Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supplementary Information

Investigating the Crystal Engineering of the Pillared Paddlewheel Metal-Organic Framework $Zn_2(NH_2BDC)_2DABCO$

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Section S1. Additional synthetic details

Table S1 Experimental modifications to original prep, along with exact masses for synthesis, BET surface area, and NMR ratios. Reagent A is DABCO, reagent B is $Zn(NO_3)_2 \bullet 6H_2O$, and reagent C is NH_2BDC.

	Modification	Reagent A (g)	Reagent B (g)	Reagent C (g)	BET Surface Area (m^2/g)	NMR Proton Ratio (NH_2BDC:DABCO)
Original Batch	—	0.0947	0.5010	0.2765	950	6:6.00
Reagent Amount	-30% Reagent A	0.0663	0.5011	0.2765	485	6:2.36
	-20% Reagent A	0.0758	0.5012	0.2766	515	6:4.80
	-10% Reagent A	0.0853	0.5012	0.2766	450	6:5.79
	+10% Reagent A	0.1042	0.5015	0.2765	470	6:6.78
	+20% Reagent A	0.1133	0.5011	0.2765	230	6:4.35
	+30% Reagent A	0.1237	0.5011	0.2765	230	6:9.96
	-10% Reagent B	0.0947	0.4513	0.2765	390	6:5.05
	-5% Reagent B	0.0947	0.4763	0.2761	530	6:6.43
	+5% Reagent B	0.0951	0.5260	0.2763	260	6:6.00
	+10% Reagent B	0.0947	0.5513	0.2765	500	6:4.68
	+20% Reagent B	0.0947	0.6012	0.2764	525	6:0.69
	+30% Reagent B	0.0947	0.6515	0.2765	530	6:0.58
	-30% Reagent C	0.0947	0.5010	0.1936	290	6:9.21
	-20% Reagent C	0.0948	0.5010	0.2212	1085	6:7.10
	-10% Reagent C	0.0946	0.5013	0.2488	535	6:6.95
	+10% Reagent C	0.0947	0.5007	0.3043	674	6:4.96
	+20% Reagent C	0.0947	0.5008	0.3318	900	6:4.64
	+30% Reagent C	0.0945	0.5010	0.3595	1400	6:7.35
	+40% Reagent C	0.0946	0.5008	0.3870	650	6:5.04
Reagent Grade	All reagents new	0.0949	0.5009	0.2765	341	6:7.40
	Reagents A & C new	0.0949	0.5008	0.2765	683	6:10.20
Solvent Alterations	Dry DMF	0.0949	0.5010	0.2765	325	6:3.91
	90% DMF/10% EtOH	0.0947	0.5010	0.2765	135	No NH_2BDC protons
	DEF	0.0945	0.5010	0.2767	65	No NH_2BDC protons
Heating Conditions	120°C sand bath	0.0946	0.5013	0.2764	475	6:7.55
	Suspended in oven	0.0948	0.5010	0.2765	450	6:6.23
Heating Duration	24 hours	0.0950	0.5007	0.2765	322	6:6.47
Preheating Additives	+3 drops HNO_3	0.0947	0.5010	0.2768	200	6:6.78
	+100 mg H_2O	0.0946	0.5012	0.2765	165	6:10.01
Combo Modifications	Reagents A & C new/120℃ sand bath	0.0947	0.5010	0.2765	402	6:9.06
	Reagents A & C new/Suspended in oven	0.0947	0.5012	0.2764	673	6:8.61
	+30% Reagent C/120℃ sand bath	0.0945	0.5009	0.3594	522	6:6.91
	+30% Reagent C/Suspended in oven	0.0948	0.5013	0.3595	670	6:7.28
	+30% Reagent C/+100 mg H_2O	0.0947	0.5010	0.3595	643	6:8.72
	+30% Reagent C/+100 mg H_2O/Suspended in oven	0.0947	0.5012	0.3593	630	6:7.50

