Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

Isolated-alkene-linked porous organic polymers (BIT-POPs): Facile synthesis via ROMP and distinguishing overlapped signals in solid-state ^{13}C NMR

Zhi-Hao Zhang [1], Shan-Qing Peng [1], Shumeng Chi [1], Hanyuan Chen [1], Lei Fan [1], Yan Liu [1], Xiaohua Ma[2]* & Mu-Hua Huang[1]*

[1] Experimental Center for Advanced Materials, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China

[2]State Key Laboratory of Separation Membranes and Membrane Processes, National Center for International Joint Research on Membrane Science and Technology, Tiangong University, Tianjin, 300387, P. R. China

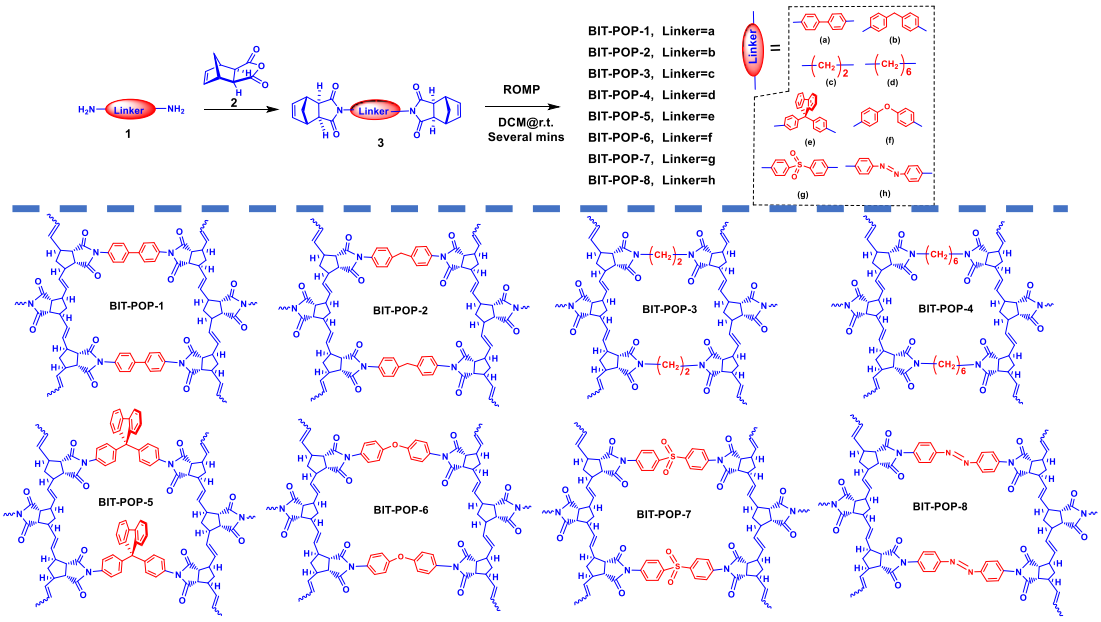
Content

1. General Information for characterization and measurements

All chemicals were purchased from commercial suppliers (Sinopharm Chemical Regent Co.) and used without further purification, unless otherwise noted. The monomer of were synthesized by modifying the reported methods[1]. 1H-NMR (400 MHz) and 13C-NMR (101 MHz) spectra were determined on an Oxford AS-400 magnetic resonance spectrometer (Varian, USA) and Bruker Avance III 400 MHz NMR. Solid-state 13C cross-polarization magic angle spinning (CP-MAS) NMR spectra of solid samples were obtained using a Bruker Avance III 400 MHz Wide Bore spectrometer (14.2 T). A 4.0 mm MAS probe and ZrO2 motor were used, and spin rates at 13 kHz. Chemical shifts (δ) are reported in ppm. Fourier Transform Infrared (FT-IR) spectra were recorded on a PerkinElmer Spectrum Two Fourier transform spectrometer from 450~4000 cm–1. Raman spectra were recorded on a Micro Raman imaging spectrometer (Thermo Fisher, USA). High-resolution ESI mass spectra (HR-ESI-MS) were recorded on a GCT CA127 Micronass UK mass spectrometer. Elemental analysis was measured by Vario EL elemental analyzer (Elementar Analysensysteme GmbH, Germany). Nitrogen adsorption/desorption isotherms at 77 K were obtained using a BELSORP Max II (MicrotracBEL Corp.) static volumetric analyzer. Prior to adsorption measurements, the samples were degassed for 12 h at 80 oC to remove residual moisture and other trapped gases. The Brunauer-Emmett-Teller (BET) surface area was calculated within the relative pressure (P/P0) range 0.05 to 0.99. The total pore volume was calculated at P/P0 of about 0.995. The non-local density functional theory (NLDFT) methods were used to establish the pore size distribution and pore diameter (DP). Scanning electron microscopy (SEM) images were taken by a Hitachi S4800 scanning electron microscope. Thermogravimetric analysis (TGA) was carried out on a Q600 SDT (TA, USA) thermogravimetric analyzer, heated from 25 ^{o}C to 800 ^{o}C at a rate of 20 ℃/min under N_2 atmosphere.

2. General Synthetic Procedures

The bisimide monomers (**BIT-BNIs**) and polymers (BIT-POPs) were synthesized by the following scheme.



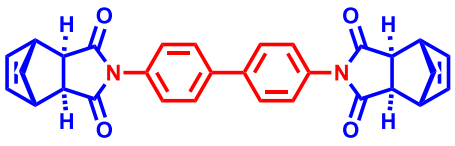
2.1 The General Synthetic Procedure for synthesis of bisimide monomers

General Synthetic Procedure:

A solution of diamine (1.0 equiv.), triethylamine (2-4 equiv.) and *exo*-Nadic anhydride (2.0 equiv.) in toluene were added to the flask. The mixture was heated to 100-120 ^{o}C and keep this temperature to reflux for 6-16 hours. After the mixture was cooled to room temperature, a solid was precipitated after adding a large amount of water. Then methanol/water (1/2, v/v) or ethanol/water (1/2, v/v) was used for washing for 2-3 times and vacuum drying for 12 h to obtain solid.

2.1.1 The synthesis of monomers-3a:

A solution of benzidine (560.7 mg, 3.1 mmol) and *exo*-Nadic anhydride (1.01 g, 6.2 mmol) in toluene (40 ml) were added to the flask. The mixture was heating to 120 ^{o}C and keep this temperature to reflux for 12 hours. After the mixture was cooled to room temperature, a solid was precipitated after adding a large amount of water (300 ml). Then methanol was used for washing for 2 times and vacuum drying for 12 h to obtain white solid (1.06 g, 72% yield).

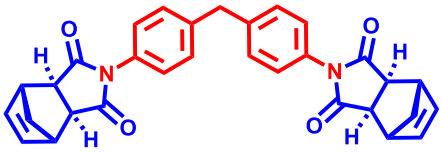


^{1}H-NMR (400 MHz, CDCl3) δ (ppm): 7.66 (d, J = 8.3 Hz, 4 H), 7.37 (d, J = 8.3 Hz, 4 H), 6.36 (s, 4 H), 3.43 (s, 4 H), 2.89 (s, 4 H), 1.64 (d, J = 9.9 Hz, 3 H), 1.51 (d, J = 9.9 Hz, 2 H); **^{13}C-NMR** (100MHz, CDCl3) δ (ppm): 177.0, 140.6, 138.0, 131.3, 128.0, 126.7, 77.3, 77.0, 76.7, 47.9, 45.9, 43.0.

FT-IR (cm^{-1}): 2982 (w), 1701 (s), 1501 (m), 1356 (m), 1179 (s), 783 (s).

2.1.2 The synthesis of monomers-3b

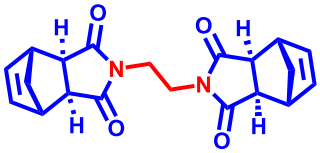
Dicaniline methane (610.6 mg, 3.1 mmol), *exo*-Nadic anhydride (1.04 g, 6.3 mmol), toluene (50 mL) and triethylamine (420 μL) were added to the reaction flask. The mixture were heating to 120 ^{o}C, and keep this temperature to reflux for 16 hours. After the mixture was cooled to room temperature, a solid was precipitated after adding a large amount of water (300 ml), the product was filtered and washed with methanol, and vacuum-dried for 12 h to obtain a milky white powder solid (1.34g, 88% yield).



^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.27 (d, J = 10.0 Hz, 4 H), 7.19 (d, J = 8.2 Hz, 4 H), 6.34 (t, J = 1.9 Hz, 4 H), 4.03 (s, 2 H), 3.42 – 3.37 (m, 4 H), 2.87 – 2.83 (m, 4 H), 1.61 (dt, J = 9.9, 1.3 Hz, 2 H), 1.47 (d, J = 9.9 Hz, 2 H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ (ppm): 177.1, 140.9, 138.0, 130.0, 129.7, 126.4, 77.3, 77.0, 76.7, 47.8, 45.8, 43.0, 41.1.

IR (cm^{-1}): 2975 (w), 1697 (s), 1507(m), 1386 (s), 1178 (s), 882 (w), 774 (s), 707 (s).

2.1.3 The synthesis of monomers-3c



A solution of ethylenediamine (205 μL, 3.1 mmol), triethylamine (210 μL) and *exo*-Nadic anhydride (1.01g, 6.2 mmol) in toluene (20 mL) were added to the flask. The mixture was heated to 100 ^{o}C, and keep this temperature to reflux for 14 hours. After the mixture was cooled to room temperature, a solid was precipitated after adding a large amount of water. Then precipitate was washed with ice water and filtered, vacuum drying for 12h to obtain white crystal product (0.84 g, 77 % yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 6.26 (s, 4H), 3.70 (s, 4 H), 3.23 (s, 4 H), 2.66 (s, 4 H), 1.50 (d, J = 10.0 Hz, 2 H), 1.27 (d, J = 9.9 Hz, 3 H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ (ppm): 178.1, 137.8, 77.3, 77.0, 76.7, 48.0, 45.0, 43.0, 37.0.

FT-IR (cm^{-1}): 3002 (w), 1699 (s), 1385 (s), 1140 (m), 1017 (w), 790 (s), 631 (s).

2.1.4 The synthesis of monomers-3d

A solution of hexylenediamine (359 mg, 3.1 mmol), triethylamine (210 μL) and *exo*-Nadic anhydride (1.01g, 6.2 mmol) in toluene (20 mL) were added to the flask. The mixture was heated to 100 ^{o}C, and keep this temperature to reflux for 16 hours. After the mixture was cooled to room temperature, a solid was precipitated after

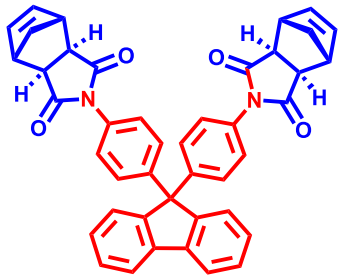
adding a large amount of water. Then precipitate was washed with methanol and ice water, then filtered and vacuum drying for 12h to obtain white crystal product (0.94g, 74% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 6.27 (t, J = 1.8 Hz, 4 H), 3.48 – 3.38 (m, 4 H), 3.29 – 3.19 (m, 4 H), 2.65 (d, J = 1.1 Hz, 4 H), 1.56 – 1.46 (m, 6 H), 1.32 – 1.24 (m, 4 H), 1.20 (d, J = 10.1 Hz, 2H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ (ppm): 178.0, 137.8, 77.3, 77.0, 76.7, 47.8, 45.1, 42.7, 38.5, 27.6, 26.4.

FT-IR (cm^{-1}): 2930 (w), 1681 (s), 1394 (m), 1244 (s), 1152 (s), 948 (w), 785 (s), 632 (s).

2.1.5 The synthesis of bisimide monomers-3e

A solution of 9- bis (4-aminobenzyl) fluorene (1.05 g 3.0 mol), triethylamine (420 μL) and *exo*-Nadic anhydride (1.01g, 6.2 mmol) in toluene (20 mL) were added to the flask. The mixture was heated to 120 ^{o}C, and keep this temperature to reflux for 12 hours. After the mixture was cooled to room temperature, a solid was precipitated after adding a large amount of water. The precipitate was washed with methanol and water, then filtered and vacuum drying for 12h to obtain white solid (1.07 g, 56% yield).



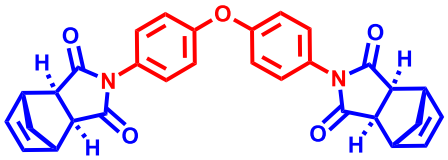
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.76 (d, J = 6.7 Hz, 2H), 7.36 (d, J = 6.9 Hz, 4 H), 7.30 (s, 6 H), 7.16 – 7.09 (m, 4 H), 6.33 (s, 4 H), 3.37 (s, 4 H), 2.83 (s, 4 H), 1.43 (d, J = 9.5 Hz, 2 H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ (ppm): 177.0, 150.1, 145.9, 140.1, 138.0, 130.5, 128.9, 127.9, 127.8, 126.3, 126.0, 120.3, 77.4, 77.0, 76.7, 65.0, 47.8, 45.8, 42.9.

FT-IR (cm^{-1}): 2979 (w), 1700 (s), 1502 (w), 1362 (s), 1169 (s), 744 (s).

2.1.6 The synthesis of monomers-3h

A solution of 4, 4 '-diaminodiphenyl ether (622 mg, 3.1 mmol), triethylamine (420 μL) and *exo*-Nadic anhydride (1.01g, 6.2 mmol) in toluene (20 mL) were added to the flask. The mixture was heated to 120 ^{o}C, and keep this temperature to reflux for 16 hours. After the mixture was cooled to room temperature, a solid was precipitated after adding a large amount of water. The precipitate was washed with methanol and

water, then filtered and vacuum drying for 12 h to obtain white solid (1.11g, 73% yield).

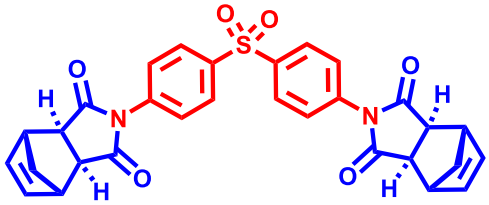


^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm): 7.29 (d, J = 8.6 Hz, 4H), 7.14 (d, J = 8.7 Hz, 4H), 6.34 (s, 4H), 3.18 (s, 4H), 2.82 (s, 4H), 1.48 – 1.35 (m, 4H); **^{13}C-NMR** (100 MHz, DMSO-d_6) δ (ppm): 177.4, 156.5, 138.3, 129.3, 128.1, 119.5, 48.0, 45.4, 43.2, 40.5, 40.3, 40.1, 39.9, 39.7, 39.5, 39.3.

FT-IR (cm^{-1}): 2981 (w), 1704 (s), 1506 (m), 1183 (s), 758 (s), 630 (s).

2.1.7 The synthesis of monomers-3f

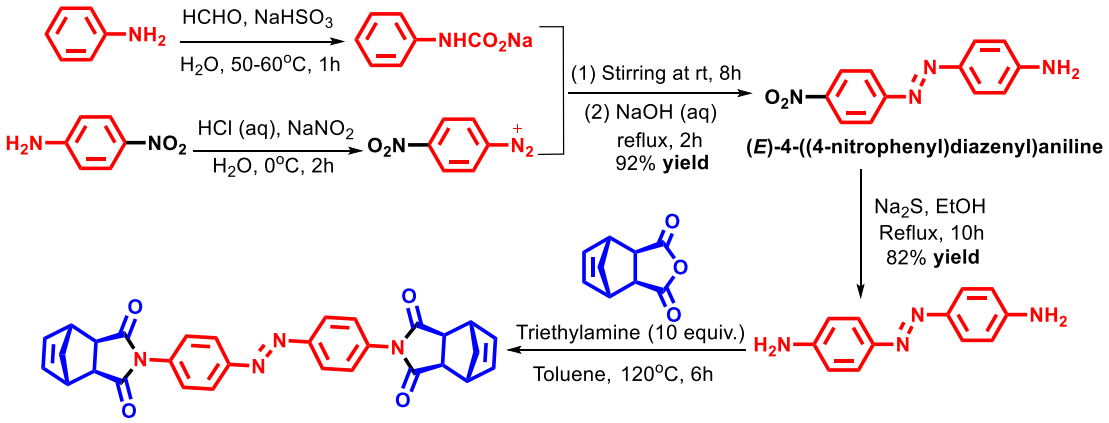
A solution of 4, 4'-diaminodiphenylsulfone (744 mg, 3.0 mol), triethylamine (420 μL) and *exo*-Nadic anhydride (1.01g, 6.2 mmol) in toluene (20 mL) were added to the flask. The mixture was heated to 120 ^{o}C, and keep this temperature to reflux for 12 hours. After the mixture was cooled to room temperature, a solid was precipitated after adding a large amount of water. The precipitate was washed with methanol and water, then filtered and vacuum drying for 12 h to obtain white solid (1.06 g, 66% yield).



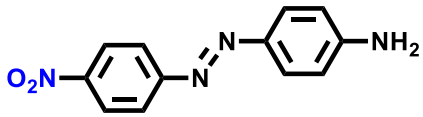
^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm): 8.08 (s, 4H), 7.57 (s, 4H), 6.33 (s, 4H), 3.17 (s, 5H), 2.84 (s, 4H), 1.40 (s, 4H), 1.21 (s, 2H); **^{13}C-NMR** (100 MHz, DMSO-d_6) δ (ppm): 176.7, 156.6, 138.3, 137.1, 128.8, 128.5, 48.2, 45.5, 43.2, 40.6, 40.4, 40.2, 40.0, 39.8, 39.6, 39.4.

FT-IR (cm^{-1}): 2983 (w), 1699 (s), 1376(m), 1167 (s), 1104 (m), 795 (m), 581 (s).

2.1.8 The synthesis of monomers-3g



(a) According to the previous reported synthetic procedure[1]: 4-nitroaniline (10.4 g) was dissolved in a solution of concentrated hydrochloric acid (19 ml) in water (75 ml). The mixture was cooled with an ice-water bath, then a solution of sodium nitrite (5.2 g) in 30 ml of water was added dropwise. The resultant solution of diazonium salt was stirred for 30 min at 0–3 ^{o}C, another solution of $NaHSO_3$ (11.4 g) dissolved in formaldehyde (2.7 g) and water (20 ml) was stirred for 30 min at 50 ^{o}C. Then the solution was heated to 60 ^{o}C and 7.0 g of aniline was added. After cooled to 0 ^{o}C, the resultant solution was added to a solution of 50 g of sodium acetate in 250 ml of water. The above solution of diazonium salt was added into this solution within 30 min. The reaction mixture was stirred at room temperature for 8 hours. The precipitate was collected by vacuum filtration and washed with water. The crude product was added to a solution of 6.8 g of sodium hydroxide in 7 ml of water. The reaction mixture was refluxed for 2 h. The resultant solution was neutralized to alkalescence by adding 5% HCl. The precipitate was collected by vacuum filtration and recrystallized from DMF/H_2O (1/1, v/v). (*E*)-4-((4-nitrophenyl) diazenyl) aniline was obtained as crimson crystals (16.6 g, 92% yield).

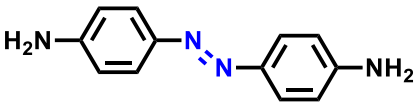


^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.39–8.30 (m, 2H), 7.99–7.90 (m, 2H), 7.88–7.82 (m, 2H), 6.85–6.70 (m, 2H), 4.23 (s, 2H).

FT-IR (cm^{-1}): 3500, 3398, 3037, 1639, 1589, 1501, 1459, 1423, 1393, 1333, 1303, 1249, 1141, 1098, 865, 835, 757.

(b) A solution of (*E*)-4-((4-nitrophenyl)diazenyl) aniline (5.0 g, 19 mmol) and sodium sulfide nonahydrate (10 g, 37 mmol, 2 equiv.) in ethanol (300 ml) was refluxed (*T* = 80 ^{o}C) for 10h. The solvent was evaporated under vacuum and resulting brown oil was redissolved in a mixture of water (300 ml) and brine (30 ml), extracted with ethyl

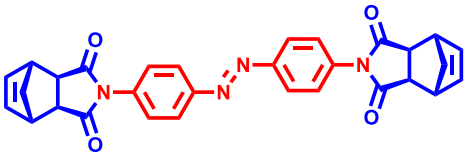
acetate (3 x 300 ml), dried ($MgSO_4$), concentrated to afford (*E*)-4,4'-(diazene-1,2-diyl) dianiline (3.3 g, 82% yield) as a reddish solid.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.2 Hz, 4H), 6.73 (d, J = 8.3 Hz, 4H), 3.94 (s, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.5, 145.8, 124.3, 114.8;

IR (neat, υ in cm^{-1}): 3478, 3461, 3383, 3341, 3204, 2959, 1729, 1616, 1599, 1438, 1300, 1235, 1137, 1109, 1067, 937, 835, 734.

(c) A solution of (*E*)-4, 4'-(diazene-1, 2-diyl) dianiline (2.12 g, 10 mmol) and *exo*-Nadic anhydride (3.4 g, 20 mmol, 1.0 equiv.) in toluene (80 ml) was refluxed (T = 120 ^oC) for 6 hours. The mixture was cooled to room temperature, a solid was precipitated after adding a large amount of water (300 ml). Then the precipitate was filtered, washed with mixed solvent (H_2O/EtOH = 2/1, v/v), and dried with 80 ^oC for 6 hours to obtain the imide monomer (3.3 g, 82% yield) as a yellow solid.

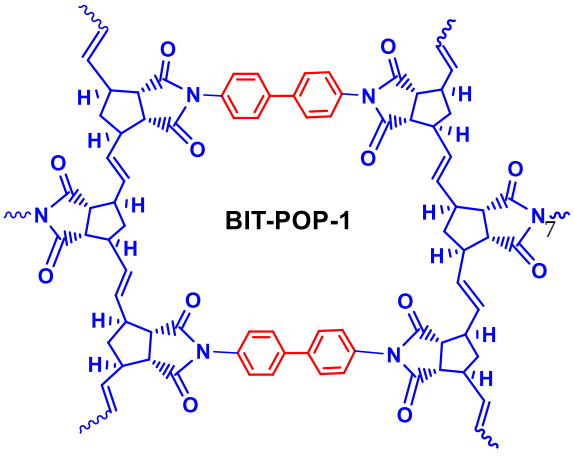


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.0 Hz, 4H), 7.47 (d, J = 8.1 Hz, 4H), 6.36 (s, 4H), 3.43 (s, 4H), 2.89 (s, 4H), 1.52 (d, J = 10.7 Hz, 2H), 1.24 (d, J = 6.7 Hz, 2H);

IR (neat, υ in cm^{-1}): 3064, 2997, 2967, 1721, 1687, 1601, 1510, 1385, 1294, 1180, 1157, 855, 792, 712.

2.2 The General Synthetic Procedure for Preparation of BIT-POPs

The synthetic procedure: To a solution of bisimidonorbornene monomers (400 mg) in DCM (10 mL) were added Grubbs-II (4 mg, 1.0 wt %) and standing at room temperature. The gel products were obtained when it's stilling 10 min to 220 min. The gel was soaked twice in ethanol and water for 12 hours each time, then the relative porous materials was obtained by freeze-drying. After the gel, take a part of solid sample to test the solution NMR in DMSO, no signal peak except for the solvent.



2.2.1 The Preparation of BIT-POP-1

To a solution of **monomer-3a** (200 mg) in DCM (5 mL) were added Grubbs-II (2 mg, 1.0 wt %) and stilling at room

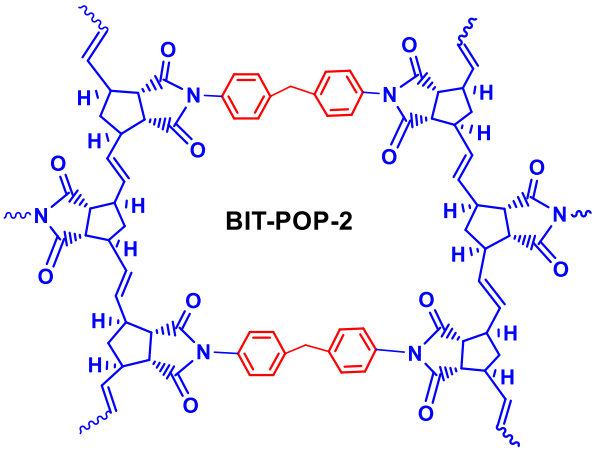
temperature. The gel products were formed when it reacted for 6 min. Using ethanol and water to exchange the solvent in the gels for 12 hours each time, then BIT-POP-1 was obtained by freeze-drying (194 mg, 97% yield).

^{13}C-CP/MS NMR, δ (ppm): 176.90, 136.57, 130.22, 125.96, 50.42, 49.97, 41.58.

FT-IR (cm^{-1}): 2945 (w), 1704 (s), 1364 (m), 1159 (s), 710 (w), 604 (m).

Elemental Analysis: found N5.74%, C76.96%, H4.91%.

2.2.2 The Preparation of BIT-POP-2



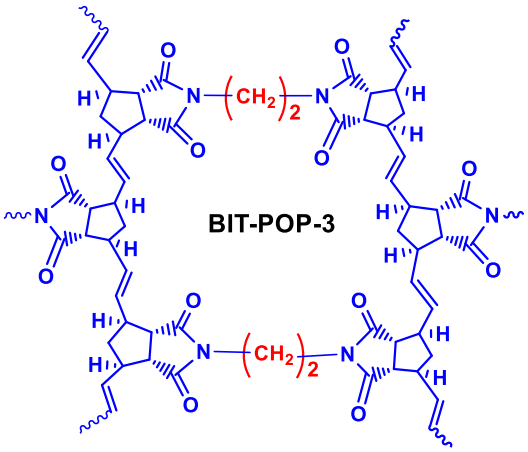
To a solution of **monomer-3b** (200 mg) in DCM (5 mL) were added Grubbs-II (2 mg, 1.0 wt %) and stilling at room temperature. The gel products were formed when it reacted for 17 min. Using ethanol and water to exchange the solvent in the gels for 12 hours each time, then BIT-POP-2 was obtained by freeze-drying (190 mg, 95% yield).

^{13}C-CP/MS NMR, δ (ppm): 178.50, 138.54, 131.63, 52.95, 46.67, 43.88, 37.01.

FT-IR (cm^{-1}): 2967 (w), 1715 (s), 1505 (m), 1378 (s), 1164 (w), 740 (s).

Elemental Analysis: found N5.54%, C75.51%, H5.23%

2.2.3 The Preparation of BIT-POP-3



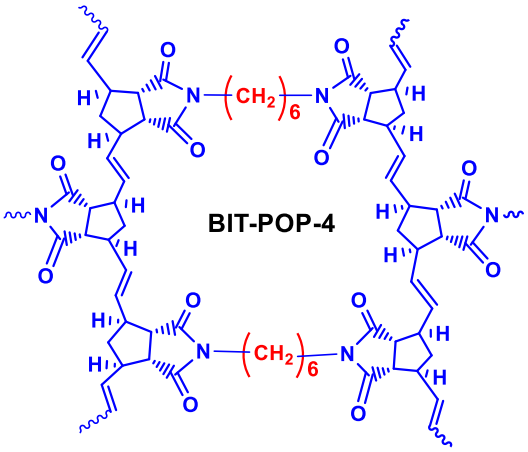
To a solution of **monomer-3c** (200 mg) in DCM (5 mL) were added Grubbs-II (2 mg, 1.0 wt %) and stilling at room temperature. The gel products were formed when it reacted for 36 min. Using ethanol and water to exchange the solvent in the gels for 12 hours each time, then BIT-POP-3 was obtained by freeze-drying (176 mg, 88% yield).

^{13}C-CP/MS NMR, δ (ppm): 175.52, 130.47, 48.82, 44.96, 42.13, 35.33.

FT-IR (cm^{-1}): 2948 (w), 1778 (w), 1694 (s), 1388 (m), 1147 (m), 788 (w), 644 (w).

Elemental Analysis: found N7.78%, C66.24%, H5.88%

2.2.4 The Preparation of BIT-POP-4



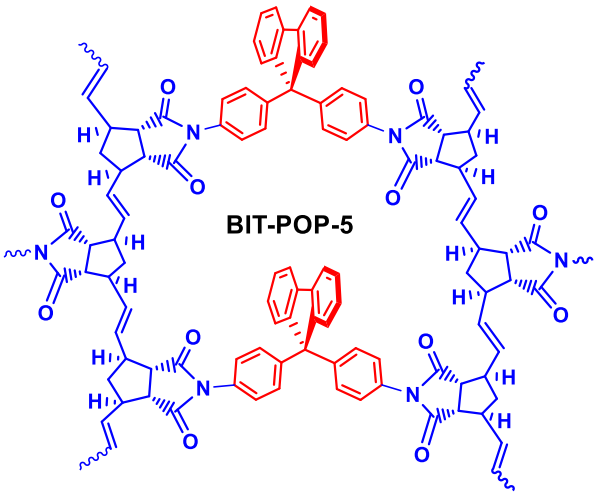
To a solution of **monomer-3d** (200 mg) in DCM (5 mL) were added Grubbs-II (2 mg, 1.0 wt %) and stilling at room temperature. The gel products were formed when it reacted for 73 min. Using ethanol and water to exchange the solvent in the gels for 12 hours each time, then BIT-POP-4 was obtained by freeze-drying (192 mg, 96% yield).

^{13}C-CP/MS NMR, δ (ppm): 175.42, 130.12, 48.86, 40.74, 35.73, 23.86.

FT-IR (cm^{-1}): 2936 (w), 1773 (w), 1686 (s), 1393 (m), 1352 (m), 1155 (m), 963 (w).

Elemental Analysis: found N6.68%, C69.47%, H7.05%

2.2.5 The Preparation of BIT-POP-5



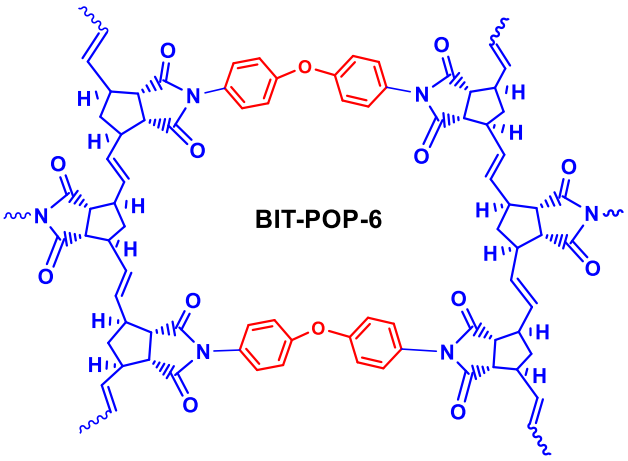
To a solution of **monomer-3e** (200 mg) in DCM (5 mL) were added Grubbs-II (2 mg, 1.0 wt %) and stilling at room temperature. The gel products were formed when it reacted for 39 min. Using ethanol and water to exchange the solvent in the gels for 12 hours each time, then BIT-POP-5 was obtained by freeze-drying (182mg, 91% yield).

^{13}C-CP/MS NMR, δ (ppm): 175.44, 150.50, 148.08, 146.04, 142.63, 139.82, 136.69, 126.87, 120.28, 119.35, 63.82, 50.92, 44.15, 43.05, 41.89.

FT-IR (cm^{-1}): 2941 (w), 1778 (w), 1709 (s), 1375 (m), 1153 (m), 954 (w), 745 (m).

Elemental Analysis: found N4.13%, C79.93%, H5.14%

2.2.6 The Preparation of BIT-POP-6

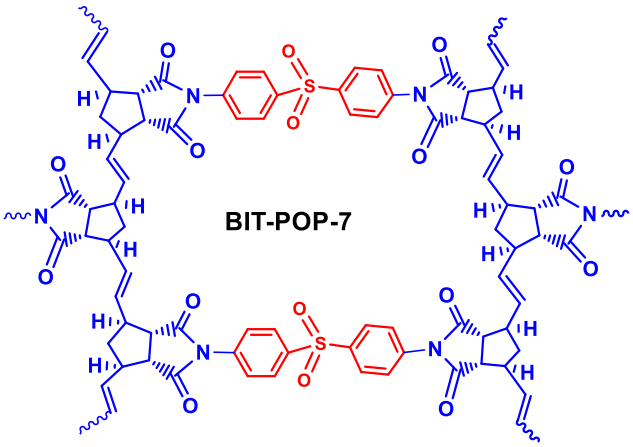


To a solution of **monomer-3f** (200 mg) in DCM (5 mL) were added Grubbs-II (2 mg, 1.0 wt %) and stilling at room temperature. The gel products were formed when it reacted for 24 min. Using ethanol and water to exchange the solvent in the gels for 12 hours each time, then BIT-POP-6 was obtained by freeze-drying (186 mg, 93% yield).

^{13}C-CP/MS NMR, δ (ppm): 175.89, 156.67, 126.91, 122.10, 50.87, 42.70.

FT-IR (cm^{-1}): 2948 (w), 1711 (w), 1704 (s), 1515 (m), 1375 (s), 1174 (s), 777 (w).

Elemental Analysis: found N5.70%, C73.37%, H4.93%



2.2.7 The Preparation of BIT-POP-7

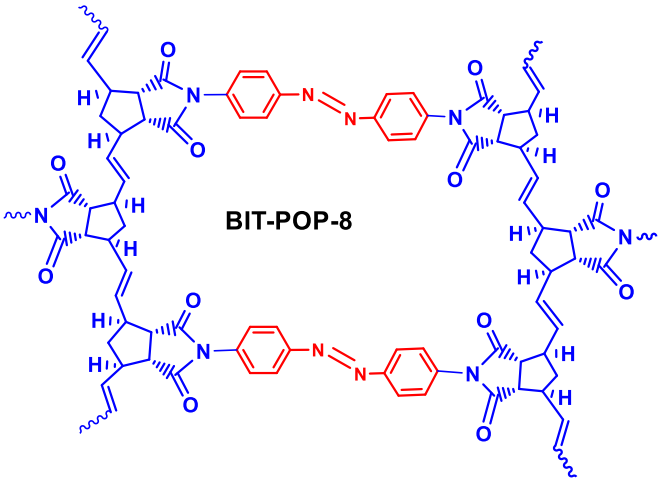
To a solution of **monomer-3g** (200 mg) in DCM (5 mL) were added Grubbs-II (2 mg, 1.0 wt %) and stilling at room temperature. The gel products were formed when it reacted for 180 min. Using ethanol and water to exchange the solvent in the gels for 12 hours each time, then BIT-POP-7 was obtained by freeze-drying (166 mg, 83% yield).

^{13}C-CP/MS NMR, δ (ppm): 175.72, 135.99, 127.07, 51.15, 42.65.

FT-IR (cm^{-1}): 2953 (w), 1779 (w), 1710 (s), 1502 (m), 1364 (m), 1161 (m), 812 (w), 604 (w).

