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## Introduction

Large pore (consisting of 12 tetrahedra, 12R) and extra-large pore (consisting of more than 12 tetrahedra) zeolites have attracted considerable interest because of their potential uses in hydrocracking of heavy oil fractions,<sup>1,2</sup> facilitating the production of fine chemicals and biomass processes,<sup>3</sup> preparing materials in microelectronics with low values of the highfrequency dielectric constant,<sup>4</sup> manufacturing encapsulated light-emitting devices (LEDs)<sup>5</sup> and in medicine for diagnostic treatments and controlled drug delivery.<sup>6</sup> Although they are still limited in number, the past decade has witnessed the miraculous development and prosperity of the large and extralarge pore zeolites, owing to the use of germanium in the concentrated fluoride system during the synthesis.<sup>7</sup> The presence of Ge and/or F aids the formation of the 3-membered ring (3R) or double-4-membered ring (D4R), which is thought to

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## Facile preparation of extra-large pore zeolite ITQ-37 based on supramolecular assemblies as structure-directing agents†

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The chiral germanosilicate zeolite ITQ-37 was prepared using a readily-obtained, semi-rigid achiral organic structure-directing agent (SDA) 1,1',1"-(2,4,6-trimethylbenzene-1,3,5-triyl)tris(methylene)tris-(3-methyl-1*H*-imidazol-3-ium) (denoted tmbi). The synthetic factors, including crystallization temperature, water content, germanium and tmbi concentrations for the crystallization of ITQ-37, were studied by means of single crystal X-ray diffraction, powder X-ray diffraction, thermogravimetric analysis, liquid and <sup>13</sup>C/<sup>19</sup>F/<sup>29</sup>Si solid NMR and photoluminescence spectroscopy. The results showed that high Ge content, high tmbi concentration and low temperature (150 °C) conditions favor the formation of extra-large pore ITQ-37 when supramolecular interactions between tmbi molecules occur. On the other hand, a much diluted tmbi solution and a higher reaction temperature favor the crystallization of an unknown lamellar phase, wherein tmbi is present as monomers. These studies revealed that supramolecular assemblies of tmbi were formed during the zeolite synthesis and acted as SDAs for crystallization of ITQ-37, providing a general and applicable strategy for synthesizing large and extra-large pore zeolites.

be a key to the synthesis of large and extra-large pore zeolites.<sup>8,9</sup> A number of germanosilicate zeolites have recently been synthesized, which constitute a very important group of zeolites. Although most germanosilicates are unstable after removing the organic templates at high temperature owing to the easy hydrolysis of the Ge–O bonds, post-synthetic modifications by isomorphous substitution of Al or Si for Ge has been successfully applied to some germanosilicates to yield highly stable aluminosilicate or siliceous zeolites.<sup>10–12</sup>

In addition to Ge and F, organic cations, such as quaternary ammonium, known as structure-directing agents (SDAs), also play an important, and in most cases, decisive role in the formation of zeolites with special structural topology. Studies show that the shape, size, rigidity, hydrophilicity, and charge, as well as some other features of SDAs all make important impacts on their structure-directing roles. Therefore, many efforts have been made to rationally design suitable SDAs for zeolite synthesis.<sup>13</sup>

The rigidity of the SDA makes an impact on zeolite synthesis. Flexible SDAs usually have good structure-directing effects and have been widely used for crystallizing zeolites<sup>13</sup> as they can easily adopt various conformations to fit the channels of zeolites. For instance, hexamethonium has been successfully used to synthesize EU-1,<sup>14</sup> ZSM-48,<sup>15</sup> ITQ-13,<sup>16</sup> ITQ-17,<sup>17</sup> IM-10,<sup>18</sup> ITQ-22,<sup>19</sup> ITQ-24,<sup>20</sup> EMM-3 (ref. 21) and ITQ-33.<sup>22</sup> The drawback of flexible SDAs is, however, the lack of structure-directing specificity for a particular zeolite. As a result, they often result in a mixture of different structures,

