Synthesis, structure and optical activity of HPM-1 a pure silica chiral zeolite
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Supporting Information

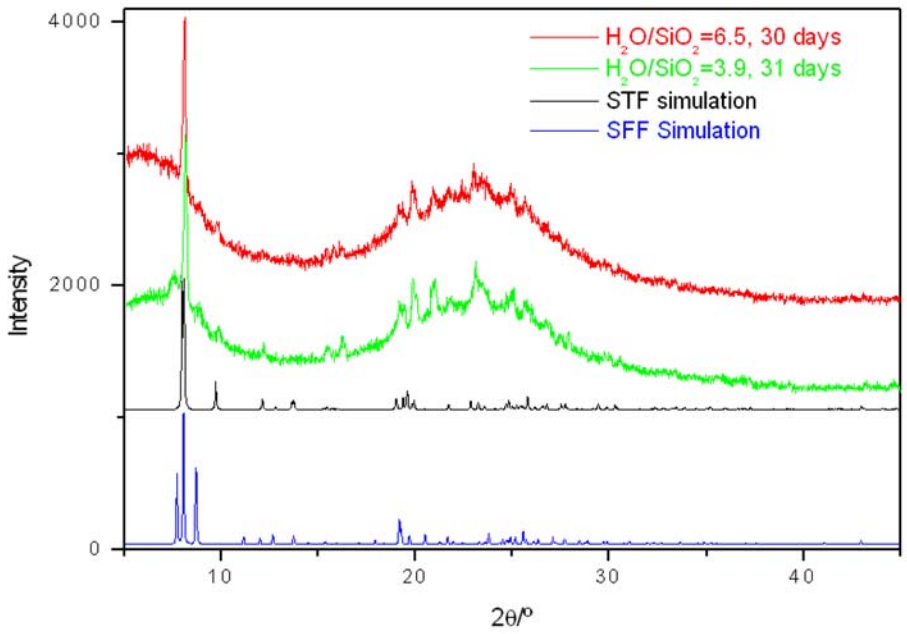

Figure S1. Experimental XRD patterns of two solids obtained at 150ºC (water/silica ratios and crystallization times as indicated), with the simulated patterns of STF and SFF shown for comparison.

