Benzylimidazolium Cations as Zeolite Structure-Directing Agents. Differences in Performance Brought About by a Small Change in Size.

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Electronic Supplementary Information.

Multinuclear magic angle spinning NMR spectroscopy

The spectra of as-made samples were recorded at room temperature on a Bruker AV-400-WB equipment using 4mm ZrO rotors and Kel-F lids spinning at 10kHz for ^{13}C and ^{29}Si and 2.5 mm ZrO rotors and Vespel lids spining at 25kHz for ^{19}F. The ^{19}F spectra were acquired at a resonance frequency of 376.45 MHz with a π/8 pulse at 60kHz, 75 kHz spectral width, relaxation delay of 20s and are referenced using Na_2SiF_6 as a secondary reference (-152.46 ppm referenced to $CFCl_3$ at δ =0 ppm as primary reference). The ^{13}C spectra were acquired at 100.61 MHz resonance frequency using a CP-MAS sequence, with a 3μs ^{1}H excitation pulse, 3.5 ms contact time, 4s recycle delay and 35kHz spectral width, using proton decoupling at 80kHz tppm15 during acquisition. The spectra were referenced to the CH_2 resonance of adamantane as secondary reference (29.5 ppm with respect to TMS at δ =0 ppm as primary reference). The ^{29}Si spectra were acquired at a resonance frequency of 79.49 MHz with a π/12 pulse at 20kHz, spectral width of 15kHz and 60 or 180s relaxation delay, and are referenced using kaolin as a secondary reference (-91.2 ppm, referenced to TMS at δ =0 ppm as primary reference).

Table S1. Syntheses with 1,2-dimethylimidazole[a]

H_2O/Si_2O	*F source*	*Time (days)*	*pH*	*Phase*
21	NH4F	7	9	Amorphous
		27	8,7	Amorphous
14,5	HF 48%	6	6,7	Amorphous
		31	6,7	Amorphous + dense
16[b]	HF 48%	7	6,8	Amorphous
		18	7,0	Amorphous + dense
		33	6,7	dense

[a] 150ºC, composition: SiO_2 : 0.5(1,2-dimethylimidazole) : 0.5(HF or NH_4F) : xH_2O; silica source: fumed silica (Aldrich, 99.8%) [b] with ITW seeds added (2% based on silica).

