Influence of Organic Structure-Directing Agents on Fluoride Dynamics in As-Synthesized Silicalite-1

Michael Fischer

Crystallography Group, Department of Geosciences, University of Bremen, Klagenfurter Straße 2-4, D-28359 Bremen, Germany

and

MAPEX Center for Materials and Processes, University of Bremen, Germany

michael.fischer@uni-bremen.de

SUPPORTING INFORMATION

Content:

1) Description of preliminary optimizations using the DREIDING force field

Structure models of MFI_(TMA,F), MFI_(TEA,F), and MFI_(TBA,F) were constructed using the DFT-optimized structure of MFI_(TPA,F) as starting point. The alkyl chain length was modified using the *Materials Studio Visualizer* (© DS BIOVIA), and hydrogen atoms were added using an automated placement procedure ("Adjust hydrogen"). Prior to the DFT calculations, a force-field based optimization of the OSDA coordinates was performed using *Materials Studio Forcite*. In these calculations, the positions of the framework atoms as well as the lattice parameters were held fixed. The structure optimizations used a mixed optimization algorithm ("Smart": cascade of steepest descent, adjusted basis set Newton-Raphson, and quasi-Newton algorithms) and the following convergence criteria ("Fine" settings according to *Materials Studio* default settings):

- Energy convergence: 10^{-4} kcal mol^{-1}
- Force convergence: $5 \cdot 10^{-3}$ kcal mol^{-1} Å^{-1}
- Displacement convergence: $5 \cdot 10^{-5}$ Å

For MFI_(TBA,F), a simulated annealing was carried out using *Materials Studio Forcite* in order to obtain a realistic initial configuration of the butyl chains. This simulated annealing was performed for 20 molecular dynamics cycles with an initial temperature of 300 K and a mid-cycle temperature of 1000 K (*NVE* ensemble). Each cycle consisted of 200,000 steps (time step 1 fs). The structure obtained at the end of each cycle was optimized using the same routine as described above, and the lowest-energy structure was then taken as starting point for the DFT optimization of MFI_(TBA,F).

All force field calculations described above used parameters from the DREIDING force field (S. L. Mayo, B. D. Olafson, W. A. Goddard, *J. Phys. Chem.* **1990**, *94*, 8897), employing the atom types N_3, C_3, and H_ for OSDA atoms, and Si3, O_3, and F_ for framework atoms. A cutoff of 15.5 Å was used for the Lennard-Jones potentials representing van der Waals interactions. Electrostatic interactions were not considered.

2) DFT-optimized models of MFI-type systems

Table S1: DFT-optimized unit cell parameters of MFI-type systems.

	a / Å	*b* / Å	*c* / Å	*α* / deg	*β* / deg	*γ* / deg	*V* / Å^3
Calcined Silicalite-1[a)]	20.053	19.73	13.357	91.14	90	90	5284
MFI_(TMA,F)	19.860	19.672	13.407	90	90	90	5238
MFI_(TEA,F)	19.913	19.795	13.423	90	90	90	5291
MFI_(TPA,F)[b)]	19.842	19.775	13.487	90	90	90	5292
MFI_(TBA,F)	20.151	20.011	13.531	90	90	90	5456
MFI_(MTBA,F)	20.036	19.887	13.468	90	90	90	5366
MFI_(ETBA,F)	20.028	19.879	13.474	90	90	90	5364
MFI_(PTBA,F)	20.047	19.926	13.477	90	90	90	5383
MFI_(MTPA,F)	19.866	19.795	13.400	90	90	90	5270

a) Experiment: *a* = 20.107 Å, *b* = 19.879 Å, *c* = 13.369 Å, *α* = 90.67 deg
(H. van Koningsveld, J. C. Jansen, H. van Bekkum, *Zeolites* **1990**, *10*, 235)
b) Experiment: *a* = 20.003 Å, *b* = 19.993 Å, *c* = 13.392 Å
(E. Aubert, F. Porcher, M. Souhassou, V. Petříček, C. Lecomte *J. Phys. Chem. B* **2002**, *106*, 1110)

