

Inside polyMOFs: Layered Structures in Polymer-Based Metal-Organic Frameworks

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SUPPORTING INFORMATION

Materials Synthesis

All solvents and starting materials were purchased from chemical suppliers and used without further purification (Sigma Aldrich, Alfa Aesar, EMD, and TCI).

Polymer and polyMOF Synthesis

Monomers, polymers, and polyMOFs were synthesized according to a previously published report (S. Ayala Jr., K. C. Bentz, S. M. Cohen. *Chem. Sci.* **2019**, *10*, 1746). Briefly, the general procedure for polyUiO-66 preparation is described. The polymer ligand (0.03 mmol by monomer repeat unit), ZrCl₄ (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.

Characterization Methods

Powder X-ray Diffraction (PXRD): PXRD data were collected at room temperature on a Bruker D8 Advance diffractometer running at 40 kV, 40 mA for Cu K α ($\lambda = 1.5418 \text{ \AA}$), with a scan speed of 0.5 sec/step, a step size of 0.01° in 2 θ , and a 2 θ range of 3-50° at room temperature.

Scanning Electron Microscopy (SEM). MOFs were placed on conductive carbon tape on a sample holder and coated using an Ir-sputter coating for 7 sec. A Zeiss Sigma 500

ESEM microscope was used for acquiring images using a 2-3 kV energy source under vacuum at a working distance of 5 mm.

Small-angle X-ray scattering. Crystals in capillaries were analyzed at beamline 5-ID-D of the Advanced Photon Source (Argonne National Laboratory). Data were collected using collimated X-ray radiation (0.7293 Å, 17 keV) calibrated with both a glassy carbon standard and a silicon diffraction grating. Scattered radiation was detected using a CCD area detector. One-dimensional scattering data were obtained through the azimuthal averaging of the two-dimensional data to produce plots of the scattering intensity as a function of the scattering vector length, $q = 4\pi\sin(\theta/\lambda)$, where θ is one-half of the scattering angle and λ is the wavelength of the X-rays used. Analysis of the one-dimensional data was performed using the powder diffraction processing software JADE (MDI) or Origin (OriginLab). Scattering vectors, q , were converted to Bragg diffraction D-spacings through the relationship $q = 2\pi/D$.

Gel-permeation chromatography (GPC). 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.

¹H NMR. ¹H nuclear magnetic resonance (NMR) spectra were collected using a Varian spectrometer running at 400 MHz.

TEM Imaging. TEM was performed using a JEOL ARM300F GrandARM TEM (operated at 300 kV) with Gatan OneView-IS camera and Gatan K3 in situ direct electron detector. An electron flux of 0.5 to 2 e⁻ Å⁻² s⁻¹ (with a beam current of 1.52 nA) such that the cumulative dose not exceeding ~10 e⁻ Å⁻² was used over the course of acquisition. HAADF-STEM and elemental mapping were performed using a JEOL ARM200CF Aberration-Corrected TEM (operated at 200 kV). X-ray signals were collected using a Dual SDD EDS detector. HAADF-STEM data were collected with a probe semi-convergence angle of 10 mrad and at a camera length of 20 cm. A beam current of 0.3 nA and pixel dwell times between 1 and 5 μs. TEM samples were prepared by pipetting ~3 μL of polyMOF sample dispersed in methanol onto a 200-mesh copper TEM grids with lacey carbon support layer. Prior to drop cast, TEM grids were glow discharged for 60 sec with a 25 mA current. Thin sections of ~100 to ~200 nm polyMOF samples were prepared by microtoming using a Leica EM UC7/FC7 Cryo-Ultramicrotome.

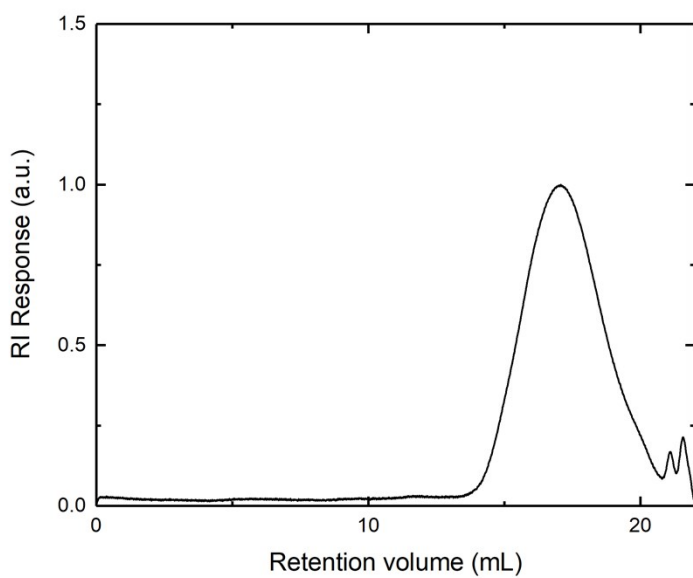


Figure S1. GPC chromatogram of pbdc-8e, methyl ester protected polymer ligand.

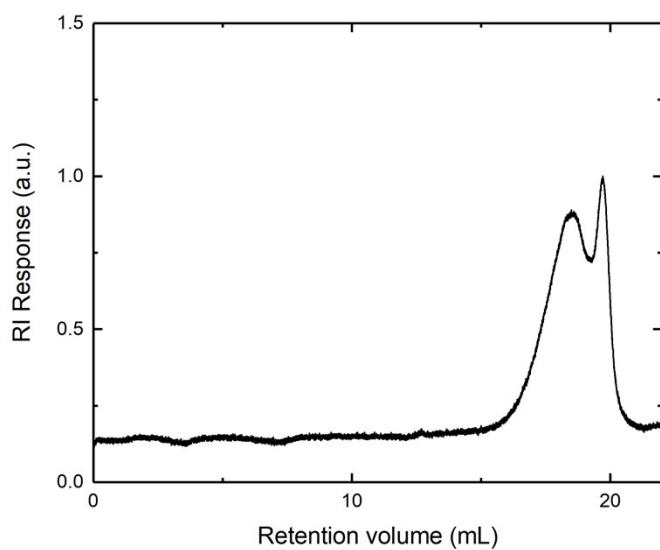


Figure S2. GPC chromatogram of pbdc-8e-PEG_{4k}-10%, methyl ester protected polymer ligand.

