ELECTRONIC SUPPLEMENTARY INFORMATION

Polymethylaluminoxane organic frameworks (sMAOF) – highly active supports for slurry phase ethylene polymerisation

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1. Experimental details

1.1. General procedures

All manipulations were carried out using standard Schlenk techniques under N_2,[1] or in an MBraun UNIlab glovebox under N_2. All glassware was dried at 160 °C overnight prior to use. Sonications were carried out in a 9.2 L volume VWR ultrasonic bath (dry running frequency 45 kHz) with built-in digital timer and thermostat. Hexane and toluene were dried and degassed using an MBraun SPS-800 solvent purification system.[2] Dried solvents were collected, degassed and stored over N_2 in K mirrored ampules. THF–d_8 (Fluorochem) was degassed by three freeze−pump−thaw cycles, dried by refluxing over CaH_2 for 3 days, vacuum distilled into a J. Young ampoule and stored under N_2. Trimethylaluminium (TMA), tri*iso*butylaluminium (TIBA), benzoic acid (99%), Tetrafluoroterephthalic acid (**B**), hydroquinone (**C**), resorcinol (**D**), 4,4-dihydroxybiphenyl (**E**), bisphenol A (**F**), 4,4-(hexafluoroisopropylidene)diphenol (**G**), 2,6-dihydroxynaphthalene (**H**) and 2,7-dihydroxynaphthalene (**I**) were supplied by Sigma-Aldrich and used as received. Solid polymethylaluminoxane (sMAO, TOSOH Finechem 39.5 $\text{wt\%}_{\text{Al,}}$)[3,4] Tetrafluorohydroquinone (**A**, Apollo Scientific), 2,3,5,6-Tetrafluoro-4-(2,3,5,6-tetrafluoro-4-hydroxy-phenyl)phenol (Manchester Organics) and *rac*-ethylenebis(indenyl)-zirconium(IV) dichloride ((EBI)$ZrCl_2$, Strem) were used as received. Nitric acid (68% *d*=1.42, Primar Plus™, for trace metal analysis) was supplied by Fisher Scientific.

1.2. Analytical techniques

Solution NMR samples were prepared in the glovebox, using 5 mm J. Young tap NMR tubes. Spectra were measured either on a Bruker Avance III HD nanobay 400 MHz NMR spectrometer, or a Bruker Avance III 500 MHz NMR spectrometer and were referenced internally to the residual protic solvent (^1H) or the signals of the solvent (^{13}C), and aqueous $Al(NO_3)_3$ for ^{27}Al. Peak fittings and integrations of NMR spectra were carried out using the MestReNova software package.[5]

Solid state NMR samples were prepared in the glovebox, using powdered solid material loaded into 3.2 or 4.0 mm zirconia rotors. Spectra were measured on a Bruker Avance III HD 400 MHz NMR spectrometer at room temperature. Magic angle spinning was carried out using dry dinitrogen. ^{27}Al Hahnecho of sMAOF samples employed a recycle delay of 0.01 s, 32000 scans and a spinning speed of 15 kHz. ^1H DP-MAS used a recycle delay of 10 s, 32 scans and a spinning speed of 24 kHz. Spectral referencing is with respect to external adamantane for ^{13}C (38.48 ppm) and aqueous $Al(NO_3)_3$ for ^{27}Al (0.00 ppm).

Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy samples were prepared as powders in an alumina crucible and sealed under N_2 in a Pike Technologies gas-tight cell. Spectra were measured at room temperature through a NaCl window on a Bruker VERTEX 80 FT-IR spectrometer fitted with a Pike Technologies DiffusIR accessory, using 64 scans, resolution 4 and spectral range 4500–400 cm^{-1}. These spectra were collected in reflectance units and submitted to Kubelka–Munk transform.[6] A background spectrum (128 scans) of a pristine gold surface under N_2 was recorded before each set of measurements.

Specific surface areas were analyzed using a Micromeritics 3Flex. The samples were measured for the N_2 adsorption and desorption at 77 K. Before each measurement, the samples were first *in situ* degassed at 90 °C for 6 h. The adsorption isotherm was analyzed via the Brunauer–Emmett–Teller (BET) method to calculate the specific surface area.[7]

Samples for ICP-MS analysis were prepared by digestion in high purity HNO_3 solution (2 h reflux), and dilution with 18.2 Mohm DI water, calibrated using external calibration analysis (a series of standards of known Al and Zr concentrations were prepared and measured externally to the samples to produce a linear calibration) and measured by Mr P. Holdship (University of Oxford) on a Perkin Elmer Elan 6100DRC ICP-MS.

Scanning electron microscopy energy dispersive X-ray (SEM-EDX) spectroscopy was performed by Mrs Jennifer A. Holter (David Cockayne Centre for Electron Microscopy, Oxford Materials) on a Carl Zeiss Merlin high resolution field emission gun SEM at a voltage of 20 kV fitted with Zeiss A-STEM detector. EDX spectra were measured using an Oxford instruments Xmax 150. Samples of sMAOF were spread on silicon nitride membranes (200 μm substrate thickness), and quickly transferred from a vial sealed under N_2 to the instrument vacuum antechamber. SEM-EDX elemental mapping and line scan analysis were carried out using the AZtecLive software package.

Scanning electron microscopy (SEM) analysis of polyethylene samples was performed by Dr Jessica V. Lamb on a JOEL JSM 6610LV scanning electron microscope with an accelerating voltage of 3.0 kV. Samples were spread on carbon tape adhered to an SEM stage. Before imaging, the polyethylene samples were coated with a thin platinum layer (10 nm thickness) to prevent charging and to improve image quality.

Gel permeation chromatography (GPC) analysis was performed by Norner AS, GPC-IR from Polymer Char with Highly- Sensitive IR5 MCT Detector. Polymer soluble in the mobile phase at 140 °C. Dissolve polymer in tetrachlorobenzene at 160 °C for 1 to 4h. Concentration ~ 0.25 – 1.8 mg/mL. Detector: IR5 MCT infrared detector Solvent: tetrachlorobenzene. Column temperature: 150 °C Columns: 1 PL gel Guard, 3 PLgel 13 µm OLEXIS Calibrations: Flow Marker (IR5) Mass constant (IR5) Narrow Standards (IR5) Composition (IR5) Linear Ref (IR5) Processing methods: GPC-IR Parallels: 2-3.

X-ray total scattering data were collected at the I15-1 beamline at the Diamond Light Source, UK (λ = 0.161669 Å, 76.7 keV). Samples were loaded under argon into 1.5 mm borosilicate capillaries. Capillaries were sealed and mounted onto the instrument and data were collected at room temperature for each sample, empty instrument and an argon-filled capillary. These data were processed using GudrunX[8,9] in order to correct for background scattering, Compton scattering, multiple scattering and beam attenuation by the sample container. The resulting X-ray total scattering functions were transformed to PDFs; we use the normalisation referred to as $D(r)$ in Ref. 10.

1.3. Syntheses and Characterisation data

Post-synthesis modification of sMAO with linker compounds

Control sMAO A Schlenk flask containing a dispersion of sMAO (1.296 g, 19.0 $\mathrm{mmol_{Al}}$) in toluene (50 mL) was sonicated in a water bath at ambient temperature for 1 h. Over the course of the sonication the water bath had reached a temperature of 45 °C. After cooling to ambient temperature, hexane (80 mL) was added and the resultant colourless suspension was allowed to settle. The supernatant solution was removed by filtration and the remaining solids were washed with toluene-hexane (1:1 v/v mixture, 3 × 80 mL) and dried *in vacuo* overnight, to afford control sMAO as a free-flowing white solid. Total yield: 1.320 g, 18.8 $\mathrm{mmol_{Al}}$ (99% based on aluminium).
^{1}H and ^{27}Al{^{1}H} NMR spectra in THF-d_8 were consistent with those previously reported for sMAO.[3,4]

sMAOF(0.025/A) To a Schlenk flask containing a dispersion of sMAO (756 mg, 11.1 $\mathrm{mmol_{Al}}$) in toluene (15 mL) was added a solution of tetrafluorohydroquinone (**A**, 51 mg, 0.280 mmol) in toluene (3 × 5 mL). Effervescence was observed and the flask was sonicated in a water bath at ambient temperature for 1 h. Over the course of the reaction the water bath had reached a temperature of 45 °C. After cooling to ambient temperature, hexane (80 mL) was added and the resultant off-white suspension was allowed to settle. The supernatant solution was removed by filtration and the remaining solids were washed with toluene-hexane (1:1 v/v mixture, 3 × 50 mL) and dried *in vacuo* overnight, to afford sMAOF(0.025/**A**) as a free-flowing white solid. Total yield: 683 mg, 7.97 $\mathrm{mmol_{Al}}$ (72% based on aluminium). ^{1}H NMR (THF-d_8, 400.2 MHz, 298 K): δ_H 8.50 – 7.40 (br, Ar-*H*), −0.19 – −1.09 (br, oligomeric AlMe_x), –0.60 (s, bound Al-Me^A), –0.85 (s, bound Al-Me^B), −0.96 (s, 'free' AlMe_x). ^{19}F{^{1}H} NMR (THF-d_8, 376.5 MHz, 298 K): δ_F −123.2 (m, *o*-C_6F_5), −158.3 (m, *p*-C_6F_5), −164.2 (m, *m*-C_6F_5). ^{27}Al{^{1}H} NMR (THF-d_8, 104.3 MHz, 298 K): δ_Al 190.6 (*Al*Me). Elemental anal.: Al, 31.5; F, 2.47 wt%.

sMAOF(0.01/A) Following an analogous procedure starting with sMAO (800 mg, 11.7 $\mathrm{mmol_{Al}}$) and 1,4-HO(C_6F_4)OH (21.6 mg, 0.119 mmol). Total yield: 689 mg, 9.44 $\mathrm{mmol_{Al}}$ (81% based on aluminium).
sMAOF(0.05/A) Following an analogous procedure starting with sMAO (867 mg, 12.7 $\mathrm{mmol_{Al}}$) and 1,4-HO(C_6F_4)OH (115 mg, 182.1 mmol). Total yield: 793 mg, 8.61 $\mathrm{mmol_{Al}}$ (68% based on aluminium). 'Free' AlMe_x content = 16.3 mol% by integration.
sMAOF(0.10/A) Following an analogous procedure starting with sMAO (786 mg, 11.5 $\mathrm{mmol_{Al}}$) and 1,4-HO(C_6F_4)OH (212 mg, 1.16 mmol). Total yield: 698 mg, 7.39 $\mathrm{mmol_{Al}}$ (64% based on aluminium).
sMAOF(0.20/A) Following an analogous procedure starting with sMAO (770 mg, 11.3 $\mathrm{mmol_{Al}}$) and 1,4-HO(C_6F_4)OH (415 mg, 2.28 mmol). Total yield: 877 mg, 6.82 $\mathrm{mmol_{Al}}$ (60% based on aluminium).
sMAOF(0.40/A) Following an analogous procedure starting with sMAO (780 mg, 11.4 $\mathrm{mmol_{Al}}$) and 1,4-HO(C_6F_4)OH (848 mg, 4.66 mmol). Total yield: 1.10 g, 6.52 $\mathrm{mmol_{Al}}$ (57% based on aluminium).