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which makes it very difficult to separate and characterize them. This is contrary to rigid SDAs, which are often of higher specificity for directing the formation of a particular zeolite structure. However, the rigid SDAs have their own limitations because steric hindrance makes them less successful in synthesizing zeolites. For the synthesis of large and extralarge pore zeolites, a rigid and bulky SDA with an appropriate polarity/hydrophilicity is usually required<sup>7</sup> because in most cases it acts as the space-filling agent to fill the voids of large pores.<sup>23</sup> However, there are some limitations for using bulky SDAs in zeolite synthesis. First, bulky SDAs are not readily available and are expensive; their preparations are tedious and often involve multi-step reactions with low yields. Second, as the size of an SDA increases, its hydrophobicity often increases, which limits its solubility and thus results in the formation of an amorphous phase during zeolite synthesis.<sup>24</sup>

ITQ-37 has so far the largest 30R (30-membered ring) channel and is also the first chiral germanosilicate zeolite,<sup>25</sup> which has long been sought after because it could be used to shape-selective, asymmetric catalysis perform and separation.<sup>26-28</sup> The SDA for ITQ-37 used by Corma et al. (SDA1, Fig. 1) is a rigid, bulky and chiral quaternary ammonium salt. The synthesis of SDA1 involves multi-step reactions and a very long reaction time with a low total yield (35%).<sup>25</sup> Yu et al.<sup>29</sup> successfully synthesized the chiral ITQ-37 using an achiral, yet asymmetric, SDA (SDA2, Fig. 1). Although there are no chiral atoms within it, SDA2 is not commercially available and its precursors are expensive. In this study, we use a semi-rigid imidazolium, namely, 1,1',1"-(2,4,6trimethylbenzene-1,3,5-triyl)-tris(methylene)tris(3-methyl-1Himidazol-3-ium) (denoted tmbi, Fig. 2), which is easily obtained from inexpensive raw materials, as an efficient SDA for ITQ-37 crystallization. It is noted that one isomer of tmbi has previously been successfully applied in directing the crystallization of zeolites LTA and ITQ-24.30 Herein, we show that supramolecular self-assemblies of tmbi were formed during the synthesis and acted as SDAs for crystallization of extralarge pore ITQ-37, which provides a general strategy for synthesizing extra-large pore zeolites.

### Experimental

#### Synthesis of the SDAs

1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene (denoted tmbBr) was synthesized by a modified procedure reported by Alexander *et al.*<sup>31</sup> As shown in Fig. 2, typically, a mixture of concentrated sulfuric acid and acetic acid (1:1 v/v, 90 mL) was added dropwise to a mixture of mesitylene (12.48 mL, 90







mmol), paraformaldehyde (12.60 g, 420 mmol), sodium bromide (74.08 g, 720 mmol), and acetic acid (96 mL), which was first stirred at 60 °C for 2h and then the temperature was slowly increased to 90–95 °C; the mixture was allowed to stand overnight and then poured into water (2.0 L) at room temperature. The white solid product was filtered, dried in vacuum, and recrystallized by ether-dichloromethane (1:1 v/v) to afford 34.13 g of product (94% yield). <sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>, ppm): 2.46 (s, 9H, –CH<sub>3</sub>), 4.57 (s, 6H, –CH<sub>2</sub>). <sup>13</sup>C NMR (125 MHz; CDCl<sub>3</sub>, ppm): 15.3, 29.9, 133.4, and 138.1.

The precursor tmbBr reacts with stoichiometric 1-methyl-1*H*-imidazole under reflux in tetrahydrofuran for 2 d, to yield the bromide salt of 1,1',1"-(2,4,6-trimethylbenzene-1,3,5-triyl)tris(methylene)tris(3-methyl-1*H*-imidazol-3-ium) (denoted tmbiBr<sub>3</sub>) as a white precipitate (yield 96%). ESI-MS: M-Br (*m*/*z*: 562.34, 30%), (M-2Br)/2 (*m*/*z*: 241.22, 55%), (M-3Br)/3 (*m*/*z*: 134.18, 100%).

The template  $\text{tmbiBr}_3$  was converted into the corresponding hydroxides  $\text{tmbi}(\text{OH})_3$  by anion exchange. The final concentration of the hydroxide solution was determined by titration with HCl with phenolphthalein as the indicator.

