Electronic Supplementary Material (ESI) for Chemical Science.

Block co-polyMOFs: Morphology Control of Polymer-MOF Hybrid Materials

Sergio Ayala, Kyle C. Bentz, and Seth M. Cohen*

SUPPORTING INFORMATION

Department of Chemistry and Biochemistry

University of California, San Diego

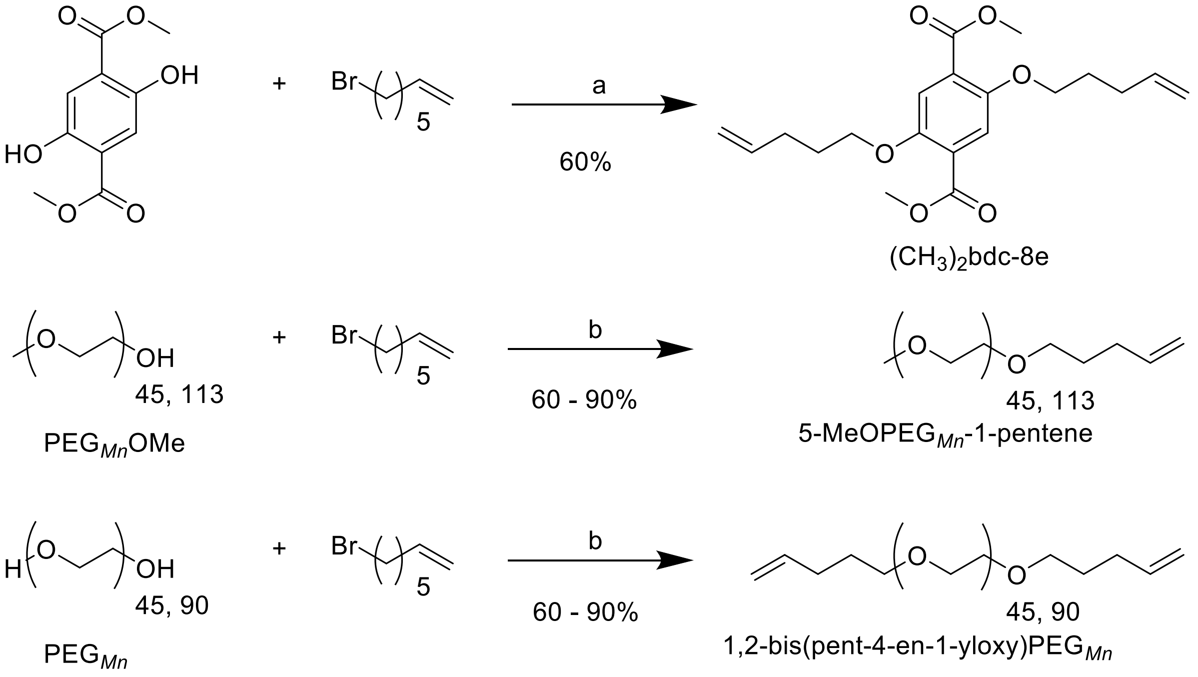
9500 Gilman Drive

La Jolla, CA 92093 (USA)

E-mail: scohen@ucsd.edu

Experimental

General Materials and Methods. Starting materials were purchased and used from commercially available suppliers (Sigma-Aldrich, Acros Organics, Matrix Scientific, and others) without further purification. Chromatography was performed using a CombiFlash R_f 200 automated system from Teledyne Isco. ^1H nuclear magnetic resonance (NMR) spectra were collected using a Varian spectrometer running at 400 MHz.



Scheme S1. Synthesis of monomers $(CH_3)_2$bdc-8e and PEG macromonomers: (a-b) Reagents and conditions: a) K_2CO_3, DMF, 80 °C, 12h; b) NaH, DMF, 45 °C, 4h.

Synthesis of $(CH_3)_2$bdc-8e. The procedure was modified from a previous report. To a 250 mL round bottom flask was added dimethyl 2,5-dihydroxyterephthalate (5.00 g, 22.1 mmol, 1.00 eq), 5-bromo-1-pentene (10.5 mL, 79 mmol, 4 eq), and potassium carbonate (5.4g, 39.3 mmol, 5 eq) in 60mL DMF. The suspension was stirred and heated at 80 °C overnight and monitored by TLC using 20% ethyl acetate (EtOAc) in hexanes. Once completed, potassium carbonate was removed by filtration, and DMF was removed via evaporation. The tar produced by the reaction was removed by silica gel chromatography eluting 10% ethyl acetate (EtOAc) in hexanes, affording the desired monomers.

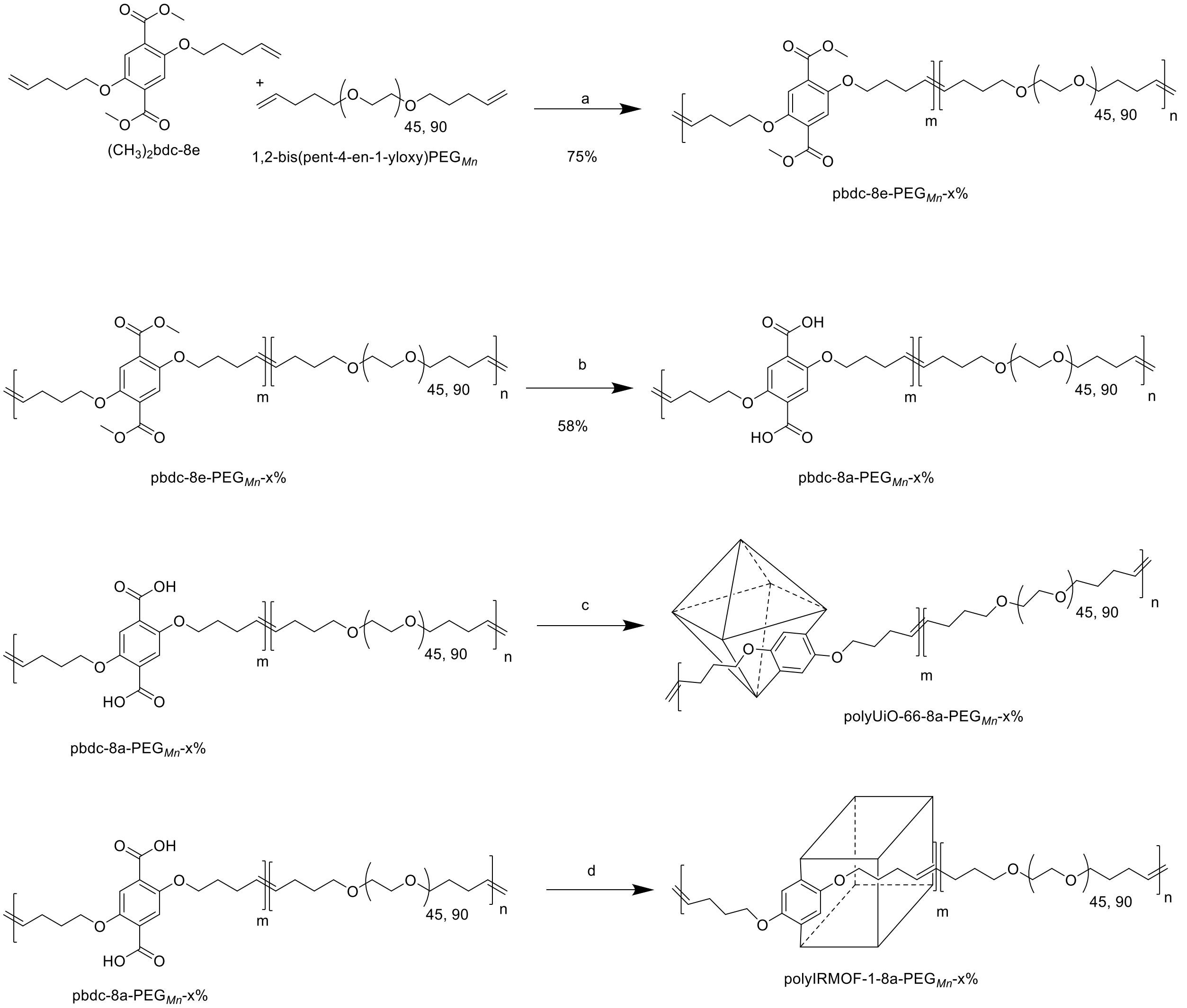
Synthesis of alkene-functionalized PEG macromonomers. To a 100 mL round bottom flask was added polyethylene glycol (PEG) (2.4 mmol, 1 eq), 5-bromo-1-pentene (1.6 mL, 12 mmol, 10. eq), and dissolved in 20 mL of DMF. Then, 60% wt. NaH in mineral oil (360 mg, 9.0 mmol, 7.5 eq.) was slowly added to the solution. The reaction was stirred and heated to 45 °C for 2 h. Then, the solution was quenched using 0.6 mL of 2 M NH_4Cl solution and he solution was stirred for 30 min to ensure quenching. The mixture was filtered through a Buchner funnel to remove any precipitating salts. DMF was removed via evaporation. The functionalized polymer was dissolved in CH_2Cl_2 to precipitate any remaining salts left in the polymer mixture. The salts were filtered, and the solvent was evaporated yielding the functionalized PEG polymers.

1,2-bis(pent-4-en-1-yloxy)PEG$_{2000}$. Yield: 70 % (3.5 g, 0.88 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.05 – 4.91 (m, 2H), 3.64 (s, J = 3.8 Hz, 180H), 2.20 – 1.97 (m, 4H), 1.67 (dt, J = 13.9, 6.8 Hz, 2H).

1,2-bis(pent-4-en-1-yloxy)PEG$_{4000}$. Yield: 73% (3.5 g, 0.88 mmol). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 5.79 (dt, *J* = 16.9, 8.3 Hz, 1H), 4.98 (dd, *J* = 23.8, 13.5 Hz, 2H), 3.67 (t, 2H), 3.50 (s, 246H), 2.11 – 1.99 (m, 2H), 1.63 – 1.50 (m, 2H).

5-MeOPEG$_{2000}$-1-pentene. Yield: 94% (4.5 g, 2.3 mmol). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 5.81 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.21 – 4.90 (m, 2H), 3.50 (s, 180H), 3.23 (s, 3H), 2.13 – 1.99 (m, 2H), 1.64 – 1.50 (m, 2H). *Mn*~ 2000 g/mol.

5-MeOPEG$_{5000}$-1-pentene. Yield: 67% (8.0 g, 1.6 mmol). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 5.81 (d, *J* = 6.8 Hz, 1H), 5.25 – 4.85 (m, 2H), 3.71 – 3.65 (m, 9H), 3.50 (s, 452H), 2.06 (s, 2H),b 1.57 (dd, *J* = 14.6, 6.8 Hz, 2H).



Scheme S2. Synthesis of of pbdc-8a-PEG$_{Mn}$-x%: a-d) Reagents and conditions: a) G2 catalyst, CH$_2$Cl$_2$, 50 °C, 5 h; b) KOH, THF/H$_2$O, 40 °C, 12h; c) ZrCl$_4$, 1:1 DEF/formic acid, 135 °C, 48h; d) Zn(NO$_3$)$_2$*6H$_2$O, DMF, 100 °C, 24 h.

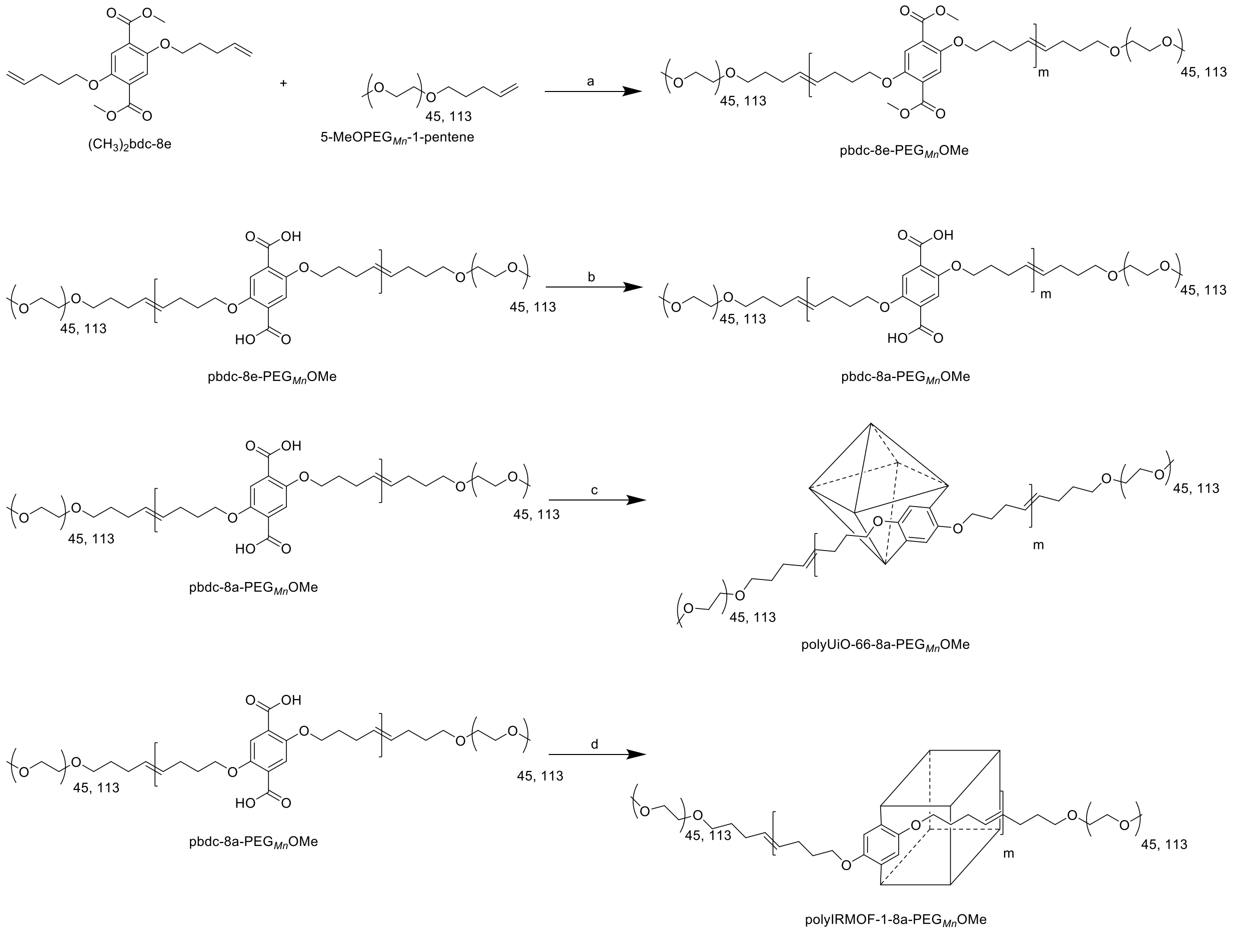
General polymerization procedure for pbdc-8e-PEG*Mn*-x% (Random AB copolymers). Dimethyl 2,5-bis(pent-4-en-1-yloxy) terephthalate ($(CH_3)_2$bdc-8e) (1.09 g, 3.00 mmol, 1.0 eq), 1,2-bis(pent-4-en-1-yloxy)PEG$_{Mn}$ (1-10 mol%) was added to a 10 mL round bottom flask, and dissolved in 5 mL CH_2Cl_2 and 100 µL methanol to enhance the solubility of the PEG. Grubbs second-generation catalyst was loaded neat (25 mg, 0.030 mmol, 0.01 eq). The reaction was set at 50 °C under mild nitrogen for 5 h while stirring. After 5 h, the solution was cooled to room temperature, and 2 mL of ethyl vinyl ether was added to quench the catalyst. The solution was stirred for 30 minutes. The polymer was precipitated in diethyl ether, followed by centrifugation at 7000 rpm for 10 min. at 8 °C. The supernatant was decanted, and the polymer was dissolved using 5 mL CH_2Cl_2 and 2 mL of methanol. The polymer was precipitated four more times in diethyl ether. After the final wash, the polymer was dried under high vacuum for two hours.

pbdc-8e-PEG$_{2000}$-2%. Yield: 44% (540 mg, 1.0 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 147H), 5.73 – 5.41 (m, 138H), 4.10 – 3.96 (m, *J* = 11.8, 8.8 Hz, 309H), 3.89 (s, 406H), 3.64 (s, 180H), 2.38 – 2.12 (m, 184H), 1.86 (bs, *J* = 5.3 Hz, 193H). M_n: 18,700 g/mol, M_w/M_n: 1.3.

pbdc-8e-PEG$_{2000}$-20%. Yield: 61% (970 mg, 1.8 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 15H), 5.75 – 5.34 (m, 16H), 4.00 (s, *J* = 5.8 Hz, 32H), 3.89 (s, *J* = 8.2 Hz, 43H), 3.64 (s, *J* = 4.4 Hz, 180H), 2.34 – 2.12 (m, 23H), 1.97 – 1.80 (m, 23H). M_n: 14,700 g/mol, M_w/M_n: 1.4.

pbdc-8e-PEG$_{4000}$-1%. Yield: 63% (760 mg, 2.3 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 191H), 5.96 – 5.35 (m, 209H), 4.10 – 3.95 (m, 406H), 3.95 – 3.82 (m, *J* = 2.9 Hz, 531H), 3.64 (s, 364H), 2.40 – 2.13 (m, 265H), 2.01 – 1.75 (m, 299H). *M_n*: 18,700 g/mol, *M_w/M_n*: 1.5.

pbdc-8e-PEG$_{4000}$-10%. Yield: 50% (800 mg, 1.5 mmol). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32 (s, 24H), 5.82 (dd, *J* = 16.9, 10.3 Hz, 1H), 5.69 – 5.32 (m, 26H), 4.99 (dd, *J* = 24.6, 13.6 Hz, 1H), 3.97 (t, *J* = 6.0 Hz, 49H), 3.86 (d, *J* = 8.0 Hz, 69H), 3.62 (s, 364H), 2.27 – 2.08 (m, 48H), 1.92 – 1.74 (m, 49H). *M_n*: 16,000 g/mol, *M_w/M_n*: 2.2.



Scheme S3. Synthesis of pbdc-8a-PEG$_{Mn}$OMe: a-e) Reagents and conditions: a) NaH, DMF, 45 °C, 4h; b) G2 catalyst, CH_2Cl_2, 50 °C, 5 h, then 5-MeOPEG$_{Mn}$-1-pentene, 2 h; c) KOH, THF/H_2O, 40 °C, 12h; d) $ZrCl_4$, 1:1 DEF/formic acid, 135 °C, 48h; e) $Zn(NO_3)_2$*$6H_2O$, DMF, 100 °C, 24 h.

General polymerization procedure for pbdce-PEG$_{Mn}$OMe (AB$_2$ copolymers). Dimethyl 2,5-bis(pent-4-en-1-yloxy) terephthalate ((CH$_3$)$_2$bdc-8e) (1.09 g, 3.00 mmol, 1.0 eq), was added to a 10 mL round bottom flask, and dissolved in 5 mL CH$_2$Cl$_2$. Grubbs second-generation catalyst was loaded neat (25 mg, 0.030 mmol, 0.01 eq). The reaction was set at 50 °C under mild nitrogen for 5 h while stirring. After 5 h, 5-MeOPEG$_{Mn}$-1-pentene (4.0 mol%) was added to reaction, along with 100 µL methanol to enhance solubility of PEG. The mixture was stirred at 50 °C for an additional 2 h. Then, the solution was cooled to room temperature, 2 mL of ethyl vinyl ether was added to quench the catalyst, and the solution was stirred for 30 minutes. The polymer was precipitated in diethyl ether, followed by centrifugation at 7000 rpm for 10 min. at 8 °C. The supernatant was decanted, and the polymer was dissolved using 5 mL CH$_2$Cl$_2$ and 2 mL of methanol. The polymer was precipitated four more times in diethyl ether. After the final wash, the polymer was dried under high vacuum for 2 h.

For purified AB$_2$ copolymers. The procedure was followed as before, but after the third wash, the polymer was purified using silica gel chromatography at gradient from 0-20% methanol in CH$_2$Cl$_2$, eluting pbdc-8e at 3% methanol, and the desired AB$_2$ copolymers at 6% and 10% methanol in CH$_2$Cl$_2$.

pbdc-8e-PEG$_{2000}$OMe (crude). Yield: 46% (820 mg, 1.4 mmol). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.34 (s, 97H), 5.68 – 5.39 (m, 98H), 4.00 (t, *J* = 6.1 Hz, 200H), 3.89 (s, 279H), 3.64 (s, 180H), 2.19 (d, *J* = 3.6 Hz, 173H), 1.96 – 1.74 (m, 192H). M_n: 23,200 g/mol, M_w/M_n: 1.8.

pbdc-8e-PEG$_{2000}$OMe. Yield: 18% (140 mg, 0.30 mmol). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.35 (s, 56H), 5.75 – 5.34 (m, 57H), 4.00 (s, *J* = 15.4 Hz, 106H), 3.89 (s, *J* = 8.1 Hz, 143H), 3.64 (s, 180H), 2.19 (bs, 97H), 1.95 – 1.76 (m, *J* = 7.0 Hz, 102H). M_n: 20,300 g/mol, M_w/M_n: 1.6.

pbdc-8e-PEG$_{5000}$OMe (crude). Yield: 64% (920 mg, 1.9 mmol). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.35 (s, 133H), 5.78 – 5.37 (m, 1H), 4.00 (t, *J* = 6.0 Hz, 274H), 3.90 (s, 315H), 3.65 (s, 460H), 2.36 – 2.13 (m, 234 H), 1.97 – 1.74 (m, 245 H). M_n: 29,400 g/mol, M_w/M_n: 1.7.

pbdc-8e-PEG$_{5000}$OMe. Yield: 5.5% (79 mg, 0.17 mmol). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34 (s, 30H), 5.65 – 5.35 (m, 26H), 5.02 (dd, *J* = 24.9, 13.6 Hz, 1H), 4.00 (t, *J* = 5.9 Hz, 53H), 3.88 (d, *J* = 8.0 Hz, 82H), 3.64 (s, 448H), 2.29 – 2.12 (m, 50H), 1.85 (d, *J* = 7.1 Hz, 51H). M_n: 19,900 g/mol, M_w/M_n: 1.4.

Procedure for ester deprotection of PEG copolymers. The PEG copolymer ester (300 to 800 mg) was added to a 250 mL round-bottom flask, along with potassium hydroxide (30 equiv), and placed in 60 mL a 1:1 of THF:water solution. The mixture was heated at 45 °C overnight. The THF was reduced by evaporation. The solution was acidified to a pH value of ~1 using a 2M HCl solution. The resultant polymer suspension was collected by centrifugation at 7000 rpm for 10 min. at 8 °C. The solid was transferred to a vial and dried under high vacuum. If no solid was observed after acidification, then the water was removed by evaporation. To the resultant polymer/salt mixture was added a 20 mL solution containing 1:1 DMF:Acetone, dissolving the polymer only. The salts were removed by filtration. The remaining solution was evaporated to yield the polymer ligand.

pbdc-8a-PEG$_{2000}$-2%. Yield: 96% (210 mg, 0.41 mmol). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 7.26 (s, *J* = 6.4 Hz, 162H), 5.99 – 5.76 (m, 8H), 5.74 – 5.33 (m, 150H), 5.08 – 4.94 (m, 1H), 3.97 (d, *J* = 6.4 Hz, 295H), 3.50 (s, 180H), 2.13 (s, *J* = 6.8 Hz, 174H), 1.86 – 1.57 (m, 212H).

pbdc-8a-PEG$_{2000}$-20%. Yield: 90.1% (350 mg, 0.69 mmol). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 7.25 (s, *J* = 6.7 Hz, 15H), 5.65 – 5.36 (m, 15H), 4.08 – 3.89 (m, 30H), 3.50 (s, 180H), 2.13 (s, *J* = 39.3 Hz, 21H), 1.90 – 1.56 (m, 23H).

pbdc-8a-PEG$_{4000}$-1%. Yield: 78% (230 mg, 0.59 mmol). ^{1}H NMR (400 MHz, DMSO-d$_6$). δ 7.25 (s, *J* = 6.6 Hz, 236H), 6.02 – 5.82 (m, 4H), 5.73 – 5.23 (m, 214H), 3.97 (d, *J* = 6.4 Hz, 429H), 3.50 (s, 364H), 2.25 – 2.05 (m, 255H), 1.83 – 1.56 (m, 313H).

