

Supporting Information

Atomic Insights into Nanoparticles Formation of Hydroxy-Fluorinated Anatase featuring Titanium Vacancies

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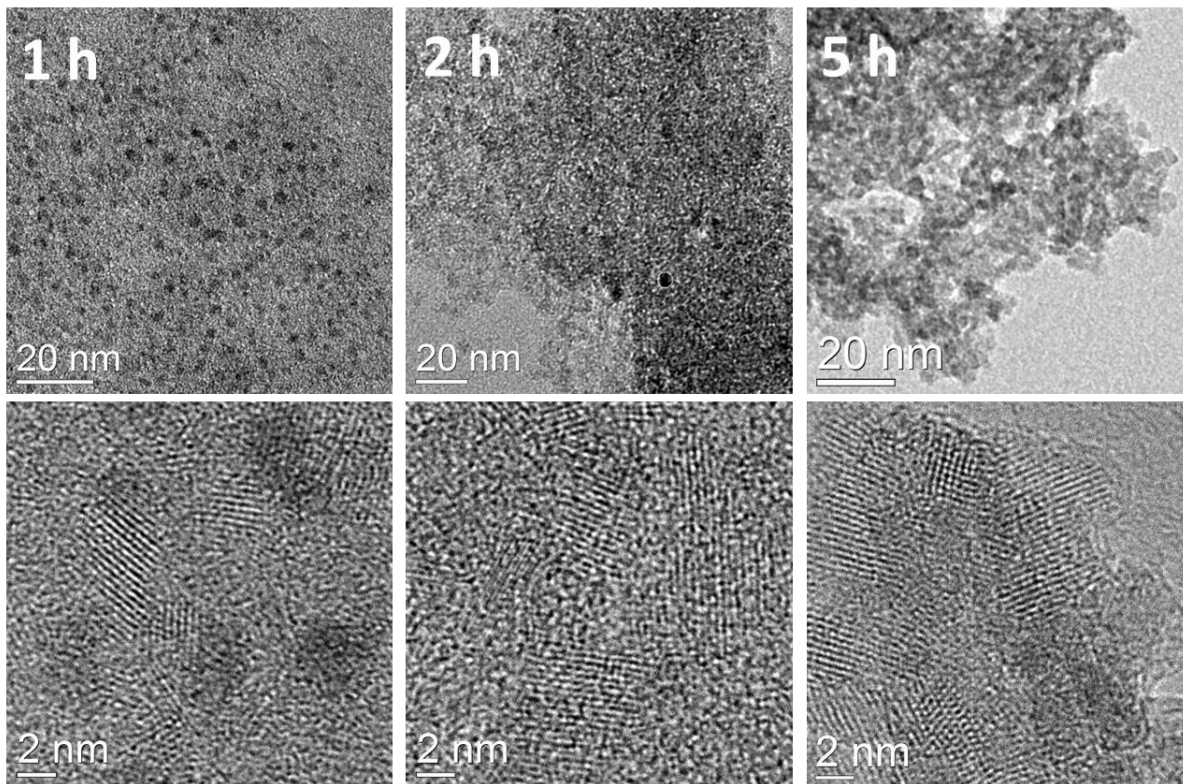


Figure S1. High-resolution TEM images of the samples synthesized after 1, 2 and 5 h.