#### Zeolite synthesis

Unless otherwise stated, all the SDAs were used in OH<sup>-</sup> forms for zeolite synthesis. In a typical synthesis of ITQ-37, 0.2615 g (2.5 mmol) of GeO<sub>2</sub> (Sigma-Aldrich, >98%) were added to a 2.5 mmol (based on OH<sup>-</sup> concentration) SDAOH solution and stirred for half an hour. Then, 0.7315 g (2.5 mmol) of tetraethylorthosilicate (TEOS, Sigma-Aldrich, >99%) were added to the solution. After the mixture was stirred for 2 h for adequate hydrolysis of the TEOS, 0.1250 g (2.5 mmol) of HF solution (40 wt%) were added. The mixture was allowed to reach the desired water ratio by evaporation of ethanol and some water at 80 °C. The obtained gel (1.0224 g) with a molar composition of 1SiO<sub>2</sub>:1GeO<sub>2</sub>:1SDA<sub>1/3</sub>(OH):1HF:3H<sub>2</sub>O was transferred into a 15 mL Teflon lined vessel in a steel autoclave and heated at 150 or 175 °C in static conditions for 15 days. The final powder was filtered, washed with distilled water and ethanol, and dried in air.

#### Characterization

Elemental analyses of C, H, and N were performed on an Elementar Vario MICRO Elemental Analyzer. The inductively coupled plasma (ICP) analysis was carried out on a Perkin-Elmer Optima 3300 DV. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance instrument using Cu $K_{\alpha 1}$  radiation ( $\lambda = 1.54056$  Å) at room temperature. Scanning electron microscopy (SEM) images of the products were obtained on a field emission scanning electron microanalyser (Hitachi S-4800), employing an accelerating voltage of 10 kV. Electrospray ionization mass spectrometry (ESI-MS) was recorded in positive ion mode (LC-ESI-MS, ThermoQuestLCO Duo, USA) without a liquid chromatography (LC) process. Fluorescence measurements were performed on a FluoroMax-4 spectrofluorometer with a 3 nm slit. Thermogravimetric (TG) analyses were performed on a Perkin-Elmer thermal analyzer under air with a heating rate of 5 °C min<sup>-1</sup>. A Micromeritics ASAP 2020 surface area porosimetry system was used to measure N<sub>2</sub> gas adsorption at 77 K. Solid state NMR spectra were obtained on a Bruker Av-400 spectrometer using the magic-angle spinning (MAS) technique at room temperature. <sup>19</sup>F spectra were obtained using a Bruker Av-400 spectrometer at 376.47 MHz in 4.0 mm diameter zirconia rotors at a spinning rate of 14 kHz. The spectra were obtained using 2.1 µs pulses, which correspond to a magnetization flip angle of  $\pi/2$ rad and a recycle delay of 15 s. The spectra were referenced to CFCl<sub>3</sub>. The <sup>13</sup>C spectra were obtained at a 100.62 MHz resonance frequency using a CP-MAS sequence, with a 3.0 µs <sup>1</sup>H excitation pulse, 2.0 ms contact time, 5 s recycle delay and 100 kHz spectral width, using proton decoupling at 60 kHz spinal-64 during acquisition. The <sup>29</sup>Si spectra were obtained at a resonance frequency of 79.49 MHz with a  $\pi/2$  pulse at 56 kHz, spectral width of 100 kHz and a 150 s relaxation delay.

X-ray crystal structure determination. The data collections for single crystal X-ray diffraction were carried out on a Bruker Smart APEX II CCD diffractometer at 296 K, using graphite-monochromated Mo-K<sub> $\alpha$ </sub> radiation ( $\lambda = 0.71073$  Å). Data reduction and absorption correction were performed using the SAINT and SADABS programs,<sup>32</sup> respectively. The structures were solved by direct methods using the SHELXS-97 program and refined with full-matrix least squares on  $F^2$ using the SHELXL-97 program.<sup>33</sup> All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed in geometrically calculated positions and refined using the riding model.