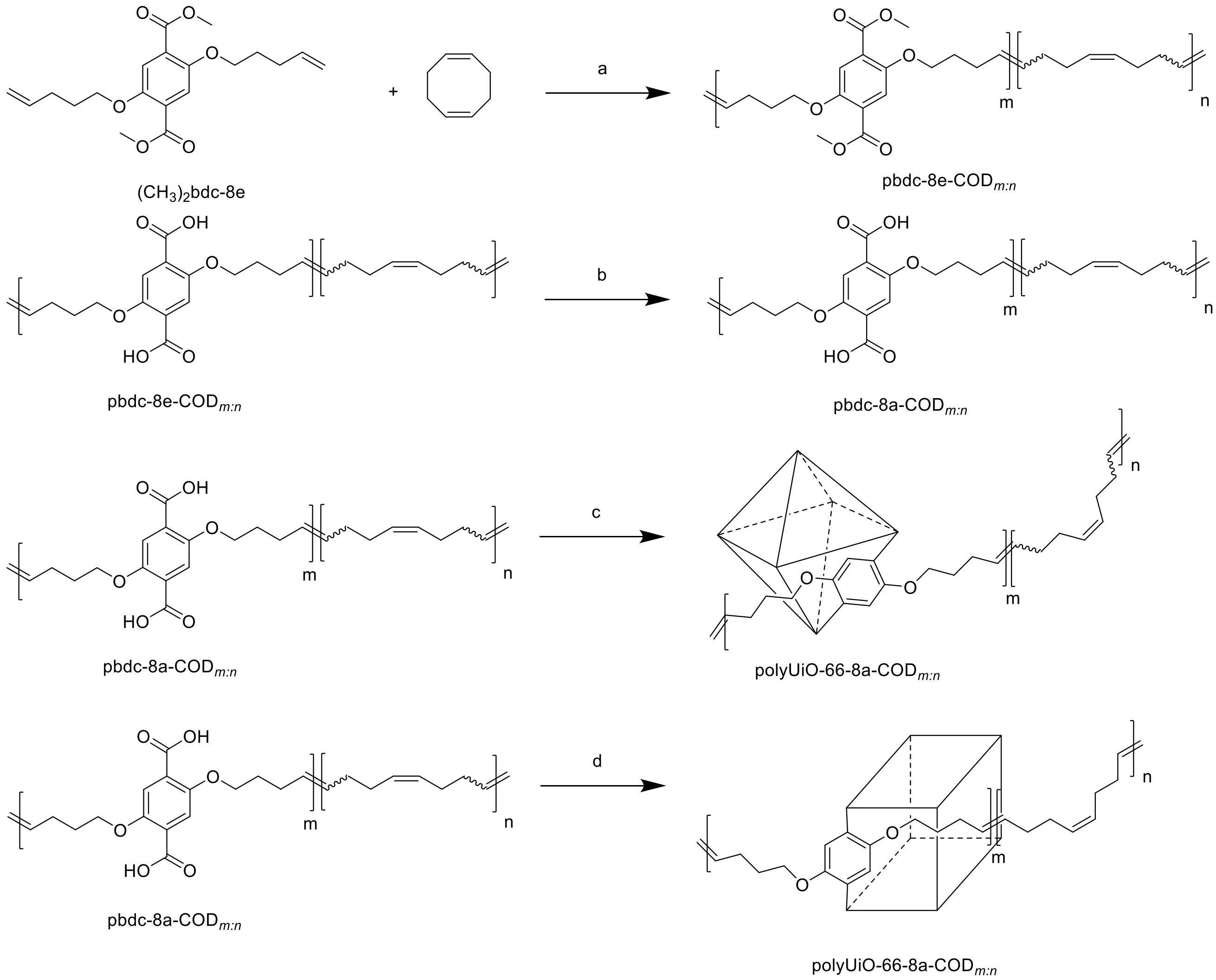
pbdc-8a-PEG$_{4000}$-10%. Yield: 49% (230 mg, 0.94 mmol). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 7.25 (s, 51H), 5.67 – 5.30 (m, 54H), 5.00 (dd, *J* = 25.7, 14.7 Hz, 1H), 3.96 (t, *J* = 5.7 Hz, 98H), 3.50 (s, 364H), 2.12 (s, *J* = 39.5 Hz, 97H), 1.85 – 1.51 (m, 104H).

pbdc-8a-PEG$_{2000}$OMe (crude). Yield: 87% (330 mg, 0.840 mmol) ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 7.25 (s, 104H), 5.70 – 5.34 (m, 113H), 3.96 (bs, 347H), 3.50 (s, 180H), 2.12 (s, 182H), 1.71 (s, *J* = 88.2 Hz, 200H).

pbdc-8a-PEG$_{2000}$OMe. Yield: 70% (82 mg, 0. 26 mmol). ^{1}H NMR (400 MHz, DMSO) δ 7.25 (s, 58H), 5.68 – 5.32 (m, 58H), 3.97 (d, *J* = 6.2 Hz, 111H), 3.50 (s, 180H), 2.12 (s, 102H), 1.72 (s, 110H).

pbdca-PEG$_{5000}$OMe (crude). Yield: 89% (400 mg, 0.98 mmol). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 7.25 (s, 112H), 5.99 – 4.97 (m, 105H), 3.96 (t, *J* = 6.0 Hz, 243H), 3.50 (s, 454H), 2.12 (s, 188H), 1.84 – 1.53 (m, 203H).

pbdca-PEG$_{5000}$OMe. Yield: 33% (20 mg, 0.045 mmol). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 7.25 (s, 44H), 5.71 – 5.29 (m, 42H), 5.00 (dd, *J* = 24.0, 13.6 Hz, 1H), 3.96 (t, *J* = 6.1 Hz, 80H), 3.50 (s, 451H), 2.30 – 2.03 (m, 75H), 1.86 – 1.61 (m, 76H).



Scheme S4. Synthesis of pbdc-8a-COD$_{m:n}$: a-d) Reagents and conditions: b) HG2 catalyst, CH_2Cl_2, 50 °C, 5 h, then COD, 1 h; c) KOH, THF/H_2O, 40 °C, 12h; d) $ZrCl_4$, 1:1 DEF/formic acid, 135 °C, 48h; e) $Zn(NO_3)_2$*$6H_2O$, DMF, 100 °C, 24 h.

General procedure for synthesis of pbdc-8e-COD$_{m:n}$. To a 10 mL round bottom flask was added $(CH_3)_2$bdc-8e monomer (1.087g, 3.0 mmol, 1.00 eq), and dissolved in 5 mL of CH_2Cl_2. Hoveyda-Grubbs second-generation catalyst was loaded neat (18 mg, 0.030 mmol, 0.01 eq). The reaction was set at mild reflux (45 °C) under mild nitrogen for 5 h. After 5 h, the appropriate amount of COD (0.300-6.00 mmol) along with 1 mL of CH_2Cl_2

was added to the reaction mixture, and stirred for an additional 30 min at 45 °C. The solution was cooled to room temperature, and ethyl vinyl ether (2 mL) was added to quench the catalyst, stirring for 30 minutes. The polymer was precipitated in methanol, followed by centrifugation at 7000 rpm for 10 min. at room temperature. The supernatant was decanted, and the polymer was dissolved in CH_2Cl_2 and precipitated four more times in methanol. After the final wash, the polymer was transferred to a vial, and dried under vacuum for further analysis.

pbdc-8e-COD$_{10:1}$. Yield: 57% (800 mg, 1.7 mmol): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 2H), 5.84 – 5.23 (m, 4H), 4.00 (t, *J* = 6.0 Hz, 5H), 3.89 (s, 4H), 2.19 (s, 4H), 2.03 (s, 1H), 1.85 (d, *J* = 6.3 Hz, 4H).

pbdc-8e-COD$_{2:1}$. Yield: 60.% (880 mg, 3.00 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (s, 2H), 5.90 – 4.95 (m, 4H), 4.00 (t, *J* = 5.8 Hz, 4H), 3.88 (d, *J* = 8.1 Hz, 6H), 2.18 (s, 4H), 2.02 (s, 4H), 1.86 (bs, 3H). M_n: 17,500 g/mol, M_w/M_n: 2.8.

pbdc-8e-COD$_{1:1}$. Yield: 96% (1.26 g, 2.68 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (s, 2H), 5.63 – 5.33 (m, 6H), 4.00 (t, *J* = 6.0 Hz, 4H), 3.89 (s, 5H), 2.15 (bs, 4H), 2.02 (s, 8H), 1.93 – 1.76 (m, 4H). M_n: 17,200 g/mol, M_w/M_n: 2.8.

General Procedure for ester deprotection of pbdc-8e-COD$_{m:n}$. The polymer ester (600mg -1.6g) was added to a 250-mL round-bottom flask, along with sodium hydroxide (30 equivalents), and placed in 60 mL a 1:1 of THF:water solution. The mixture was heated at 60 °C for 12h, or until the solution became clear. A biphasic solution containing THF and water was observed. The THF was reduced by evaporation. The solution was acidified *dropwise* to a pH value of ~5 using a 2M HCl solution. The resultant solid was collected by vacuum filtration.

pbdc-8a-COD$_{10:1}$. Yield: 81% (560 mg, 1.6 mmol). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 7.24 (s, 2H), 5.78 – 5.16 (m, 3H), 4.94 (s, 1H), 3.94 (s, 5H), 2.11 (s, 4H), 1.93 (d, *J* = 25.5 Hz, 1H), 1.70 (s, 4H).

pbdc-8a-COD$_{2:1}$. Yield: 99% (630 mg, 1.4 mmol). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 7.25 (s, 2H), 5.45 (dd, *J* = 62.1, 34.5 Hz, 4H), 3.96 (s, 4H), 2.11 (s, 3H), 1.97 (s, 4H), 1.71 (s, 3H).

pbdc-8a-COD$_{1:1}$. Yield: 93% (530 mg, 1.3 mmol). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.25 (s, 2H), 5.93 – 4.76 (m, 6H), 3.86 (d, *J* = 67.8 Hz, 4H), 2.07 (d, *J* = 29.1 Hz, 3H), 1.96 (s, 7H), 1.71 (s, 3H).

General procedure for Zr-polyMOF synthesis. Procedure was adapted and modified from a previously published report (Ayala et al., *Chem. Commun.*, **2017**, *53*, 3058-3061). The polymer ligand (0.03 mmol by monomer repeat unit), $ZrCl_4$ (0.037 mmol), and 2 mL of DEF were added to a 20 mL scintillation vial. After the solution became clear, 2 mL of formic acid was added. The vial was heated at 135 °C for 48 h. The resultant film was washed by exchanging solvent with copious amounts of DMF, followed by copious amounts of methanol.

General procedure for IRMOF-type polyMOF synthesis. The IRMOF-type polyMOFs were prepared by adapting a previously reported procedure (Zhang et al., *Angew. Chem. Int. Ed.*, **2015**, *54*, 6152-6157). The appropriate copolymer ligand (0.0250 mmol by monomer repeat unit), $Zn(NO_3)_2 \cdot 6H_2O$ (0.125 mmol), and 1.3 mL of DMF were mixed in a 20 mL scintillation vial. The vial was placed in a pre-heated oven at 100 °C for 24 h.

The resultant off-white powders were cleaned by centrifugation (4000 rpm), and extensive washing by solvent-exchange of DMF (5x5 mL of DMF). The samples were kept in DMF until further studies were performed.

Analytical Characterization

Gel-permeation chromatography (GPC) conditions for analysis of copolymer esters. Gel-permeation chromatography was performed in DMF (0.7 mL/min) using a Malvern GPC equipped with D4000 single-pore column and D-6000M general-purpose mixed-bed weight divinylbenzene column connected in series to determine molecular weights and molecular weight distributions, M_w/M_n, of our polymers. The solutions were filtered through 0.4 μm PTFE membrane before being injected into either GPC instrument. Narrow poly (methyl methacrylate) (PMMA) was used as the calibration standard.

PXRD Analysis. *For UiO-66 polyMOFs:* The synthesized materials were collected by filtration, washed with copious amounts of DMF, followed by copious amounts of methanol, and dried for ~20 minutes before data collection. *For IRMOF-1 polyMOFs:* the samples were loaded on silicon crystal sample holders while still wet with DMF. PXRD data were collected at ambient temperature on a Bruker D8 Advance diffractometer at 40 kV and 40 mA for Cu Kα (λ = 1.5418 Å), with a scan speed of 0.5 s/step, a step size of 0.02° in 2θ, and a 2θ range of 5−50°.

^{1}H NMR Digestions. *For block-polyUiO-66-PEG.* To ~5 mg of material was added 500 μL solution containing 100 μL of 1M NaOD and 400 μL DMSO-d_6. Samples were sonicated at 40 °C for 1 h. Then, samples were placed in an oven at 40 °C overnight. The remaining solids were filtered through 0.4 μm PTFE membranes and the solution was analyzed by ^{1}H NMR. *For block-polyUiO-66-COD$_{m:n}$.* Samples were filtered and washed with copious amounts of DMF, methanol, and acetone to remove any impurities. About 10 mg of material was dissolved in 600 μL DMSO-d$_6$ using 10 μL of 50% HF in water to digest the polyMOF. *For all polyIRMOF-1 samples.* About 5 mg of polyMOF was washed with DMF and CH_2Cl_2. To the samples was added a solution containing 600 μL of DMSO-*d*$_6$ and 5 μL of DCl. The mixture was sonicated at room temperature for 1 h. The solution was used for ^{1}H NMR analysis.

Scanning Electron Microscopy (SEM). polyUiO-66 samples were transferred to conductive carbon tape on a sample holder, and coated using a Ir-sputter coating for 7 sec. A Philips XL ESEM instrument was used for acquiring images using a 10 kV energy source under vacuum at a working distance at 10 mm.

Dynamic Light Scattering (DLS). Polymers were dissolved in *N*,*N*-diethylformamide at 5 mg/mL, sonicated for 30 minutes, and filtered through 0.45 micron PTFE filters into pre-cleaned quartz cuvettes prior to analysis. DLS was performed on a Malvern Zetasizer ZS90 (Malvern, UK) at both 13° and 90°. Hydrodynamic radii were determined from distribution fits to the autocorrelation functions using number-averaged weighed values.

N$_2$-Sorption Measurements. Prior to analysis, the materials were washed by exchanging the solvent with DMF three times for one day, then with methanol five times day for two one day, and finally with CH_2Cl_2 five times a day for one day. About 40-50 mg of the samples were transferred to pre-weighed sample tubes, and the samples were evacuated in a vacuum line until solvent was evaporated. The crystals were activated using an ASAP 2020 Adsorption analyzer under vacuum at 70 °C for 10h. After degassing, the sample tube was reweighed to obtain an accurate mass measurement for the degassed sample. All measurements were obtained at 77K using a liquid nitrogen bath.

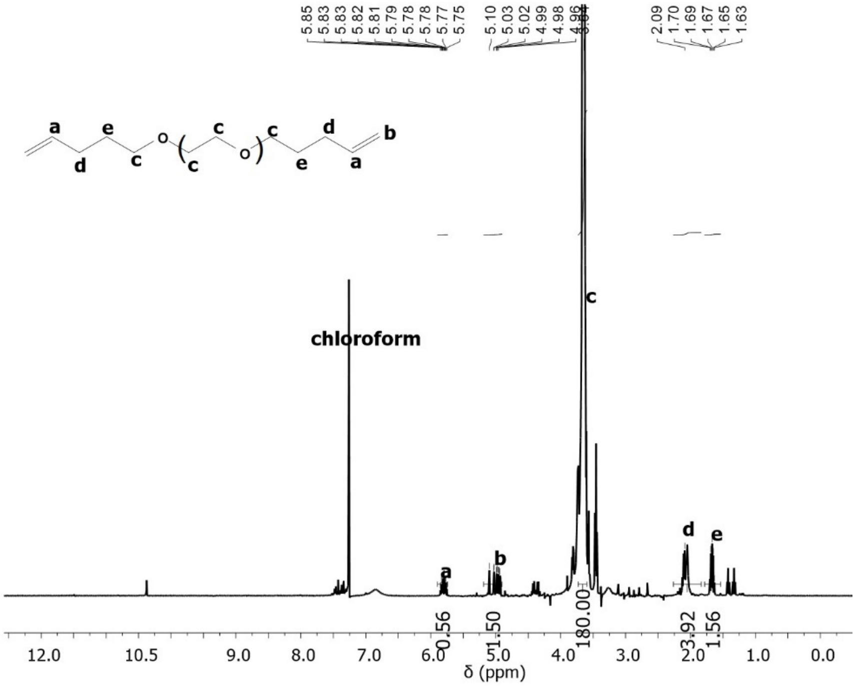


Figure S1. ^{1}H NMR of 1,2-bis(pent-4-en-1-yloxy)PEG$_{2000}$.

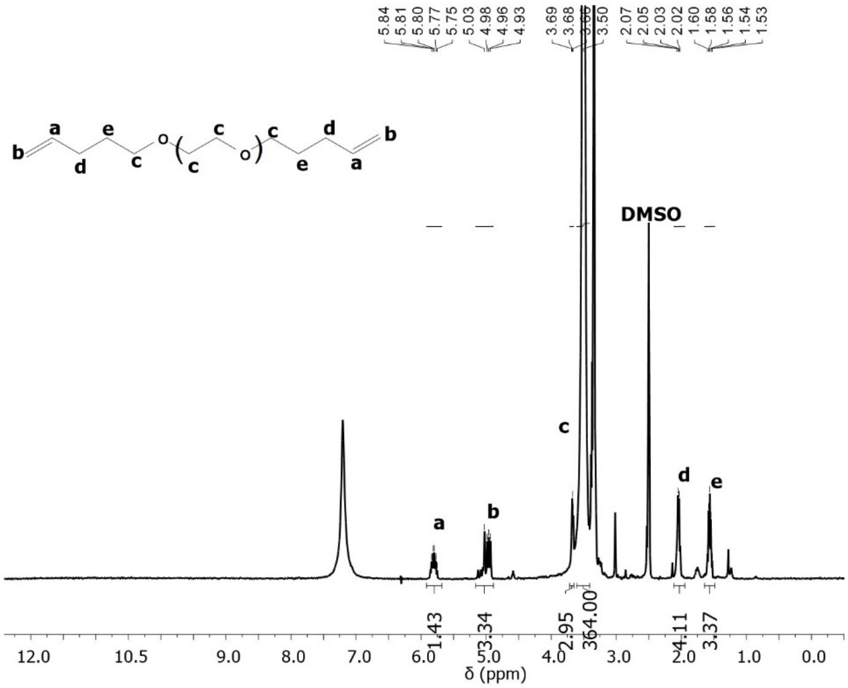


Figure S2. ^{1}H NMR of 1,2-bis(pent-4-en-1-yloxy)PEG$_{4000}$.

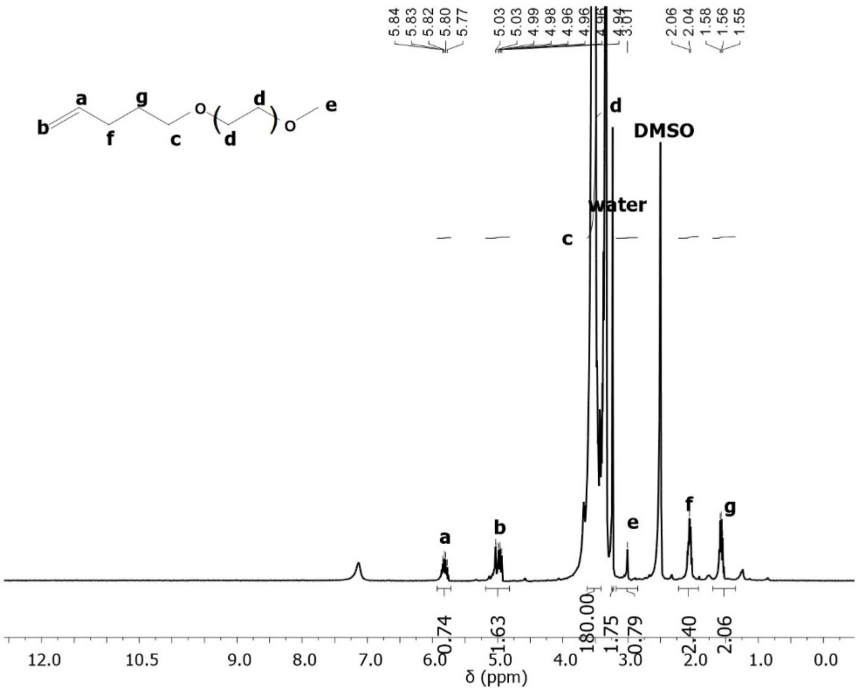


Figure S3. ^{1}H NMR of 5-MeOPEG$_{2000}$-1-pentene.

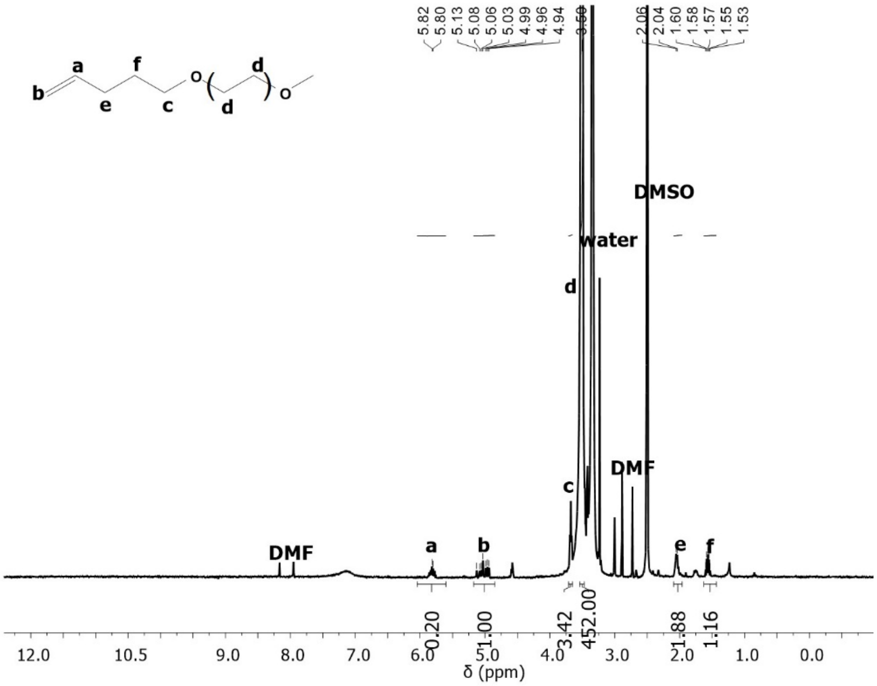


Figure S4. ^{1}H NMR of 5-MeOPEG$_{5000}$-1-pentene.

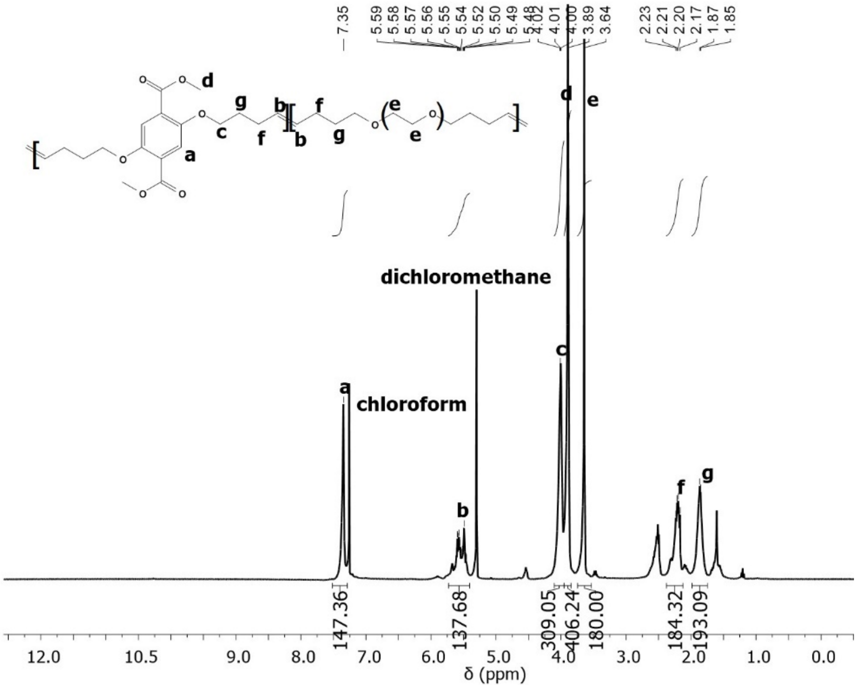


Figure S5. ^{1}H NMR of pbdc-8e-PEG$_{2000}$-2%.

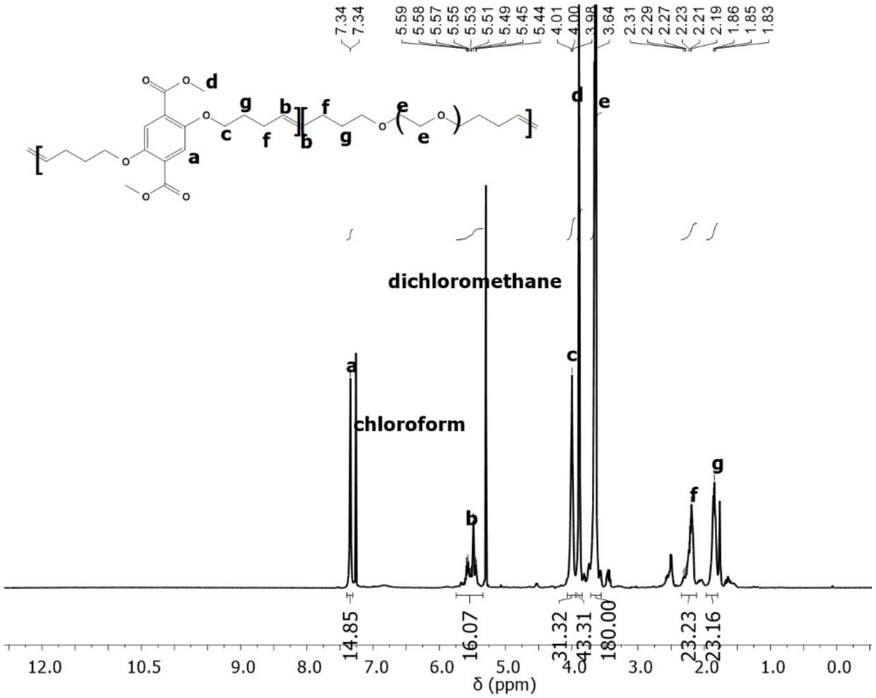


Figure S6. ^{1}H NMR of pbdc-8e-PEG$_{2000}$-20%.

