Hierarchical Structure and Porosity in UiO-66

polyMOFs

Sergio Ayala, Zhenjie Zhang, 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 and ¹³C nuclear magnetic resonance (NMR) spectra were collected using a Varian spectrometer running at 400 MHz.

General Procedure for Synthesis of Monomers. To a 250 mL round bottom flask was added ester-protected 2,5-dihydroxyterephthalate (5.0 g, 7.9 mmol, 1 eq), the appropriate bromoalkene (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 20% ethyl acetate (EtOAc) in hexanes, affording the desired monomers.

Dimethyl 2,5-bis(but-3-en-1-yloxy)terephthalate (bdc-6e): Physical state: solid crystals. Yield: 46% (3.4 g, 8.1 mmol). ¹H NMR (400 MHz, DMSO-d₆) δ 7.32 (s, 2H), 6.20 – 5.80 (m, 2H), 5.42 (ddd, *J* = 17.2, 3.5, 1.7 Hz, 2H), 5.23 (q, *J* = 10.6, 1.6 Hz, 2H), 4.68 – 4.54 (m, 4H), 4.27 (q, *J* = 7.1 Hz, 4H), 1.28 (t, *J* = 7.1 Hz, 6H).

Dimethyl 2,5-bis(pent-4-en-1-yloxy)terephthalate (bdc-8e): Physical state: solid crystals. Yield: 58% (5.7 g, 13 mmol). ¹H NMR (400 MHz, CDCl₃) δ 7.35 (s, 2H), 5.85

(ddt, *J* = 16.9, 10.1, 6.7 Hz, 2H), 5.05 (dd, *J* = 17.1, 1.6 Hz, 2H), 4.99 (d, *J* = 10.2 Hz, 2H), 4.02 (t, *J* = 6.3 Hz, 4H), 3.90 (s, 6H), 2.31 – 2.20 (m, 4H), 1.95 – 1.85 (m, 4H).

Dimethyl 2,5-bis(hex-5-en-1-yloxy)terephthalate (bdc-10e): Physical state: yellowamber liquid. Yield: 89% (7.7 g, 4.2 mmol). ¹H NMR (400 MHz, CDCl₃): δ = 7.35 (s, 2H), 5.91 – 5.75 (m, 2H), 5.06 – 4.99 (m, 2H), 4.96 (ddd, *J* = 10.2, 2.0, 1.1 Hz, 2H), 4.01 (t, *J* = 6.4 Hz, 4H), 3.89 (s, 6H), 2.12 (td, *J* = 7.6, 1.1 Hz, 4H), 1.86 – 1.77 (m, 4H), 1.63 – 1.53 (m, 4H).

General Polymerization Procedure for Synthesis of pbdc-*xe-u***.** To a 25 mL round bottom flask was added monomer (3.00 mmol, 1.00 eq), and dissolved in 5 mL of DCM. The solution was degassed for 2 minutes. Grubbs second-generation catalyst was loaded neat (25 mg, 0.030 mmol, 0.01 eq). The reaction was set at mild reflux (45 °C) under mild nitrogen for 5 h. After the solution was cooled to room temperature, ethyl vinyl ether (2 mL) was added to quench the catalyst, and the solution was stirred 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 DCM and precipitated four more times in methanol. After the final wash, the polymer was transferred to a vial, and dried under vacuum for two hours.

For narrow dispersity polymers: The procedure was followed as before, but the catalyst loading was varied to 0.003 mmol to obtain small oligomers. 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 DCM and

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precipitated one more time in methanol. The polymer was purified using silica gel chromatography at gradient from 0% to 3% methanol in dichloromethane, affording the desired polymers.

Poly-dimethyl 2,5-bis(but-3-en-1-yloxy)terephthalate (pbdc-6e-u): Yield: 74% (740 mg, 2.2 mmol) ¹H NMR (400 MHz, CDCl₃) δ 7.36 (s, 1H), 6.06 – 5.79 (m, 1H), 5.75 – 5.59 (m, 1H), 5.16 (d, *J* = 17.1 Hz, 1H), 5.10 (d, *J* = 10.4 Hz, 1H), 4.03 (t, *J* = 6.7 Hz, 3H), 3.88 (s, 4H), 2.66 – 2.47 (m, 2H). *M_n*: 20,500 g/mol, *M_w/M_n*: 2.1, DP: 67 rpt units.

