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# Structure-direction in the crystallization of ITW zeolite using 2-ethyl-1,3,4-trimethylimidazolium<sup>†</sup>

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2-ethyl-1,3,4-trimethylimidazolium is so far the fifth and largest imidazolium cation able to produce pure silica zeolite ITW. The crystallization is not direct, but occurs as an in situ transformation from either the chiral HPM-1 (STW) zeolite or the new layered zeolite precursor HPM-2 (preMTF) and results in large interpenetrated crystals with a habit so far unseen in this zeolite. The results of chemical, physicochemical and structural characterization allow to discuss structure-direction issues. The large cation is occluded intact in the zeolite, causing an expansion of the zeolite volume. The degree of polarization of the Si–O bond is similar to that observed in other as-made ITW zeolites.

## 1 Introduction

Zeolite ITQ-12, with Zeolite Framework Type ITW,<sup>1</sup> is a pure silica zeolite that contains double-four membered rings (D4R) together with small pores running along (100) and (001).<sup>2</sup> While only the pores along (001) seem to be large enough for the passage of small hydrocarbons, ITW displays interesting selective adsorption properties that gives this material potential for the non-cryogenic separation of propane and propylene.<sup>3</sup> Pure silica zeolites containing D4R in their structures have only been prepared in the presence of fluoride, and this anion ends up occluded inside the D4R units,<sup>4</sup> prompting the idea of a structure-direction ability of fluoride towards this type of silica zeolites.<sup>5,6</sup> Recently, Density Functional Theory (DFT) studies of pure silica ITW synthesized using 1,3,4-trimethylimidazolium (134TMI) as an organic structure-directing agent (SDA), showed that host-guest interactions in this material enhance the flexibility of the framework by polarizing the Si–O bond.<sup>7</sup> This polarization effect allows relaxation of the otherwise strained D4R structure, making it reachable for crystallization. The effect was shown to be strong enough to revert the relative stabilities of two zeolites (TON and ITW).<sup>8</sup> Later on, after the synthesis of ITW with other imidazolium cations, 1,2,3-trimethylimidazolium (123TMI) and 1,3-dimethylimidazolium (13DMI),<sup>9</sup> the idea

was corroborated and an additional role of the hydrophilicity of the imidazolium cation was proposed: the more hydrophilic the cation, the largest the flexibility enhancement, resulting in a more specific structure-direction. Thus, the structure-directing ability of the imidazolium cations was correlated to its hydrophilic character. The idea got further support when ITW was later on synthesized with 1-ethyl-2,3-dimethylimidazolium (1E23DMI):<sup>10</sup> the hydrophilicity and structure-direction ability of the cation and the framework flexibility of the as-made 1E23DMI-ITW fitted very well within the overall picture. This cation provided another example of reverting the relative stabilities of two zeolites (in this case MTW and ITW). Here we characterize a new ITW zeolite synthesized using a larger imidazolium cation, 2-ethyl-1,3,4-trimethylimidazolium (2E134TMI, see Figure 1). In the range of conditions studied, the new 2E134TMI-ITW zeolite only crystallizes as a result of an in situ transformation from either the chiral HPM-1 STW zeolite,<sup>11,12</sup> or the new layered zeolite precursor HPM-2.<sup>13</sup> The structural characterization of 2E134TMI-ITW suggests a flexibility enhancement similar to those of the previously reported ITW materials.

