Supporting Information

"Influence of Space-Filling of Pendant Groups on the Structure and Sorptive Properties of Two Semi-Flexible Isoreticular Metal-Organic Frameworks"

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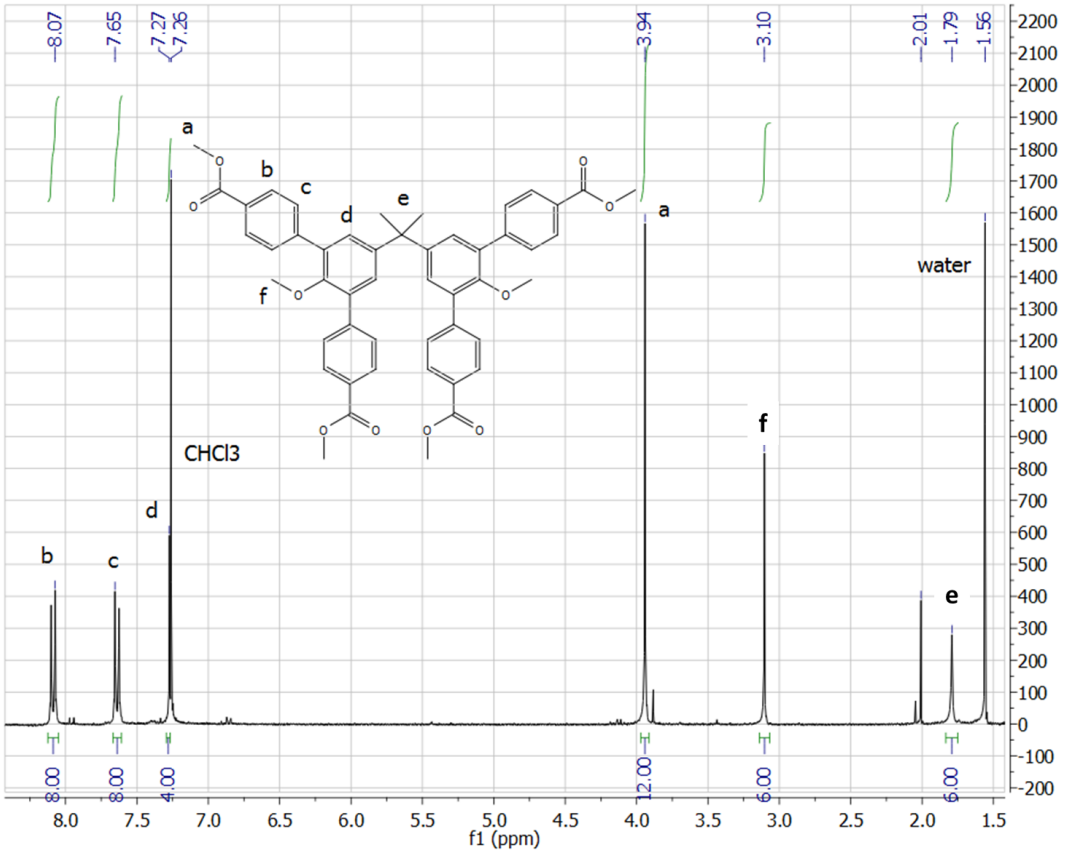

