

Sol-gel Chemistry of Titanium alkoxide towards HF: impacts of reaction parameters

Wei Li,[†] Monique Body,[§] Christophe Legein,[§] and Damien Dambournet^{*,†}

[†]Sorbonne Universités, UPMC Univ Paris 06, CNRS, UMR 8234, PHENIX, F-75005 Paris, France

[§] Université Bretagne Loire, Université du Maine, UMR CNRS 6283, Institut des Molécules et des Matériaux du Mans (IMMM), Avenue Olivier Messiaen, 72085 Le Mans Cedex 9, France

Supporting Information

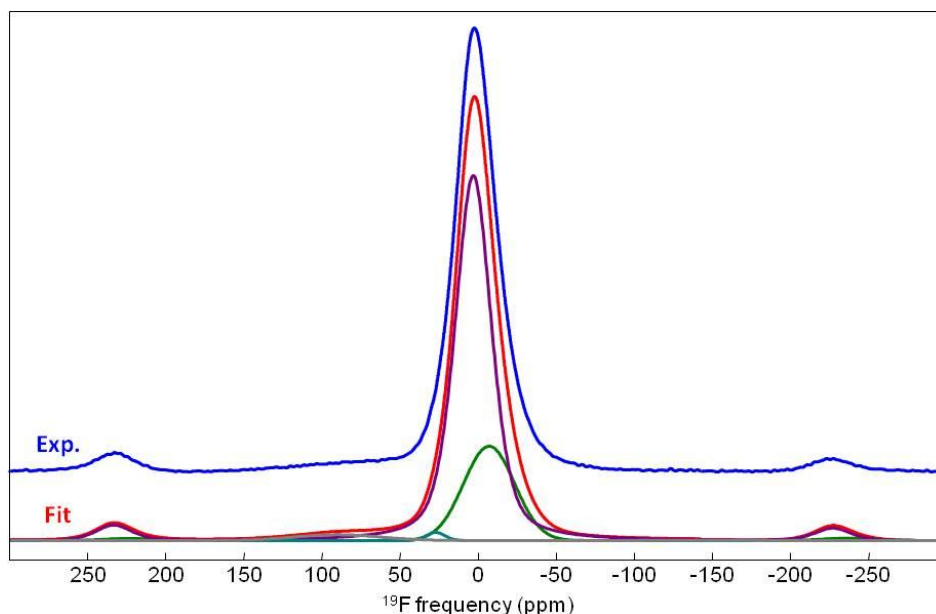


Figure S1. Experimental (blue) and fitted (red) ^{19}F MAS (64 kHz) solid state NMR spectra of the HTB phase prepared using titanium butoxide as precursor, a molar ratio R equal to 3.7 and 2-butanol as solvent. The individual resonances used for the fit (see Table S1) are shown below.

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 HTB phase prepared using titanium butoxide as precursor, a molar ratio R equal to 3.7 and 2-butanol as solvent and assignment of these NMR resonances.

δ_{iso}	LW	I	Assignment
-6.8	38.4	22.1	$\text{Ti}_2\text{-F}$
3.3	27.5	75.2	$\text{Ti}_2\text{-F}$
27.5	14.2	0.7	$\text{Ti}_2\text{-F}$
90.3	65.3	2.1	$\text{Ti}\square\text{-F}$