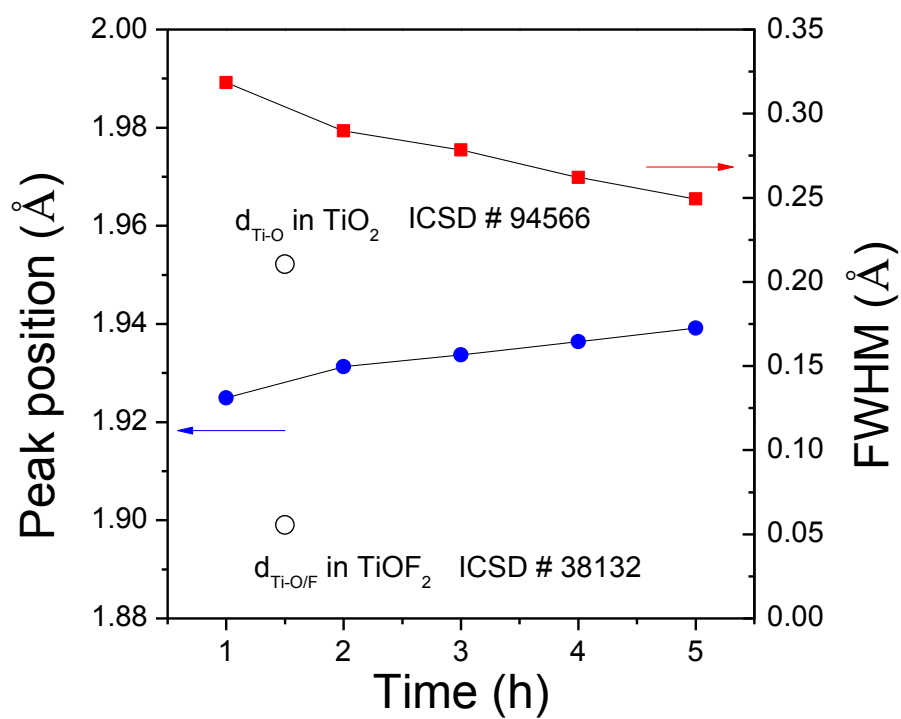


Figure S2. Peak positions and FWHM obtained from fitting (using a Gaussian function) the 1st peak of the PDF. The average Ti-O/F bond distances in reference (taken from the ICSD¹) anatase ($d_{\text{Ti-O}}$ in TiO_2 ²) and in bulk TiOF_2 ($d_{\text{Ti-O/F}}$ in TiOF_2 ³) are pointed by black circles for comparison purposes.

¹ Inorganic Crystal Structure Database (ICSD), Version 1.9.5, FIZ Karlsruhe and NIST, Germany and Maryland, 2007.

² Weirich, T.E.; Winterer, M.; Seifried, S.; Mayer, J. *Acta Crystallogr. A* **2002**, 58, 308-315.

³ Vorres, K.; Donohue, J. *Acta Crystallogr.* **1955**, 8, 25-26.

