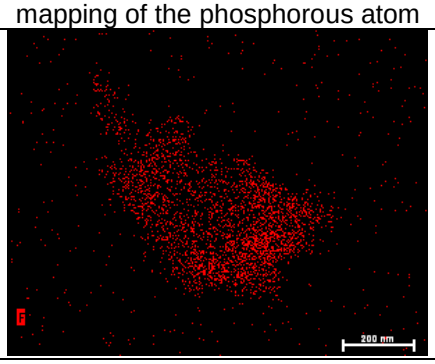


mapping of the phosphorous atom

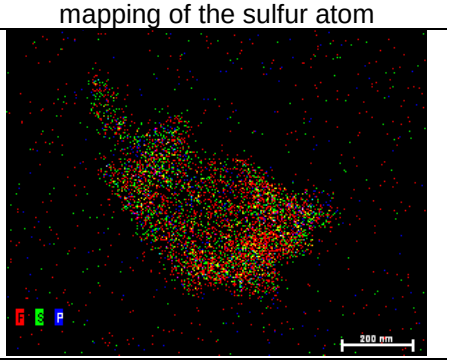


mapping of the sulfur atom



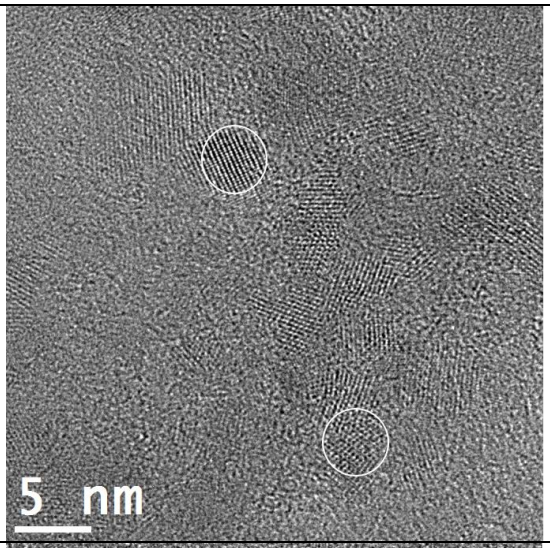


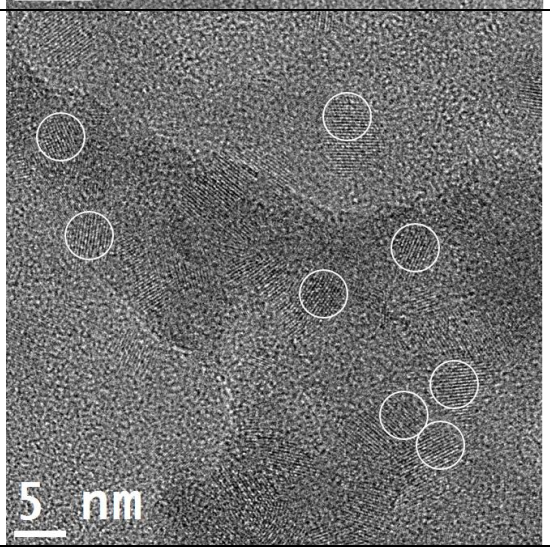
mapping of the fluorine atom



