Supplementary Materials for

Cu$_3$(BTC)$_2$ nanoflakes synthesized in ionic liquid/water binary solvent and their catalytic properties

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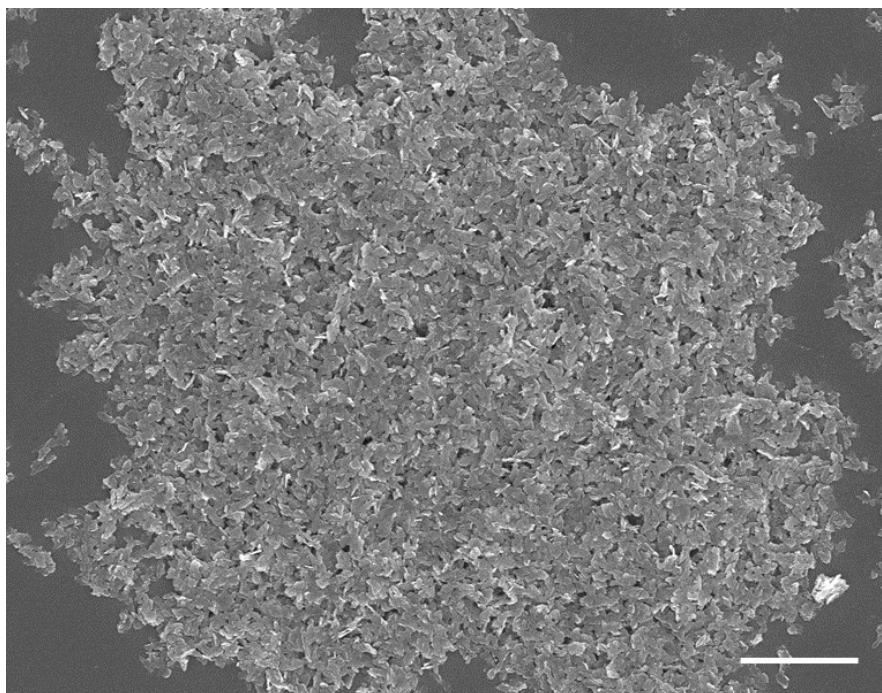
Results and Discussion

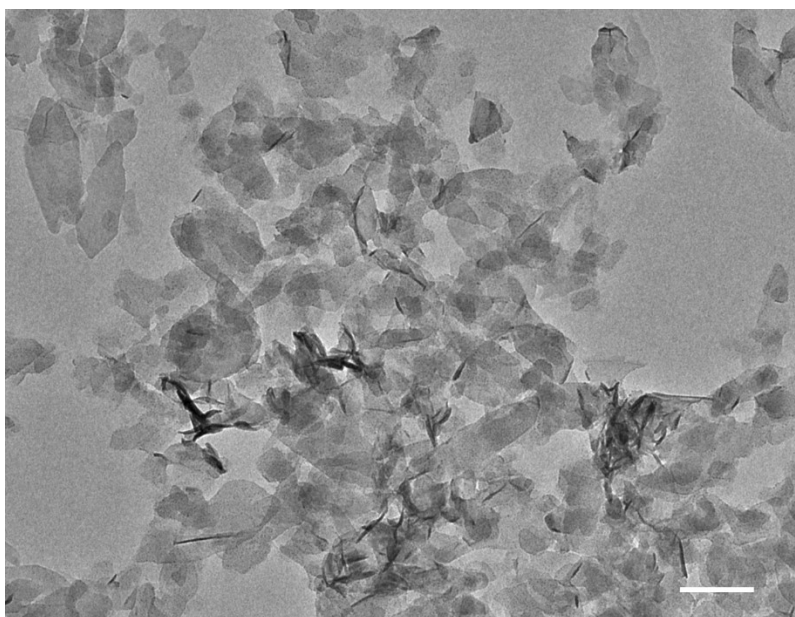**Fig. S1.** SEM image of n-$Cu_3(BTC)_2$. Scale bar: 3 μm.

Fig. S2. TEM image of *n*-Cu$_3$(BTC)$_2$. Scale bar: 200 nm.

