Supporting Information

Extremely efficient crystallization of HKUST-1 and keggin-loaded related phases through the epoxide´s route

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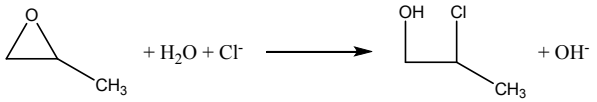
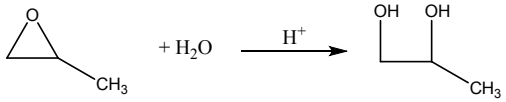


Eq. S1

$$13.5\ Cu^{2+} + 8\ H_3BTC\ (s) + 27\ OH^- + H_3PW_{12}O_{40} \longrightarrow [Cu_{12}(BTC)_8(H_2O)_{12}][PW_{12}O_{40}](Cu)_{1.5}\ (s) + 15\ H_2O \qquad \text{Eq. S2}$$



Eq. S3

Scheme S1. Chloride attack and PO ring rupture driven alkalinization (1), H_3BTC/POM ($H_3PW_{12}O_{40}$ to exemplify) deprotonation and HKUST-1 precipitation (2) and parallel acid catalyzed PO hydrolysis (3).

Table S1. Initial molar content of reagents and solvent, on the basis of one mol of polyoxometalate (POM)

$CuCl_2$	H_3BTC	PO	H_2O	POM	% Cu(II) as MOF*	STY kg m^3 day^{-1}
12	8	30	216	-	96,0±0,5	2,03 x 10^5
12	8	36	216	-	99,5±0,5	2,10 x 10^5
24	16	60	216	-	84,7±0,5	3,57 x 10^5
24	16	72	216	-	98,0±0,5	4,14 x 10^5
12	8	36	216	1=PW	95,5±0,5	2,57 x 10^6
12	8	36	216	1=SiMo	86,0±0,5	1,88 x 10^6
12	8	36	216	1=PMo	89,5±0,5	1,96 x 10^6

* In order to define the absolute precipitation yield the content of remnant Cu(II) in the washing solution was assessed by UV-Vis, after the addition of NH_3 excess.

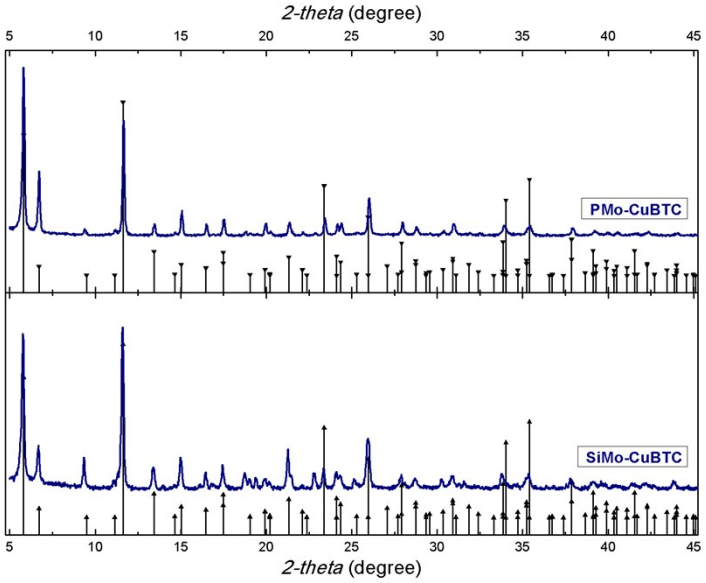


Figure S1. PXRD of sample PMo-CuBTC (upper pattern) and SiMo-CuBTC (lower pattern). Reference diffraction lines from NENU-5 and NENU-4 reference phases are also presented (C. Y. Sun, S. X. Liu, D. D. Liang, K. Z. Shao, Y. H. Ren and Z. M. Su, J. Am. Chem. Soc., 2009, 131, 1883-1888.).