Elemental Analysis: found N5.19%, C66.64%, H4.47%

2.2.8 The Preparation of BIT-POP-8



To a solution of **monomer-3h** (200 mg) in DCM (5 mL) were added Grubbs-II (2 mg, 1.0 wt %) and stilling at room temperature. The gel products were formed when it reacted for 220 min. Using ethanol and water to exchange the solvent in the gels for 12 hours each time, then BIT-POP-8 was obtained by freeze-drying (154 mg, 77% yield).

^{13}C-CP/MS NMR, δ (ppm): 175.69, 150.63, 133.65, 126.96, 125.43, 122.48, 50.71, 42.92, 42.45.

FT-IR (cm^{-1}): 2935 (w), 1774 (w), 1704 (s), 1496 (w), 1360 (m), 1161 (m), 964 (w), 842 (w).

Elemental Analysis: found N11.03%, C71.40%, H4.60%

2.3 gas separation

10 wt.% (20 mg) of porous materials (BIT-POP-1~8) was mixed with 200 mg polysulfone and dried at 80 ^{o}C for 12 hours. 6.45 g of chloroform was added to the mixture. The solution was stirred for 24h at ambient condition. Composite films were formed via solution casting at a ambient condition.

5 wt.% (10 mg) of porous materials (BIT-POP-1~8) was mixed with 200 mg polysulfone and dried at 80 ^{o}C for 12 hours. 6.45 g of chloroform was added to the mixture. The solution was stirred for 24h at ambient condition. Composite films were formed via solution casting at a ambient condition.

The gas permeabilities were determined by the constant-volume/variable-pressure time-lag method with the set-up illustrated in Fig. 2. The downstream pressure was recorded using an Inficon transducer ranging from 0–10 torr; the leak rate of the instrument was $\sim 1 \times 10^{-7}$ torr s^{-1} with a downstream volume of 30 cm. Before testing, a polysulfone film was used as a standard membrane material to check the system. The O_2 permeability obtained at 35 ℃ was 1.25 barrer with an O_2/N_2 selectivity of 5.5 which agreed well with previously reported data[2].

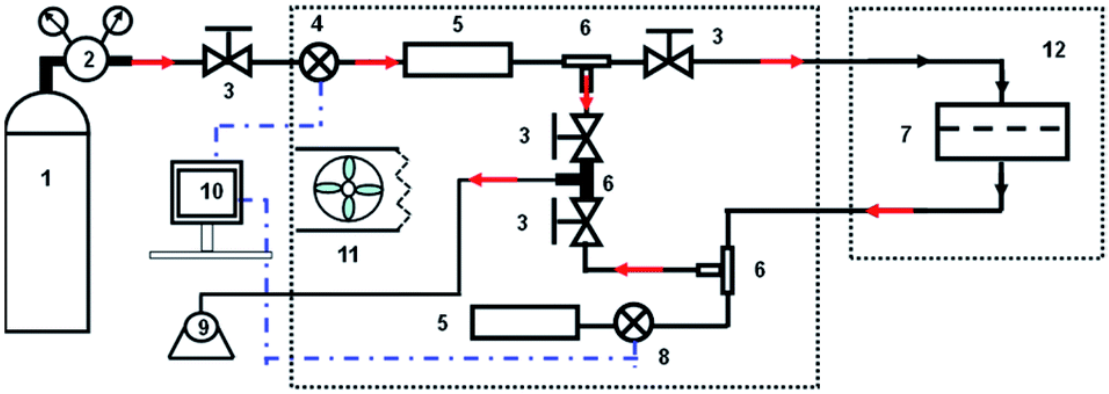


Figure S 1 Gas separation set-up for low-temperature testing;

(1) cylinder, (2) regulator, (3) bellows sealed valve, (4) upstream transducer, (5) gas cylinder, (6) welded T-pipe, (7) membrane cell, (8) downstream transducer, (9) pump, (10) computer, (11) temperature control, and (12) chiller.

3 Table in ESI

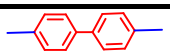
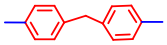
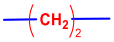
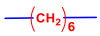
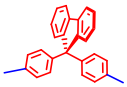
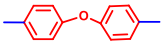
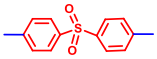
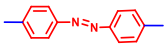
Table S 1. Elemental analysis of BIT-POPs

Entry	Obtained mass ratio (%)			Theoretical mass ratio (%)		
	N	C	H	N	C	H
BIT-POP-1	5.74	74.96	4.91	5.88	75.62	5.08
BIT-POP-2	5.54	75.51	5.23	5.71	75.90	5.34
BIT-POP-3	7.78	66.24	5.88	7.95	68.17	5.72
BIT-POP-4	6.68	69.47	7.05	6.86	70.57	6.91
BIT-POP-5	4.13	79.93	5.14	4.37	80.61	5.03
BIT-POP-6	5.70	73.37	4.93	5.69	73.16	4.91
BIT-POP-7	5.19	66.64	4.47	5.18	66.65	4.48
BIT-POP-8	11.03	71.40	4.60	11.10	71.42	4.79

Table S 2. Gas separation of BIT-POP-1、BIT-POP-5

Entry	He	H_2	N_2	O_2	CH_4	CO_2
BIT-POP-1(5 wt%)	9.72	11.08	0.16	1.02	0.17	5.26
BIT-POP-1(10 wt%)	15.36	17.73	0.33	1.84	0.36	8.87
BIT-POP-5(5 wt%)	19.27	21.40	0.38	2.15	0.48	11.83
BIT-POP-5(10 wt%)	21.07	22.40	0.40	2.40	0.44	12.67
PSF	13.00	14.00	0.25	1.40	0.25	5.60

Table S 3. The influence the linkers on the outcome of the porosity parameters of BIT-POPs

Sample	Linker	Length of linker (Astron)	S_{BET} [a] (m^2/g)	V_{total} [b] (cm^3/g)	Mean Pore Size (nm)	Yield (%)
BIT-POP-1		9.622	594	0.76	5.8	97
BIT-POP-2		10.515	432	0.547	4.8	95
BIT-POP-3		3.737	166	0.107	11.3	88
BIT-POP-4		8.739	33	0.023	22.0	96
BIT-POP-5		9.476	579	1.051	5.8	91
BIT-POP-6		9.158	310	0.296	7.6	93
BIT-POP-7		7.837	233	0.197	9.4	83
BIT-POP-8		11.427	432	0.404	3.8	77

[a] BET surface area were determined by N_2 adsorption–desorption isotherms (77K); [b] Calculated from the N_2 adsorbed at P/P_0 = 0.99.