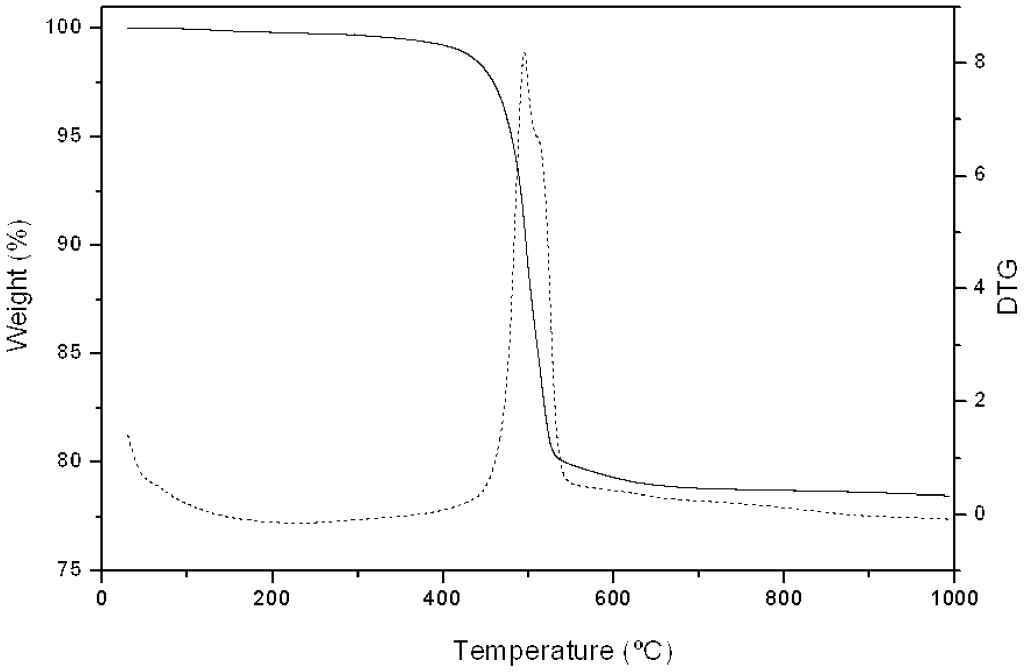

Figure S2. Thermogravimetric analysis of as-made HPM-1 (STW).

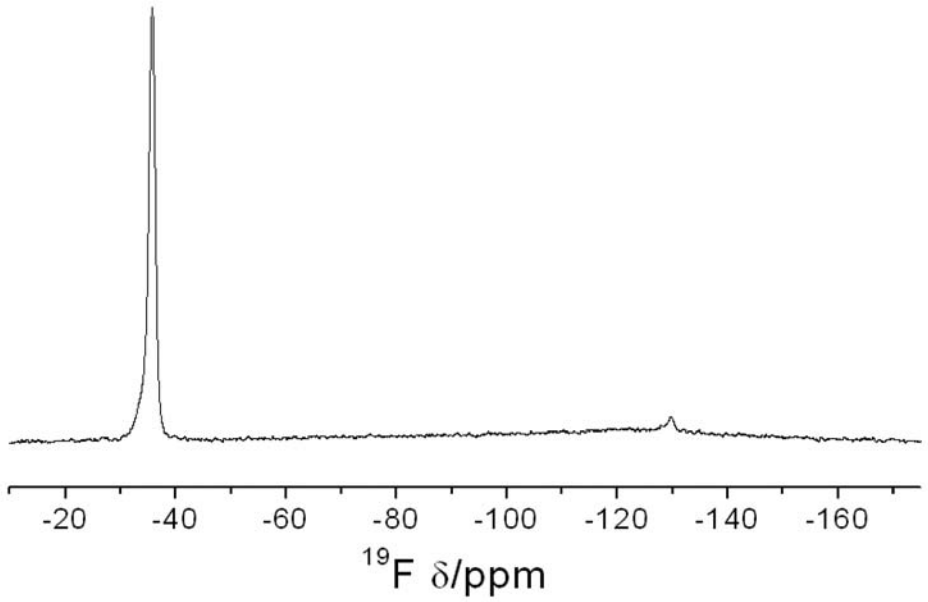

Figure S3. ^{19}F MAS NMR spectrum of as-made HPM-1 (2E134TMI-STW), showing a strong resonance at –35.7ppm assigned to F^- occluded in D4R of HPM-1. A small resonance around –130 ppm is assigned to traces of a hexafluorosilicate impurity in this particular sample (estimated as < 0.4% weight percent in the solid, based on the relative intensities of both resonances and assuming a $|C_8H_{15}N_2F|_2[SiF_6]$ composition for the hexafluorosilicate).