Poly-dimethyl 2,5-bis(pent-4-en-1-yloxy)terephthalate (pbdc-8e-u): Yield: 75% (820 mg, 2.3 mmol). ¹H NMR (400 MHz, CDCl₃) δ = 7.34 (s, 1H), 5.72 – 5.34 (m, 1H), 4.00 (t, J = 6.0 Hz, 2H), 3.89 (s, 2H), 2.32 – 2.10 (m, 2H), 1.86 (dd, J = 22.9, 16.1 Hz, 2H). M_n : 19,600 g/mol, M_w/M_n : 2.9, DP: 58 rpt units.

Poly-dimethyl 2,5-bis(hex-5-en-1-yloxy)terephthalate (pbdc-10e-u): Yield: 40% (470 mg, 0.48 mmol). ¹H NMR (400 MHz, CDCl₃): δ = 7.35 (s, 1H), 5.43 (m, *J* = 14.0 Hz, 1H), 4.00 (t, *J* = 5.9 Hz, 2H), 3.89 (s, 3H), 2.05 (bs, 2H), 1.90 – 1.71 (m, 2H), 1.62 – 1.47 (m, 2H). *M_n*: 10,800, *M_w/M_n*: 3.1, DP: 30 rpt units.

General Polymer Hydrolysis Procedure for pbdc-*xa-u* **synthesis.** The polymer ester (300mg-800 mg) was added to a 250 mL round-bottom flask, along with sodium hydroxide (15 equivalents), and placed in 60 mL a 1:1 of n,n-dimethylformamide (DMF): water solution. The mixture was heated at 90 °C for 24h, or until the solution became clear. The solvent was reduced by evaporation. The solution was acidified to a pH value of ~1 using a 2M HCI solution. The resultant solid was collected by vacuum filtration. The solid was washed with copious amounts of 2M HCI solution, and water to remove any salts.

Poly-2,5-bis(but-3-en-1-yloxy)terephthalic acid (pbdc-6a-u): Yield: 97% (630 mg, 2.0 mmol), ¹H NMR (400 MHz, DMSO-d₆) δ 7.22 (s, 1H), 5.97 – 5.71 (m, 1H), 5.72 – 5.40 (m, 1H), 5.13 (d, *J* = 17.4 Hz, 1H), 5.04 (d, *J* = 10.1 Hz, 1H), 3.97 (s, 2H), 2.38 (s, 2H).

Poly-2,5-bis(pent-4-en-1-yloxy)terephthalic acid (pbdc-8a-u): Yield: 94% (670 mg, 2.0 mmol) ¹H NMR (400 MHz, DMSO-d₆) δ 7.25 (s, 1H), 5.47 (m, 1H), 3.96 (t, *J* = 5.8 Hz, 2H), 2.12 (m, 2H), 1.86 – 1.60 (m, 2H).

Poly-2,5-bis(hex-5-en-1-yloxy)terephthalic acid (pbdc-10a-u): Yield: 97% (360 mg, 0.99 mmol) ¹H NMR (400 MHz, DMSO-d₆) δ 7.23 (s, 1H), 5.79 (m, 1H), 5.61 – 5.21 (m, 1H), 5.01 (d, *J* = 18.4 Hz, 1H), 4.94 (d, *J* = 9.9 Hz, 1H), 3.95 (t, *J* = 5.7 Hz, 2H), 2.05 (m, 2H), 1.65 (m, 2H), 1.53 – 1.36 (m, 2H).

General procedure for Zr-polyMOF synthesis. Procedure was adapted and modified from a previously published report.¹ Briefly, polymer-ligand (0.03 mmol) and zirconium (IV) chloride (ZrCl₄) (0.037 mmol) were dissolved in 20 mL scintillation vials using 2 mL of n,n-diethylformamide (DEF). After dissolving, 2 mL of formic acid was added to the vial. The reaction was set in a pre-heated oven at 135 °C for 2 days. A powder or brittle film was obtained at the bottom of the vial. The resultant materials were washed by exchanging the solvent with copious amounts of DMF.

Analytical Characterization

Gel-permeation chromatography (GPC) conditions for pbdc-xe-u. 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. The synthesized polyMOFs were collected by filtration, washed with copious amounts of methanol to remove DEF, and dried for ~20 minutes before data collection. PXRD data were collected at ambient temperature on a Bruker D8 Advance diffractometer at 40 kV and 40 mA for Cu K α (λ = 1.5418 Å), with a scan speed of 1 s/step, a step size of 0.02° in 20, and a 20 range of 5–50°.

¹**H NMR Digestions.** 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 μ L DMSO-d₆ using 10 μ L of 50% HF in water to digest the polyMOF.

