Supplementary Information

Combined Solid State NMR and X-ray Diffraction Investigation of the Local Structure of the Five-Coordinate Silicon in Fluoride-Containing As-Synthesized STF Zeolite

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Equations and Parameters for Fitting CP and REDOR NMR Data

Table S1. Complete fitting parameters for the $^{19}F \rightarrow ^{29}Si$ CP curves

Peak	M_{CP} (arb. units)	x	T_{CP} (ms)	$T_{1\rho}$ (ms)	T_{damp} (ms)	D (Hz)	r (Å)
A	162	0.25	2.6	1000	7	4420 ± 220	1.72 ± 0.03
B	75	0.28	0.75	1000	4	820 ± 80	3.02 ± 0.10
C	71	0.21	0.75	1000	5	820 ± 80	3.02 ± 0.10
F	43	0.30	0.80	1000	8	600 ± 80	3.35 ± 0.15
H	63	0.40	2.0	1000	5	820 ± 100	3.02 ± 0.13
J	160	0.32	3.7	1000	3.4	1200 ± 100	2.66 ± 0.07
K	60	0.10	3.7	1000	5	800 ± 50	3.04 ± 0.06

The following description of the equations for CP and REDOR can also be found in reference 16.

Equations for Cross Polarization

Since the $^{19}F/^{29}Si$ spin pairs are not completely isolated, these CP curves will have contributions from both the isolated spin pairs and from the extended network of ^{19}F nuclei. Therefore they were fit to a linear combination of two functions:

$$S_{CP}(t) = M_{CP} [\, x\, S_{\text{isolated}}(t) + (1\text{-}x)\, S_{\text{network}}(t) \,] \qquad \text{(S1)}$$

M_{CP} is a scaling factor and S_{network} describes the signal arising from the extended network of ^{19}F nuclei and is described by the exponential growth-decay equation:

$$S_{\text{network}}(t) = \frac{\exp(-t/T_{1\rho}) - \exp(-t/T_{CP})}{1-(T_{CP}/T_{1\rho})} \qquad \text{(S2)}$$

where T_{CP} is the rate constant for the growth of magnetization and $T_{1\rho}$ is the rate constant for magnetization decay due to spin lock relaxation. S_{isolated} is the signal arising from the isolated spin pair and can be described by the equation

$$S_{\text{isolated}}(t) = \tfrac{1}{2}\left(\exp(-t/T_{1\rho}) - \exp(-t/T_{\text{damp}})\, g_{\pm 1}(t)\right) \tag{S3}$$

where T_{damp} is the rate constant for the damping of the oscillation function, $g_{\pm 1}(t)$

$$g_{\pm 1}(t) = \tfrac{1}{2}\int_0^{\pi} \cos\left(\frac{\pi \boldsymbol{D} t}{\sqrt{2}}\sin(2\theta)\right) \sin\theta \, d\theta \tag{S4}$$

The integral in Equation S4 can be expressed as a sum of Bessel functions of the first-kind, therefore

$$g_{\pm 1}(t) = J_0\left(\frac{\pi \boldsymbol{D} t}{\sqrt{2}}\right) + 2\sum_{k=1}^{\infty} \frac{1}{1-4(2k)^2} J_{2k}\left(\frac{\pi \boldsymbol{D} t}{\sqrt{2}}\right) \tag{S5}$$

Finally, $\boldsymbol{D}$ is the heteronuclear dipolar coupling constant (in Hz) between the two isolated spin-½ nuclei, which is related to $\boldsymbol{r}$, the distance between the two nuclei:

$$\boldsymbol{D} = (\mu_0 \gamma_I \gamma_S h) / (16\pi^3 \boldsymbol{r}^3) \tag{S6}$$

Equation for REDOR

Integral form:

$$\Delta S / S_0 = M_R\left(1 - \frac{1}{2\pi}\int_0^{\pi}\int_0^{\pi} \cos(n\boldsymbol{D}\tau_r \sin\beta \sin\alpha)\sin\beta \, d\beta \, d\alpha\right)$$