## Results and discussion

#### Crystallization of ITQ-37

Zeolite syntheses were carried out in the presence of Ge and F because both are thought to be beneficial for the formation of large and extra-large pore zeolites.<sup>8,9</sup> The typical gel molar compositions are in the form of  $1\text{SiO}_2:x\text{GeO}_2:y\text{SDA}_{1/3}(\text{OH}):$  yHF:zH<sub>2</sub>O, where x = 1, 0.5, 0.2; y = 1, 0.5; z = 3, 5, 10. The crystallization occurred at either 150 °C or 175 °C for up to 45 d. In addition to crystallization temperature, the effects of water content, germanium and SDA concentrations were studied. Table 1 lists various synthetic parameters that we have surveyed using the designed SDA.

As shown in Table 1, when Si/OH<sup>-</sup> is 2, ITQ-37 can be produced only with a high Ge content (Si/Ge = 1) and a low water content ( $H_2O/Si = 3$ ) either at 150 or 175 °C. Upon increasing Paper

Table 1 Survey of zeolite synthesis with tmbi as an SDA

Si/OH <sup>-</sup>	Ge/Si H <sub>2</sub> O/Si	1			0.5			0.2		
		3	5	10	3	5	10	3	5	10
2	150 °C	ITQ-37	U1	U1	_	U1	U1	_	_	
2	175 °C	ITQ-37	_	_	_	_	_	_	_	_
1	150 °C	ITQ-37	ITQ-37	_	ITQ-37	ITQ-37	U1	_		_
1	175 °C	ITQ-37	_`	_	ITQ-37	_`	_		_	_
		-		_	-					

-" represents an amorphous phase.

the water content or decreasing the Ge content, however, an unknown phase, U1, which appeared to be a lamellar phase (as shown in Fig. 3) was formed at 150 °C and an amorphous phase was obtained at 175 °C. On the other hand, when the syntheses were carried out with a higher concentration of tmbi, *i.e.* Si/OH<sup>-</sup> = 1 (Table 1), ITQ-37 was obtained in a broader range of synthetic conditions, *e.g.* under lower Ge concentration and higher water content. The phase U1 was only formed at conditions of Ge/Si = 0.5 and H<sub>2</sub>O/Si = 10 at 150 °C, whereas the other systems with low Ge concentration and very high water content led to the formation of amorphous phases. It is clear that a high concentration of tmbi, a higher Ge content, and much less water content together with a lower temperature (150 °C) favor the formation of the extra-large pore zeolite ITQ-37.

#### **Characterization of ITQ-37**

As shown in Fig. 4, the powder XRD patterns of the assynthesized ITQ-37 are consistent with the simulated one based on the reported crystal structure data,<sup>25</sup> proving that the as-synthesized ITQ-37 is a pure phase.

<sup>19</sup>F MAS NMR spectra of both ITQ-37 and U1 (Fig. 5) show strong resonance bands at -7.8 ppm for ITQ-37 and -8.3 ppm for U1, characteristic of fluoride anions entrapped in germanium-rich double-4-rings (D4R).<sup>34</sup> Another band at



Fig. 3 XRD pattern and SEM image of as-synthesized phase U1.



Fig. 4 (a) Experimental and (b) simulated PXRD patterns for ITQ-37.



Fig. 5 Solid state <sup>19</sup>F MAS NMR spectra of (a) U1 and (b) ITQ-37. \* represent spinning sidebands.

–126.8 ppm for ITQ-37 and –122.4 ppm for U1 likely belongs to the mobile fluoride ions in channels,  $^{35}$  which just act as

charge-balancing counterparts for the tmbi cations. The presence of the strong peak owing to the mobile fluoride in the as-synthesized ITQ-37 is different from that of Corma's ITQ-37 (ref. 25) and implies that there were many more fluorides in our as-synthesized ITQ-37, which may be attributed to the use of the tmbi tri-cations.

The solid-state <sup>13</sup>C NMR spectra of the as-synthesized ITQ-37 and U1 are in good agreement with that of the liquid tmbi (Fig. 6), indicating that the organic tmbi cations are maintained intact in both products. In comparison to that of the liquid, however, peak broadening in both materials occurred. Such a phenomenon usually occurs in the solid state, which arises from decreased mobility of the tmbi molecule within the framework due to steric restrictions or some strong intermolecular interactions.<sup>36</sup> In U1, peak splittings for C<sub>1</sub> and C<sub>3</sub> are observed, which indicate that tmbi may locate in different chemical environments in U1.