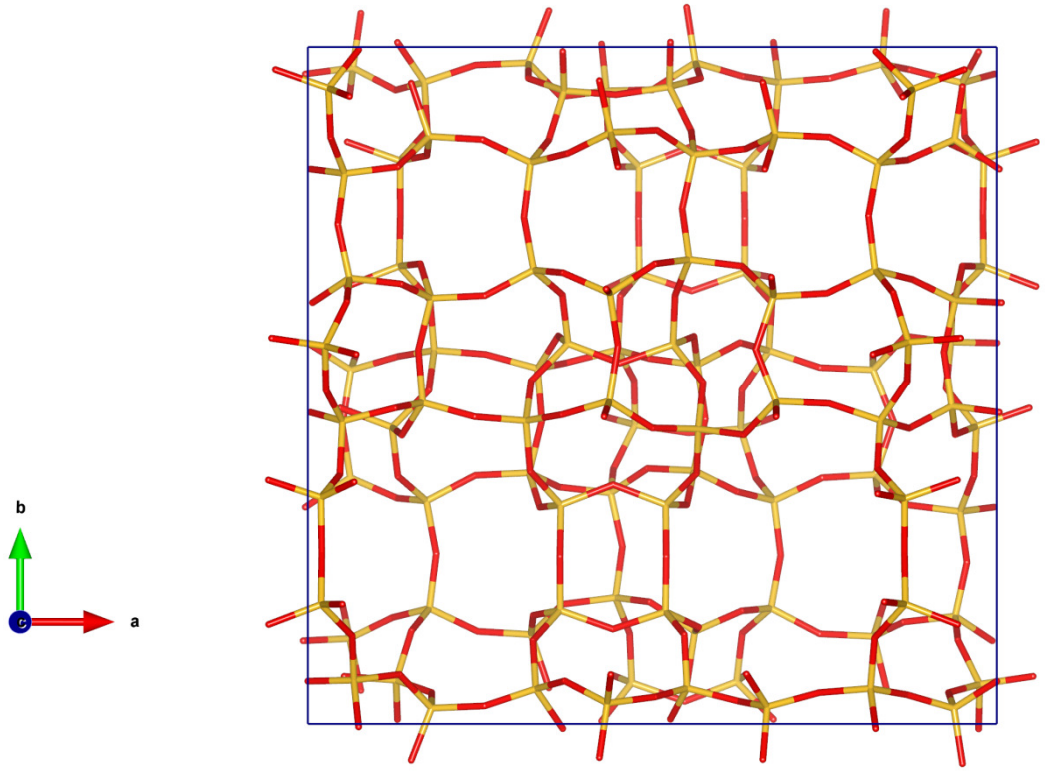

Figure S1: DFT-optimized structure of calcined Silicalite-1.

