Supporting Information for

Ethylene Polymerization with a Crystallographically

Well-Defined Metal–Organic Framework Supported Catalyst

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Materials

Acetone, *N,N*-dimethylformamide (DMF), hydrochloric acid were purchased from Fisher Scientific (Waltham, MA) and used as received. Benzoic acid, trifluoroacetic acid (TFA), zirconyl chloride octahydrate, chromium(II) chloride (99.99% trace metals), and 1.0 M diethylaluminum chloride (DEAC) in heptane were purchased from Sigma-Aldrich (St. Louis, MO) and used as received. ***Caution diethylaluminum chloride is pyrophoric and should only be handled under an inert atmosphere and with care***. Anhydrous heptane was purchased from Sigma-Aldrich and further dried by soaking over 3 Å molecular sieves. *N,N*-diethylformamide (DEF) was purchased from TCI America (Portland, OR) and used as received. UHP N_2 (99.999%), UHP Ar (99.999%), and UHP ethylene (99.9%) were purchased from Airgas (Radnor, PA) and used as received. 1,3,6,8-tetrakis(p-benzoic acid)pyrene (H_4TBAPy) was synthesized based on literature procedure.[1]

Methods

NU-1000 Powder Synthesis. 1,3,5,8-tetrakis(p-benzoic acid)pyrene, was synthesized according to reported procedure.[1] NU-1000 was synthesized, acid activated, and washed according to previously published procedures.[1,2]

Cr-SIM-NU-1000 Powder Synthesis. Cr-SIM-NU-1000 was prepared by previously reported procedure.[3] Cr-SIM-NU-1000 was prepared by mixing 200 mg NU-1000 into 25 mL of a 0.1 M $CrCl_2$ solution in *N,N*-dimethylformamide (DMF) and heated overnight at 100 °C. The sample was washed with fresh DMF (3 x 40 mL). Then the sample was washed with acetone (3 x 40 mL) to exchange the solvent to remove DMF and left to soak overnight in fresh acetone. The sample was dried at 80 °C in a vacuum oven for 2 hours, and then thermally activated at 120 °C under dynamic vacuum on a Smart VacPrep for 16 hours.

DEAC@Cr-SIM-NU-1000 Powder Synthesis. Freshly DMF washed Cr-SIM-NU-1000 powder was solvent exchanged to acetone by washing 3 times and then soaking overnight. Then, after decanting the acetone, the powder was placed in a vacuum oven at 80 °C for 3 hours. Then, it was thermally activated at 120 °C under dynamic vacuum on a Smart VacPrep for 16 hours. The powder was then transferred into an Ar filled glovebox. Next, it was soaked in anhydrous heptane before decanting the solvent and exposing the powder to 1.0 M diethylaluminum chloride in heptane consistent with the catalysis experiments. After 1 h, the solvent was decanted and exchanged for fresh heptane 3 times with a 30 min. soaking period in between. The solvent was then exchanged to pentane, where the powder was allowed to soak for a total of 1.5 h during which 3 washes and subsequent soaks were performed. After decanting as much pentane as possible, the powder was held under dynamic vacuum on a Smart VacPrep for 16 hours.

NU-1000 Single Crystal Synthesis. Single crystals of NU-1000 were prepared by previously reported procedure.[3] 70 mg $ZrCl_4$ and 2 g benzoic acid were dissolved in 6 mL *N,N*-diethylformamide (DEF) *via* sonication in an 8-dram vial. 40 mg H_4TBAPy was suspended in 4 mL DEF *via* sonication in a separate 8-dram vial. Both vials were incubated in a preheated oven at 100 °C for 1 h. The vials were then removed from the oven and allowed to cool to room temperature. Subsequently, the linker solution was added to the node solution and 40 µL TFA was also added. After brief sonication to ensure homogeneous distribution of the solutions, the vial was placed in a sand bath before being placed in a preheated oven at 120 °C overnight. After allowing

the vial to cool to room temperature the crystals were DMF washed and acid activated similarly to the powder, with 0.5 mL 8 M HCl in 12 mL DMF at 100 °C overnight. Lastly, they were washed 3 times with fresh DMF.

Cr-SIM-NU-1000 Single Crystal Synthesis. Freshly washed NU-1000 single crystals were subjected to a 0.1 M $CrCl_2$ solution in DMF at 100 °C overnight. After cooling to room temperature, the unreacted $CrCl_2$ was washed away with fresh DMF aliquots.

DEAC@Cr-SIM-NU-1000 Single Crystal Synthesis. Freshly DMF washed Cr-SIM-NU-1000 single crystals were solvent exchanged to ethanol by washing 3 times and then soaking overnight. Then, in as minimal ethanol as possible, the crystals were transferred to a glass dish for supercritical CO_2 activation. Using a supercritical CO_2 drier, the ethanol was exchanged with liquid CO_2 and dry crystals were obtained. The crystals were then transferred into an Ar filled glovebox. Next, they were soaked in anhydrous heptane before decanting the solvent and exposing the crystals to 1.0 M diethylaluminum chloride in heptane consistent with the powder experiments. After 1 h, the solvent was decanted and exchanged for fresh heptane 3 times with a 30 min. soaking period in between.

Ethylene Polymerization
In an Ar filled glovebox, 10 mg Cr-SIM-NU-1000, 5 mL anhydrous heptane, and 1.0 mL of diethylaluminum chloride (1.0 M in heptane) were charged into a 50 mL 4590 micro bench top autoclave Parr reactor. The reactor was then sealed, transferred out of the glovebox and connected to the gas inlet, pressure gauge, and thermocouple at the reactor station. The reactor was then set to stir at 200 rpm and pressurized to between 5 and 40 bar with C_2H_4. After 1 hour, the reaction was vented and opened, after which the solid polymer was recovered for analysis.

Analytical Measurements
Powder X-ray diffraction (PXRD) data was collected at the IMSERC X-ray Facility at Northwestern University on a STOE-STADI-P powder diffractometer equipped with an asymmetric curved Germanium monochromator (CuKα1 radiation, λ = 1.54056 Å) and one-dimensional silicon strip detector (MYTHEN2 1K from DECTRIS). The line focused Cu X-ray tube was operated at 40 kV and 40 mA. Powder was packed in a 3 mm metallic mask and sandwiched between two layers of polyimide tape. Intensity data from 1 to 40 degrees 2θ were collected over a period of 5 mins.

N_2 adsorption isotherms were measured on a Micromeritics Tristar II 3020 (Micromeritics, Norcross, GA) at 77 K with 30-80 mg pre-activated sample at 120 °C for 16 h under high vacuum using a Smart VacPrep (Micromeritics, Norcross, GA). BET area was calculated in the region P/P_0 = 0.005-0.05 and pore-size distributions were obtained *via* density functional theory (DFT) calculations using a carbon slit-pore model with a N_2 kernel.

Inductively coupled plasma optical-emission spectroscopy (ICP-OES) was performed at the QBIC facility at Northwestern University on a Thermo iCAP 7600 Spectrometer (ThermoFisher, Waltham, MA). In each preparation, ~3 mg samples were digested in 2 mL concentrated nitric acid in a 2-5 mL Biotage (Uppsala, Sweden) microwave vial. Biotage SPX microwave reactor

(software version 2.3, build 6250) was used to heat the mixture to 150 °C for 15 min. 300 μL of the digested sample was removed and diluted to 10 mL with ultrapure Millipore water.

Supercritical CO_2 drying was performed using a Tousimis Samdri-PVT-3D supercritical CO_2 drier, exchanging ethanol for supercritical CO_2 five times with a minimum soaking time of 1 h between exchanges. The temperature was then increased to the supercritical point and the instrument pressure was bled at 0.5 cm^3/min.

Single-crystal X-ray diffraction (SC-XRD) intensity data of a yellow-green rod crystal were collected at 200 K. A suitable single crystal was mounted on a MiTeGen loop with paratone oil on an XtaLAB Synergy diffractometer equipped with a micro-focus sealed X-ray tube PhotonJet (Cu) X-ray source and a Hybrid Pixel Array Detector(HyPix) detector. Temperature of the crystal was controlled with an Oxford Cryosystems low-temperature device. Data reduction was performed with the CrysAlisPro software using an empirical absorption correction. The structure was solved with the ShelXT structure solution program using the Intrinsic Phasing solution method and by using Olex2 as the graphical interface. The model was refined with ShelXL using least squares minimization. The CIF has been deposited in the Cambridge Crystallography Data Centre under Deposition #2115104 and is freely accessible at https://www.ccdc.cam.ac.uk/.

Scanning electron microscopy (SEM) images were collected at Northwestern University's EPIC/NUANCE facility using an FEI Quanta 650 ESEM microscope. All samples were coated with 9 nm OsO_4 before imaging.

Catalysis experiments were conducted at the Reactor Engineering and Catalyst Testing (REACT) core facility at Northwestern University using a 50 mL 4590 micro bench top autoclave Parr reactor (Parr Instruments, Moline, IL) connected to a gas manifold and a 4838 Reactor Controller (Parr Instruments, Moline, IL).

