

Electronic Supporting Information

Preferential orientations of structure directing agents in zeolites

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1. Synthesis and characterisation of the asymmetric SDA

The alkyltripropylammonium halides $\text{RN}(\text{C}_3\text{H}_7)_3^+\text{Br}^-$ ($\text{R} \equiv \text{Et, Bu, EtOH}$) were prepared by reacting the corresponding alkyl halide with tripropylamine. As an example, ethyltripropylammonium bromide was prepared by refluxing 0.1 mole of tripropylamine and 0.1 mole of ethylbromide in acetonitrile for 24 hours. Then, the solution was cooled and the solvent was removed by rotary evaporation at reduced pressure. The recovered solids were recrystallised in ethyl acetate, and further characterised using solution-state ^1H and ^{13}C NMR (*vide infra*).

tripropylethylammonium bromide (TPEABr) in CDCl_3

Chain Position	α	Propyl		Ethyl	
		β	γ	α	β
$^1\text{H } \delta_{\text{iso}}$ (ppm)	3.3	1.8	1.1	3.3	1.4
$^{13}\text{C } \delta_{\text{iso}}$ (ppm)	60.2	15.9	10.9	54.8	8.2

butyltripropylammonium bromide (BTABr) in CDCl_3

Chain Position	α	Propyl		Butyl			
		β	γ	α	β	γ	δ
$^1\text{H } \delta_{\text{iso}}$ (ppm)	3.2	1.8	0.9	3.2	1.7	1.3	0.9
$^{13}\text{C } \delta_{\text{iso}}$ (ppm)	60.8	16.0	10.9	59.1	24.2	19.8	13.7

2-hydroxy-ethyl-tripropylammonium (EtOHTPABr) in CDCl_3

Chain Position	α	Propyl		EtOH		OH
		β	γ	α	β	
$^1\text{H } \delta_{\text{iso}}$ (ppm)	3.4	1.8	1.0	3.4	3.6	4.1
$^{13}\text{C } \delta_{\text{iso}}$ (ppm)	55.5	15.8	10.8	60.7	61.2	---

tetrapropylammonium bromide (TPABr) in CDCl_3

Chain Position	α	Propyl	
		β	γ
$^1\text{H } \delta_{\text{iso}}$ (ppm)	3.3	1.8	1.1
$^{13}\text{C } \delta_{\text{iso}}$ (ppm)	60.2	15.9	10.9

