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# Accurate structure determination of a borosilicate zeolite EMM-26 with two-dimensional 10×10 ring channels using rotation electron diffraction

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## S1. Synthesis of EMM-26

EMM-26 was first synthesized using 1,6-bis(N-methylpyrrolidinium)hexane hydroxide as an organic structure directing agent (OSDA). Firstly boric acid was dissolved in an aqueous solution of the OSDA in a Teflon insert for a 23-mL steel Parr autoclave. Then tetamethylorthosilicate (TMOS) was mixed with the solution in an OSDA/Si molar ratio of 0.25, and hydrolyzed for 10-15 min. Afterwards drops of 50% HF were then added to neutralize the hydroxide until the $F^-$/Si ratio reached 0.5. The resultant gel was mixed together by hand to form a uniform paste. Water and methanol from the TMOS hydrolysis were then allowed to evaporate in a vented hood over the course of 1-2 days until the $H_2O$/Si ratio was below a desired value. At this point drops of water were added to bring the $H_2O$/Si to the appropriate level and the gel was homogenized by hand. Finally the reaction gel was sealed in an autoclave, which was tumbled (~35-40 rpm) at 175 °C for 11 days in a preheated oven.

EMM-26 was also prepared in a hydroxide media without fluoride. A reaction mixture was prepared using boric acid as the boron source, Ludox AS-40 as the silica source, HCl as a source of halide ions and 1,6-bis(N-methylpyrrolidinium)hexane hydroxide as the OSDA. The molar ratio of the reaction mixture was 1,6-bis(N-methylpyrrolidinium)hexane hydroxide/Si = 0.2, Si/B = 5, HCl/Si = 0.10, and $H_2O$/Si = 35. The reaction mixture was sealed in a 1.5-mL stainless steel reactor vessel and heated in a convection oven at 160 °C under tumbling conditions (about 30 rpm) for 56 days. The product was recovered by a series of three centrifugations, decantations, re-suspensions, and washings with deionized water. Powder X-ray diffraction (PXRD) showed the product to be a mixture of a new phase, EMM-26, with amorphous material and a minor amount of zeolite beta impurity.

Pure EMM-26 was synthesized using seeds of the EMM-26 prepared under the fluoride media. First 1.67 g of a solution of 1,6-bis(N-methylpyrrolidinium)hexane hydroxide (25.8 wt%) was mixed with 5.39 g deionized water in a Teflon liner for a 23-mL steel Parr autoclave. Next 0.19 g boric acid was added to the solution and mixed until nearly complete dissolution. Then 2.25 g Ludox AS-40 was added to the mixture followed by adding 1.50 g of 1 M HCl. About 0.04 g seeds were added to the suspension and the liner was then sealed inside the 23-mL autoclave, and heated at 160 °C under tumbling conditions (about 40 rpm). The reactor was removed and quenched after 14 days. The solids were isolated by filtration, washed exhaustively with deionized water, dried, and analyzed with PXRD. The PXRD pattern indicated the product was pure EMM-26.

## S2. Structure determination by rotation electron diffraction (RED)

The structure of as-made EMM-26 was determined from a sub-Ångström sized crystal using the rotation electron diffraction (RED) method[1] developed in our group. The as-made EMM-26 sample for RED data collection was dispersed in absolute ethanol and treated by ultrasonic treatment for 5 min. A droplet of the suspension was transferred onto a carbon-coated copper grid and dried in air. The collection of 3D RED data was controlled by the software *RED data collection*[2] on a JEOL JEM2100 TEM at 200 kV. A single-tilt tomography sample holder was used for the data collection, which could tilt from -70° to +70° in the TEM. ED frames were recorded on a 12-bit Gatan ES500W Erlangshen camera side-mounted at a 35 mm port.

The RED dataset of EMM-26 contains 484 ED frames and covers a tilt range of 88.90°. 1444 reflections (of which 524 unique) were obtained from this RED dataset. The beam tilt step was 0.20° and the exposure time was 1.0 s per ED frame. The total data collection time was less than half an hour for this RED dataset. Detailed RED data collection and crystallographic information for EMM-26 are given in Table S1.

