Supporting Information for:

Effect of Countercation on the Water Stability of an Anionic Metal-Organic Framework

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1. Characterization

The cation exchange experiments and the characterization of the cation-exchanged materials were conducted based on previous reported procedures which yielded complete exchange of DMA cations. See the following reference for details:

An et al. *J. Am. Chem. Soc*. **2010**, *131*, 5578

The integration for one set of the H_2-BPDC aromatic hydrogens was set as 6 H's, which is consistent with the formula unit $[Zn_2(Ad)_1(BPDC)_{1.5}O_{0.25}]^{-0.5}$. We then integrated the peaks corresponding to each cation to determine the number of cations in each material. We expect 0.5 cations per formula unit. The data is consistent with this expectation.

Single Cation MOFs (integration shown for italicized 'H' in formula)

I: $NH_2(CH_3)_2^+$, δ 2.55 (s, 2.8 H's)
Example calculation: 6 H per cation
Integration: 2.8 H
2.8/6 = 0.47 cations per formula unit

II: $N(CH_3)_4^+$, δ 3.1 (s, 6.0 H's)
III: $N(CH_2CH_3)_4^+$, δ 1.2 (t, 6.4 H's)
IV: $N(CH_2CH_2CH_2CH_3)_4^+$, δ 0.97 (t, 5.2 H's)
V: $N(CH_3)(CH_2CH_2OH)_3^+$, δ 3.1 (s, 1.8 H's)

Mixed Cation MOFs (integration shown for italicized 'H' in formula)

VI: $N(CH_2CH_3)_4^+$, δ 1.2 (t, 3.5 H's) ; $N(CH_3)(CH_2CH_2OH)_3^+$, δ 3.1 (s, 0.72 H's)
Example calculation: 12 H per $N(CH_2CH_3)_4^+$
Integration: 3.5 H
3.5/12 = 0.29 $N(CH_2CH_3)_4^+$ per formula unit

3 H per $N(CH_3)(CH_2CH_2OH)_3^+$
Integration: 0.72 H
0.72/3 = 0.24

Therefore, $N(CH_2CH_3)_4^+ : N(CH_3)(CH_2CH_2OH)_3^+ = 1.2 : 1$

VII: $N(CH_2CH_3)_4^+$, δ 1.2 (t, 5.1 H's) ; $N(CH_3)(CH_2CH_2OH)_3^+$, δ 3.1 (s, 0.4 H's)
VIII: $N(CH_2CH_3)_4^+$, δ 1.2 (t, 3.3 H's) ; $N(CH_3)(CH_2CH_2OH)_3^+$, δ 3.1 (s, 1.2 H's)

The crystallinity for **I-V** was confirmed via PXRD.

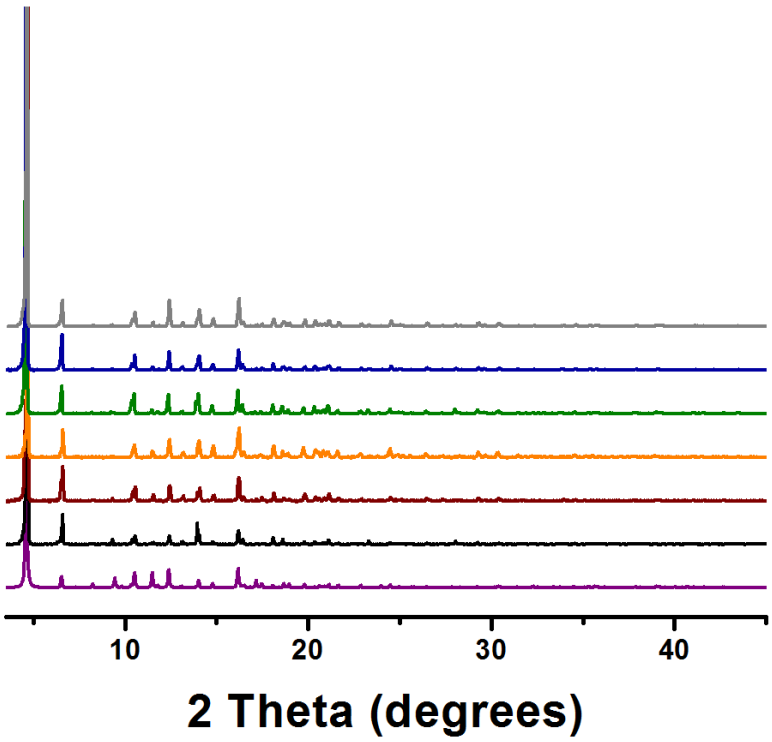

Figure S1: PXRD patterns for **I** (black), **II** (red), **III** (orange), **IV** (green), **V** (blue), and **I** after heating to 150 °C (grey) compared to the simulated pattern (purple).

2. Water Soaking

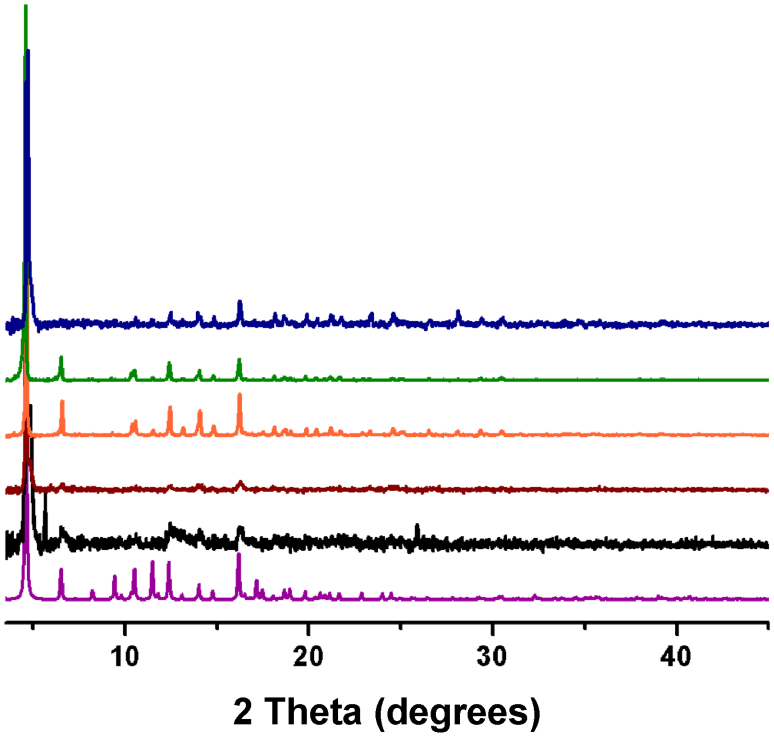

Figure S2: PXRD of **I** (black), **II** (red), **III** (orange), **IV** (green), and **V** (blue) after soaking in H_2O for 7 days, compared to simulated pattern (purple).

