Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

NMR Reveals the Surface Functionalisation of Ti_3C_2 MXene

Supplementary Information

1. *Effect of drying on ^1H NMR*

^1H NMR spectra were recorded for the HF synthesised $Ti_3C_2T_x$ dried to different degrees (Figure S.1a). In the as received sample only a single resonance at 6.9 ppm is seen; after drying 1 hr at 100 °C *in vacuo* this signal is reduced in intensity and after drying overnight at 200 °C *in vacuo* it is observed at 6.5 ppm with comparable intensity to other proton signals.

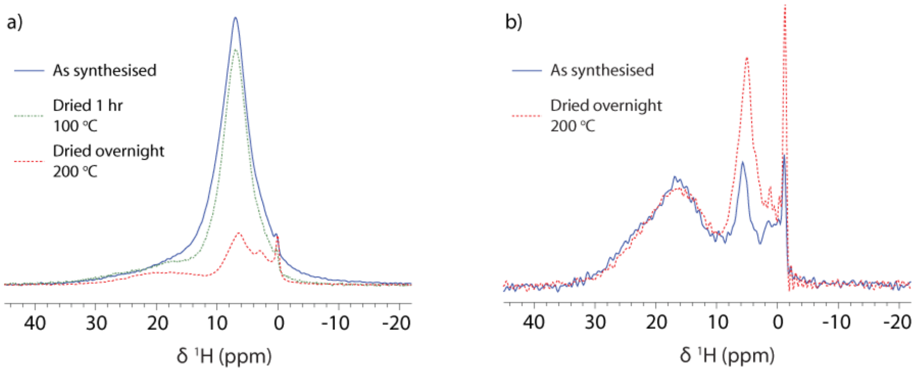

Figure S.1: The effect of drying on the ^1H NMR spectrum of $Ti_3C_2T_x$ without (a) and with (b) a T_2 filter. Spectra were recorded in a field of 7.05 T at 60 kHz MAS using a spin-echo experiment with delays of 16.7 µs and 835 µs for regular and T_2 filtered spectra respectively.

The H_2O signal is found to have a short T_2 relaxation constant of ~0.5 ms, so a spin-echo experiment with a long delay was used to filter out most of the H_2O intensity such that the Ti-OH resonance could be resolved in the as synthesised sample. To determine if vacuum drying removed Ti-OH terminations, an as synthesised sample of HF etched $Ti_3C_2T_x$ MXene was packed into a rotor and the T_2 filtered ^1H spectrum recorded. The packed rotor was then dried overnight *in vacuo* at 200 °C and the spectrum rerecorded. Comparing the spectra (Figure S.1b), it is clear that there is no significant difference in Ti-OH intensity, and we conclude that drying *in vacuo* at 200 °C does not lead to a loss of Ti-OH terminations. The observed increase in the H_2O signal in the dried sample is due to an increase in T_2 (~1.5 ms), which outweighs the decrease in water intensity from drying. It is noted that the H_2O signal in V_2CT_x MXene was also found to have a short T_2[1].

2. *^1H Exchange and Double Quantum NMR Spectroscopies*

Exchange spectroscopy (EXSY) experiments show the 1D spectrum along the diagonal, with off-diagonal signal due to chemical or dipolar exchange between sites. The ^1H EXSY spectrum of HF synthesised $Ti_3C_2T_x$ (Figure S.2a) shows a diagonal resonance at 18 ppm due to the Ti-OH peak, which indicates there are no Ti-OH peaks near Ti-OH peaks to exchange with, whereas the water peak at 6.5 ppm appears symmetrical due to H_2O-H_2O exchange. Repeating the experiment with longer contact times only reduced the signal, suggesting dipolar rather than chemical exchange, as also concluded in the study on V_2CT_x[1].

Unlike EXSY experiments, signal in double quantum (DQ) experiments only occurs when two nuclei are coupled via the dipolar interaction. In the double quantum dimension (y axis), the frequency is given by the sum of the frequencies of the two nuclei, with self-correlations therefore appearing at double their frequency. The ^{1}H DQ spectrum of HF synthesised $Ti_3C_2T_x$ was recorded using the back-to-back (BABA) method for DQ coherence generation[2] (Figure S.2b). This supports the deductions from the EXSY spectrum with both the Ti-OH signal at 18 ppm and the supposed contaminant at 0 ppm being filtered out, indicating there are few nuclei adjacent to nuclei in the same environment.