Gel permeation chromatography (GPC) measurements were conducted in the Chemical Science and Engineering Division at Argonne National Laboratory (ANL) using a high-temperature GPC (Agilent-Polymer Laboratories 220) equipped with refractive index and viscometer detectors. Monodisperse polystyrene standards were used for calibration (ranging from 400 Da to 1.1 MDa). The column set included 3 Agilent PL-Gel Mixed B columns and 1 PL-Gel Mixed B guard column. 1,2,4-trichlorobenzene (TCB) containing 0.01 wt% 3,5-di-tert-butyl-4-hydroxytoluene (BHT) was chosen as the eluent with a flow rate of 1.0 mL/min at 150 °C. Samples were prepared in TCB at a concentration of ~1 – 2 mg/mL and heated at 130 °C for 24 h prior to injection.

[13]C Cross Polarization/Magic Angle Spinning (CP/MAS) solid-state nuclear magnetic resonance (NMR) spectroscopy was conducted at room temperature on a a Bruker Avance III 400 MHz spectrometer equipped with a 4mm HX probe. Sample data was acquired using TopSpin™ by Bruker. ^{13}C CP/MAS NMR data were collected using a spin rate of 10 KHz and a contact time (p15) of 5 ms at room temperature. D1 was set to 5.00 sec, SW was set to 296 ppm, and O1P was set to 100 ppm. 12,000 scans were used for ^{13}C CP/MAS NMR data collection. Samples were loaded neat into a 4 mm cylindrical zirconia rotor sealed with a Kel-F cap, both from Bruker. ^{13}C CP/MAS NMR spectra were referenced to an external adamantane peak at δ 38.3 and were

converted to tetramethylsilane at δ 0.0. NMR spectra were reported after phase correction in MestReNova (MNova) by Mestrelab Research.

^{1}H and ^{13}C solution state NMR spectroscopy was conducted on a Bruker Avance III 600 MHz system equipped with two RF channels (^{1}H = 600 MHz, ^{13}C = 150 MHz). Sample data was acquired using TopSpin™ by Bruker. All collected spectra were referenced to residual solvent signals. NMR spectra were processed and integrated using Mnova by Mestrelab Research, following phase correction and baseline correction (Whittaker smoother). Initial ^{1}H solution state NMR spectra of the polymer product were collected in 1,1,2,2-tetrachloroethane-d_2 at 120 °C with 25 scans. D1 was set to 5.00 sec, SW was set to 16 ppm, and O1P was set to 6 ppm. Next, ^{13}C solution state NMR spectra of the polymer product were collected in 1,1,2,2-tetrachloroethane-d_2 at 120 °C with 18,000 scans. D1 was set to 2.00 sec, SW was set to 240 ppm, and O1P was set to 100 ppm. After ^{13}C solution state NMR data collection finished, final ^{1}H solution state NMR spectra of the polymer product were collected in 1,1,2,2-tetrachloroethane-d_2 at 120 °C with 25 scans. D1 was set to 5.00 sec, SW was set to 16 ppm, and O1P was set to 6 ppm. The polymer product was heated at 120 °C in 1,1,2,2-tetrachloroethane-d_2 prior to NMR data collection to aid in solubilization.

Differential scanning calorimetry (DSC) experiments were conducted using a Mettler Toledo TGA/DSC 1 LF and corresponding STARe software (v16.10). For DSC of polymers, samples were heated in 70 µL alumina crucibles under N_2 at 10 °C/min. from 25 °C to 200 °C and then cooled from 200 °C to 25 °C for two cycles.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were conducted using a Thermo Scientific Nicolet iS50 FT-IR spectrometer equipped with an MCT-A detector cooled to 77 K. A Harrick Scientific Praying Mantis™ Diffuse Reflectance accessory was used to acquire spectra under air- and moisture-free conditions. Samples were prepared inside of a glovebox with argon atmosphere and DRIFTS spectra were collected under this atmosphere. KBr was used as a background for spectra. The collected spectra were processed using the Kubelka-Munk function.

X-ray photoelectron spectra were collected at the Keck-II/NUANCE facility at Northwestern University using a Thermo Scientific ESCALAB 250Xi (Al Kα radiation, 1486.6 eV). All measurements were performed with an electron flood gun and were calibrated to C1s peak at 284.8 eV.

Productivity Calculations
Productivity (g PE mol^{-1} Cr h^{-1}) = mass of polymer isolated / (mol Cr in MOF catalyst * experiment duration)