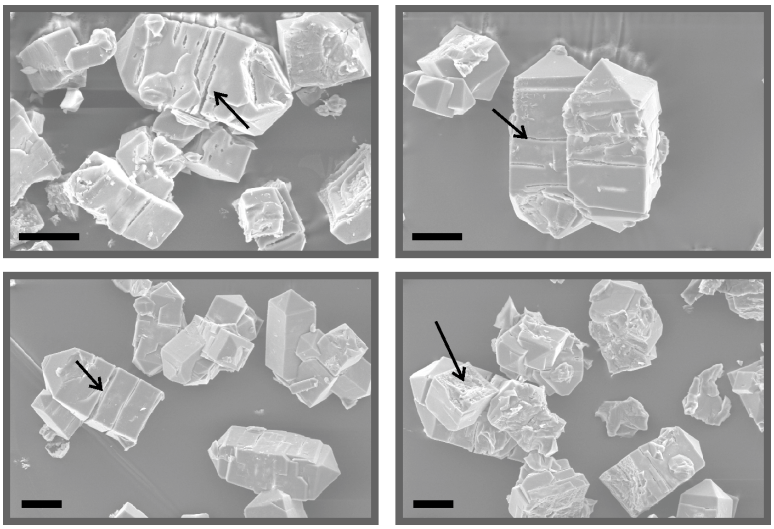

Figure S3: SEM images for **I** after soaking in H_2O for seven days. Black arrows indicate cracking and fracturing of crystallites. Scale bar: 20 μm.

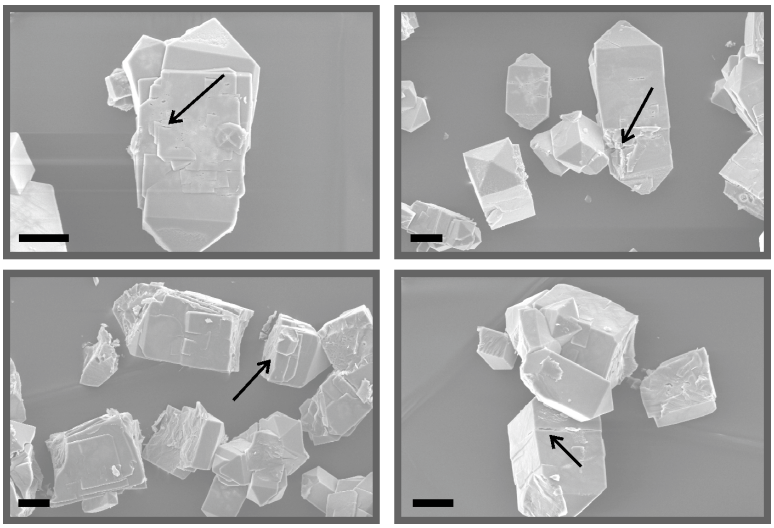

Figure S4: SEM images for **II** after soaking in H_2O for seven days. Black arrows indicate cracking and fracturing of crystallites. Scale bar: 20 μm.

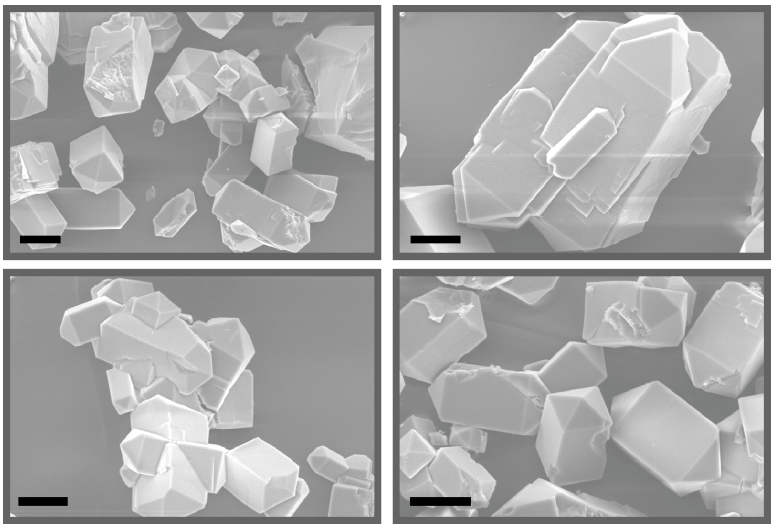

Figure S5: SEM images for **III** after soaking in H_2O for seven days. Scale bar: 20 μm.

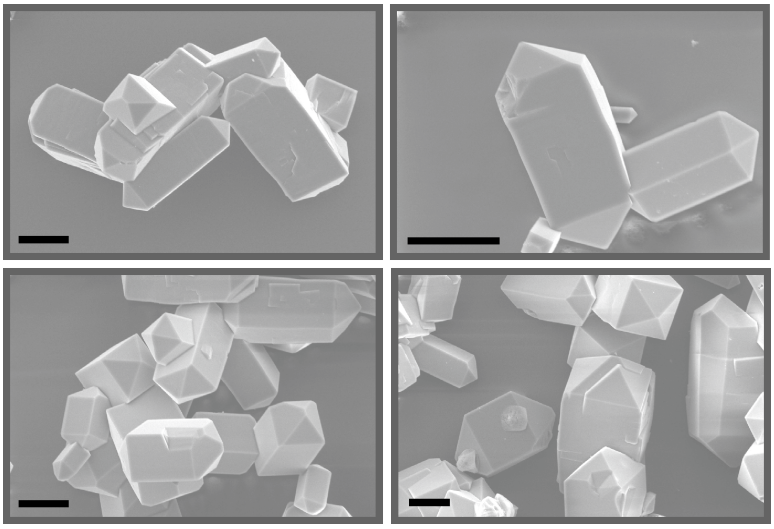

Figure S6: SEM images for **IV** after soaking in H_2O for seven days. Scale bar: 20 μm.

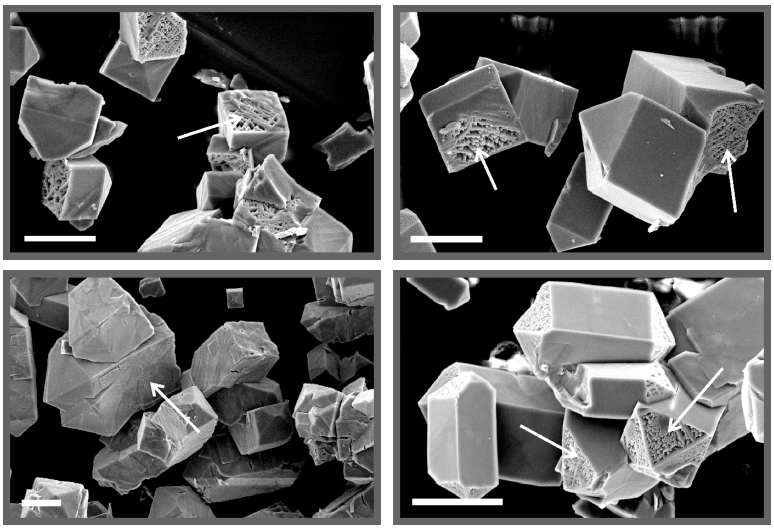

Figure S7: SEM images for **V** after soaking in H_2O for seven days. White arrows indicate regions of degradation and pitting. Scale bar: 20 μm.