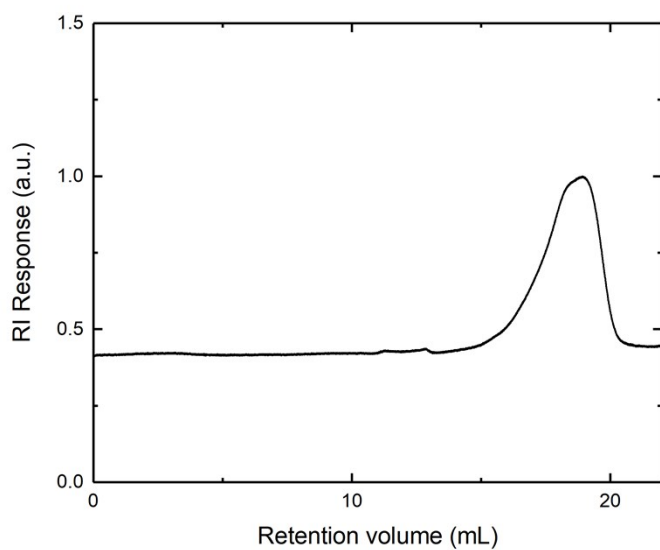


Figure S3. GPC chromatogram of pbdc-8e-PEG_{2k}-OMe, methyl ester protected polymer ligand.

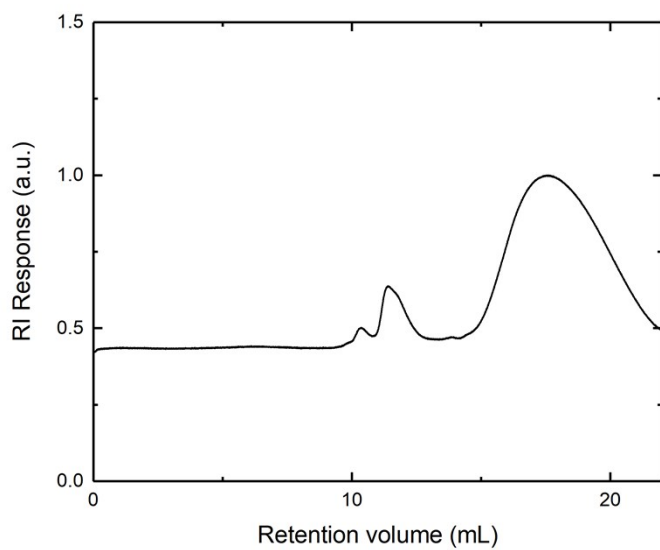


Figure S4. GPC chromatogram of pbdc-8e-COD_{1:1}, methyl ester protected polymer ligand.

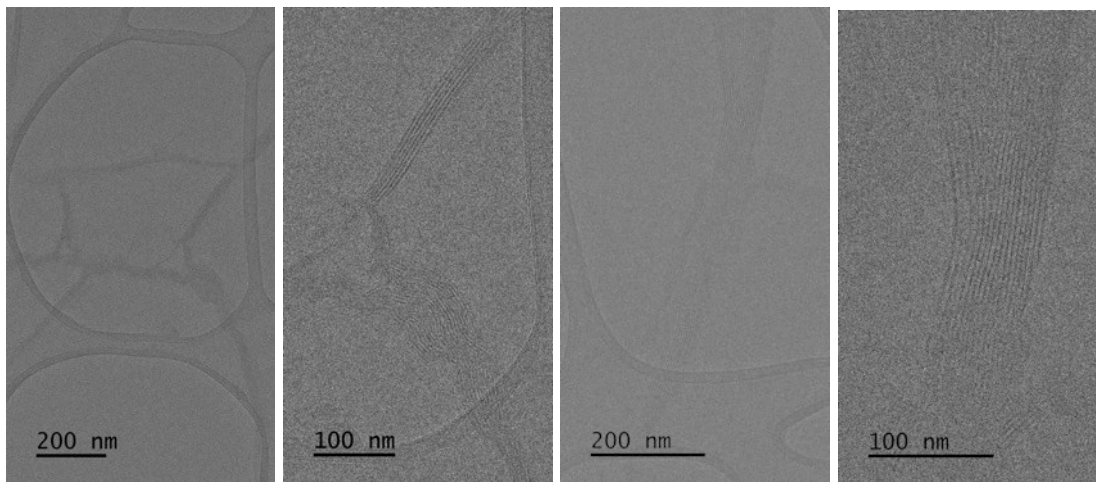


Figure S5. HR-TEM images of thin films (100 nm) of polyUiO-66 derived from pbdc-8a-PEG_{4k}-10%.

