

Supplementary Information for

Selectivity for Water Isotopologues Within Metal Organic Nanotubes

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1. Materials and Methods

CAUTION: The synthesis of the UMON material requires the use of radioactive ^{238}U , which is an α emitter, and like all radioactive materials must be handled with care. These experiments were conducted by trained personnel in a licensed research facility with special precautions taken toward the handling, monitoring, and disposal of radioactive materials.

UMON materials were synthesized according to previously published methodology. Briefly, 2.5 mL of a 0.2 M uranyl nitrate hexahydrate solution was mixed with 2.5 mL of a 0.2 M iminodiacetic acid solution in a glass scintillation vial and followed by the addition of 5 mL of 0.2 M piperazine. Methanol was added to the solution in a H₂O:methanol of 1:2 to aid in crystallization. Crystalline materials in pure yields were formed on the bottom of the sample vial with yields of 95% based upon U. The material was filtered, washed with acetone, and air dried. Purity of the bulk material was assessed by powder X-ray diffraction on a Bruker Avance diffractometer (Cu K α).

Flow-through D₂O uptake studies: Dehydrated UMON crystallites were placed in a tared 1.5-dram glass vial and dehydrated at 120° for 18 hrs. The vial was sealed with a septum cap while at temperature, and the initial mass of the sample/vial was recorded using a METTLER AT20 microbalance. The sample was placed on a vapor sorption apparatus and dry air (Praxair 439 compressed air ultra-zero) was bubbled through a sealed vial by perforating the seal with a needle (Fig. S1). The relative humidity (RH) was maintained at 80% by passing the dry gas through 10 mL of D₂O (99.6%) and the temperature and humidity was monitored by a Sensirion sensor. A Cole Parmer flow-rate gauge was used to control the volume of vapor passed over the UMON material. The weight change of the sample every 10 minutes for one hour.

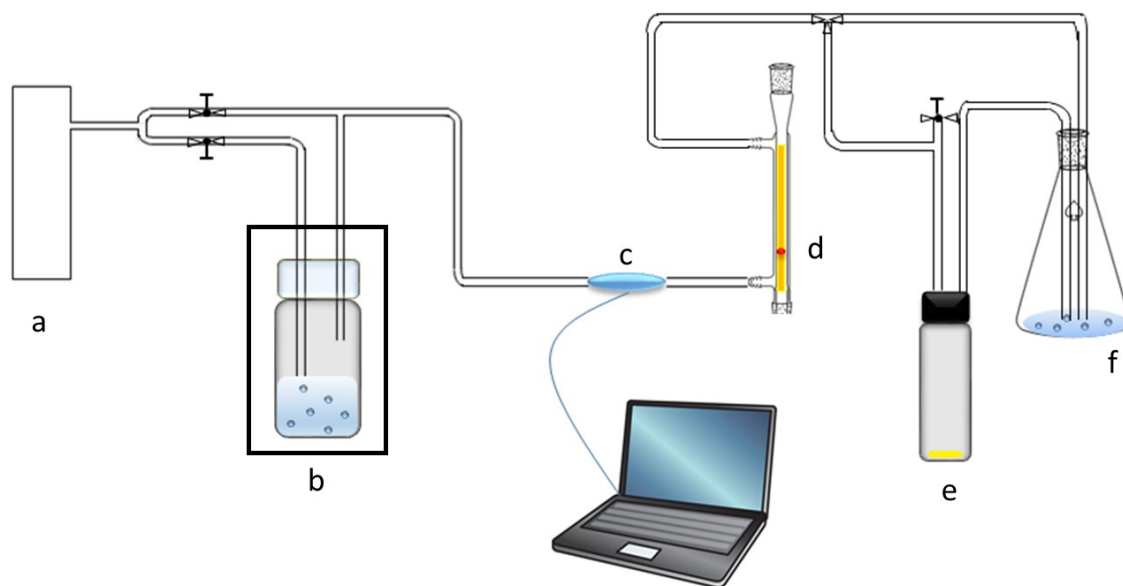


Fig. S1. Vapor sorption apparatus used for D₂O flow-through experiments includes (a) dry N₂ source, (b) sealed D₂O chamber, (c) relative humidity sensor, (d) flow meter, (e) sample chamber, and (f) overflow chamber.

Batch D₂O uptake studies: Crystals were gently ground to achieve a uniform crystallite size range of $250 \pm 75 \mu\text{m}$, and dehydrated at 120 °C for 18 hrs. A large glove bag (520 L, SigmaAldrich) was purged and backfilled with UHP nitrogen gas (99.999%, Praxair) three times. The N₂ gas was passed through activated molecular sieves (3 Å, 8-12 mesh, Acros Organics) and Drierite™ (8 mesh) to ensure and monitor the dryness. Approximately 80 mg of the crystals in three 1.5-dram glass vials were removed from the oven and immediately placed into the glove bag (Fig. S2). Two uncapped 20-mL glass scintillation vials with D₂O (2.5 mL) were also placed into the glove bag. The vials containing the UMON crystals were uncapped and placed inside the 20-mL vials containing D₂O. The larger vials

were then capped and allowed to equilibrate for 18 hours. The third UMON sample was left uncapped in the glovebox to serve as a blank. D₂O uptake experiments were performed five times over one calendar year with freshly prepared UMON samples. Uptake of 50%/50% H₂O/D₂O mixture was also performed using the same methodology as described for the pure D₂O system.

After uptake, UMON crystals were removed from the 1.5-dram vials, placed into two tared Al pans, and sealed in glass vials for transport to the TGA/FTIR instrument. Transfer time was ~30sec and based upon our prior vapor sorption experiments (and blank), we are confident that prohibited measurable uptake of atmospheric H₂O. Samples were analyzed using a TA instruments TGA Q500 (purged with N₂ prior to use) interfaced with a Nicolet FT-IR spectrometer via a Thermo Scientific evolved gas analyzer. The sample was heated from 25 °C to 180 °C (ramp rate of 20 °C per minute) and the evolved gas was analyzed with FTIR spectroscopy. TGA/FTIR data was also collected on H₂O, D₂O, and HDO standards.

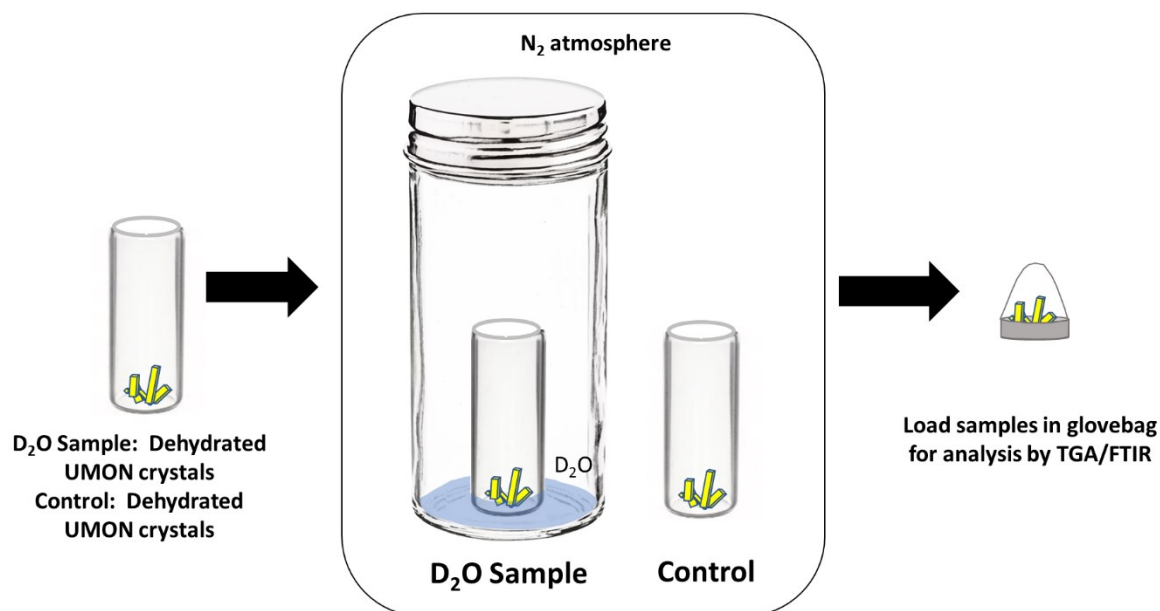


Fig. S2. Illustration of the experimental methodology for the D₂O adsorption experiments. Two sets of 1.5-dram vials containing dehydrated UMON crystals were placed into a N₂ atmosphere. One set of vials was placed into a 20 mL scintillation vial containing 2.5 mL D₂O and the other set were exposed to the N₂ atmosphere inside the glovebag. Both sets of vials were equilibrated overnight before being transferred to an aluminum TGA pan for analysis by TGA/FTIR spectroscopy.

FTIR studies of solid state UMON samples: Freshly synthesized UMON crystals were vacuum filtered from their mother liquor, rinsed with dry acetone (3 Å, 8-12 mesh, Acros Organics), and dehydrated at 80 °C for 18 hrs. Approximately 30 mg of the heated material was immediately placed into immersion oil and deposited between two KBr discs for FTIR analysis. Two additional 30 mg samples were placed into separate 20 mL vials for hydration with either H₂O or D₂O vapor (5-mL of liquid larger sealed glass vials) for 18 hrs in the glove bag. After hydration, the crystals were prepared for FTIR analysis on KBr disks. FTIR spectra were measured using a Bruker Tensor spectrometer equipped with a standard glow bar source and DTGS detector. The spectrometer and sample cavity were purged with air (<1 ppm water and CO₂). All spectra are referenced to a common background taken immediately before the sample measurements.

NMR spectroscopy of solid state UMON samples: Experiments were conducted on a Bruker AV III instrument (Bruker Biospin, Billerica, MA) operating at a proton frequency of 500.01 MHz using a 4mm

MAS BB/1H Bruker probe head. Measurements were performed without spinning (static) in a 4 mm ZrO₂ rotor. Samples (50 mg) and standards were confined to a Teflon insert placed inside the rotor to provide additional isolation of the sample. Relaxation delay was maintained at 0.1 seconds for the ²D experiments. The spectral sweep width was 200 ppm centered at 4 ppm. 1024 data points were acquired, zero filled to 16,384 prior to apodization with 100 Hz line broadening and typically 60,000 free induction decays were coadded. Pulse width was 3.75 μsec resulting in an effective bandwidth of 66 KHz. Various relaxation delays and a solid echo did not significantly improve the spectral quality. For the H-1 measurement, the relaxation delay was maintained at 20 seconds, spectral sweep width was 200 ppm centered at 4 ppm, 4096 data points were acquired, and zero filled to 16,384 prior to apodization with 100 Hz line broadening. Typically, 32 free induction decays were coadded. Pulse width was 4 μsec resulting in an effective bandwidth of 62.5 KHz. Spectra were referenced indirectly to TMS using the ¹H or ²D resonance of water at 4.8 ppm. ²D spectra were deconvoluted using the Sola program within Topspin 3.2. For plotting, the fit data was simulated using QUEST (V1.1.7, F. A. Perras, University of Ottawa and Ames Laboratory).