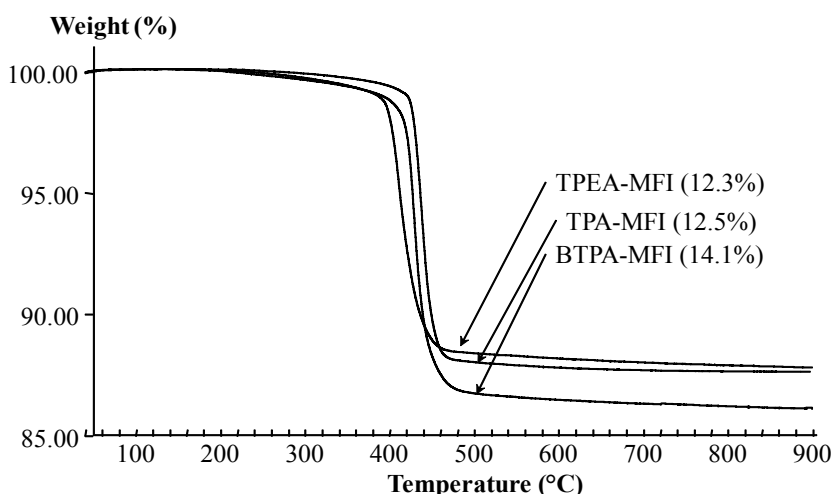
2. Synthesis of zeolites

The synthesis of zeolites was done by hydrothermal treatment of an aqueous gel. Typically 2.2g of NH_4F were dissolved in 39.6g of water by stirring at ambient temperature in presence of 8.3×10^{-3} mole of the used SDA. After a total dissolution, 4.0 g of fumed silica (Aerosil 200) were added. Then, the mixture was transferred to a 50 mL Teflon coated autoclave and heated at 175°C during 5 days. The obtained powders were washed abundantly with distilled water and heated at 80°C overnight. The yields of all the synthesis were similar (75 - 80%). The theoretical formula of the as-synthesised zeolites is $\text{SiO}_2[\text{R}(\text{Pr})_3\text{NF}]_{1/24}$ (*vide infra*).

3. TGA and elemental analyses

The experimental weight losses measured by thermogravimetric analyses (TGA, curves below) are very close to the expected theoretical losses considering a molar ratio $\text{Si}/\{\text{R}(\text{Pr})_3\text{N}^+\}$ equal to 24 (see Table below). The experimental Si/F molar ratios obtained from elemental analyses are also consistent with an expected Si/F molar ratio of 24.

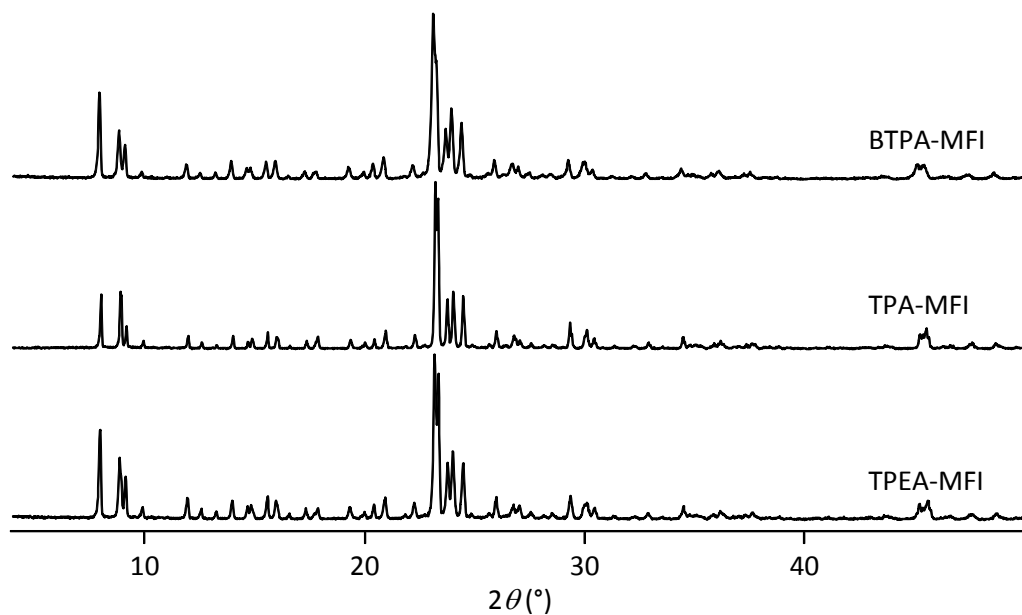
TGA were performed on a NETZSCH TG 209, under air with a 293-1173 K temperature ramp and a heating rate of $10 \text{ K}\cdot\text{min}^{-1}$. Elemental analyses were done at the CNRS facility "Service Central d'Analyse" (Vernaison, France), using Inductive Coupled Plasma (for Si) and ionic chromatography with a specific electrode (for F). See: <http://www.sca.cnrs.fr/> for more details.