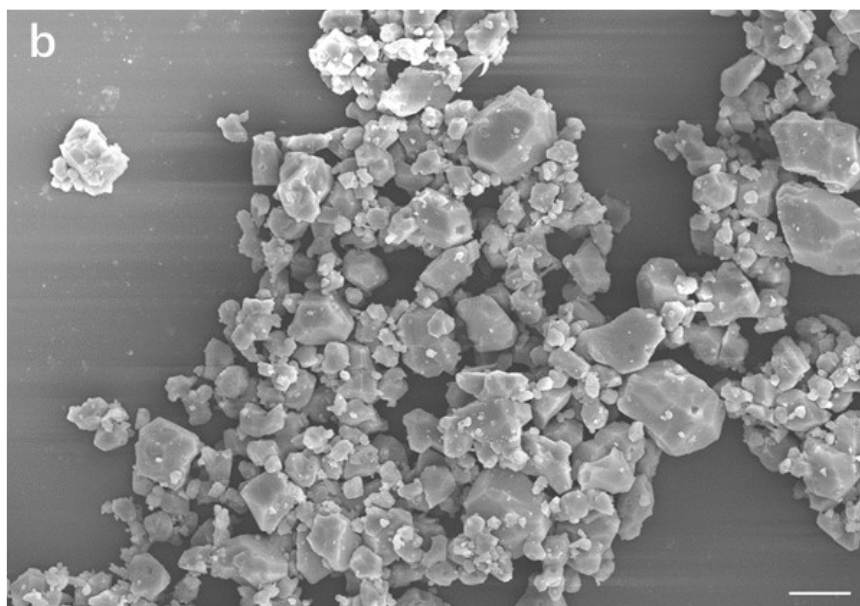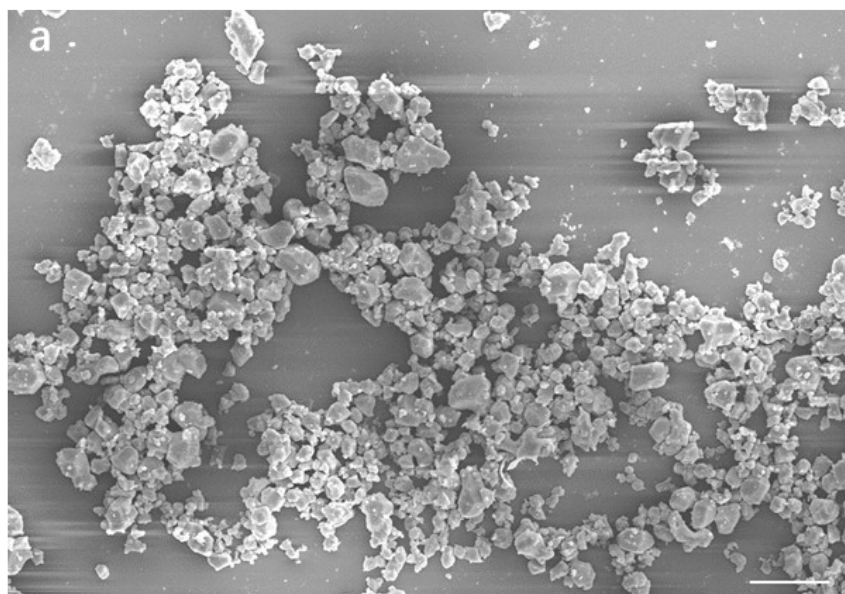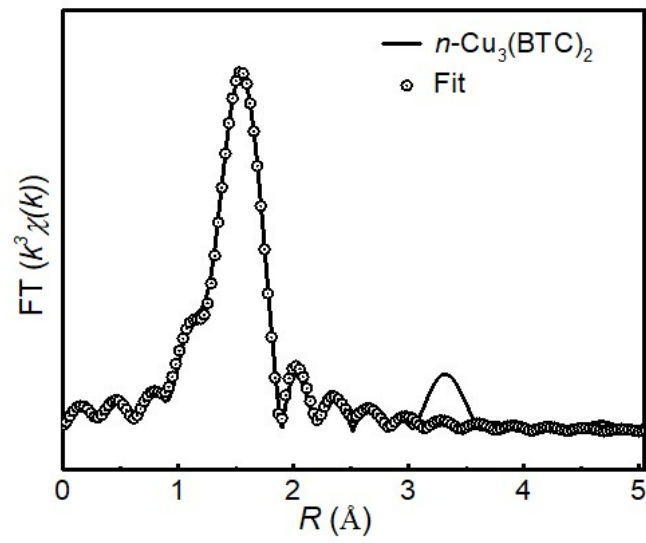**Fig. S3.** SEM images of *m*-$Cu_3(BTC)_2$. Scale bars: 30 μm in a and 10 μm in b.
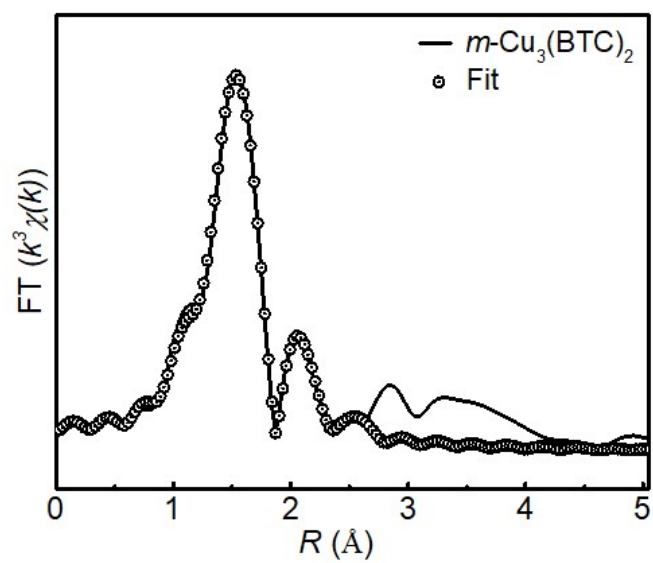
Fig. S4. EXAFS fitting curve of n-Cu$_3$(BTC)$_2$.
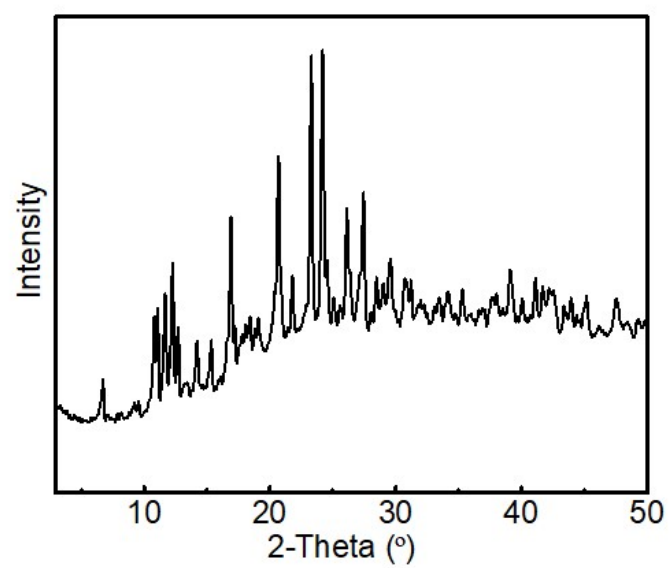
Fig. S5. EXAFS fitting curve of *m*-Cu$_3$(BTC)$_2$.