## 2 Experimental

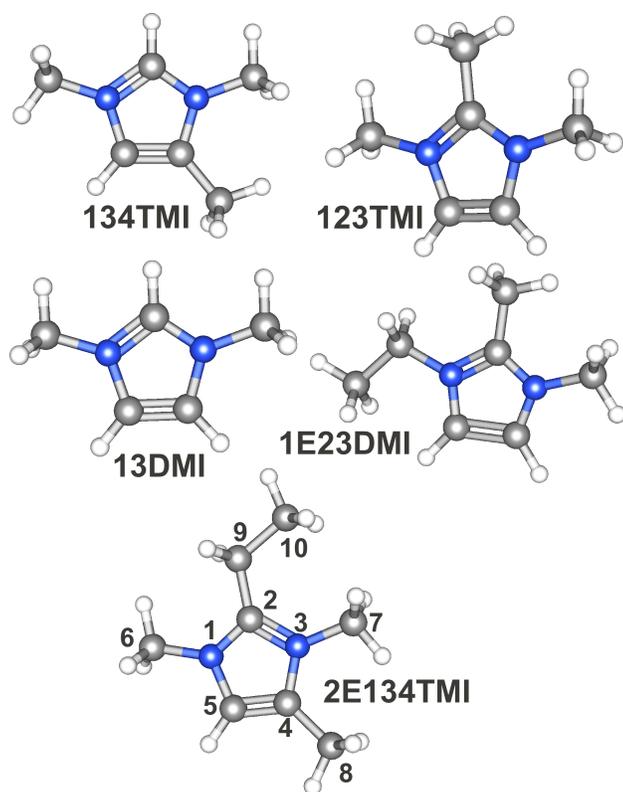
### 2.1 Synthesis of Materials

2E134TMI-ITW was synthesized during a thorough investigation of 2E134TMI as an organic SDA in the synthesis of pure silica zeolites by the fluoride route.<sup>12</sup> Briefly, while that cation behaved as a poor SDA at 150 °C, increasing the crystallization to 175 °C afforded the fast crystallization of two new phases: the chiral silica zeolite HPM-1 (STW)<sup>11</sup> and the new zeolite layered precursor HPM-2.<sup>13</sup> Both phases were

<sup>†</sup> Electronic Supplementary Information (ESI) available: <sup>19</sup>F MAS NMR spectrum, thermogravimetric and thermo differential analysis curves, details of Rietveld refinement and Rietveld plot for 2E134TMI-ITW. See DOI: 10.1039/b000000x/

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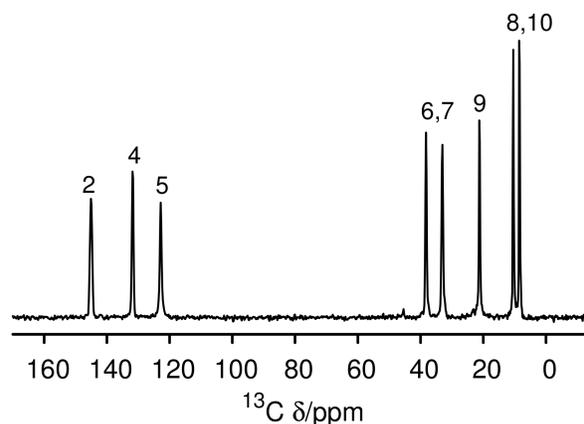


**Fig. 1** Five imidazolium cations able to crystallize pure silica ITW (with C, N numbering for 2E134TMI indicated). Blue, N; gray, C; white, H.

found unstable in the crystallizing medium, showing signs of transformation into 2E134TMI-ITW. The phase initially crystallizing could be controlled by adjusting the chemical composition of the synthesis mixture, which was  $\text{SiO}_2$ : 0.5 2E134TMI-OH: 0.5 HF:  $x$   $\text{H}_2\text{O}$ . For low  $\text{H}_2\text{O}/\text{SiO}_2$  ratios HPM-1 was the starting phase, while at intermediate ratios HPM-2 tend to crystallize. After prolonged heating transformation of both phases into ITW occurred. 2E134TMI-ITW could be synthesized in pure form, for instance, from a synthesis mixture with  $x=5.7$  after 39 days of heating at 175 °C (shorter crystallization times of 7 and 11 days produced instead HPM-1 and HPM-1 plus traces of ITW, respectively).

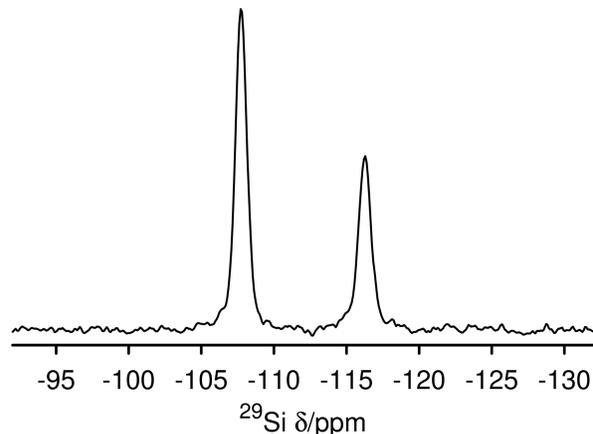
## 2.2 Characterization

Phase identification was done by powder X-ray diffraction (XRD, Bruker D8 Advance diffractometer,  $\text{Cu K}\alpha$ ,  $2\theta$  2–45° range). The structure analysis was done using high resolution synchrotron XRD data collected at the ESRF on the BM25A beam line. The data was collected in capillary mode (0.8 mm) with  $\lambda = 0.82548$  Å, from 2° to 62°  $2\theta$ . Details of the room temperature multinuclear ( $^{19}\text{F}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$ ) magic angle spin-