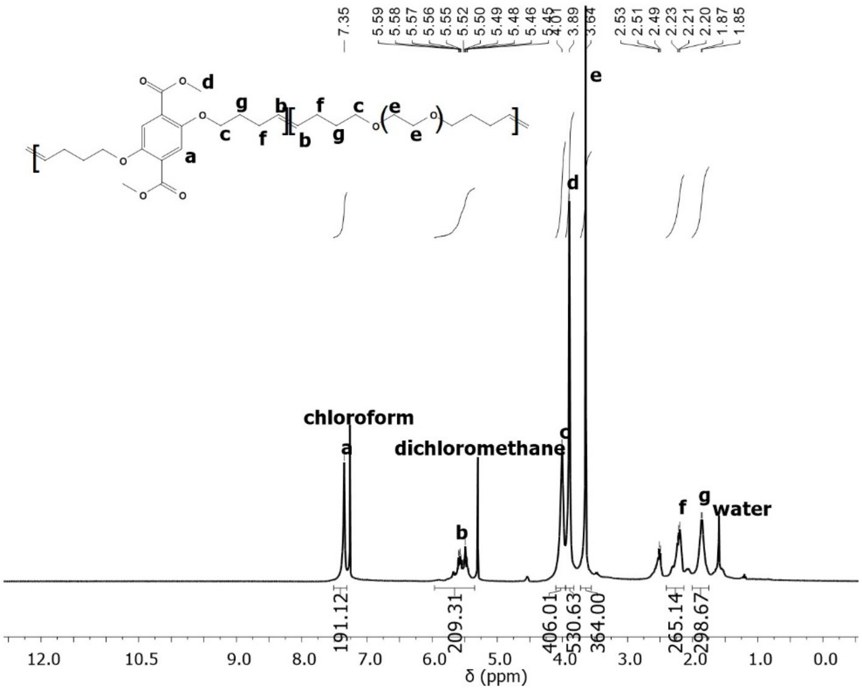


Figure S7. ^{1}H NMR of pbdc-8e-PEG$_{4000}$-1%.

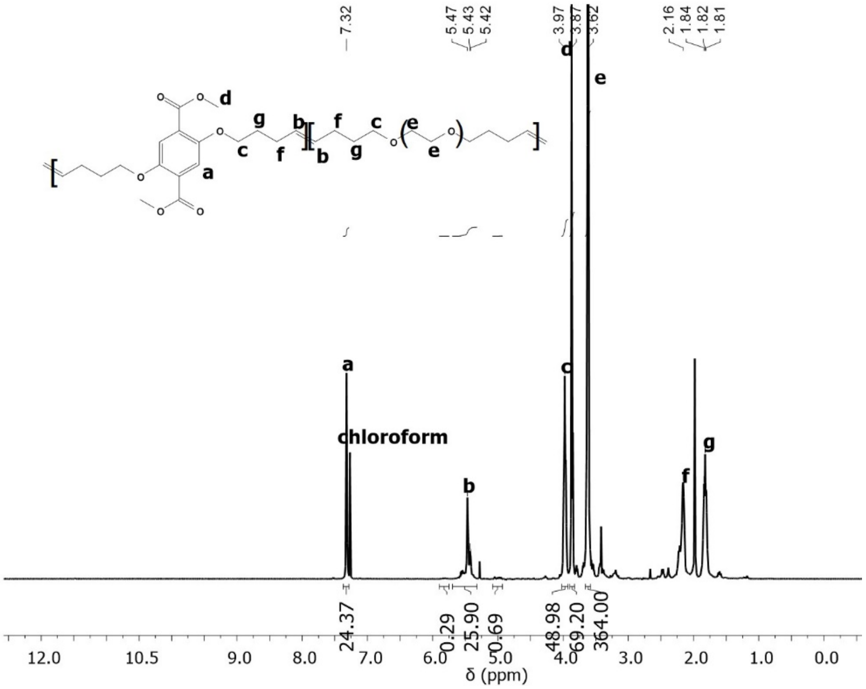


Figure S8. ^{1}H NMR of pbdc-8e-PEG$_{4000}$-10%.

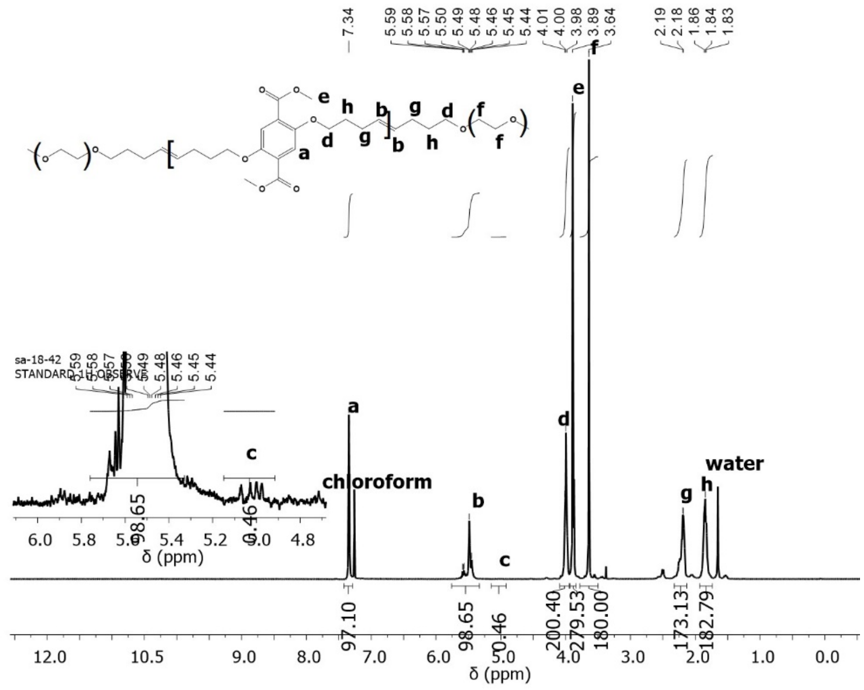


Figure S9. ^{1}H NMR of crude pbdc-8e-PEG$_{2000}$OMe.

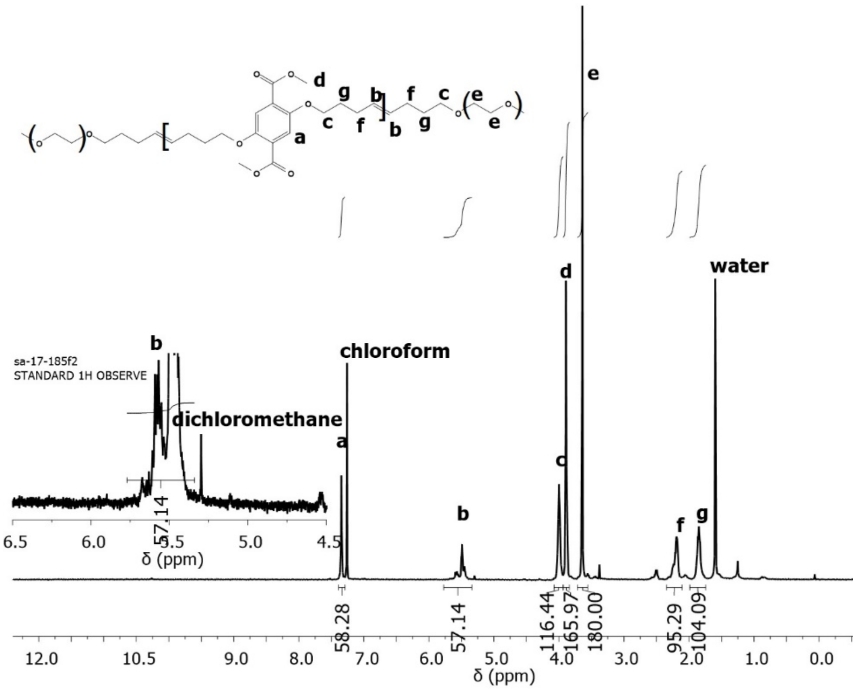


Figure S10. ^{1}H NMR of pbdc-8e-PEG$_{2000}$OMe. End-group analysis was used to determine the purity of the AB$_2$ copolymer.

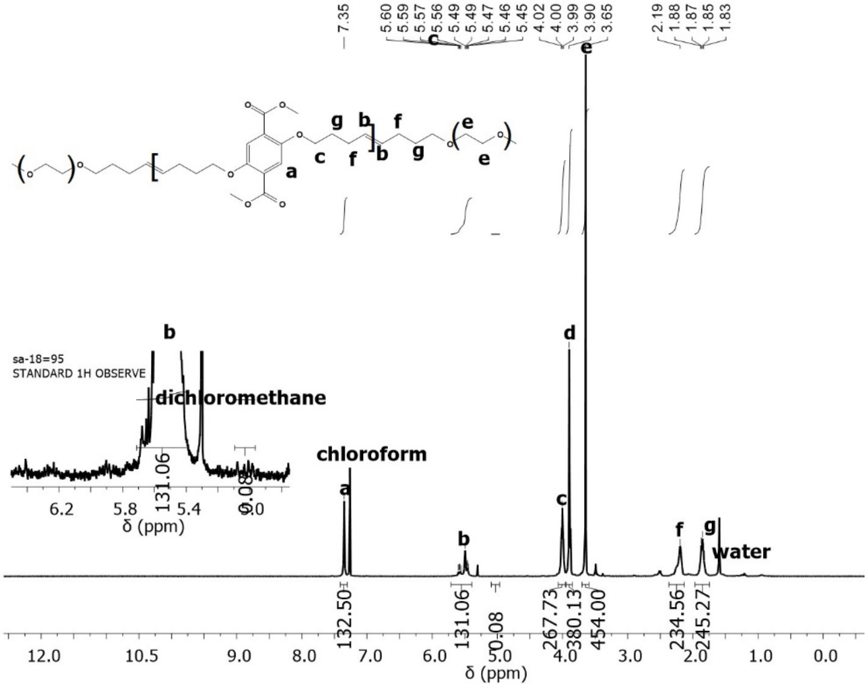


Figure S11. ^{1}H NMR of crude pbdc-8e-PEG$_{5000}$OMe.

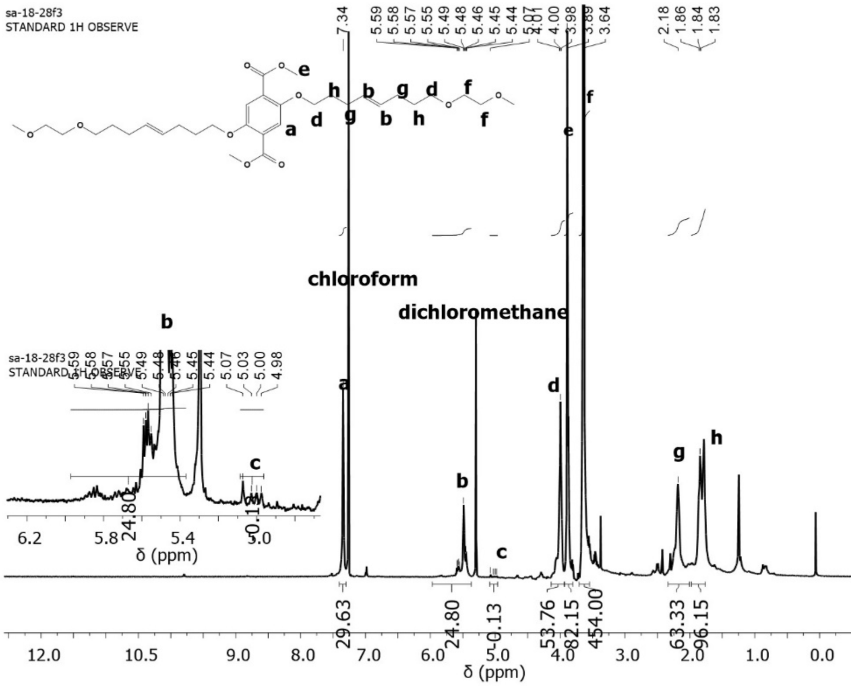


Figure S12. ^{1}H NMR of pbdc-8e-PEG$_{5000}$OMe. End-group analysis was used to determine the purity of the AB$_2$ copolymer.

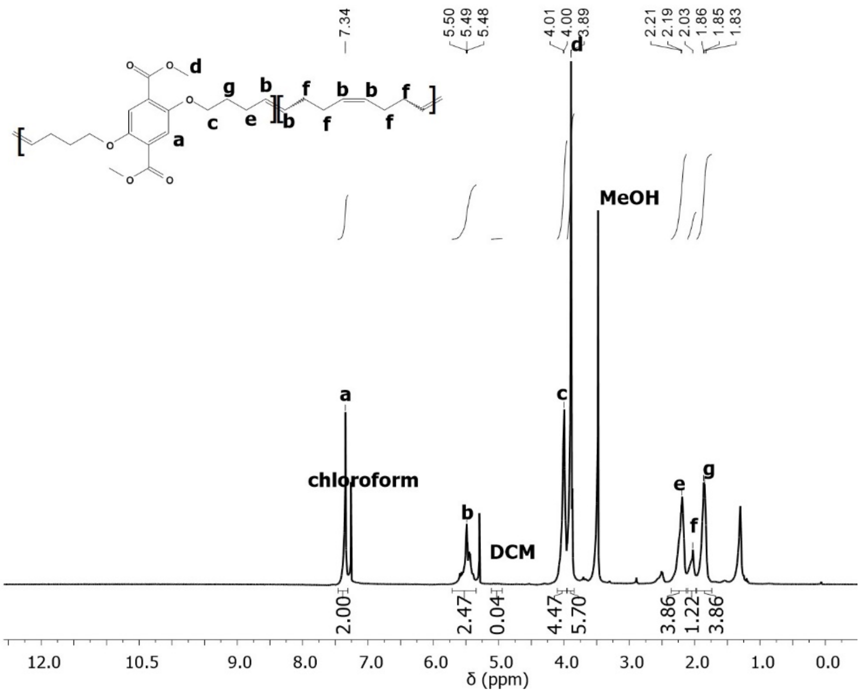


Figure S13. ^{1}H NMR of pbdc-8e-COD$_{10:1}$.

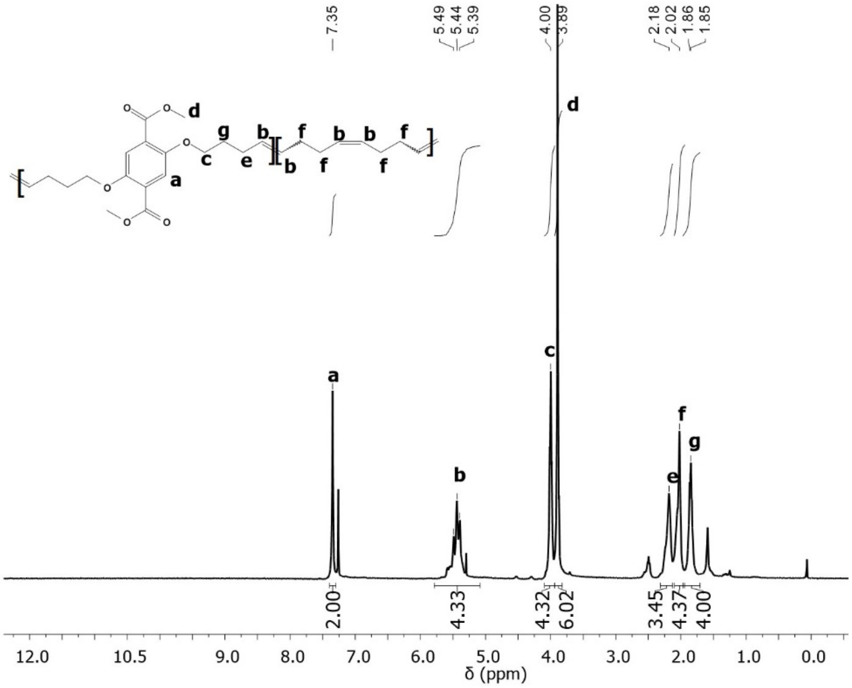


Figure S14. ^{1}H NMR of pbdc-8e-COD$_{2:1}$.

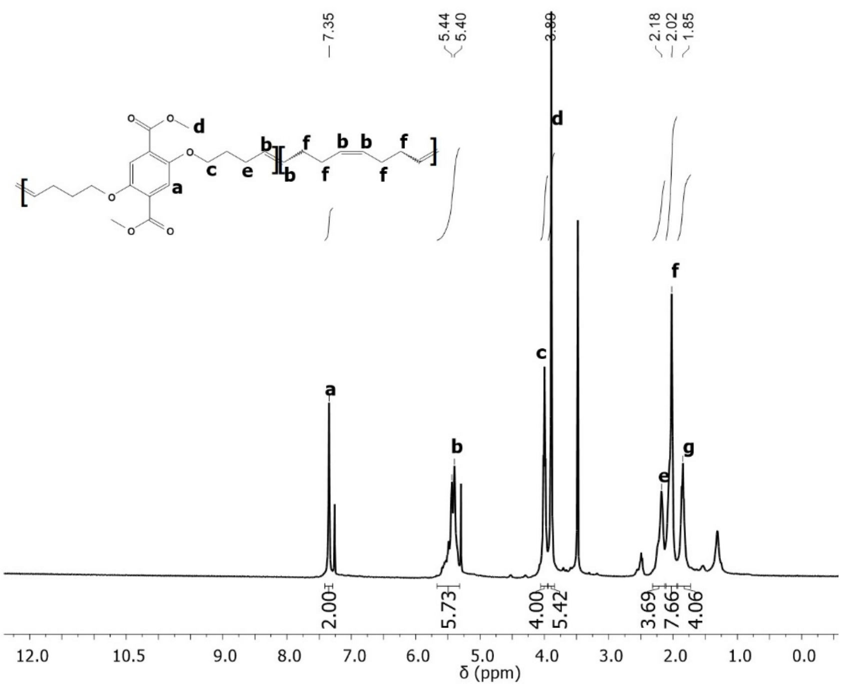


Figure S15. ^{1}H NMR of pbdc-8e-COD$_{1:1}$.

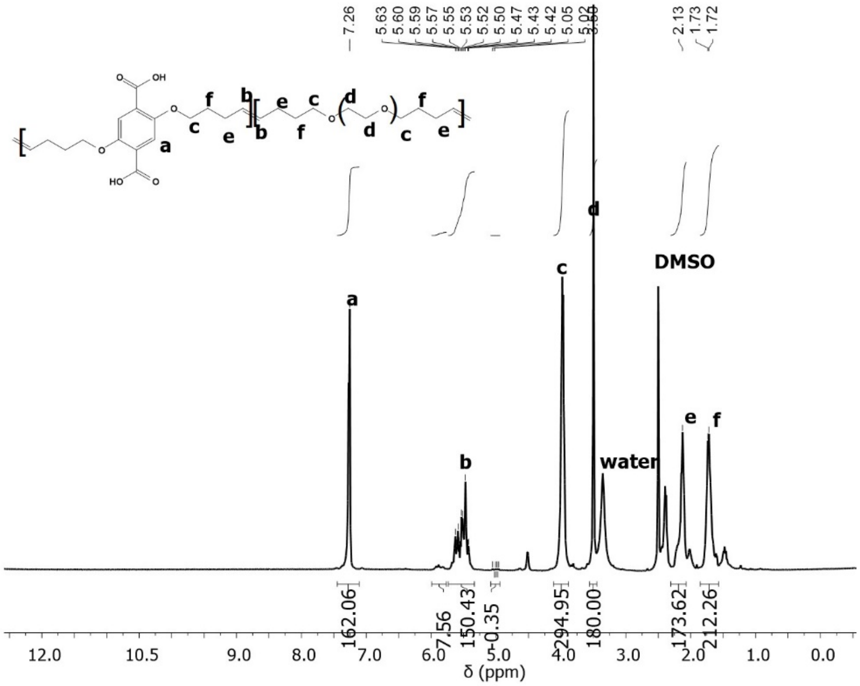


Figure S16. ^{1}H NMR of pbdc-8a-PEG$_{2000}$-2%.

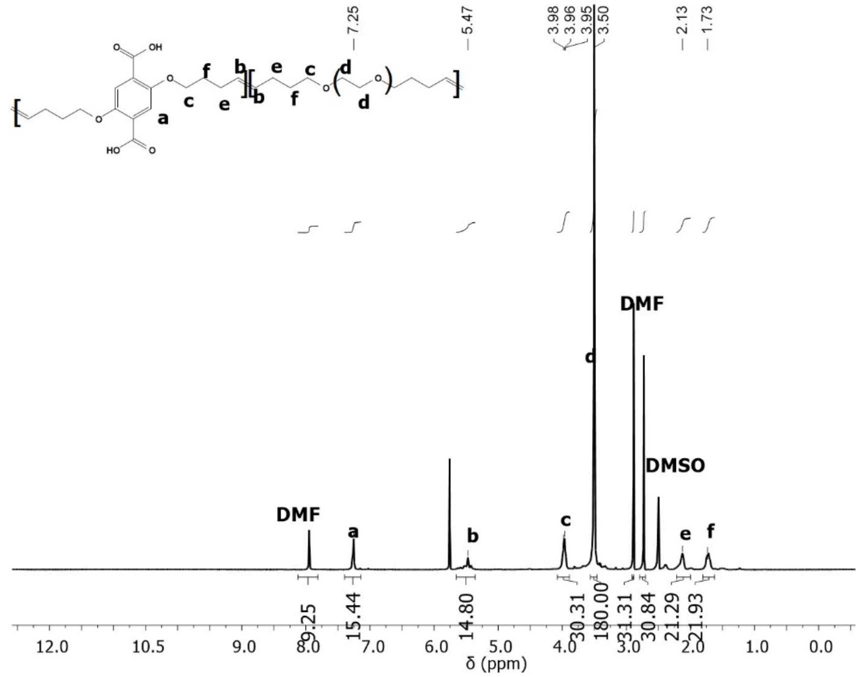


Figure S17. ^{1}H NMR of pbdc-8a-PEG$_{2000}$-20%.

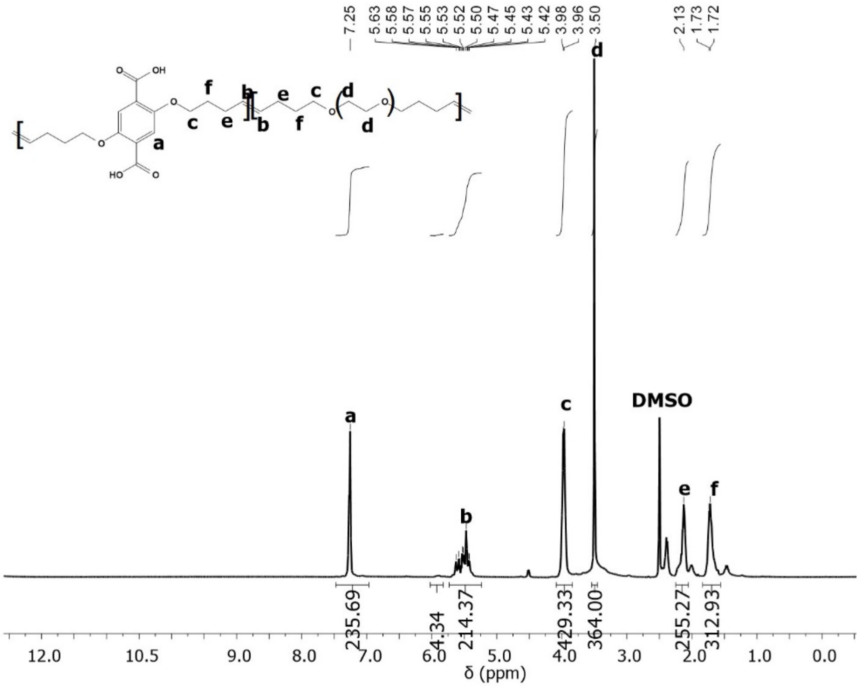


Figure S18. ^{1}H NMR of pbdc-8a-PEG$_{4000}$-1%.

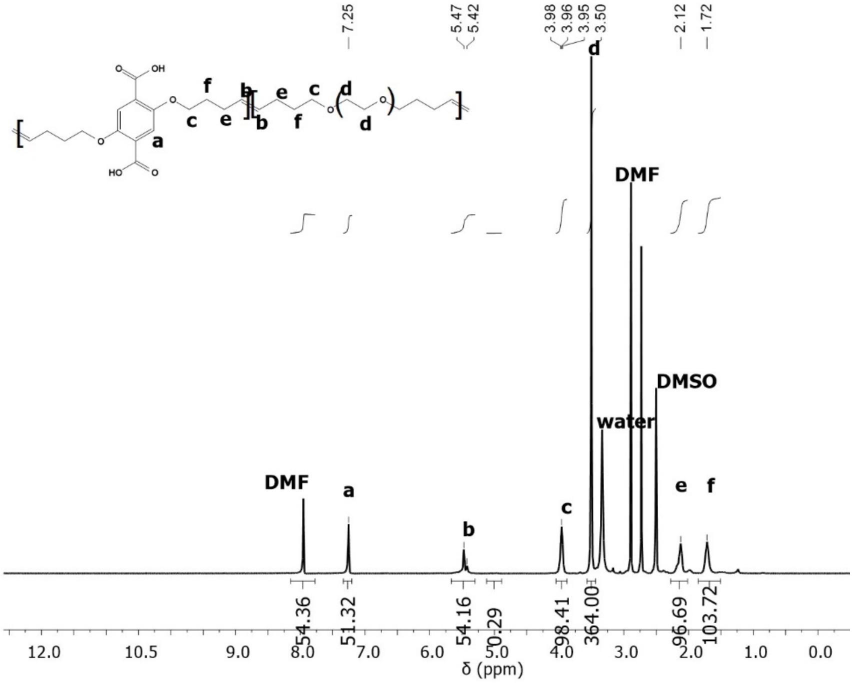


Figure S19. ^{1}H NMR of pbdc-8a-PEG$_{4000}$-10%.