The data processing was performed using the software *RED-data processing*[2], which includes zero shift correction, peak search, unit cell determination, indexation of reflections and intensity extraction. The rotation axis and reciprocal space sampling (number of pixels per reciprocal Å, pixel*Å) were pre-calibrated using a standard sample. The unit cell was determined from the positions of diffraction spots detected in the ED frames. The intensity for each reflection was extracted from the ED frame with the maximum intensity value. Reflections that were within the experimental tilt range but too weak to be detected by the RED software were assigned zero intensity. The final list of reflections with the indices and intensities was output to an HKL file in a standard HKLF4 format for the program *SHELX*. The structure solution and refinement were performed using *SHELX*97. Atomic scattering factors for electrons were used. All seven T-atoms (T = Si, B) and 13 framework oxygen positions were found by direct methods. In the initial refinement against RED data, soft restraints were applied to all the T-O (1.59 Å) and tetrahedral oxygen atoms O···O (2.60 Å) distances considering the ratio of Si/B = 11. The occupancy of Si and B at each T site was also refined. After several refinement cycles, we found that the occupancies of Si and B turned to be 1.0 and 0.0 respectively at the T1-3 and T5 sites. Boron was mainly located at three T-sites, T4, T6 and T7. Therefore in the final refinement, these three sites were refined as mixed Si/B positions, and the other four sites T1, T2, T3 and T5 were refined as Si positions. The residual peaks in the pores were assigned to two oxygen atoms belonging to guest water molecules and two carbon atoms belonging to the OSDAs. The final refinement converged to an R1 value of 0.2185 for all 524 reflections, with the occupancies of boron to be 12% at T4, 5% at T6, and 39% at T7 positions.

## S3. Location of OSDA position and Rietveld refinement

Powder X-ray diffraction patterns of as-made EMM-26 were collected on the powder diffractometer ($\lambda$ = 0.4009 Å**)** at the beamline ID-22 at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. To prevent preferred orientations, transmission geometry was used with a capillary sample holder (the diameter of the capillary was 0.7 mm). Rietveld refinement of the as-made EMM-26 structure was performed using the program TOPAS Academic 4.1.

During the Rietveld refinement, soft distance restraints were placed on the distances of T-O (1.59 Å) and tetrahedral oxygen atoms O···O (2.60 Å). All T and O positions and the Si/B occupancies of each T position were refined. Atomic displacement parameters ($U_{iso}$) were fixed to 0.0114 for Si atoms, 0.0171 for framework O atoms, 0.1013 for C (N) atoms and 0.1267 for an O atom belonging to a guest water molecule.

Firstly the framework geometry of EMM-26 obtained from the RED data was optimized by using TOPAS Academic 4.1. Then Rietveld refinement was carried out from the optimized model using only the high angle synchrotron diffraction data ($15.0° \leq 2\theta \leq 28.0°$), from which the scale factor between experimental and calculated data was determined. Finally a difference electron density map, which is shown in Figure S1, was calculated from the entire PXRD data and all parameters including the scale factor obtained from the high angle diffraction data. Residual densities can be found in the middle of the pores, suggesting the location of the OSDA. Before placing the OSDA at the residual peaks, an energy optimization for the OSDA was done with Cerius2 software from Accelerys[3]. Contributions from van der Waals interactions, valence bond, angle, and torsion energies were determined with the combination of the Burchart and Universal force fields[4]. Then the OSDA was introduced into the pore at the location of the residual peaks. After an initial refinement considering the OSDA as a rigid body with all parameters fixed except for those describing the rotation and translation of the OSDA, the atomic coordinates of T and O atoms, the occupancies of boron in all the T sites, and the rotation and translation of the OSDA are further refined.

Initial refinement against the synchrotron data without any soft restrains showed that the preferential boron positions were T4 (14%), T6 (8%) and T7 (30%). The occupancies of boron at the other T-sites (T1-3, T5) were less than 4%. Therefore only T4, T6 and T7 were considered as mixed Si/B positions, while the other T-sites as pure Si positions in the final refinement. The final refinement converged with a reasonable fit. The $R_{wp}$, $R_p$, $R_{brag}$, and GOF values are 0.0658, 0.0505, 0.0279, and 3.60, respectively (Table S2). The refined occupancies of boron were 14% at T4, 8% at T6, and 35% at T7 positions, which agree with those obtained from the RED data.

## S4. High resolution transmission electron microscopy (HRTEM)

Selected area electron diffraction (SAED) patterns and high-resolution transmission electron microscopy (HRTEM) images of as-made EMM-26 were recorded on a JEOL JEM-2100F microscope equipped with a field emission gun operated at 200 kV (point resolution 1.9 Å) using a Gatan Ultrascan 1000 2k × 2k CCD camera. The HRTEM image was corrected for the effects of contrast transfer function (CTF) using the software QFocus[5].