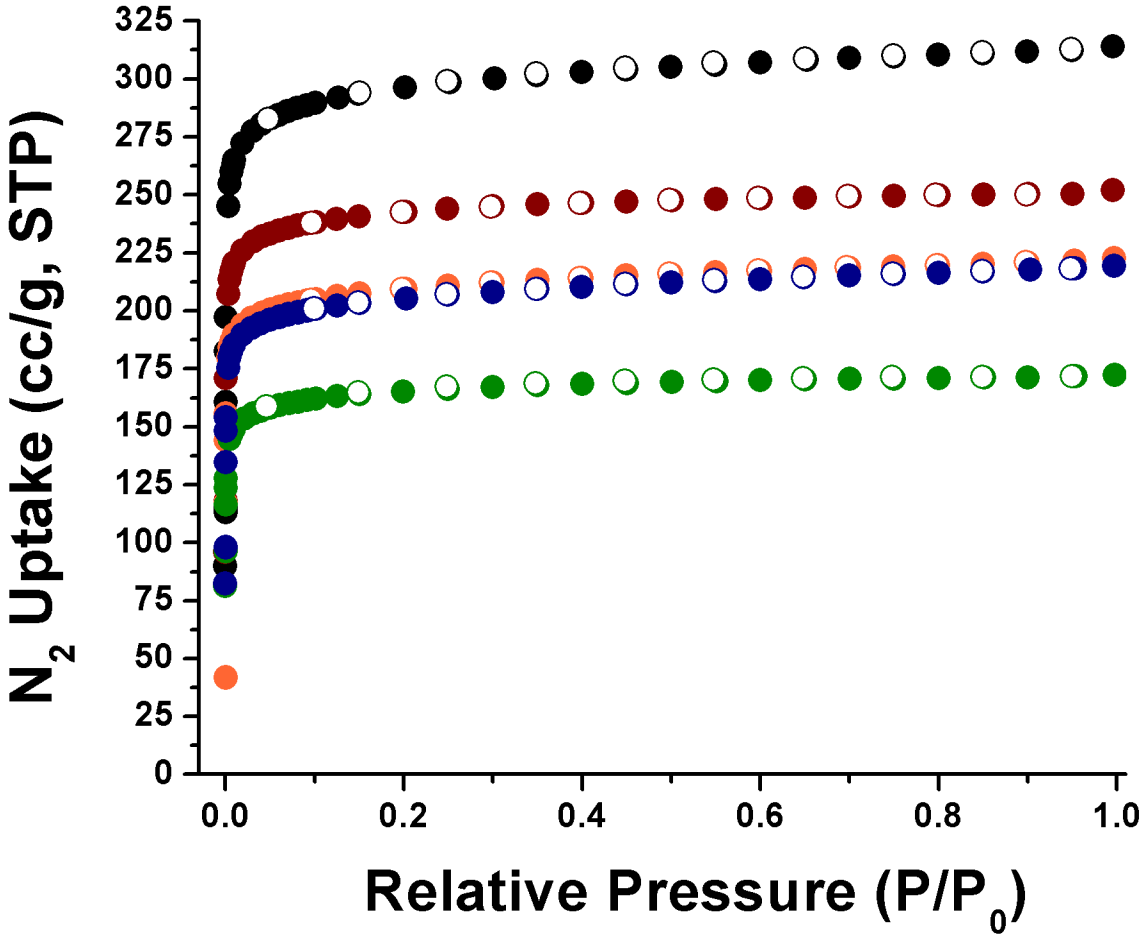

Figure S8: N_2 isotherms at 77 K after cation exchange for **I** (black), **II** (red), **III** (orange), **IV** (green), and **V** (blue).

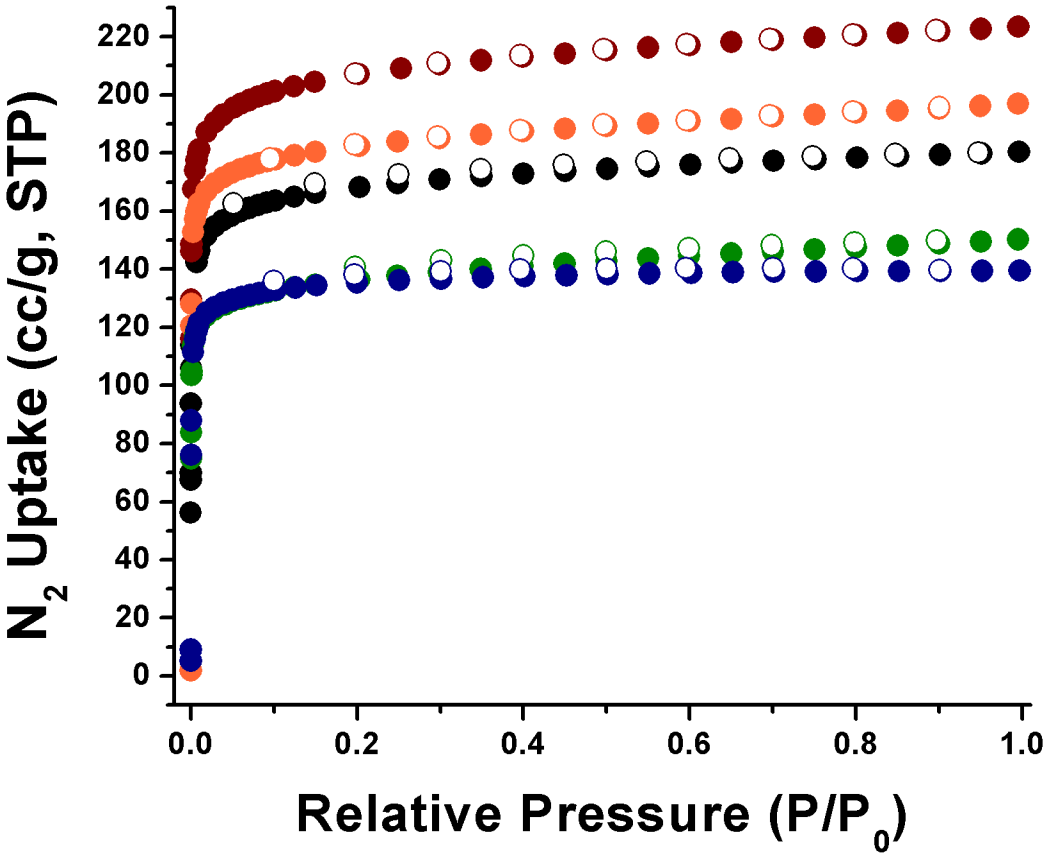

Figure S9: N_2 isotherms at 77 K of **I** (black), **II** (red), **III** (orange), **IV** (green), and **V** (blue) after soaking in H_2O for 7 days.