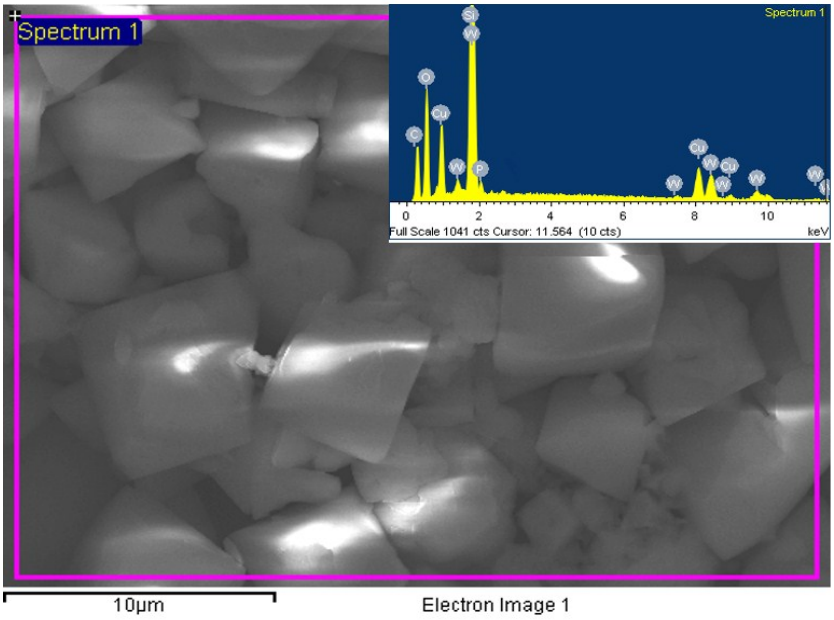


Figure S2. FESEM image and EDS spectrum of sample PW-CuBTC. Expected ratio Cu:W:P=13.5:12:1; obtained ratio Cu:W:P=13.5±0.4:12.0±0.6:1.0±0.1.

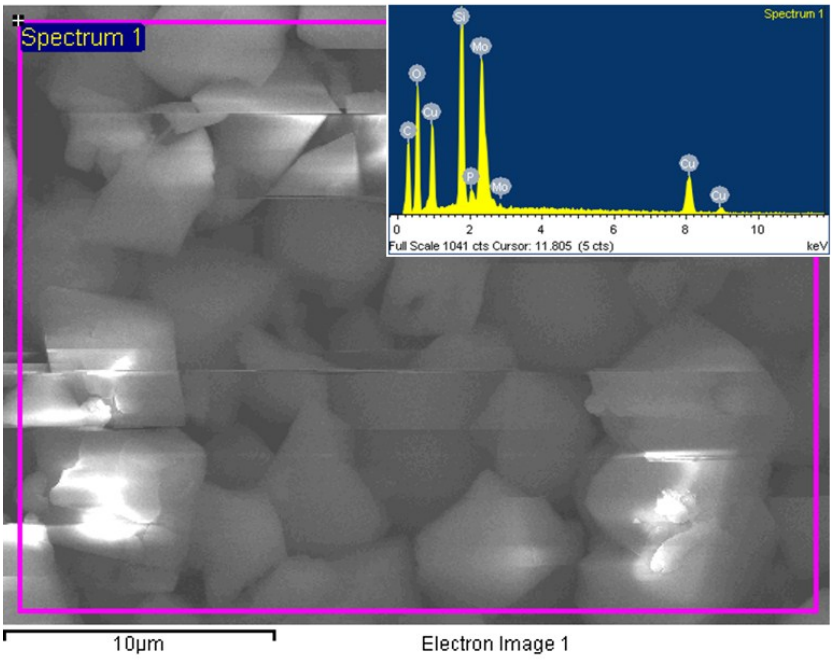


Figure S3. FESEM image and EDS spectrum of sample PMo-CuBTC. Expected ratio Cu:Mo:P=14:12:1; obtained ratio Cu:Mo:P=14.0±0.4:12.3±0.6:1.1±0.1.

