Isoreticular Expansion of polyMOFs Achieves High Surface Area Materials

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SUPPORTING INFORMATION

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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 Rf 200 automated system from Teledyne Isco. Allyloxy-functionalized UiO-68 and UiO-67 were prepared using previous reports (Gui et al. J. Solid State Chem., 2015, 223, 79-83; Yu et al. Chem. Commun., 2015, 51, 9880-9883.). $^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectra were collected using a Varian spectrometer running at 400 MHz.

Scheme S1. Synthetic scheme of ptpdc-xa-u synthesis, where x = 8 or 10. a-f) Reagents and conditions: a-f) Reagents and conditions: a) Pd(dppf)Cl$_2$, K$_2$CO$_3$, 2:1 dioxane/H$_2$O, 80 °C, 12 h; b) BBr$_3$, CH$_2$Cl$_2$, reflux, 48 h; c) K$_2$CO$_3$, DMF, 80 °C 12 h; d) HG2 catalyst, CHCl$_3$, 80 °C, 5 h; e) KOH, 1:1 THF/H$_2$O, 60 °C, 12 h; f) ZrCl$_4$, 1:1 DEF/formic acid, 135 °C, 48 h.

[1,1',4',1"-Terphenyl]-4,4"-dicarboxylic acid-2',5'-dimethoxy-4,4"-dimethyl ester (1). To a 250 mL round bottom flask was added methoxycarbonyl phenyl boronic acid (3.00 g, 16.7 mmol, 2.5 eq), bromobenzene (2 g, 7 mmol, 1 eq), K$_2$CO$_3$ (6.91 g, 50.0 mmol, 7.4 eq), and PdCl$_2$(dppf) (275 mg, 1.1 mmol, 0.16 eq) in 25 mL of water and 50 mL of 1,4-dioxane. The solution was degassed for 5 min and heated at 80 °C under nitrogen atmosphere for 14 h. After cooling down, 50 mL of water was added to the solution followed by filtration. The product was then purified by
recrystallization using DMF and a few drops of water. The desired product \(1\) was isolated as white gray crystals. Yield: 88% (2.42 g, 5.95 mmol). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.89 (dd, \(J = 176.6, 7.8\) Hz, 8H), 6.99 (s, 1H), 3.95 (s, 6H). See Figure S1 for NMR spectrum with assignments.

\[\text{[1,1\:'\text{-}	ext{Terphenyl}]\text{-}4,4\:'\text{-dicarboxylic acid-2',5'-hydroxy-4,4''-dimethyl ester (2).}\] Compound 1 (1.2 g, 3.0 mmol, 1 eq), 1 M BBr\(_3\) (29 mL, 29 mmol, 10 eq), and 14 mL of CH\(_2\)Cl\(_2\) were added to a 250 mL flask and the reaction mixture was heated at 50 °C for 48 h. After cooling down the solution, the reaction was quenched with 100 mL of MeOH. The product 2 was isolated as an orange powder. Yield: 75% (0.77 g, 2.0 mmol). \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) 9.26 (s, 2H), 8.05 – 7.68 (m, 8H), 6.94 (s, 2H), 3.87 (s, 6H). See Figure S2 for \(^1\)H NMR spectrum with assignments.

\[\text{[1,1\:'\text{-}	ext{Terphenyl}]\text{-}4,4\:'\text{-dicarboxylic acid-2',5'-bis(pent-4-en-1-yloxy)-4,4''-dimethyl ester (3).}\] Compound 2 (0.68 g, 1.85 mmol, 1 eq), 5-bromo-1-pentene (0.86 mL, 7.2 mmol, 4 eq), K\(_2\)CO\(_3\) (1.52 g, 11.0 mmol, 6.1 eq), and 40 mL of DMF were added in a 250 mL round bottom flask. The solution was stirred and heated at 80 °C for 14 h and monitored by TLC using 20% of ethyl acetate and 80% hexane. Potassium carbonate was then removed by filtration, DMF was removed by rotary evaporation, and the resulting residue was subjected to column chromatography (hexane/ethyl acetate). The product 3 was isolated as a white powder. Chromatography gradient: 0-1 min of 5% EtOAc, 1-6 min of 10% EtOAc, 6-12 min of 15% EtOAc, 17-20 min of 20% EtOAc. Yield: 53% (0.49 g, 0.95 mmol). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.88 (dd, \(J = 170.3, 8.2\) Hz, 8H), 6.99 (s, 2H), 5.76 (ddt, \(J = 16.9, 10.2, 6.7\) Hz, 2H), 5.00 – 4.92 (m, 4H), 3.95 (bs, \(J = 3.4\) Hz, 10H), 2.17 – 2.06 (dt, 4H), 1.78 (dt, \(J = 13.5, 6.4\) Hz, 4H). See Figure S3 for \(^1\)H NMR spectrum with assignments.

