New insights into Fluoride's Role in MFI Zeolites: Unveiling the Link Between Location and Synthesis Conditions.

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1. MATERIALS AND METHODS

1.1. Organic cations synthesis

The preparation of the organic cations and the synthesis procedure of silicalite-1 using the family of ethyl and propyl ammonium or phosphonium OSDAs has been previously described^{1,2} and the butyl OSDAs are commercially available (Sigma Aldrich). The tributylmethyl and di quaternary (diquats) cations family were prepared following the procedure described in literature³. The tributylmethyl ammonium/phosphonium OSDAs were synthesized by alkylating the tributyl amine (Sigma Aldrich) or phosphine (Sigma Aldrich) with iodomethane (Sigma Aldrich). For the diquats either the triethyl (ABCR) or tributyl phosphine (Sigma Aldrich) was employed by reacting them with 1,4-diiodobutane, the following reaction scheme is shown as a general example of the alkylation of an amine or phosphine:



Scheme S1. Synthesis scheme of the butane-1,4-diylbis(triethylphosphonium) cation.

Table S1 presents the chemical composition and the fluorine content as well as the volume and unit cell parameters for the complete set of samples studied including the zeolites prepared with mixture of ammonium and phosphonium cations. The sample name has been stablished by the letter code of the OSDA and in case of using a mixture, the subindex number will indicate the P-OSDA proportion.

Table S1. Chemical composition and volume and unit cell parameters of as- synthesized silicalite-1 zeolites.

Sample	OSDA / u.c	F / u.c	F/OSDA ¹	% F ₋₆₅	% F ₋₈₀	a (Å)2	b (Å)	c (Å)	Volume (ų)
TEA-MFI	4.4	3.9	0.9	99.0	1.0	19,923 (8)	19,847 (7)	13,333 (5)	5272
TEX-MFI ₂₆	4.2	3.0	0.7	98.8	1.2	19,825 (9)	19,940 (9)	13,316 (5)	5264
TEX-MFI ₄₂	4.0	3.3	0.8	98.5	1.5	19,814 (8)	19,971 (6)	13,339 (6)	5278
TEP-MFI	4.1	2.7	0.6	97.1	2.9	19,846 (7)	19,969 (6)	13,349 (4)	5291
TPA-MFI	4.5	3.3	0.74	93.1	6.9	19,920 (4)	20,034 (4)	13,376 (2)	5338
TPX-MFI ₂₆	4.1	2.6	0.64	90.3	9.7	19,927	20,043	13,385	5346

						(4)	(4)	(3)	
TPX-MFI ₄₅	4.1	2.5	0.60	87.6	12.4	19,945 (8)	20,037 (6)	13,404 (4)	5357
TPP-MFI	4.3	2.4	0.56	81.2	18.8	19,965 (9)	20,106 (9)	13,398 (6)	5378
TBA-MFI	3.6	1.8	0.50	57.4	42.4	20,094 (9)	19,969 (8)	13,421 (7)	5385
TBX-MFI ₃₃	3.4	1.9	0.54	57.2	42.8	20,108 (4)	19,955 (4)	13,432 (3)	5390
TBP-MFI	3.0	1.5	0.49	53.2	46.8	19,987 (6)	20,133 (6)	13,448 (4)	5411
TBMA-MFI	4.2	2.4	0.56	81.1	18.9	19,870 (6)	20,048 (9)	13,372 (7)	5327
TBMP-MFI	4.2	1.5	0.36	45.8	54.2	20,124 (3)	19,924 (4)	13,437 (3)	5387
EPPE-MFI	3.8	1.9	0.49	80.9	19.1	19,830 (7)	20,038 (5)	13,378 (4)	5316
BPPB-MFI	3.2	1.9	0.59	54.8	45.2	19,992 (8)	20,189 (9)	14,473 (6)	5438

2. RESULTS

2. 1. X ray diffraction patterns

Figure S1 shows the XRD patterns of the silicalite-1 samples, which are typical of the MFI type zeolite.



Figure S1. XRD patterns of the silicalite-1 zeolites synthesized using different OSDAs.

