

Zeolite structure-direction by simple bis(methylimidazolium) cations. The effect of the spacer length on structure-direction and of the imidazolium ring orientation on the ^{19}F NMR resonances.

Alex Rojas, Luis Gómez-Hortigüela and Miguel A. Camblor
Supporting Information

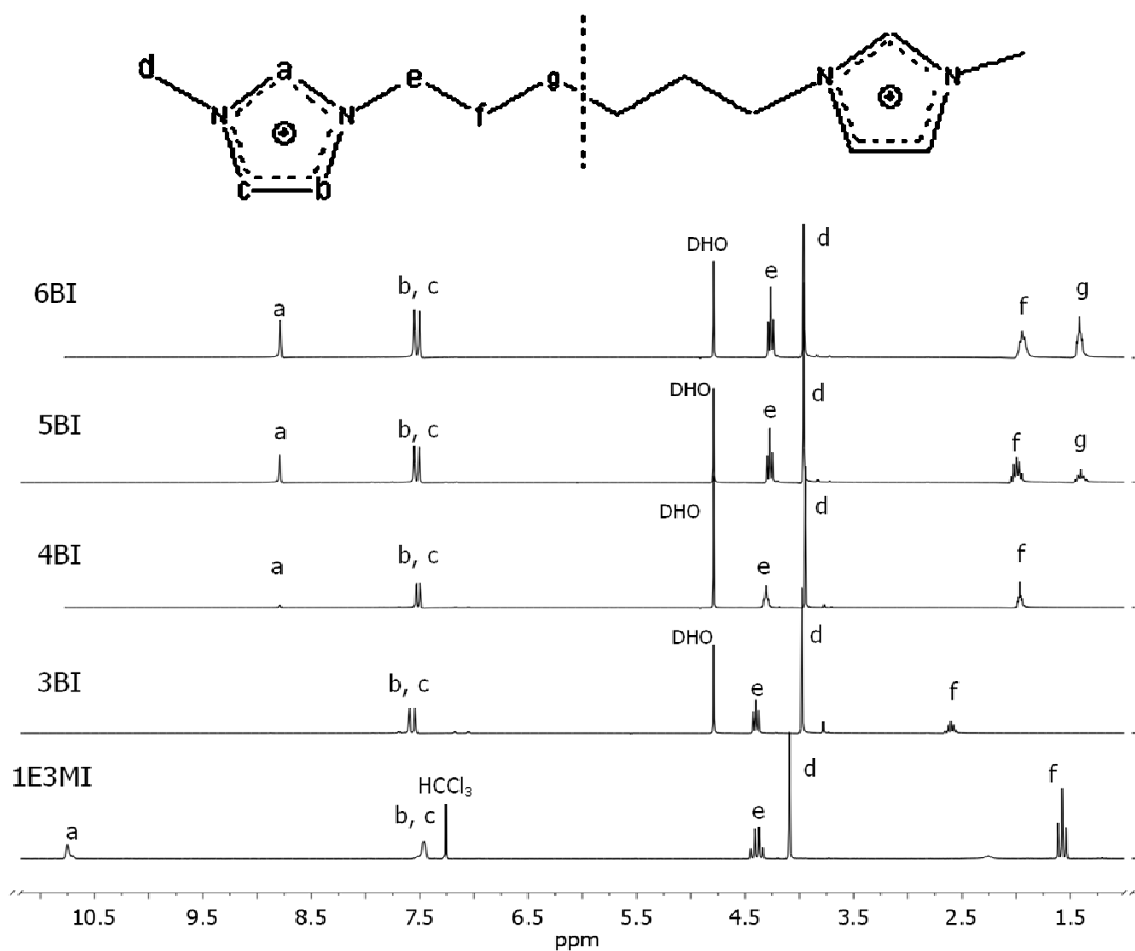


Figure S1. ^1H NMR spectra in DCCl_3 or D_2O of the organic SDA cations used in this work.