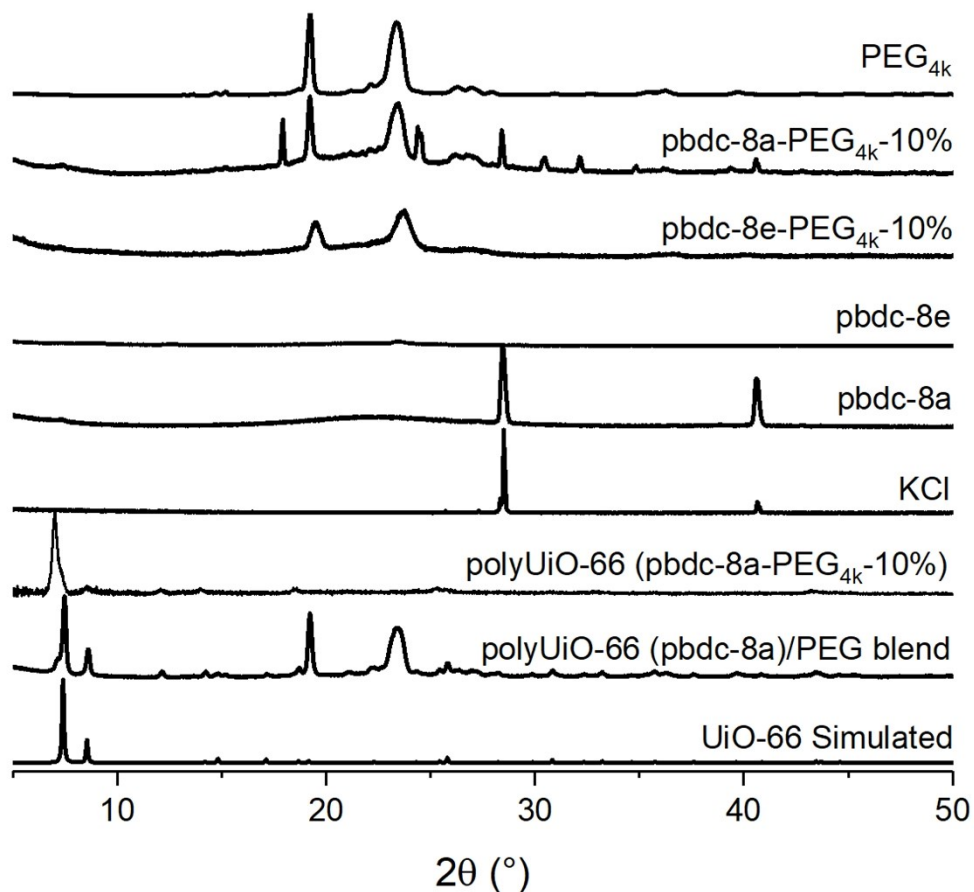


Figure S6. PXRD patterns of (top to bottom): 4,000 g/mol semi-crystalline PEG; pbdc-8a-PEG_{4k}-10% block polymer (free acid); pbdc-8e-PEG_{4k}-10% block polymer (methyl ester protected); pbdc-8e homopolymer (methyl ester protected); pbdc-8a homopolymer (free acid, with trapped potassium chloride); potassium chloride; polyUiO-66 derived from pbdc-8a-PEG_{4k}-10% block polymer; polyUiO-66 derived from pbdc-8a homopolymer physically blended with 4,000 g/mol PEG at the same weight percent in the pbdc-8a-PEG_{4k}-10% block polymer; simulated powder pattern for UiO-66. Small amounts of potassium chloride are present in the free acid polymers due to deprotection conditions from the methyl ester precursor.