4 Figures in ESI

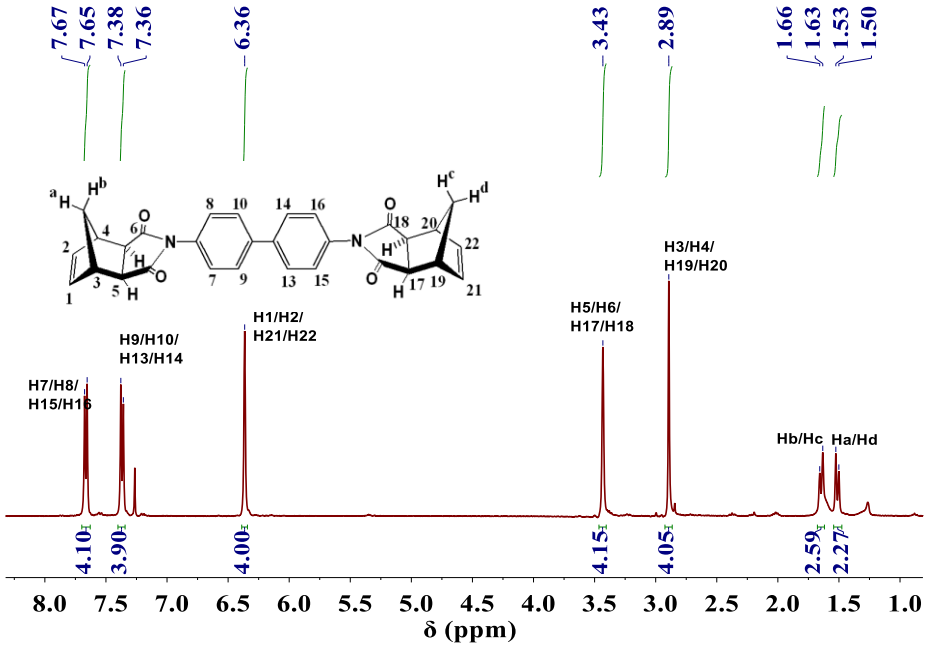


Figure S 2 ^{1}H-NMR of monomers-3a

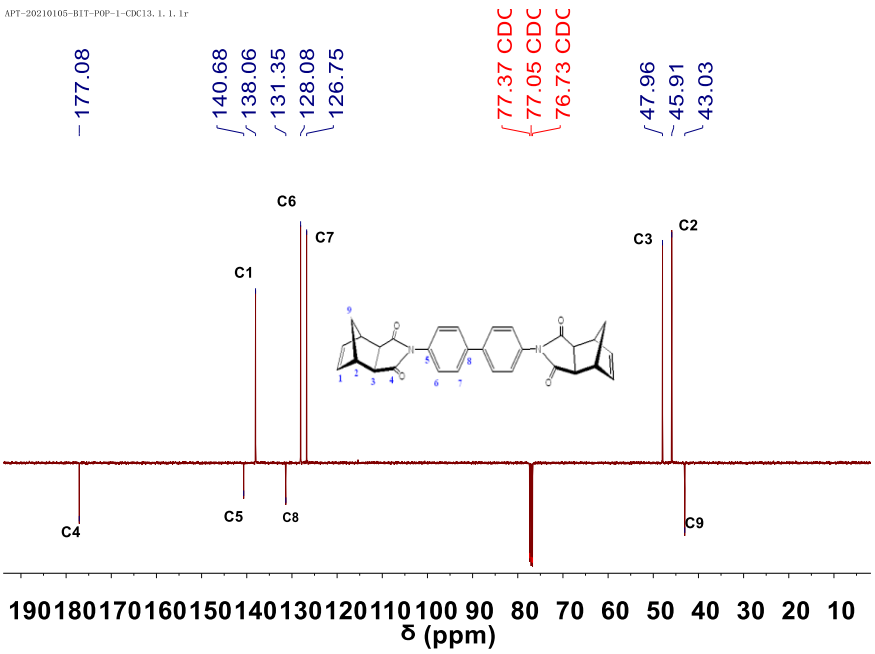


Figure S 3 APT-NMR of monomers-3a

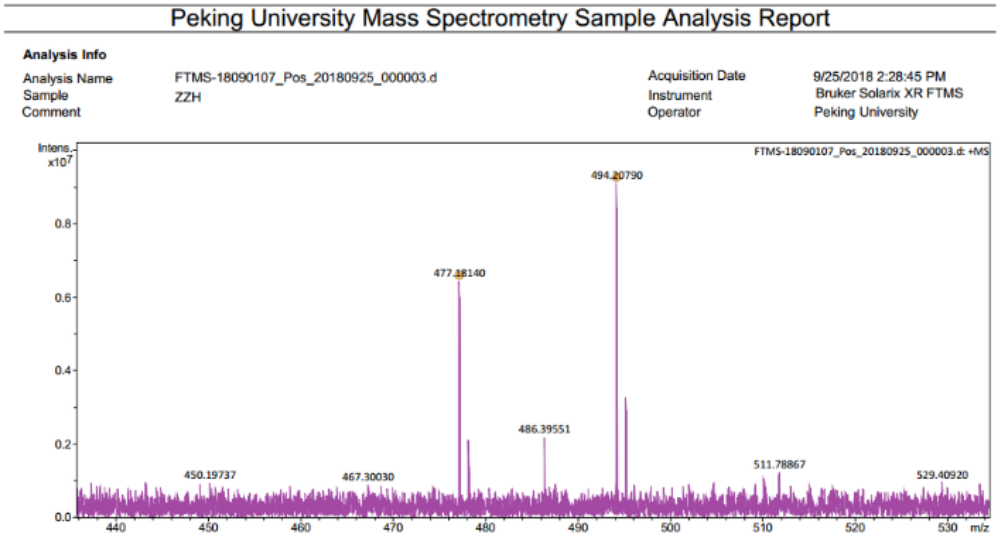


Figure S 4 FT-MS of monomer-3a

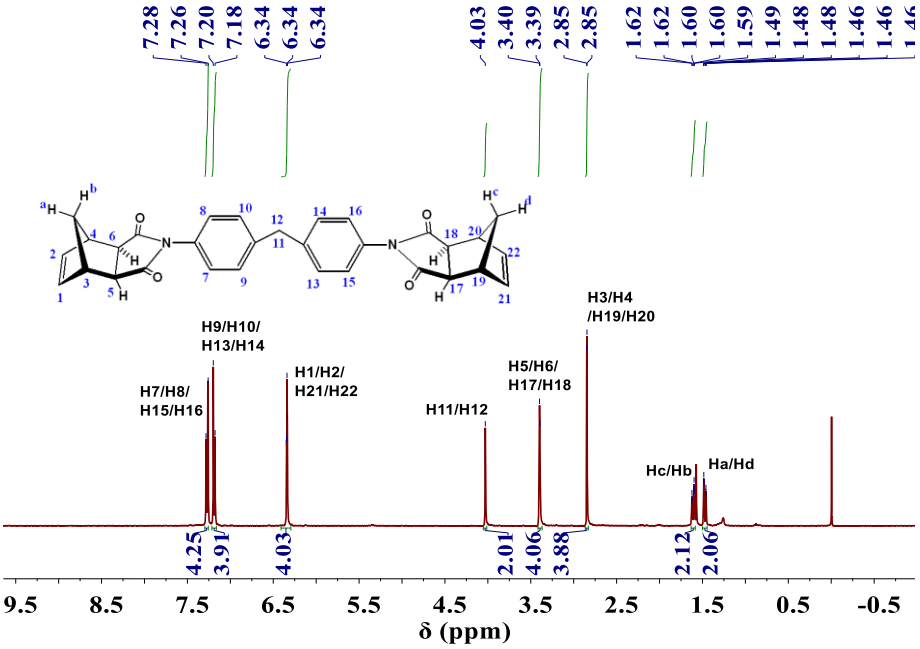


Figure S 5 ^{1}H-NMR of monomers-3b

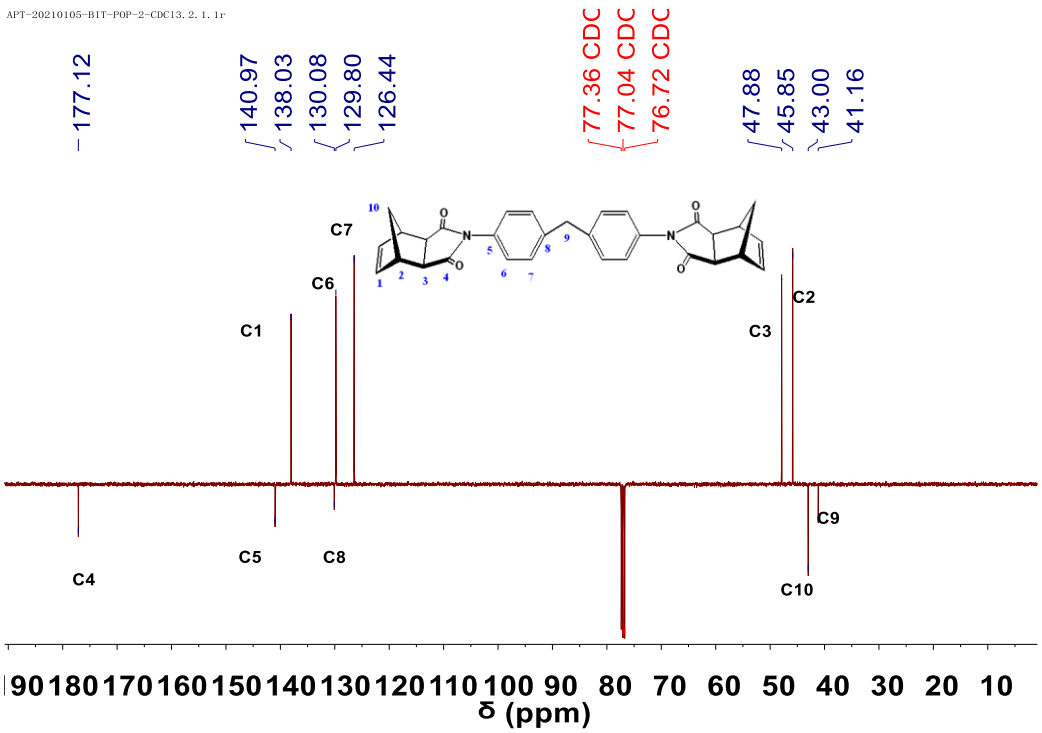


Figure S 6 APT-NMR of monomers-3b

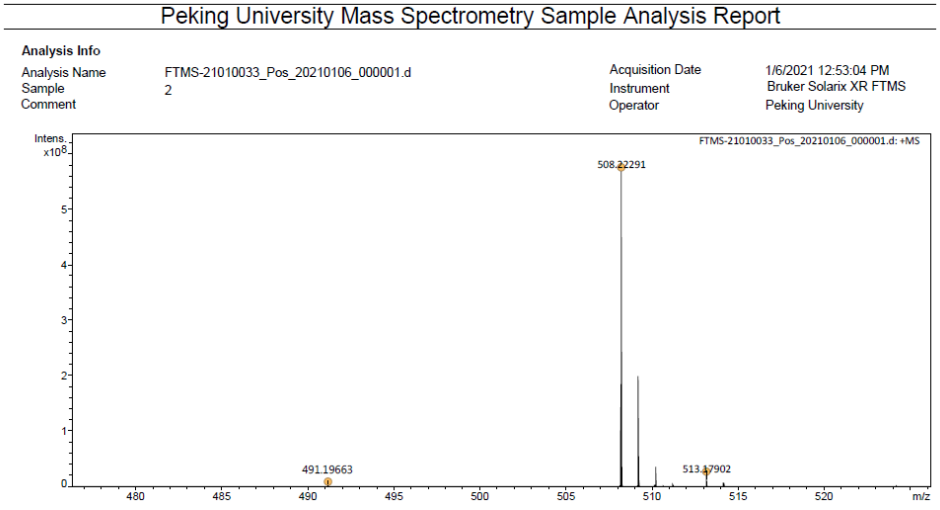


Figure S 7 FT-MS of monomer-3b

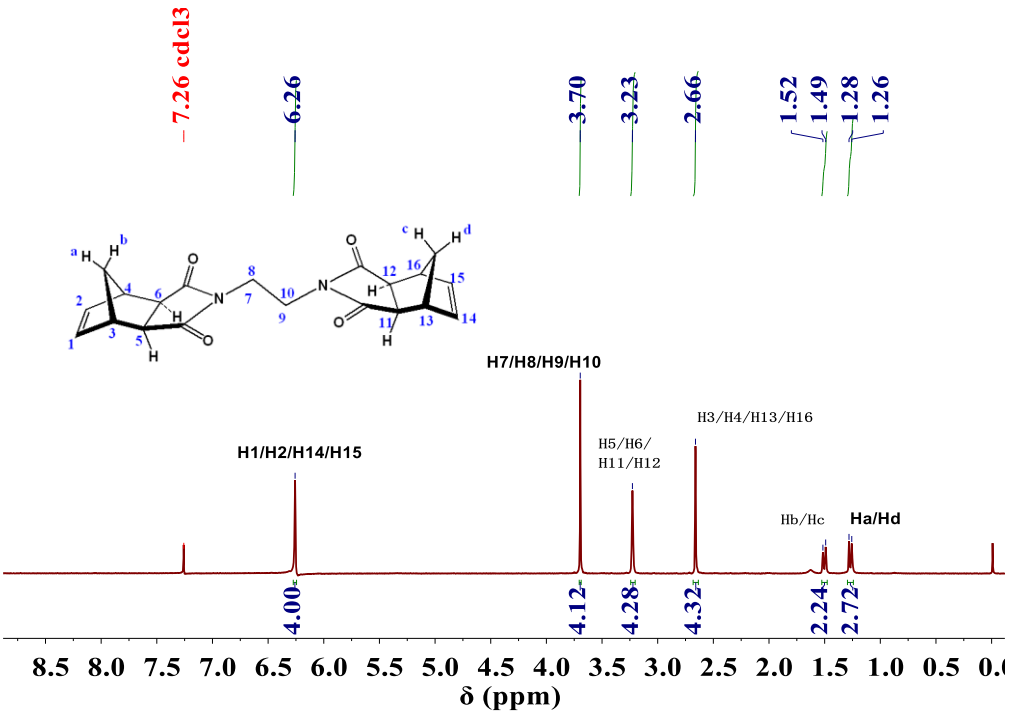


Figure S 8 ^{1}H-NMR of monomers-3c

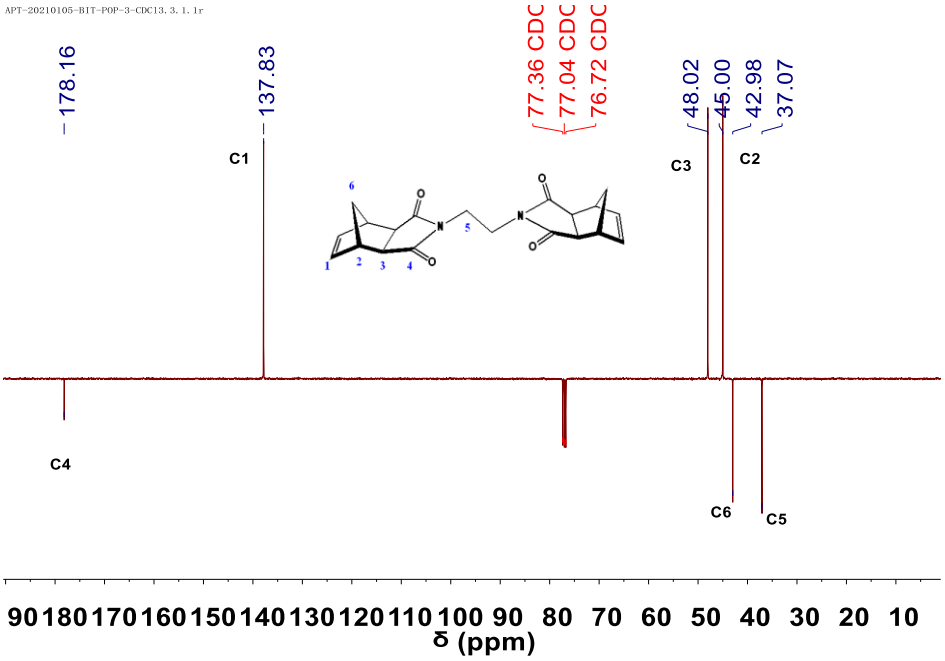


Figure S 9 APT-NMR of monomers-3c

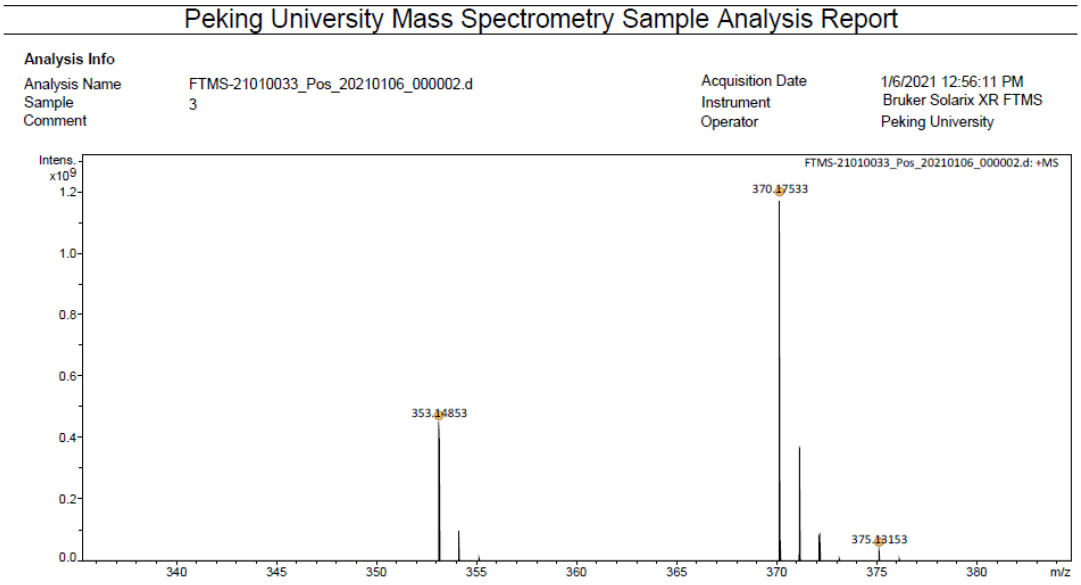


Figure S 10 FT-MS of monomer-3c

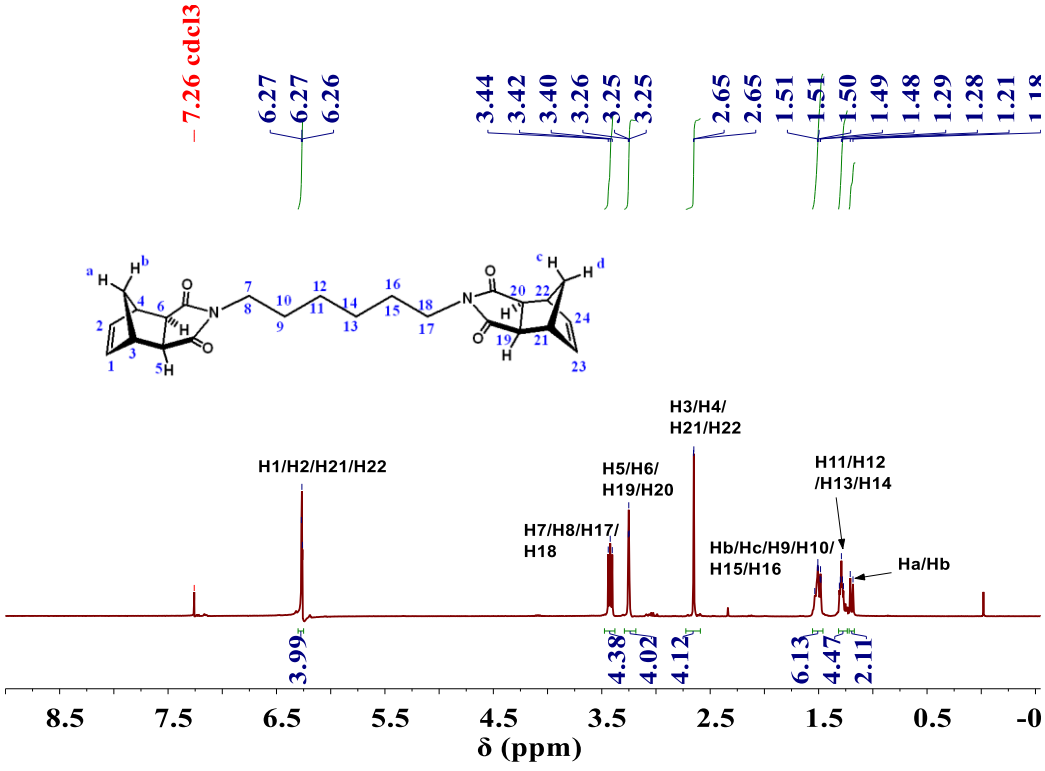


Figure S 11 ^{1}H-NMR of monomers-3d

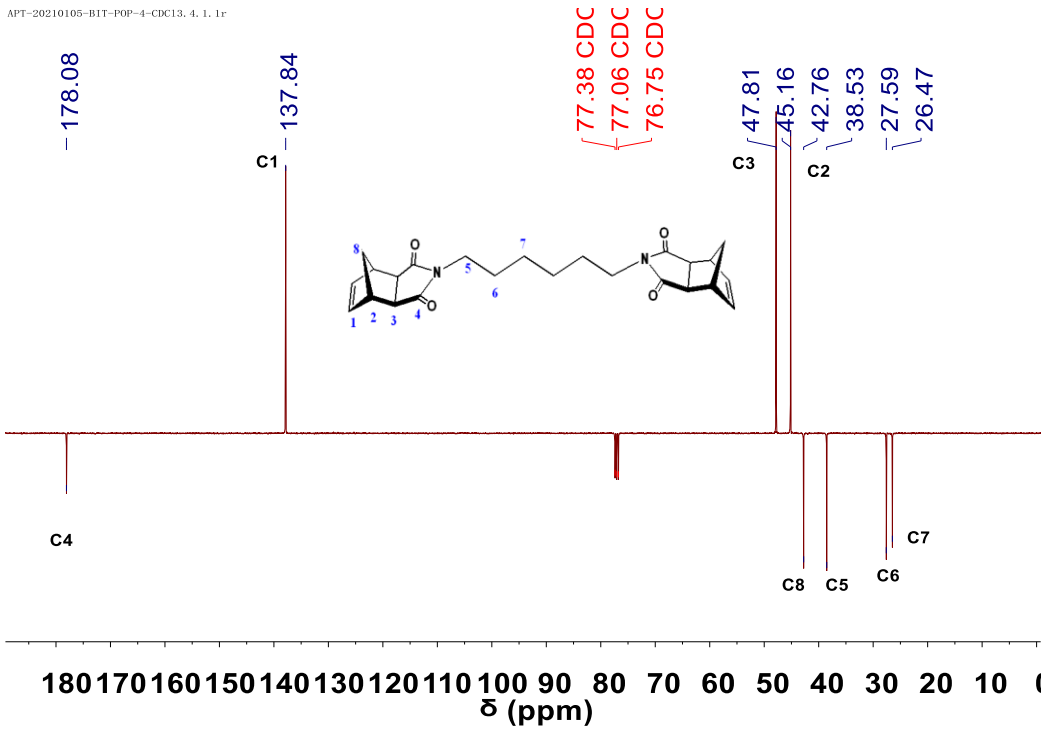


Figure S 12 APT-NMR of monomers-3d

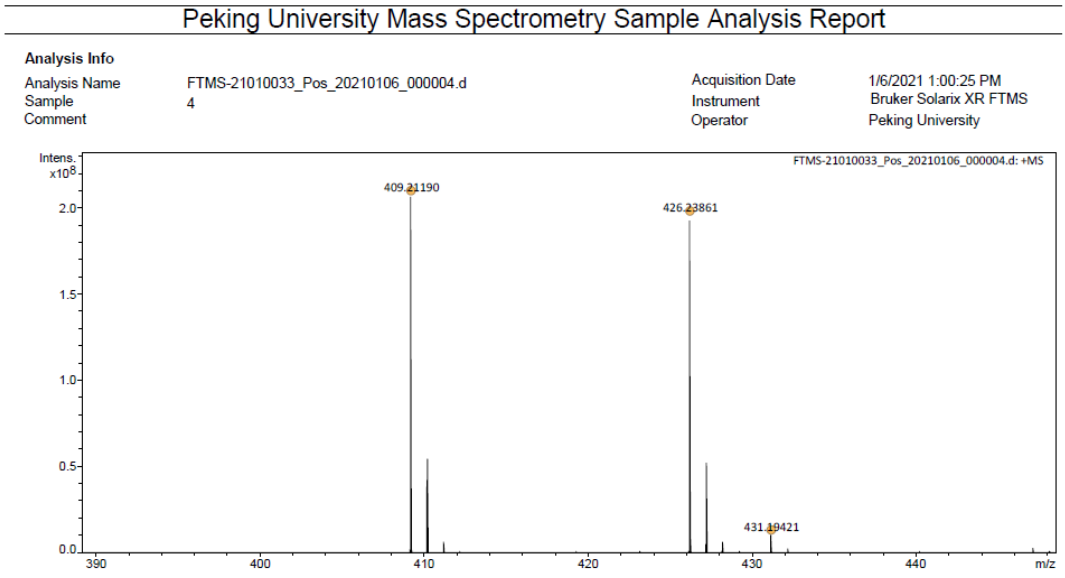


Figure S 13 FT-MS of monomer-3d

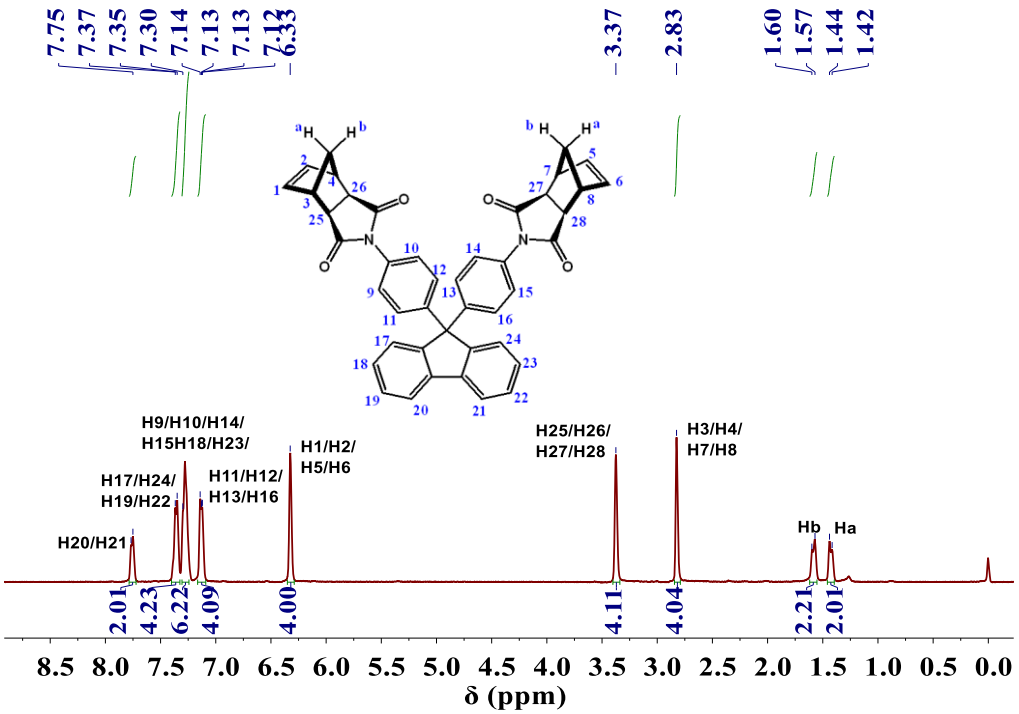


Figure S 14 ^{1}H-NMR of monomers-3e

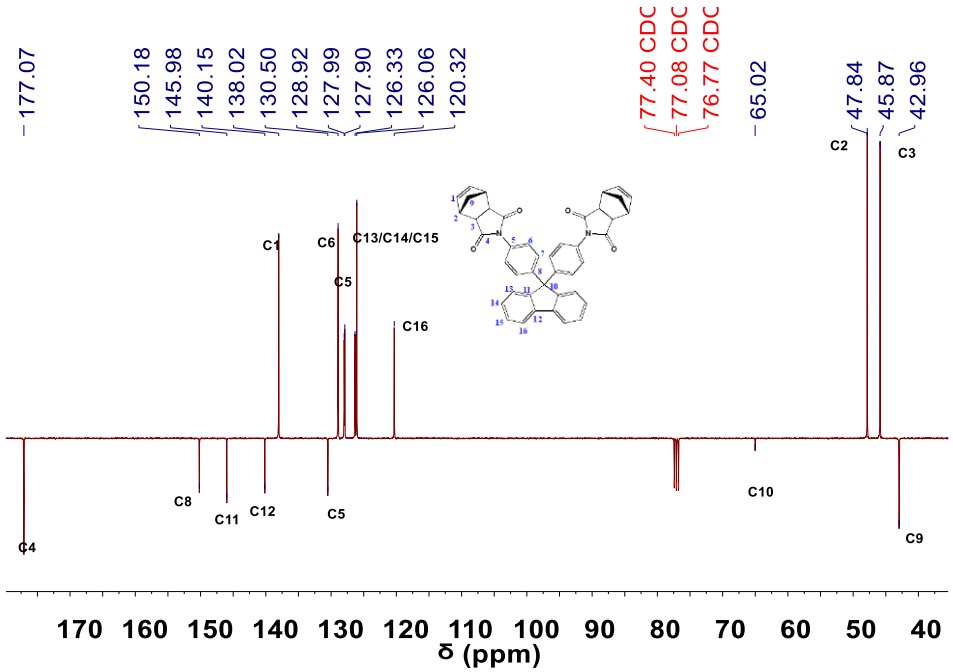


Figure S 15 APT-NMR of monomers-3e

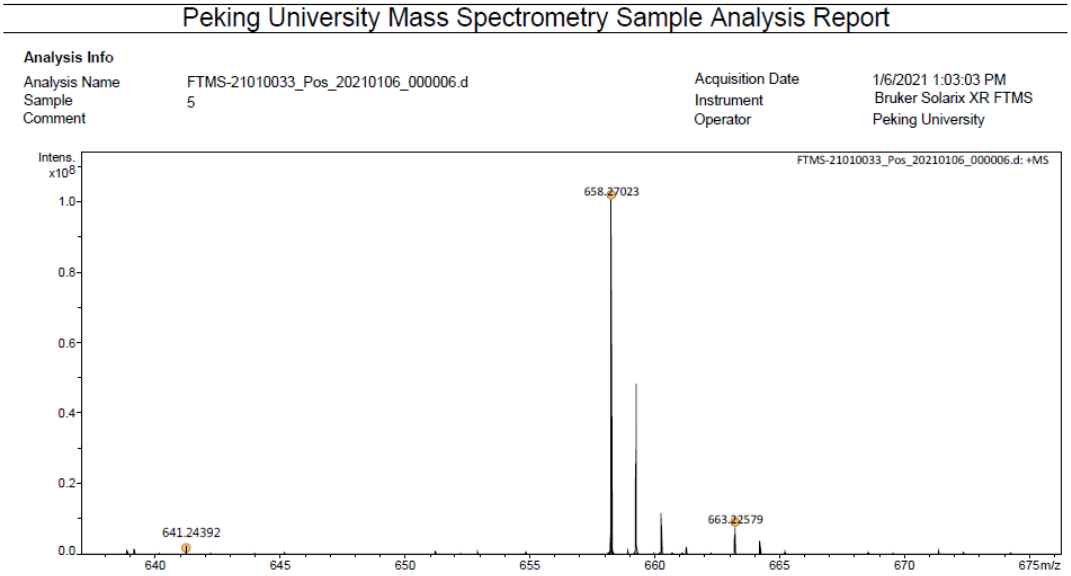


Figure S 16 FT-MS of monomer-3e

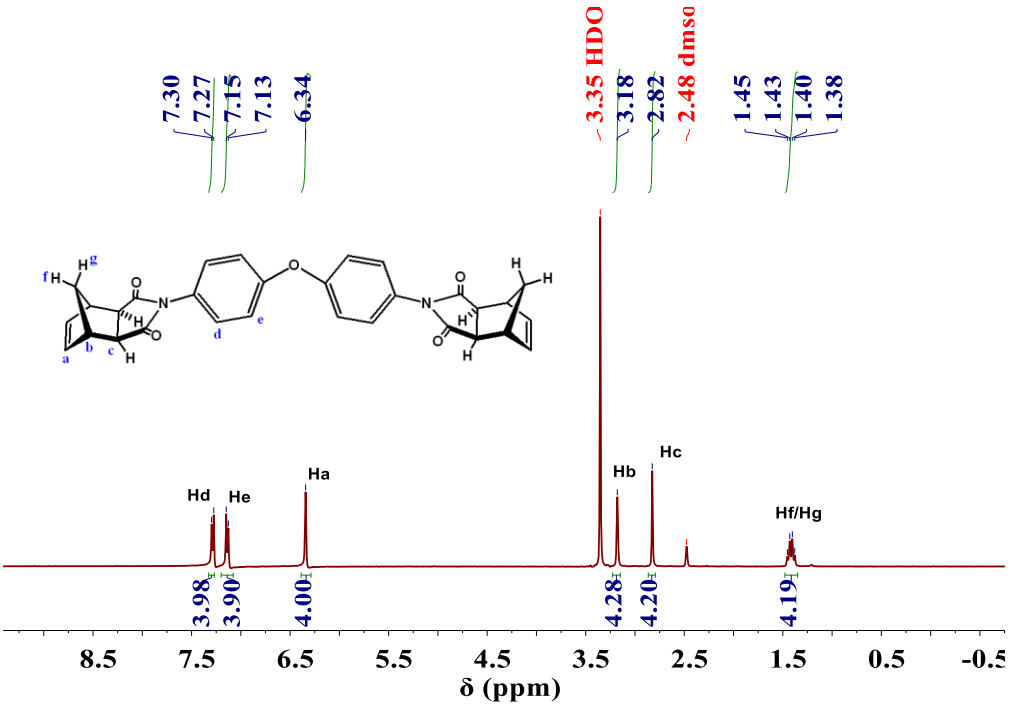


Figure S 17 ^{1}H-NMR of monomers-3f

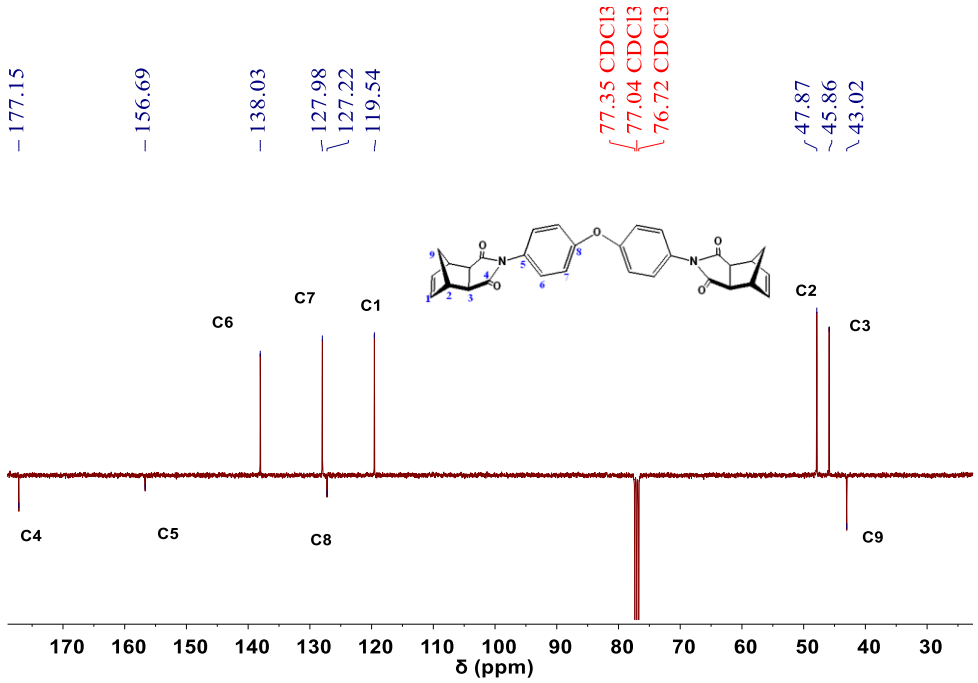


Figure S 18 APT-NMR of monomers-3f

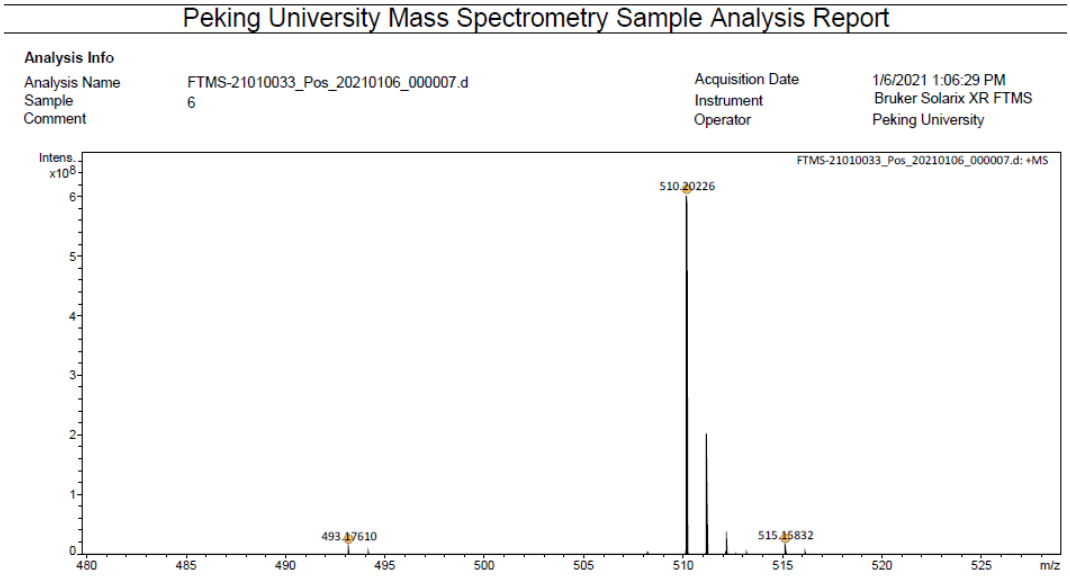


Figure S 19 FT-MS of monomer-3f

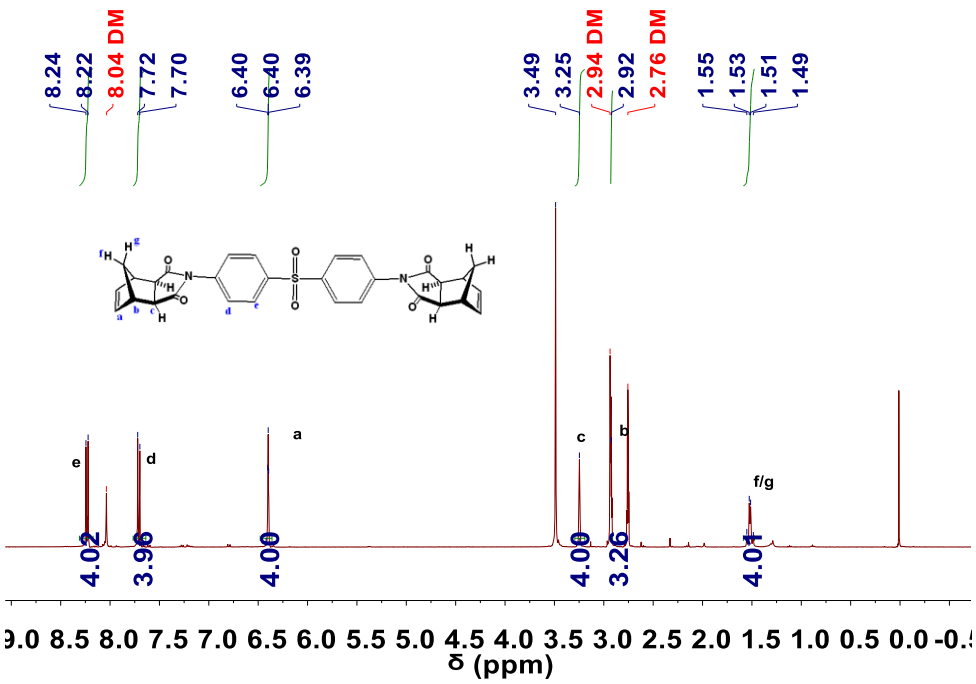


Figure S 20 ^{1}H-NMR of monomers-3g

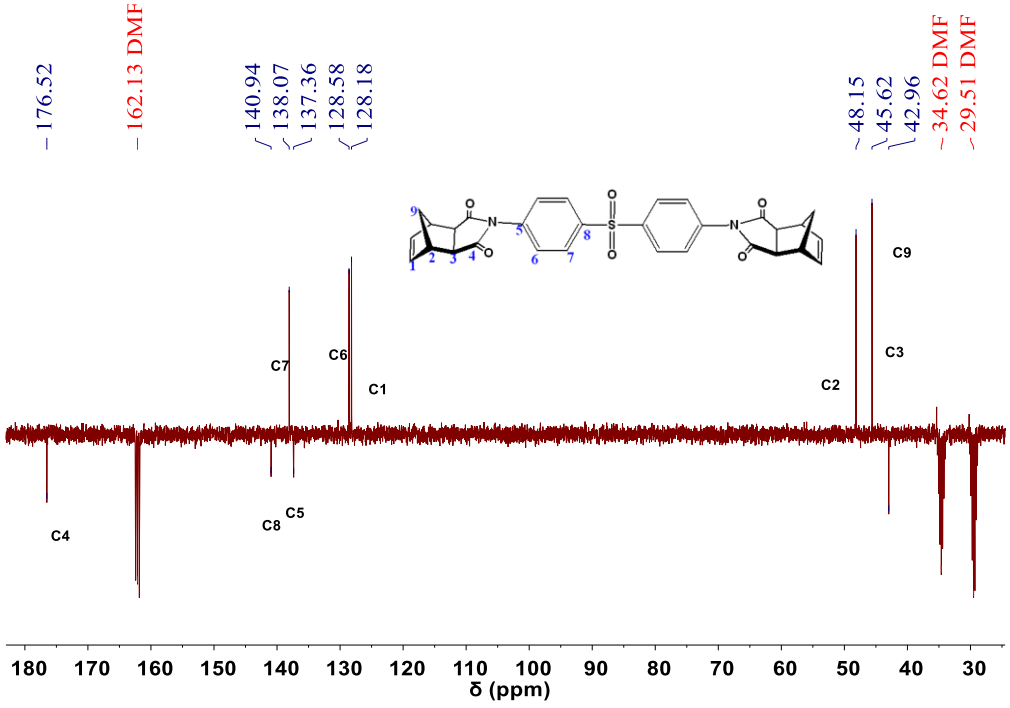


Figure S 21 APT-NMR of monomers-3g

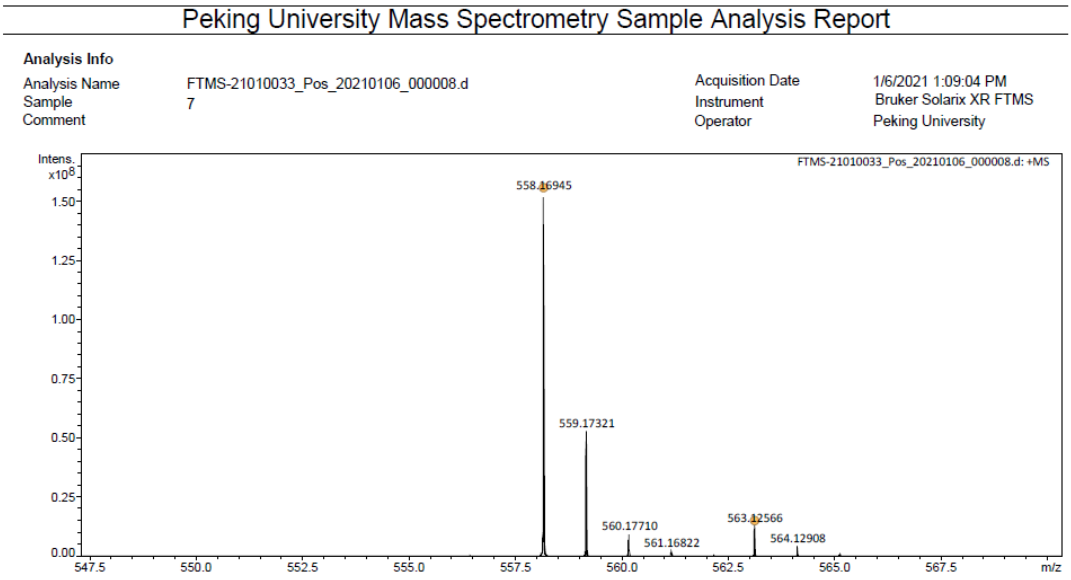


Figure S 22 FT-MS of monomer-3g

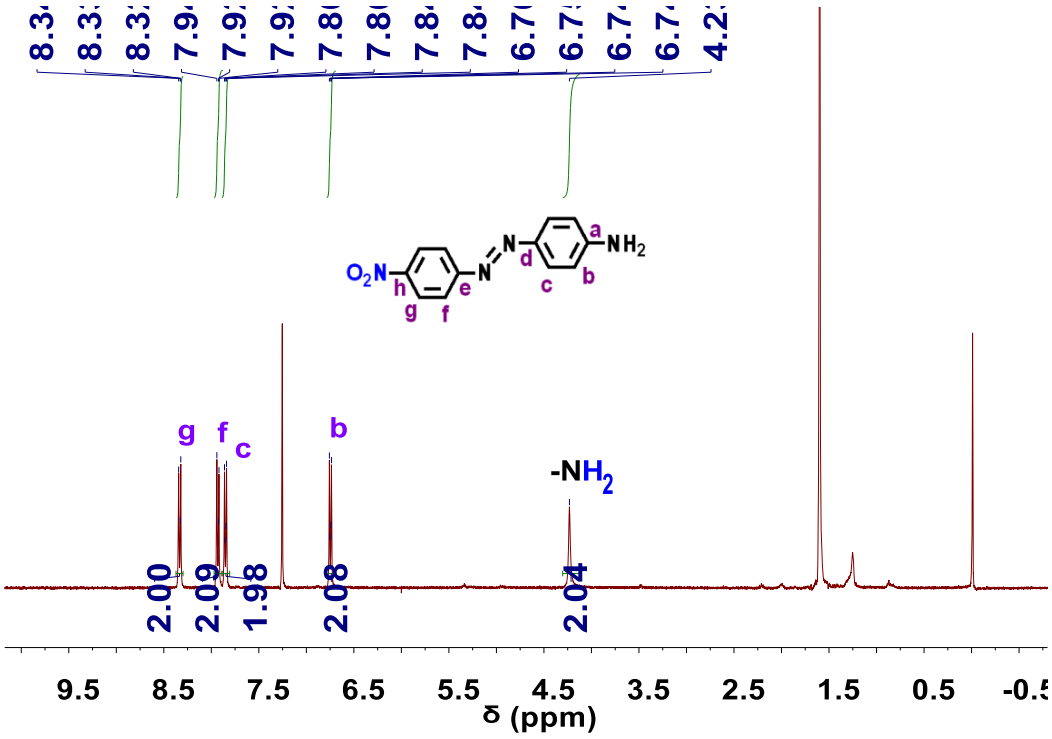


Figure S 23 ^{1}H NMR of (*E*)-4-((4-nitrophenyl) diazenyl) aniline

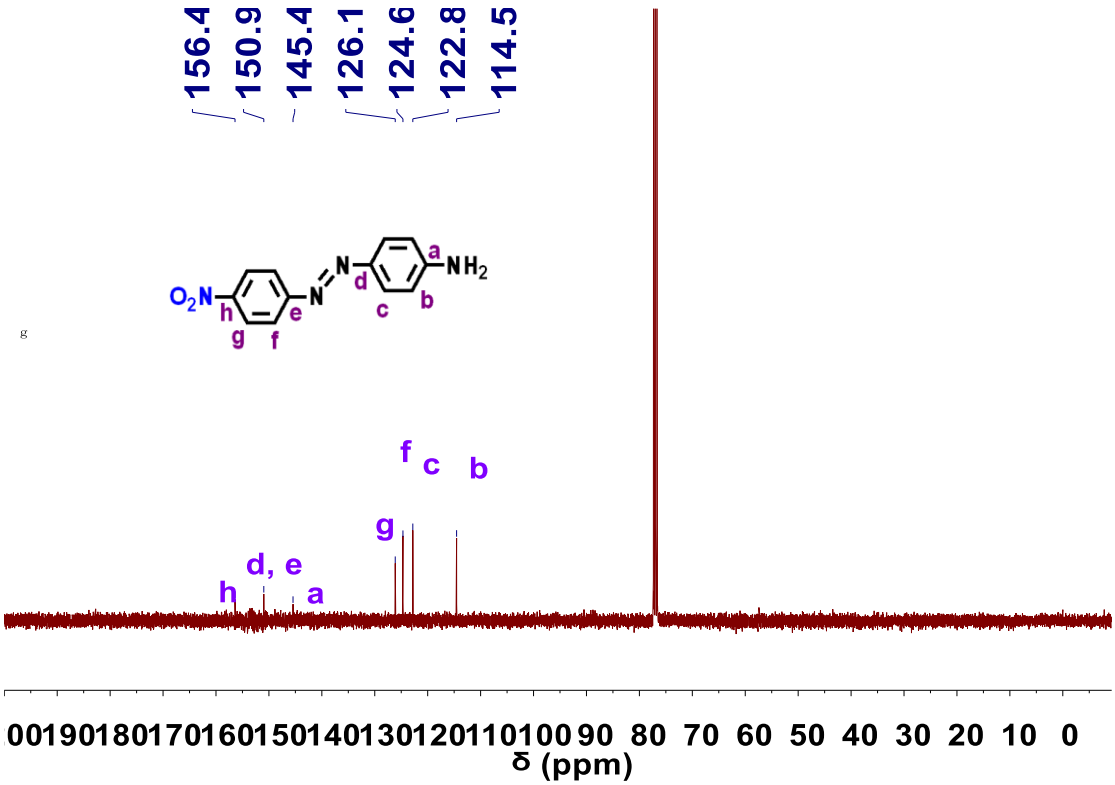


Figure S 24 ^{13}C NMR of (*E*)-4-((4-nitrophenyl) diazenyl) aniline

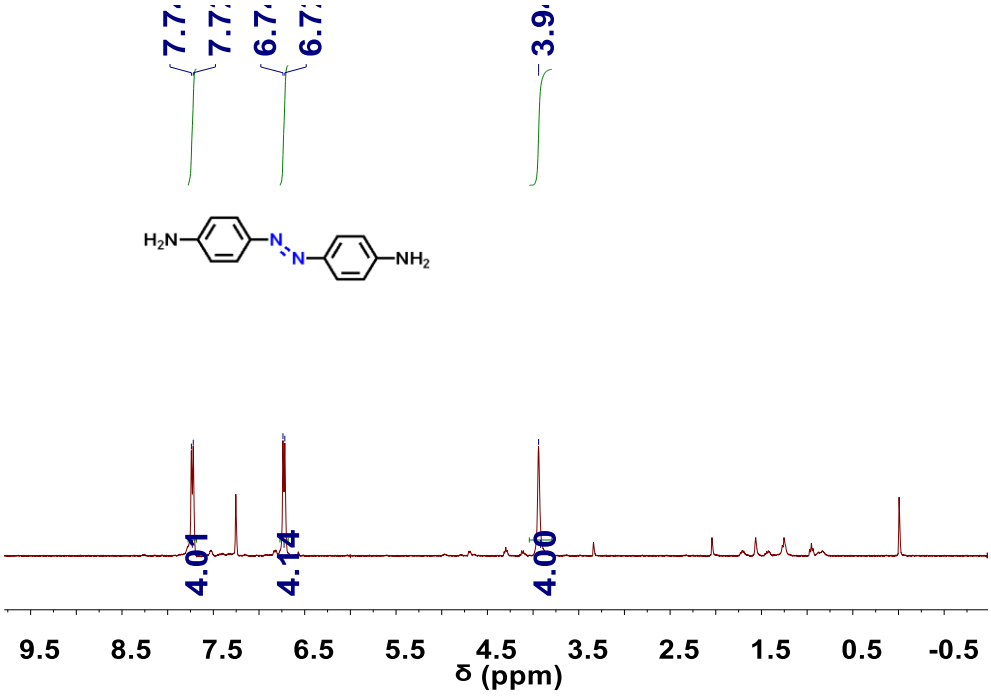


Figure S 25 ^{1}H NMR of (*E*)-4, 4'-(diazene-1, 2-diyl) dianiline

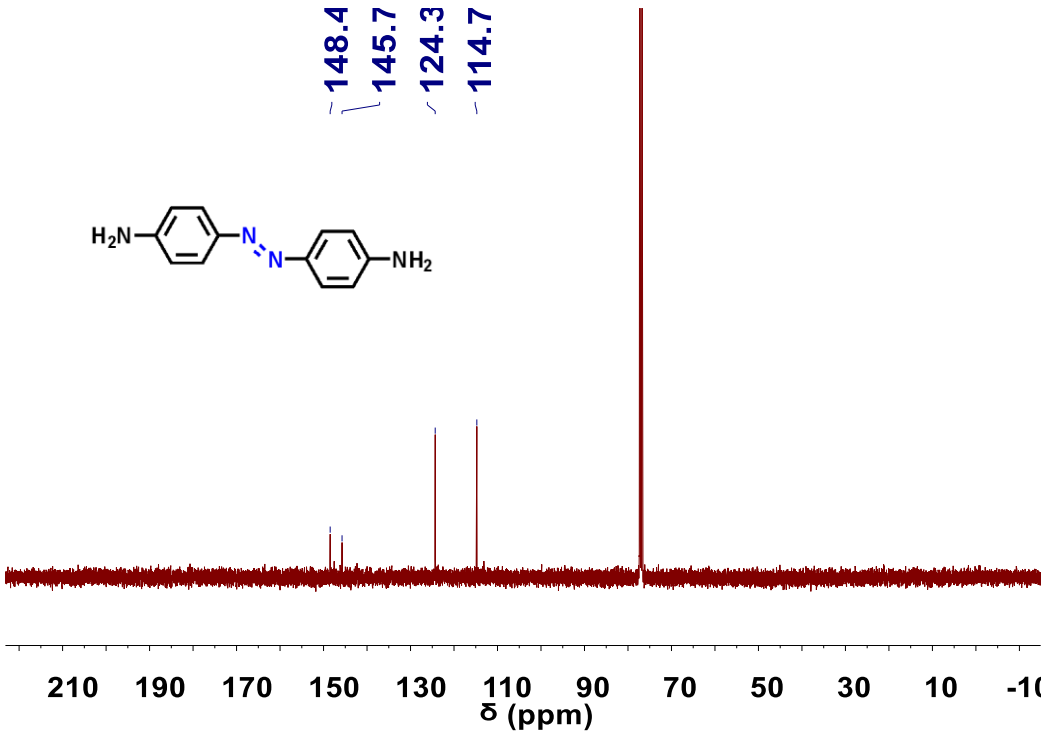


Figure S 26 ^{13}C NMR of (*E*)-4, 4'-(diazene-1, 2-diyl) dianiline

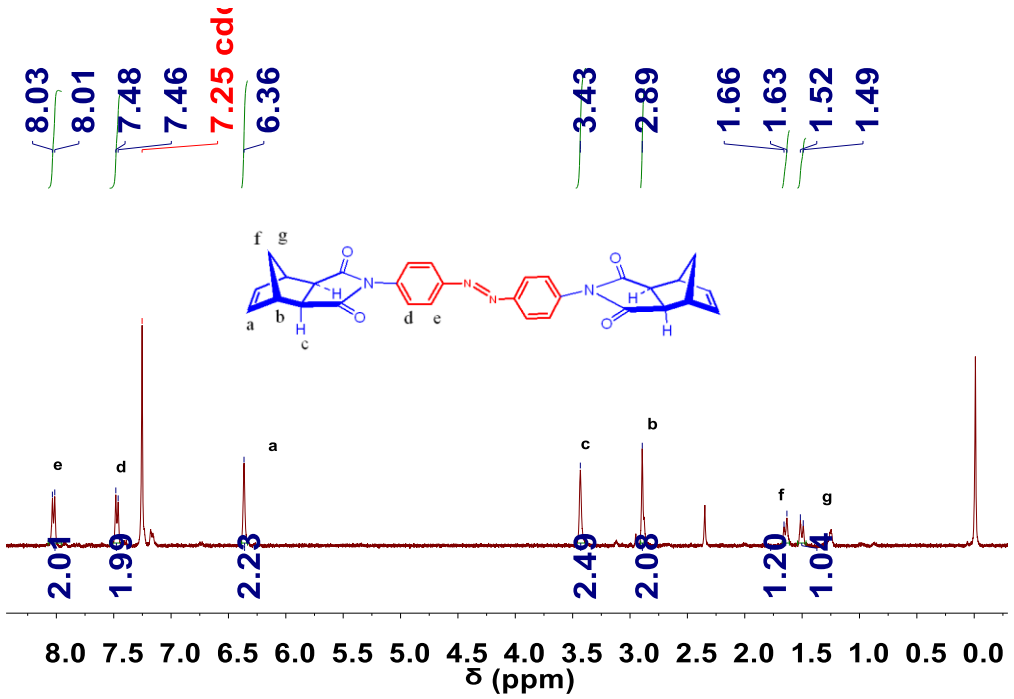


Figure S 27 ^{1}H-NMR of monomers-3h

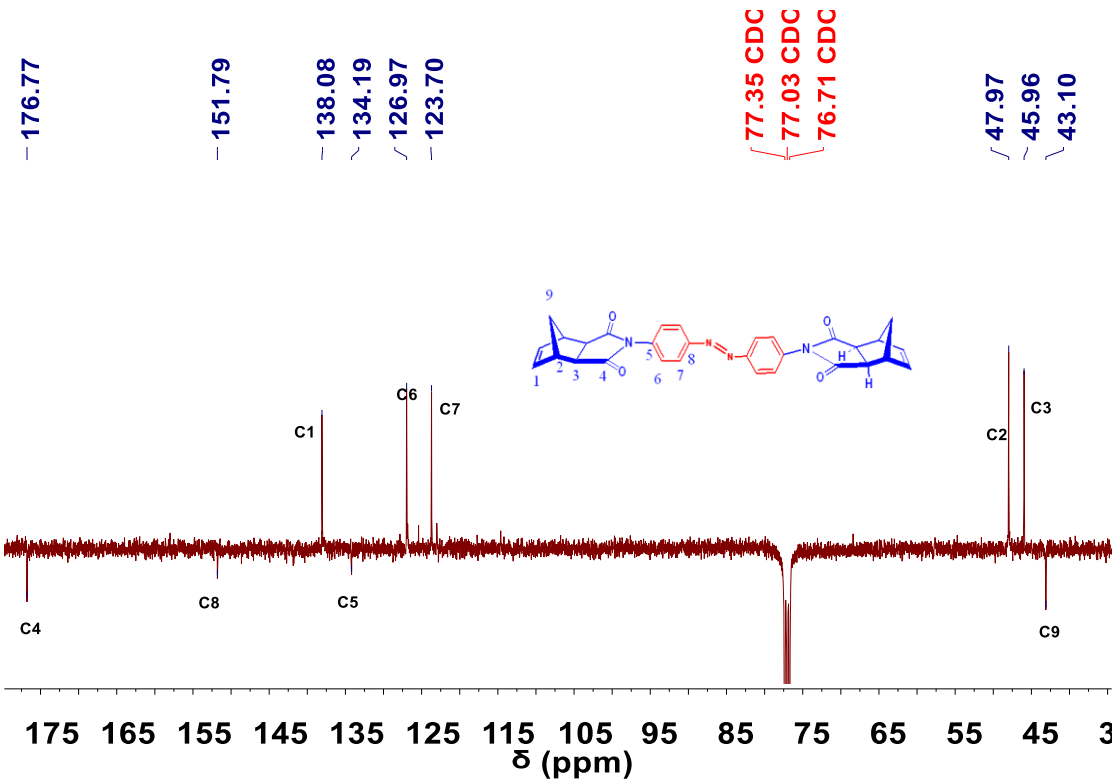


Figure S 28 APT-NMR of monomers-3h

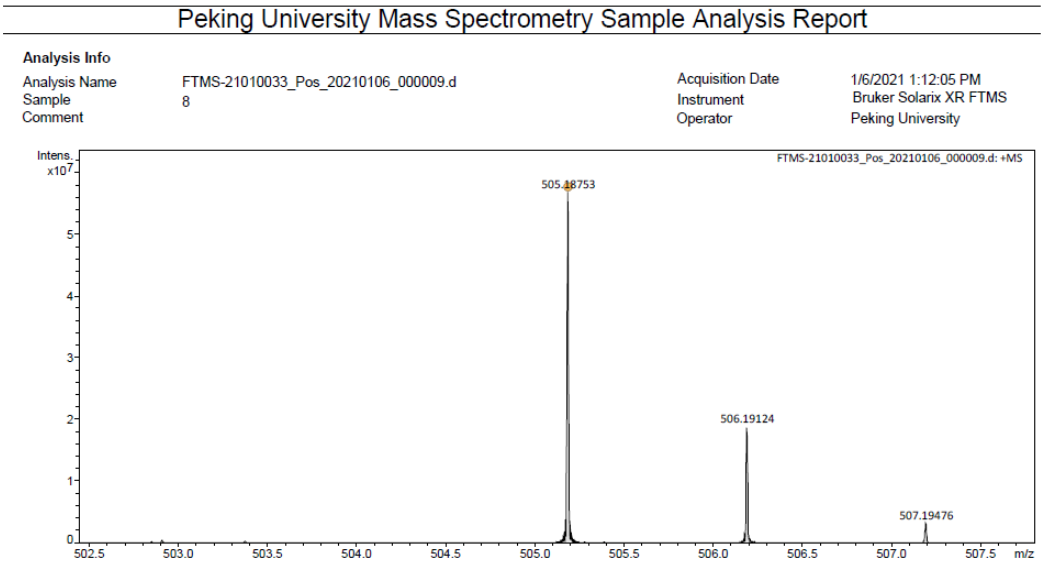


Figure S 29 FT-MS of monomer-3g

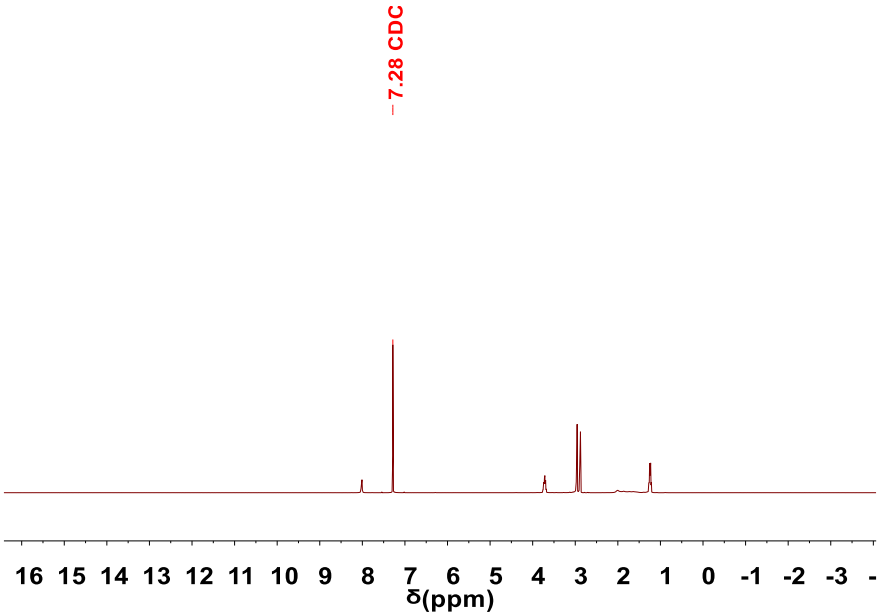


Figure S 30 ^{1}H-NMR of the BIT-POP-gel

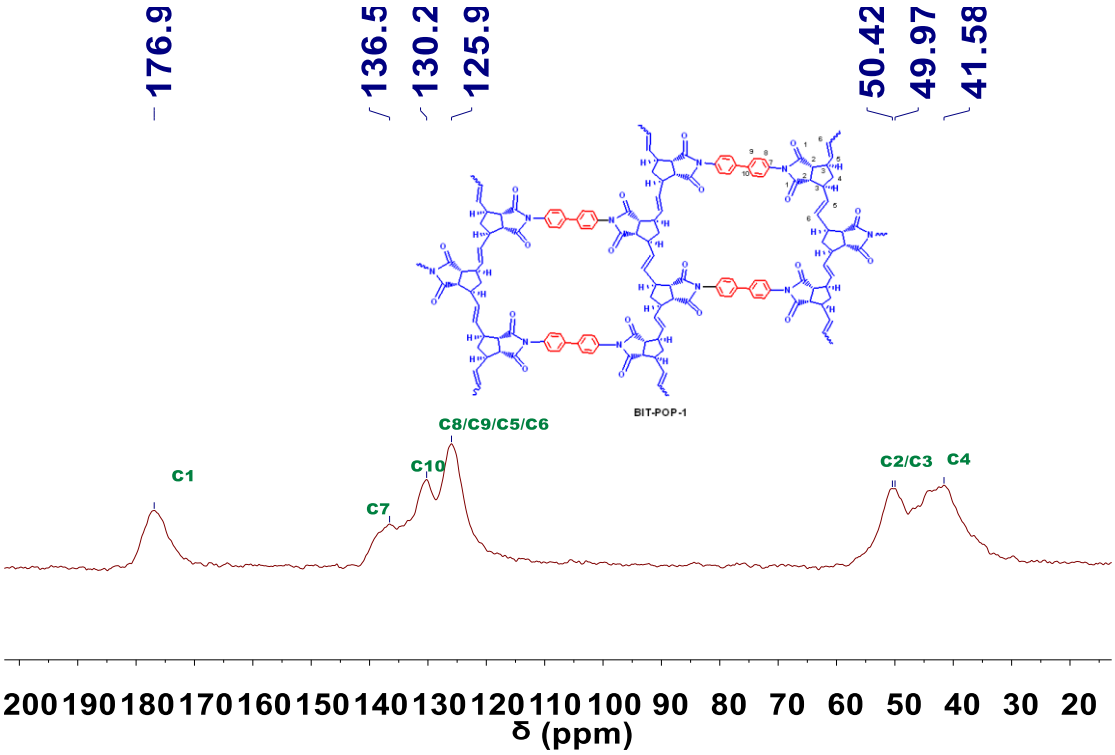


Figure S 31 CP-MS-^{13}C-NMR of BIT-POP-1(P15=3ms)