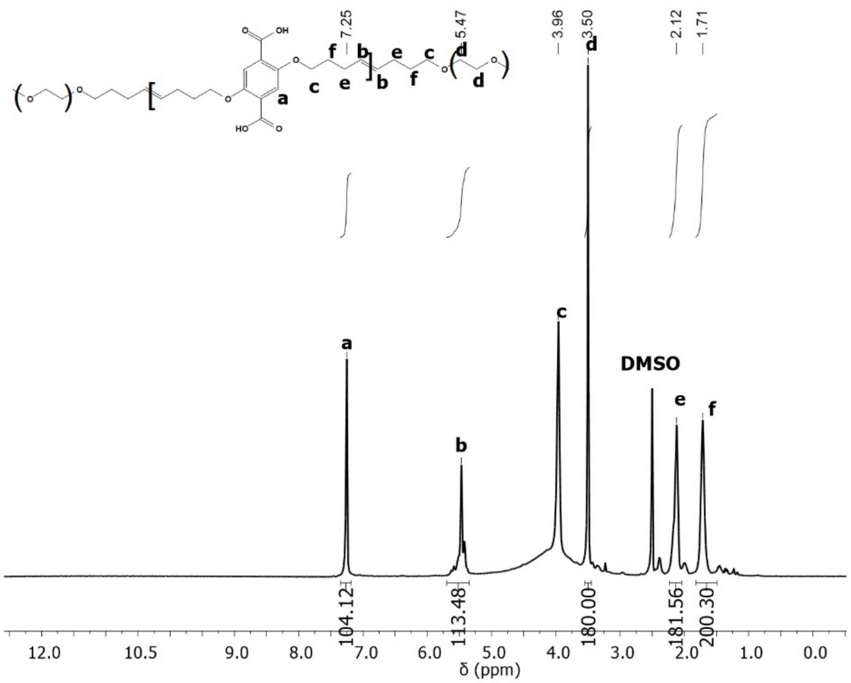


Figure S20. ^{1}H NMR of crude pbdc-8a-PEG$_{2000}$OMe.

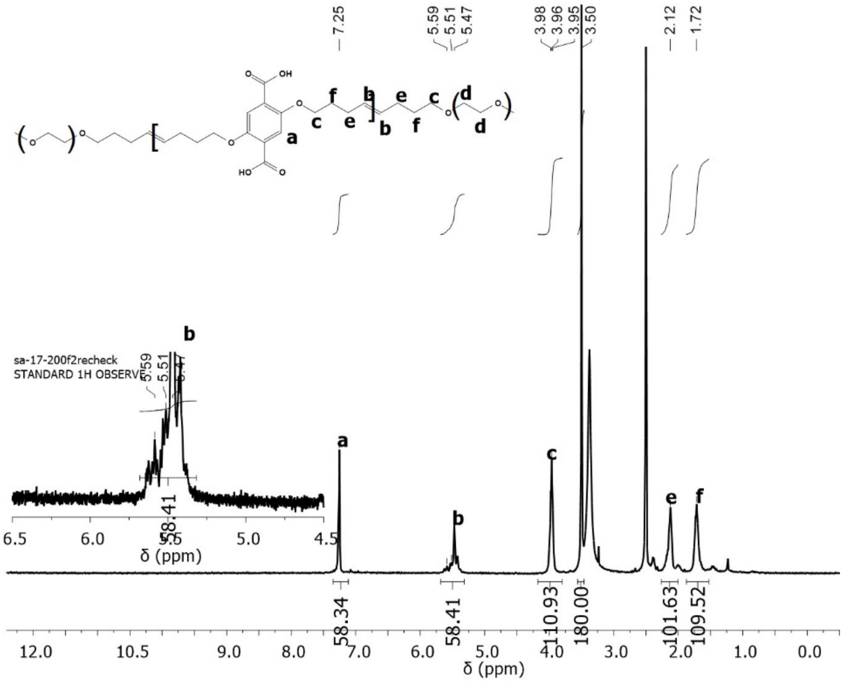


Figure S21. ^{1}H NMR of pbdc-8a-PEG$_{2000}$OMe.

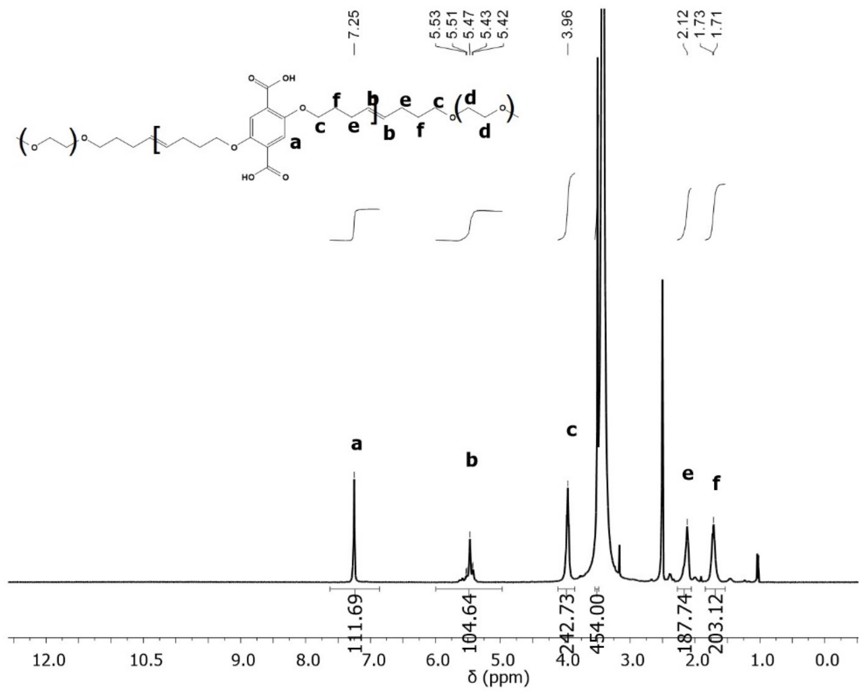


Figure S22. ^{1}H NMR of crude pbdc-8a-PEG$_{5000}$OMe.

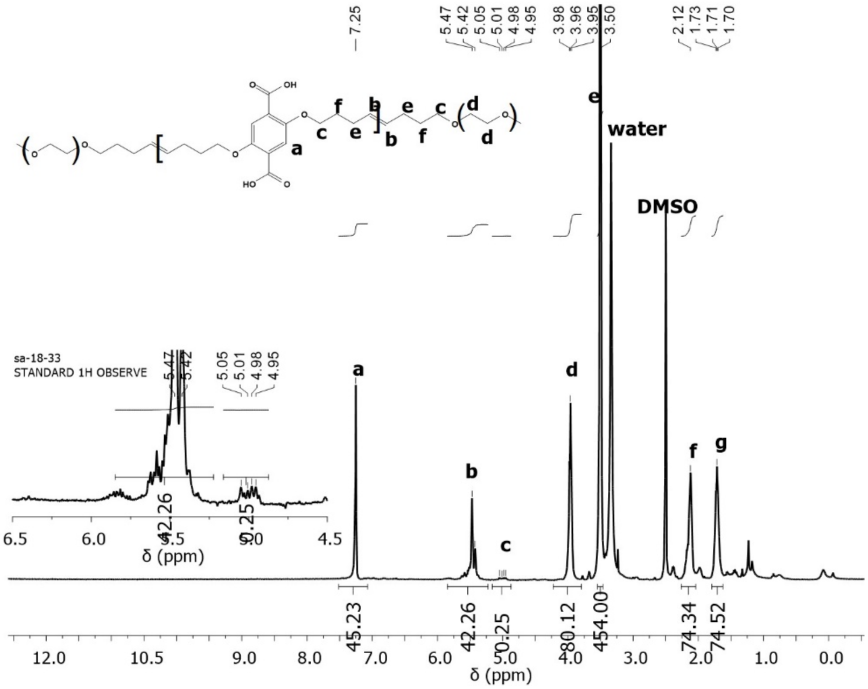


Figure S23. ^{1}H NMR of pbdc-8a-PEG$_{5000}$OMe.

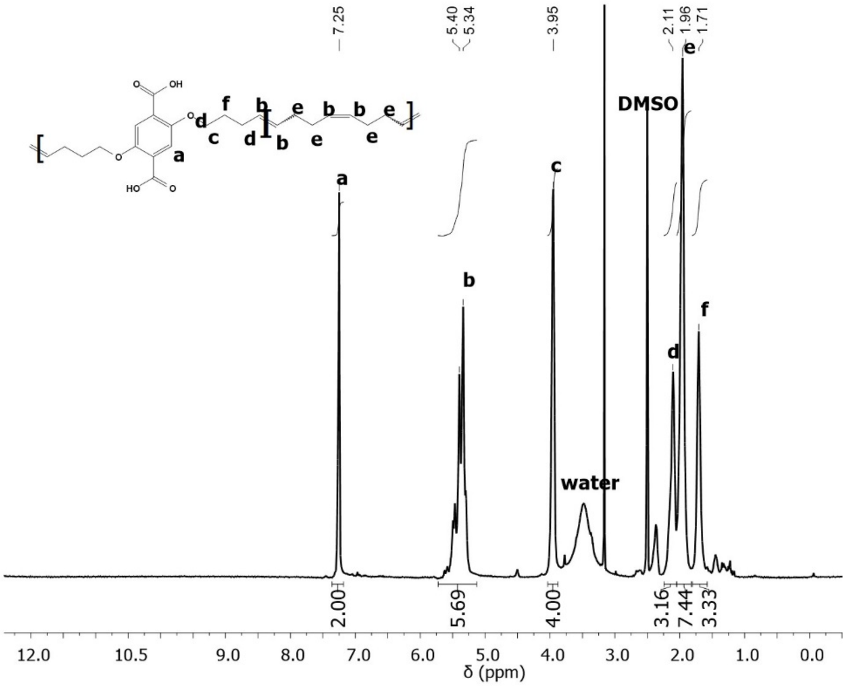


Figure S24. ^{1}H NMR of pbdc-8a-COD$_{1:1}$.

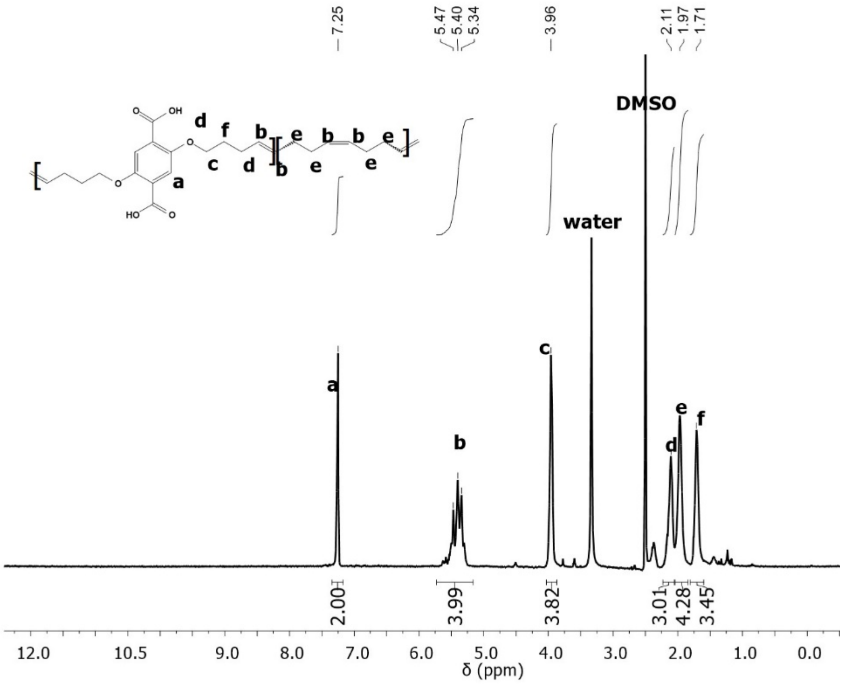


Figure S25. ^{1}H NMR of pbdc-8a-COD$_{2:1}$.

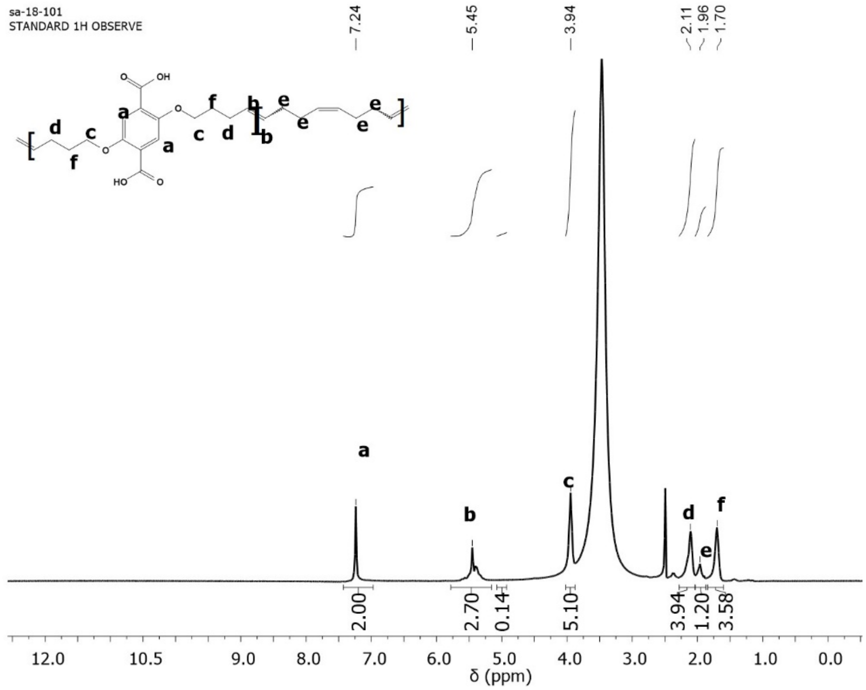


Figure S26. ^{1}H NMR of pbdc-8a-COD$_{10:1}$.

Table S1. Ratio of bdc-8e to co-monomer.

Ligand	**[a] Ratio of bdc-8e: co-monomer (^{1}H NMR)**
pbdc-8e-PEG$_{2000}$-2%	1: 0.63
pbdc-8e-PEG$_{2000}$-20%	1: 6.4
pbdc-8e-PEG$_{4000}$-1%	1: 0.91
pbdc-8e-PEG$_{4000}$-10%	1: 7.5
pbdc-8e-PEG$_{2000}$OMe (crude)	1: 0.91
pbdc-8e-PEG$_{2000}$OMe	1: 1.6
pbdc-8e-PEG$_{5000}$OMe (crude)	1: 1.6
pbdc-8e-PEG$_{5000}$OMe	1: 7.5
pbdc-8e-COD$_{1:1}$	1:1
pbdc-8e-COD$_{2:1}$	1:0.50
pbdc-8e-COD$_{10:1}$	1:0.19

[a] Ratio of $(CH_3)_2$bdc-8e to co-monomer (ethylene glycol or COD) was determined by ^{1}H NMR.

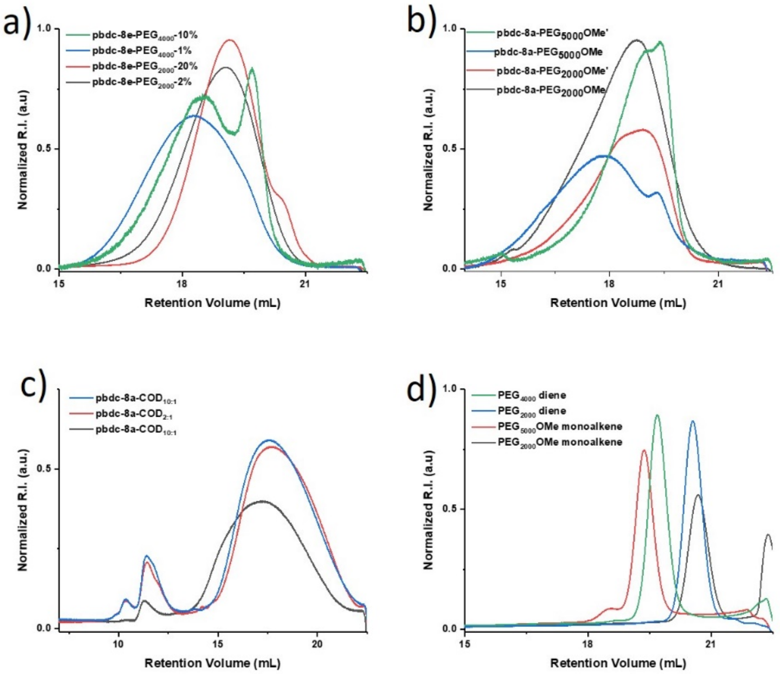


Figure S27. GPC traces obtained for polymers: a) pbdc-8e-PEG$_{Mn}$-x%; b) pbdc-8e-PEG$_{Mn}$OMe; c) pbdc-8e-COD$_{m:n}$; d) alkene-functionalized PEG macromonomers.

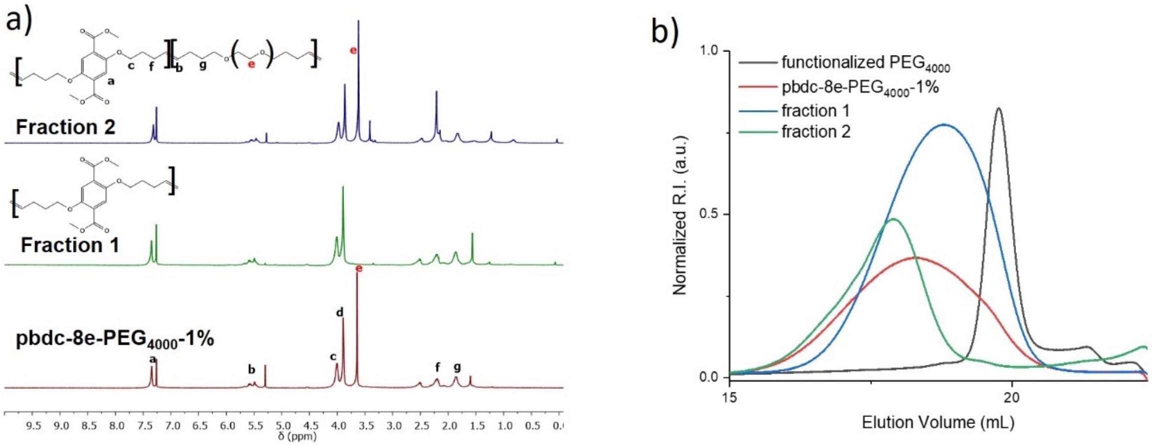


Figure S28. a) ^{1}H NMR and b) GPC trace of representative fractionated sample pbdc-8e-PEG$_{4000}$-1% is presented.

Table S2. Yields, compositions, and molecular weight of fractionated 8e-PEG$_{4000}$-1%

Ligand	**Yield %**	**(CH$_3$)$_2$bdc: ethylene glycol**	***M$_n$* (g/mol)**	***Đ***
Functionalized PEG$_{4000}$	**-**	-	10,600	1.07
pbdc-8e-PEG$_{4000}$ crude-1%	**-**	1.1: 1	24,300	1.44
pbdc-8e-PEG$_{4000}$-1% fraction 1	64	1:0	20,800	1.10
pbdc-8e-PEG$_{4000}$-1% fraction 2	26	1:2	38,100	1.20

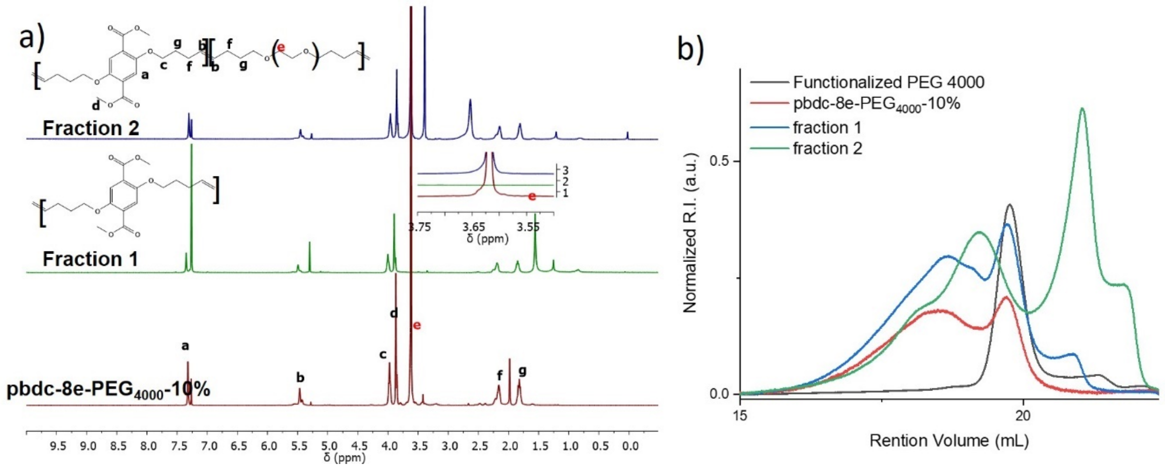


Figure S29. a) ^{1}H NMR and b) GPC trace of representative fractionated sample pbdc-8e-PEG$_{4000}$-10% is presented.

Table S3. Yields, compositions, and molecular weight of fractionated 8e-PEG$_{4000}$-10%

Ligand	**Yield%**	**$(CH_3)_2$bdc: ethylene glycol**	***M_n* (g/mol)**	***Đ***
Functionalized PEG$_{4000}$	-	-	10,600	1.07
pbdc-8e-PEG4000 crude	-	1: 7.5	18,700	1.50
pbdc-8e-PEG$_{4000}$-10% fraction 1	4	1: 0	16,000	2.15
pbdc-8e-PEG$_{4000}$-10% fraction 2	45	1: 6.1	22,000	1.54

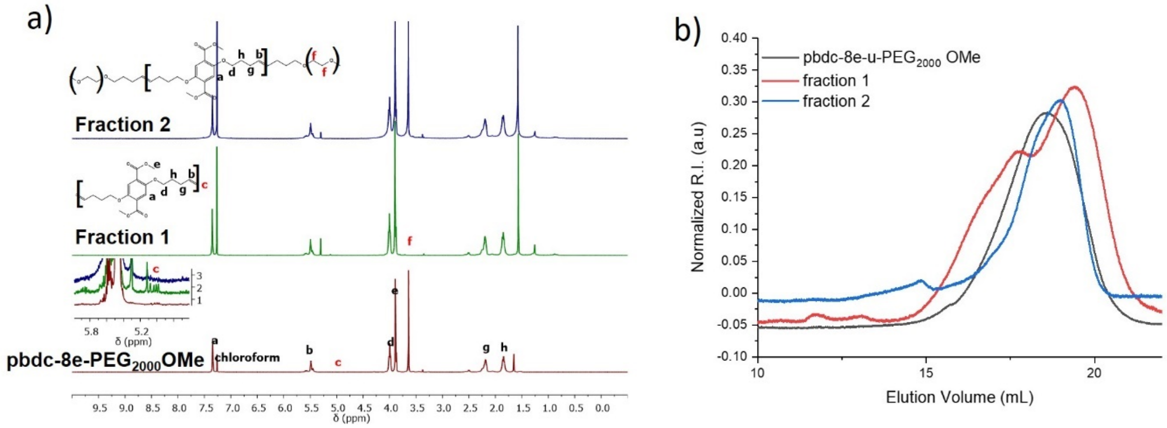


Figure S30. a) ^{1}H NMR and b) GPC trace of representative fractionated sample pbdc-8e-PEG$_{2000}$OMe is presented.

Table S4. Yields, compositions, and molecular weight of fractionated 8e-PEG$_{2000}$OMe.

Ligand	**Yield%**	**$(CH_3)_2$bdc: ethylene glycol**	**M_n (g/mol)**	**Đ**
pbdc-8e-PEG$_{2000}$OMe	-	1.1: 1	23,200	1.8
fraction 1	37	1: 0	17,100	2.1
fraction 2	18	1.1: 1	23,000	1.3

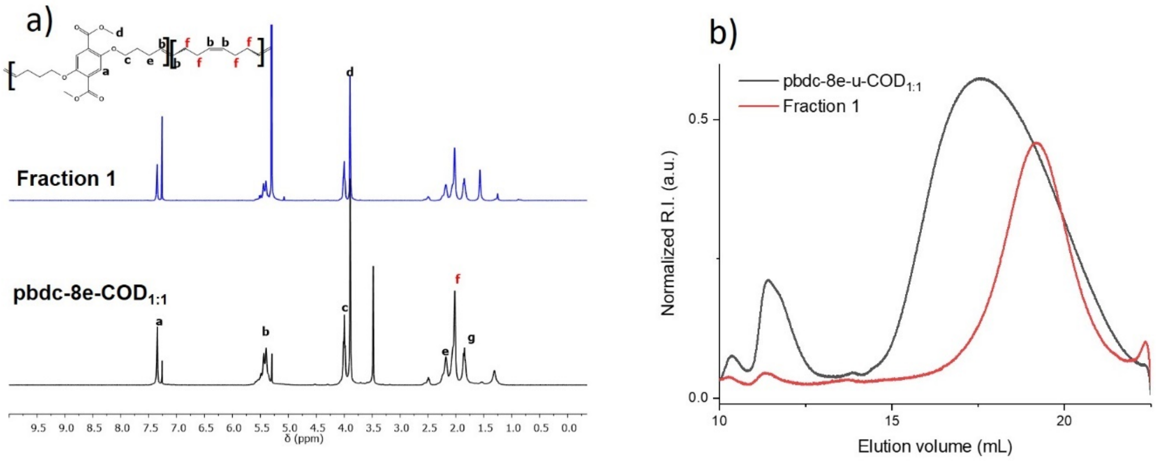


Figure S31. a) ^{1}H NMR and b) GPC trace of representative fractionated sample pbdc-8e-COD$_{1:1}$ is presented.

