

Electronic Supplementary Information For

Ferrocene Metallopolymers of Intrinsic Microporosity (MPIMs)

Tianran Zhai,^a Kenson Ambrose,^b Audithya Nyayachavadi,^b Kelly G. Walter,^c Simon Rondeau-Gagné,^b and Jeremy I. Feldblyum^{*a}

^a*Department of Chemistry, The University at Albany, State University of New York, Albany, NY, 12222, United States. Email: jfeldblyum@albany.edu*

^b*Department of Chemistry and Biochemistry, University of Windsor, Windsor, ON, N9B 3P4, Canada. Email: Simon.Rondeau-Gagne@uwindsor.ca*

^c*Department of Microbiological Sciences, North Dakota State University, Fargo, ND, 58108*

Contents

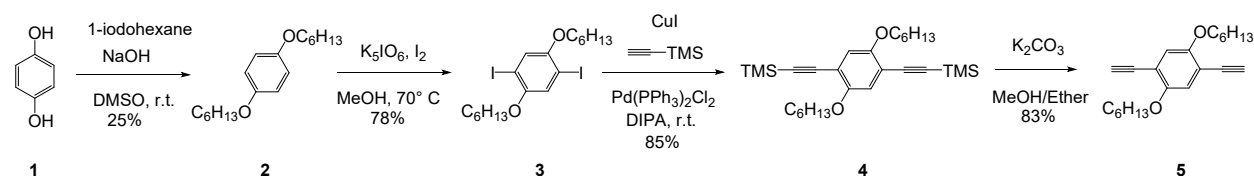
1. Experimental section	3
1.1 General methods	3
1.2 Synthesis of monomers	3
1.3 Synthesis of polymers	7
1.4 Polymer activation and gas sorption	7
2. Spectroscopic, gas sorption, thermogravimetric analysis, and cyclic voltammetry data	9
2.1 ^1H NMR and ^{13}C NMR spectra	9
2.2 FT-IR spectra	18
2.3 Gas sorption data.....	31
2.4 Thermogravimetric analysis (TGA).....	40
2.5 Raman spectra	45
2.6 Cyclic voltammetry	46

1. Experimental section

1.1 General methods

All ^1H NMR spectra were recorded at 500 MHz under ambient conditions. ^{13}C NMR spectra were recorded at 126 MHz under ambient conditions. FT-IR data were collected with a Spectrum Two FT-IR spectrometer (Perkin Elmer, Waltham, MA) in attenuated total internal reflectance (ATIR) mode using a diamond ATIR crystal. High resolution mass data were acquired using direct analysis in real time-high resolution mass spectrometry (DART-HRMS; AccuTOF-DAART 4G, JEOL USA, Peabody, MA) in positive mode. The ion source was operated with ultra-high purity helium (Airgas, Albany, NY, USA) and at a temperature of 300 °C. Raman spectroscopy was performed using an inVia Raman microscope (Renishaw, West Dundee). For spectral acquisition, the following settings were used: 475 nm laser, 50x objective, 1% laser power filter, 30 s acquisition time. UV-Vis-NIR data were measured using a Jasco V-770 UV-vis near-infrared (UV-vis-NIR) spectrophotometer with scanning rate 10 nm/min, UV/Vis bandwidth 5 nm and NIR bandwidth 20 nm. Gas sorption analysis was performed using a 3Flex gas sorption analyzer (Micromeritics, Norcross, GA). Samples were affixed to the gas sorption analyzer, evacuated to 10^{-6} bar, cooled to 77 K, and analyzed using high purity N_2 gas (99.999%+, Airgas). Number average molecular weight (M_n), weight average molecular weight (M_w), and dispersity (D_M) were evaluated by high temperature size exclusion chromatography (SEC) using 1,2,4-trichlorobenzene and performed on an EcoSEC HLC-8321GPC/HT (Tosoh Bioscience Inc., San Francisco, CA) equipped with a single TSK gel GPC column (GMHHR-H; 300 mm \times 7.8 mm) calibrated with monodisperse polystyrene standards. The samples were prepared using 1 mg/mL of sample in trichlorobenzene (TCB), which were allowed to stir at 80 °C for 12 h prior to injection. The analysis of the samples was performed at 180 °C with a flow rate of 1.0 mL/min with injection quantities of 300 μL . Data were collected and processed using the EcoSEC 8321GPC HT software suite. Cyclic voltammetry measurements were carried out using a sealed CHode three electrode electrochemical set up utilizing a glassy carbon working electrode, a saturated KCl standard electrode, and a platinum wire counter electrode in anhydrous dimethylformamide solvent having 0.1 M tetrabutylammonium tetrafluoroborate.

1.2 Synthesis of monomers



1,4-dihexyloxybenzene (2): 1-iodohexane (16.0 mL, 0.108 mmol, 3 eq.) and NaOH (5.45 g, 0.108 mmol, 3 eq.) were added to a solution of hydroquinone (3.98 g, 0.0362 mmol, 1 eq.) in 120 mL DMSO under air atmosphere at r.t. The mixture was stirred for 2 h and then poured into ice and water (1000 mL). The resulting solid precipitate was filtered and washed with water. The resulting residue was purified by flash column chromatography using hexanes as the eluent to afford the product (2.49 g, 25%) as a white solid.

^1H NMR (500 MHz, Chloroform-*d*) δ 6.82 (s, 4H), 3.90 (t, J = 6.6 Hz, 4H), 1.83 – 1.68 (m, 4H), 1.45 (dt, J = 8.0, 3.9 Hz, 4H), 1.33 (dq, J = 7.2, 4.3, 3.8 Hz, 8H), 0.95 – 0.86 (m, 6H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 153.34, 115.54, 68.82, 31.77, 29.53, 25.90, 22.77, 14.20.

1,4-diiodo-2,5-dihexyloxybenzene (3): A solution of H_5I_6 (2.18 g, 9.56 mmol, 0.65 eq.) in methanol (35 mL) was stirred for 10 min. I_2 (4.64 g, 19.7 mmol, 1.3 eq.) was added and the resulting solution was stirred for another 10 min. 1,4-dihexyloxybenzene (4.11 g, 14.8 mmol, 1 eq.) was added and the mixture was stirred at 70 °C for 4 h. The resulting solution was poured into a solution of $\text{Na}_2\text{S}_2\text{O}_5$ (3.8 g) in water (75 mL). The resulting precipitate was washed with methanol and dissolved in DCM. After filtration, the filtrate was collected and evaporated under vacuum to afford a white solid (6.20 g, 78%).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.17 (s, 2H), 3.93 (t, J = 6.4 Hz, 4H), 1.84 – 1.75 (m, 4H), 1.49 (q, J = 7.3 Hz, 4H), 1.37 – 1.32 (m, 8H), 0.93 – 0.89 (m, 6H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 153.02, 122.95, 86.46, 70.52, 31.62, 29.27, 25.87, 22.74, 14.19.

1,4-bis(trimethylsilylethynyl)-2,5-bis(hexyloxy)benzene (4): A flame-dried 100 mL Schlenk flask was charged with 30 mL diisopropylamine, 1,4-diiodo-2,5-dihexyloxybenzene (4.09 g, 7.70 mmol, 1 eq.), trimethylsilylethyne (3.20 mL, 23.1 mmol, 3 eq.), copper(I) iodide (146.7 mg, 0.77 mmol, 10 mol%) and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (270.2 mg, 0.385 mmol, 5 mol%). The mixture was stirred for

24 h at room temperature. The solvent was removed in vacuo and the residue was dissolved in hexanes and extracted with water. The combined organic phases were dried over NaSO₄ and the solvent was removed in vacuo. The residue was purified by column chromatography using hexanes/DCM (20/1-15/1) as eluent to afford compound **4** (3.08 g, 85%).

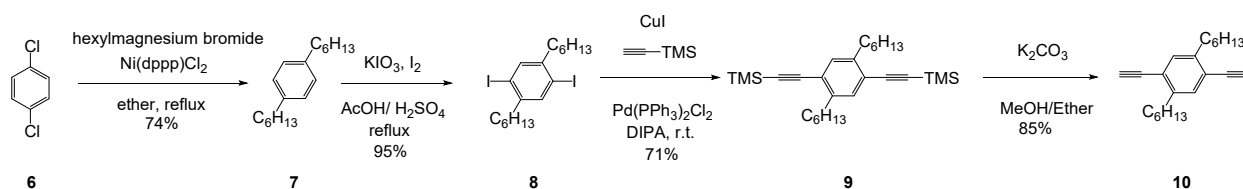
¹H NMR (500 MHz, Chloroform-*d*) δ 6.89 (s, 12H), 3.94 (t, *J* = 6.3 Hz, 4H), 1.84 – 1.73 (m, 4H), 1.52 – 1.46 (m, 4H), 1.39 – 1.29 (m, 8H), 1.02 – 0.85 (m, 6H), 0.25 (s, 18H)

¹³C NMR (126 MHz, Chloroform-*d*) δ 154.14, 117.34, 114.07, 101.20, 100.22, 69.59, 31.76, 29.44, 25.84, 22.79, 14.23, 0.10, 0.10.

1,4-diethynyl-2,5-bis(hexyloxy)benzene (5): A 500 mL round bottom flask was charged with 1,4-bis(trimethylsilylethynyl)-2,5-bis(hexyloxy)benzene (2.85 g, 6.05 mmol, 1 eq.) and suspended in 100 mL methanol and 100 mL ether, and then K₂CO₃ (3.17 g, 23.0 mmol, 3.8 eq.) was added. The mixture was stirred for 1 h at room temperature. The solvent was removed by rotary evaporation. The residue was dissolved in hexanes. K₂CO₃ was removed by filtration, and the residue was purified by column chromatography using hexanes/DCM (10/1) as the eluent to afford compound **5** (968.7 mg, 83%).

¹H NMR (500 MHz, Chloroform-*d*) δ 6.95 (s, 2H), 3.97 (t, *J* = 6.6 Hz, 4H), 3.33 (s, 2H), 1.80 (dt, *J* = 14.3, 6.6 Hz, 4H), 1.49 – 1.41 (m, 4H), 1.41 – 1.27 (m, 8H), 0.94 – 0.86 (m, 6H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 154.12, 117.87, 113.39, 82.54, 79.92, 69.81, 31.67, 29.24, 25.73, 22.74, 14.17.



1,4-dihexylbenzene (7): To a dry flask NiCl₂(dppp) (77.4 mg, 0.143 mmol, 0.3 mol%) and a solution of 1,4-dichlorobenzene (7.00 g, 47.6 mmol, 1.0 eq.) in THF (30 mL) were added, and then hexylmagnesiumbromide (105 mL, 1 M in THF, 2.2 eq.) was added dropwise. The resulting reaction mixture was stirred under reflux for 15 h. After cooling to room temperature, the reaction mixture was hydrolyzed with ice/HCl (aq. 1 M, 70 mL), then extracted with hexanes. The combined organic phase was washed with saturated NaHCO₃ solution and brine, then dried over MgSO₄. The solvent was then removed in vacuo. The resulting residue was purified by column chromatography using hexanes as the eluent to afford compound **7** (8.71 g, 74 %).

¹H NMR (500 MHz, Chloroform-*d*) δ 7.09 (s, 4H), 2.63 – 2.50 (m, 4H), 1.59 (p, *J* = 7.8, 7.4 Hz, 4H), 1.39 – 1.26 (m, 12H), 0.88 (t, *J* = 6.8 Hz, 6H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 140.23, 128.36, 35.73, 31.91, 31.72, 29.23, 22.78, 14.26.

1,4-dihexyl-2,5-diiodobenzene (8): 1,4-dihexylbenzene (236.0 mg, 0.958 mmol, 1 eq.) was dissolved in a mixture of acetic acid (6 mL), conc. H₂SO₄ (0.4 mL), and water (0.1 mL). I₂ (248.5 mg, 1.05 mmol, 1.1 eq.) and potassium iodate (101.8 mg, 0.479 mmol, 0.5 eq.) were added, and the resulting mixture was stirred under reflux for 20 h. The reaction was then allowed to cool to room temperature and stopped by the addition of 10 mL water. The aqueous phase was extracted with hexanes, and the combined organic layers were washed with Na₂S₂O₃ (aq., sat.), Na₂HCO₃ (aq., sat.), and Na₂SO₄ (aq., sat.), and dried over MgSO₄. The crude product was purified by column chromatography using hexanes as the eluent. Compound **8** was isolated as a colorless solid (451 mg, 95%).

¹H NMR (500 MHz, Chloroform-*d*) δ 7.59 (s, 2H), 2.69 – 2.54 (m, 4H), 1.53 (d, *J* = 7.2 Hz, 8H), 1.39 – 1.29 (m, 12H), 0.97 – 0.86 (m, 8H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 144.99, 139.45, 100.48, 39.99, 31.75, 30.32, 29.15, 22.74, 14.23.

1,4-bis(trimethylsilylethynyl)-2,5-bis(hexyloxy)benzene (9): A flame-dried 25 mL Schlenk flask was charged with diisopropylamine (10 mL), **8** (1.27 g, 2.54 mmol, 1 eq.), trimethylsilylethyne (1.1 mL, 7.62 mmol, 3 eq.), copper(I) iodide (38.7 mg, 0.203 mmol, 8 mol%) and Pd(PPh₃)₂Cl₂ (178.3 mg, 0.254 mmol, 10 mol%). The mixture was stirred for 24 h at room temperature. The solvent was removed in vacuo, and the residue was dissolved in hexanes and extracted with water. The aqueous phase was extracted with hexanes twice. The combined organic phases were dried over NaSO₄ and the solvent was removed in vacuo. The residue was purified by column chromatography using hexanes as the eluent to afford compound **9** (786.8 mg, 71%).

¹H NMR (500 MHz, Chloroform-*d*) δ 7.26 (s, 2H), 2.74 – 2.55 (m, 4H), 1.67 – 1.55 (m, 4H), 1.38 – 1.25 (m, 12H), 0.98 – 0.83 (m, 6H), 0.25 (s, 18H).

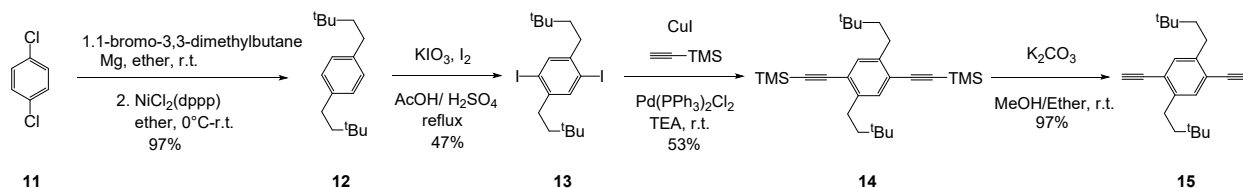
¹³C NMR (126 MHz, Chloroform-*d*) δ 144.99, 139.45, 125.89, 106.29, 100.47, 39.99, 31.75, 30.32, 29.15, 22.74, 14.23.

1,4-diethynyl-2,5-dihexylbenzene (10): A 250 mL round bottom flask was charged with **9** (2.57 g, 5.87 mmol, 1 eq.) and suspended in methanol (50 mL) and ether (50 mL). then K₂CO₃ (3.08 g, 22.3 mmol, 3.8 eq.) was then added. The mixture was

stirred for 1 h at room temperature. The solvent was then removed by rotary evaporation. The resulting mixture was suspended in hexanes, and K_2CO_3 was removed by filtration. The resulting solution was dried by rotary evaporation, and the resulting residue was purified by column chromatography using hexanes as the eluent to afford compound **10** (1.47 g, 85%).

1H NMR (500 MHz, Chloroform-*d*) δ 7.29 (s, 2H), 3.28 (s, 2H), 2.76 – 2.64 (m, 4H), 1.61 (m, 4H), 1.41 – 1.27 (m, 12H), 0.95 – 0.79 (m, 6H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.69, 132.95, 121.93, 82.27, 81.54, 33.86, 31.69, 30.44, 29.11, 22.59, 14.07.



1,4-bis(3,3-dimethylbutyl)benzene (12): To a flame-dried flask, dichlorobenzene (7.00 g, 47.6 mmol, 1 eq.) and $NiCl_2(dppp)$ (258.0 mg, 0.476 mmol, 1 mol%) were dissolved in ether (20 mL). Then Grignard reagent [1-bromo-2,2-dimethylpentane (17.0 mL, 119 mmol, 2.5 eq.) in ether (50 mL)] was added at 0 °C. The reaction was stirred at r.t. overnight. The mixture was then poured into water at 0 °C, then extracted with hexanes. Combine organic phases were washed with 1M HCl and then $NaHCO_3$ (aq., sat.) and brine. The residue was purified by column chromatography using hexanes as the eluent to afford compound **12** (11.34 g, 97%).

IR (neat): ν_{max} 3025 cm^{-1} , 2956 cm^{-1} , 2862 cm^{-1} , 2844 cm^{-1} , 1473 cm^{-1} , 1363 cm^{-1} , 1236 cm^{-1} , 844 cm^{-1} , 728 cm^{-1} , 552 cm^{-1} .

1H NMR (500 MHz, Chloroform-*d*) δ 7.09 (s, 4H), 2.66 – 2.42 (m, 4H), 1.61 – 1.41 (m, 4H), 0.95 (s, 18H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 140.80, 128.35, 46.68, 30.92, 30.68, 29.50.

HRMS (*m/z*): Calcd. for $C_{18}H_{31}$ [$M+H$] $^+$: 247.2420, found: 247.2401.

1,4-bis(3,3-dimethylbutyl)-2,5-diiodobenzene (13): **12** (11.35 g, 46.0 mmol, 1 eq.) was dissolved in acetic acid (90 mL), conc. H_2SO_4 (6 mL), and water (1.5 mL). I_2 (11.9 g, 50.5 mmol, 1.1 eq.) and potassium iodate (4.92 g, 23.0 mmol, 0.5 eq.) were added, and the resulting mixture stirred under reflux for 20 h. The reaction was cooled to room temperature and stopped by the addition of water (50 mL). The aqueous phase was extracted with hexanes, and the combined organic layers were washed with $Na_2S_2O_3$ (aq. sat.), Na_2HCO_3 (aq. sat.), and Na_2SO_4 (aq. sat.), and dried over $MgSO_4$. The crude product was purified by column chromatography using hexanes as the eluent, and compound **13** was isolated as colorless solid (10.8 g, 47%).

IR (neat): ν_{max} 2950 cm^{-1} , 2898 cm^{-1} , 2866 cm^{-1} , 1459 cm^{-1} , 1363 cm^{-1} , 1230 cm^{-1} , 1041 cm^{-1} , 886 cm^{-1} , 797 cm^{-1} , 476 cm^{-1} .

1H NMR (500 MHz, Chloroform-*d*) δ 7.59 (s, 2H), 2.72 – 2.48 (m, 4H), 1.45 – 1.32 (m, 4H), 0.98 (s, 18H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 145.42, 139.44, 100.42, 44.89, 35.58, 30.78, 29.43.

HRMS (*m/z*): Calcd. for $C_{18}H_{29}I_2$ [$M+H$] $^+$: 499.0353, found: 499.0370.

((2,5-bis(3,3-dimethylbutyl)-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane) (14): A flame-dried 100 mL Schlenk flask was charged with triethylamine (30 mL), **13** (3.40 g, 6.82 mmol, 1 eq.), trimethylsilylethyne (2.8 mL, 20.5 mmol, 3 eq.), copper(I) iodide (103.9 mg, 0.545 mmol, 8 mol%) and $Pd(PPh_3)_2Cl_2$ (478.7 mg, 0.682 mmol, 10 mol%). The mixture was stirred for 24 h at room temperature. The solvent was removed in vacuo and the residue was dissolved in hexanes and extracted with water. The aqueous phase was extracted with hexanes twice. The combined organic phases were dried over Na_2SO_4 and the solvent was removed in vacuo. The residue was purified by column chromatography using hexanes as the eluent to afford compound **14** (1.59 g, 53%).

IR (neat): ν_{max} 2950 cm^{-1} , 2863 cm^{-1} , 2148 cm^{-1} , 1476 cm^{-1} , 1250 cm^{-1} , 829 cm^{-1} , 759 cm^{-1} , 699 cm^{-1} , 626 cm^{-1} .

1H NMR (500 MHz, Chloroform-*d*) δ 7.24 (s, 2H), 2.79 – 2.57 (m, 4H), 1.49 – 1.40 (m, 4H), 0.96 (s, 18H), 0.24 (s, 18H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.09, 132.82, 122.69, 103.84, 98.78, 45.47, 30.75, 29.56, 29.44, 0.17.

HRMS (*m/z*): Calcd. for $C_{28}H_{47}Si_2$ [$M+H$] $^+$: 439.3211, found: 439.3217.

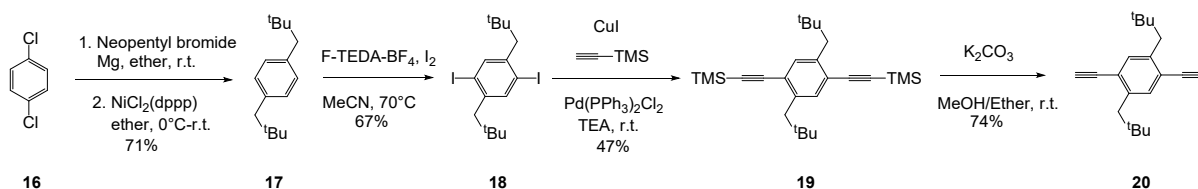
1,4-bis(3,3-dimethylbutyl)-2,5-diethynylbenzene (15): A 100 mL round bottom flask was charged with **14** (1.65 g, 3.77 mmol, 1 eq.) and suspended in methanol (50 mL) and ether (50 mL). K_2CO_3 (1.98 g, 14.3 mmol, 3.8 eq.) was then added. The mixture was stirred for 1 h at room temperature. The solvent was removed by rotary evaporation. The resulting mixture was suspended in hexanes, and K_2CO_3 was removed by filtration. The resulting solution was dried by rotary evaporation, and the resulting residue was purified by column chromatography using hexanes as the eluent to afford compound **15** (1.07 g, 97%).

IR (neat): ν_{max} 3295 cm^{-1} , 2959 cm^{-1} , 2866 cm^{-1} , 2104 cm^{-1} , 1474 cm^{-1} , 1365 cm^{-1} , 1215 cm^{-1} , 901 cm^{-1} , 647 cm^{-1} , 605 cm^{-1} , 483 cm^{-1} .

1H NMR (500 MHz, Chloroform-*d*) δ 7.29 (s, 2H), 3.28 (s, 2H), 2.84 – 2.57 (m, 4H), 1.50 – 1.38 (m, 4H), 0.96 (s, 18H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.40, 133.09, 122.08, 82.24, 81.68, 45.36, 30.77, 29.46, 29.36.

HRMS (*m/z*): Calcd. for $\text{C}_{22}\text{H}_{31}$ [$\text{M}+\text{H}$] $^+$: 295.2420, found: 295.2434.



1,4-dieneopentylbenzene (17): To a flame-dried flask, dichlorobenzene (7.00 g, 47.6 mmol, 1 eq.) and NiCl₂(dppp) (258.0 mg, 0.476 mmol, 1 mol%) were dissolved in ether (20 mL). Grignard reagent [1 1-bromo-2,2-dimethylpentane (15.0 mL, 119 mmol, 2.5 eq.) in ether (50 mL)] was then added at 0 °C. Reaction was stirred at r.t. overnight. Mixture was poured into water at 0 °C, followed by extraction with hexanes. Combined organic layer was washed with 1M HCl and then NaHCO₃ (aq., sat.) and brine. Residue was purified by column chromatography using hexanes as eluent to afford compound **17** (7.41 g, 71%).

IR (neat): ν_{max} 3020 cm⁻¹, 2954 cm⁻¹, 2907 cm⁻¹, 2861 cm⁻¹, 1515 cm⁻¹, 1467 cm⁻¹, 1361 cm⁻¹, 1244 cm⁻¹.

^1H NMR (500 MHz, Chloroform-*d*) δ 7.02 (s, 4H), 2.46 (s, 4H), 0.90 (s, 18H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 137.15, 129.84, 50.00, 31.85, 29.55.

HRMS (*m/z*): Calcd. for $\text{C}_{16}\text{H}_{27}$ [$\text{M}+\text{H}$] $^+$: 219.2107, found: 219.2680.

1,4-diiodo-2,5-dieneopentylbenzene (18): To a solution of **17** (2.88 g, 13.2 mmol, 1 eq.) in MeCN (120 mL) were added I₂ (7.76 g, 32.9 mmol, 2.5 eq.) and F-TEDA-BF₄ (11.7 g, 32.9 mmol, 2.5 eq.) and the reaction mixture was stirred at 70 °C overnight. The solvent was removed under reduced pressure and the crude mixture was extracted with hexanes and water. The combined organic phase was washed with Na₂S₂O₃·5H₂O (10 %, aq.) and brine and subsequently dried over Na₂SO₄. The residue was purified by column chromatography using hexanes as the eluent to afford compound **18** (4.16 g, 67%).

IR (neat): ν_{max} 2950 cm⁻¹, 2864 cm⁻¹, 1454 cm⁻¹, 1364 cm⁻¹, 1246 cm⁻¹, 880 cm⁻¹, 801 cm⁻¹, 453 cm⁻¹.

^1H NMR (500 MHz, Chloroform-*d*) δ 7.65 (s, 2H), 2.66 (s, 4H), 0.99 (s, 18H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.54, 141.35, 102.13, 51.44, 33.60, 29.83.

HRMS (*m/z*): Calcd. for $\text{C}_{16}\text{H}_{25}\text{I}_2$ [$\text{M}+\text{H}$] $^+$: 471.0040, found: 471.0055

((2,5-dieneopentyl-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane) (19): A flame dried 100 mL Schlenk flask was charged with 30 mL triethylamine, **18** (3.34 g, 7.10 mmol, 1 eq.), trimethylsilylethyne (2.4 mL, 17.8 mmol, 2.5 eq.), copper(I) iodide (108.2 mg, 0.568 mmol, 8 mol%) and Pd(PPh₃)₂Cl₂ (498.3 mg, 0.498 mmol, 10 mol%). The mixture was stirred for 24 h at room temperature. The solvent was removed in vacuo and the residue was dissolved in hexanes and extracted with water. The aqueous phase was extracted with hexanes for twice. The combined organic phases were dried by NaSO₄ and the solvent was removed. The residue was purified by column chromatography using hexanes as eluent to afford compound **19** (1.35 g, 47%).

IR (neat): ν_{max} 3013 cm⁻¹, 2950 cm⁻¹, 2901 cm⁻¹, 2866 cm⁻¹, 2152 cm⁻¹, 1466 cm⁻¹, 1246 cm⁻¹, 832 cm⁻¹, 761 cm⁻¹, 546 cm⁻¹.

^1H NMR (500 MHz, Chloroform-*d*) δ 7.23 (s, 2H), 2.68 (s, 4H), 0.95 (s, 18H), 0.25 (s, 18H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 139.82, 134.48, 123.72, 105.59, 98.65, 46.59, 33.34, 29.76, 0.09.

HRMS (*m/z*): Calcd. for $\text{C}_{26}\text{H}_{43}\text{Si}_2$ [$\text{M}+\text{H}$] $^+$: 411.2897, found: 411.2893.

1,4-diethynyl-2,5-dieneopentylbenzene (20): A 100 mL round bottom flask was charged with **19** (1.35 g, 3.29 mmol, 1 eq.) and suspended in methanol (30 mL) and ether (30 mL), and then K₂CO₃ (1.73 g, 12.5 mmol, 3.8 eq.) was added. The mixture was stirred for 1 h at room temperature. The solvent was removed by rotary evaporation. The resulting mixture was suspended in hexanes, and K₂CO₃ was removed by filtration. The resulting solution was dried by rotary evaporation, and the resulting residue was purified by column chromatography using hexanes as the eluent to afford compound **20** (824.0 mg, 94%).

IR (neat): ν_{max} 3295 cm⁻¹, 2948 cm⁻¹, 2863 cm⁻¹, 2101 cm⁻¹, 1466 cm⁻¹, 1363 cm⁻¹, 1247 cm⁻¹, 900 cm⁻¹, 833 cm⁻¹, 644 cm⁻¹.

^1H NMR (500 MHz, Chloroform-*d*) δ 7.29 (s, 2H), 3.24 (s, 2H), 2.70 (s, 4H), 0.95 (s, 18H).