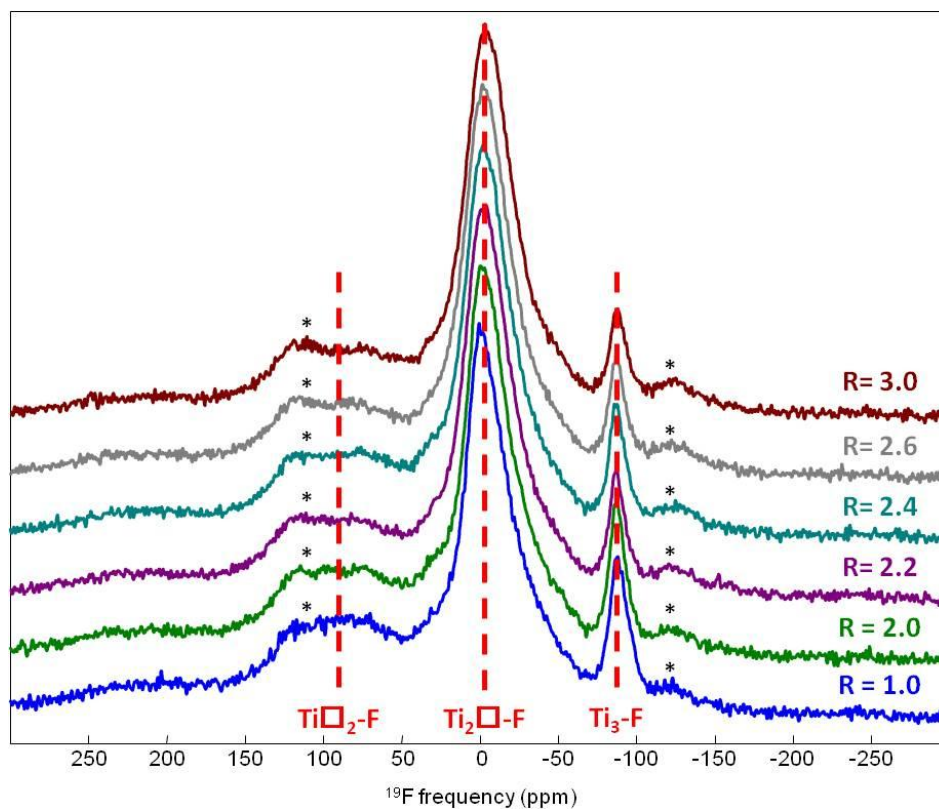


Figure S2. ^{19}F MAS (34 kHz) solid state NMR spectra of the samples prepared using various molar ratio $R = \text{F}/\text{Ti}$. The precursor and solvent used were $\text{Ti}(\text{OEt})_4$ and ethanol, respectively. Asterisks refer to the first spinning sidebands of the main isotropic line. The red dashed lines indicate the three main NMR lines corresponding to the three fluorine species occurring in $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$ anatase.

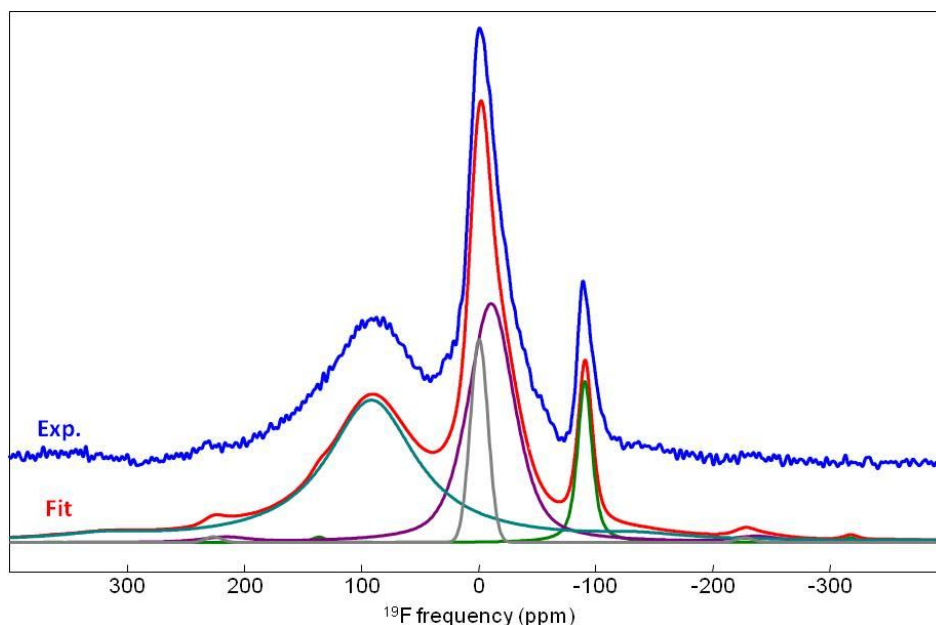


Figure S3. Experimental (blue) and fitted (red) ^{19}F MAS (64 kHz) solid state NMR spectra of the sample (anatase) prepared using $\text{Ti}(\text{OEt})_4$ as precursor, a molar ratio R equal to 1.0 and ethanol as solvent. The individual resonances used for the fit (see Table S2) are shown below.

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 using $\text{Ti}(\text{OEt})_4$ as precursor, a molar ratio R equal to 1.0 and ethanol as solvent. and assignment of these NMR resonances.

δ_{iso}	LW	I	Assignment
-90.8	14.6	7.9	$\text{Ti}_3\text{-F}$
-10.9	46.8	35.0	$\text{Ti}_2\text{□-F}$
-0.7	17.6	9.3	$\text{Ti}_2\text{□-F}$
91.2	92.8	47.8	$\text{Ti□}_2\text{-F}$