2. 2. ¹H & ²⁹Si MAS-NMR spectra of the tetrabutyl, tributylmethyl and diquats OSDAs families

The ¹H NMR spectra of the samples indicated in Figure S2a display a group of resonances in the region $\delta^1H = 0$ - 5 ppm from the organic cations, a weaker signals at $\delta^1H \sim 4.5$ ppm assigned to occluded water and another one at $\delta^1H \sim 10$ ppm of silanol groups stabilizing the negative siloxy groups, Si-O····HO-Si.^{4,5} The presence of Si-O····HO-Si groups in the zeolite is also reflected in the ²⁹Si MAS-NMR spectra (Figure S2b and S2c) by the appearance of a resonance at $\delta^{29}Si \sim -103$ ppm of Q³ sites and the broadening of the Q⁴ signals due to the existence of defects in the structure.



Figure S2. a) ¹H and b) ²⁹Si MAS-NMR spectra of the MFI zeolites synthesized with tetrabutyl, tributylmethyl and diquats families of OSDAs. c) ²⁹Si MAS-NMR spectra of selected samples displaying different intensity of the Q³ resonance.

2. 3. Synthesis of the MFI zeolite using TPA as OSDA and varying the synthesis times

We have investigated the crystallization of the MFI zeolite following the synthesis procedure detailed in the experimental section using the TPA cation as OSDA, heating at 175°C and with synthesis times of 5, 48, 168, 720 hours. The main results are depicted in **Figure S3.** Longer synthesis times favours the incorporation of fluoride into the zeolite.



Figure S3. Results obtained for the silicalite-1 obtained at different synthesis time: a) powder XRD patterns, b) ¹⁹F MAS-NMR spectra, c) quantification of the total fluoride and the¹⁹F NMR signals at about -65 ppm and -80 ppm vs time and d) quantification of the ¹⁹F NMR signals at about -65 ppm and -80 ppm vs the total amount of fluoride, e) ²⁹Si NMR spectra.

Figure S3a shows the diffractograms of the samples obtained at increasing crystallization times, which are already fully crystalline after 5 hours. The FESEM images (not shown) show that the zeolitic crystals are identical to those of the TPA-MFI sample reported in our previous studies² and no changes in size or shape were observed after enhancing the synthesis time from 5 h to 720 h.

Figure S3b displays the ¹⁹F MAS-NMR spectra of the four samples obtained at different times, which contain the signals at $\delta^{19}F \sim -65$ ppm and $\delta^{19}F \sim -80$ ppm. The relative intensity of the resonance at $\delta^{19}F \sim -80$ ppm decreases with synthesis time being practically null in the spectrum of the sample obtained at 720 h. Figure S3c shows the evolution of the intensities of the signals at $\delta^{19}F \sim -65$ and -80 ppm and the sum of both vs the synthesis time. As the synthesis time increases, the total amount of fluoride and the population of fluoride giving the signal at $\delta^{19}F \sim -65$ ppm increases, while the intensity of the signal at $\delta^{19}F \sim -80$ ppm decreases. Figure S3d shows the linear dependence of the amount of fluoride giving the ¹⁹F NMR signals at $\delta^{19}F \sim -65$ ppm and at $\delta^{19}F \sim -80$ ppm with the total amount of fluoride in the sample.

Figure S3e shows the ²⁹Si MAS NMR spectra of the MFI samples obtained at different synthesis times. The shape of the signals corresponding to Q⁴ environments becomes better resolved and the signal attributed to Q³ (defects) progressively disappears as the crystallization times increases. Moreover, when zooming the spectra in the $\delta^{29}Si \sim -120$ to -140 ppm region intermediate between the O₄Si_x-F and O₄Si resonances, a very tiny but broad band is present due to the existence of mobile fluoride species.

2.4 Theoretical Calculations

Simulation of ¹⁹F chemical shift

The structure of the MFI was taken originally from the IZA database and subsequently the lattice parameters were optimized at the PBE level of theory described in section 2.3 of the main manuscript. The four OSDA cations and four fluoride atoms were added manually to the optimized MFI framework to run simulated annealing molecular dynamics (SA-MD) to get a stable conformation of the OSDA inside the framework.

The SA-MD simulations were performed with the GFN-FF force field implemented in GULP. Simulations ran for 100 ps with six annealing cycles ranged from 100 K to 2100 K. The 100 most stable configurations were then extracted from the trajectories and subsequently optimized with GFN-FF and the most stable was optimized with PBE. The resulting optimized structures (**Figure S4**) were taken for the calculation of the absolute shielding (**Table S2**).