Tritiated water uptake: CAUTION: This methodology requires the use of radioactive ³T, which is an β emitter, and like all radioactive materials must be handled with care. These experiments were conducted by trained personnel in a licensed research facility with special precautions taken toward the handling, monitoring, and disposal of radioactive materials.

Tritiated water was obtained from Perkin Elmer NET001B001MC, Lot: 2396166 (predicted specific activity: 1 mCi/ml; measured specific activity 4 mCi/ml). All tritiated samples were analyzed by a Packard 2900 TR Series Liquid Scintillation Counter (with a PerkinElmer Ultima Gold cocktail). The experimental design was tested with H₂O to confirm the uptake methodology.

Freshly prepared crystals were placed in glass vial in a gravimetric oven set at 120° for 30 min to dehydrate. Four experimental and three control replicates of these crystals (~5-15mg) were placed into a cut Eppendorf tube (~0.4 ml) (Fig. S3) and then a second 0.6-mL Eppendorf tube for transport. The tubes were closed and sealed with parafilm before removal from the oven. As-synthesized (fully hydrated) nanotubes were used as the control.

Tritiated water (50 μl) was placed into four 2.0 mL tubes and the 0.4 mL Eppendorf containing the dehydrated UMON crystals was added. The 2.0 mL tubes were sealed and then placed on an orbital shaker for hydration. After 40 minutes, the 0.4 mL Eppendorf tube was removed, and 100 μL of pure deionized/distilled H₂O was added directly to the crystals. The tube was gently shaken to ensure mixing and a 5-μL aliquot of solution was transferred to a 20 mL scintillation vial containing 15 mL of PerkinElmer Ultima Gold scintillation cocktail. The process was repeated every four minutes for a total of 70 minutes. Finally, 150 μL of 1M HCl was added to dissolve the UMON material and a five μl aliquot was analyzed by LSC to measure total ³T.

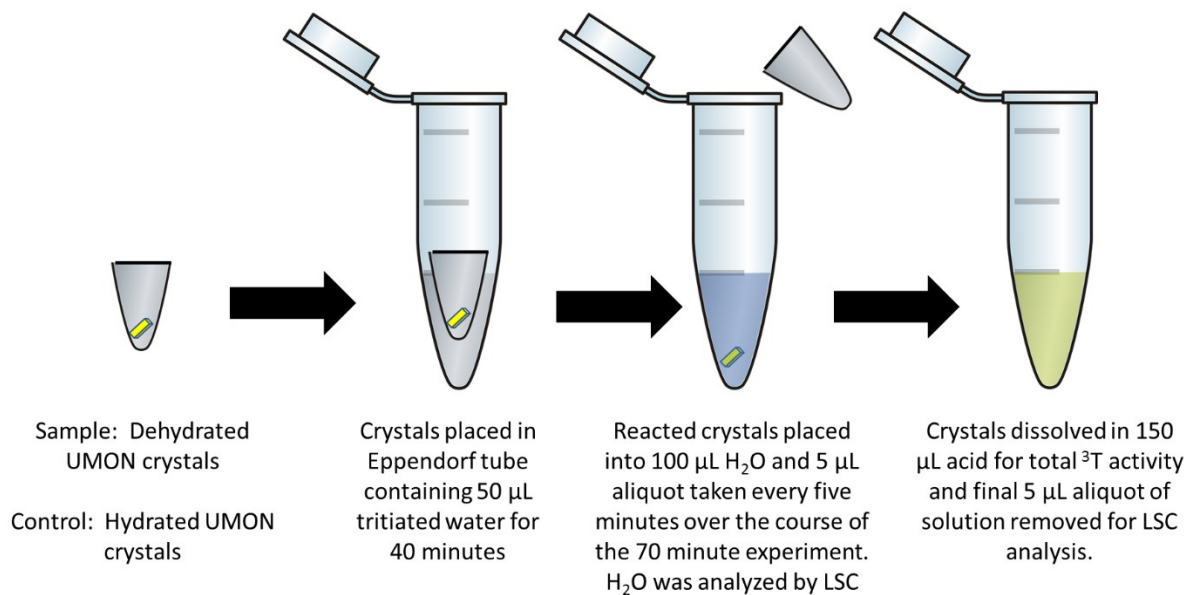


Fig. S3. Illustration depicting tritiated water adsorption methodology. UMON crystals were placed into a 0.4 mL Eppendorf tube and then placed into a larger vial containing tritiated water (1 mCi/mL). After exposure for 40 minutes, the reacted crystals were placed into Millipure H₂O and aliquots were taken every 4 minutes for a 72 minute experiment. Total ³T in the sample was then analyzed by dissolving the crystals in acid and then measuring the activity by Liquid Scintillation Counting (LSC).

2. Structural Details of UMON material

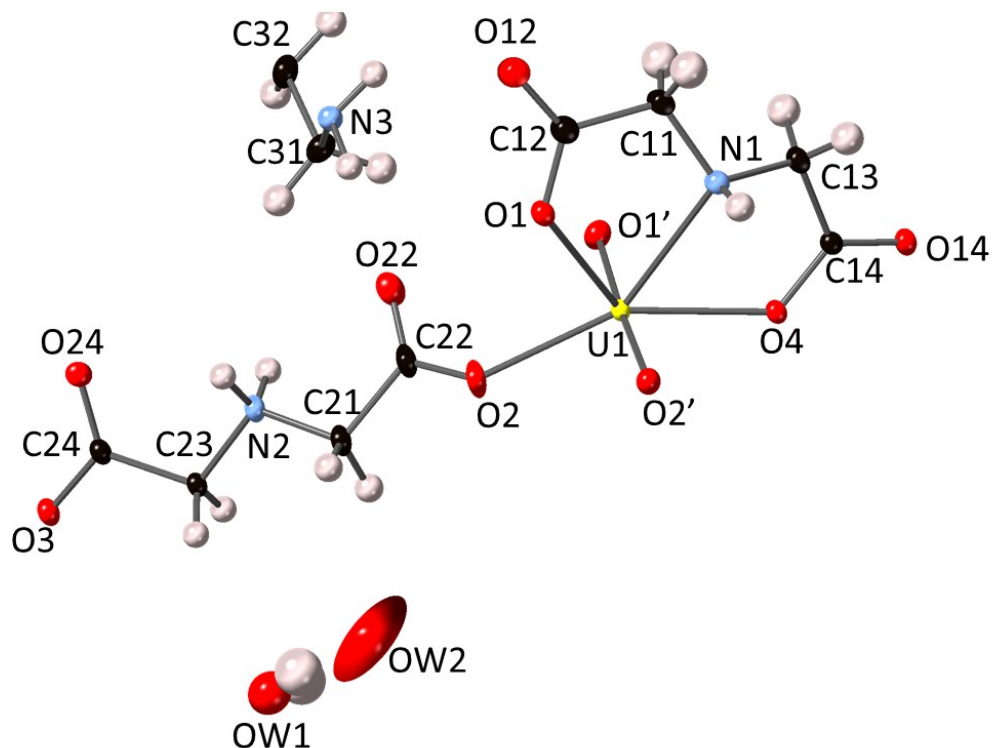


Fig. S4. The asymmetric unit of the UMON material depicted using thermal ellipsoids (50%) based upon structure determination using single-crystal X-ray diffraction.

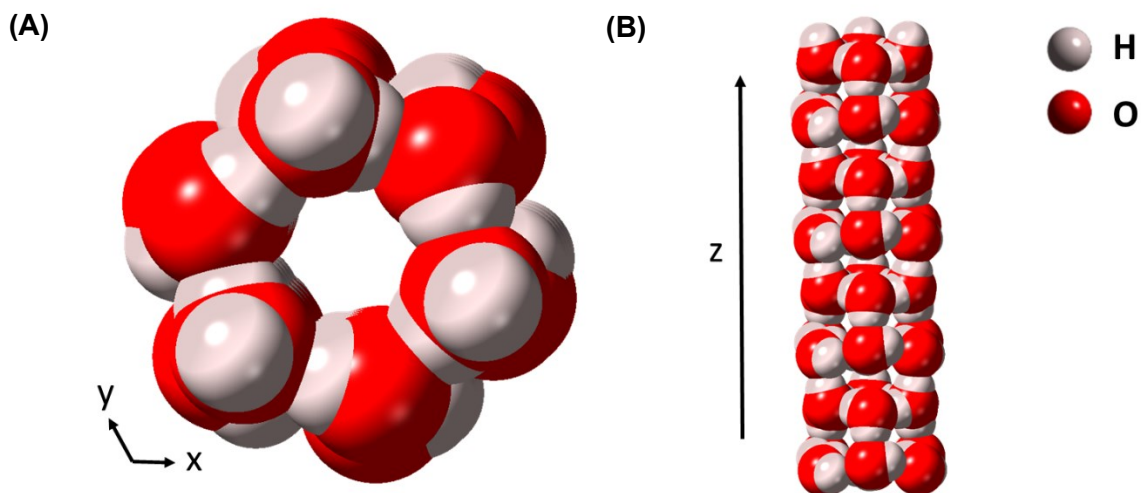


Fig. S5. (a) Image of water packing viewed down the UMON channel obtained from single crystal X-ray diffraction indicates a hexameric arrangement of water molecules. (b) The extended view of the ice-like arrangement of the water molecules within the UMON channels shows an extended network of H-bonding.