Fig. S1 ^{1}H NMR spectrum of Me_4pbtd-OMe

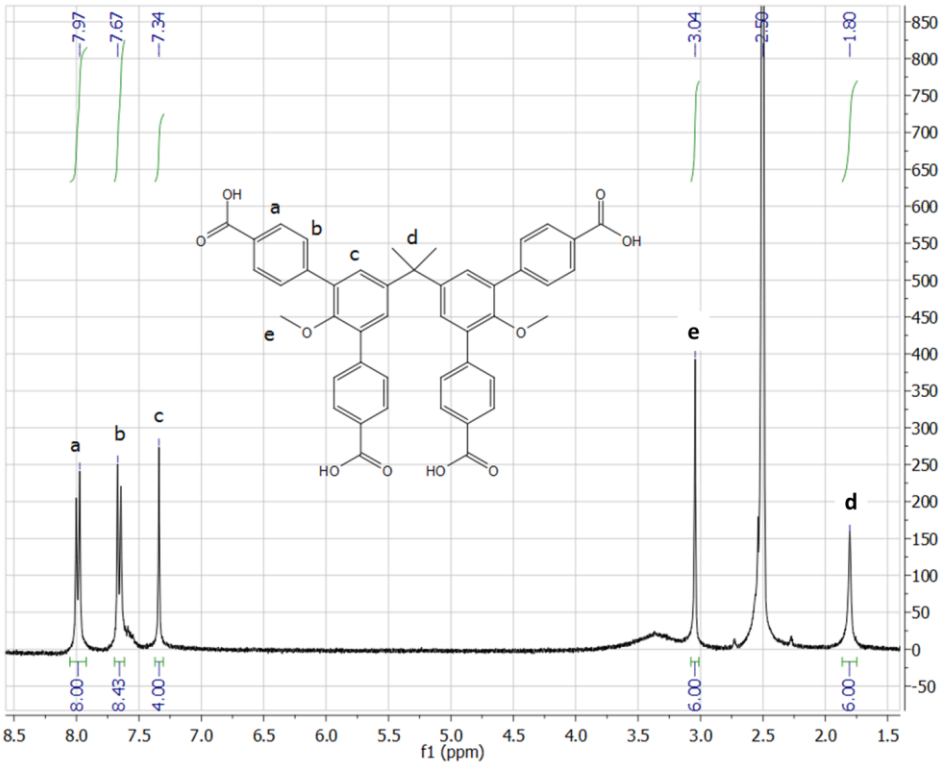

Fig. S2 ^{1}H NMR spectrum of H_4pbtd-OMe

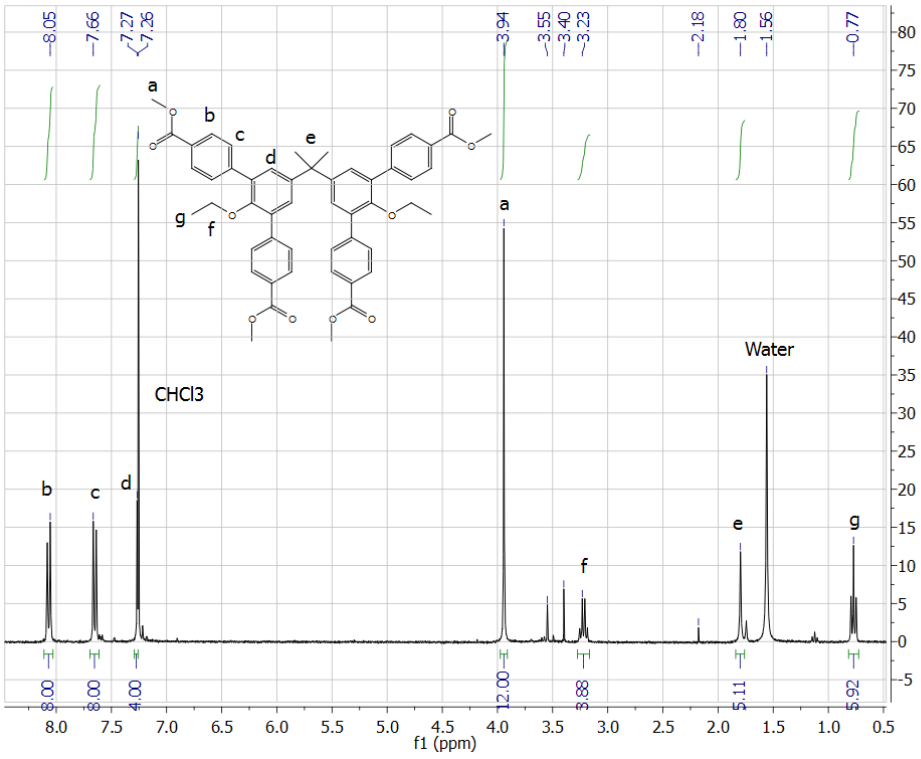

Fig. S3 ^{1}H NMR spectrum of Me_4pbtd-OEt

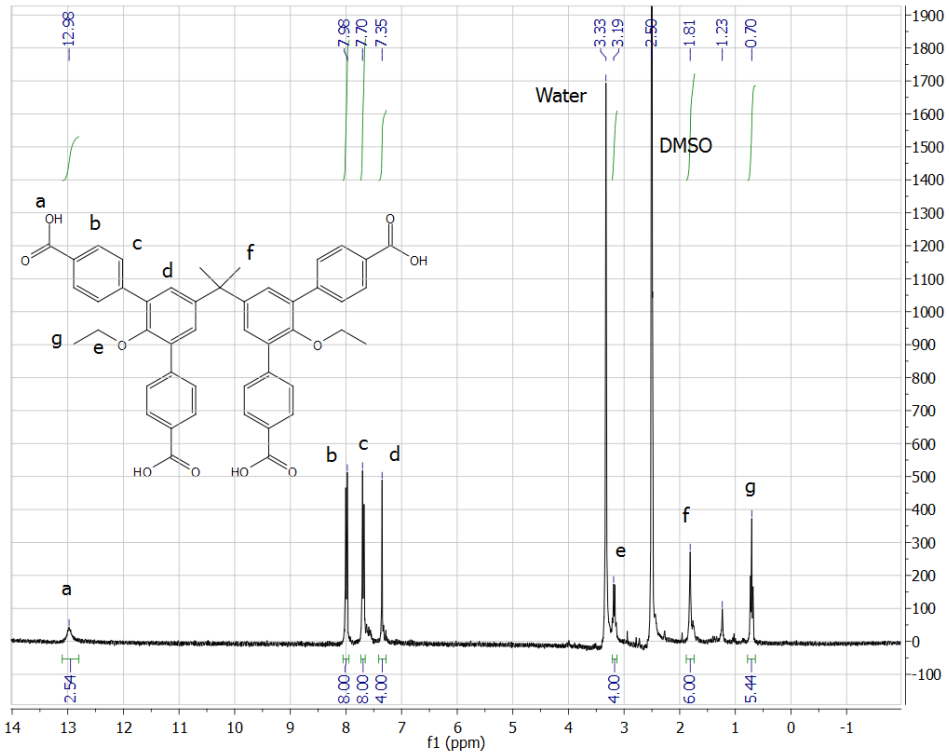

Fig. S4 ^{1}H NMR spectrum of H_4pbtd-OEt

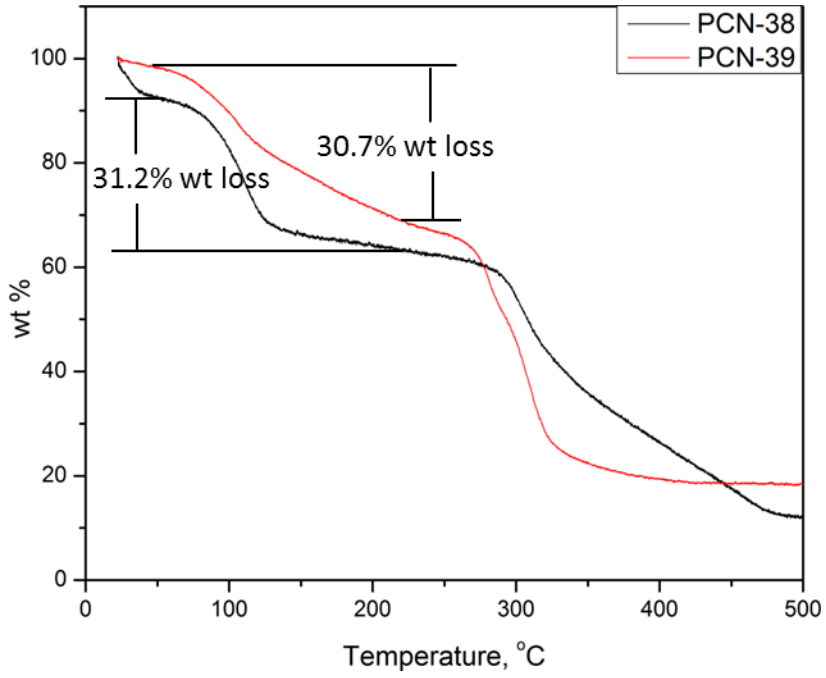

Fig S5 Thermogravimetric analysis of PCN-38 and -39

E

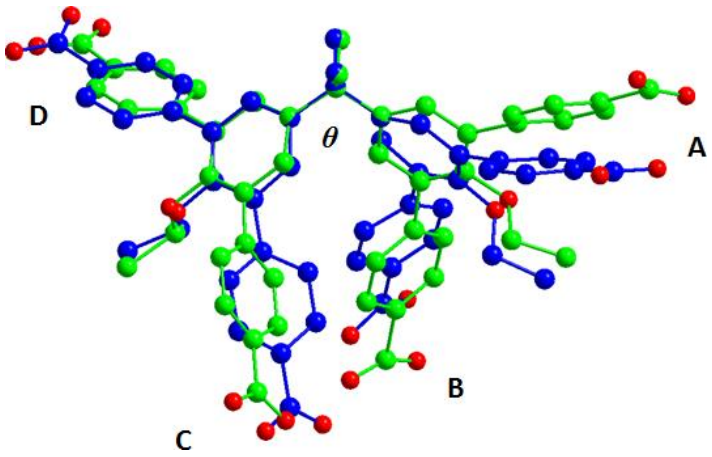

Fig S6 Overlap of PMTD-OEt ligands in PCN-39(*P* -1) (green) and PCN-39(*C* 2/*c*) (blue). Labels A-D reference planes formed from