Caution: Samples of sMAOF(**A**) with 1,4-HO(C_6F_4)OH modifier loading ≥ 0.10 are flocculent and extremely pyrophoric and react violently in contact with air or moisture. Extra care should be taken when handling and safely disposing of these samples.

sMAOF(0.025/C) To a Schlenk flask containing a dispersion of sMAO (1.00 g, 14.6 mmol_{Al}) in toluene (15 mL) was added a solution of hydroquinone (**C**, 40 mg, 0.36 mmol) in toluene (3 × 5 mL). Effervescence was observed and the flask was sonicated in a water bath at ambient temperature for 1 h. Over the course of the reaction the water bath had reached a temperature of 45 °C. After cooling to ambient temperature, hexane (80 mL) was added and the resultant off-white suspension was allowed to settle. The supernatant solution was removed by filtration and the remaining solids were washed with toluene-hexane (1:1 v/v mixture, 3 × 50 mL) and dried *in vacuo* overnight, to afford sMAOF(0.025/**C**) as a free-flowing white solid. Total yield: 918 mg, 11.2 mmol_{Al} (77% based on aluminium). Elemental anal.: Al, 32.7 wt%.

sMAOF(0.025/D) To a Schlenk flask containing a dispersion of sMAO (647 mg, 9.47 mmol_{Al}) in toluene (15 mL) was added a solution of resorcinol (**D**, 26 mg, 0.236 mmol) in toluene (3 × 5 mL). Effervescence was observed and the flask was sonicated in a water bath at ambient temperature for 1 h. Over the course of the reaction the water bath had reached a temperature of 45 °C. After cooling to ambient temperature, hexane (80 mL) was added and the resultant off-white suspension was allowed to settle. The supernatant solution was removed by filtration and the remaining solids were washed with toluene-hexane (1:1 v/v mixture, 3 × 50 mL) and dried *in vacuo* overnight, to afford sMAOF(0.025/**D**) as a free-flowing white solid. Total yield: 680 mg, 8.24 mmol_{Al} (87% based on aluminium). Elemental anal.: Al, 32.0 wt%.

sMAOF(0.025/E) To a Schlenk flask containing a dispersion of sMAO (766 mg, 11.2 mmol_{Al}) in toluene (15 mL) was added a solution of 4,4-dihydroxybiphenyl (**E**, 53 mg, 0.285 mmol) in toluene (3 × 5 mL). Effervescence was observed and the flask was sonicated in a water bath at ambient temperature for 1 h. Over the course of the reaction the water bath had reached a temperature of 45 °C. After cooling to ambient temperature, hexane (80 mL) was added and the resultant off-white suspension was allowed to settle. The supernatant solution was removed by filtration and the remaining solids were washed with toluene-hexane (1:1 v/v mixture, 3 × 50 mL) and dried *in vacuo* overnight, to afford sMAOF(0.025/**E**) as a free-flowing white solid. Total yield: 602 mg, 5.28 mmol_{Al} (47% based on aluminium) Elemental anal.: Al, 23.7 wt%.

sMAOF(0.025/F) To a Schlenk flask containing a dispersion of sMAO (756 mg, 11.1 mmol_{Al}) in toluene (15 mL) was added a solution of bisphenol A (**F**, 63 mg, 0.276 mmol) in toluene (3 × 5 mL). Effervescence was observed and the flask was sonicated in a water bath at ambient temperature for 1 h. Over the course of the reaction the water bath had reached a temperature of 45 °C. After cooling to ambient temperature, hexane (80 mL) was added and the pink suspension was allowed to settle. The supernatant solution was removed by filtration and the remaining solids were washed with toluene-hexane (1:1 v/v mixture, 3 × 50 mL) and dried *in vacuo* overnight, to afford sMAOF(0.025/**F**) as a free-flowing pink solid. Total yield: 688 mg, 8.56 mmol_{Al} (77% based on aluminium). Elemental anal.: Al, 33.6 wt%.

sMAOF(0.025/G) To a Schlenk flask containing a dispersion of sMAO (767 mg, 11.2 mmol_{Al}) in toluene (15 mL) was added a solution of 4,4-(hexafluoroisopropylidene)diphenol (**G**, 94 mg, 0.280 mmol) in toluene (3 × 5 mL). Effervescence was observed and the flask was sonicated in a water bath at ambient temperature for 1 h. Over the course of the reaction the water bath had reached a temperature of 45 °C. After cooling to ambient temperature, hexane (80 mL) was added and the resultant off-white suspension was allowed to settle. The supernatant solution was removed by filtration and the remaining solids were washed with toluene-hexane (1:1 v/v mixture, 3 × 50 mL) and dried *in vacuo* overnight, to afford sMAOF(0.025/**G**) as a free-flowing white solid. Total yield: 657 mg, 6.33 mmol$_{Al}$ (57% based on aluminium). Elemental anal.: Al, 26.0 wt%.

sMAOF(0.025/H) To a Schlenk flask containing a dispersion of sMAO (780 mg, 11.4 mmol$_{Al}$) in toluene (15 mL) was added a solution of 2,6-dihydroxynaphthalene (**H**, 46 mg, 0.287 mmol) in toluene (3 × 5 mL). Effervescence was observed and the flask was sonicated in a water bath at ambient temperature for 1 h. Over the course of the reaction the water bath had reached a temperature of 45 °C. After cooling to ambient temperature, hexane (80 mL) was added and the resultant dark green suspension was allowed to settle. The supernatant solution was removed by filtration and the remaining solids were washed with toluene-hexane (1:1 v/v mixture, 3 × 50 mL) and dried *in vacuo* overnight, to afford sMAOF(0.025/**H**) as a free-flowing green solid. Total yield: 639 mg, 7.95 mmol$_{Al}$ (70% based on aluminium). Elemental anal.: Al, 33.6 wt%.

sMAOF(0.025/I) To a Schlenk flask containing a dispersion of sMAO (780 mg, 11.4 mmol$_{Al}$) in toluene (15 mL) was added a solution of 2,7-dihydroxynaphthalene (**I**, 46 mg, 0.287 mmol) in toluene (3 × 5 mL). Effervescence was observed and the flask was sonicated in a water bath at ambient temperature for 1 h. Over the course of the reaction the water bath had reached a temperature of 45 °C. After cooling to ambient temperature, hexane (80 mL) was added and the resultant egg-yolk yellow suspension was allowed to settle. The supernatant solution was removed by filtration and the remaining solids were washed with toluene-hexane (1:1 v/v mixture, 3 × 50 mL) and dried *in vacuo* overnight, to afford sMAOF(0.025/**I**) as a free-flowing yellow solid. Total yield: 611 mg, 6.38 mmol$_{Al}$ (56% based on aluminium). Elemental anal.: Al, 28.2 wt%.

General procedures for immobilisation of metallocene pre-catalysts

To a Schlenk flask charged with sMAO (60.6 mg$_{Al}$, 0.887 mmol$_{Al}$) and (EBI)ZrCl$_2$ (4.7 mg, 0.011 mmol) was added toluene (40 mL), and the resulting orange dispersion was heated at 80 °C for 1 h with regular swirling. The mixture was allowed to cool to room temperature and a pink-orange solid settled below a colourless supernatant solution. The supernatant was removed by filtration and the remaining slurry was dried *in vacuo* overnight, to afford a free-flowing orange solid.
Complete immobilisation of (EBI)ZrCl$_2$ on the support after heating/swirling was judged by a colourless toluene filtrate and confirmed for the control sMAO catalyst by ICP-MS: Al, 38.89 wt%; Zr, 0.67 wt%; mol$_{Al}$/mol$_{Zr}$ = 196.

Immobilisation of metallocene pre-catalysts on modified sMAOF supports was carried out using an adaption of the above procedure, based on the wt% Al of the support determined by ICP-MS analysis, and calculated with a target catalyst loading of $[Al_{sMAO}]_0/[Zr]_0 = 200$.
(EBI)ZrCl$_2$–sMAOF(0.025,**A**) ICP-MS: mol$_{Al}$/mol$_{Zr}$ = 199.
(EBI)ZrCl$_2$–sMAOF(0.025,**D**) ICP-MS: mol$_{Al}$/mol$_{Zr}$ = 191.
(EBI)ZrCl$_2$–sMAOF(0.025,**E**) ICP-MS: mol$_{Al}$/mol$_{Zr}$ = 178.
(EBI)ZrCl$_2$–sMAOF(0.025,**F**) ICP-MS: mol$_{Al}$/mol$_{Zr}$ = 178.
(EBI)ZrCl$_2$–sMAOF(0.025,**G**) ICP-MS: mol$_{Al}$/mol$_{Zr}$ = 179.