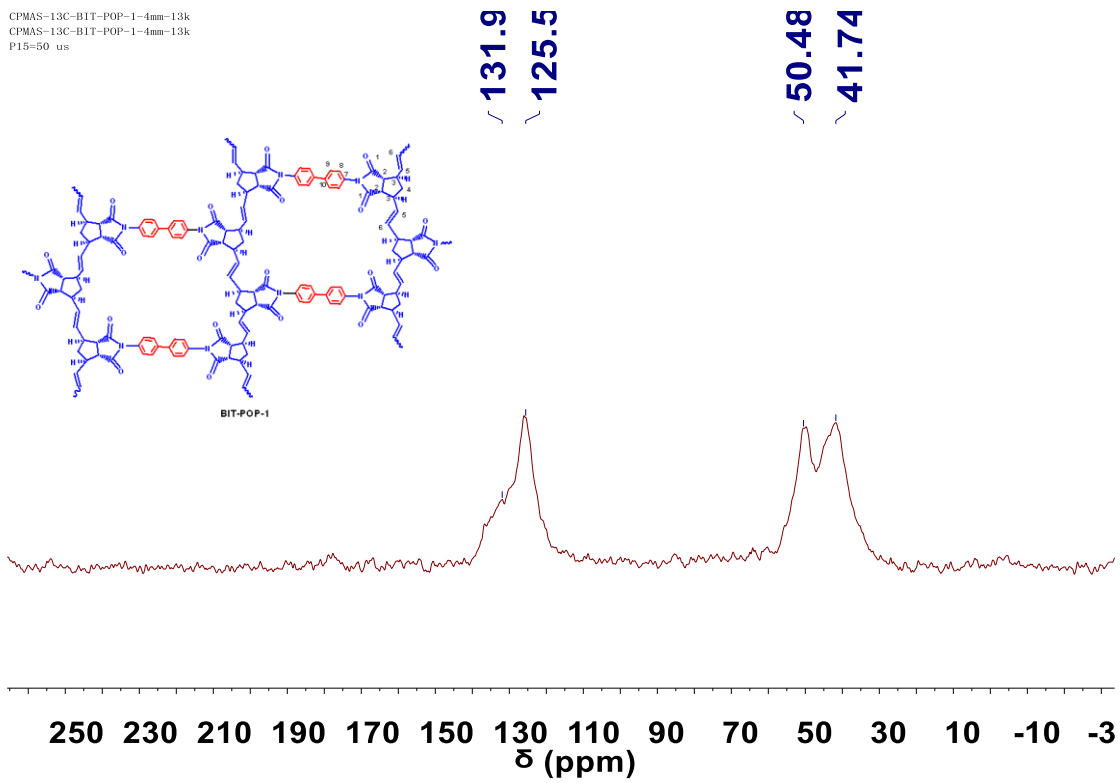


Figure S 32 CP-MS-^{13}C-NMR of BIT-POP-1(P15=0.05ms)

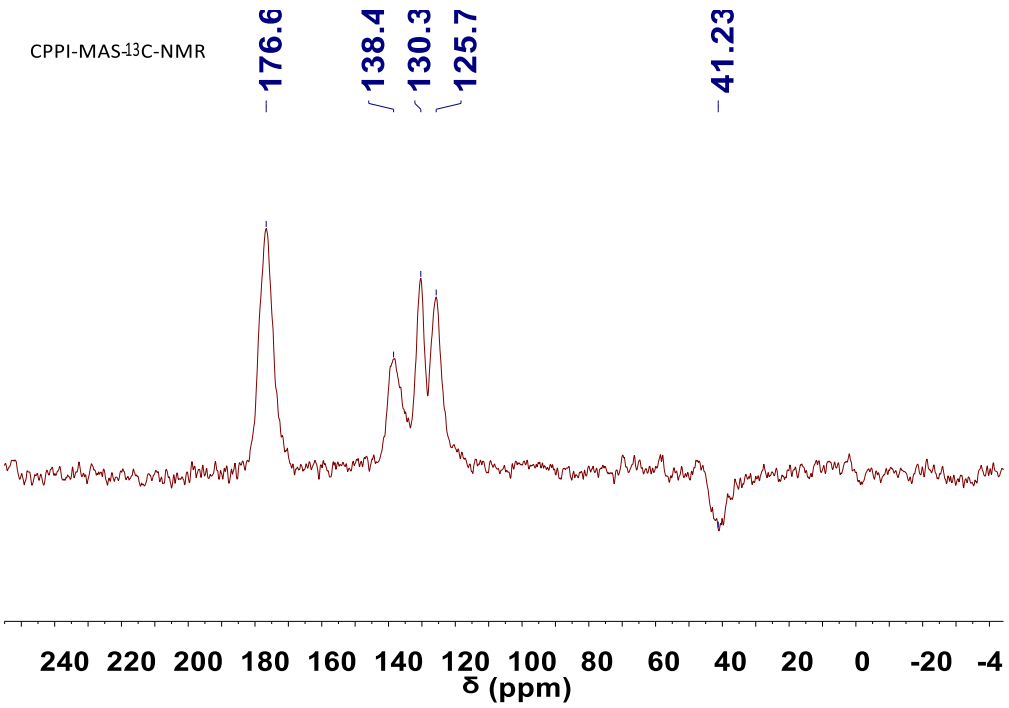


Figure S 33 CPPI-MAS-^{13}C-NMR of BIT-POP-1

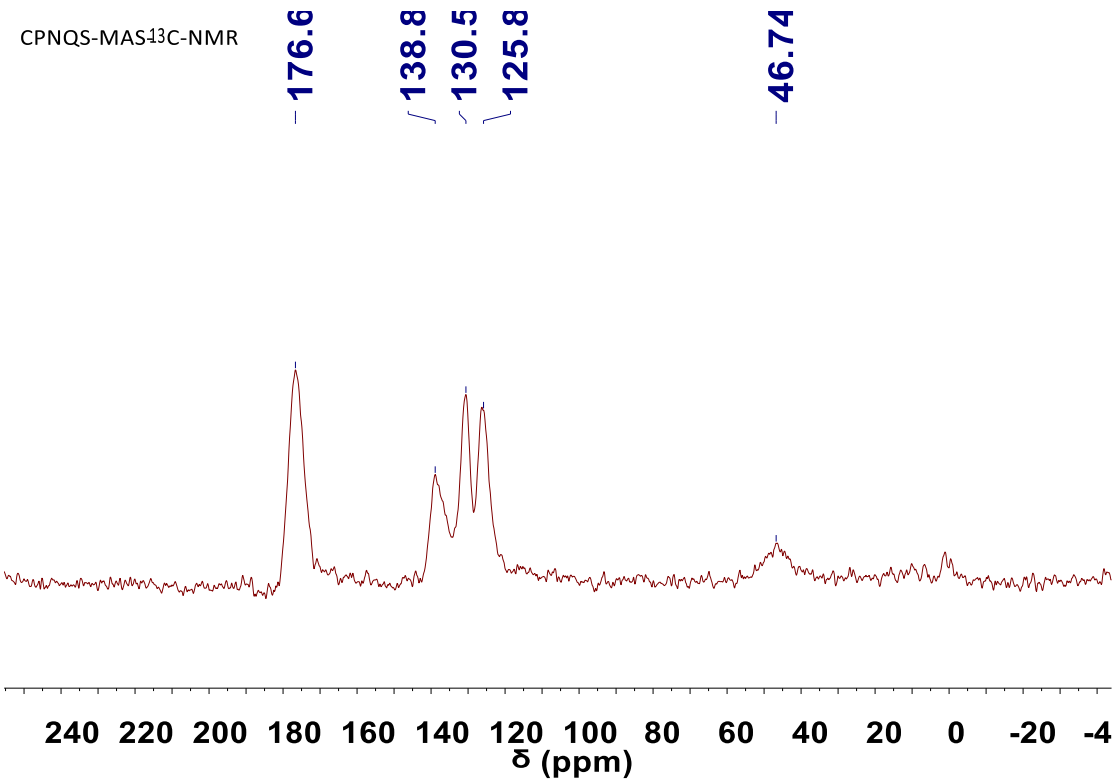


Figure S 34 CPNQS-MAS-13C-NMR of BIT-POP-1

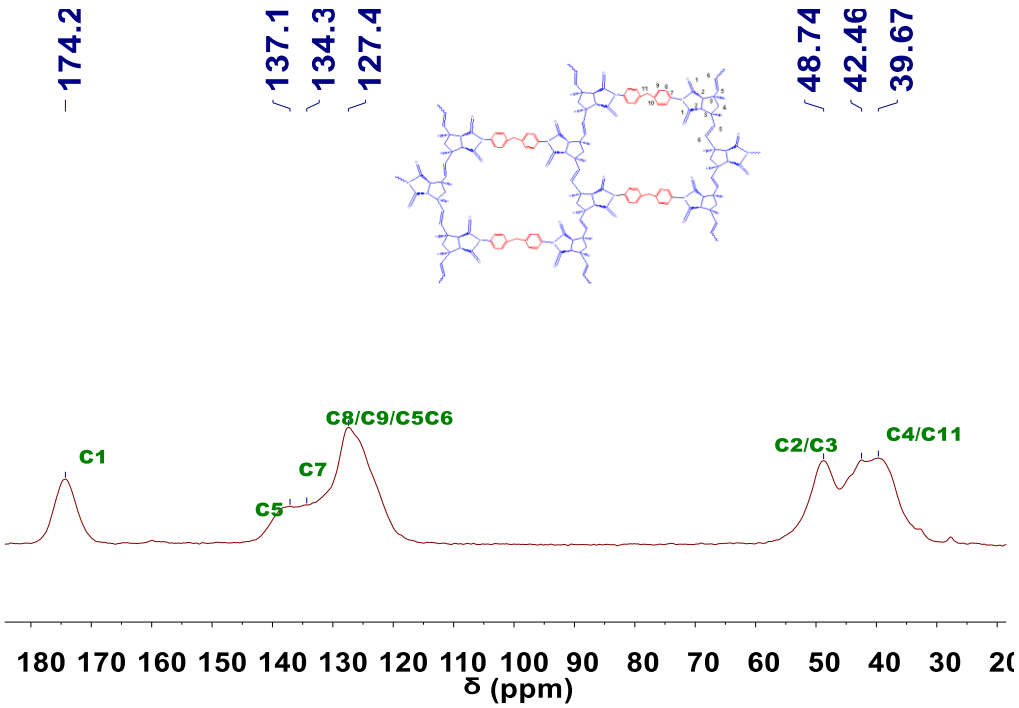


Figure S 35 CP-MS-^{13}C-NMR of BIT-POP-2 (P15=3ms)

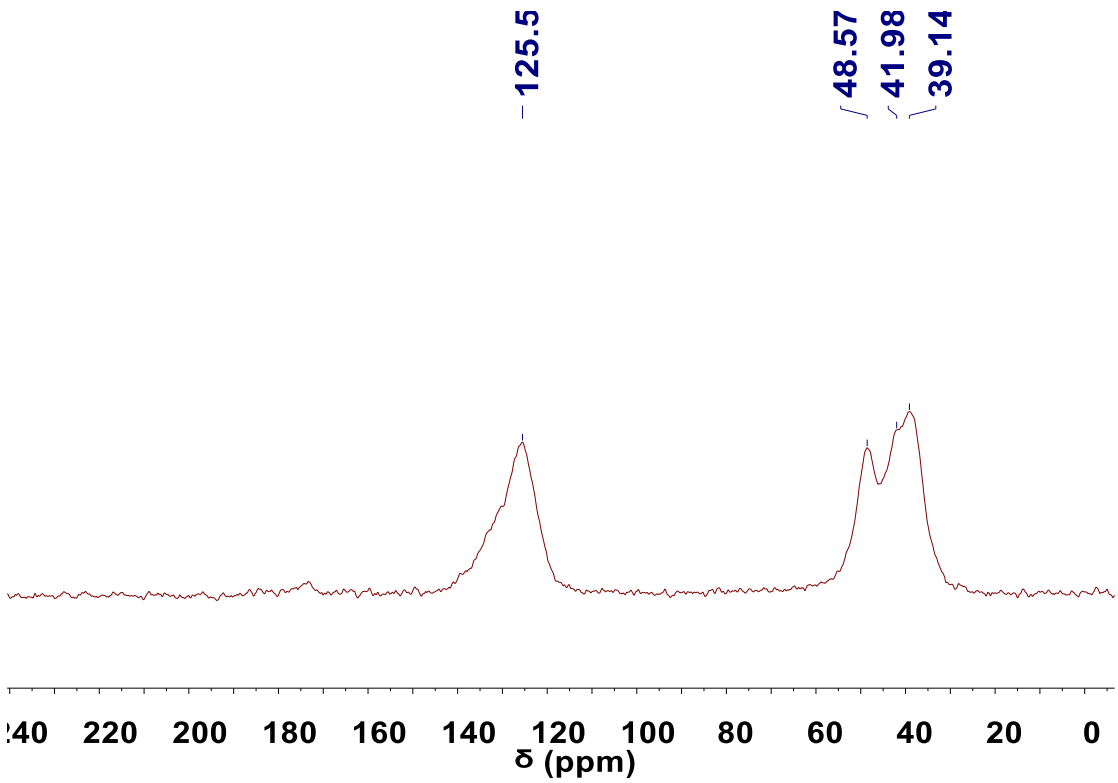


Figure S 36 CP-MS-^{13}C-NMR of BIT-POP-2(P15=0.05ms)

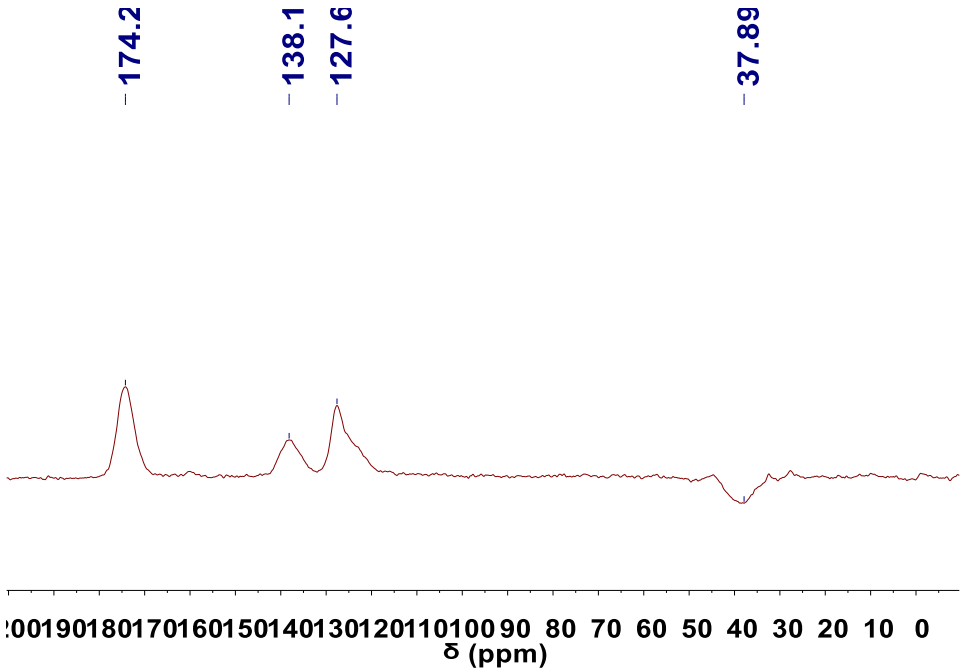


Figure S 37 CPPI-MAS-^{13}C-NMR of BIT-POP-2

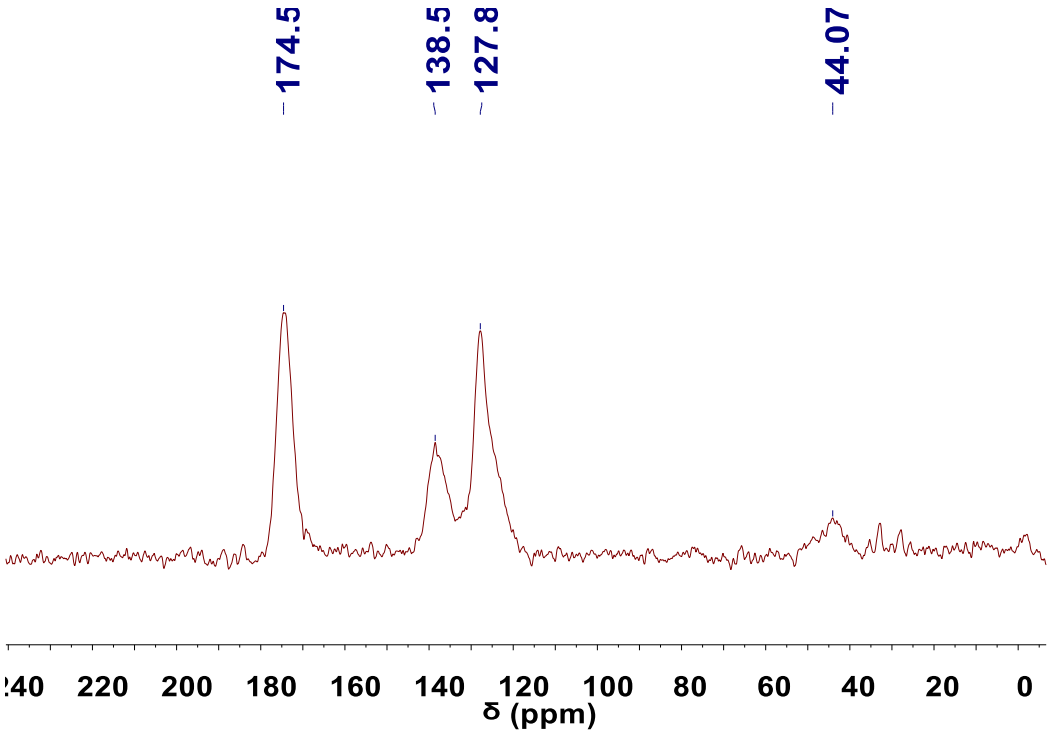


Figure S 38 CPNQS-MAS-13C-NMR of BIT-POP-2

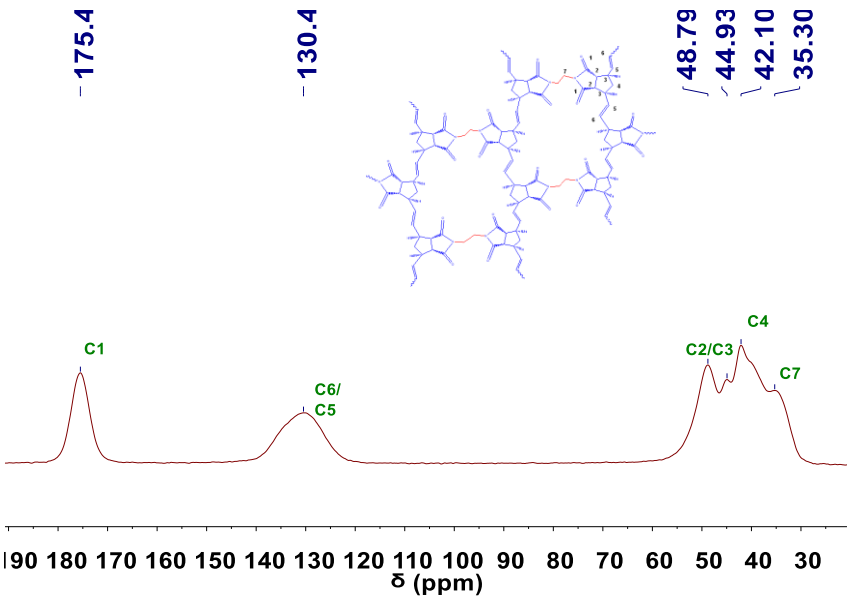


Figure S 39 CP-MS-^{13}C-NMR of BIT-POP-3 (P15=3ms)

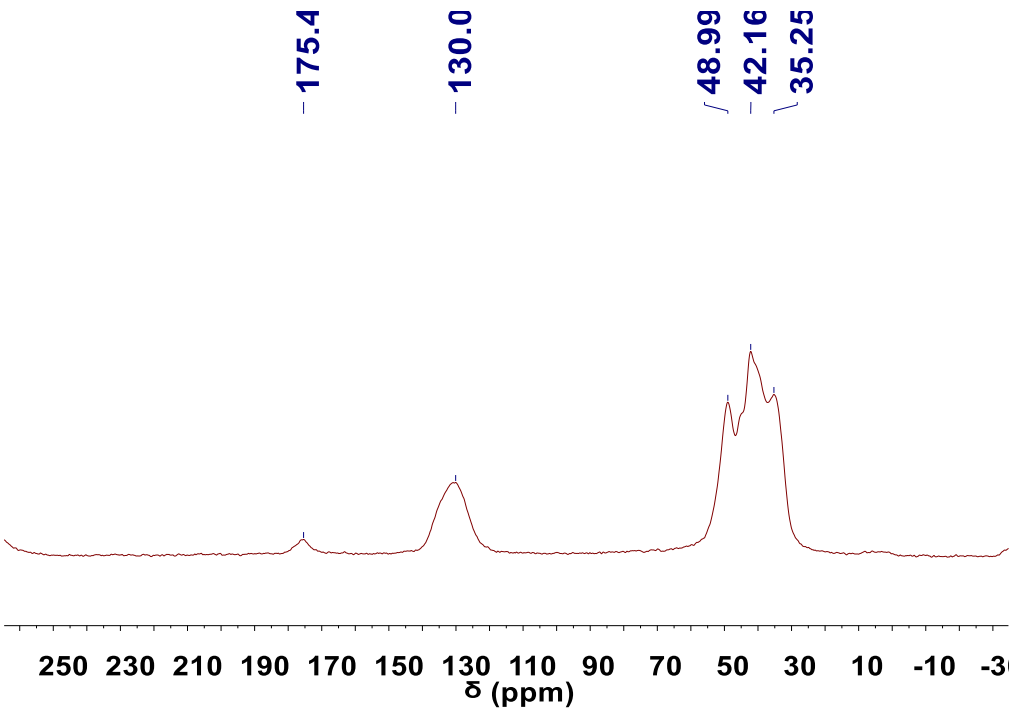


Figure S 40 CP-MS-^{13}C-NMR of BIT-POP-3(P15=0.05ms)

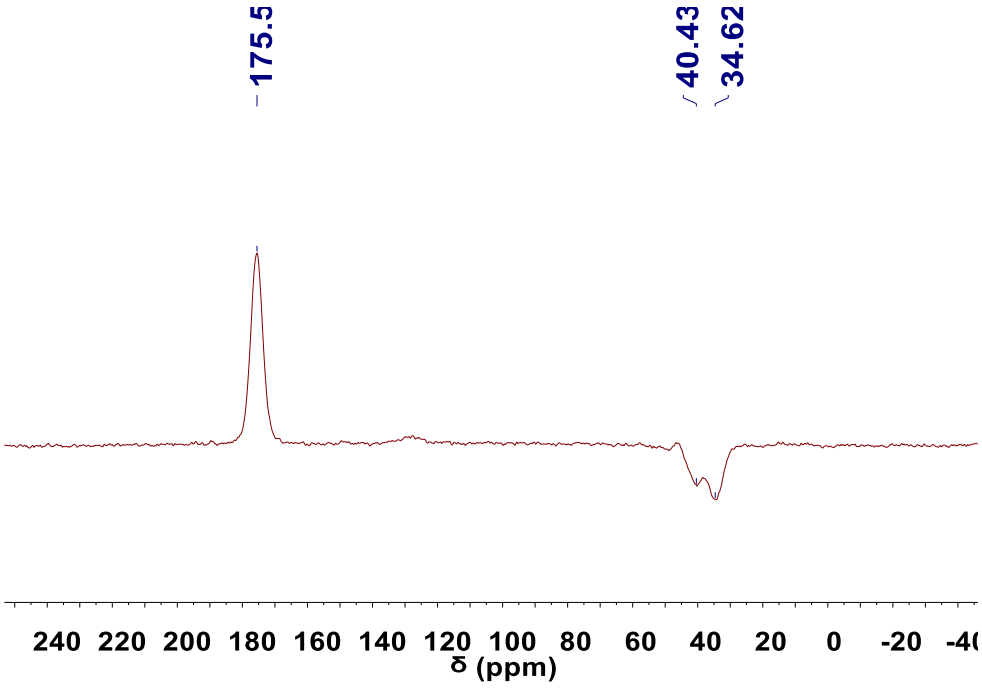


Figure S 41 CPPI-MAS-^{13}C-NMR of BIT-POP-3

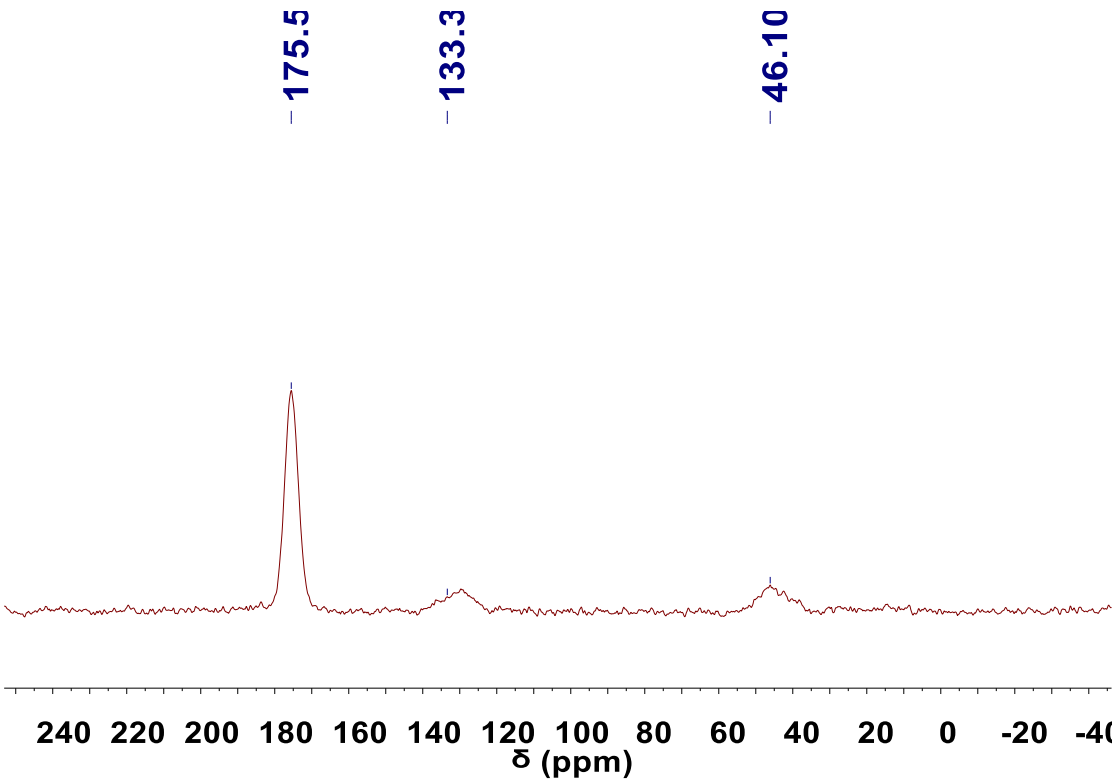


Figure S 42 CPNQS-MAS-13C-NMR of BIT-POP-3

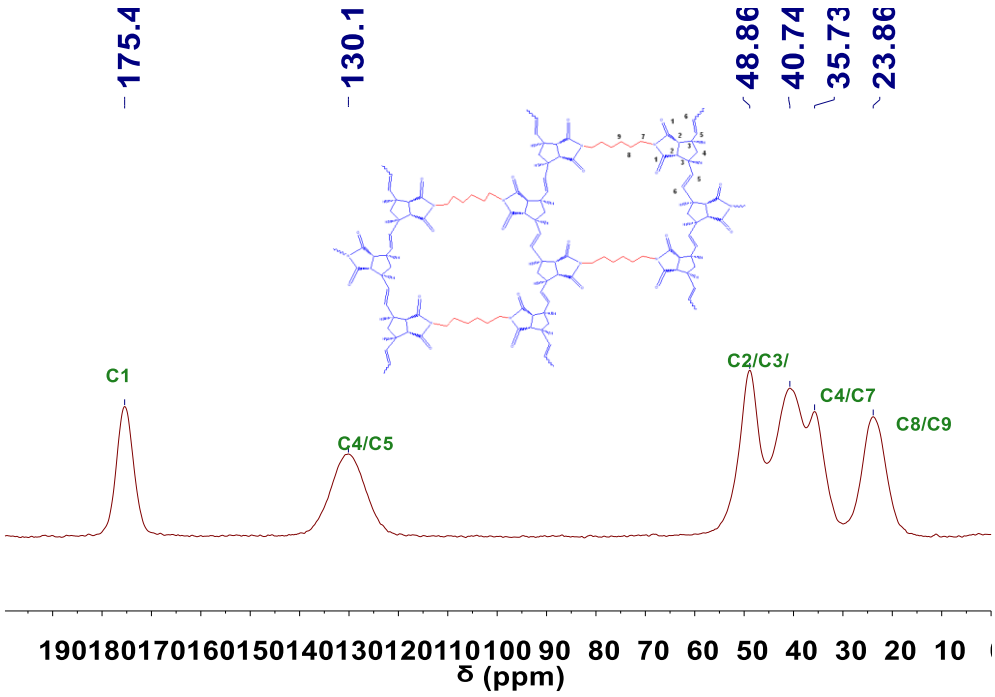


Figure S 43 CP-MS-^{13}C-NMR of BIT-POP-4 (P15=3ms)