**Table S1** Crystallographic data and structure refinement base on the RED data for as-made EMM-26 ($\lambda$=0.0251 Å).

| Sample | As-made EMM-26 |
|---|---|
| Tilt range (°) | -35.50~ 53.39 |
| Tilt step (°) | 0.20 |
| Exposure time/frame (s) | 1.0 |
| No. of frames | 484 |
| Program for structure determination | SHELX-97 |
| Crystal system | orthorhombic |
| Space group | *Cmce* |
| Unit cell parameters from RED | $a$=19.4 Å, $b$=15.8 Å, $c$=17.9 Å<br>$\alpha$= 90.5°, $\beta$= 89.7°, $\gamma$= 89.8° |
| Volume (Å$^3$) | 5786.7 |
| Crystal size (nm$^3$) | 500×350×50 |
| Resolution (Å) | 1.10 |
| Completeness (%) | 76.0 |
| No. total reflections | 1444 |
| No. unique reflections | 524 |
| No. refined parameters | 69 |
| No. restraints | 72 |
| $R_{int}$ | 0.217 |
| R1 (observed reflections) | 0.1459 |
| R1(all reflections) | 0.2185 |
| GOF | 0.956 |

**Table S2** Crystallographic data and results for the Rietveld refinement of as-made EMM-26 against synchrotron powder diffraction.

| Sample | As-made EMM-26 |
|---|---|
| Unit cell contents (measured) | $\|N_2H_{36}C_{16}\|_4Si_{88}B_8O_{192}$ |
| Unit cell contents (refined) | $\|N_2H_{36}C_{16}\|_4Si_{88}B_8O_{192}\cdot(H_2O)$ |
| Diffractometer | Synchrotron, ID-22, ESRF, Grenoble |
| Wavelength | 0.4009 Å |
| Space Group | *Cmce* |
| *a* / Å | 19.391(1) |
| *b* / Å | 15.700(1) |
| *c* / Å | 17.767(0) |
| $R_p$ | 0.0505 |
| $R_{wp}$ | 0.0659 |
| $R_{brag}$ | 0.0183 |
| GOF | 3.602 |

**Table S3** Comparison of atomic positions of EMM-26 refined against the PXRD and RED data. The unit cell parameters used to calculate the deviations were obtained from PXRD.

| Coordinates from the PXRD data | | | | Coordinates from the RED data | | | | Deviation Δ (Å) |
|---|---|---|---|---|---|---|---|---|
| Atom | x | y | z | Atom | x | y | z | |
| Si1 | 0.418 | 0.157 | 0.429 | Si1 | 0.419 | 0.158 | 0.429 | 0.025 |
| Si2 | 0.348 | 0 | 0.5 | Si2 | 0.349 | 0 | 0.5 | 0.019 |
| Si3 | 0.234 | 0.073 | 0.604 | Si3 | 0.235 | 0.07 | 0.604 | 0.051 |
| Si4 | 0.25 | 0.326 | 0.25 | Si4 | 0.25 | 0.323 | 0.25 | 0.047 |
| Si5 | 0.177 | 0.204 | 0.499 | Si5 | 0.179 | 0.205 | 0.499 | 0.042 |
| Si6 | 0.197 | 0.112 | 0.353 | Si6 | 0.197 | 0.11 | 0.353 | 0.031 |
| Si7 | 0.335 | 0.176 | 0.292 | Si7 | 0.336 | 0.178 | 0.292 | 0.037 |
| O1 | 0.4 | 0.172 | 0.342 | O1 | 0.4 | 0.176 | 0.342 | 0.063 |
| O2 | 0.301 | 0.059 | 0.553 | O2 | 0.301 | 0.051 | 0.553 | 0.126 |
| O3 | 0.397 | 0.063 | 0.452 | O3 | 0.396 | 0.066 | 0.452 | 0.051 |
| O4 | 0.382 | 0.228 | 0.482 | O4 | 0.385 | 0.231 | 0.482 | 0.075 |
| O5 | 0.162 | 0.165 | 0.418 | O5 | 0.159 | 0.162 | 0.418 | 0.075 |
| O6 | 0.317 | 0.268 | 0.265 | O6 | 0.316 | 0.271 | 0.265 | 0.051 |
| O7 | 0.154 | 0.12 | 0.277 | O7 | 0.153 | 0.124 | 0.277 | 0.066 |
| O8 | 0.264 | 0.115 | 0.68 | O8 | 0.265 | 0.114 | 0.68 | 0.025 |
| O9 | 0.197 | -0.013 | 0.623 | O9 | 0.19 | -0.011 | 0.623 | 0.139 |
| O10 | 0.274 | 0.143 | 0.345 | O10 | 0.271 | 0.143 | 0.345 | 0.058 |
| O11 | 0.5 | 0.165 | 0.44 | O11 | 0.5 | 0.173 | 0.44 | 0.126 |
| O12 | 0.25 | 0.25 | 0.5 | O12 | 0.25 | 0.25 | 0.5 | 0.000 |
| O13 | 0.179 | 0.133 | 0.563 | O13 | 0.181 | 0.13 | 0.563 | 0.061 |