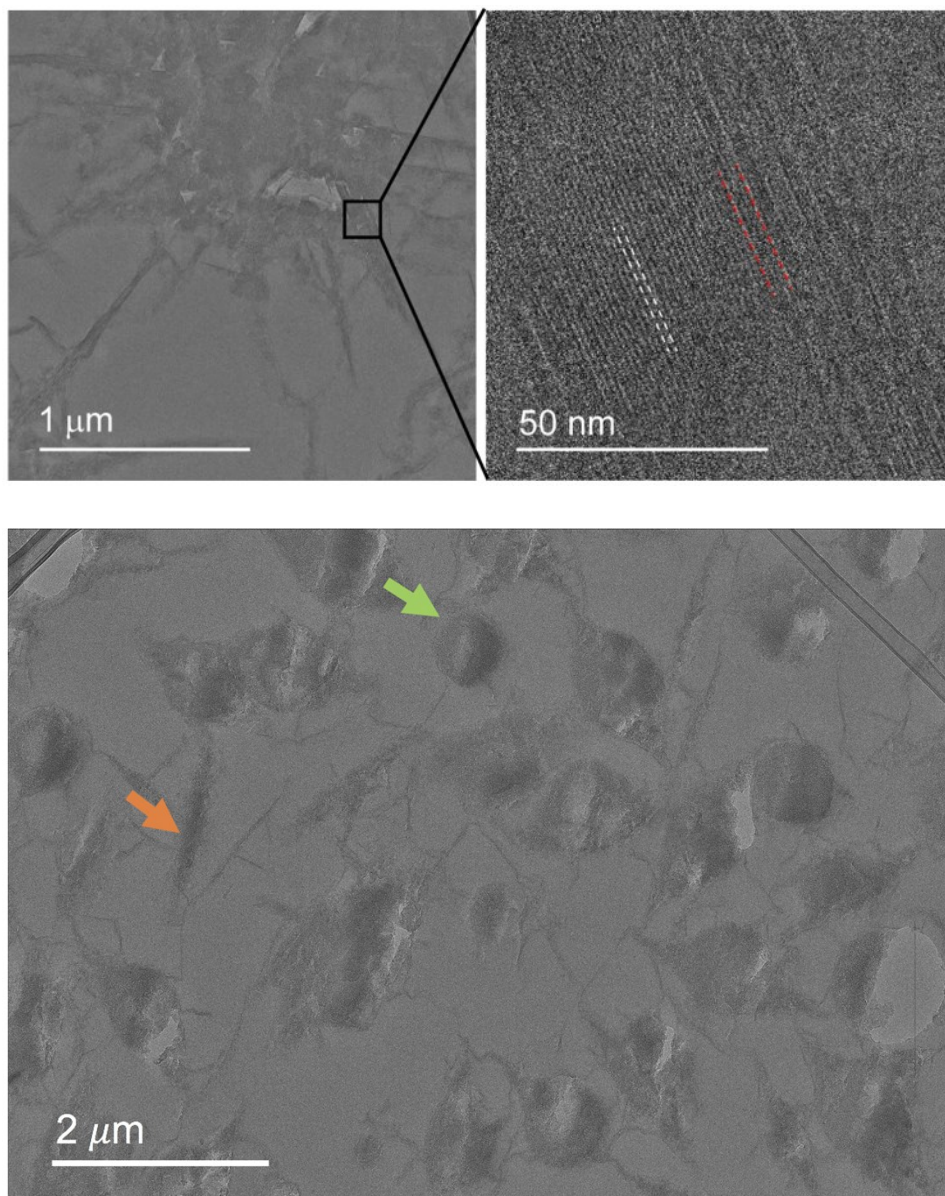


Figure S7. HR-TEM images of thin films of polyUiO-66 derived from pbdc-8a-PEG_{2k}-OMe. Green arrow denotes the x-y plane of a crystal where the lattice spacing of 1.2 to 1.4 nm represents the distance between neighboring Zr clusters; orange arrow denotes the crystal in x-z axis where the 2D stacked architecture of UiO-66 and polymer are evident by 4.2 nm spacing.

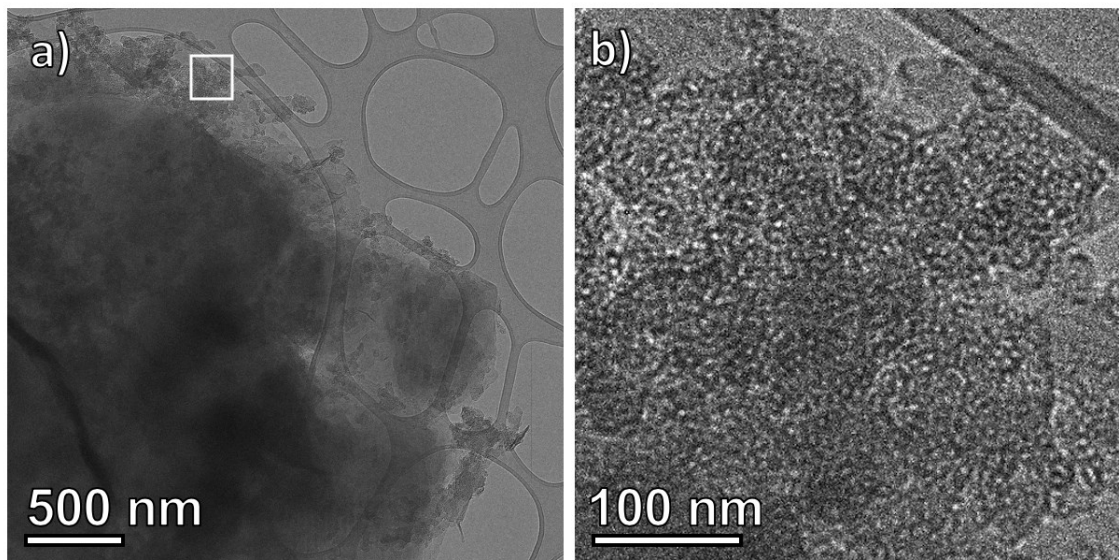


Figure S8. Top-down view of polyUiO-66 derived from pbdc-8a-PEG_{2k}-OMe showing the presence of nanochannels: a) HRTEM of microtomed section of bulk crystal, b) high magnification image of white inset in (a).