Turnover Frequency Calculations
TOF (h^{-1}) = mol ethylene consumed / (mol Cr in MOF catalyst * experiment duration)
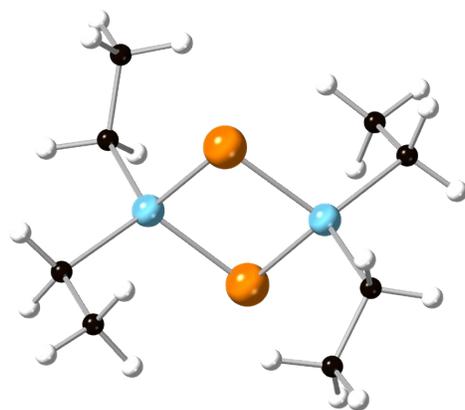
Figure S1. Structure of diethylaluminum chloride, which exists as a dimer at room temperature. Atom colors: Hydrogen (white), Carbon (black), Chlorine (orange), Aluminum (light blue).
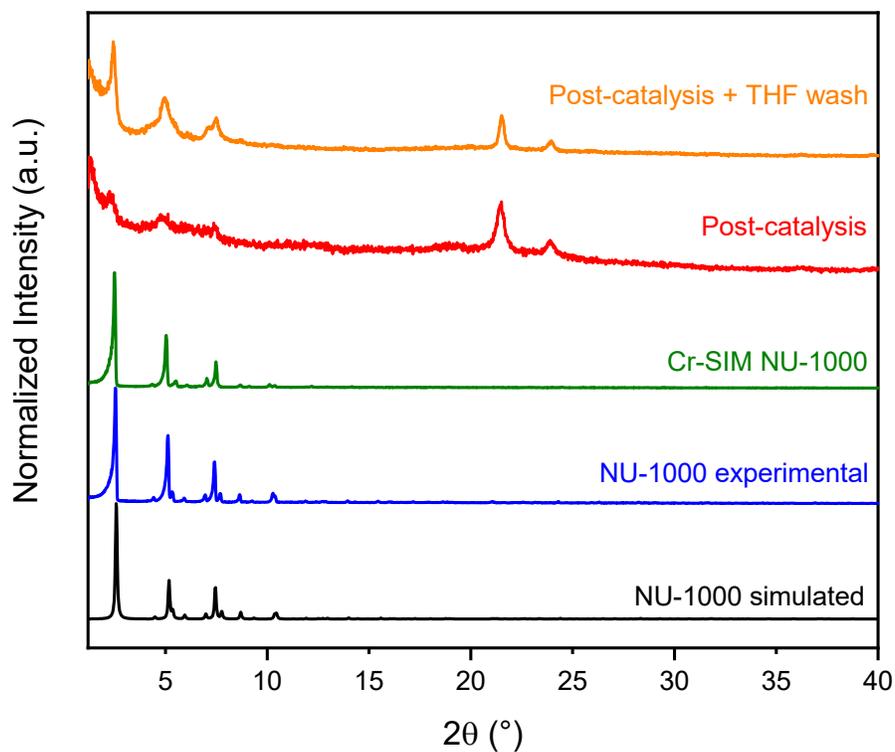
Figure S2. Powder X-ray diffraction patterns of NU-1000 simulated (black) and experimental (blue), Cr-SIM-NU-1000 (green), Cr-SIM-NU-1000 post-catalysis (red), and Cr-SIM-NU-1000 post-catalysis washed with THF (orange).
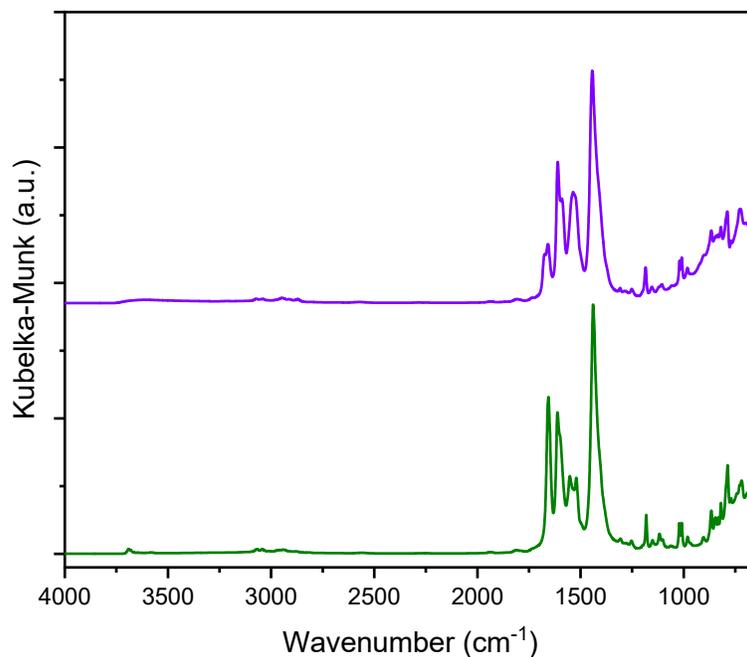
Figure S3. Diffuse reflectance infrared Fourier transform (DRIFT) spectra of Cr-SIM-NU-1000 (green) and DEAC@Cr-SIM-NU-1000 (purple).
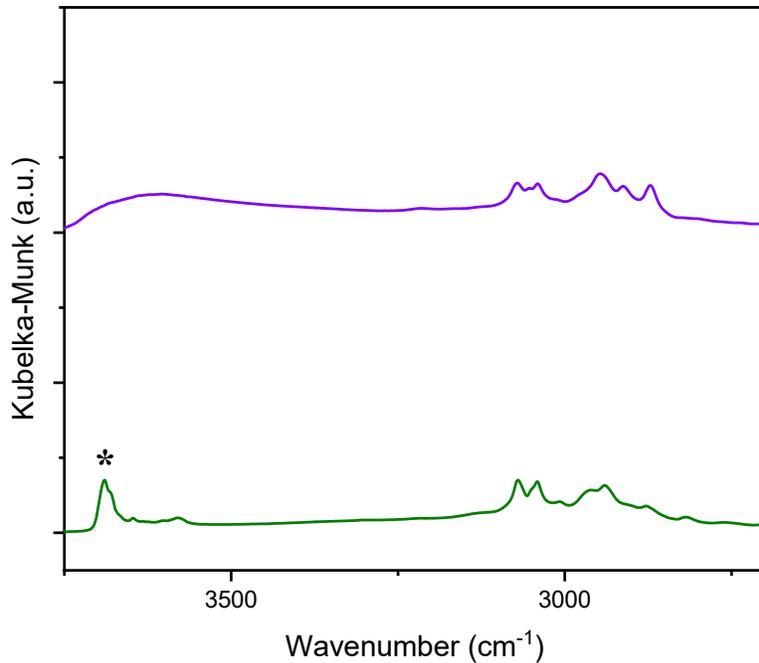
Figure S4. Zoomed in higher wavenumber region of the diffuse reflectance infrared Fourier transform (DRIFT) spectra of Cr-SIM-NU-1000 (green) and DEAC@Cr-SIM-NU-1000 (purple) showing the loss of the hydroxyl peak upon treatment with DEAC.
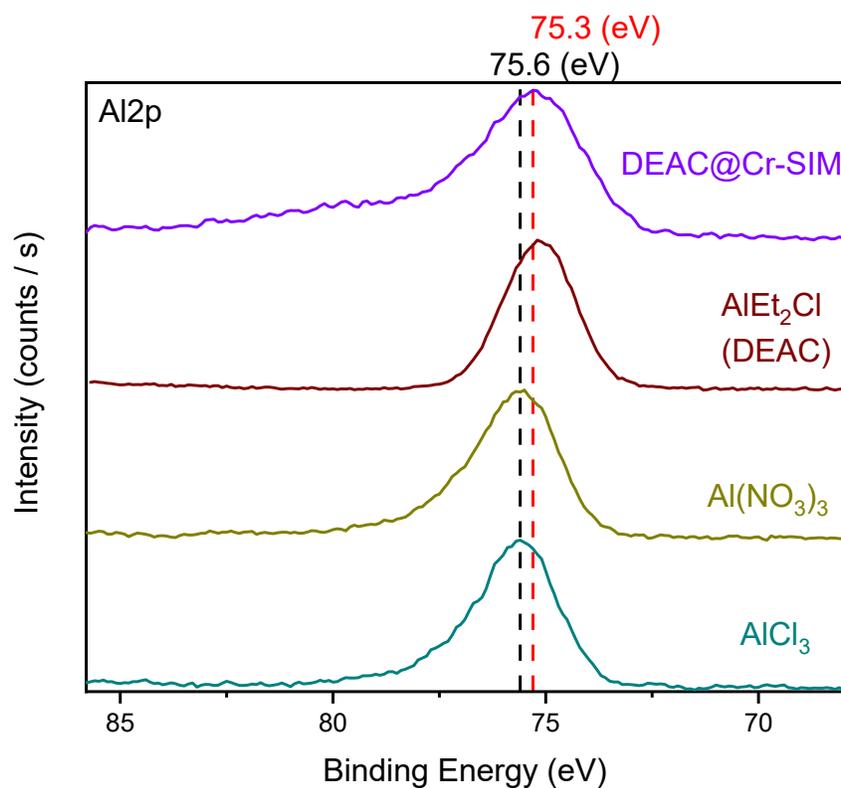