carboxylate group of respective position, θ is the angle between phenyl rings on methylene bridge

Table S1

Angle Measured	PCN-39(*P* -1)	PCN-39(*C* 2/*c*)
θ	111.6	107.3
∠AB	44.0	53.3
∠AC	84.6	78.6
∠AD	45.9	35.5
∠BC	51.4	49.4
∠BD	82.1	78.6
∠CD	53.3	53.3

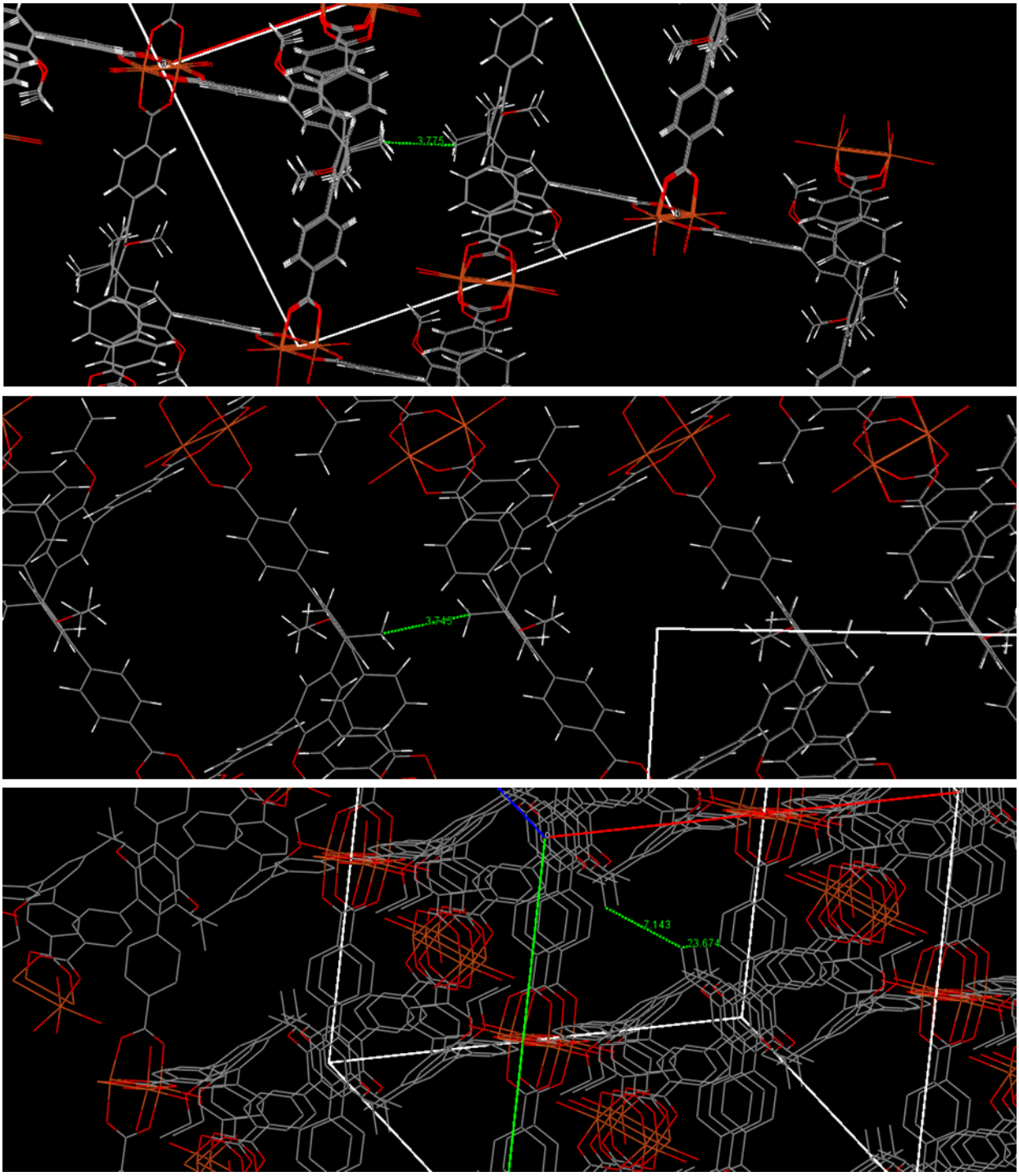

Fig. S7 View of closest Me-Me contacts in PCN-38 along [0 1 1] (top), PCN-39(*P* -1) along [0 0 1], and PCN-39(*C* 2/*c*) along [2 3 6]. Indicated distances are 3.775 Å in PCN-38, 3.745 Å in PCN-39(*P* -1), and 7.143 and 23.674 Å in PCN-39(*C* 2/*c*) (C-C distances).