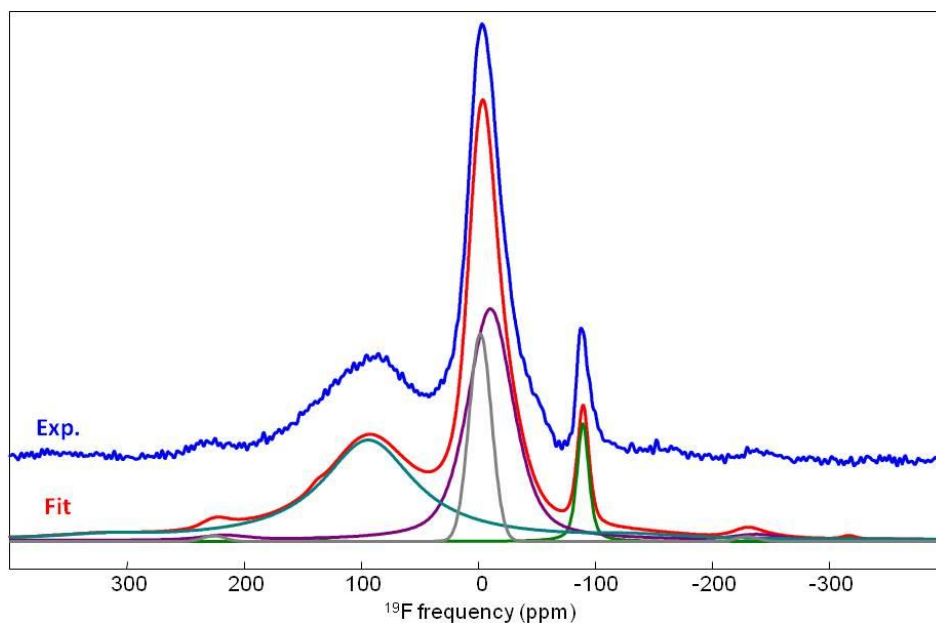


Figure S4. Experimental (blue) and fitted (red) ^{19}F MAS (64 kHz) solid state NMR spectra of the sample (anatase) prepared using $\text{Ti}(\text{OEt})_4$ as precursor, a molar ratio R equal to 2.2 and ethanol as solvent. The individual resonances used for the fit (see Table S3) are shown below.

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 using $\text{Ti}(\text{OEt})_4$ as precursor, a molar ratio R equal to 2.2 and ethanol as solvent. and assignment of these NMR resonances.

δ_{iso}	LW	I	Assignment
-89.2	11.9	5.3	$\text{Ti}_3\text{-F}$
-10.3	46.3	39.5	$\text{Ti}_2\text{□-F}$
-1.7	22.3	14.2	$\text{Ti}_2\text{□-F}$
93.8	95.7	41.0	$\text{Ti□}_2\text{-F}$

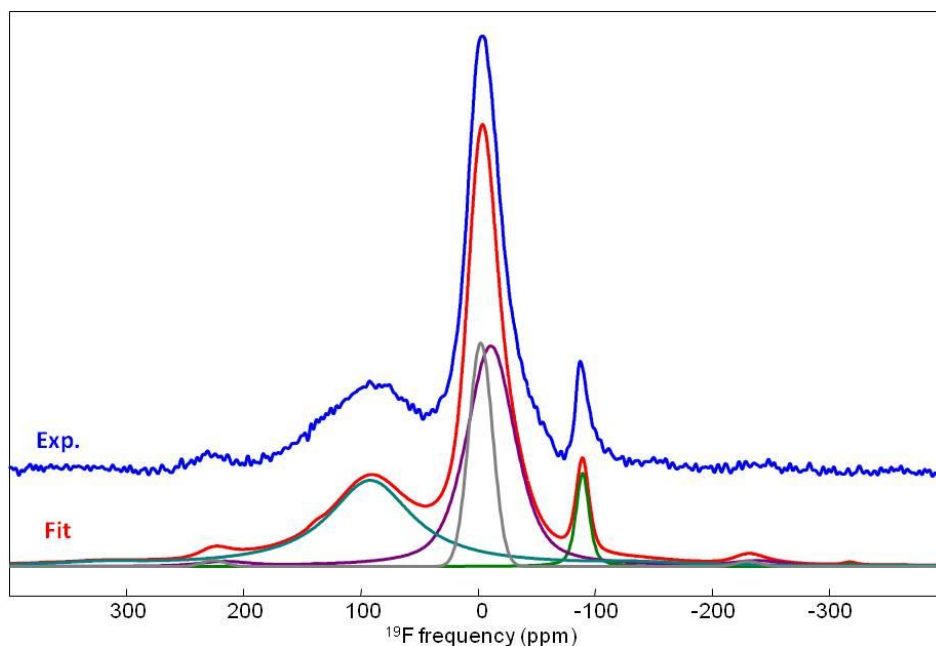


Figure S5. Experimental (blue) and fitted (red) ^{19}F MAS (64 kHz) solid state NMR spectra of the sample (anatase) prepared using $\text{Ti}(\text{OEt})_4$ as precursor, a molar ratio R equal to 3.0 and ethanol as solvent. The individual resonances used for the fit (see Table S4) are shown below.

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 using $\text{Ti}(\text{OEt})_4$ as precursor, a molar ratio R equal to 3.0 and ethanol as solvent. and assignment of these NMR resonances.