	Expected weight loss (%)	Experimental weight loss (%)	Experimental Si/F
TPEA-MFI	11.7	12.3	28.7
TPA-MFI	12.4	12.5	25.3
BTPA-MFI	13.2	14.1	28.6

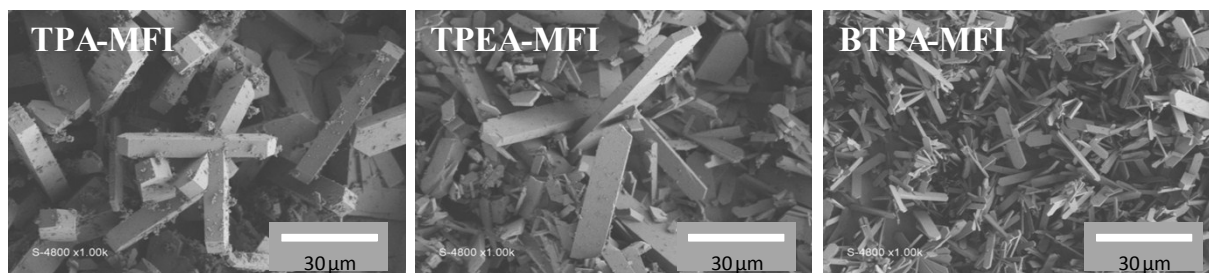
4. X-Ray diffraction

The X-Ray diffraction (XRD) powder patterns presented below were collected on a Bruker AXS D8 diffractometer using a Cu-K α radiation.



5. Scanning Electron Microscopy

The Scanning Electron Microscopy pictures were recorded using a HITACHI 4800 S microscope and metallised samples.



6. Solid-state NMR data

6.1 Standard experimental conditions

The NMR spectra were recorded using MAS probes (zirconia rotors) on Varian 600 spectrometer (14.1 T) for ^{19}F , ^{14}N and ^1H nuclei, and on a Varian 300 spectrometer (7.0 T) for ^{29}Si and ^{13}C nuclei. Spectrum modelling was achieved using the freely accessible *DmFit* software.¹

^1H NMR spectra were recorded using 1.2 mm rotors, $\pi/2$ pulses of 2.0 μs , and recycling delays of 2 s. Chemical shifts are referenced towards external TMS.

$^{13}\text{C}\{^1\text{H}\}$ NMR cross-polarization (CP) MAS spectra were recorded using 7.5 mm rotors. Experiments were conducted using: contact times of 5 ms, a linear ramp on the ^1H contact pulse (10 % slope), ^1H decoupling during acquisition (^1H RF field strengths $\nu_{RF} \sim 50$ kHz), and recycle delay of 5 s. Chemical shifts were referenced towards external neat TMS.

^{14}N NMR MAS single pulse spectra were recorded using 9.5 mm rotors spun at $\nu = 2, 3$ and 4 kHz (stability within 1-2 Hz). RF field strengths were $\nu_{RF} \sim 84$ kHz, flip angles to $\pi/8$ (3 μs , bandwidth ~ 170 kHz) and recycling delays to 0.5 s. Smaller flip angles were also tested (down to 2 μs , bandwidth ~ 250 kHz). These conditions insure a wide irradiation, and proper longitudinal relaxation. The FID was left shifted so as to consider only the acquired points after the first rotational echo maximum. ^1H decoupling ($\nu_{RF} \sim 25$ kHz) was used during acquisition. ^{14}N NMR chemical shifts were referenced towards solid NH_4Cl spun at 3 kHz.

^{19}F NMR spectra were recorded using 2.5 mm rotors, $\pi/2$ pulses of 1.7 μs , and recycling delays of 10 s were used. Chemical shifts are referenced towards external CFCl_3 .

$^{29}\text{Si}\{^1\text{H}\}$ NMR CP-MAS spectra were recorded using 7.5 mm rotors. Experiments were conducted using: contact times of 15 ms, a linear ramp on the ^1H contact pulse (10 % slope), ^1H decoupling during acquisition (^1H $\nu_{RF} \sim 50$ kHz), and recycle delay of 2 s. Chemical shifts were referenced towards external neat TMS.