Figure S5. Al 2p X-ray photoelectron spectra (XPS) of DEAC@Cr-SIM-NU-1000 (purple), DEAC (brown), and two other Al salts: $Al(NO_3)_3$ (yellow) and $AlCl_3$ (teal).
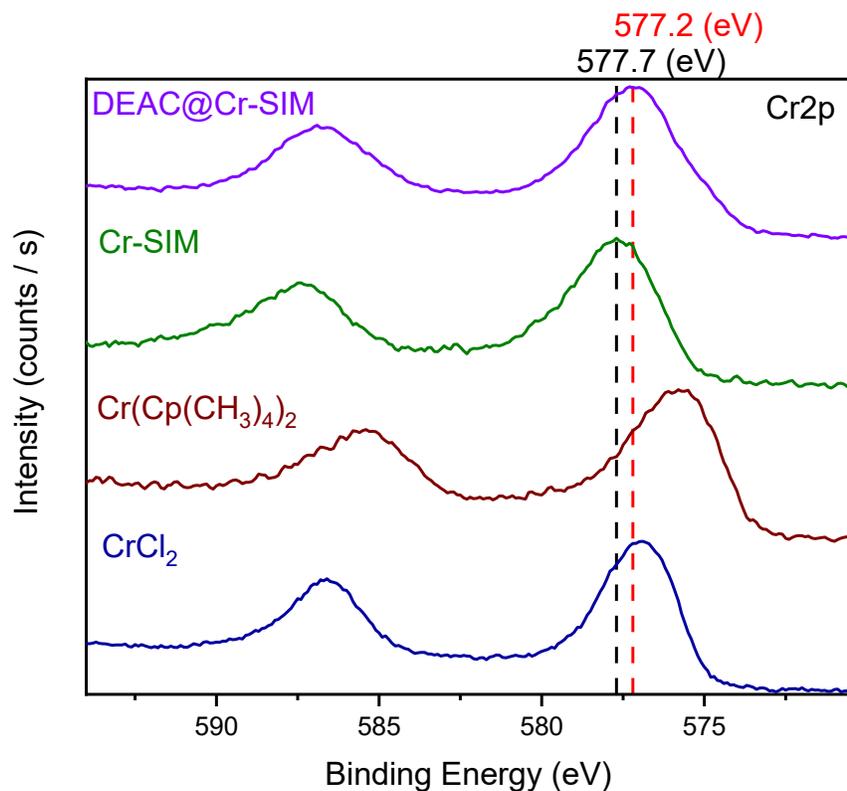
Figure S6. Cr 2p X-ray photoelectron spectra (XPS) of DEAC@Cr-SIM-NU-1000 (purple), Cr-SIM-NU-1000 (green), and two Cr precursors: $Cr(Cp(CH_3)_4)_2$ (brown) and $CrCl_2$ (navy blue).
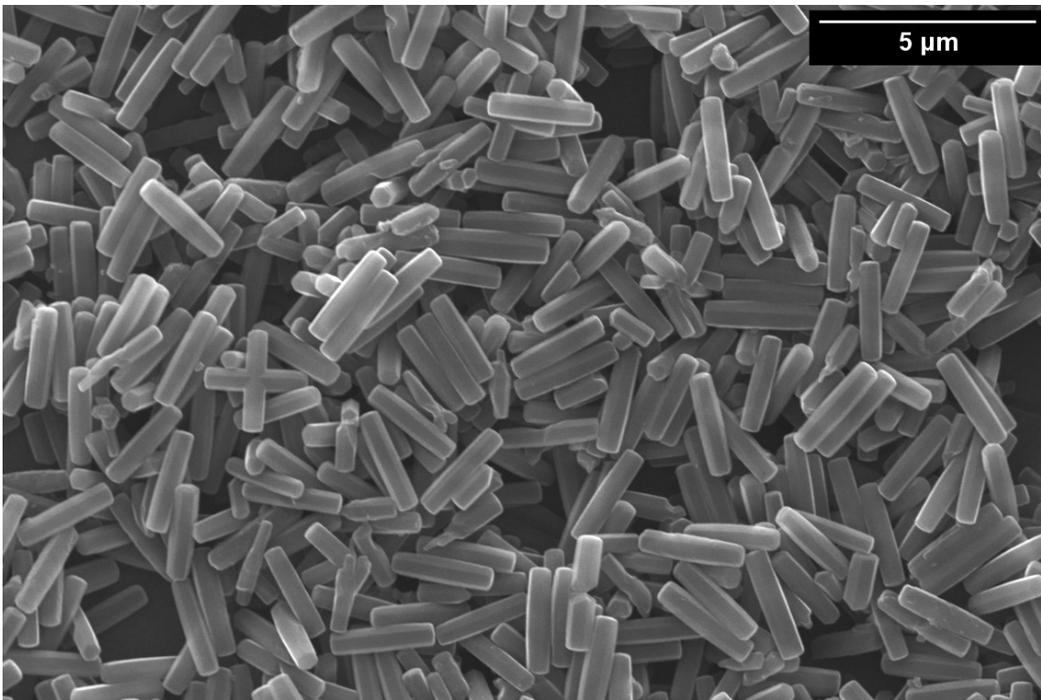
Figure S7. SEM image of NU-1000. Scale bar 5 micron.
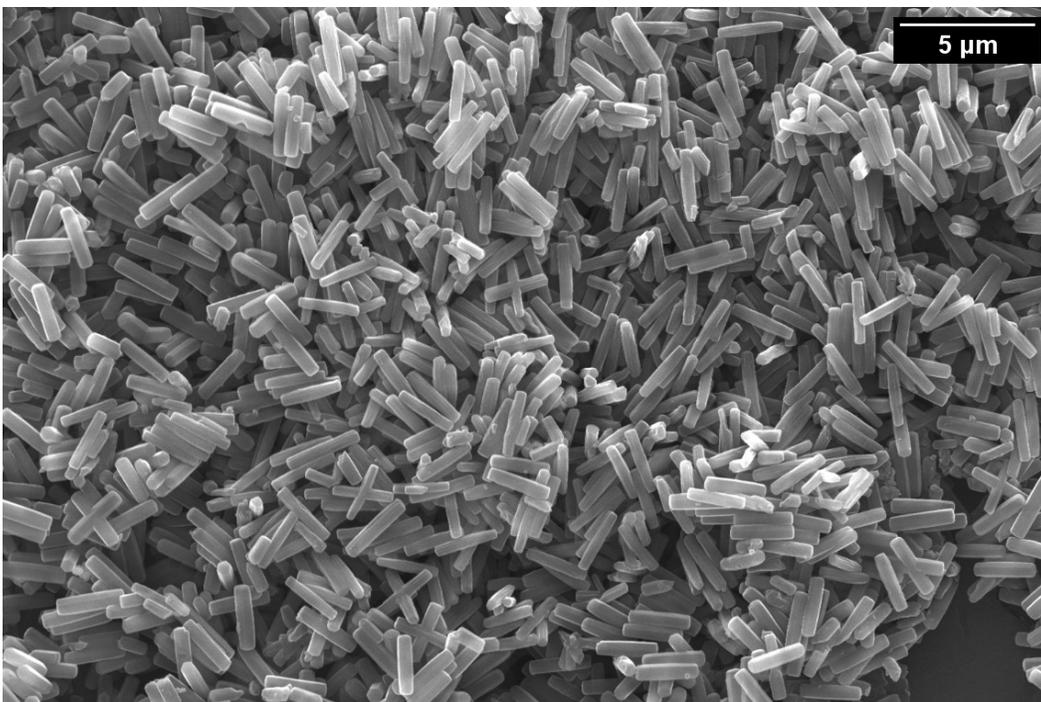
Figure S8. SEM image of Cr-SIM-NU-1000. Scale bar 5 micron.
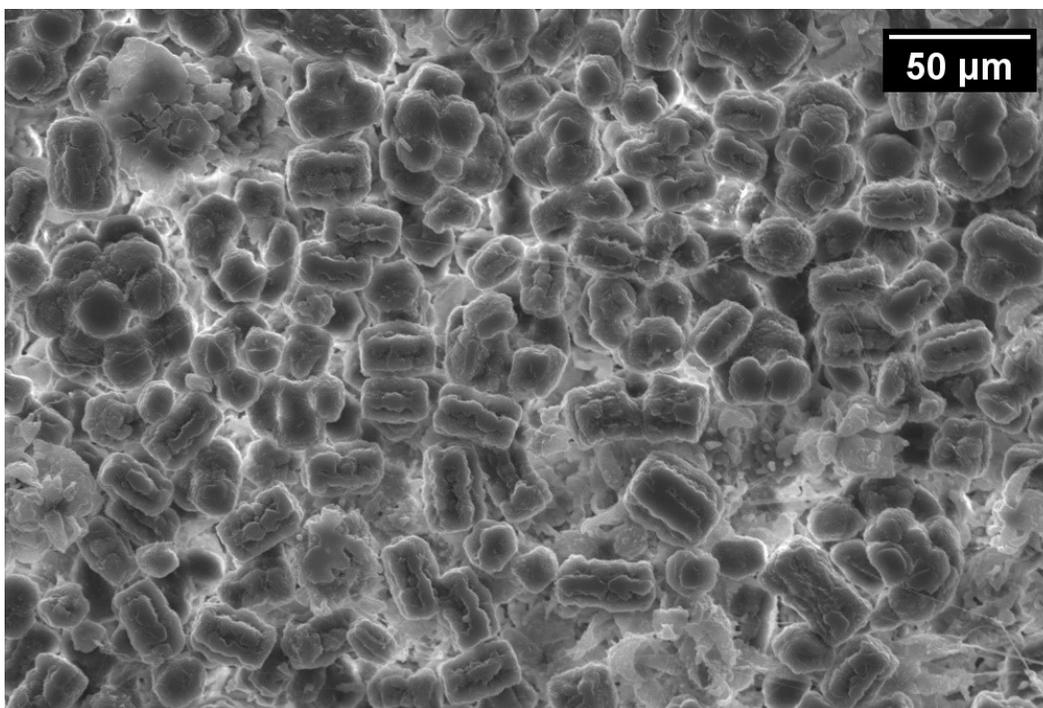
Figure S9. SEM image of post-catalysis Cr-SIM-NU-1000. Scale bar 50 micron.
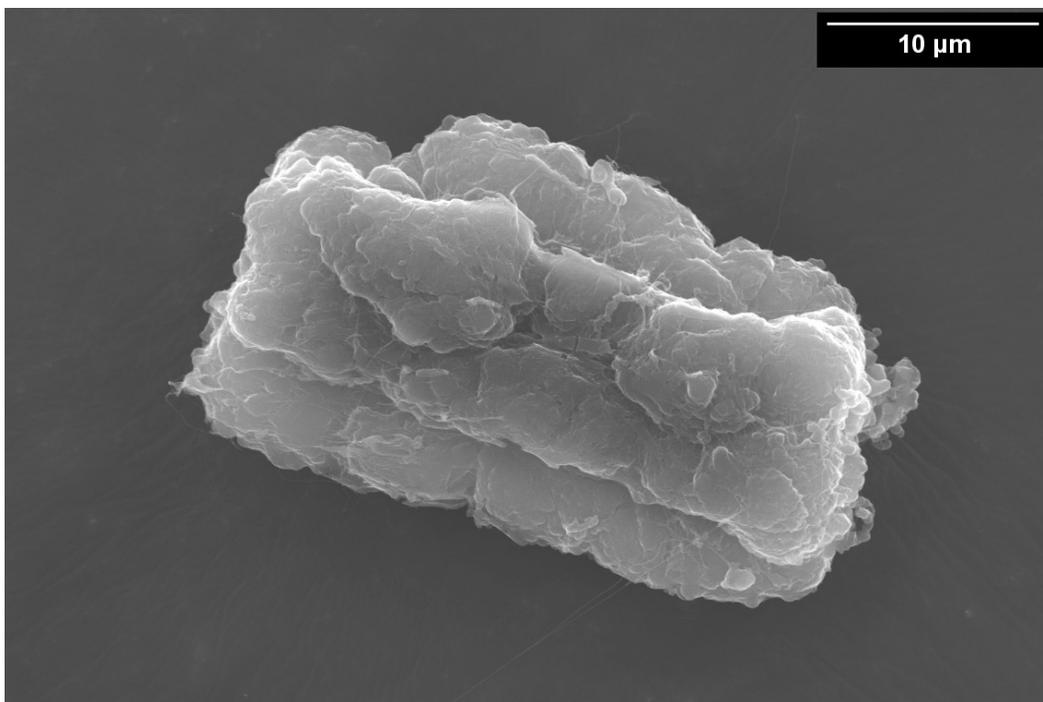
Figure S10. SEM image of post-catalysis Cr-SIM-NU-1000 at higher magnification. Scale bar 10 micron.
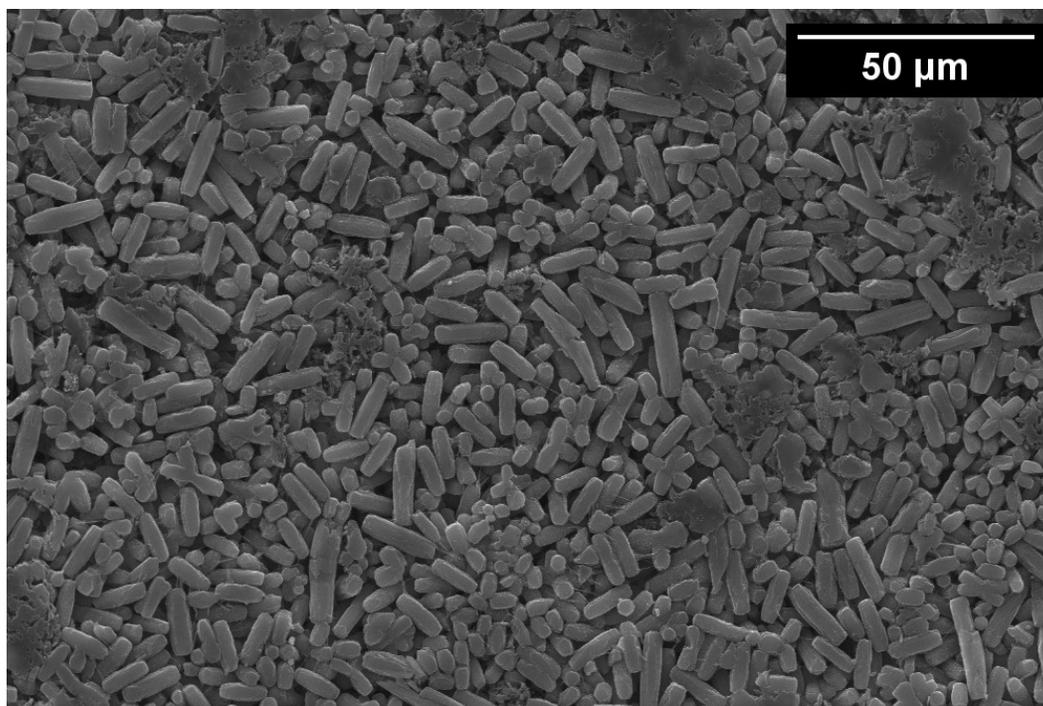
Figure S11. SEM image of post-catalysis Cr-SIM-NU-1000 washed with THF. Scale bar 50 micron.
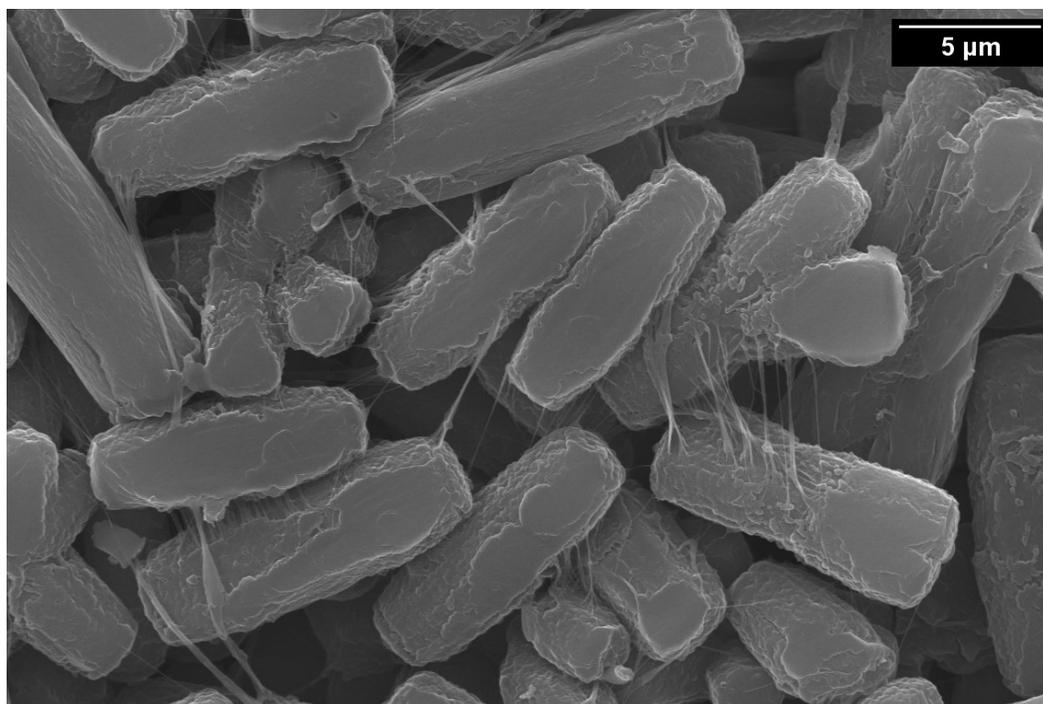
Figure S12. SEM image at higher magnification of post-catalysis Cr-SIM-NU-1000 washed with THF. Scale bar 5 micron.