\[\text{[1,1\:'\text{-}	ext{Terphenyl}]\text{-}4,4\:'\text{-dicarboxylic acid-2',5'-bis(hex-5-en-1-yloxy)-4,4''-dimethyl ester (4).}\] The same procedure was applied as for compound 3, using 6-bromo-1-hexene. Yield: 70% (0.65 g, 1.7 mmol). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.09 (d, \(J = 8.7\) Hz, 4H), 7.67 (d, \(J = 8.1\) Hz, 4H), 6.99 (s, 2H), 5.76 (ddt, \(J = 16.9, 10.2, 6.6\) Hz, 2H), 4.95 (s, 4H), 3.95 (s, 10H), 2.04 (q, \(J = 7.4\) Hz, 4H), 1.77 – 1.63 (p, 4H), 1.46 (p, \(J = 7.5\) Hz, 4H). See Figure S4 for \(^1\)H NMR spectrum with assignments.

**General Polymerization Procedure for Synthesis of ptpdc-xe-u (where x = 8 or 10; polymer ester precursor for polyUIO-68).** The desired monomer (200 mg, 0.39 mmol, 1 eq), Hoveyda-Grubbs second generation catalyst (11 mg, 0.017 mmol, 0.045 eq) and 0.8 mL of CHCl\(_3\) were added into a flask and heated at 70 °C for 5 h. The reaction was then quenched with ethyl vinyl ether (0.29 mL, 3 mmol, 7.7 eq). After allowing the reaction to cool to room temperature, 15 mL of MeOH was added to the solution. The polymer was isolated by centrifugation (Beckman Coulter Allegra X-22R Centrifuge, fixed-
angle rotor, 5300 rpm for 6 min) and washed three times with MeOH. The polymer was then dried by removing MeOH under high vacuum.

**Poly-[1,1’:4’,1”-Terphenyl]-4,4’“-dicarboxylic acid-2’,5’-bis(pent-4-en-1-yloxy) 4,4’“-dimethyl ester (ptpdc-8e-u).** Yield: 75% (150 mg, 0.29 mmol). 

\( ^1H \) NMR (400 MHz, CDCl\(^3\)): \( \delta \) 8.05 (s, 4H), 7.64 (s, 4H), 6.96 (s, 2H), 5.31 (m, 2H), 4.52 (d, \( J = 99.5 \) Hz, 0.15H), 3.89 (bs, 2H), 2.35 (bs, 4H), 2.02 (dt, 4H). See Figure S5 for \(^1H\) NMR spectrum with assignments.

**Poly-[1,1’:4’,1”-Terphenyl]-4,4’“-dicarboxylic acid-2’,5’-bis(hex-5-en-1-yloxy) 4,4’“-dimethyl ester (ptpdc-10e-u).** Yield: 98% (420 mg, 0.77 mmol). 

\( ^1H \) NMR (400 MHz, CDCl\(^3\)): \( \delta \) 8.06 (s, 4H), 7.65 (s, 4H), 6.97 (s, 2H), 5.32 (m, 2H), 4.49 (s, 0.14H), 3.90 (s, 10H), 2.02 (bs, 40H), 1.67 (bs, 4H), 1.31 (bs, 4H). See Figure S6 for \(^1H\) NMR spectrum with assignments.

**General Polymer Hydrolysis Procedure for ptpdc-xa-u synthesis (where x = 8 or 10; polymer acid precursor for polyUiO-68).** To hydrolyze the terminal ester groups, the polymer (100-400 mg, 0.20 mmol, 1 eq) was placed in a 1:1 mixture of water and THF (15 mL total) with excess KOH (30 eq). The mixture was heated at 80 °C for 5 h. The solution was acidified with 1.0 M HCl. The resulting precipitate was collected by centrifugation and washed three times with MeOH. The isolated solid was dried by removing methanol under high vacuum.