1.4. Ethylene polymerisation studies

For laboratory scale polymerisations the solid supported catalyst (10.0 mg), triisobutylaluminium scavenger (150 mg), and hexane (50 mL) were added to a high-pressure Rotaflo ampoule. Ethylene gas was continuously fed into the ampoule at 2 bar overpressure during polymerisation at 70 °C. After 30 min, the reaction was stopped by removing the ampoule from the oil bath, and degassing *in vacuo*. The polymer was isolated on a frit, washed with pentane (50 mL) and vacuum dried at room temperature for 1 h. Each polymerisation experiment was conducted at least twice to ensure the reproducibility of the corresponding outcome, and mean activities are quoted in units of $kg_{PE}mol_{Zr}^{-1}h^{-1}$.

For scale-up polymerisations the solid supported catalyst (25.0 mg), triethylaluminium scavenger (2.5 mL), and hexane (1000 mL) were added to a 2 Litre high-pressure reactor. Ethylene gas was continuously fed into the reactor at 8 bar overpressure during polymerisation at 80 °C for 60 min. The polymer was isolated on a frit, washed with hexanes (100 mL) and vacuum dried at room temperature overnight. Each polymerisation experiment was conducted at least twice to ensure the reproducibility of the corresponding outcome, and mean activities are quoted in units of $kg_{PE}mol_{Zr}^{-1}h^{-1}$.

2. Additional characterising data

2.1. Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy

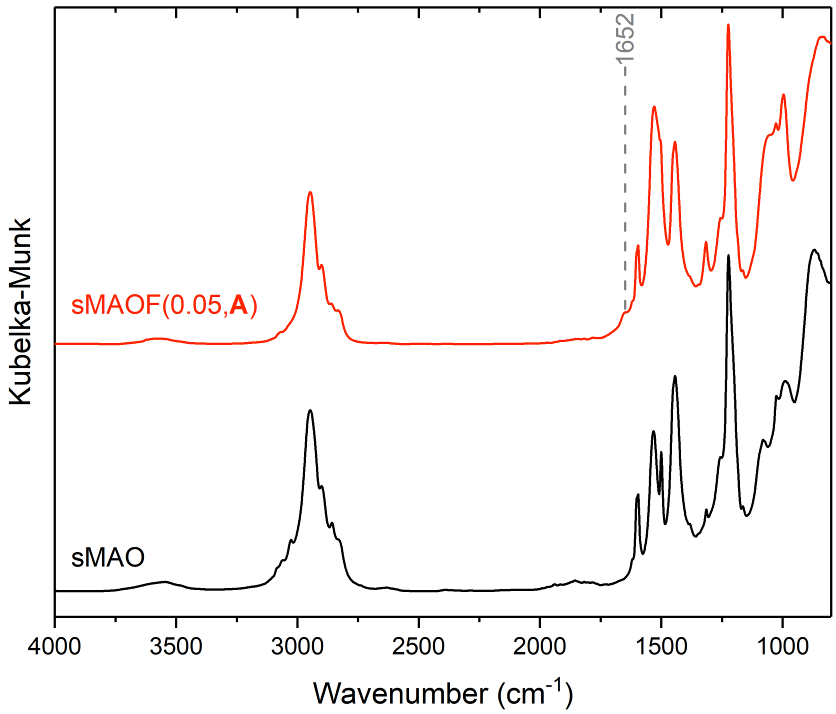


Figure S1 Overlayed DRIFT spectra (NaCl window) of sMAOF(0.05/**A**) (red) and sMAO (black), with IR band assigned to the ν(C=C) stretch of the bridging -OC_6F_4O- group highlighted.

2.2. Solution NMR spectroscopy

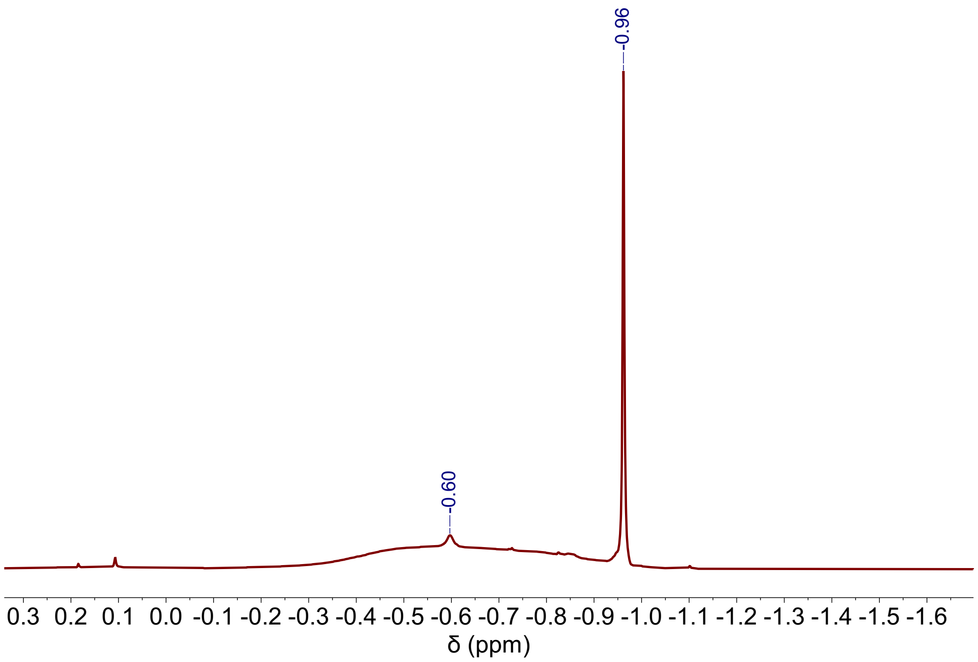


Figure S2 Selected region of ^{1}H NMR spectrum of sMAOF(0.025/**A**) in d_8-THF.

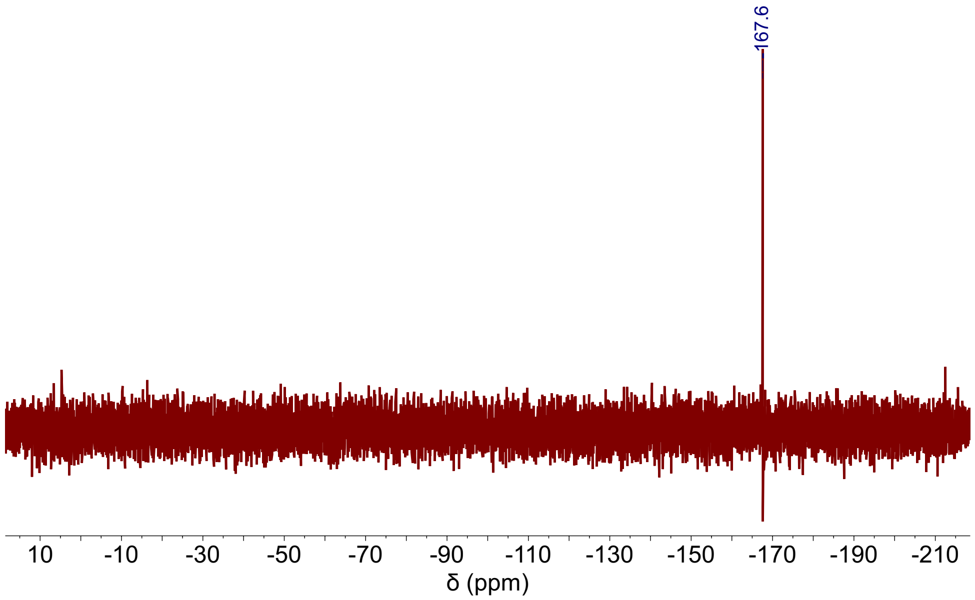


Figure S3 ^{19}F{^{1}H} NMR spectrum of sMAOF(0.025/**A**) in d_8-THF.

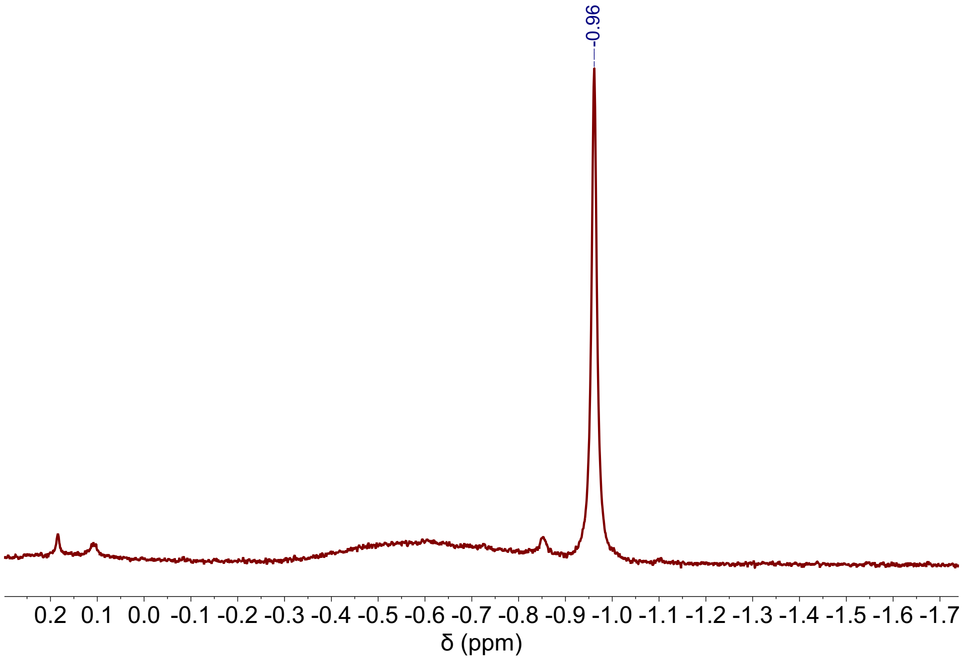


Figure S4 Selected region of ^{1}H NMR spectrum of sMAOF(0.05/**A**) in *d*$_8$-THF.