Table S5. Yields, compositions, and molecular weight of fractionated 8e-PEG$_{2000}$OMe.

Ligand	**Yield %**	**$(CH_3)_2$bdc: ethylene glycol**	***M_n* (g/mol)**	***Đ***
pbdc-8e-COD1:1	-	1:1	17,200	2.8
Fraction 1	45	1:1	14,400	1.6

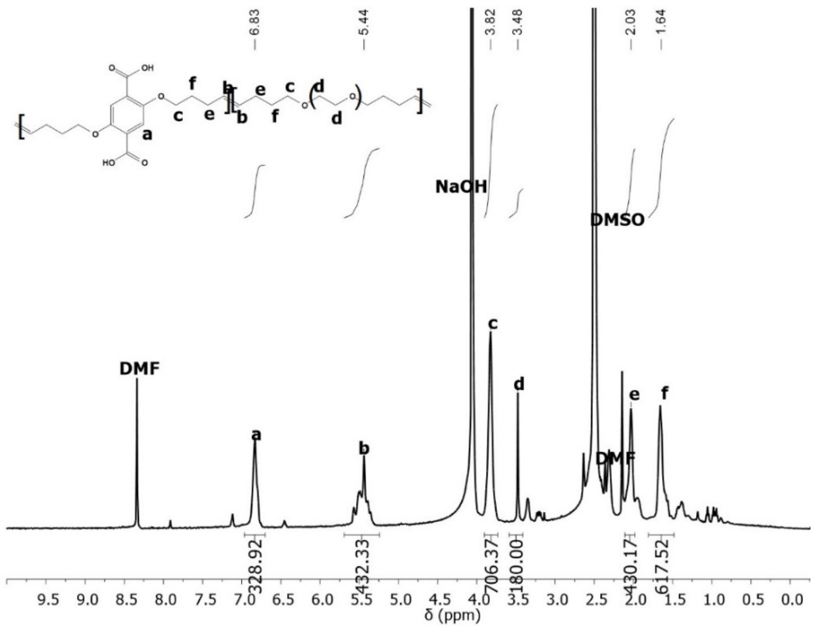


Figure S32. ^{1}H NMR of digested polyUiO-66 prepared from pbdc-8a-PEG$_{2000}$-2%.

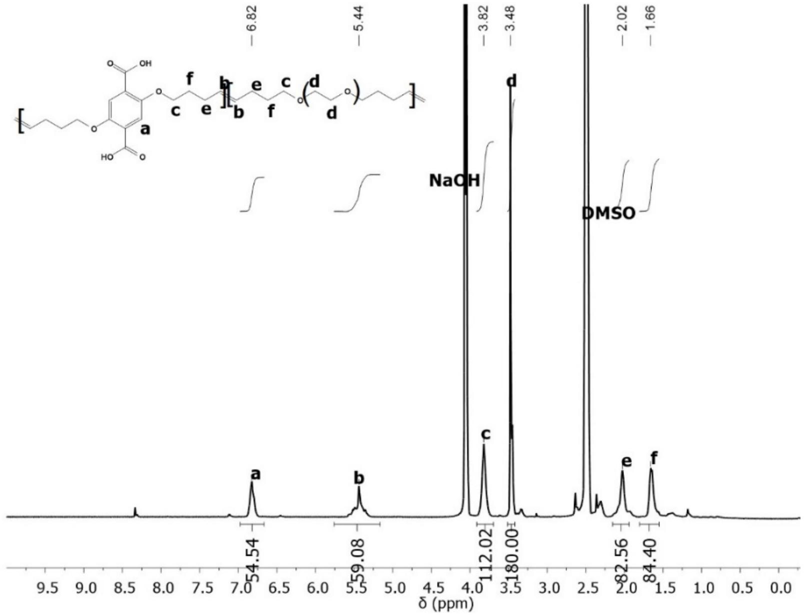


Figure S33. ^{1}H NMR of digested polyUiO-66 prepared from pbdc-8a-PEG$_{2000}$-20%.

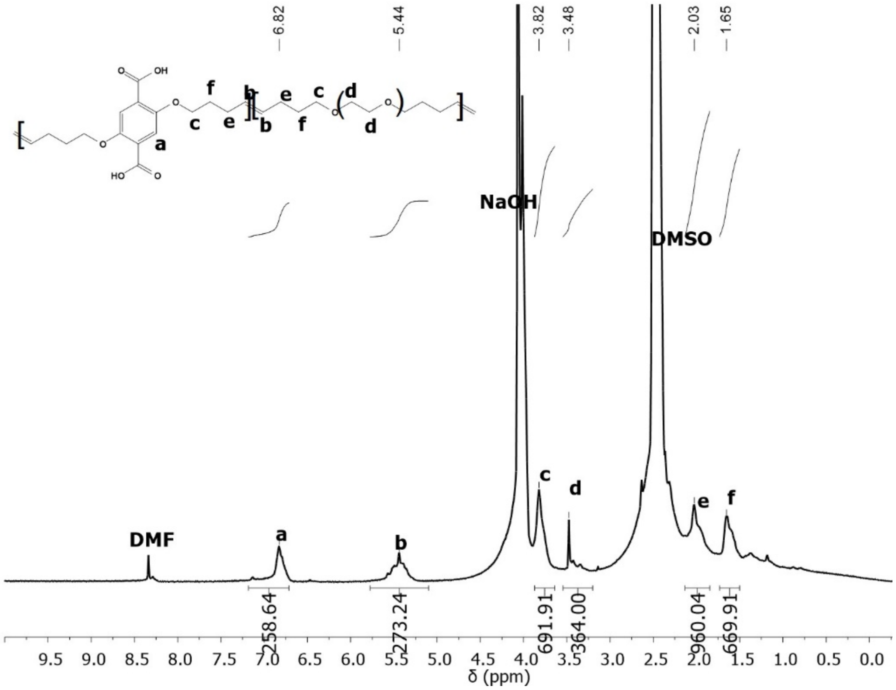


Figure S34. ^{1}H NMR of digested polyUiO-66 prepared from pbdc-8a-PEG$_{4000}$-1%.

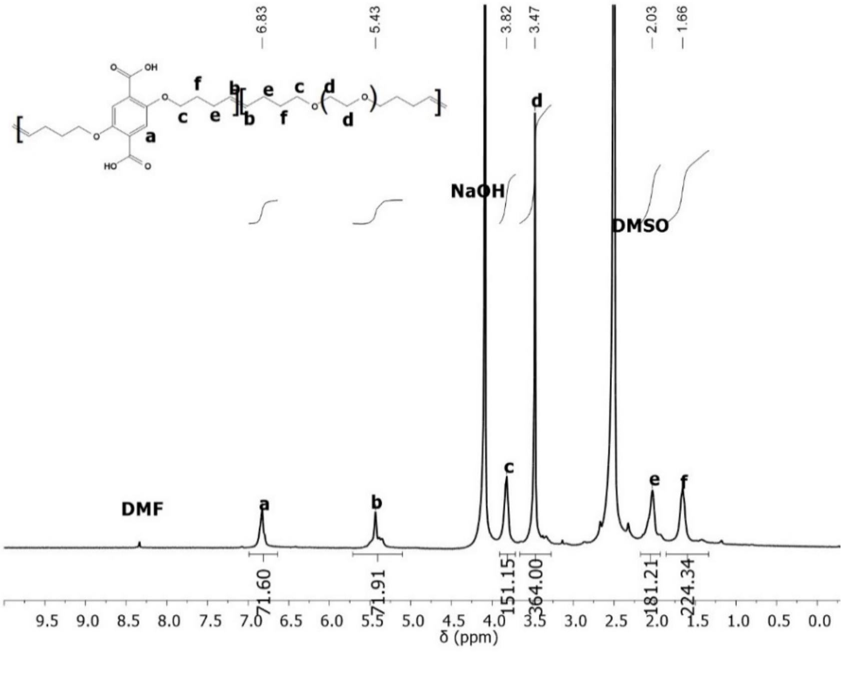


Figure S35. ^{1}H NMR of digested polyUiO-66 prepared from pbdc-8a-PEG$_{4000}$-10%.

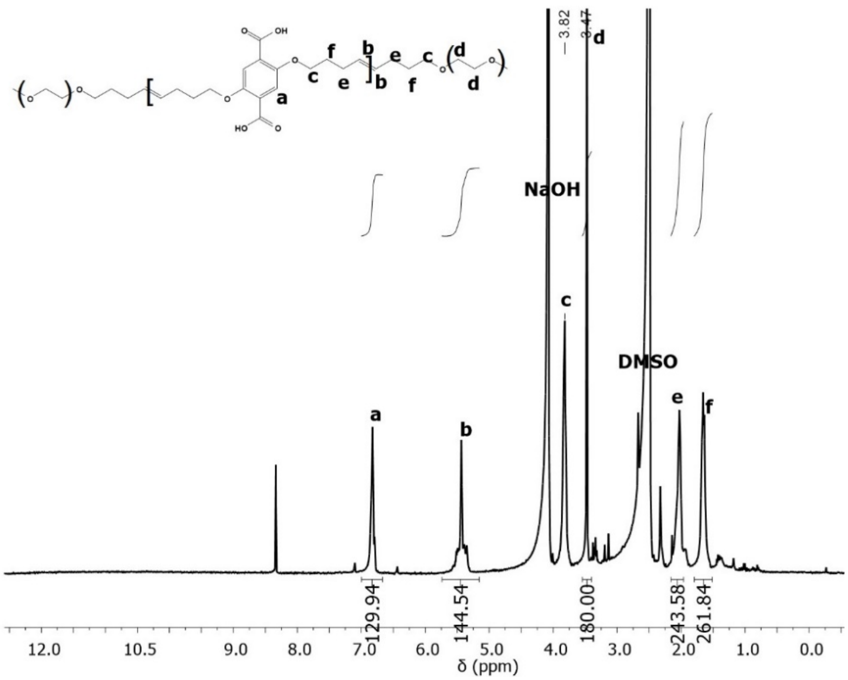


Figure S36. ^{1}H NMR of digested polyUiO-66 prepared from crude pbdc-8a-PEG$_{2000}$OMe.

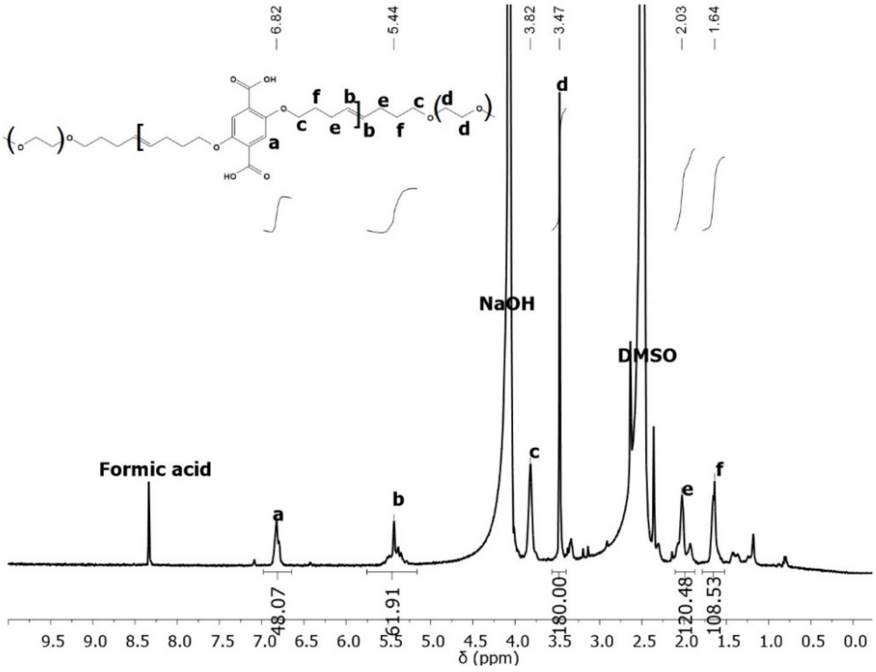


Figure S37. ^{1}H NMR of digested polyUiO-66 prepared from pbdc-8a-PEG$_{2000}$OMe.

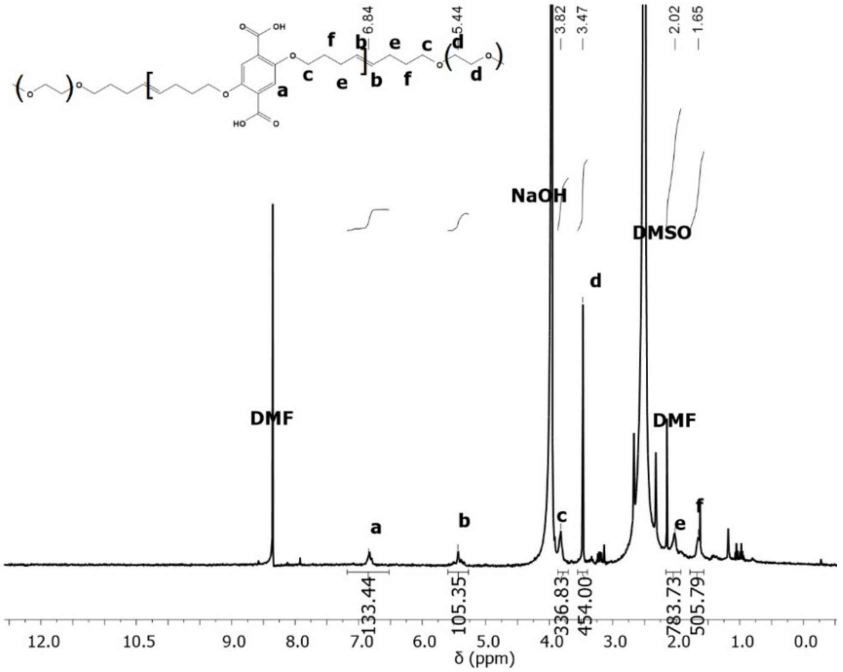


Figure S38. ^{1}H NMR of digested polyUiO-66 prepared from crude pbdc-8a-PEG$_{5000}$OMe.

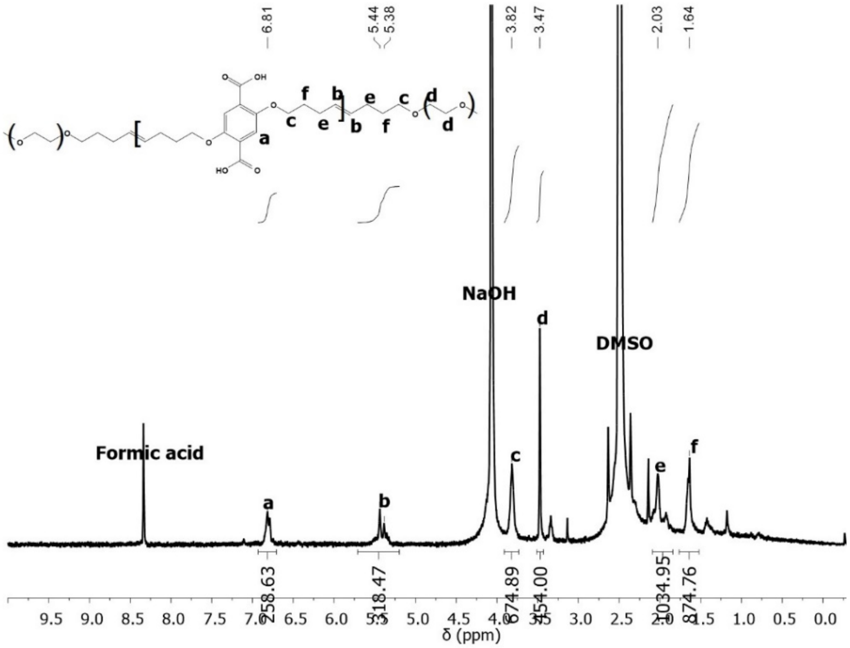


Figure S39. ^{1}H NMR of digested polyUiO-66 prepared from pbdc-8a-PEG$_{5000}$OMe.

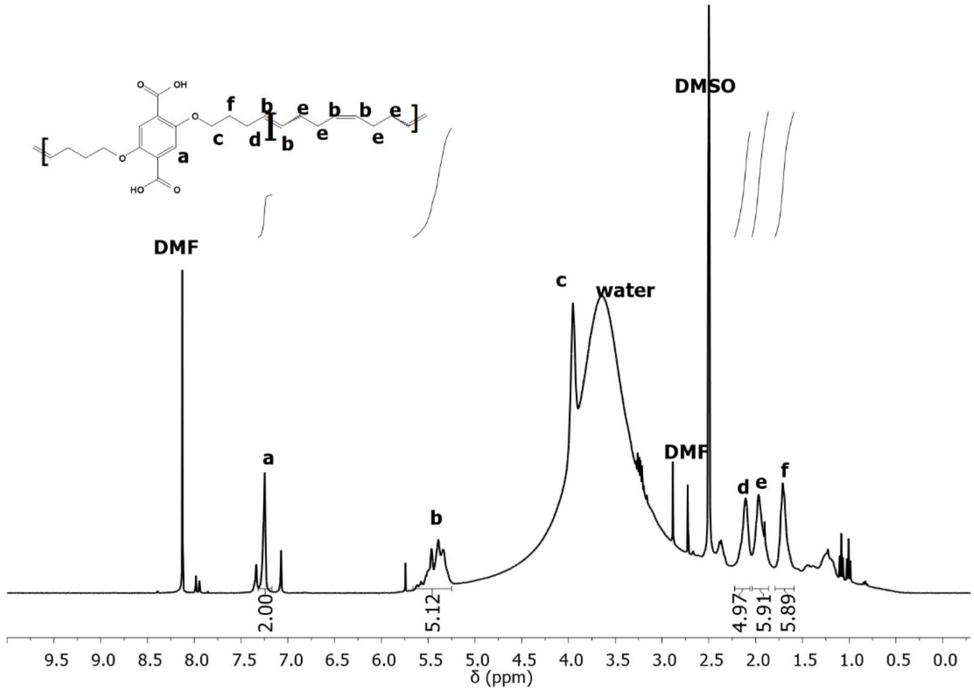


Figure S40. ^{1}H NMR of digested polyUiO-66 prepared from pbdc-8a-COD$_{1:1}$.

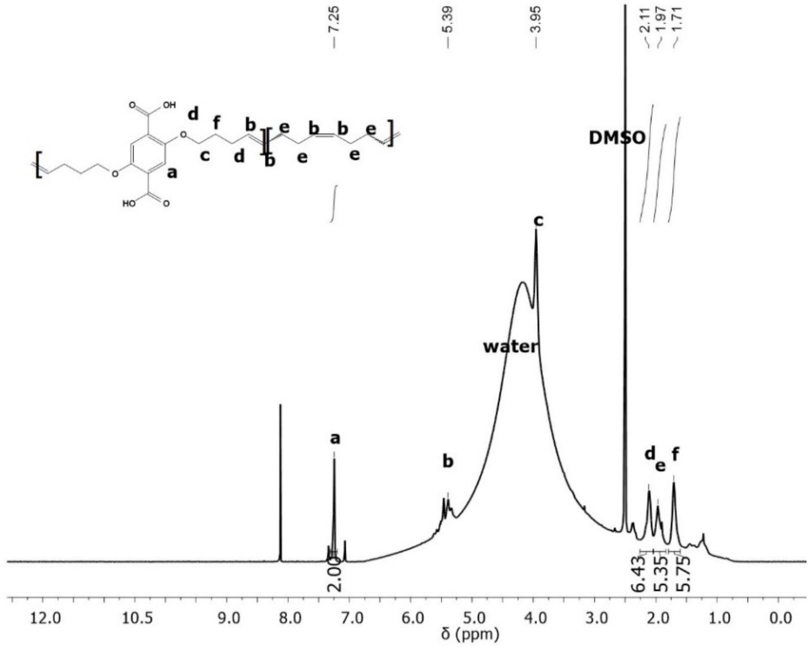


Figure S41. ^{1}H NMR of digested polyUiO-66 prepared from pbdc-8a-COD$_{2:1}$.

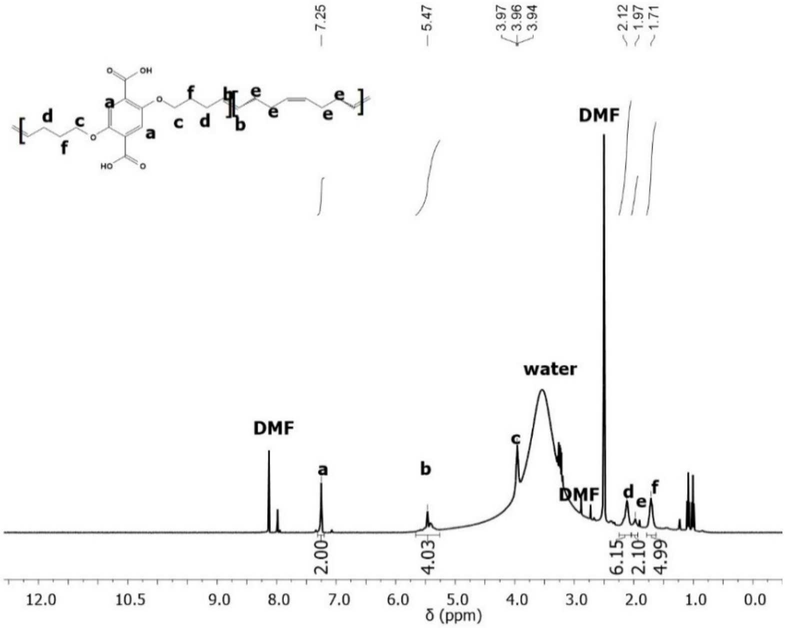


Figure S42. ^{1}H NMR of digested polyUiO-66 prepared from pbdc-8a-COD$_{10:1}$.

Table S6. Ratios of H_2bdc to co-monomer before and after digestion.

Ligand	**H_2bdc:co-monomer before digestion (^{1}H NMR)**	**H_2bdc:co-monomer after digestion (^{1}H NMR)**
[a] pbdc-8e-PEG$_{2000}$-2%	1.8:1	3.7:1
[a] pbdc-8e-PEG$_{2000}$-20%	1:5.8	1:1.6
pbdc-8e-PEG$_{4000}$-1%	1.3:1	1.4:1
pbdc-8e-PEG$_{4000}$-10%	1:3.3	1:2.5
[b] pbdc-8e-PEG$_{2000}$OMe (crude)	1.1:1	1.4:1
[b] pbdc-8e-PEG$_{2000}$OMe	1:1.6	1:1.8
pbdc-8e-PEG$_{5000}$OMe (crude)	1:2.0	1:1.7
pbdc-8e-PEG$_{5000}$OMe	1:5	1.7:1
[c] pbdc-8e-COD$_{1:1}$	1:1	1.5:1
[c] pbdc-8e-COD$_{2:1}$	2:1	2:1
[c] pbdc-8e-COD$_{10:1}$	10:1	5:1

[a] Dissolution of polyUiO-66 prepared from pbdc-8a-PEG$_{2000}$-2% and pbdc-8a-PEG$_{2000}$-20% ligands showed that the presence of PEG had significantly decreased in comparison to the amount of PEG present in the starting block polymer ligands (Fig. S37-S40). A possible explanation for this result may be that some of polymer chains were never incorporated into the lattice of the polyMOF and were washed prior to analysis by ^{1}HNMR digestions. [b] Digested samples of polyUiO-66 prepared from pbdc-8a-PEG$_{Mn}$OMe or pbdc-8a-PEG$_{2000}$OMe reveal that the ratio of H_2bdc to PEG in the polymer is retained even after digestion of the polymer (Fig. S41-S44). [c] For digested samples of polyUiO-66 prepared from pbdc-8a-COD$_{m:n}$, the ratio of H_2bdc to COD remains largely unchanged even after digestion of polyMOF samples, validating retention of structural integrity in the block polymer ligands (Fig. S45-S46).