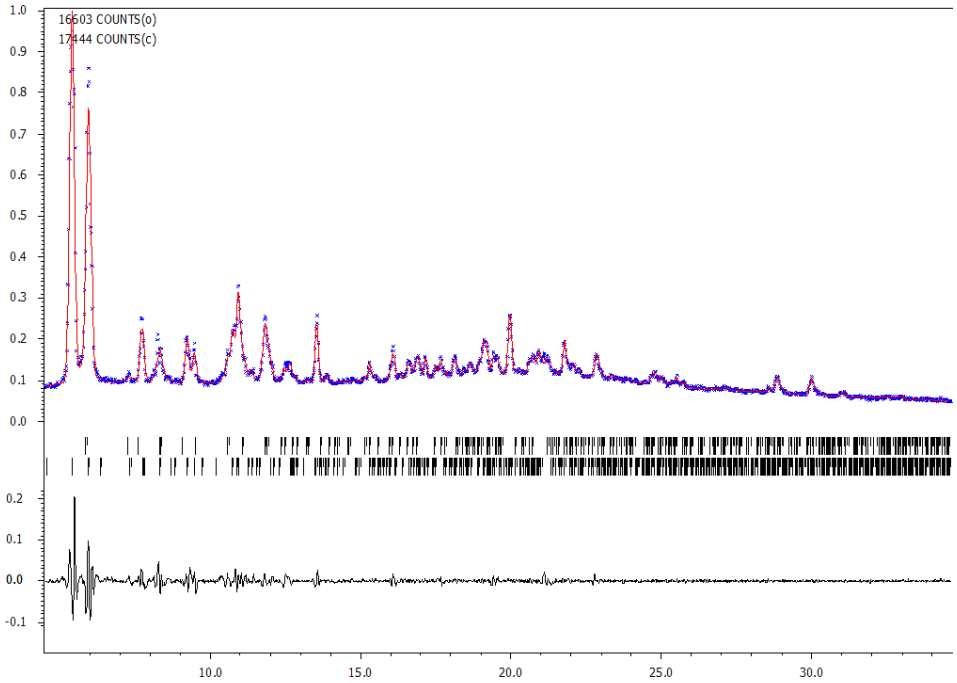

Fig. S8 PXRD pattern of freshly synthesized PCN-39 (blue) shown with Le Bail fit (red) for PCN-39(*C* 2/*c*) (top positions) and PCN-39(*P* -1) (bottom positions)

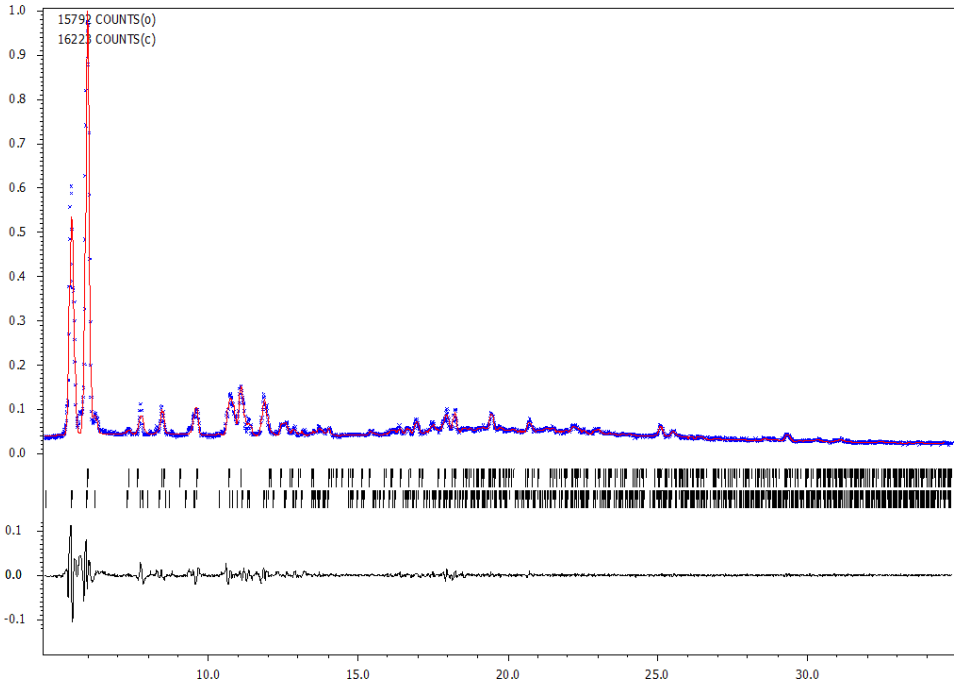

Fig. S9 PXRD pattern of PCN-39 (blue) shown with Le Bail fit (red) for PCN-39(*C* 2/*c*) (top positions) and PCN-39(*P* -1) (bottom positions) after ~30 min exposure to air