δ_{iso}	LW	I	Assignment
-89.4	13.2	5.1	$\text{Ti}_3\text{-F}$
-11.1	48.8	43.0	$\text{Ti}_2\text{□-F}$
-2.4	23.8	17.6	$\text{Ti}_2\text{□-F}$
91.8	87.1	34.3	$\text{Ti□}_2\text{-F}$

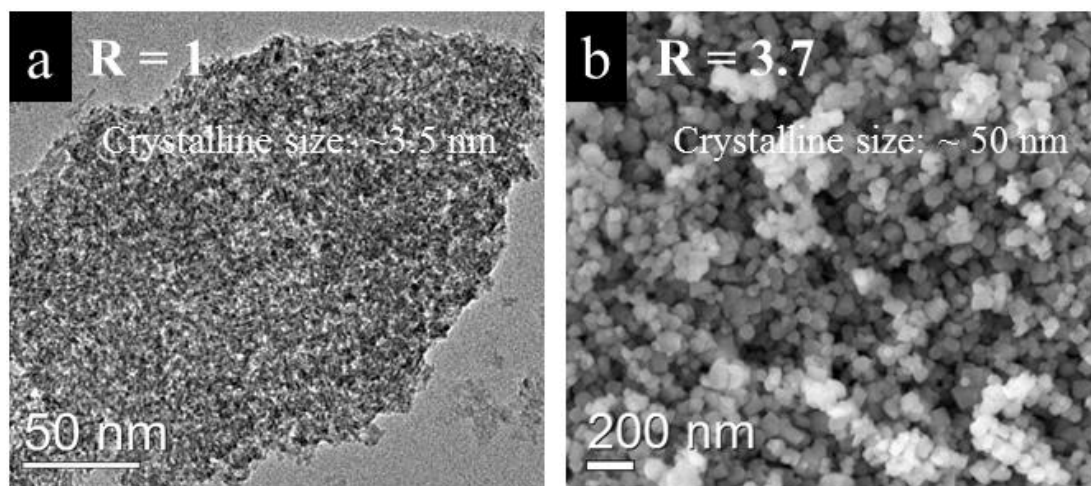


Figure S6. TEM (a) and SEM (b) images of the materials synthesized using titanium isopropoxide and isopropanol at $R = 1$ and $R = 3.7$, respectively.

The hydrolysis rate (molar ratio of water to titanium alkoxide, h) strongly affects the functionality of titanium precursor. The study of the influence of hydrolysis rate was carried out by using $\text{Ti}(\text{O}^i\text{Pr})_4$ as precursor and isopropanol as solvent at a fluorine content of $R = 3.0$. Because aqueous HF solution contains 60 wt. % of water, the hydrolysis rate without additional water is $h = 5$. h was then increased to 10 and 15. The evolution of XRD patterns as a function of h is shown in **Figure S6**. For $h = 5$, the diffraction peaks are indexed with the HTB-type phase in majority as well as a minority phase of $\text{TiO}_2\text{-B}$. By increasing the hydrolysis rate to $h = 10$, the formation of anatase phase is observed. It coexists with HTB and $\text{TiO}_2\text{-B}$. When more water is added ($h = 15$), the proportion of anatase increases.

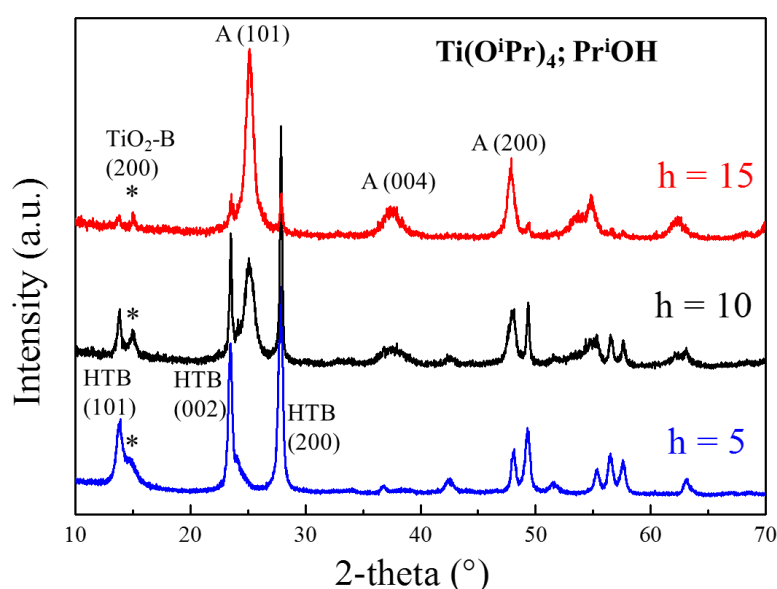


Figure S7. XRD patterns of the samples prepared using various hydrolysis ratio (h). The precursor and solvent used were titanium isopropoxide and isopropanol, respectively, and the molar ratio $R = \text{F/Ti}$ used was equal to 3. ‘A’ and ‘HTB’ refer to anatase and hexagonal-tungsten-bronze type phases, respectively and asterisks refer to (200) planes of $\text{TiO}_2\text{-B}$.