Figure S4. Optimized structures of final models without defects. Si, O, N, C, H, F are depicted in orange, red, blue, gray, light gray, light blue respectively.

Table S2. Predicted isotropic absolute shielding (σ_{iso}) of ¹⁹F for the models with fluoride located in the five sitting positions of the *t-mel* cage. The corresponding chemical shifts are shown in Table 2.

Structure	OSDA	σ _{iso} ¹⁹ F (ppm)
Τ8	TEA	-306.9, -307.9, -307.2, -308.1
Т9	TEA	-291.3, 291.0, -289.4, -292.2
T10	TEA	-289.6, -291.3, -291.3, -291.2
T11	TEA	-311.2, -311.3, -314.6, -312.9

T12	TEA	-308.2 -308.8, -308.7, -308.4
T8	TPA	-307.0, -307.0, -307.3, -306.8
Т9	TPA	-292.8, -293.8, -294.2, -293.1
T10	TPA	-282.7, -287.0, -285.9, -288.1
T11	TPA	-311.3, -312.3, -311.9, -312.8
T12	TPA	-304.6, -306.2, -304.7, -305.0
Т8	TBA	-312.0, -312.8, -312.1, -312.6
Т9	TBA	-295.0, -294.4, -297.9, -294.7
T10	TBA	-300.7, -301.4, -299.2, -302.2
T11	TBA	-312.0, -312.7, -312.0, -313.2
T12	TBA	-308.3, -306.4, -307.8, -305.6

To predict the ¹⁹F NMR chemical shifts, a calibration line, illustrated **Figure S5**, was constructed by correlating the experimental isotropic chemical shifts (δ_{iso}) of 18 fluorinated compounds with their calculated absolute isotropic shielding (σ iso), summarized in **Table S3**.

Table S3: Theoretical ¹⁹F σ_{iso} (ppm) values calculated with the modified Becke-Johnson exchange potential (TB-mBJ) of the reference compounds and their experimental ¹⁹F δ_{iso} (ppm) found in the bibliography.^{6,7,8} The linear regression is shown in **Figure S5**.

Fluorinated compound	σ_{iso} (TB-mBJ) (ppm)	Experimental δ_{iso} (ppm)
LiF	426.7	-204.36
NaF	449.8	-224.26
KF	358.4	-133.36
RbF	328.9	-90.9 ⁶
RbF.H ₂ O	334.1	-113.07
MgF_2	422.0	-197.36
SrF ₂	317.3	-108.0^{6}
AlF ₃	397.8	-172.0^{6}
CdF_2	416.9	-192.17
HgF ₂	411.3	-196.47

KF.2H ₂ O	350.9	-133.07
Na ₃ AlF ₆	417.8	-189.07
	417.6	-190.07
$Na_5Al_3F_{14}$	394.2	-166.07
	416.4	-182.0
	417.6	-190.0
Na_2SiF_6	378.3	-151.07
α -PbF ₂	290.7	-57.77
	263.1	-20.5
CF ₃ Cl	259.2	-28.68
CFCl ₂ CFCl ₂	298	-67.8 ⁸
SiF ₄	383.1	-163.3 ⁸



Figure S5. Correlation between experimental isotropic chemical shifts (δi_{so} , *in* ppm) and theoretical NMR shielding (σ_{iso} in ppm) calculated with TB-mBJ exchange potential for ¹⁹F in the reference fluorinated compounds listed in **Table S3**. All structures are optimized with PBE-D3. The references for the experimental values of ¹⁹F are indicated in **Table S3**.



Figure S6. Correlation of the ¹⁹F NMR chemical shift with Si–F bond length for all models, with and without defects and for all OSDA cations and fluoride positioning. The data shows a relatively high correlation coefficient of 0.80 for a lineal relationship.

In an effort to identify the structural parameters influencing the differing stabilities of fluoride positioning, we calculated the degree of distortion of the fluoride-bound T site relative to an ideal trigonal-bipyramidal geometry, which is characterized by six angles of 90 °, three angles of 120° and one angle of 180°. The *distortion degree of the fluoride environment* was defined as the average deviation of the ten F-Si-O and O-Si-O angles from those of the perfect trigonal-bipyramidal geometry. Using the geometrical parameters of the structure models of MFI with TEA, TPA, and TBA OSDAs and the fluoride located at the five different positions within the *t-mel cages*, we calculated the distortion degree (see **Table S4**) and plotted these values against the relative energy in **Figure S7**.