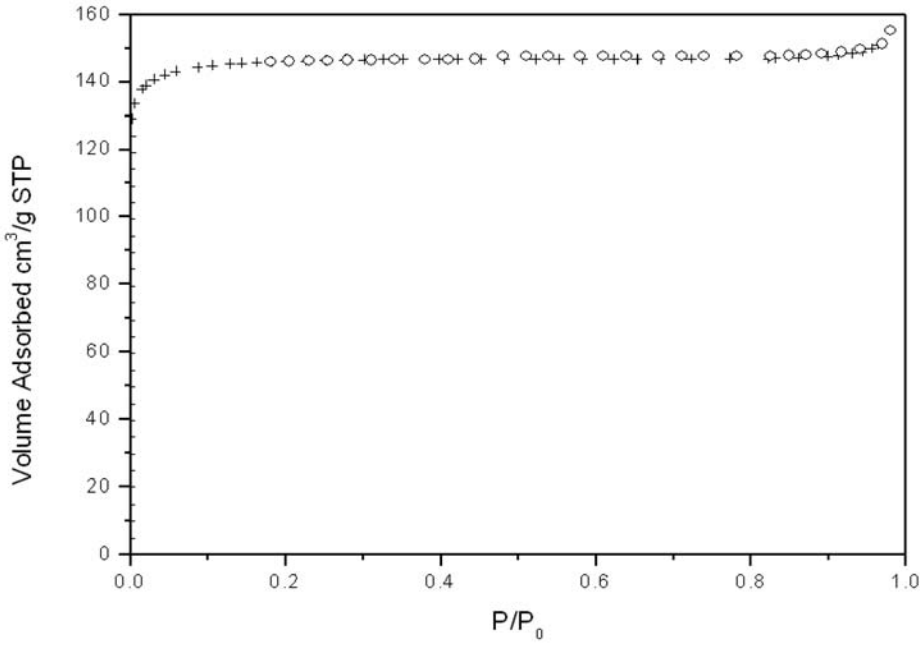

Figure S4. N_2 adsorption (+) and desorption (o) isotherm at 77.35 K on calcined HPM-1.

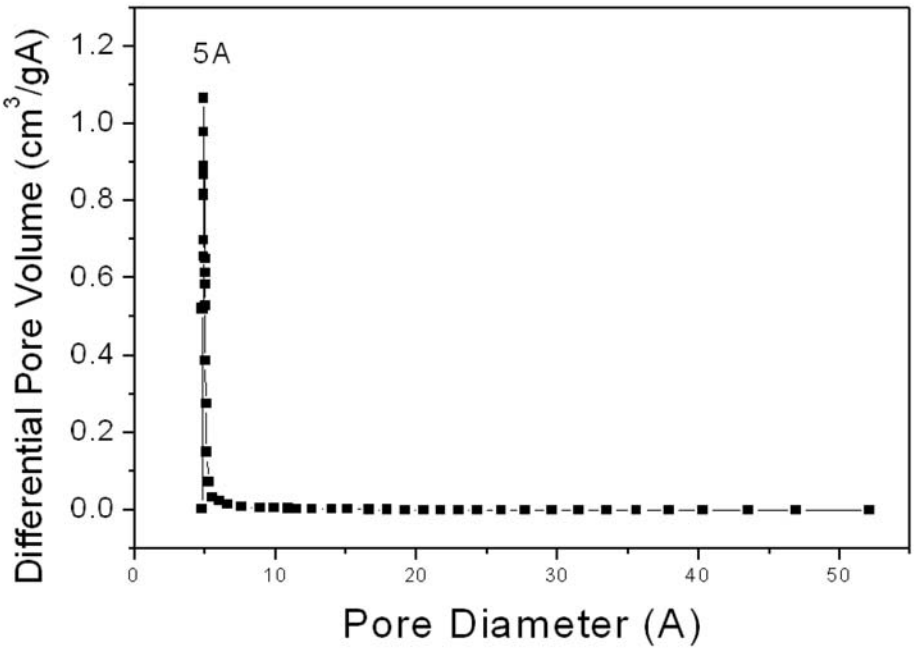

Figure S5. Horvath-Kawazoe Differential Pore Volume Plot (Slit Pore Geometry) of calcined HPM-1.