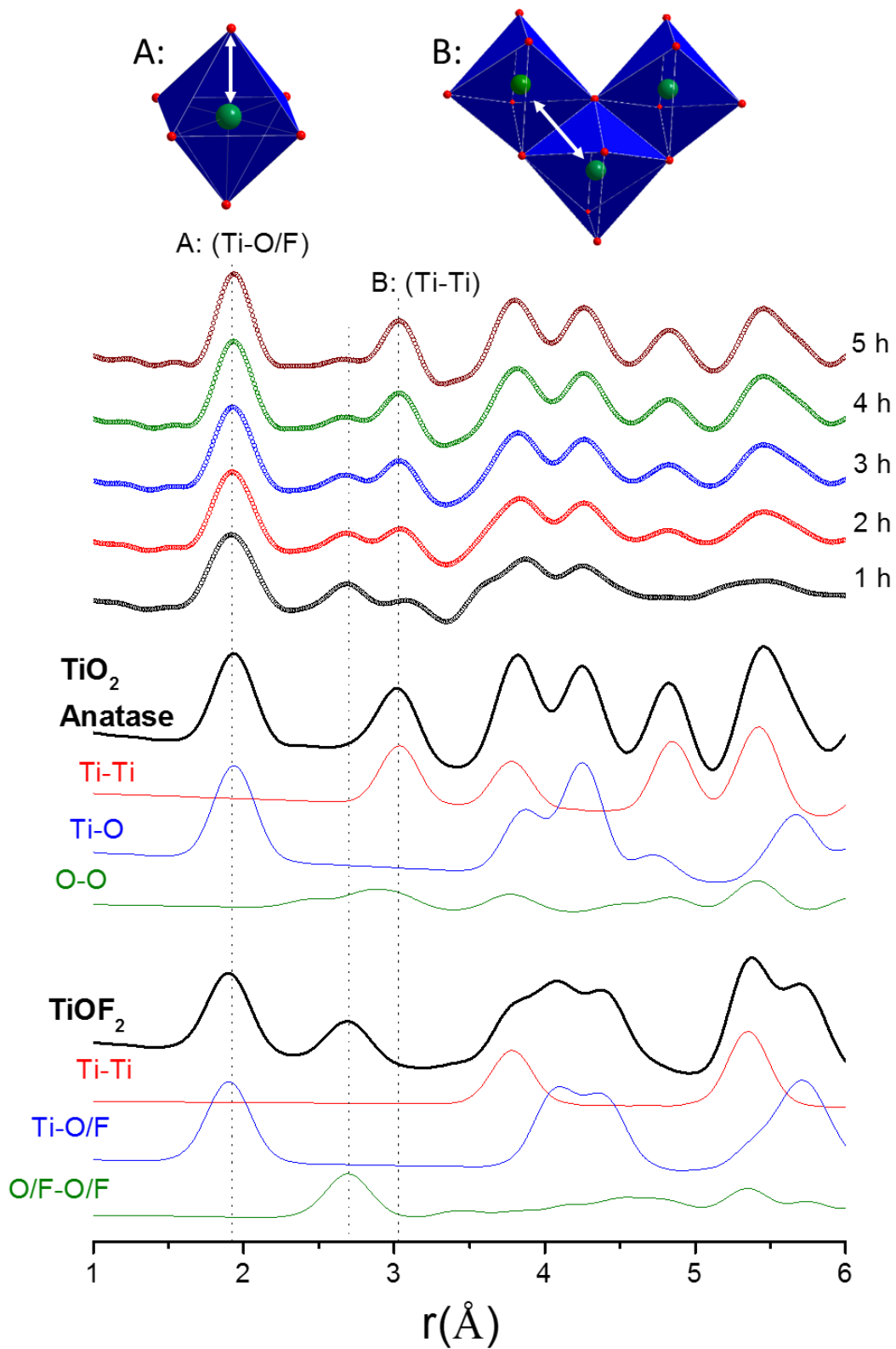


Figure S3. Comparison between time-dependent PDFs and reference TiOF_2 ³ (ICSD¹ # 38132) and TiO_2 ² (ICSD¹ # 94566) as well as their calculated partial PDFs.

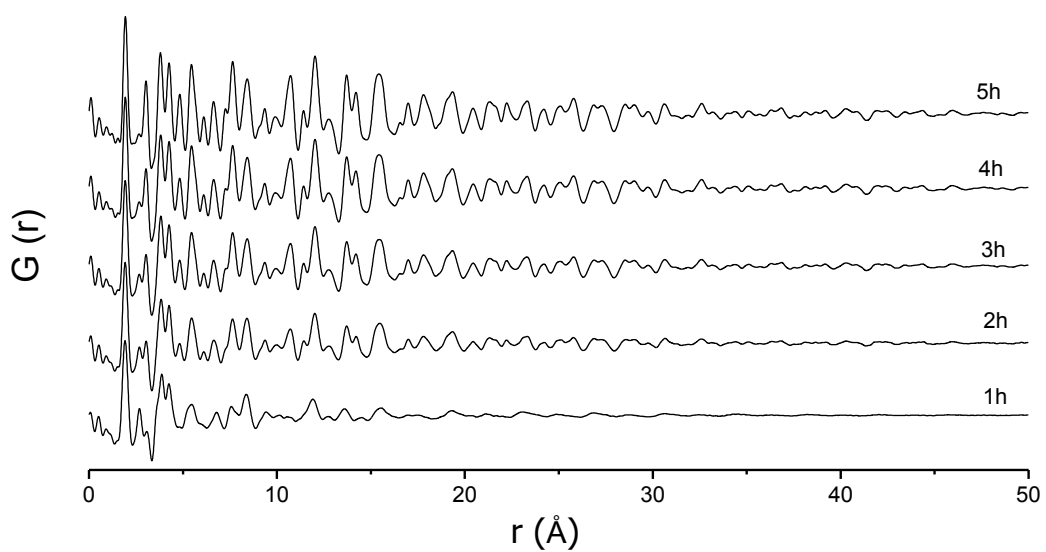


Figure S4. Evolution of the PDFs for the samples prepared at different reaction time.