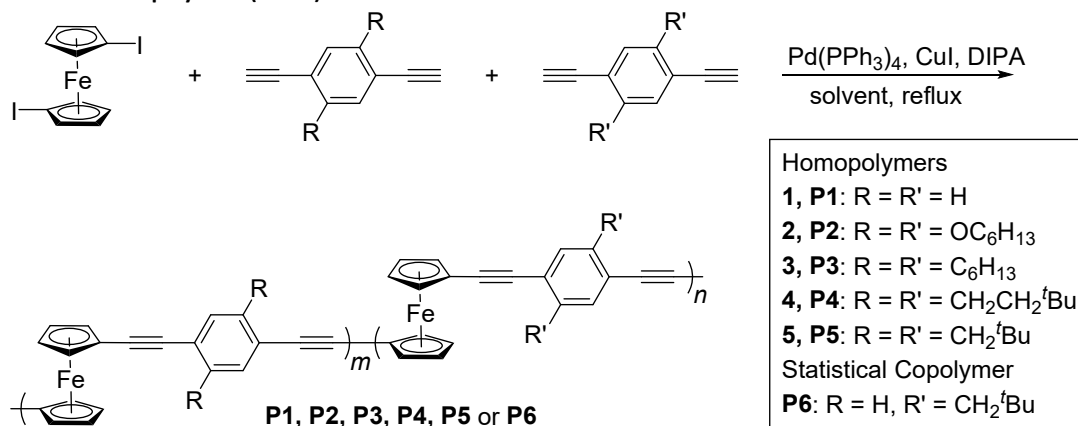
^{13}C NMR (126 MHz, Chloroform-*d*) δ 139.85, 135.26, 123.01, 83.78, 81.41, 46.53, 33.33, 29.69.

HRMS (*m/z*): Calcd. for $\text{C}_{20}\text{H}_{27}$ [$\text{M}+\text{H}$] $^+$: 267.2107, found: 267.2099.

1,1-diiodoferrocene was prepared according to the literature.¹

1.3 Synthesis of polymers

Synthesis of ferrocene polymers (P1-P6):

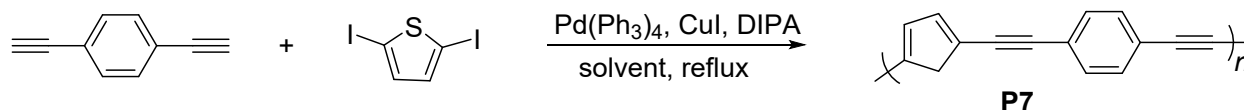


Method A (synthesis of **P2** and **P3**): A Schlenk tube was flame-dried and filled with argon. Substituted 1,4-diethynylbenzene (2.05 mmol, 1 eq.), 1,1'-diiodoferrocene (2.05 mmol, 1 eq.), Pd(PPh₃)₄ (0.0882 mmol, 0.043 eq.) and CuI (0.0882 mmol, 0.043 eq.) were dissolved in diisopropylamine (25 mL) and toluene (25 mL) for **P2** and diisopropylamine (25 mL) and DCM (25 mL) for **P3**. The reaction mixture was stirred at 70 °C for 93 h for **P2** and 107 h for **P3**. The reaction was then cooled to r.t.. The majority of solvent was removed by rotary evaporation, and the resulting residue was extracted with DCM and water. The organic phase was isolated and the solvent removed by rotary evaporation. The resulting residue was washed by organic solvents using the following washing sequence: methanol (30 mL, 4x), ethyl acetate (30 mL, 3x) and hexanes (30 mL, 3x). The washed solid was isolated by centrifugation (6000 rpm, 10 min). The red-brown solid was dried at reduced pressure (~50 mTorr) overnight. **P2** was obtained in 85% yield and **P3** was obtained in 49% yield. Anal. Calcd. for **P2** (C₃₂H₃₆FeO₂): C, 75.59%; H, 7.14%; Fe, 10.98%; O, 6.29%. Found: C, 71.29%; H, 7.40%. Anal. Calcd. for **P3** (C₃₂H₃₆Fe): C, 80.66%; H, 3.93%; Fe, 7.62 Found: C, 72.35%; H, 7.19%.

P6Chemical Formula: C₅₀H₄₄Fe₂•
 Elemental Analysis: C, 79.38; H, 5.86; Fe, 14.76

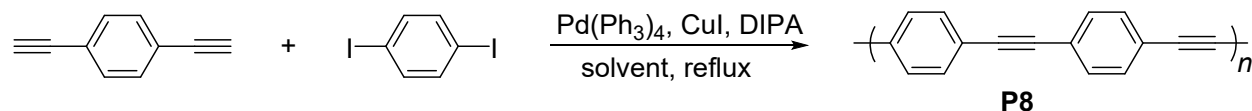
Method B (synthesis of **P1**, **P4**, **P5**, and **P6**): A Schlenk tube was flame-dried and filled with argon. Substituted 1,4-diethynylbenzene (2.05 mmol, 1 eq.), 1,1'-diiodoferrocene (2.05 mmol, 1 eq.), Pd(PPh₃)₄ (0.0882 mmol, 0.043 eq.), CuI (0.0882 mmol, 0.043 eq.) were dissolved in diisopropylamine (0.33 mL, 2.39 mmol, 1.2 eq.) and DCM (45 mL). The reaction mixture was stirred at 70 °C for 72 h. The reaction was then cooled to r.t.. The majority of solvent was removed by rotary evaporation, and the resulting residue was extracted with DCM and water. The organic phase was isolated and the solvent removed by rotary evaporation. The resulting residue was washed by organic solvents using the following washing sequence: methanol (30 mL, 4x), ethyl acetate (30 mL, 3x, except for **P4** due to its non-negligible solubility in ethyl acetate), and hexanes (30 mL, 3x). The washed solid was isolated by centrifugation (6000 rpm, 10 min). The red-brown solid was dried under vacuum overnight. **P1** was obtained in 46% yield, **P4** was obtained in 16% yield, **P5** was obtained in 35% yield, and **P6** was obtained in 28% yield. Anal. Calcd. for **P1** (C₂₀H₁₂Fe): C, 77.95%; H, 3.93%; Fe, 18.12%. Found: C, 70.76%; H, 3.88%. Anal. Calcd. for **P4** (C₃₂H₃₆Fe): C, 80.66%; H, 7.62%; Fe, 11.72 Found: C, 76.56%; H, 7.87%. Anal. Calcd. for **P5** (C₃₀H₃₂Fe): C, 80.35%; H, 7.19%; Fe, 12.45%. Found: C, 62.85%; H, 6.26%. Anal. Calcd. for **P3** (C₂₅H₂₂Fe): C, 79.38%; H, 5.86%; Fe, 7.62 Found: C, 69.98%; H, 5.15%.

Synthesis of other polymers (P7 and P8):



A Schlenk tube was flame-dried and filled with argon. 1,4-Diethynylbenzene (264.92 mg, 2.1 mmol, 1 eq.), 2,5-diiodothiophene (705.5 mg, 2.1 mmol, 1 eq.), Pd(PPh₃)₄ (97.1 mg, 0.084 mmol, 0.04 eq.), CuI (16.0 mg, 0.084 mmol, 0.04 eq.) were dissolved in diisopropylamine (0.53 mL, 2.52 mmol, 1.2 eq.) and DCM (45 mL). The reaction mixture was stirred at 70 °C for 72 h. The reaction was then cooled to r.t.. The majority of solvent was removed by rotary evaporation, and the resulting residue was extracted with DCM and water. The organic phase was isolated and the solvent removed by rotary evaporation. The resulting residue was washed by organic solvents using the following washing sequence: methanol (30 mL, 4x), ethyl acetate (30 mL, 3x), and hexanes

(30 mL, 3x). The washed solid was isolated by centrifugation (6000 rpm, 10 min). The red-brown solid was dried under vacuum overnight. **P7** was obtained in 53% yield. Analysis of the soluble portion of the polymer by SEC (180 °C in 1,2,4-trichlorobenzene, polystyrene standard) was used to estimate $M_n = 4900$ g/mol, $M_w = 6300$ g/mol, and $D_M = 1.27$.



A Schlenk tube was flame-dried and filled with argon. 1,4-Diethynylbenzene (264.92, 2.1 mmol, 1 eq.), 1,4-Diiodobenzene (692.8 mg, 2.1 mmol, 1 eq.), Pd(PPh₃)₄ (97.1 mg, 0.084 mmol, 0.04 eq.), CuI (16.0 mg, 0.084 mmol, 0.04 eq.) were dissolved in diisopropylamine (0.53 mL, 2.52 mmol, 1.2 eq.) and DCM (45 mL). The reaction mixture was stirred at 70 °C for 72 h. The reaction was then cooled to r.t.. The majority of solvent was removed by rotary evaporation, and the resulting residue was extracted with DCM and water. The organic phase was isolated and the solvent removed by rotary evaporation. The resulting residue was washed by organic solvents using the following washing sequence: methanol (30 mL, 4x), ethyl acetate (30 mL, 3x), and hexanes (30 mL, 3x). The washed solid was isolated by centrifugation (6000 rpm, 10 min). The red-brown solid was dried under vacuum overnight. **P8** was obtained in 49 % yield. The resulting polymer was completely insoluble in 1,2,4-trichlorobenzene at 180 °C, precluding analysis by SEC.

1.4 Polymer activation and gas sorption

Polymers were activated under reduced pressure (~50 mTorr) with heating at different temperatures prior to N₂ sorption analysis according to the following tables. Polymers **P3** and **P4** were determined to be non-porous (<10 m²/g BET surface area, the lower limit of our measurements) irrespective of activation method (Figures S36-41).

Table S1. P1 N₂ sorption BET surface area

Temperature (°C)	Time (h)	BET surface area (m ² /g) ^a
r.t.	7	416 ± 3
100	10	427 ± 3
100	17	422 ± 3
100	36	418 ± 3
150	2	416 ± 2

^aThe reported errors are those associated with the BET equation fit.

Table S2. P2 N₂ sorption BET surface area

Temperature (°C)	Time (h)	BET surface area (m ² /g) ^a
r.t.	17	21 ± 0.3
50	17	21 ± 0.3
100	17	18 ± 0.3
150	21	16 ± 0.3
200	20	17 ± 0.3

^aThe reported errors are those associated with the BET equation fit.

Table S3. P5 N₂ sorption BET surface area

Temperature (°C)	Time (h)	BET surface area (m ² /g) ^a
r.t.	6	110 ± 1
50	7	40 ± 1
100	7	nonporous

^aThe reported errors are those associated with the BET equation fit.

Table S4. P6 N₂ sorption BET surface area

Temperature (°C)	Time (h)	BET surface area (m ² /g) ^a
r.t.	5	391 ± 3
30	7	376 ± 2
40	48	354 ± 2
80	36	343 ± 3
100	48	311 ± 3

^aThe reported errors are those associated with the BET equation fit.

Table S5. P7 N₂ sorption BET surface area

Temperature (°C)	Time (h)	BET surface area (m ² /g) ^a
r.t.	7	98 ± 1
100	3	65 ± 1

^aThe reported errors are those associated with the BET equation fit.

Table S6. P8 N₂ sorption BET surface area

Temperature (°C)	Time (h)	BET surface area (m ² /g) ^a
r.t.	15	160 ± 2
100	2	94 ± 1

^aThe reported errors are those associated with the BET equation fit.

1.5 Polymer solubility

Table S7. Solubility of **P1-P6** in organic solvents at room temperature (ca. 23 °C).

Solvent	P1	P2	P3	P4	P5	P6
Hexanes	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble
Toluene	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble
Chlorobenzene	Sparingly soluble	Sparingly soluble	Sparingly soluble	Partially soluble	Partially soluble	Sparingly soluble
Dichloromethane	Sparingly soluble	Partially soluble	Sparingly soluble	Soluble	Sparingly soluble	Sparingly soluble
Chloroform	Sparingly soluble	Partially soluble	Sparingly soluble	Soluble	Sparingly soluble	Partially soluble
Acetone	Insoluble	Partially soluble	Sparingly soluble	Soluble	Sparingly soluble	Sparingly soluble
Ethyl acetate	Insoluble	Sparingly soluble	Sparingly soluble	Soluble	Sparingly soluble	Sparingly soluble
Tetrahydrofuran	Partially soluble	Partially soluble	Partially soluble	Soluble	Partially soluble	Partially soluble
Methanol	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble
Dimethylformamide	Partially soluble	Partially soluble	Partially soluble	Soluble	Partially soluble	Partially soluble
Dimethyl sulfoxide	Partially soluble	Partially soluble	Partially soluble	Soluble	Partially soluble	Partially soluble
1,2,4-Trichlorobenzene	Sparingly soluble	Partially soluble	Partially soluble	Partially soluble	Sparingly soluble	Partially soluble

2. Spectroscopic, gas sorption, thermogravimetric analysis, and cyclic voltammetry data

2.1 ^1H NMR and ^{13}C NMR spectra

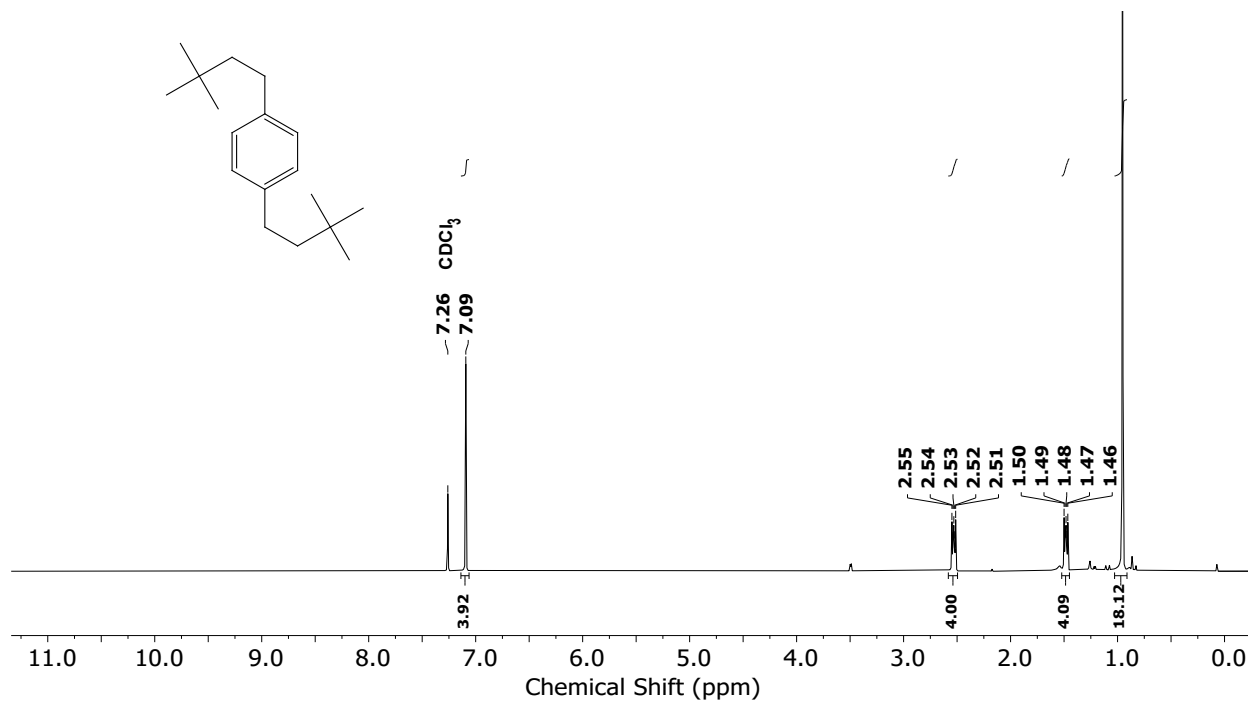


Figure S1. ^1H NMR spectrum of compound 12.

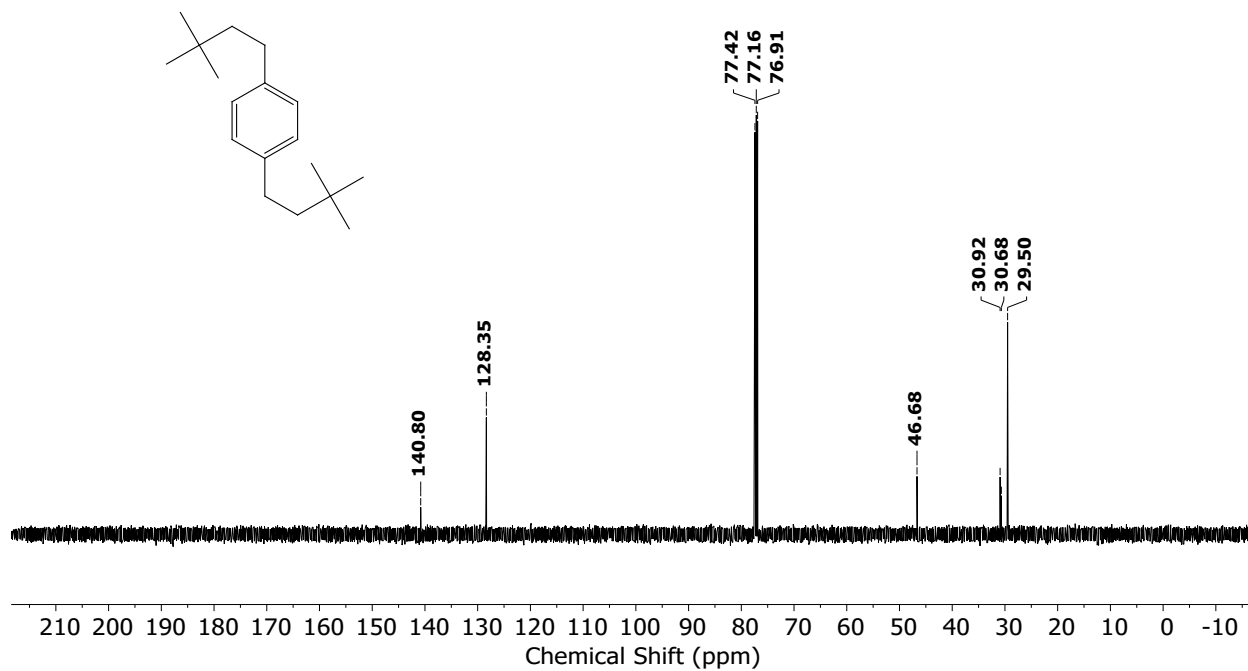


Figure S2. ^{13}C NMR spectrum of compound 12.

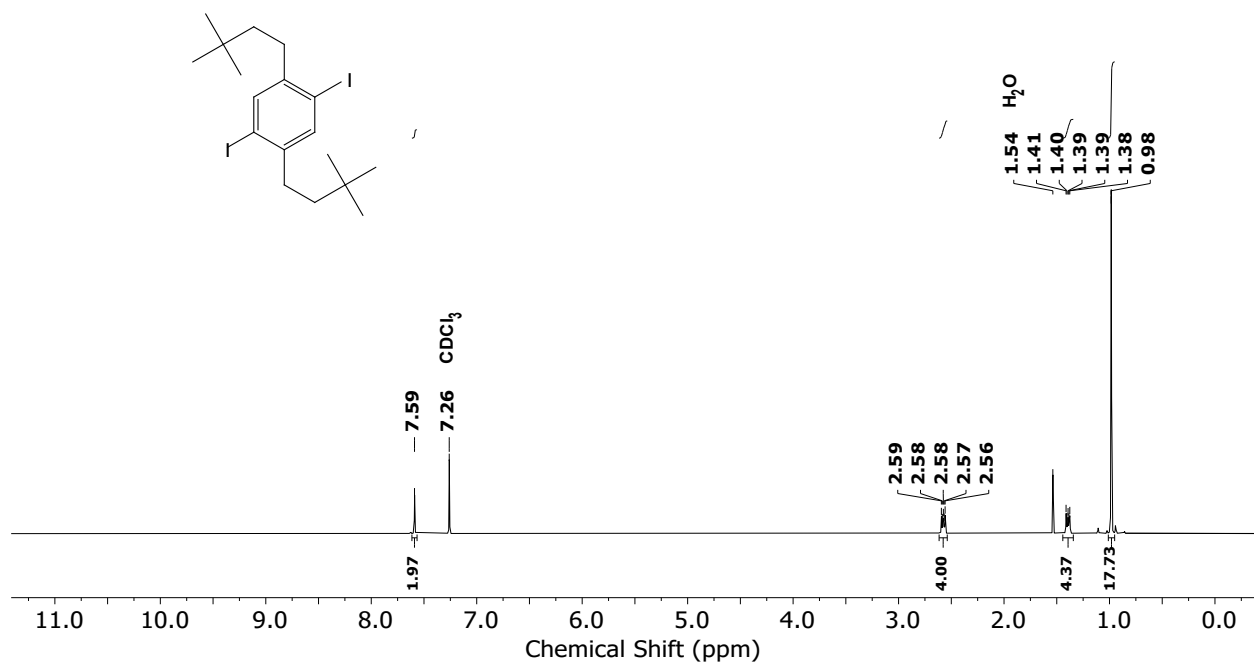


Figure S3. ¹H NMR spectrum of compound 13.

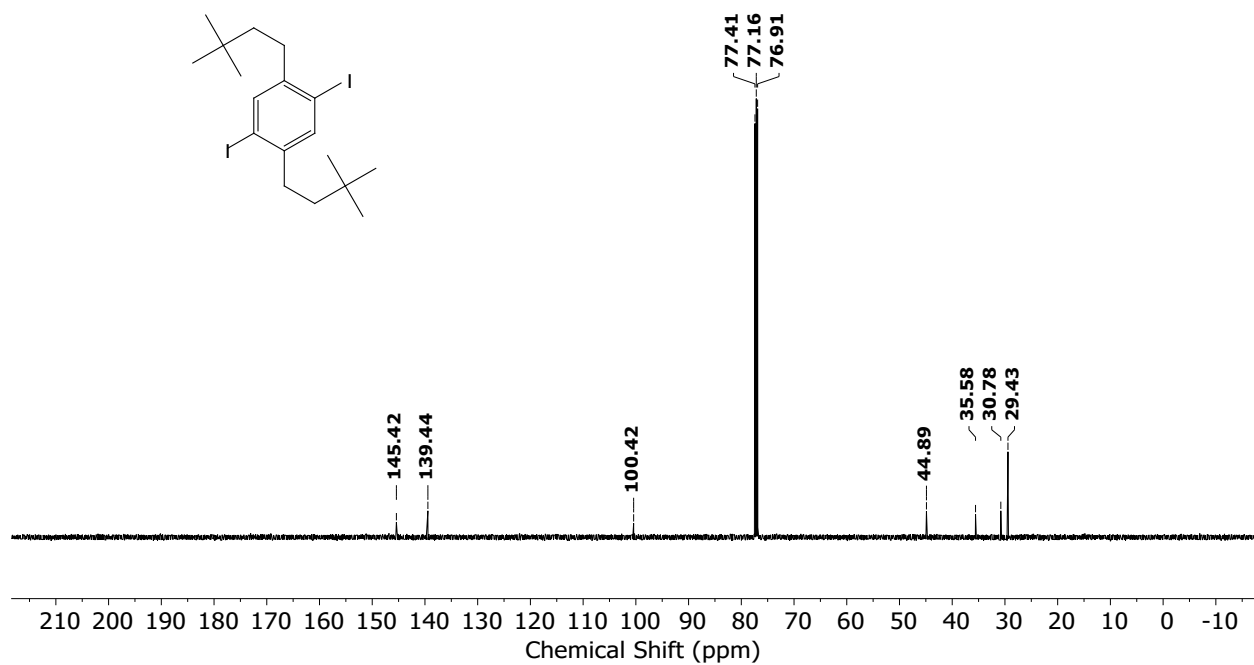


Figure S4. ¹³C NMR spectrum of compound 13.

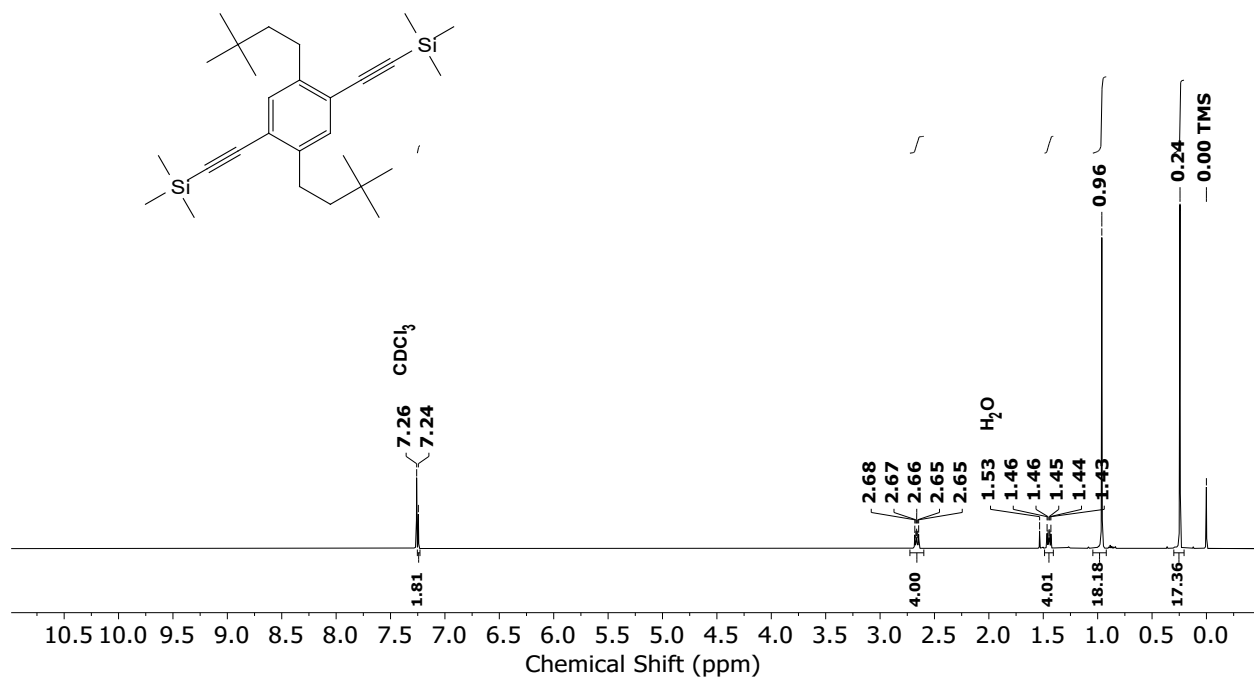


Figure S5. ^1H NMR spectrum of compound 14.

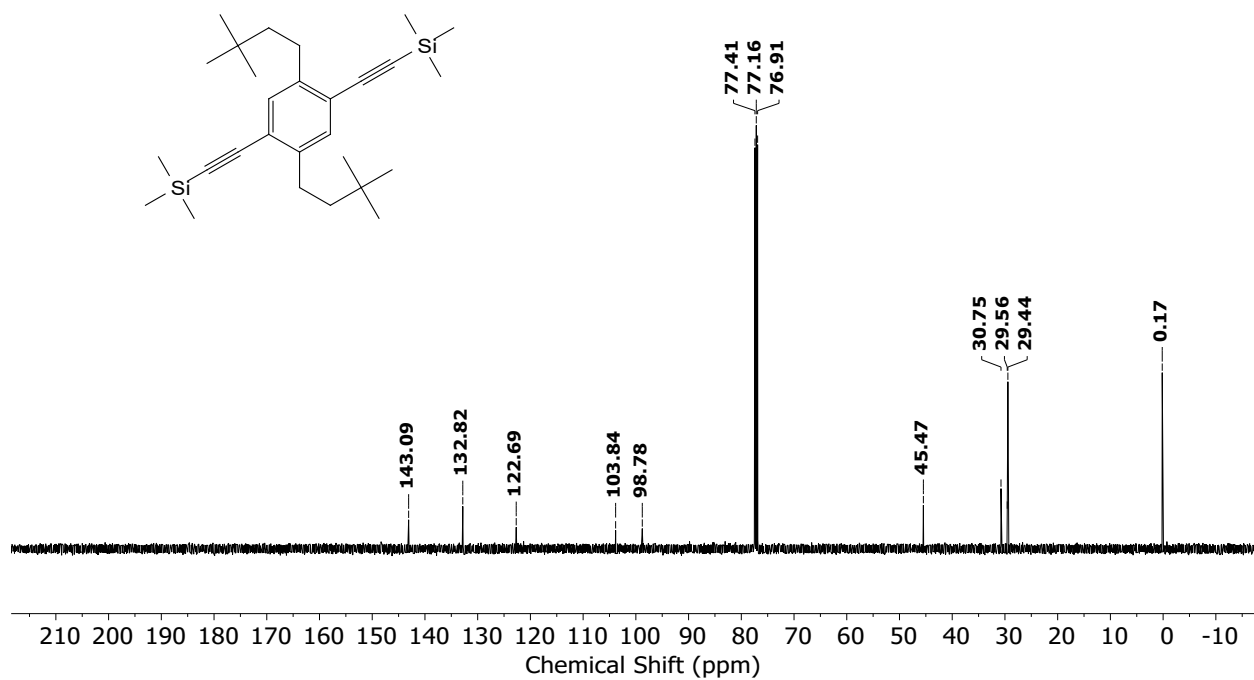


Figure S6. ^{13}C NMR spectrum of compound 14.

