

Electronic Supplementary Information

Grignard Synthesis of Fluorinated Nanoporous Element Organic Frameworks based on the Heteroatoms P, B, Si, Sn and Ge

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1. Experimental Procedure

1.1. General Information and Chemicals

All syntheses were carried out under argon atmosphere using standard schlenk techniques. All solvents for syntheses were degassed and stored under argon atmosphere prior to use.

Bromopentafluorobenzene (99 %), isopropylmagnesium chloride lithium chloride complex (1.3 M in THF, ≥ 99 %), hydrochloric acid (37%), anhydrous dioxane (99.8 %), diethylene glycol dimethyl ether (anhydrous, 99.5 %), Nafion NR50 (98 %), Amberlyst 15 hydrogen form and tin(VI)chloride (98 %) were purchased from Sigma Aldrich. Germanium(VI)chloride (99.9999 %), silicium(VI)chloride (99 %) and boron trichloride (1.0 M in hexane) were obtained from Alfa Aesar. Phosphorus trichloride (> 99.0 %) was purchased from Merck. 4,4'-Dibromooctafluorobiphenyl (99 %) was obtained from abcr. Methanol (anhydrous, 99.8 %), tetrahydrofuran (anhydrous, 99.9 %), ethanol (99.9 %), sodium hydroxide (99.5 %), acetic acid (99.5 %), ethyl acetate (99.5 %) and hydrochloric acid standard solution (0.1 M) were purchased from ChemSolute. Dichlormethan (anhydrous) was obtained from Applichem. The chemicals and solvents were used without further purification.

1.2. Characterization

Scanning electron microscopy (SEM) was performed on a Zeiss DSM 982 Gemini with a field emission cathode. For energy dispersive X-ray spectroscopy (EDX) of the surface, the system Oxford Link ISIS with HPGc-detector and UT-Window was applied.

Powder X-ray diffraction (XRD) pattern were recorded on a Siemens D5000 instrument with a Cu K_{α} radiation ($\lambda = 0.154$ nm). The scanning range was set from 3° to $90^{\circ} 2\theta$ with 0.02° intervals and a collection time of 1 s per step.

Thermogravimetric analyses (TG) and differential scanning calorimetry (DSC) were carried out using a STA 409 cell from Netzsch with a heating rate of 5 K min^{-1} in air up to 1273 K.

Nitrogen physisorption isotherms were measured at 77 K using a ASAP2000 apparatus (Micrometrics) and water vapor physisorption isotherms were performed at 298 K on an Autosorb iQ (Quantachrome Instruments). Prior to the measurements, the samples were outgassed under vacuum at 393 K overnight. High purity gas (nitrogen: 99.999 %) was used for the adsorption measurements.

A Vertex 70 with attenuated total reflection (ATR) unit was used to obtain infrared (IR) spectroscopy spectra. A measuring range of $4500 - 400 \text{ cm}^{-1}$ was chosen.

Elemental analysis was measured at the Mikroanalytisches Laboratorium Kolbe, Mülheim an der Ruhr. The elements C and F were determined for all materials and P, B, Si, Sn and Ge were detected depending on the connector element. The element C was measured on a CHNOS-Maschine (Elementar Model Vario EL), F on an ion chromatography (Metrohm Model 883 Plus), Ge on with atomic absorption spectroscopy (AAS, PerkinElmer Model Analyst 200) and P, Si, Sn und B were determined photometrically with UV/VIS spectroscopy (Analytik Jena Model Specord 50 Plus).

X-ray photoelectron spectroscopy (XPS) was obtained on an Ultra Axis Spectrometer (Kratos Analytical, Manchester, UK) using Al K α radiation (1.486 keV) operated at 12 kV. The binding energies were referenced to the F1s line at 690.9 eV.¹

Solid-state $^{119}\text{Sn}\{^{19}\text{F}\}$, $^{31}\text{P}\{^{19}\text{F}\}$, ^{19}F , CP from ^{19}F to ^{13}C , $^{11}\text{B}\{^{19}\text{F}\}$ and ^1H nuclear magnetic resonance (NMR) spectroscopy with magic angle spinning (MAS) was measured on a 500 and 700 MHz BRUKER Avance III (4 and 3.2 mm MAS rotor, 5-11 kHz spinning at rt). The chemical shifts δ are presented in parts per million (ppm) relative to calibration standards. To identify spinning side-bands, ^{31}P , ^{19}F , ^{11}B and ^1H spectra were recorded at two different spinnings. The main peak maintained at the same chemical shift, while spinning side-bands were shifted.

Gas chromatography (GC) of the esterification solutions was performed on a Foxi system with a 50m CP-Way-57-CB coloum. The temperature was 50-200 °C with a heating rate of 8 °C min⁻¹. Diethylene glycol dimethyl ether was used as internal standard.

1.3. Polymer Syntheses and Analytical Date

The linker 4,4'-dibromooctafluorobiphenyl (2.00 g, 4.40 mmol, 1 eq) dissolved in THF (5 mL) was activated by cooling to 0 °C and subsequent addition of isopropylmagnesium chloride lithium chloride complex (1.3 M in THF; 6.75 mL, 8.80 mmol, 2 eq). After 30 min at 0 °C, the reaction solution was warmed to room temperature and stirred overnight. The end-capping agent bromopentafluorobenzene (1.08 g, 4.40 mmol, 1 eq) was activated following the same activation procedure with isopropylmagnesium chloride lithium chloride complex (1.3 M in THF; 3.38 mL, 4.40 mmol, 1 eq). The element chloride was dissolved in THF (20 mL) and the activated linker solution was added dropwise under fast stirring. The solution was further stirred for 90 min before the activated end-capping agent was added and left to stir overnight. The reaction was quenched with methanol (60 mL) and filtered over a glass filter. The solid was suspended in water (250 mL) and 0.78 mL conc. hydrochloric acid was added and left to stir for 30 min. After filtration, the solid was washed with water (250 mL), THF (250 mL) and chloroform (250 mL) for 30 min each. The resulting solid was dried at 60 °C under *vacuo*. The yield was related to the theoretical composition of $\text{E}(\text{C}_6\text{F}_4)_3$ (E=P, B) and $\text{E}(\text{C}_6\text{F}_4)_4$ (E=Sn, Si, Ge) per unit.

poly-tris(2,3,5,6-tetrafluorophenyl)phoshine (P_F-EOF)

Reaction with phosphorus trichloride (0.391 g, 2.85 mmol) resulted in the polymer P_F-EOF (1.76 g, 125 %). CP from ^{19}F to ^{13}C MAS NMR (126 MHz, 11 kHz spinning, 25 °C) δ : 153.2, 121.2, 117.8 ppm. $^{31}\text{P}\{^{19}\text{F}\}$ MAS NMR (202 MHz, 8 kHz spinning, 25 °C) δ : -79.0 ppm. Anal. calcd for $\text{C}_{18}\text{F}_{12}\text{P}$: C 45.5, F 48.0, P 6.5; found: C 44.6, F 34.9, P 8.7.

poly-tris(2,3,5,6-tetrafluorophenyl)borane (B_F-EOF)

Reaction with boron trichloride (1.0 M in hexane, 2.94 mL, 2.16 g, 2.92 mmol) resulted in the polymer B_F-EOF (1.68 g, 122 %). CP from ^{19}F to ^{13}C MAS NMR (126 MHz, 11 kHz spinning, 25 °C) δ : 157.2, 153.0, 117.3, 115.2 ppm. $^{11}\text{B}\{^{19}\text{F}\}$ MAS NMR (160 MHz, 8 kHz spinning, 25 °C) δ : 18.4, -5.2 ppm. Anal. calcd for $\text{C}_{18}\text{F}_{12}\text{B}$: C 47.5, F 50.1, B 2.4; found: C 48.8, F 41.9, B 2.5.