**Poly-[1,1’:4’,1”-Terphenyl]-2’,5’-bis(pent-4-en-1-yloxy)4,4’“-dicarboxylic acid (ptpdc-8a-u).** Yield: 97% (92 mg, 0.19 mmol). \( ^1H \) NMR (400 MHz, DMSO-\(d_6\)): \( \delta \) 8.05 (s, 4H), 7.64 (s, 4H), 6.96 (s, 2H), 5.31 (m, 2H), 4.52 (d, \( J = 99.5 \) Hz, 0.15H), 3.89 (bs, 2H), 2.35 (bs, 4H), 2.02 (dt, 4H). See Figure S7 for \(^1H\) NMR spectrum with assignments.

**Poly-[1,1’:4’,1”-Terphenyl]-2’,5’-bis(hex-5-en-1-yloxy)4,4’“-dicarboxylic acid (ptpdc-10a-u).** Yield: 90% (0.390 g, 0.79 mmol). \( ^1H \) NMR (400 MHz, DMSO-\(d_6\)): \( \delta \) 8.04 (s, 4H), 7.66 (s, 4H), 7.05 (s, 0H), 5.25 (bs, 2H), 4.49 (s, 0.25H), 3.91 (s, 3H), 3.41 (s, 3H), 1.87 (bs, 4H), 1.56 (bs, 4H), 1.23 (bs, 4H). See Figure S8 for \(^1H\) NMR spectrum with assignments.
Scheme S2. Illustration of pbpdc-x8-u synthesis. a-f) Reagents and conditions:  a) Pd(dppf)Cl₂, K₂CO₃, 2:1 dioxane/H₂O, 80 °C, 12 h; b) BBr₃, CH₂Cl₂, reflux, 48 h; c) K₂CO₃, DMF, 80 °C 12 h; d) HG2 catalyst, CHCl₃, 80 °C, 5 h; e) KOH , 1:1 THF/H₂O, 60 °C, 12 h; f) ZrCl₄, 1:1 DEF/formic acid, 135 °C, 48 h.

[1,1'-Biphenyl]-4,4'-dicarboxylic acid-3,3'-dimethoxy-4,4'-dimethyl ester (5). Methyl 4-bromo-2-methoxybenzoate (1.00 g, 4.1 mmol, 1 eq), (3-methoxy-4- (methoxycarbonyl)phenyl boronic acid (1.04 g, 4.9 mmol, 1.2 eq), K₂CO₃ (3.46 g, 525 mmol, 6.3 eq), and PdCl₂(dppf) (175 mg, 0.70 mmol, 0.17 eq) were added to a round bottom flask with 10 mL of water and 25 mL of 1,4-dioxane. The solution was degassed for 5 minutes and heated at 80 °C under nitrogen atmosphere for 14h. After cooling to room temperature, 20 mL of water was added and the solution was filtered. The product was then purified by recrystallization using a large excess of DMF and 2 mL of water. Compound 5 was isolated as white-gray crystals. Yield: 98% (1.31 g, .40 mmol). ¹H NMR (400 MHz, CDCl₃): δ 7.90 (d, J = 8.0 Hz, 2H), 7.20 (dd, J = 8.0, 1.6 Hz, 2H), 7.15 (d, J = 1.6 Hz, 2H), 3.99 (s, 6H), 3.92 (s, 6H). See Figure S9 for ¹H NMR spectrum with assignments.

[1,1'-Biphenyl]-4,4'-dicarboxylic acid-3,3'-dihydroxy- 4,4'-dimethyl ester (6). Compound 5 (700 mg, 2.1 mmol, 1 eq), 1 M BBr₃ in heptane (22 mL, 22 mmol, 10 eq), and 15mL of CH₂Cl₂ were added to a flask and stirred at room temperature for 48h. After allowing the solution to cool, the reaction was quenched with excess methanol. The solution was co-evaporated with excess
of methanol until a yellow solid precipitated. The solid was then added to 650 mL of MeOH, H$_2$SO$_4$ (4 drops), and heated in refluxing MeOH for four days. The solution was concentrated by evaporation of MeOH, and water was added to yield an off-white solid. Yield: 95% (550 mg, 2.0 mmol). $^1$H NMR (400 MHz, DMSO-d$_6$): δ 7.87 (d, J = 7.2 Hz, 2H), 7.30 (d, J = 6.9 Hz, 2H), 7.30 (d, J = 6.9 Hz, 2H), 3.91 (s, 3H). See Figure S10 for $^1$H NMR spectrum with assignments.