Details of Rietveld refinement of as-made 2E134TMI-STW.
The structure of as-made 2E134TMI-STW was refined using the GSAS program[1] and the EXPGUI graphical interface[2] against synchrotron data in space group *P6$_1$22*. The structural model, initially containing only Si and O atoms, was based on our solution of calcined SiO_2-ITW,[3] but with the cell parameters found by indexing the as-made sample (a=11.90, c=29.69Å). Fluoride atoms were introduced near the center of the D4R units at (0.46, 0.91, 0.25), in agreement with the ^{19}F MAS NMR spectrum (Figure S3). The background was modeled graphically using the shifted Chebyshev function with 22 coeficientes, and was kept fixed until the final steps of the refinement. After initial refinement of the scale factor, cell parameters and several coefficients of a pseudovoigt profile function,[4] that allows for asymmetry correction[5] and microstrain broadening,[6] a difference Fourier analysis revealed a relatively flat area with four arms of electron density missing inside the large [$4^6 5^8 8^2 10^2$] cage, plus some smaller areas nearby. The organic cation, after minimization using GAMESS,[7] as implemented in the ChemBio 3D Ultra suite of packages,[8] was introduced in the model as a combination of two rigid bodies: the imidazolium ring with the three methyl groups plus the ethyl group as a satellite able to freely rotate along the C(2)-C(9) bond. The C at position two of the imidazolium ring was initially positioned at (0.43, 0.05, 0) and the ethyl group was placed at 90º of the plane of the imidazolium ring, i.e., in its most stable conformation in vacuum (see Figure 6 in the main text). Fractional occupancies of 0.5 were used to yield a final occupancy of 1 cation per cage, in agreement with the chemical analysis. The refinement of Si and O atomic positions was initially performed with soft restrains on the Si-O (1.610 Å) and O···O distances (2.612 Å), and the rigid bodies were allowed to freely move, with the only constrain that the ethyl group remained properly attached to C(2). When the distance restrains were gradually softened O12 (in an edge of the D4R unit) was observed to displace to unrealistic positions (well towards the center of the D4R, occupied by F). Hence this atom was kept fixed until the final stages of the refinement. As the refinement proceeded, microstrain broadening profile coeficients were introduced. The background coefficients were increased to 24 and the isotropic atomic displacement parameters were refined while constrained to be equal according to atom type (C and N together). Preferred orientation along [001], using the March-Dollase formalism,[9] make little difference in the refinement (ratio: 0.99782), as expected for a capillary experiment. Finally, all the restraints on distances were completely removed and the position of atom O12 was also refined. Due to the ^{29}Si MAS NMR results (Figure 3) and the problems found with O12 attempts were made to lower the symmetry to *P6$_1$*, but the refinement was found very unstable. The final Rietveld plot in space group *P6$_1$22* is shown in Figure S6, complete crystallographic information is provided in a cif file, and details on crystallographic and experimental parameters are gathered in Table S1. Comparison of experimental and calculated chemical shifts for ^{29}Si MAS NMR resonances is given in Table S2.

A Rietveld refinement in which the ethyl group was initially oriented closer to C(6) rather than C(7) was also attempted, since a conformation with a torsion angle of around 54º has a similar energy as the one found (torsion angle: 126º). However, this implies exchanging the position of C(4) (with a methyl substiuent) and C(5) (unsubsituted) and, hence, directing that methyl substituent towards the silica wall. In this case, unrealistic distances (such as C to O distances as small as 2.8 Å) could not be avoided, and this model was discarded.