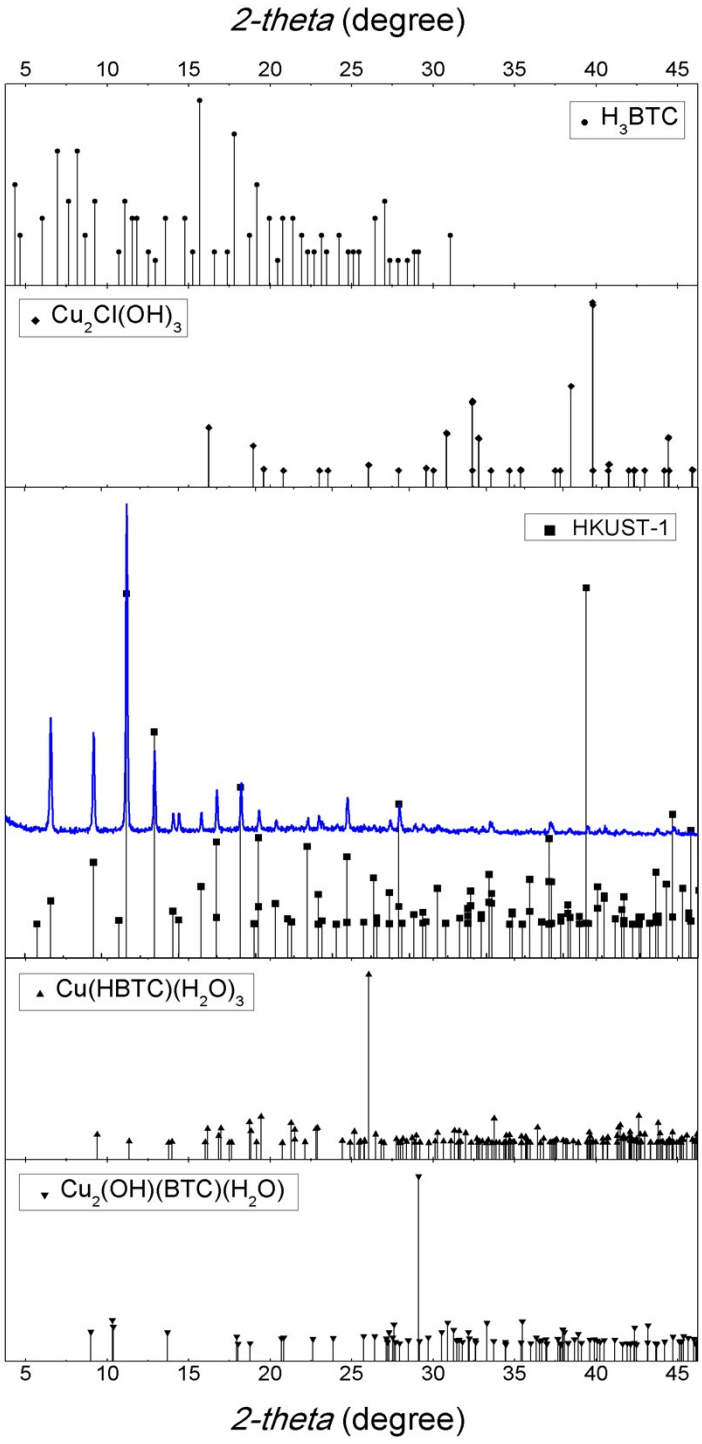


Figure S4. PXRD pattern of sample CuBTC (blue line) compared with reference lines of H-KUST, starting reagents and related compounds.