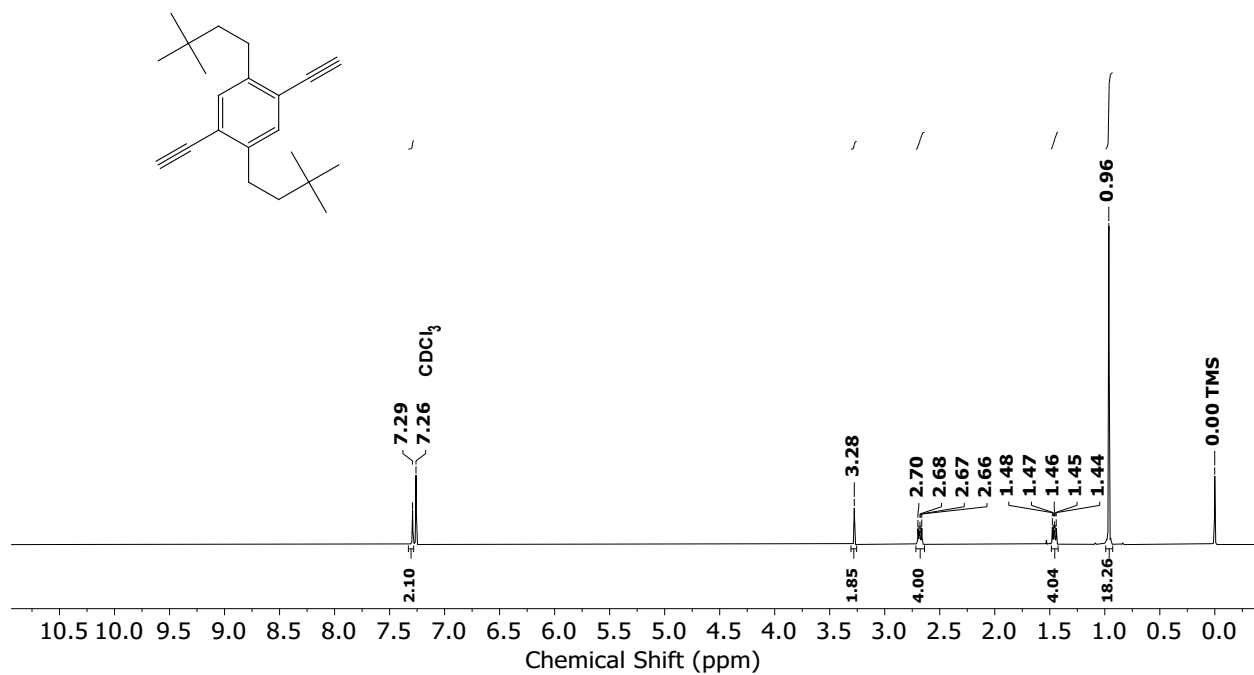


Figure S7. ^1H NMR spectrum of compound 15.

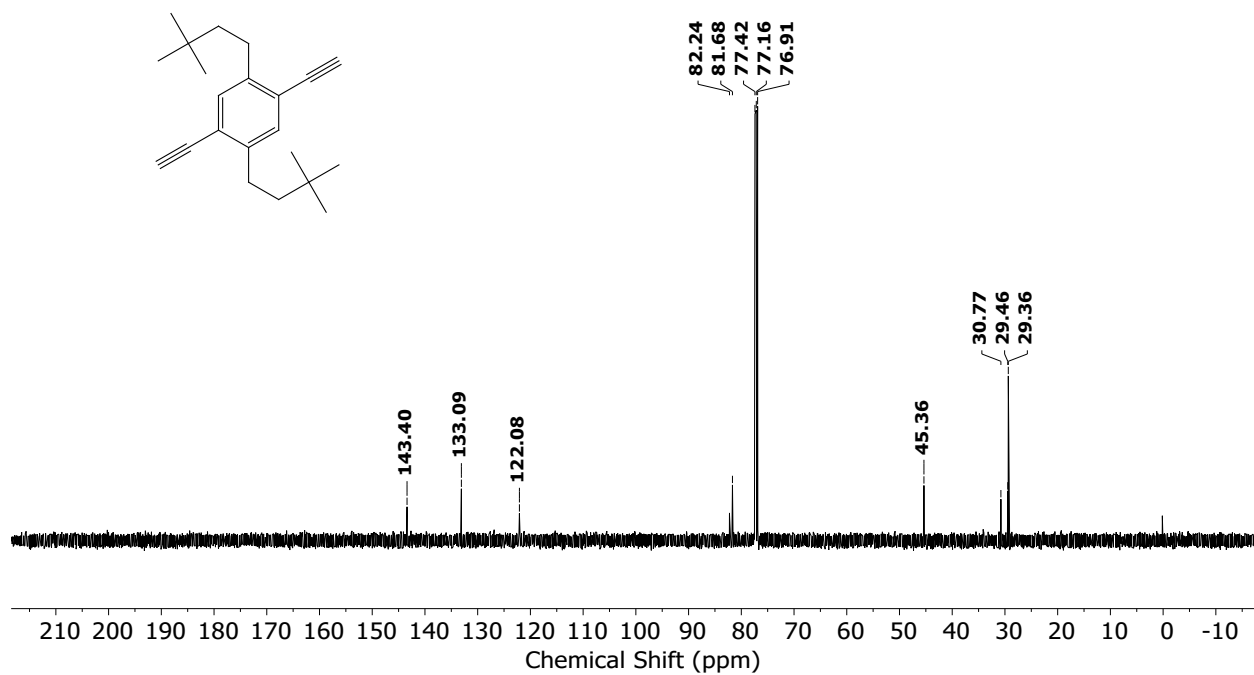


Figure S8. ^{13}C NMR spectrum of compound 15. Figure S9. ^1H NMR spectrum of compound 17.

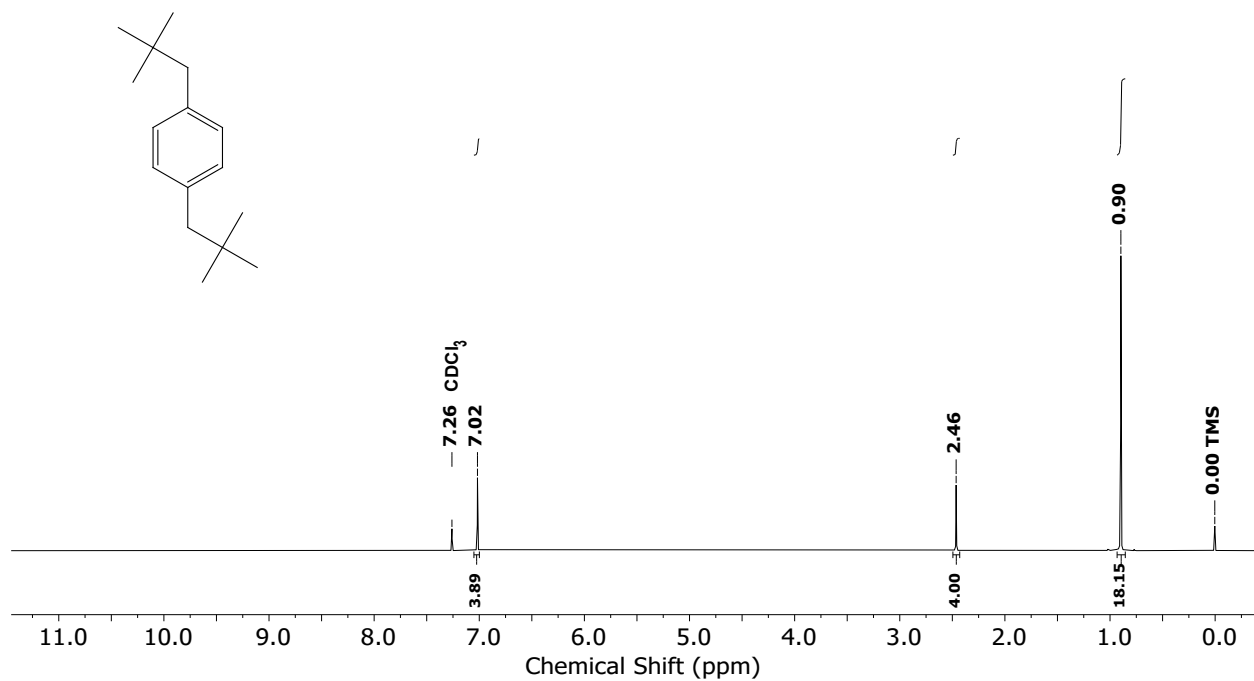


Figure S9. ^1H NMR spectrum of compound 17.

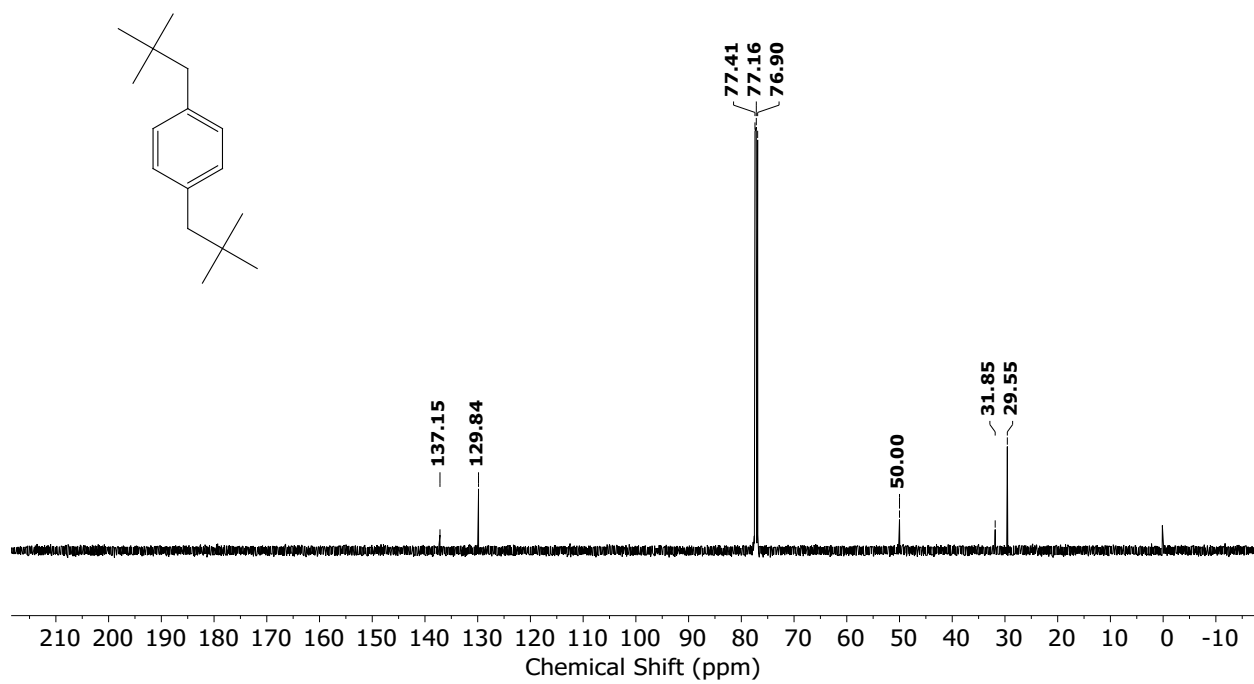


Figure S10. ^{13}C NMR spectrum of compound 17.

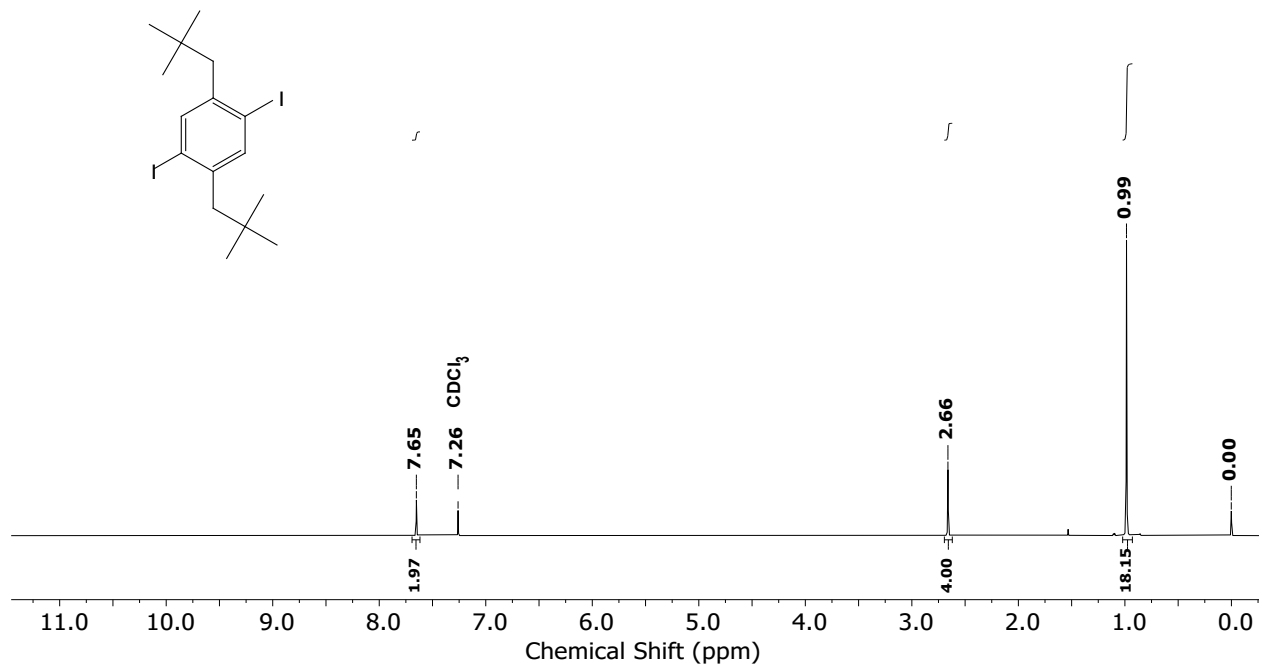


Figure S11. ¹H NMR spectrum of compound 18.

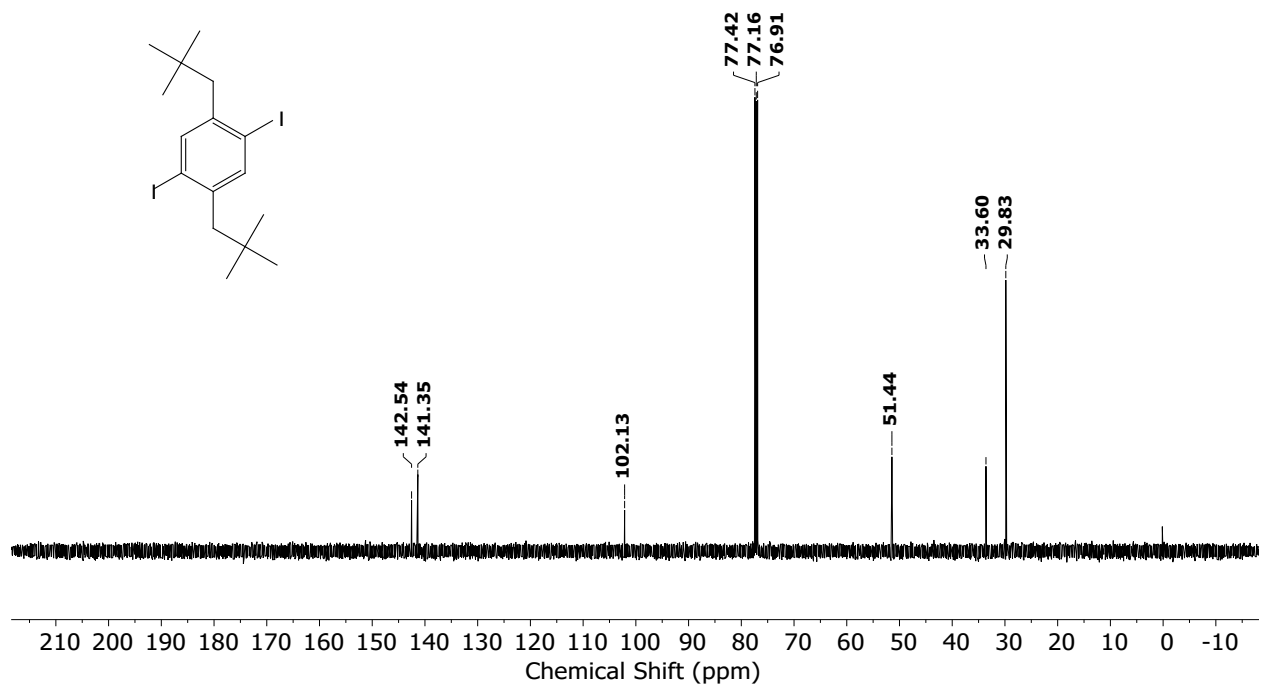


Figure S12. ¹³C NMR spectrum of compound 18.

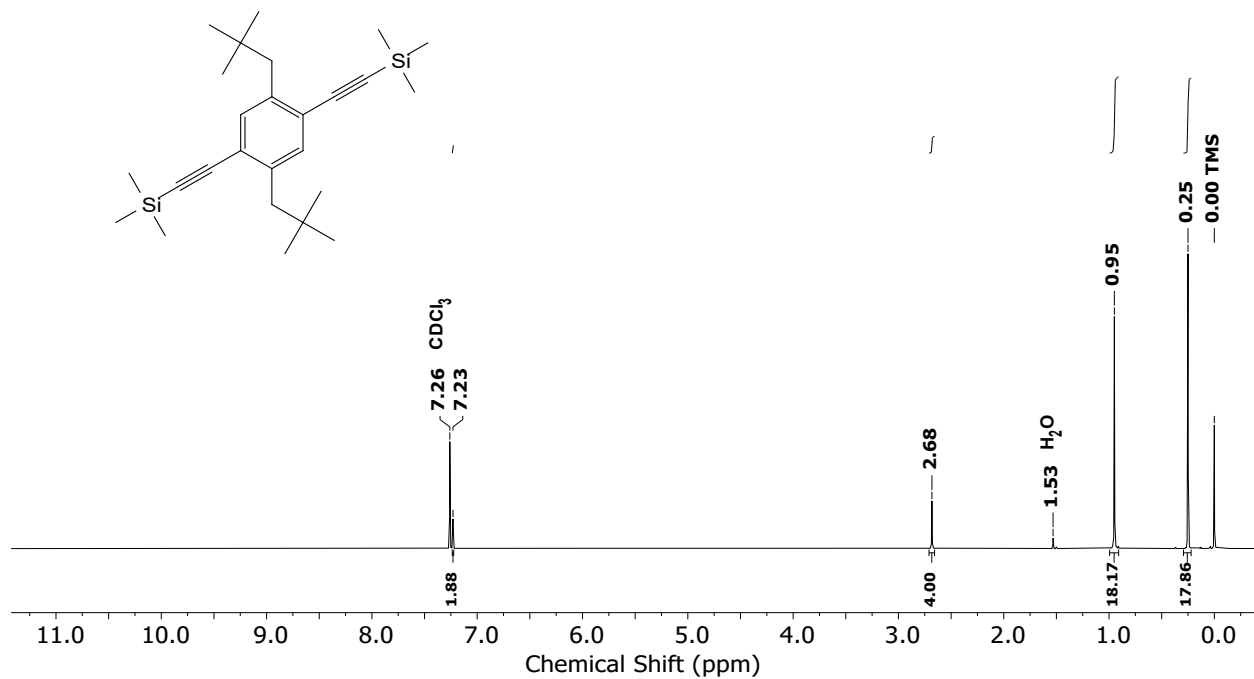


Figure S13. ¹H NMR spectrum of compound 19.

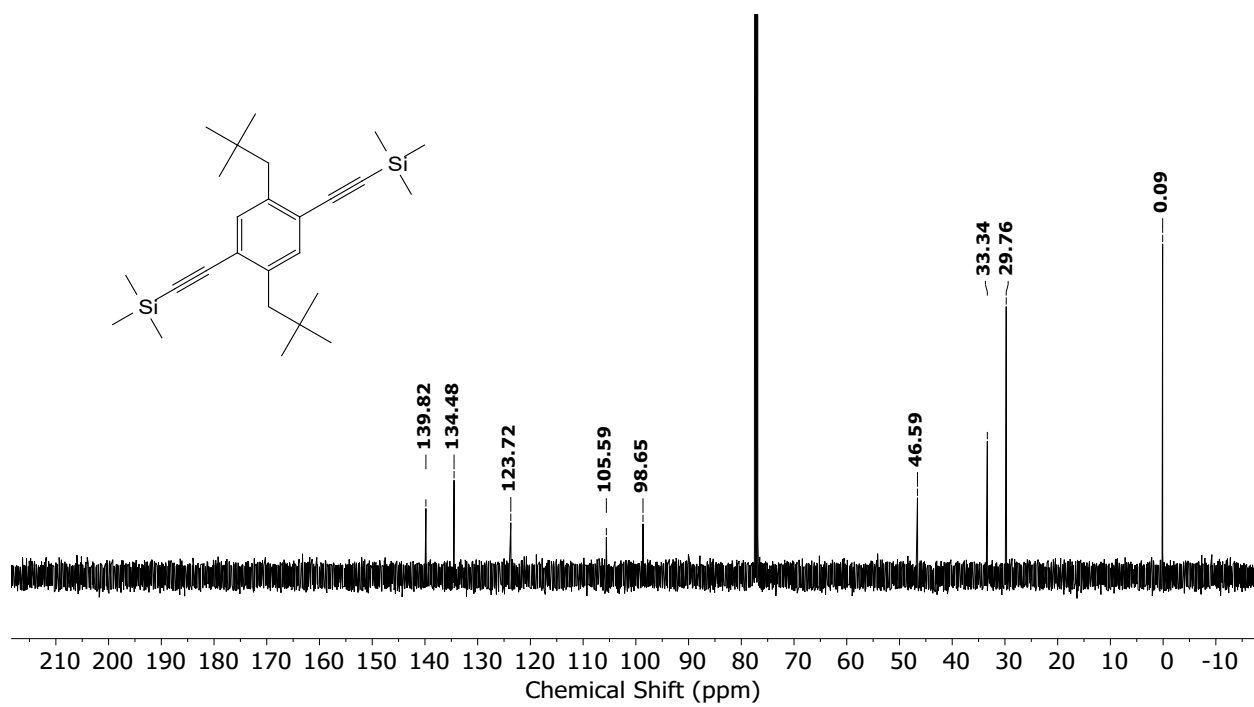


Figure S14. ¹³C NMR spectrum of compound 19.

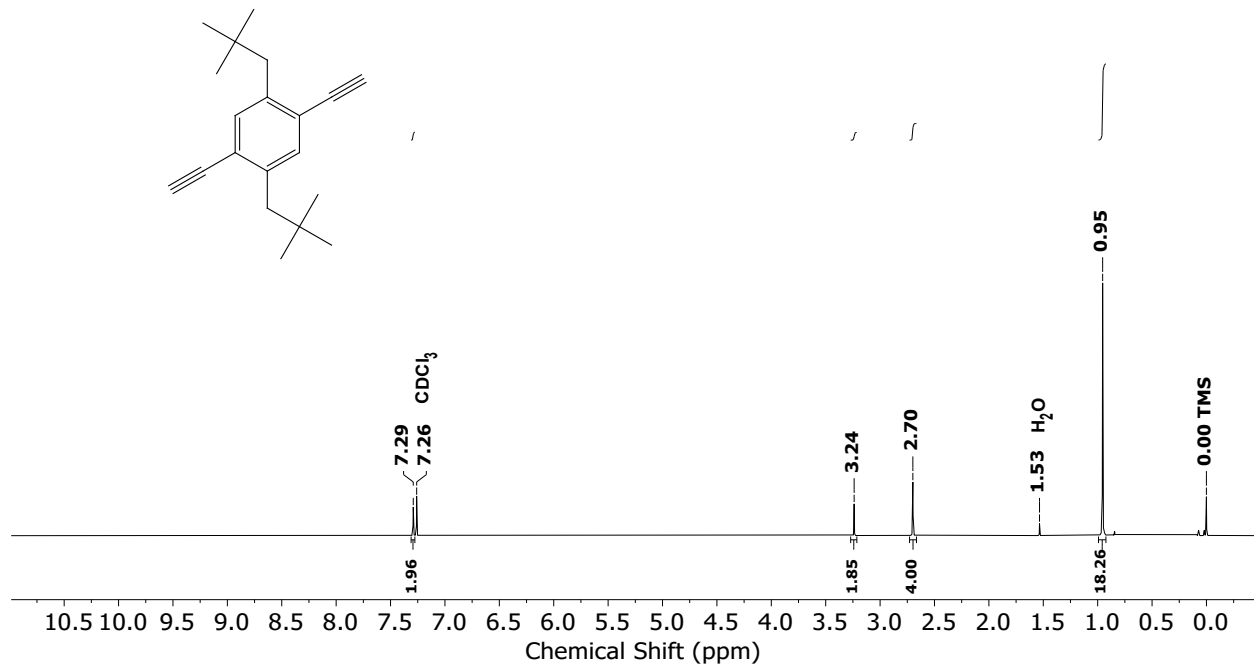


Figure S15. ¹H NMR spectrum of compound 20.

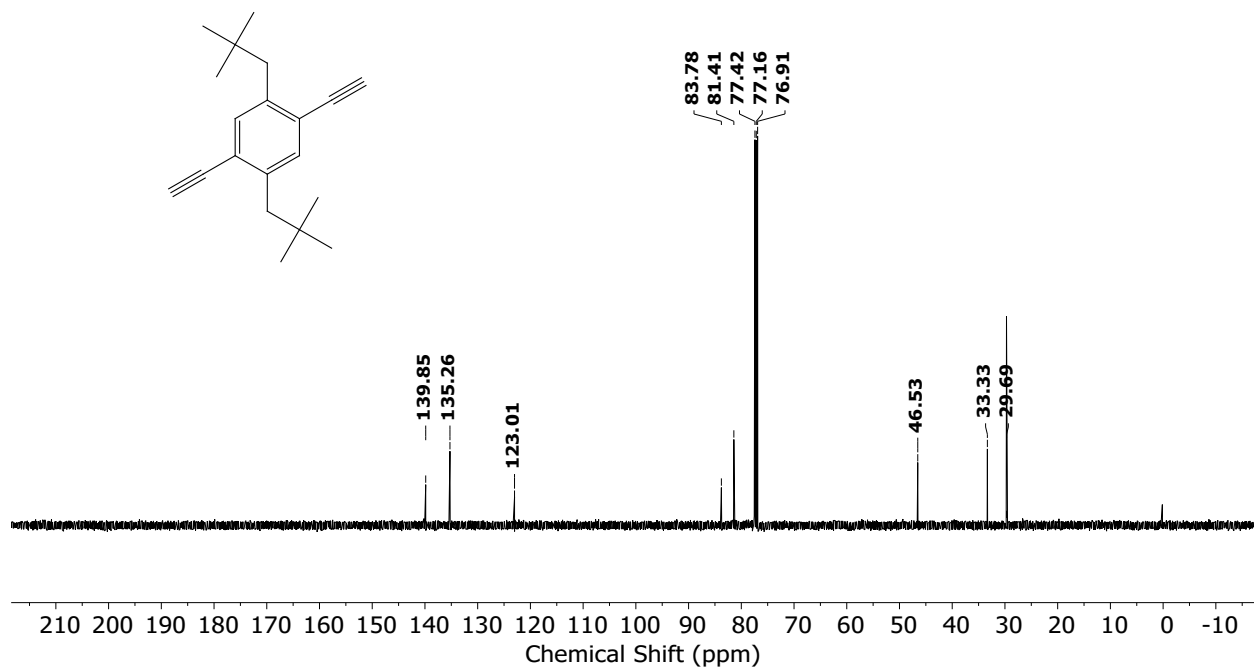


Figure S16. ¹³C NMR spectrum of compound 20.