[1,1'-Biphenyl]-4,4'-dicarboxylic acid-3,3'-bis(pent-4-en-1-yloxy) 4,4'-dimethyl ester (7). Compound 6 (0.50 g, 1.6 mmol, 1 eq), 5-bromo-1-pentene (2.48 g, 16.7 mmol, 9 eq), K$_2$CO$_3$ (1.53 g, 11.1 mmol, 6 eq) and 40 mL of DMF were added to a 250 mL round bottom flask. The solution was stirred and heated at 80 °C for 14 h and monitored by TLC using 20% of ethyl acetate and 80% hexane. Potassium carbonate was then removed by filtration and the DMF was removed by rotary evaporation and the resulting residue was subjected to column chromatography (hexane/ethyl acetate). The biphenyl monomer 7 was isolated as a white powder. Chromatography gradient: 0-5 min of 5% EtOAc, 5-10 min of 10% EtOAc, 10-20 min of 15% EtOAc. Yield: 53% (0.40 g, 0.90 mmol). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.88 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 7.11 (s, 2H), 5.95 – 5.80 (m, 2H), 5.08 (d, J = 17.1 Hz, 2H), 5.01 (d, J = 10.2 Hz, 2H), 4.13 (t, J = 6.3 Hz, 4H), 3.91 (s, J = 2.3 Hz, 6H), 2.32 (q, J = 7.0 Hz, 4H), 1.97 (p, 4H). See Figure S11 for $^1$HNMR spectrum with assignments.

Poly-[1,1'-Biphenyl]-4,4'-dicarboxylic acid-3,3'-bis(pent-4-en-1-yloxy)-4,4'-dimethyl ester (pbpdc-8e-u). The conditions used are identical to those used for the polymerization synthesis of ptpdc-xe-u, using compound 7. Yield: 84% (135 mg, 0.31 mmol). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.83 (s, 2H), 7.12 (bs, 4H), 5.52 (s, 2H), 4.64 (s, 0.10H), 4.08 (s, 4H), 3.87 (s, 6H), 2.23 (bs, 4H), 1.88 (bs, 4H). See Figure S12 for $^1$H NMR spectrum with assignments.

Poly-[1,1'-Biphenyl] -3,3'-bis(pent-4-en-1-yloxy)-4,4'-dicarboxylic acid (pbpdc-8a-u). The conditions used are identical to those used for the hydrolysis of ptpdc-xe-u, using pbpdc-8e-u. Yield: 79% (79 mg, 0.19 mmol). $^1$H NMR (400 MHz, DMSO-d$_6$): δ 7.68 (bs, 2H), 7.31 (bs, 4H), 5.49 (bm, 2H), 4.69 (m, 0.10H), 4.12 (s, 4H), 2.16 (bs, 4H), 1.76 (bs, 4H). See Figure S13 for $^1$H NMR spectrum with assignments.

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). In a 20 mL scintillation vial, the polymer ligand (0.03 mmol) and ZrCl$_4$ (0.037 mmol) were added to 2 mL of DEF. After the solution became clear, 2 mL of formic acid was added. The vial was heated at 135 °C for 48 h. For Single crystal growth prepared from ptpdc-xa-u. Single crystals of ptpdc-10a-u were prepared as described above. After removal from the oven, the 20 mL scintillation vial containing the polyMOF was sonicated to
suspend microparticles of polyUiO-68-10a-u, allowing for large crystals to sink to the bottom of the vial. The mother liquor and microparticles were removed, leaving the large crystals at the bottom of the vial.