The left plot in **Figure S7** shows that for TEA-based models, an increase in the distortion of the fluoride environment leads to a decrease in system stability. A similar tendency is observed for TPA (middle panel), excluding the T11 site because of its highly distortion exceeding 6°. In contrast, the bulky OSDA (right panel) enforces a nearly ideal trigonal-bipyramidal environment with distortion below 2.5° for all fluoride positions, resulting in smaller energy differences in the various fluoride locations. The data illustrated in **Figure S7** are consistent with the higher relative intensity of the ¹⁹F NMR signal at δ ¹⁹F \approx -80 ppm in the TBA-MFI zeolite compared to TEA-MFI and TPA-MFI (see Figure 2), indicating that fluoride can occupy multiple positions due to the small energy difference. A breakdown of the distortion contributions is shown in **Table S4**.



Figure S7. Relative stabilization energy of the MFI models with TEA, TPA or TBA as OSDAs against the degree of distortion of the fluoride environment with respect to a perfect trigonalbipyramidal geometry. The central atom is the fluoride-bound T site. The reference angles are the following: six angles of 90 °, three angles of 120 ° and one angle of 180°. Square symbols correspond to T9 site and triangles to T12 site.

Table S4. Breakdown of the individual contributions to the deviations from the reference angles defining a perfect trigonal-bipyramidal geometry.

	90°	90°	90°	90°	90° TEA	90°	120°	120°	120°	180°	Distortion
T8	3.1	2.2	0	0.6	1.4	3.9	6.5	1.7	8.1	5.1	3.3
T9	3.6	2.9	0.8	0.4	2.9	4.1	1.1	0.6	1.2	3.3	2.1
T10	4.2	2.6	0.8	1.4	2.7	3.6	4	1.5	2	2.9	2.6
T11	3.2	1.1	0.6	0.1	2.1	4.2	6.2	5.3	11.3	6.4	4.0
T12	2	1.9	0.5	1	1.2	2.5	4	3.1	7	3.7	2.7
					TPA						
T8	2.8	2.3	0.2	0.9	1.1	3.5	5.7	2.5	7.9	4.6	3.1
T9	3.1	2.7	0.8	0.4	2.8	3.5	1.8	0.3	1.1	2.9	1.9
T10	5.6	2.7	0.8	2.3	2.9	4	5.1	1.6	2.7	3.4	3.1
T11	2.8	2.3	1.5	1	4.2	6.7	9.9	8.9	18.7	10.9	6.7
T12	2.8	1.9	0.1	0.9	1.6	2.9	4.4	2.8	7	4	2.8
					TBA						
T8	1.2	0.9	0.7	0.6	1	1.2	1	0.2	1.1	0.6	0.8
T9	3.1	2.7	1.5	0.4	2.3	4.7	2.6	0.3	2.3	2.5	2.3
T10	2.4	2.1	1.5	0.7	1.3	4.1	2.3	1	2.9	2.2	2.0
T11	1.3	0.9	0.5	0.4	0.9	1.5	1.3	0	1.2	1	0.9
T12	2.5	1.6	0.4	0.2	1.8	3.1	2.4	0.1	2.1	2.1	1.6

Simulation of connectivity defects

To study the possible influence of connectivity defects in the local environment of the fluoride anions, we calculated the δ^{19} F including such defects in the models. We chose TPA as OSDA because by including three fluorides and one connectivity defect in the unit cell we have a realistic model that matches the composition of the TPA-MFI sample, 3 F/u.c and a F/OSDA ratio of 0.75. To build the model with the most stable connectivity defects for TPA we started with the MFI framework containing one TPA cation with the same configuration as the optimized models with four OSDA. For this starting structure one connectivity defect was created by removing one Si atom from all possible Si positions in radius of 7 Å centered at the N atom of the TPA, resulting in 24 structures. Three different TPA cations conformations were considered for each of the 24 structures, totaling 72 structures containing four uncoordinated oxygen atoms due to the removal of Si. For each of these structures we considered four ways of compensating with H three of the four uncoordinated O atoms. Thus, the models had connectivity defects as proposed in the literature⁹ and the final pool contained 288 models (**Figure S8**).