P4

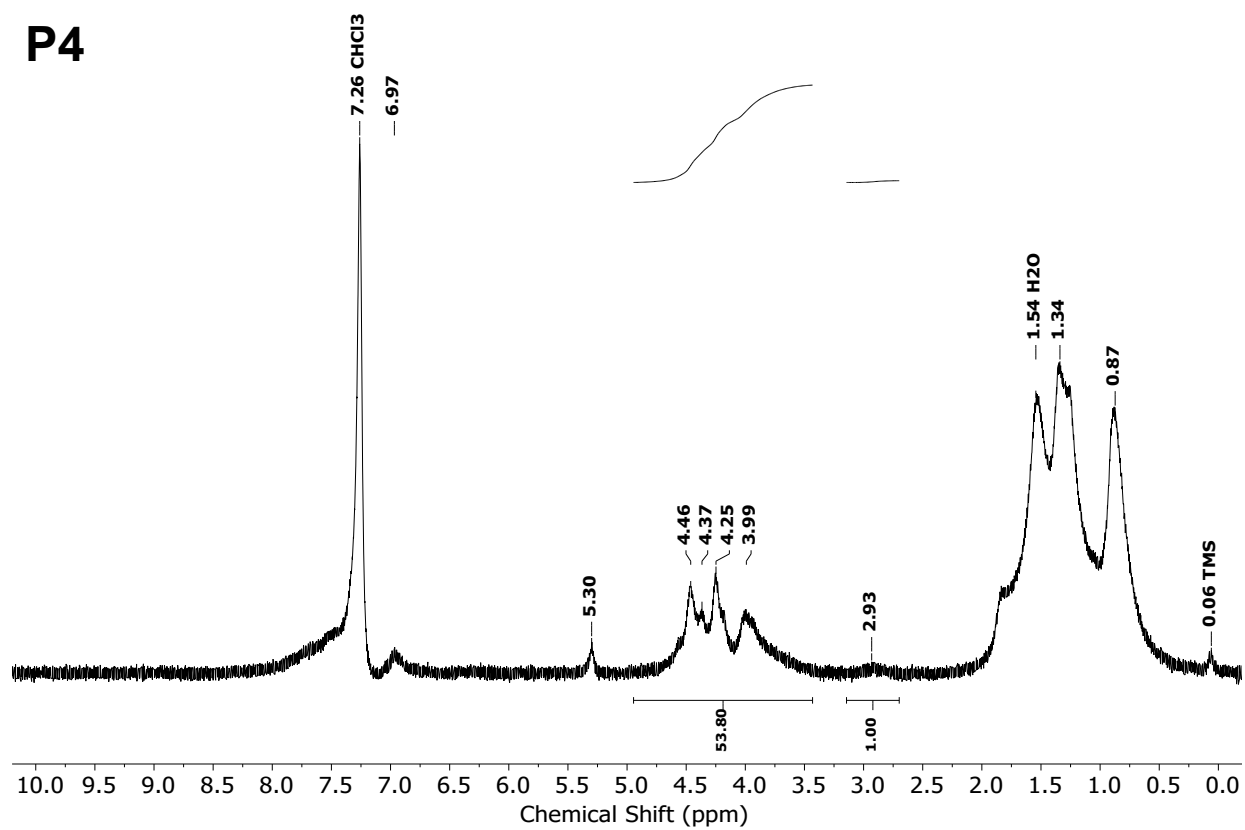


Figure S17. ¹H NMR spectrum of P4.

2.2 FT-IR spectra

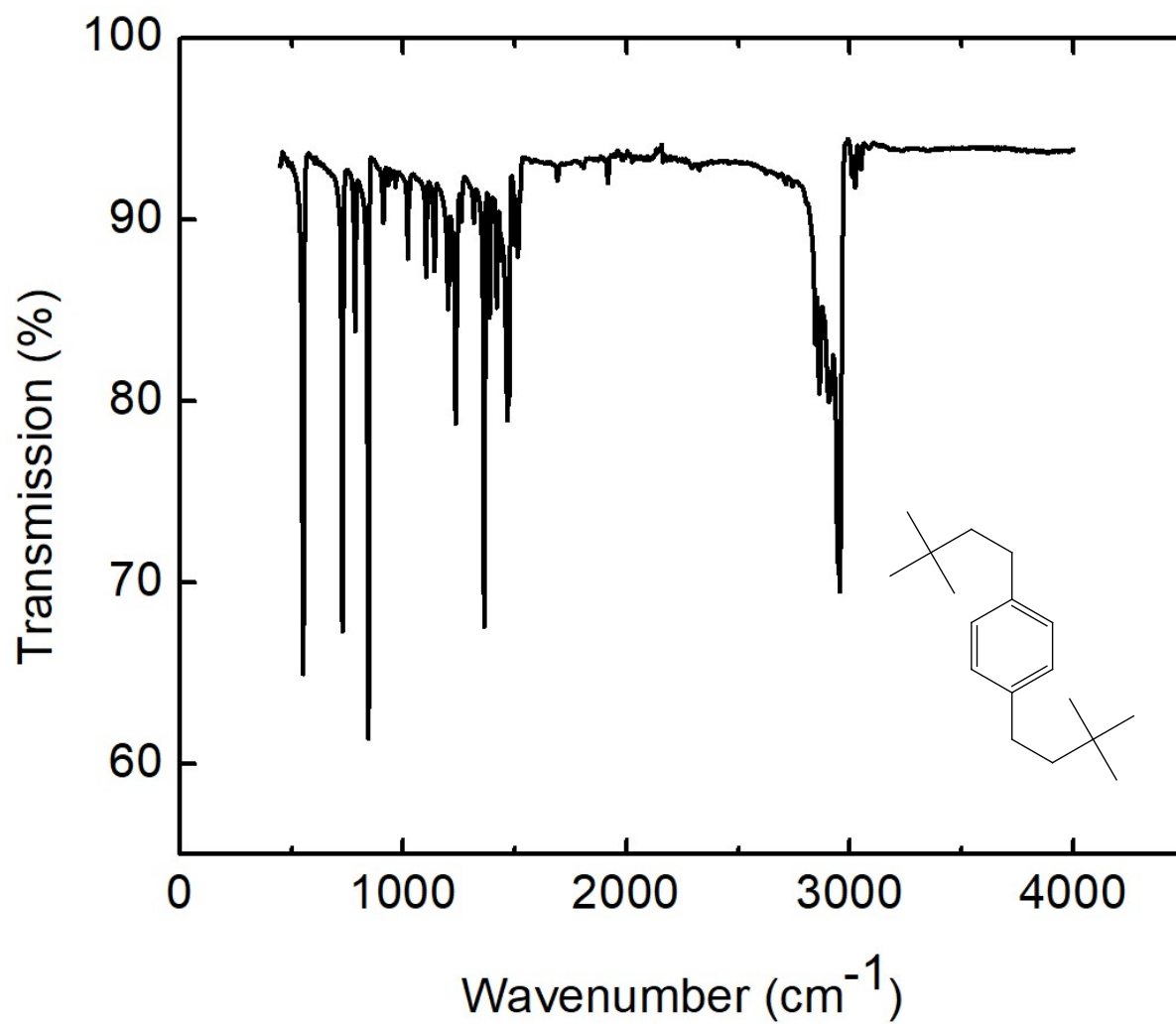


Figure S18. FT-IR spectrum of compound 12.

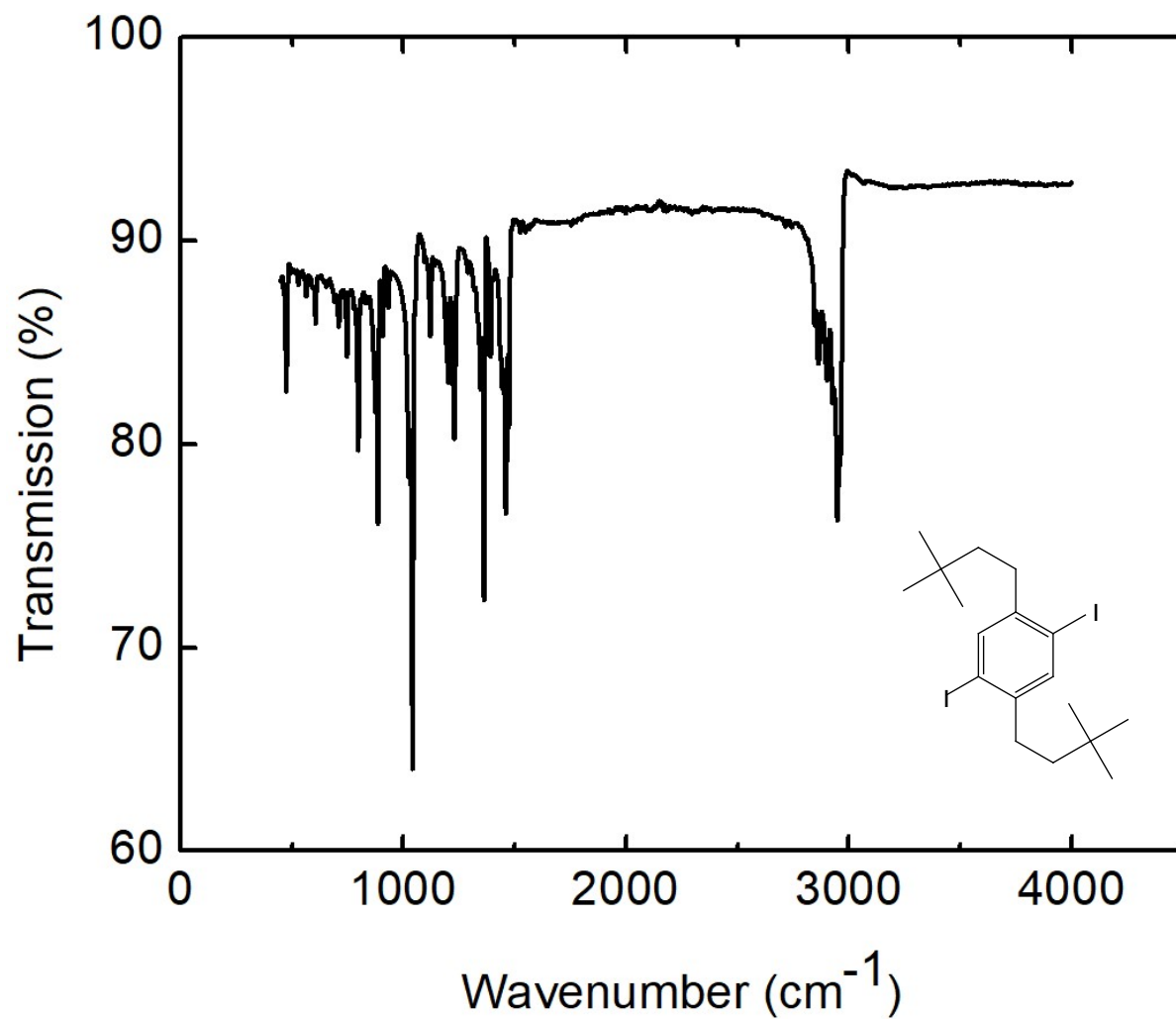


Figure S18. FT-IR spectrum of compound 12.

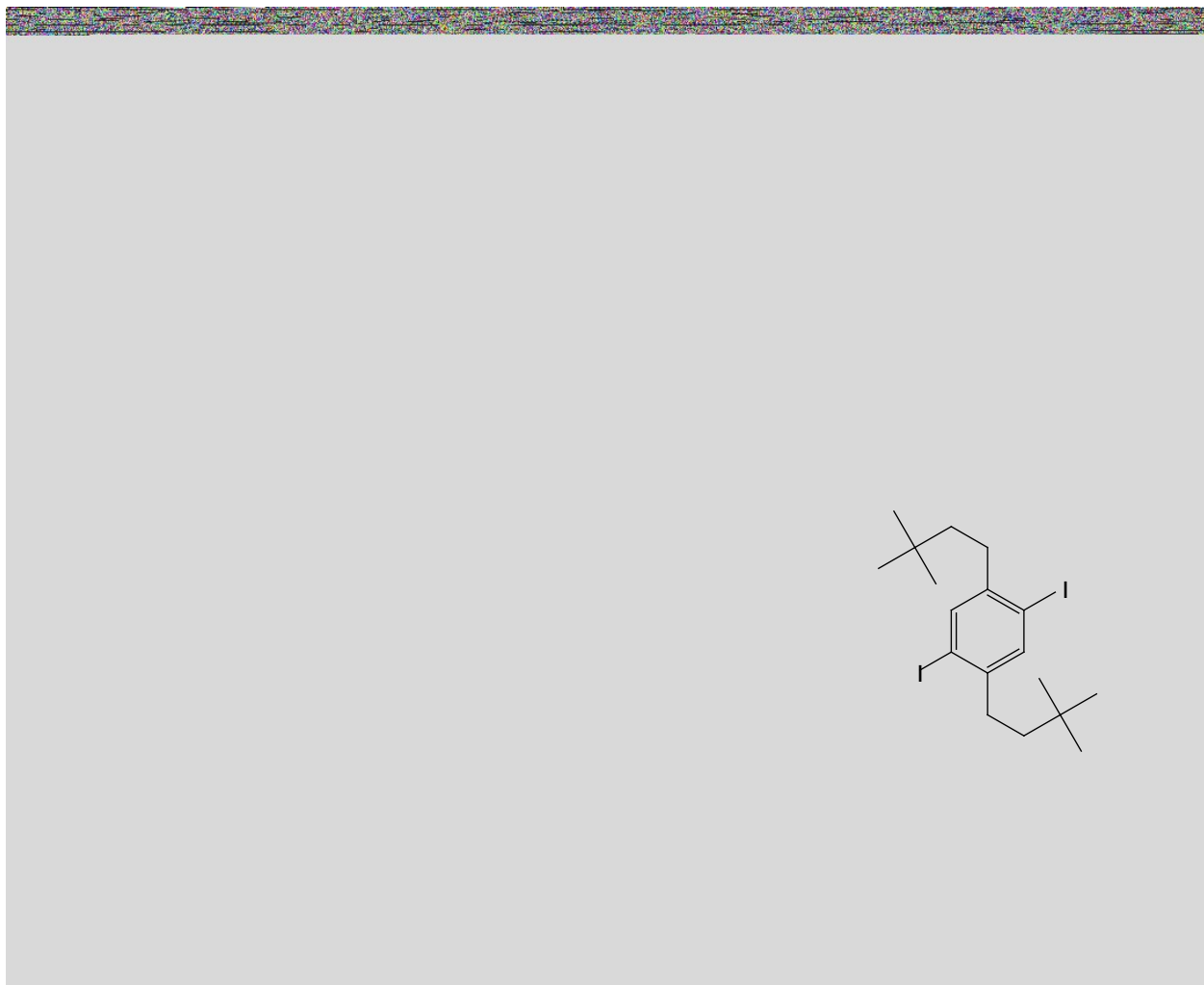


Figure S18. FT-IR spectrum of compound **12**.

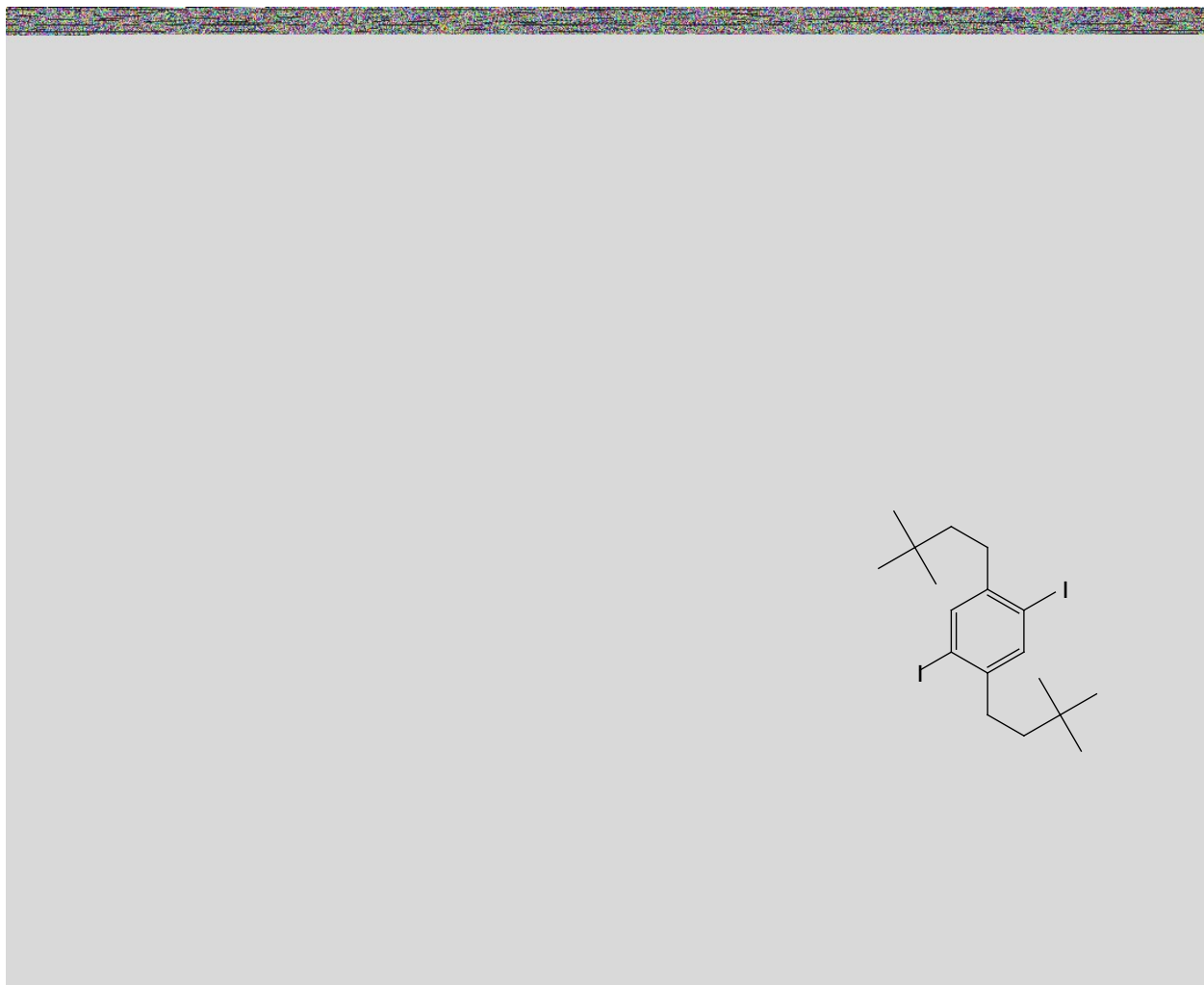


Figure S18. FT-IR spectrum of compound **12**.

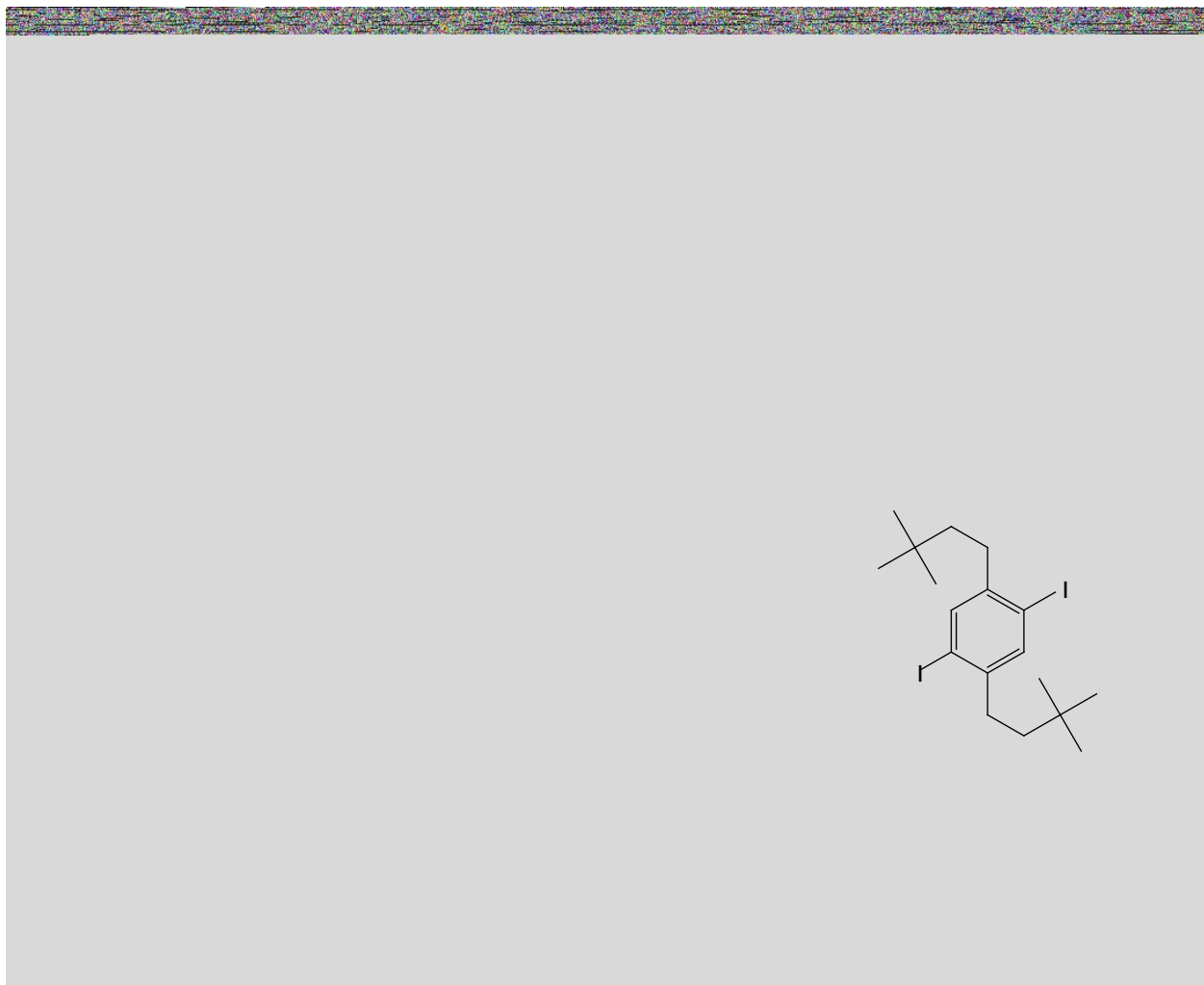


Figure S19. FT-IR spectrum of compound **13**.

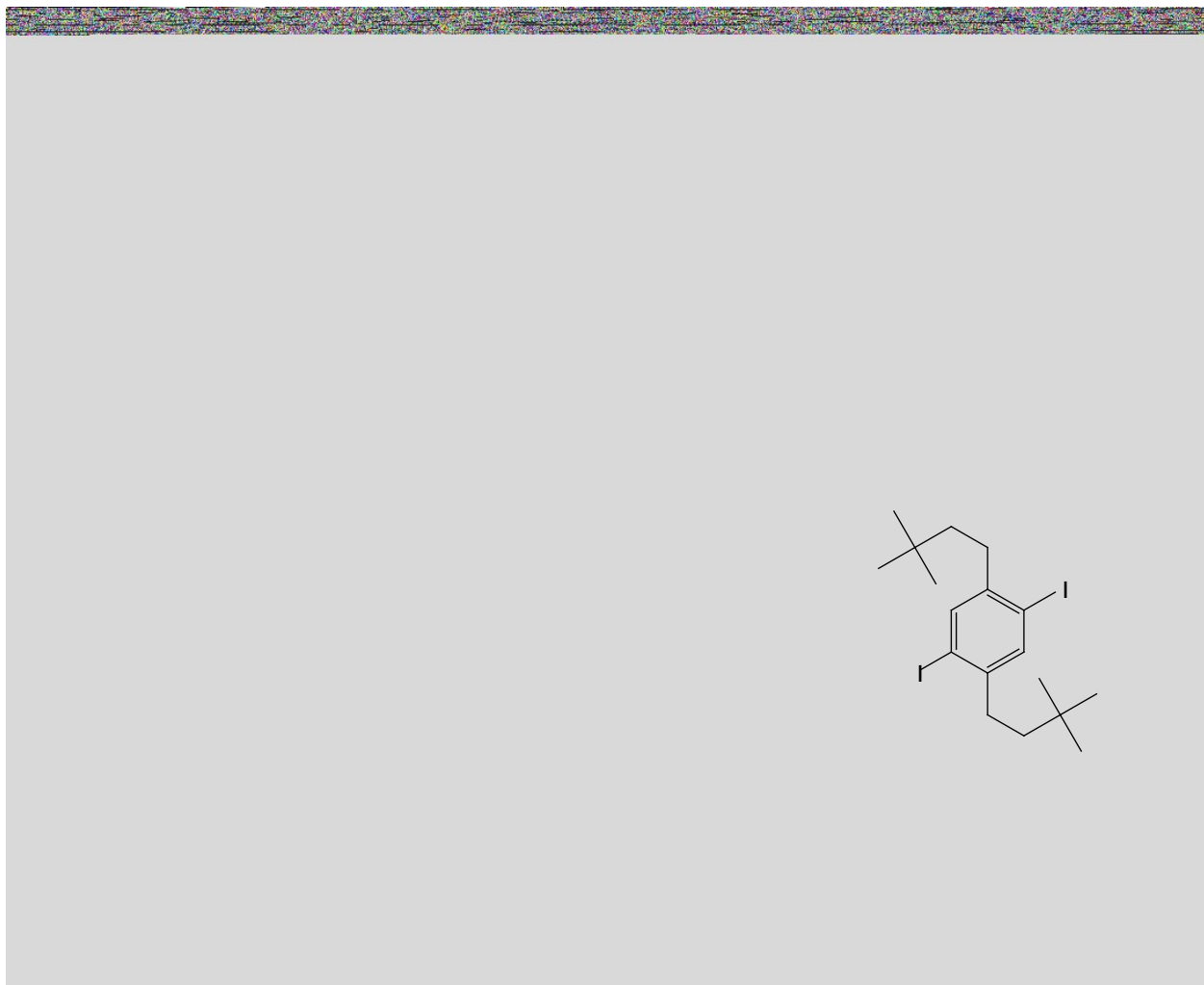


Figure S18. FT-IR spectrum of compound **12**.

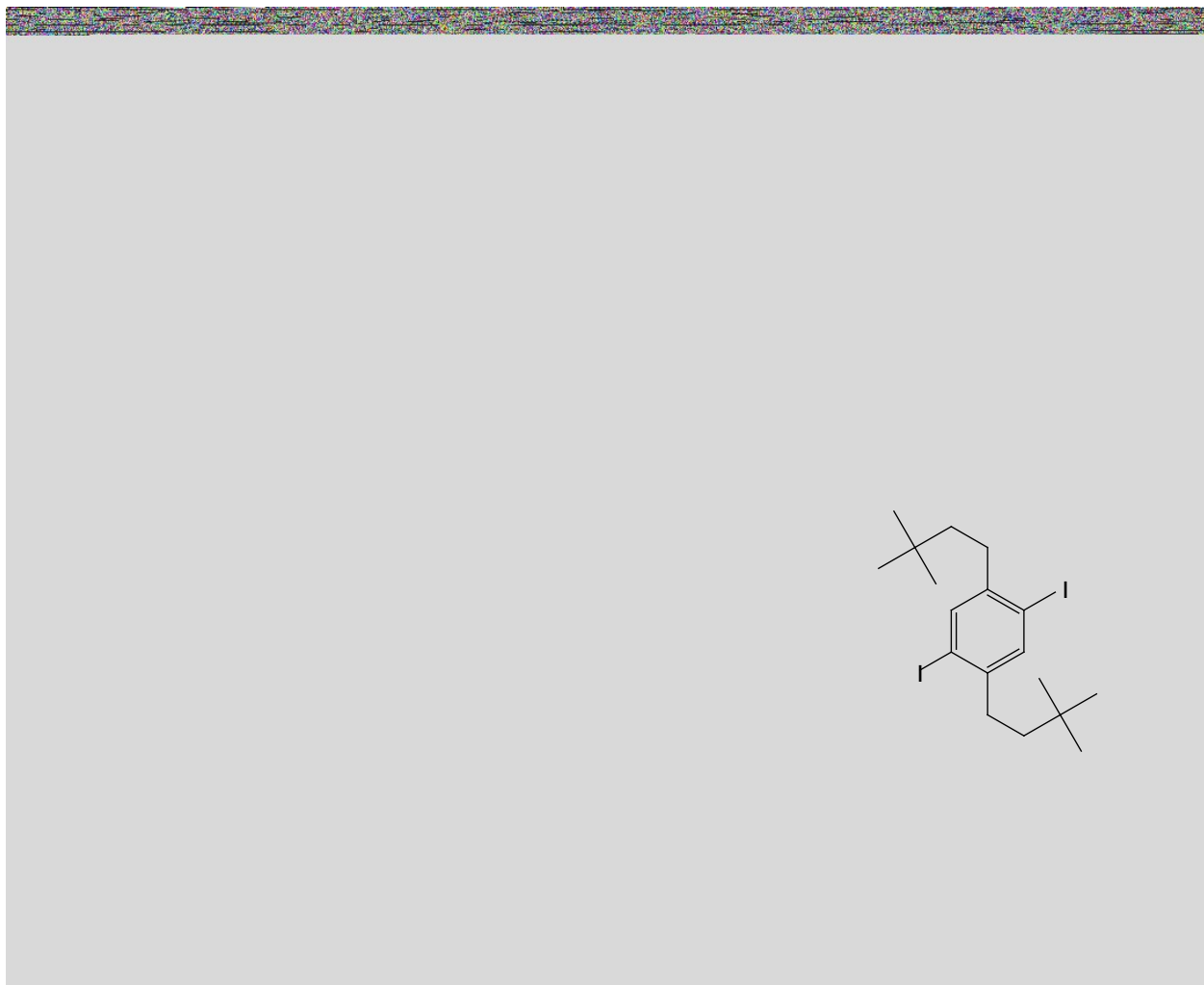


Figure S19. FT-IR spectrum of compound **13**.