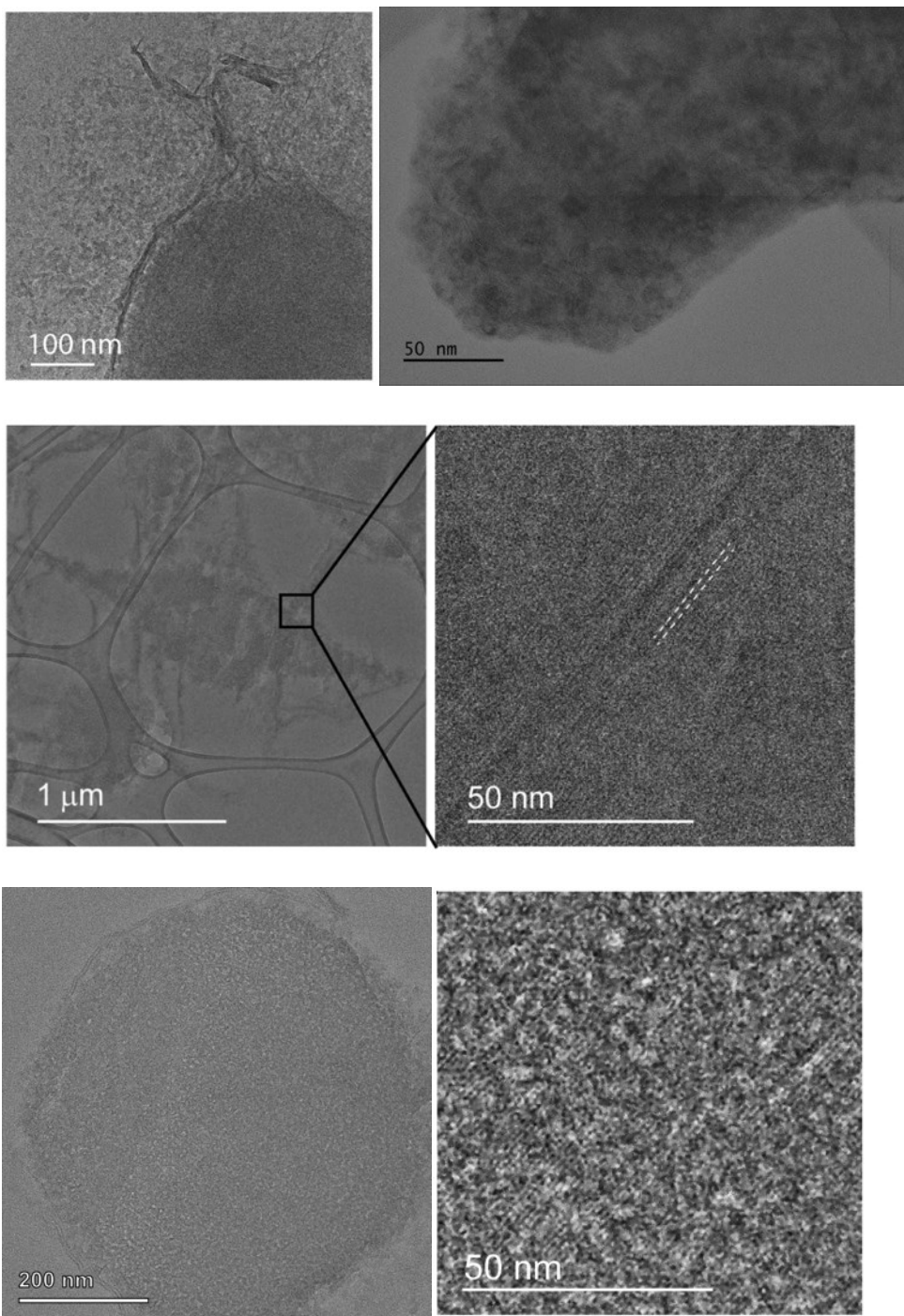


Figure S9. HR-TEM images of thin films (100 nm) of polyUiO-66 derived from pbdc-8a-COD_{1:1}.

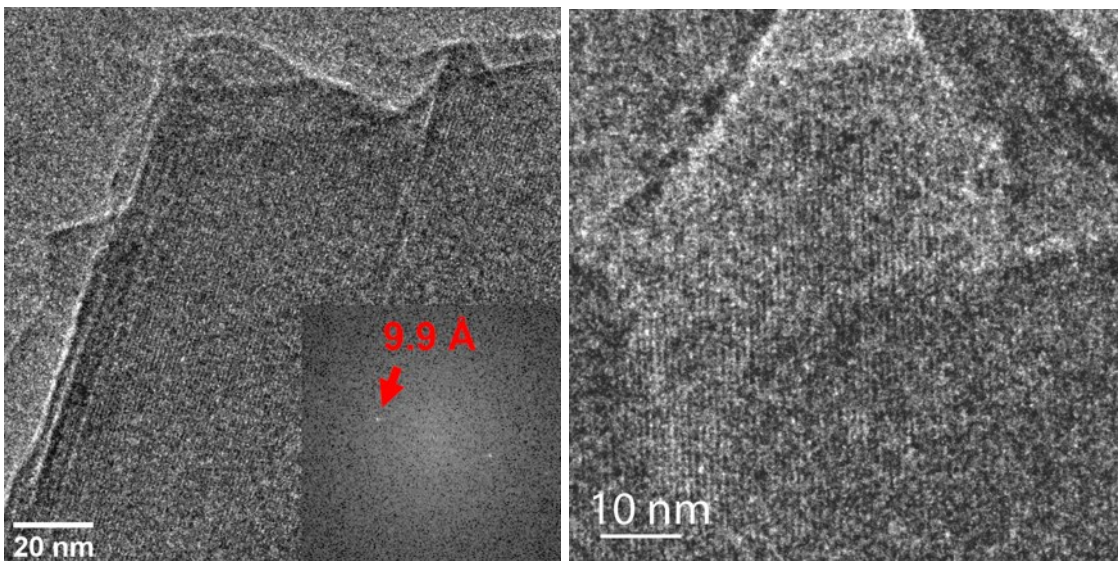


Figure S10. HR-TEM images of thin films (100 nm) of polyUiO-66 derived from homopolymer pbdc-8a (inset: electron diffraction pattern).

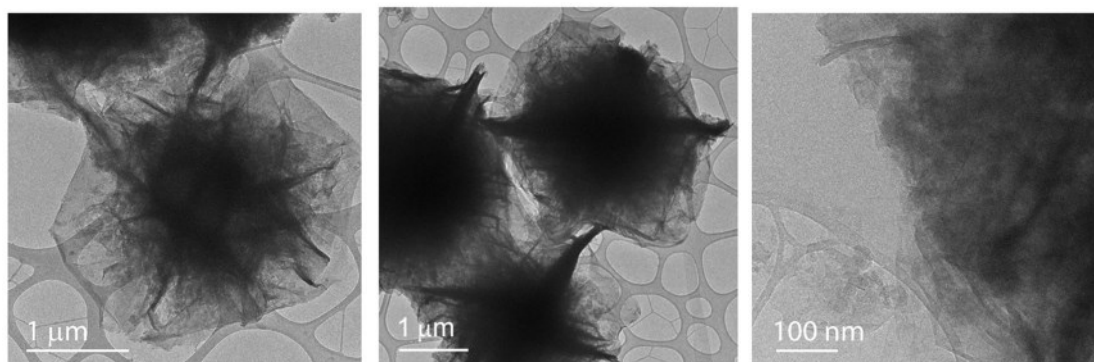


Figure S11. TEM images of bulk crystals of polyUiO-66 derived from pbdc-8a-PEG_{2k}-OMe.