Multinuclear magic angle spinning (MAS) NMR spectroscopy

The spectra of as-made and calcined samples were carried out at room temperature on a Bruker AV-400-WB equipment using a triple channel probe with 4mm ZrO rotors and Kel-F lids spinning at 10kHz for ^1H , ^{13}C y ^{29}Si and a double channel probe with 2.5 mm ZrO rotors and Vespel lids spinning at 25kHz for ^{19}F . The ^{19}F spectra of the as-made zeolites were acquired at a resonance frequency of 376.45 MHz with a $\pi/8$ pulse at 60kHz, 75 kHz spectral width, relaxation delay of 20s and 256 scans and are referenced using Na_2SiF_6 as a secondary reference (-152.46 ppm referenced to CFCl_3 at $\delta = 0\text{ppm}$ as primary reference). The ^{13}C spectra of the as-made zeolites were acquired at 100.61 MHz resonance frequency using a CP-MAS sequence, with a $3\mu\text{s}$ ^1H 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 $\delta = 0\text{ppm}$ as primary reference). The ^{29}Si spectra were acquired at a resonance frequency of 79.49 MHz with a $\pi/12$ pulse at 20kHz, spectral width of 15kHz and 60s relaxation delay, and are referenced using kaolin as a secondary reference (-91.2ppm, referenced to TMS at $\delta = 0\text{ppm}$ as primary reference). The $^{29}\text{Si}\{^1\text{H}\}$ CP MAS experiments were carried with a ^1H $\pi/2$ pulse width at 120kHz, 50 kHz spectral width, 6.5 ms contact time, 5s relaxation delay and tppm15 decoupling. The $^{29}\text{Si}\{^{19}\text{F}\}$ CP MAS experiments were done with a $\pi/2$ ^{19}F excitation pulse at 60kHz, with contact time of 10 ms continuous-wave decoupling, delay time of 15s and 50kHz spectral width.