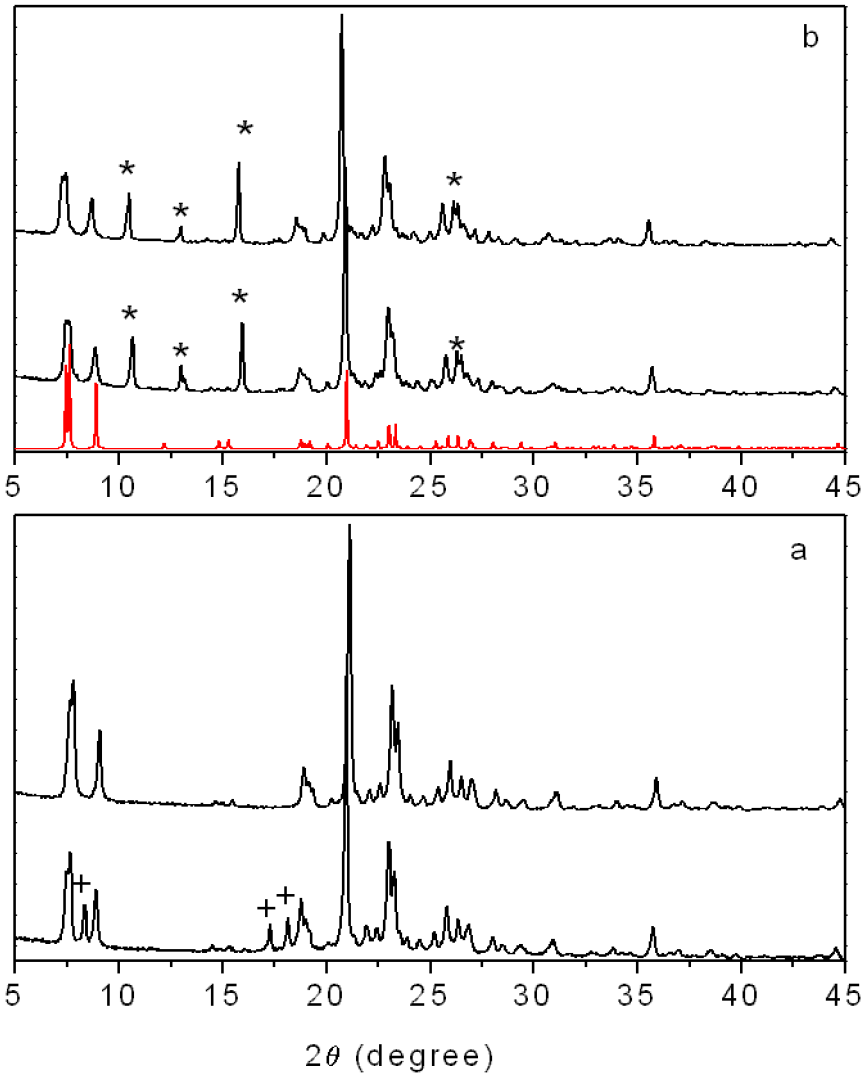

Fig. S1. Powder X-Ray Diffraction patterns of the solids obtained at 150ºC with 1B23DMI at (a) H_2O/SiO_2 ratio of 5.8 and crystallization time of 11 days before (bottom) and after extensive washing with hot water (top) and (b) H_2O/SiO_2 ratio of 5.3 and crystallization time of 5 days (black bottom trace) and 12 days (top). Most reflections belong to MTW (its simulated pattern is shown in red for comparison), while the ones marked correspond to soluble (+) or ITW (*) phases.

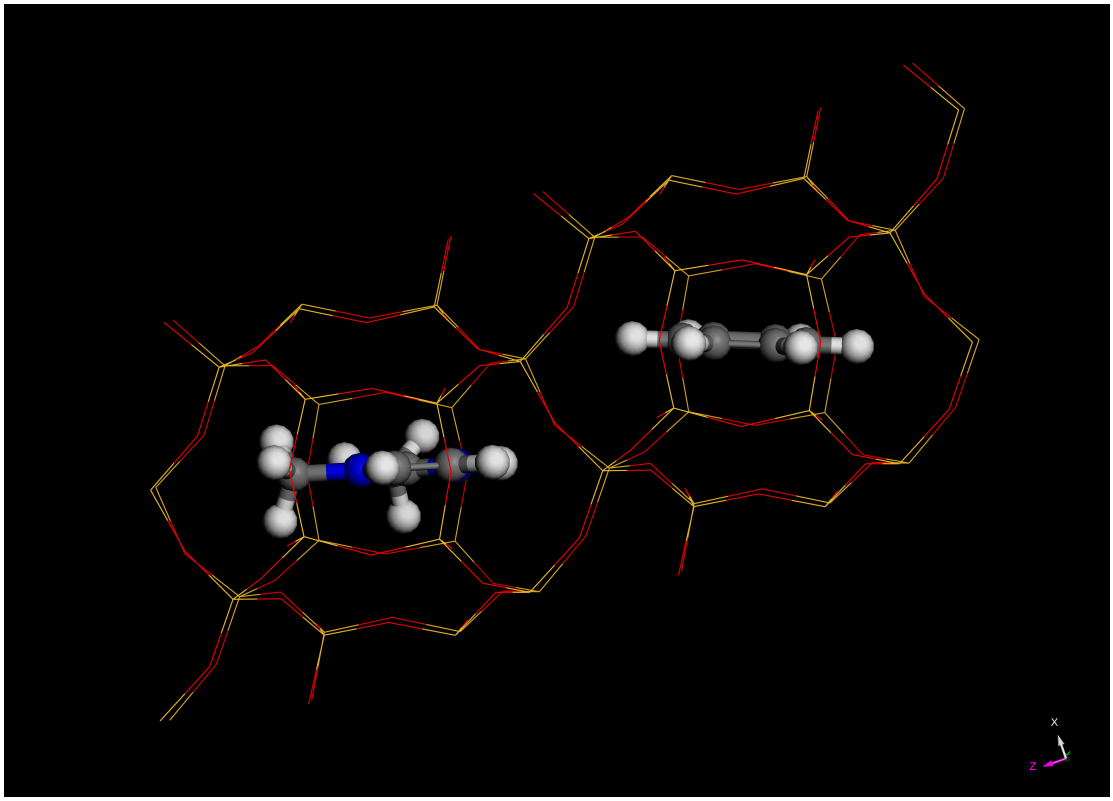

Fig. S2. One 1,2-dimethylimidazole and one benzene in close adjacent cavities of ITW, showing they are too far apart and in an unfavourable orientation to be connected trough a CH_2 bridge.