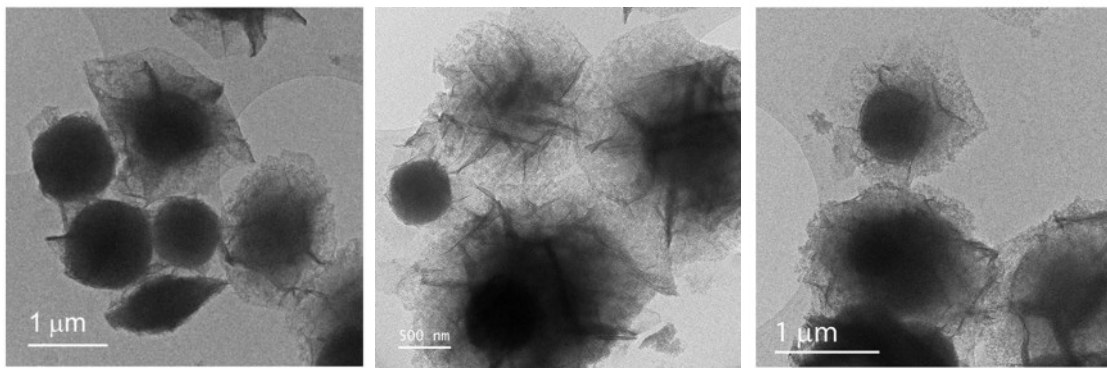


Figure S12. TEM images of bulk crystals of polyUiO-66 derived from pbdc-8a-COD_{1:1}.

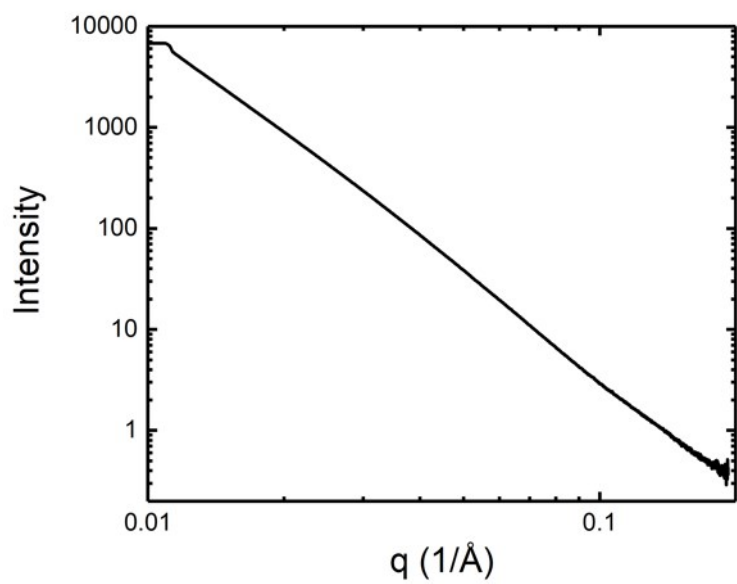


Figure S13. SAXS scattering profile of polyUiO-66 derived from homopolymer pbdc-8a.

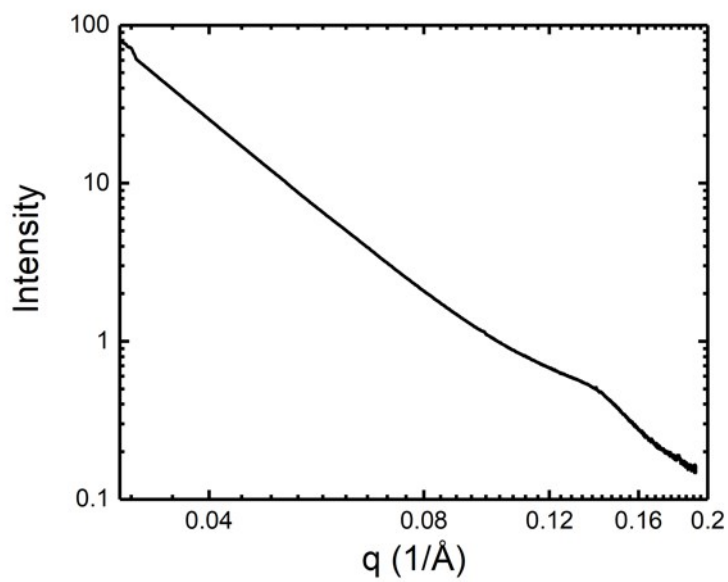


Figure S14. SAXS scattering profile of polyUiO-66 derived from polyBDC-*b*-PEG_{4k}-10%

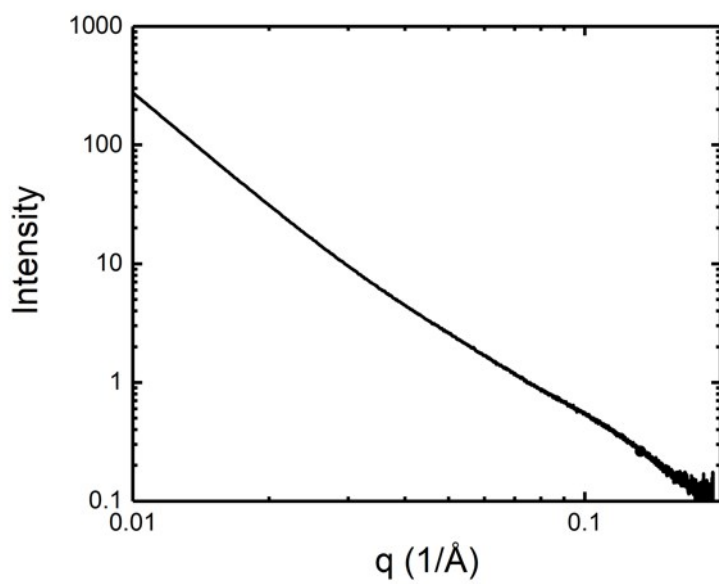


Figure S15. SAXS scattering profile of polyUiO-66 derived from polyBDC-*b*-PEG_{2k}-OMe.