Table S1. Productivity and turnover frequencies of Cr-SIM-NU-1000 compared to relevant

Metric (@ RT)	Cr-SIM-NU-1000	Cr-MFU-4l [4]	MIL-101(Cr)-NDC[5]	MIL-53(Cr)[5]
Productivity*	4	90	5	17
TOF**	0.7	14	9×10^{-5}	2×10^{-4}

literature materials.

*Productivity shown in g PE g_{cat}^{-1} h^{-1} atm^{-1}
**TOF shown in s^{-1}

Ethylene Pressure (bar)	Melting Temperature (°C)	Heat of Fusion (J/g)	Crystallinity* (%)
5	136.9 ± 0.3	103 ± 38	35 ± 13
10	136.7 ± 0.3	108 ± 12	37 ± 4
20	136.4 ± 0.3	152 ± 31	52 ± 10
30	136.8 ± 0.6	139 ± 16	48 ± 6
40	136.9 ± 1.3	118 ± 30	40 ± 10

Table S2. Melting temperatures, heats of fusion, and percent crystallinity of polymer samples produced by Cr-SIM-NU-1000 at various ethylene pressures.

*Determined by the melting enthalpy calculated from DSC in comparison to $\Delta H°_m = 293$ J/g for 100% crystalline UHMWPE.

Reaction Pressure (bar)	Number Average Molecular Weight, M_n (kDa)	Weight Average Molecular Weight, M_w (kDa)	Polydispersity
5	0.54	3.2	7.1
10	1.4	2.2	2.4
20	3.2	7.8	2.5