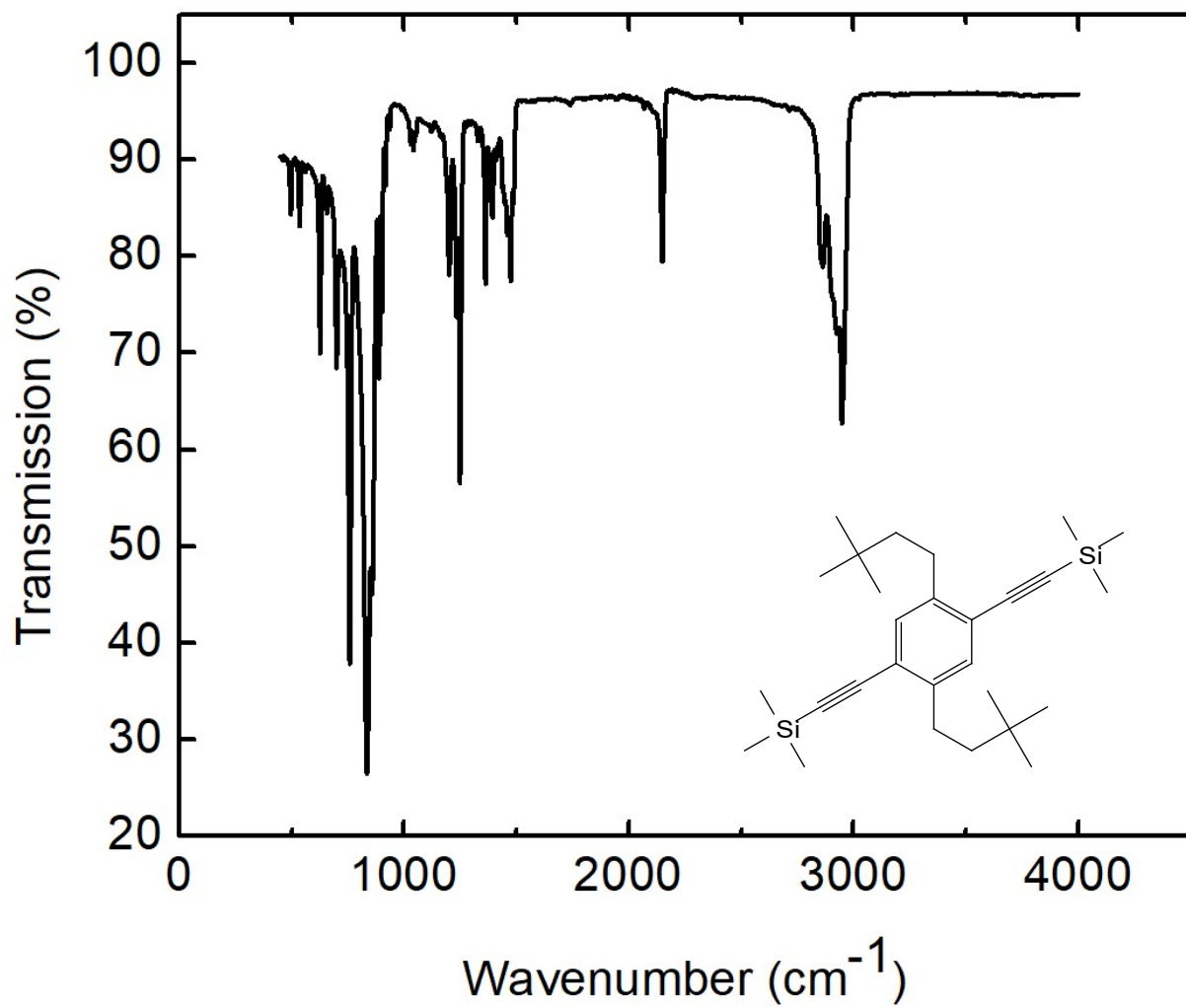


Figure S20. FT-IR spectrum of compound 14.

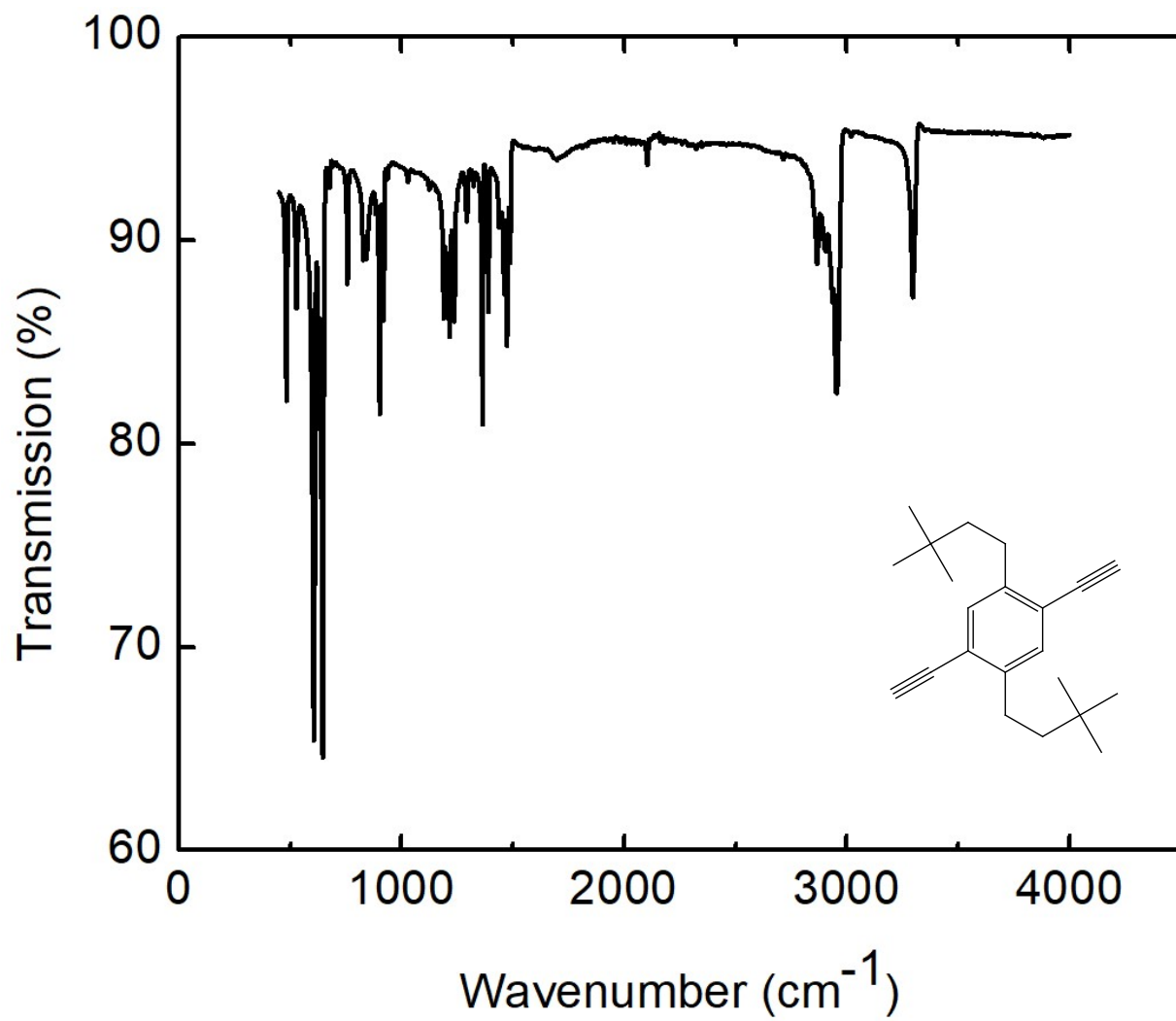


Figure S21. FT-IR spectrum of compound 15.

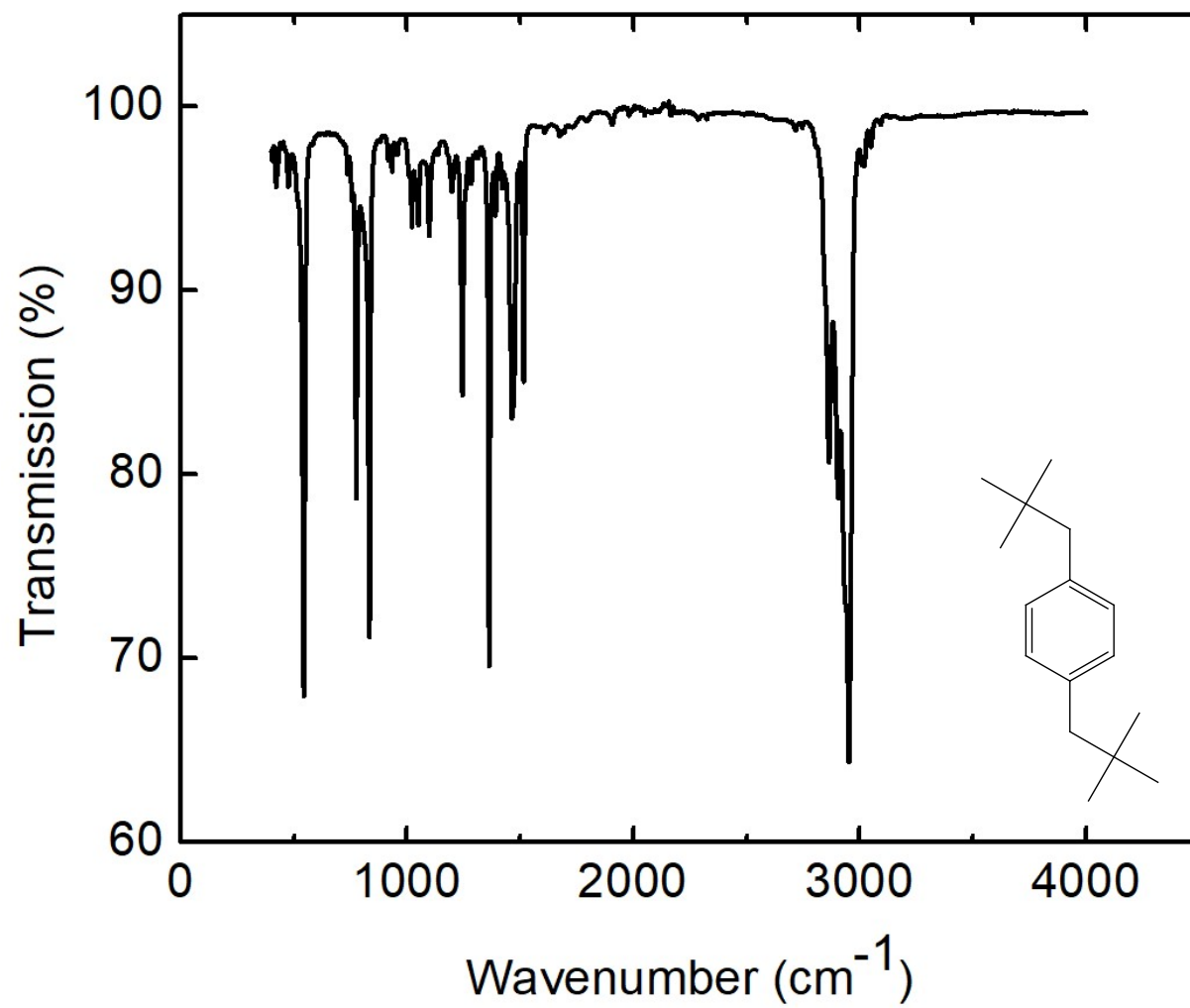


Figure S22. FT-IR spectrum of compound 17.

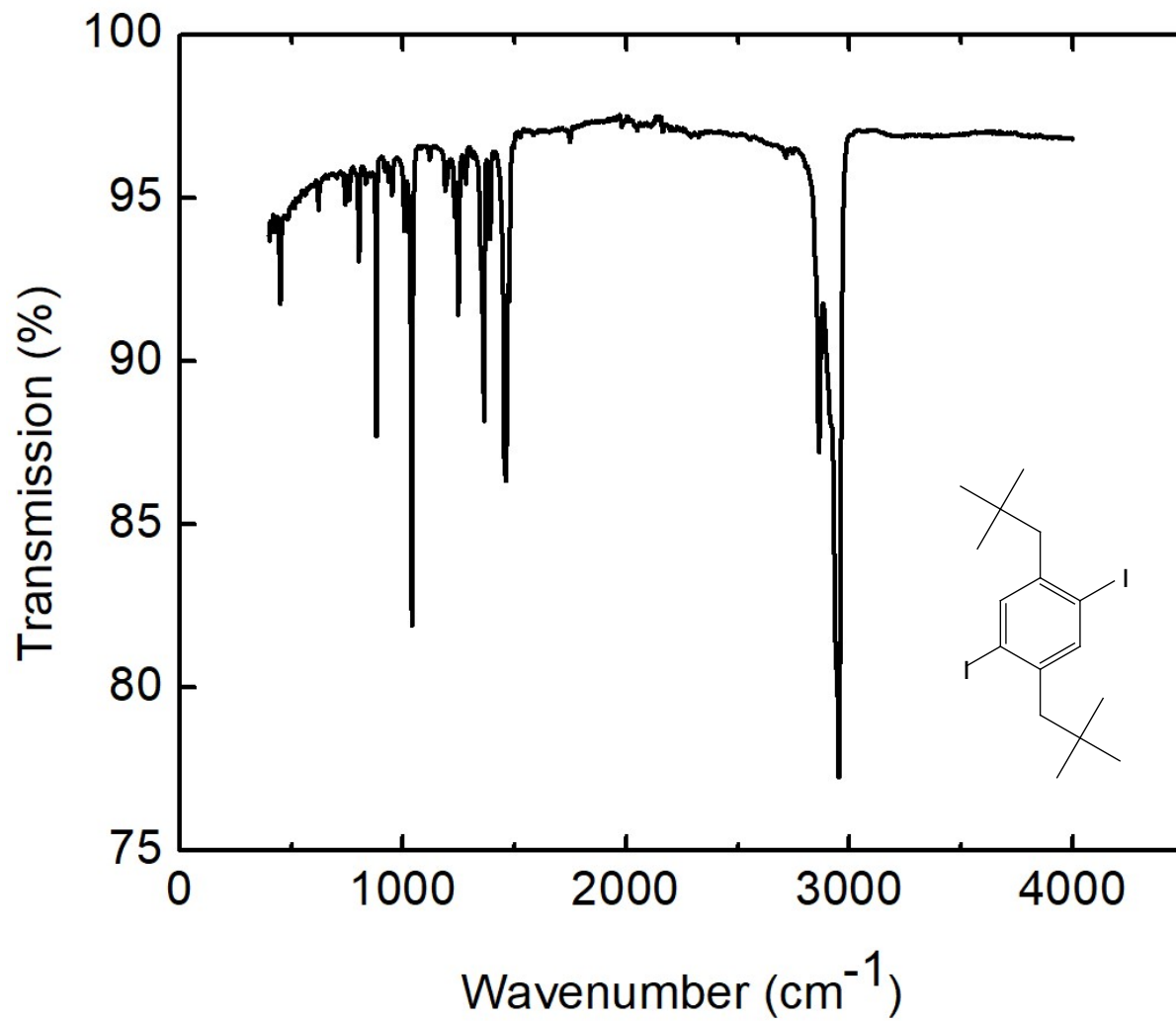


Figure S23. FT-IR spectrum of compound 18.

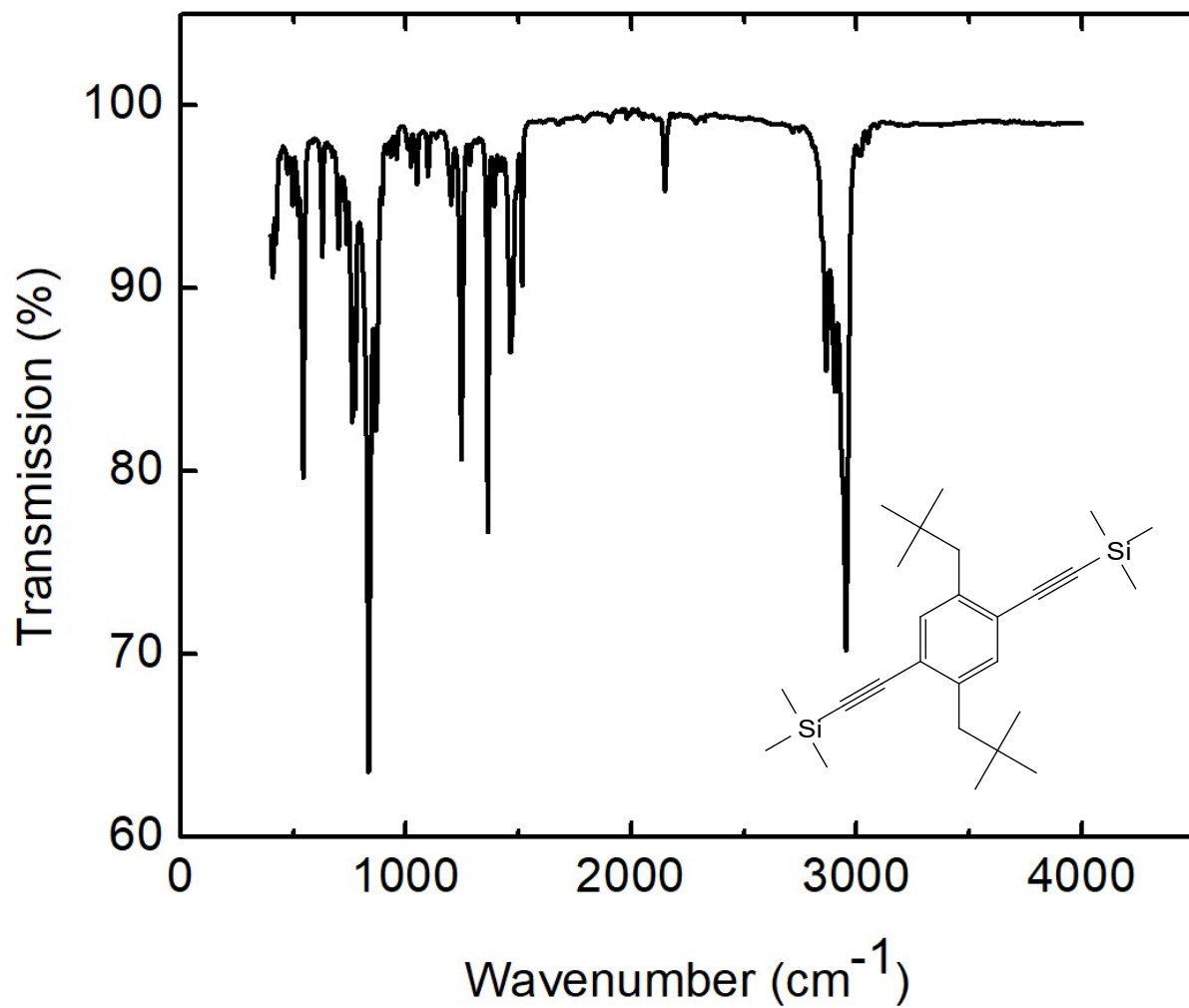


Figure S24. FT-IR spectrum of compound 19.

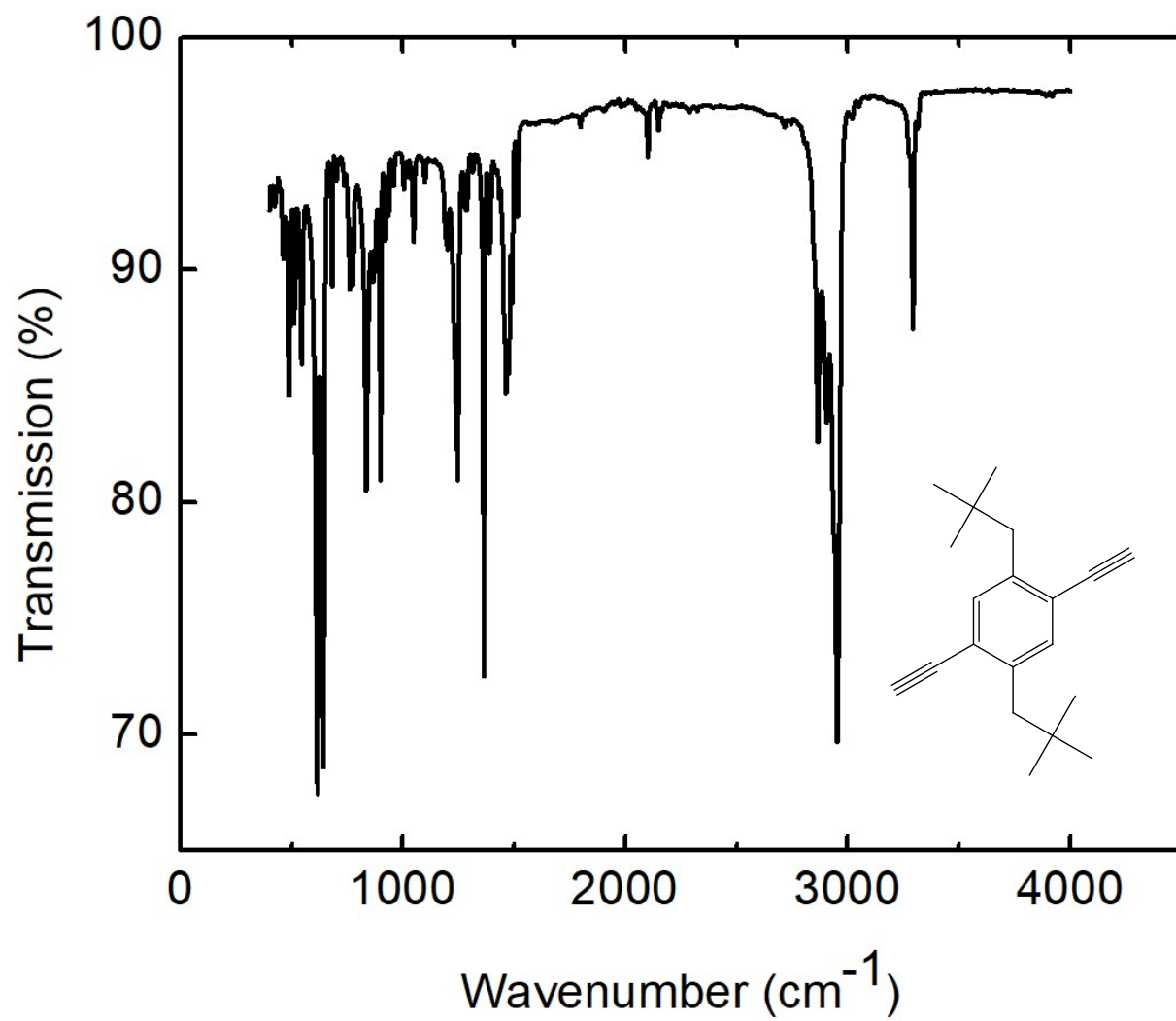


Figure S25. FT-IR spectrum of compound 20.

2.3 Gas sorption data

P1, r.t., 7 h

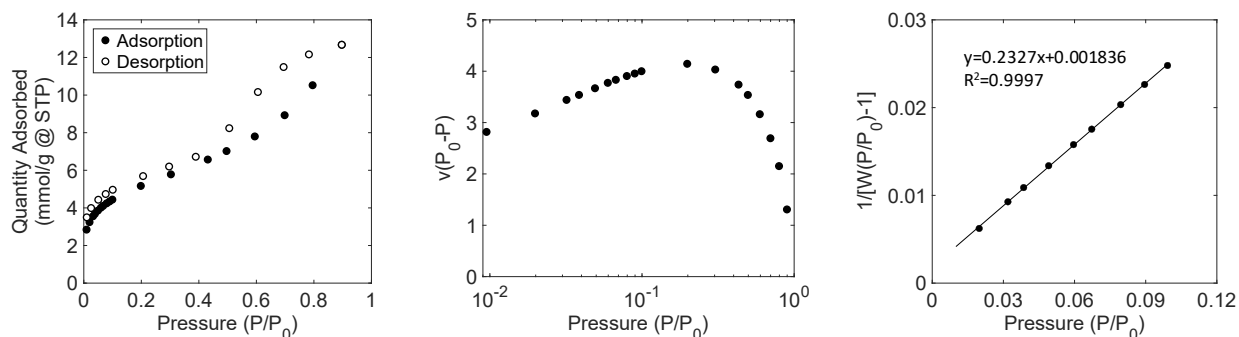


Figure S26. N₂ gas adsorption isotherm (left) of polymer **P1** activated at room temperature for 7 hours under reduced pressure (50 mTorr), determination of BET plot range (middle) based on consistency criteria^{2,3}, and BET fit (right) for obtaining BET surface area.

P1, 100 °C, 10 h

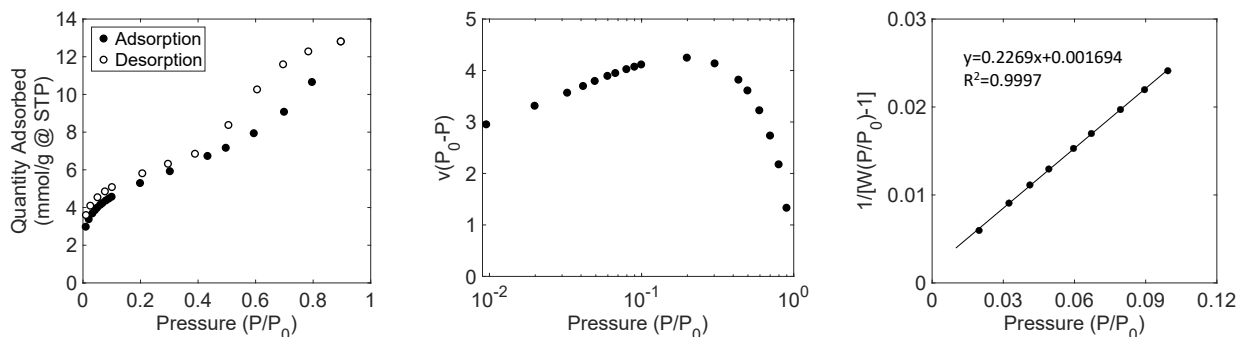


Figure S27. N₂ gas adsorption isotherm (left) of polymer **P1** activated at 100 °C for 10 hours under reduced pressure (50 mTorr), determination of BET plot range (middle) based on consistency criteria^{2,3}, and BET fit (right) for obtaining BET surface area.

P1, 100 °C, 17 h

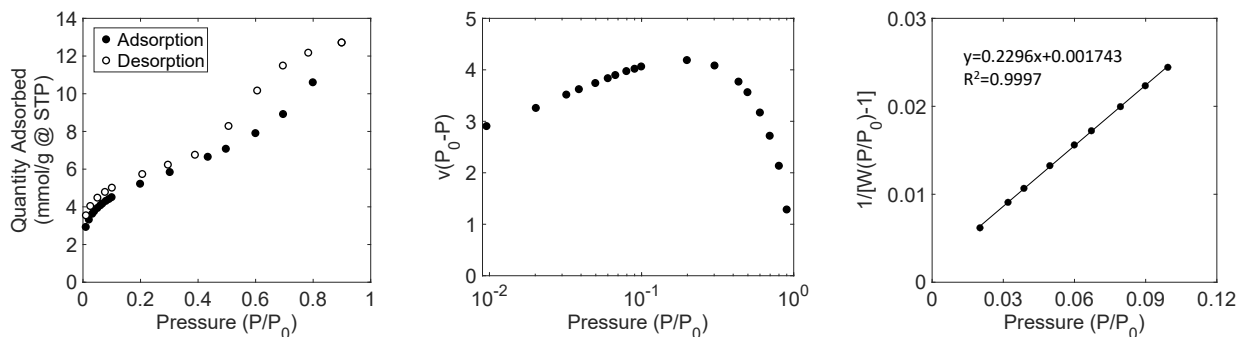


Figure S28. N₂ gas adsorption isotherm (left) of polymer **P1** activated at 100 °C for 17 hours under reduced pressure (50 mTorr), determination of BET plot range (middle) based on consistency criteria^{2,3}, and BET fit (right) for obtaining BET surface area.

P1, 100 °C 36 h

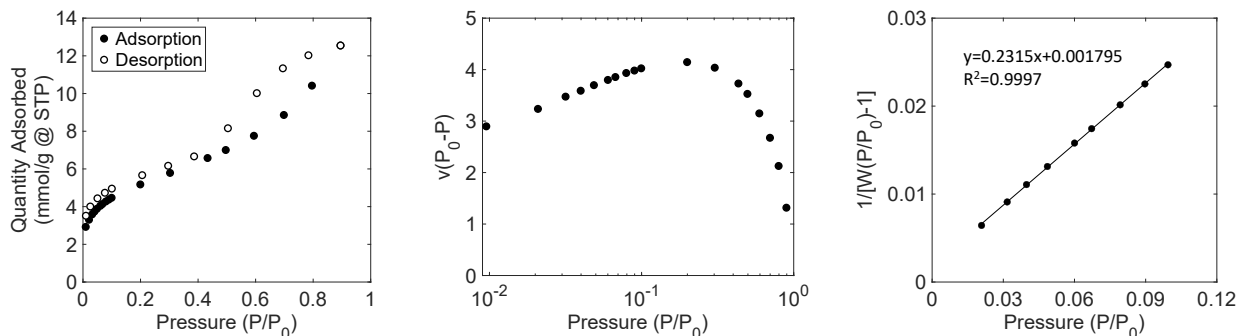


Figure S29. N₂ gas adsorption isotherm (left) of polymer **P1** activated at 100 °C for 36 hours under reduced pressure (50 mTorr), determination of BET plot range (middle) based on consistency criteria^{2,3}, and BET fit (right) for obtaining BET surface area.