This integral expression can also be expressed as a sum of Bessel Functions of the first kind:

$$\Delta S / S_0 = M_R\left(1 - [J_0(\sqrt{2}\, n\boldsymbol{D}\tau_r)]^2 + 2\sum_{k=1}^{\infty} \frac{1}{16k^2 - 1}[J_k(\sqrt{2}\, n\boldsymbol{D}\tau_r)]^2\right) \tag{S7}$$

For the fit presented in Figure 5, τ_r = 1/15000 Hz = 6.67 × 10^{-5} s, M_R = 1, and $\boldsymbol{D}$ = 4.4 ± 0.4 kHz.

Crystal Structure Determination of [F,DMABO]-STF

Please note the following tables use the notation Si3A and Si3B for Si3' and Si3 respectively.

The maximum electron density was measured 0.7Å from the framework and could not be refined as a chemically sensible atom.

Table S2. Crystal data and structure refinement for [F,DMABO]-STF.

Identification code	[F,DMABO]-STF
Empirical formula	C24 H48 F2 N2 O64 Si32
Formula weight	2325.52
Temperature	150(2) K
Wavelength	0.68920 A
Crystal system, space group	monoclinic, P2(1)/c
Unit cell dimensions	a = 7.4573(2)A alpha = 90 deg.
	b = 18.0966(5)A beta = 99.254(1) deg.
	c = 14.0233(4)A gamma = 90 deg.
Volume	1867.84(9) A^3
Z, Calculated density	1, 2.067 Mg/m^3
Absorption coefficient	0.531 mm^-1
F(000)	1184
Crystal size	0.02 x 0.02 x 0.015 mm
Theta range for data collection	2.61 to 29.54 deg.
Limiting indices	-10<=h<=10, -25<=k<=24, -19<=l<=18
Reflections collected / unique	18869 / 5414 [R(int) = 0.0469]
Completeness to theta = 29.54	92.1 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5414 / 222 / 339
Goodness-of-fit on F^2	1.064
Final R indices [I>2sigma(I)]	R1 = 0.0708, wR2 = 0.1602
R indices (all data)	R1 = 0.0892, wR2 = 0.1676
Largest diff. peak and hole	1.703 and -1.706 e.A^-3

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for [F,DMABO]-STF. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Si(1)	4164(2)	7540(1)	9016(1)	10(1)
Si(2)	3217(2)	11624(1)	7097(1)	12(1)
Si(3A)	4126(4)	12558(2)	8818(2)	8(1)
O(1A)	3595(14)	11852(5)	8169(7)	15(3)
O(10A)	4804(11)	12314(5)	9903(6)	15(2)
O(14A)	5678(11)	13029(5)	8418(6)	23(2)
O(16A)	2428(10)	13108(4)	8715(6)	23(2)
Si(3B)	4272(5)	12664(2)	8910(2)	10(1)
O(1B)	3840(14)	11837(5)	8251(7)	10(3)
O(10B)	4976(11)	12181(5)	9911(6)	11(2)
O(14B)	5935(11)	12895(4)	8341(5)	13(2)
O(16B)	2125(12)	12913(5)	8616(6)	26(2)
Si(4)	-594(2)	8503(1)	6149(1)	17(1)
Si(5)	7774(2)	10073(1)	5755(1)	13(1)
Si(6)	3215(2)	8495(1)	7276(1)	11(1)
Si(7)	3951(2)	10032(1)	6432(1)	11(1)
Si(8)	9452(2)	11639(1)	5897(1)	17(1)
O(2)	3843(4)	8302(2)	8405(2)	16(1)
O(3)	3379(4)	10745(2)	6992(2)	19(1)
O(4)	3715(5)	9344(2)	7116(2)	20(1)
O(5)	1055(5)	8373(2)	7024(3)	24(1)
O(6)	8968(5)	10793(2)	6080(3)	23(1)
O(7)	6020(5)	10107(2)	6277(3)	24(1)
O(8)	1154(5)	11870(2)	6697(3)	27(1)
O(9)	7309(5)	10057(2)	4600(2)	22(1)
O(11)	2206(5)	7171(2)	9009(3)	33(1)
O(12)	-1042(5)	9369(2)	6128(3)	24(1)
O(13)	32(5)	8256(2)	5152(3)	29(1)
O(15)	5425(6)	7001(2)	8528(2)	31(1)
F(1)	4678(9)	13473(3)	9588(4)	27(1)
N(1)	-500(20)	10743(7)	9466(9)	71(5)
C(2)	-150(20)	10069(8)	8836(9)	62(4)
C(3)	1110(30)	9370(11)	10870(10)	114(10)
C(4)	-980(20)	9422(7)	9289(10)	81(5)
C(5)	1470(30)	8759(12)	11621(13)	127(12)
C(6)	-2300(20)	9780(11)	9898(14)	208(17)
C(7)	-1080(20)	10397(8)	10407(11)	95(7)
C(8)	1230(30)	11201(10)	9767(18)	59(10)
C(9)	-2000(30)	8954(12)	8529(15)	150(13)
C(10)	400(30)	9019(10)	9943(10)	196(16)
C(11)	-2030(30)	11222(14)	8940(16)	120(30)
C(12)	-150(50)	9910(16)	11196(12)	310(30)
C(13)	2910(50)	9731(19)	10820(30)	300(30)