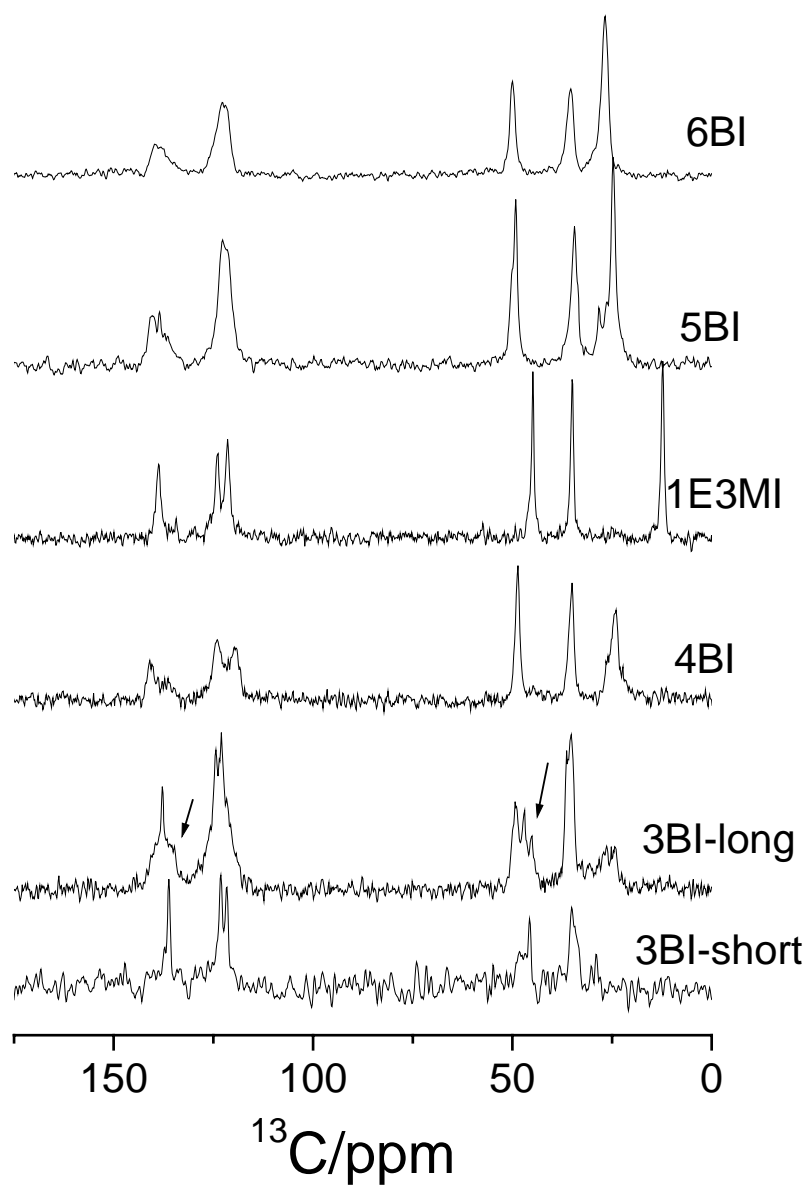


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ CPMAS NMR spectra of as-made TON zeolites. Signals of possible decomposition products are marked with arrows. The traces marked as 3BI-short and 3BI-long correspond to zeolite TON crystallized with 3BI for 3 and 9 days, respectively, and suggest 3BI decomposition under the synthesis conditions.

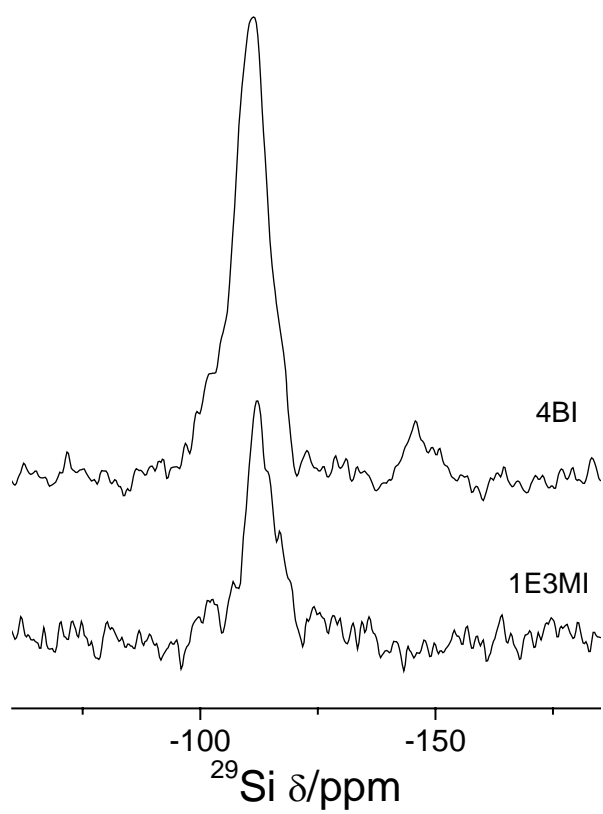


Figure S3. ^{29}Si { ^1H } CPMAS NMR spectra of as-made MFI zeolites synthesized with the SDA indicated.