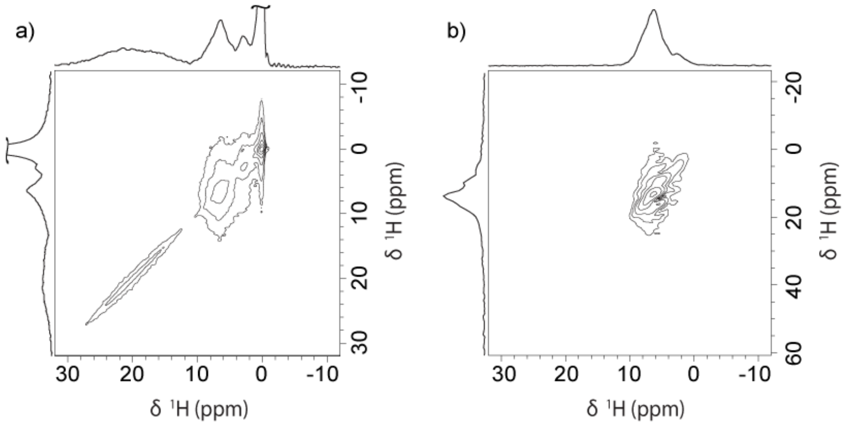

Figure S.2: ^{1}H a) exchange spectroscopy and b) double quantum spectra of HF synthesised $Ti_3C_2T_x$. Spectra were recorded in a field of 7.05 T at 60 kHz MAS.

3. *Variable Temperature ^{1}H NMR*

Figure S.3 shows ten ^{1}H NMR spectra of HF synthesised $Ti_3C_2T_x$ MXene recorded between −8 and 62 °C at 40 kHz MAS. The actual sample temperature was found from a calibration with $Pb(NO_3)_2$, which has a highly temperature dependent chemical shift[3]. Increasing the temperature decreases the intensity slightly and causes a small change in chemical shift; both of these effects are most likely due to the change in shim coil temperature affecting the shimming. The change in chemical shift affects all the signals equally and is too small for a hyperfine interaction to be a significant contribution to the Ti-OH chemical shift.

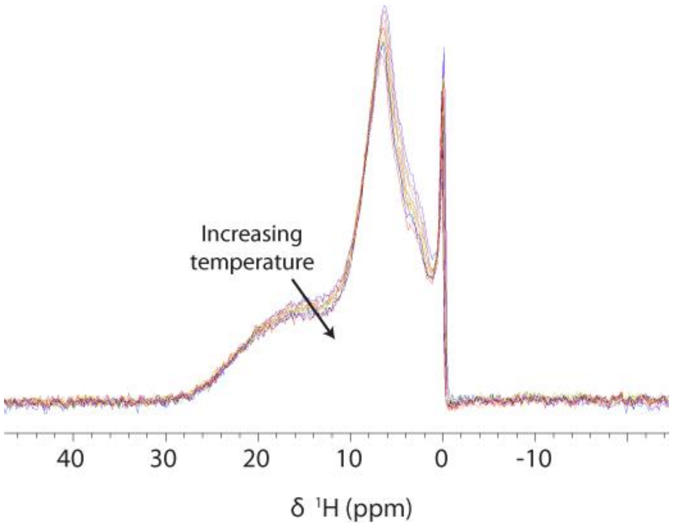

Figure S.3: Variable temperature ^{1}H NMR of the HF synthesised $Ti_3C_2T_x$ between −8 and 62 °C. Spectra were recorded in a field of 7.05 T at 40 kHz MAS using a spin-echo experiment with a delay of 16.7 µs.

4. *^{19}F NMR of TiF_3*

Figure S.4 shows the ^{19}F NMR spectrum of TiF_3 with an isotropic chemical shift of 17 ppm; this is sufficiently close to the chemical shift of 8 ppm observed in the HF synthesised Ti_3C_2 to permit assignment.