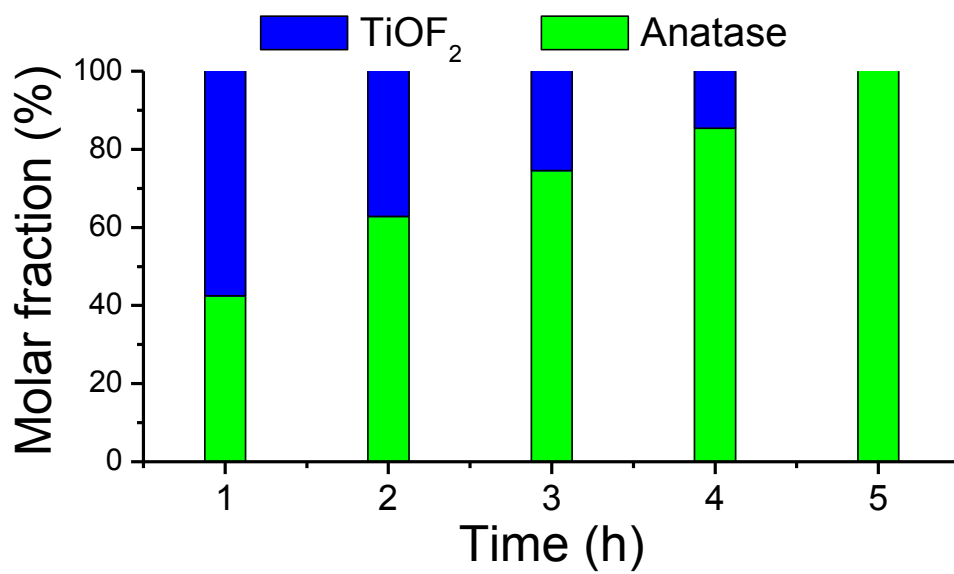


Figure S5. Quantitative phase analysis obtained by PDF refinements.

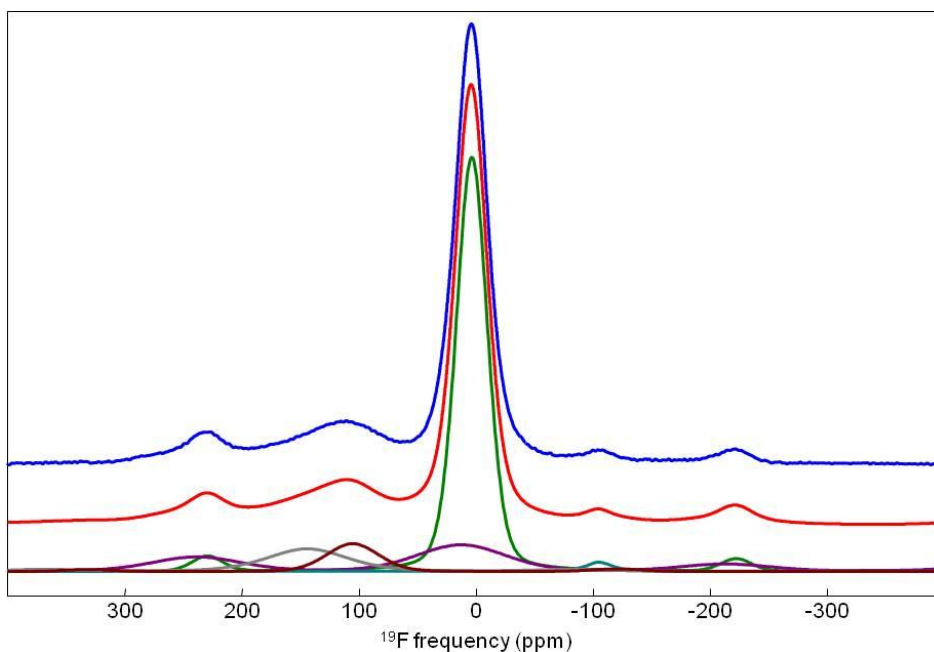


Fig. S6. Experimental (blue) and fitted (red) ^{19}F MAS (64 kHz) NMR spectra of the sample prepared at 1 hour reaction time. The individual resonances used for the fit are shown below (see Table S1).

Table S1. Isotropic chemical shifts (δ_{iso} , ppm), line widths (LW, ppm) and relative intensities (I, %) of the NMR resonances used for the fit of the ^{19}F MAS (64 kHz) NMR spectrum of the sample prepared at 1 hour reaction time and assignment of these NMR resonances.

