Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Synthesis, Characterization, and Post-Synthetic Modification of a Micro/Mesoporous Zirconium-Tricarboxylate Metal-Organic Framework: Towards the Addition of Acid Active Sites

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Table of Contents

1. Results and Discussion

1.1. Influence of the concentration of modulator on the properties of zirconium tricarboxylate MOFs

1.1.1 Assessment of surface area and porosity

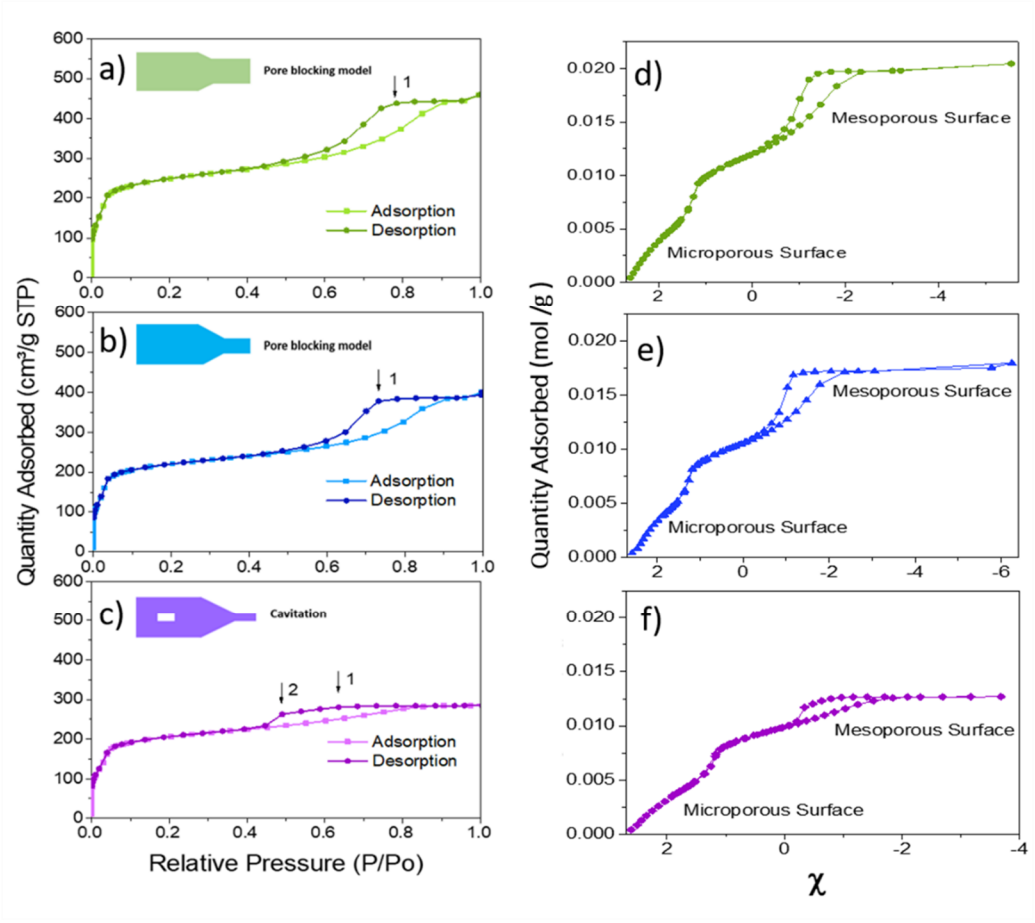

Figure S1. N_2 adsorption/desorption isotherms of (a) ZrBTC-114.6 (b) ZrBTC-83.5 and, (c) ZrBTC-52.4, in the all range of the linear P/Po. χ-method adsorption/desorption isotherms of the same materials (d) ZrBTC-114.6, (e) ZrBTC-83.5, and (f) ZrBTC-52.4.

Table S1. Comparison of the apparent surface areas calculated using BET method taking into account the full consistency criteria proposed by Rouquerol of the ZrBTC-114.6, ZrBTC-83.5, and ZrBTC-52.4 materials and using argon as probe molecule.

BET - Rouquerol Consistency Criteria						
Sample	SA (m^2/g)	C value > 0	n(min) < monolayer < n(max)	P/Po(mono) ~1/(√C+1)	Linear fitting R^2	Rsq
ZrBTC-114.6	**804**	True-105.17	True	True	False	0.96590
ZrBTC-83.5	**744**	True-106.77	True	True	False	0.95738
ZrBTC-52.4	**717**	True-101.04	True	True	False	0.98691