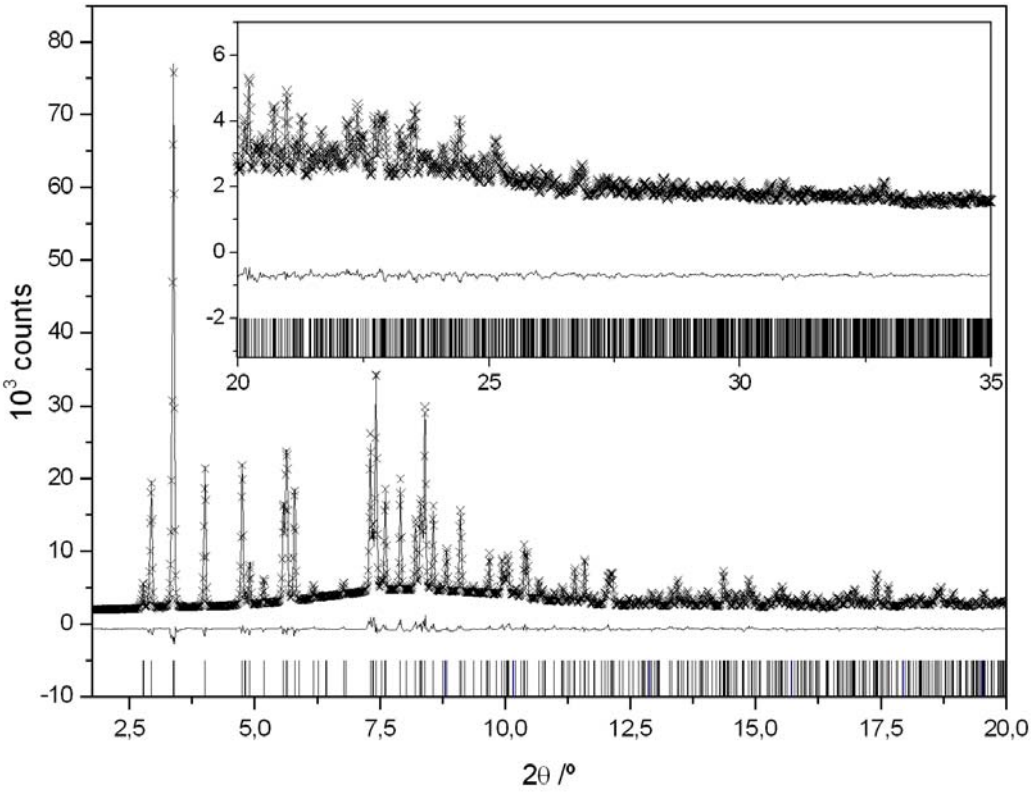

Figure S6. Observed (x) and calculated (solid line) powder X-ray diffractograms for as-made 2E134TMI-STW refined in space group $P6_122$. Vertical tic marks indicate the positions of allowed reflections. The lower trace is the difference plot. λ=0.4995Å.

Table S1. Crystallographic and Experimental Parameters for the Rietveld Refinement of 2E134TMI-STW

	As-made HPM-1, $\|C_8N_2H_{15}F\|_6[SiO_2]_{60}$
wavelength	0.49950 Å
temperature	298 K
2θ range	1.76-34.99º
step size	0.01°
no. of data points	3324
no. of reflections	1397
space group	*P6$_1$22*
unit cell parameters (Å)	
a	11.90205(11)
c	29.6920(4)
cell volume (Å^3)	3642.62(8)
residuals	
R_{wp}	0.0317
R_p	0.0238
R_F^2	0.0621
reduced χ2	3.4770

Table S2. Comparison of ^{29}Si chemical shifts observed experimentally and calculated from the average SiOSi angles determined by Rietveld refinement.

			Refined Structure		
^{29}Si δ exp		**sites**	**SiOSi**	**^{29}Si δ calc[a]**	**Δppm**
-113.7	Non D4R	Si5	154.6	-115.0	-1.3
		Si1	139.4	-106.2	0
		Si2	140.6	-106.9	-0.7
-106.2	D4R	Si3	141.2	-107.3	-1.1
		Si4	143.8	-108.7	-2.5

[a] According to the empirical correlation of Thomas et al.[10]