ion-exchanged poly-tris(2,3,5,6-tetrafluorophenyl)borane (BH_F-EOF)

Except of the drying procedure, the general synthesis route was followed as described above. Instead, the polymer was stirred in 1 M HCl (250 mL) for 1 h. Afterwards, the polymer was filtered and washed with water three times until pH 7 of the washing solution was reached. The polymer was filtered, suspended in dioxane (100 mL) and freeze-dried. Reaction with boron trichloride (1.0 M in hexane, 8.18 mL, 8.18 mmol) resulted in a yellowish powder of the polymer BH_F-EOF (2.5117 g, 68 %). CP from ¹⁹F to ¹³C MAS NMR (126 MHz, 11 kHz spinning, 25 °C) δ: 156.5, 152.6, 116.5 ppm. ¹¹B{¹⁹F} MAS NMR (160 MHz, 8 kHz spinning, 25 °C) δ: 20.8, -6.1 ppm. ¹H MAS NMR (500 MHz, 11 kHz spinning, 25 °C) δ: 6.9, 3.6 ppm.

poly-tetrakis(2,3,5,6-tetrafluorophenyl)stannane (Sn_F-EOF)

4,4'-Dibromooctafluorobiphenyl (1.00 g, 2.20 mmol, 1 eq) and bromopentafluorobenzene (0.54 g, 2.20 mmol, 1 eq) were activated with isopropylmagnesium chloride lithium chloride complex (1.3 M in THF; 3.38 mL, 4.40 mmol, 2 eq and 1.69 mL, 2.20 mmol, 1 eq, respectively). Reaction with tin(IV)tetrachloride (0.29 g, 1.10 mmol) resulted in the polymer Sn_F-EOF (0.66 g, 76 %). CP from ¹⁹F to ¹³C MAS NMR (126 MHz, 11 kHz spinning, 25 °C) δ: 157.1, 153.0 ppm. ¹¹⁹Sn{¹⁹F} MAS NMR (186 MHz, 5 kHz spinning, 25 °C) δ: -243.3 ppm. Anal. calcd for C₂₄F₁₆Sn: C 40.5, F 42.8, Sn 16.7; found: C 39.3, F 41.5, Sn 12.6.

poly-tetra(2,3,5,6-tetrafluorophenyl)silane (Si_F-EOF)

Reaction with silicium(IV)tetrachloride (0.374 g, 2.20 mmol) resulted in the polymer Si_F-EOF (0.43 g, 32 %). CP from ¹⁹F to ¹³C MAS NMR (126 MHz, 11 kHz spinning, 25 °C) δ: 153.1, 117.6 ppm. Anal. calcd for C₂₄F₁₆Si: C 46.5, F 49.0, Si 4.5; found: C 44.7, F 48.0, Si 1.8.

poly-tetra(2,3,5,6-tetrafluorophenyl)germane (Ge_F-EOF)

4,4'-Dibromooctafluorobiphenyl (1.00 g, 2.20 mmol, 1 eq) and bromopentafluorobenzene (0.54 g, 2.20 mmol, 1 eq) were activated with isopropylmagnesium chloride lithium chloride complex (1.3 M in THF; 3.38 mL, 4.40 mmol, 2 eq and 1.69 mL, 2.20 mmol, 1 eq, respectively). Cross-linking with germanium(IV)tetrachloride (0.24 g, 1.10 mmol) resulted in the polymer Ge_F-EOF (0.62 g, 78 %). CP from ¹⁹F to ¹³C MAS NMR (126 MHz, 11 kHz spinning, 25 °C) δ: 157.1, 153.0, 119.6, 117.3 ppm. Anal. calcd for C₂₄F₁₆Ge: C 43.3, F 45.7, Ge 11.0; found: C 46.2, F 43.9, Ge 7.7.

1.4. Boehm Titration

The Boehm titration was performed following the procedure described by Delidovich *et al.*² 100 mg of the acidic material (BH_F-EOF, Amberlyst 15 H form, Nafion NR50) were suspended in 0.1 M NaOH (20 mL) and stirred at room temperature for 20 h in a closed vessel. After filtration, 5 mL of the filtrate were transferred into a Erlenmeyer flask and 0.1 M HCl (10 mL) was added. The acidic solution was back-titrated with 0.1 M NaOH. The procedure was performed three times for each material and each batch was titrated three times. The calculated acidic sites are summarized in Table S1.

Table S1: Amount of acidic sites for the catalysts BH_F-EOF, Amberlyst 15 H form and Nafion NR50 determined by Boehm titration.

Catalyst	n_{H^+} [mmol g ⁻¹]
BH _F -EOF	1.30
Amberlyst 15 H form	5.22
Nafion NR50	1.48

1.5. Esterification of Acetic Acid with Ethanol

The esterification reactions were performed in 10 mL pressure-tubes with stirring bar. For each reaction, 30 mg of the catalyst were mixed with acetic acid (2 mL) and ethanol (2 mL) and placed in a preheated aluminium box at 60 °C. After the desired reaction time, the reactors were cooled in water followed by ice. The reaction solution was filtered with a syringe filter. The sample was analyzed by GC with diethylene glycol dimethyl ether as internal standard.

As the same amount of catalyst (30 mg) was used, the amount of ethyl acetate (AcOEt) formed during the reaction was referred to the amount of acidic sites, determined by Boehm titration (equation 1). This ratio is defined as turnover number (TON).

$$TON = \frac{n_{AcOEt}}{n_{H^+}} \quad (1)$$

In order to discuss the activity of the different catalysts, the initial turnover frequency (TOF) after 30 minutes was determined according to equation 2.