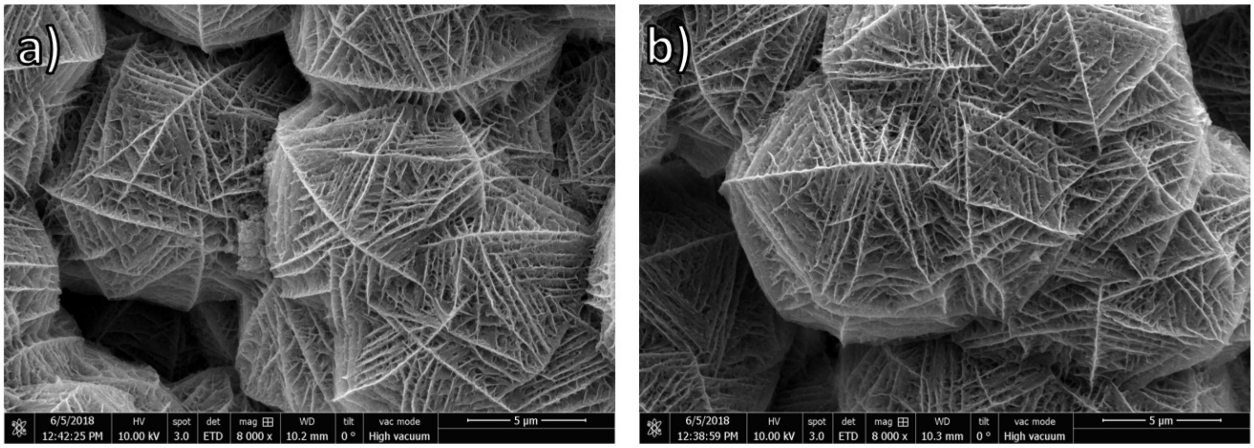


Figure S43. SEM images for polyIRMOF-1 prepared from pbdc-8a and physically mixed PEG$_{4000}$ at a) 1% loading and b) 10% loading.

Table S7. Hydrodynamic radii at 90° and 13° scattering angle for polymer ligands, and polyIRMOF-1 derived from pbdc-8a-PEG$_{4000}$-10%.

	Hydrodynamic radius (nm)	
Ligand	**90°**	**13°**
pbdc-8e-PEG$_{2000}$-2%	4.7	26.6
pbdc-8e-PEG$_{2000}$-20%	5.5	101
pbdc-8e-PEG$_{4000}$-1%	4.8	12.5
pbdc-8e-PEG$_{4000}$-10%	5.3	71.5
pbdc-8e-PEG$_{2000}$OMe	4.3	129
pbdc-8e-PEG$_{5000}$OMe	5.5	33.2
pbdc-8e-COD$_{1:1}$	7.9	>500
pbdc-8e-COD$_{2:1}$	6.8	53

pbdc-8e-COD$_{10:1}$	7.5	114
MOF		
polyIRMOF-1 (pbdc-8a-PEG$_{4000}$-10%)	274	308

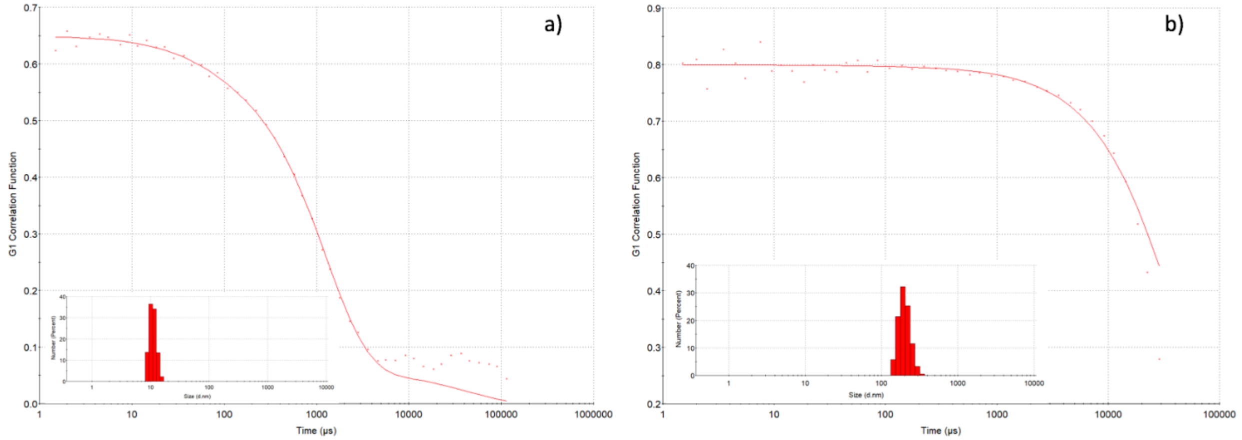


Figure S44. Correlation functions, distribution fits, and number-average size distributions (inset) at 90° (a) and 13° (b) scattering angle for pbdc-8a-PEG$_{2000}$-20%.

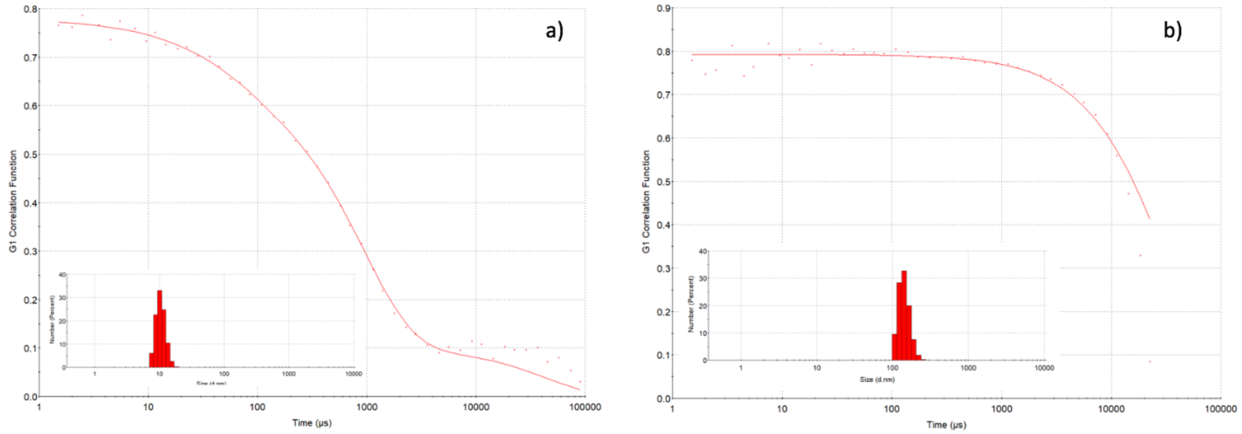


Figure S45. Correlation functions, distribution fits, and number-average size distributions (inset) at 90° (a) and 13° (b) scattering angle for pbdc-8a-PEG$_{4000}$-10%.

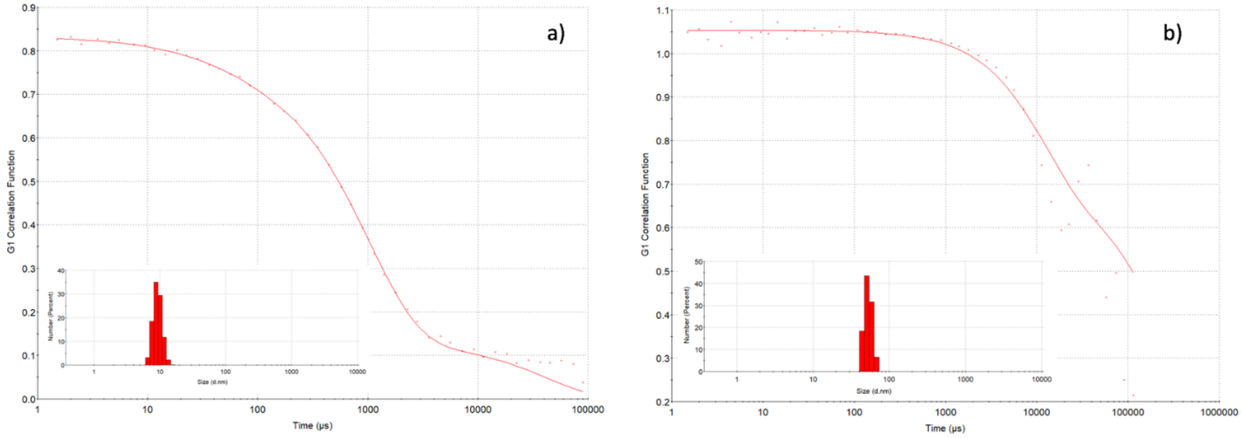


Figure S46. Correlation functions, distribution fits, and number-average size distributions (inset) at 90° (a) and 13° (b) scattering angle for pbdc-8a-PEG$_{2000}$-2%.

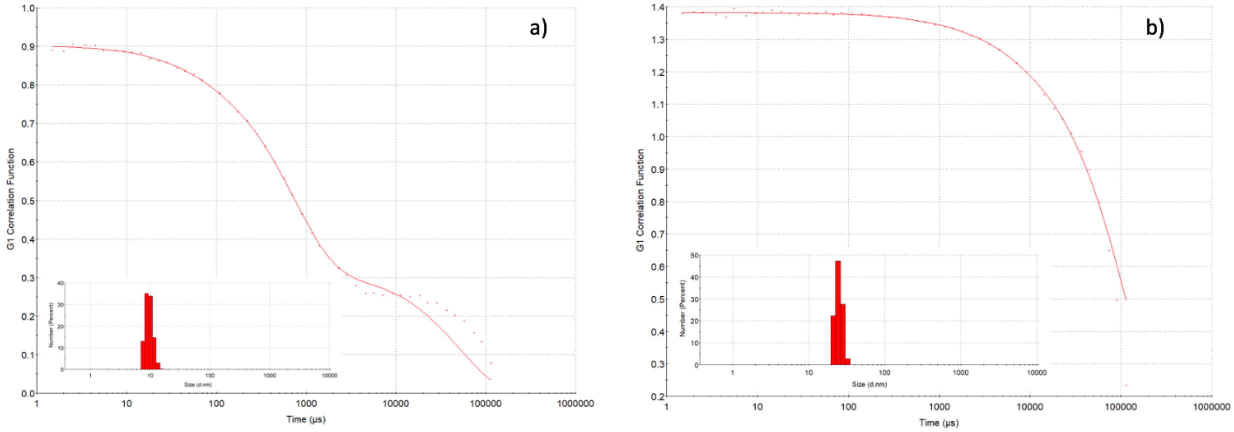


Figure S47. Correlation functions, distribution fits, and number-average size distributions (inset) at 90° (a) and 13° (b) scattering angle for pbdc-8a-PEG$_{4000}$-1%.

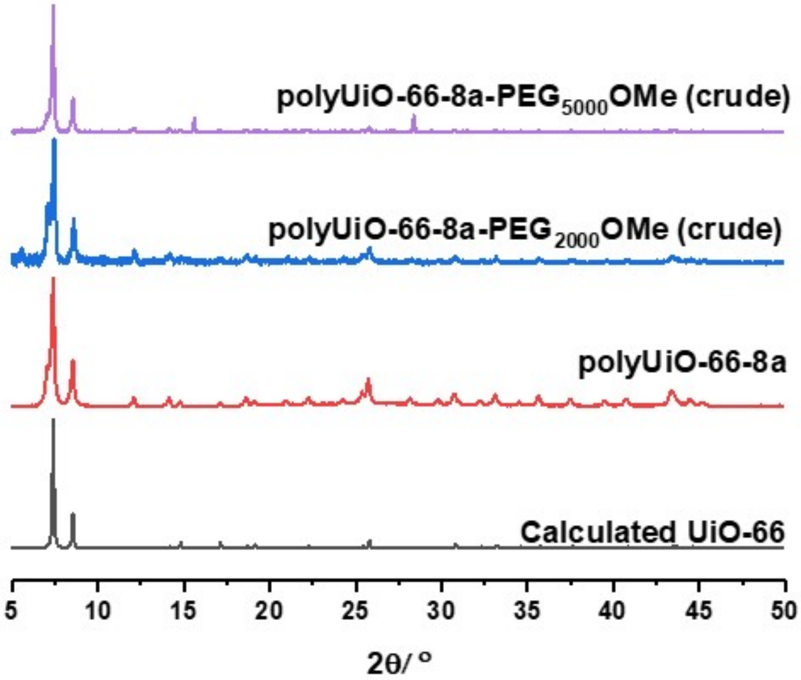


Figure S48. PXRD data was obtained for polyUiO-66 prepared from crude pbdc-8a-PEG$_{Mn}$OMe.

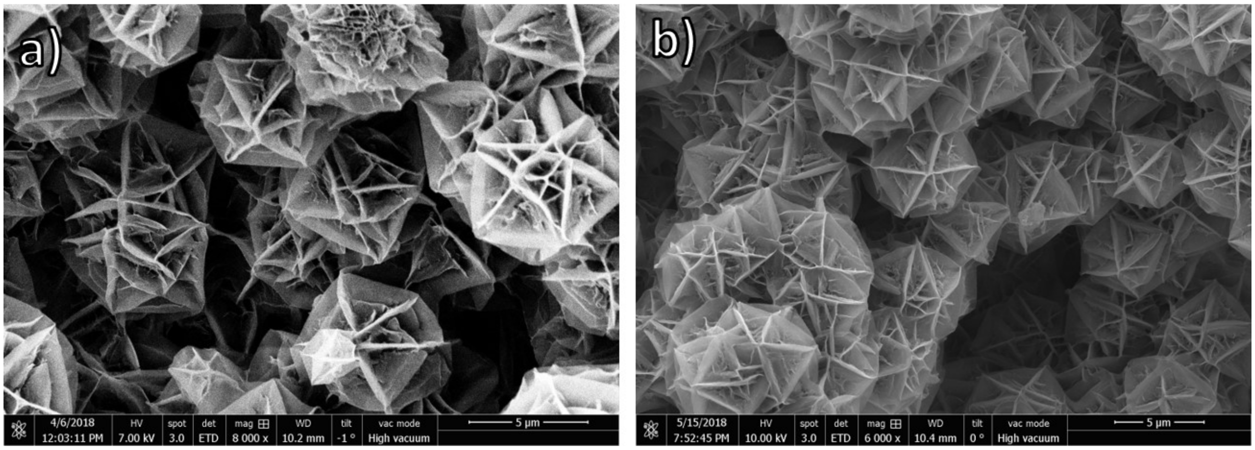


Figure S49. SEM images for polyUiO-66 prepared from crude: a) pbdc-8a-PEG$_{2000}$OMe; b) pbdc-8a-PEG$_{5000}$OMe.

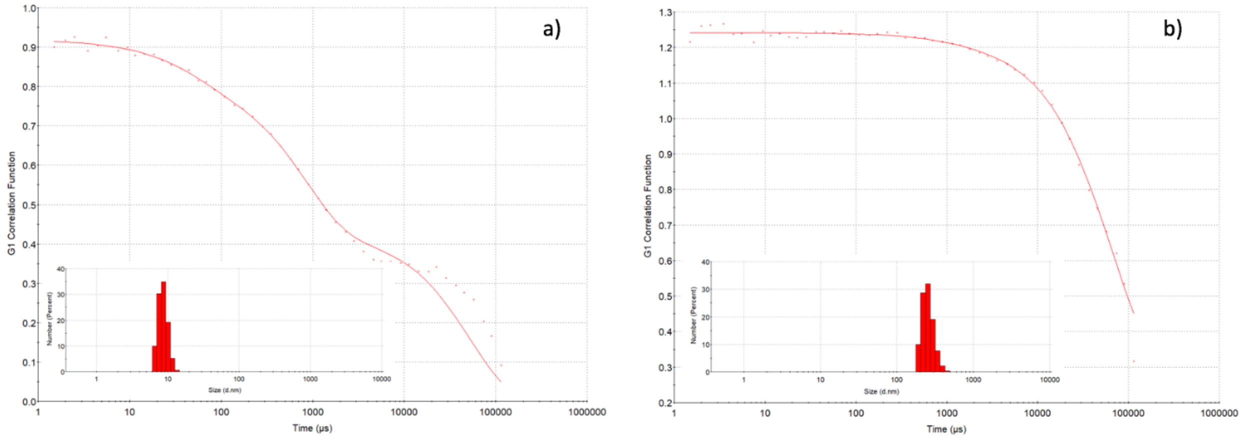


Figure S50. Correlation functions, distribution fits, and number-average size distributions (inset) at 90° (a) and 13° (b) scattering angle for pbdc-8a-PEG$_{2000}$OMe.

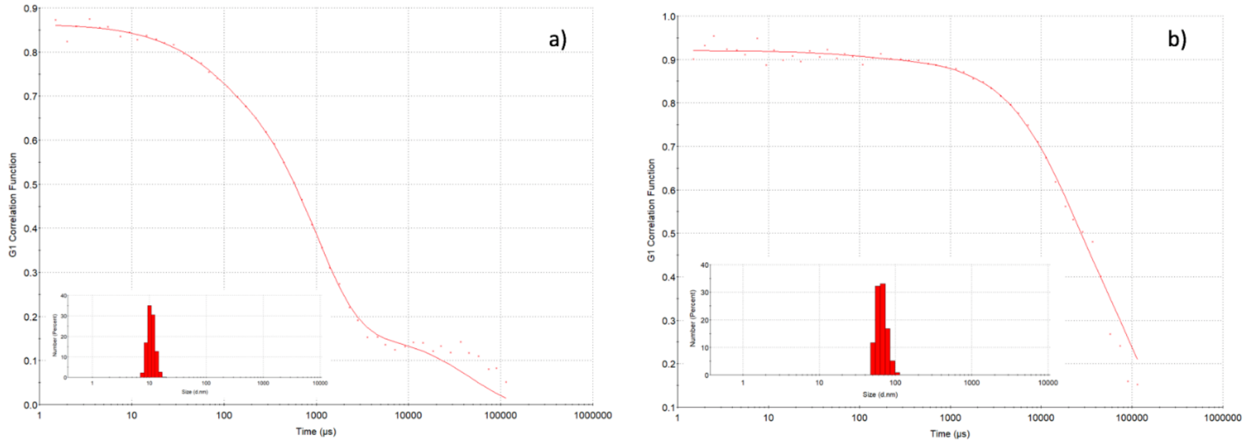


Figure S51. Correlation functions, distribution fits, and number-average size distributions (inset) at 90° (a) and 13° (b) scattering angle for pbdc-8a-PEG$_{5000}$OMe.

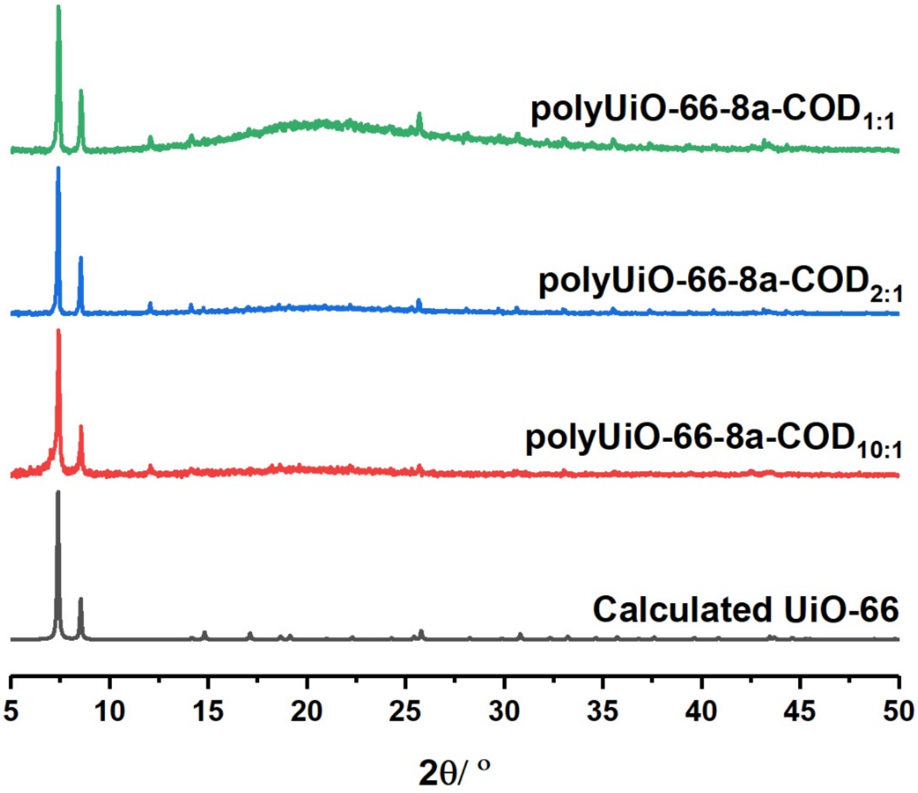


Figure S52. PXRD data was obtained for polyUiO-66 prepared from pbdc-8a-COD$_{m:n}$.

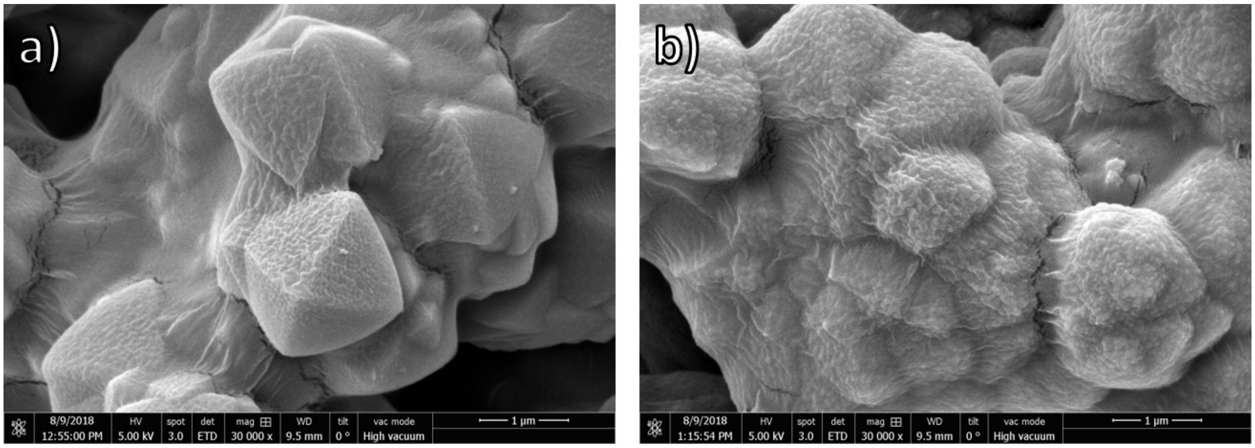


Figure S53. SEM images of polyUiO-66 prepared from: a) pbdc-8a-COD$_{2:1}$; b) pbdc-8a-COD$_{1:1}$.

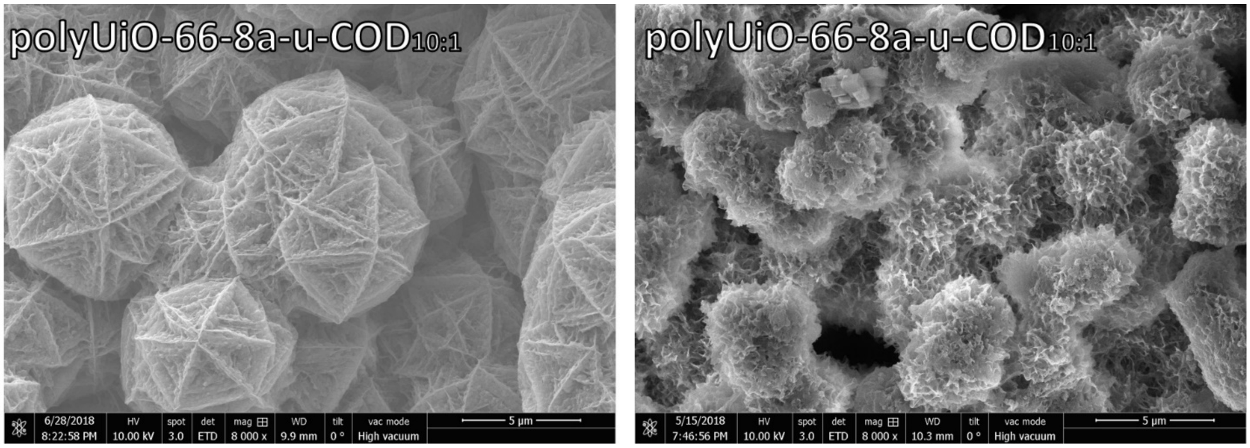


Figure S54. SEM images of two different morphologies for polyUiO-66 prepared from pbdc-8a-COD$_{10:1}$.

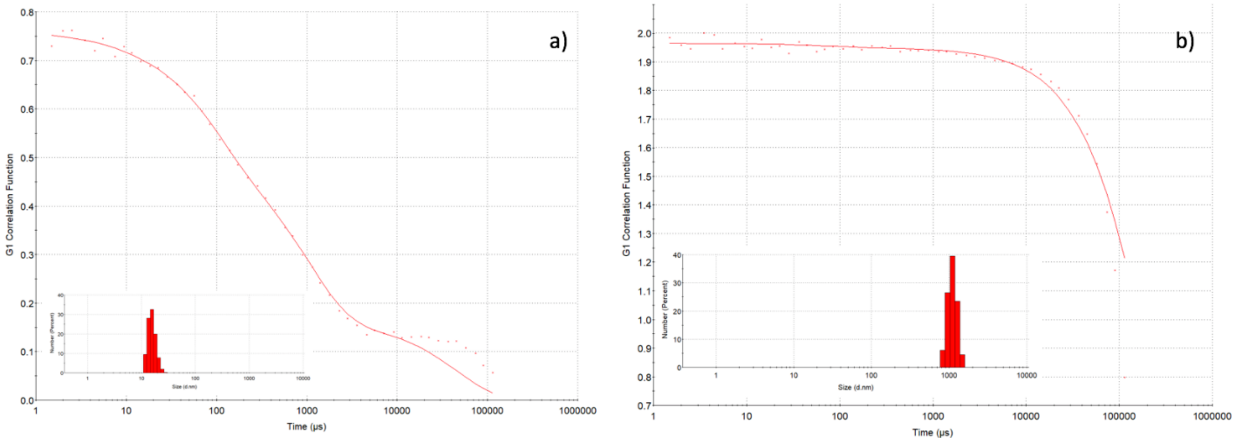


Figure S55. Correlation functions, distribution fits, and number-average size distributions (inset) at 90° (a) and 13° (b) scattering angle for pbdc-8a-COD$_{1:1}$.