Section S2. Gas adsorption data

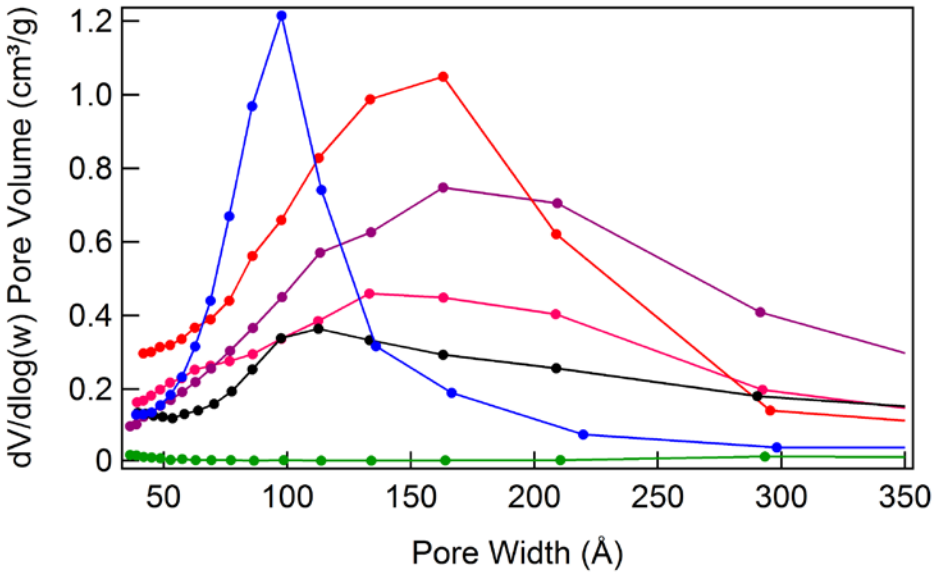

Fig. S1 BJH-PSD of the adsorption branch of the isotherms illustrated in Fig. 2 of the main text.

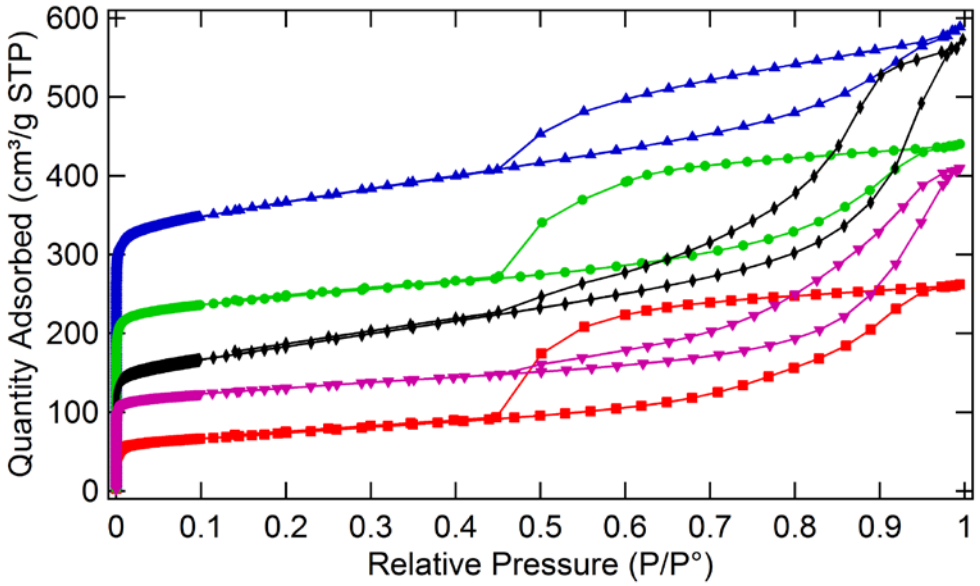

Fig. S2 N_2 gas-adsorption isotherms measured at 77 K for **P1** (red squares), **P2** (purple upside-down triangles), **P3** (black diamonds), **P4** (green circles), and **P5** (blue triangles) illustrating the hysteresis loops within these samples.