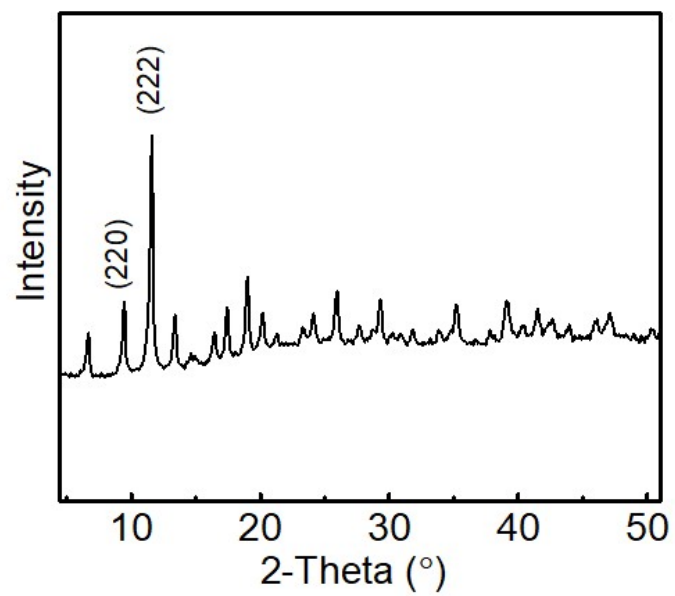**Fig. S6.** XRD pattern of the $Cu_3(BTC)_2$ synthesized in absence of IL.

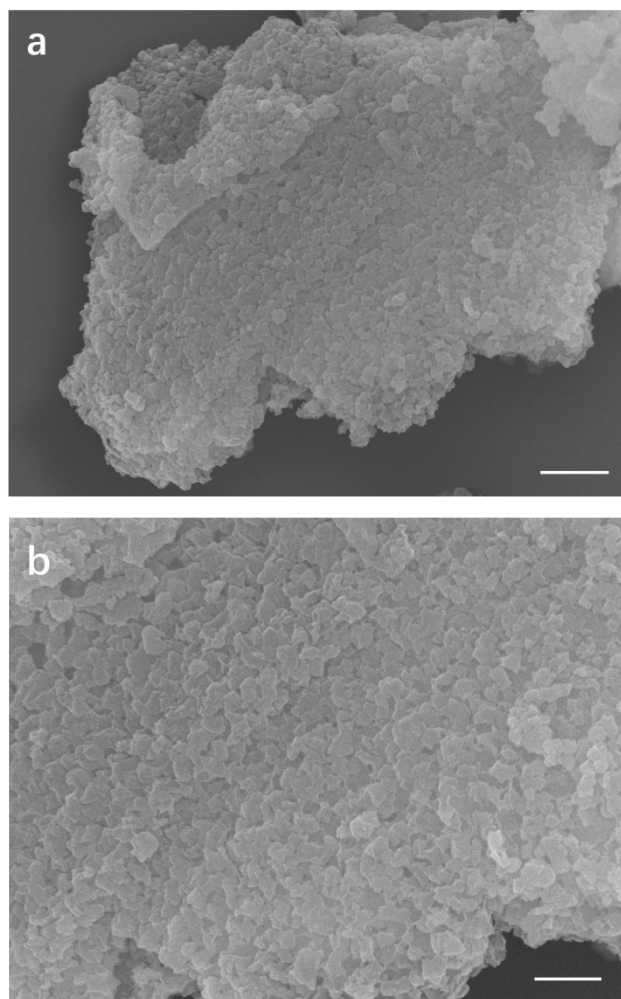**Fig. S7.** XRD pattern of the $Cu_3(BTC)_2$ synthesized in absence of water.

Fig. S8. SEM images of Cu$_3$(BTC)$_2$ synthesized in absence of water. Scale bars: 1 µm in a and 500 nm in b.

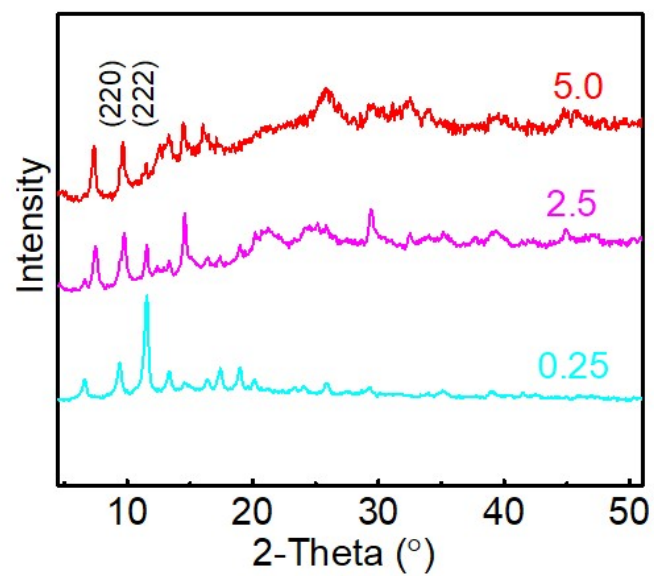**Fig. S9.** XRD patterns of the $Cu_3(BTC)_2$ synthesized in IL/water solvent with water to IL mass ratio from 0.25 to 5.0.