**General procedure for IRMOF-type polyMOFs synthesis.** The IRMOF-type polyMOFs were prepared by adapting a previously reported procedure (Zhang et al., *Angew. Chem. Int. Ed.*, **2015**, *54*, 6152-6157). To a 20 mL scintillation vial was added 0.05 mmol of the appropriate extended polymer ligand (pbpdc-xa-u or ptpdc-xa-u), Zn(NO₃)₂·6H₂O (0.30 mmol), and 2.5 mL of DMF. The vial was placed in a pre-heated oven at 100 °C for 24 h. The off-white crystals were cleaned by extensive washing and solvent-exchange of DMF (5x5 mL of DMF), and kept in solvent until further studies were performed.
Analytical methods

Gel-permeation chromatography (GPC) conditions for pbpdc-8e-u and ptpdc-xe-u (x = 8 and 10). 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. Before injection into the GPC instrument the solutions were filtered using a 0.4 μm PTFE membrane. Narrow poly(methyl methacrylate) (PMMA) was used as standard for the calibration curve.

Powder x-ray diffraction Analysis. The synthesized polyMOFs were filtered, washed with DEF, and PXRD data was collected at ambient temperature on a Bruker D8 Advance with a step size of 0.03° in 2θ, a scan speed of 0.5 s/step, and a 2θ range of 3° to 50°.

1H NMR Digestions. To 10 mg of polyMOF was added a solution containing 440 μL of 6 M NaOD and 160 μL of DMSO-d6. The mixture was sonicated at 50 °C for 24 h. The solvent was evaporated, and the mixture was re-suspended in a solution containing 500 μL of DMSO-d6 and 100 μL of D2O. The supernatant was collected by centrifugation for 1H NMR analysis, leaving Zr-O byproducts behind. For single-crystal digestion of polyUiO-68 prepared from ptpdc-10a-u. Single crystals (<100 μg) were washed by exchanging the solvent with DMF (3x50 μL), and absolute ethanol (5x100 μL). The solvent was evaporated, and to the crystals was added a solution containing 15 μL of 6 M NaOD and 5 μL of DMSO-d6. The mixture sat at room temperature for 24 h. The mixture was evaporated, and re-suspended in 40 μL of 1:1 DMSO-d6:D2O and the supernatant was collected by centrifugation for 1H NMR. For polyIRMOFs. To 10 mg of polyMOF was added a solution containing 600 μL of DMSO-d6 and 5 μL of DCI. The mixture was sonicated at room temperature for 1 h. The solution was used for 1H NMR analysis.

Scanning Electron Microscopy (SEM). The polyMOFs materials were filtered and transferred to conductive carbon tape on a sample holder and coated using a Ir-sputter coating for 14 sec. A Philips XL ESEM instrument was used for acquiring images. A 10 kV energy source under vacuum at a working distance at 10 mm was used during the measurements.

N2 gas adsorption Measurements. Between 15-50 mg of sample was transferred to pre-weighed sample tubes. The samples were activated for 10 h at 105 °C using an ASAP 2020 Adsorption analyzer. After degassing, the sample tube was reweighed to obtain an accurate mass of the degassed sample. All measurements were obtained at 77 K using a liquid nitrogen bath. Solvent-exchange for polyUiO-67. polyUiO-67 was washed by exchanging the solvent with DMF overnight and then with MeOH three times a day over three days. The samples were transferred to a pre-weighed sample tube and
evacuated in a vacuum line until no solvent was observed. **Solvent-exchange for polyUiO-68.** polyUiO-68 was washed by exchanging the solvent with EtOH three times a day over three days. The EtOH-exchanged samples were then soaked in liquid CO$_2$ in a Samdri-PVT-3D supercritical dryer for 6 h, purging the chamber with fresh liquid CO$_2$ every 30 min for the first 2 h, then purging every hour for 4 h. The temperature in the dryer was maintained between 0-10 °C during the solvent exchange with liquid CO$_2$. The temperature was then increased to 40 °C and maintained for 15 min. Finally, the supercritical CO$_2$ in the drying chamber was released over a period of 30 min. The samples were removed from the chamber and immediately transferred to a dried, pre-weighed sample tube to prevent degradation. **Solvent-exchange and activation for polyIRMOFs.** polyIRMOFs were washed with CHCl$_3$ by soaking over three days with fresh CHCl$_3$ exchanged every 24 h. The crystals were transferred wet to a pre-weighed sample tube and evacuated in a vacuum line to remove residual solvent.