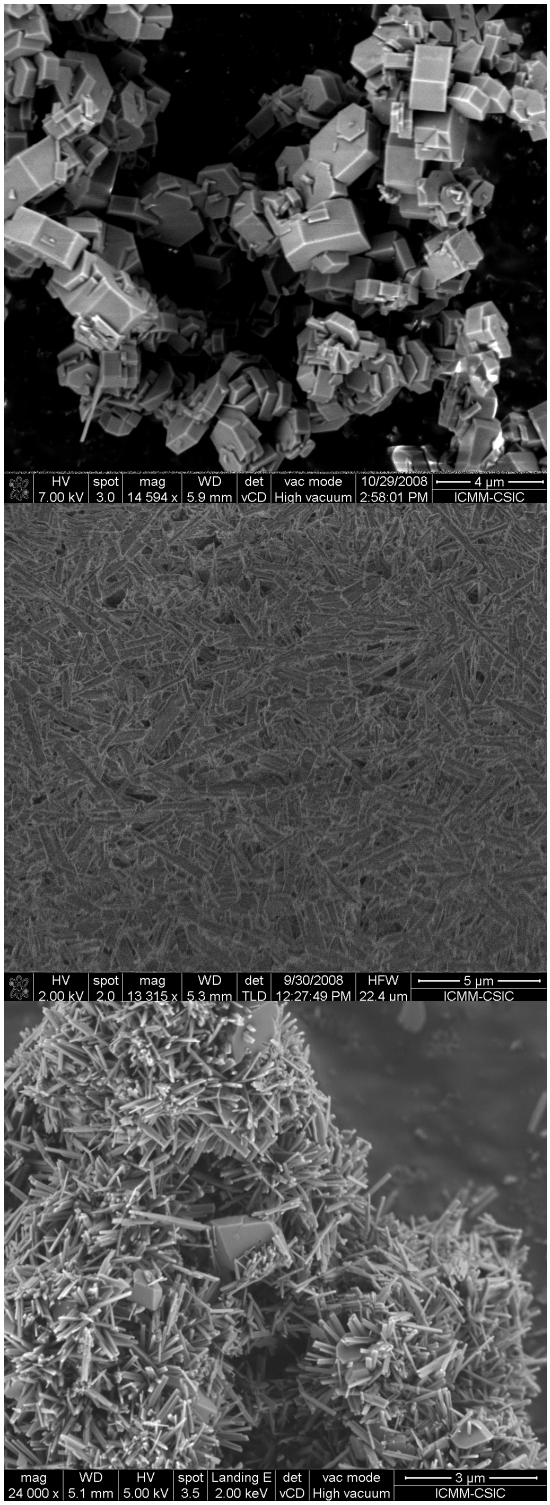

Fig. S3. Field Emission Scannning Electron Microscopy (acquired with a FEI NOVA NANOSEM 230) images of (from top to bottom): 1B3MI-MFI, 1B3MI-MTW and the MTW+ITW mixture obtained with 1B23DMI at a water/silica ratio of 5.3, 150ºC, 5 days of crystallization (the crystals with smaller and larger aspect ratio are ITW and MTW, respectively).