$$\Delta = \sqrt{\Delta x^2 a^2 + \Delta y^2 b^2 + \Delta z^2 c^2}$$

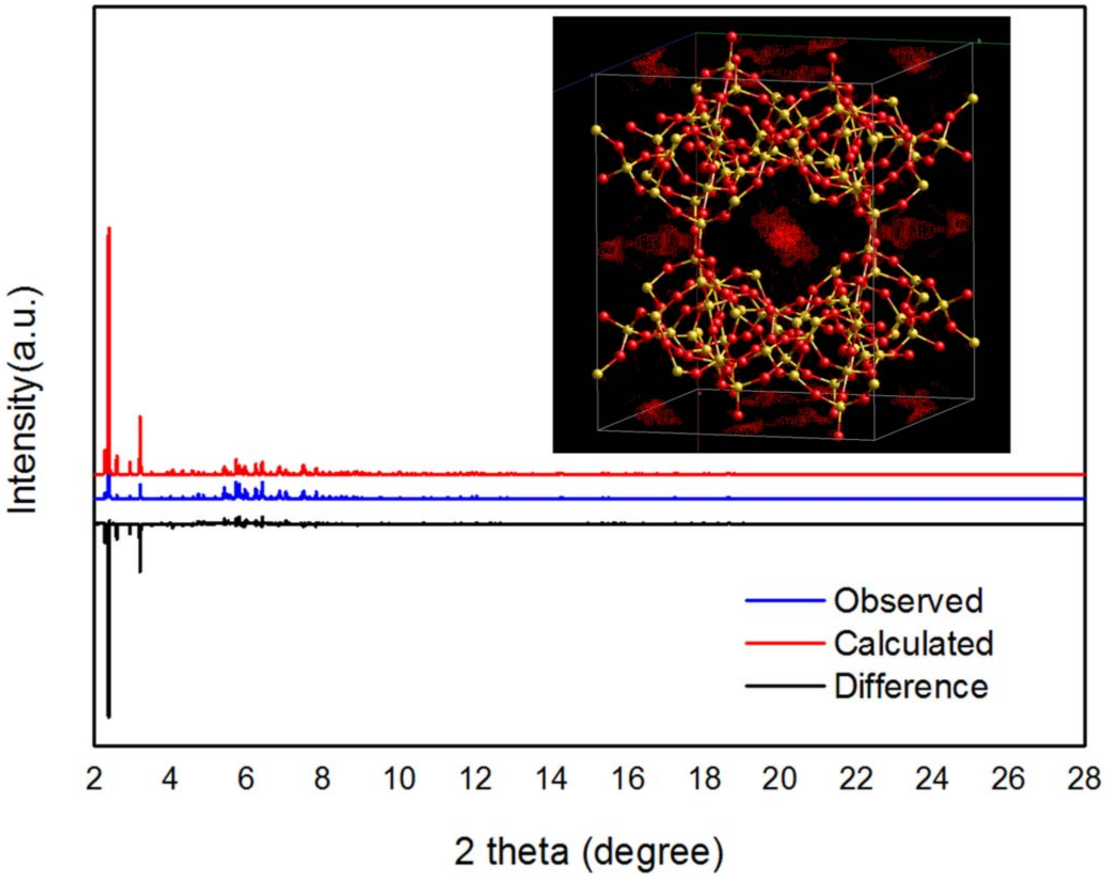


**Figure S1** Difference electron density map showing the residual densities within the pores. The observed, calculated and difference curves are in blue, red and black, respectively (λ = 0.4009 Å).