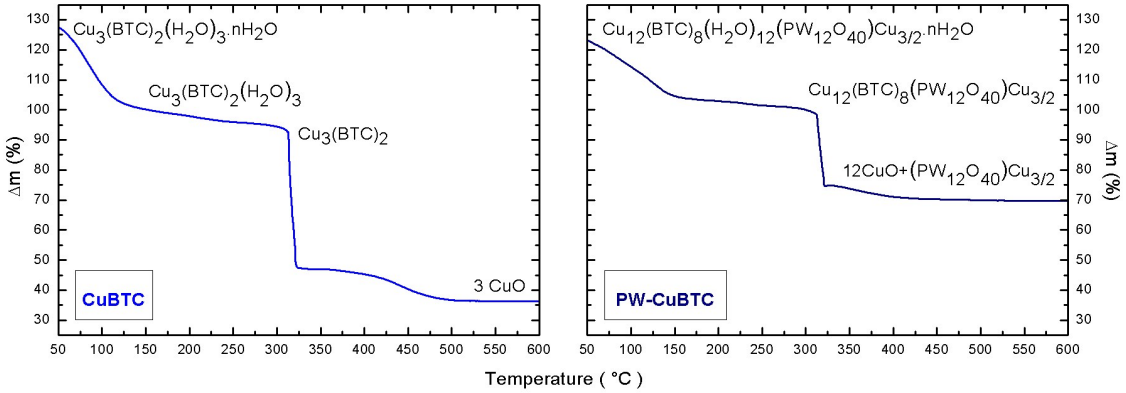


Figure S5. TGA trace (10 ºC/min, air atmosphere) for samples CuBTC (left panel) and PW-CuBTC (right panel), including the compounds expected for each step along the thermal decomposition process.

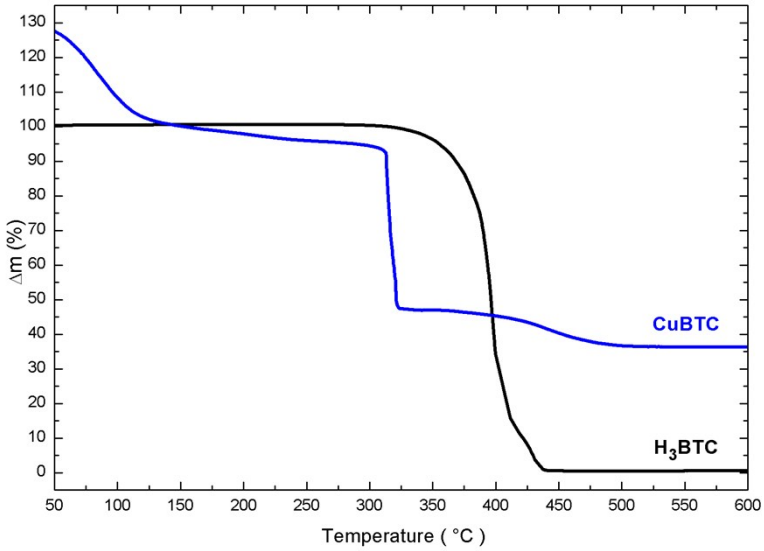


Figure S6. TGA trace (10 ºC /min, air atmosphere) for sample CuBTC (blue line) and pure H_3BTC (black line).