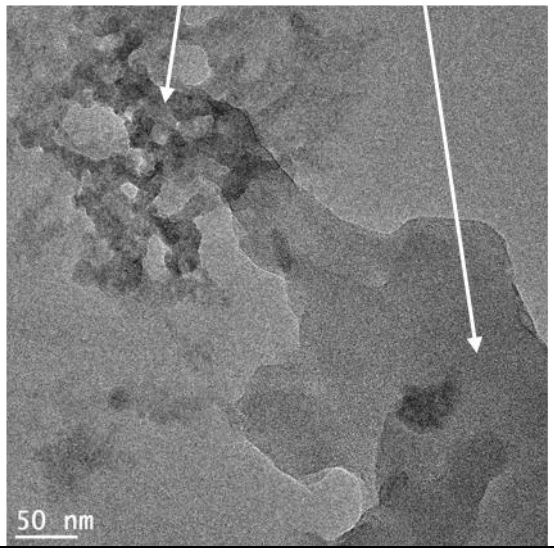
mapping of P, S and F atoms

Additional TEM Images





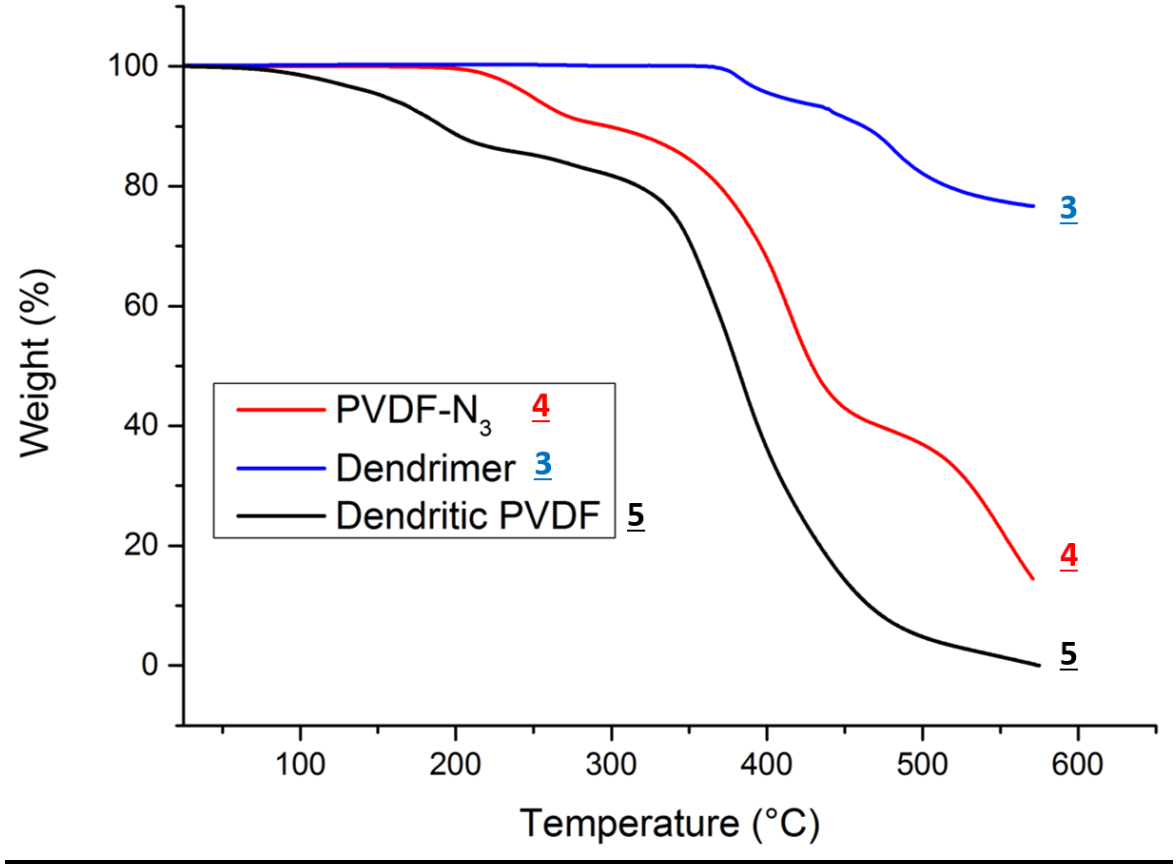
Coexistence of crystalline and amorphous areas



S6. Thermogravimetric Analyses and Differential Scanning Calorimetry

Thermogravimetric Analyses (under air)