3. Water Vapor Studies – Single Cation Exchange

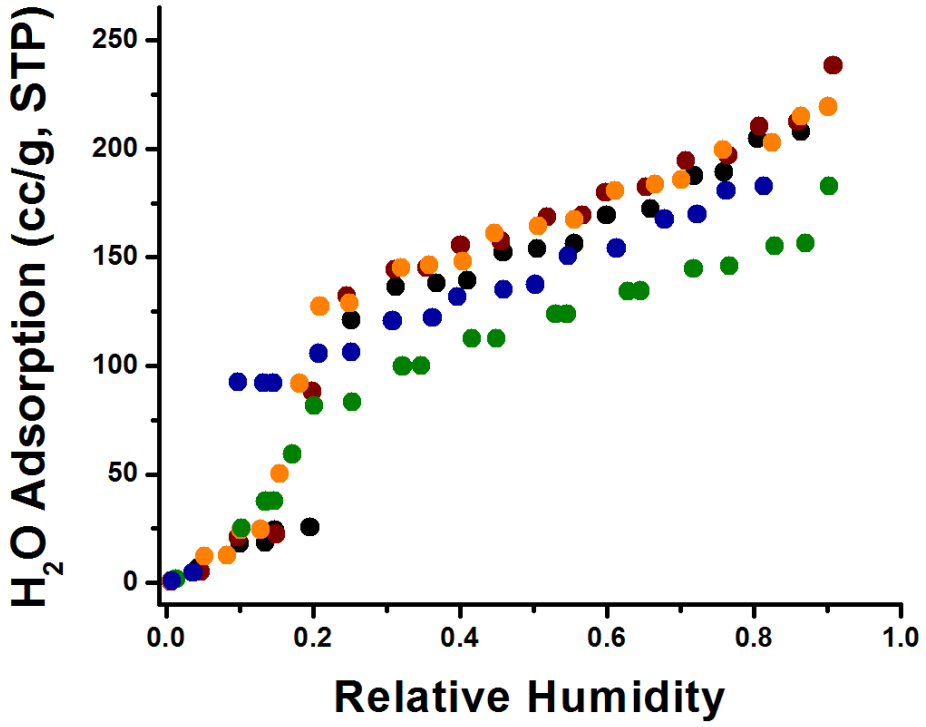

Figure S10: H_2O adsorption isotherms at 293 K for **I** (black), **II** (maroon), **III** (orange), **IV** (green), and **V** (blue). The points for **V** at 0.85 and 0.9 are not shown (585 cc/g and 2580 cc/g, respectively).

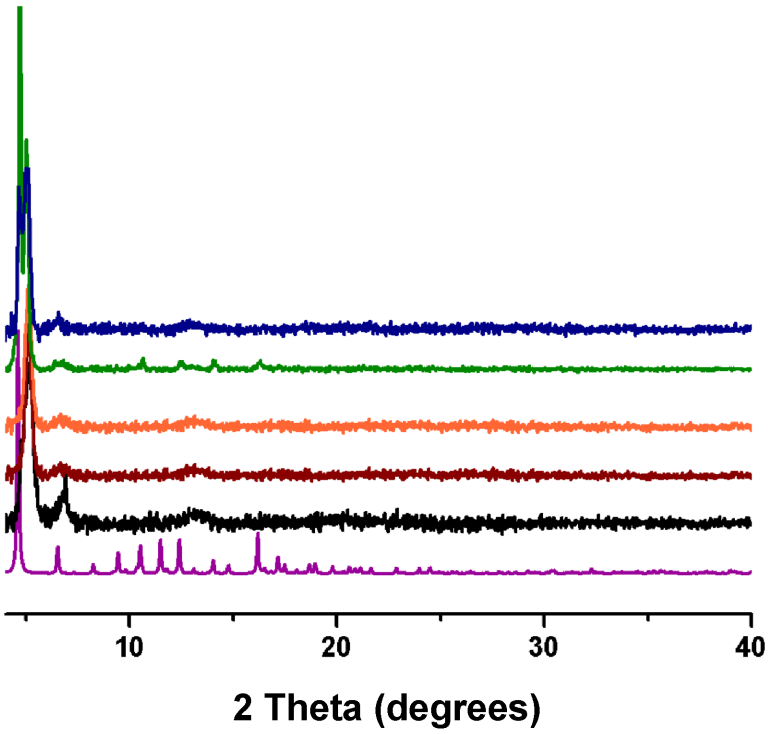

Figure S11: PXRD for **I** (black), **II** (red), **III** (orange), **IV** (green), and **V** (blue) compared to simulated **bMOF-1** pattern (purple) after exposure to 90% humidity.