$$TOF = \frac{TON}{0.5 h} \quad (2)$$

2. Results and Discussions

2.1. SEM/ EDX

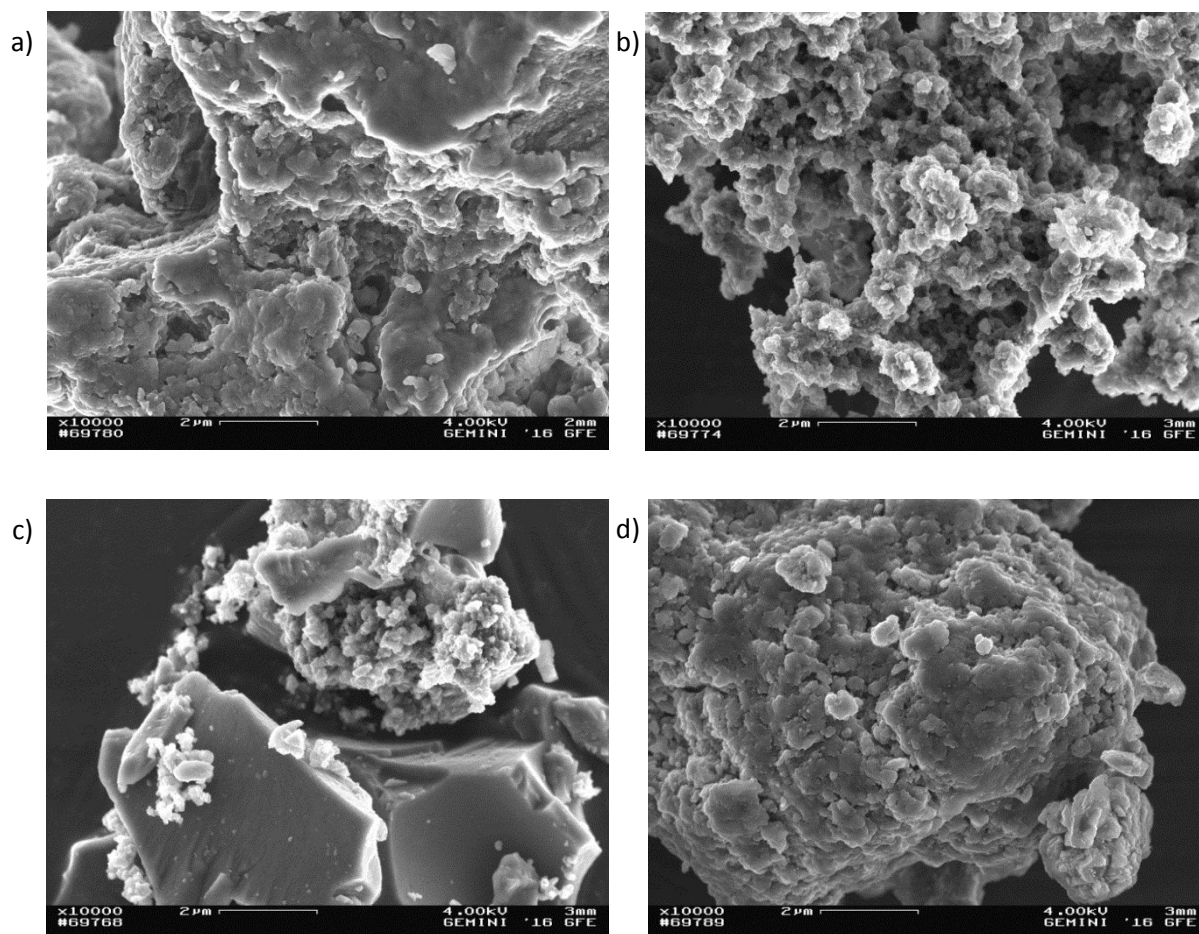


Figure S1: SEM images of fluorinated polymers with a magnification of 10 000. a) B_F-EOF, b) Si_F-EOF, c) Sn_F-EOF, d) Ge_F-EOF.

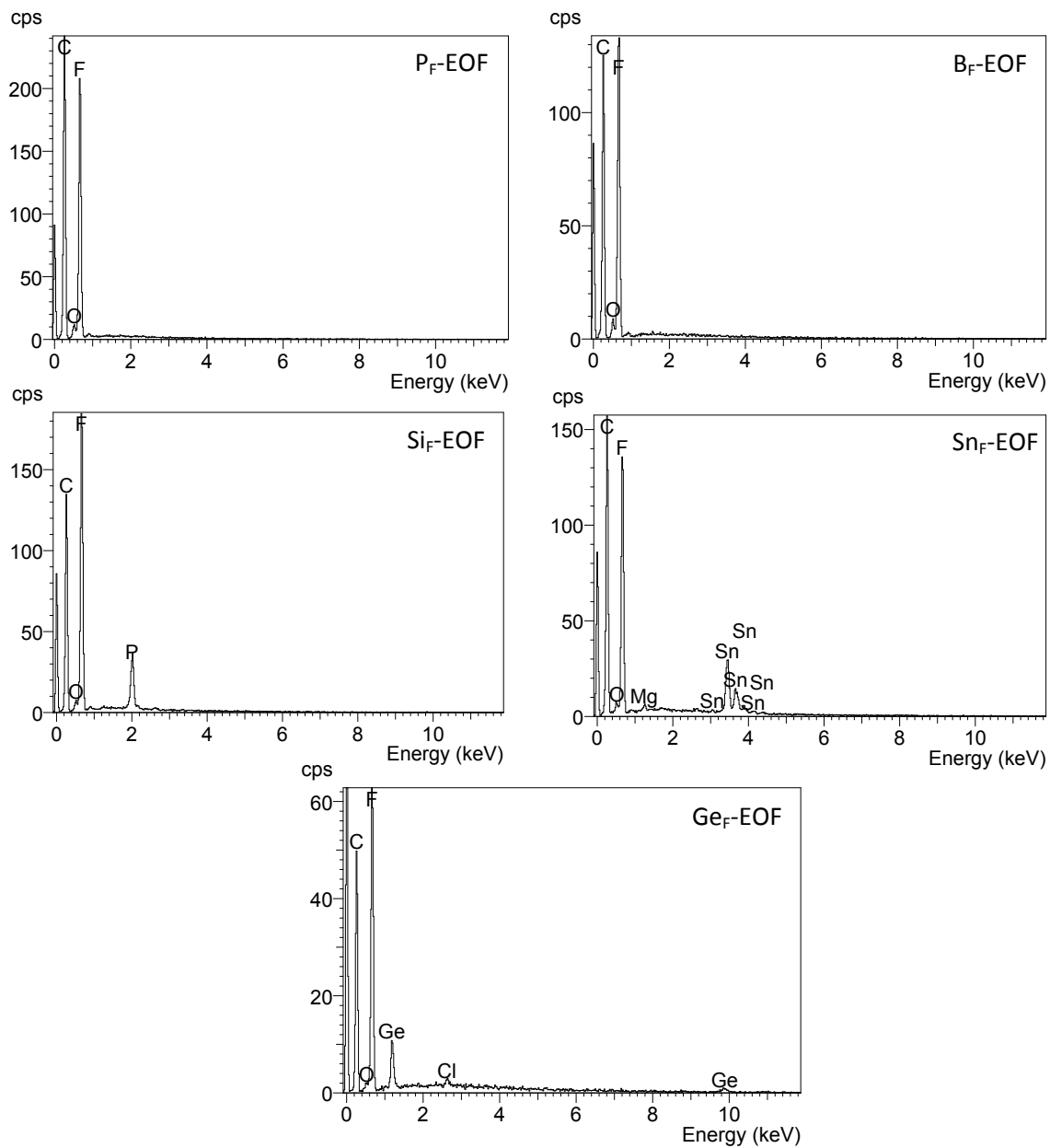


Figure S2: EDX of fluorinated polymers E_F-EOF (E= P, B, Si, Sn, Ge).