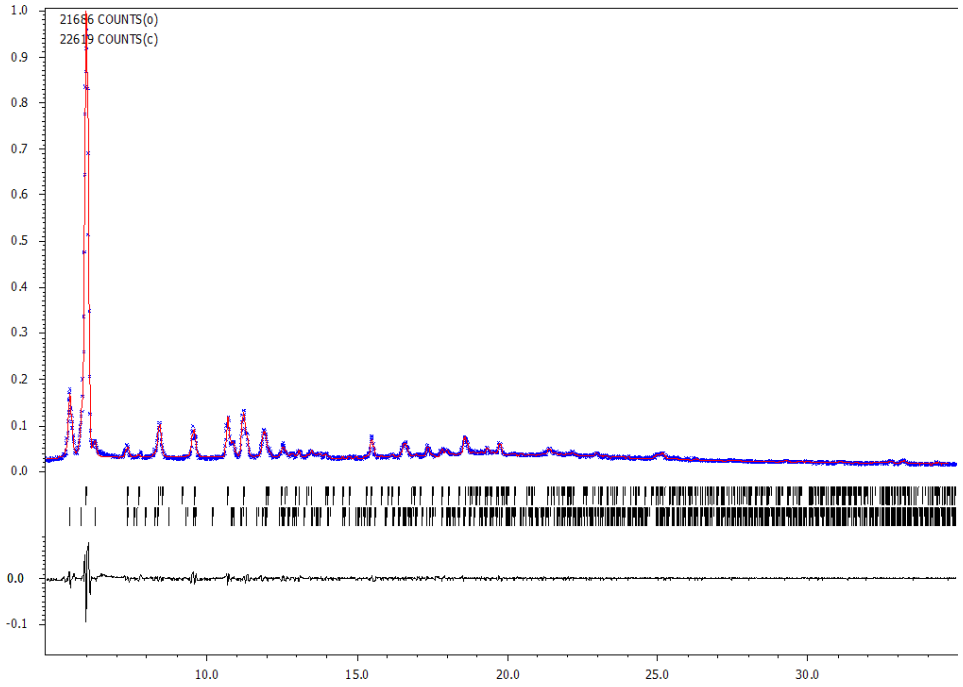

Fig S10 PXRD pattern of PCN-39 (blue) shown with Le Bail fit (red) for PCN-39(*C* 2/*c*) (top positions) and PCN-39(*P* -1) (bottom positions) after ~41 min exposure to air

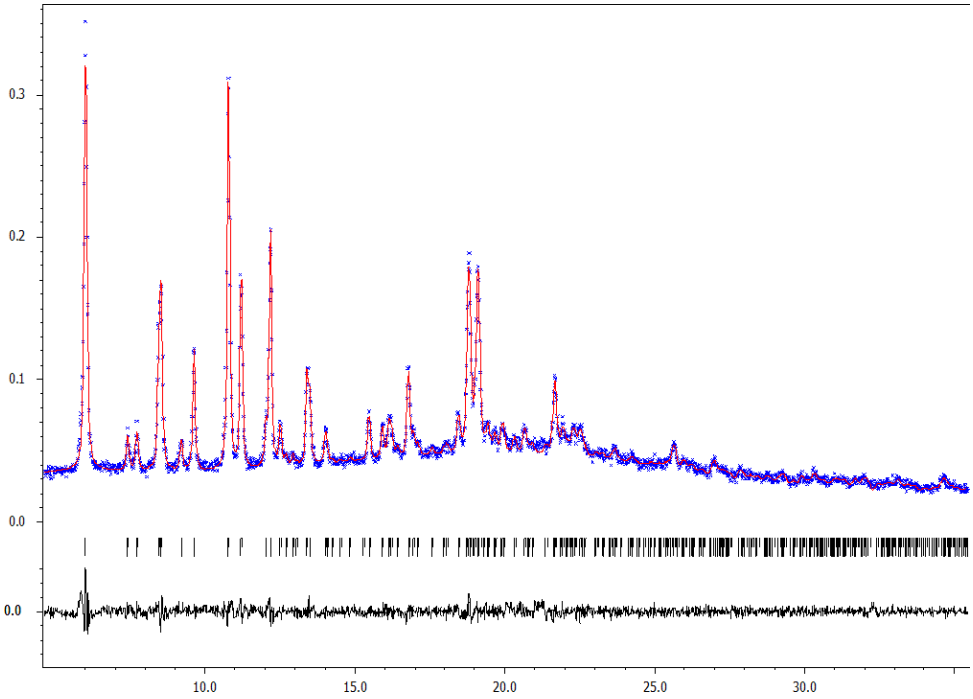

Fig S11 PXRD pattern of PCN-39 (blue) shown with Le Bail fit (red) for PCN-39(*C* 2/*c*) after solvent exchange with MeOH and evacuated for 1 h

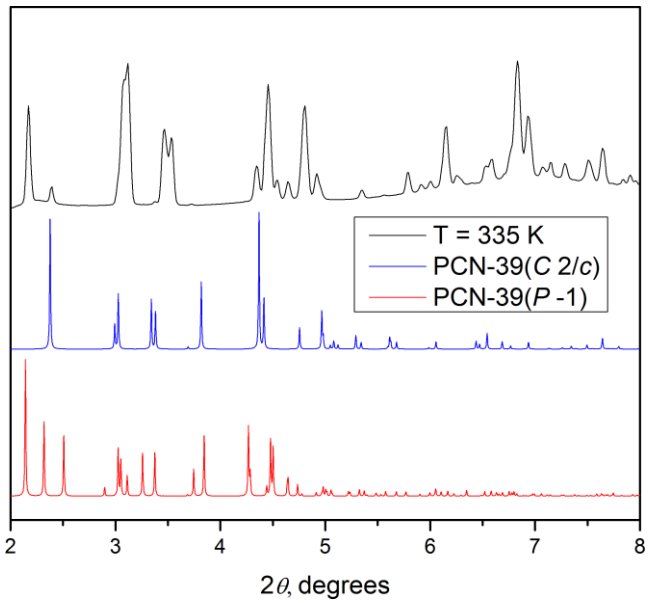

Fig. S12 Comparison of synchrotron PXRD pattern of PCN-39 heated to 335 K in closed system with simulated pattern of PCN-39(*C* 2/*c*) and PCN-39(*P* -1).