P1, 150 °C 2 h

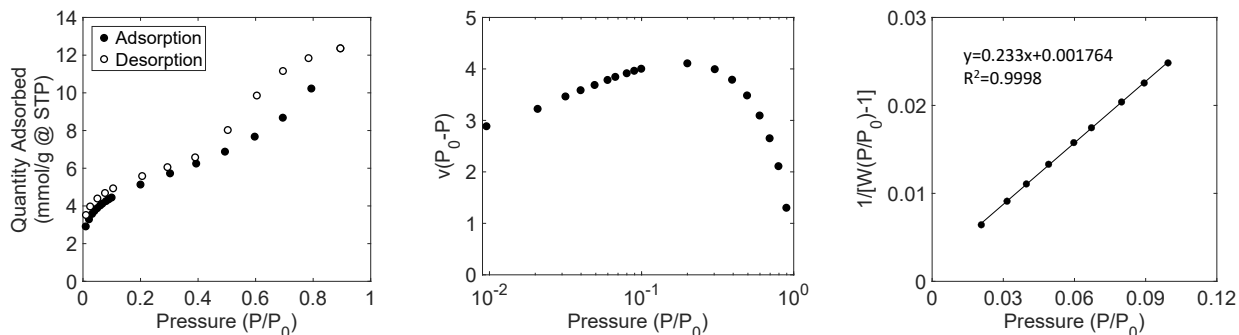


Figure S30. N₂ gas adsorption isotherm (left) of polymer **P1** activated at 150 °C for 2 hours under reduced pressure (50 mTorr), determination of BET plot range (middle) based on consistency criteria^{2,3}, and BET fit (right) for obtaining BET surface area.

P2, r.t. 17 h

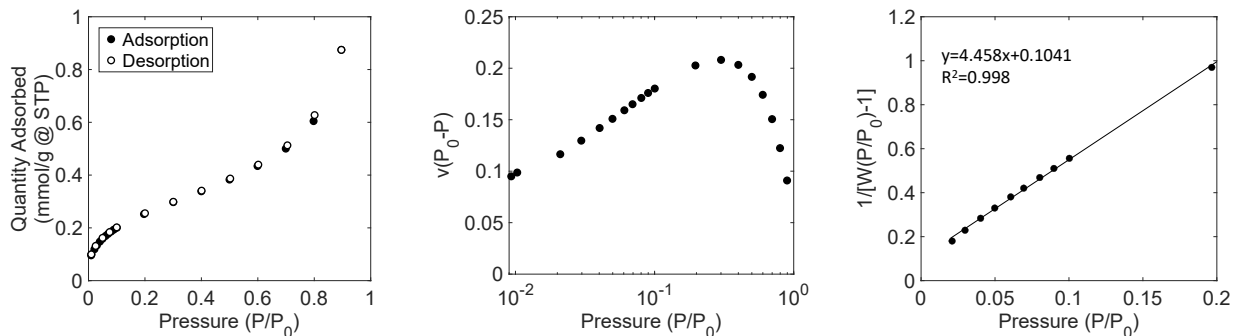


Figure S31. N₂ gas adsorption isotherm (left) of polymer **P2** activated at r.t. for 17 hours under reduced pressure (50 mTorr), determination of BET plot range (middle) based on consistency criteria^{2,3}, and BET fit (right) for obtaining BET surface area.

P2, 50 °C 17 h

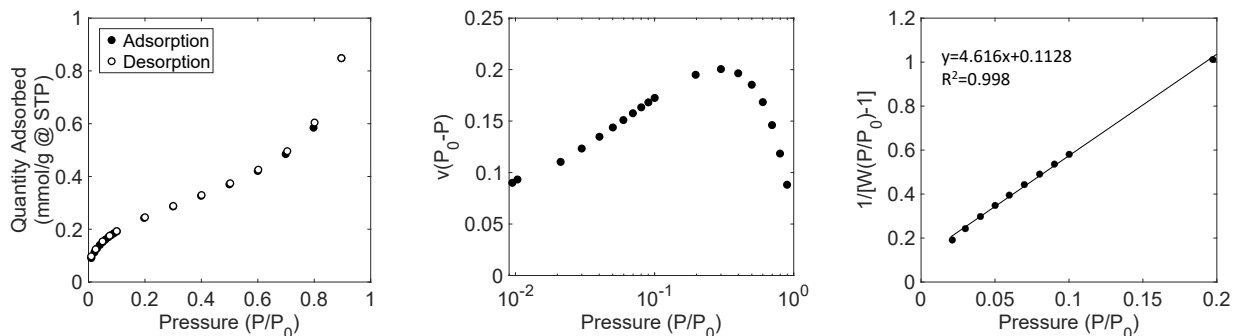


Figure S32. N₂ gas adsorption isotherm (left) of polymer P2 activated at 50 °C for 17 hours under reduced pressure (50 mTorr), determination of BET plot range (middle) based on consistency criteria^{2,3}, and BET fit (right) for obtaining BET surface area.

P2, 100 °C 17 h

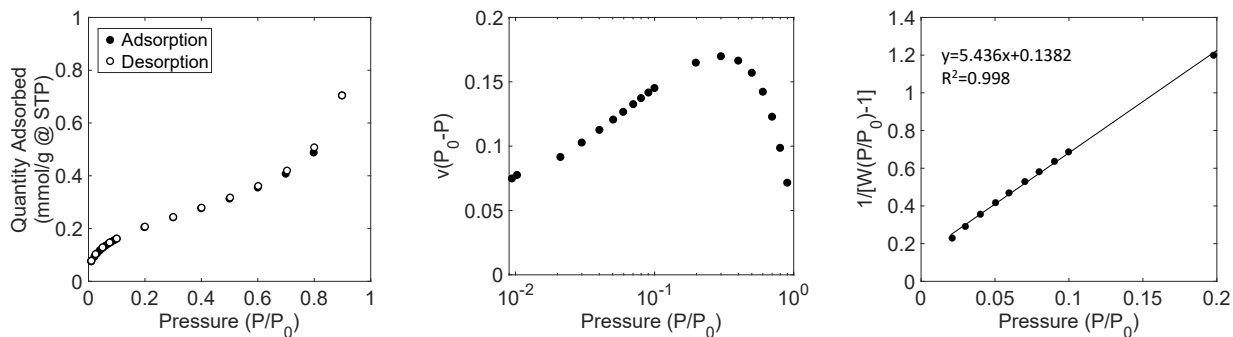


Figure S33. N₂ gas adsorption isotherm (left) of polymer P2 activated at 100 °C for 17 hours under reduced pressure (50 mTorr), determination of BET plot range (middle) based on consistency criteria^{2,3}, and BET fit (right) for obtaining BET surface area.

P2, 150 °C 20 h

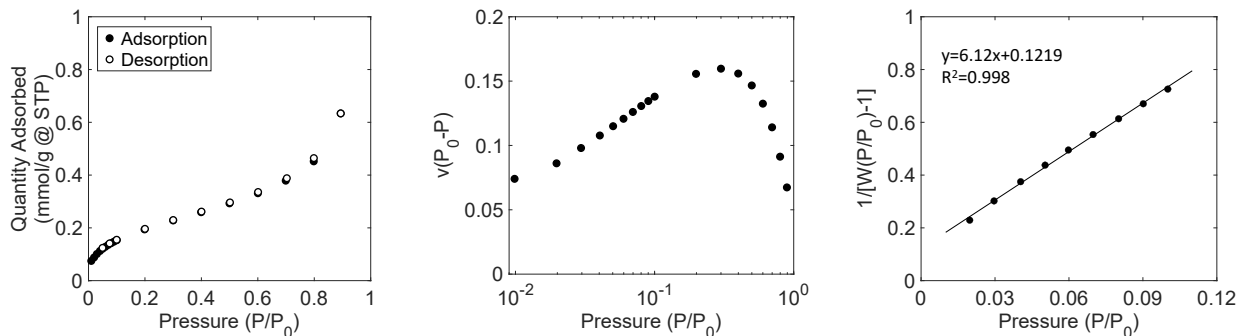


Figure S34. N₂ gas adsorption isotherm (left) of polymer P2 activated at 150 °C for 21 hours under reduced pressure (50 mTorr), determination of BET plot range (middle) based on consistency criteria^{2,3}, and BET fit (right) for obtaining BET surface area.

P2, 200 °C 21 h

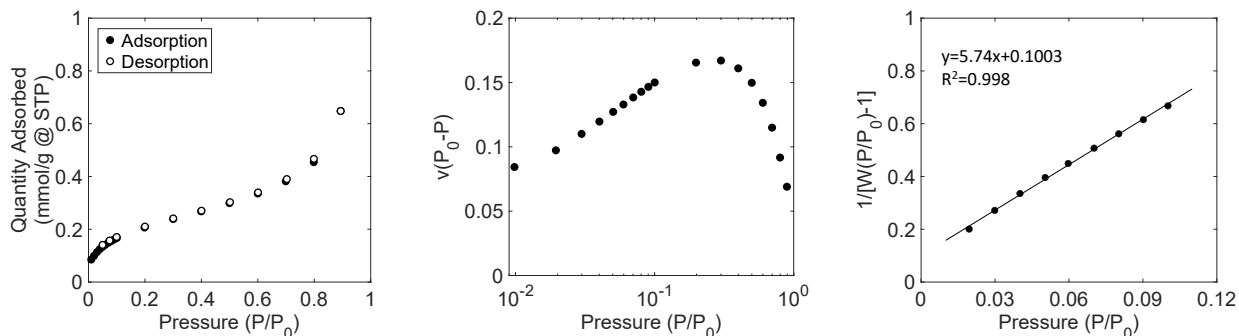


Figure S35. N₂ gas adsorption isotherm (left) of polymer **P2** activated at 200 °C for 20 hours under reduced pressure (50 mTorr), determination of BET plot range (middle) based on consistency criteria^{2,3}, and BET fit (right) for obtaining BET surface area.

P3, r.t. 20 h

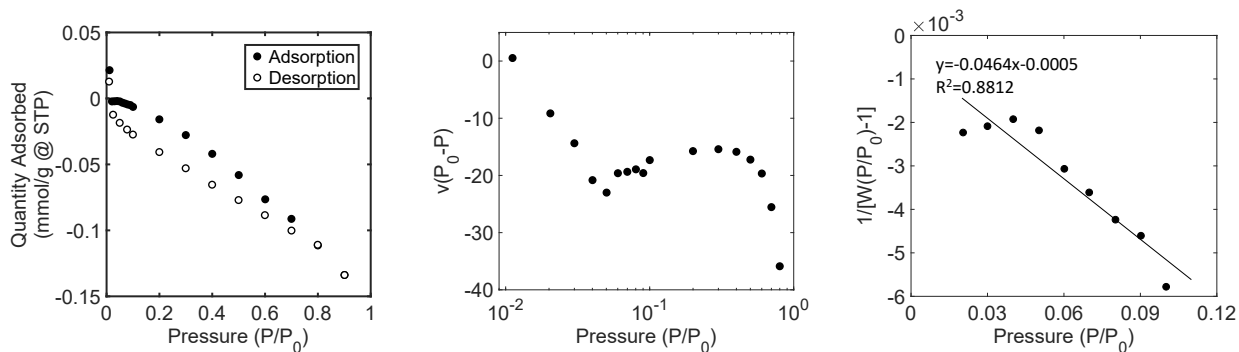


Figure S36. N₂ gas adsorption isotherm (left) of polymer **P3** activated at r.t. for 20 hours under reduced pressure (50 mTorr), determination of BET plot range (middle) based on consistency criteria^{2,3}, and BET fit (right) for obtaining BET surface area.

P3, 100 °C 7 h

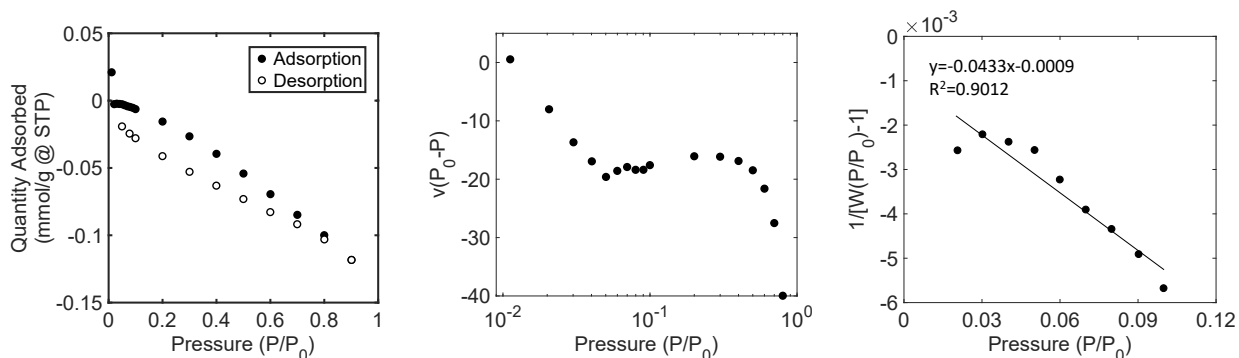


Figure S37. N₂ gas adsorption isotherm (left) of polymer **P3** activated at 100 °C for 7 hours under reduced pressure (50 mTorr), determination of BET plot range (middle) based on consistency criteria^{2,3}, and BET fit (right) for obtaining BET surface area.

P3, 150 °C 7 h

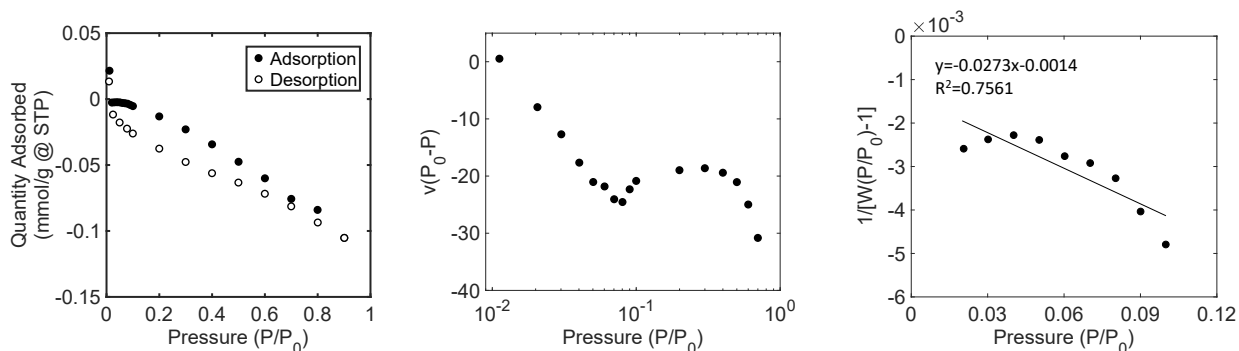


Figure S38. N₂ gas adsorption isotherm (left) of polymer **P3** activated at 150 °C for 7 hours under reduced pressure (50 mTorr), determination of BET plot range (middle) based on consistency criteria^{2,3}, and BET fit (right) for obtaining BET surface area.

P3, 200 °C 7 h

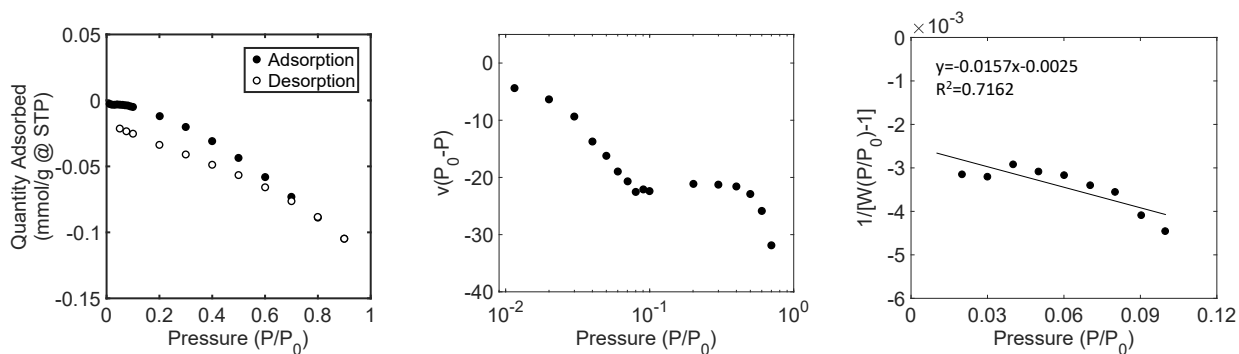


Figure S39. N₂ gas adsorption isotherm (left) of polymer **P3** activated at 200 °C for 7 hours under reduced pressure (50 mTorr), determination of BET plot range (middle) based on consistency criteria^{2,3}, and BET fit (right) for obtaining BET surface area.

P4, r.t. 15 h

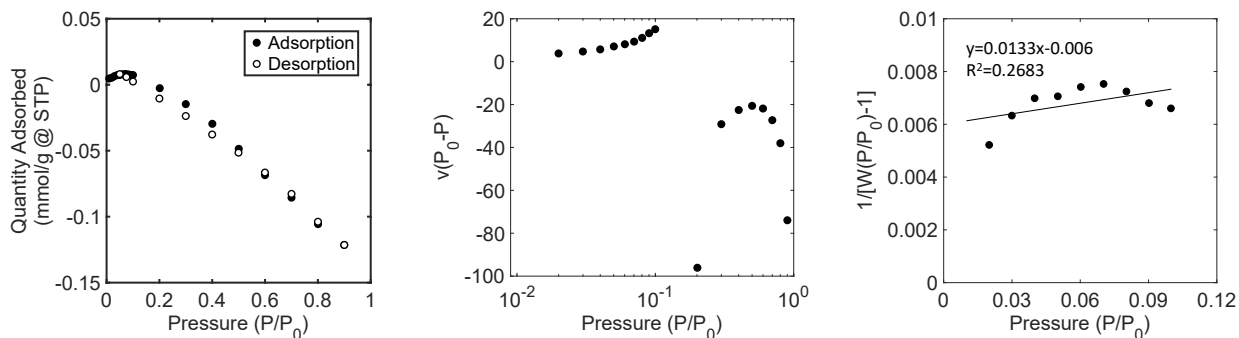


Figure S40. N₂ gas adsorption isotherm (left) of polymer **P4** activated at r.t. for 15 hours under reduced pressure (50 mTorr), determination of BET plot range (middle) based on consistency criteria^{2,3}, and BET fit (right) for obtaining BET surface area.

P4, 100 °C 7 h

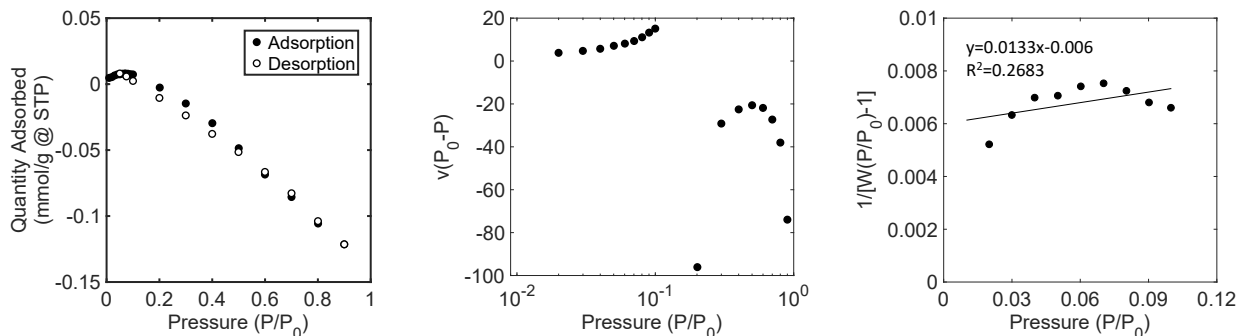


Figure S41. N₂ gas adsorption isotherm (left) of polymer **P4** activated at 100 °C for 7 hours under reduced pressure (50 mTorr), determination of BET plot range (middle) based on consistency criteria^{2,3}, and BET fit (right) for obtaining BET surface area.

P5, r.t. 6 h

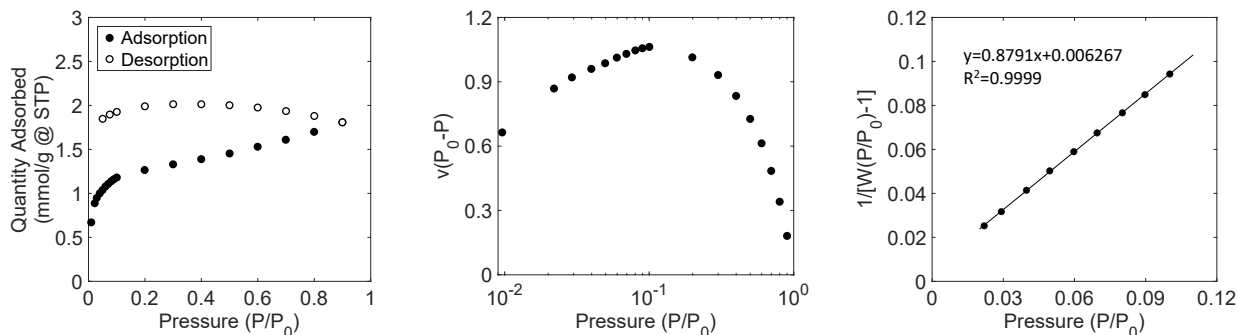


Figure S42. N₂ gas adsorption isotherm (left) of polymer **P5** activated at r.t. for 6 hours under reduced pressure (50 mTorr), determination of BET plot range (middle) based on consistency criteria^{2,3}, and BET fit (right) for obtaining BET surface area.

P5, 50 °C 7 h

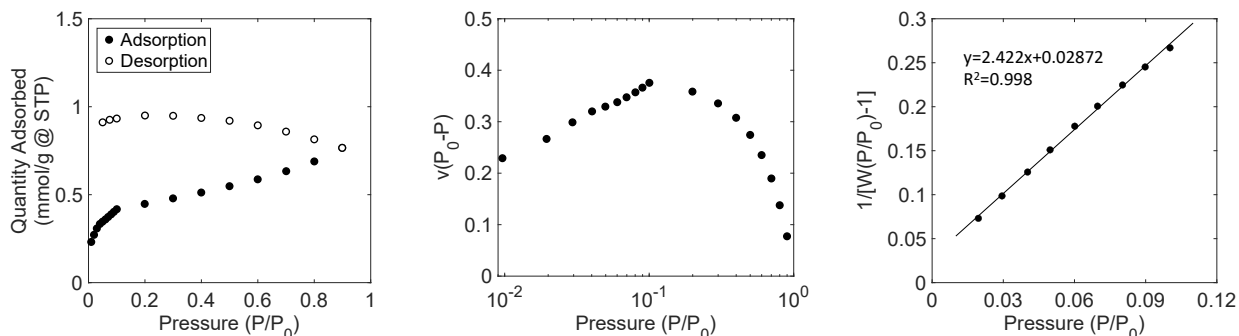


Figure S43. N₂ gas adsorption isotherm (left) of polymer **P5** activated at 50 °C for 7 hours under reduced pressure (50 mTorr), determination of BET plot range (middle) based on consistency criteria^{2,3}, and BET fit (right) for obtaining BET surface area.

P6, r.t. 5 h

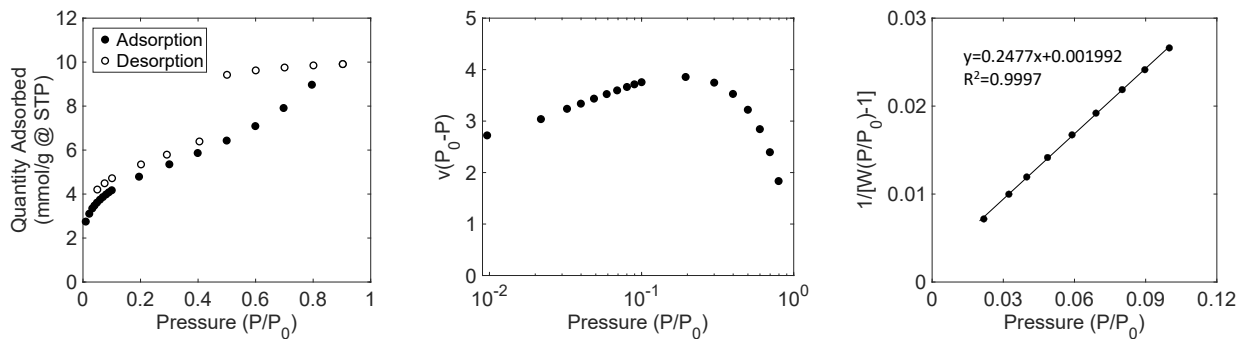


Figure S44. N₂ gas adsorption isotherm (left) of polymer P6 activated at r.t. for 5 hours under reduced pressure (50 mTorr), determination of BET plot range (middle) based on consistency criteria^{2,3}, and BET fit (right) for obtaining BET surface area.

P6, 30 °C 7 h

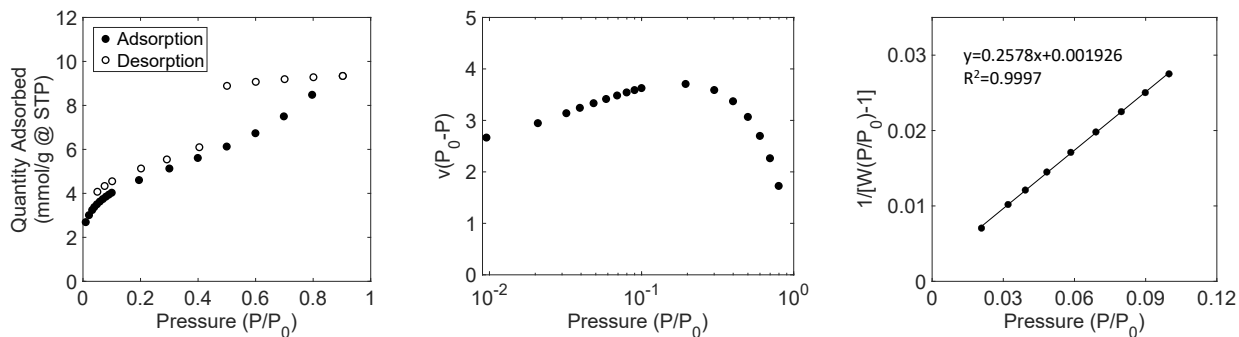


Figure S45. N₂ gas adsorption isotherm (left) of polymer P6 activated at 30 °C for 7 hours under reduced pressure (50 mTorr), determination of BET plot range (middle) based on consistency criteria^{2,3}, and BET fit (right) for obtaining BET surface area.

P6, 40 °C 48 h

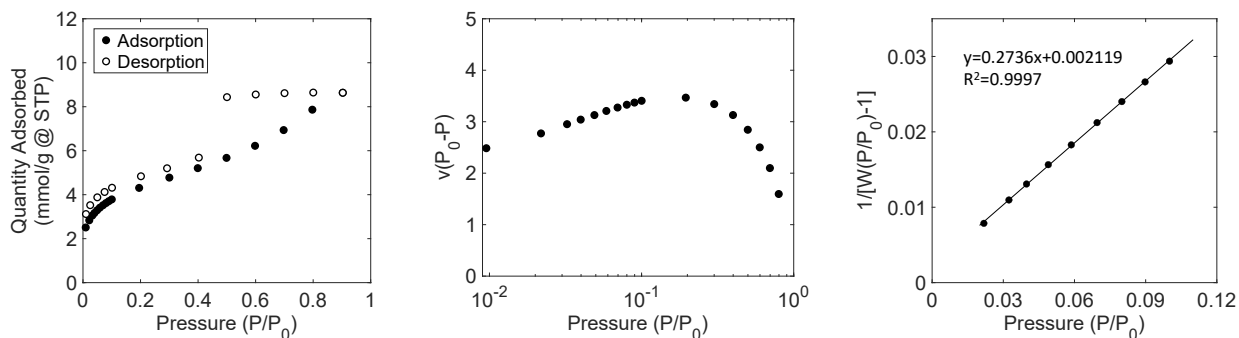


Figure S46. N₂ gas adsorption isotherm (left) of polymer P6 activated at 40 °C for 48 hours under reduced pressure (50 mTorr), determination of BET plot range (middle) based on consistency criteria^{2,3}, and BET fit (right) for obtaining BET surface area.