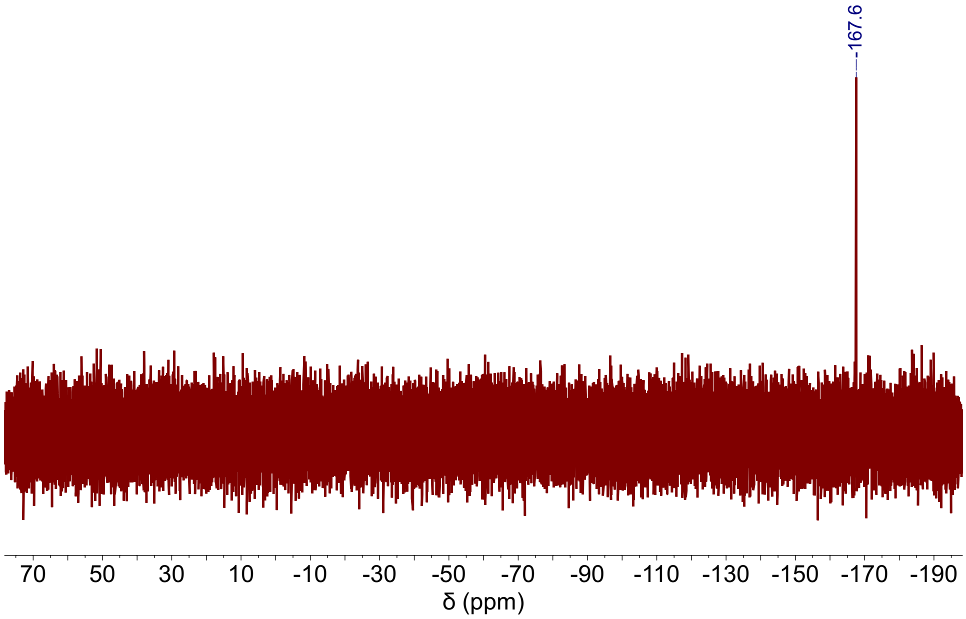


Figure S5 ^{19}F{^{1}H} NMR spectrum of sMAOF(0.05/**A**) in *d*$_8$-THF.

2.3. *Solid state NMR spectroscopy*

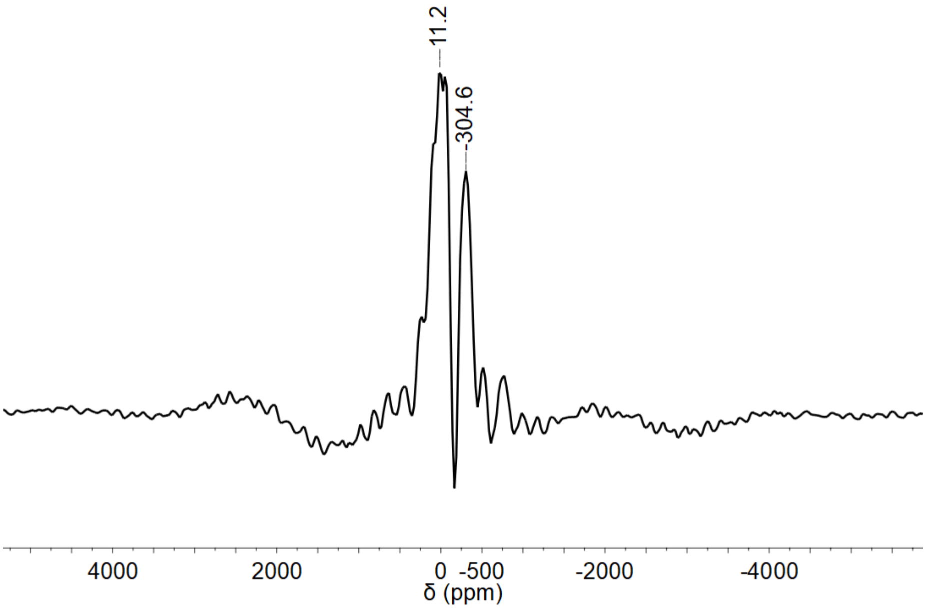


Figure S6 ^{27}Al Hahnecho SSNMR spectrum (15 kHz spinning) of sMAOF(0.05/**A**).

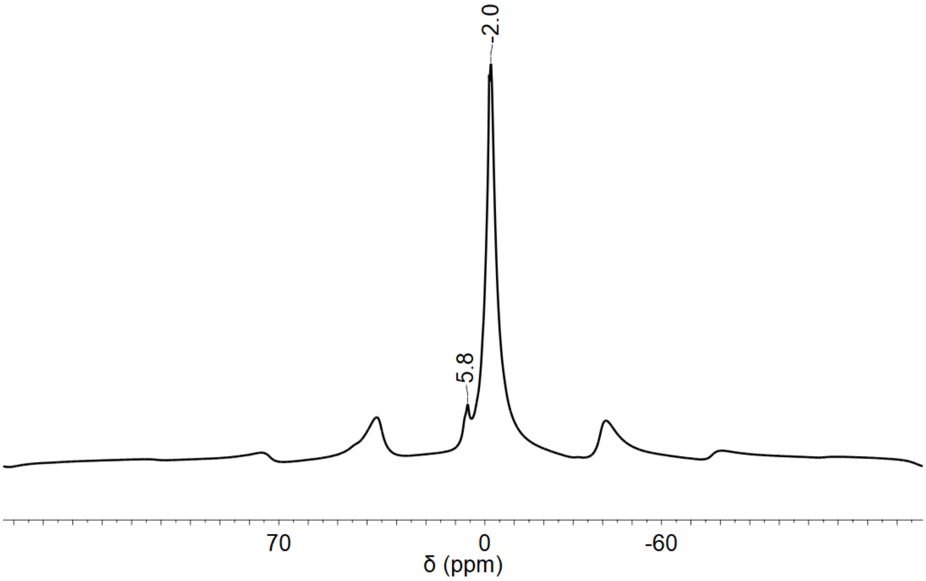


Figure S7 ^{1}H DP-MAS SSNMR spectrum (15 kHz spinning) of sMAOF(0.05/**A**).

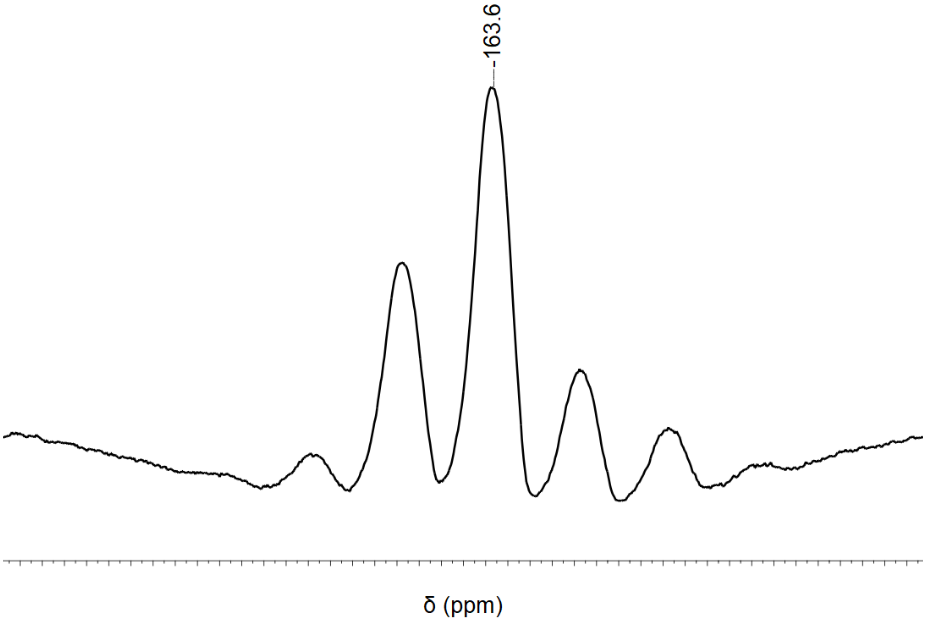


Figure S8 $^{19}F\{^{1}H\}$ DP-MAS SSNMR spectrum (15 kHz spinning) sMAOF(0.05/**A**).

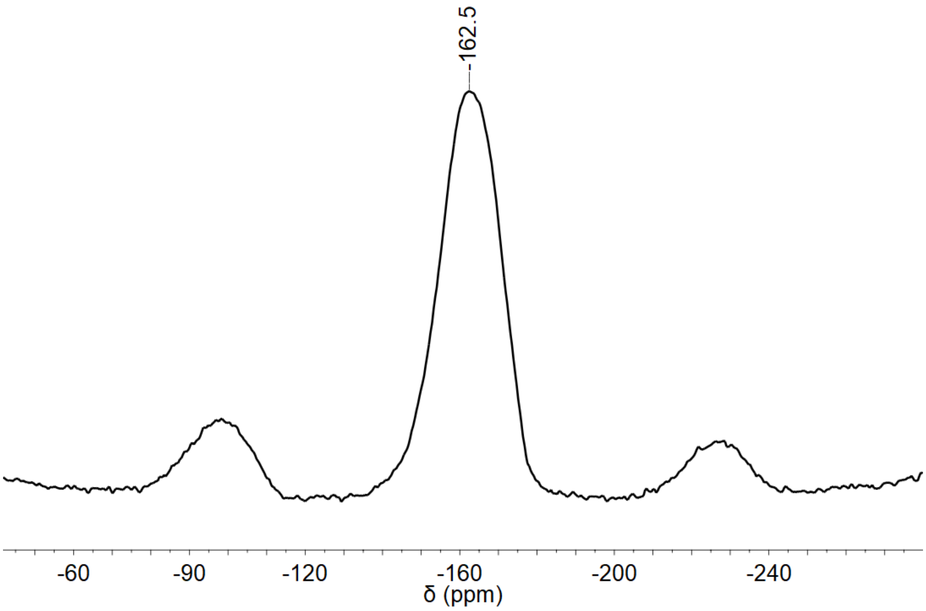


Figure S9 $^{19}F\{^{1}H\}$ DP-MAS SSNMR spectrum (24 kHz spinning) of sMAOF(0.05/**A**).