ICP analyses of the as-synthesized ITO-37 show a Ge: Si molar ratio of 1:1. CHN analyses of the as-synthesized ITQ-37 and U1 give C:N molar ratios of 4.2 and 4.3, respectively, which are in accordance with the expected C:N ratio of 4.0 in the tmbi. The TG curve of the as-synthesized U1 (Fig. S1, ESI<sup>†</sup>) shows a total weight loss of *ca.* 15.6% in the region of 200-800 °C, whereas that of the synthesized ITQ-37 (Fig. S2, ESI<sup>†</sup>) shows a total weight loss of *ca.* 20.2% in the same region. With reference to the empirical formula given by the structural analysis of ITQ-37,<sup>25</sup> as well as TG and compositional analyses, the formula of our as-synthesized ITQ-37 can be given as  $[Ge_{96}Si_{96}O_{400}H_{32}](C_{24}N_6H_{33}F_3)_{8.81}$ . Because of the high content of Ge, the calcined ITQ-37 gradually lost its crystallinity in a moisture containing atmosphere upon removal of the organic templates (Fig. S3, ESI<sup>†</sup>). However, the framework was stable in a dry atmosphere. The N<sub>2</sub> adsorption measurements showed that the Brunauer-Emmett-Teller (BET) surface area of the calcined ITQ-37 is 820 m<sup>2</sup> g<sup>-1</sup> with a *t*-plot micropore area of 603



Fig. 6 Solid-state  $^{13}$ C MAS NMR spectra of (a) U1, (b) ITQ-37 and (c)  $^{13}$ C NMR spectra in D<sub>2</sub>O solution of tmbiBr<sub>3</sub>.

m<sup>2</sup> g<sup>-1</sup> (Fig. S4, ESI<sup>†</sup>), which is comparable to values reported by Corma *et al.*<sup>25</sup> and Yu *et al.*<sup>29</sup>

#### Templating effect during the crystallization of ITQ-37

ITQ-37 is the first reported chiral germanosilicate zeolite and has, to date, the largest 30-ring channel with a pore size reaching the mesoporous scale.<sup>25</sup> It crystallizes in a cubic chiral space group,  $P4_132$ , with a unit cell volume of 18636 Å<sup>3</sup>. Each unit cell of ITO-37 contains 20 D4Rs, inside which the F<sup>-</sup> ions are located. This requires at least 20 SDA cations in the channels for charge balancing. In our as-synthesized ITO-37, there are approximately 8.8 tmbi cations estimated from the analyses. The location and conformation of these SDA cations in zeolites are very much desired, because they may obtain information about the structure-directing mechanism. Unfortunately, it is a significant challenge to accurately locate the SDAs by X-ray diffraction analysis due to the disorder. Recently, Corma et al. showed that photoluminescence spectroscopy is an useful method to investigate the possible aggregation state of aromatic-containing SDAs used for the synthesis of zeolite ITQ-29.37

Solid-state photoluminescence spectra ( $\lambda_{ex} = 272$  nm) of the as-synthesized ITQ-37 (Fig. 7) showed a strong broad blue emission centered at 440 nm upon excitation at ~270 nm, which is almost the same as that of the tmbiBr<sub>3</sub> salt. Both spectra are quite different with that of the diluted tmbi(OH)<sub>3</sub> solution with a concentration of (OH<sup>-</sup>) of about 1 × 10<sup>-4</sup> M (Fig. 8). The latter exhibited a strong single emission band at approximately 300 nm, which can be assigned to the  $\pi^*-\pi$ transition of the tmbi molecule.