3. X-ray Powder Diffraction of UMON material.

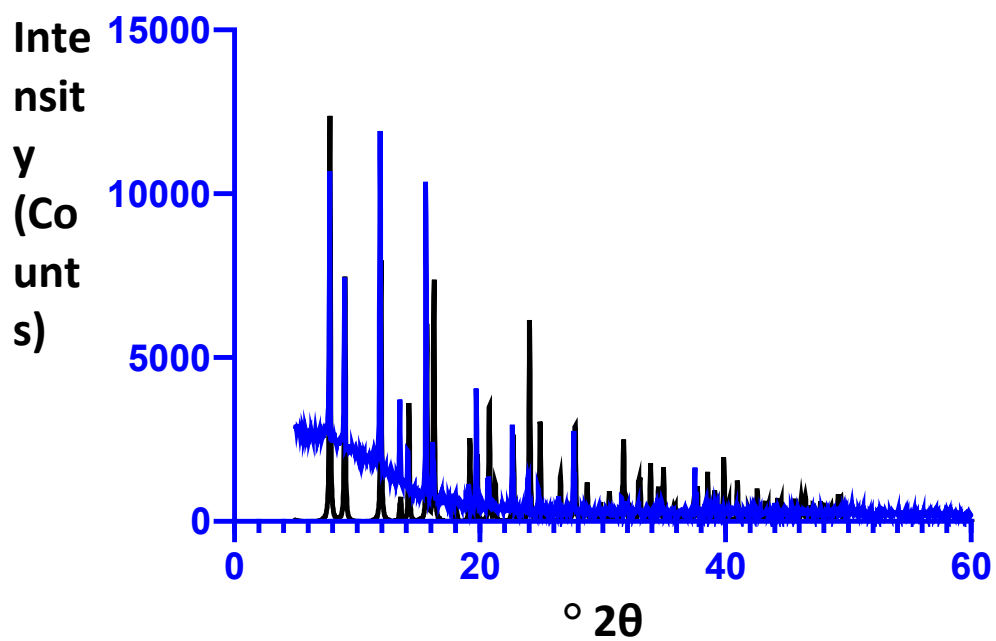


Fig. S6. Representative powder diffraction pattern of UMON showing purity before uptake experiments.

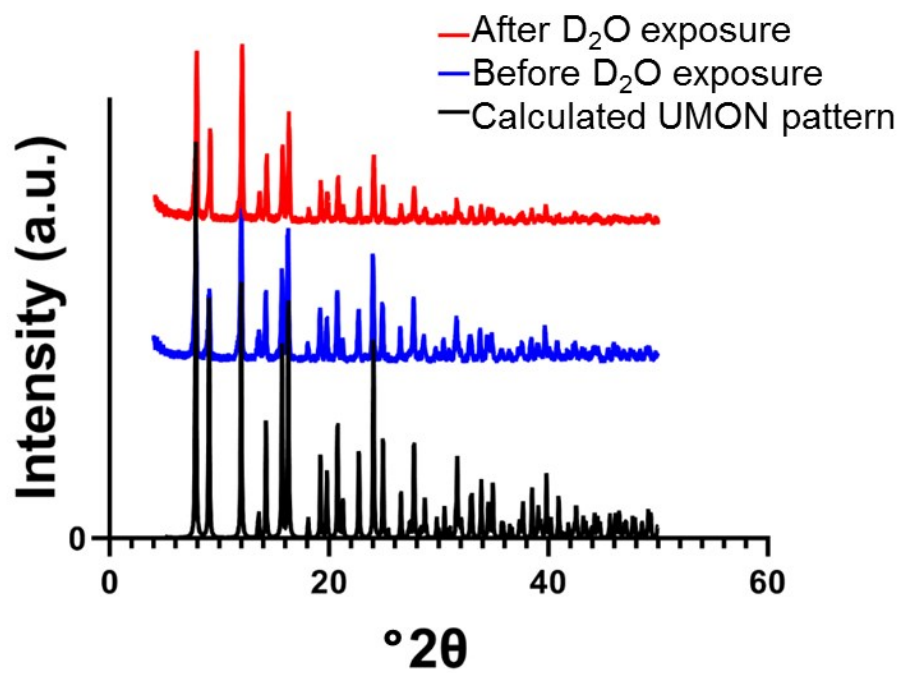


Fig. S7. Representative powder diffraction pattern of UMON after vapor sorption experiment, indicating that the material maintained its crystallinity and purity.

4. TGA with FTIR of evolved gases

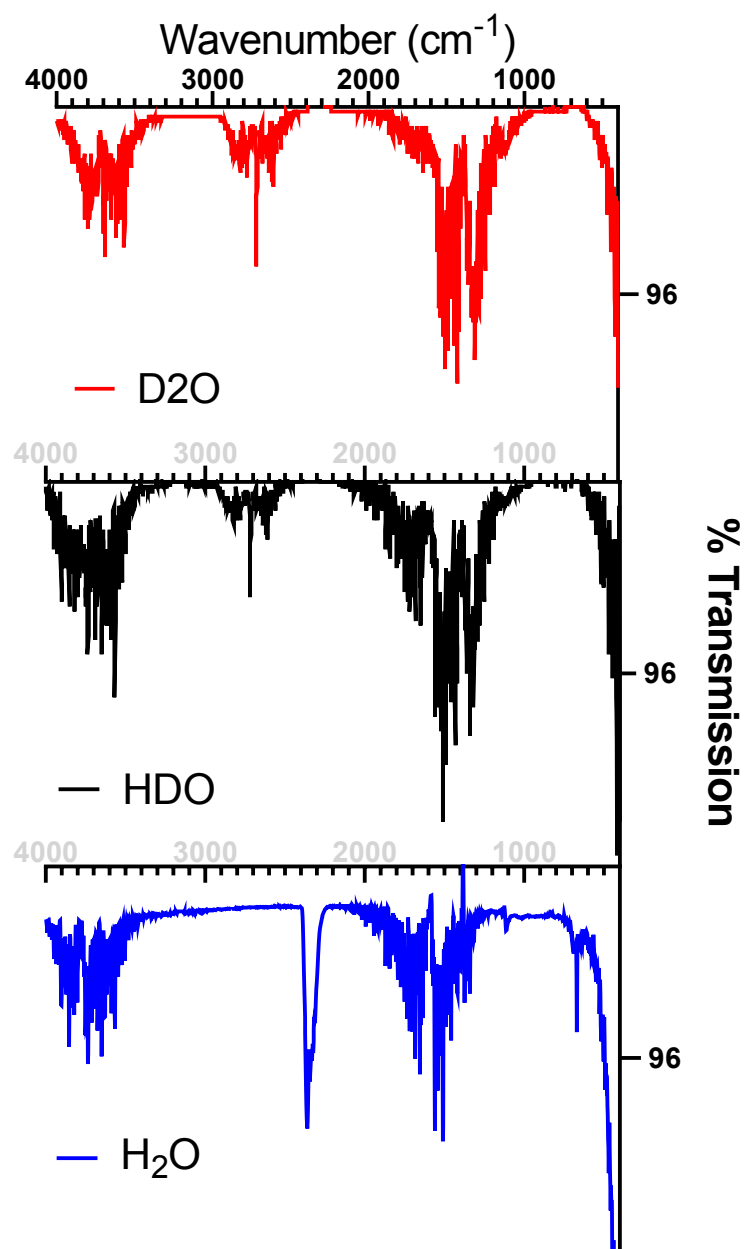


Fig. S8. FTIR spectra of H_2O , HDO, and D_2O standards used in this study. Spectral band located at 2350 cm^{-1} corresponds to imperfect background subtraction of carbon dioxide in the evolved gas.

4.1 Flow-through (Vapor sorption) experiments

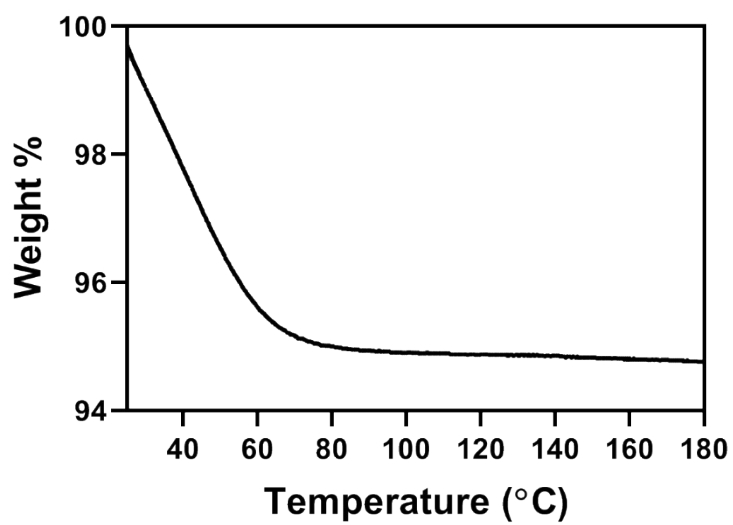


Fig. S9. Thermogravimetric analysis of the UMON material after exposure to H₂O in the flow-through experiments.

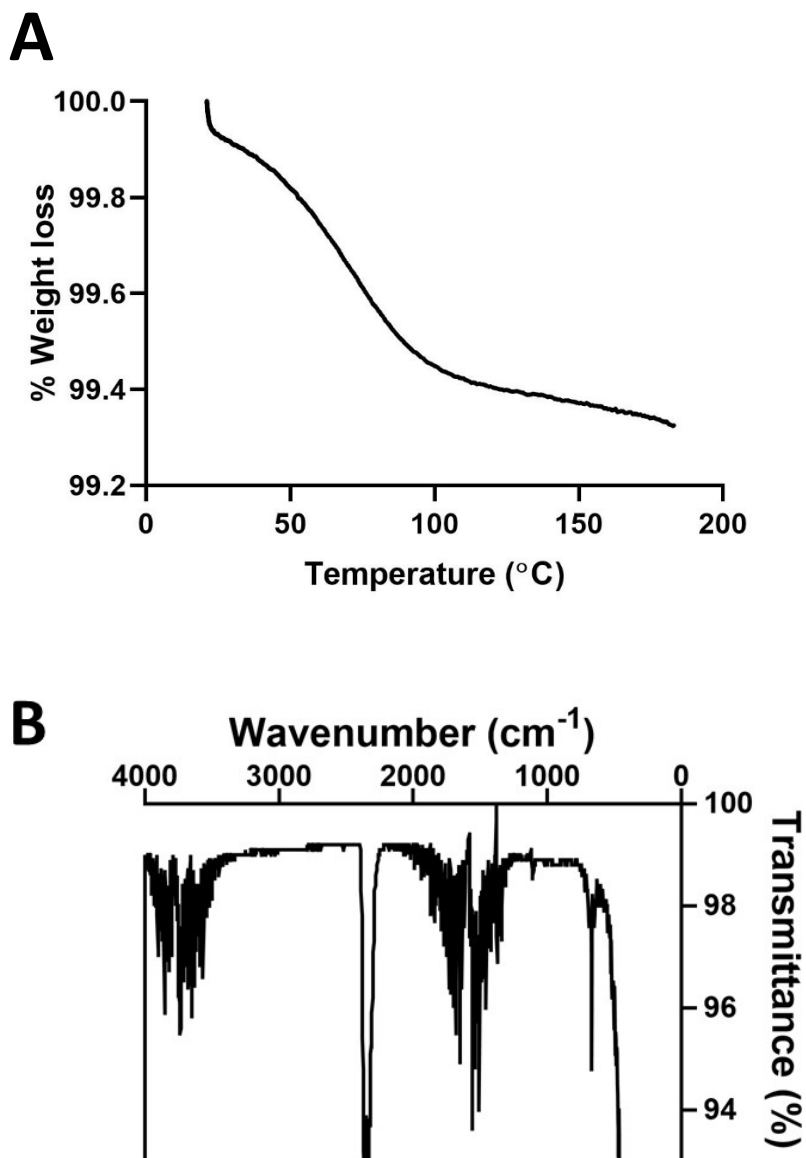


Fig. S10. (a) TGA of UMON sample exposed to D₂O in the vapor sorption apparatus (flow-through experiments). (b) FTIR of the evolved gases released during heating on the TGA of the UMON sample exposed to D₂O in the vapor sorption apparatus (flow-through experiments). Vibrational bands in the FTIR spectra indicate that the evolved gases are H₂O. Spectral band located at 2350 cm⁻¹ corresponds to residual carbon dioxide (from loading the sample) in the evolved gas.