30	2.6	4.6	1.9
40	440	920	2.0

Table S3. Gel permeation chromatography data for polymer samples produced by Cr-SIM-NU-1000 at various pressures.
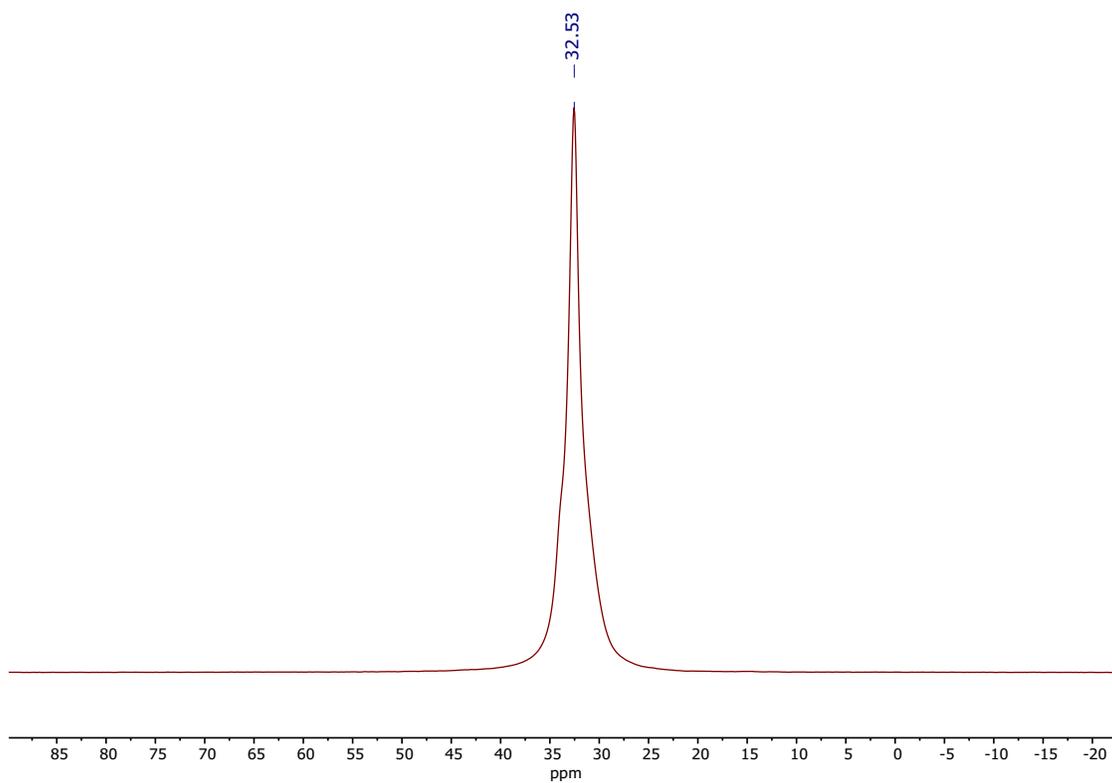
Figure S13. ^{13}C CP/MAS NMR spectrum of polyethylene product.
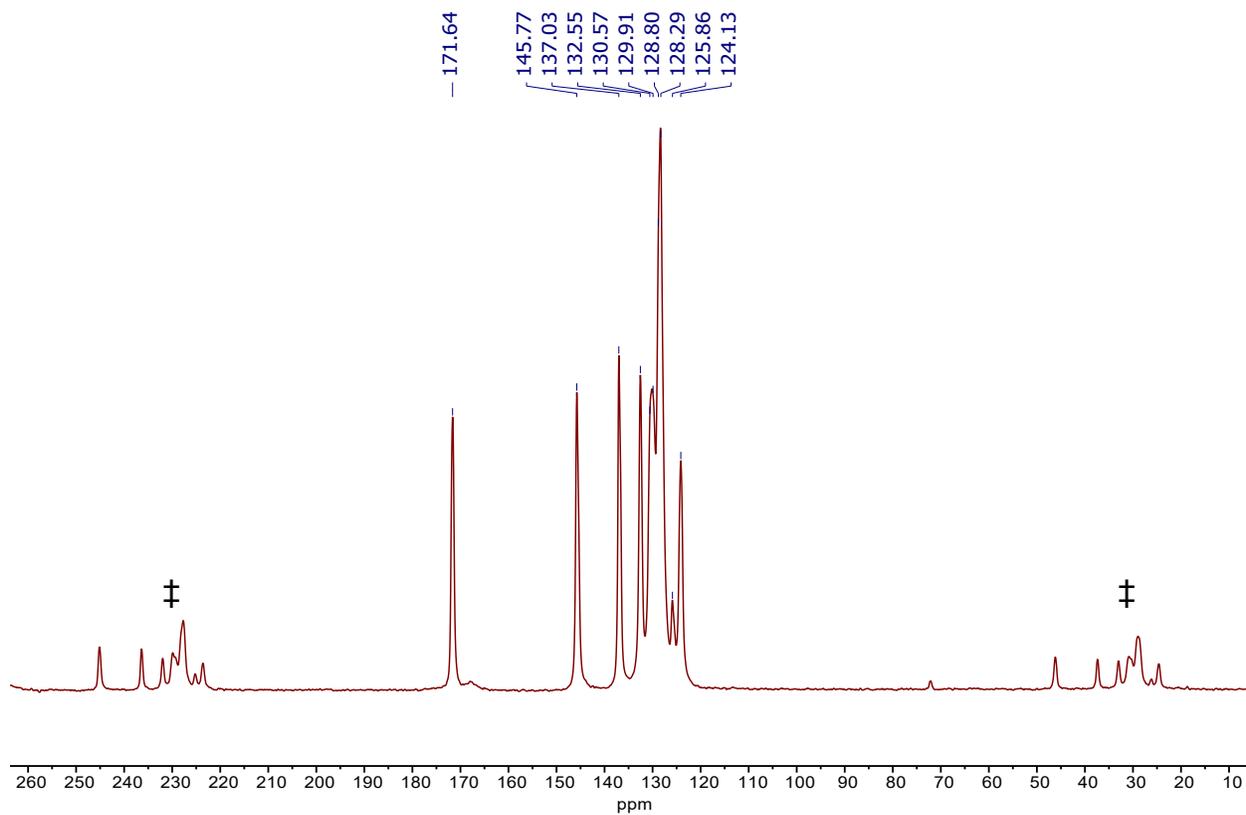
Figure S14. ^{13}C CP/MAS NMR spectrum of NU-1000 (spinning side bands indicated by ‡).
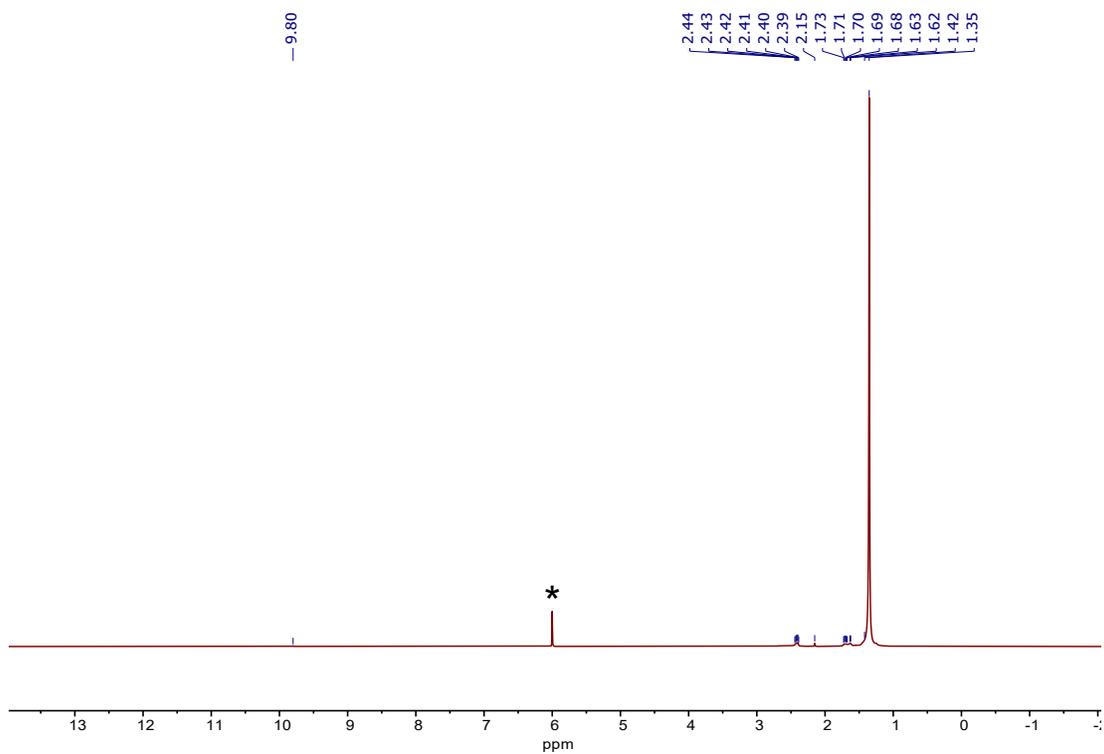
Figure S15. Initial ^{1}H NMR spectrum of polyethylene product in 1,1,2,2-tetrachloroethane-d_2 at 120 °C. * indicates residual solvent signal for 1,1,2,2-tetrachloroethane-d_2.
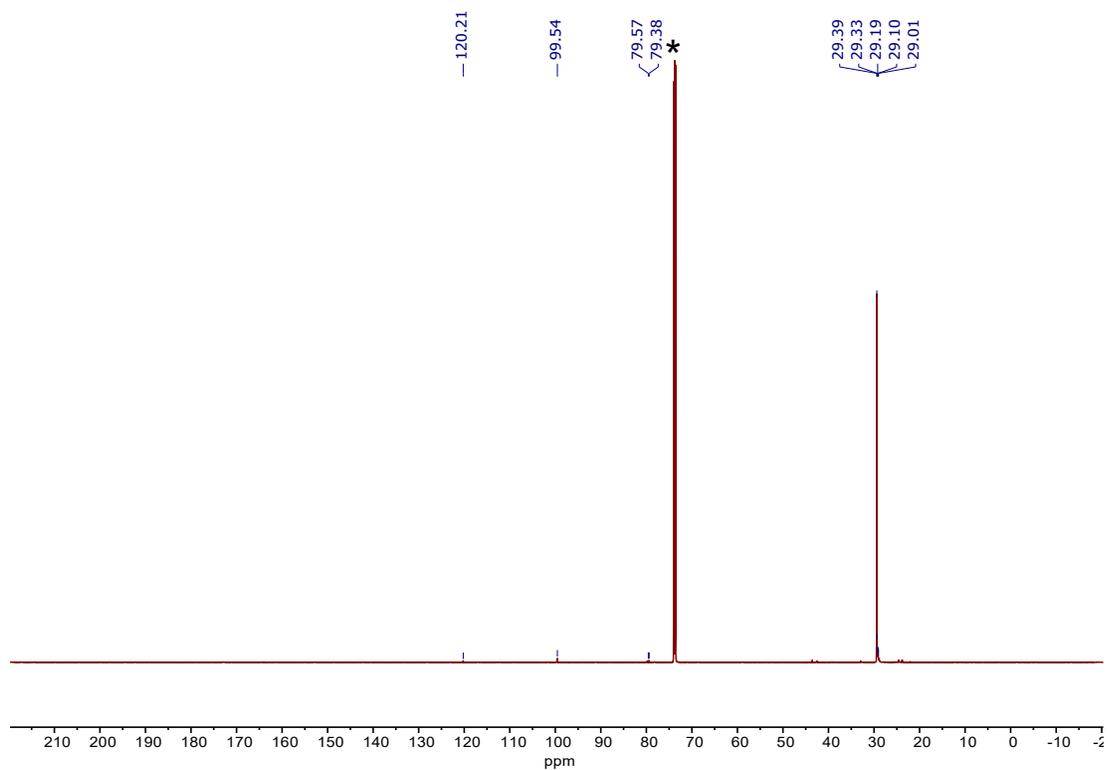
Figure S16. ^{13}C NMR spectrum of polyethylene product in 1,1,2,2-tetrachloroethane-d_2 at 120 °C. * indicates residual solvent signal for 1,1,2,2-tetrachloroethane-d_2.
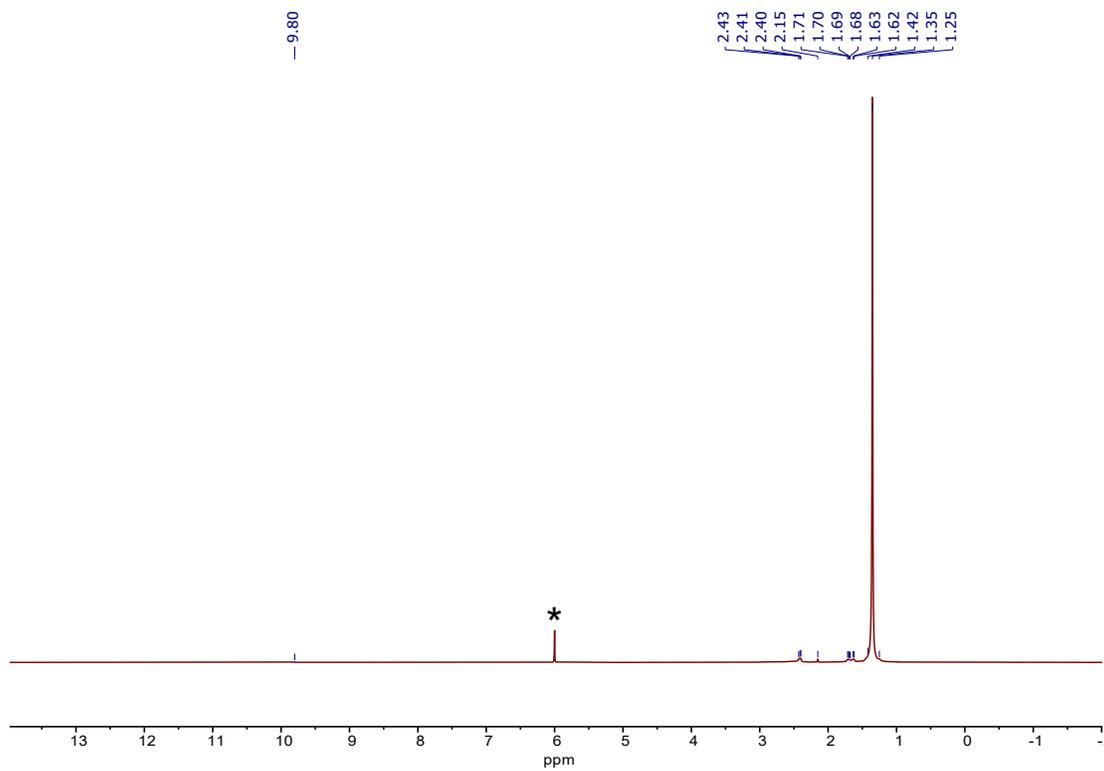
Figure S17. Final ^1H NMR spectrum of polyethylene product in 1,1,2,2-tetrachloroethane-d_2 at 120 °C. * indicates residual solvent signal for 1,1,2,2-tetrachloroethane-d_2.