**Fig. 2**  $^{13}\text{C}$  MAS NMR spectrum of as-made 2E134TMI-ITW. C-atom numbering as shown in Figure 1, bottom

ning nuclear magnetic resonance (MAS NMR) spectroscopy have been given elsewhere.<sup>9</sup> For field emission scanning electron microscopy (FE-SEM) imaging on uncoated samples a FEI NOVA NANOSEM 230 was used. C, H, N elemental chemical analysis was done in a LECO-CHNS-932 analyzer. Thermogravimetric analyses were performed under oxygen flow (100ml/min) in an SDT Q600 TA Instruments equipment up to 1000°C (heating rate 10°C/min).



**Fig. 3**  $^{29}\text{Si}$  MAS NMR spectrum of as-made 2E134TMI-ITW.

## 3 Results and Discussion

So far 2E134TMI cation is the fifth organic SDA cation able to produce pure silica zeolite ITW, after the reports on synthesis of ITW using 1,3,4-trimethylimidazolium (134TMI),<sup>2</sup> 1,2,3-trimethylimidazolium (123TMI) and 1,3-dimethylimidazolium (13DMI),<sup>9</sup> and, more recently, 1-ethyl-

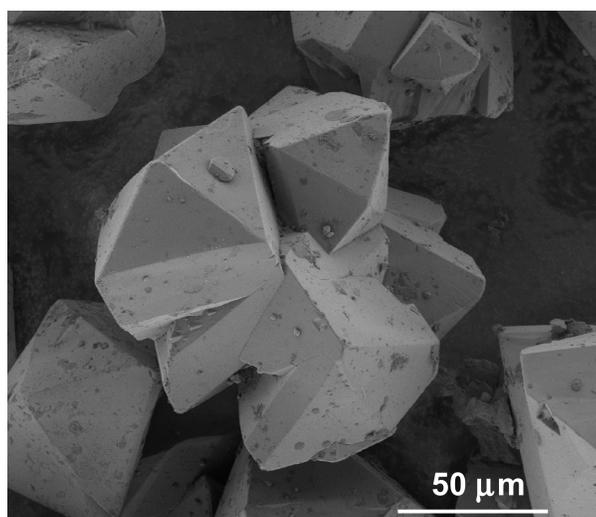
**Table 1** Chemical composition of as-made 2E134TMI–ITW

%C	%H	%N	C/N <sup>a</sup>	H/N <sup>a</sup>	TG <sup>b</sup>	u.c. <sup>c</sup>
9.93	1.8	3.1	3.7 (4.0)	8.1 (7.5)	81.64 (81.50)	$[\text{C}_8\text{H}_{15}\text{N}_2\text{F}]_{2.0}[\text{SiO}_2]_{24}0.6\text{H}_2\text{O}$

<sup>a</sup>Molar ratios. Theoretical values for 2E134TMI between parentheses; <sup>b</sup>Residue (in wt%) in the thermogravimetric analysis (the amount in parenthesis corresponds to the SiO<sub>2</sub> content in the unit cell composition given in the last column); <sup>c</sup>Unit cell composition: SDA calculated from the N analysis assuming the SDA is intact and the TG residue is SiO<sub>2</sub>. The H<sub>2</sub>O content is calculated from H excess versus N and may represent both water content and connectivity defects. Fluoride was not analyzed and is assumed to match the content of the organic cation. The empirical formula is based on the unit cell determined by crystallography (24 SiO<sub>2</sub>).

2,3-dimethylimidazolium (1E23DMI).<sup>10</sup> This cation is the largest of the five SDA but, since 2E134TMI–ITW crystallized at 175 °C after very long crystallization times (well over 30 days), the possibility that the effective SDA may be one degradation product rather than the pristine 2E134TMI needs to be considered.