Table S4. Interatomic distances (Å) and angles (°) for [F,DMABO]-STF.

Si(1)-O(15)	1.585(4)
Si(1)-O(11)	1.604(4)
Si(1)-O(10A)#1	1.608(8)
Si(1)-O(10B)#1	1.618(8)
Si(1)-O(2)	1.621(3)
Si(2)-O(1A)	1.540(9)
Si(2)-O(15)#2	1.595(4)
Si(2)-O(3)	1.604(3)
Si(2)-O(8)	1.613(3)
Si(2)-O(1B)	1.656(10)
Si(3A)-O(1A)	1.581(9)
Si(3A)-O(10A)	1.587(8)
Si(3A)-O(16A)	1.598(8)
Si(3A)-O(14A)	1.609(8)
Si(3A)-F(1)	1.983(6)
O(10A)-Si(1)#1	1.608(8)
O(14A)-Si(6)#2	1.612(8)
O(16A)-Si(4)#3	1.582(7)
Si(3B)-O(14B)	1.633(8)
Si(3B)-O(16B)	1.650(9)
Si(3B)-O(10B)	1.666(9)
Si(3B)-F(1)	1.744(7)
Si(3B)-O(1B)	1.762(10)
O(10B)-Si(1)#1	1.618(8)
O(14B)-Si(6)#2	1.582(7)
O(16B)-Si(4)#3	1.635(9)
Si(4)-O(16A)#4	1.582(7)
Si(4)-O(12)	1.601(4)
Si(4)-O(13)	1.607(4)
Si(4)-O(5)	1.609(3)
Si(4)-O(16B)#4	1.635(9)
Si(5)-O(12)#5	1.590(3)
Si(5)-O(7)	1.600(4)
Si(5)-O(9)	1.601(3)
Si(5)-O(6)	1.602(3)
Si(6)-O(14B)#6	1.582(7)
Si(6)-O(4)	1.605(3)
Si(6)-O(5)	1.608(4)
Si(6)-O(14A)#6	1.612(8)
Si(6)-O(2)	1.615(3)
Si(7)-O(7)	1.598(3)
Si(7)-O(4)	1.599(3)
Si(7)-O(9)#7	1.601(3)
Si(7)-O(3)	1.605(3)
Si(8)-O(11)#2	1.590(4)
Si(8)-O(13)#7	1.591(4)
Si(8)-O(6)	1.602(4)
Si(8)-O(8)#5	1.608(3)
O(8)-Si(8)#8	1.608(3)
O(9)-Si(7)#7	1.601(3)
O(11)-Si(8)#6	1.590(3)
O(12)-Si(5)#8	1.590(3)
O(13)-Si(8)#7	1.591(4)