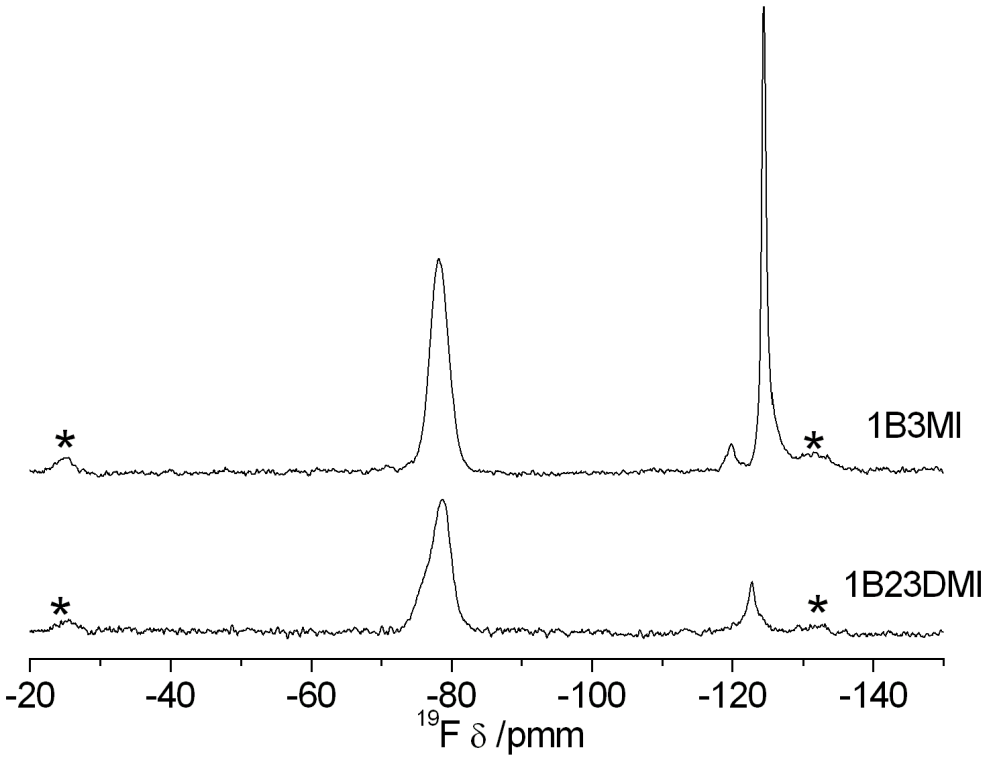

Fig. S4. ^{19}F MAS NMR spectra of routinely washed MTW phases (spinning side bands marked with *)