According to the chemical analysis of the as-made zeolite, Table 1, there is one cation per large cavity of the zeolite (2 per unit cell) but there are small deviations of the C/N molar ratio that might rise doubts about its integrity. However, the <sup>13</sup>C MAS NMR spectrum, Figure 2, clearly shows the eight expected resonances in chemical shift ranges close to those observed in the spectra of the cation in solution or occluded in other materials (the chiral HPM–1 zeolite<sup>12</sup> or the layered organosilicate zeolite precursor HPM–2).<sup>13</sup> This demonstrates the integrity of the cation occluded in the zeolite and its notable chemical and thermal stability and suggests it is in fact the organic SDA during the crystallization of ITW.

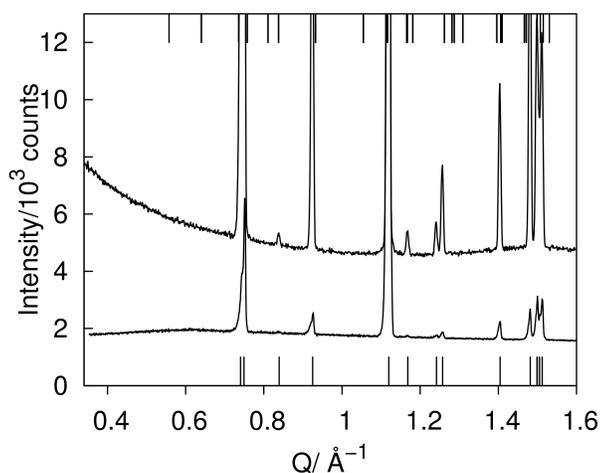
**Fig. 4** FE–SEM picture of 2E134TMI–ITW.

The presence of fluoride occluded in the zeolite is demonstrated by <sup>19</sup>F MAS NMR, see ESI Figure S1.† The single resonance at –39.8 ppm is characteristic of fluoride occluded in D4R units of pure silica zeolites.<sup>4,14–17</sup> Additionally, the

<sup>29</sup>Si MAS NMR spectrum (Figure 3) only shows two resonances in the Q<sup>4</sup> region, evidencing the lack of connectivity defects in the as-made material (absence of any noticeable resonance in the Q<sup>3</sup> region around –102ppm),<sup>18</sup> implying that charge balance of the occluded cations is attained by equimolar amounts of occluded fluoride. Thermogravimetric analysis shows a minor weight loss step of around 0.5% in the 150 – 500 °C region, followed by a large step of 17.9 % in the 600 – 850 °C (see ESI Figure S2 †). The first minor step is assigned to the desorption of residual organic matter in the outer surface, while the second one is assigned to the combustion/degradation and desorption of the organic cation and desorption of the fluoride anion and accounts for the complete filling of the two large [4<sup>4</sup>5<sup>4</sup>6<sup>4</sup>8<sup>4</sup>] and two small [4<sup>6</sup>] cavities per unit cell of ITW (see Table 1).