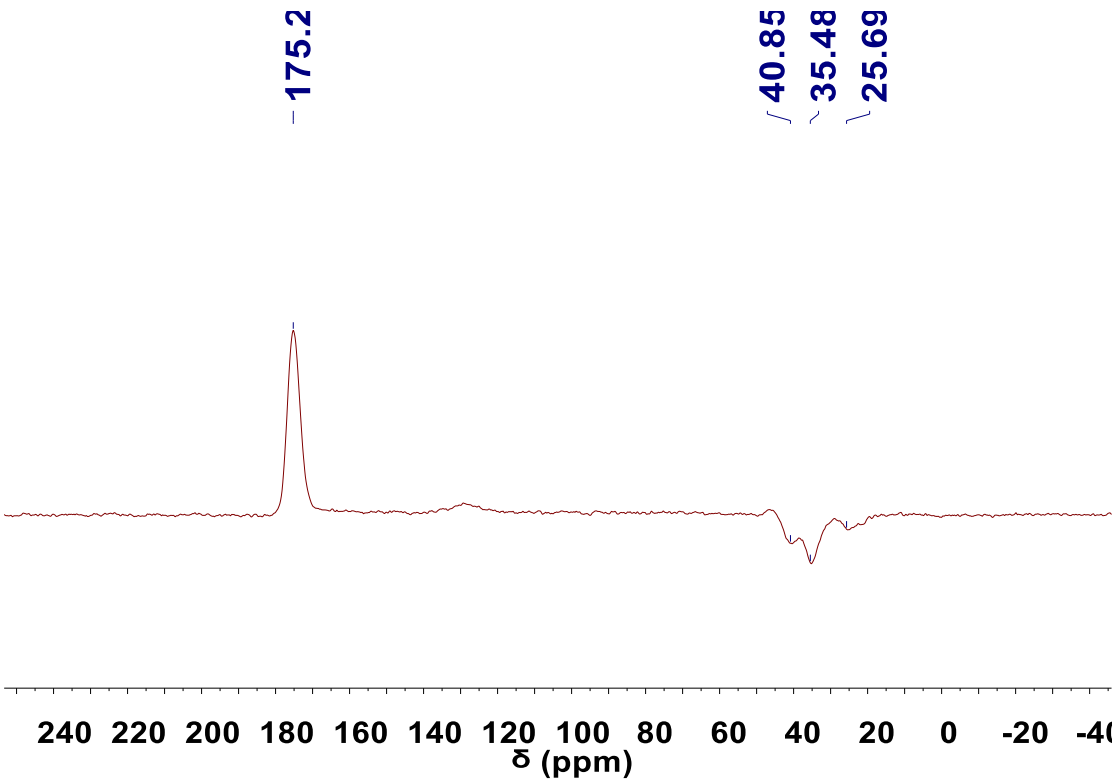


Figure S 44 CPPI-MAS-^{13}C-NMR of BIT-POP-4

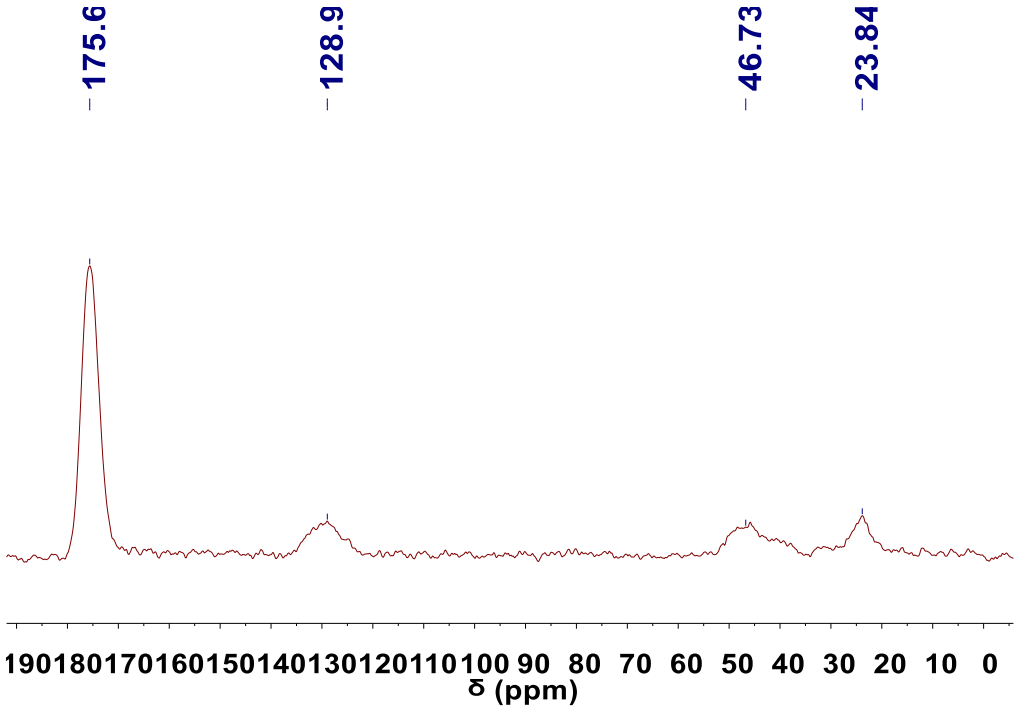


Figure S 45 CPNQS-MAS-^{13}C-NMR of BIT-POP-4

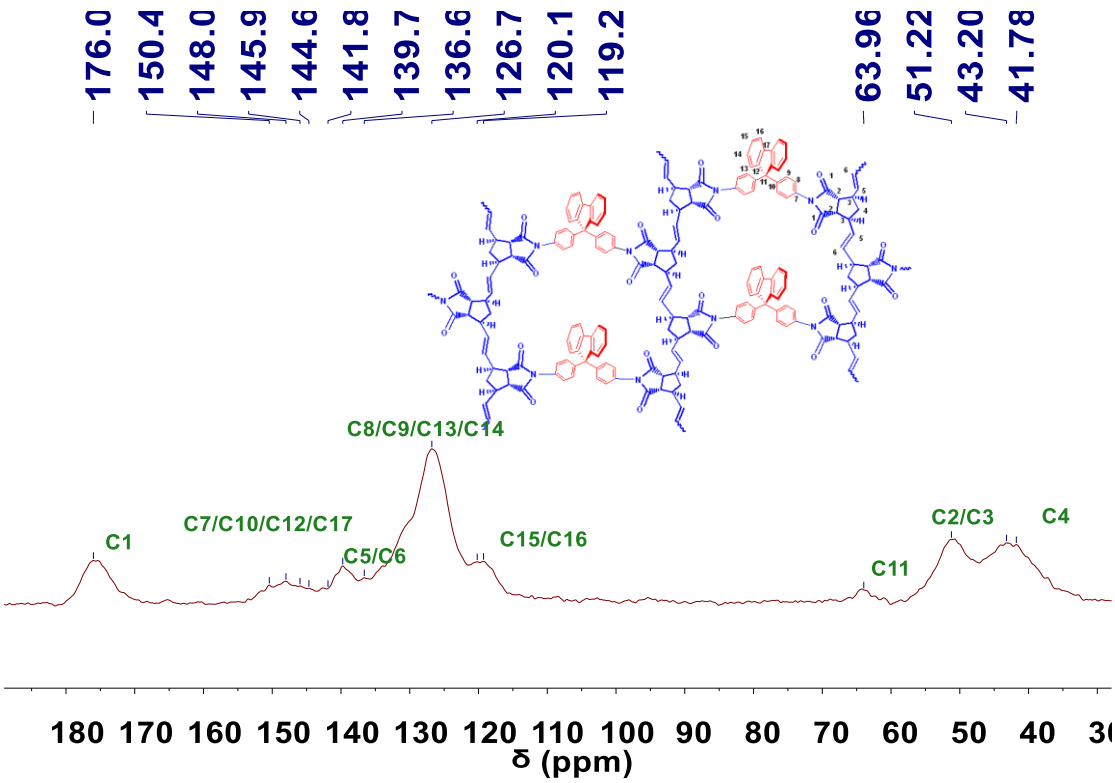


Figure S 46 CP-MS- ^{13}C-NMR of BIT-POP-5 (P15=3ms)

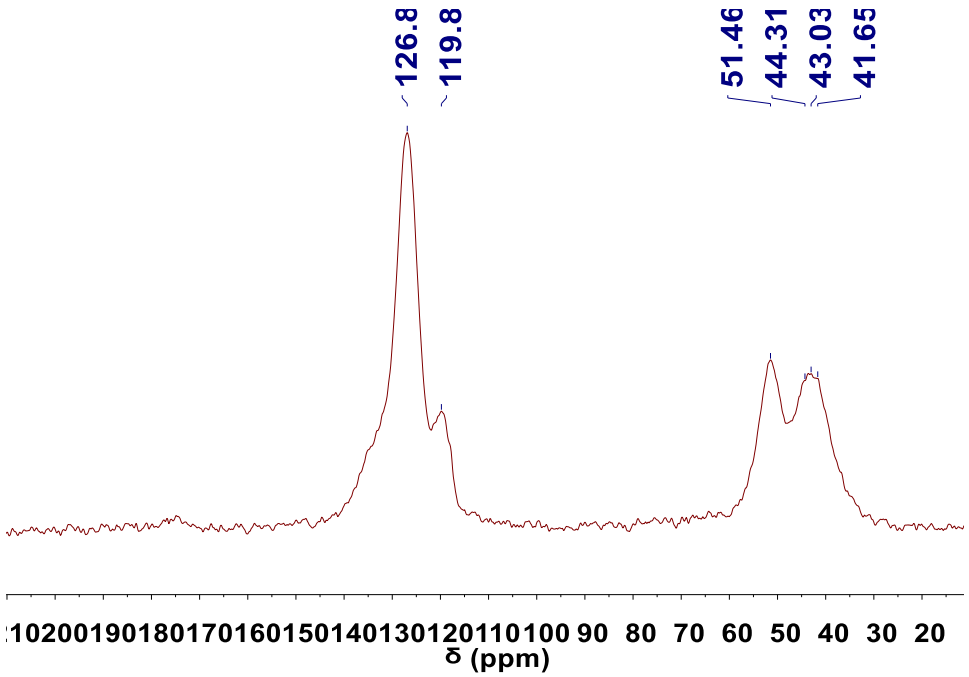


Figure S 47 CP-MS-^{13}C-NMR of BIT-POP-5(P15=0.05ms)

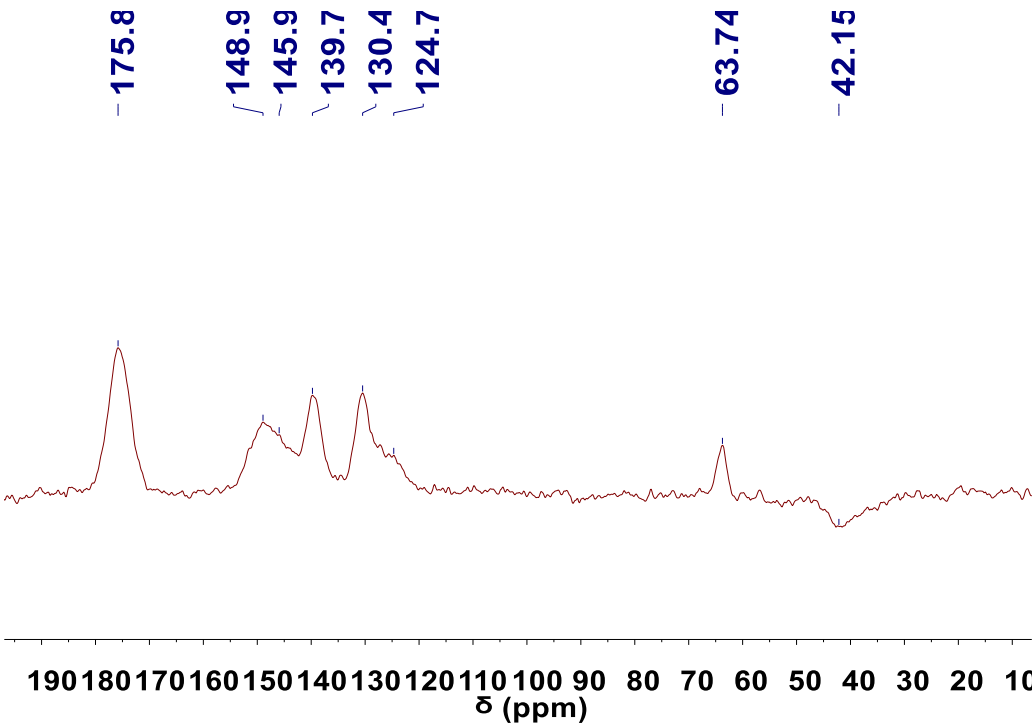


Figure S 48 CPPI-MAS-^{13}C-NMR of BIT-POP-5

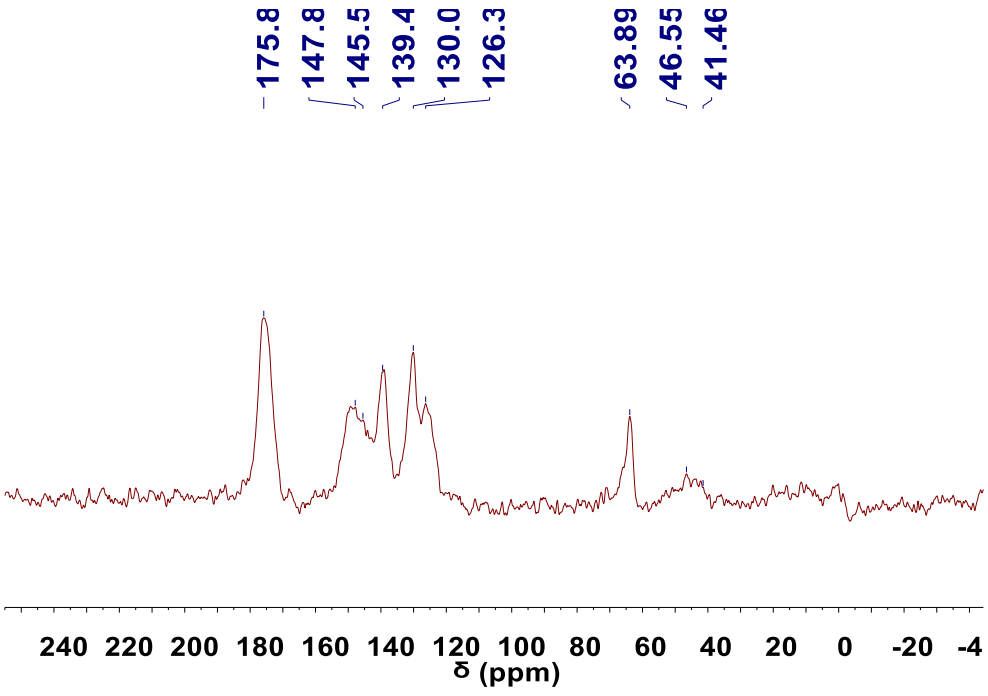


Figure S 49 CPNQS-MAS-^{13}C-NMR of BIT-POP-5

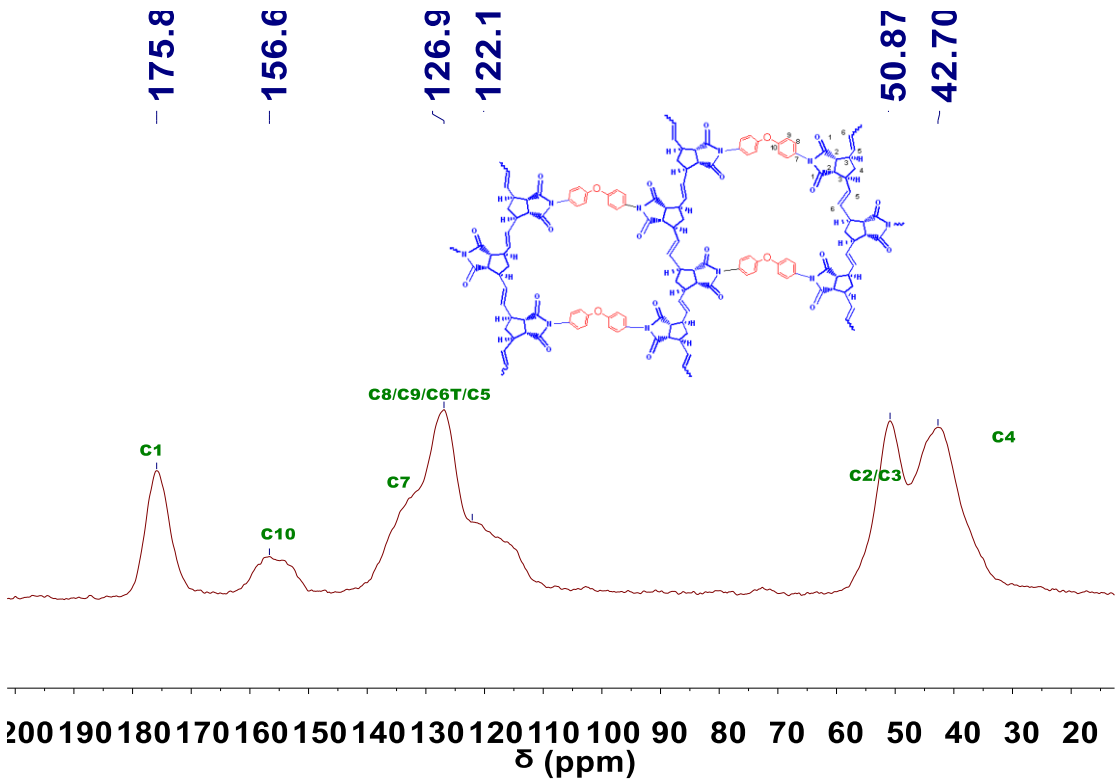


Figure S 50 CP-MS- ^{13}C-NMR of BIT-POP-6 (P15=3ms)

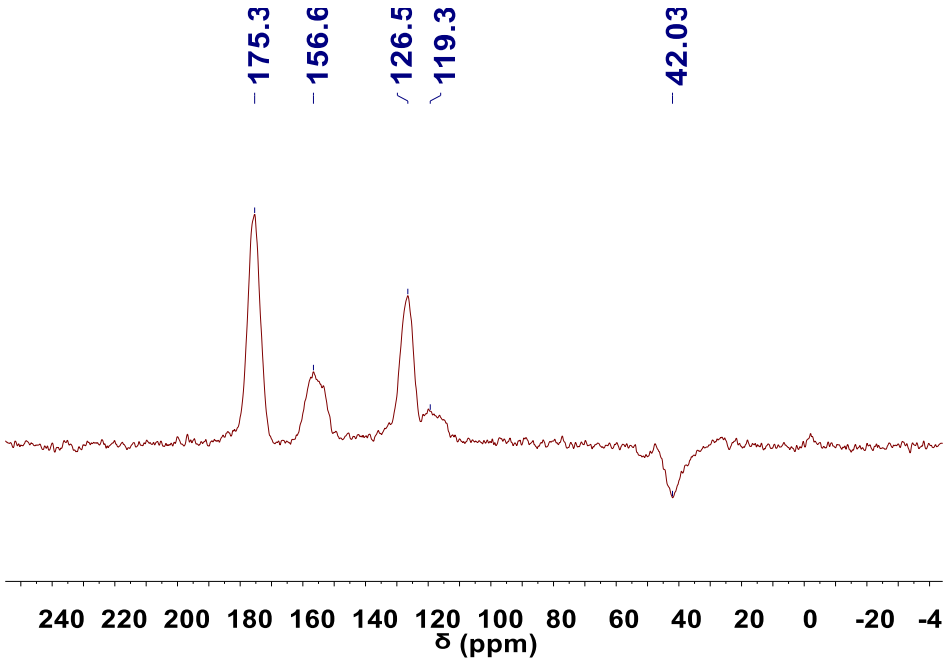


Figure S 51 CPPI-MAS-^{13}C-NMR of BIT-POP-6

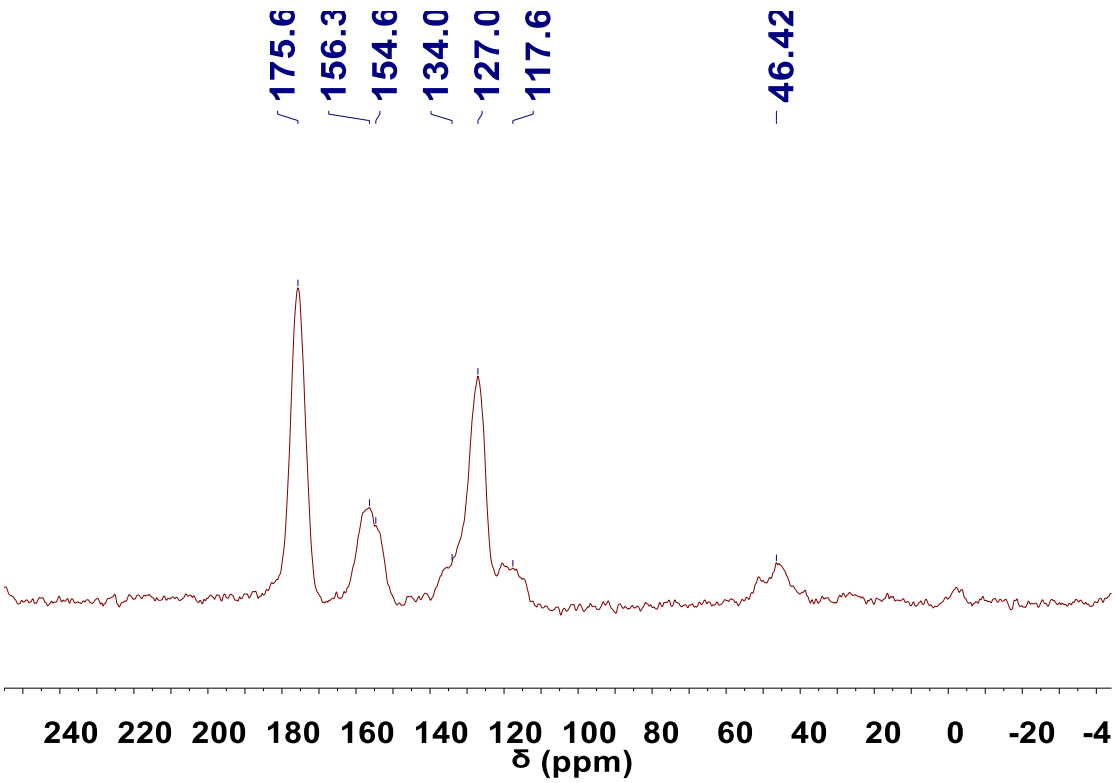


Figure S 52 CPNQS-MAS-^{13}C-NMR of BIT-POP-6

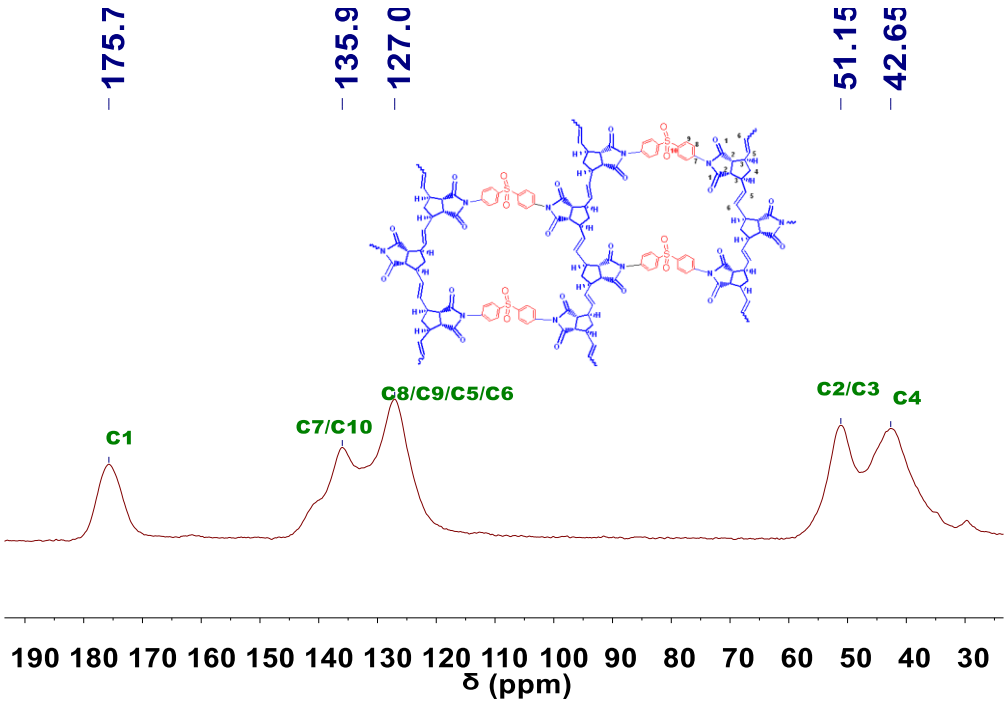


Figure S 53 CP-MS- ^{13}C-NMR of BIT-POP-7 (P15=3ms)

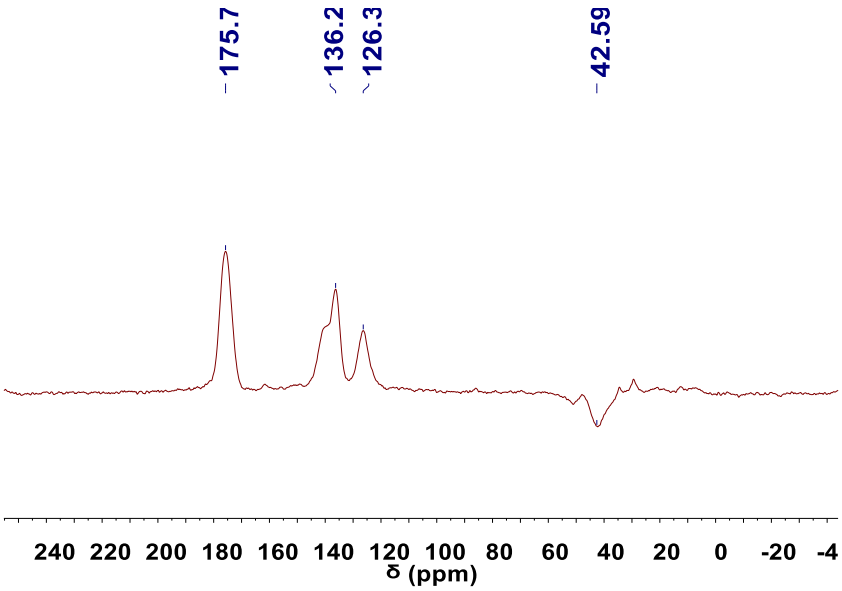


Figure S 54 CPPI-MAS-^{13}C-NMR of BIT-POP-7

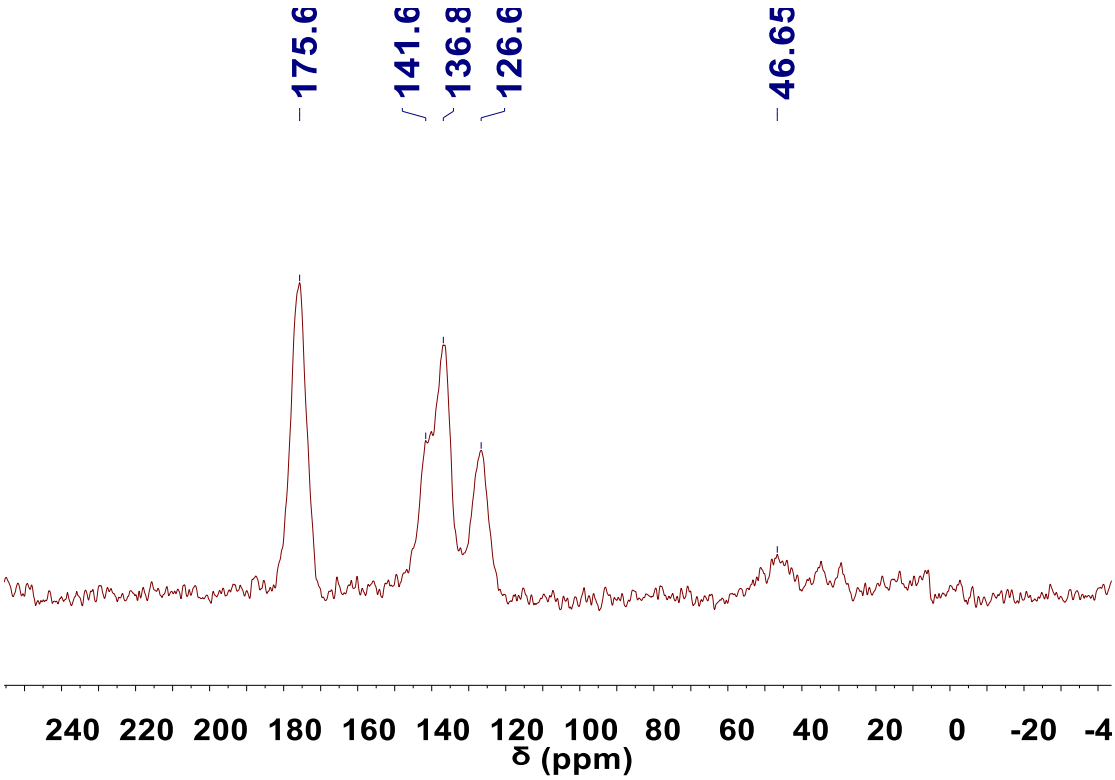


Figure S 55 CPNQS-MAS-^{13}C-NMR of BIT-POP-7

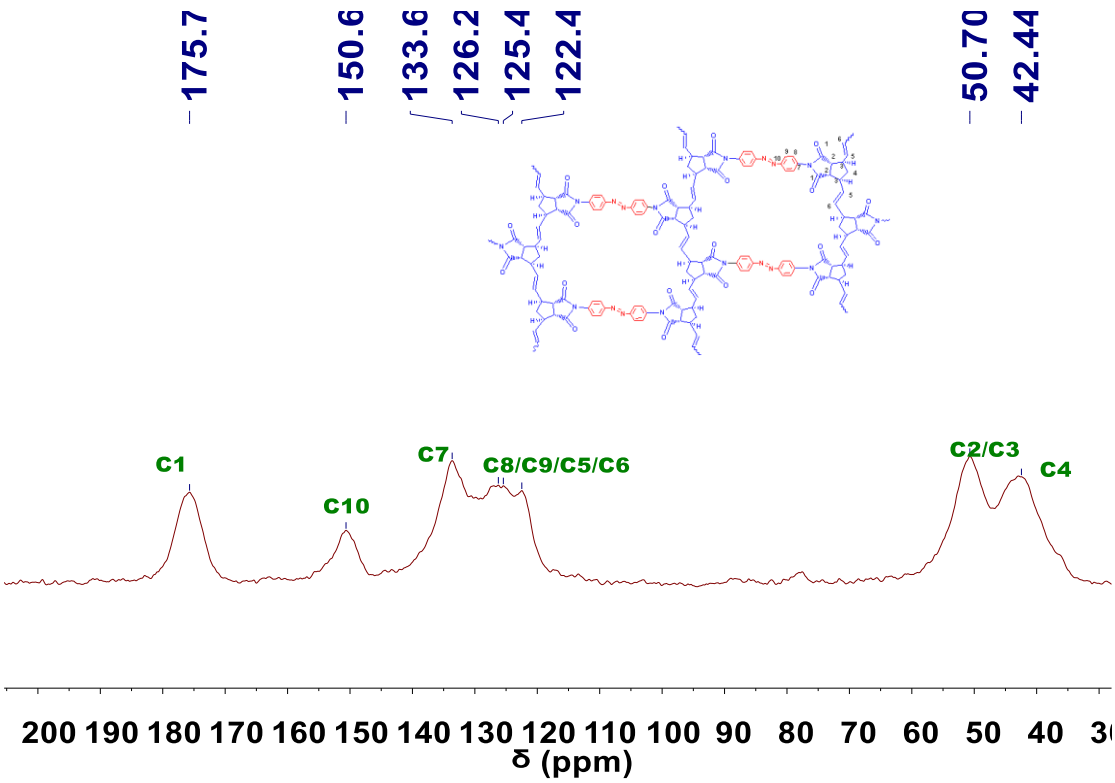


Figure S 56 CP-MS- ^{13}C-NMR of BIT-POP-8 (P15=3ms)