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.

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N₂-Sorption Measurements. Prior to analysis, the materials were washed by exchanging the solvent with DMF three times for one day, then with methanol twice a day for two days. About 40-50 mg of the samples were transferred to pre-weighed sample tubes, and the samples were evacuated in a vacuum line for 2h. The crystals were activated using an ASAP 2020 Adsorption analyzer under vacuum at 105 °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.

TGA/DSC Measurements. Between 5–10 mg of dried material weighed for thermogravimetric analysis (TGA) measurements. Samples were analyzed under a stream of dried N₂ gas at a flow rate of 80 mL/min using a Mettler Toledo TGA/DSC 1 STAR System running from 35 to 800 °C with a ramping rate of 10 °C/min.



Figure S1. ¹HNMR of pbdc-6e-u. End-group analysis was used to determine number of repeat units and M_n .



Figure S2. ¹HNMR of pbdc-8e-u. End-group analysis was used to determine number of repeat units and M_n .



Figure S3. ¹HNMR of pbdc-10e-u. End-group analysis was used to determine number of repeat units and M_n .



Figure S4. ¹HNMR of pbdc-8e- u_{2700} . End-group analysis was used to determine number of repeat units and M_n .



Figure S5. ¹HNMR of pbdc-8e- u_{7800} . End-group analysis was used to determine number of repeat units and M_n after column chromatography.



Figure S6. ¹HNMR of pbdc-8e- u_{42000} . End-group analysis was used to determine number of repeat units and M_n after column chromatography.



Figure S7. GPC traces obtained for **a)** broad molecular weight pbdc-*xe-u* ligands and **b)** narrow molecular weight pbdc-8e-u ligands. Negative refraction are solvent markers.



Figure S8. ¹H NMR of pbdc-6a-u.



Figure S9. ¹H NMR of pbdc-8a-u.



Figure S10. ¹H NMR of pbdc-10a-u.



Figure S11. ¹HNMR of pbdc-8a-u₂₈₀₀.



Figure S12. ¹H NMR of pbdc-8a-u₇₈₀₀.



Figure S13. ¹H NMR of pbdc-8a-u₄₂₀₀₀.



Figure S14. MALDI-TOF MS of a) pbdc-8e-u₂₈₀₀, b) pbdc-8e-u₇₈₀₀, and c) pbdc-8e-u₄₂₀₀₀.

No signal was obtained for the largest polymer.



Figure S15. PXRD data was obtained for polyUiO-66 prepared from pbdc-xa ligands.²



Figure S16. ¹H NMR of digested polyUiO-66 prepared from broad pbdc-6a-u.



Figure S17. ¹H NMR of digested polyUiO-66 prepared from broad pbdc-8a-u.



Figure S18. ¹H NMR of digested polyUiO-66 prepared from broad pbdc-10a-u.



Figure S19. ¹H NMR of digested UiO-66 polyMOF prepared from narrow molecular weight pbdc-8a-u.



Figure S20. (a) TGA and (b) (DSC) traces of polyUiO-66 prepared from narrow pbdc-8a-

u.



Figure S21. (a) TGA and (b) (DSC) traces of narrow molecular weight pbdc-8a-u ligands.



Figure S22. PXRD data of pbdc-8a-u₄₂₀₀₀ after being stored for six months in air under ambient conditions.



Figure S23. SEM image of polyUiO-66 prepared from pbdc-6a-u.



Figure S24. SEM Images for polyUiO-66 prepared from a) pbdc-7a; b) pbdc-8a.



Figure S25. Pore-size distribution of polyUiO-66 prepared from a) pbdc-6a-u and b) pbdc-8a-u.



Figure S26. Pore-size distribution of polyUiO-66 prepared from narrow molecular weight pbdc-8a-u ligands.



Figure S27. N₂-Isotherm of polyUiO-66 prepared from pbdc-8a.

References:

1. C. A. Trickett, K. J. Gagnon, S. Lee, F. Gandara, H. B. Burgi and O. M. Yaghi, *Angew. Chem. Int. Ed.*, 2015, **54**, 11162-11167.

2. (a) Z. Zhang, H. T. H. Nguyen, S. A. Miller and S. M. Cohen, *Angew. Chem. Int. Ed.*, 2015, **54**, 6152-6157; (b) Z. J. Zhang, H. T. H. Nguyen, S. A. Miller, A. M. Ploskonka, J. B. DeCoste and S. M. Cohen, *J. Am. Chem. Soc.*, 2016, **138**, 920-925.