P6, 80 °C 36 h

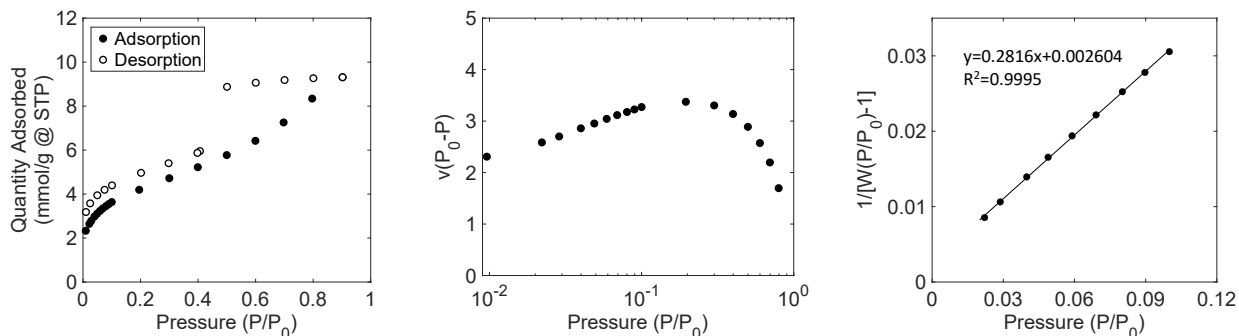


Figure S47. N₂ gas adsorption isotherm (left) of polymer **P6** activated at 80 °C for 36 hours under reduced pressure (50 mTorr), determination of BET plot range (middle) based on consistency criteria^{2,3}, and BET fit (right) for obtaining BET surface area.

P6, 100 °C 48 h

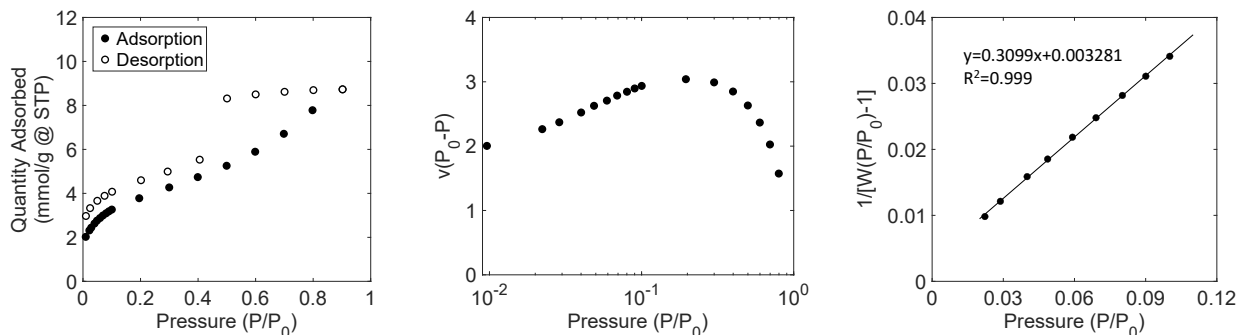


Figure S48. N₂ gas adsorption isotherm (left) of polymer **P6** activated at 100 °C for 48 hours under reduced pressure (50 mTorr), determination of BET plot range (middle) based on consistency criteria^{2,3}, and BET fit (right) for obtaining BET surface area.

P7, r.t. 7 h

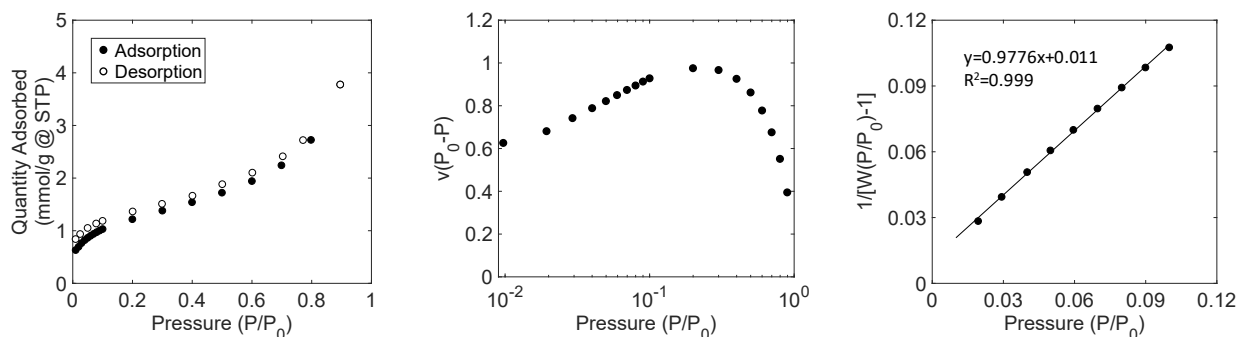


Figure S49. N₂ gas adsorption isotherm (left) of polymer **P7** activated at r.t. for 7 hours under reduced pressure (50 mTorr), determination of BET plot range (middle) based on consistency criteria^{2,3}, and BET fit (right) for obtaining BET surface area.

P7, 100 °C 3 h

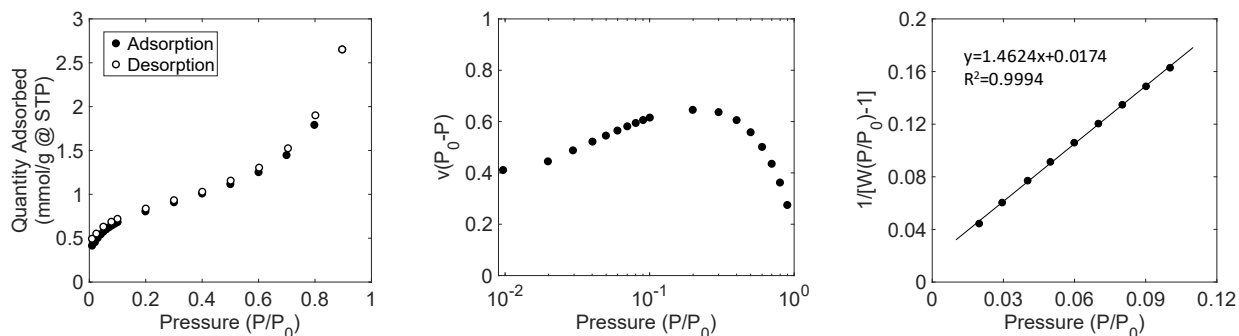


Figure S50. N₂ gas adsorption isotherm (left) of polymer **P7** activated at 100 °C for 3 hours under reduced pressure (50 mTorr), determination of BET plot range (middle) based on consistency criteria^{2,3}, and BET fit (right) for obtaining BET surface area.

P8, r.t. 15 h

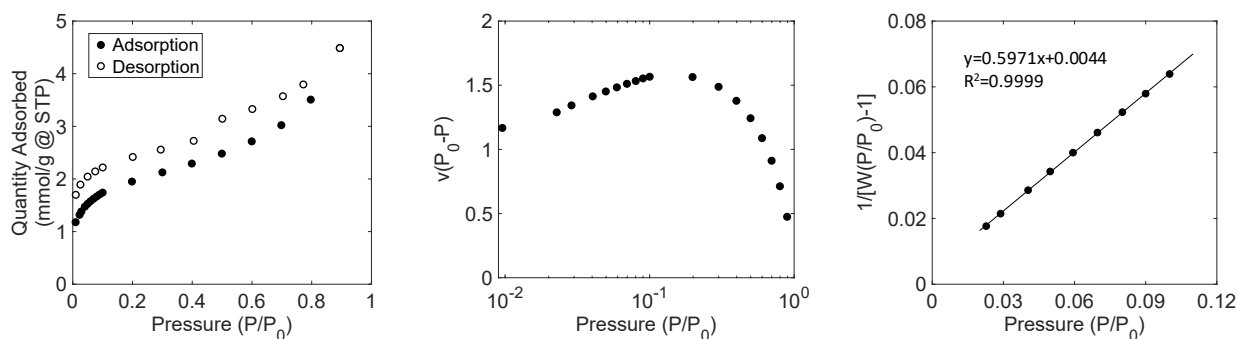


Figure S51. N₂ gas adsorption isotherm (left) of polymer **P8** activated at r.t. for 15 hours under reduced pressure (50 mTorr), determination of BET plot range (middle) based on consistency criteria^{2,3}, and BET fit (right) for obtaining BET surface area.

P8, 100 °C 2 h

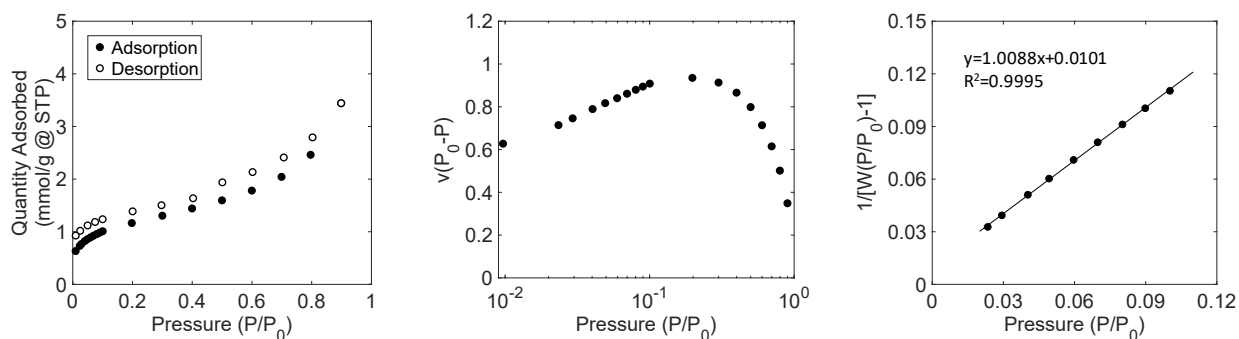


Figure S52. N₂ gas adsorption isotherm (left) of polymer **P8** activated at 100 °C for 2 hours under reduced pressure (50 mTorr), determination of BET plot range (middle) based on consistency criteria^{2,3}, and BET fit (right) for obtaining BET surface area.

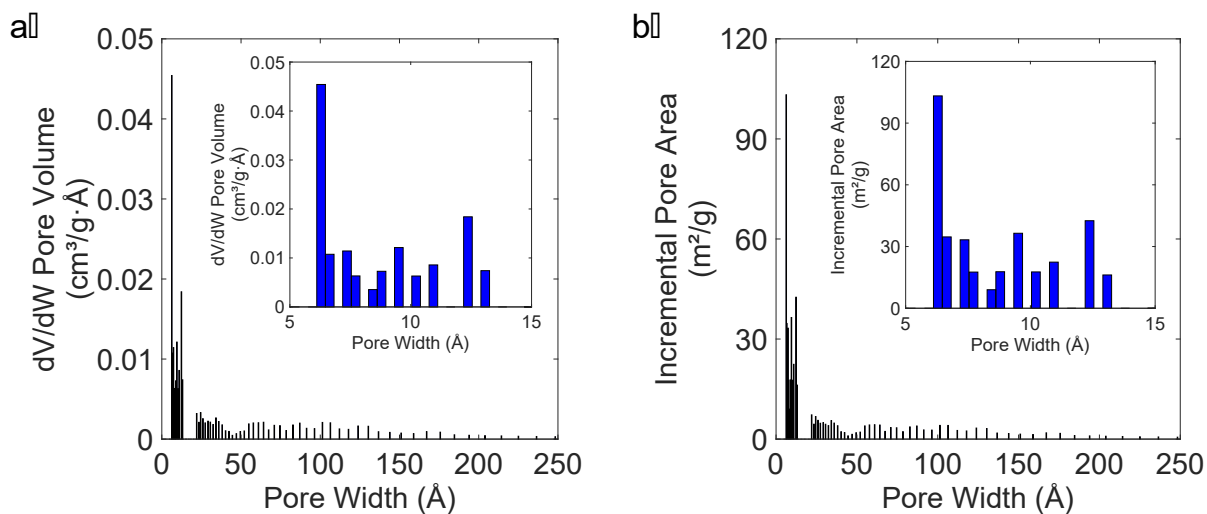


Figure S53. a) Polymer **P1** pore volume vs. pore width and b) polymer **P1** pore area vs. pore width obtained from the N₂ isotherm at 77 K using the Tarazona NLDFT mode⁴ as implemented in Micromeritics' 3Flex software.

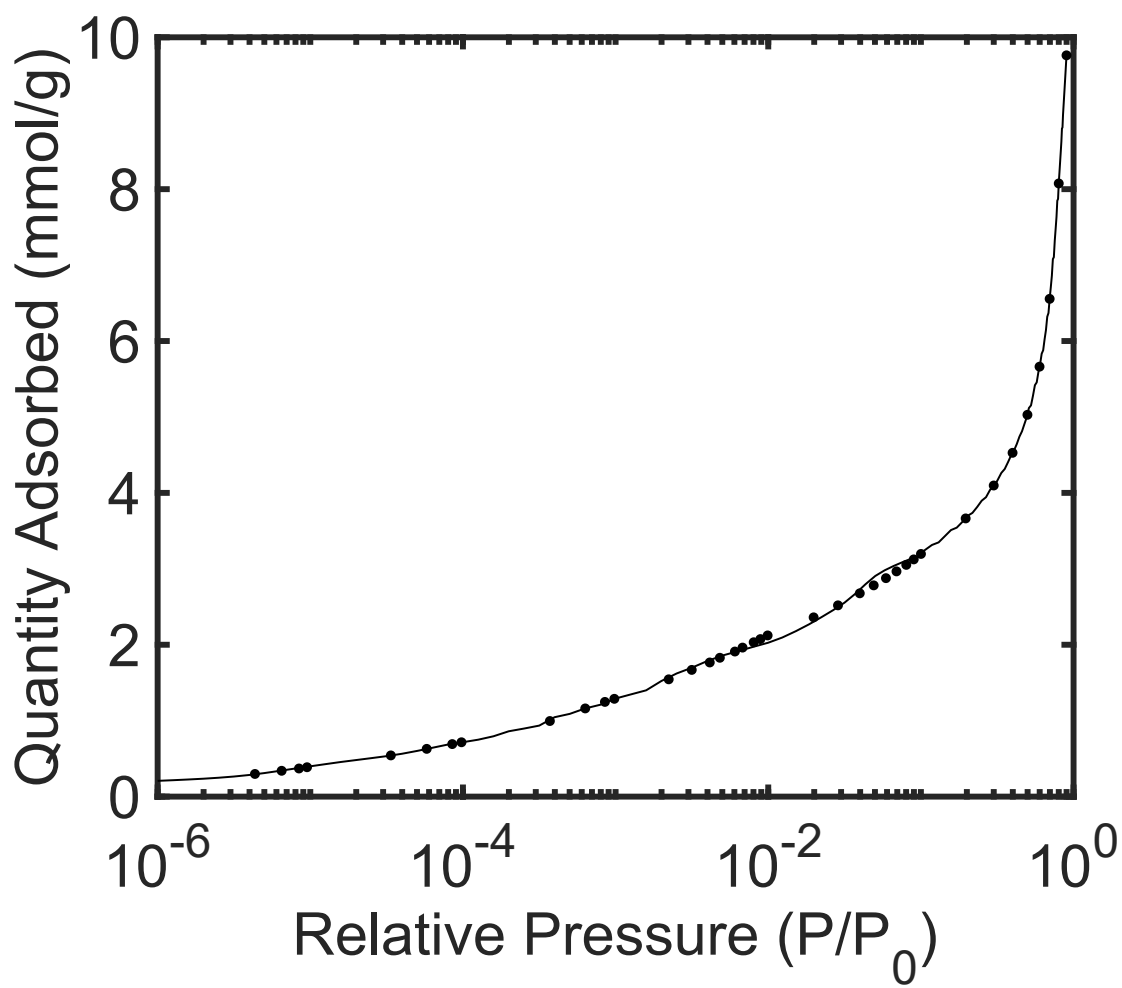


Figure S54. Goodness of fit curve of pore size distribution data (Figure S49). The standard deviation of fit is 0.33426 mmol/g.

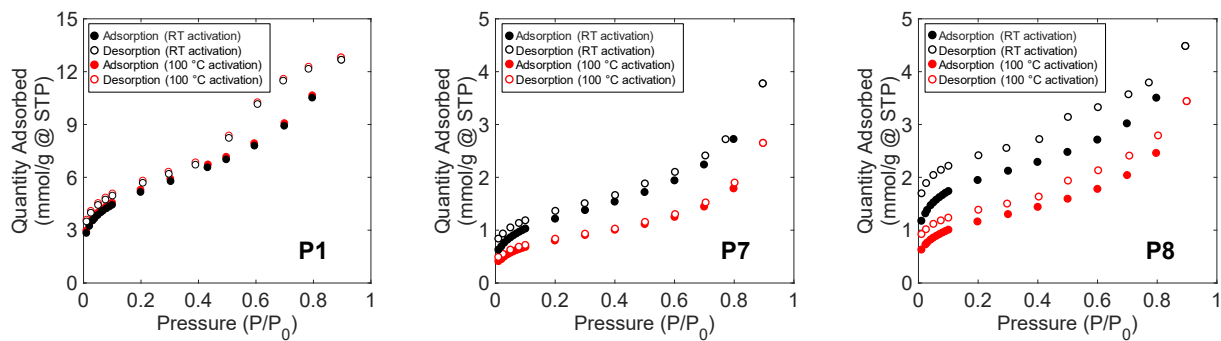


Figure S55. Comparison of N₂ gas adsorption isotherms obtained at 77 K for polymers **P1**, **P7**, and **P8** activated at room temperature (ca. 23 °C) and 100 °C.

2.4 Thermogravimetric analysis (TGA)

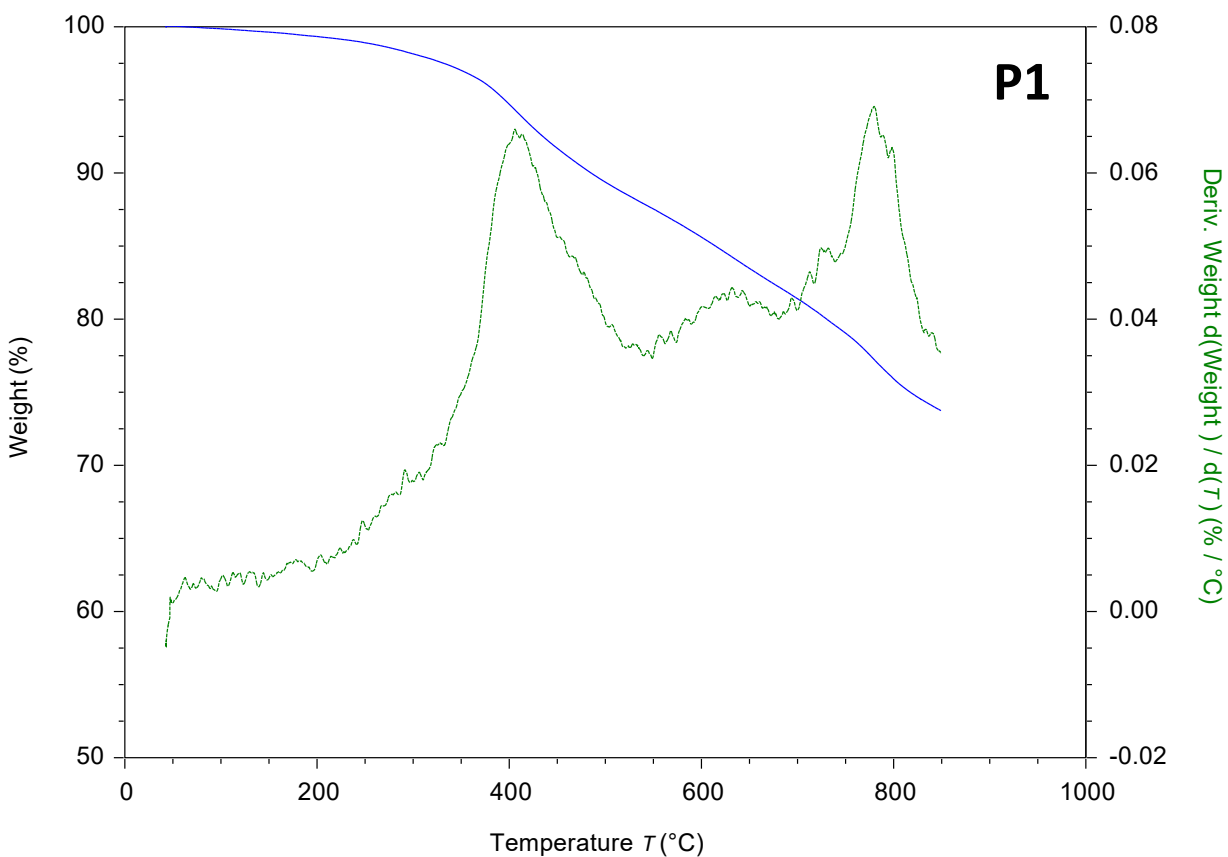


Figure S56. TGA of polymer **P1** from 35 to 850 °C with a heating rate of 5 °C/min.

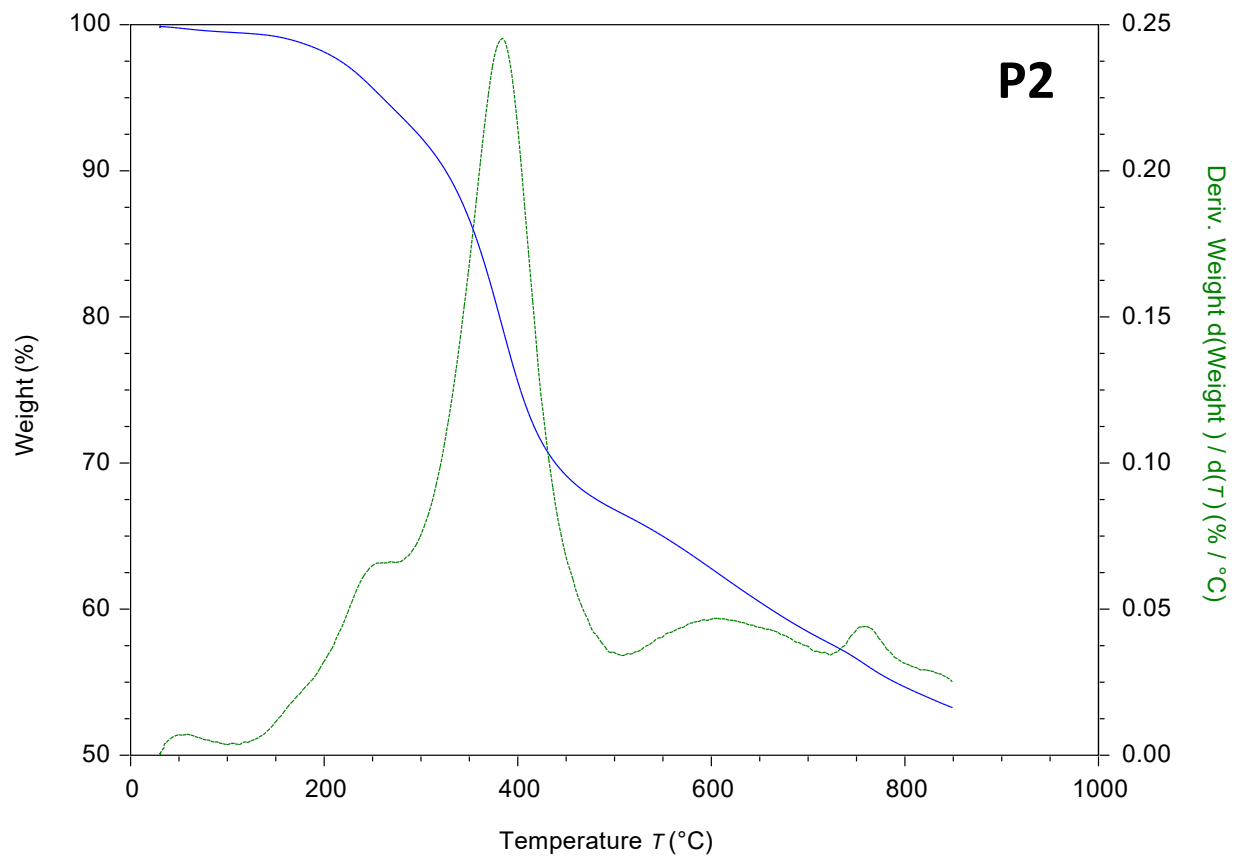


Figure S57. TGA of polymer P2 from 35 to 850 °C with a heating rate of 5 °C/min.

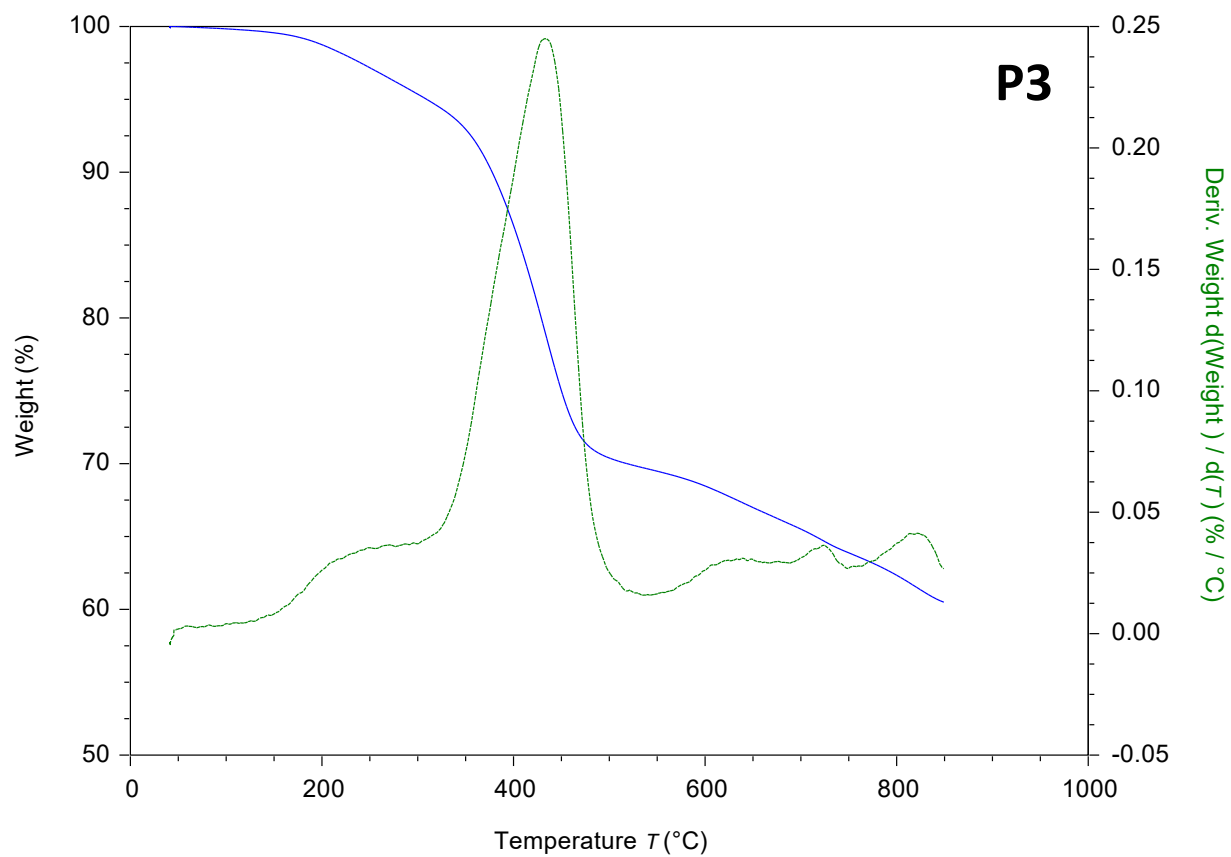


Figure S58. TGA of polymer P3 from 35 to 850 °C with a heating rate of 5 °C/min.