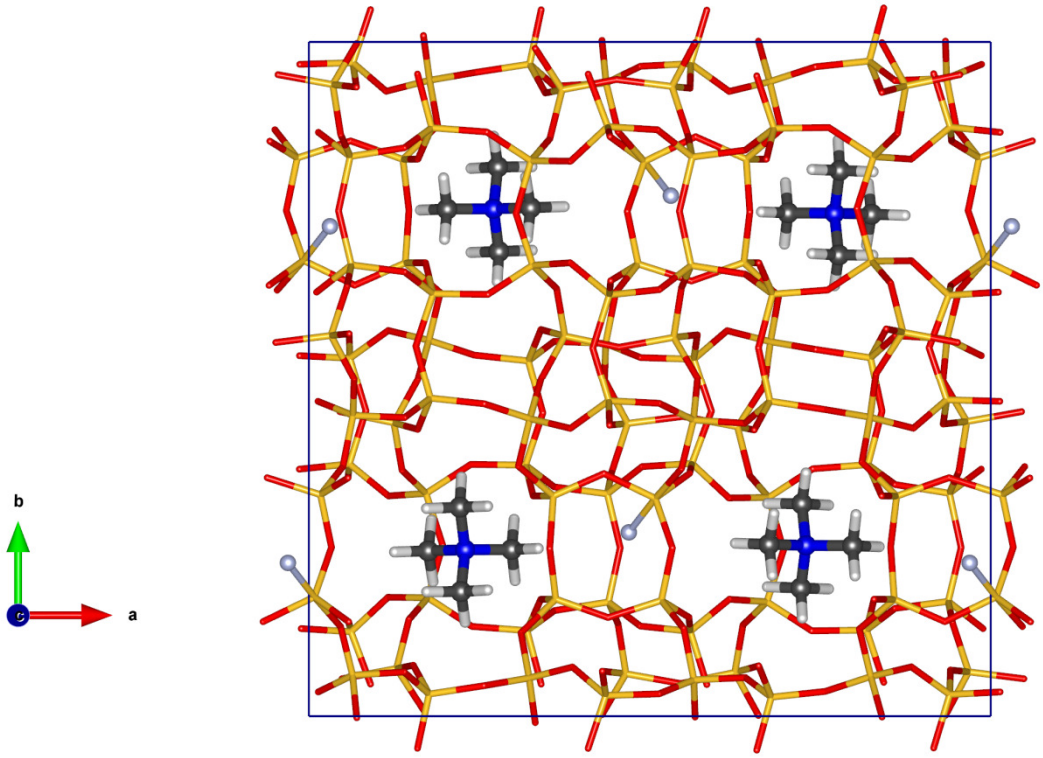

Figure S2: DFT-optimized structure of MFI_(TMA,F).

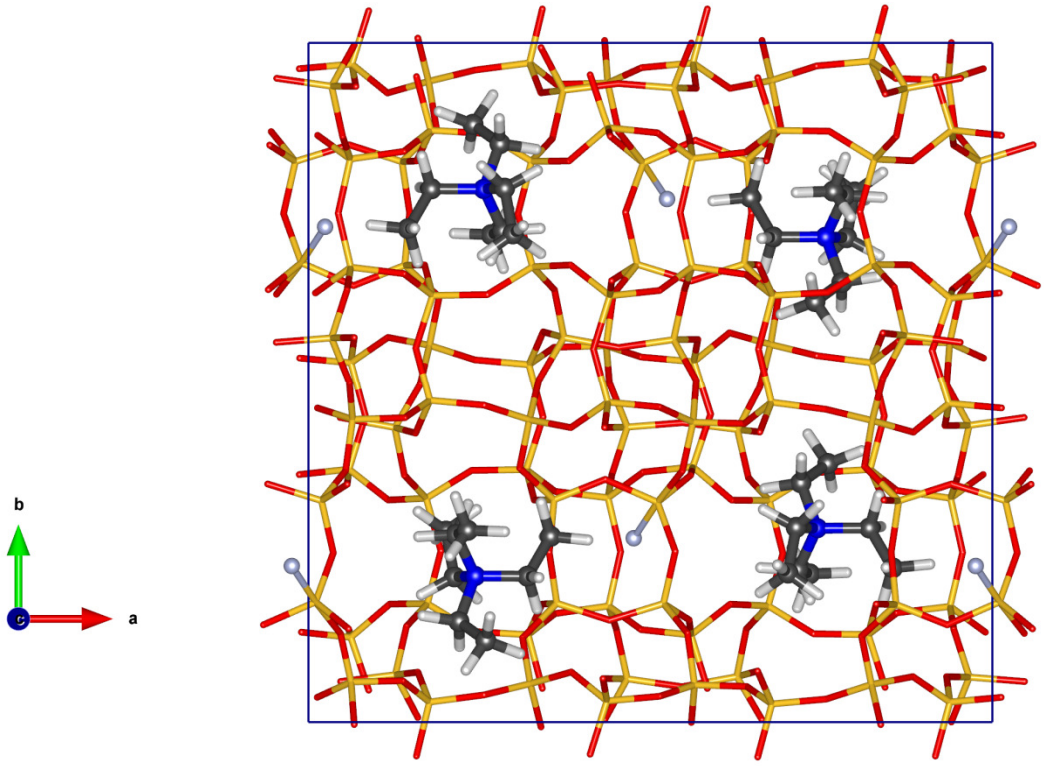

Figure S3: DFT-optimized structure of MFI_(TEA,F).