¹ D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calve, B. Alonso, J.O. Durand, B. Bujoli, Z. Gan and G. Hoatson, *Magn. Reson. Chem.* 2002, **40**, 70.

6.1 ^{29}Si NMR

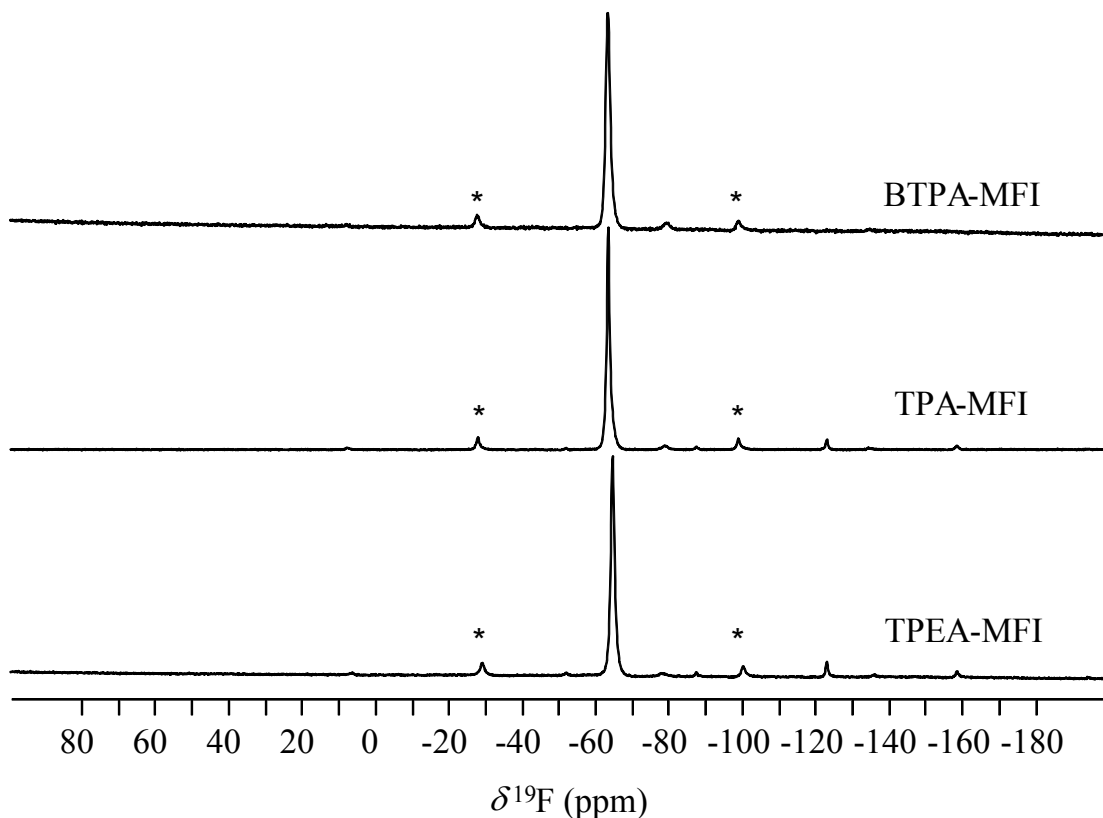
^{29}Si isotropic chemical shifts (in ppm) obtained from spectrum deconvolution and assigned following a previous assignment for TPA-MFI.²

<i>T site*</i>	<i>TPEA-MFI</i>	<i>TPA-MFI</i>	<i>BTPA-MFI</i>
---	-101.1	-102.2	-102.2
10	-107.4	-108.2	-108.4
1	-109.2	-109.7	-110.2
12	-111.4	-112.2	-112.5
7	-111.8	-112.5	-112.8
6	-112.3	-113.0	-113.2
5	-113.1	-113.2	-113.5
2	-114.4	-114.9	-113.9
3	-114.9	-115.3	-115.5
11	-116.3	-115.8	-116.1
8	-117.1	-116.9	-116.9
4	-117.7	-117.6	-117.8
9	-127	-125	-127
Average over all sites (1-12)	-114.4	-114.5	-114.8
Average for sites close to F (cage [4 ¹ 5 ² 6 ²])	-114.9	-115.6	-116.3

² C. Fyfe, D. Brouwer, A. Lewis and J.M. Chézeau, *J. Am. Chem. Soc.*, 2001, **123**, 6882.