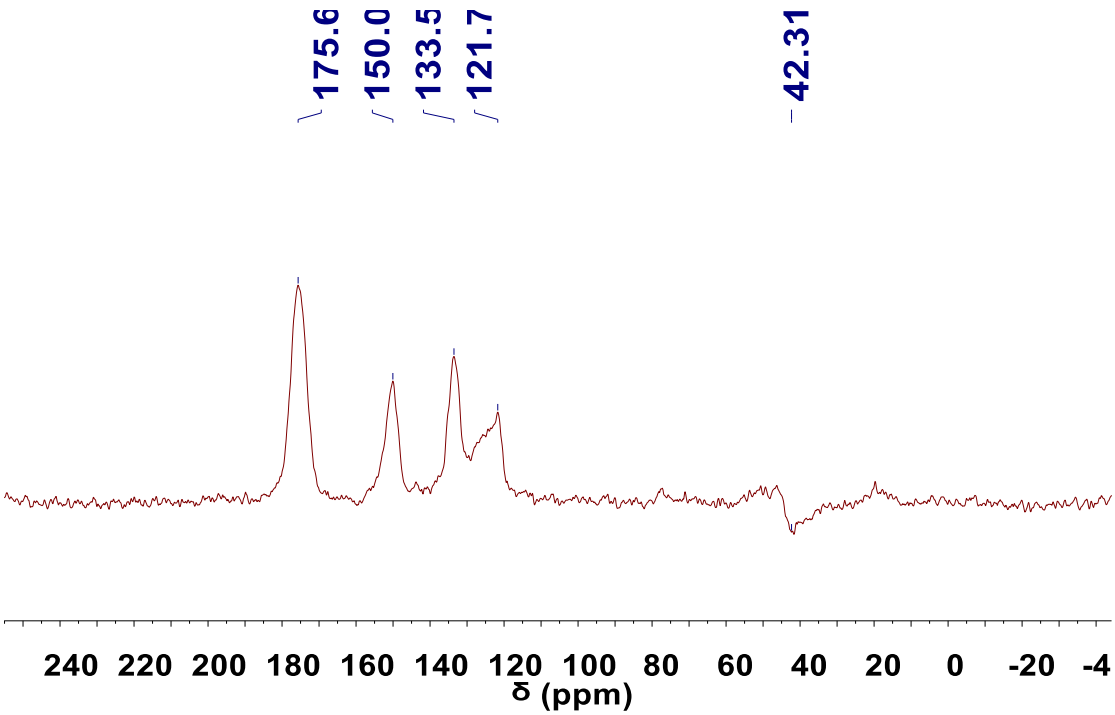


Figure S 57 CPPI-MAS-^{13}C-NMR of BIT-POP-8

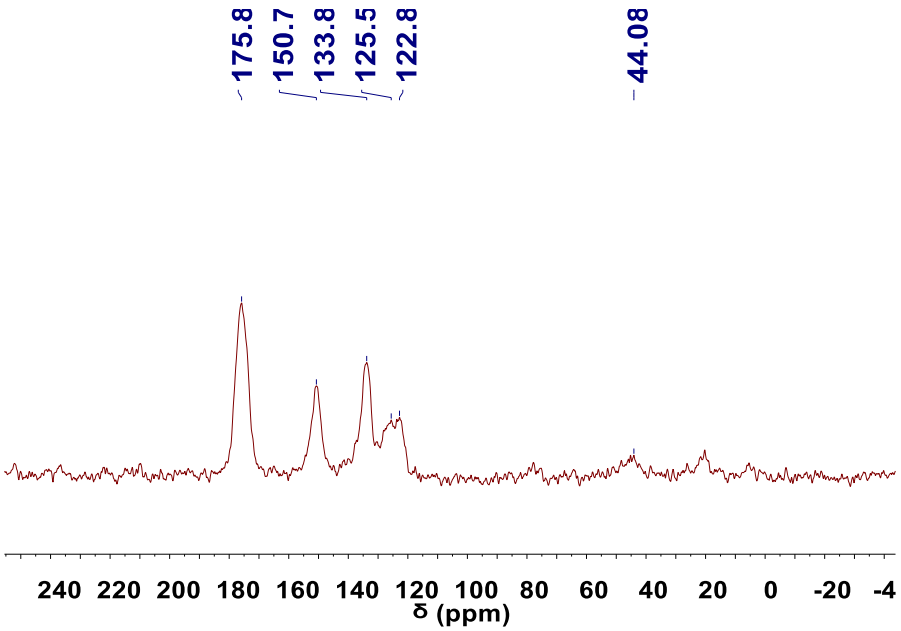


Figure S 58 CPNQS-MAS-^{13}C-NMR of BIT-POP-8

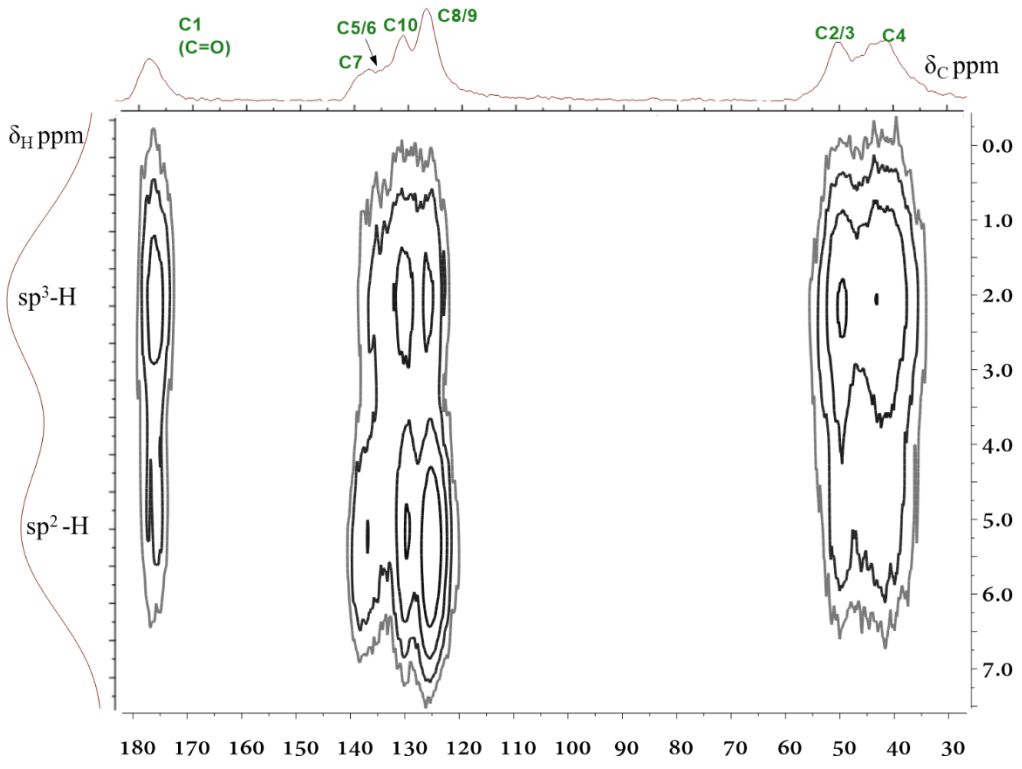


Figure S 59 HETCOR of BIT-POP-1

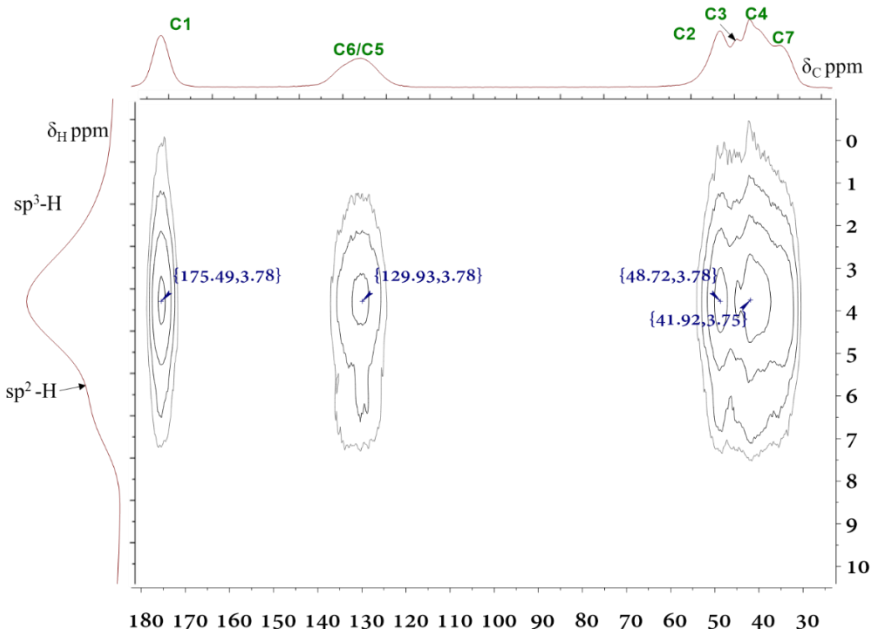


Figure S 60 HETCOR of BIT-POP-3

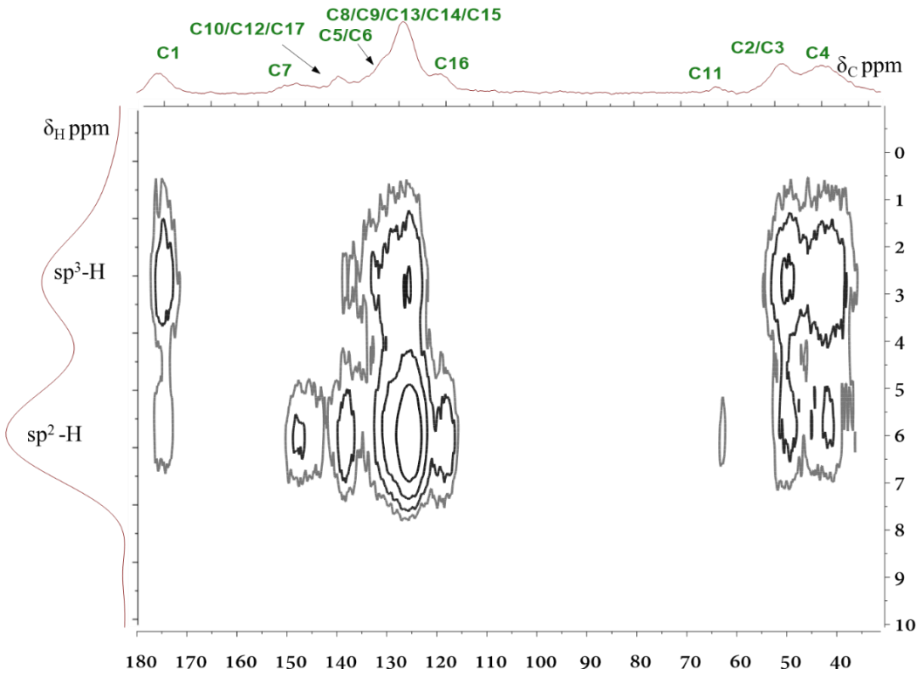


Figure S 61 HETCOR of BIT-POP-5

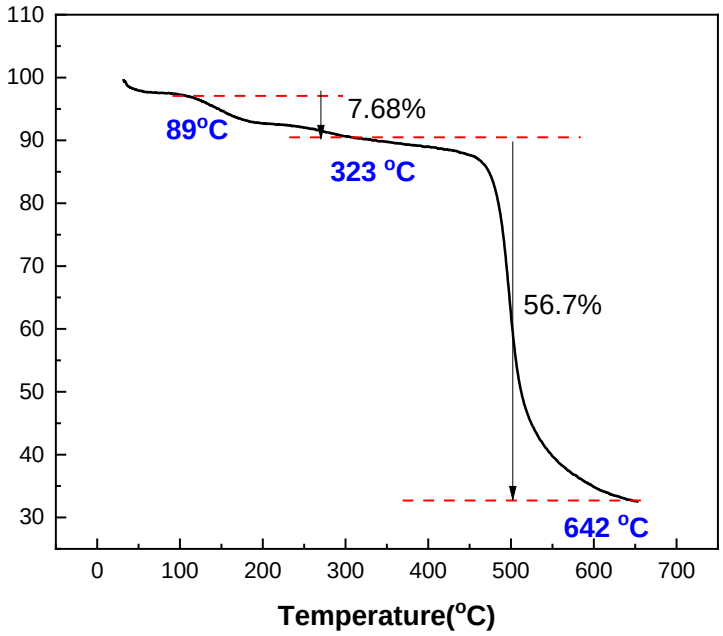


Figure S 62 TGA of BIT-POP-1

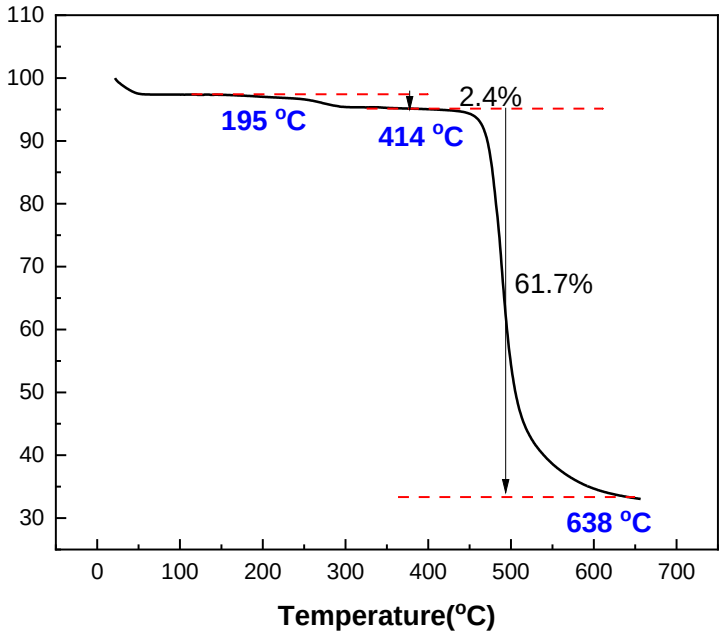


Figure S 63 TGA of BIT-POP-2

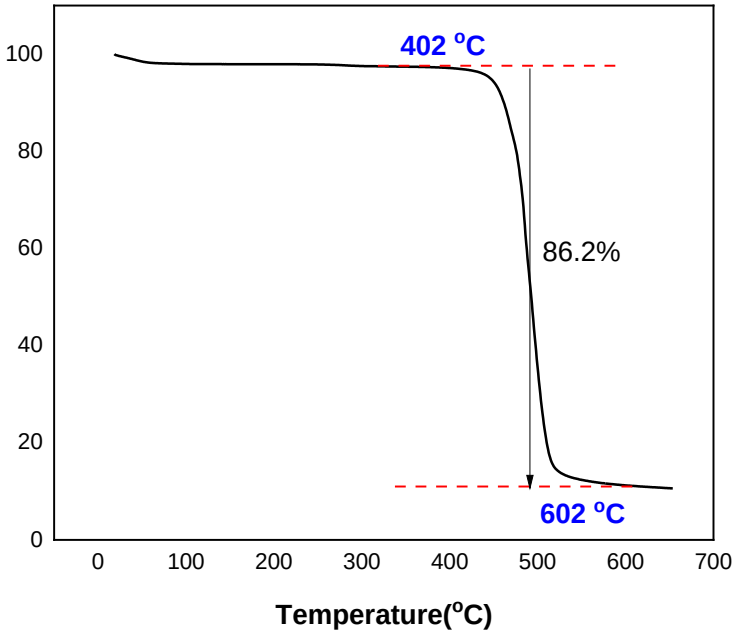


Figure S 64 TGA of BIT-POP-3

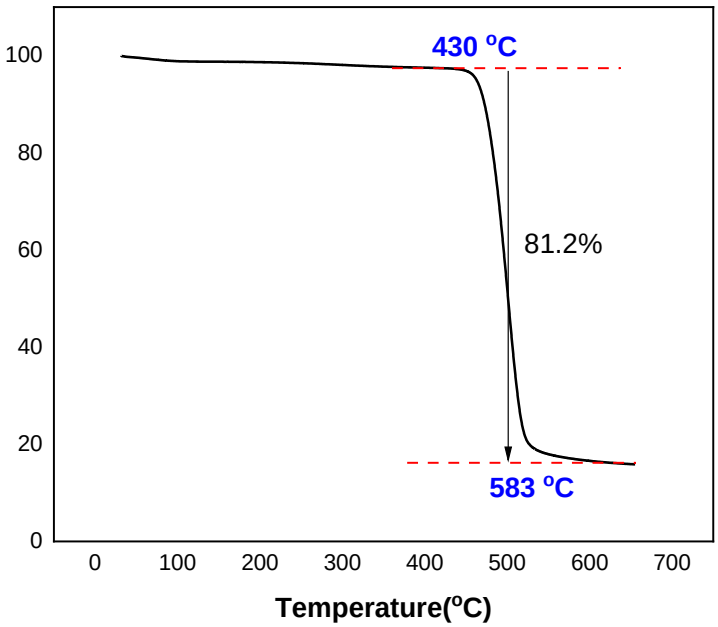


Figure S 65 TGA of BIT-POP-4

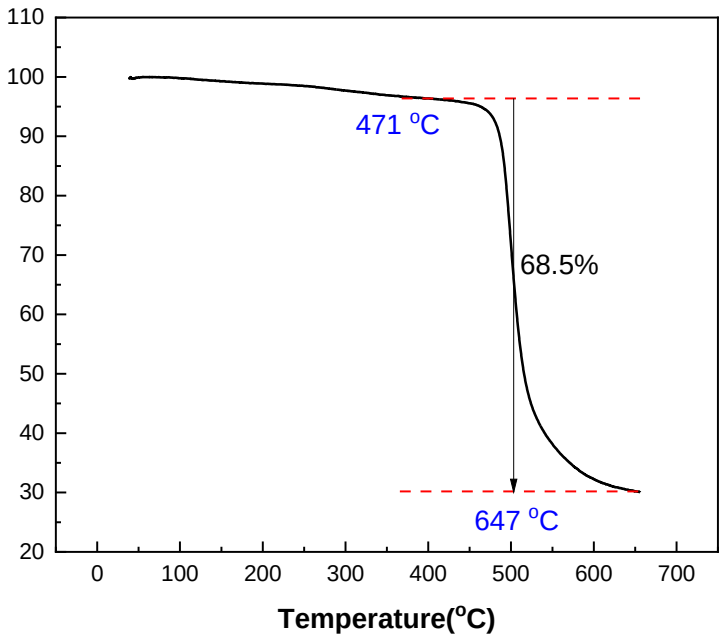


Figure S 66 TGA of BIT-POP-5

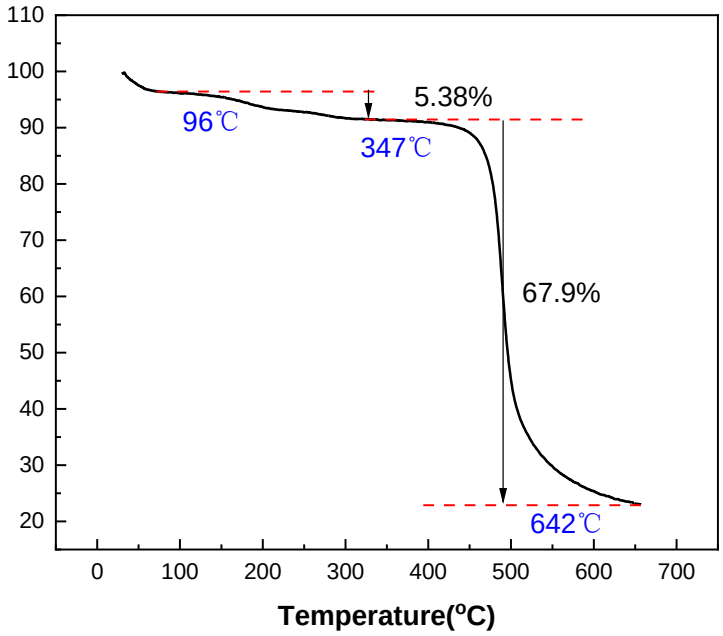


Figure S 67 TGA of BIT-POP-6

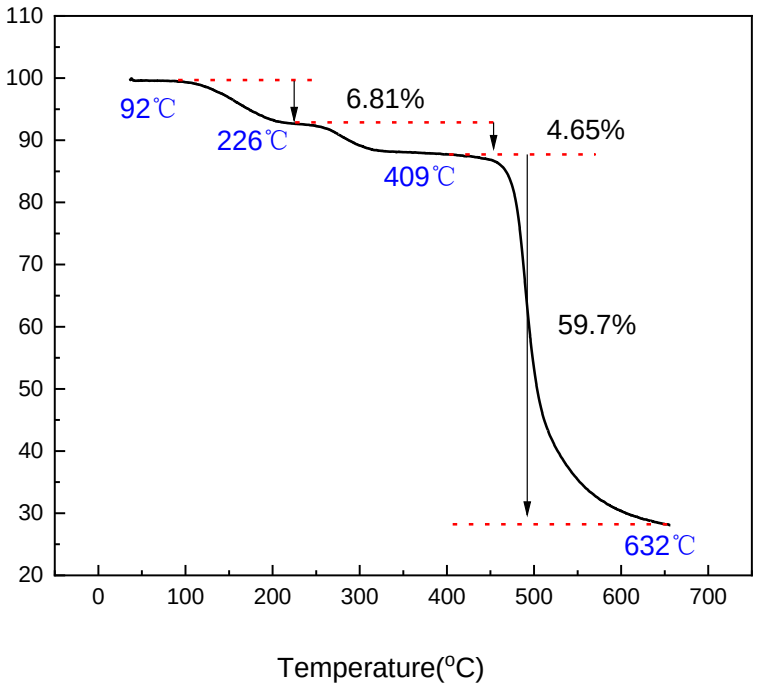


Figure S 68 TGA of BIT-POP-7

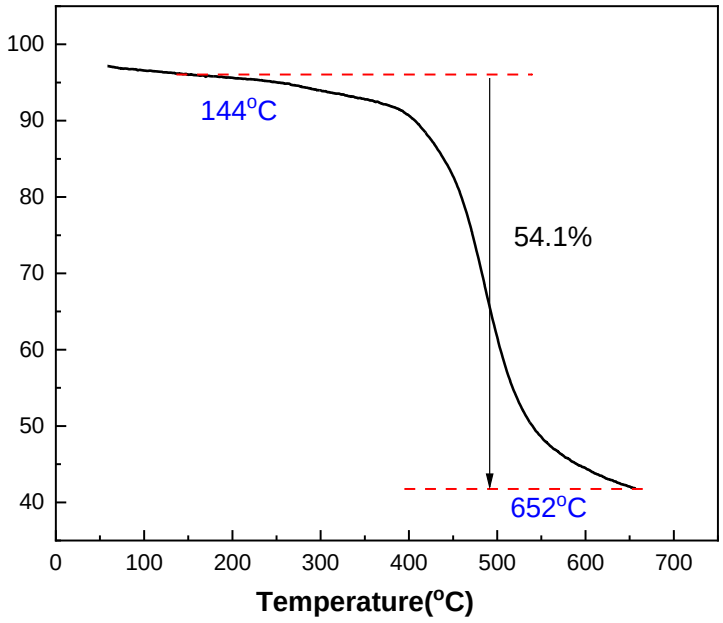


Figure S 69 TGA of BIT-POP-8

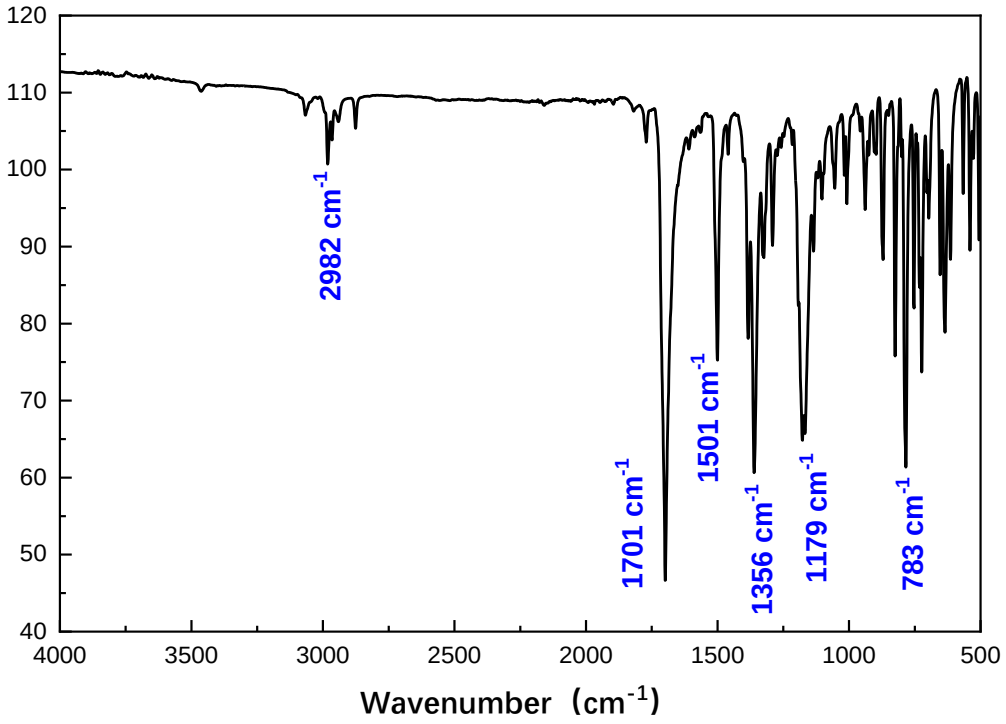


Figure S 70 FT-IR of monomers-3a

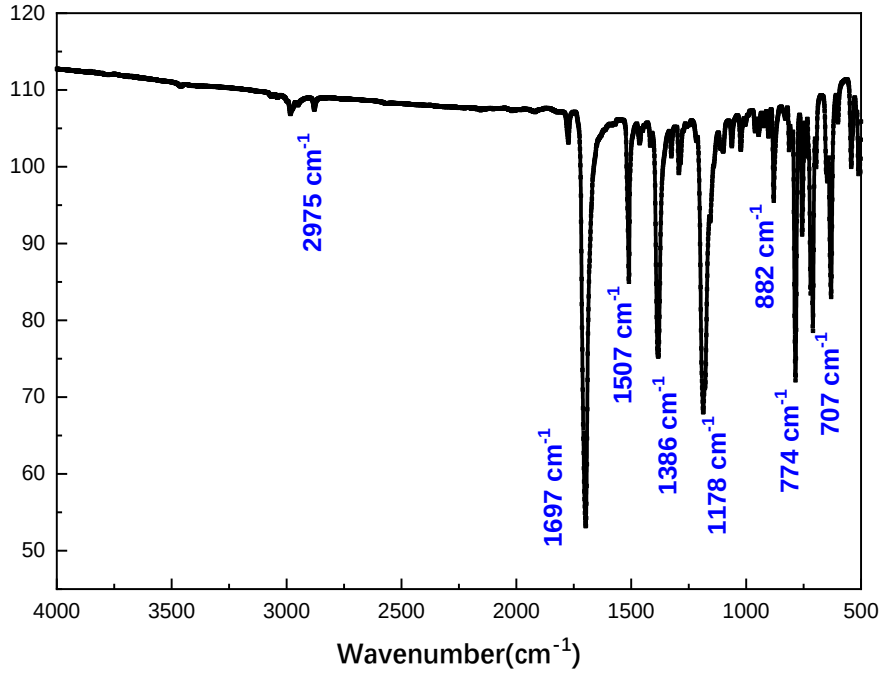


Figure S 71 FT-IR of monomers-3b

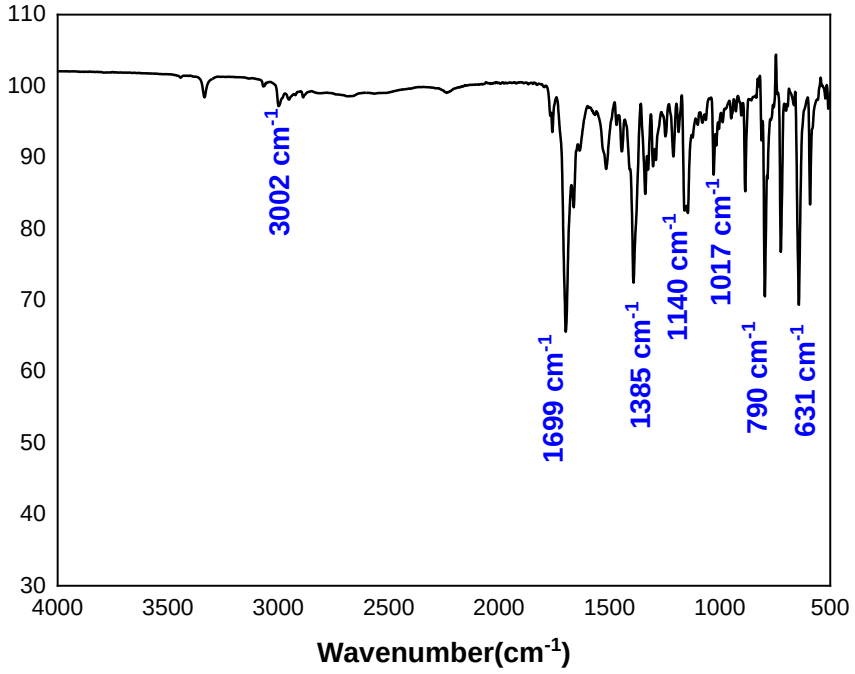


Figure S 72 FT-IR of monomers-3c

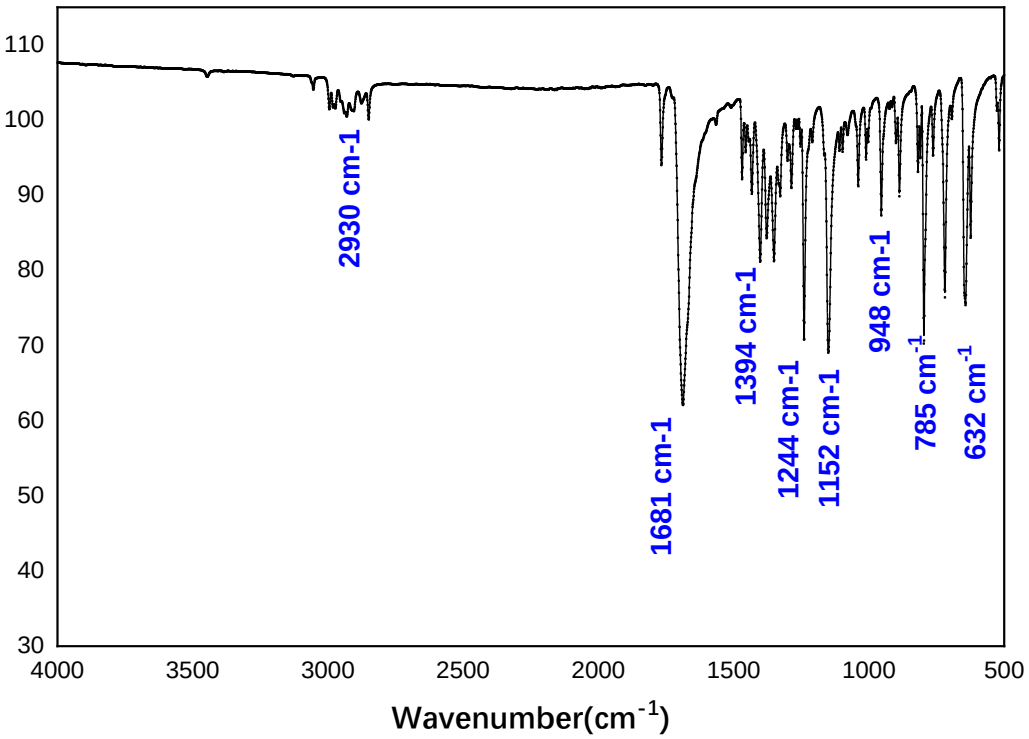


Figure S 73 FT-IR of monomers-3d

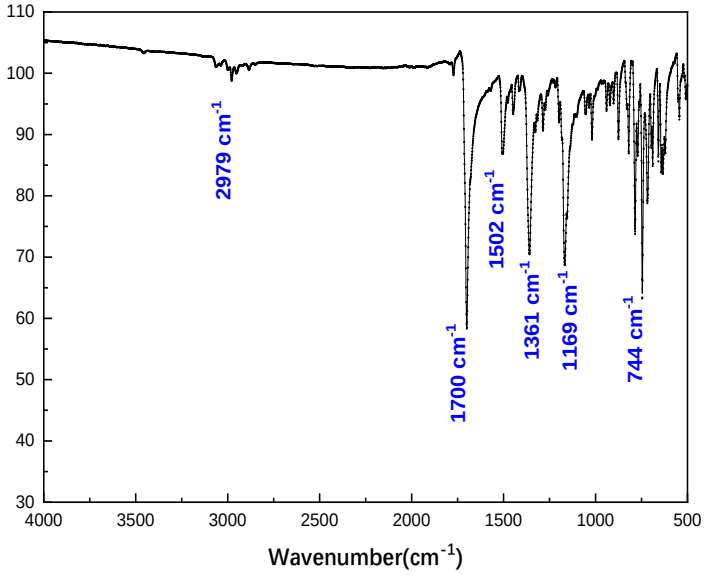


Figure S 74 FT-IR of monomers-3e

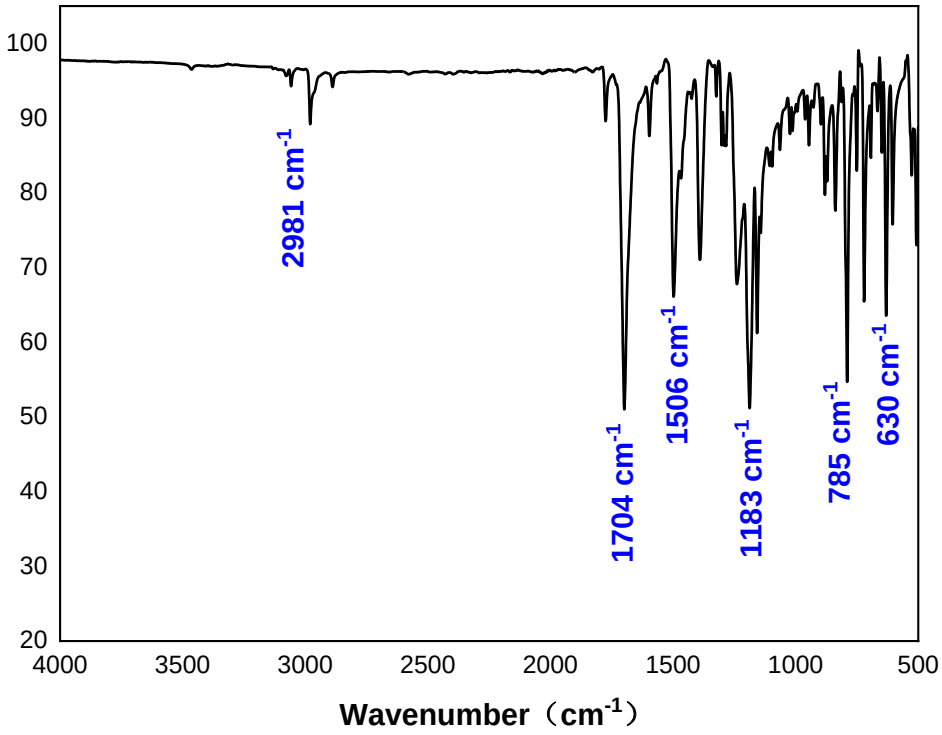


Figure S 75 FT-IR of monomers-3f

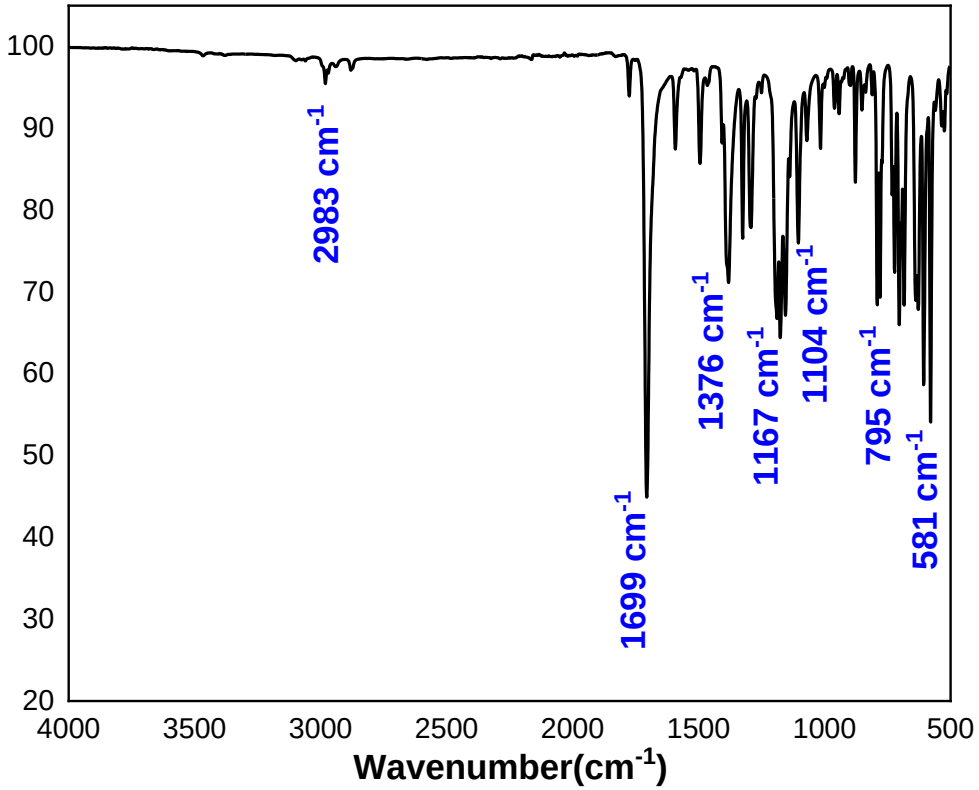


Figure S 76 FT-IR of monomers-3g

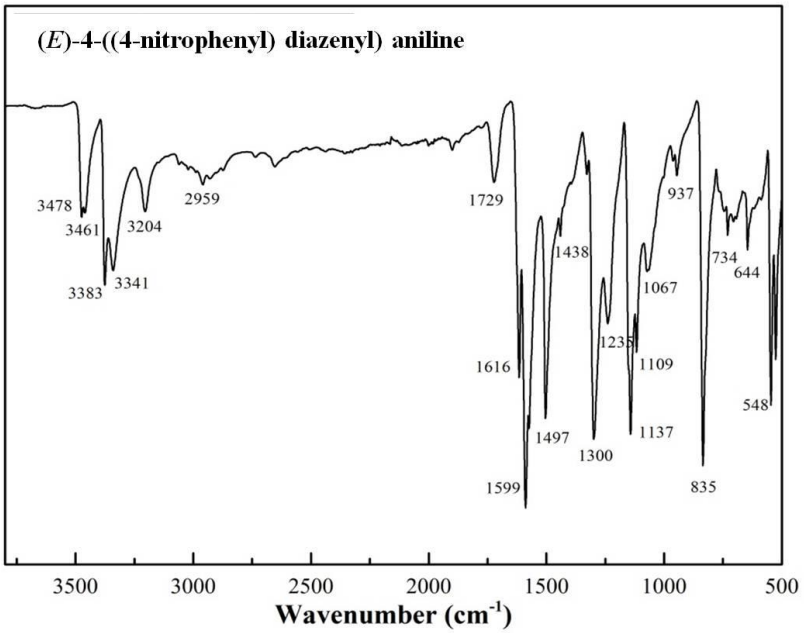


Figure S77 FT-IR of (*E*)-4-((4-nitrophenyl) diazenyl) aniline

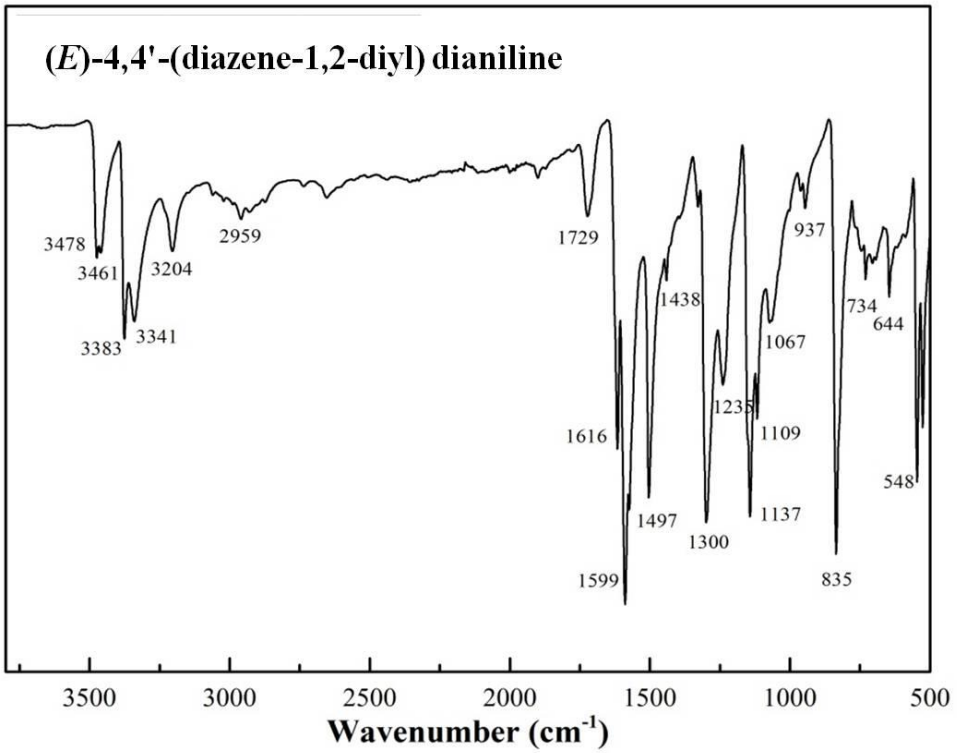


Figure S 78 FT-IR of (E)-4,4’-(diazene-1,2-diyl) dianiline

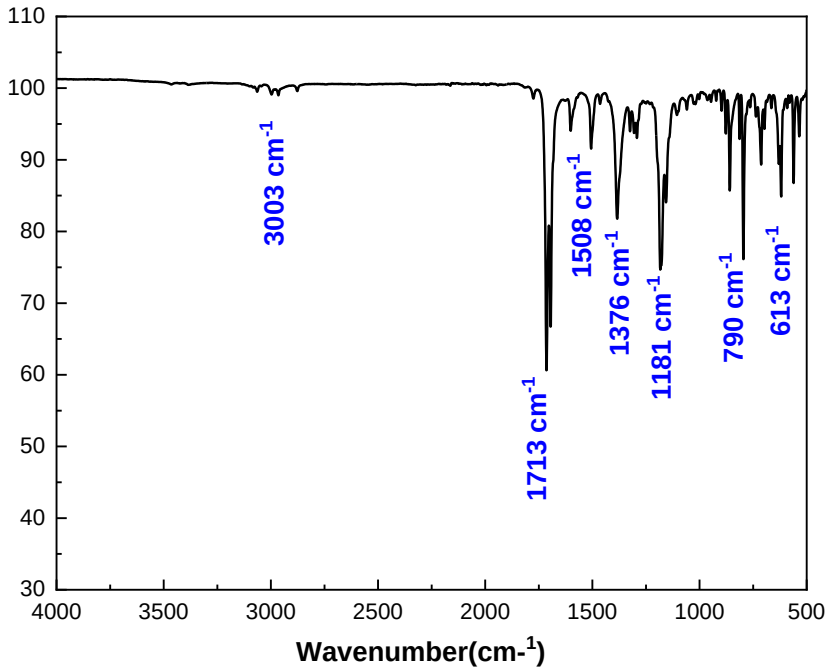