2.2. XRD

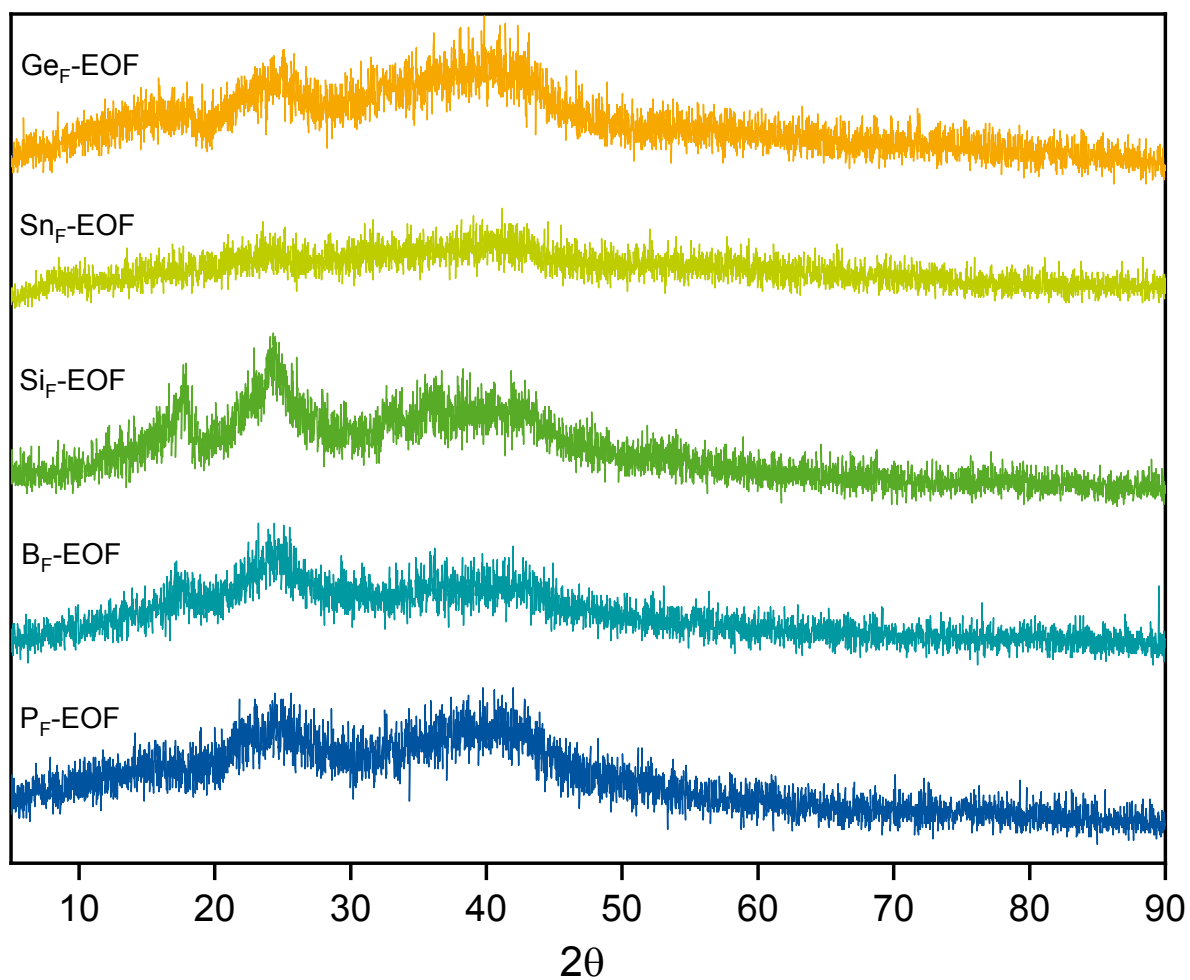


Figure S3: XRD pattern of fluorinated polymers $\text{E}_F\text{-EOF}$ (E= P, B, Si, Sn, Ge).

2.3. TG/ DSC

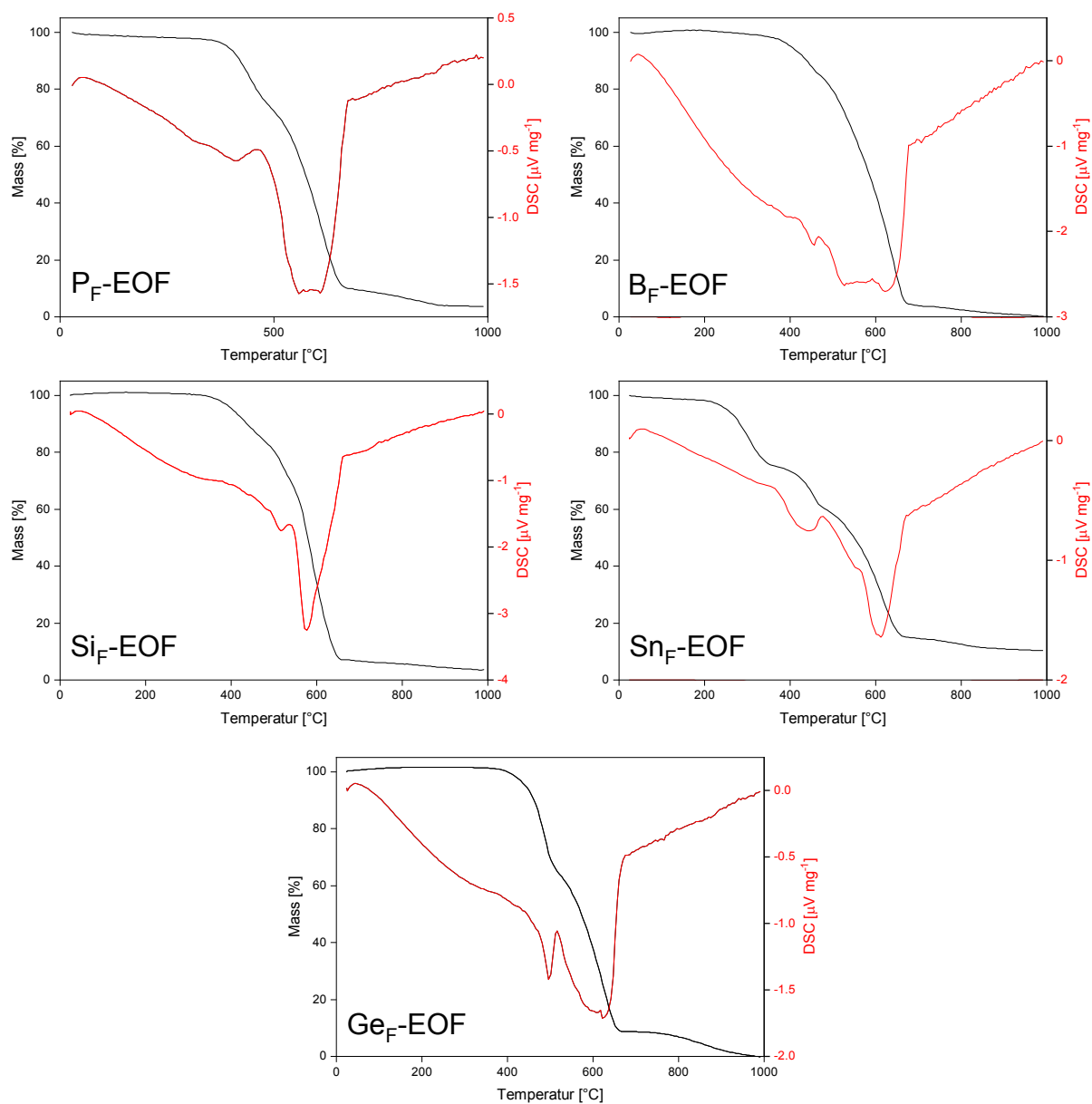


Figure S4: TG/ DSC of fluorinated polymers E_F-EOF (E= P, B, Si, Sn, Ge).

2.4. N₂ physisorption

Table S2: Specific surface areas, external surface areas and micropore volumes of synthesized fluorinated polymers E_F-EOF (E= P, B, Si, Sn, Ge).