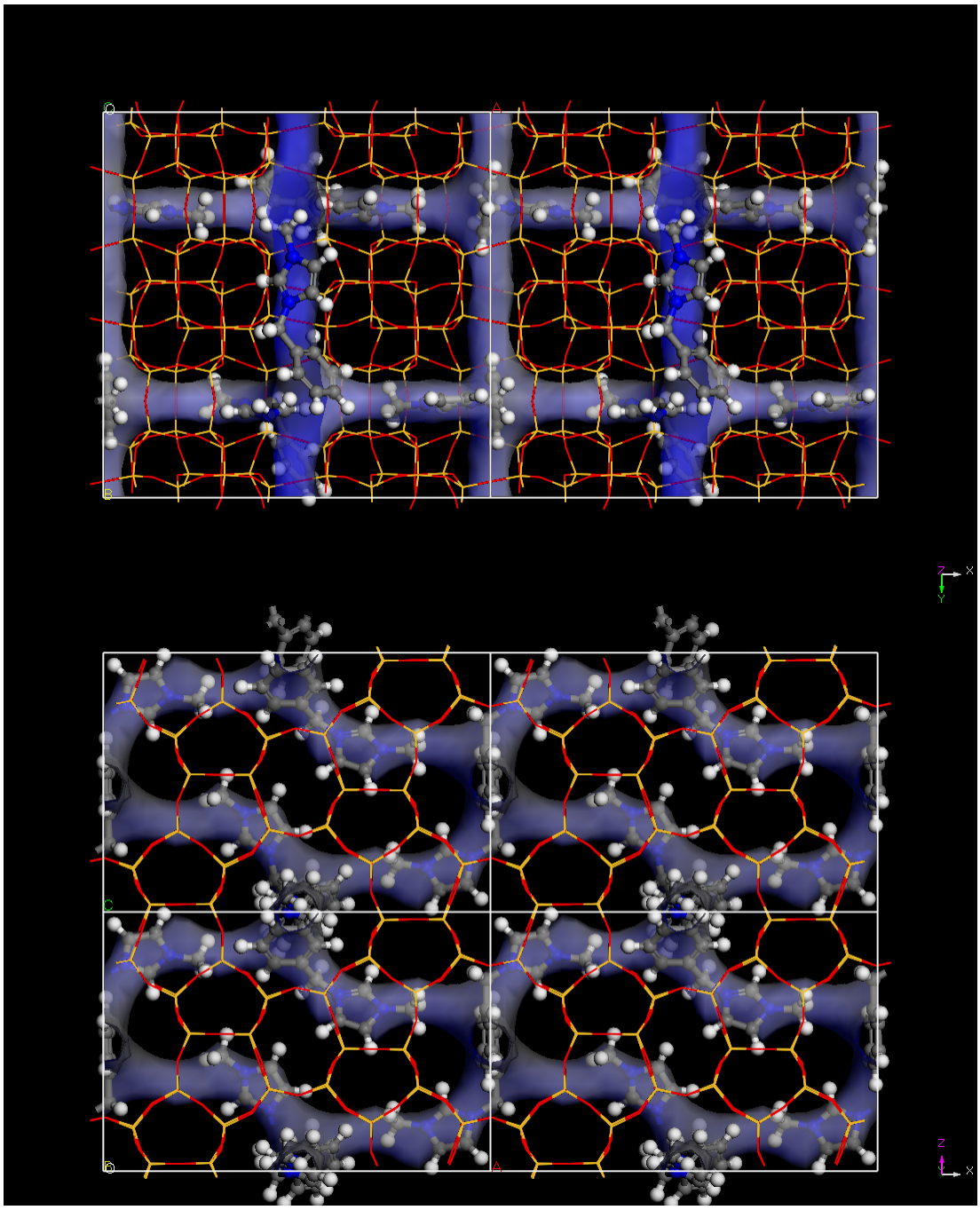

Fig. S5. Two views of the optimized location of five 1B3MI cations per unit cell.

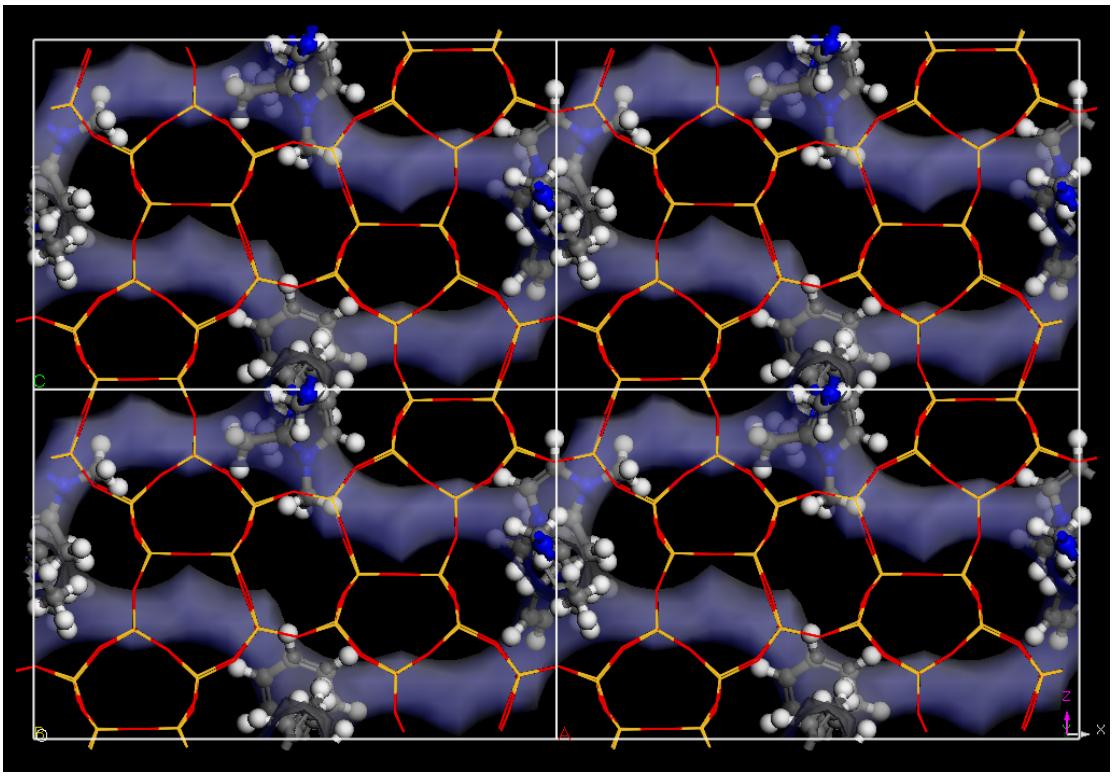

Fig. S6. Final location of 1B23DMI cations (oriented as in entry 1, Table 4), with 4 cations per u.c.