As shown in Fig. 9, single crystal X-ray diffraction analysis of the tmbiBr<sub>3</sub> crystals reveals that the organic cation tmbi adopts a *cis,cis,cis* configuration and forms head-to-head dimers *via* the parallel benzene rings. The distance between the benzene rings is approximately 3.79 Å, which indicates strong  $\pi$ - $\pi$  interactions.<sup>38</sup> Therefore, the blue emission at 440 nm in both the synthesized ITQ-37 and the bromide salt of



Fig. 8 Photoluminescence spectra of the diluted tmbi(OH)<sub>3</sub> in water: (a) c(OH<sup>-</sup>) = 1.0 × 10<sup>-4</sup> M,  $\lambda_{ex}$  = 272 nm and (b) c(OH<sup>-</sup>) = 0.3 M,  $\lambda_{ex}$  = 344 nm.

tmbi can be attributed to the formation of tmbi excimers. This implies that the tmbi cations formed dimers during the synthesis, which then acted as SDAs and filled the channels of ITQ-37. In comparison, there was only one strong emission



Fig. 7 Solid-state photoluminescence spectra ( $\lambda_{\rm ex}$  = 272 nm) of (a) tmbiBr\_3, (b) ITQ-37 and (c) U1.



Fig. 9 Packing of tmbi in tmbiBr<sub>3</sub> based on single crystal refinement. The solvent molecules, bromine and hydrogen atoms are omitted for clarity.

at 310 nm in U1, which resembles that of the dilute tmbi solution, indicating the presence of only tmbi monomer in U1.

Further studies showed that upon increasing the concentration of the tmbi(OH)<sub>3</sub> solution to 0.1 M, the emission band at 300 nm due to the tmbi monomer disappears (Fig. 8), replaced by a new emission band at *ca.* 450 nm similar to those of the solid tmbiBr<sub>3</sub> and the synthesized ITQ-37 (Fig. 7). This new emission could be attributed to the formation of excimers, similar to other polyaromatics.<sup>39–42</sup> These results indicate that there exist tmbi dimers or similar aggregates in the concentrated tmbi(OH)<sub>3</sub> solution because of the  $\pi$ -stacking interactions between adjacent aromatic rings. It is noted that the gels that yield ITQ-37 (*e.g.* y = 0.5 and z = 5) have a tmbi concentration much higher than the tmbi(OH)<sub>3</sub> solution used in the photoluminescence spectroscopic studies.

Based on the above-mentioned results, we postulated that the tmbi molecules self-assembled into the supramolecular aggregates via  $\pi$ - $\pi$  interactions between the benzene rings at high concentrations of tmbi in the gels  $(Si:OH^{-} = 1)$ , which then acted as SDAs for the formation of ITQ-37. This is supported by the photoluminescence studies of the synthesized ITQ-37 and the concentrated tmbi solution, both of which showed the presence of tmbi excimers. A high tmbi concentration and a low temperature would favor the formation of supramolecular interactions between SDA molecules. Consistently, extra-large pore ITQ-37 crystallizes under these conditions. On the other hand, a low concentration of tmbi or higher crystallization temperature disfavors the formation of self-assembled dimers. As a result, only a lamellar phase U1 was crystallized, in which tmbi monomers are present, as shown by NMR (Fig. 6) and photoluminescence studies (Fig. 7).

It is noted that the extra-large pore germanosilicate zeolite ITQ-37 was first synthesized by Corma et al. using a bulky, rigid pentacyclic diquaternary ammonium molecule (Fig. 1) as SDA.<sup>25</sup> Furthermore, Yu et al.<sup>29</sup> reported the synthesis of ITQ-37 using another bulky and rigid tetracyclic quaternary ammonium SDA (Fig. 1). Interestingly, the tmbi is a readilyprepared, semi-rigid cation that can efficiently direct the formation of extra-large pore ITQ-37 through the supramolecular assembly templating (SAT) approach. The concept of SAT was introduced by Corma et al. during the synthesis of highsilica zeolite ITQ-29 (framework code LTA), which is based on a supramolecular self-assembly of two small identical aromatic anilinium-derived molecules through  $\pi$ - $\pi$  interactions. The resulting bulky "dimer" succeeded in directing the formation of ITQ-29, with large spherical cavities of 1.14 nm diameter.<sup>37</sup> Similar effects were observed during the synthesis of large-cage AlPO<sub>4</sub>-LTA molecular sieve<sup>43</sup> and large-pore AlPO<sub>4</sub>-5,<sup>40-42</sup> wherein supramolecular assemblies of aromatic SDA molecules were found in the as-prepared AlPO<sub>4</sub> molecular sieves. Recently, by using the SAT approach, we have successfully synthesized a new extra-large pore zeolite NUD-1 with interconnecting 18-, 12-, and 10-membered ring channels.44 The successful synthesis of extra-large pore zeolite ITQ-37 using supramolecular assemblies of a semi-rigid

imidazolium tmbi as an SDA confirms that SAT strategy is a general, facile approach to synthesize extra-large pore zeolites.