O(15)-Si(2)#6	1.595(4)
N(1)-C(11)	1.524(16)
N(1)-C(8)	1.535(17)
N(1)-C(2)	1.553(14)
N(1)-C(7)	1.584(16)
C(2)-C(4)	1.510(12)
C(3)-C(10)	1.466(13)
C(3)-C(12)	1.476(14)
C(3)-C(13)	1.508(14)
C(3)-C(5)	1.520(13)
C(4)-C(10)	1.458(13)
C(4)-C(9)	1.473(12)
C(4)-C(6)	1.545(14)
C(6)-C(7)	1.540(15)
C(7)-C(12)	1.497(14)

O(15)-Si(1)-O(11)	110.1(2)
O(15)-Si(1)-O(10A)#1	106.3(4)
O(11)-Si(1)-O(10A)#1	111.8(3)
O(15)-Si(1)-O(10B)#1	114.8(4)
O(11)-Si(1)-O(10B)#1	111.1(3)
O(10A)#1-Si(1)-O(10B)#1	9.6(4)
O(15)-Si(1)-O(2)	110.05(18)
O(11)-Si(1)-O(2)	107.10(19)
O(10A)#1-Si(1)-O(2)	111.5(3)
O(10B)#1-Si(1)-O(2)	103.3(3)
O(1A)-Si(2)-O(15)#2	112.9(4)
O(1A)-Si(2)-O(3)	110.5(4)
O(15)#2-Si(2)-O(3)	108.0(2)
O(1A)-Si(2)-O(8)	106.3(4)
O(15)#2-Si(2)-O(8)	110.2(2)
O(3)-Si(2)-O(8)	108.91(18)
O(1A)-Si(2)-O(1B)	6.0(6)
O(15)#2-Si(2)-O(1B)	109.5(4)
O(3)-Si(2)-O(1B)	107.8(3)
O(8)-Si(2)-O(1B)	112.2(4)
O(1A)-Si(3A)-O(10A)	109.8(5)
O(1A)-Si(3A)-O(16A)	109.2(5)
O(10A)-Si(3A)-O(16A)	112.7(4)
O(1A)-Si(3A)-O(14A)	110.8(5)
O(10A)-Si(3A)-O(14A)	110.2(5)
O(16A)-Si(3A)-O(14A)	104.0(4)
O(1A)-Si(3A)-F(1)	176.8(5)
O(10A)-Si(3A)-F(1)	72.8(4)
O(16A)-Si(3A)-F(1)	67.8(4)
O(14A)-Si(3A)-F(1)	69.5(4)
Si(2)-O(1A)-Si(3A)	140.1(7)
Si(3A)-O(10A)-Si(1)#1	152.7(6)
Si(3A)-O(14A)-Si(6)#2	162.6(6)
Si(4)#3-O(16A)-Si(3A)	163.3(6)
O(14B)-Si(3B)-O(16B)	126.2(5)
O(14B)-Si(3B)-O(10B)	112.6(4)
O(16B)-Si(3B)-O(10B)	121.0(5)
O(14B)-Si(3B)-F(1)	88.4(4)
O(16B)-Si(3B)-F(1)	89.1(4)
O(10B)-Si(3B)-F(1)	88.7(4)
O(14B)-Si(3B)-O(1B)	92.9(5)