Figure S8. Relative energies of the optimized geometries of the 288 defective models.

A first screening was carried out by optimizing these models with GFN-FF force field proposed by Grimme¹⁰ and implemented in the GULP¹¹ version 6.1.2. Next, the five most stable structures labeled D1 to D5 (**Figure S9**) with distinct positioning were chosen to be included in the models with four OSDAs and three fluoride anions for subsequent DFT optimization and calculation of the chemical shift.



Figure S9. DFT Optimized structures of the five geometries with connectivity defects (D1, D2, D3, D4 and D5 from left to right). The F atoms and TPA are not shown for clarity. The four fused 6-ring units and H atoms are shown with balls. The rest of the framework is shown with lines. Si, O and H are depicted in orange, red, gray, light gray respectively.

Table S5 shows the relative energy and the predicted δ^{19} F of each of the four most stable connectivity defects models with TPA. In these models, the calculated δ^{19} F are very similar to those reported in **Table 2**. The values of δ^{19} F for the models with F in T9 and T10 range from - 58 to -69 ppm which can be related to the signal of -65 ppm. Like the defectless models, the predicted δ^{19} F for positions T8, T11 and T12 lie between -75 and -83 ppm which can be associated with the signal at -80 ppm.

The inclusion of connectivity defects in the models do not change the relative energy trend observed in **Table 2**. The model with fluoride in T9 is the most stable and those with fluoride in T8 and T11 are noticeable the most unstable. Note that in the calculations with connectivity defects, relative energies are generally lower than the models without connectivity defects, especially for the models with the defect created by omission of T3 site. **Figure S10** shows the five connectivity defects considered after a screening of all possible connectivity defects in the MFI topology.



Figure S10. (Upper panel) Optimized structures of the models with F located in T9 position and the three OSDAs considered (from left to right TEA, TPA, and TBA). (Lower panel) DFT Optimized structures of the five geometries with connectivity defects (D1, D2, D3, D4 and D5 from left to right). These are also represented in another orientation in **Figure S9**. The atoms involved in the connectivity defect and those of the OSDAs are shown with balls. The rest of the framework is shown with lines. Si, O, N, C, H, F are depicted in orange, red, blue, gray, light gray, light blue respectively.

E_{rel} (kJ/mol) σ_{iso} ¹⁹F (ppm) δ_{iso}^{19} F Pred. (ppm) Structure defects -306, -305, -306 **T8** -76, -75, -76 D1 86 -294, -299, -296 T9 D1 0 -63, -68, -65 -289, -295, -290 D1 -58, -64, -59 T10 63 -313, -312, -312 85 -83, -81, -81 T11 D1 T12 -303, -309, -309 D1 58 -72, -78, -79 -307, -303, -307 86 -76, -73, -77 **T8** D2 -292, -296, -294 Т9 D2 0 -60, -65, -63 -289, -291, -291 T10 D2 11 -58, -60, -60 -312, -311, -311 T11 D2 92 -82, -81, -81 9 -302, -308, -308 T12 D2 -71, -77, -77 -307, -303, -306 72 **T8** D3 -76, -72, -76 -292, -295, -292 T9 D3 0 -61, -63, -60 -294, -295, -293 T10 D3 -62, -64, -61 16 -311, -311, -314 T11 D3 96 -81, -81, -83 -306, -302, -308 T12 D3 22 -75, -71, -77 **T8** D4 75 -76, -71, -76 -307, -302, -306 0 -293, -300, -292 **T9** D4 -61, -69, -61 -291, -296, -289 D4 22 T10 -60, -65, -57 -311, -312, -310 T11 D4 105 -81, -81, -80 -304, -309, -305 T12 D4 35 -74, -79, -74 -307, -305, -307 **T8** D5 67 -77, -74, -77 -293, -299, -292 **T9** D5 0 -61, -68, -61 T10 D5 17 -62, -58, -64 -293, -290, -295 -311, -313, -310 T11 D5 103 -80, -83, -79 -306, -306, -310 T12 D5 30 -75, -76, -79

Table S5. Predicted isotropic chemical shift (δ_{iso}^{19} F), and relative energy (E_{rel}) of defective models with F located in the five sitting positions of *t-mel* cage. The δ_{iso}^{19} F were calculated using regression shown in **Figure S5** as predictor variable the absolute isotropic shielding calculated with the TB-mBJ functional.

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