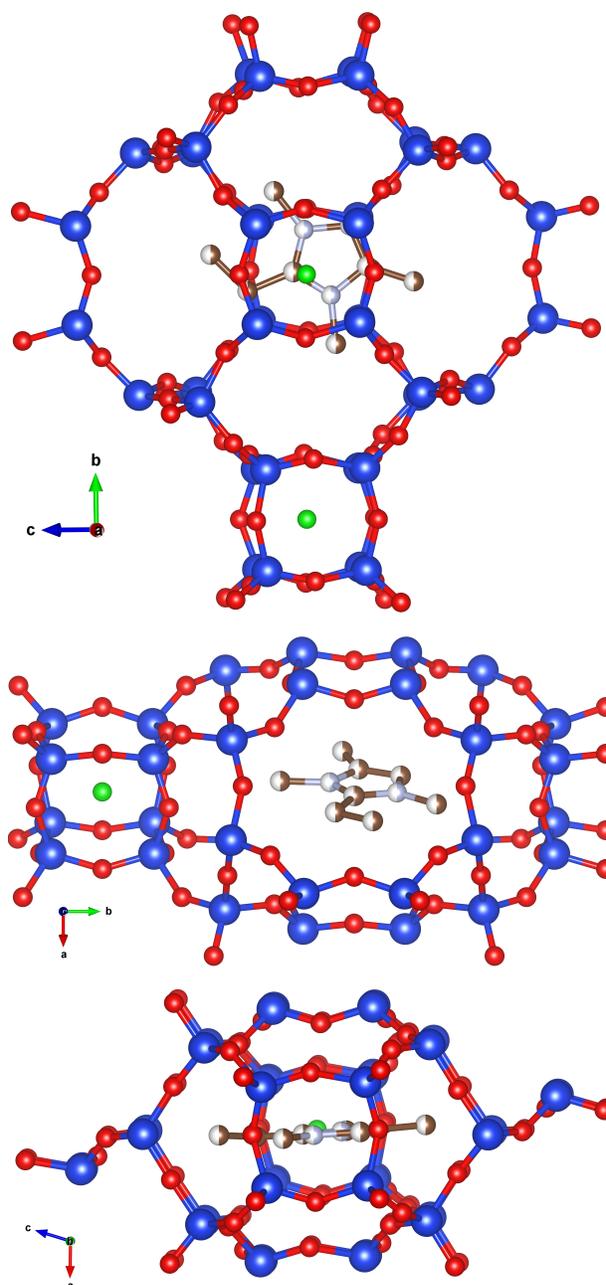
Figure 4 shows that 2E134TMI crystallizes as rather large, twinned and frequently interpenetrated crystals. Their large size is possibly a result of the long crystallization as the product of a transformation from another crystalline zeolite (HPM–1, STW). It is worth to note that each one of the five SDA used so far to make ITW produces a different crystal habit, with the long thin needles obtained with 123TMI and the low aspect ratio crystals in Figure 4 obtained with 2E134TMI as the most distant extremes.<sup>9,10</sup> Considering the cage-like nature of ITW with regard to SDA sitting and that the SDA is the only difference in the composition of the final zeolites, these differences in morphology, which reflect the different relative rates of growth of different crystal planes in the presence of different cations, are rather unusual. According to Gies,<sup>19</sup> zeolites with one-dimensional pores generally grow as needles parallel to the pore, because growth perpendicular to this direction depends on the rate of deposition of guests species, which is slow, and their clathration through the deposition of silica. In zeolites with multidimensional pores, different SDAs may promote different crystal habits by preferential sitting of the SDA.<sup>20</sup> Also, it has been shown that with the same SDA but different chemical composition, zeolites may produce different habits. Such is, for instance, the case in the synthesis of pure silica vs aluminosilicate IFR, where as the Al content increases (and fluoride content decreases) the aspect ratio of the crystal largely increases.<sup>21</sup> This effect has been interpreted as a result of the different sitting of Al and F in the frame-

work, with F sitting at specific positions favoring the formation of new channels through adsorption of new SDA guests at planes parallel to the main crystal growth direction.<sup>22</sup> Thus, the different morphologies in ITW might reflect large differences in the energy of adsorption of different guests in the silica framework. However, we contend that, despite the seemingly similar synthesis conditions, the different morphologies may result from a different composition in the liquid phase at crystallization conditions: since 2E134TMI–ITW crystallizes by transformation of the previously crystallized STW zeolite (with yields of over 80 % based on silica), this zeolite nucleates and grows from a solution highly depleted in silica that stills have, however, and excess of SDA and F ions.



**Fig. 5** XRD patterns of as-made 2E134TMI–ITW obtained with a conventional diffractometer (bottom) and with synchrotron radiation (top). Vertical marks correspond to the position of allowed reflections without cell doubling (bottom, unit cell determined in this work in space group  $Cm$ ) or with cell doubling (top, unit cell of calcined ITW in space group  $I2/m$ ).<sup>9</sup>

The XRD pattern of as-made ITW, Figure 5, showed no signs of the cell doubling that was observed in some, but not all, of the other as-made ITW materials. The zeolites prepared with 123TMI and 13DMI showed cell doubling and were indexed in space group  $I2/m$ ,<sup>9</sup> although other authors proposed a symmetry lowering to  $P2_1$  for 123TMI–ITW, also with cell doubling, based on a 2D  $2Q$   $^{29}\text{Si}$  NMR study of a  $^{29}\text{Si}$  enriched zeolite.<sup>25</sup> The 134TMI–ITW zeolite occasionally showed very faint reflections assignable to cell doubling, and the inconsistency of this observation was deemed likely to be due to preferred orientation effects. However, in 1E23DMI–ITW and also in the new 2E134TMI–ITW zeolites, no cell doubling was observed using conventional or synchrotron radiation. It is interesting to note that the two as-made zeolites that consistently showed cell doubling (123TMI– and 13DMI–ITW) also showed more complex  $^{29}\text{Si}$  MAS NMR spectra, with resolu-