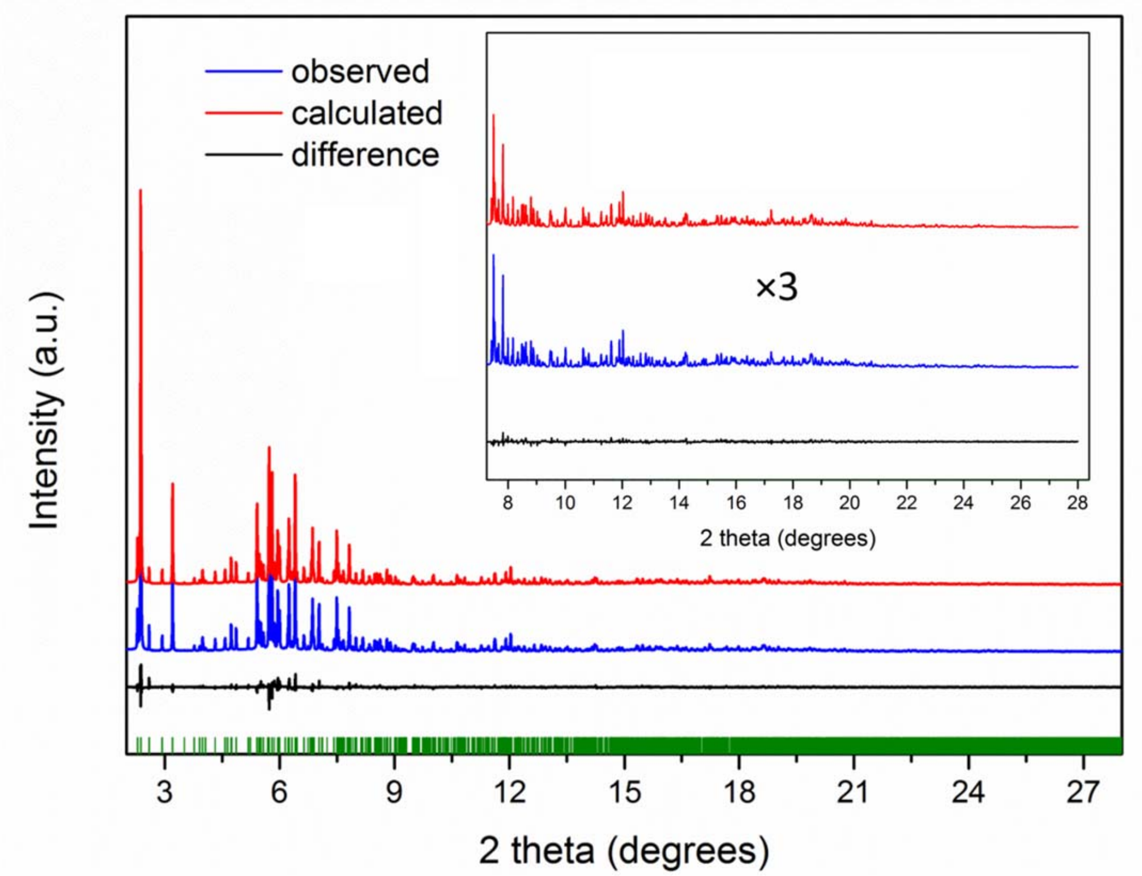
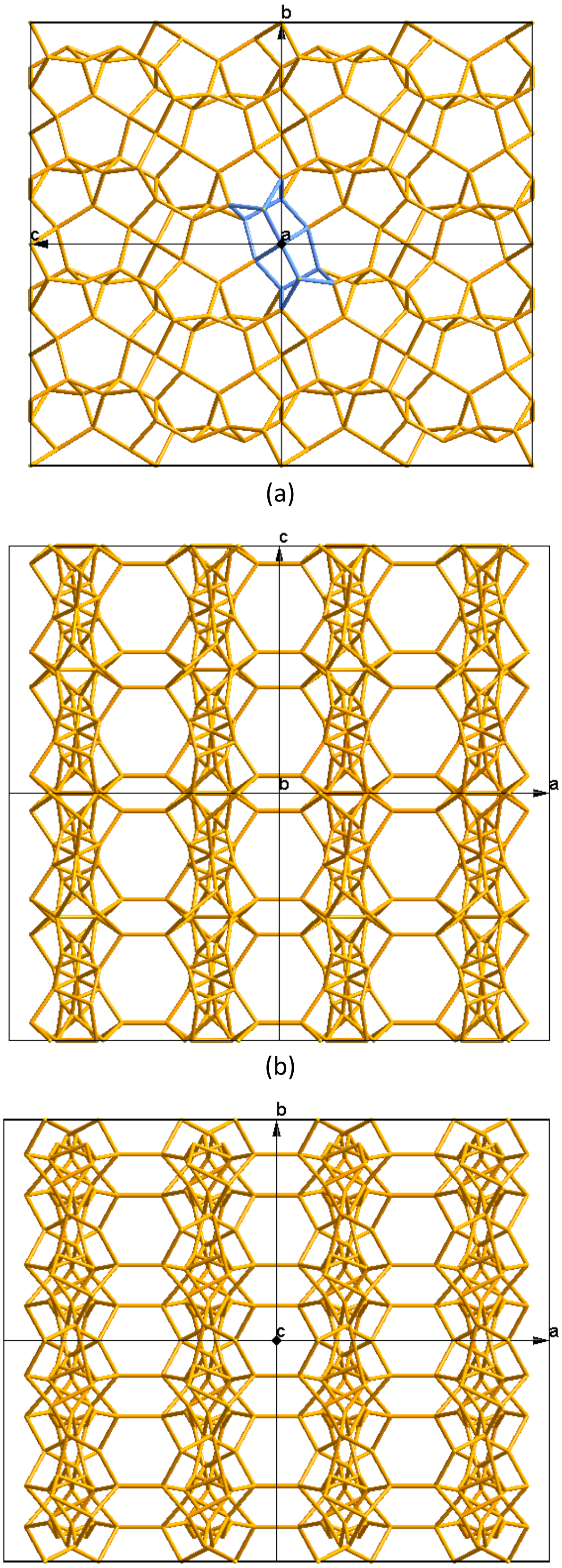