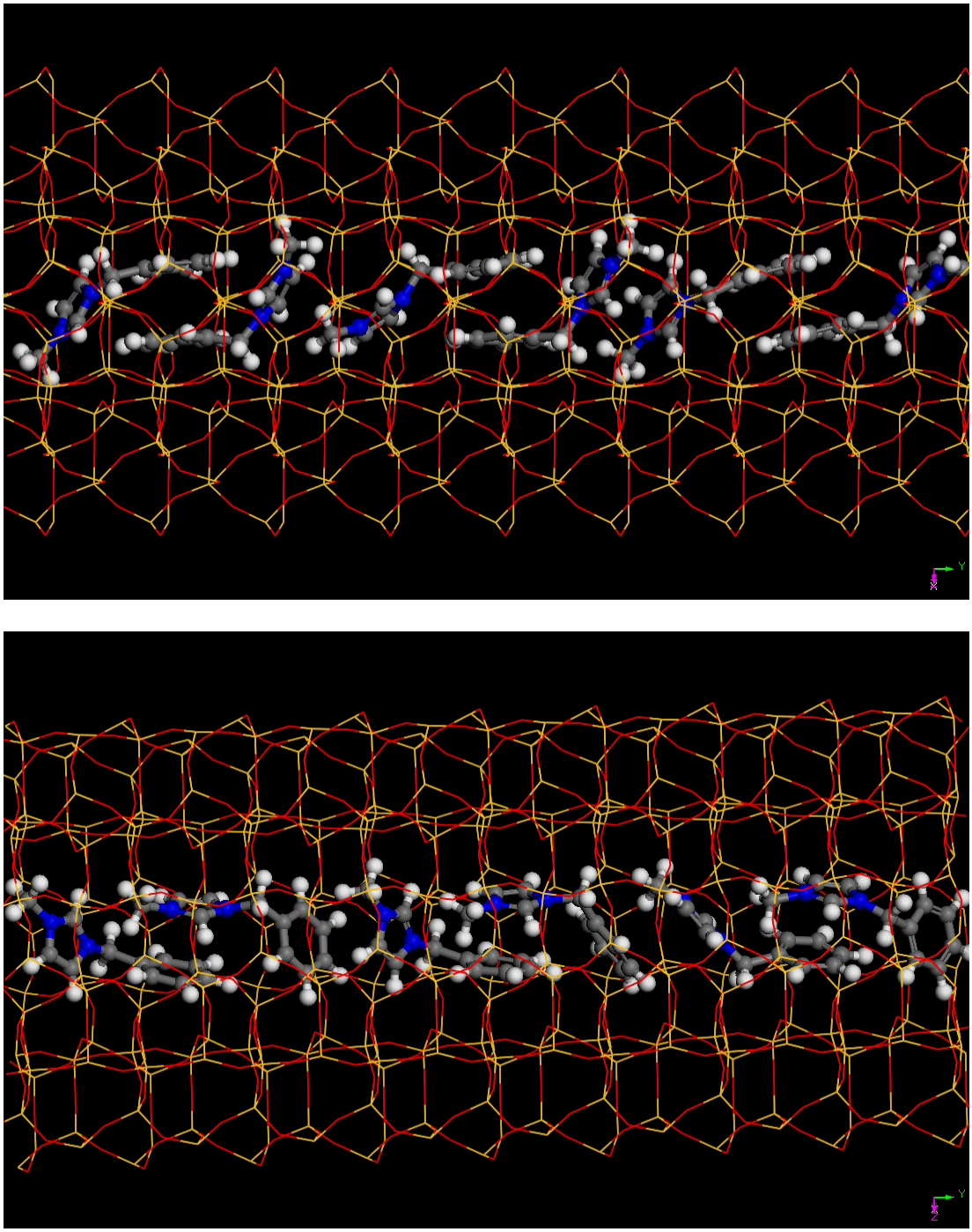

Fig. S7. Location of 1B3MI cations along the MTW channel under an unfavorable packing value of 3.0 cations per unit cell with head-to-head (top) or head-to-tail (bottom) orientation.