Polymer	S _{BET} [m ² g ⁻¹]	S _{external} [m ² g ⁻¹]	V _{micro} [cm ³ g ⁻¹]
P _F -EOF	538	312	0.109
B _F -EOF	566	285	0.137
Si _F -EOF	447	258	0.091
Sn _F -EOF	437	236	0.098
Ge _F -EOF	452	292	0.076

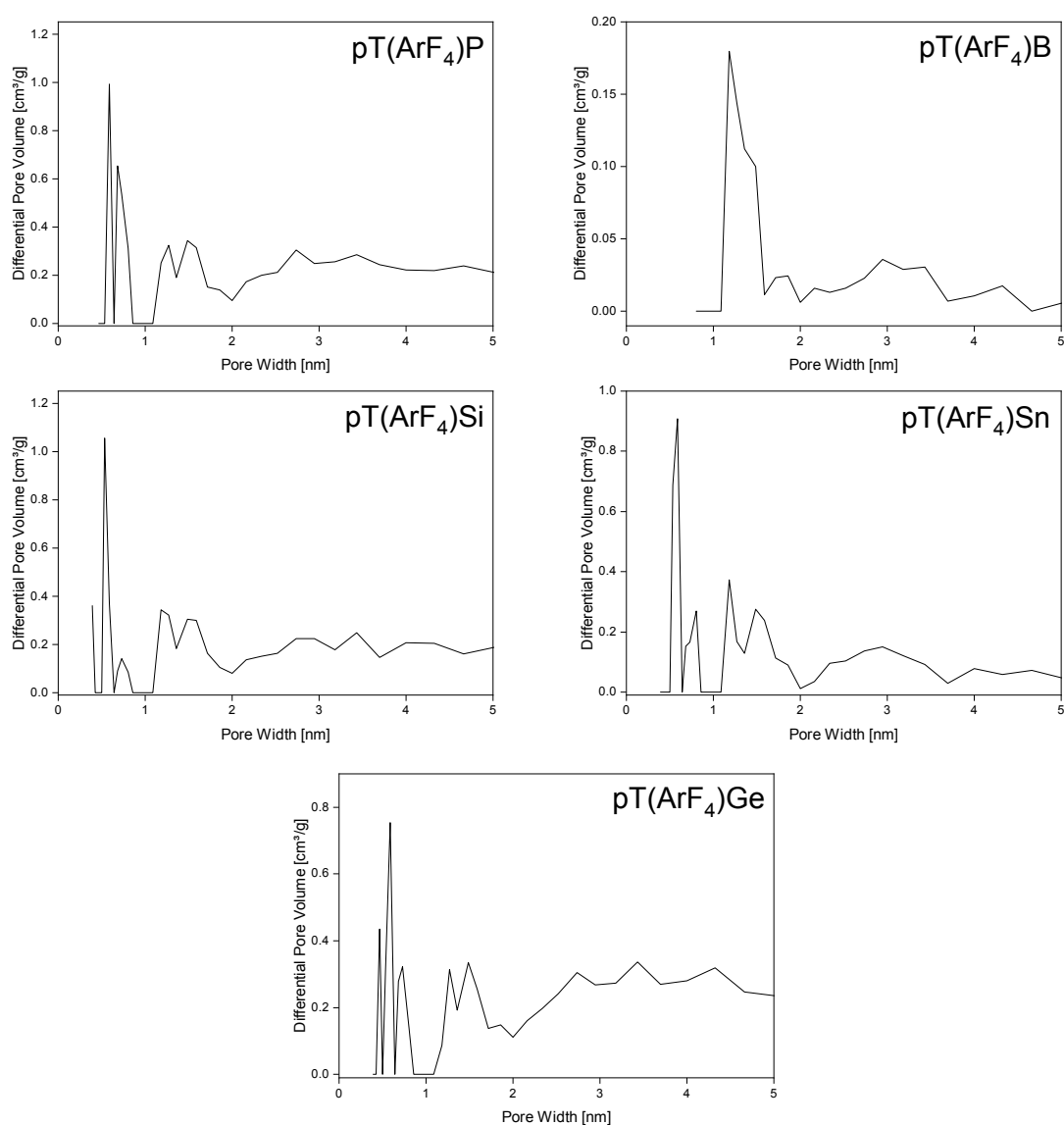


Figure S5: Pore size distribution calculated by DTF of fluorinated polymers E_F-EOF (E= P, B, Si, Sn, Ge).

2.5. ATR-IR

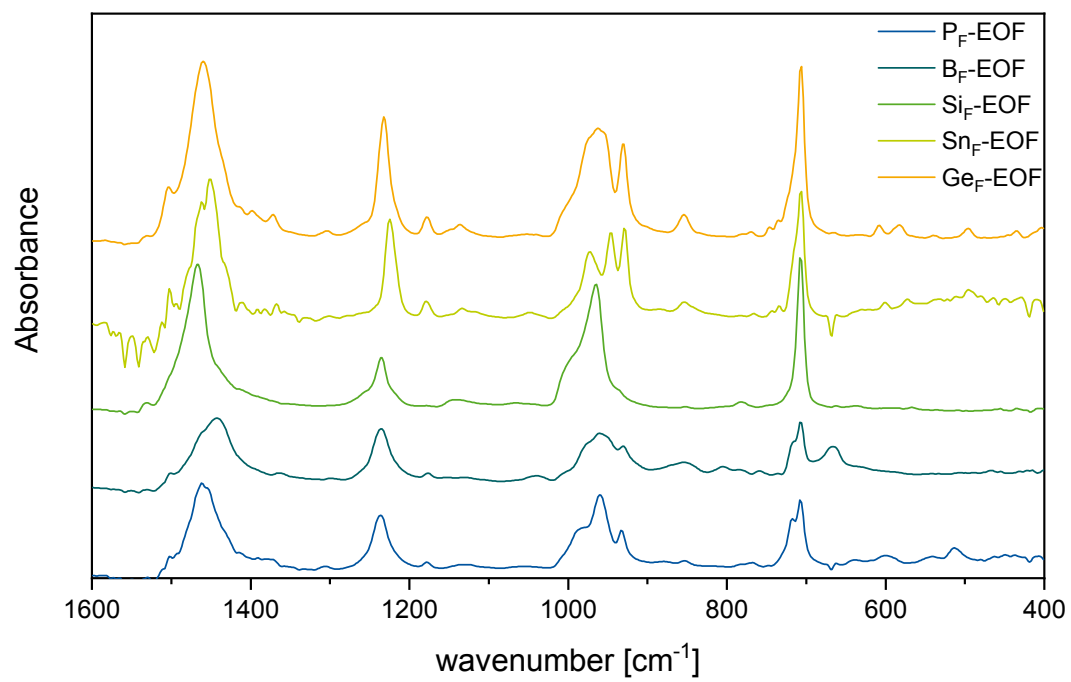


Figure S6: ATR-IR of fluorinated polymers E_F-EOF (E= P, B, Si, Sn, Ge).

2.6. XPS

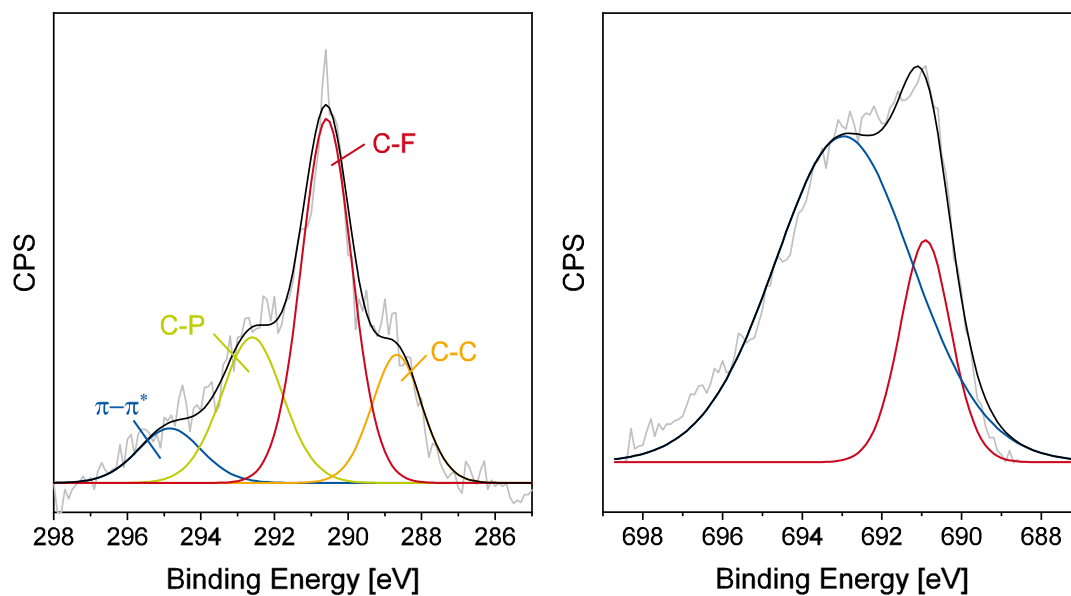


Figure S7: XPS spectra of P_F-EOF. a) C 1s und b) F 1s.