4.2 Batch uptake experiments

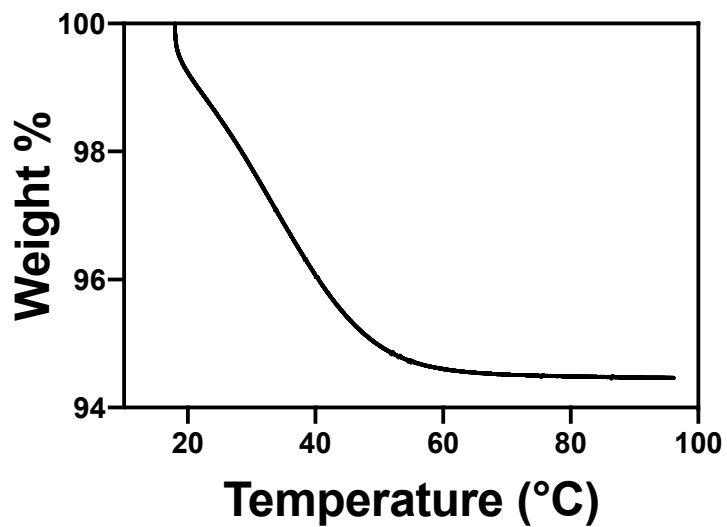


Fig. S11. Representative TGA analysis of an as-synthesized UMON sample (batch experiment) with weight loss corresponding to H₂O.

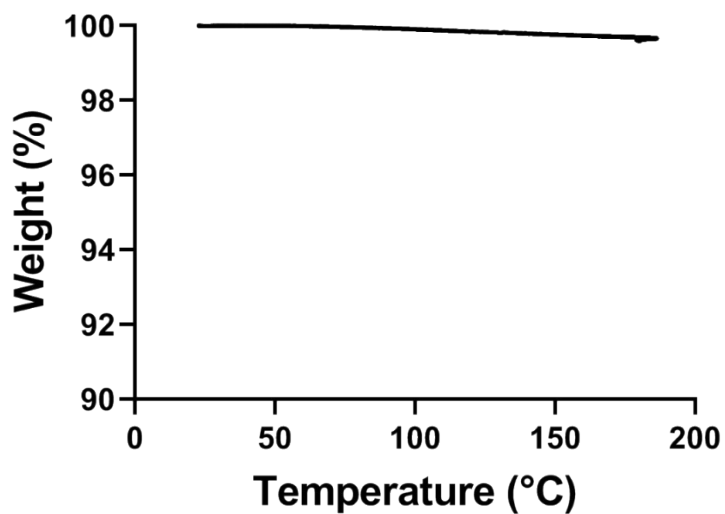


Fig. S12. Representative TGA analysis of a dehydrated UMON control sample (batch experiment) that was placed in the glove bag for 18 hours.

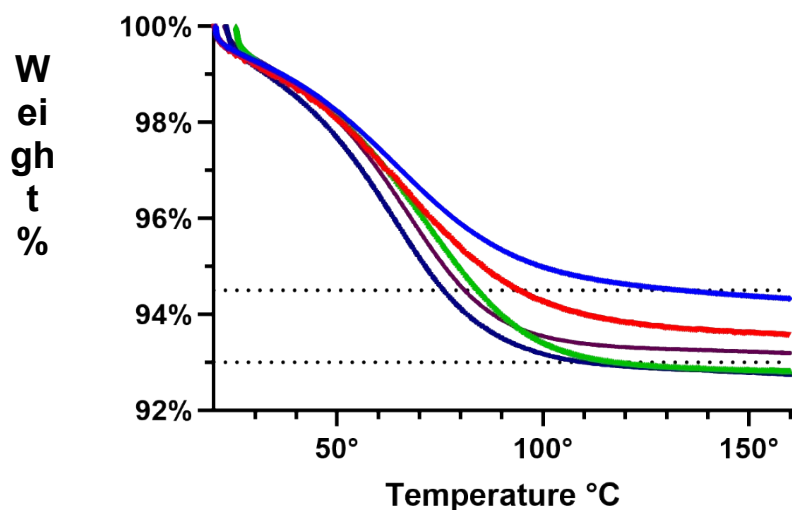


Fig. S13. Collated replicate TGA data for dehydrated UMON samples exposed to D₂O vapor for 18 hours in batch experiments.

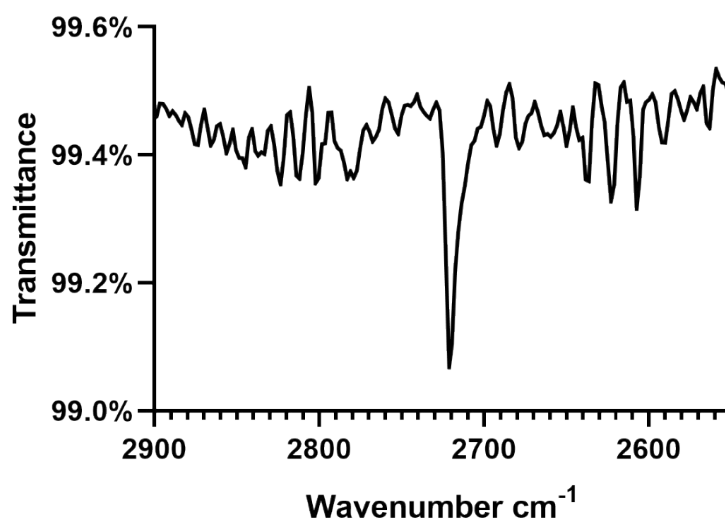


Fig. S14. FTIR spectrum of evolved gases released from UMON exposed to D₂O vapor for 18 hours in batch experiments. The window of interest is associated with the ν_1 O-D stretch located at 2723 cm⁻¹ which was collected at 120 °C.

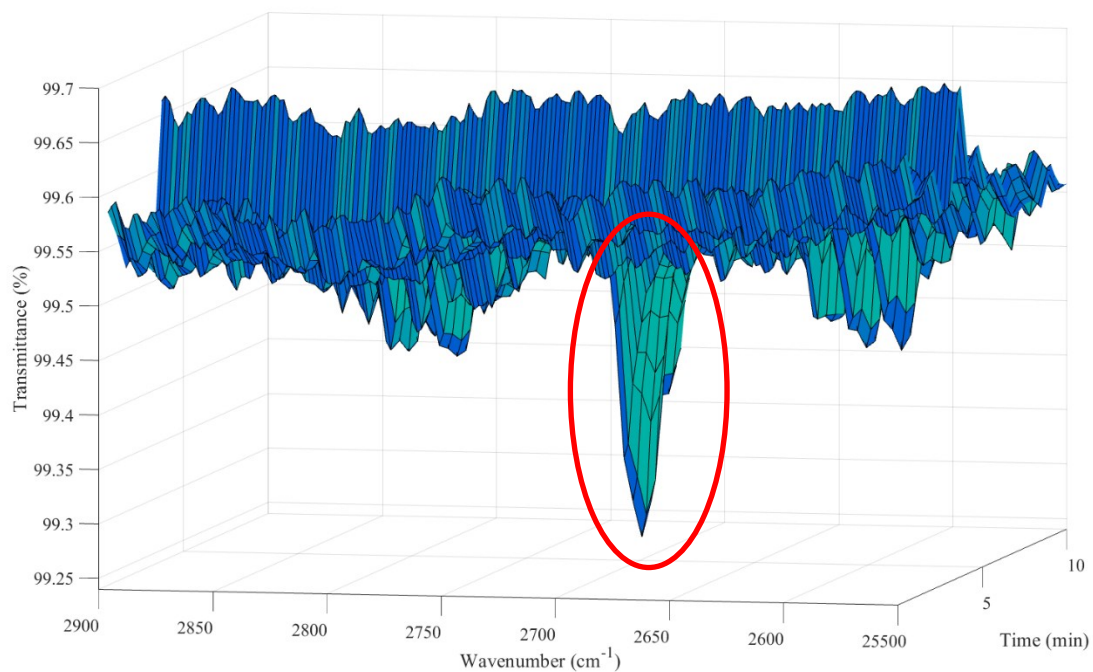


Fig. S15. FTIR spectrum of evolved gases released from UMON exposed to D₂O vapor in batch experiments collected over time. The window of interest is again associated with the ν_1 O-D stretch located at 2723 cm⁻¹. The peak begins to grow in after 5 minutes (80 °C) of heating.