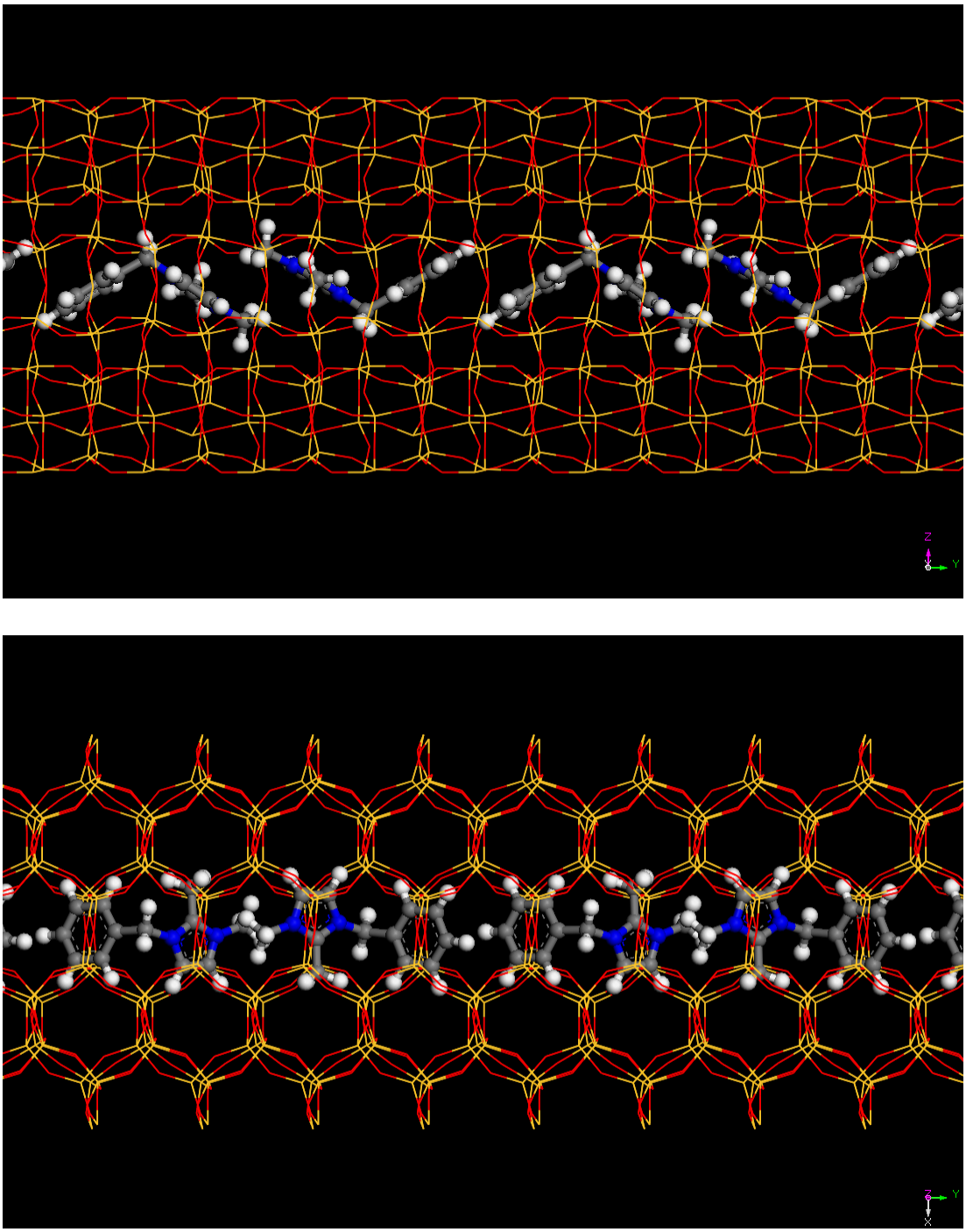

Fig. S8. Two views of the location of 1B23DMI cations along the MTW channel under a packing value of 2.0 cations per unit cell with unfavorable head-to-head orientation.