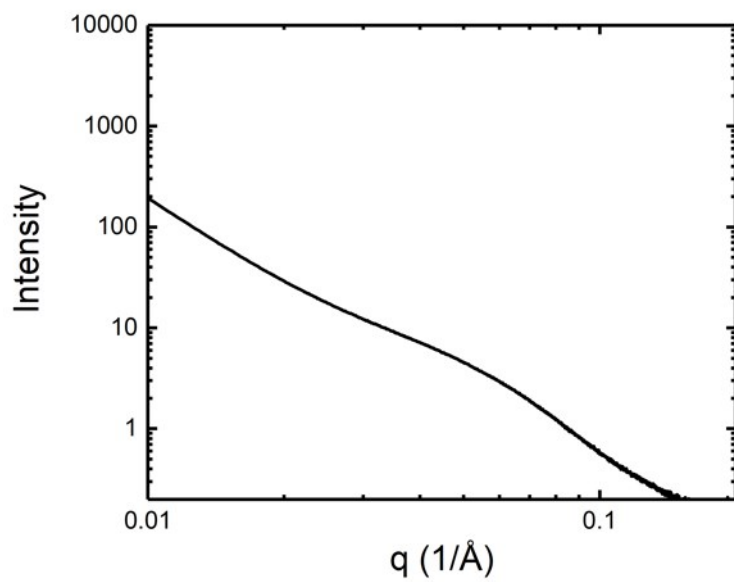


Figure S16. SAXS scattering profile of polyUiO-66 derived from polyBDC-*co*-COD_{1:1}.

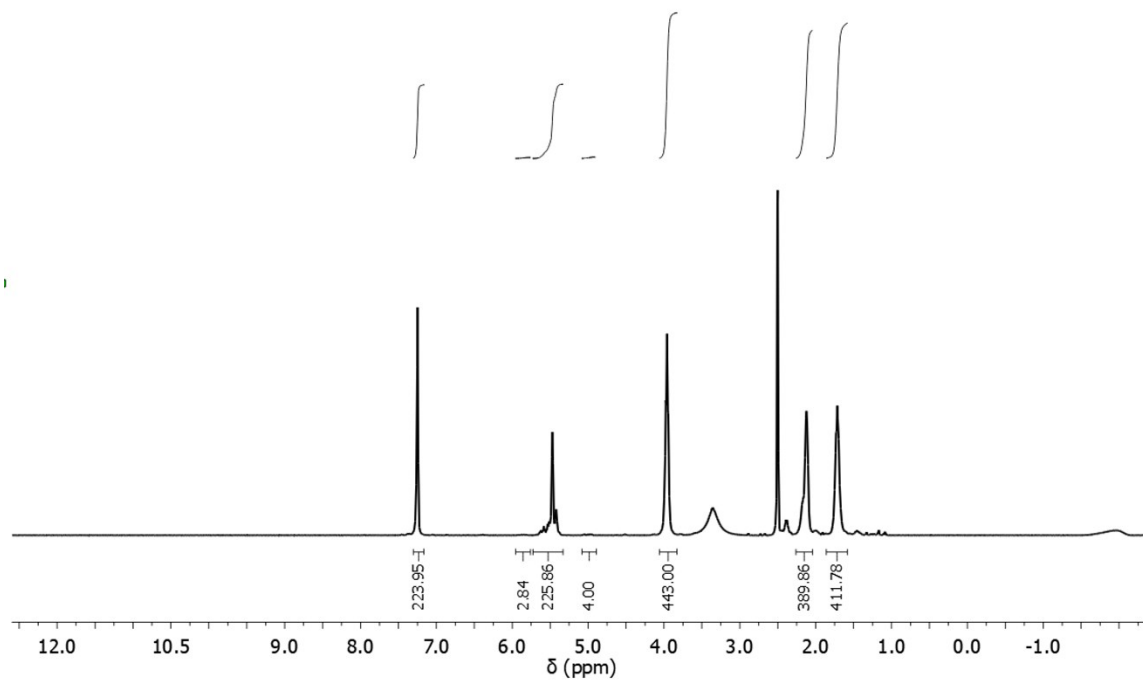


Figure S17. ^1H NMR spectrum of pbdc-8a ligand.

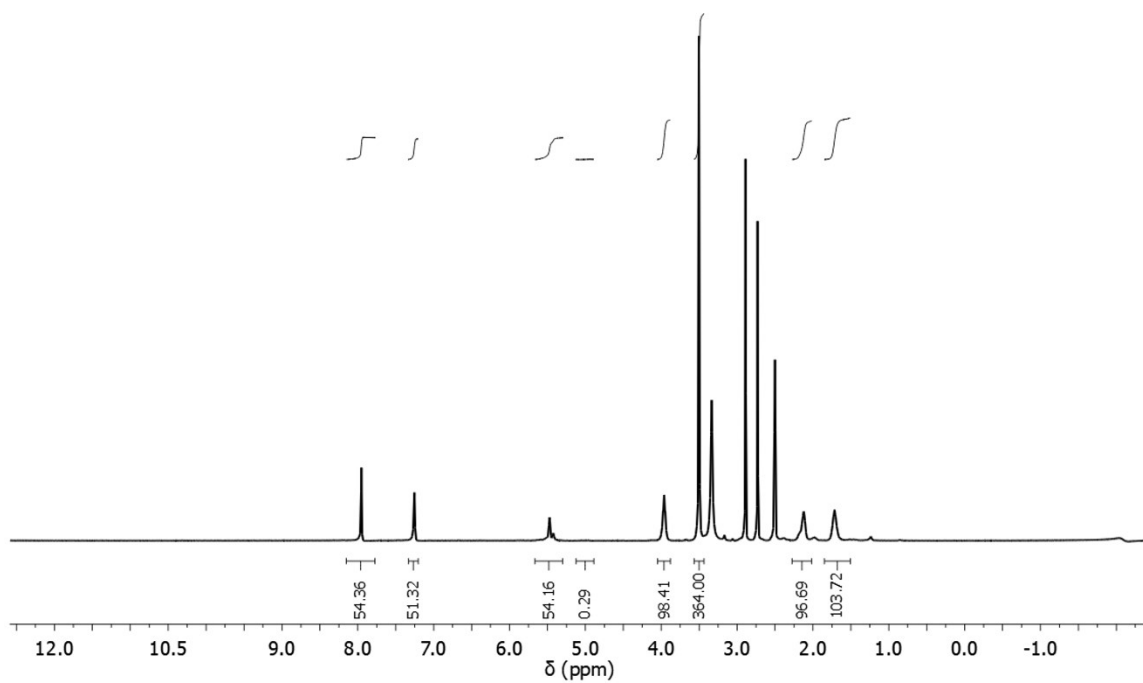


Figure S18. ^1H NMR spectrum of pbdc-8a-PEG_{4k}-10%, ligand.