The phase change from HTB to anatase with the increase of hydrolysis rate highlights the role of water on modifying the hydro/fluorolysis and condensation reactions of alkoxide precursor. Reverse phase change observed in tuning fluorine ratio indicates competitive reaction between fluorolysis and hydrolysis. Increase of the amount of water in the synthesis favors hydrolysis reaction and leads to much hydroxylated titanium octahedra subunits, thus suppressing the fluoride-rich HTB phase and favoring the formation of an oxide-rich anatase phase.

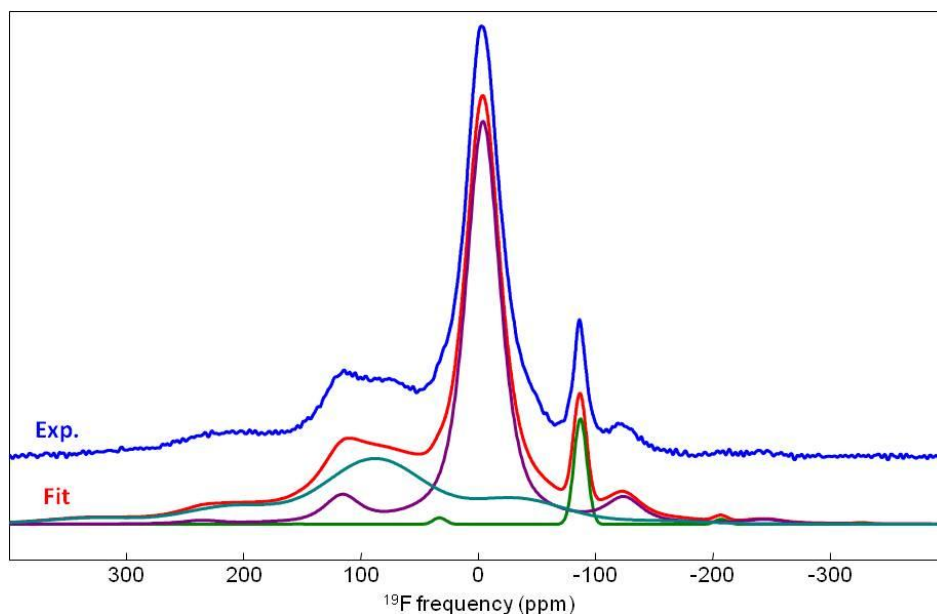


Figure S8. Experimental (blue) and fitted (red) ^{19}F MAS (34 kHz) solid state NMR spectra of the sample prepared using titanium isopropoxide as precursor, a molar ratio R equal to 2.0 and isopropanol as solvent. The individual resonances used for the fit (see Table S5) are shown below.

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 (34 kHz) NMR spectrum of the sample prepared using titanium isopropoxide as precursor, a molar ratio R equal to 2.0 and isopropanol as solvent and assignment of these NMR resonances.

δ_{iso}	LW	I	Assignment
-87.1	13.1	4.6	$\text{Ti}_3\text{-F}$
-4.0	34.8	60.1	$\text{Ti}_2\text{□-F}$
88.2	97.7	35.2	$\text{Ti□}_2\text{-F}$

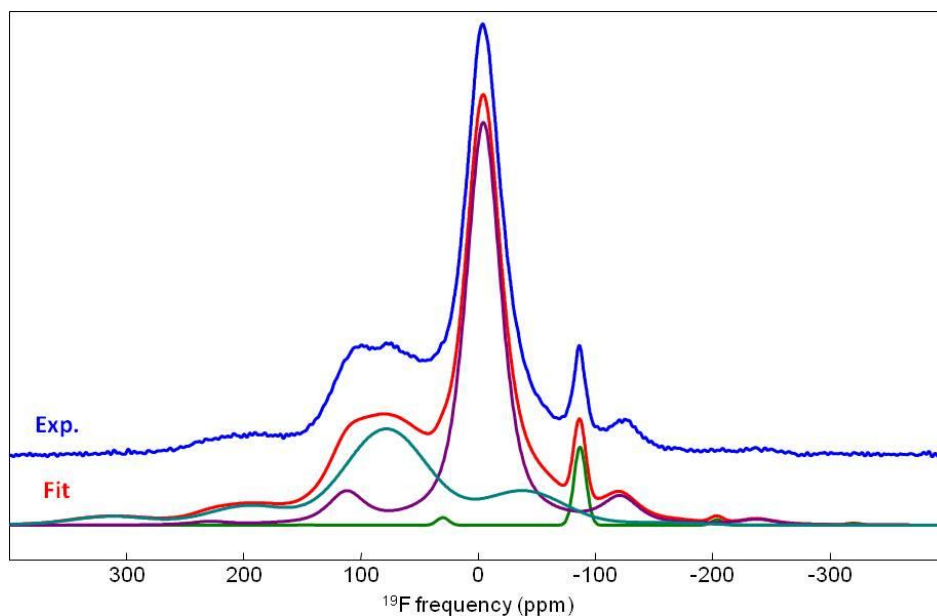


Figure S9. Experimental (blue) and fitted (red) ^{19}F MAS (34 kHz) solid state NMR spectra of the sample prepared using titanium isopropoxide as precursor, a molar ratio R equal to 2.2 and isopropanol as solvent. The individual resonances used for the fit (see Table S6) are shown below.