Figure S 79 FT-IR of monomers-3h

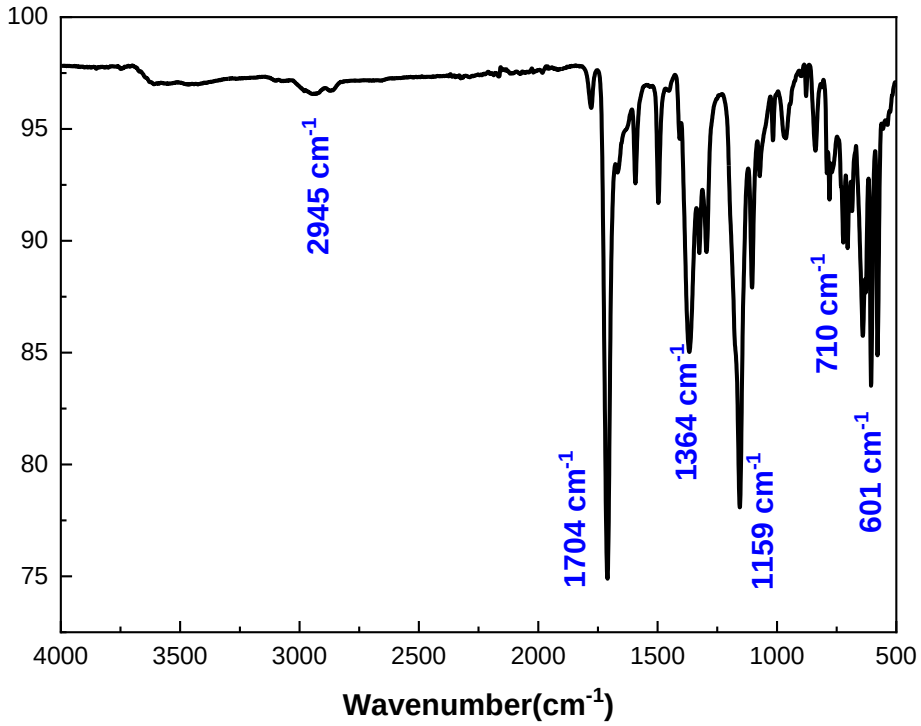


Figure S 80 IR of BIT-POP-1

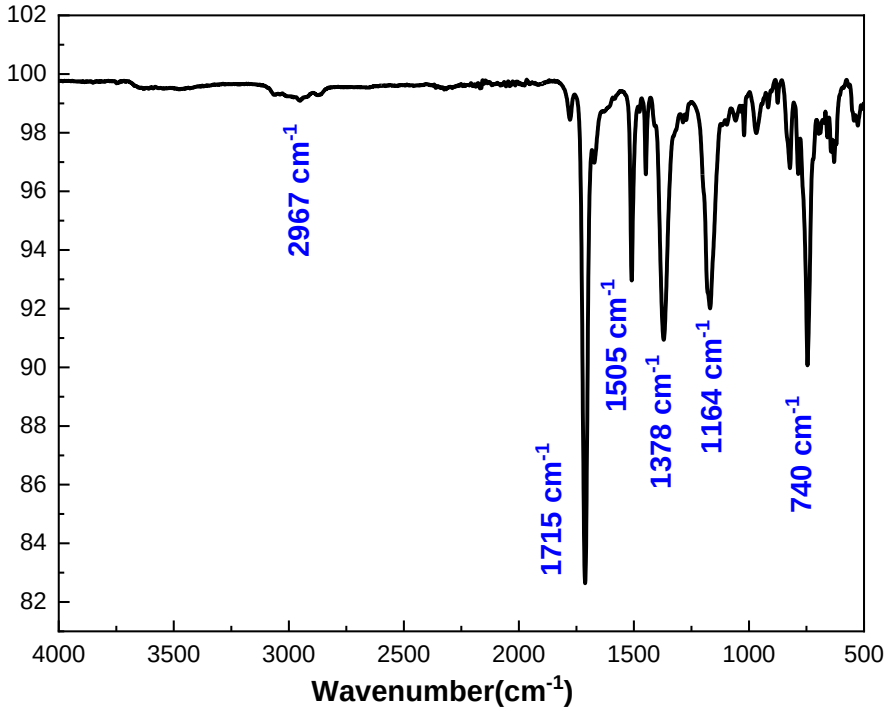


Figure S 81 IR of BIT-POP-2

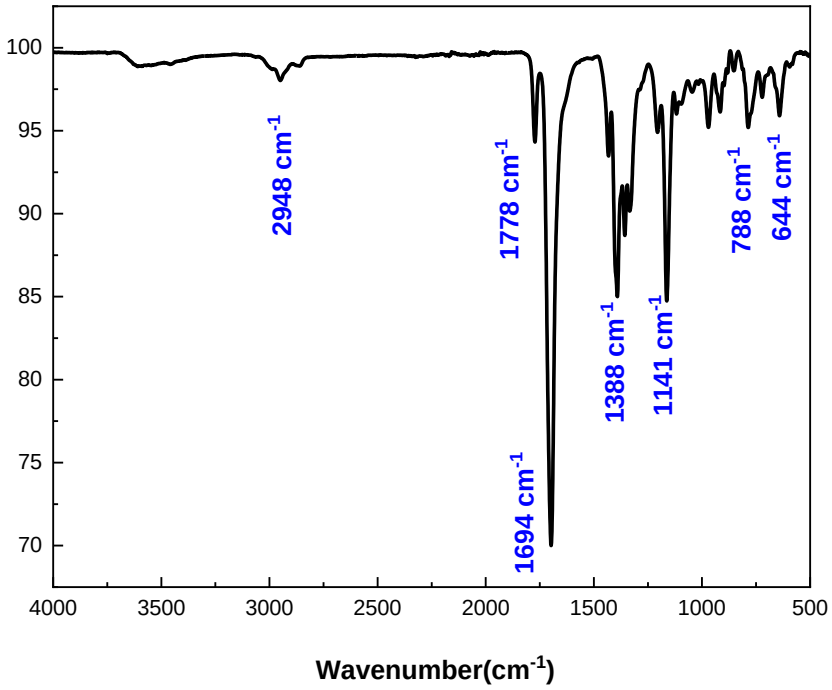


Figure S 82 IR of BIT-POP-3

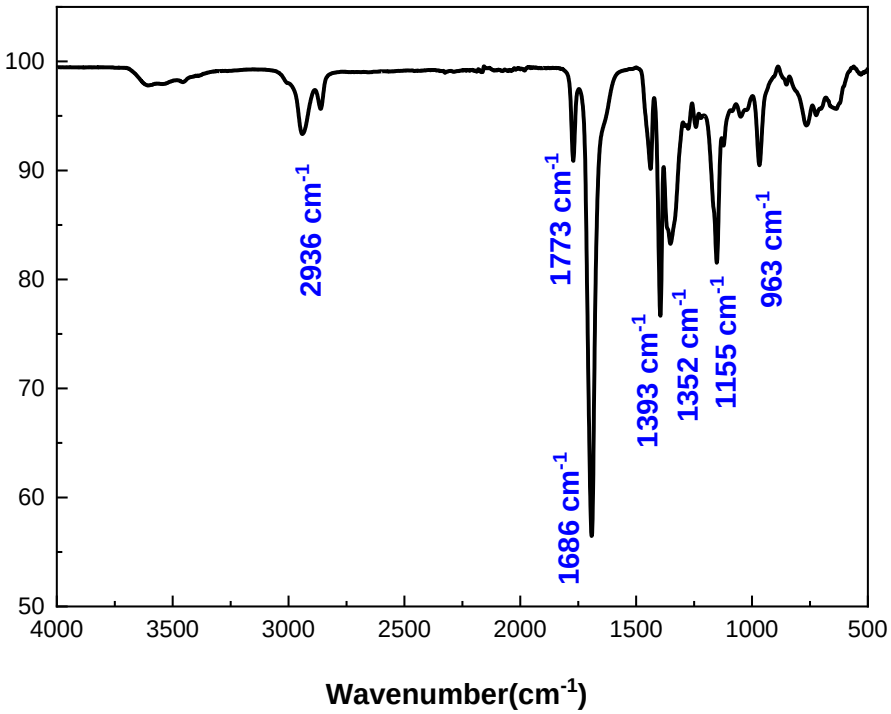


Figure S 83 IR of BIT-POP-4

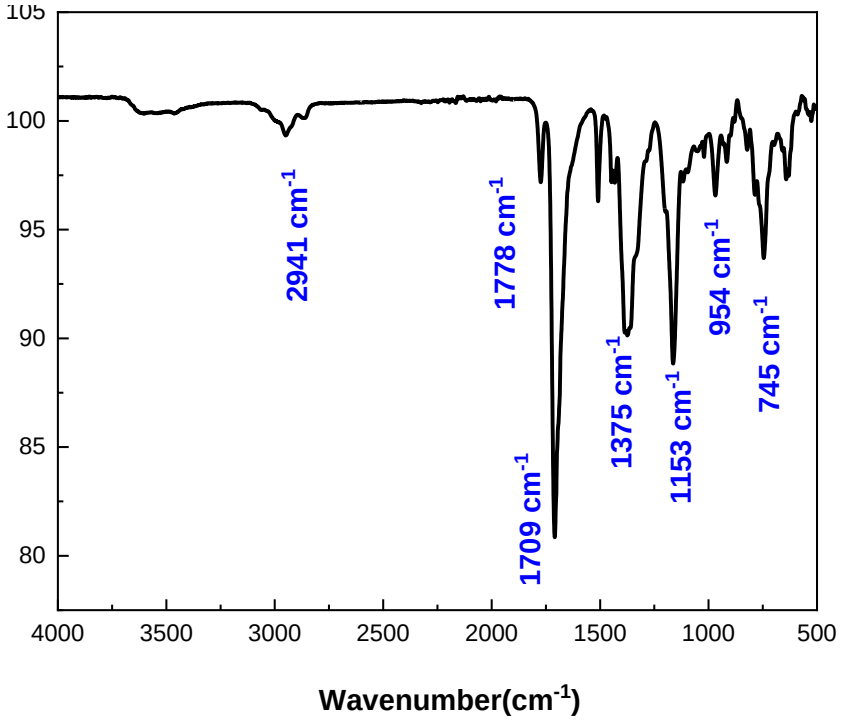


Figure S 84 IR of BIT-POP-5

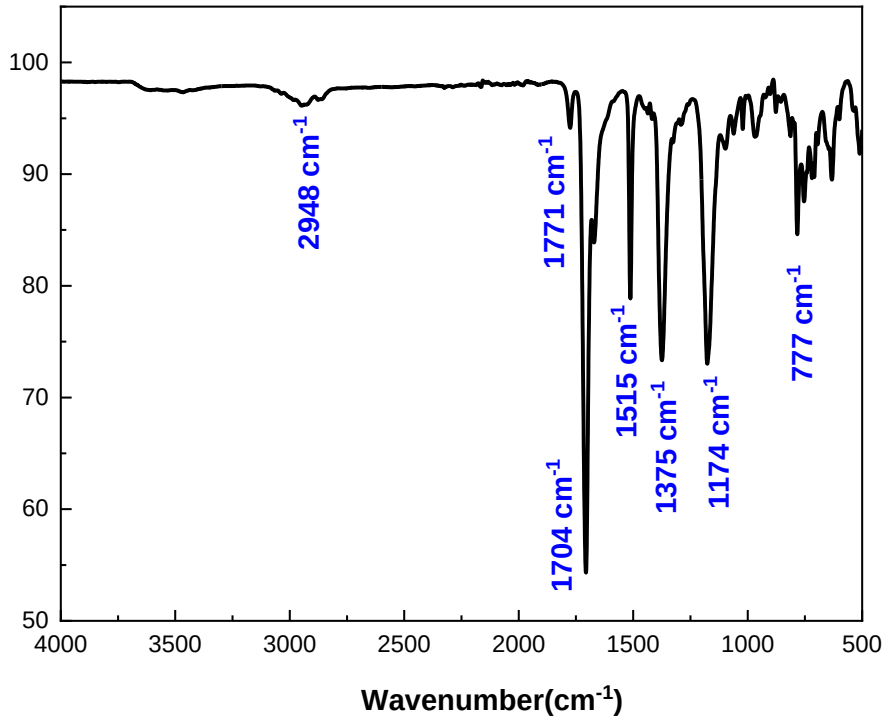


Figure S 85 IR of BIT-POP-6

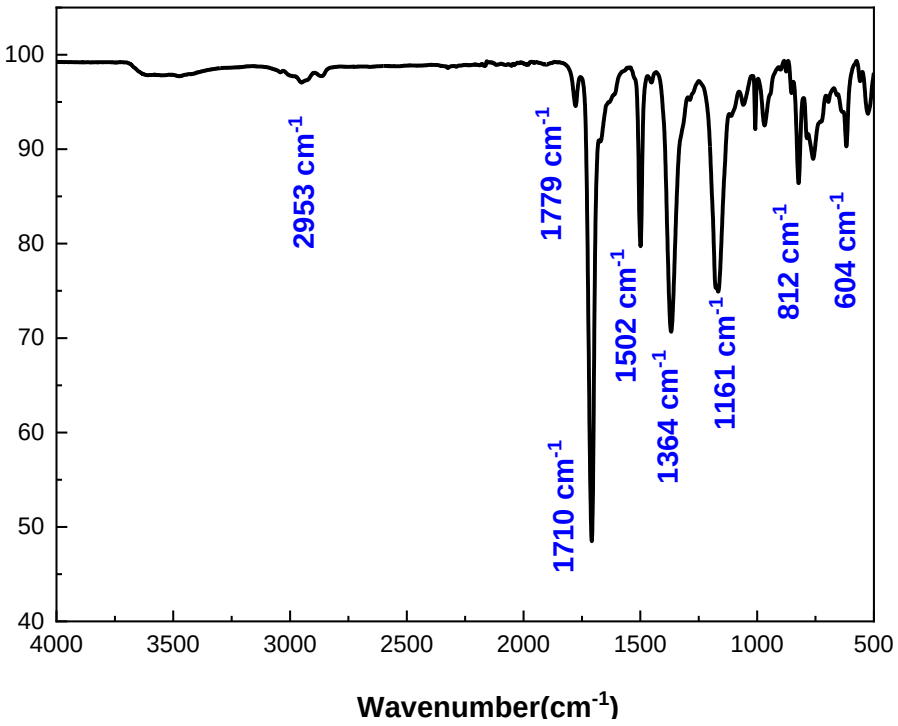


Figure S 86 IR of BIT-POP-7

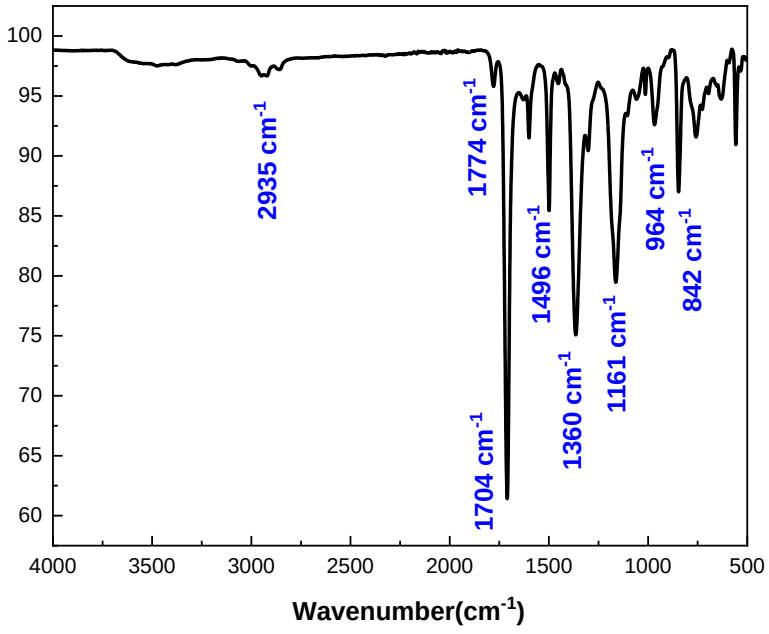


Figure S 87 IR of BIT-POP-8

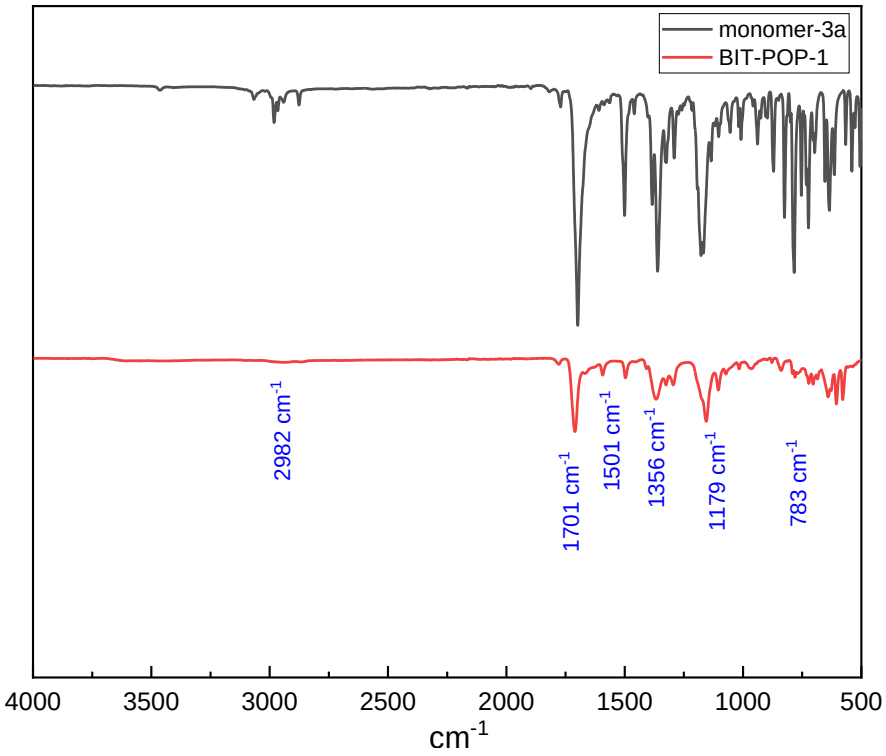


Figure S 88 IR of monomer-3a and BIT-POP-1

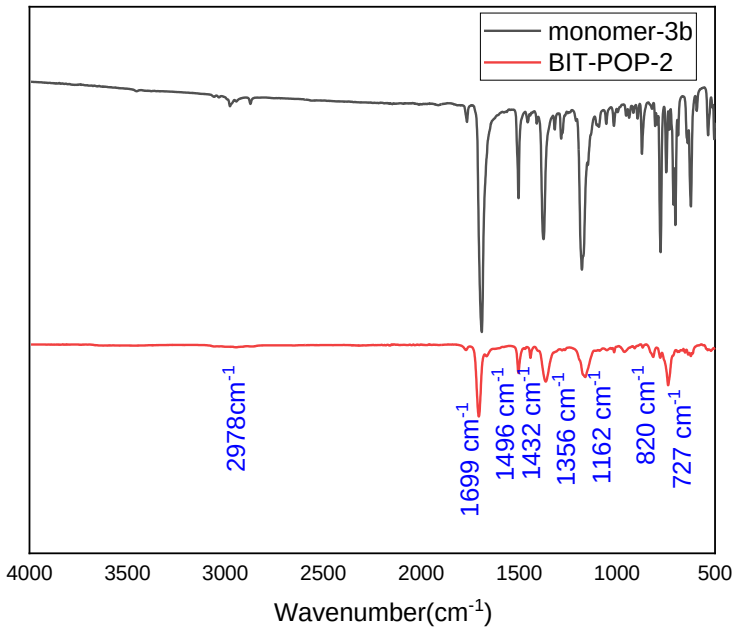


Figure S 89 IR of monomer-3b and BIT-POP-2

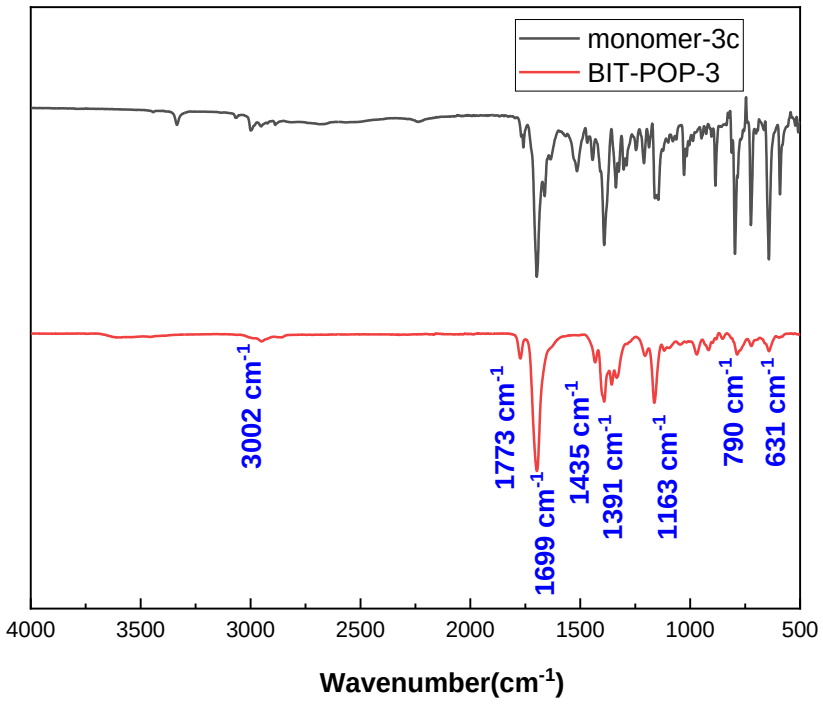


Figure S 90 IR of monomer-3c and BIT-POP-3

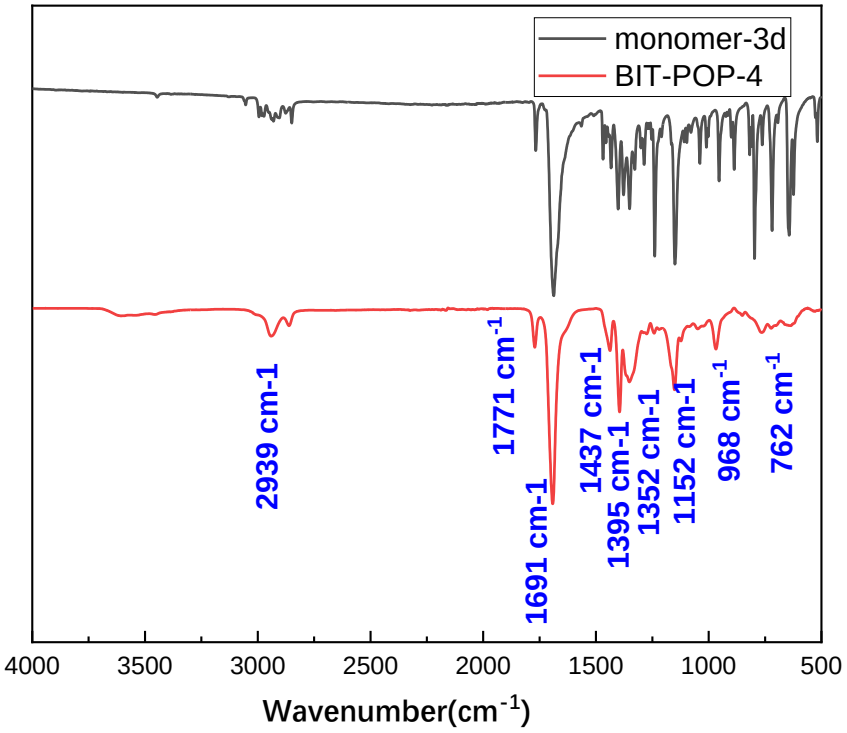


Figure S 91 IR of monomer-3d and BIT-POP-4

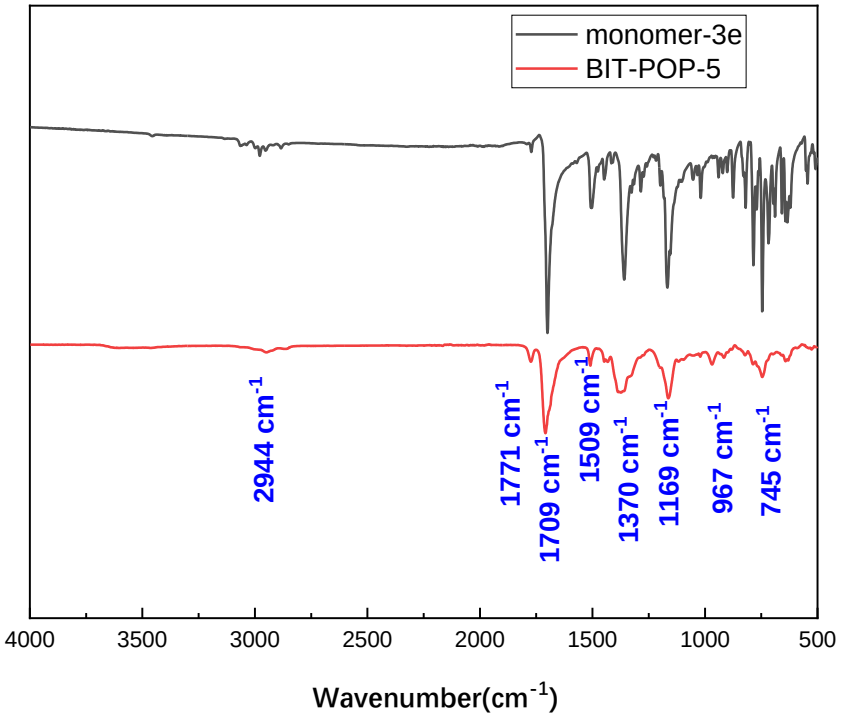


Figure S 92 IR of monomer-3e and BIT-POP-5

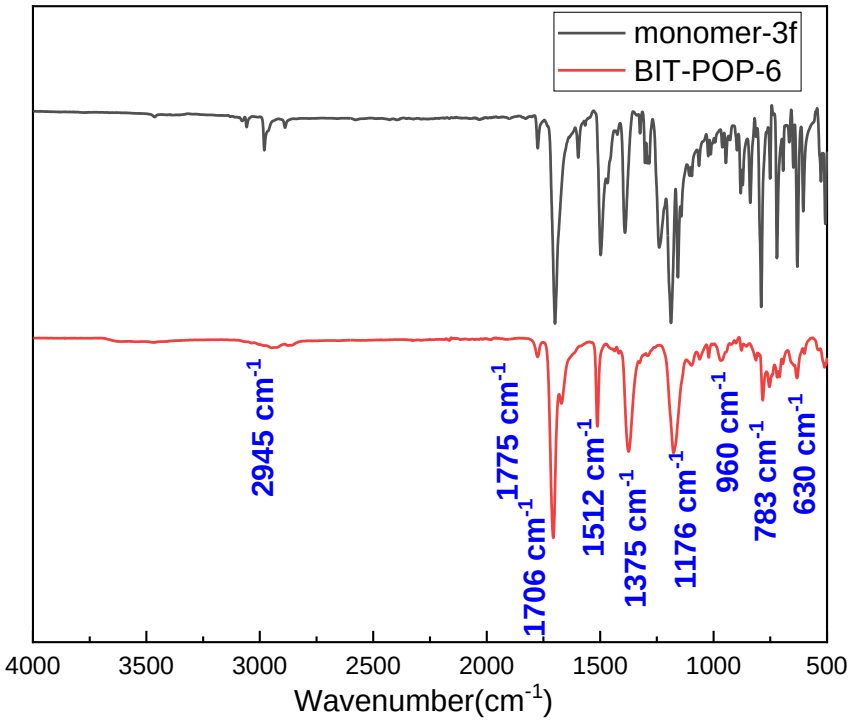


Figure S 93 IR of monomer-3f and BIT-POP-6

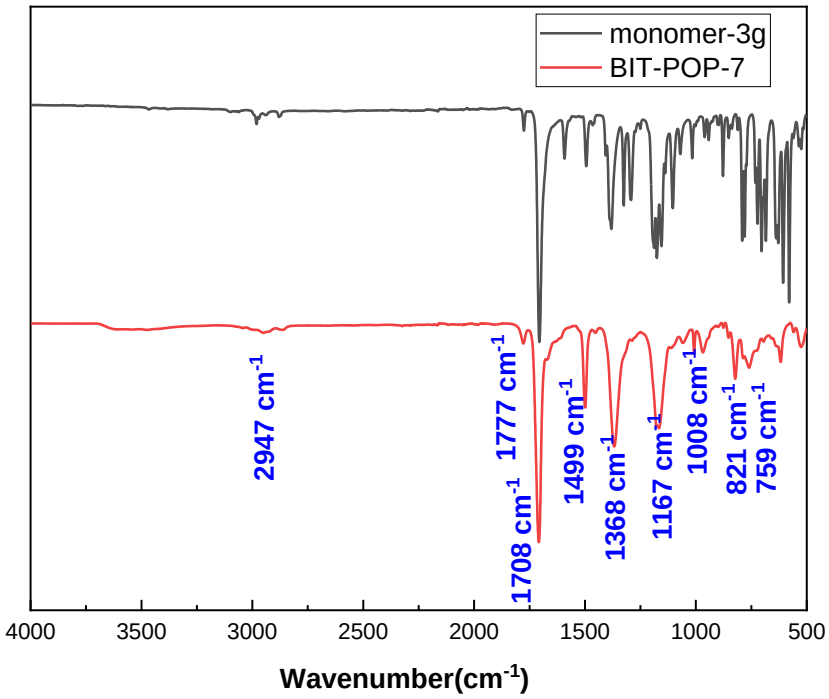


Figure S 94 IR of monomer-3g and BIT-POP-7

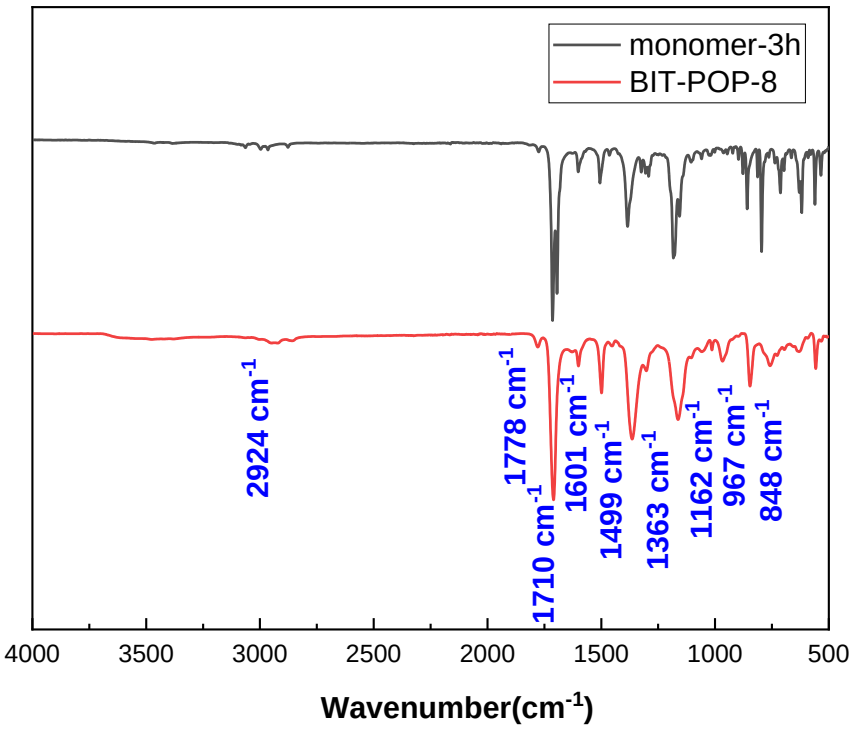


Figure S 95 IR of monomer-3h and BIT-POP-8

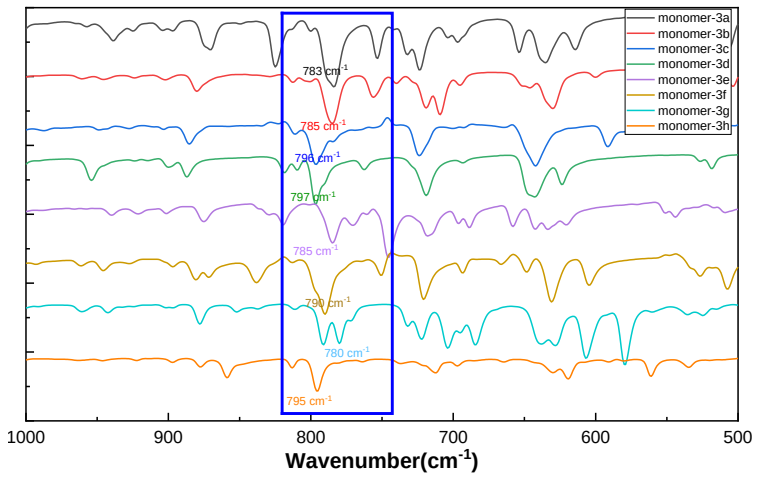


Figure S 96 IR of monomer-3a~3h

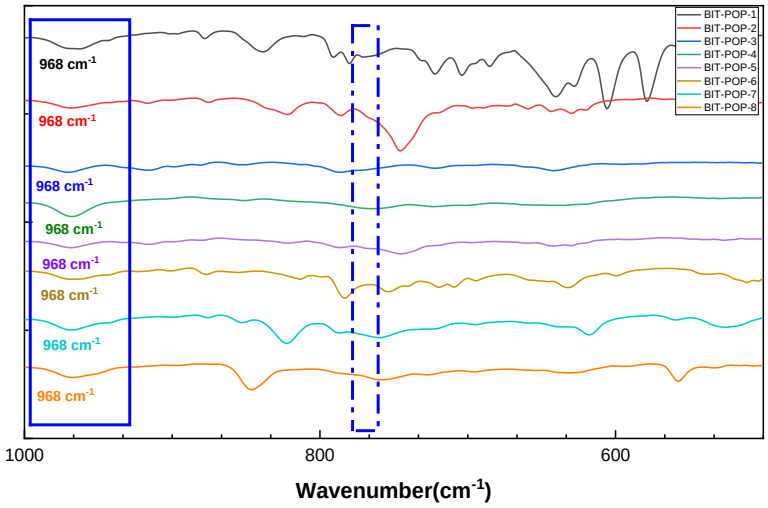


Figure S 97 IR of BIT-POP-1~8

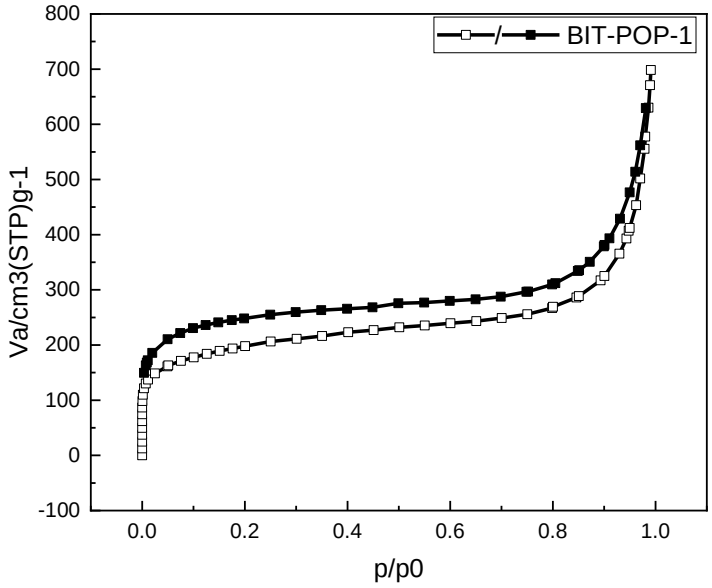


Figure S 98 Nitrogen adsorption–desorption isotherms of BIT-POP-1 at 77 K

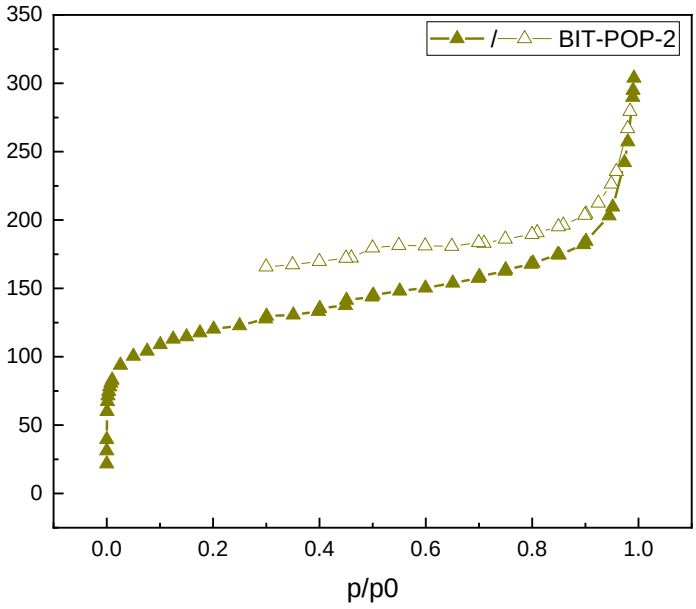


Figure S 99 Nitrogen adsorption–desorption isotherms of BIT-POP-2 at 77 K

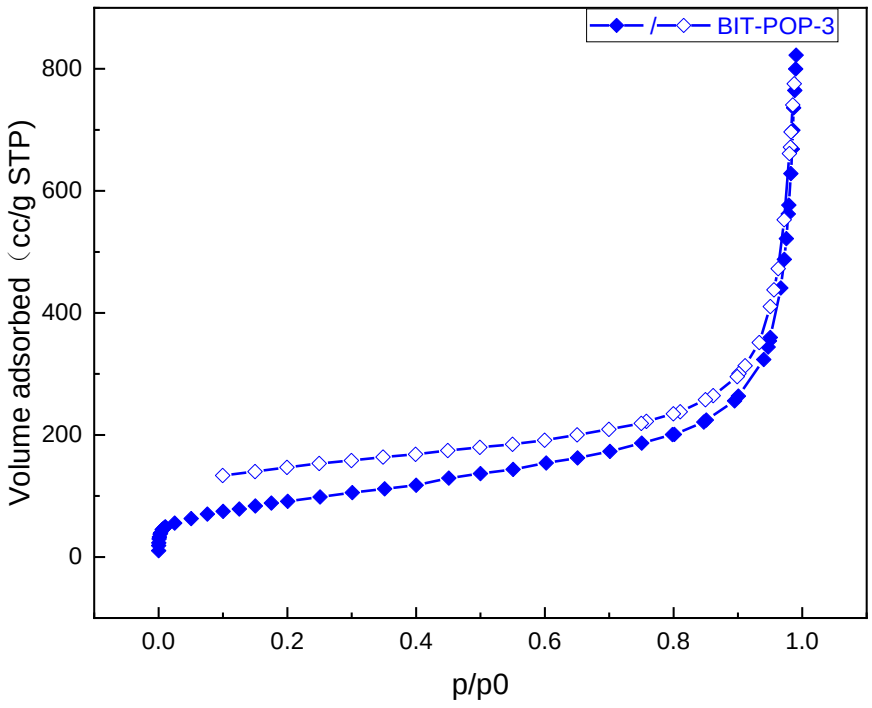


Figure S 100 Nitrogen adsorption–desorption isotherms of BIT-POP-3 at 77 K