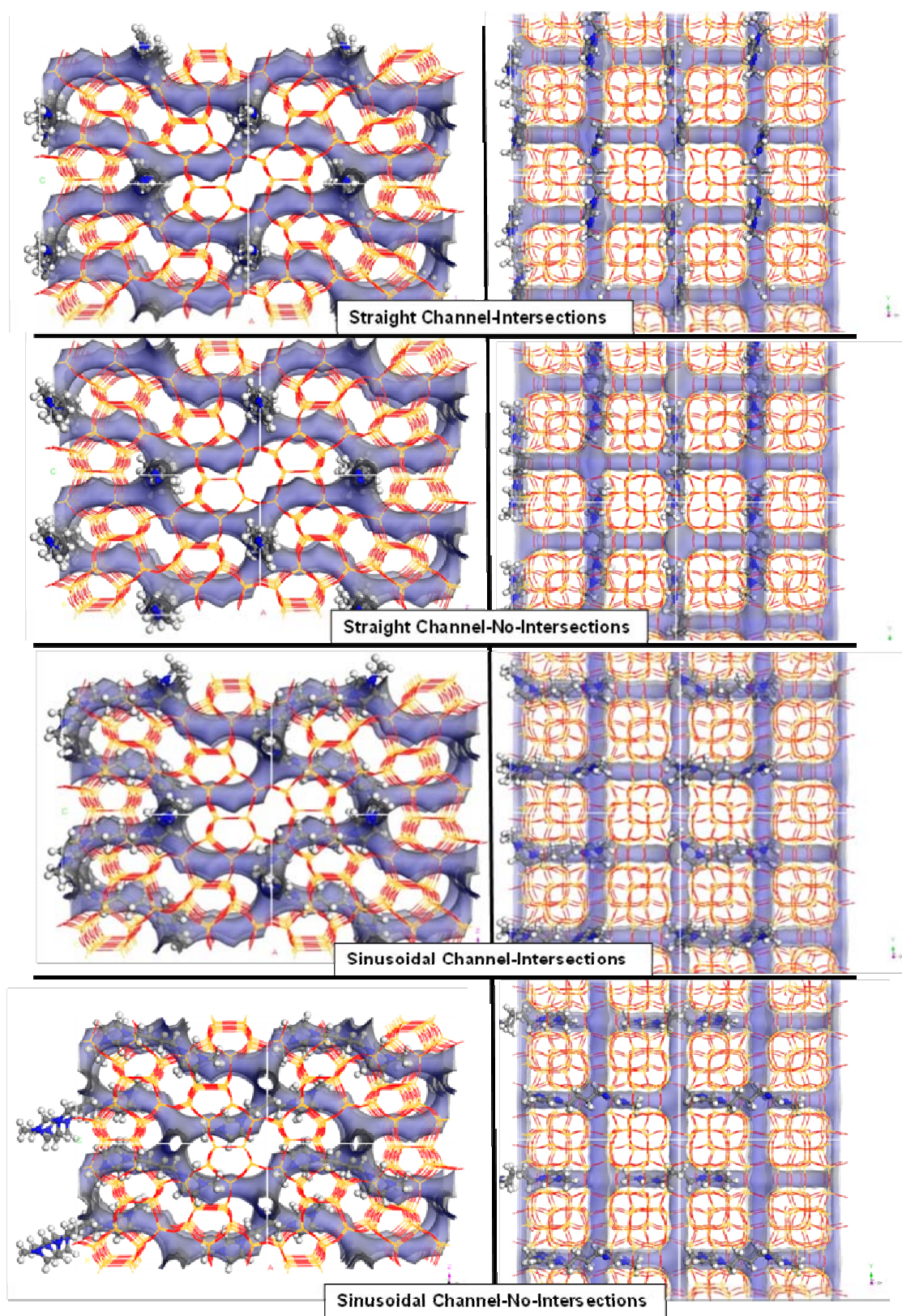


Figure S4. Different locations tried for the 4BI molecules in the MFI structure under a loading of 2 molecules per unit cell.