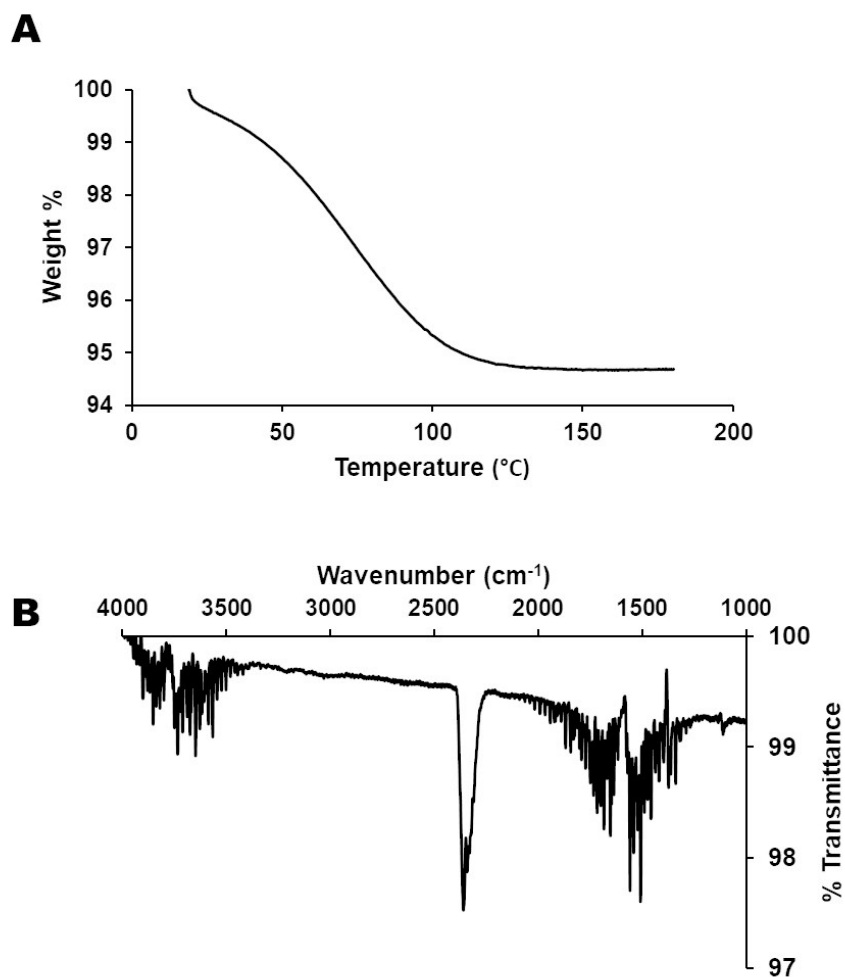


Fig. S16. Uptake of 50/50 wt% D₂O/H₂O solution using the batch uptake methodology resulted in (a) 5.5% weight loss in the TGA that corresponds to full uptake within the channels. (b) FTIR spectrum of evolved gases released from UMON during the TGA analysis of the UMON material exposed to the 50/50 wt% D₂O/H₂O solution indicate the presence of H₂O with no bands associated with D₂O present in the spectrum. Spectral band located at 2350 cm⁻¹ corresponds to residual carbon dioxide in the evolved gas.

4.3. Extended Flow-through experiments to support batch experiments

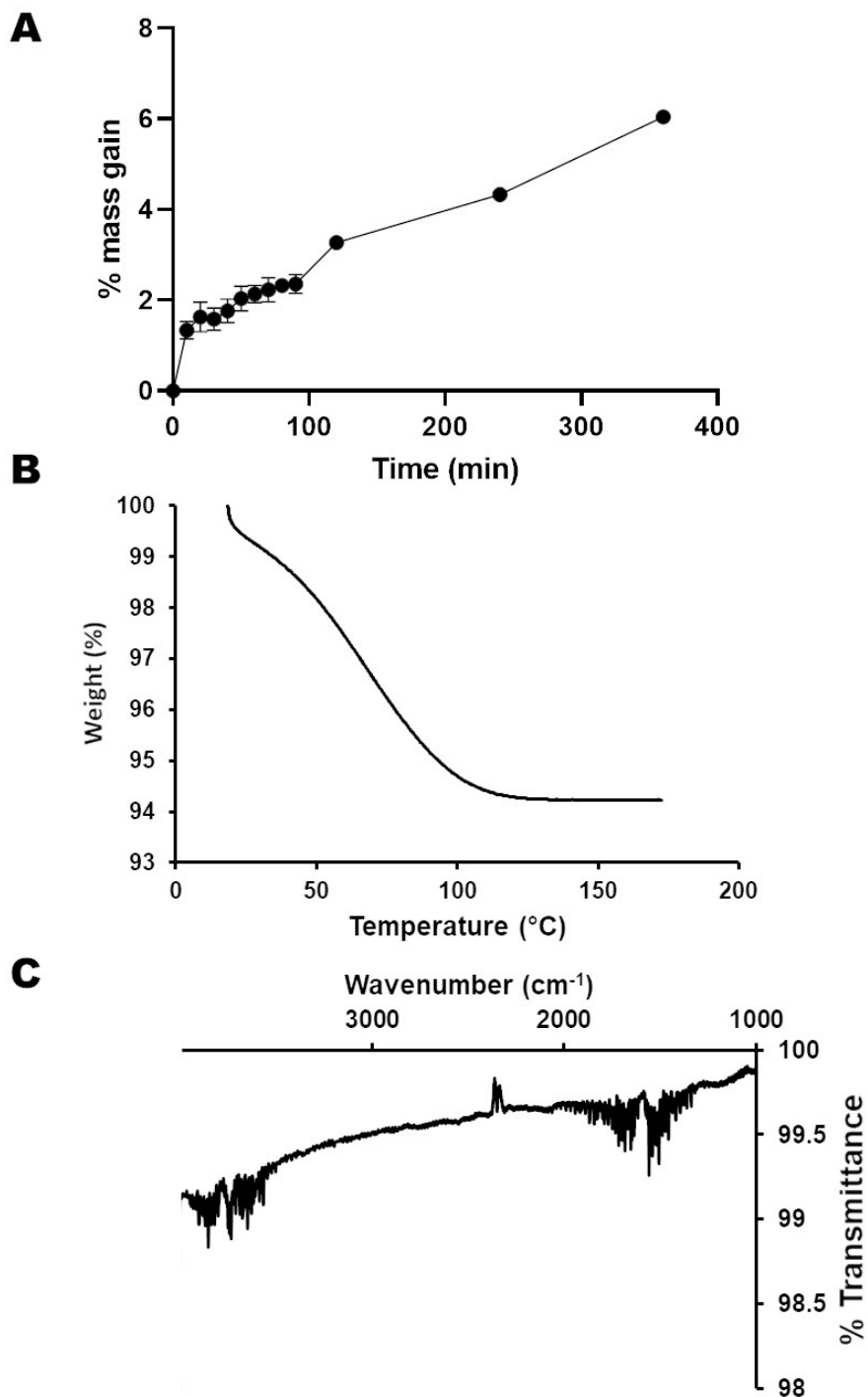


Fig. S17. (a) Extended analysis of D₂O uptake using the vapor sorption apparatus (flow-through experiments). Full uptake (6%) was achieved after 6 hours of exposure (b) TGA of the extended analysis of the D₂O uptake using the vapor sorption apparatus. A weight loss of 5.8% was achieved by 100 °C, which corresponds to the presence of H₂O in the nanotubes. (c) The FTIR of the evolved gases released during heating on the TGA of the UMON sample exposed to D₂O in the vapor sorption apparatus (extended flow-through experiments). Vibrational bands in the FTIR spectra indicate that the evolved gases are H₂O. There is no evidence of D₂O bands within the FTIR spectra, supporting the results of the batch experiments.

5. Solid-state FTIR analysis of UMON material

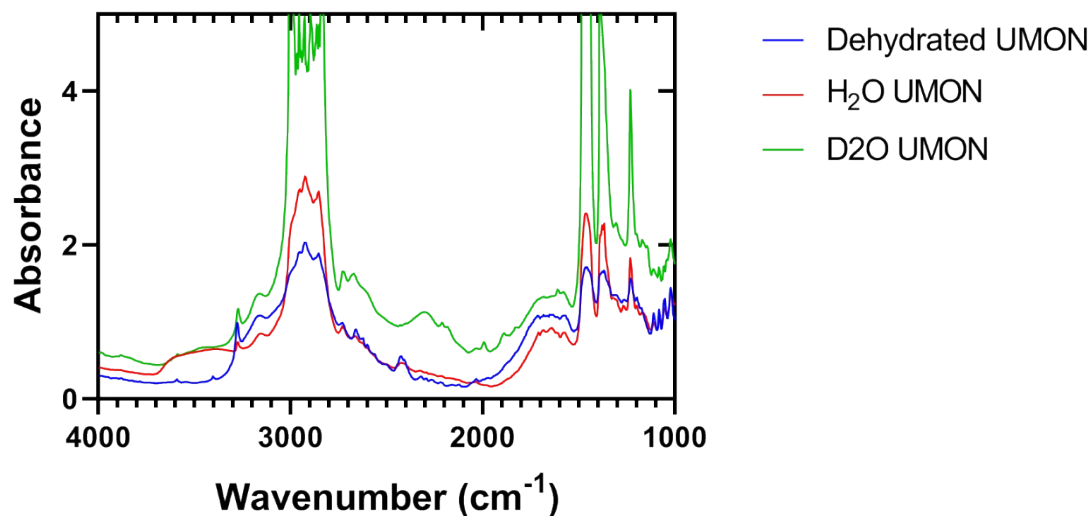


Fig. S18. Full FTIR spectrum of the solid UMON samples in immersion oil.

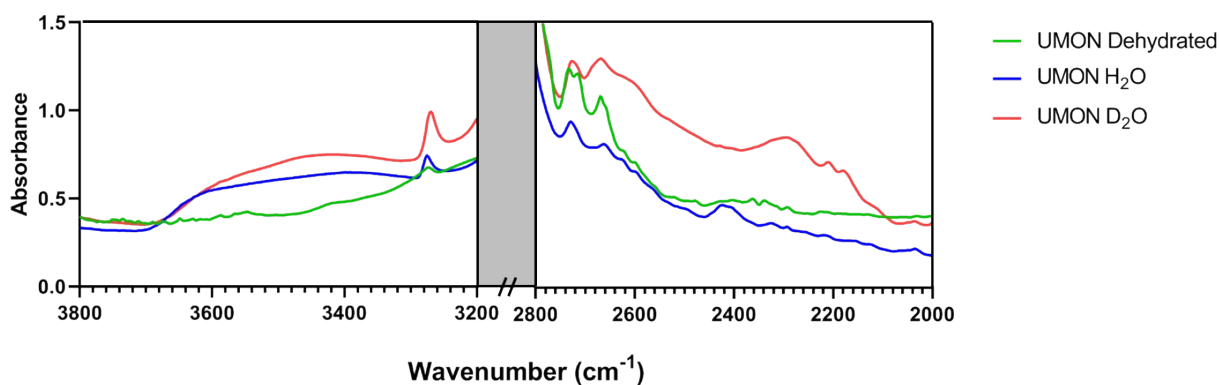


Fig. S19. Condensed phase FTIR of UMON exposed to either H₂O or D₂O vapor contains broad bands between 3400 and 4000 cm⁻¹ that are indicative of light water. An additional peak at 2280 cm⁻¹ is suggestive of ²D exchange with amine groups.