6.2 ^{19}F NMR

The ^{19}F NMR spectra recorded at $\nu_{MAS} = 20$ kHz are presented below. The main peak located at ~ -63 ppm represents the fluoride in the $[4^15^26^2]$ cage while the minor peaks (less than 3-8 %) observed at around -80 ppm and -120 ppm are assigned to structure defect (following the proposition of ref. 3) and residual NH_4F respectively.



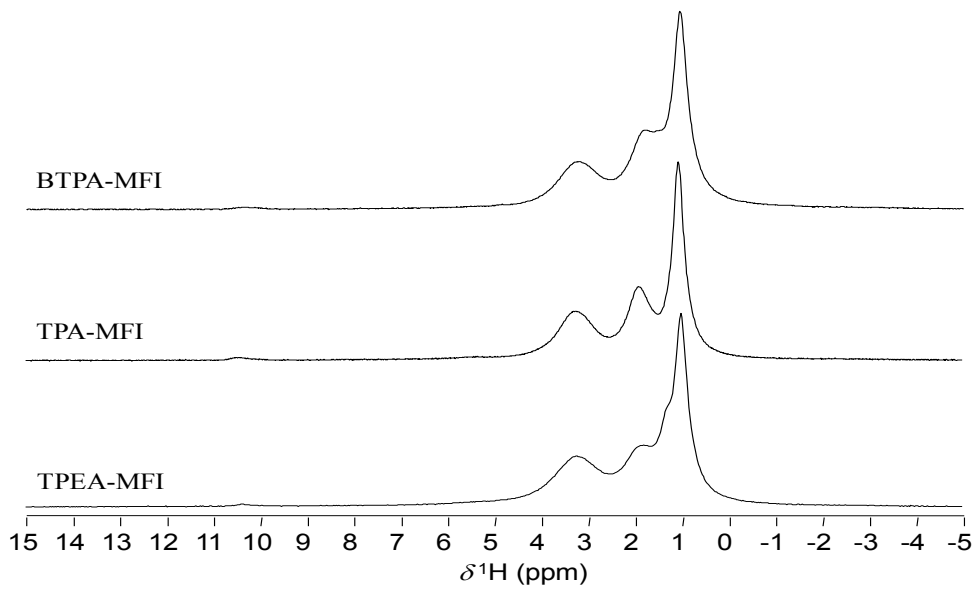
The table below presents the ^{19}F chemical shift anisotropy parameters extracted from spectra recorded at $\nu_{MAS} = 5$ and 20 kHz.

<i>Sample</i>	δ_{iso} (ppm)	Δ_{CSA} (ppm)	η_{CSA}
BTPA-MFI	-62.6 (5 kHz)	-27	0.8
	-63.0 (20 kHz)		
TPA-MFI	-62.8 (5 kHz)	-25	0.9
	-63.4 (20 kHz)		
TPEA-MFI	-63.9 (5 kHz)	-28	0.9
	-64.6 (20 kHz)		