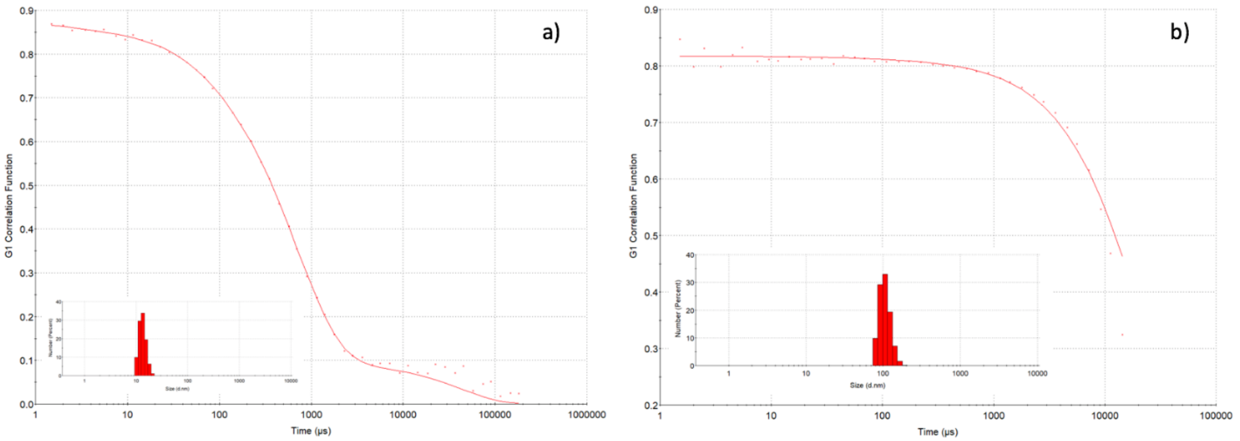


Figure S56. Correlation functions, distribution fits, and number-average size distributions (inset) at 90° (a) and 13° (b) scattering angle for pbdc-8a-COD$_{2:1}$.

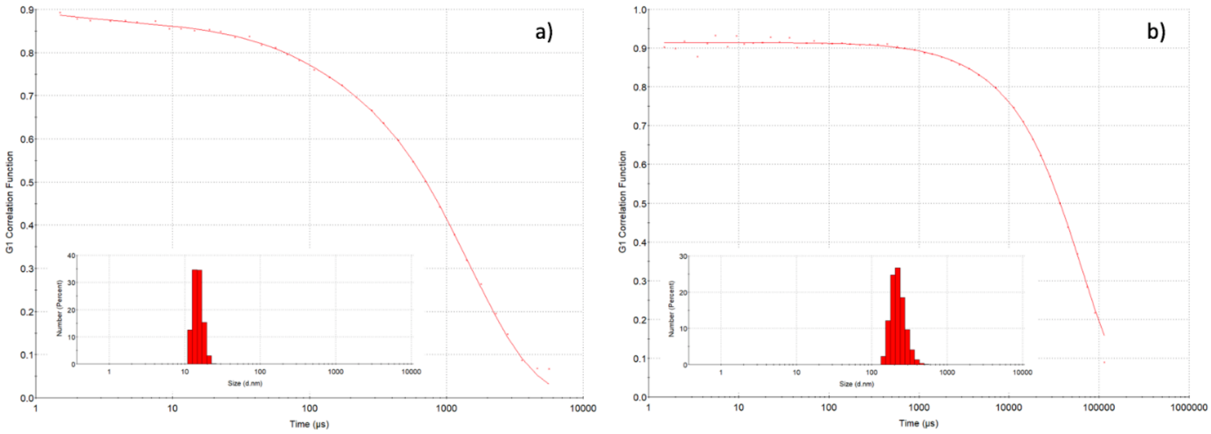


Figure S57. Correlation functions, distribution fits, and number-average size distributions (inset) at 90° (a) and 13° (b) scattering angle for pbdc-8a-COD$_{10:1}$.

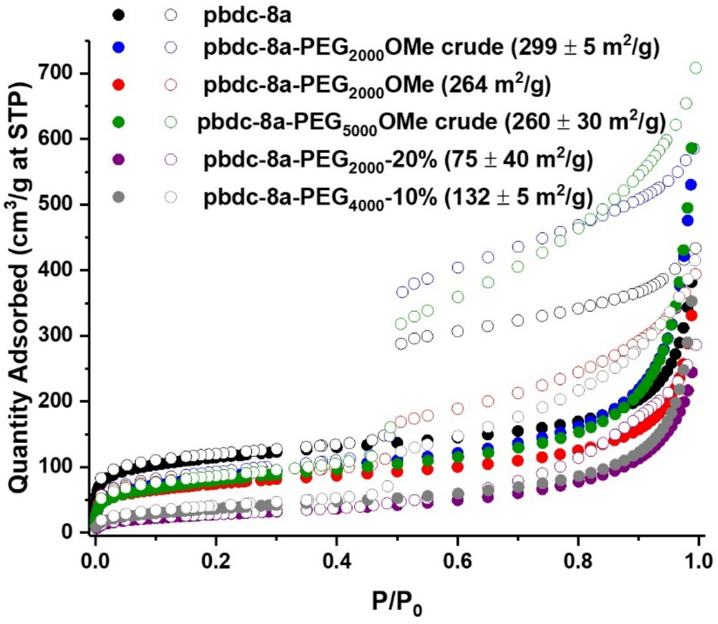


Figure S58. N_2 adsorption isotherms for all block-polyUiO-66 with an interlaced morphology.

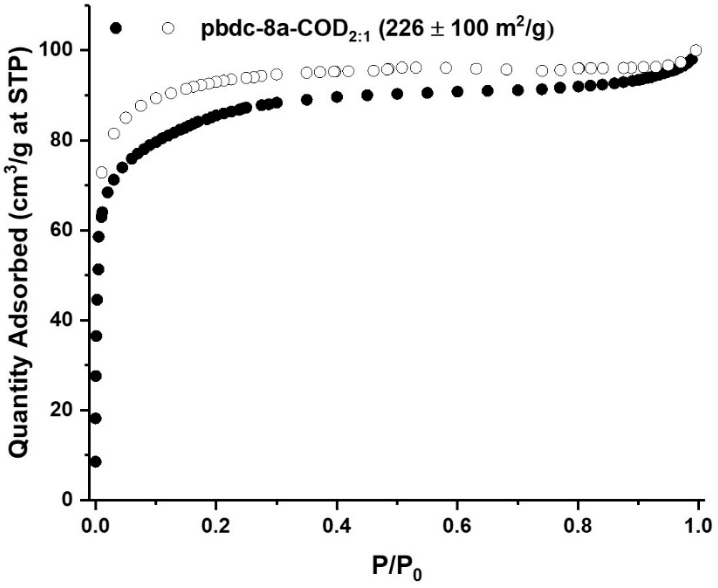


Figure S59. N_2 adsorption isotherm for block-polyUiO-66 prepared from pbdc-8a-COD$_{2:1}$ is presented.

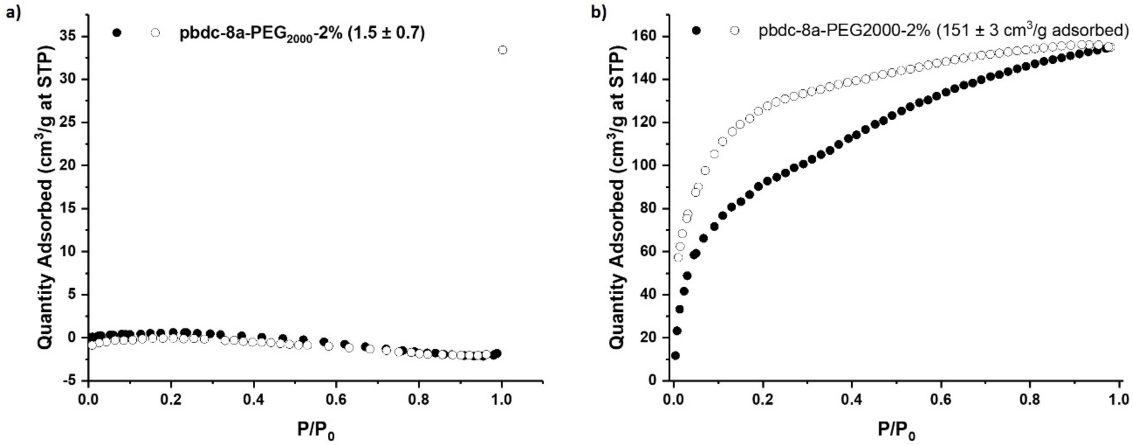


Figure S60. a) N_2 adsorption isotherms and b) CO_2 adsorption for block-polyUiO-66 prepared from pbdc-8a-PEG$_{2000}$-2%.

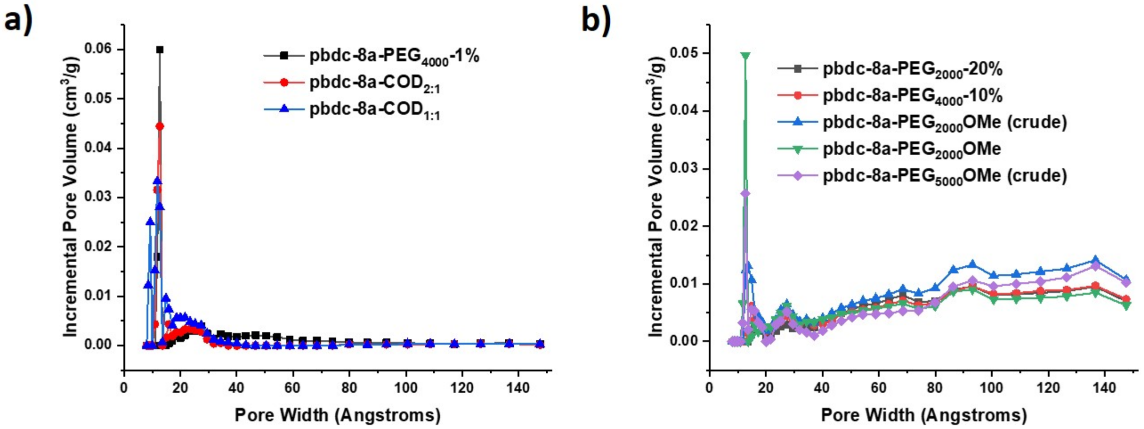


Figure S61. Pore-size distribution for block-polyUiO-66 with a(n): a) octahedral morphology; b) interlaced morphology.

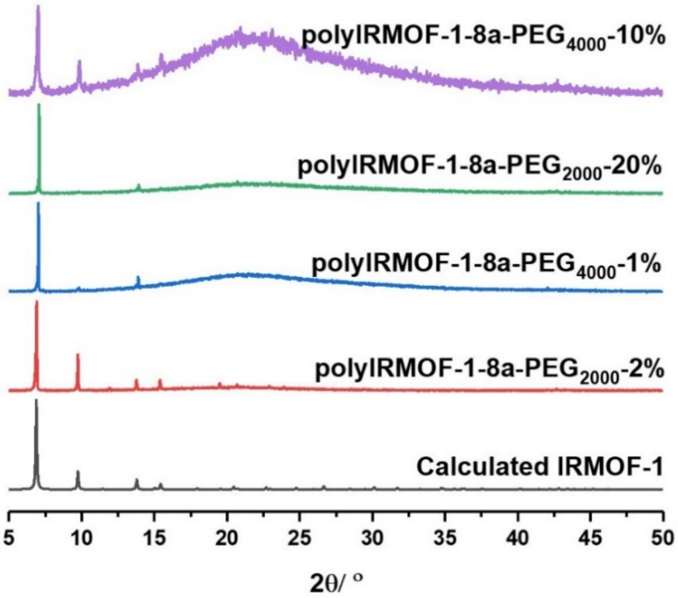


Figure S62. PXRD data was obtained for polyIRMOF-1 prepared from pbdc-8a-PEG$_{Mn}$-x%.

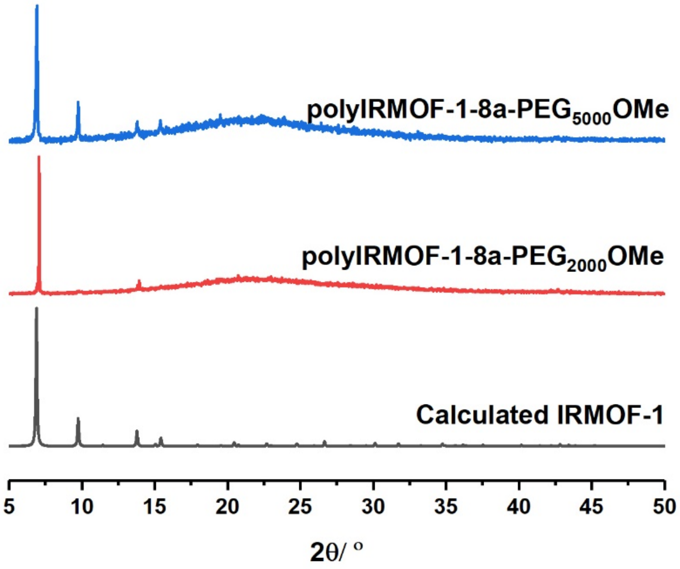


Figure S63. PXRD data was obtained for polyIRMOF-1 prepared from pbdc-8a-PEG$_{Mn}$OMe.

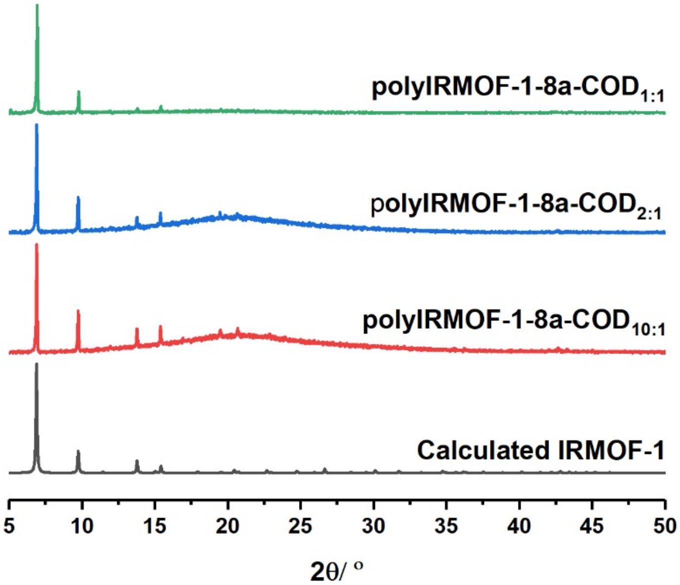


Figure S64. PXRD data was obtained for polyIRMOF-1 prepared from pbdc-8a-COD$_{m:n}$.

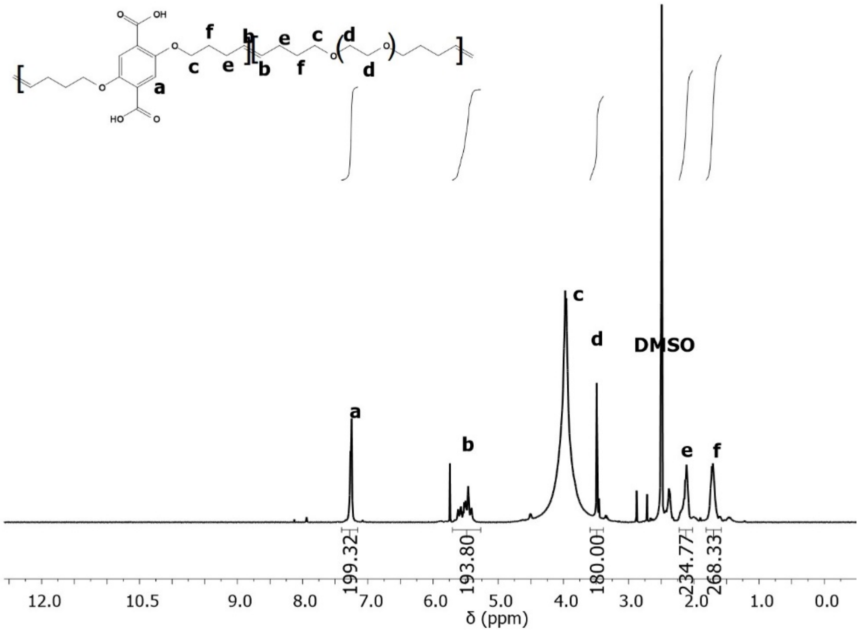


Figure S65. ^{1}H NMR of digested polyIRMOF-1 prepared from pbdc-8a-PEG$_{2000}$-2%.

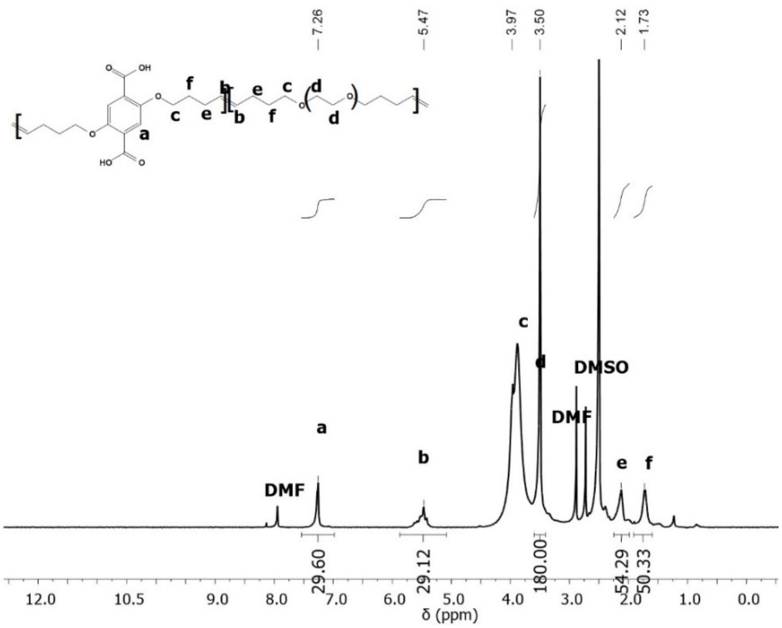


Figure S66. ^{1}H NMR of digested polyIRMOF-1 prepared from pbdc-8a-PEG$_{2000}$-20%.

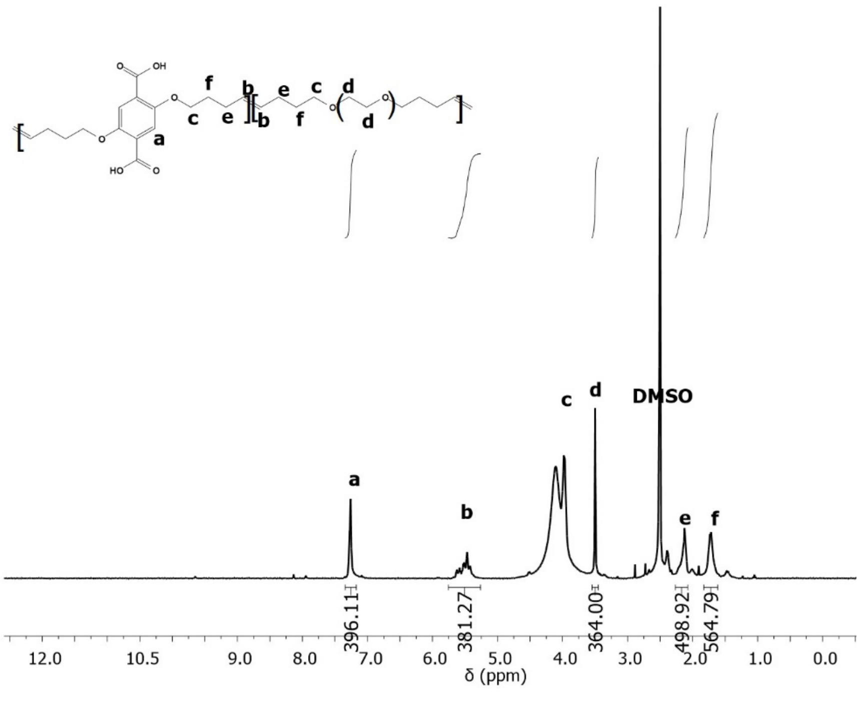


Figure S67. ^{1}H NMR of digested polyIRMOF-1 prepared from pbdc-8a-PEG$_{4000}$-1%.

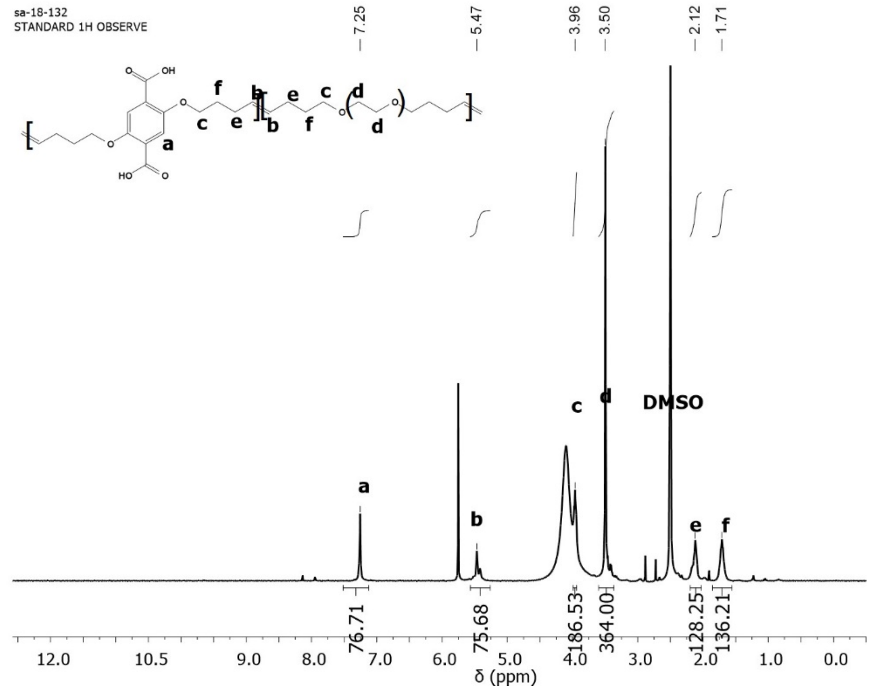


Figure S68. ^{1}H NMR of digested polyIRMOF-1 prepared from pbdc-8a-PEG$_{4000}$-10%.

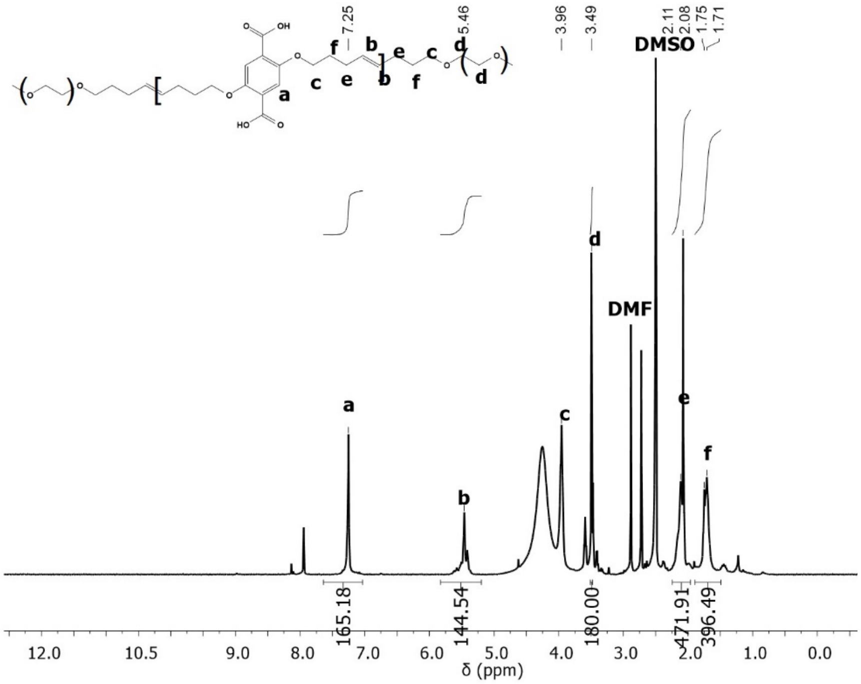


Figure S69. ^{1}H NMR of digested polyIRMOF-1 prepared from pbdc-8a-PEG$_{2000}$OMe.