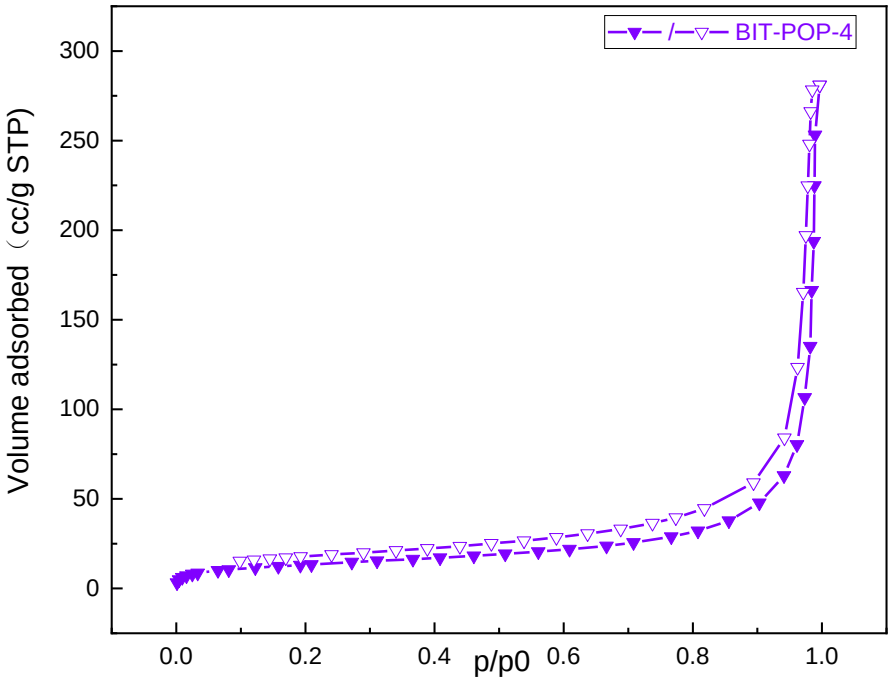


Figure S 101 Nitrogen adsorption–desorption isotherms of BIT-POP-4 at 77 K

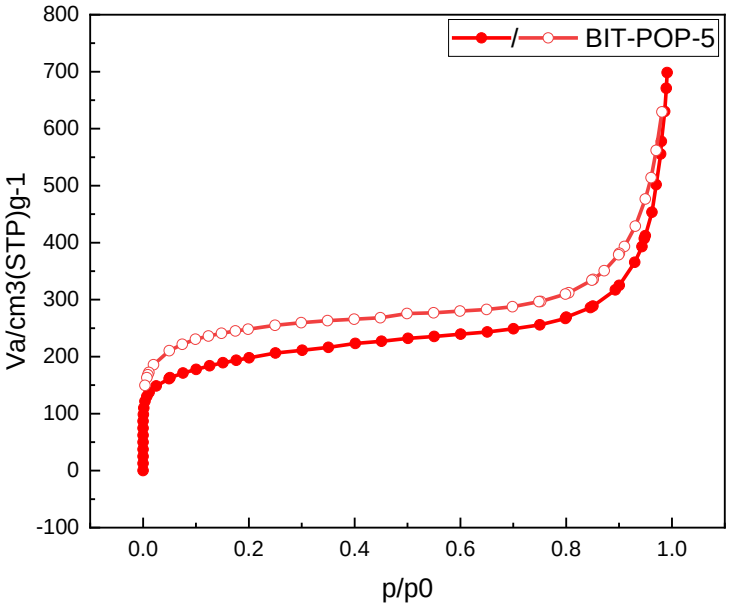


Figure S 102 Nitrogen adsorption–desorption isotherms of BIT-POP-5 at 77 K

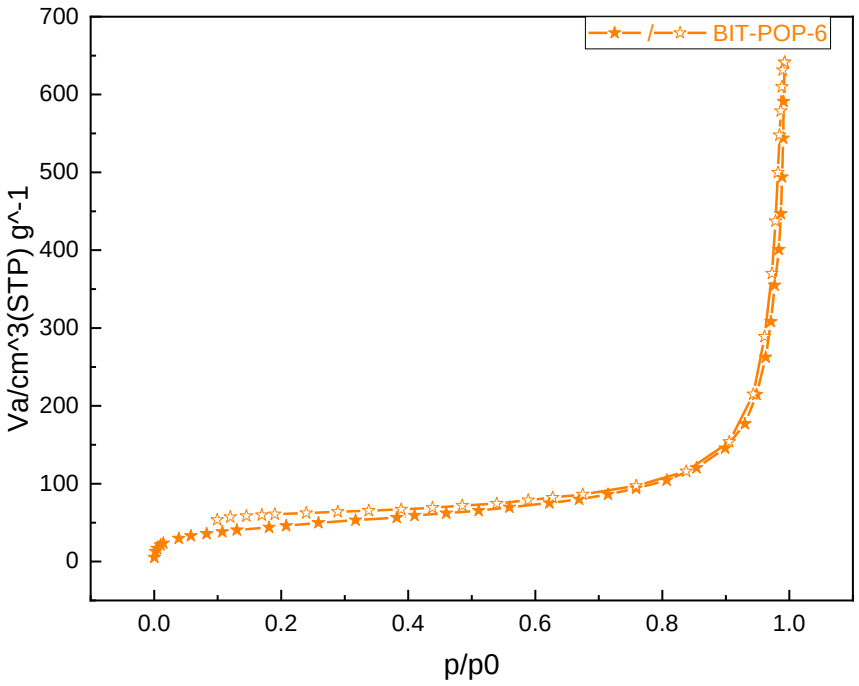


Figure S 103 Nitrogen adsorption–desorption isotherms of BIT-POP-6 at 77 K

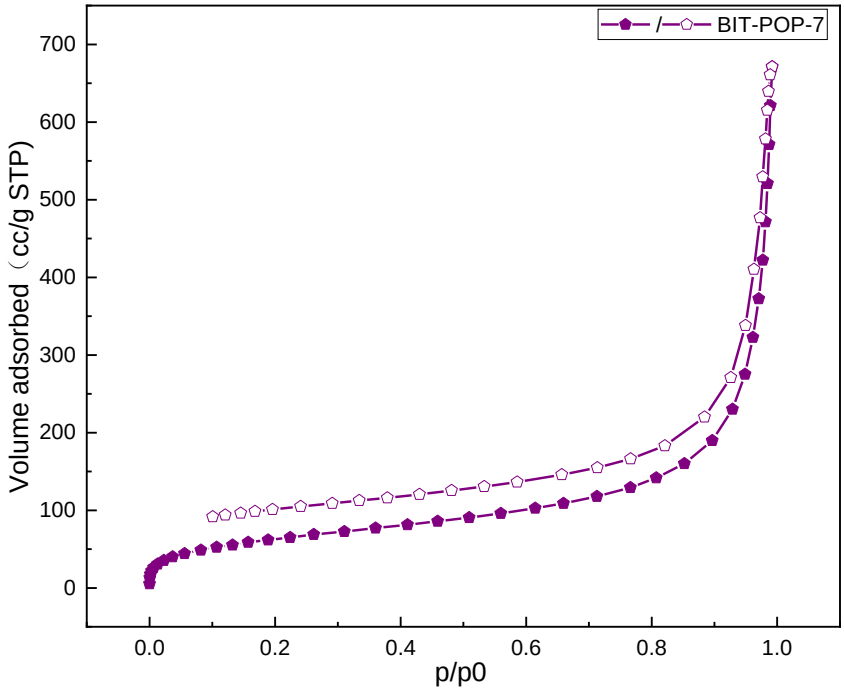


Figure S 104 Nitrogen adsorption–desorption isotherms of BIT-POP-7 at 77 K

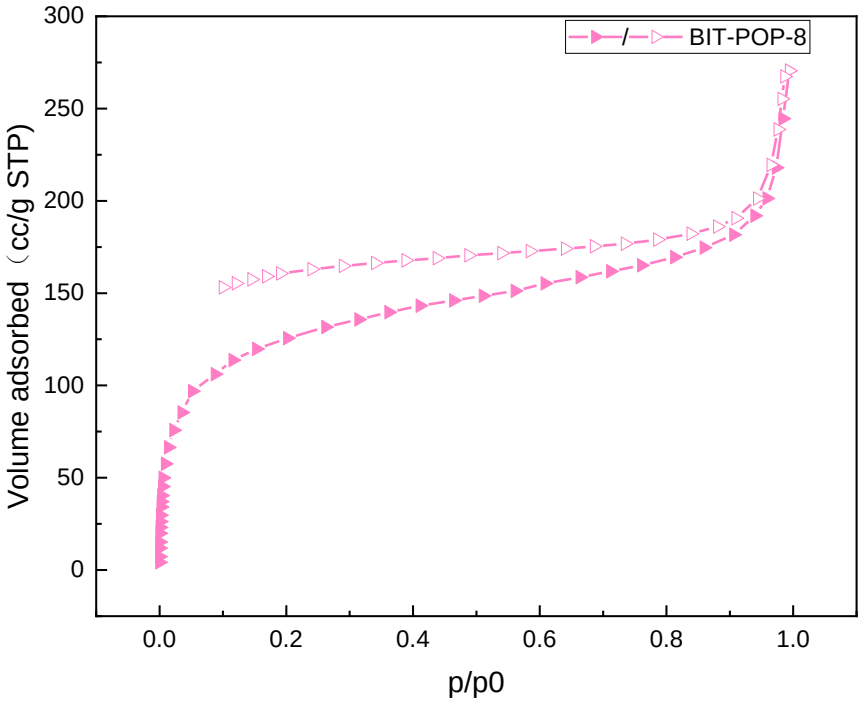


Figure S 105 Nitrogen adsorption–desorption isotherms of BIT-POP-8 at 77 K

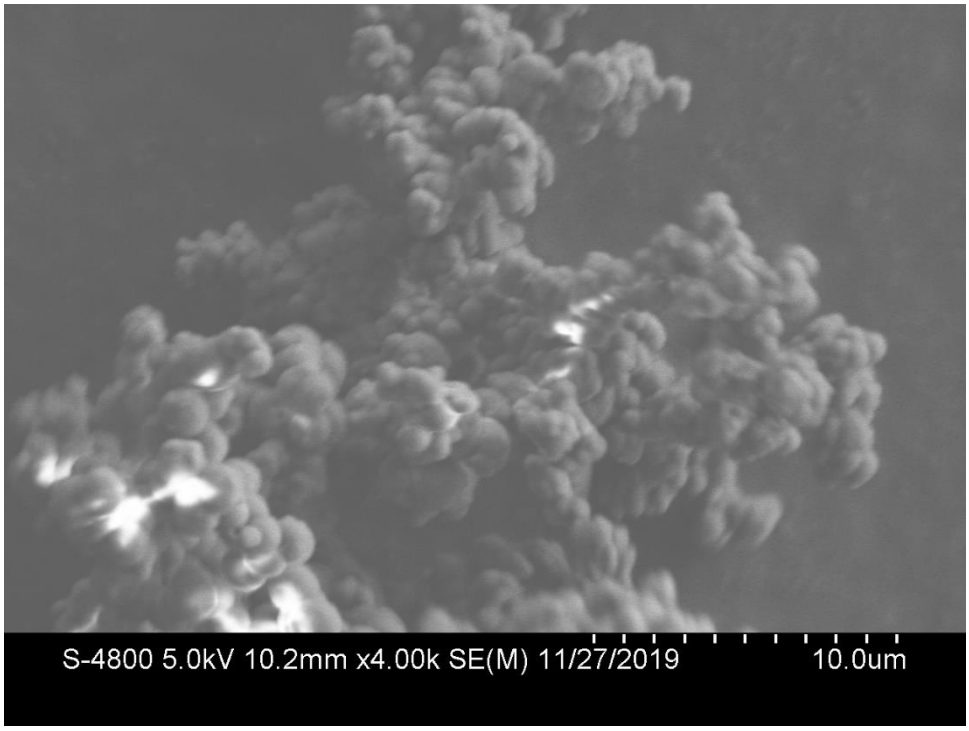


Figure S 106 SEM image of BIT-POP-1

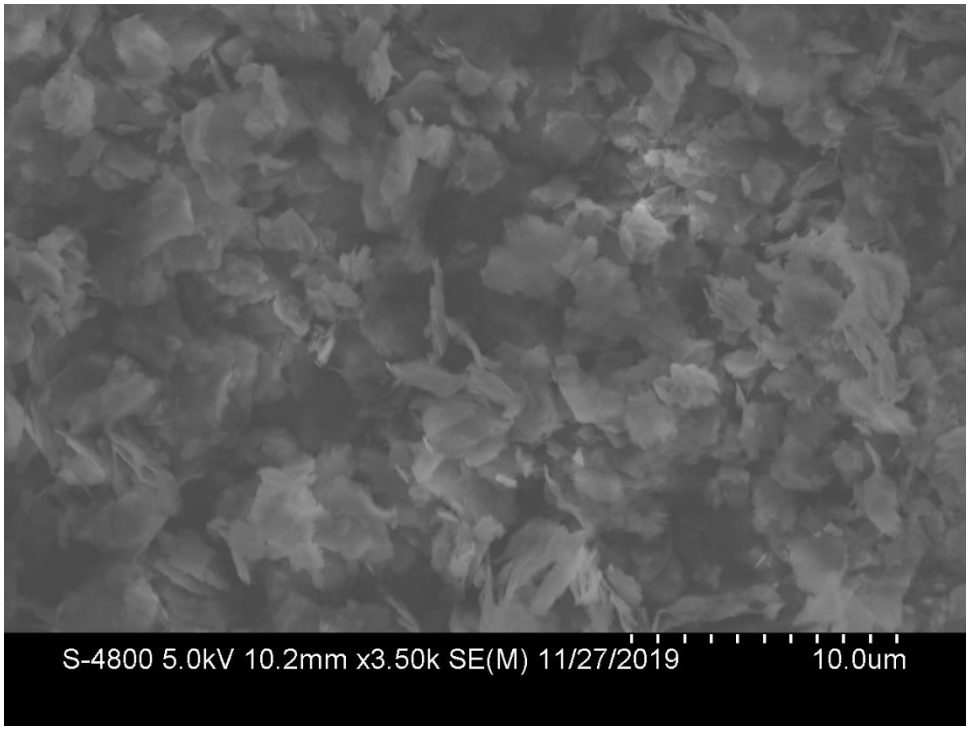


Figure S 107 SEM image of BIT-POP-8

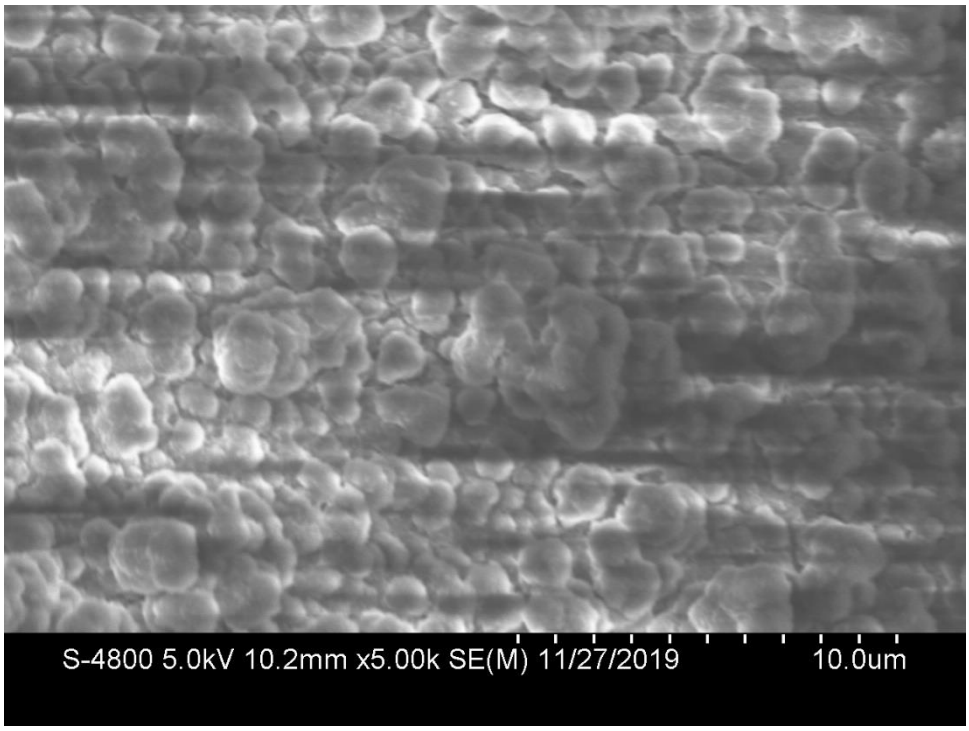


Figure S 108 SEM image of BIT-POP-5

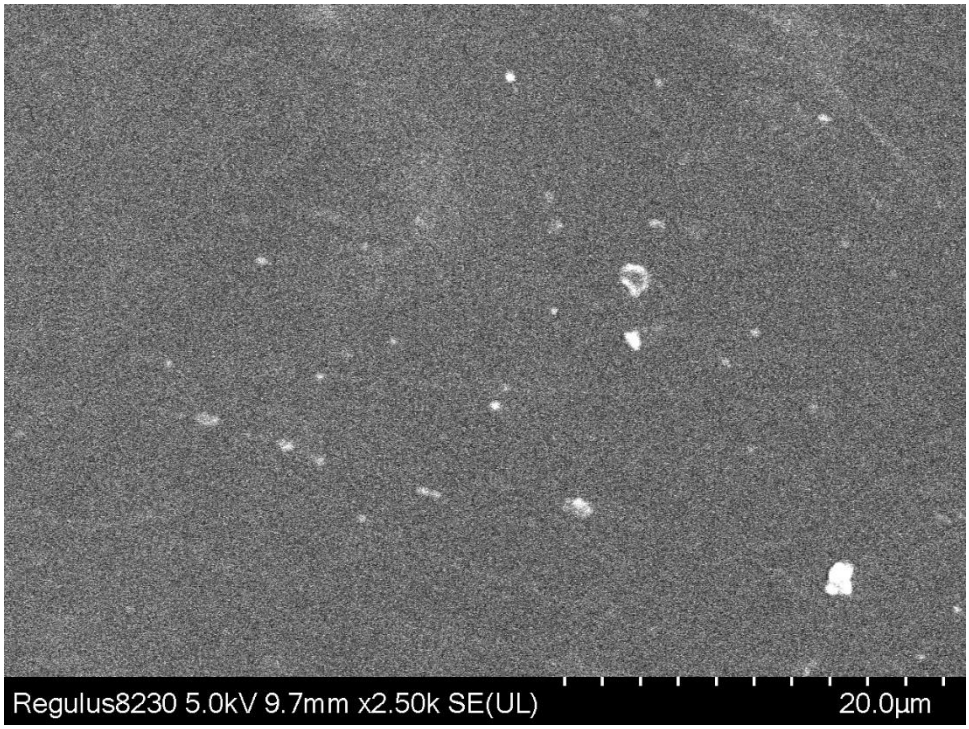


Figure S 109 SEM image of BIT-POP-5-MMM

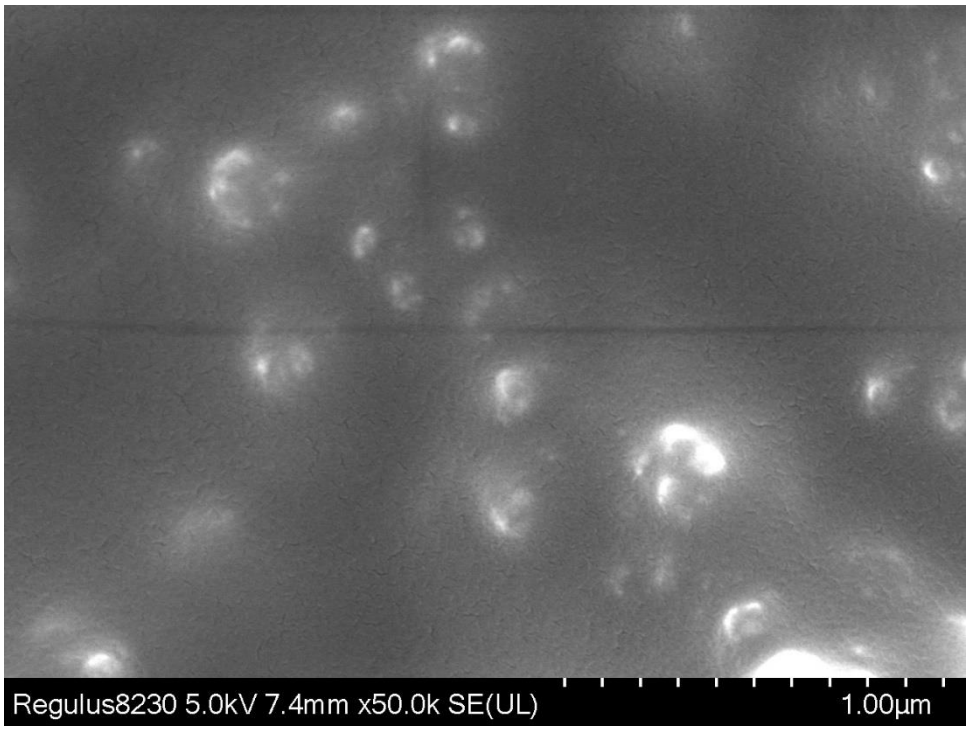


Figure S 110 SEM image of BIT-POP-5-MMM-2

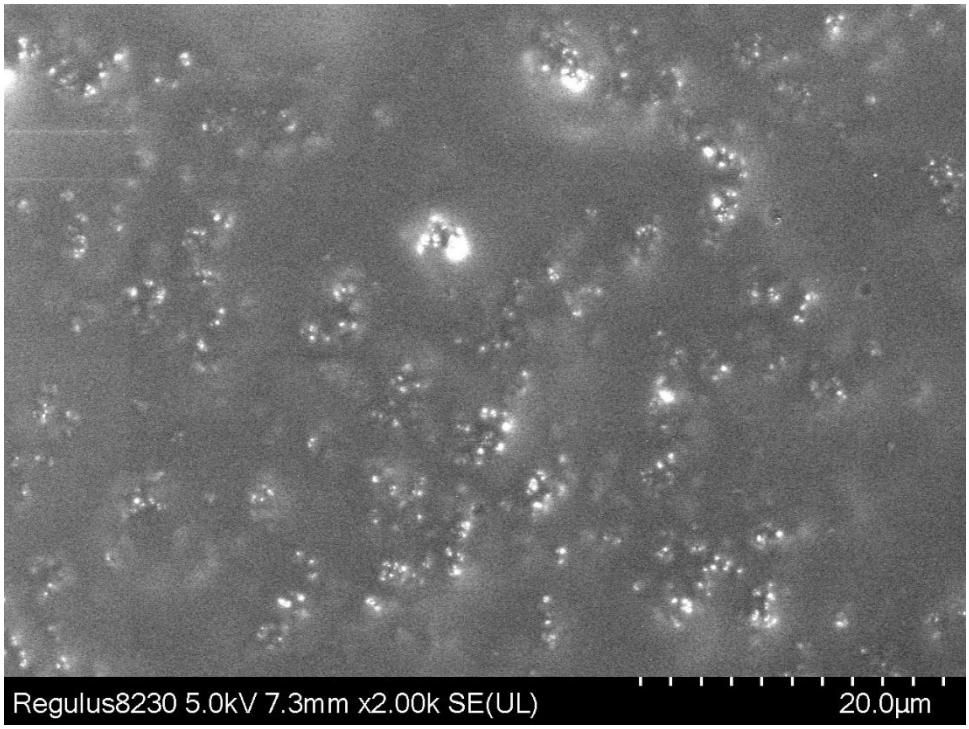


Figure S 111 SEM image of BIT-POP-5-MMM-3

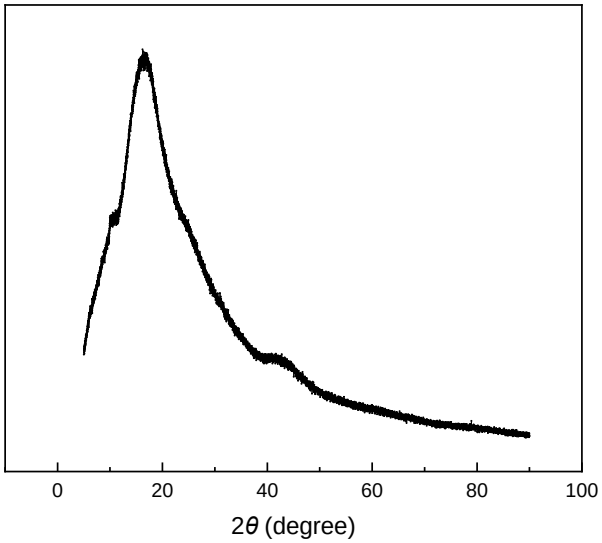


Figure S 112 PXRD of BIT-POP-1

References:

(1) Zheng, Z.; Wang, L.; Su, Z.; Xu, J.; Yang, J.; Zhang, Q. Photoinduced chirality in achiral liquid crystalline polymethacrylates containing bisazobenzene and azobenzene chromophores. *Journal of Photochemistry and Photobiology, A: Chemistry* **2007**, *185*, 338-344.

(2) Ma, X.; Zhu, Z.; Shi, W.; Ji, W.; Li, J.; Wang, Y.; Pinnau, I. Unprecedented gas separation performance of a difluoro-functionalized triptycene-based ladder PIM membrane at low temperature. *Journal of Materials Chemistry A: Materials for Energy and Sustainability* **2021**, *9*, 5404-5414.