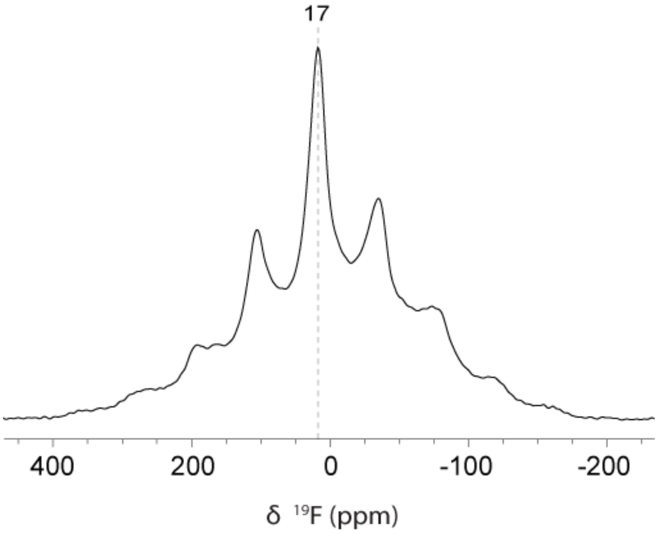

Figure S.4: ^{19}F NMR of TiF_3 with an isotropic chemical shift of 17 ppm. The spectrum was recorded in a field of 16.5 T at 60 kHz MAS using a spin-echo experiment with a delay of 16.7 µs.

5. *EDS analysis*

In order to make an estimate on the conversion of Ti_3AlC_2 to $Ti_3C_2T_x$, we used Ti and Al signals from energy-dispersive spectroscopy (EDS) as reported previously[4]. All values obtained from EDS were normalized to the Ti signal, and the results averaged to present the data in Table S1. In addition to the values previously reported for the procedures, where the products were cleaned by washing with distilled water after etching, we have included data for LiF-HCl samples which have been first washed with 6 M HCl, followed by water washing (italicized). This procedure may cause changes to the interlayer chemistry of the $Ti_3C_2T_x$ sheets, but shows a decrease in the Al and F signals, presumably due to solubilising and removal of both LiF and AlF_3. We can assume that all Al signal present originates from un-etched Ti_3AlC_2 in the normal washing samples to obtain a first estimate, but after assumed removal of AlF_3, the value estimated for the acid-washed samples should be more accurate. The HF-etching data presented here show a large amount of both F and Al, due to residual AlF_3, which is variable between samples, but it can be assumed to be nearly 100% conversion as no Ti_3AlC_2 peaks are present in the XRD pattern of the HF etched sample (main text, Figure 1c).

Table 1: Summarized EDS values of various etching and washing procedures

	HF etching	**LiF-HCl@40 °C**	
	Normal washing	Normal washing	*Acid washing*
Ti	3.00	3.00	*3.00*
Al	0.40	0.25	*0.10*
C	2.80	2.12	*1.76*
O	1.98	1.08	*1.15*
F	3.25	5.80	*0.86*
Cl	--	0.16	*0.18*

6. *Synthesis*

? **Ti_3AlC_2**. Ti_2AlC (Kanthal, Sweden) was mixed with TiC (Alfa Aesar, 99.5% purity) to afford Ti_3AlC_2, according to previously-reported procedures.[5]

? **Ti_3C_2 (HF)**. **Ti_3AlC_2** was slowly added to concentrated hydrofluoric acid (48-51 wt%, Acros) in a ratio of 10 mL HF solution : 1 g **Ti_3AlC_2** and stirred at ~ 25 °C for 18 hours. The reaction mixture was washed in a centrifugation/decantation process as described previously, followed by a final wash with ethanol to transfer the sediment for drying.[5]

? **Ti_3C_2 (LiF)**. Ti_3AlC_2 was slowly added to a mixture of HCl (6 M, Fisher technical grade) and LiF (Alfa Aesar, 99+%) in a ratio of 1 mol **Ti_3AlC_2** : 5 mol LiF and 10 mL HCl solution : 1 g **Ti_3AlC_2**. The reaction mixture was stirred and held at 40 °C for 24 hours (temperature maintained by a heated oil bath). These samples were etched for a shorter time period than originally reported (24 hrs c.f. 45 hrs) to prevent over-etching[6], as this has been found to give higher and more reliable yields of delaminated material at the expense of more unreacted $Ti_3AlC_{2.}$ The resulting sediment was washed with water as in the case for **Ti_3C_2 (HF)** until a green supernatant appeared at pH ~ 5, corresponding to some dispersion of flakes. The sediment was collected and filtered to remove water, followed by drying in air.