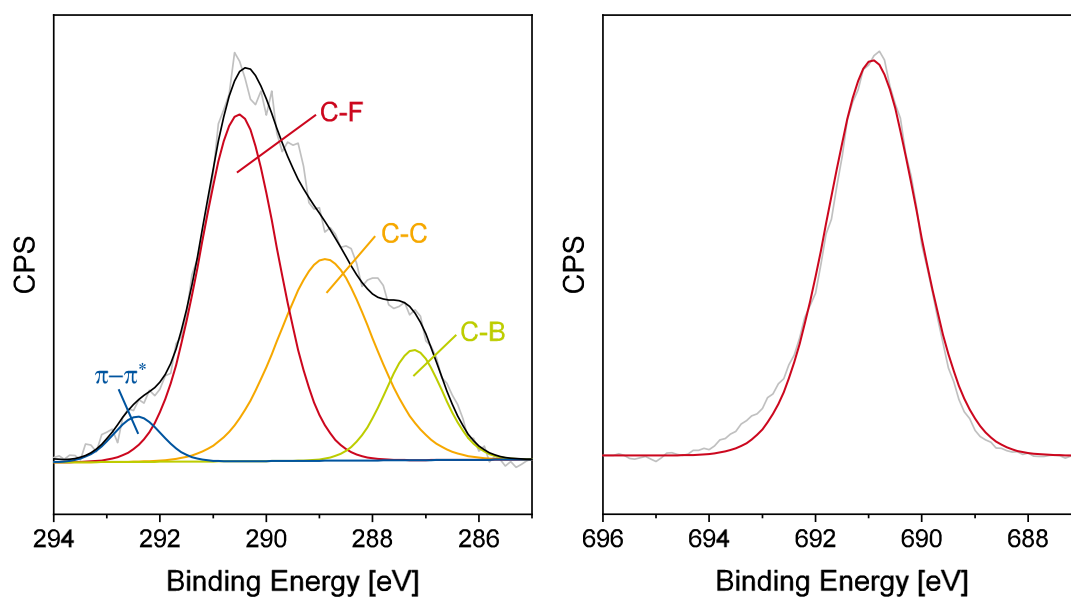


Figure S8: XPS spectra of B_F-EOF. a) C 1s und b) F 1s.

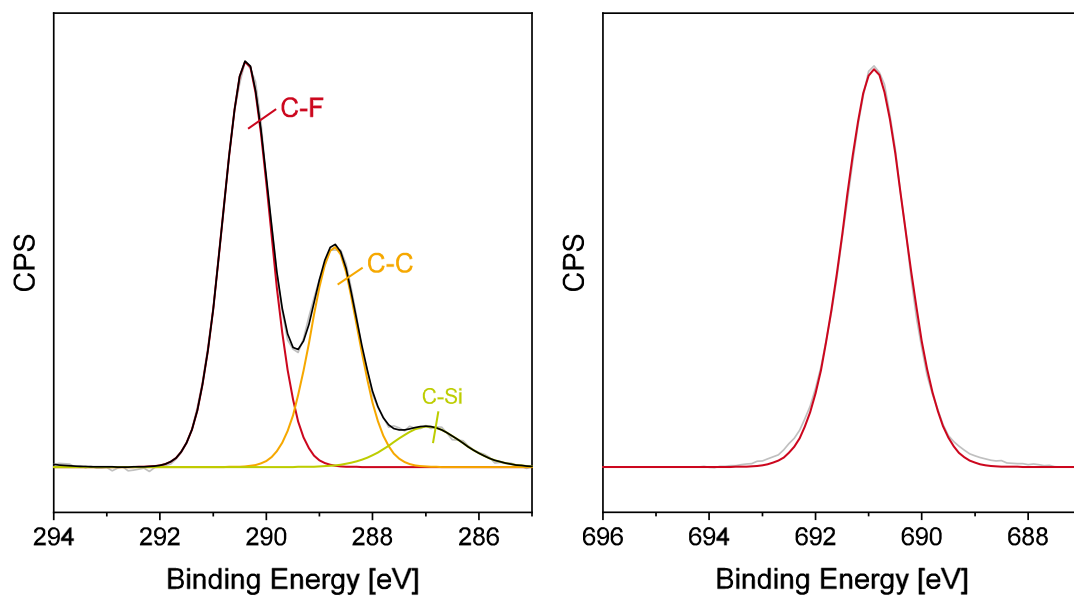


Figure S9: XPS spectra of Si_F-EOF. a) C 1s und b) F 1s.

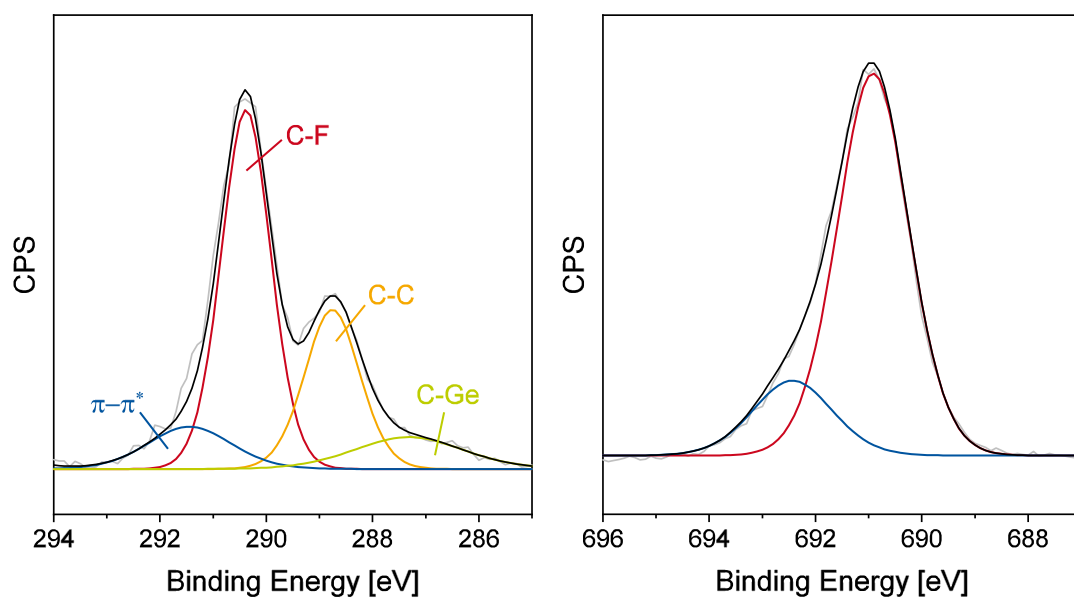


Figure S10: XPS spectra of Ge_F-EOF. a) C 1s und b) F 1s.