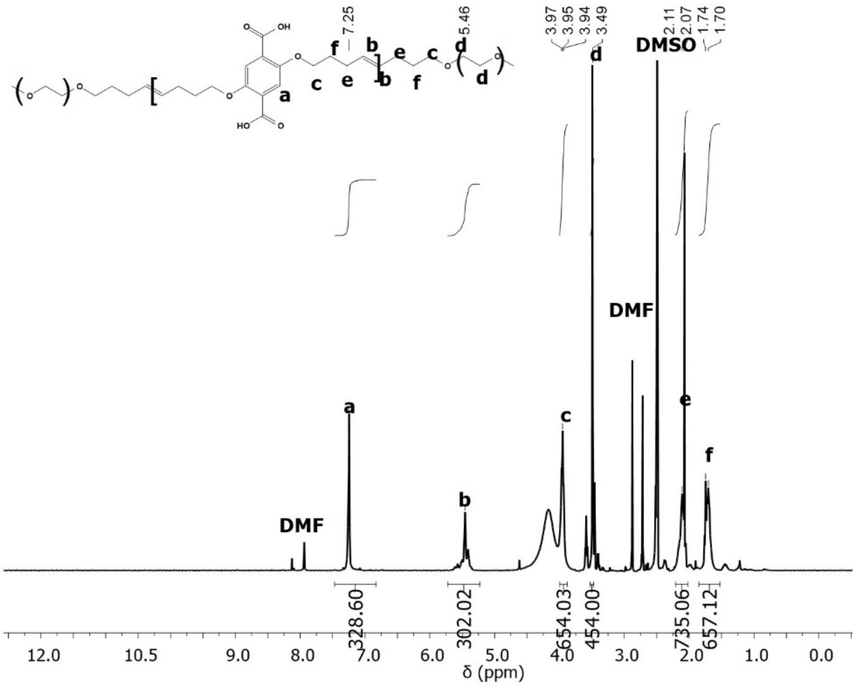


Figure S70. ^{1}H NMR of digested polyIRMOF-1 prepared from pbdc-8a-PEG$_{5000}$OMe.

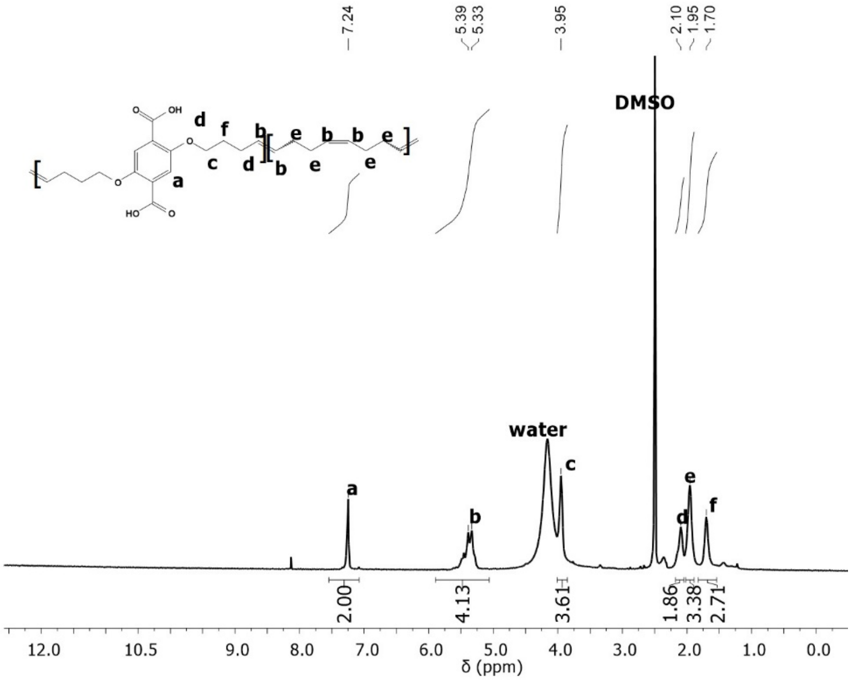


Figure S71. ^{1}H NMR of digested polyIRMOF-1 prepared from pbdc-8a-COD$_{1:1}$.

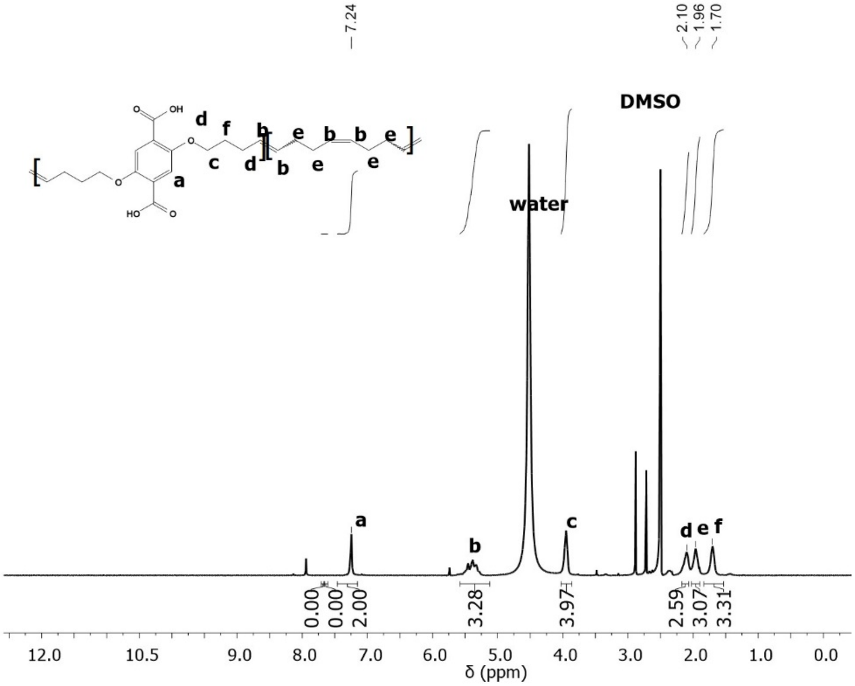


Figure S72. ^{1}H NMR of digested polyIRMOF-1 prepared from pbdc-8a-COD$_{2:1}$.

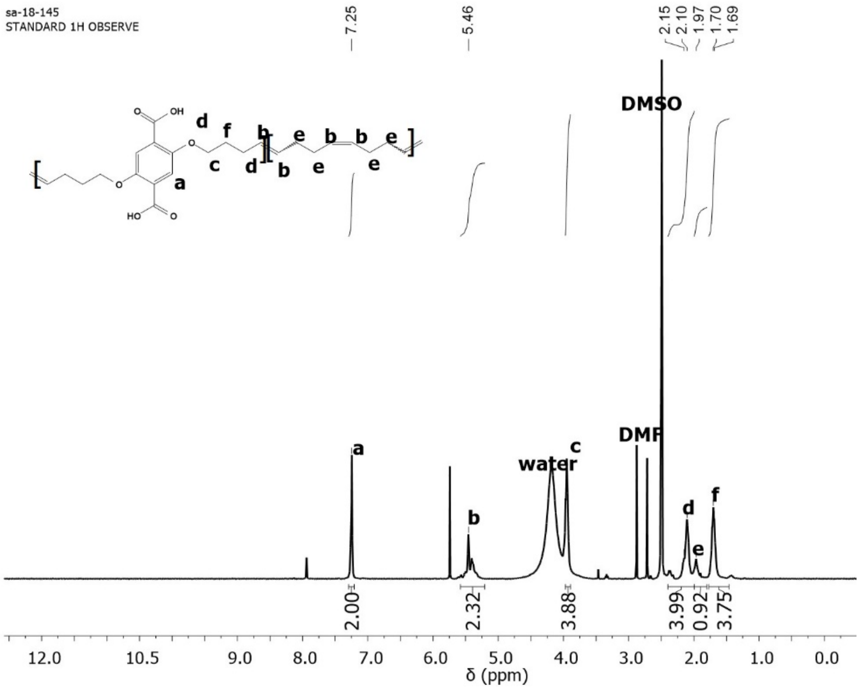


Figure S73. ^{1}H NMR of digested polyIRMOF-1 prepared from pbdc-8a-COD$_{10:1}$.

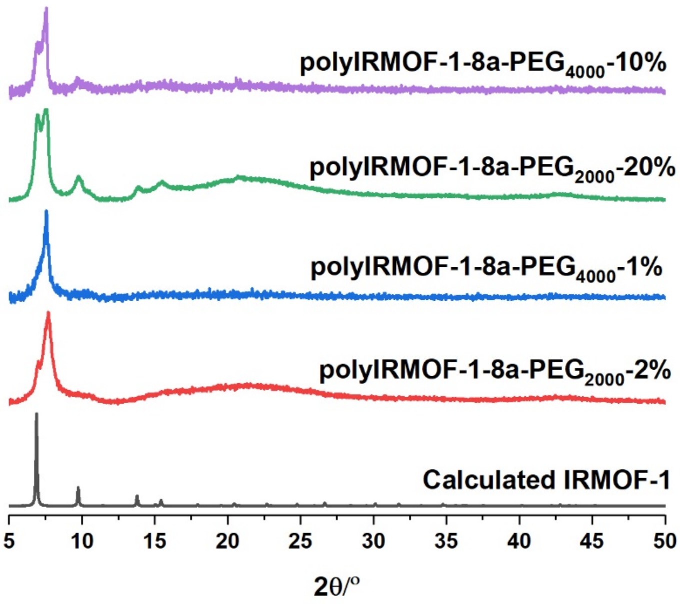


Figure S74. PXRD data was obtained for polyIRMOF-1 prepared from pbdc-8a-PEG$_{Mn}$-x% after activation.

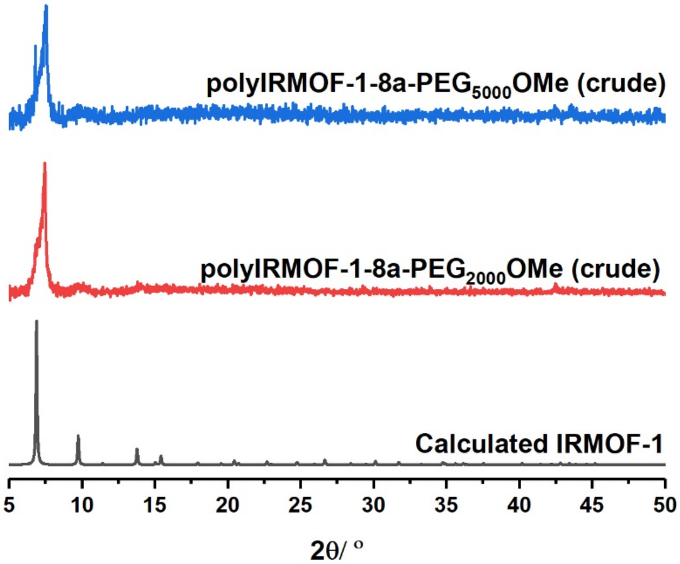


Figure S75. PXRD data was obtained for polyIRMOF-1 prepared from pbdc-8a-PEG$_{Mn}$-x% after activation.

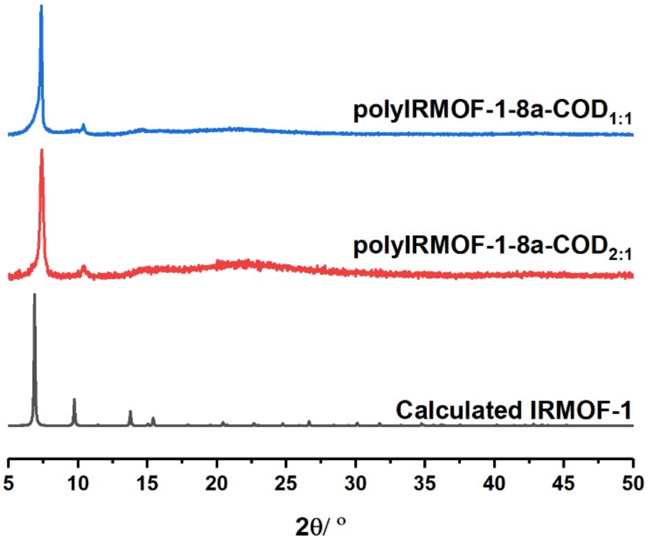


Figure S76. PXRD data was obtained for polyIRMOF-1 prepared from pbdc-8a-PEG$_{Mn}$-x% after activation.

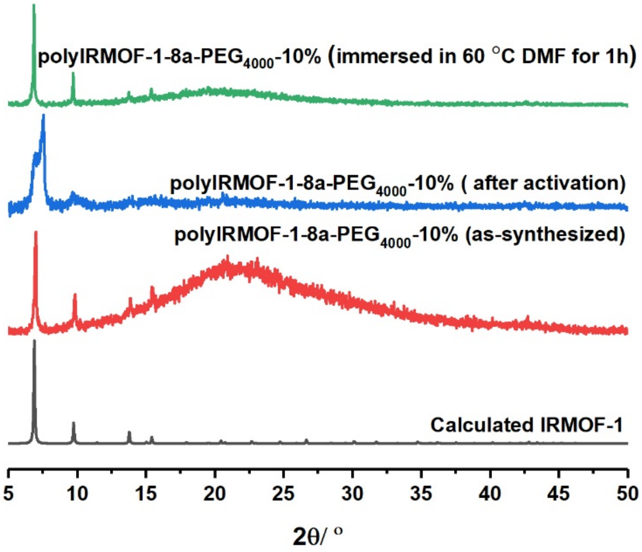


Figure S77. Representative PXRD data was obtained for polyIRMOF-1 prepared from pbdc-8a-PEG$_{4000}$-10% and shown here as synthesized, after activation, and after immersion in DMF at 60 °C for 1 h.

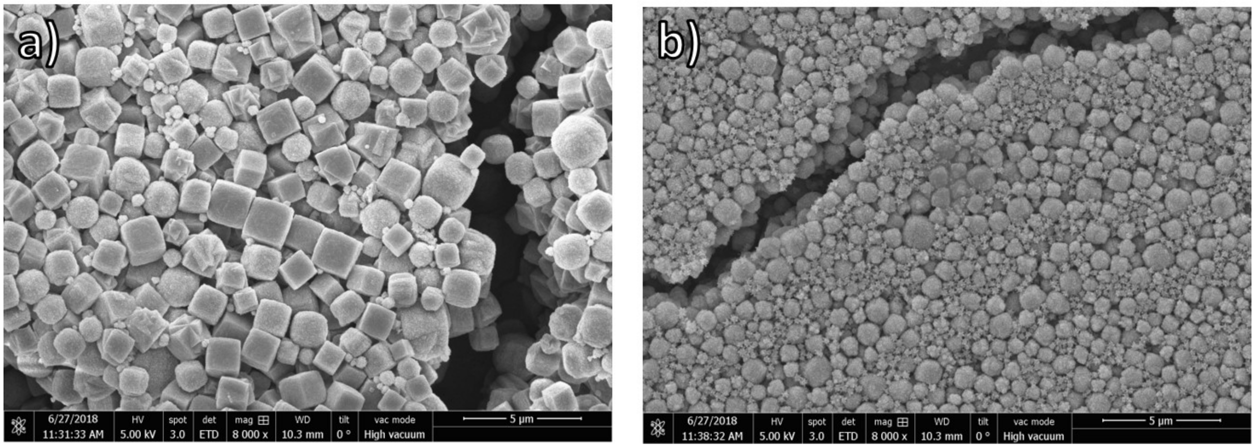


Figure S78. SEM images for polyIRMOF-1 prepared from a) pbdc-8a-PEG$_{2000}$OMe and b) pbdc-8a-PEG$_{5000}$OMe.

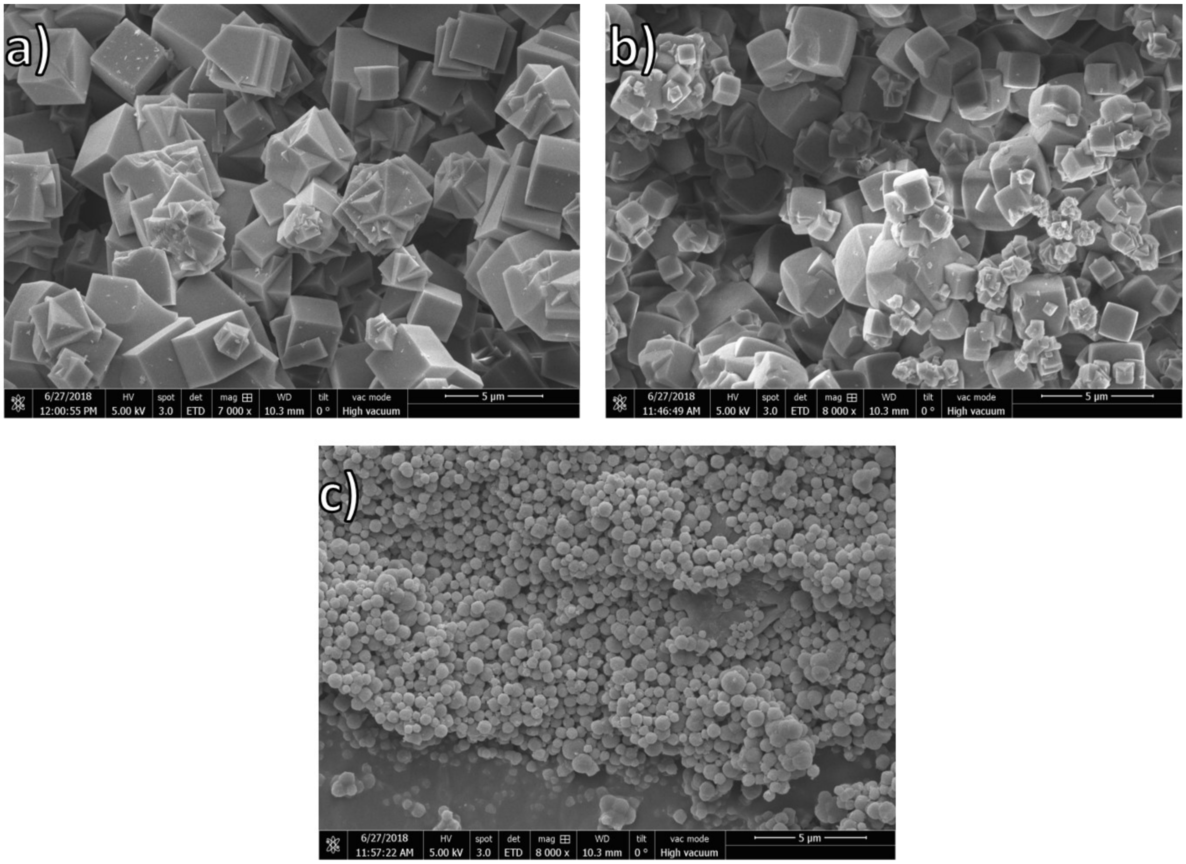


Figure S79. SEM images for polyIRMOF-1 prepared from a) pbdc-8a-COD$_{10:1}$, b) pbdc-8a-COD$_{2:1}$ and c) pbdc-8a-COD$_{1:1}$.

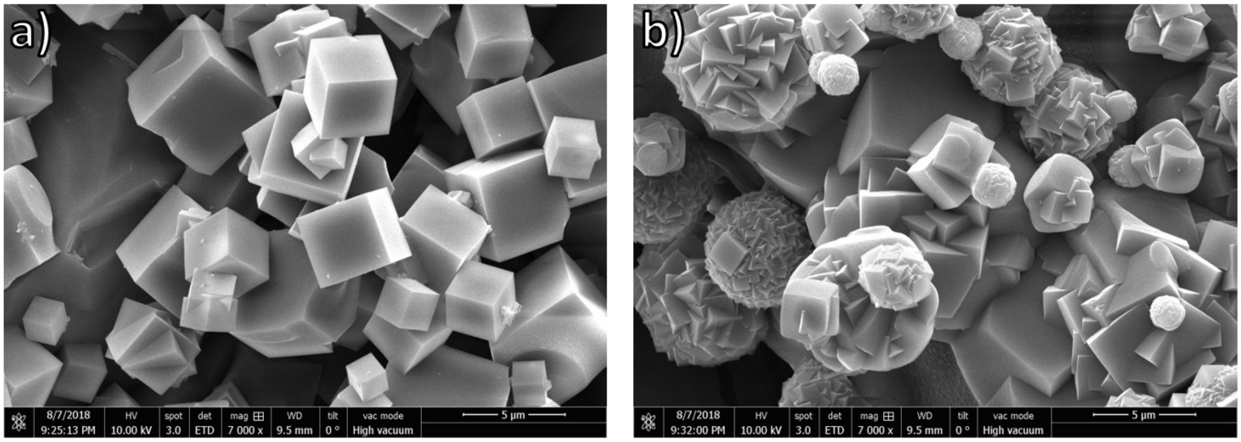


Figure S80. SEM images for polyIRMOF-1 prepared from pbdc-8a and physically mixed PEG$_{4000}$ at a)1% loading and b) 10% loading.

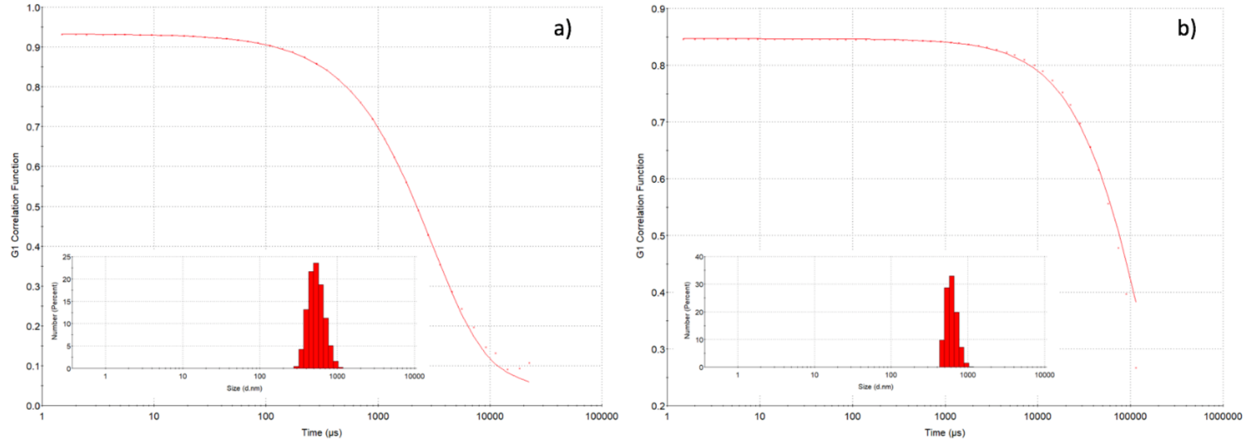


Figure S81. Correlation functions, distribution fits, and number-average size distributions (inset) at 90° (a) and 13° (b) scattering angle for polyIRMOF-1 prepared from pbdc-8a-PEG_{4000}-10%.

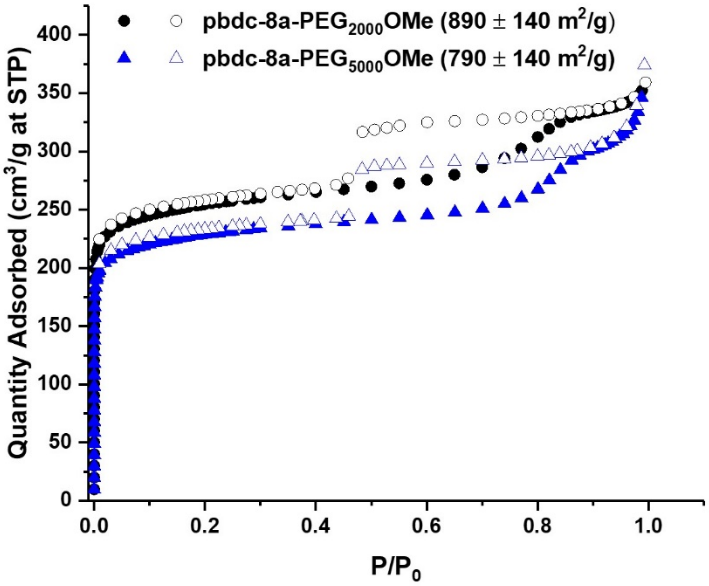


Figure S82. N_2 adsorption isotherm for polyIRMOF-1 prepared from pbdc-8a-PEG_{2000}OMe is presented.

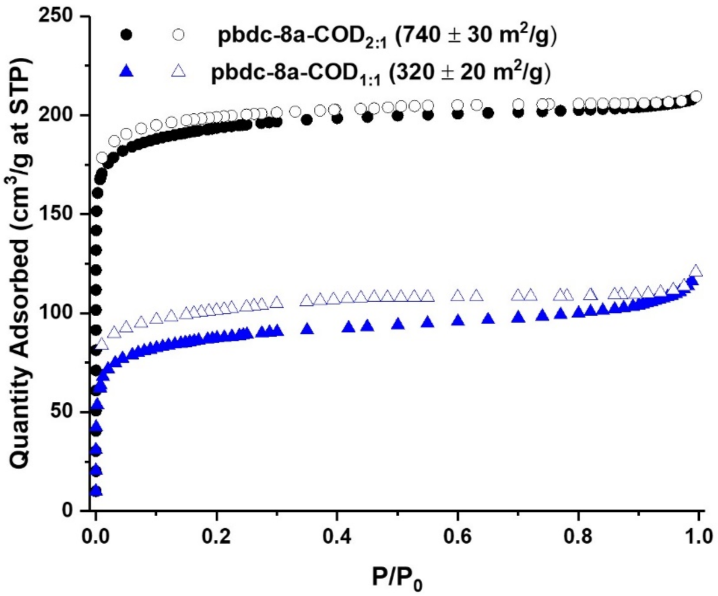


Figure S83. N$_2$ adsorption isotherm for polyIRMOF-1 prepared from pbdc-8a-COD$_{m:n}$ is presented.