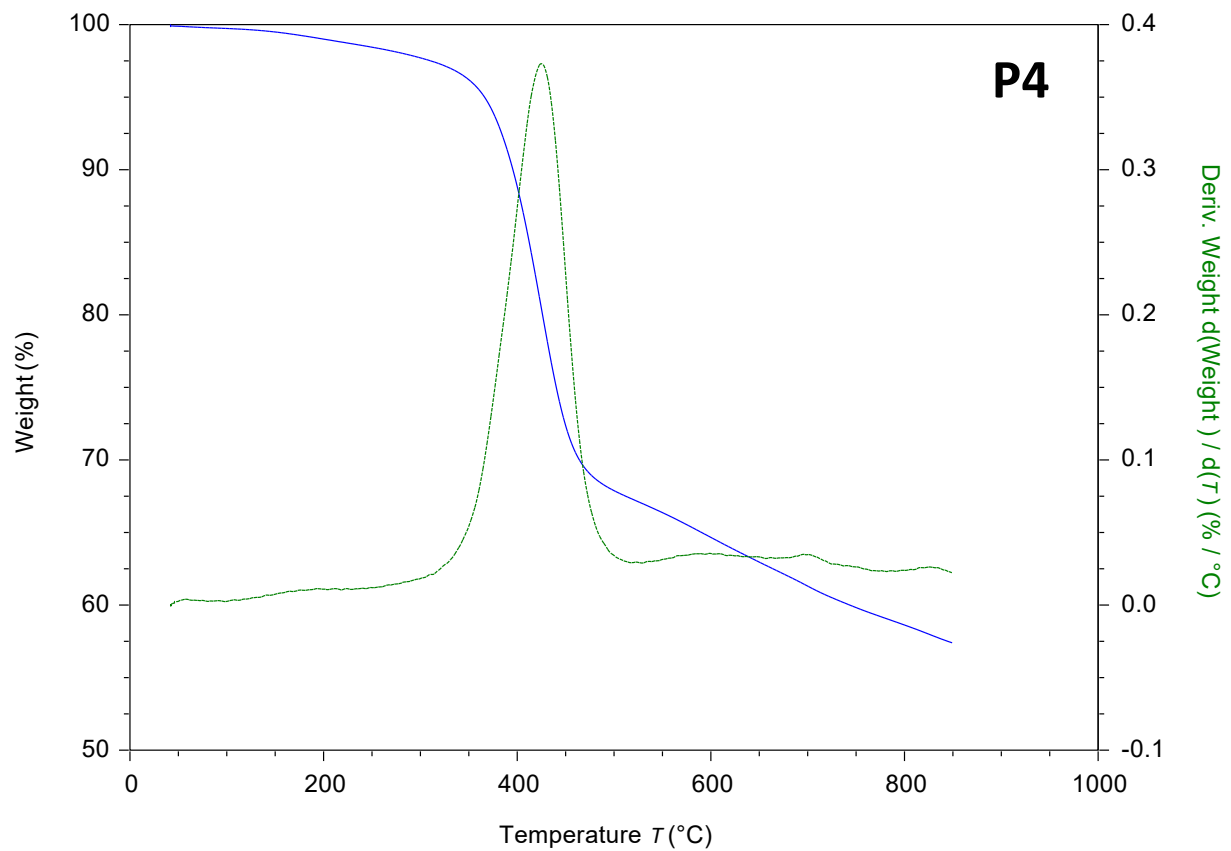


Figure S59. TGA of polymer P4 from 35 to 850 °C with a heating rate of 5 °C/min.

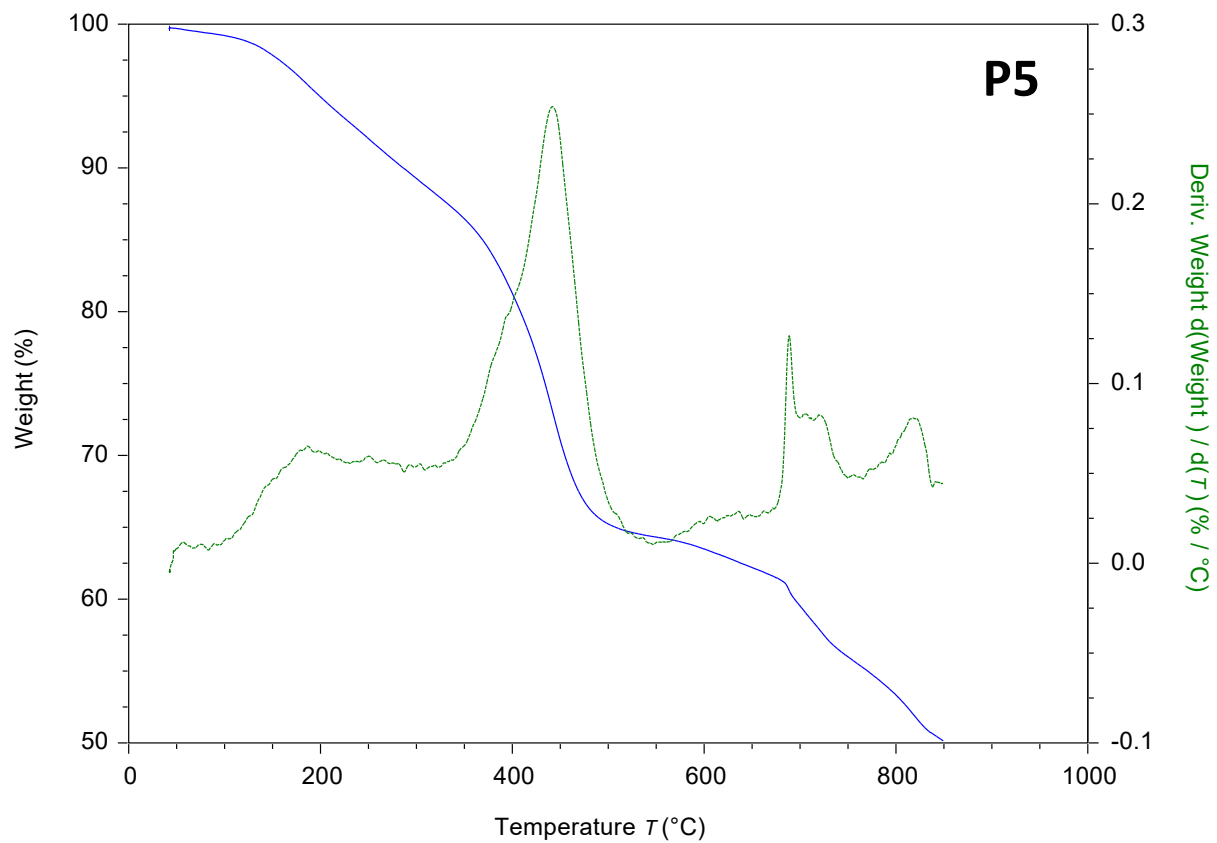


Figure S60. TGA of polymer P5 from 35 to 850 °C with a heating rate of 5 °C/min.

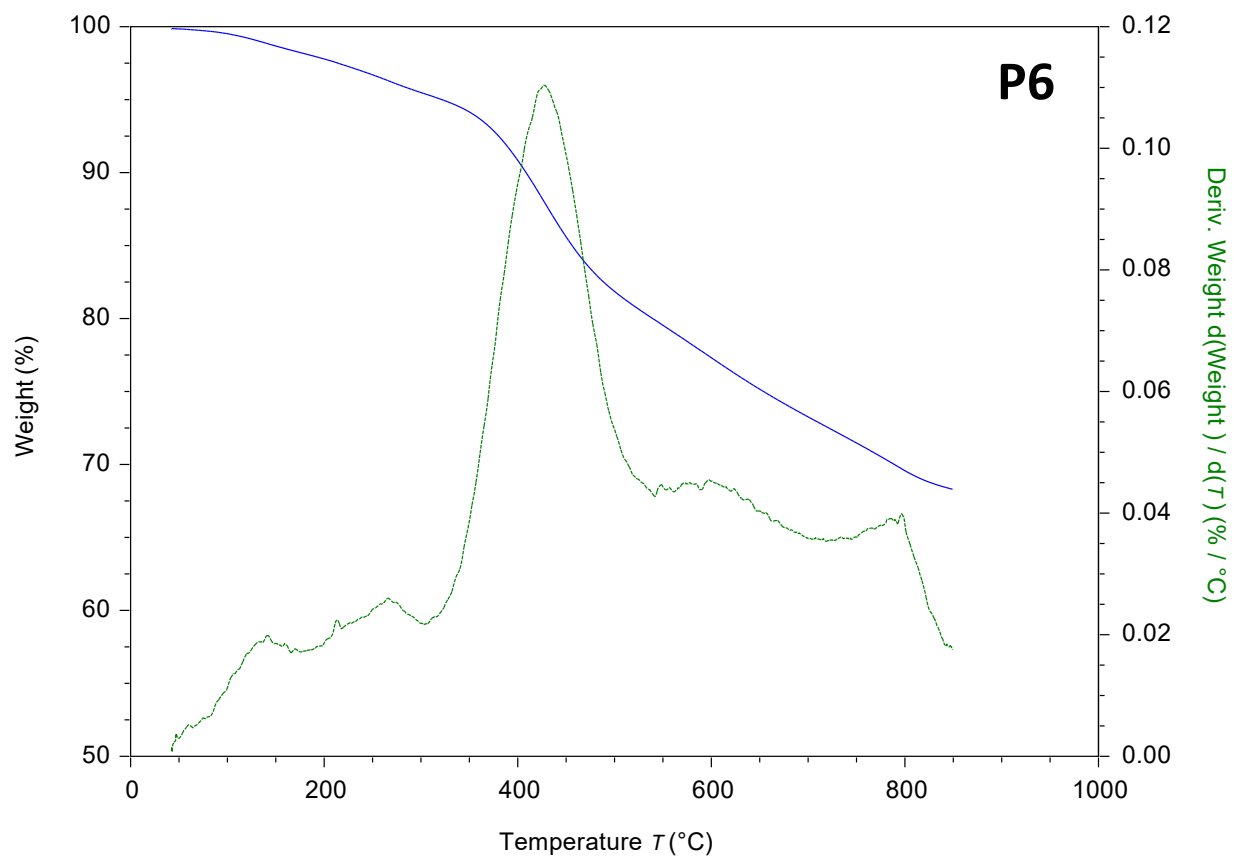


Figure S61. TGA of polymer P6 from 35 to 850 $^\circ\text{C}$ with a heating rate of 5 $^\circ\text{C}/\text{min}$.

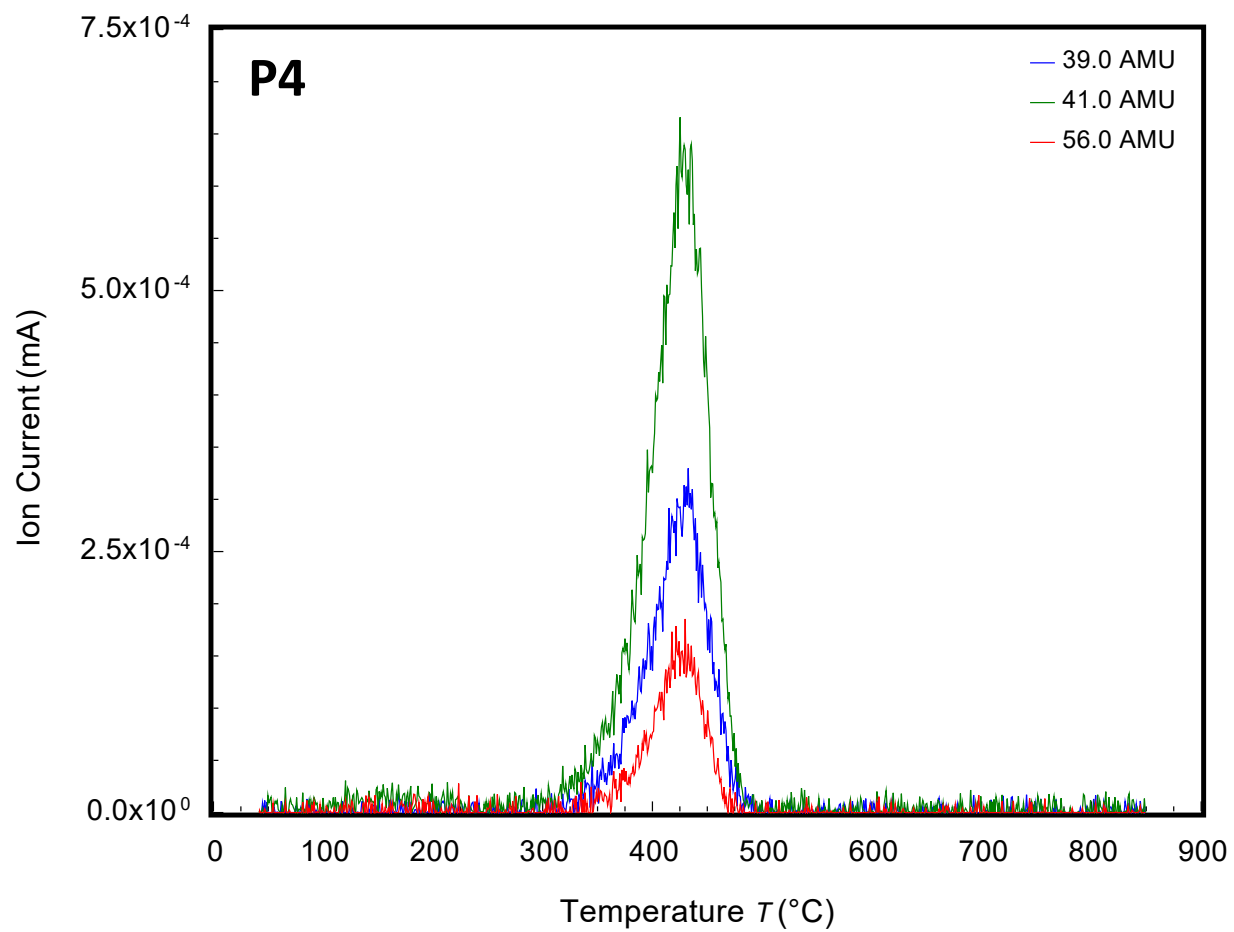


Figure S62. TGA mass spectrum of polymer P4 decomposition products from 35 to 850 $^{\circ}\text{C}$ with a heating rate of 5 $^{\circ}\text{C}/\text{min}$.

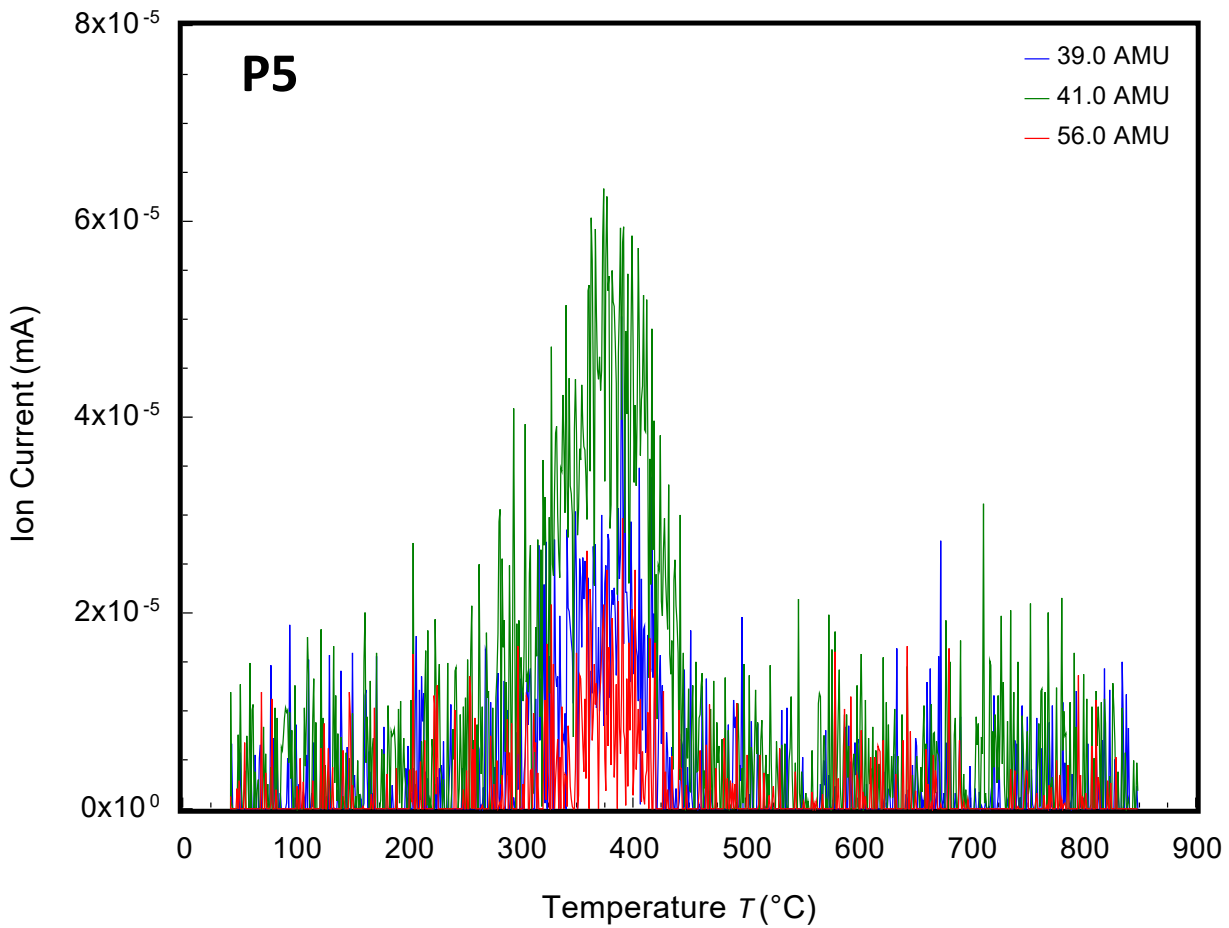


Figure S63. TGA mass spectrum of polymer **P5** decomposition products from 35 to 850 °C with a heating rate of 5 °C/min.

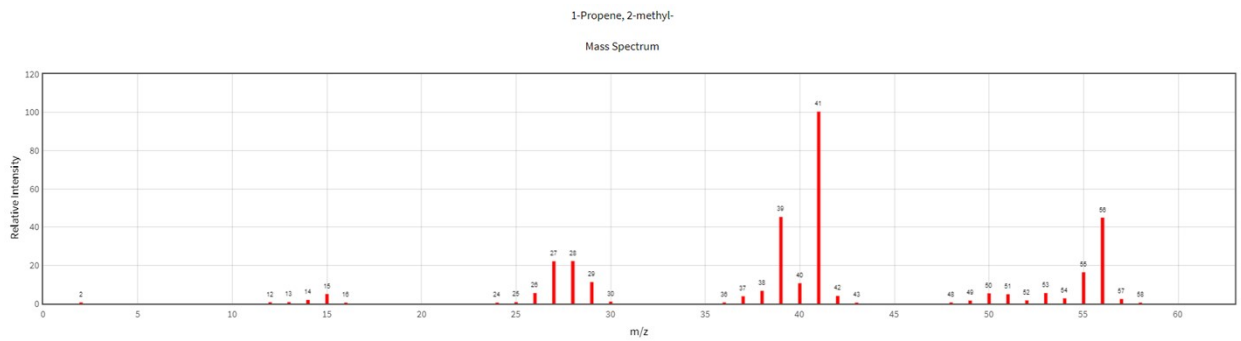


Figure S64. Electron ionization mass spectrum of isobutene. Figure reproduced directly from the NIST Mass Spectrometry Data Center.⁵

2.5 Raman spectra

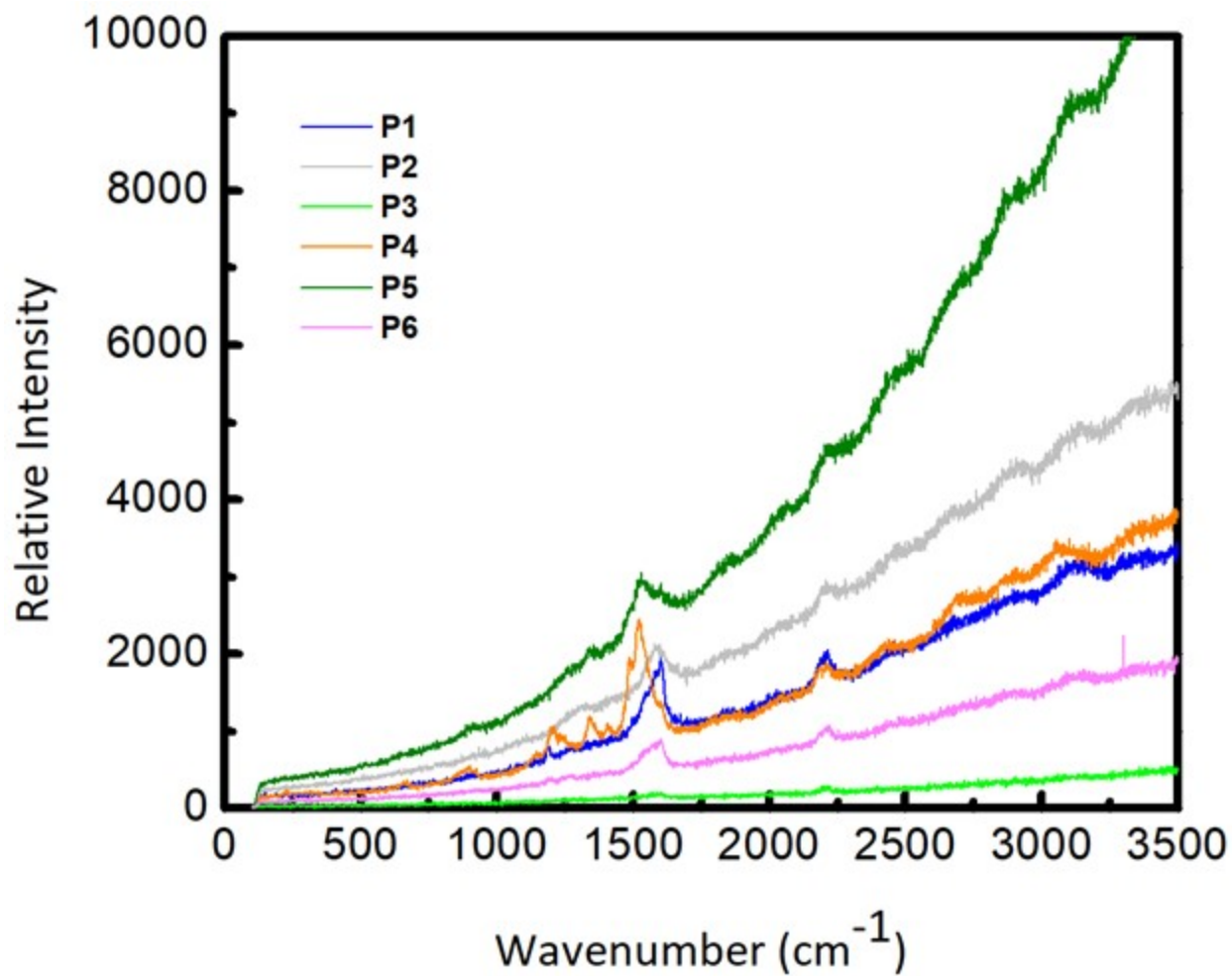


Figure S65. Original (non-background-corrected) Raman spectra of P1-P6.

2.6 Cyclic voltammetry

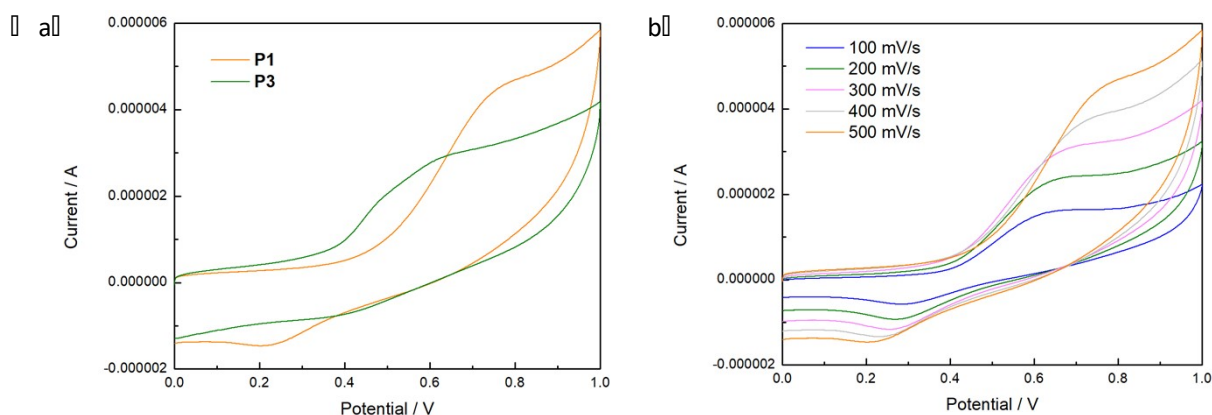


Figure S66. Cyclic voltammograms of (a) **P1** and **P3** in DMF (soluble part) containing 0.10 M [N(n-C₄H₉)₄]BF₄ under N₂ with 500 mV/s scanning rate. Potential is given vs Ag/Ag⁺. (b) **P1** in DMF (soluble part) containing 0.10 M [N(n-C₄H₉)₄]BF₄ under N₂ with different scanning rates.

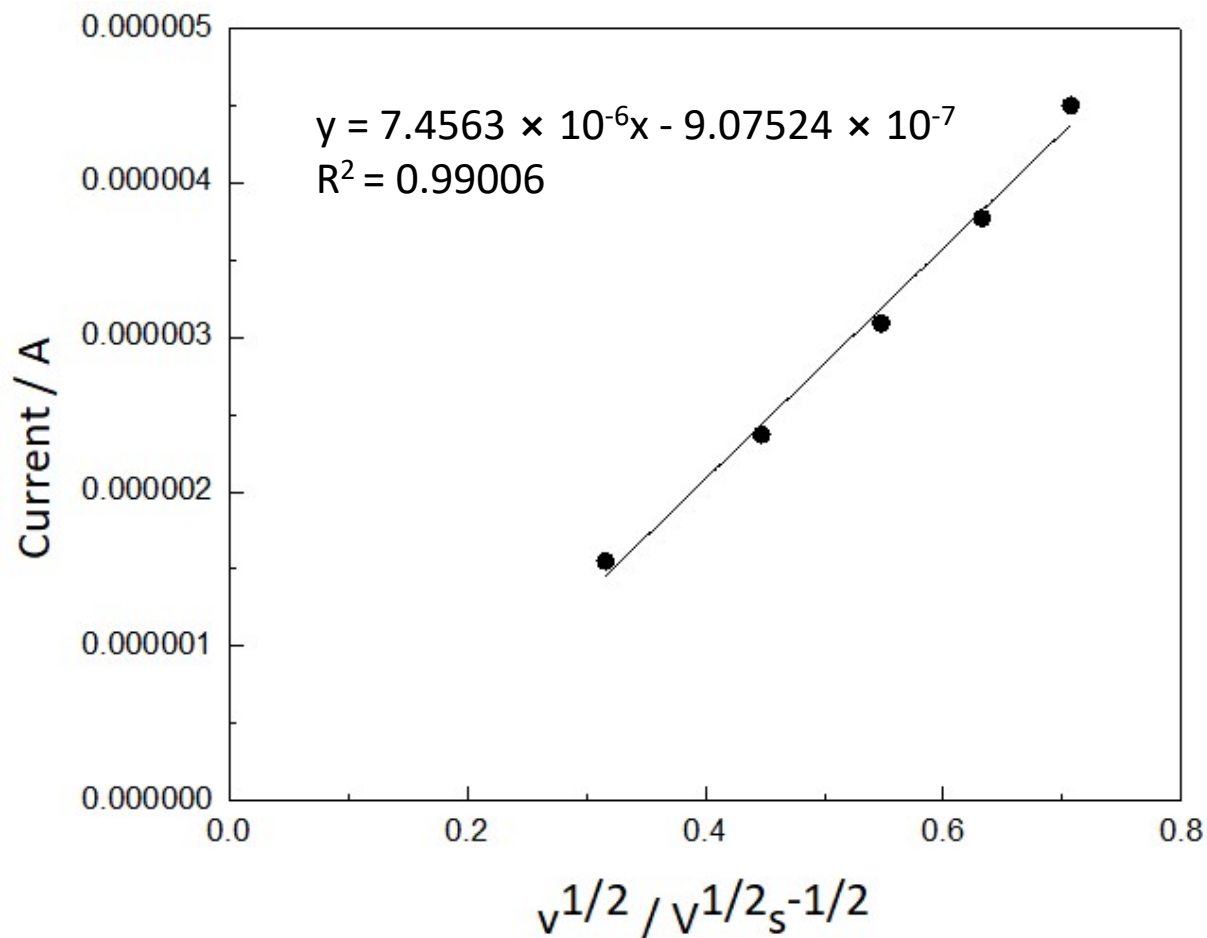


Figure S67. Plot of anodic peak current of **P1** against $v^{1/2}$ (v = scan rate).

References

1. M. S. Inkpen, S. Du, M. Driver, T. Albrecht and N. J. Long, *Dalton Trans.*, 2013, **42**, 2813-2816.
2. P. Llewellyn, F. Rodriguez-Reinoso, J. Rouquerol and N. Seaton, *Studies in Surface Science and Catalysis*, 2007, **160**, 49-56.
3. K. S. Walton and R. Q. Snurr, *J. Am. Chem. Soc.*, 2007, **129**, 8552-8556.
4. P. Tarazona, *Phys. Rev. A*, 1985, **31**, 2672-2679.
5. R. S. Deinhammer, E. Y. Ting and M. D. Porter, *Anal. Chem.*, 1995, **67**, 237-246.