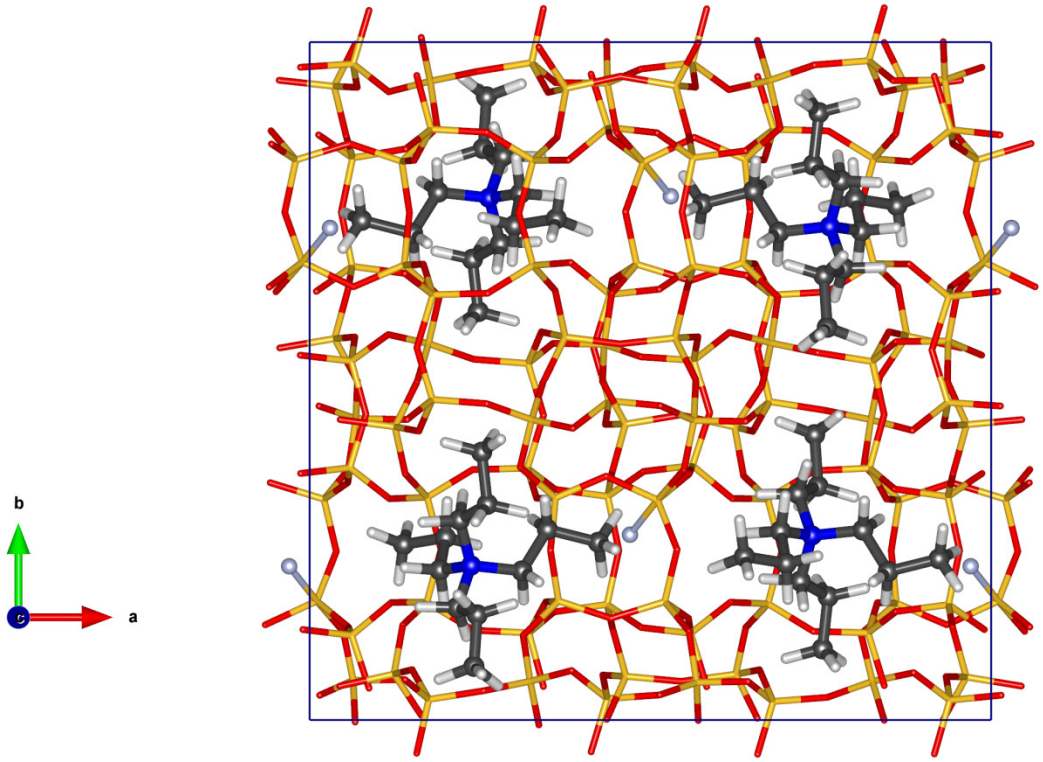

Figure S4: DFT-optimized structure of MFI_(TPA,F).