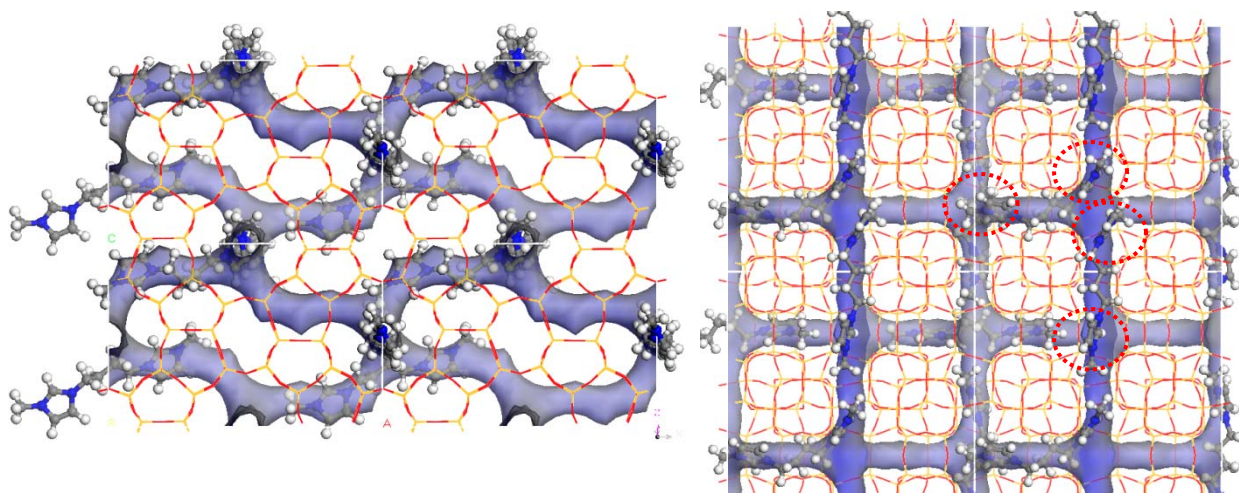


Figure S5. Two views of the less stable arrangement of 4BI molecules within the MFI structure, with half of the imidazolium rings located in the channel intersections (entry 5 in Table 3); dashed red circles highlights the imidazolium rings that are sited in the intersections.

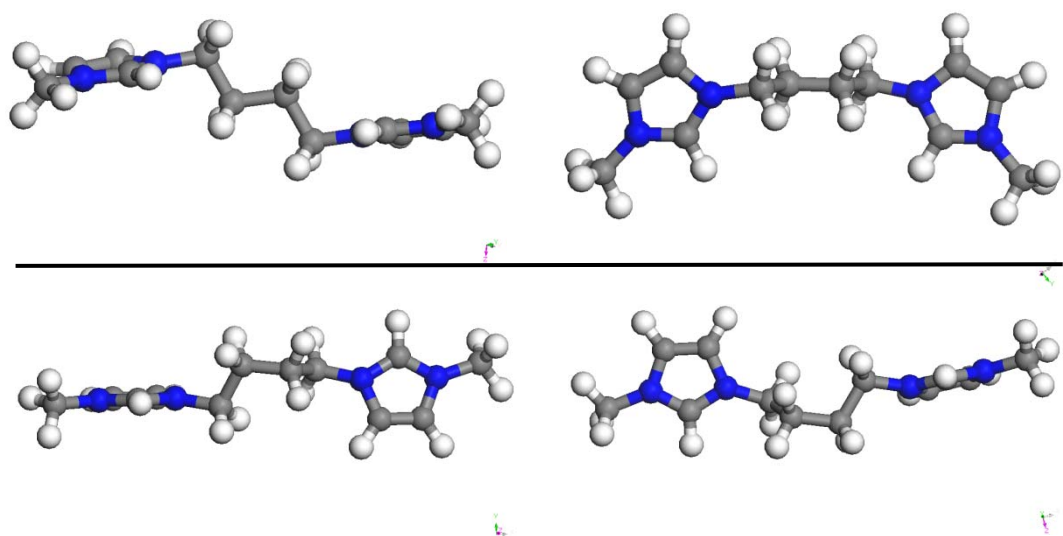


Figure S6. Conformation of 4BI SDA molecules in vacuo (top) and within the sinusoidal channels of the MFI structure (under an organic content of 4 SDA/u.c.) (bottom).