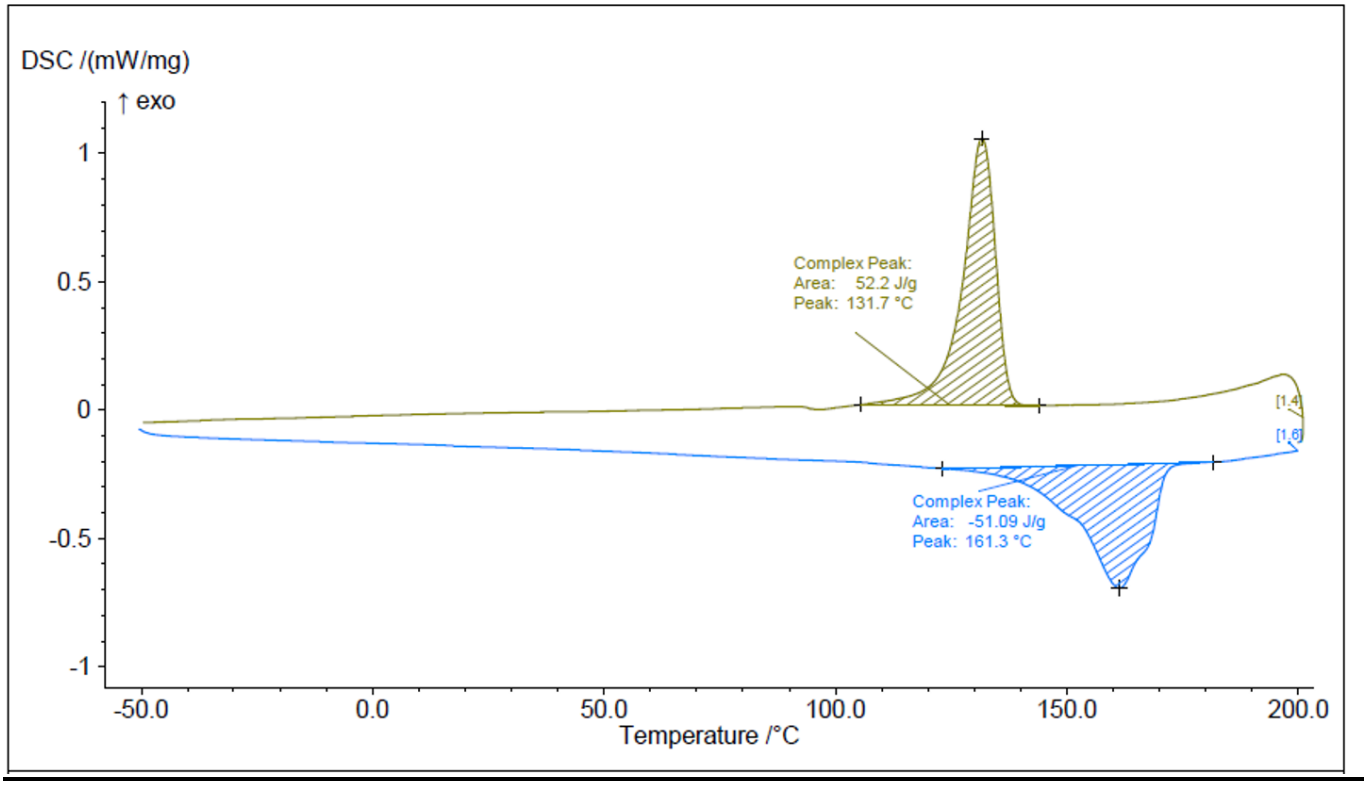
PPH dendrimer **3**, displaying a very high thermal stability (up to ca. 407 °C), lies among the most stable PPH studied to date.[7] PVDF-N_3 polymer was found to be stable up to ca. 249 °C. Surprisingly, dendritic PVDF **5** started to decompose from 91 °C. (5 % of weight loss)