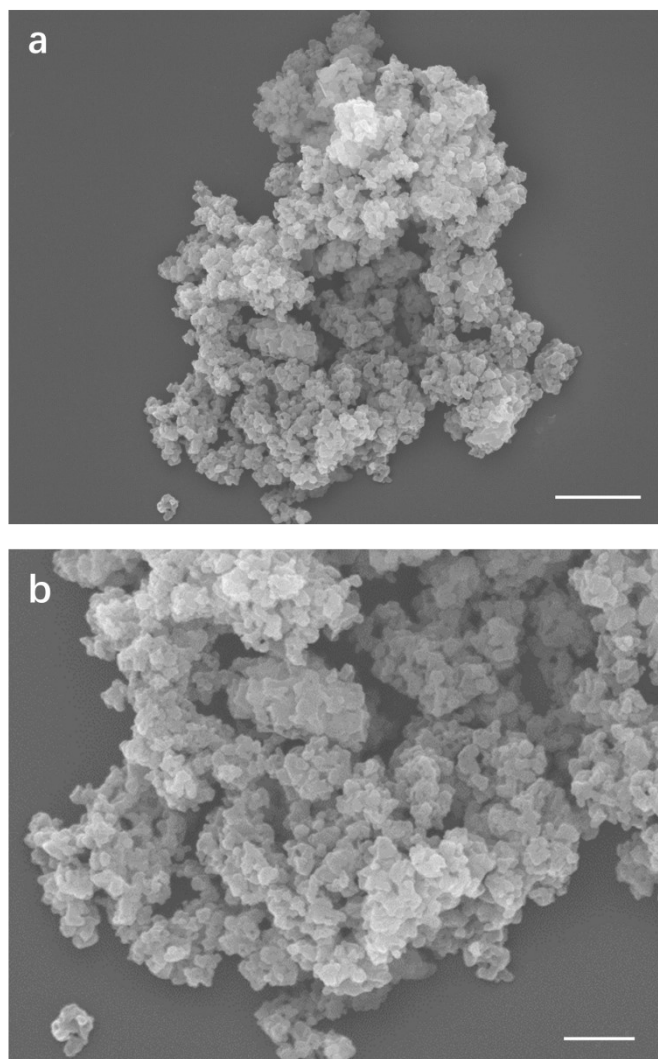**Fig. S10.** SEM images of Cu$_3$(BTC)$_2$ synthesized in IL/water solvent with water to IL mass ratio of 0.25. Scale bars: 1 μm in a and 500 nm in b.
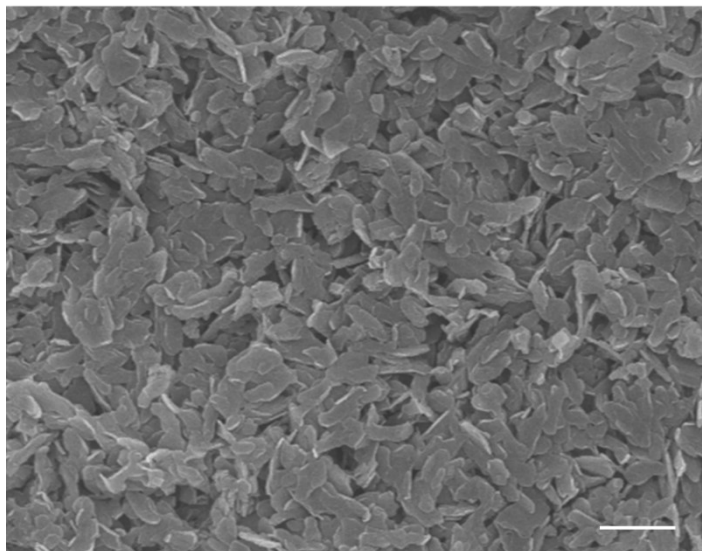
Fig. S11. SEM image of $Cu_3(BTC)_2$ synthesized in IL/water solvent with water to IL mass ratio of 2.5. Scale bar: 500 nm.

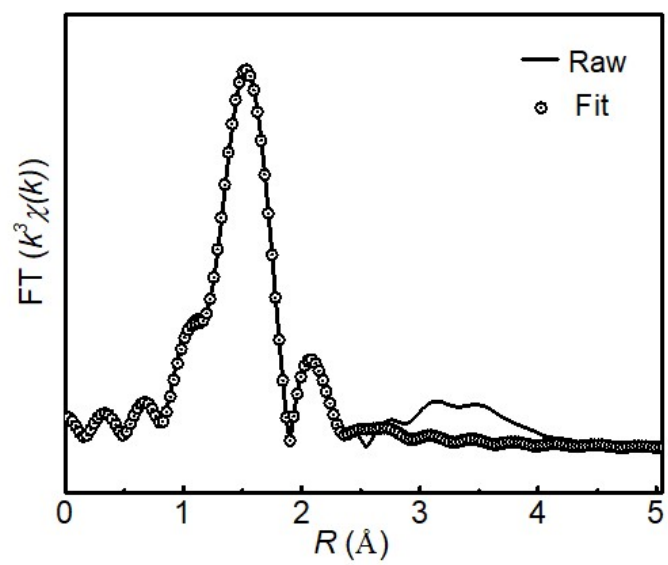**Fig. S12.** EXAFS fitting curve of $Cu_3(BTC)_2$ synthesized in absence of water.

Fig. S13. EXAFS fitting curve of $Cu_3(BTC)_2$ synthesized in IL/water solvent with water to IL mass ratio of 0.25.