δ_{iso}	LW	I	Assignment
-104.5	27.0	1.4	FTi_3
3.9	31.2	62.4	$\text{FTi}_2\text{□}$, FTi_2
13.0	88.8	18.2	$\text{FTi}_2\text{□}$, FTi_2
105.6	52.8	7.7	FTi□_2 , FTi□
144.2	81.7	10.3	FTi□ , FTi□_2

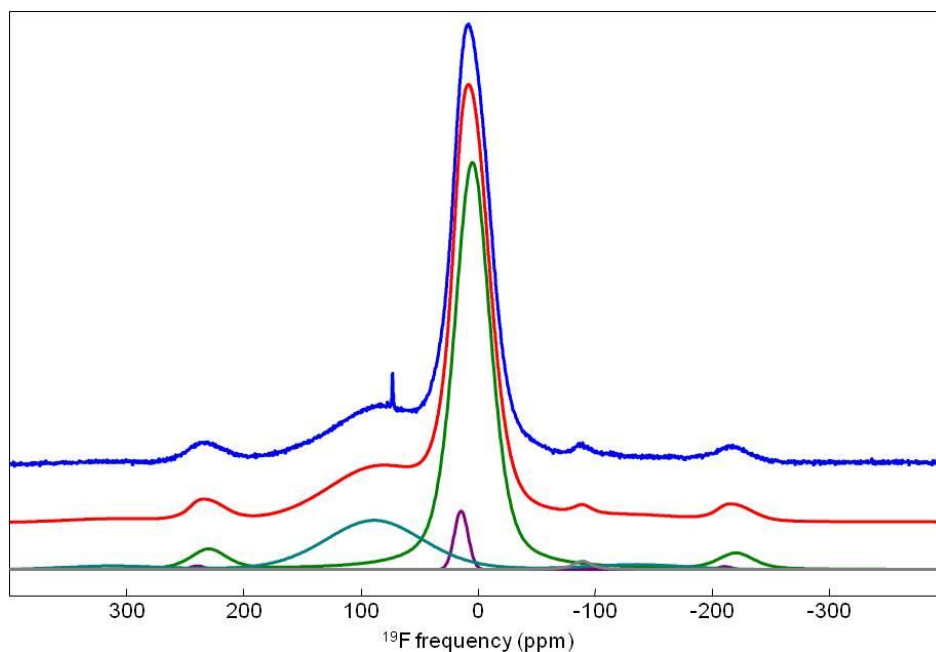


Fig. S7. Experimental (blue) and fitted (red) ^{19}F MAS (64 kHz) NMR spectra of the sample prepared at 2 hours reaction time. The individual resonances used for the fit are shown below (see Table S2).

Table S2. Isotropic chemical shifts (δ_{iso} , ppm), line widths (LW, ppm) and relative intensities (I, %) of the NMR resonances used for the fit of the ^{19}F MAS (64 kHz) NMR spectrum of the sample prepared at 2 hours reaction time and assignment of these NMR resonances.

δ_{iso}	LW	I	Assignment
-89.3	19.0	0.9	FTi_3
4.7	36.1	72.4	$\text{FTi}_2\text{□}$, FTi_2
14.3	13.8	3.5	$\text{FTi}_2\text{□}$, FTi_2
88.5	99.0	23.2	FTi□_2 , FTi□ (?)