7. *SEM Experimental*

Scanning Electron Microscopy (SEM) analysis was performed on a Zeiss Supra 50VP; Energy-Dispersive Spectroscopy (EDS) was performed with this instrument (Oxford EDS, with INCA software). EDS scans were obtained at low magnification (200-400 x) at random points in the sample; three points per sample were used to obtain averages to calculate rough elemental ratios. Elemental standards were as follows: C: $CaCO_3$; Al: Al_2O_3; O: SiO_2; F: MgF_2; Nb: Nb metal. XPP matrix correction (Pouchou and Pichoir (1988)) was used for element quantitative analysis.

8. *XRD Experimental*

All samples were mixed with 10 wt. % crystalline silicon as an internal standard. A Rigaku SmartLab diffractometer (Rigaku Corporation, Tokyo, Japan) was used to measure XRD patterns (Cu Kα radiation source). MAX and MXene samples were scanned at a step size of 0.04° and collection time of 0.5 s per step.

9. *NMR Experimental*

Quantitative ^1H and ^{19}F 1D experiments, ^{13}C 1D experiments and ^1H-^{19}F 2D experiments were performed using a Bruker Avance III spectrometer operating at a magnetic field strength of 11.7 T, corresponding to a 1H Larmor frequency of 500 MHz. ^1H experiments showing the effect of drying, ^1H-^{13}C HETCOR experiments and ^1H EXSY experiments were performed with a Bruker Avance spectrometer operating at a magnetic field strength of 7.05 T, corresponding to a ^1H Larmor frequency of 300 MHz. 1D ^1H, ^{13}C and ^{19}F and ^1H EXSY experiments were performed with a Bruker 1.3 mm double resonance probe and ^1H-^{19}F HETCOR experiments (and the 1D experiments they are directly compared with) were performed with a Bruker 2.5 mm double resonance probe, which can simultaneously tune to ^1H and ^{19}F.

^{13}C experiments were performed at 50 kHz MAS, as the metallic MAX phase could not be spun faster, with a Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence[7] (Figure S.5). This allowed good signal to noise to be achieved overnight despite the long T_1 relaxation time and low natural abundance of ^{13}C. A radio-frequency strength of 96 kHz was used for the $\pi/2$ pulse and the recycle delay was 10 s. 200 echoes were recorded per scan, with 160 rotor periods per echo (3.2 ms). However, the Ti_3C_2 resonance was found to have a shorter T_2 relaxation time than the Ti_3AlC_2 resonance so in order to observe both, an exponential multiplication of 5 Hz was applied to the total time domain, effectively reducing the number of echoes used. The echoes were then all summed to avoid the artefact of CPMG which outlines the spectrum in so-called “spikelets”, and a centred exponential line broadening of 1000 Hz was applied to the combined echo to further increase signal to noise (Figure S.6).

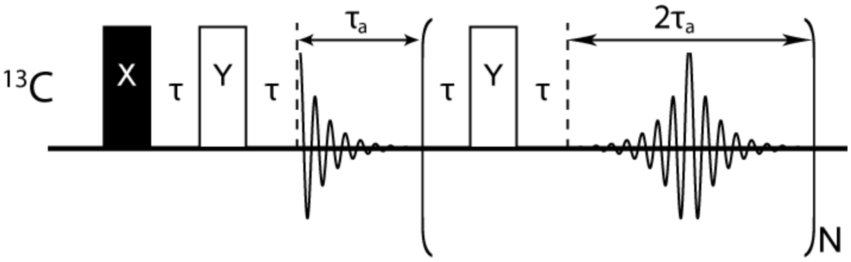

Figure S.5: CPMG pulse sequence.

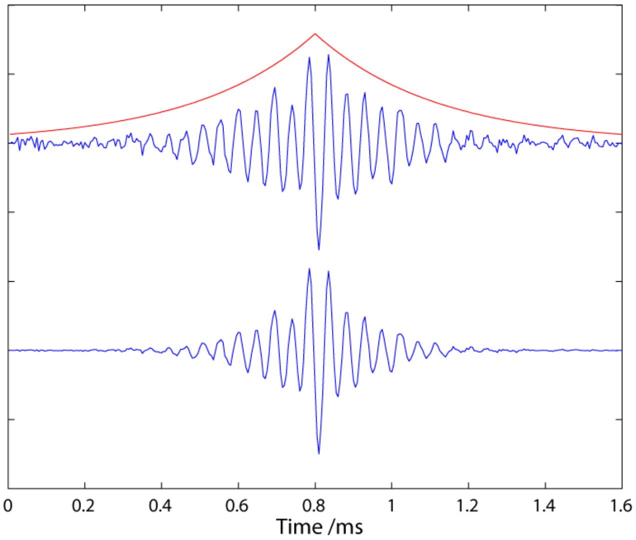

Figure S.6: Line broadening of the summed echo in a CPMG experiment. Top - summed echo and centred exponential function. Bottom – exponential multiplied echo with greater signal to noise.