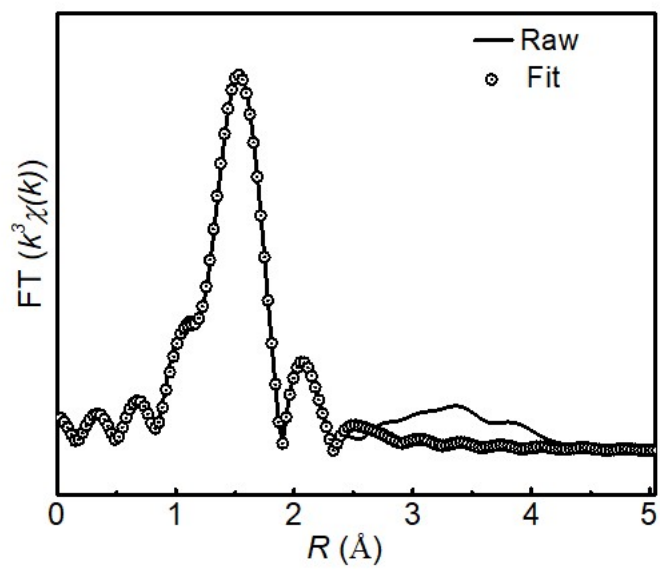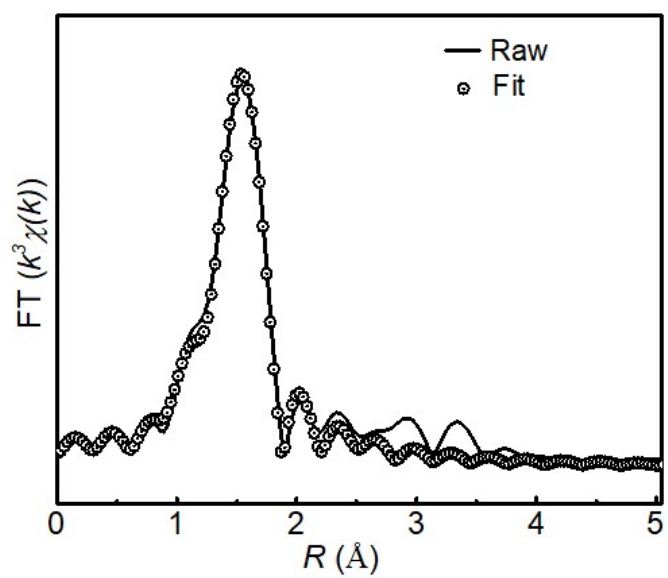**Fig. S14.** EXAFS fitting curve of $Cu_3(BTC)_2$ synthesized in IL/water solvent with water to IL mass ratio of 2.5.
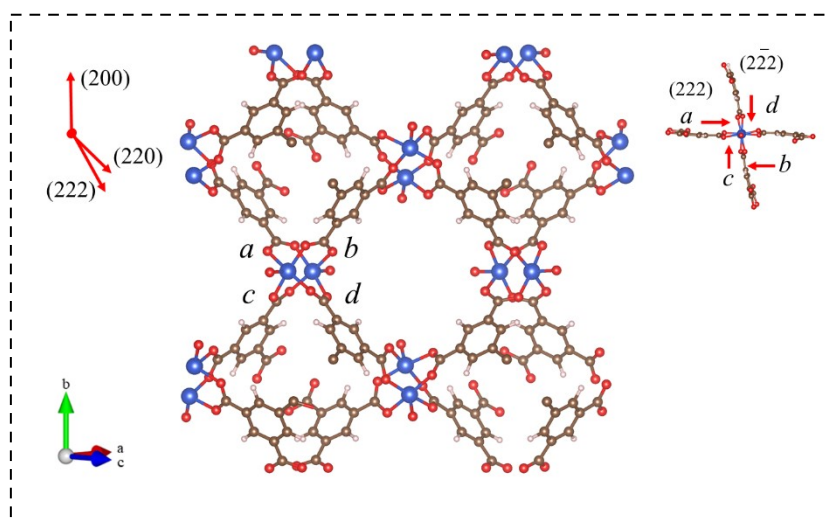
Fig. S15. Schematic diagram of crystal plane directions of Cu$_3$(BTC)$_2$.
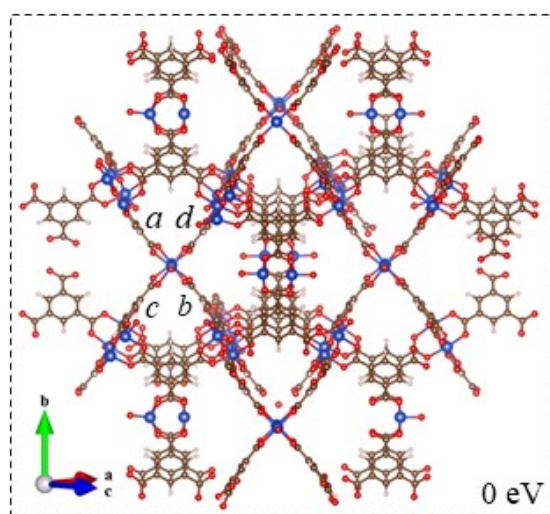
Fig. S16. Structure diagram of $Cu_3(BTC)_2$ when the Cu-O bond is unbroken.