1.1.2. Crystallinity

Table S2. Crystal data and structure refinement of the synthesized Zr-MOFs

	ZrBTC-114.6	ZrBTC-83.5	ZrBTC-52.4
Crystal system	Cubic	Cubic	Cubic
Space group	Fd-3m	Fd-3m	Fd-3m
a (Å)	35.14027	35.05387	35.07650
b (Å)	35.14027	35.05387	35.07650
c (Å)	35.14027	35.05387	35.07650
α (°)	90	90	90
β (°)	90	90	90
Ψ (°)	90	90	90
Volume ($Å^3$)	43392.578	43073.266	43156.750
Chi2	1,33	1,38	1,30
% Approximate crystallinity	74.5	62	61

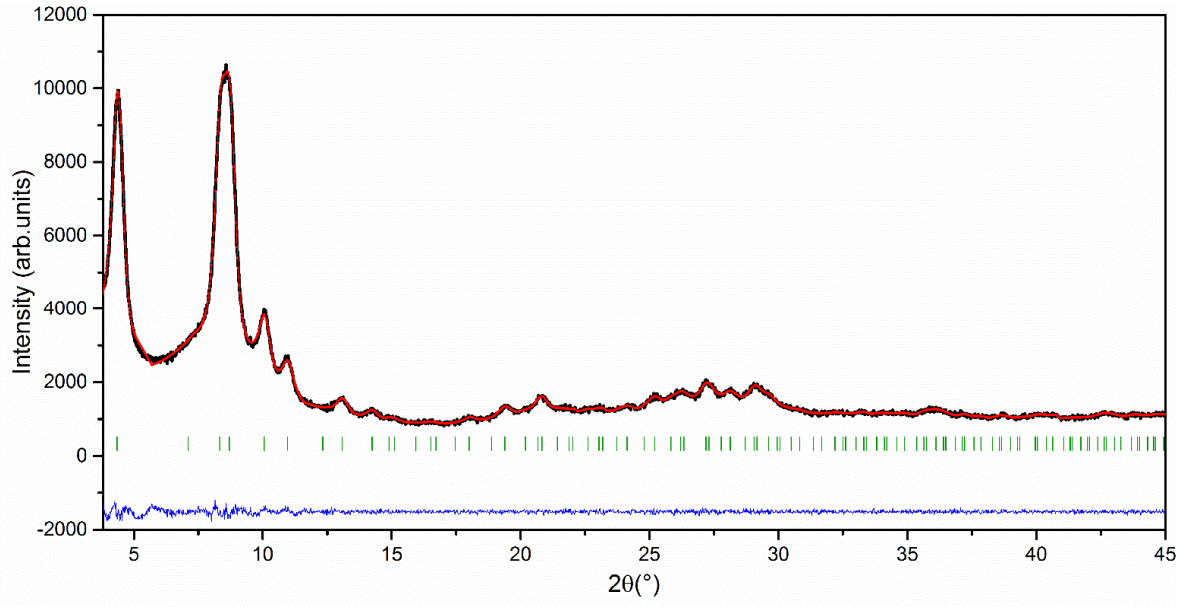

Figure S2. Le Bail profile is fitting for ZrBTC-114.6 sample using Laboratory PXRD data. Experimental data is shown in red squares, the calculation in black, the difference in the blue line, and Bragg reflection markers in green.

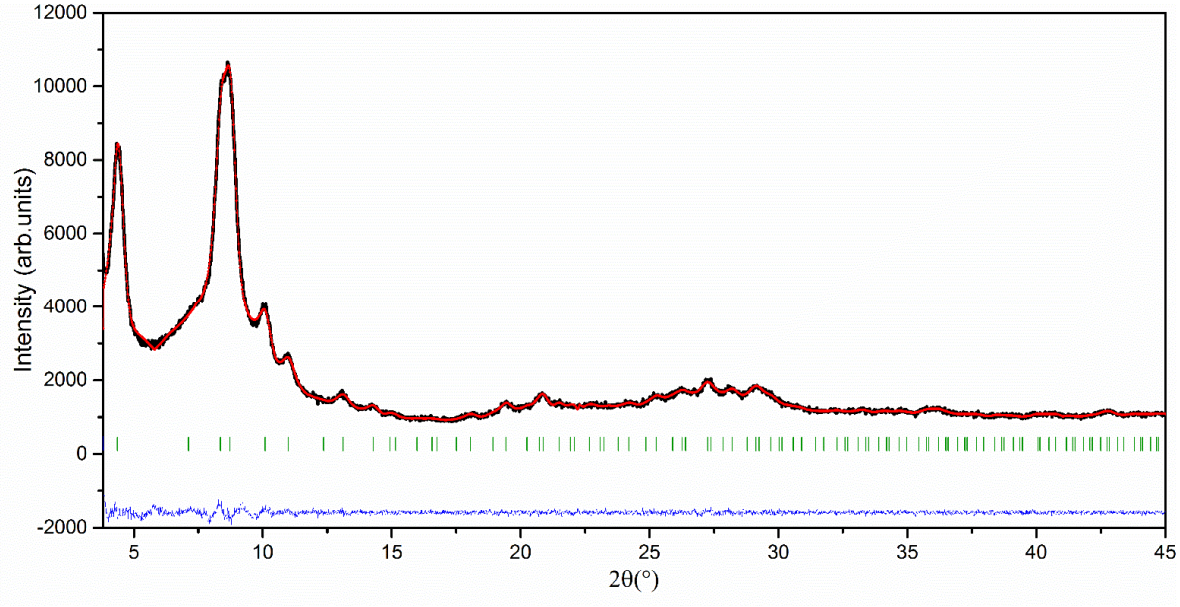

Figure S3. Le Bail profile is fitting for ZrBTC-83.5 sample using Laboratory PXRD data. Experimental data is shown in red squares, the calculation in black, the difference in the blue line, and Bragg reflection markers in green.