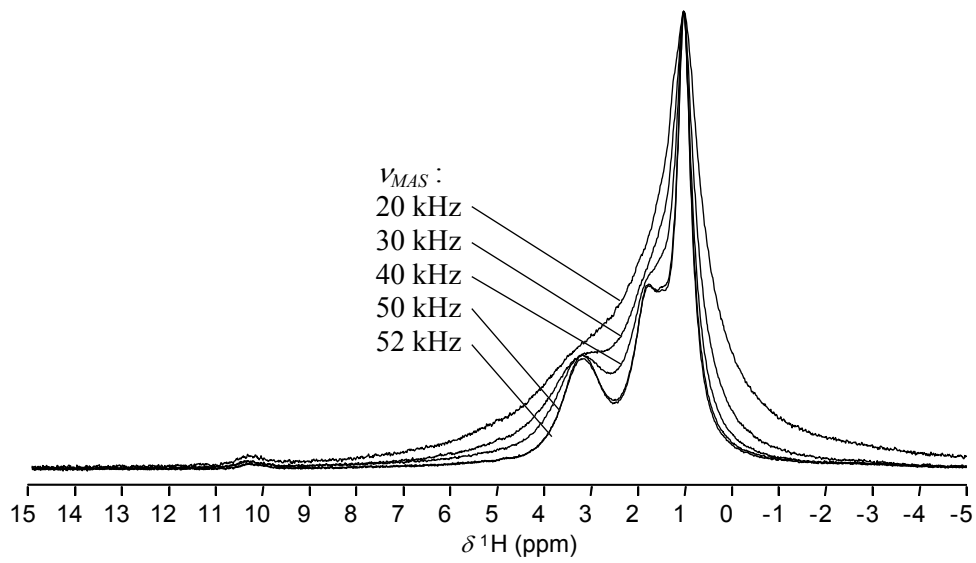
³ L. Delmotte, M. Soulard, F. Guth, A. Seive, A. Lopez and J.L. Guth, *Zeolites*, 1990, **10**, 778.

6.3 ^1H NMR

6.3.1 ^1H single pulse spectra for the as-synthesised zeolites ($\nu_{MAS} = 50$ kHz).



6.3.2 ^1H single pulse spectra recorded at variable ν_{MAS} (sample BTPA-MFI).



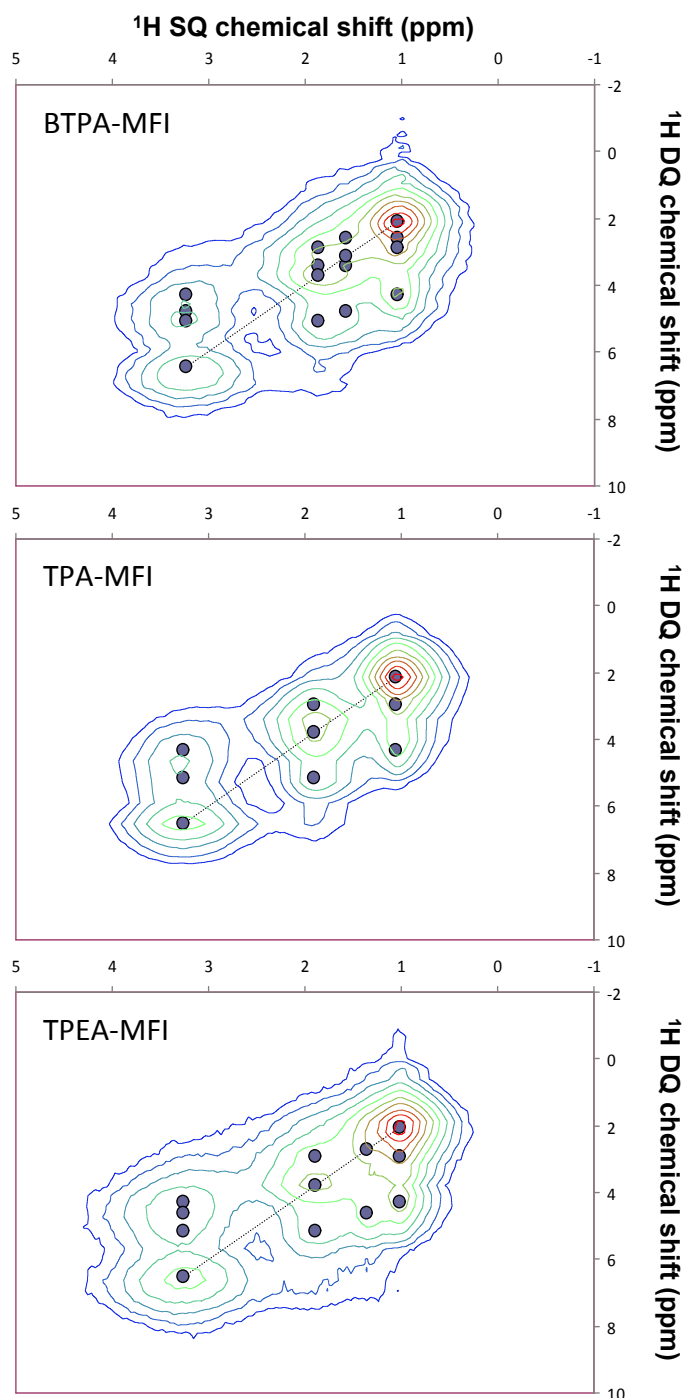
6.3.3 ¹H NMR Table for the as-synthesised zeolites.