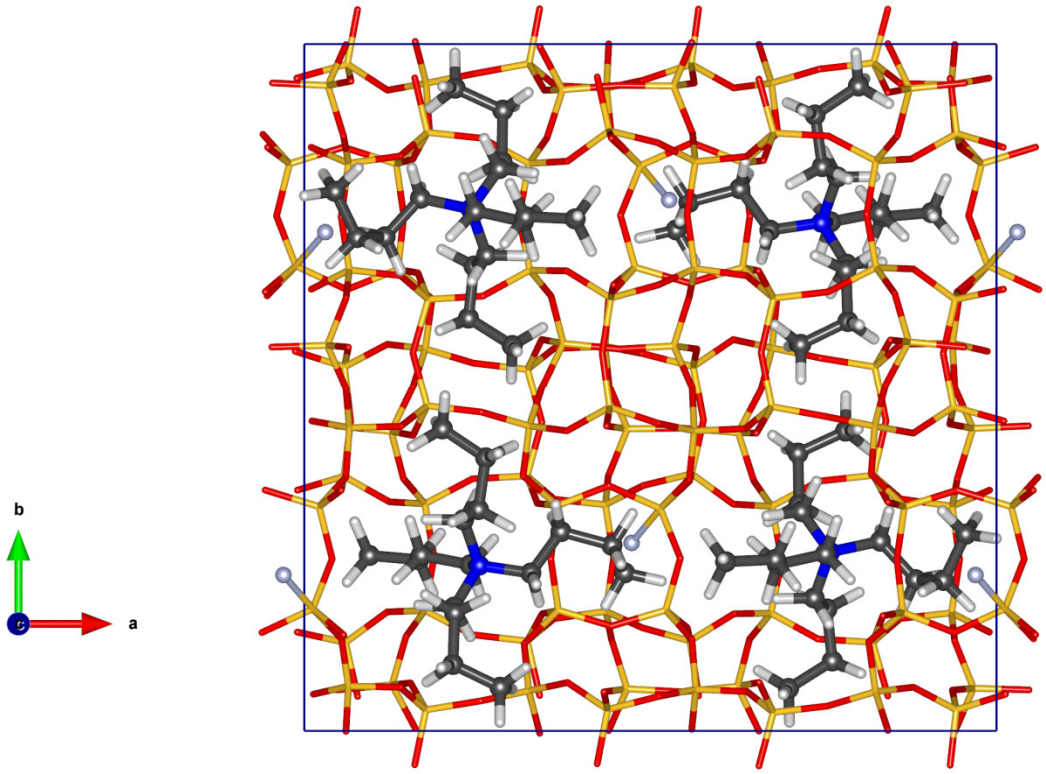

Figure S5: DFT-optimized structure of MFI_(TBA,F).

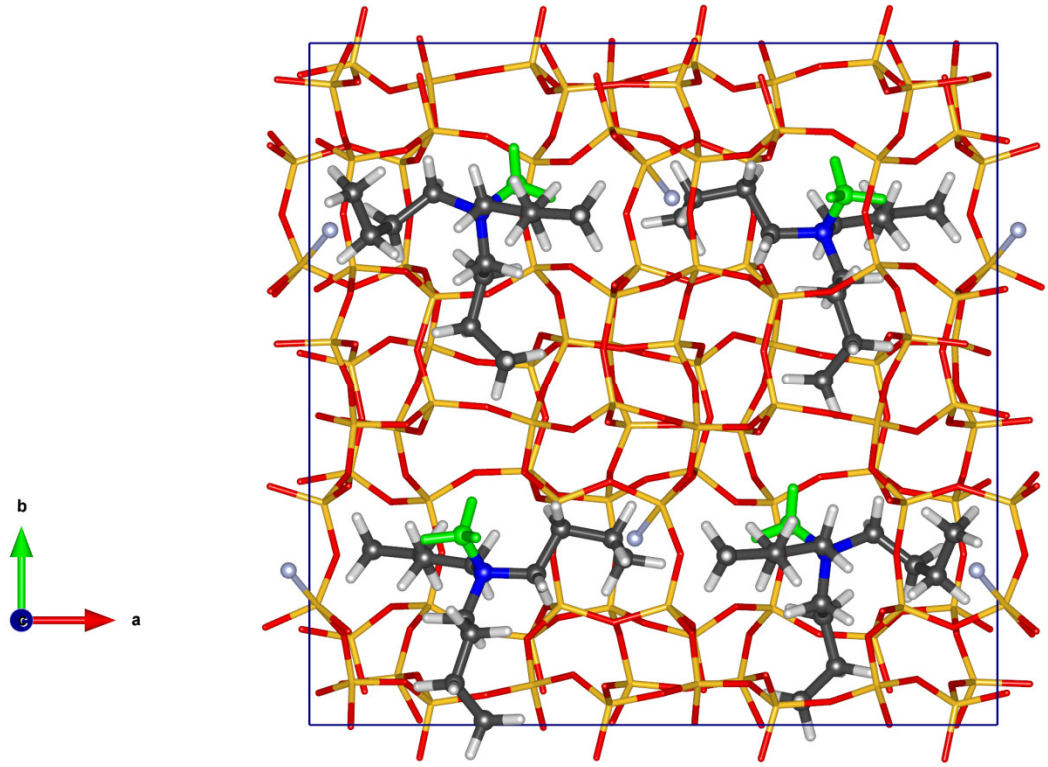

Figure S6: DFT-optimized structure of MFI_(MTBA,F). The methyl chain is shown in green.