### Conclusions

In this study, we successfully utilized a readily-prepared, semi-rigid imidazolium tmbi as an SDA in synthesizing a chiral, extra-large pore germanosilicate zeolite, ITQ-37. The formation of ITQ-37 showed a strong dependence on tmbi concentration and crystallization temperature. XRD, elemental analysis, TGA, and NMR and photoluminescence spectroscopic studies showed that the formation of supramolecular assemblies *via*  $\pi$ - $\pi$  interactions between the aromatic rings of tmbi occurred in the tmbi concentrated gels at low crystallization temperatures, and the supramolecular assemblies thus formed acted as SDAs for the crystallization of ITQ-37. This study demonstrates that the supramolecular assembly templating approach is a general, applicable strategy, which has great potential in synthesizing new, large and extra-large pore zeolites.

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### Notes and references

- 1 J. Sterte and J. E. Otterstedt, Appl. Catal., 1988, 38, 131-142.
- 2 H. Du, C. Fairbridge, H. Yang and Z. Ring, *Appl. Catal., A*, 2005, **294**, 1–21.
- 3 A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, 107, 2411–2502.
- 4 Z. Li, M. C. Johnson, M. Sun, E. T. Ryan, D. J. Earl, W. Maichen, J. I. Martin, S. Li, C. M. Lew, J. Wang, M. W. Deem, M. E. Davis and Y. Yan, *Angew. Chem., Int. Ed.*, 2006, 45, 6329–6332.
- 5 P. Atienzar, M. J. Díaz-Cabañas, M. Moliner, E. Peris, A. Corma and H. García, *Chem. Eur. J.*, 2007, **13**, 8733–8738.
- 6 S. W. Young, F. Qing, D. Rubin, K. J. Balkus, J. S. Engel, J. Lang, W. C. Dow, J. D. Mutch and R. A. Miller, *J. Magn. Reson. Imaging*, 1995, 5, 499–508.
- 7 J. Jiang, J. Yu and A. Corma, Angew. Chem., Int. Ed., 2010, 49, 3120–3145.
- 8 M. O'Keeffe and O. M. Yaghi, *Chem. Eur. J.*, 1999, 5, 2796–2801.
- 9 G. O. Bnmner and W. M. Meier, Nature, 1989, 337, 146-147.
- 10 P. Eliasova, M. Opanasenko, P. S. Wheatley, M. Shamzhy, M. Mazur, P. Nachtigall, W. J. Roth, R. E. Morris and J. Cejka, *Chem. Soc. Rev.*, 2015, 44, 7177–7206.
- 11 R. E. Morris and J. Cejka, Nat. Chem., 2015, 7, 381-388.
- M. Mazur, P. S. Wheatley, M. Navarro, W. J. Roth, M. Položij, A. Mayoral, P. Eliášová, P. Nachtigall, J. Čejka and R. E. Morris, *Nat. Chem.*, 2016, 8, 58–62.