**TGA/DSC Measurements.** Between 5–10 mg of dried material was weighed for thermogravimetric analysis (TGA) measurements. The samples were analyzed under a stream of dried N$_2$ gas at a flow rate of 80 mL/min and heated from 35 to 800 °C with a ramping rate of 5 °C/min using a Mettler Toledo TGA/DSC 1 STAR System.

**Single X-ray Diffraction Crystallography.** A suitable crystal of polyUiO-68-10a-u was selected and placed on a Bruker APEX-II Ultra diffractometer, with a Mo-Kα Microfocus Rotating Anode and a APEX-II CCD area detector. The crystal was kept at 100 K during data collection. Using Olex2, the structure was solved with the ShelXT structure solution program using direct methods and refined with the XL refinement package using Least Squares minimisation (Dolomanov et al. *J. Appl. Crystallogr.*, 2009, 42, 339-341; G. Sheldrick, *Acta Crystallographica Section C*, 2015, 71, 3-8.; G. Sheldrick, *Acta Crystallographica Section A*, 2008, 64, 112-122). Minor restraints, including bond distances restraints and planar restraints were applied along with occupancies <1, to the linker central phenyl ring and methylene spacer to allow for their refinement. The disordered alkyl spacer and solvent molecules within the framework were treated with the SQUEEZE protocol in PLATON to account for electron density (P. van der Sluis et al., *Acta Crystallographica Section A*, 1990, 46, 194-201). The crystal data file of polyUiO-68-10a-u was deposited into the Cambridge Crystallographic Data Centre (CCDC) and assigned a number (1552853). Crystallographic data collection and refinement information is listed in Table S1.
Figure S1. $^1$H NMR of compound 1.

Figure S2. $^1$H NMR of compound 2.
Figure S3. $^1$H NMR of tpdc-8e-u, compound 3.

Figure S4. $^1$H NMR of compound tpdc-10e-u, compound 4.
Figure S5. $^1$H NMR of ptpdc-8e-u. End-group analysis was used to determine number of repeat units and $M_n$.

Figure S6. $^1$H NMR of ptpdc-10e-u. End-group analysis was used to determine number of repeat units and $M_n$. 
Figure S7. $^1$H NMR of ptpdc-8a-u.

Figure S8. $^1$H NMR of ptpdc-10a-u.
Figure S9. $^1$H NMR of compound 5.

Figure S10. $^1$H NMR of compound 6.
Figure 11. $^1$H NMR of compound 7.

Figure S12. $^1$H NMR of pbpd-c-8e-u. End-group analysis was used to determine number of repeat units and $M_n$. 
Figure S13. $^1$H NMR of pbpdc-8a-u.

Figure S14. GPC curves of polymer ligand ester derivatives pbpdc-xe-u and ptpdc-xe-u.
Figure S15. $^1$H NMR of digested polyUiO-67-8a-u.

Figure S16. $^1$H NMR of digested polyUiO-68-8a-u.
Figure S17. $^1$H NMR of digested polyUiO-68-10a-u.

Figure S18. Optical image of single crystals of polyUiO-68-10a-u used for $^1$H NMR.
Figure S19. $^1$HNMR of digested polyUIO-68-10a-u single crystals. a) The $^1$H NMR of the digested single crystals match with integration of the polymer ptpdc-10a-u. b) The $^1$HNMR of the digested crystals (black trace) is compared to the $^1$H NMR of the ptpdc-10a-u (red trace).
Figure S20. TGA curves of UiO-67, UiO-68, polyUiO-67-8a-u and polyUiO-68-xa-u, where $x = 8$ or $10$.

Figure S21. Stability test of: a) native UiO-67 after 20 h; b) polyUiO-67 after 3 days; c) allyloxy-functionalized UiO-68 after 1.5 h; d) polyUiO-68 after 5 h. Both polyUiO-67 and polyUiO-68 exhibit high crystallinity for extended times, when compared to their native counterparts, UiO-67 and allyloxy-functionalized UiO-68, respectively.
Figure S22. Chemical stability test for: a) allyloxy-functionalized UiO-68 and b) polyUiO-68-8a-u after being submerged in water for 12 h and allowed to dry over time.