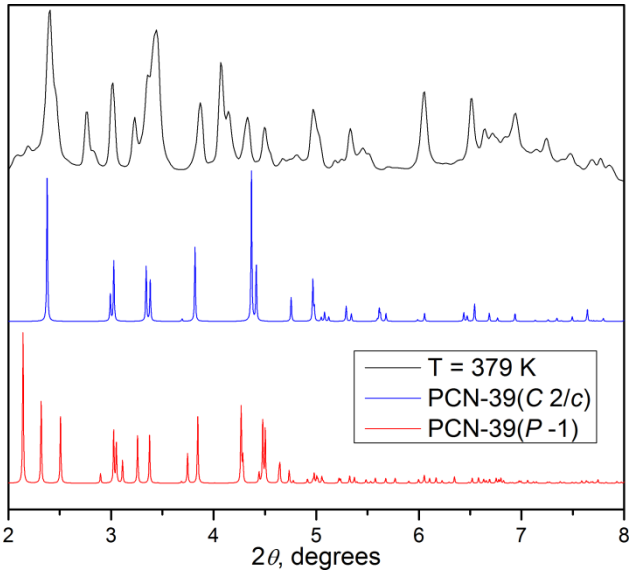

Fig. S13 Comparison of synchrotron PXRD pattern of PCN-39 heated to 379 K in closed system with simulated pattern of PCN-39(*P* -1) and -39(*C* 2/*c*).

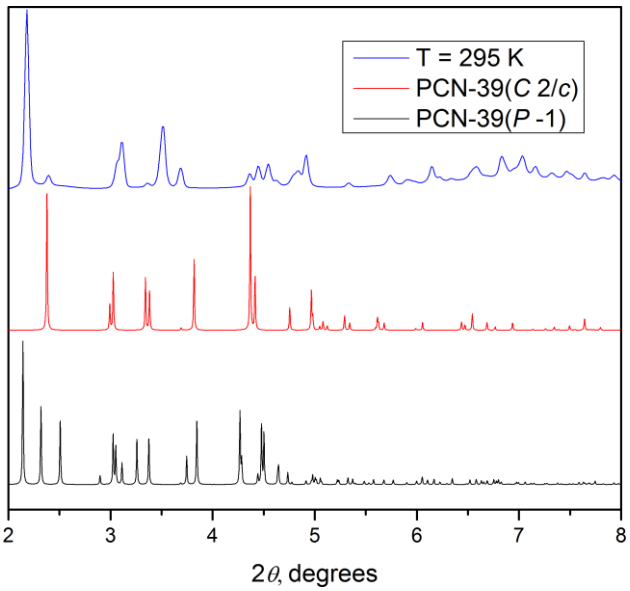

Fig. S14 Comparison of synchrotron PXRD pattern of PCN-39 cooled to 295 K after heating to 479 K in closed system with simulated pattern of PCN-39(*P* -1) and PCN-39(*C* 2/*c*).

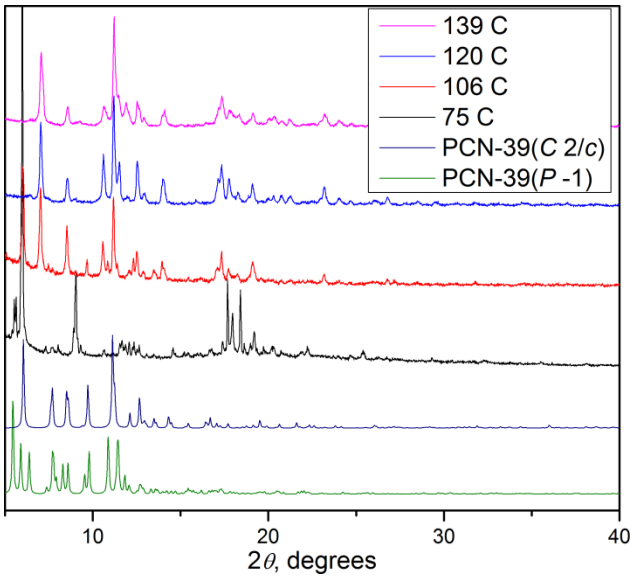

Fig. S15 Combined TGA/PXRD stop experiments. Samples were heated to specified temperature, cooled, transferred to Si single crystal PXRD sample cell, and PXRD pattern collected.

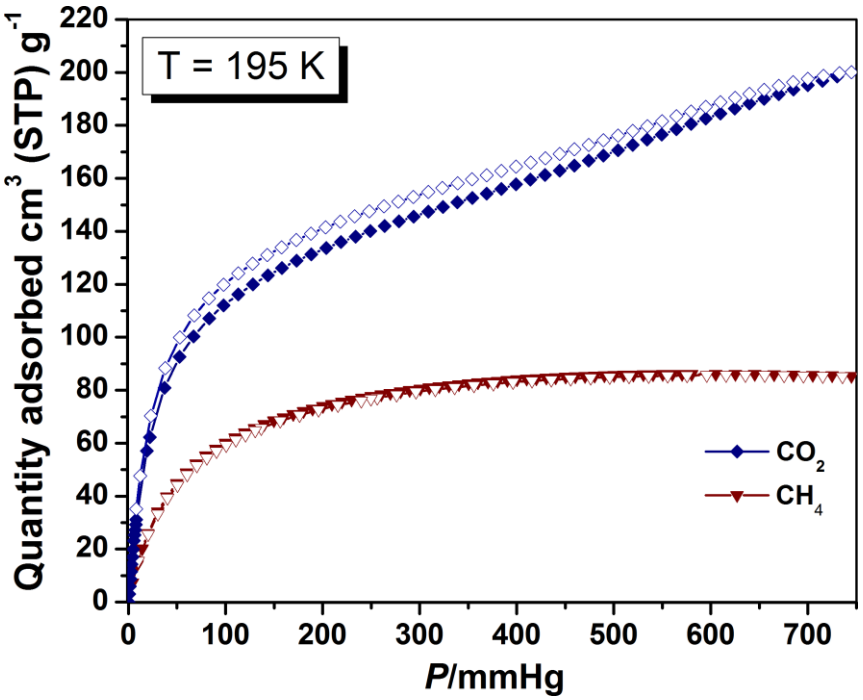

Fig S16 Methane and carbon dioxide uptake isotherms for PCN-38, measured at 195 K (solid symbols, adsorption; open symbols, desorption)