**Fig. 6** Three views of the location of guests in 2E134TMI–ITW. Only one of the two symmetrical orientations of the organic cation is shown. Blue, Si; red, O; bronze, C; gray, N; green F.<sup>23</sup>

tion of up to five crystallographic sites, while the rest of the as-made zeolites only contained two resonances in their spectra, due to Si sites involved and not involved, respectively, in D4R units. This suggests that, beyond preferred orientation effects, 123TMI–ITW and 13DMI–ITW have a higher degree of ordering. For the rest of materials, including 2E134TMI–ITW,

**Table 2** Unit cell and cation data for ITW zeolites

Cation	CatVol <sup>a</sup>	Space Group	<i>a</i>	<i>b</i>	<i>c</i> <sup>b</sup>	$\beta$	Vol <sup>b</sup>	$\Delta T$ <sup>c</sup>	reference
None <sup>d</sup>	0	<i>I2/m</i>	10.32658	14.99940	17.71021	105.3959	2644.74	2.82	<sup>9</sup>
123TMI	123.6	<i>I2/m</i>	10.43748	14.80768	17.50255	106.0895	2599.15	4.74	<sup>9</sup>
13DMI	105.5	<i>I2/m</i>	10.42127	14.8998	17.5897	105.8066	2627.97	3.63	<sup>9</sup>
134TMI	123.5	<i>Cm</i>	10.4478	14.9854	17.6732	105.935	2660.68	6.17 <sup>e</sup>	<sup>24</sup>
1E23DMI	144.5	<i>Cm</i>	10.498797	14.91631	17.69389	106.05730	2662.816	4.67	<sup>10</sup>
2E134TMI	164.3	<i>Cm</i>	10.532250	14.964344	17.653694	106.0718	2673.628	4.76	this work

<sup>a</sup> Connolly volume ( $\text{\AA}^3$ ) of the cation for a conformation close to that found in the zeolite<sup>10,12</sup>; <sup>b</sup> cell edges in  $\text{\AA}$ . For zeolites with *Cm* symmetry the *c* parameter and the cell volume ( $\text{\AA}^3$ ) have been doubled; <sup>c</sup> deviation from tetrahedrality, determined crystallographically; <sup>d</sup> calcined 123TMI–ITW <sup>e</sup> the structure of 134TMI–ITW was refined with constrains on Si–O and O–O distances.

the lower degree of ordering may prevent the observation of a cell doubling. The more disordered frameworks appear for the materials that show a cell expansion in the as-made form compared to the calcined form (i.e., for 2E134TMI–, 134TMI– and 1E23DMI–ITW) and we hypothesize that it may be a result of the SDA "pushing" against the framework.<sup>24</sup>

The pattern of 2E134TMI–ITW was indexed in space group *Cm* with cell parameters *a*= 10.527  $\text{\AA}$ , *b*= 14.972  $\text{\AA}$ , *c*= 8.826  $\text{\AA}$ ,  $\beta$ = 106.02° using the program ITO in the CMPR toolkit.<sup>26,27</sup> Powder XRD data collected with synchrotron radiation was used for the structural characterization of as-made 2E134TMI–ITW, using the Si and O fractional coordinates reported for 134TMI–ITW.<sup>24</sup> The silica framework was initially refined with restrains on Si–O (1.610 $\text{\AA}$ ) and O–O (2.612  $\text{\AA}$ ) distances and at the final stages of the refinement the weight of the restrains was gradually reduced and finally completely eliminated. A fluoride anion was introduced at (0.5,0.5,0.5), i.e., close to the center of the [4<sup>6</sup>] cage. The organic cation was introduced as a combination of two rigid bodies, one for the imidazole ring with the three methyl substituents and the other, corresponding to the ethyl group, as a satellite able to rotate around the C(2)–C(9) bond. The cation was introduced inside the slit-shaped [4<sup>4</sup>5<sup>4</sup>6<sup>4</sup>8<sup>4</sup>] cavity initially oriented almost normal to the equatorial plane but it rapidly sited close to that plane when allowed to move. The fractional occupancies of the organic atoms was fixed to 0.5 so as to have one per cavity (there are two symmetric orientations). Further details of the refinement are provided as ESI (Tables S1 and S2, Figure S3). †In the refined structure ( $R_{wp}$ = 5.86 %,  $R_p$ = 4.42 %,  $R_{F2}$ = 6.51 %,  $\chi^2$ = 5.416) the organic cation resides close to the equatorial plane of the large cavity, with the ethyl group only slightly rotated with respect to the plane of the imidazole ring (6.3° out of plane, computed as the C(10)–C(9)–C(2)–N(1) dihedral angle, Figure 6). This conformation is far from the most stable one (with the ethyl group about normal to the imidazolium ring)<sup>12</sup> and also far from that found in STW, where the ethyl group is some 54° out of the plane of the ring