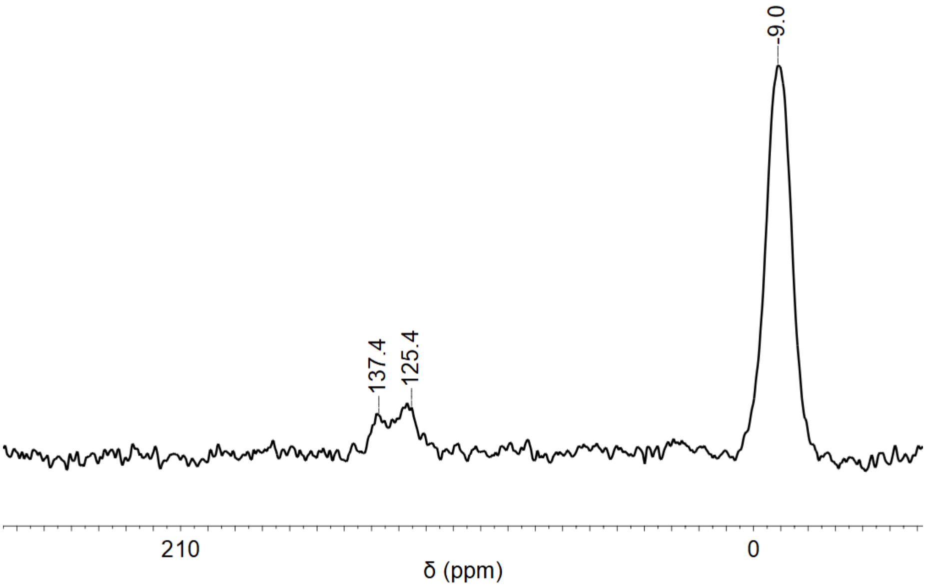


Figure S10 $^{1}H \rightarrow ^{13}C-\{^{19}F\}$ CP-MAS SSNMR spectrum (10 kHz spinning) of sMAOF(0.05/**A**).

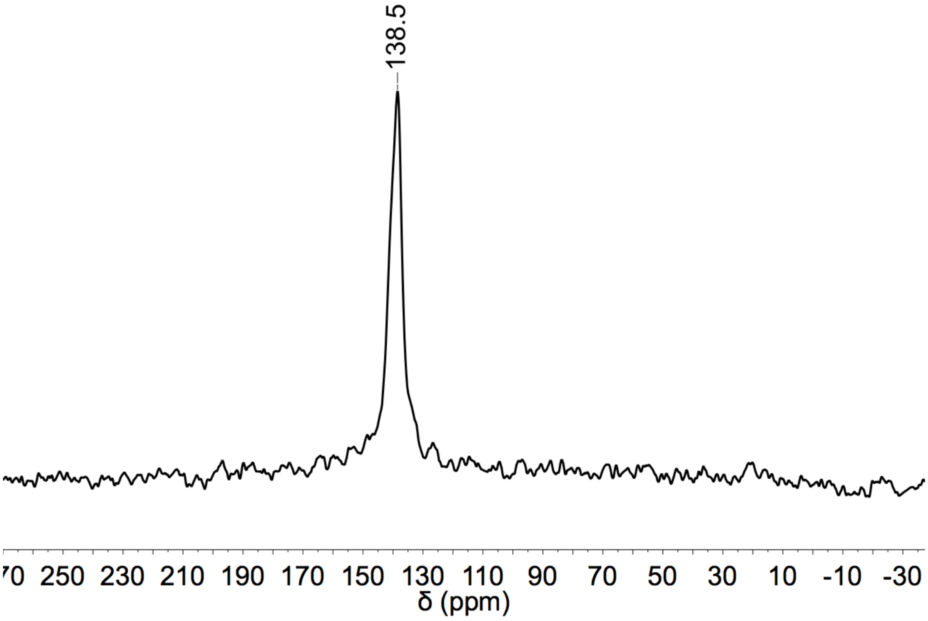


Figure S11 $^{19}F \rightarrow ^{13}C-\{^{1}H\}$ CP-MAS SSNMR spectrum (10 kHz spinning) of sMAOF(0.05/**A**).

2.4. Brunauer–Emmett–Teller (BET) isotherm

Table S1 Calculated BET and *t*-plot parameters for control sMAO sample.

BET surface area: 688.9140 ± 2.3414 m^2/g
Slope: 0.14119 ± 0.00048 g/mmol
Y-intercept: 0.00042 ± 0.00048 g/mmol
C: 336.819112
Qm: 7.06150 mmol/g
Correlation coefficient: 0.9999769
Molecular cross-sectional area: 0.1620 nm^2
t-plot Micropore area: 227.0608 m^{2}g^{-1}
t-plot External area: 461.8532 m^{2}g^{-1}
t-plot Micropore volume: 0.095250 cm^{3}g^{-1}
t-plot Micropore area / External surface area: 0.4916

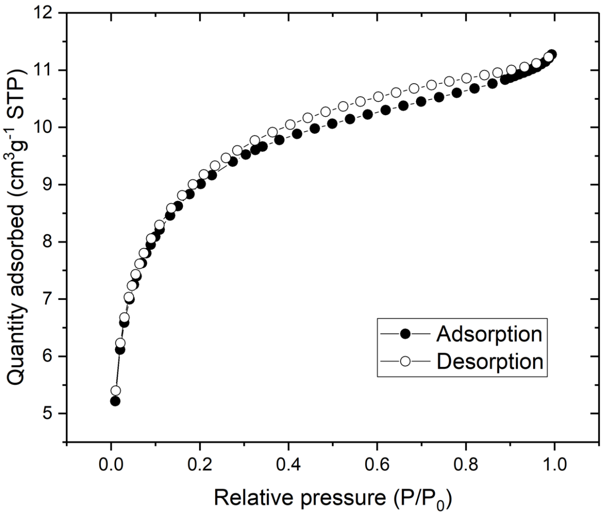


Figure S12 N_2 adsorption/desorption isotherm for sMAOF(0.01,**A**)

Table S2 Calculated BET and *t*-plot parameters for sMAOF(0.01,**A**) sample.

BET surface area: 750.5742 ± 15510 m^2/g
Slope: 0.129157 ± 0.000268 g/mmol
Y-intercept: 0.000823 ± 0.000022 g/mmol
C: 157.987449
Qm: 7.69353 mmol/g
Correlation coefficient: 0.9999893
Molecular cross-sectional area: 0.1620 nm^2
t-plot Micropore area: 358.9935 m^{2}g^{-1}
t-plot External area: 391.5811 m^{2}g^{-1}
t-plot Micropore volume: 0.141227 cm^{3}g^{-1}
t-plot Micropore area / External surface area: 0.9168

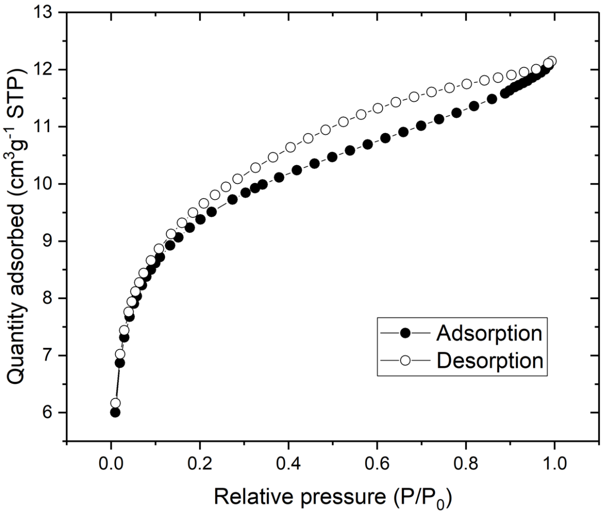


Figure S13 N_2 adsorption/desorption isotherm for sMAOF(0.025,**A**)

Table S3 Calculated BET and *t*-plot parameters for sMAOF(0.025,**A**) sample.

BET surface area: 785.5732 ± 1.8299 m²/g
Slope: 0.12370 ± 0.00029 g/mmol
Y-intercept: 0.00049 ± 0.00002 g/mmol
C: 253.592902
Qm: 8.05228 mmol/g
Correlation coefficient: 0.9999918
Molecular cross-sectional area: 0.1620 nm²
t-plot Micropore area: 456.3522 m^{2}g^{-1}
t-plot External area: 329.2210 m^{2}g^{-1}
t-plot Micropore volume: 0.181389 cm^{3}g^{-1}
t-plot Micropore area / External surface area: 1.386

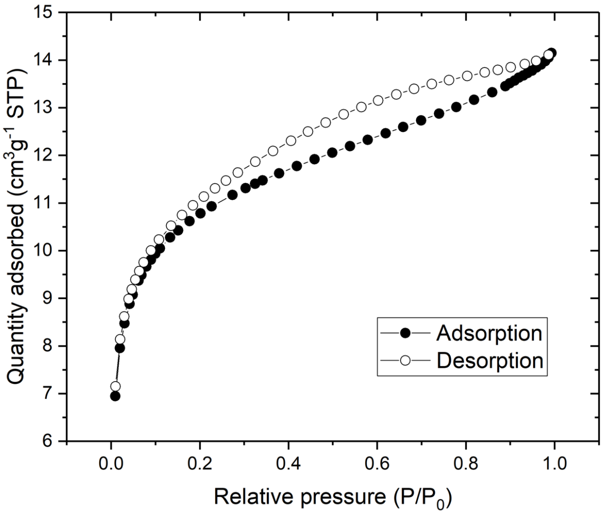


Figure S14 N_2 adsorption/desorption isotherm for sMAOF(0.05,**A**)

Table S4 Calculated BET and *t*-plot parameters for sMAOF(0.05,**A**) sample.