H position in alkyl chains	¹H isotropic chemical shift δ_{iso} (ppm)		
	BTPA-MFI	TPA-MFI	TPEA-MFI
C-CH ₃ (Bu, Pr)	1.0	1.1	1.0
C-CH ₃ (Et)	-	-	1.4
C-CH ₂ -C (γ in Bu)	1.6	-	-
C-CH ₂ -C (β in Bu, Pr)	1.9	1.9	1.9
N-CH ₂ -C (Bu, Et, Pr)	3.2	3.3	3.3
OH defects (< 1 %)	10.3	5.6, 10.4	5.6, 10.4

6.3.4 ^1H - ^1H Double Quantum (DQ) – Single Quantum (SQ) correlations.

^1H - ^1H DQ-SQ 2D correlation experiments based on homonuclear dipolar couplings were recorded using the BABA scheme⁴ and identical excitation and reconversion times (τ_e and τ_r). Results presented for $\tau_e = \tau_r = 40 \mu\text{s}$ were similar to those found for $\tau_e = \tau_r = 80 \mu\text{s}$. As no correlations peaks are observed for the small -OH defects, the 2D spectra are centred on the ^1H signals of the alkyl groups.

The greyed circles correspond to calculated correlation peaks from 1D spectrum deconvolution (see table above), and making the hypothesis that all ^1H nuclei are coupled together within the same alkyl chain (Et, Pr or Bu) but not between all chains. This hypothesis is enough to explain the experimental 2D data (in particular in the case of TPEA-MFI).



⁴ W. Sommer, J. Gottwald, D.E. Demco and H.W. Spiess, *J. Magn. Reson. A*, 1995, **113**, 131.

6.4 ^{14}N NMR quadrupolar interaction parameters

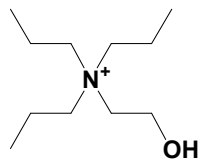
6.4.1 Zeolites

<i>Sample</i>	<i>C_Q (kHz)</i>	<i>η_Q</i>
TPA-MFI	53.0	0.3
TPEA-MFI	58.0	0.4
BTPA-MFI	54.0	0.6
EtOHTPA-MFI	84.0	0.7

6.4.2 Halides

<i>Crystal</i>	<i>C_Q (kHz)</i>	<i>η_Q</i>
TPABr	48.0	0.0
TPEABr	65.0	0.5
BTPABr	71.0	0.7
EtOHTPABr	129.0	0.8

7. Extension to 2-hydroxyethyl-tripropylammonium bromide (EtOHTPABr)



²⁹Si {¹H} NMR CP-MAS: comparison between EtOHTPA-MFI (bottom) and the TPA-MFI (up).