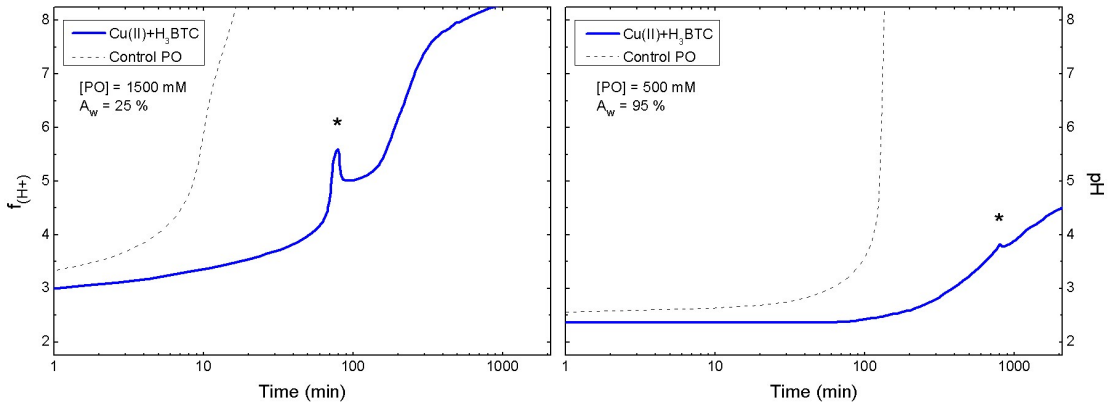


Figure S7. Evolution of pH as a function of time at 298 K for EtOH:H_2O solutions containing PO, $[CuCl_2]_o$=5 mM and $[H_3BTC]_o$=3.3 mM. Asterisks represent the nucleation overshoot that triggers CuBTC precipitation.

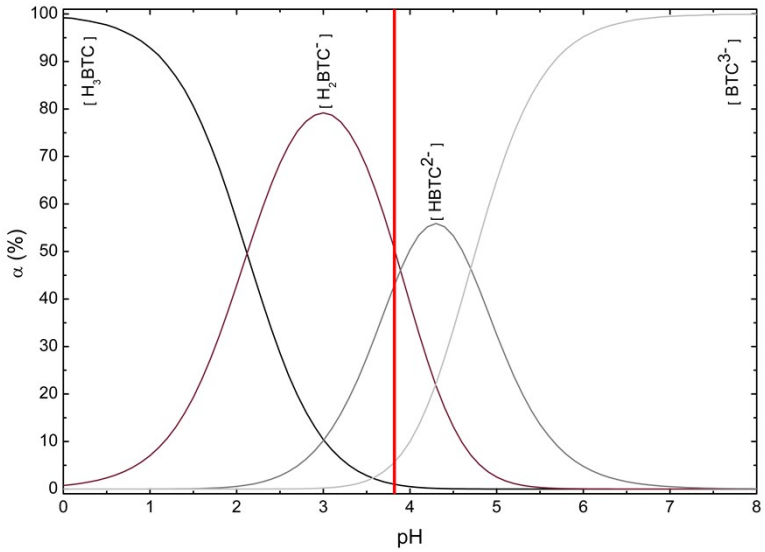


Figure S8. Speciation diagram of H_3BTC in water at 298 K.

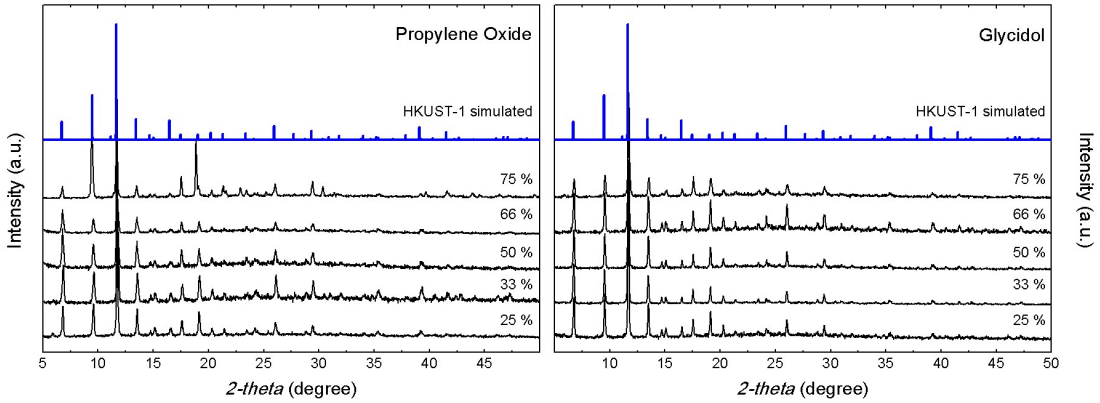


Figure S9. PXRD of samples prepared after aging EtOH:H_2O mixtures with increasing water volume percentage (%) and $[CuCl_2]_o$=5 mM, $[H_3BTC]_o$=3.3 mM, $[Epoxide]_o$=500 mM at 25 ^oC for 24 h.