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 (34 kHz) NMR spectrum of the sample prepared using titanium isopropoxide as precursor, a molar ratio R equal to 2.2 and isopropanol as solvent and assignment of these NMR resonances.

δ_{iso}	LW	I	Assignment
-86.7	12.1	3.2	$\text{Ti}_3\text{-F}$
-4.3	35.5	59.0	$\text{Ti}_2\text{□-F}$
78.5	82.3	37.8	$\text{Ti□}_2\text{-F}$

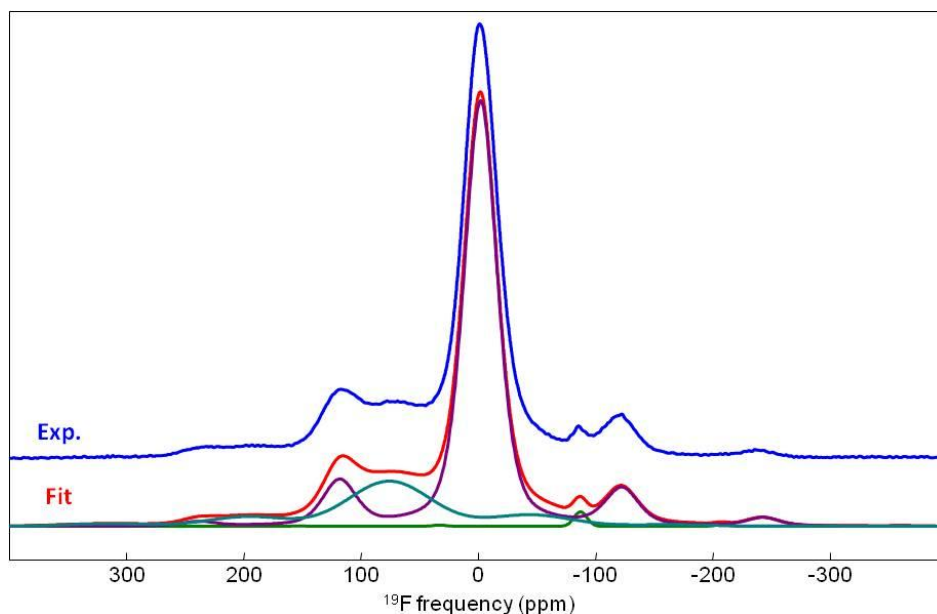


Figure S10. Experimental (blue) and fitted (red) ^{19}F MAS (34 kHz) solid state NMR spectra of the sample prepared using titanium isopropoxide as precursor, a molar ratio R equal to 2.4 and isopropanol as solvent. The individual resonances used for the fit (see Table S7) are shown below.

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 (34 kHz) NMR spectrum of the sample prepared using titanium isopropoxide as precursor, a molar ratio R equal to 2.4 and isopropanol as solvent and assignment of these NMR resonances.

δ_{iso}	LW	I	Assignment
-87.1	13.1	0.9	$\text{Ti}_3\text{-F}$
-2.0	33.4	77.3	$\text{Ti}_2\text{□-F}$
75.8	81.8	21.9	$\text{Ti□}_2\text{-F}$

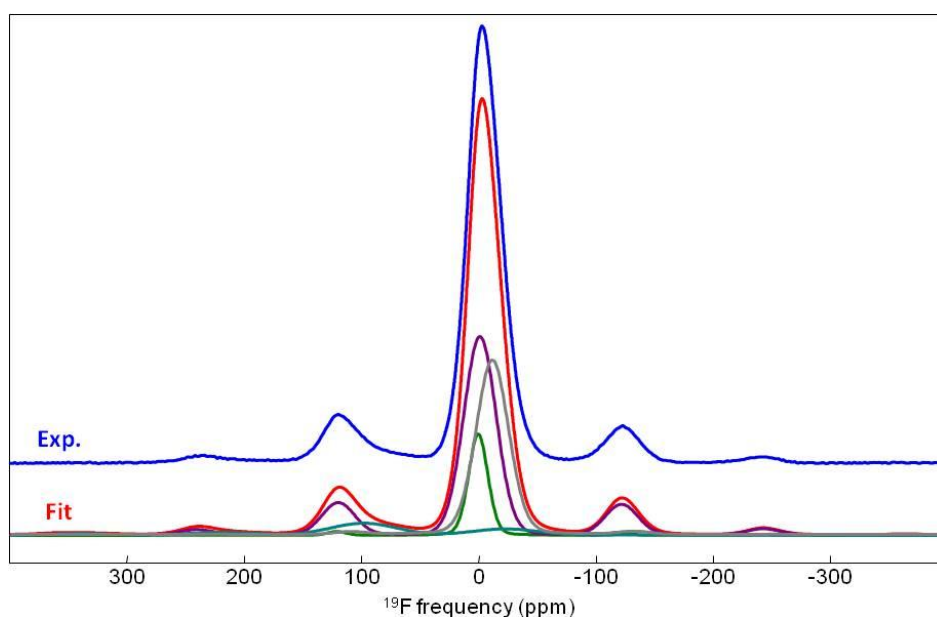


Figure S11. Experimental (blue) and fitted (red) ^{19}F MAS (34 kHz) solid state NMR spectra of the sample prepared using titanium isopropoxide as precursor, a molar ratio R equal to 2.6 and isopropanol as solvent. The individual resonances used for the fit (see Table S8) are shown below.