6. Solid-state NMR of UMON material

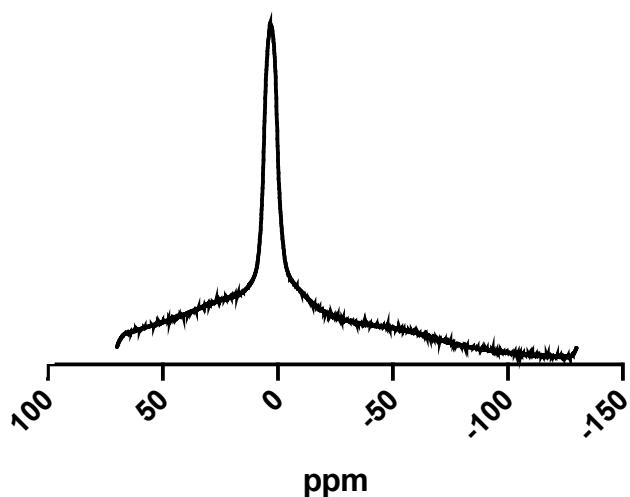


Fig. S20. The solid state ^1H NMR spectra for the hydrated UMON displays a large single peak near 5 ppm corresponding to H_2O in the channels.

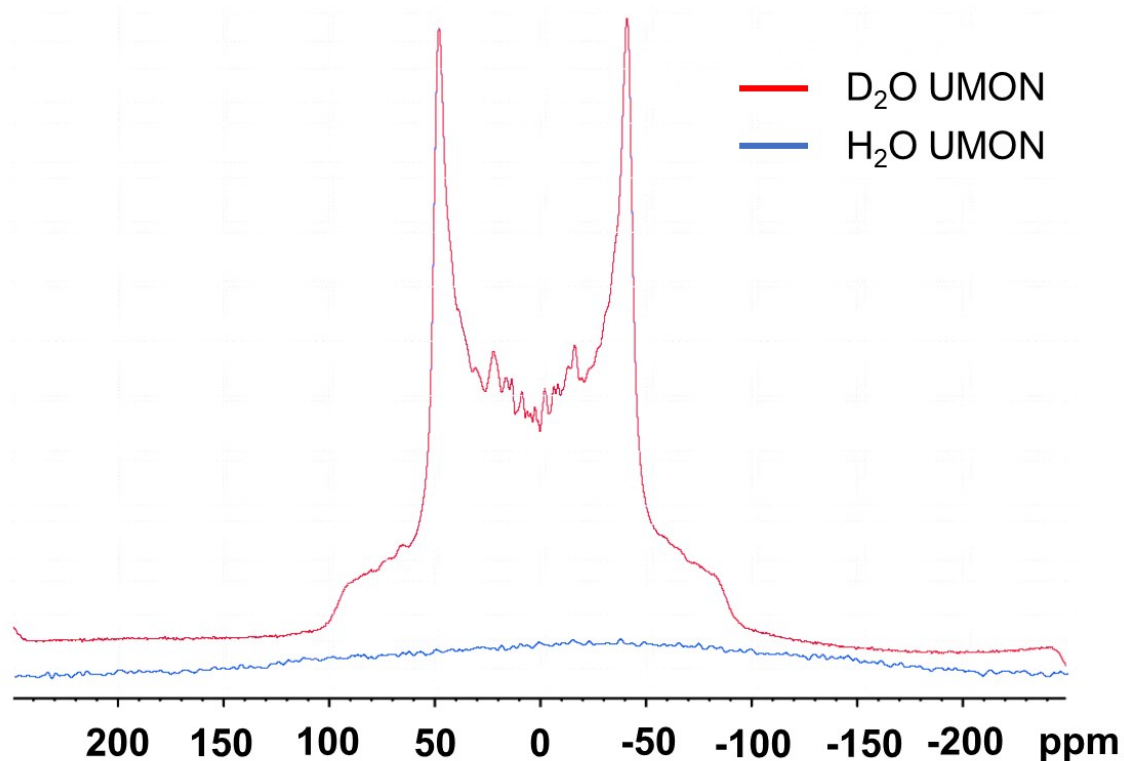


Fig. S21. No signal is observed for the solid-state ^2D -NMR of the UMON material exposed to H_2O , but peaks are present when exposed to D_2O . The shape of the band indicates that the ^2D is in a different chemical environment than just the DHO or D_2O molecule.

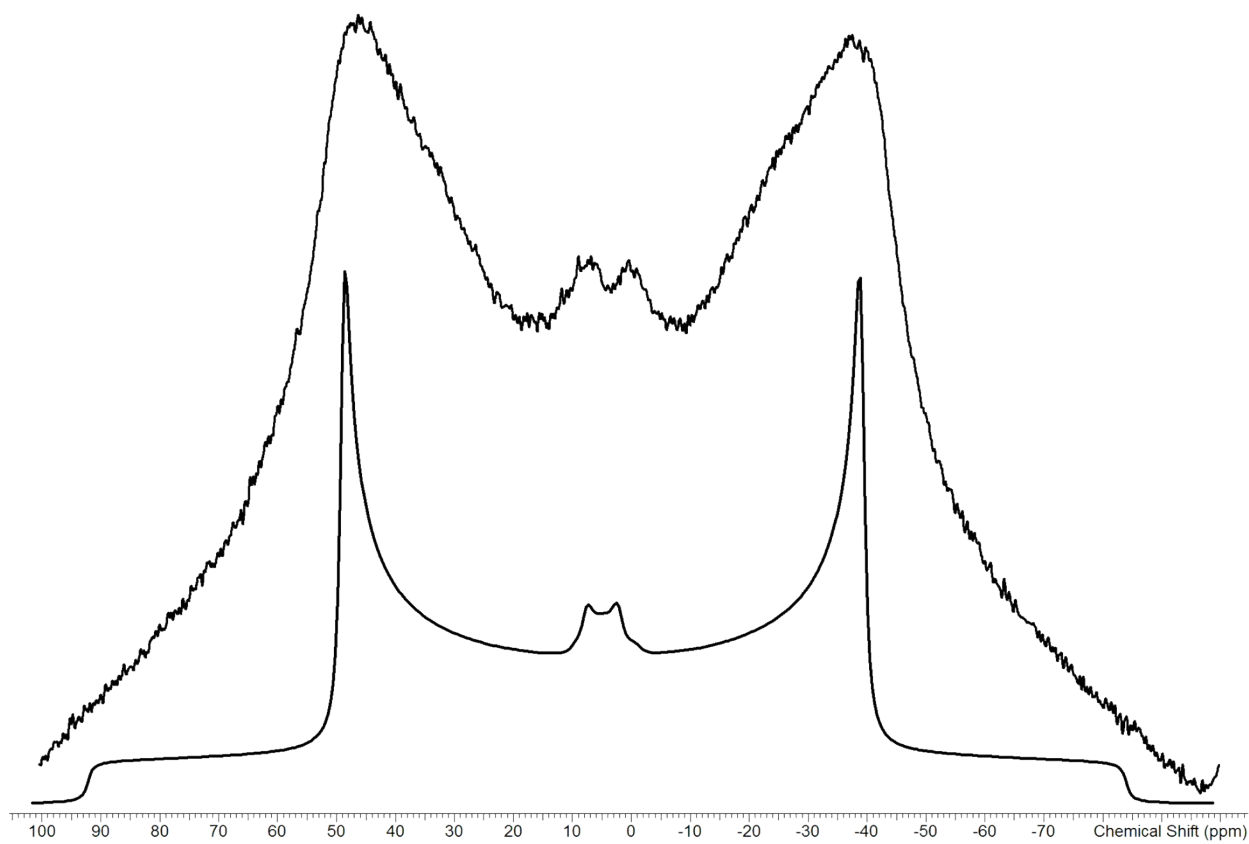


Fig. S22. The solid state ^2D NMR spectra for the UMON material exposed to D_2O vapor for 18 hours (top) and modeled fit of the data (bottom).