^{1}H-^{13}C HETCOR experiments were performed at 40 kHz MAS, also using a CPMG pulse sequence for the 1D slices. The echoes in each 1D slice were summed and a centred exponential line broadening of 3000 Hz applied before the 2D fourier transform to remove the spikelet pattern and increase signal to noise. Cross polarisation was established under the Hartmann-Hahn matching condition using ^{1}H and ^{13}C radio-frequency strengths of 90 kHz and 50 kHz respectively. A 10 ms contact time was necessary to achieve cross polarisation through the intervening Ti layer.

^{1}H and ^{19}F 1D experiments were performed at 60 kHz MAS with a spin–echo pulse sequence (90°–τ–180°–τ–acquire) to avoid baseline distortions and to remove background signals associated with the probe. For both, spin–echo τ delays of a single rotor period, 16.7 μs, were used. Radio-frequency strengths of 102 kHz and 125 kHz were used for the ^{1}H and ^{19}F $\pi/2$ pulses respectively. T_2 filtered ^{1}H spectra used a spin-echo τ delay of 50 rotor periods, 835 μs.

^1H-^{19}F HETCOR experiments were performed at 20 kHz MAS with 2 ms contact time. Cross polarisation was established under the Hartmann-Hahn matching condition using ^1H and ^{19}F radio-frequency strengths of ~80 kHz and ~50 kHz respectively. A spin echo of a single rotor period, 16.7 μs, was again appended to avoid baseline distortion.

^1H spectra were referenced relative to adamantane at 1.81 ppm, ^{13}C spectra were referenced relative to the tertiary carbon atom in adamantane at 38.5 ppm and ^{19}F spectra were referenced relative to LiF at −203 ppm.

The 1D ^1H and ^{19}F spectra used for spin counting are quantitative as a recycle delay of $>5T_1$ was used: 15 s for the ^1H spectra and 120 s for the ^{19}F spectra. Thus the intensity of a signal is proportional to the number of spins in the environment, with the constant of proportionality being determined by running the same experiments on three samples of different known masses of adamantane and PTFE respectively. This spin counting was first used to find the mass of H_2O, AlF_3, LiF and TiF_3, then the mass of $Ti_3C_2T_x$ was found by subtracting these from the sample mass, further accounting for any remaining Ti_3AlC_2 as previously determined by EDS.

^1H EXSY experiments were performed using a mixing time of 160 ms and a radio-frequency power of 89 kHz for the $\pi/2$ pulse. 100 Hz of line broadening was applied to both the direct and indirect dimensions. ^1H BABA experiments used a single rotor period for back-to-back recoupling.

10. *Structure Visualisation*

The schematic of etching Ti_3AlC_2 to $Ti_3C_2T_x$ was made using the VESTA software package[8].

References

1 K. J. Harris, M. Bugnet, M. Naguib, M. W. Barsoum and G. R. Goward, *J. Phys. Chem. C*, 2015, 13713–13720.

2 M. Feike, D. E. Demco, R. Graf, J. Gottwald, S. Hafner and H. W. Spiess, *J. Magn. Reson. Ser. A*, 1996, **122**, 214–221.

3 A. Bielecki and D. P. Burum, *J. Magn. Reson. Ser. A*, 1995, **116**, 215–220.

4 M. Naguib, J. Halim, J. Lu, K. M. Cook, L. Hultman, Y. Gogotsi and M. W. Barsoum, *J. Am. Chem. Soc.*, 2013, **135**, 15966–15969.

5 M. Naguib, M. Kurtoglu, V. Presser, J. Lu, J. Niu, M. Heon, L. Hultman, Y. Gogotsi and M. W. Barsoum, *Adv. Mater.*, 2011, **23**, 4248–4253.

6 O. Mashtalir, M. Naguib, B. Dyatkin, Y. Gogotsi and M. W. Barsoum, *Mater. Chem. Phys.*, 2013, **139**, 147–152.

7 R. Siegel, T. T. Nakashima and R. E. Wasylishen, *Concepts Magn. Reson. Part A*, 2005, **26A**, 62–77.

8 K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 2011, **44**, 1272–1276.