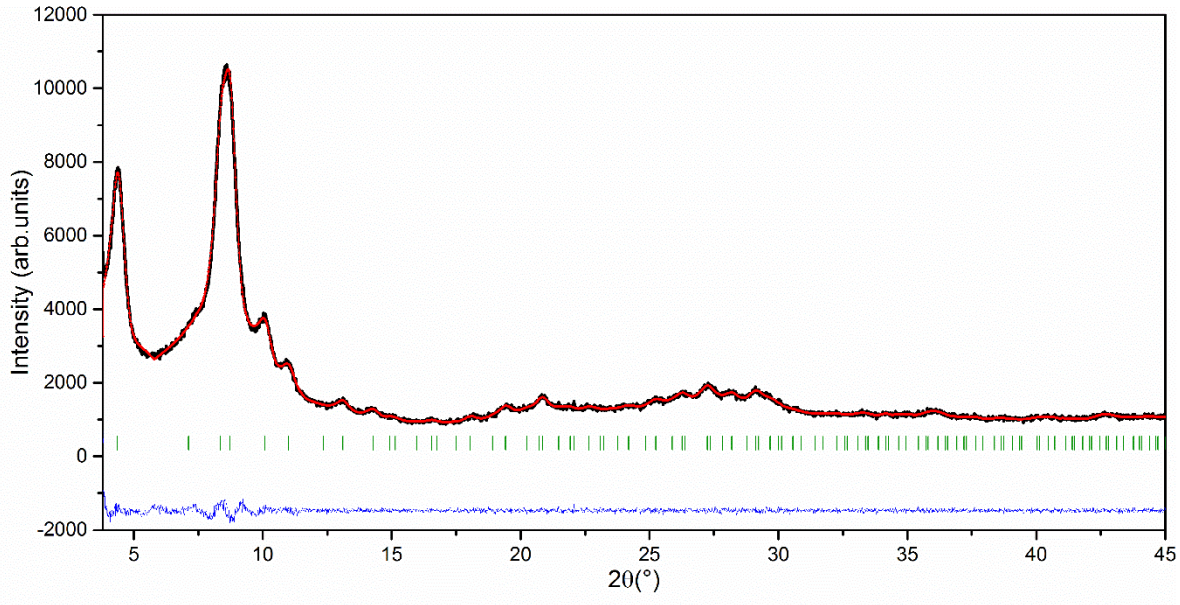

Figure S4. Le Bail profile is fitting for ZrBTC-52.4 sample using Laboratory PXRD data. Experimental data is shown in red squares, the calculation in black, the difference in the blue line, and Bragg reflection markers in green.

1.2. Properties Comparison of Unmodified and Sulfated Samples.

1.2.1. Assessment of the effect of sulfation on surface area and porosity

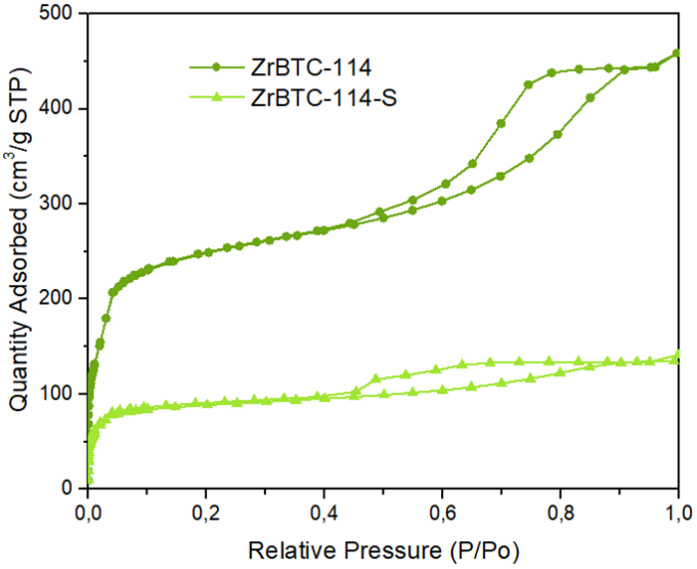

Figure S5. N_2 adsorption-desorption isotherms of MOF ZrBTC-114.6 without and with PSM.