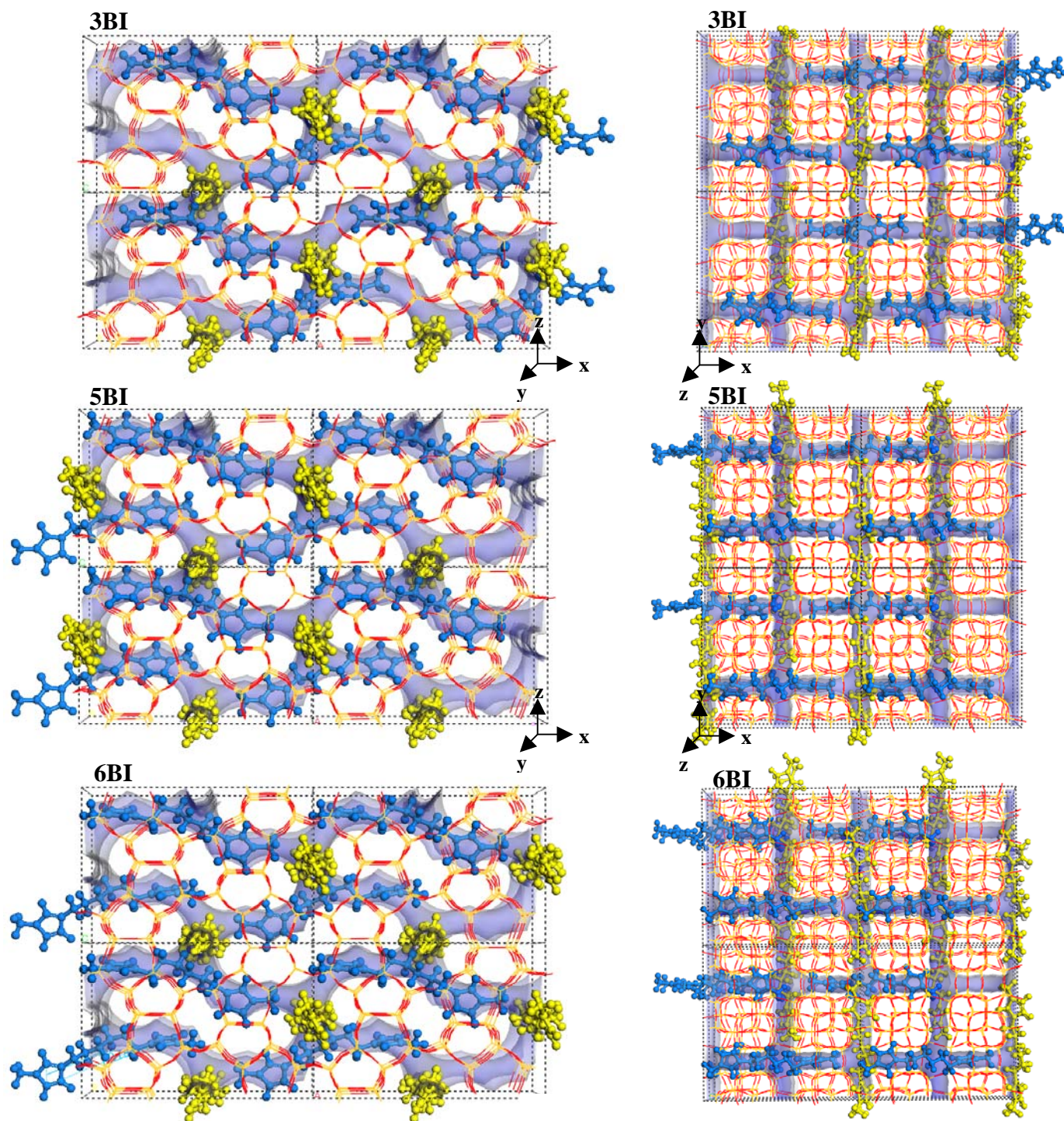


Figure S7. Final location of 3BI (top), 5BI (middle) and 6BI (bottom) molecules within the MFI structure. Molecules located in the sinusoidal and straight channels are displayed in blue and yellow, respectively.

Molecular Mechanics Study on Structure directing effects in the synthesis of TON.

For completeness, we also studied the interaction energies of the molecules when occluded within the TON zeolite, by using the molecular mechanics methodology described in the main text. In this case, due to the smaller size of the TON unit cell as well as to the presence of only one-dimensional channels, supercells of a primitive cell, containing one channel per cell and half the volume and SiO₂ of the reported orthorhombic structure,¹ were built in order to reach packing values as close as possible to the ones experimentally observed (2 1E3MI in 1x1x4 u.c., 2 3BI in 1x1x6 u.c., 2 4BI in 1x1x6 u.c., 2 5BI in 1x1x7 u.c. and 2 6BI in 1x1x8 u.c., where u.c. refers to a primitive cell with 12 SiO₂) (Table S1). The SDA molecules can only be located aligned with the channel axis. The interaction energies are shown in Table S1, while Figure S6 shows the location of the 3BI molecules within the TON zeolite.