and directed towards an 8MR window.<sup>12</sup> The unfavorable conformation adopted by 2E134TMI occluded in ITW reflects the highly constrained void space within the cavity.

A calculation of <sup>29</sup>Si chemical shifts using the average Si–O–Si angle for every crystallographic site and the empirical correlation of Thomas et al.<sup>28</sup> reveal the chemical shifts are grouped around two values, justifying the existence of only two resonances in the <sup>29</sup>Si MAS NMR spectrum (Figure 3): silicon sites belonging to D4R units have more acute Si–O–Si average angles (141.5°) and are significantly downfield shifted with respect to the position of other sites (average Si–O–Si angle: 156.0°).

The refined cell of 2E134TMI–ITW is the most expanded among the reported ITW zeolites (1336.8  $\text{\AA}^3$  per 24 SiO<sub>2</sub>, see Table 2), being almost 3% larger than the most contracted one (2599.15  $\text{\AA}^3$  per 48 SiO<sub>2</sub> in 123TMI–ITW).<sup>9</sup> While 2E134TMI is the largest of the five SDA considered here, there is not, however, a direct relationship between cation volume and cell volume. In fact, there is not a clear relation between any cell parameter and the cation's volume, except for the *a* parameter. This shows a weak linear dependency on the cation volume, despite the fact that the *a* edge goes across the imidazolium ring which, presumably, should not change much in size between the different cations.

The flexibility of zeolites has been previously proposed as a key property of "realizable zeolites".<sup>29,30</sup> If we admit that zeolites are metastable phases,<sup>31,32</sup> "realizable zeolites" are materials that may actually crystallize by kinetical control. Thus, flexibility is important with regard to structure-direction effects that drive the crystallization to a particular zeolite: the possibility that host-guest interactions can improve the flexibility of the zeolite and hence the chance to find an optimum host-guest packing needs to be considered.<sup>33</sup> The case of STW, lacking any flexibility in calcined pure silica form,<sup>30</sup> but being nonetheless realizable by virtue of an enhanced flexibility in its as-made form illustrates the importance of this point.<sup>11,12</sup> In this regard it is important to distinguish two

kinds of framework flexibilities, i.e., of the ability of a framework to deform. Sartbaeva et al. define a "flexibility window" as "a range of densities in which the structural units (for example, tetrahedra) can retain their ideal shape".<sup>29</sup> For the description of pure silica calcined zeolites, generally considered as highly covalent tetrahedral frameworks where tetrahedra behave as rigid units, this kind of framework flexibility may suffice. However, at least for as-made zeolites prepared with fluoride, the relevant framework flexibility needs to encompass any deformation of the framework, including deformations of the tetrahedra themselves. As it has been shown before by DFT calculations, the F<sup>-</sup> promoting effect towards silica zeolites with D4R units mainly consists on an increased ionization of the Si–O bond that allows the structure to relax, decreasing the stress associated with such silica units.<sup>8–10</sup> With a lessened covalent character, [SiO<sub>4</sub>] units can deviate more from tetrahedrality, affording a wider range of deformations. The magnitude of this deviation was shown to be also dependent on the SDA cation: the more hydrophilic the cation, the larger the deviation.