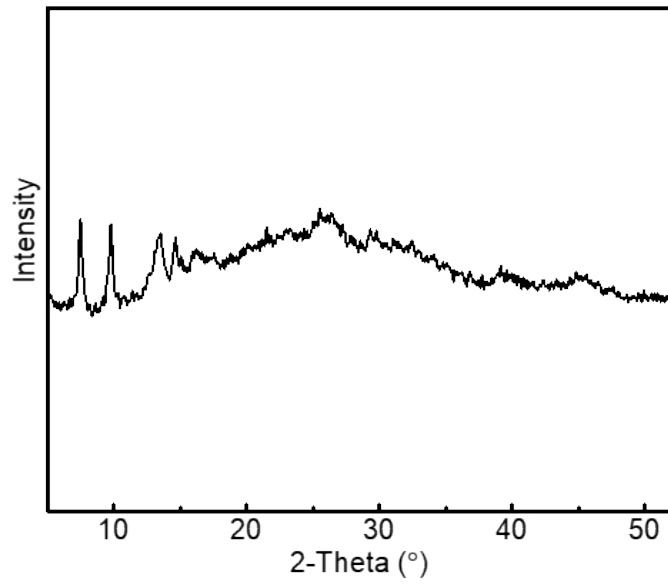
Fig. S17. XRD pattern of n-Cu$_3$(BTC)$_2$ after used for five cycles.
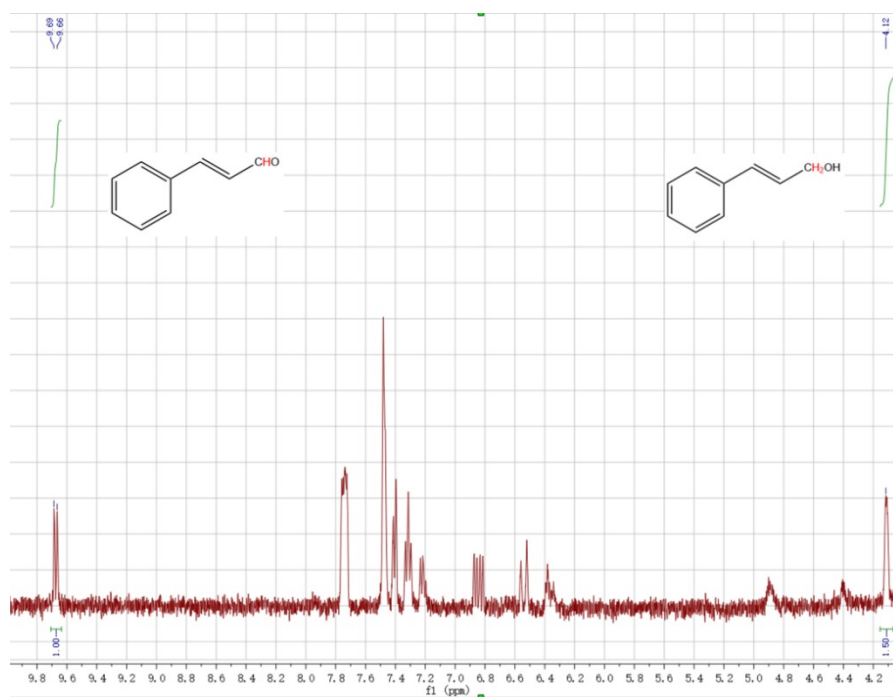
Fig. S18. ^{1}H NMR spectrum for the oxidation of cinnamyl alcohol catalyzed by *m*-Cu$_3$(BTC)$_2$ at 12 h.
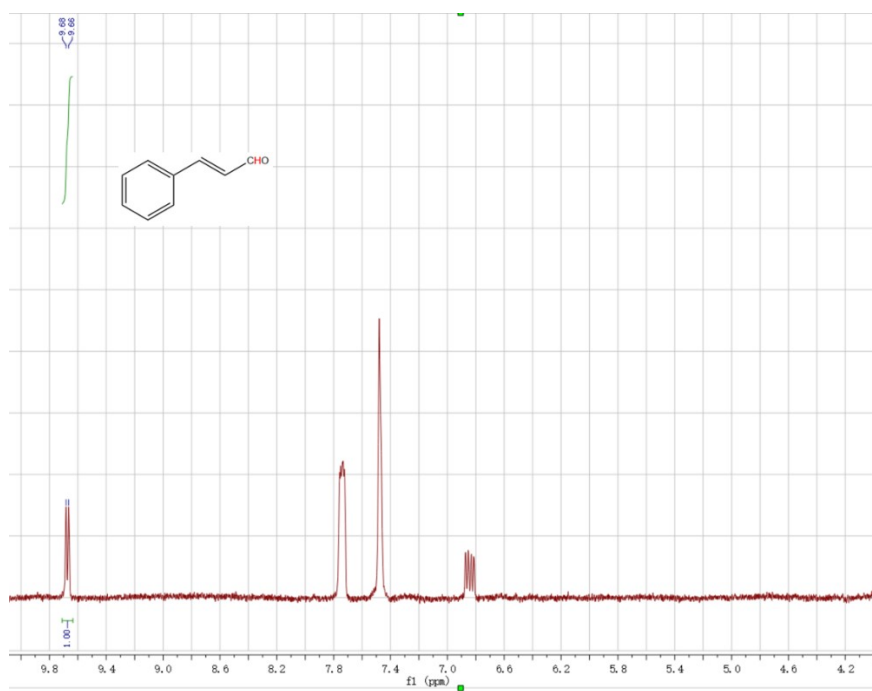
Fig. S19. ^{1}H NMR spectrum for the oxidation of cinnamyl alcohol catalyzed by *n*-Cu$_3$(BTC)$_2$ at 12 h.