**Figure S2** Rietveld refinement plot of as-made EMM-26. The observed, calculated and difference curves are in blue, red and black, respectively. The vertical bars indicate the positions of Bragg peaks (λ = 0.4009 Å).



(a)

(b)

(c)

**Figure S3** The 3D framework of EMM-26 viewed along the (a) ***a***-axis, (b) ***b***-axis and ***c***-axis. Only T-T connections are shown for clarity. A *fer* composite building unit is highlighted in blue in (a).

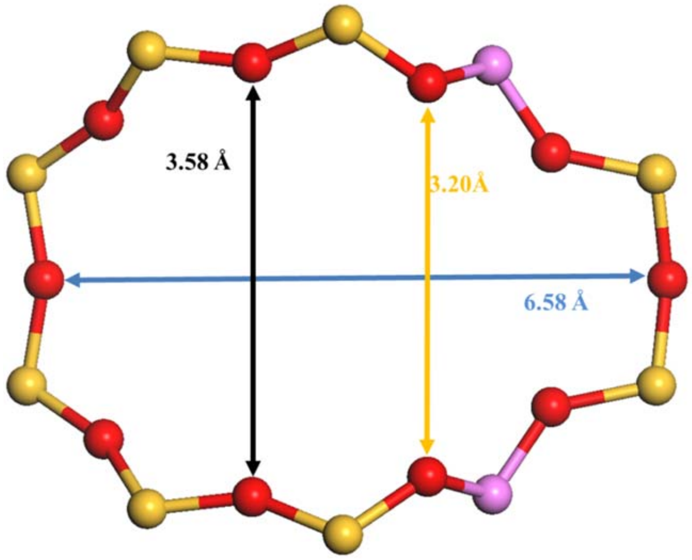


**Figure S4** Maximum effective pore diameters of the 10-rings in EMM-26. A van der Waals diameter of 2.70 Å for oxygen atoms has been subtracted. The positions with the highest boron content (T7, 37%) are shown in pink.