O(16B)-Si(3B)-O(1B)	90.7(5)
O(10B)-Si(3B)-O(1B)	90.1(5)
F(1)-Si(3B)-O(1B)	178.5(4)
Si(2)-O(1B)-Si(3B)	135.1(6)
Si(1)#1-O(10B)-Si(3B)	130.1(6)
Si(6)#2-O(14B)-Si(3B)	147.7(6)
Si(4)#3-O(16B)-Si(3B)	144.0(6)
O(16A)#4-Si(4)-O(12)	105.2(3)
O(16A)#4-Si(4)-O(13)	110.9(3)
O(12)-Si(4)-O(13)	110.2(2)
O(16A)#4-Si(4)-O(5)	114.3(3)
O(12)-Si(4)-O(5)	106.85(19)
O(13)-Si(4)-O(5)	109.3(2)
O(16A)#4-Si(4)-O(16B)#4	15.2(4)
O(12)-Si(4)-O(16B)#4	119.5(4)
O(13)-Si(4)-O(16B)#4	107.7(3)
O(5)-Si(4)-O(16B)#4	102.9(3)
O(12)#5-Si(5)-O(7)	109.3(2)
O(12)#5-Si(5)-O(9)	109.67(19)
O(7)-Si(5)-O(9)	113.8(2)
O(12)#5-Si(5)-O(6)	107.7(2)
O(7)-Si(5)-O(6)	107.24(19)
O(9)-Si(5)-O(6)	108.87(19)
O(14B)#6-Si(6)-O(4)	117.2(3)
O(14B)#6-Si(6)-O(5)	105.1(3)
O(4)-Si(6)-O(5)	110.35(19)
O(14B)#6-Si(6)-O(14A)#6	12.0(4)
O(4)-Si(6)-O(14A)#6	105.3(3)
O(5)-Si(6)-O(14A)#6	112.8(3)
O(14B)#6-Si(6)-O(2)	108.0(3)
O(4)-Si(6)-O(2)	107.83(17)
O(5)-Si(6)-O(2)	107.92(18)
O(14A)#6-Si(6)-O(2)	112.5(3)
O(7)-Si(7)-O(4)	110.5(2)
O(7)-Si(7)-O(9)#7	109.0(2)
O(4)-Si(7)-O(9)#7	111.04(19)
O(7)-Si(7)-O(3)	109.65(19)
O(4)-Si(7)-O(3)	105.60(18)
O(9)#7-Si(7)-O(3)	111.07(18)
O(11)#2-Si(8)-O(13)#7	108.1(2)
O(11)#2-Si(8)-O(6)	111.6(2)
O(13)#7-Si(8)-O(6)	110.9(2)
O(11)#2-Si(8)-O(8)#5	108.76(19)
O(13)#7-Si(8)-O(8)#5	109.4(2)
O(6)-Si(8)-O(8)#5	108.1(2)
Si(6)-O(2)-Si(1)	134.2(2)
Si(2)-O(3)-Si(7)	150.8(2)
Si(7)-O(4)-Si(6)	151.6(2)
Si(6)-O(5)-Si(4)	139.7(2)
Si(8)-O(6)-Si(5)	149.3(3)
Si(7)-O(7)-Si(5)	159.6(3)
Si(8)#8-O(8)-Si(2)	140.5(2)
Si(7)#7-O(9)-Si(5)	156.4(3)
Si(8)#6-O(11)-Si(1)	166.2(3)
Si(5)#8-O(12)-Si(4)	153.3(2)
Si(8)#7-O(13)-Si(4)	156.7(3)
Si(1)-O(15)-Si(2)#6	166.8(3)

Si(3B)-F(1)-Si(3A)	1.97(19)
C(11)-N(1)-C(8)	110.9(11)
C(11)-N(1)-C(2)	110.5(10)
C(8)-N(1)-C(2)	111.8(10)
C(11)-N(1)-C(7)	110.1(10)
C(8)-N(1)-C(7)	108.5(10)
C(2)-N(1)-C(7)	104.9(9)
C(4)-C(2)-N(1)	104.7(9)
C(10)-C(3)-C(12)	113.9(9)
C(10)-C(3)-C(13)	110.1(12)
C(12)-C(3)-C(13)	110.0(12)
C(10)-C(3)-C(5)	107.4(11)
C(12)-C(3)-C(5)	108.5(11)
C(13)-C(3)-C(5)	106.7(11)
C(10)-C(4)-C(9)	113.3(11)
C(10)-C(4)-C(2)	111.0(11)
C(9)-C(4)-C(2)	109.9(10)
C(10)-C(4)-C(6)	108.0(9)
C(9)-C(4)-C(6)	109.9(10)
C(2)-C(4)-C(6)	104.3(9)
C(7)-C(6)-C(4)	100.4(8)
C(12)-C(7)-C(6)	94.8(16)
C(12)-C(7)-N(1)	133.7(17)
C(6)-C(7)-N(1)	97.0(11)
C(4)-C(10)-C(3)	117.3(8)
C(3)-C(12)-C(7)	113.9(11)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z+2 #2 -x+1,y+1/2,-z+3/2
#3 -x,y+1/2,-z+3/2 #4 -x,y-1/2,-z+3/2
#5 x+1,y,z #6 -x+1,y-1/2,-z+3/2 #7 -x+1,-y+2,-z+1
#8 x-1,y,z