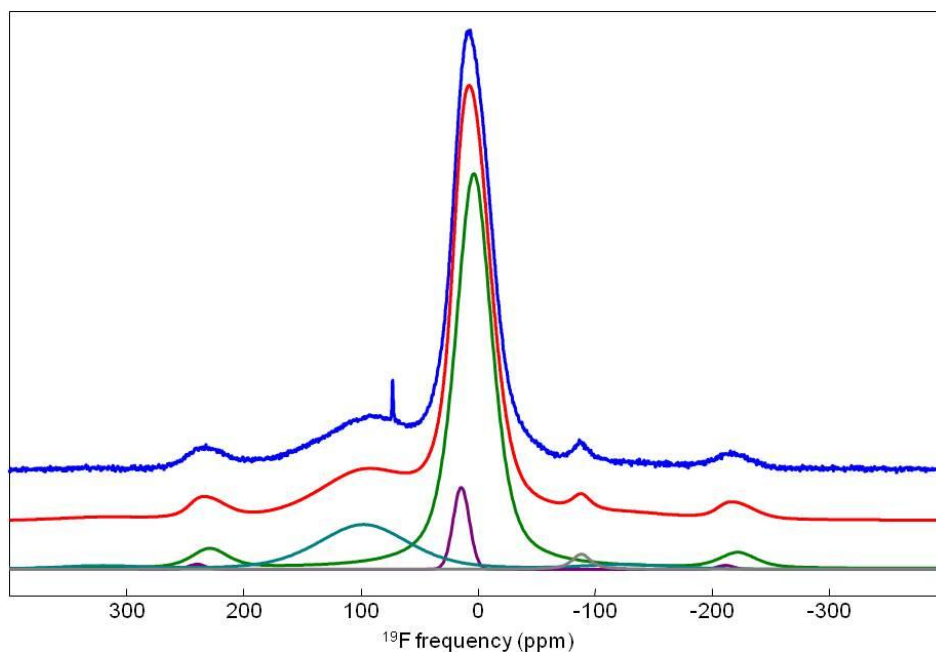


Fig. S8. Experimental (blue) and fitted (red) ^{19}F MAS (64 kHz) NMR spectra of the sample prepared at 3 hours reaction time. The individual resonances used for the fit are shown below (see Table S3).

Table S3. Isotropic chemical shifts (δ_{iso} , ppm), line widths (LW, ppm) and relative intensities (I, %) of the NMR resonances used for the fit of the ^{19}F MAS (64 kHz) NMR spectrum of the sample prepared at 3 hours reaction time and assignment of these NMR resonances.

δ_{iso}	LW	I	Assignment
-88.3	19.0	1.5	FTi_3
3.5	36.8	72.5	$\text{FTi}_2\text{□}$, FTi_2
14.2	16.3	5.5	$\text{FTi}_2\text{□}$, FTi_2
97.7	92.0	20.5	FTi□_2 , FTi□ (?)

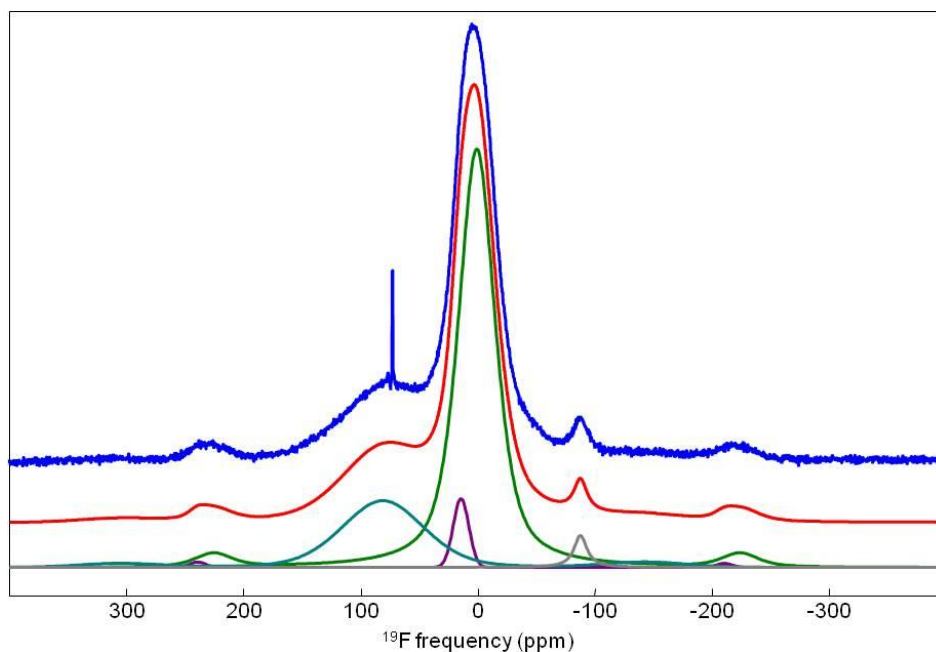


Fig. S9. Experimental (blue) and fitted (red) ^{19}F MAS (64 kHz) NMR spectra of the sample prepared at 4 hours reaction time. The individual resonances used for the fit are shown below (see Table S4).

Table S4. Isotropic chemical shifts (δ_{iso} , ppm), line widths (LW, ppm) and relative intensities (I, %) of the NMR resonances used for the fit of the ^{19}F MAS (64 kHz) NMR spectrum of the sample prepared at 4 hours reaction time and assignment of these NMR resonances.