BET surface area: 895.6912 ± 2.8605 m^2/g
Slope: 0.10861 ± 0.00035 g/mmol
Y-intercept: 0.00031 ± 0.00003 g/mmol
C: 345.793024
Qm: 9.18101 mmol/g
Correlation coefficient: 0.9999847
Molecular cross-sectional area: 0.1620 nm^2
t-plot Micropore area: 529.0826 m^2g^{-1}
t-plot External area: 366.6086 m^2g^{-1}
t-plot Micropore volume: 0.213728 cm^3g^{-1}
t-plot Micropore area / External surface area: 1.443

2.5. *Total X-ray scattering studies*

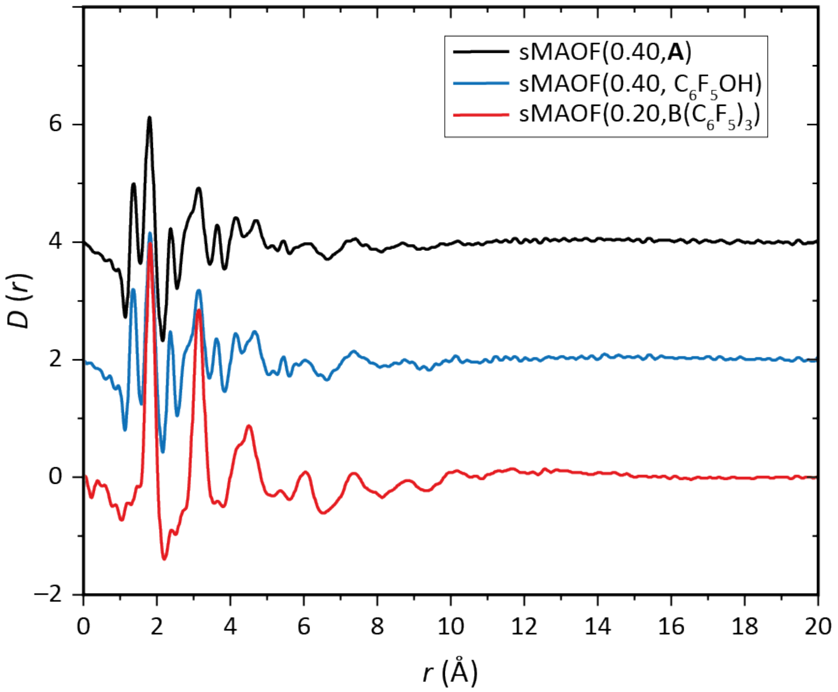


Figure S15 Overlaid X-ray PDFs of the sMAOF(0.40,**A**) and previously reported sMAOF(0.40,C_6F_5OH), and sMAOF(0.20,$B(C_6F_5)_3$).

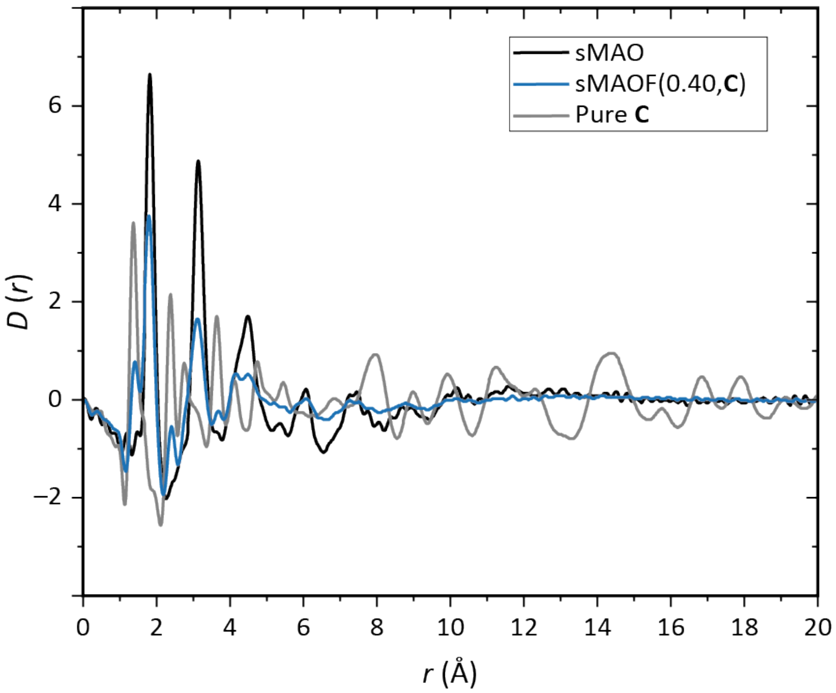


Figure S16 Overlaid X-ray PDFs of the control sMAO sample, sMAOF(0.40,**C**) and the pure modifier compound **C**.

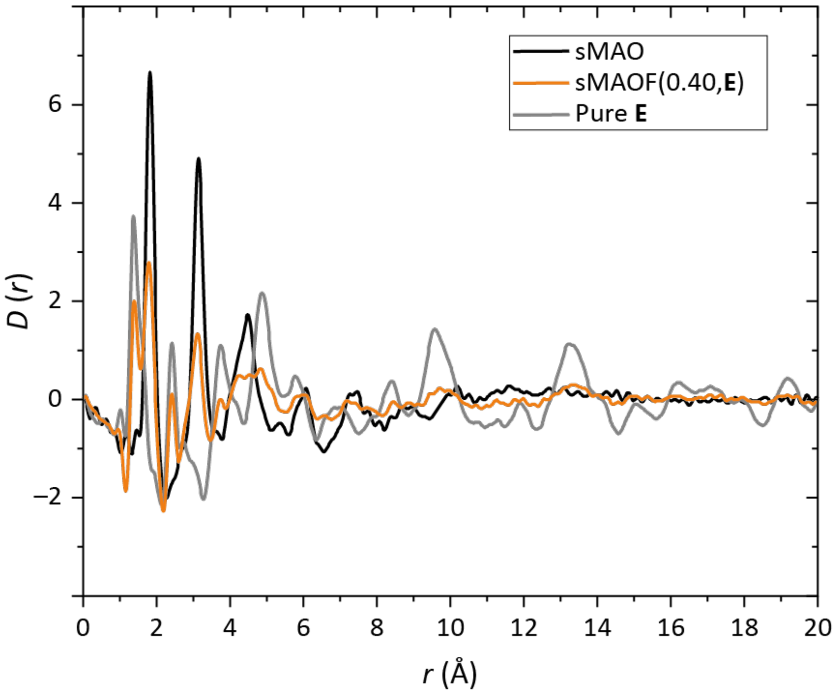


Figure S17 Overlaid X-ray PDFs of the control sMAO sample, sMAOF(0.40,**E**) and the pure modifier compound **E**.

2.6. *Scanning Electron Microscopy with Energy Dispersive X-ray (SEM-EDX) spectroscopy*

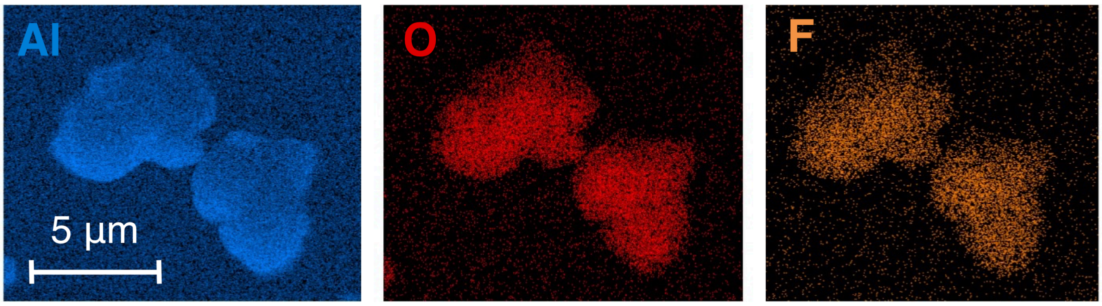
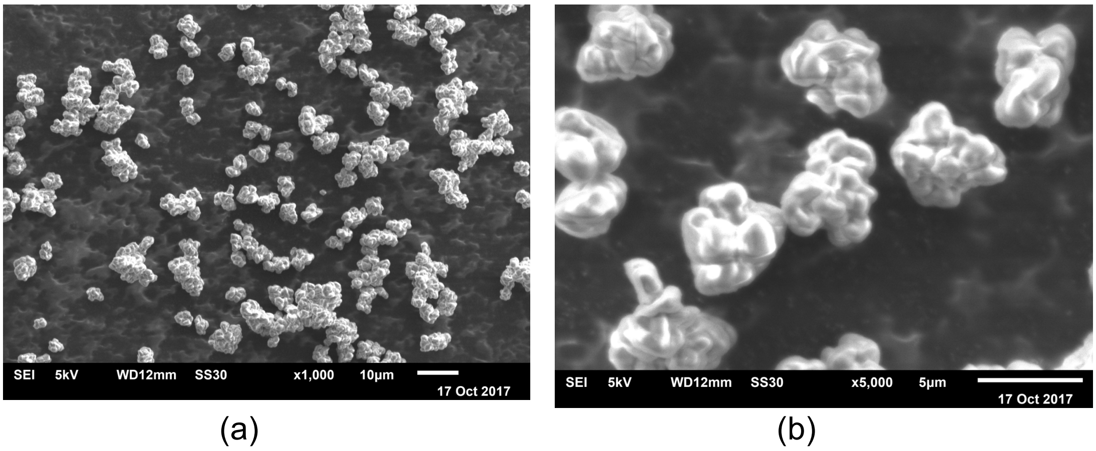


Figure S18 SEM micrograph of sMAOF(0.40,**A**) particles with corresponding Al, (blue), O (red), and F (orange) elemental maps, as determined by EDX spectroscopy.