- 13 M. Moliner, F. Rey and A. Corma, Angew. Chem., Int. Ed., 2013, 52, 13880-13889.
- 14 G. W. Dodwell, R. P. Denkewicz and L. B. Sand, Zeolites, 1985, 5, 153–157.
- 15 A. Moini, K. D. Schmitt, E. W. Valyocsik and R. F. Polomski, *Zeolites*, 1994, 14, 504–511.
- 16 A. Corma, M. Puche, F. Rey, G. Sankar and S. J. Teat, *Angew. Chem., Int. Ed.*, 2003, 42, 1156–1159.
- 17 A. Corma, M. T. Navarro, F. Rey, J. Rius and S. Valencia, *Angew. Chem., Int. Ed.*, 2001, 40, 2277–2280.
- 18 Y. Mathieu, J.-L. Paillaud, P. Caullet and N. Bats, Microporous Mesoporous Mater., 2004, 75, 13–22.
- 19 A. Corma, F. Rey, S. Valencia, J. L. Jorda and J. Rius, Nat. Mater., 2003, 2, 493-497.
- 20 R. Castañeda, A. Corma, V. Fornés, F. Rey and J. Rius, *J. Am. Chem. Soc.*, 2003, **125**, 7820–7821.
- 21 M. Afeworki, D. L. Dorset, G. J. Kennedy and K. G. Strohmaier, *Chem. Mater.*, 2006, **18**, 1697–1704.
- 22 A. Corma, M. J. Diaz-Cabanas, J. L. Jorda, C. Martinez and M. Moliner, *Nature*, 2006, 443, 842–845.
- 23 M. E. Davis and R. F. Lobo, Chem. Mater., 1992, 4, 756-768.
- 24 R. F. Lobo, S. I. Zones and M. E. Davis, J. Inclusion Phenom. Mol. Recognit. Chem., 1995, 21, 47–78.
- 25 J. Sun, C. Bonneau, A. Cantin, A. Corma, M. J. Diaz-Cabanas, M. Moliner, D. Zhang, M. Li and X. Zou, *Nature*, 2009, 458, 1154–1157.
- 26 R. Raja and J. M. Thomas, *J. Mol. Catal. A: Chem.*, 2002, 181, 3–14.
- 27 J. M. Castillo, T. J. H. Vlugt, D. Dubbeldam, S. Hamad and S. Calero, J. Phys. Chem. C, 2010, 114, 22207–22213.
- 28 A. Kuschel and S. Polarz, J. Am. Chem. Soc., 2010, 132, 6558–6565.
- 29 K. Qian, J. Li, J. Jiang, Z. Liang, J. Yu and R. Xu, *Microporous Mesoporous Mater.*, 2012, 164, 88–92.

- 30 J. E. Schmidt, S. I. Zones, D. Xie and M. E. Davis, *Microporous Mesoporous Mater.*, 2014, 200, 132–139.
- 31 N. A. Samy and V. Alexander, *Dalton. Trans.*, 2011, 40, 8630–8642.
- 32 SMART and SADABS, Bruker AXS Inc., Madison, Wisconsin, USA, 1997.
- 33 G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112.
- 34 G. Sastre, J. A. Vidal-Moya, T. Blasco, J. Rius, J. L. Jordá, M. T. Navarro, F. Rey and A. Corma, *Angew. Chem., Int. Ed.*, 2002, 41, 4722–4726.
- 35 J. Su, Y. Wang, J. Lin, J. Liang, J. Sun and X. Zou, *Dalton Trans.*, 2013, 42, 1360–1363.
- 36 A. Burton, S. Elomari, R. C. Medrud, I. Y. Chan, C.-Y. Chen, L. M. Bull and E. S. Vittoratos, *J. Am. Chem. Soc.*, 2003, 125, 1633–1642.
- 37 A. Corma, F. Rey, J. Rius, M. J. Sabater and S. Valencia, *Nature*, 2004, 431, 287–290.
- 38 M. O. Sinnokrot, E. F. Valeev and C. D. Sherrill, J. Am. Chem. Soc., 2002, 124, 10887–10893.
- 39 T. Nakano and T. Yade, J. Am. Chem. Soc., 2003, 125, 15474-15484.
- 40 T. Álvaro-Muñoz, F. López-Arbeloa, J. Pérez-Pariente and L. Gómez-Hortigüela, J. Phys. Chem. C, 2014, 118, 3069–3077.
- 41 L. Gómez-Hortigüela, F. López-Arbeloa, F. Corà and J. Pérez-Pariente, J. Am. Chem. Soc., 2008, 130, 13274–13284.
- 42 L. Gómez-Hortigüela, S. Hamad, F. López-Arbeloa, A. B. Pinar, J. Pérez-Pariente and F. Corà, *J. Am. Chem. Soc.*, 2009, 131, 16509–16524.
- 43 E. J. Fayad, N. Bats, C. E. A. Kirschhock, B. Rebours, A.-A. Quoineaud and J. A. Martens, *Angew. Chem., Int. Ed.*, 2010, 49, 4585-4588.
- 44 F.-J. Chen, Y. Xu and H.-B. Du, Angew. Chem., Int. Ed., 2014, 53, 9592–9596.