Table S4. Crystal data and structure refinement for DEAC@Cr-SIM-NU-1000.

Identification code	DEAC@Cr-SIM-NU-1000_final
Empirical formula	$C_{45.27}H_{22}AlCl_2Cr_{0.18}O_{15.33}Zr_3$
Formula weight	1192.25
Temperature/K	200.15
Crystal system	hexagonal
Space group	P6/mmm
a/Å	39.433(3)
b/Å	39.433(3)
c/Å	16.2564(5)
$\alpha/°$	90
$\beta/°$	90
$\gamma/°$	120
Volume/Å^3	21891(3)
Z	6
ρ_{calc}g/cm^3	0.543
μ/mm^{-1}	2.419
F(000)	3526.0
Crystal size/mm^3	0.101 × 0.039 × 0.018
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.848 to 79.946
Index ranges	-32 ≤ h ≤ 32, -32 ≤ k ≤ 32, -7 ≤ l ≤ 13
Reflections collected	29356
Independent reflections	2583 [R_{int} = 0.1309, R_{sigma} = 0.0374]
Data/restraints/parameters	2583/246/167
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0859, wR_2 = 0.2454
Final R indexes [all data]	R_1 = 0.1033, wR_2 = 0.2678
Largest diff. peak/hole / e Å^{-3}	0.55/-1.22

Table S5. Cr-O bond distances comparison between Cr-SIM-NU-1000 and DEAC@Cr-SIM-NU-1000 structures.