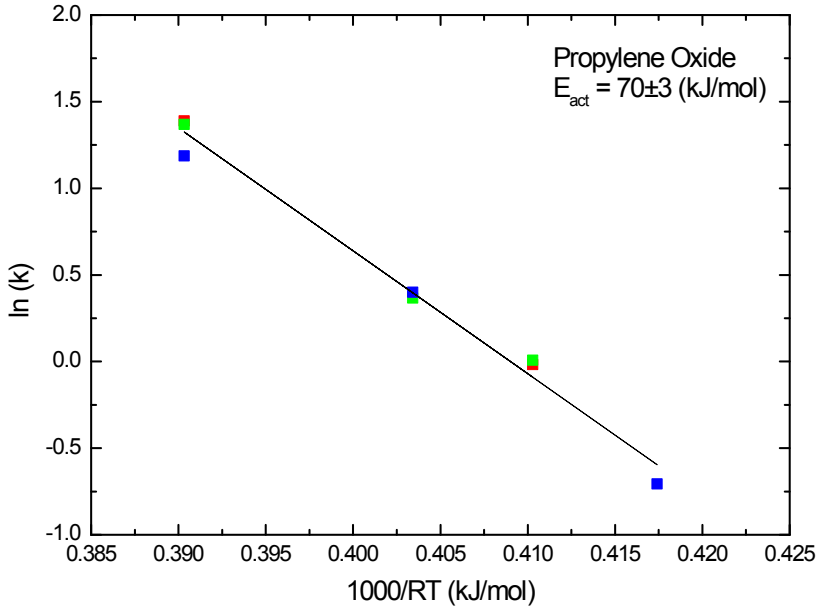


Figure S10. Alkalinization rate constant, *k*, as a function of the inverse of temperature recorded in a water solution containing propylene oxide (PO) 100 mM and NaCl 100 mM (red), 150 mM (green) or 300 mM (blue)

Table S2. Compilation of eco efficiency parameters.

Ref.	Cu(II) source	STY Kg $m^{-3}d^{-1}$	sEF	cEF	SI+WI Kg_{Sv}/Kg_{MOF}	Solvent Intensity	Water Intensity	Reaction Mass Efficiency	Mass Intensity	H_3BTC excess
7	$Cu(OH)_2$	1842	0,5	28	27	18	8,9	3,5 %	29	33 **%**
8	$Cu(CH_3COO)_2.H_2O$	2035	2,1	1192	1190	-	1190	0,1 %	1193	133 **%**
10	$Cu(OH)_2$	144000	0,2	0,7	0,5	0,5	-	58 %	1,7	0 **%**
CuBTC*	$CuCl_2.2H_2O$	210000*	1,4	3,0	1,6	-	1,6	42 %	3,2	0 **%**
PW-CuBTC*	$CuCl_2.2H_2O$	2570000*	0,6	1,2	0,7	-	0,7	64%	1,9	0 **%**

* This work

Definitions of parameters

Space-Time Yield	$$STY = \frac{Kg_{product}}{m^3_{reactor} day_{reaction}}$$
Simple Environmental Factor	$$sEF = \frac{\Sigma\left(m_{raw\ materials} + m_{reagents} - m_{product}\right)}{m_{product}}$$
Complete Environmental Factor	$$cEF = \frac{\Sigma\left(m_{raw\ materials} + m_{reagents} + m_{solvents} + m_{water} - m_{product}\right)}{m_{product}}$$
Solvent Intensity	$$SI = \frac{m_{solvents\ (excluding\ water)}}{m_{product}}$$
Water Intensity	$$WI = \frac{m_{water}}{m_{product}}$$
Total solvent demand	$$SI + WI = \frac{m_{solvents} + m_{water}}{m_{product}}$$
Reaction Mass Efficiency	$$RME = \frac{m_{product}}{m_{all\ reactants}} . 100\%$$
Mass Intensity	$$MI = \frac{m_{materials\ (including\ water)}}{m_{product}}$$