δ_{iso}	LW	I	Assignment
-87.6	13.5	2.1	FTi_3
0.9	37.2	70.3	$\text{FTi}_2\text{□}$, FTi_2
14.4	15.7	4.2	$\text{FTi}_2\text{□}$, FTi_2
81.1	82.7	23.4	FTi□_2 , FTi□ (?)

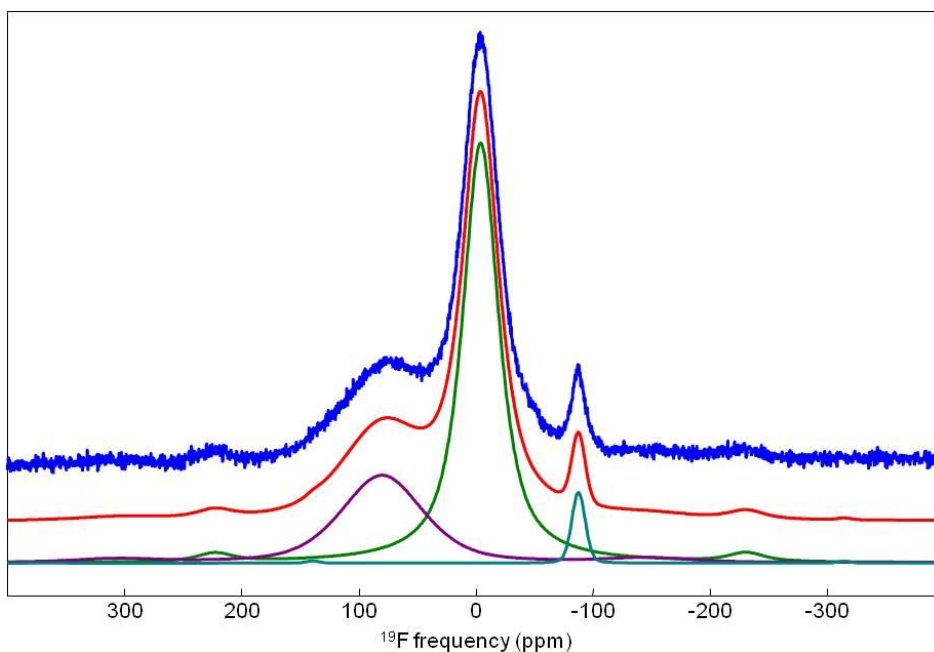


Fig. 10. Experimental (blue) and fitted (red) ^{19}F MAS (64 kHz) NMR spectra of the sample prepared at 6 hours reaction time. The individual resonances used for the fit are shown below (see Table S5).

Table S5. Isotropic chemical shifts (δ_{iso} , ppm), line widths (LW, ppm) and relative intensities (I, %) of the NMR resonances used for the fit of the ^{19}F MAS (64 kHz) NMR spectrum of the sample prepared at 6 hours reaction time and assignment of these NMR resonances.

δ_{iso}	LW	I	Assignment
-87.6	13.6	3.5	FTi_3
-4.1	36.7	67.7	$\text{FTi}_2\text{□}$
80.0	82.4	28.8	FTi□_2