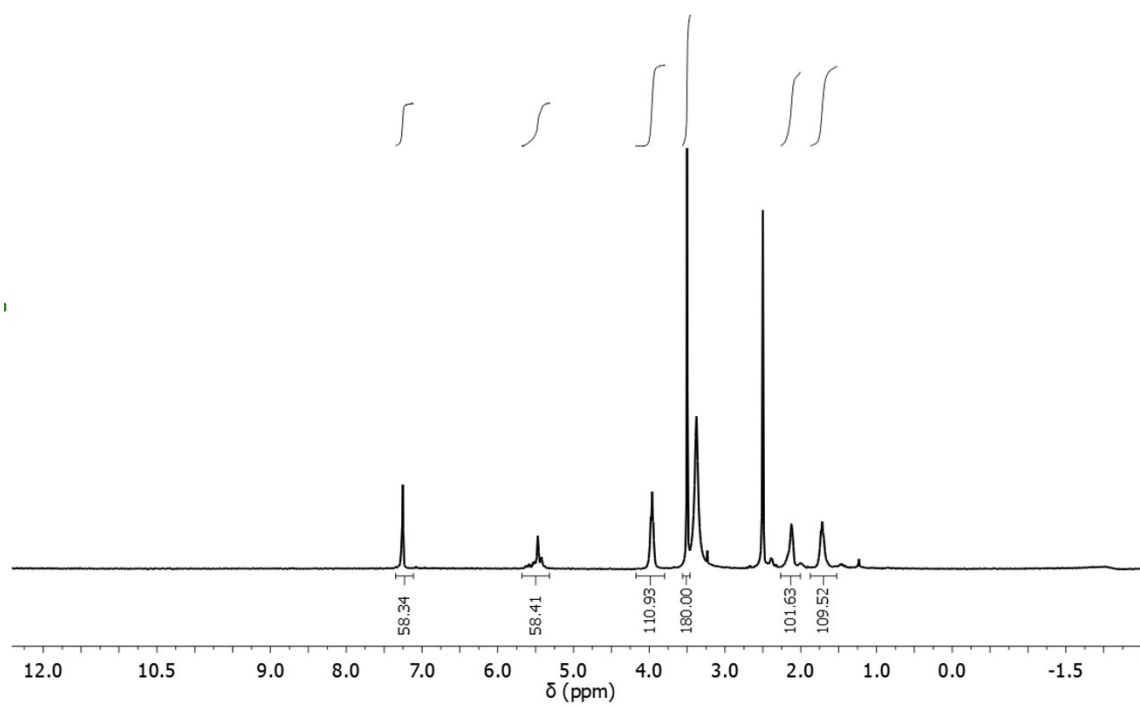


Figure S19. ^1H NMR spectrum of pbdc-8a-PEG_{2k}-OMe ligand.

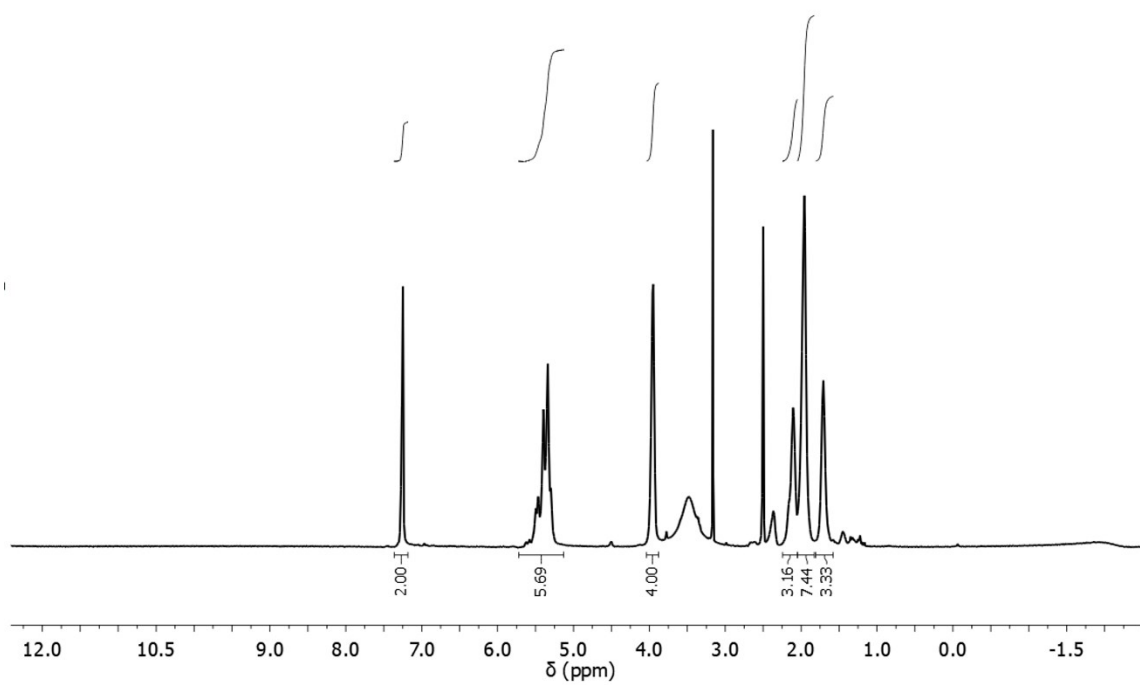


Figure S20. ^1H NMR spectrum of pbdc-8a-COD_{1:1} ligand.