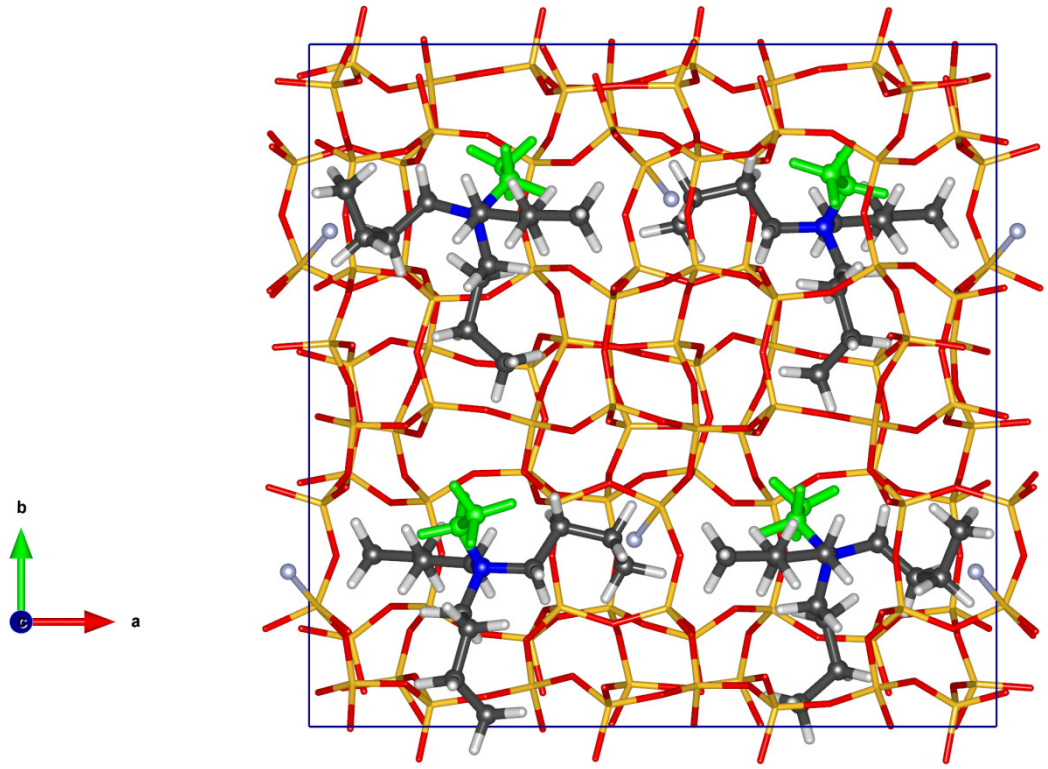

Figure S7: DFT-optimized structure of MFI_(ETBA,F). The ethyl chain is shown in green.