Fig. S20. ^{1}H NMR spectrum for the oxidation of 4-methylbenzyl alcohol catalyzed by *m*-Cu$_3$(BTC)$_2$ at 13 h.

Fig. S21. ^{1}H NMR spectrum for the oxidation of 4-methylbenzyl alcohol catalyzed by *n*-Cu$_3$(BTC)$_2$ at 13 h.
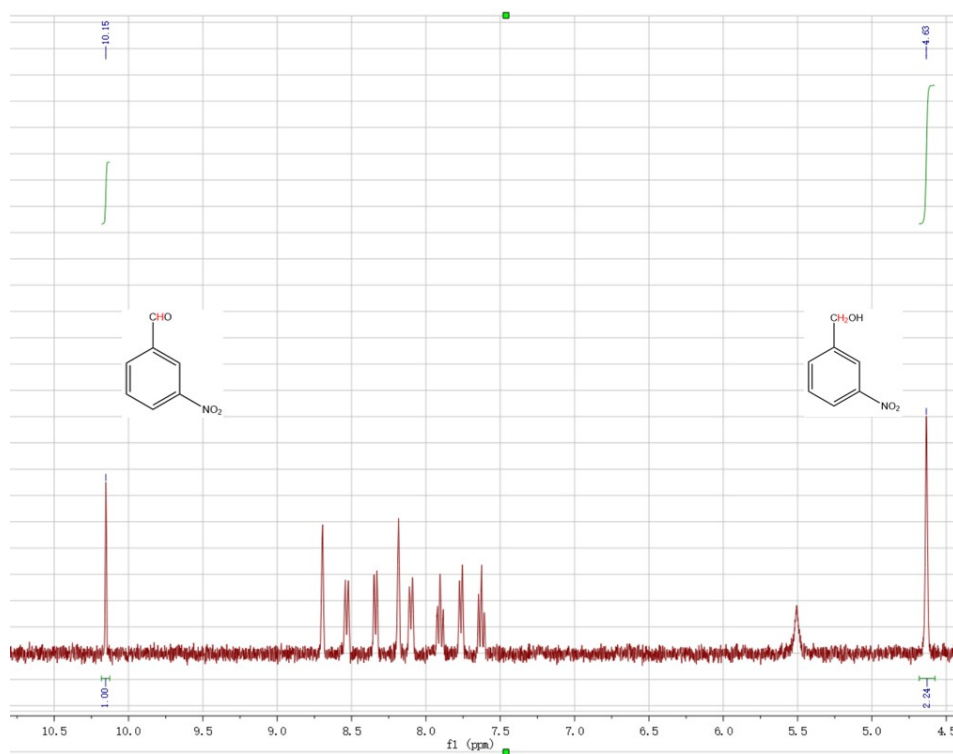
Fig. S22. ^{1}H NMR spectrum for the oxidation of 3-nitrobenzyl alcohol catalyzed by *m*-Cu$_3$(BTC)$_2$ at 16 h.
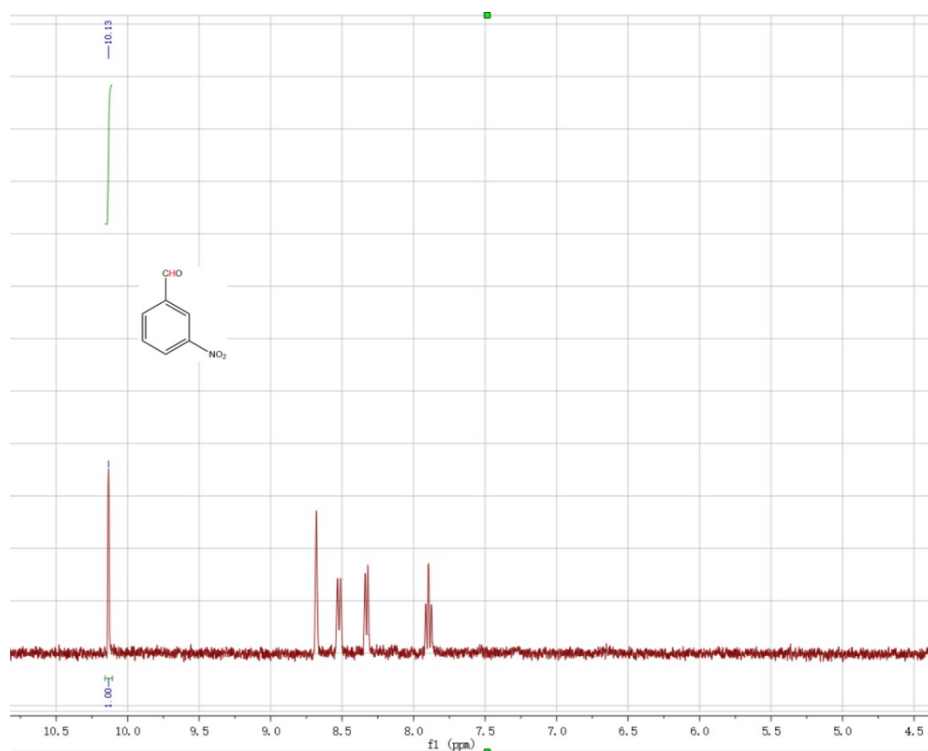
Fig. S23. ^{1}H NMR spectrum for the oxidation of 3-nitrobenzyl alcohol catalyzed by *n*-Cu$_3$(BTC)$_2$ at 16 h.