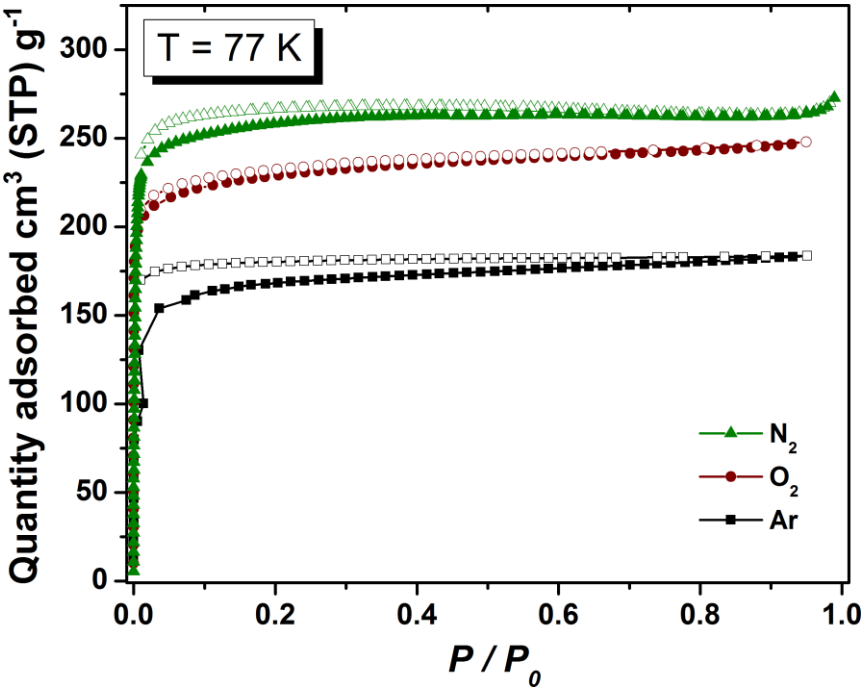

Fig S17 Oxygen and argon uptake isotherms for PCN-38, measured at 77 K (solid symbols, adsorption; open symbols, desorption)

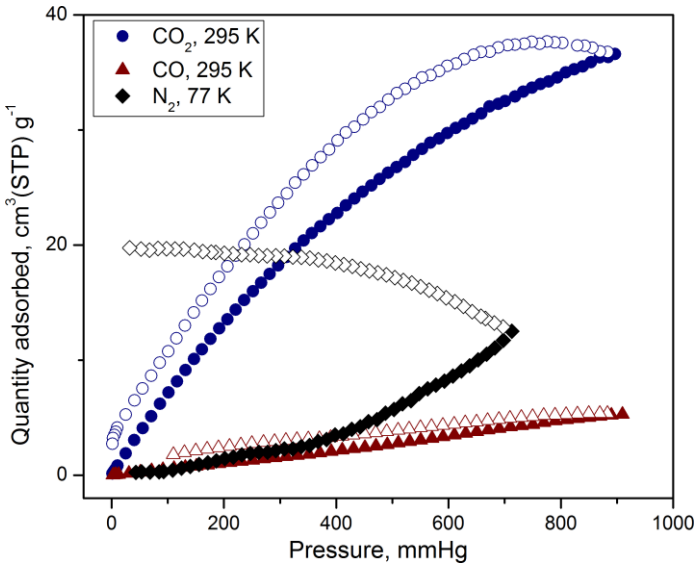

Fig S18 Carbon dioxide, carbon monoxide, and nitrogen uptake isotherms for PCN-39 measured at 295, 295, and 77 K, respectively. (solid symbols, adsorption; open symbols, desorption)

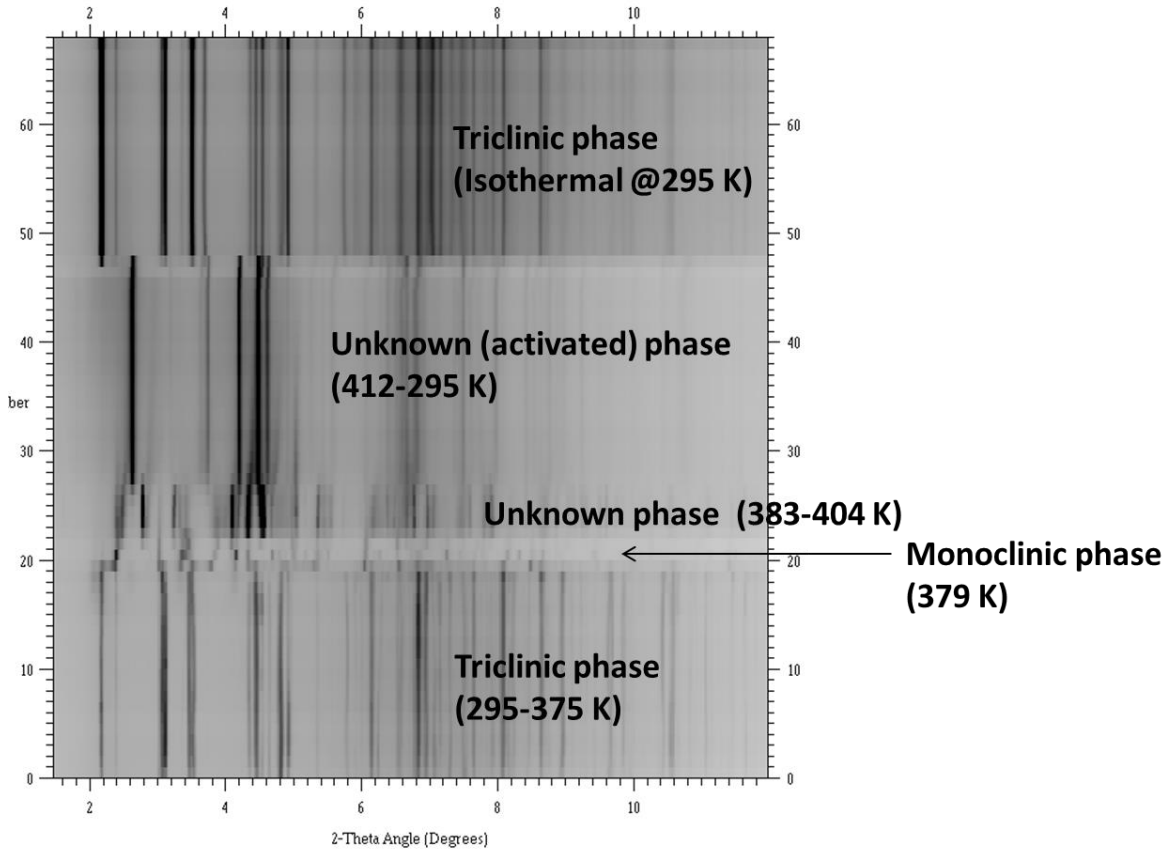

Fig S19 Top view of PXRD patterns collected from *in situ* synchrotron PXRD experiment heating PCN-39 in a closed system from 295 – 473 K at a rate of 2 K/min, maintained at 473 K for 30 min, then quickly cooled to 295 K. Labeled phases are the phases that dominate, but not necessarily phase pure.