2.7. *Scanning Electron Microscopy of sMAOF samples*



(a) (b)

Figure S19 SEM images of sMAOF(0.025,**A**) at (a) x1,000 and (b) x5,000 magnification.

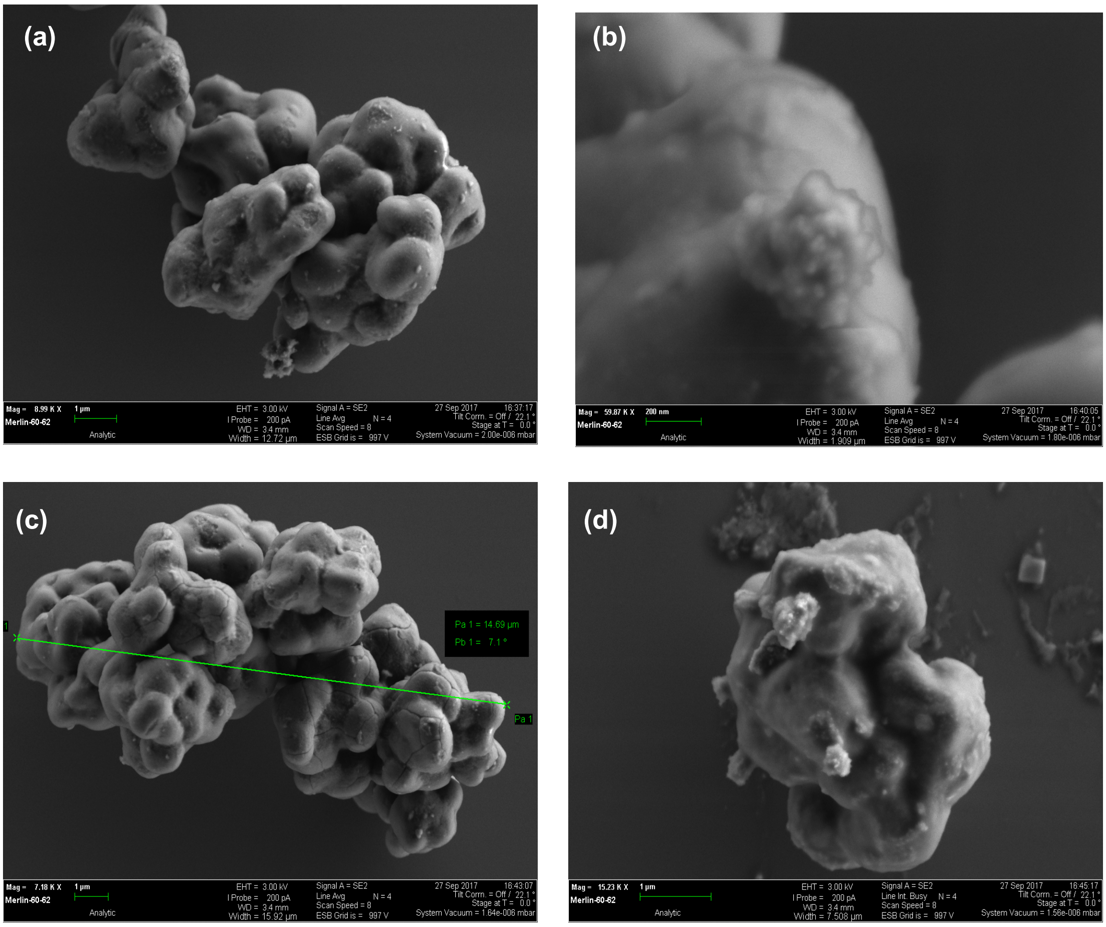
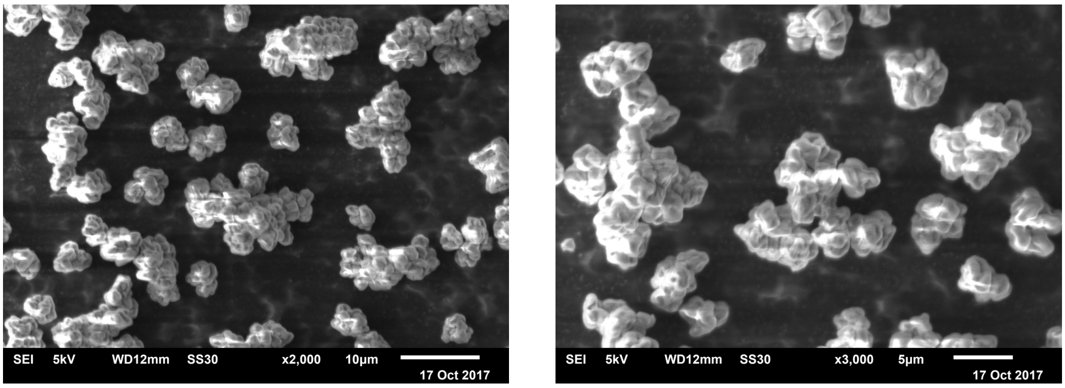
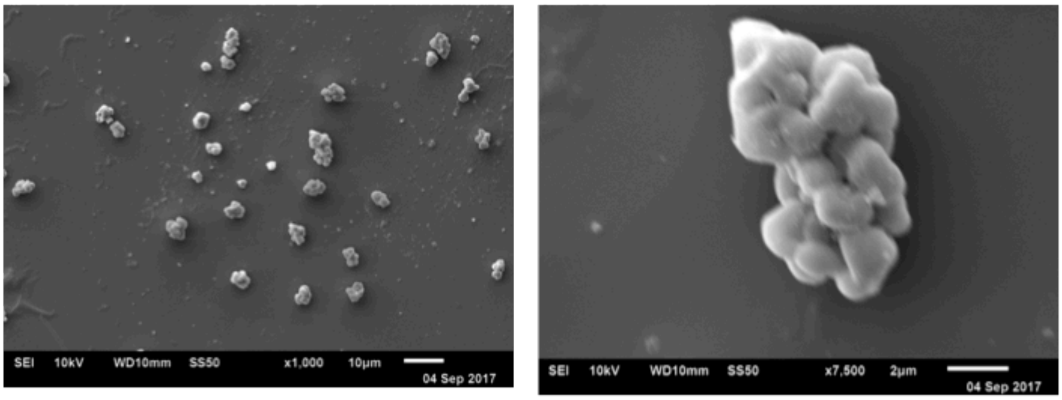


Figure S20 SEM images of sMAOF(0.025,**A**) at (a) x8.99k (b) x59.87k (c) 7.18k and (b) x15.23k magnification.



(a) (b)

Figure S21 SEM images of sMAOF(0.025,**C**) at (a) x2,000 and (b) x3,000 magnification.



(a) (b)

Figure S22 SEM images of sMAOF(0.025,**E**) at (a) x1,000 and (b) x7,500 magnification.

3. Slurry phase ethylene polymerisation studies

3.1. Additional polymerisation data

Table S5 Slurry-phase ethylene polymerisation and GPC data for (EBI)$ZrCl_2$–sMAOF(**A**) catalysts with different $HO(C_6F_4)OH$ modifier loadings.

Modifier loading $([M]_0/[Al_{sMAO}]_0)$	**Productivity** $(kg_{PE}g_{CAT}^{-1}h^{-1})$	**Activity** $(kg_{PE}mol_{Zr}^{-1}h^{-1})$	**SD**	M_w (kg mol^{-1})	**PDI** (M_w/M_w)
0	0.905	11896	572	99.4	3.6
0.01	0.920	12780	94	119.4	4.3
0.025	0.964	15675	803	108.2	4.1
0.05	0.163	3435	1407	246.2	4.1

Polymerisation conditions: 10.0 mg_{CAT}*, 2 bar,* 70 °C *50 mL hexanes, 150 mg TIBA.*

Table S6 Slurry-phase ethylene polymerisation and GPC data for (EBI)$ZrCl_2$–sMAOF(0.025,**A**) catalysts at different zirconocene complex loadings.

$[Al_{sMAOF}]_0/[Zr]_0$	**Productivity** $(kg_{PE}g_{CAT}^{-1}h^{-1})$	**Activity** $(kg_{PE}mol_{Zr}^{-1}h^{-1})$	**SD**	M_w (kg mol^{-1})	**PDI** (M_w/M_w)
50	0.694	3265	177	75.1	3.7
100	0.856	7673	300	112.2	4.2
150	0.850	11249	29	123.0	4.2
200	0.832	14209	803	108.2	4.1

Polymerisation conditions: 10.0 mg_{CAT}*, 2 bar,* 70 °C *50 mL hexanes, 150 mg TIBA.*

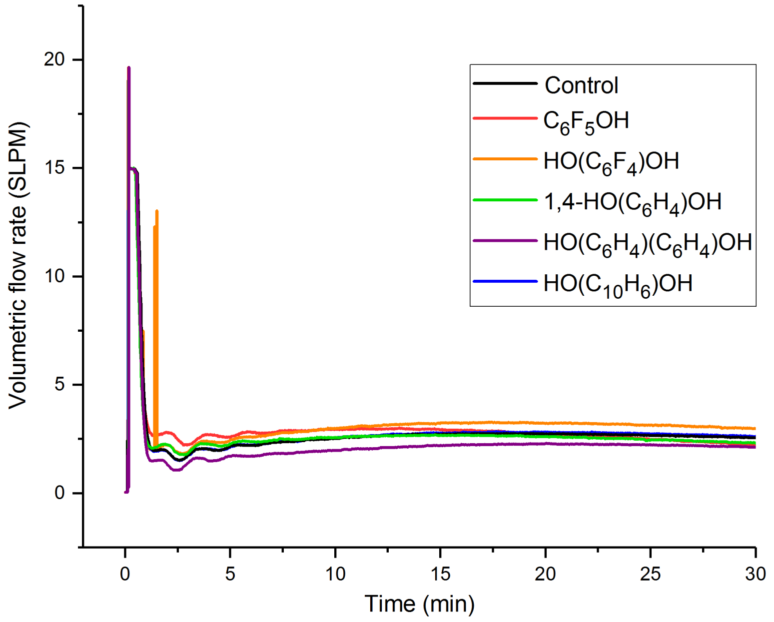


Figure S23 Ethylene flow in standard litre per minute (SLPM) during scale-up polymerisation for (EBI)$ZrCl_2$–sMAOF(0.025,M) catalysts. Polymerisation conditions: 25 mg catalyst, 8 bar C_2H_4, 80 °C, $AlEt_3$ = 2.5 mL, hexanes (1000 mL).