2.7. Solid-State-MAS NMR

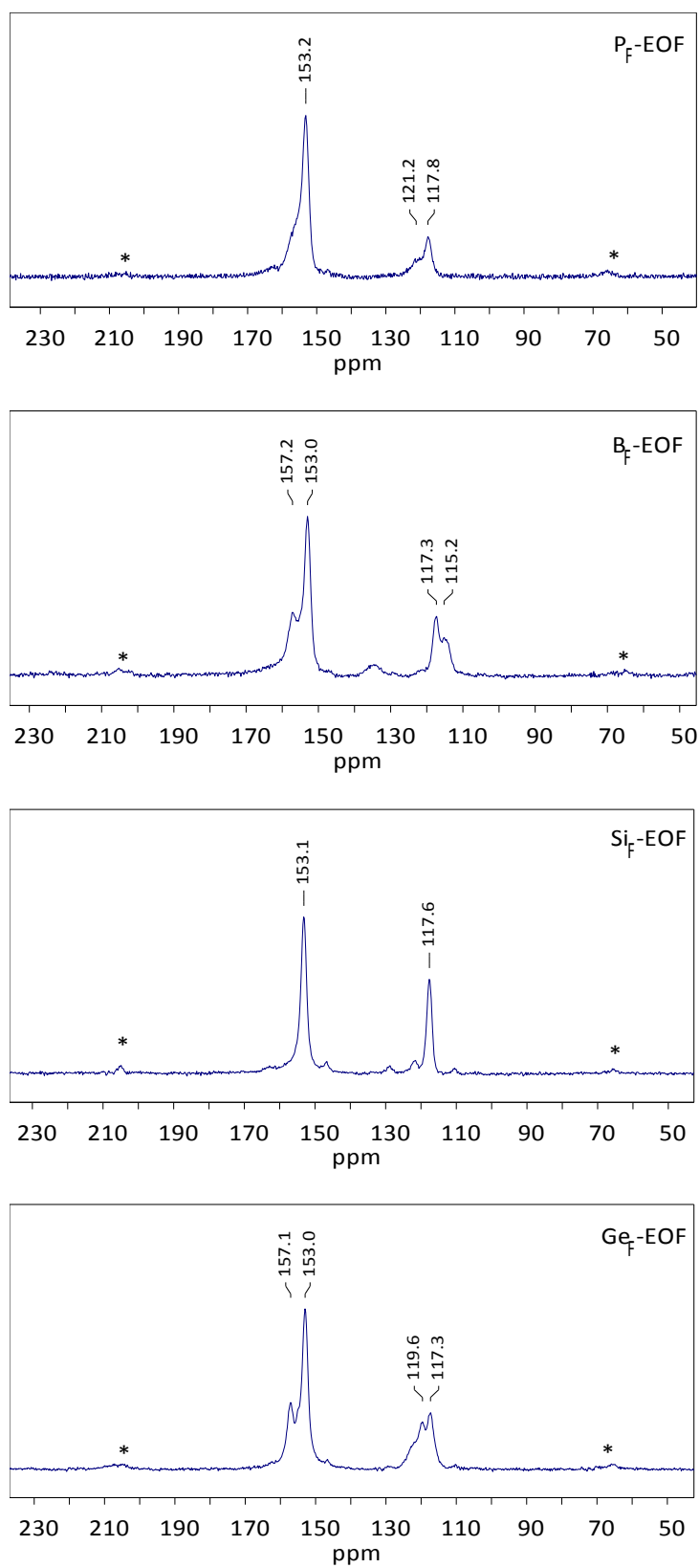


Figure S11: CP from ^{19}F to ^{13}C MAS NMR of E_F -EOF (E= P, B, Si, Sn, Ge) at 11 kHz.

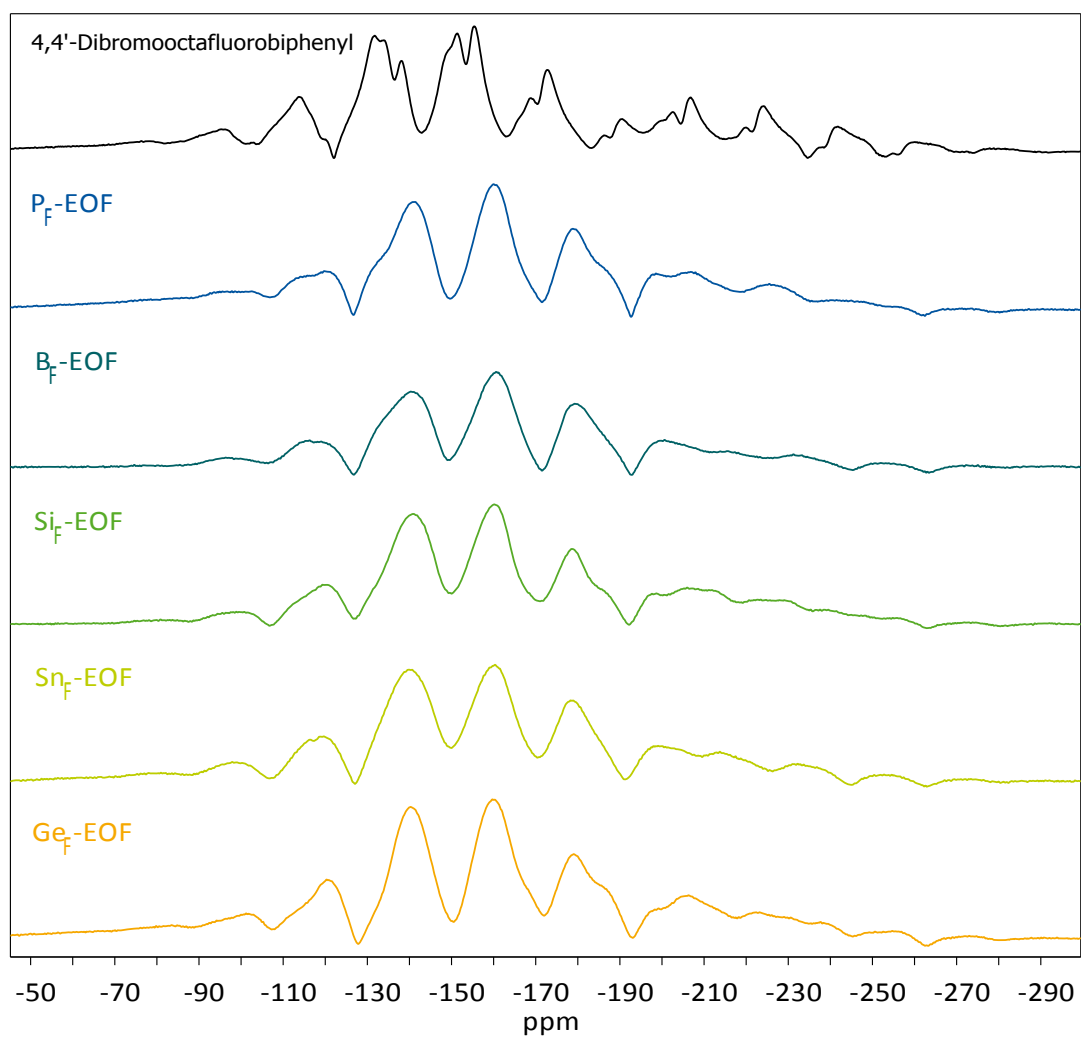


Figure S12: ^{19}F MAS NMR of E_F-EOF (E= P, B, Si, Sn, Ge) at 8 kHz, in comparison to the linker 4,4'-dibromooctafluorobiphenyl.