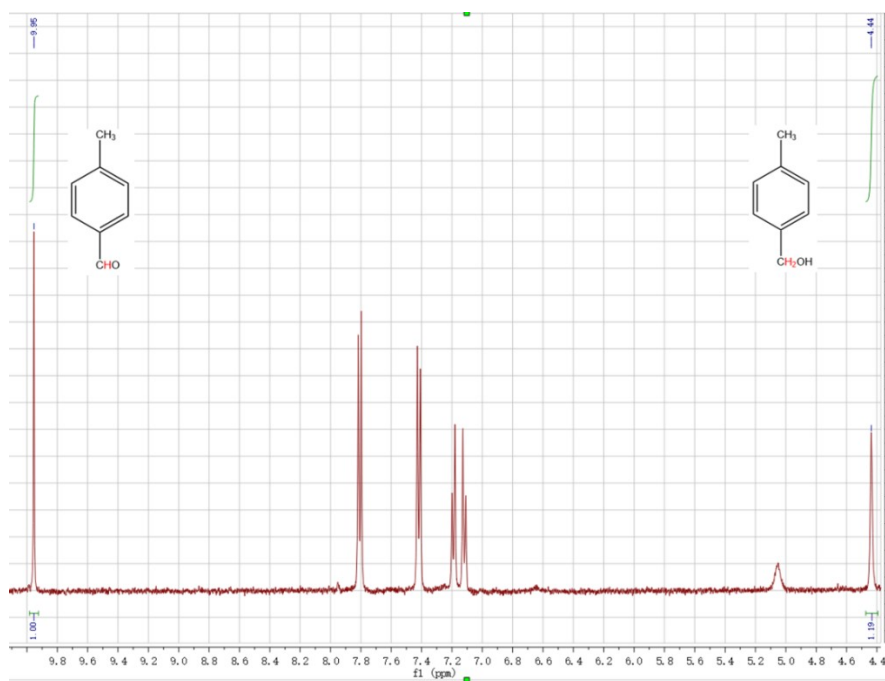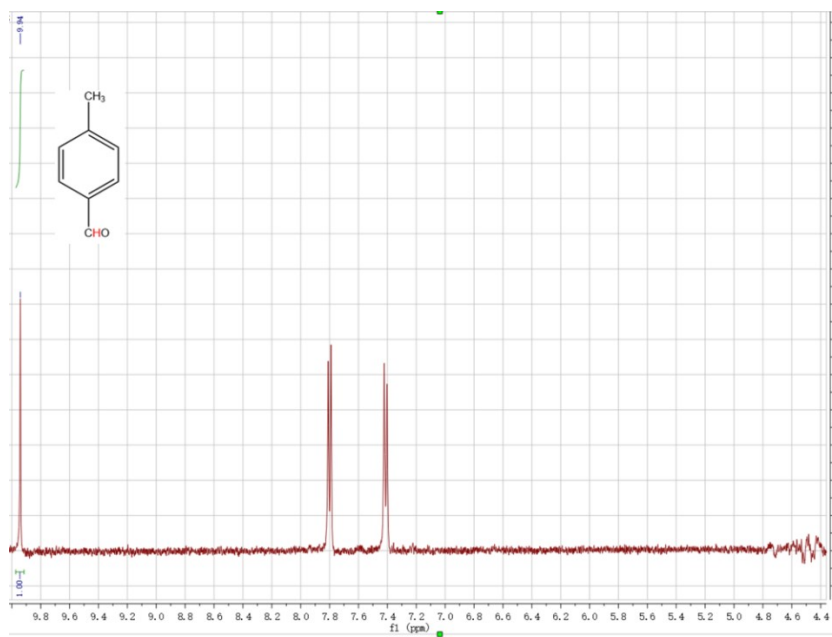**Table S1.** High-resolution XPS spectra fitting data of O 1s for n-Cu$_3$(BTC)$_2$ and m-Cu$_3$(BTC)$_2$.

Sample O 1s	n-Cu$_3$(BTC)$_2$		
	Position (eV)	FWHM (eV)	Area
COO	532.0	1.937	35212.86
Cu-O	531.6	1.369	34224.01

The ratio of peak area of Cu-O bond to that of COO bond for n-Cu$_3$(BTC)$_2$ is 0.97.

Sample O 1s	m-Cu$_3$(BTC)$_2$		
	Position (eV)	FWHM (eV)	Area
COO	532.8	2.310	21963.34
Cu-O	531.9	1.387	23446.35

The ratio of peak area of Cu-O bond to that of COO bond for m-Cu$_3$(BTC)$_2$ is 1.07.

Table S2. EXAFS fitting parameters at the Cu K-edge for n-Cu$_3$(BTC)$_2$, m-Cu$_3$(BTC)$_2$ and Cu$_3$(BTC)$_2$ synthesized in IL/water solvent with water to IL mass ratio from 0 to 2.5.

Sample	Shell	N [a]	R (Å) [b]	σ^2 (Å$^{-2}\cdot 10^{-3}$) [c]	ΔE_0 (eV) [d]	R factor (%)
n-Cu$_3$(BTC)$_2$	Cu-O	3.6	1.94	3.6	6.0	0.3
m-Cu$_3$(BTC)$_2$	Cu-O	5.0	1.95	5.0	2.8	0.5
0	Cu-O	4.5	1.95	5.6	3.9	0.1
0.25	Cu-O	4.4	1.95	5.4	3.7	0.3
2.5	Cu-O	4.1	1.93	3.8	6.5	0.4

Table S3. Energy barriers of water attacks Cu-O bond in *a*, *b*, *c* and *d* directions. The calculation process of energy barriers required for the fracture of (222) crystal plane, vertical plane of (222) crystal plane and (220) crystal plane.

	E^a (eV)	E^b (eV)	E^c (eV)	E^d (eV)
$E_{2H_2O\text{-}Cu_3(BTC)_2}$	-4551.12	-4551.44	-4550.19	-4551.06
$E_{Cu_3(BTC)_2}$	-4525.48	-4525.48	-4525.48	-4525.48
E_{H_2O}	-14.21	-14.21	-14.21	-14.21
ΔE	2.78	2.46	3.71	2.84

Calculation process:

$\Delta E_{xyz} = E_{2H_2O\text{-}Cu_3(BTC)_2} - E_{Cu_3(BTC)_2} - 2E_{H_2O}$;

$\Delta E_{222} = (\Delta E^a + \Delta E^b)/2 = 2.62$ eV;

$\Delta E_{22\bar{2}} = (\Delta E^c + \Delta E^d)/2 = 3.28$ eV (vertical plane of 222) ;

$\Delta E_{220} = \min\left(\dfrac{\Delta E^a + \Delta E^d}{2}, \dfrac{\Delta E^b + \Delta E^c}{2}\right) = \min(2.81, 3.09)\ \text{eV} = 2.81$ eV.