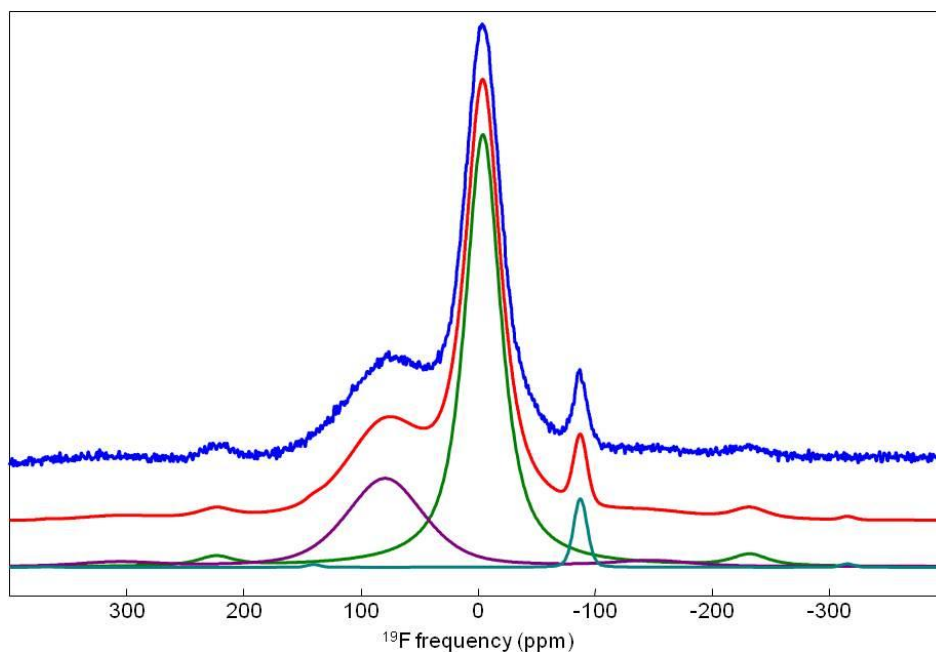


Fig. S11. Experimental (blue) and fitted (red) ^{19}F MAS (64 kHz) NMR spectra of the sample prepared at 8 hours reaction time. The individual resonances used for the fit are shown below (see Table S6).

Table S6. Isotropic chemical shifts (δ_{iso} , ppm), line widths (LW, ppm) and relative intensities (I, %) of the NMR resonances used for the fit of the ^{19}F MAS (64 kHz) NMR spectrum of the sample prepared at 8 hours reaction time and assignment of these NMR resonances.

δ_{iso}	LW	I	Assignment
-87.5	13.7	3.5	FTi_3
-4.3	36.6	68.7	$\text{FTi}_2\text{□}$
79.2	78.2	27.8	FTi□_2

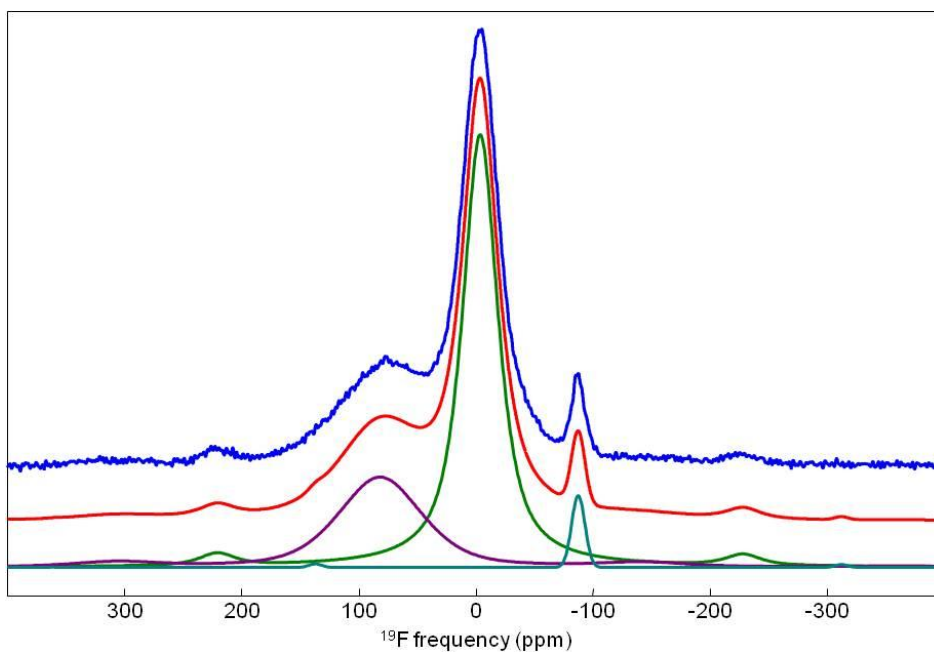


Fig. S12. Experimental (blue) and fitted (red) ^{19}F MAS (64 kHz) NMR spectra of the sample prepared at 10 hours reaction time. The individual resonances used for the fit are shown below (see Table S7).

Table S7. Isotropic chemical shifts (δ_{iso} , ppm), line widths (LW, ppm) and relative intensities (I, %) of the NMR resonances used for the fit of the ^{19}F MAS (64 kHz) NMR spectrum of the sample prepared at 10 hours reaction time and assignment of these NMR resonances.

δ_{iso}	LW	I	Assignment
-87.4	13.4	3.2	FTi_3
-3.7	36.1	67.3	$\text{FTi}_2\text{□}$
81.7	84.0	29.5	FTi□_2