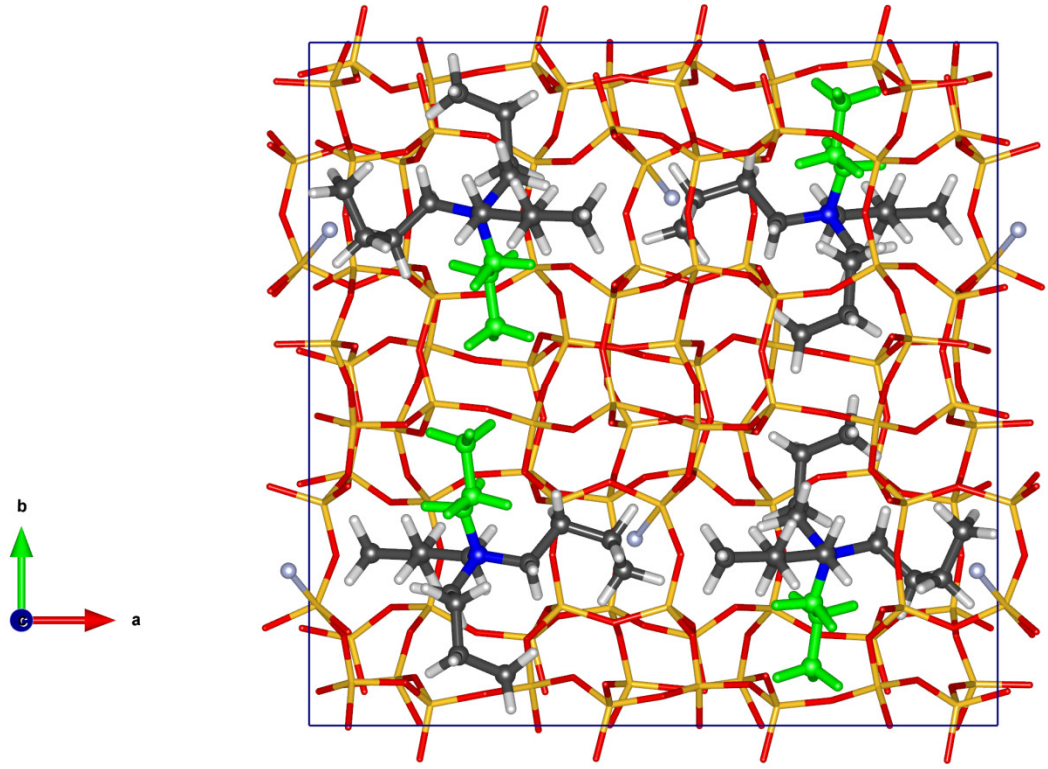

Figure S8: DFT-optimized structure of MFI_(PTBA,F). The propyl chain is shown in green.

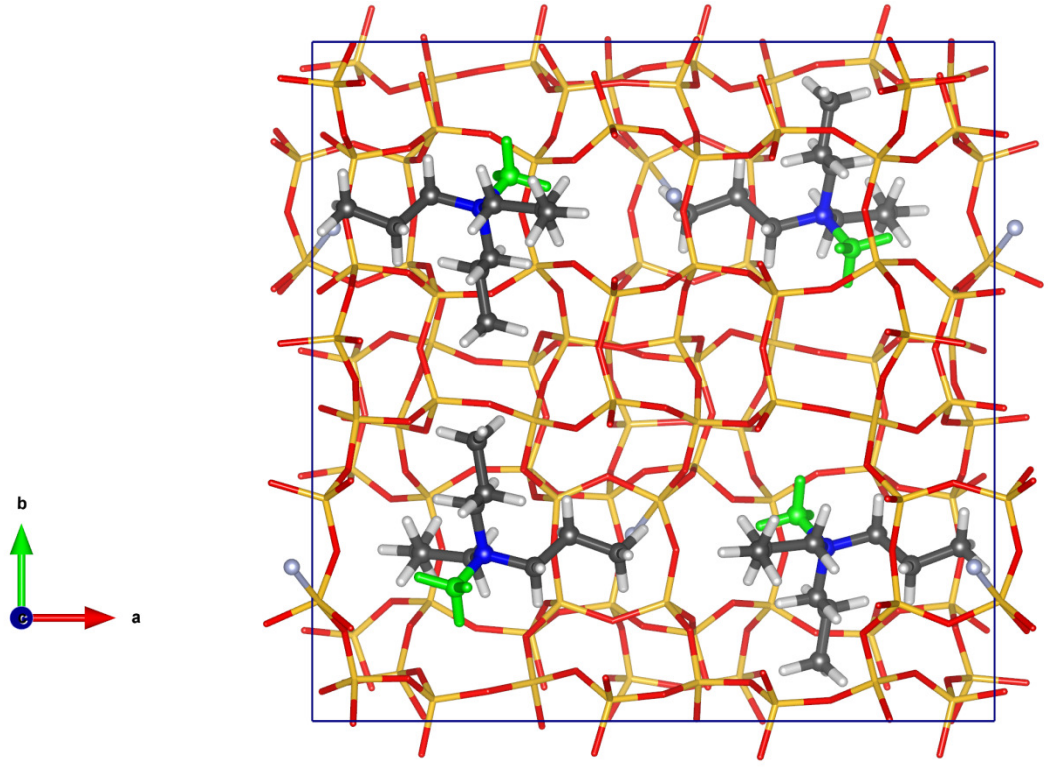

Figure S9: DFT-optimized structure of MFI_(MTPA,F). The methyl chain is shown in green.