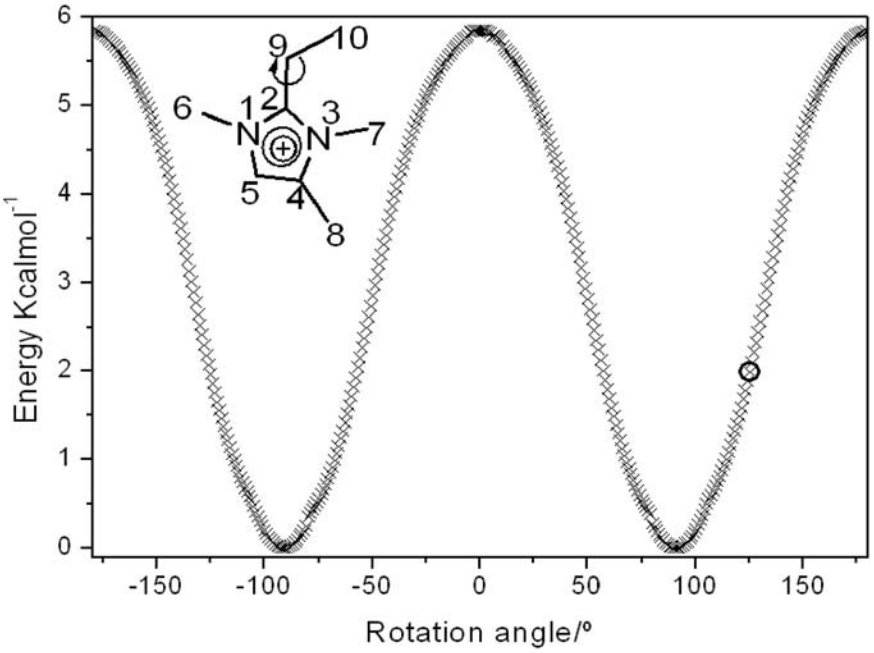

Figure S7. Excess potential energy of 2E134TMI as a function of the N(3)C(2)C(9)C(10) torsion angle (the drawing corresponds to a rotation angle of 0º, clockwise is positive). The conformation found by Rietveld refinement in the zeolite in space group $P6_122$, -126º, is marked with a circle.

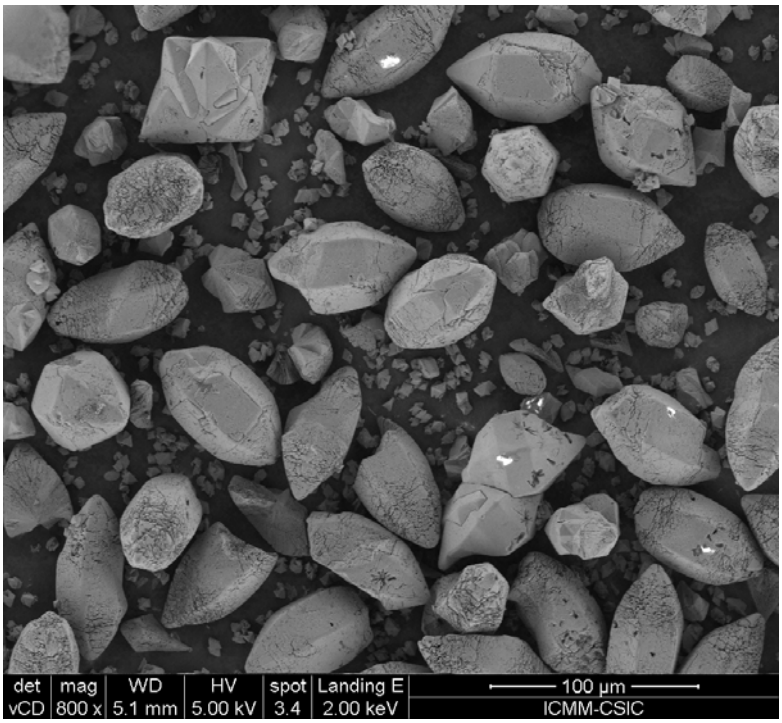

Figure S8. FE-SEM picture of the sample crystallized at 175ºC for 12 days at H_2O/SiO_2=4.0, which contains large HPM-1 "double-pencil" crystals together with much smaller ITW crystals. This is the sample that was investigated by Mueller matrix microscopy (see main text)

References

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