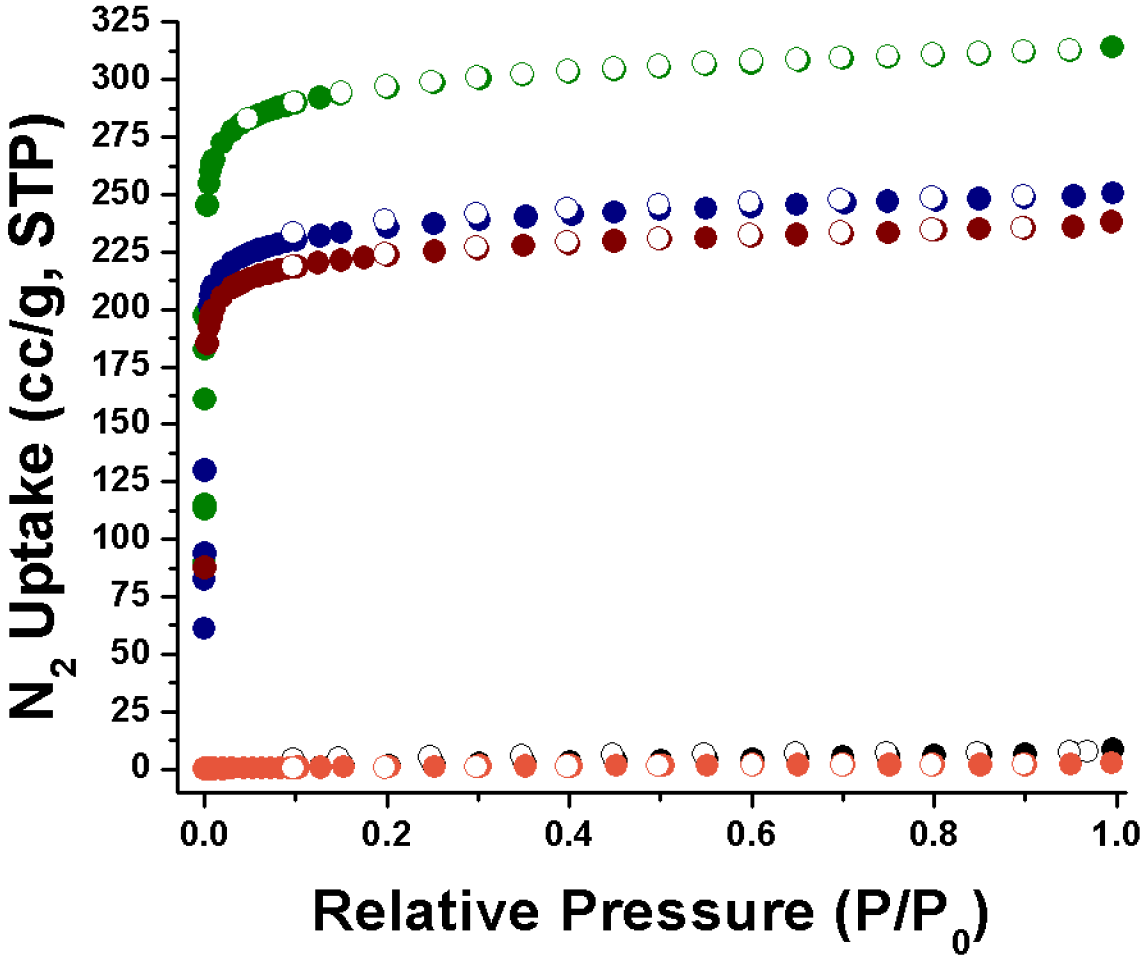

Figure S12: N_2 isotherm for **I** before exposure (green), after 90% humidity (black), 20% humidity (orange), 17.5% humidity (red), and 15% humidity (blue).

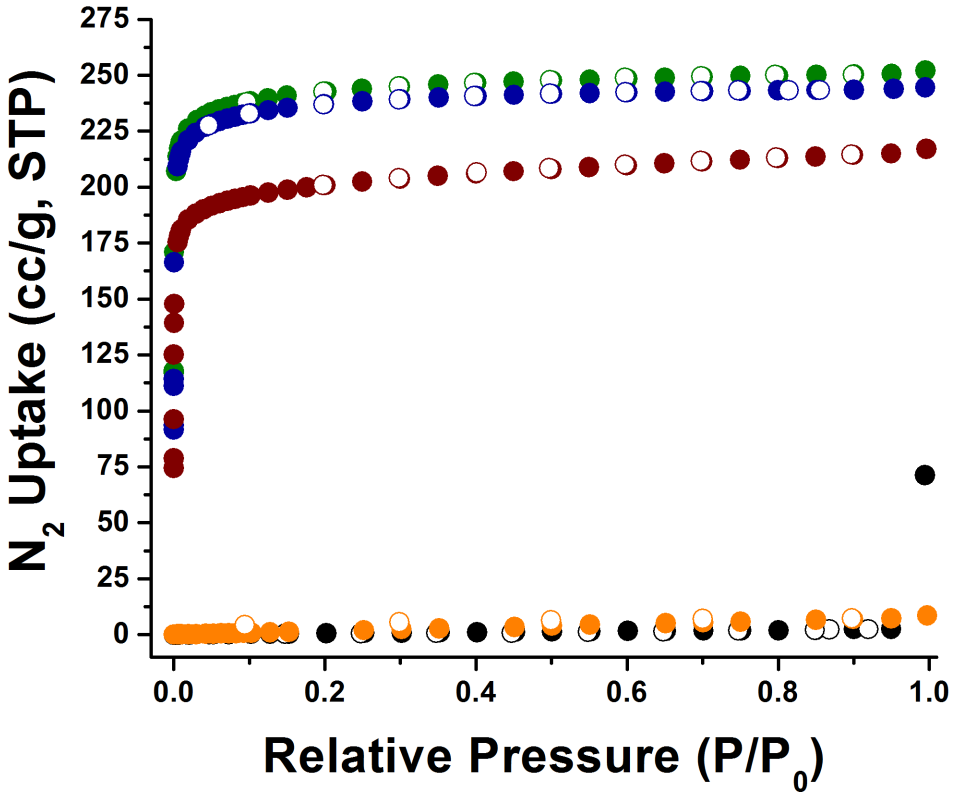

Figure S13: N_2 isotherm for **II** before exposure (green), after 90% humidity (black), 20% humidity (orange), 17.5% humidity (red), and 15% humidity (blue). Some points omitted for clarity due to overlapping plots.

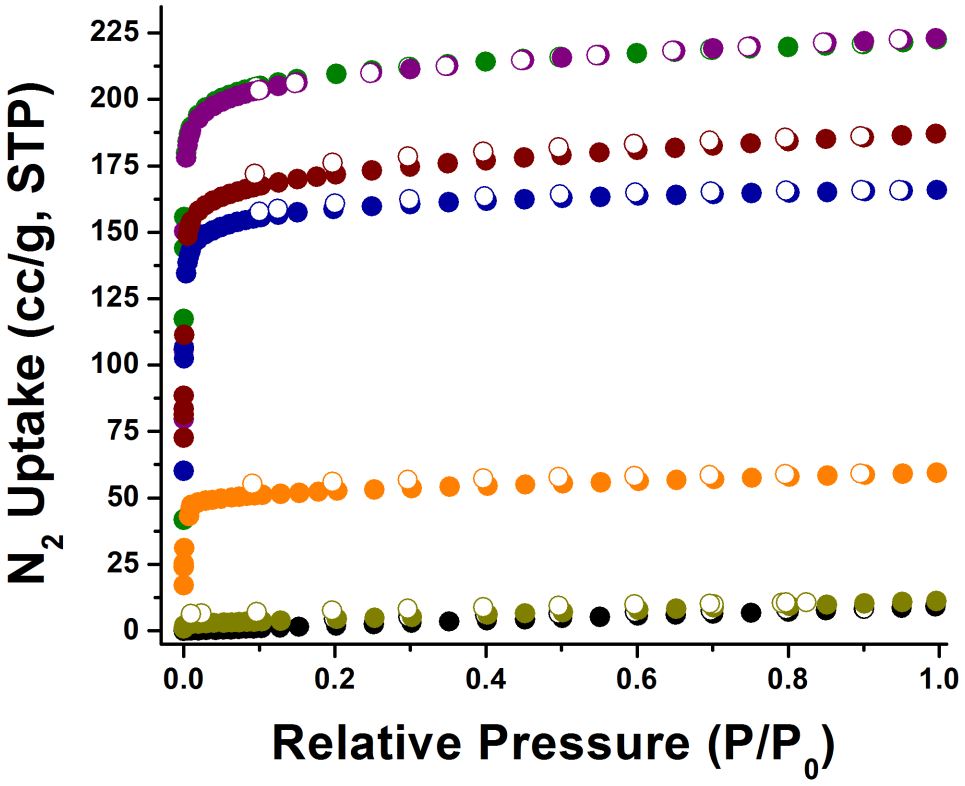

Figure S14: N_2 isotherm for **III** before exposure (green), after 90% humidity (black), 22% humidity (olive), 20% humidity (orange), 17.5% humidity (red),15% humidity (blue), 12.5% humidity (purple). Some points omitted for clarity due to overlapping plots.