Table S8. 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 (34 kHz) NMR spectrum of the sample prepared using titanium isopropoxide as precursor, a molar ratio R equal to 2.6 and isopropanol as solvent and assignment of these NMR resonances.

δ_{iso}	LW	I	Assignment
-11.9	32.8	32.9	$\text{Ti}_2\text{-F}$
-1.3	32.6	47.2	$\text{Ti}_2\text{-F}$
0.2	19.3	11.6	$\text{Ti}_2\text{-F}$
97.8	66.7	8.3	$\text{Ti}\square\text{-F}$

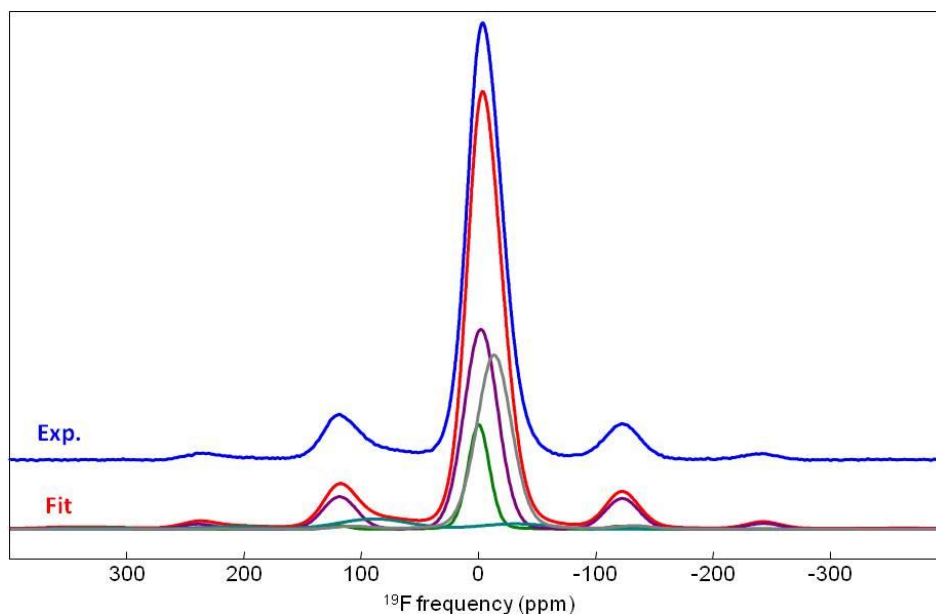


Figure S12. Experimental (blue) and fitted (red) ^{19}F MAS (34 kHz) solid state NMR spectra of the sample prepared using titanium isopropoxide as precursor, a molar ratio R equal to 3.0 and isopropanol as solvent. The individual resonances used for the fit (see Table S9) are shown below.

Table S9. 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 (34 kHz) NMR spectrum of the sample prepared using titanium isopropoxide as precursor, a molar ratio R equal to 3.0 and isopropanol as solvent and assignment of these NMR resonances.

δ_{iso}	LW	I	Assignment
-13.4	34.8	33.2	$\text{Ti}_2\text{-F}$
-0.2	21.6	12.9	$\text{Ti}_2\text{-F}$
-2.1	33.6	46.9	$\text{Ti}_2\text{-F}$
89.0	71.7	7.0	$\text{Ti}\square\text{-F}$