7. Proposed mechanism for batch uptake experiments

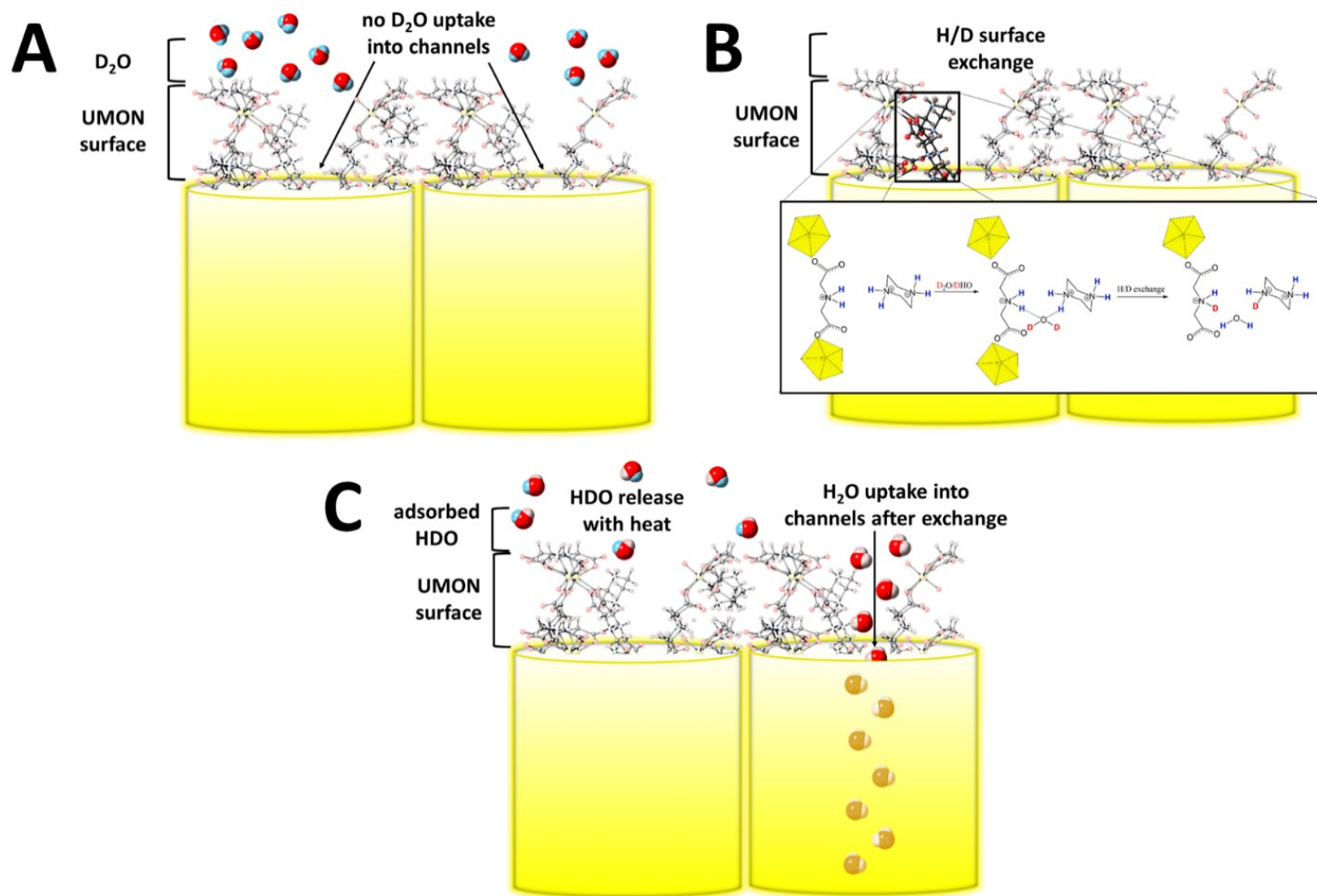


Figure S23. A summary of the proposed adsorption process (steps 1 and 2 of the overall selectivity) when UMON is exposed to D_2O . (A) D_2O adsorbs to the surface of the UMON sample but does not enter the channel. (B) Proton exchange can occur between the amine groups and the D_2O molecule. (C) After exchange, the H_2O molecule can enter the channel and adsorbed HDO remains on the surface.

8.Details on ^3T results and activity calculations

The LSC was calibrated using ^{14}C and ^3T standards and the established protocols. Raw data collected from the LSC was converted from counts per minute (CPM) to disintegrations per minute (DPM) by considering counting efficiency. Converting from DPM to disintegrations per second (DPS) led to activity in units of Becquerel (1 DPS = 1Bq). We then corrected for the sample volume loss (we removed 5 mL of solution for each time point and the final point is corrected for the addition of 150 mL of HCl). The activity was then converted to number of ^3T atoms in the sample using the decay constant for ^3T ($\lambda = 1.783 \times 10^{-9} \text{ sec}^{-1}$) with $A = \lambda N$. The specific activity of the tritiated water ($4.2 \text{ mCi/mL} = 1.554 \times 10^{-8} \text{ Bq/mL}$) was used to calculate the volume of water. Using the density and molecular weight of water allows us to calculate nanomoles of tritiated water that are adsorbed in the UMON sample. This value can then be normalized to the mass of the sample. The separation factor was estimated by considering the ^3T concentration in the water vapor (from the specific activity) divided by the ^3T concentration observed with the sample (^3T activity of the sample in Bq divided by volume of water in the sample).

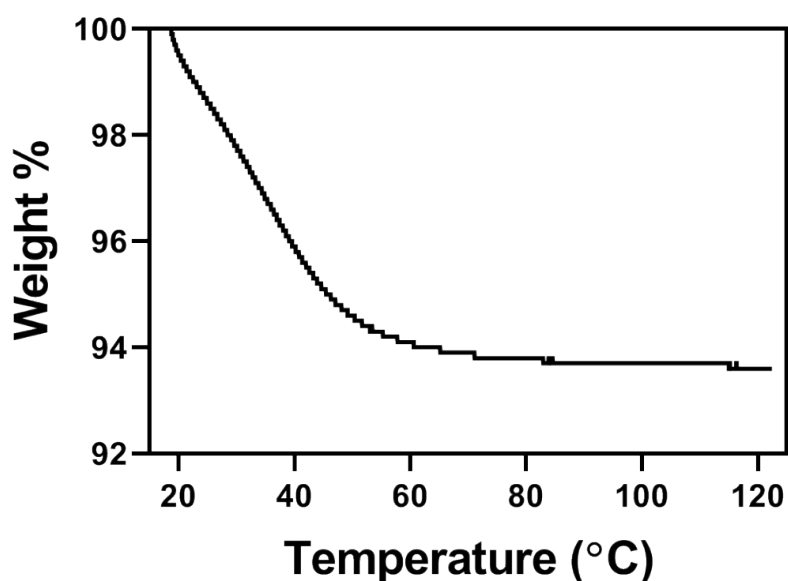


Fig. S24. Test of the UMON tritiated water adsorption methodology using pure H_2O . TGA and FTIR analysis indicate complete hydration (5.8%) after 40 minutes of exposure to H_2O in the Eppendorf vial.

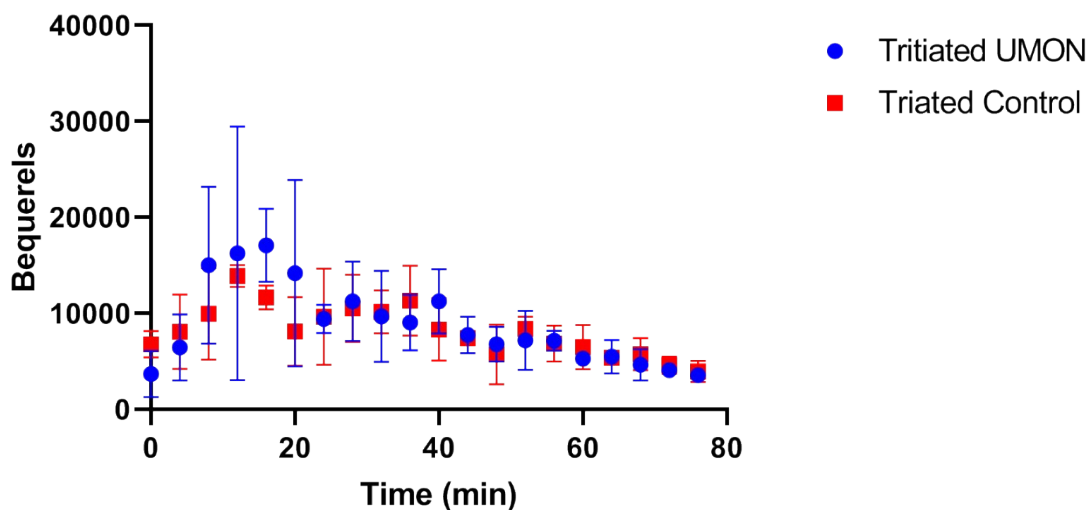


Fig. S25. Total Bq of ^3T for the tritiated UMON and control samples over the 72 minute sampling period. The sample consisted of a dehydrated UMON crystals and the control was hydrated UMON crystals. The last data point represents the addition of acid to the system to completely dissolve the UMON material and accounts for total activity in the sample.

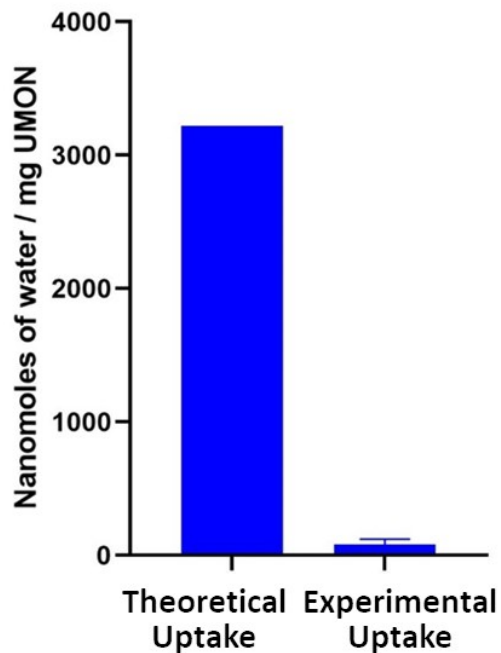


Figure S26. ^3T uptake experiments were converted from activity to total moles of water using the specific activity of the tritiated water. Expected amount of water (Theoretical Uptake) calculated from TGA analysis for UMON is 3222 nanomoles water/mg UMON. Dehydrated UMON (Experimental uptake) adsorbed 80 ± 40 nanomoles of water/mg, which suggests that the HTO is much more likely surface adsorbed water (2.8%).

Table S1. Raw counts (CPM), quenching statistics (SIS/tSIE), and activity (DPM) of the tritiated samples collected by Liquid Scintillation Counting. This data has not be corrected for dilution factors.

Sample	Sampling time point (min)	CPM	SIS	tSIE	DPM	
Dehydrated UMON 1 (mass of sample = 5.03 mg)	0	2062	14.16	658.74	4443	
	4	6622	14.05	665.99	14187	
	8	8195	13.9	667.66	17544	
	12	6520	14.13	679.87	13815	
	16	23183	13.86	662.74	49819	
	20	9774	13.99	671.33	20856	
	24	9769	14	675.33	20778	
	28	15059	14.04	674.94	32036	
	32	10808	13.86	665.18	23188	
	36	11309	13.98	673.67	24086	
	40	16078	13.75	661.57	34603	
	44	10519	13.76	665.58	22565	
	48	7069	13.89	663.28	15184	
	52	6431	14.06	677.58	13656	
	56	11635	13.86	667.76	24910	
	Dissolved UMON 1	60	10475	14.05	669.43	22383
64		6459	13.97	667.34	13830	
68		6534	14.06	668.79	13968	
72		10171	14.16	667.44	21766	
76		2099	15.68	661.77	4502	
Dehydrated UMON 2 (mass of sample = 6.44 mg)		0	2116	14.32	657.88	4559
		4	1467	14.49	668.36	3133
		8	9725	13.94	668.48	20793
		12	33974	13.79	661.86	73080
		16	20153	13.77	659.11	43442
	20	32280	13.91	671.71	68884	
	24	9358	14.06	676.59	19884	
	28	10258	13.8	663.83	22028	
	32	4518	14	663.75	9700	
	36	12819	13.96	659.27	27616	
	40	14840	13.86	662.65	31907	
	44	8287	13.85	659.29	17866	
	48	9648	14.03	666.96	20658	
	52	10155	13.95	663.64	21807	
	56	10538	14.09	664.48	22604	
	60	9078	14.06	669.68	19397	