Table S5. Anisotropic displacement parameters (A^2 x 10^3) for [F,DMABO]-STF. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Si(1)	10(1)	15(1)	6(1)	0(1)	0(1)	-2(1)
Si(2)	10(1)	9(1)	16(1)	-1(1)	1(1)	-2(1)
Si(4)	11(1)	17(1)	22(1)	1(1)	-1(1)	-4(1)
Si(5)	8(1)	16(1)	14(1)	-4(1)	1(1)	0(1)
Si(6)	13(1)	10(1)	10(1)	-1(1)	1(1)	2(1)
Si(7)	9(1)	9(1)	14(1)	-2(1)	2(1)	0(1)
Si(8)	10(1)	18(1)	21(1)	-11(1)	-2(1)	3(1)
O(2)	21(2)	15(1)	10(1)	0(1)	-1(1)	0(1)
O(3)	20(2)	11(1)	26(2)	-5(1)	3(1)	4(1)
O(4)	30(2)	12(1)	18(1)	2(1)	6(1)	-3(1)
O(5)	15(2)	25(2)	28(2)	10(1)	-4(1)	-2(1)
O(6)	19(2)	22(2)	29(2)	-9(1)	2(1)	-9(1)
O(7)	14(2)	33(2)	27(2)	-4(1)	7(1)	-3(1)
O(8)	16(2)	20(2)	39(2)	-15(1)	-13(1)	6(1)
O(9)	21(2)	30(2)	14(1)	0(1)	-1(1)	-2(1)
O(11)	18(2)	45(2)	32(2)	15(2)	-7(2)	-21(2)
O(12)	16(2)	23(2)	30(2)	0(1)	-5(1)	6(1)
O(13)	32(2)	30(2)	26(2)	-4(2)	9(2)	-3(2)
O(15)	47(2)	33(2)	16(2)	0(1)	16(2)	19(2)
F(1)	38(3)	19(3)	21(3)	-7(2)	0(2)	0(2)
N(1)	113(14)	74(10)	32(8)	4(7)	34(8)	46(10)
C(2)	57(10)	95(12)	37(7)	2(7)	18(7)	30(8)
C(3)	180(20)	130(20)	39(10)	46(11)	49(10)	70(15)
C(4)	94(15)	80(12)	75(12)	-14(8)	29(8)	4(9)
C(5)	160(20)	170(20)	70(11)	85(15)	65(14)	101(19)
C(6)	200(20)	160(30)	330(40)	-140(20)	230(30)	-122(18)
C(7)	111(18)	72(13)	111(18)	-12(10)	49(14)	19(10)
C(8)	58(18)	16(10)	110(30)	33(13)	37(18)	-2(10)
C(9)	140(20)	230(30)	91(17)	-56(18)	52(13)	-90(20)
C(10)	340(40)	150(30)	77(14)	44(14)	-40(20)	50(20)
C(11)	170(50)	120(30)	110(30)	110(30)	110(30)	130(40)
C(12)	480(60)	250(50)	200(30)	60(30)	90(30)	280(50)
C(13)	330(50)	150(40)	410(80)	70(50)	60(50)	-90(30)