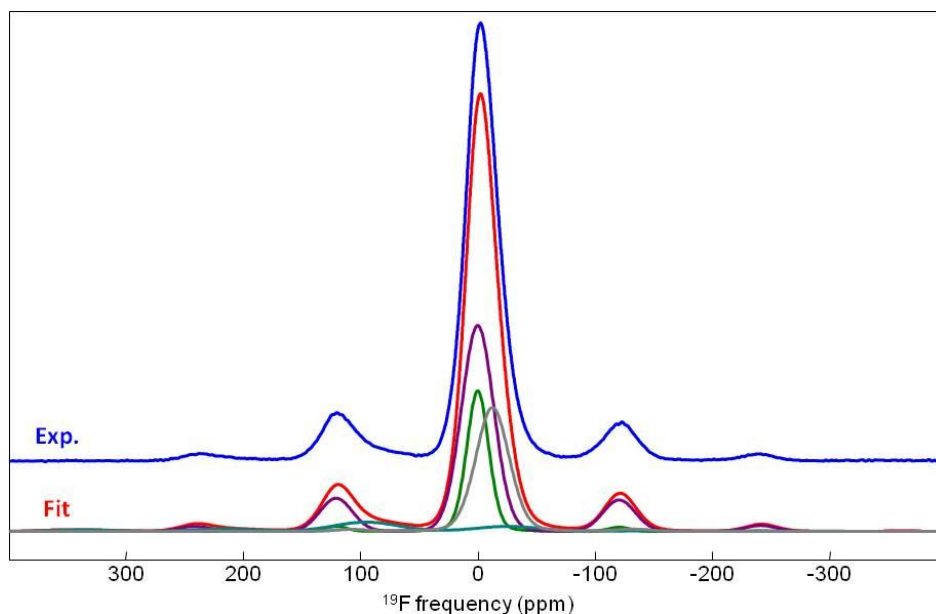


Figure S13. Experimental (blue) and fitted (red) ^{19}F MAS (34 kHz) solid state NMR spectra of the sample prepared using titanium isopropoxide as precursor, a molar ratio R equal to 3.5 and isopropanol as solvent. The individual resonances used for the fit (see Table S10) are shown below.

Table S10. 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 (34 kHz) NMR spectrum of the sample prepared using titanium isopropoxide as precursor, a molar ratio R equal to 3.5 and isopropanol as solvent and assignment of these NMR resonances.

δ_{iso}	LW	I	Assignment
-12.9	33.4	24.4	$\text{Ti}_2\text{-F}$
-0.3	22.1	19.0	$\text{Ti}_2\text{-F}$
-0.2	32.3	49.7	$\text{Ti}_2\text{-F}$
94.8	64.4	6.9	$\text{Ti}\square\text{-F}$

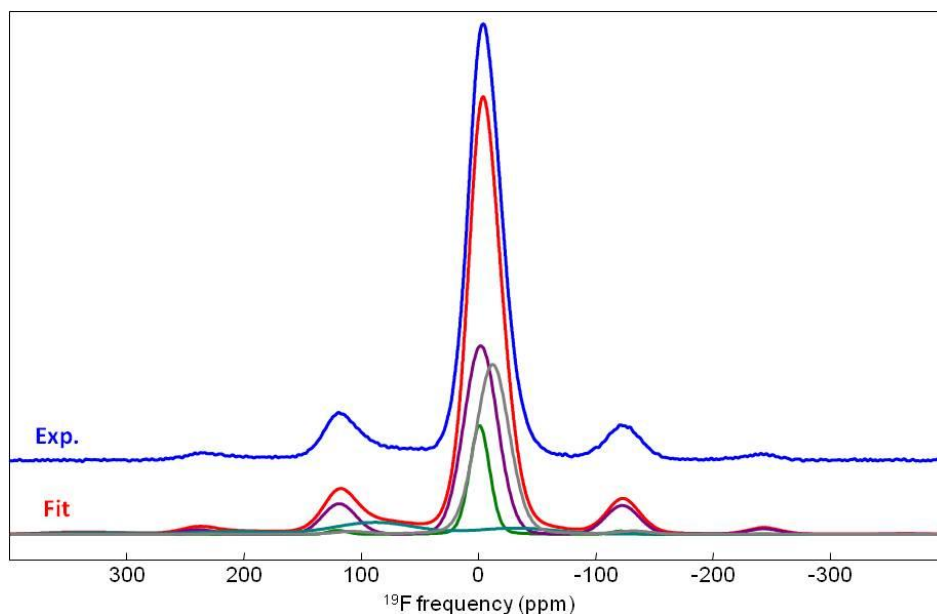


Figure S14. Experimental (blue) and fitted (red) ^{19}F MAS (34 kHz) solid state NMR spectra of the sample prepared using titanium isopropoxide as precursor, a molar ratio R equal to 3.7 and isopropanol as solvent. The individual resonances used for the fit (see Table S11) are shown below.

Table S11. 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 (34 kHz) NMR spectrum of the sample prepared using titanium isopropoxide as precursor, a molar ratio R equal to 3.7 and isopropanol as solvent and assignment of these NMR resonances.

δ_{iso}	LW	I	Assignment
-12.1	33.6	32.0	$\text{Ti}_2\text{-F}$
-2.0	33.6	45.0	$\text{Ti}_2\text{-F}$
-1.0	20.3	12.8	$\text{Ti}_2\text{-F}$
88.3	81.6	10.2	$\text{Ti}\square\text{-F}$

Table S12. 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 (34 kHz) NMR spectrum of the sample prepared using $\text{Ti}(\text{OBu})_4$ as precursor, a molar ratio R equal to 1.0 and 2-butanol as solvent and assignment of these NMR resonances.

δ_{iso}	LW	I	Assignment
-88.2	15.6	10.8	$\text{Ti}_3\text{-F}$
2.4	41.3	62.3	$\text{Ti}_2\text{-}\square\text{-F}$
95.0	95.4	27.0	$\text{Ti}\square_2\text{-F}$