The five as-made ITW materials not only share the same framework topology but also a closely similar chemical composition, which can be written as |RF|<sub>2.0</sub>[SiO<sub>2</sub>]<sub>24</sub>, i.e. only the nature, but not the concentration, of the cation R is different among the five solids. Structure-direction effects on them shall have two main actors: fluoride, whose effect must be the same in any of the five as-made ITW zeolites, and the organic cation, deemed to be responsible for any difference. Thus, a comparison of all these as-made ITW zeolites is merited. The deviation from tetrahedrality in 2E134TMI-ITW, computed as the standard deviation of OSiO angles from the ideal value of 109.47°, is 4.76°, thus similar to the values calculated from crystallographic data for other ITW zeolites refined without restraints on distances and/or angles (which are all in the 3.6–4.7 range). This accords with the relatively high hydrophilicity of 2E134TMI: the hydrophilicity of the five cations, estimated from the percentage of transfer of its iodide salt from water to chloroform,<sup>34</sup> decreases in the order 123TMI > 1E23DMI > 2E134TMI > 13DMI > 134TMI.<sup>10,12</sup> The fact that the deviation from tetrahedrality is slightly larger for 2E134TMI than for the most hydrophilic cations may be attributed to its larger cation size, which, together with the need to adopt an unfavorable conformation with the ethyl group close to the imidazolium plane, may also detract from a more specific structure-direction of 2E134TMI towards ITW. For ITW zeolites, the lowest deviation from tetrahedrality occurs for the calcined material, implying it is the less flexible one, whilst as the unit cell contracts or expands in the cation-containing materials the deviation from tetrahedrality increases, showing the increased flexibility of the as-made materials. The only other as-made pure silica zeolites for which there are detailed structural data are AST prepared with quin-

clidine (Q)<sup>14</sup> or tetramethylammonium (TMA)<sup>35</sup> and STW prepared with 2E134TMI.<sup>12</sup> For comparison, we have calculated  $\Delta T$  using the available structural data for the as-made and calcined materials.<sup>11,12,14,15,35</sup> In every case there is a substantial increase of  $\Delta T$  in the as-made form (3.03, 3.27 and 3.40° for as-made TMA-AST, Q-AST and 2E134TMI-STW) with respect to the calcined form (0.73 and 1.88° for calcined AST and STW), similar to the ITW case. This suggests a general effect of polarization of the Si–O bond in D4R zeolites containing fluoride and a cation, which make D4R zeolites realizable.<sup>8</sup>

Finally, as pointed out above, we have previously reported three instances in which host-guest interactions are able to revert the order of stability of silica zeolites:<sup>8,10</sup> TON or MTW zeolites have been transformed in situ into ITW when using 13DMI and 134TMI or 1E23DMI, respectively, in spite of the lower stability of ITW in the absence of fluoride and organics. The lower stability of ITW, confirmed by DFT calculations, is due to its less dense nature and, significantly, to the presence of D4R in the structure.<sup>8</sup> The in situ transformation of STW to ITW with 2E134TMI, however, does not likely imply a reversion in stability: the framework density of STW is significantly smaller than that of ITW, while STW also contains a larger density of D4R. Both facts suggest the STW silica framework is less stable than the ITW silica framework.

## 4 Conclusions

2E134TMI is able to transform in situ an initially crystallized zeolite STW into zeolite ITW, which is more dense and, likely, less strained due to its lower concentration of D4R units. Despite the long crystallization time at 175 °C, the occluded organics are intact and occupy every large [4<sup>4</sup>5<sup>4</sup>6<sup>4</sup>8<sup>4</sup>] cavity, with fluoride occluded in D4R as counterbalancing anion. The ethyl groups lie some 6° out of the plane of the imidazolium ring in a relatively unfavorable conformation. The structure shows no sign of cell doubling and displays the lowest framework density amongst reported ITW zeolites due to the large cation size. The deviation from tetrahedrality of the SiO<sub>2</sub> framework is larger than that observed in the calcined ITW zeolite and similar to the values observed for other as-made materials containing D4R, suggesting an enhanced flexibility afforded by host-guest interactions, which is deemed necessary for the crystallization of this zeolite.

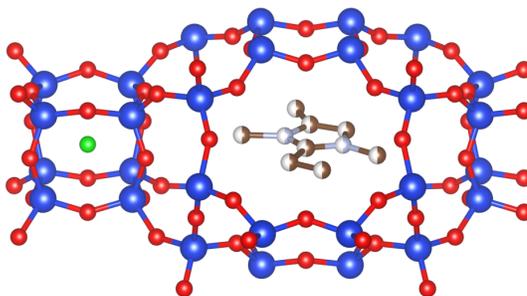
## 5 Acknowledgements

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TOC: 2-ethyl-1,3,4-trimethylimidazolium, the fifth and largest imidazolium cation able to produce pure silica zeolite ITW, affords together with fluoride a significant flexibility enhancement of the  $\text{SiO}_2$  framework.