3.2. *Scanning electron microscopy (SEM) imaging of polyethylene samples*

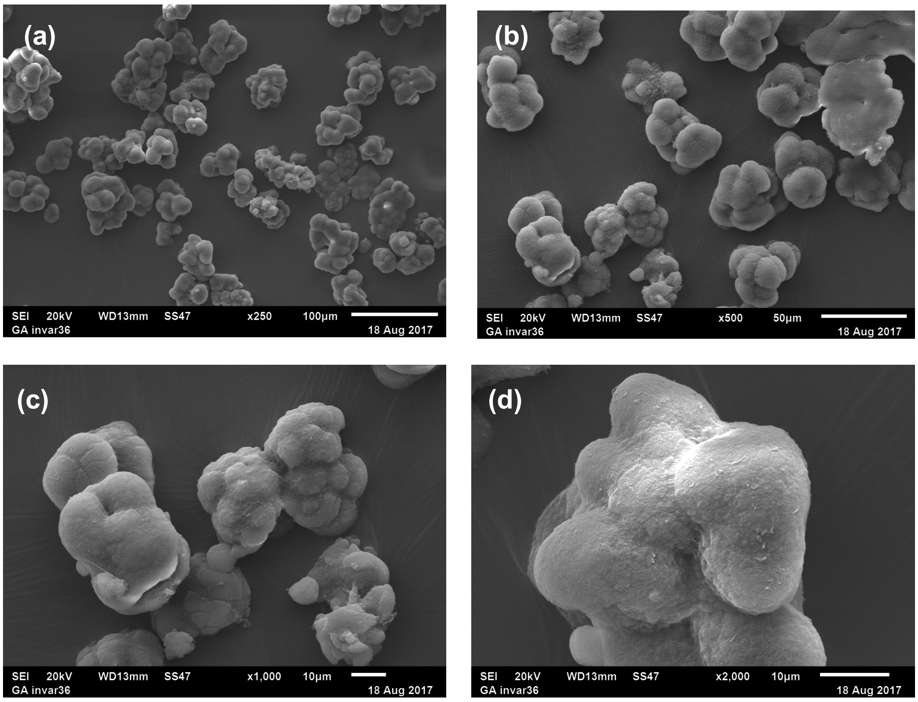


Figure S24 SEM images at (a)×250, (b)×500, (c)×1000 and (d)×2000 magnification of PE samples produced from a(EBI)ZrCl$_2$–sMAOF(0.025,**A**) catalyst system.

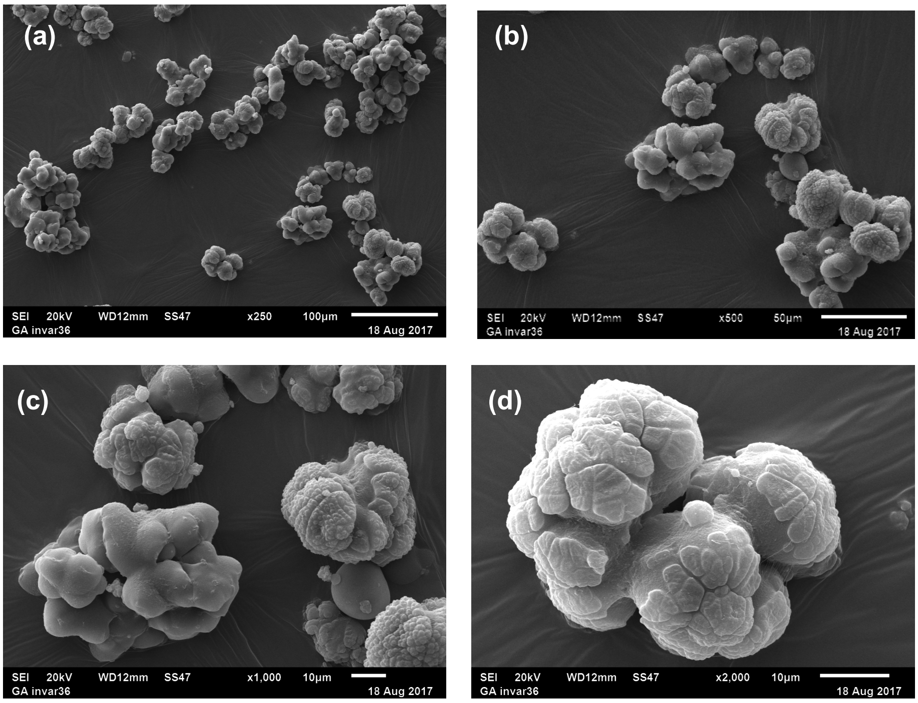


Figure S25 SEM images at (a)×250, (b)×500, (c)×1000 and (d)×2000 magnification of PE samples produced from a(EBI)ZrCl$_2$–sMAOF(0.05,**A**) catalyst system.

3.3. Gel permeation chromatography (GPC) of polyethylene samples

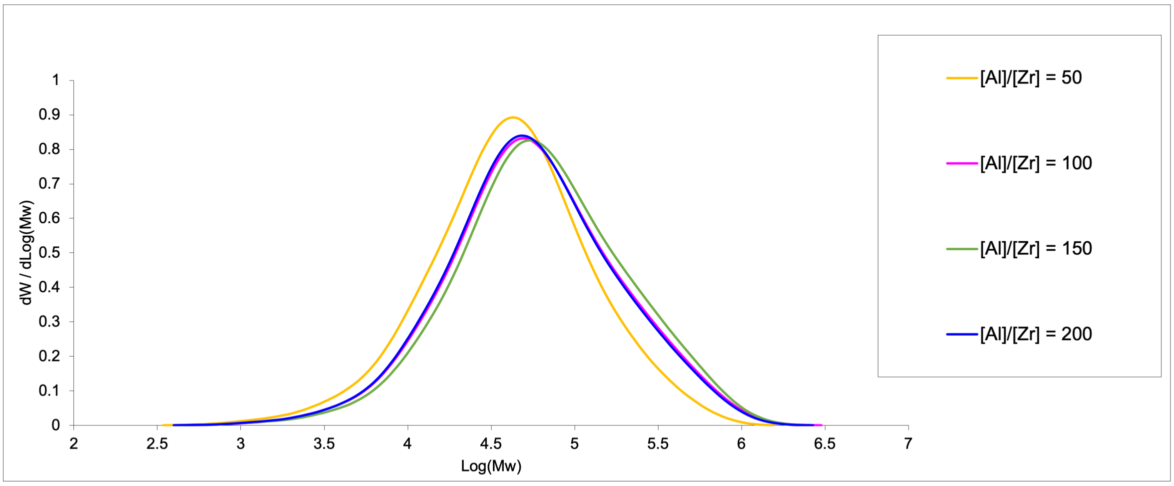


Figure S26 Overlaid GPC traces of PE samples produced from (EBI)$ZrCl_2$–sMAOF(0.025,**A**) catalysts at different zirconocene complex loadings.

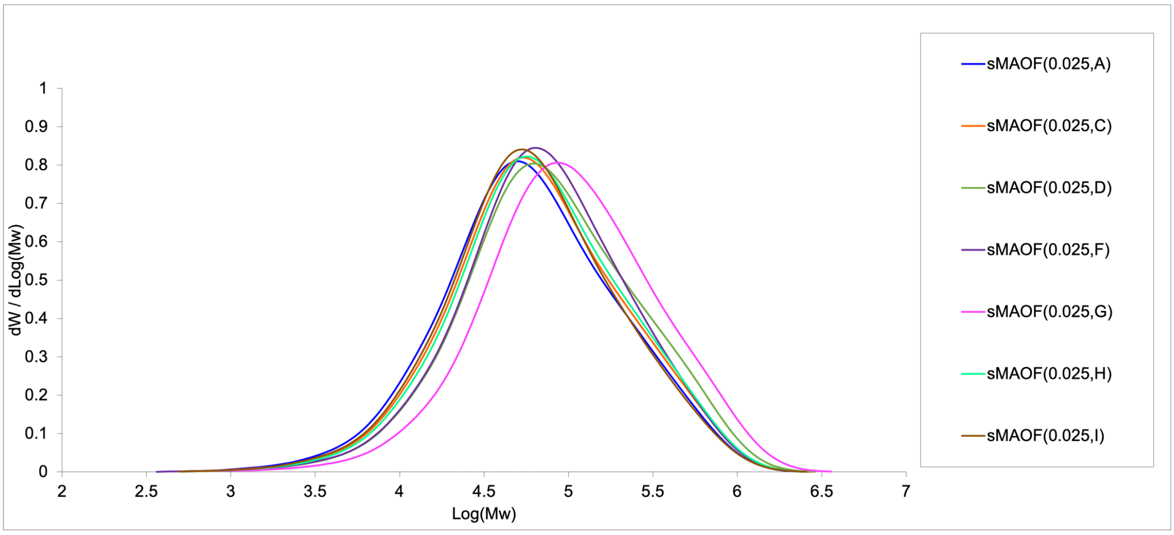


Figure S27 Overlaid GPC traces of PE samples produced from (EBI)$ZrCl_2$–sMAOF(0.025,M) catalysts at target loading $[Al_{sMAO}]_0/[Zr]_0 = 200$.

4. References

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