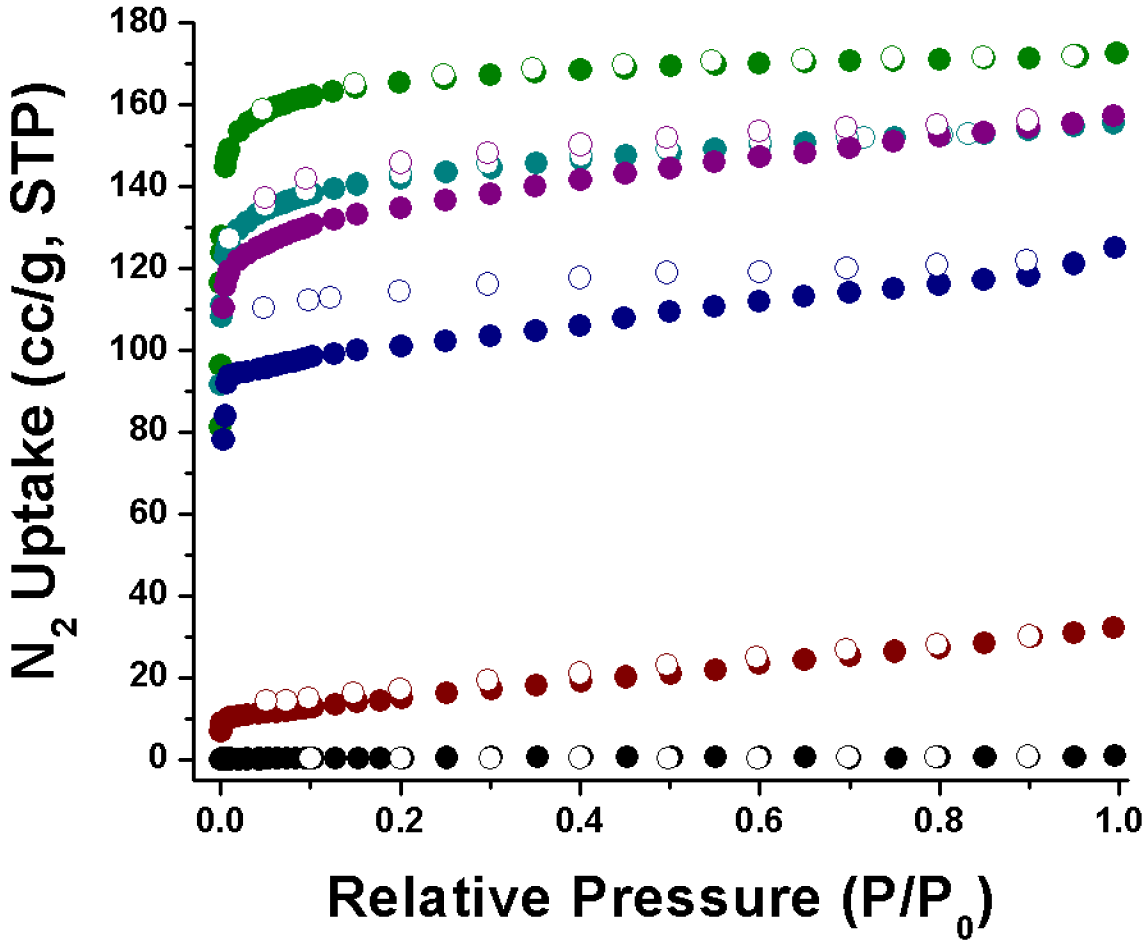

Figure S15: N_2 isotherm for **IV** before exposure (green), after 90% humidity (black), 17.5% humidity (red), 15% humidity (blue), 12.5% humidity (purple), and 10% humidity (teal).