3) Comparison of RDFs of MFI_(TPA,F) and MFI_(MTPA,F)

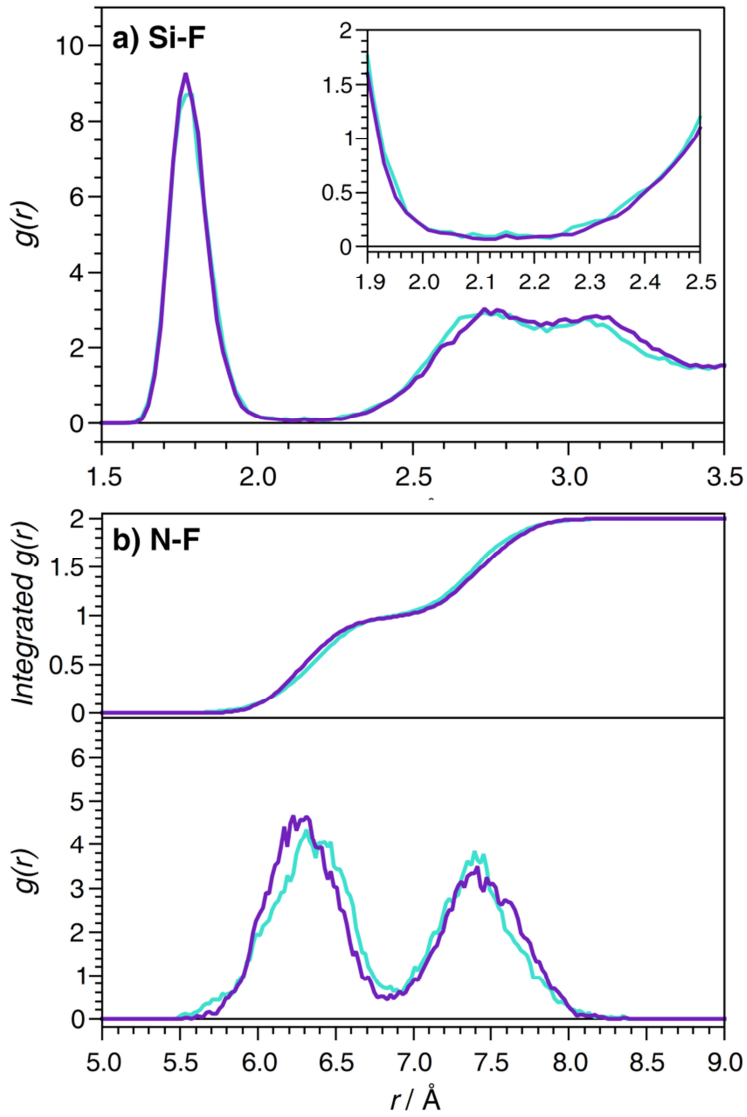

Figure S10: a) Si-F and b) N-F radial distribution functions obtained for MFI_(TPA,F) (turquoise) and MFI_(MTPA,F) (purple) for a temperature of 373 K. The inset in the upper panel shows the distance range between the first and second maximum in the Si-F RDF, and the top part of the lower panel shows the integrated N-F RDFs.

4) Guide to other supplementary files

- **RMSDs_RDFs_SuppInfo.xlsx:** EXCEL file containing RMSDs (sorted by elements) and Si-F and N-F RDFs
- **MFI_opti.inp:** Sample CP2K input file for a structure optimization
- **MFI_MD.inp:** Sample CP2K input file for an AIMD calculation
- **MFI_YYY_PBE-D3.cif:** DFT-optimized structures of OSDA-free Silicalite-1 (YYY = noOSDA) and OSDA-containing MFI models (YYY = X_F, where X = OSDA)