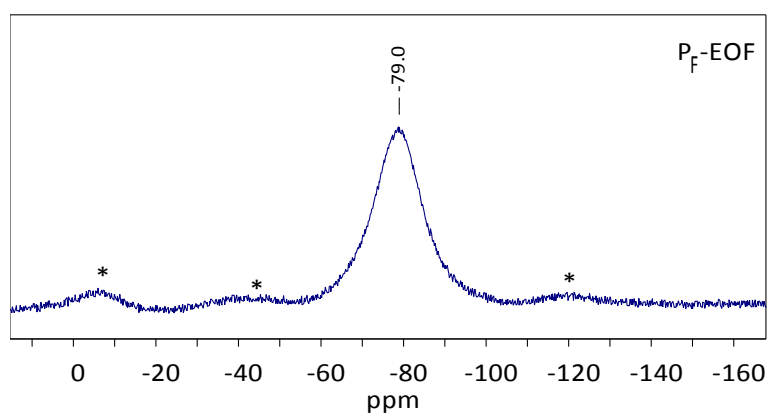


Figure S13: $^{31}\text{P}\{^{19}\text{F}\}$ MAS NMR of P_F-EOF at 8 kHz.

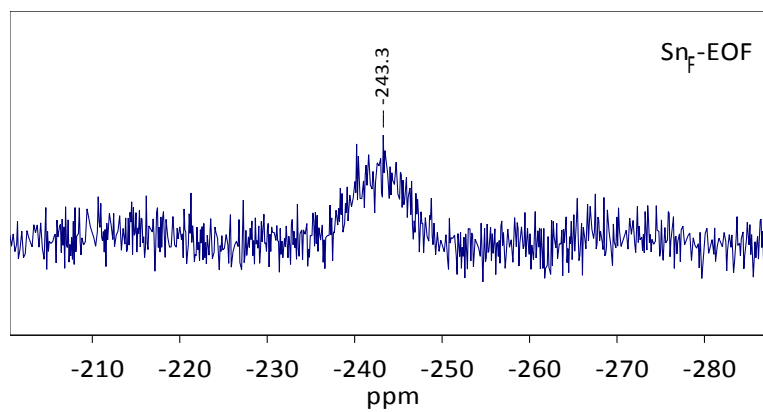


Figure S14: $^{119}\text{Sn}\{^{19}\text{F}\}$ MAS NMR of Sn_F -EOF at 5 kHz.

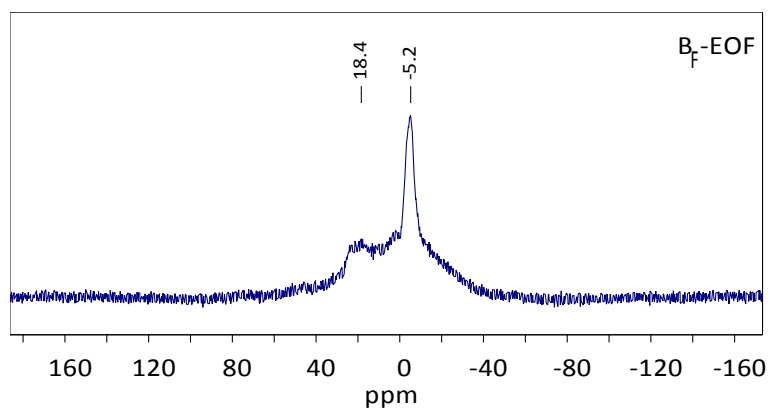


Figure S15: $^{11}\text{B}\{^{19}\text{F}\}$ MAS NMR of B_F -EOF at 8 kHz.

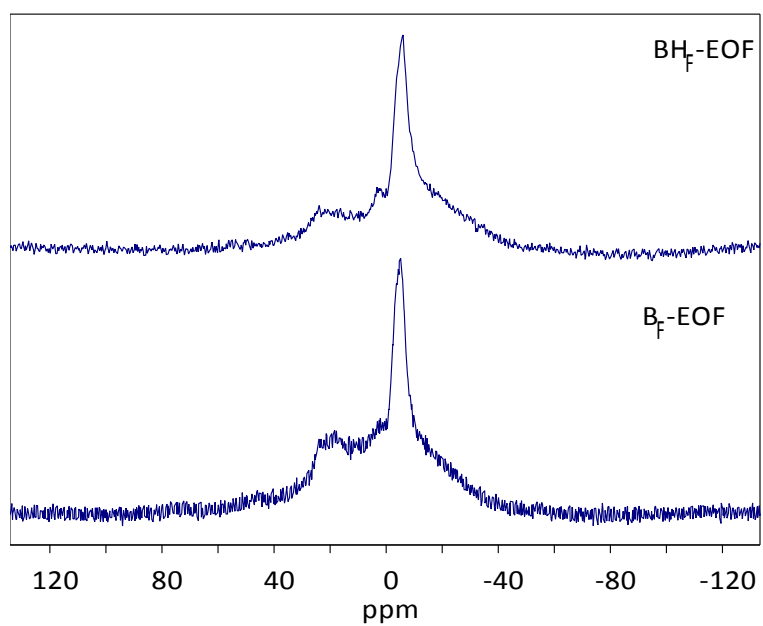


Figure S16: $^{11}\text{B}\{^{19}\text{F}\}$ MAS NMR of B_F -EOF and BH_F -EOF at 8 kHz.

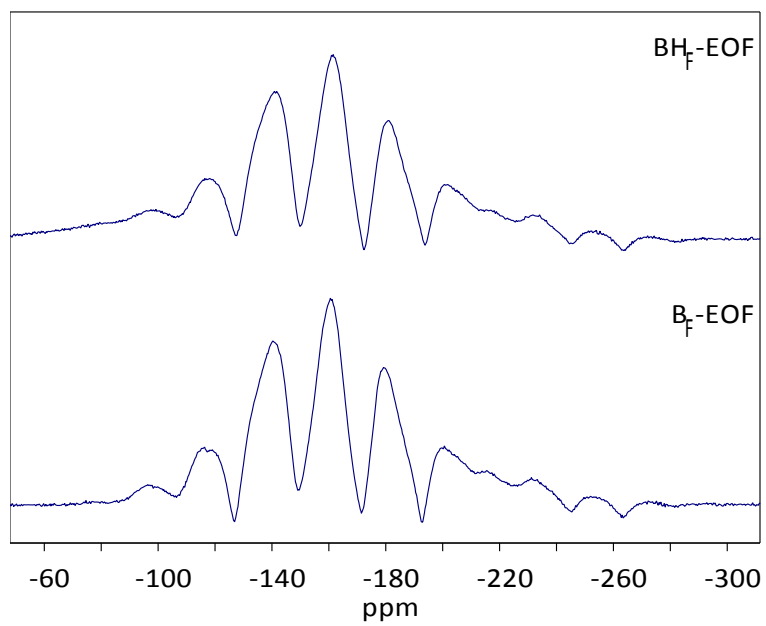


Figure S17: ^{19}F MAS NMR of $\text{B}_f\text{-EOF}$ and $\text{BH}_f\text{-EOF}$ at 8 kHz.

References

- 1 C. D. Wagner, *The Nist X-Ray Photoelectron Spectroscopy (XPS) Database*, 1991.
- 2 I. Delidovich and R. Palkovits, *Microporous Mesoporous Mater.*, 2016, **219**, 317–319.