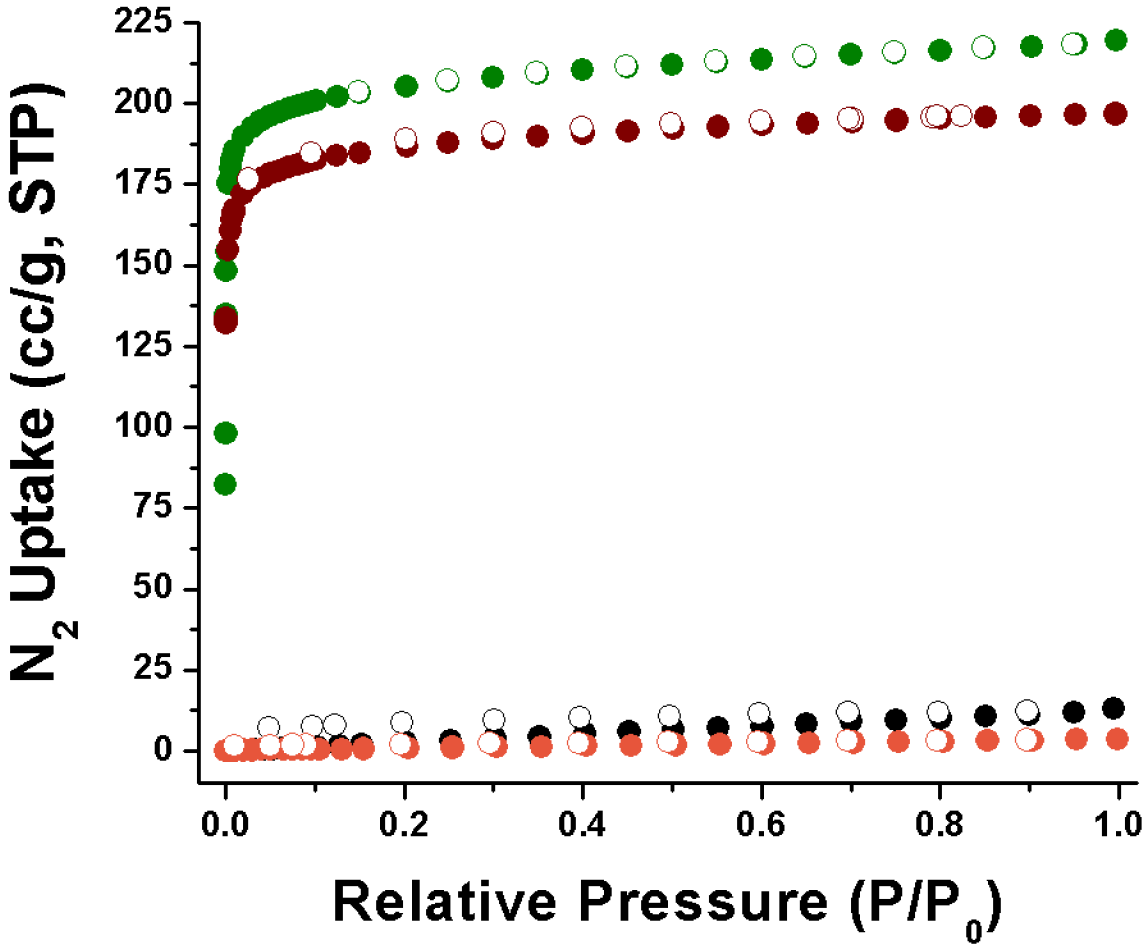

Figure S16: N_2 isotherm for **V** before exposure (green), after 90% humidity (black), 5% humidity (red), and 7.5% humidity (orange).

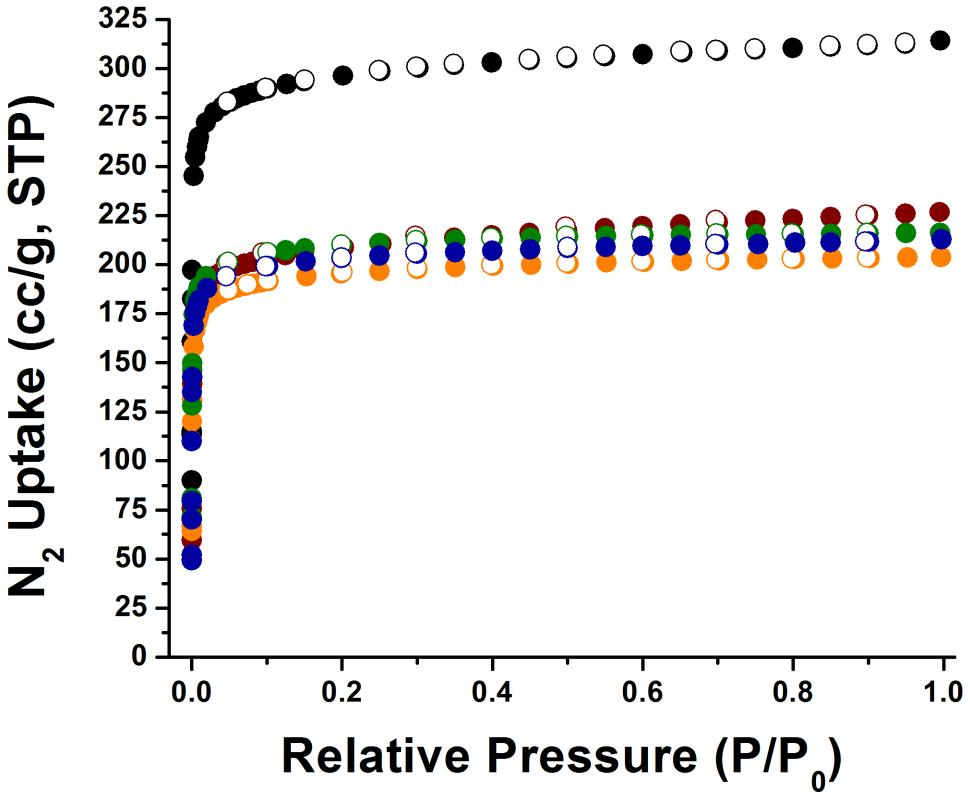

Figure S17: N_2 isotherm at 77 K for **I** (before: black) after exposure to 15% humidity four times (red, orange, green, and blue). Some points omitted for clarity due to overlapping plots.

4. Water Vapor Studies – Multi-Cation Exchange

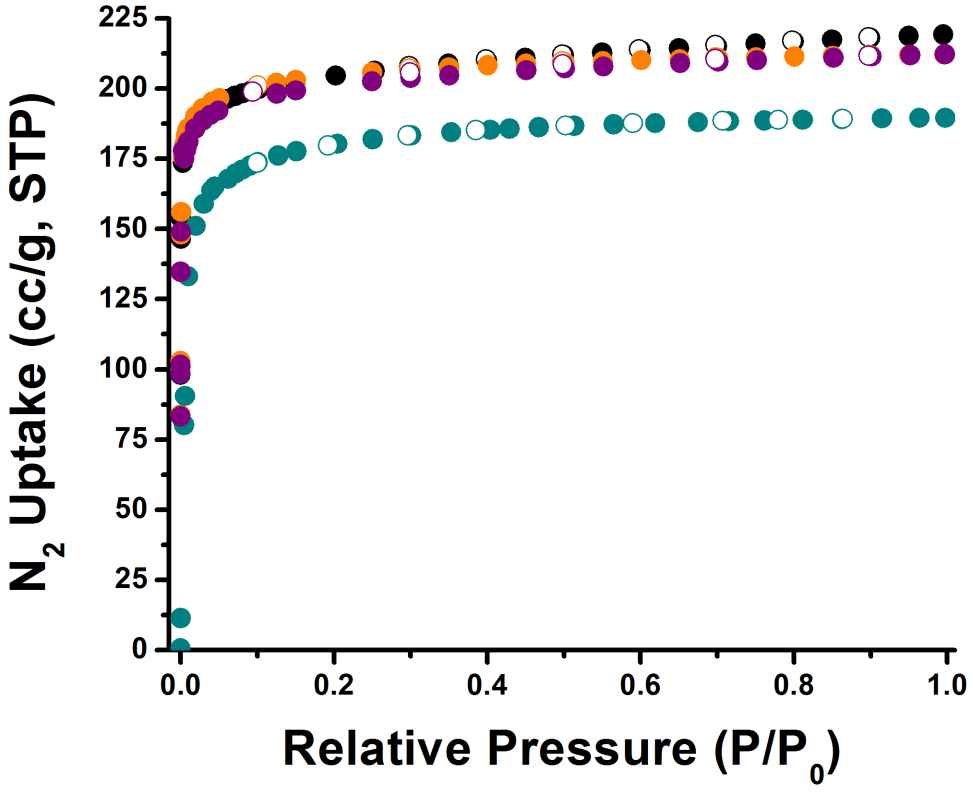

Figure S18: N_2 isotherm at 77 K for **VI** before (black) H_2O adsorption, after 7.5 % (orange), 10 % (teal), and 12.5 % (purple) humidity. Some points omitted for clarity due to overlapping plots.

