Supporting Information

Functionalization of Metal–Organic Frameworks Achieves Controllable Wettability

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1. Synthesis and Characterization

1.1 $N$-mesitylacetamide 2.

Figure S1. $^1$HNMR spectra of $N$-mesitylacetamide 2 in CDCl$_3$. 
**Figure S2.** $^{13}$CNMR spectra of $N$-mesitylacetamide 2 in CDCl$_3$.

**1.2. 2-aminobenzene-1,3,5-tricarboxylic acid 3.**

**Figure S3.** $^1$HNMR spectra of 2-aminobenzene-1,3,5-tricarboxylic acid 3 in DMSO-d$_6$. 
2. Post-synthetic modification

Scheme S2. Amide Functionalization of Cu$_3$(NH$_2$BTC)$_2$

2.1. $^1$HNMR spectra of modified ligands

The unmodified ligand peaks are denoted with a black square and appear slightly downfield of the modified ligands denoted with red circles. The appearance and intensity of a chemical shift within the $^1$HNMR spectra of the digested MOF samples at 8.39 ppm, indicative of the aromatic protons on the modified amino tricarboxylate ligands was identified. Aromatic region (8 ppm – 9 ppm) was used to quantify percent conversion to the desired amides. As the equivalents of anhydride increases, so does the percentage of modification, denoted by the peak in the aromatic region with the red circle. All modifications were performed in triplicate, and the three independent studies were averaged and summarized in Table 1.
**Figure S5.** $^1$HNMR spectra of digested Cu$_3$(NH-AM5-BTC)$_2$ in CDCl$_3$, showing the increase in modified ligand to unmodified ligand as the equivalents of anhydride increases.

**Figure S6.** $^1$HNMR spectra of digested Cu$_3$(NH-AMi-Pr-BTC)$_2$ in CDCl$_3$. 
Figure S7. $^1$HNMR spectra of digested Cu$_3$(NH-AMi-Bu-BTC)$_2$ in CDCl$_3$.

Figure S8. $^1$HNMR spectra of digested Cu$_3$(NH-AM4-BTC)$_2$ in DMSO-D6.
**Figure S9.** $^{1}H$NMR spectra of digested Cu$_3$(NH-AM6-BTC)$_2$ in DMSO-D$_6$.

**Figure S10.** $^{1}H$NMR spectra of digested Cu$_3$(NH-AM7-BTC)$_2$ in DMSO-D$_6$. 
2.2. Mass spectrometry of acid digested modified ligands.

Figure S12. Digested Cu$_3$(NH-AM$_{10}$-BTC)$_2$; ESI/APCI-MS.
Figure S13. Digested Cu$_3$(NH-AM/Bu-BTC)$_2$: ESI/APCI-MS.

Figure S14. Digested Cu$_3$(NH-AM4-BTC)$_2$: ESI/APCI-MS.
Figure S15. Digested Cu$_3$(NH-AM5-BTC)$_2$ ESI/APCI-MS.

Figure S16. Digested Cu$_3$(NH-AM6-BTC)$_2$ ESI/APCI-MS.
Figure S17. Cu$_3$(NH-AM7-BTC)$_2$ ESI/APCI-MS.

Figure S18. Digested Cu$_3$(NH-AM10-BTC)$_2$ ESI/APCI-MS.
3. Thermal gravimetric analysis (TGA)

Figure S19. Thermal gravimetric analysis (TGA) of Cu$_3$(NH$_2$BTC)$_2$ and all modified materials. TGA shows that the modified materials retain thermal stability.
4. IR

Figure S20. IR spectroscopy from bottom to top of Cu$_3$(BTC)$_2$, Cu$_3$(NH$_2$BTC)$_2$, preligand NH$_2$H$_3$BTC and modified MOF Cu$_3$(NH-AMI-Bu(BTC)$_2$. The MOF samples to not appear to contain any free-ligand (little to no decomposition). All modified spectra are consistent with that of Cu$_3$(NH-AMI-Bu-BTC)$_2$(shown).
5. Wettability

5.1 Water Contact Angles (WCA)

Figure S21. Water contact angle and sorption study images highlighting the ability to select different modifications and percent of functionalization to obtain different amounts of hydrophobicity.

5.2. WCA vs Number of Carbons in Amide

Figure S22. Relationship where the observed water contact angle in degrees (y) increases as the number of carbons (x) increases (when maximum modification is performed) with linear alkyl chains from 5–10 carbons. y = 5.7x + 89.5, R^2 = 0.97. Each data point represents the average of three trials. Error bars represent the standard deviation of 3 water droplets on the material after 1 second.
6. Water Stability PXRD

![Figure S23](image)

**Figure S23.** Powder X-ray diffraction data before (top, shown in blue) and after (bottom, shown in black) water submersion. (A) \( \text{Cu}_3(\text{NH}_2\text{BTC})_2 \) before water exposure. Little to no diffraction pattern is observed after water exposure with the unmodified material. (B) \( \text{Cu}_3(\text{NH-AM10-BTC})_2 \). The result shown is with 14% conversion and minor changes in intensity and slight shift in the 2θ diffraction pattern is observed after water exposure with the unmodified material. To our knowledge, this increased amount of water stability has never been observed for copper MOFs via synthetic functionalization of the ligand, and foreshadows exciting possibilities for applications of \( \text{Cu}_3(\text{NH}_2\text{BTC})_2 \) in place of \( \text{Cu}_3(\text{BTC})_2 \).

7. 3-D Crystal Drawings

![3-D Crystal Drawings](image)

**Figure S24.** \( \text{Cu}_3(\text{NH}_2\text{BTC})_2 \) 3-dimensional drawings showing potential access views of the amino functional handle. Oxygen is highlighted in red, nitrogen in blue, copper in green, hydrogen in grey, and carbon in black.
8. SEM of MOF

![SEM images of MOF](image)

**Figure S25.** Cu$_3$(NH$_2$BTC)$_2$ and Cu$_3$(NH-AM5-BTC)$_2$ (left to right) SEM images after gentle grinding taken at 1400X.

11. References