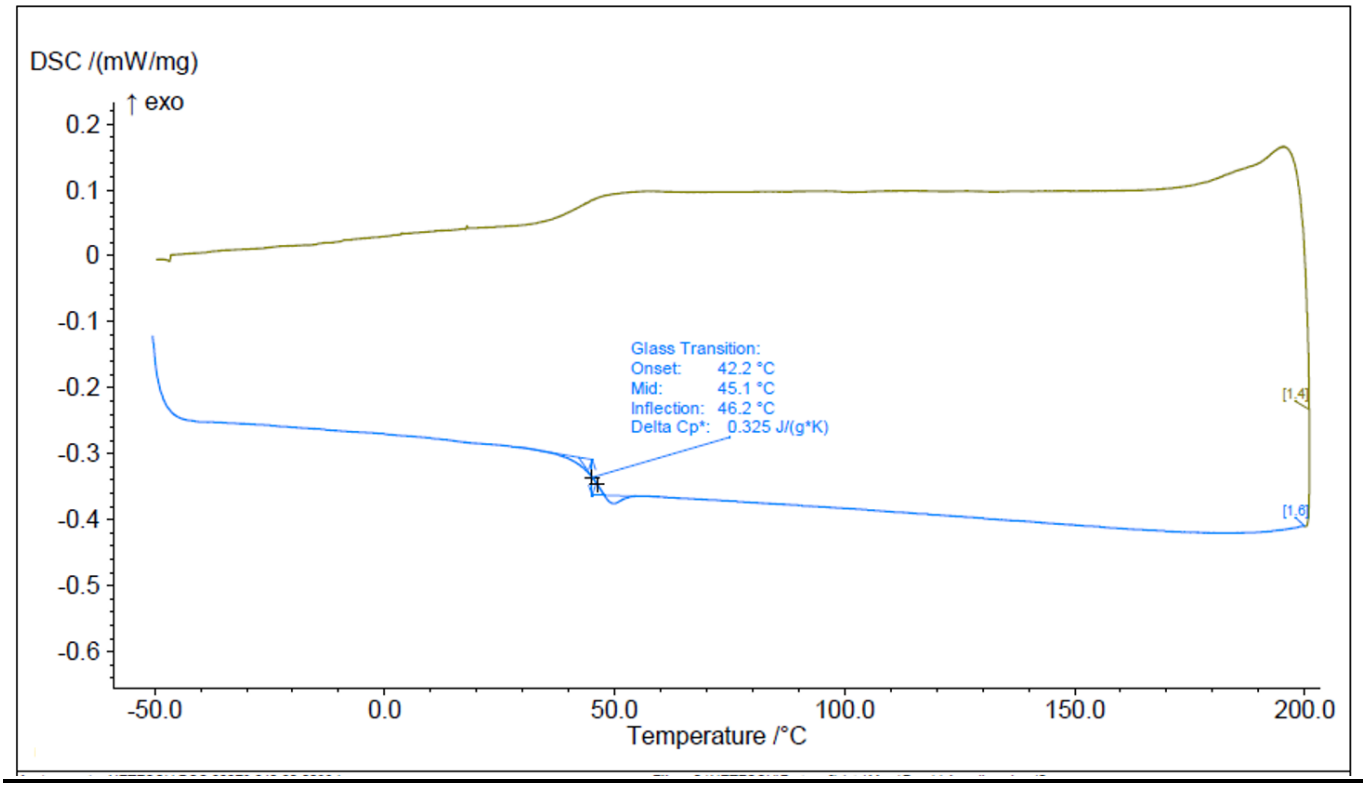
[7] C.-O. Turrin, V. Maraval, J. Leclaire, E. Dantras, C. Lacabanne, A.-M. Caminade, J.-P. Majoral, *Tetrahedron,* 2003, **59**, 3965-3973.

Differential Scanning Calorimetry

DSC PVDF-N_3 4



DSC PPH-dendrimer 3



DSC Dendritic PVDF 5