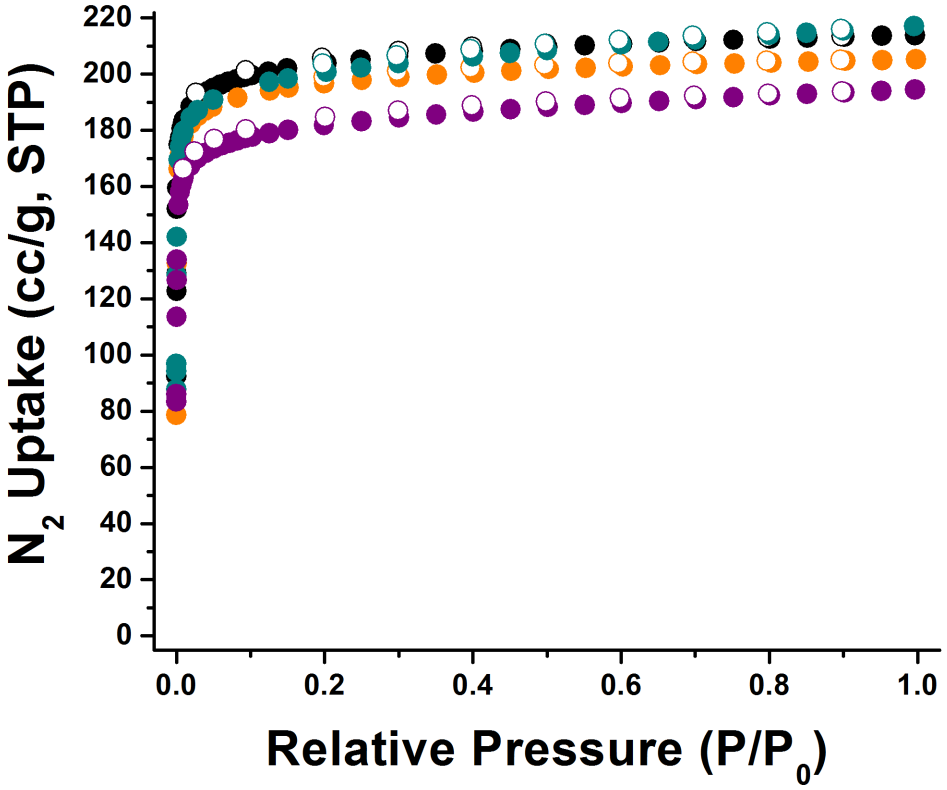

Figure S19: N_2 isotherm at 77 K for **VII** before (black) H_2O adsorption, after 7.5 % (orange), 10 % (teal), and 12.5 % (purple) humidity. Some points omitted for clarity due to overlapping plots.

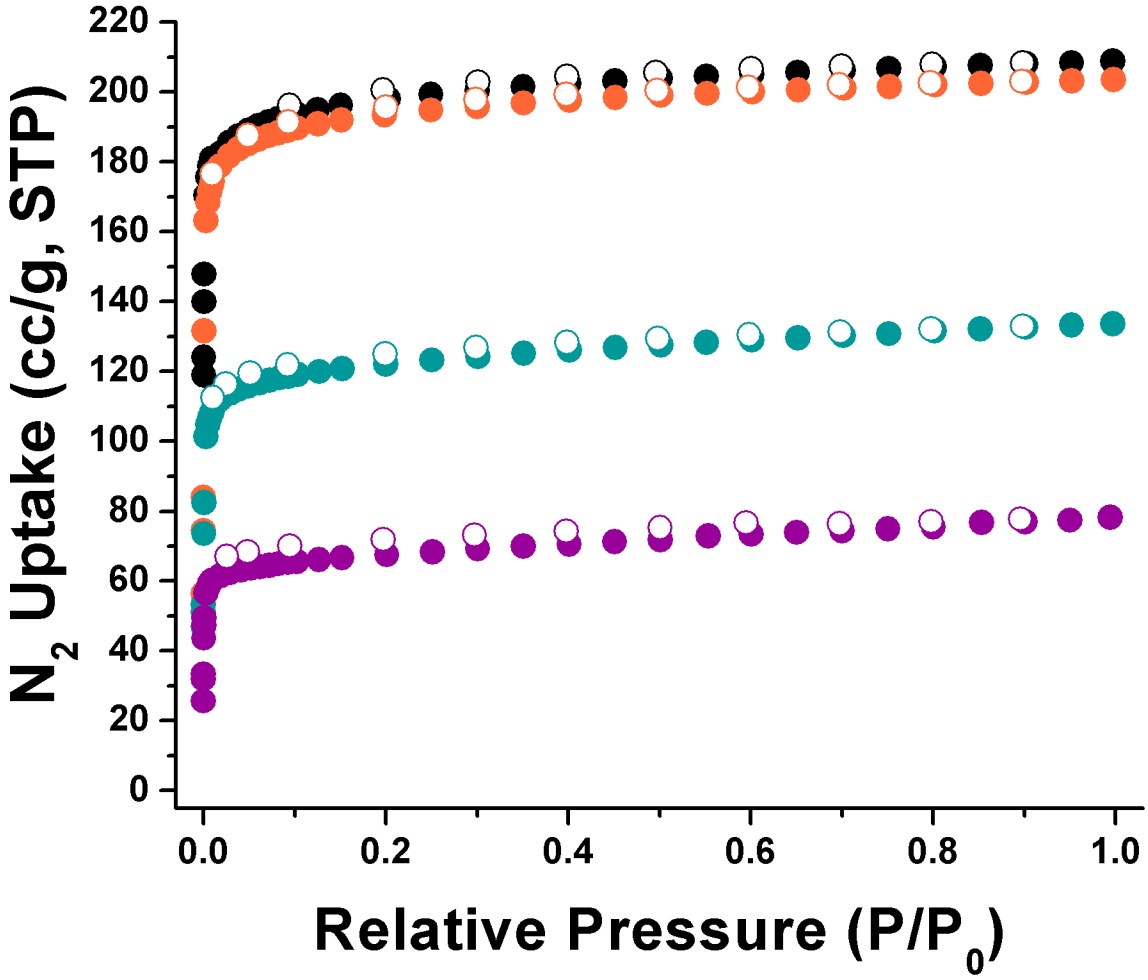

Figure S20: N_2 isotherm at 77 K for **VIII** before (black) H_2O adsorption, after H_2O adsorption to 7.5 % (orange), 10 % (teal), and 12.5 % (purple) humidity.