Table S1. Interaction energies of the different molecules occluded within the TON zeolite.

Molecule	Experimental packing ^a	Theoretical packing ^a	Interaction E. (kcal/mol per Si)
1E3MI	0.48	0.5	-3.37
3BI	0.31	0.33	-4.86
4BI	0.32	0.33	-4.59
5BI	0.27	0.285	-3.88
6BI	0.245	0.25	-3.8

^amolecules per primitive cell (12SiO₂)

The interaction energies in this case are considerably smaller than the ones observed for the MFI zeolite. This is as expected since the framework density of the TON structure is higher (it is denser), and so a lower void volume is available in this framework (1.88 and 4.42 Å³ per Si atom for TON and MFI, respectively), thus allowing a smaller

incorporation of organic molecules. In practice, this would be balanced by the higher intrinsic stability expected for dense (TON) compared to open (MFI) frameworks.²

Comparison of the interaction energies indicates that, in this case, the largest interaction energy is achieved by the 3BI molecule, thus suggesting that this molecule is the best SDA for this structure. This is again in good agreement with the non-observation of the MFI structure in the synthesis carried out with this SDA.

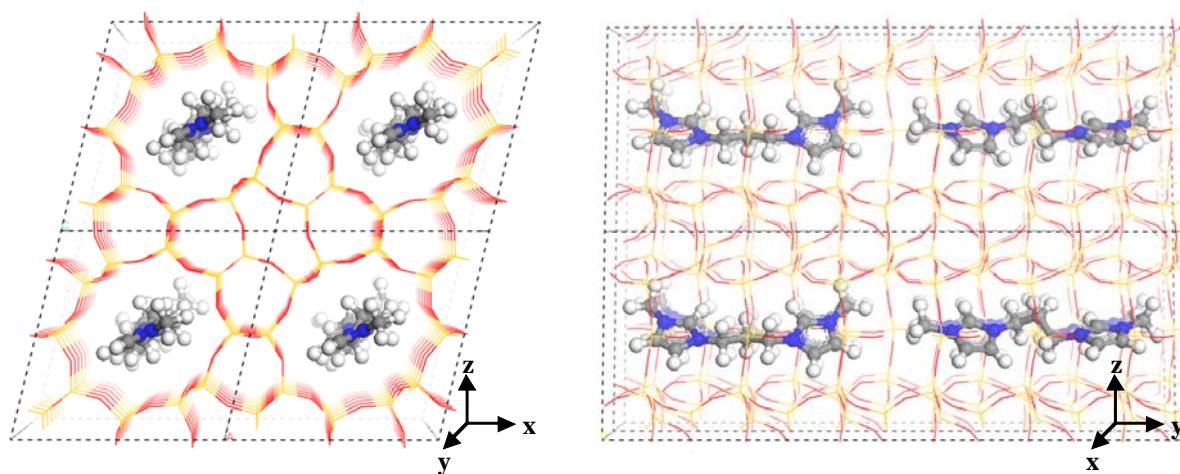


Figure S8. Location of 3BI molecules within the TON zeolite.