	64	10336	14.04	662.8	22211
	68	8519	14.01	666.96	18237
	72	8361	14.04	660.43	17995
Dissolved UMON 2	76	2156	15.78	668.64	4600
Dehydrated UMON 3 (mass of sample = 11.85 mg)	0	2829	14.3	673.55	6019
	4	8945	13.85	662.63	19224
	8	26490	13.95	679.31	56189
	12	21606	13.85	668.38	46220
	16	14533	13.81	664.68	31192
	20	10966	13.9	669.29	23442
	24	12292	13.97	670.38	26247
	28	20405	13.99	672.14	43516
	32	18205	13.88	671.81	38846
	36	16842	13.92	674.06	35872
	40	21539	13.89	659.93	46389
	44	15039	13.82	662.27	32345
	48	13402	13.91	663.79	28774
	52	18446	13.98	664.28	39590
	56	14766	13.95	673.65	31470
	60	8559	14.03	674.64	18208
	64	14596	14.11	666.57	31268
	68	10177	14.15	676.14	21627
	72	10807	13.94	662.32	23224
Dissolved UMON 3	76	2850	16.22	660.15	6116
Dehydrated UMON 4 (mass of sample = 7.97 mg)	0	6698	13.86	657.86	14452
	4	7854	13.97	662.67	16869
	8	15860	13.78	664.08	34051
	12	5206	13.92	661.72	11200
	16	15469	13.9	667.26	33123
	20	10669	13.95	665.6	22874
	24	12631	13.81	664.41	27109
	28	9259	13.97	662.72	19891
	32	15844	13.88	672.42	33803
	36	7319	13.91	664.22	15709
	40	10204	13.92	661.61	21934
	44	11614	13.85	660.52	25003
	48	12099	13.9	663.21	25994
	52	12293	13.91	663.17	26409
	56	13057	13.76	660.87	28113
	60	11515	13.9	661.12	24781

	64	12398	13.88	661.93	26658
	68	14890	14.05	670.2	31803
	72	8803	13.95	672.1	18775
Dissolved UMON 4	76	2579	15.52	665.45	5518
Control 1	0	5392	14.08	664.3	11565
(mass of sample = 12.26 mg)	4	11032	13.98	661.34	23729
	8	13223	13.98	676.82	28106
	12	14955	13.91	663.54	32115
	16	11160	13.91	674.06	23779
	20	9352	14.07	665.44	20049
	24	4793	14.23	674.21	10199
	28	7897	14.05	667.58	16897
	32	14877	13.98	664.85	31917
	36	9548	13.82	658.33	20590
	40	16179	13.92	663.62	34741
	44	11850	13.98	673.46	25249
	48	12820	13.94	666.21	27478
	52	12838	13.92	665.22	27537
	56	15679	14.07	665.31	33620
	60	17062	14.04	667.02	36535
	64	12177	13.99	666.97	26071
	68	16457	14.02	662.64	35363
	72	13160	14.01	663.36	28265
Dissolved Control 1	76	3532	16.03	658.54	7597
Control 2	0	7789	13.98	660.06	16768
(mass of sample = 9.14 mg)	4	8639	14.06	662.81	18557
	8	4485	14.2	676.53	9525
	12	13091	14	670.41	27953
	16	13647	13.82	661.3	29370
	20	12904	13.85	662.85	27731
	24	12937	13.87	663.98	27783
	28	15166	13.86	656.47	32761
	32	14196	13.93	666.03	30429
	36	16726	13.93	658.44	36067
	40	11610	13.88	658.92	25027
	44	9602	14.01	664.54	20605
	48	10331	14.04	664.33	22159
	52	16372	14.18	673	34875
	56	10747	14.17	661.9	23089
	60	10300	14.31	663.17	22111

	64	9307	14.18	658.28	20056
	68	9932	14.32	666.25	21270
	72	9112	14.01	664.58	19561
Dissolved Control 2	76	2471	16.55	663.41	5289
Control 3	0	5825	14.18	668.61	12451
(mass of sample = 6.94 mg)	4	3724	14.18	664.29	7988
	8	12183	13.81	659.57	26249
	12	15211	13.99	669.96	32493
	16	12812	13.95	662.59	27530
	20	4925	14.25	666.42	10543
	24	16051	13.95	664.6	34437
	28	15249	13.92	667.31	32643
	32	9595	13.92	662.5	20625
	36	18750	13.86	659.13	40414
	40	7106	14.1	666.03	15224
	44	11457	13.97	665.15	24567
	48	3422	14.1	659.27	7368
	52	12396	14.07	669.2	26493
	56	9470	14.09	660.77	20369
	60	8994	14.21	665.38	19269
	64	10779	14.15	661.16	23186
	68	10710	14.23	663.17	23002
	72	10016	14.27	656.45	21622
Dissolved Control 3	76	2109	16.44	673.87	4476
1 uL dilute tritiated water (1:100)		43982	13.79	667.89	94142
Blank 1 (H ₂ O)		19	45.14	659.79	38
Blank 2 (H ₂ O)		74	30.2	667.78	153

CPM = Counts per minute (spectral window 1); DPM = Disintegrations per minute; SIS = Spectral index of the sample; tSIE = transformed Spectral Index

Table S2. Activity of tritiated UMON and control samples in Becquerel with activities corrected for total dilution factors (total aliquot volume or acid added for total dissolution of the solid material).

Sampling time point (min)	Dehydrated UMON Samples (Bq)						Control samples activity (Bq)				
	1	2	3	4	average	stdev	1	2	3	Average	stdev
0	2222	2280	3010	7226	3684	2388	5783	8384	6226	6797	1392
4	6857	1514	9292	8153	6454	3440	11469	8969	3861	8100	3878
8	8187	9703	26222	15890	15001	8189	13116	4445	12250	9937	4776
12	6217	32886	20799	5040	16235	13213	14452	12579	14622	13884	1134
16	21588	18825	13517	14353	17071	3808	10304	12727	11930	11654	1235
20	8690	28702	9768	9531	14173	9697	8354	11555	4393	8100	3588
24	8311	7954	10499	10844	9402	1480	4080	11113	13775	9656	5009
28	12280	8444	16681	7625	11258	4146	6477	12558	12513	10516	3498
32	8502	3557	14244	12394	9674	4728	11703	11157	7563	10141	2250
36	8430	9666	12555	5498	9037	2925	7207	12623	14145	11325	3647
40	11534	10636	15463	7311	11236	3353	11580	8342	5075	8332	3253
44	7146	5658	10243	7918	7741	1913	7996	6525	7780	7433	794
48	4555	6197	8632	7798	6796	1803	8243	6648	2210	5701	3126
52	3869	6179	11217	7483	7187	3074	7802	9881	7506	8397	1294
56	6643	6028	8392	7497	7140	1029	8965	6157	5432	6851	1866
60	5596	4849	4552	6195	5298	742	9134	5528	4817	6493	2314
64	3227	5183	7296	6220	5481	1733	6083	4680	5410	5391	702
68	3026	3951	4686	6891	4639	1648	7662	4609	4984	5751	1665
72	4353	3599	4645	3755	4088	493	5653	3912	4324	4630	910
Dissolved	3076	3143	4179	3771	3542	527	5191	3614	3059	3955	1106
Average	6468	6074	9520	7229	7323	1541	7698	7668	7042	7469	370
Bq/mg	1286	943	803	907	985	209	628	839	1015	827	194

9. H₂O isotherm

The H₂O isotherm was collected by varying the relative humidity within the vapor absorption apparatus to collect H₂O uptake after reaching equilibrium values (90 minutes). The shape of the isotherm (Figure S27) suggests the formation of a Type IV isotherm as a result of multilayer adsorption followed by capillary condensation, but additional desorption data is necessary to confirm. Based upon this assessment, data was fit to the Brunauer-Emmet-Teller isotherm model:

$$m = \frac{a_w m_0 c}{(1 - a_w)[1 + a_w(c - 1)]}$$

where m = mass of H₂O (g)/100 g material, a_w = water activity, m_0 = monolayer value, and c = energy term. The c value was calculated based upon:

$$c = \exp\left(\frac{Q_s}{RT}\right)$$

where Q is the energy of the surface interaction, R is the gas constant and T is temperature. The Q value was taken from previous experimental work¹⁷ that determined the interaction between the interior walls of the nanochannels and the H₂O inside the pores was -7.8 kJ/mol.

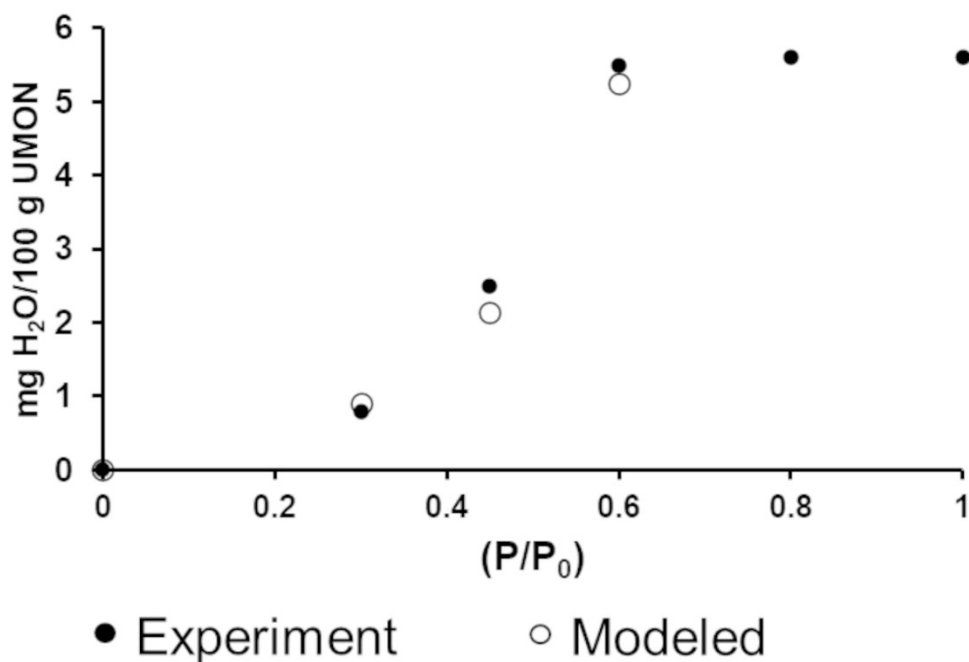


Figure S27. Isotherm data for H₂O using the vapor sorption apparatus at 30, 45, 60, and 80% RH. The modeled values utilize the BET model.