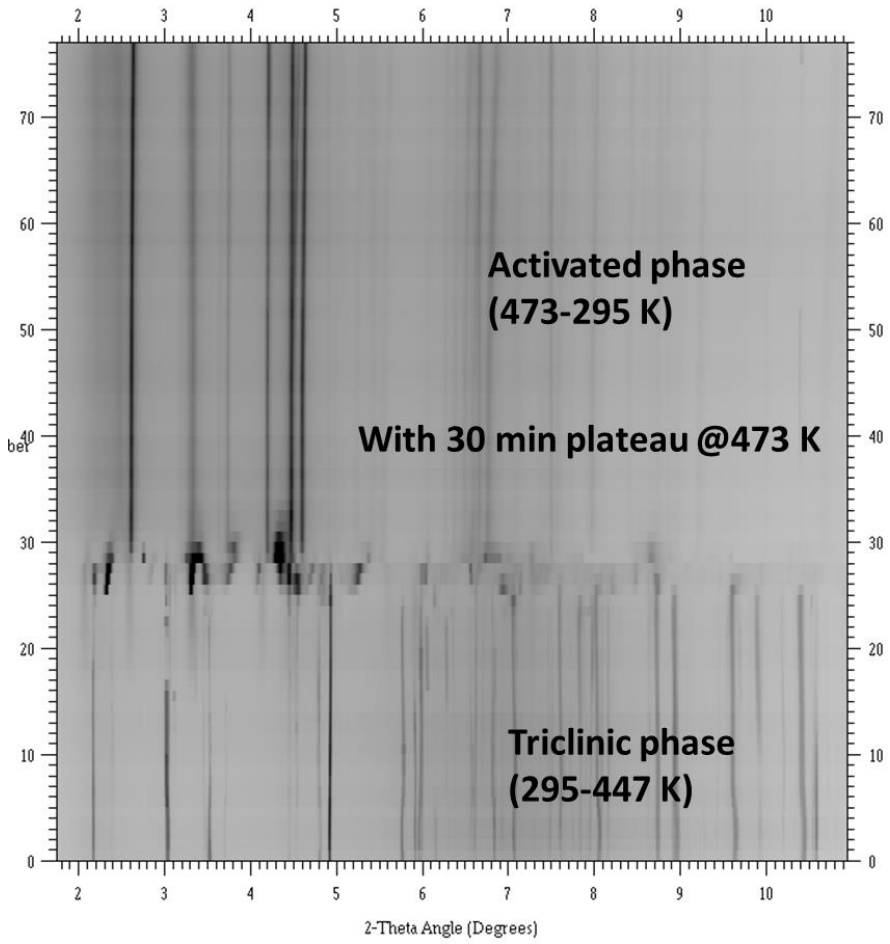

Fig S20 Top view of PXRD patterns collected from *in situ* synchrotron PXRD experiment heating PCN-39 under He flow from 295 – 473 K at a rate of 3 K/min, maintained at 473 K for 30 min, then cooled to 295 K at a rate of 3 K/min. Labeled phases are the phases that dominate, but not necessarily phase pure.

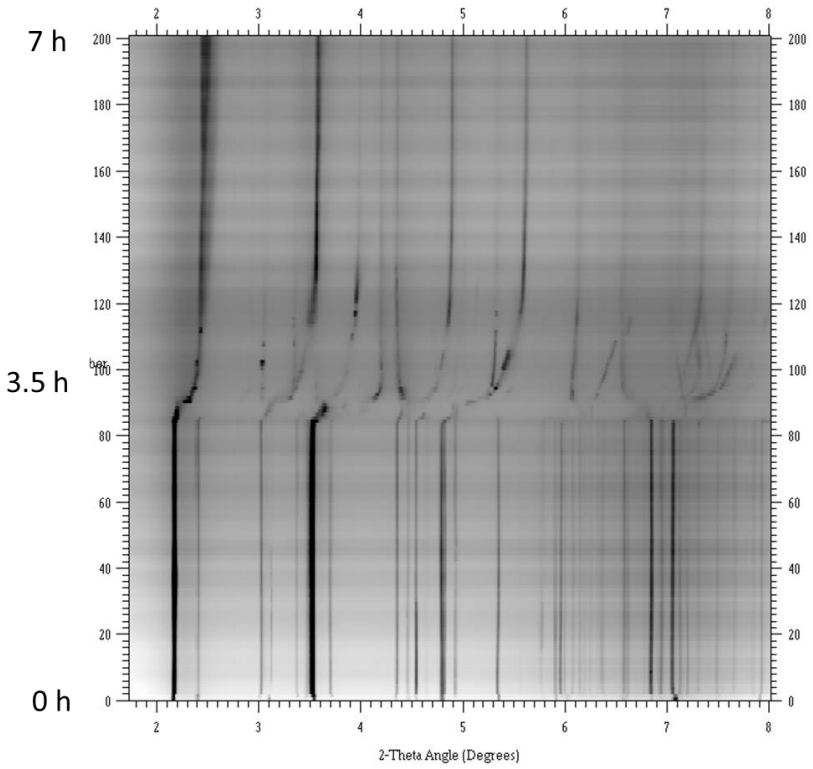

Fig S21 Top view of PXRD patterns collected from *in situ* synchrotron PXRD experiment flowing He over a sample of PCN-39 at 295 K