Figure S23. a) Rouquerol plot for UiO-67. Only points below $P/P_0 = 0.030$ satisfy the criteria for applying the BET theory. b) Plot of the linear region for the BET equation for UiO-67.

Figure S24. a) Rouquerol plot for allyloxy-functionalized UiO-68. Only points below $P/P_0 = 0.030$ satisfy the criteria for applying the BET theory. b) Plot of the linear region for the BET equation for allyloxy-functionalized UiO-68.
Figure S25. a) Rouquerol plot for polyUiO-67-8a-u. Only points below $P/P_0 = 0.046$ satisfy the criteria for applying the BET theory. b) Plot of the linear region for the BET equation for polyUiO-67-8a-u.

Figure S26. a) Rouquerol plot for polyUiO-68-8a-u. Only points below $P/P_0 = 0.050$ satisfy the criteria for applying the BET theory. b) Plot of the linear region for the BET equation for polyUiO-68-8a-u.

Figure S27. a) Rouquerol plot for polyUiO-68-10a-u. Only points below $P/P_0 = 0.050$ satisfy the criteria for applying the BET theory. b) Plot of the linear region for the BET equation for polyUiO-68-10a-u.
Figure S28. The pore size distributions of: a) UiO-67 and polyUiO-67-8a-u, and b) polyUiO-68-xa-u are presented.

Figure S29. PXRD patterns for polyIRMOF-10-8a-u.

Figure S30. PXRD patterns for polyIRMOF-16-xa-u.
Figure S31. $^1$HNMR of digested polyIRMOF-10-8a-u.

Figure S32. $^1$H NMR of digested polyIRMOF-16-8a-u.
Figure S33. $^1$H NMR of digested polyIRMOF-16-10a-u.
Figure S34. SEM images of polyIRMOF-10-8a-u prepared from pbpdc-8a-u.

Figure S35. SEM images of polyIRMOF-16-8a-u prepared from ptpdc-8a-u.

Figure S36. SEM images of polyIRMOF-16-8a-u prepared from ptpdc-8a-u.
Figure S37. N$_2$-isotherm of polyIRMOF-16-10a-u.

Table S1. $^1$H NMR end-group analysis of the polymer acid ligands pbpdc-xa-u and ptpdc-xa-u.

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### Table S2. Crystal data and structure refinement for polyUiO-68-10a-u.

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<tr>
<td>(a/\text{Å})</td>
<td>32.6990(13)</td>
</tr>
<tr>
<td>(b/\text{Å})</td>
<td>32.6990(13)</td>
</tr>
<tr>
<td>(c/\text{Å})</td>
<td>32.6990(13)</td>
</tr>
<tr>
<td>(\alpha/°)</td>
<td>90</td>
</tr>
<tr>
<td>(\beta/°)</td>
<td>90</td>
</tr>
<tr>
<td>(\gamma/°)</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>34963(4)</td>
</tr>
<tr>
<td>(Z)</td>
<td>4</td>
</tr>
<tr>
<td>(\rho_{\text{calc}}/\text{g/cm}^3)</td>
<td>0.480</td>
</tr>
<tr>
<td>(\mu/\text{mm}^{-1})</td>
<td>0.199</td>
</tr>
<tr>
<td>(F(000))</td>
<td>4912.0</td>
</tr>
<tr>
<td>Crystal size/Å³</td>
<td>0.1 × 0.075 × 0.075</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoK(\alpha) (\lambda = 0.71073)</td>
</tr>
<tr>
<td>2θ range for data collection/°</td>
<td>2.49 to 50.066</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-38 ≤ h ≤ 37, -38 ≤ k ≤ 34, -38 ≤ l ≤ 37</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>70023</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>1586 [(R_{\text{int}} = 0.0862, R_{\text{sigma}} = 0.0190)]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>1586/84/68</td>
</tr>
<tr>
<td>Goodness-of-fit on (F^2)</td>
<td>1.159</td>
</tr>
<tr>
<td>Final (R) indexes [(I&gt;=2\sigma (I))]</td>
<td>(R_1 = 0.0597, wR_2 = 0.1709)</td>
</tr>
<tr>
<td>Final (R) indexes [all data]</td>
<td>(R_1 = 0.0702, wR_2 = 0.1801)</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>0.66/-0.68</td>
</tr>
</tbody>
</table>