Cr-SIM-NU-1000 Cr-O Distances (Å)	DEAC@Cr-SIM-NU-1000 Cr-O Distances (Å)
1.968	1.992
2.270	2.508
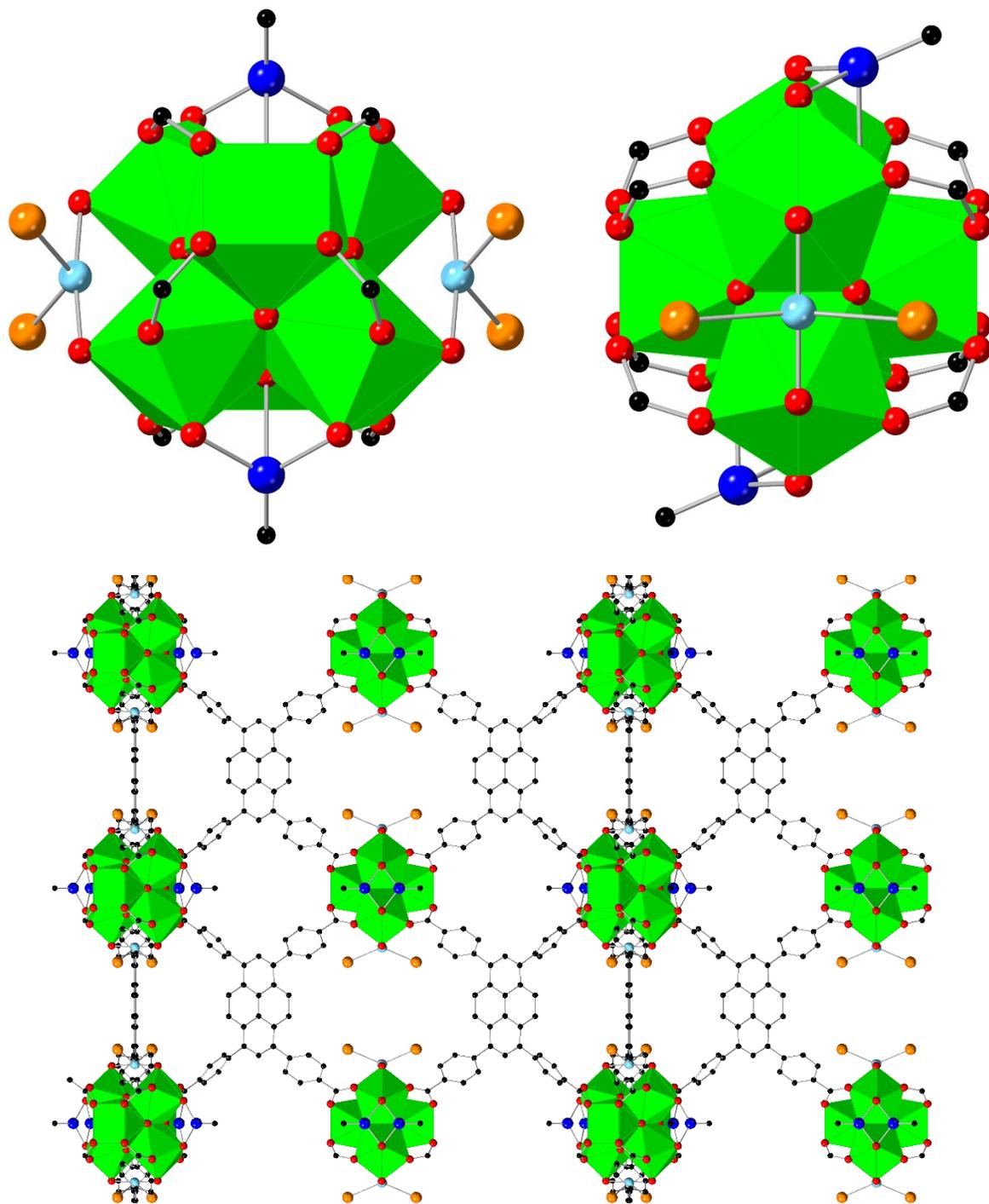
Figure S18: Views of the node (top) and window, or c-pore, along the a-axis (bottom) of DEAC@Cr-SIM-NU-1000 single crystal structure. DEAC viewed in crystallographically equivalent positions. Atom colors: C (black), O (red), Cl (orange), Al (light blue), Cr (dark blue), Zr (green), with hydrogens omitted for clarity.
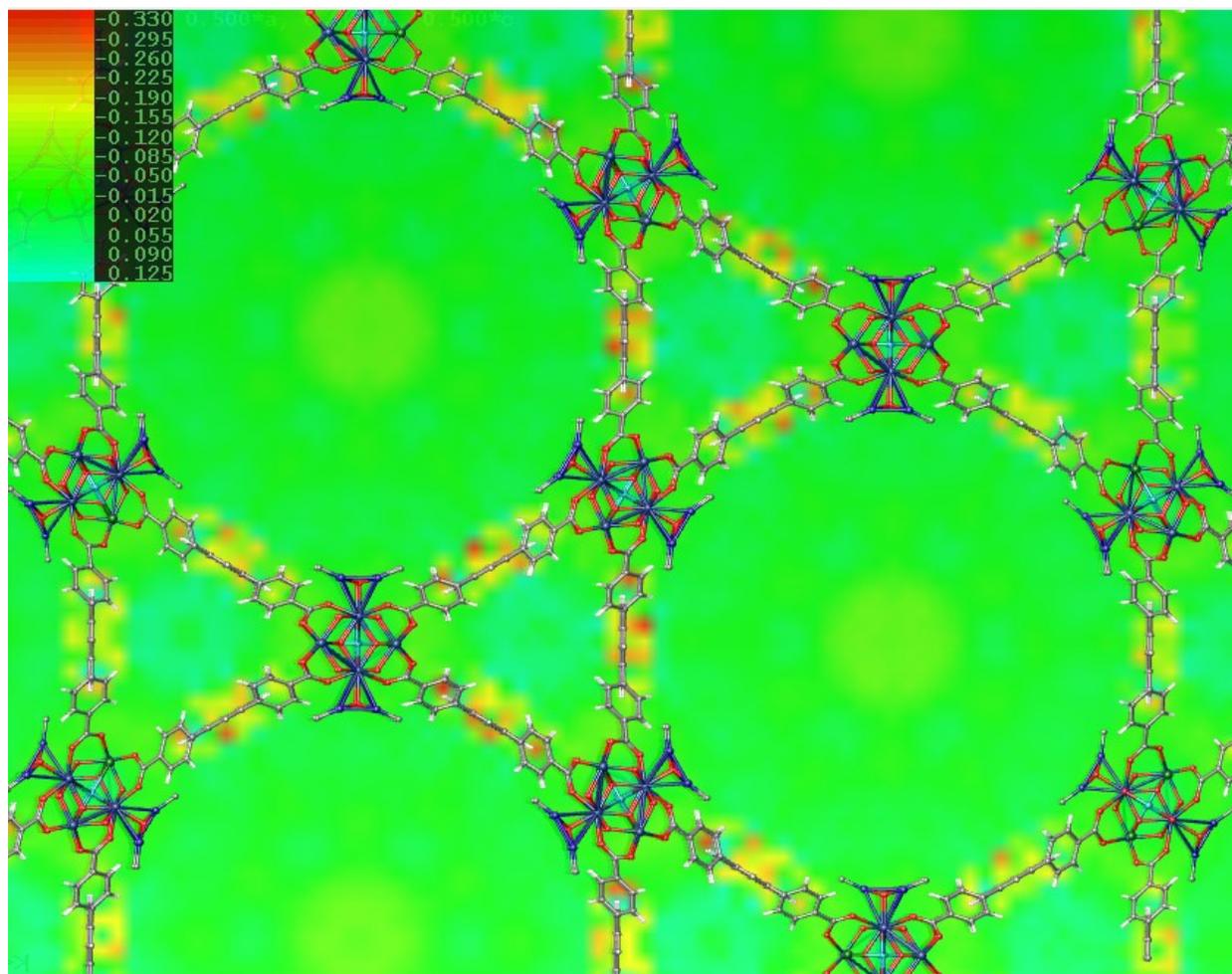
Figure S19: Residual electron density map of DEAC@Cr-SIM-NU-1000 single crystal structure viewing the hexagonal and triangular pores. Map shows minimal unassigned electron density within the hexagonal and triangular pores suggesting no remaining Al co-catalyst left within these pores. Electron density map generated by Olex2.
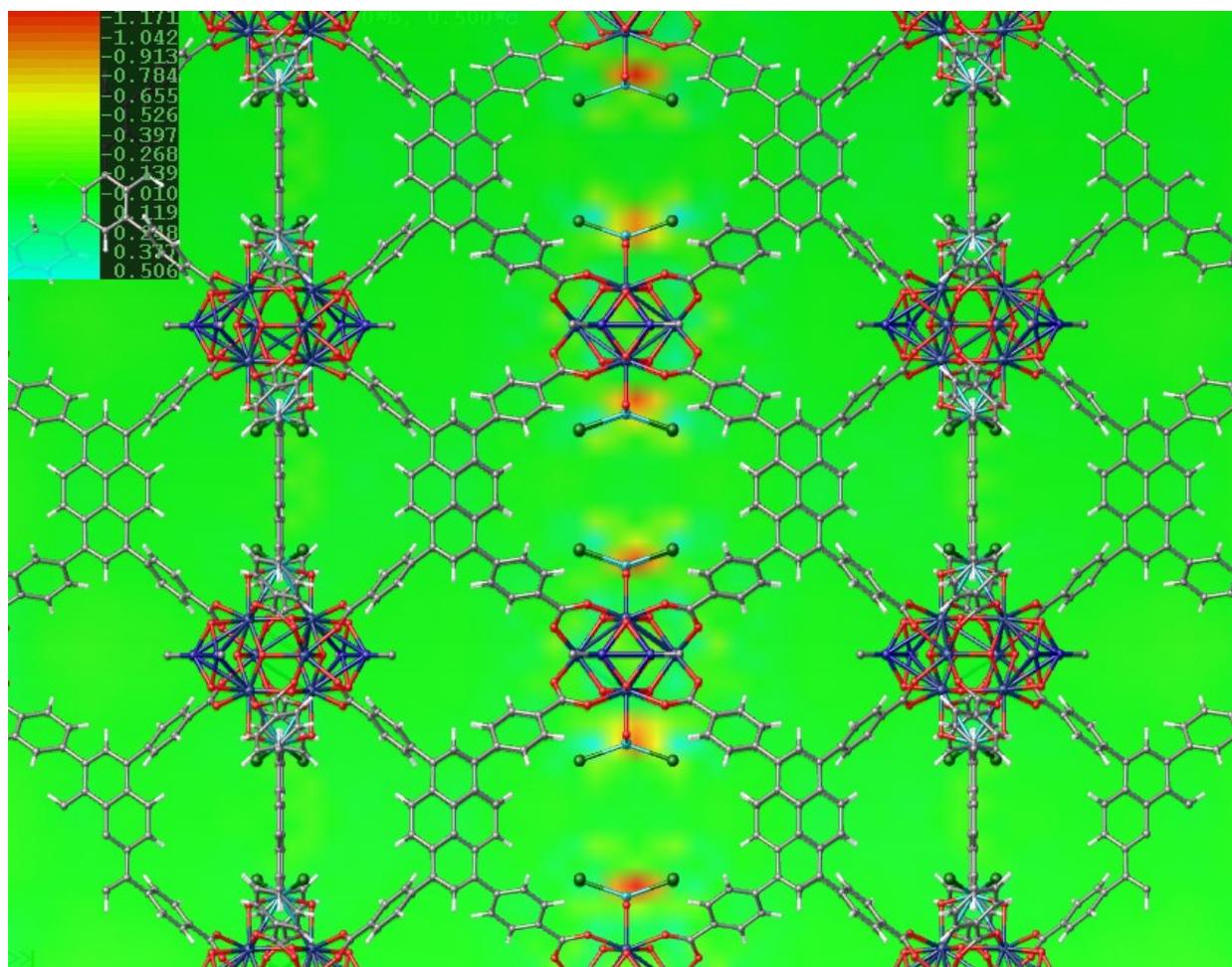
Figure S20: Residual electron density map of DEAC@Cr-SIM-NU-1000 single crystal structure viewing the internode spaces, or c-pores. Map shows additional unassigned electron density within c-pores indicating remaining Al co-catalyst left within these pores. Electron density map generated by Olex2.

References

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