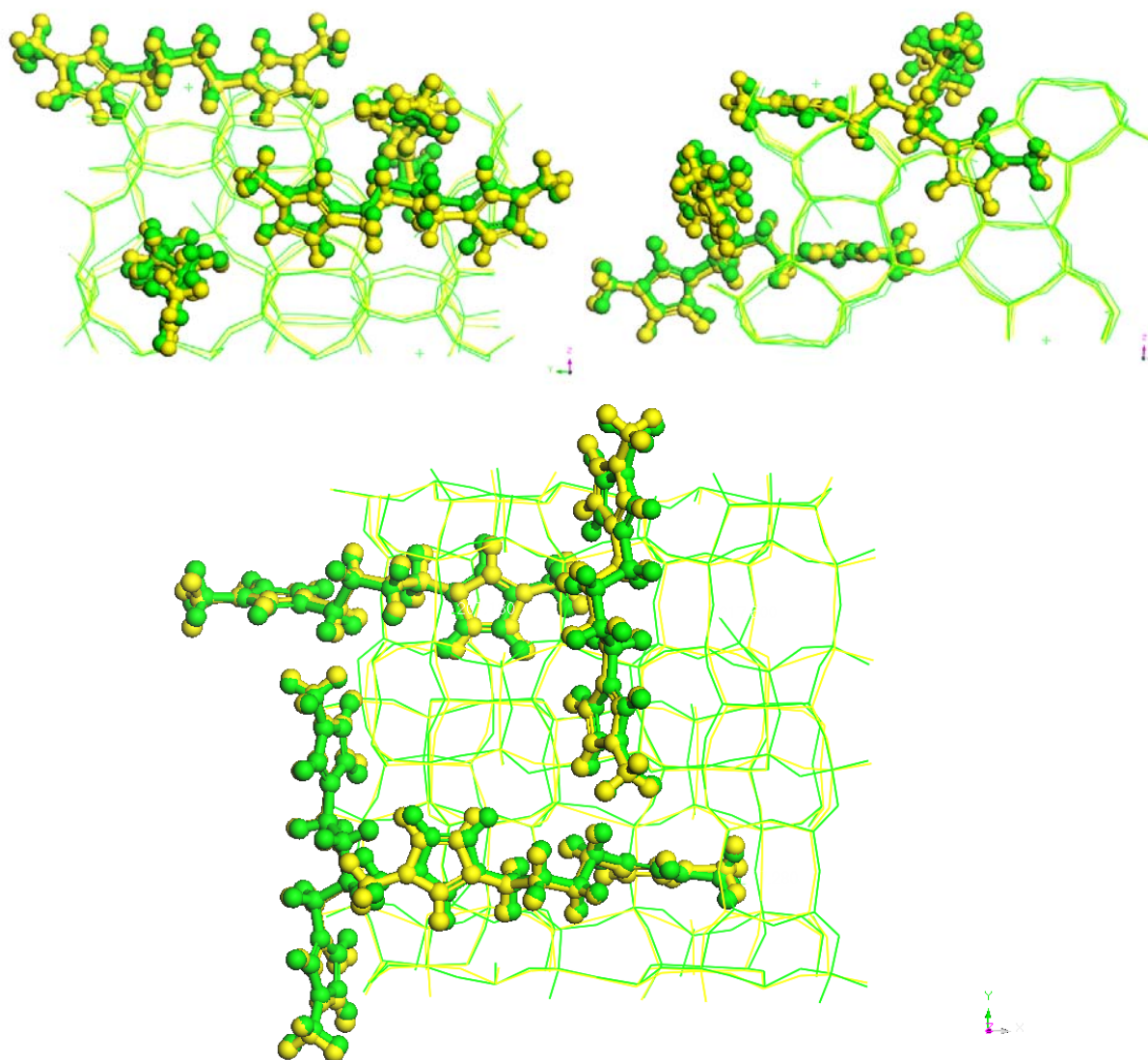


Figure S9. Three different views of the atomic coordinates of the template molecules obtained by molecular mechanics (in yellow) and by DFT+D (in green) calculations. It can be observed that the location of the template molecules is very similar in both cases, showing the high performance of molecular mechanics models in predicting the location of bulky template molecules since this is mainly a consequence of the fitting between the void volume of the framework and the molecular volume of the organic cations.

References

- ¹C.M. Zicovich-Wilson, F. Gándara, A. Monge M.A. Camblor, *J. Am. Chem. Soc.*, **2010**, *132*, 3461-3471.
- ²P.M. Piccione, C. Laberty, S. Yang, M.A. Camblor, A. Navrotsky, M.E. Davis *J. Phys. Chem.* **2000**, *104*, 10001-01011.