Section S3. NMR Data

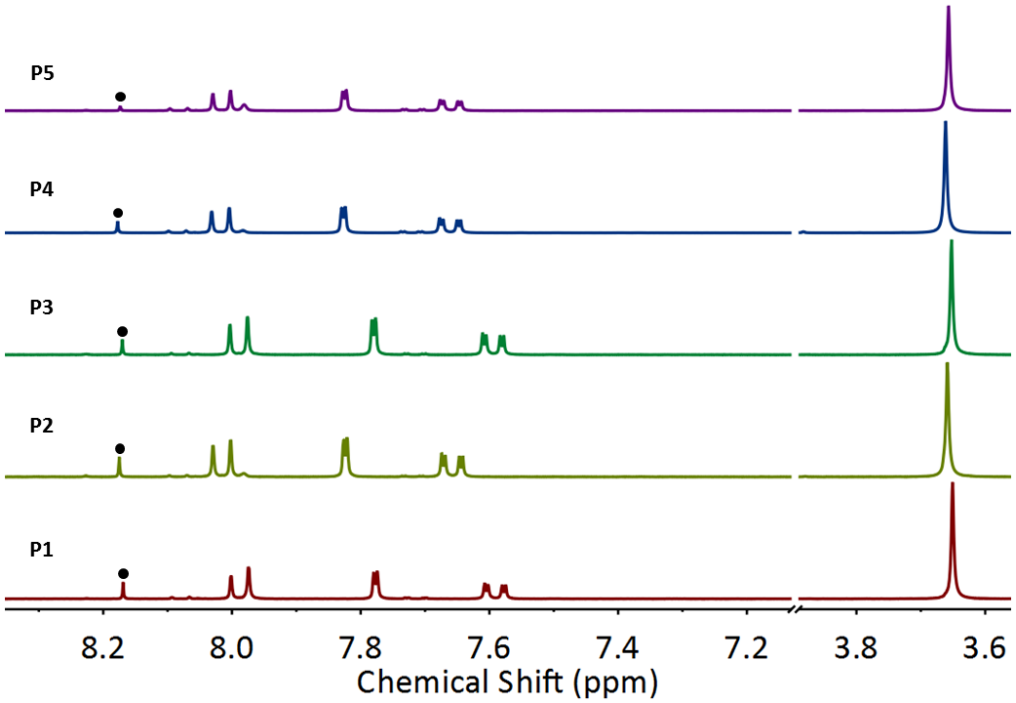

Fig. S3 ^{1}H NMR of acid digested (D_2SO_4/DMSO-d_6) **P1** – **P5** $Zn_2(NH_2BDC)_2DABCO$. The peak at 3.65 is due to DABCO. The peaks ranging from 7.5 – 8.1 are due to NH_2BDC. Variations in chemical shifts between samples are due to the slight variation in D_2SO_4 concentration. Peaks marked with a black circle indicate the presence of residual DMF.

Section S4. SEM Data

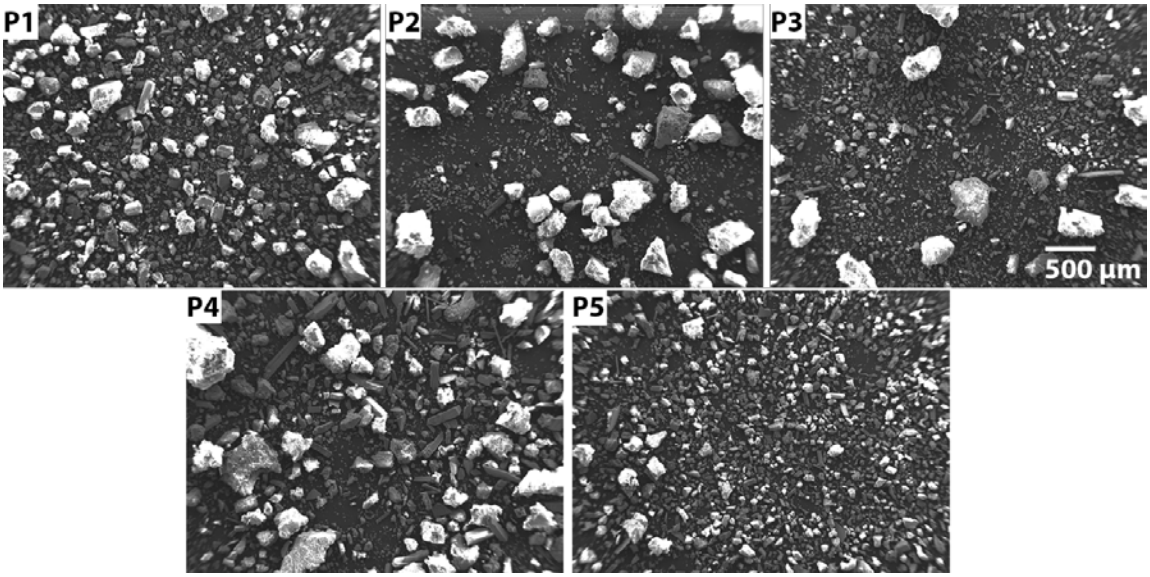

Fig. S4 SEM images of P1 – P5 at the same magnification (scale bar shown in P3). All the samples were carbon coated to minimize charging. Generally speaking, two features are observed within each sample: large insulating chunks and smaller rectangular prisms that are consistent with the morphology of $Zn_2(NH_2BDC)_2DABCO$. We cannot conclude that other compounds are not present. In general, compared with the surface area data, as more insulating chunks are present and less rectangular prisms of $Zn_2(NH_2BDC)_2DABCO$, the lower the overall surface area. Thus, we hypothesize that the insulating chunks are responsible for the less than ideal surface area observed in this work.