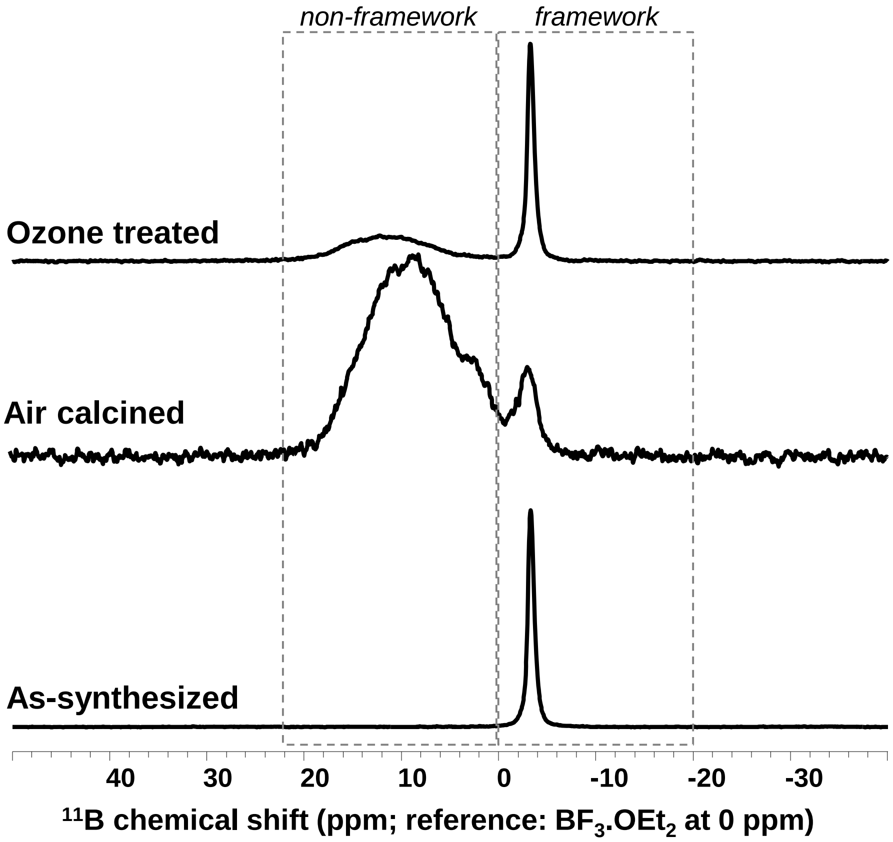


**Figure S5** $^{11}$B NMR on EMM-26 after different treatments: 160.1 MHz $^{11}$B MAS NMR (11.7T, $^{1}$H at 500MHz), MAS = 10kHz. The percentage of boron atoms in the zeolite framework with tetahedral environment is 100% for the as-synthesized, 8% for the air-calciend and 47% for the ozone treated EMM-26.

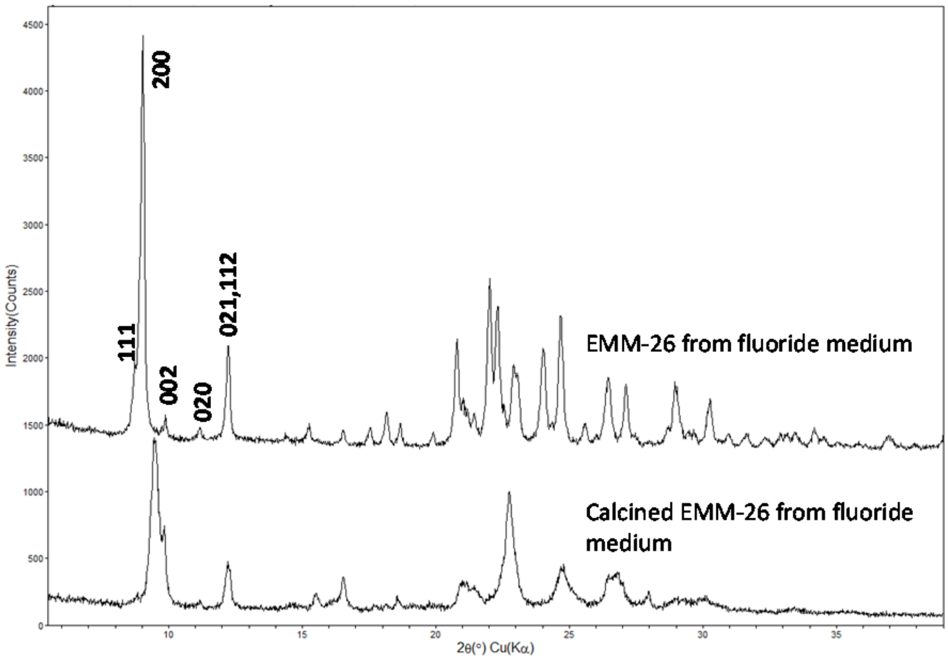


**Figure S6** PXRD patterns of the as-made and calcined EMM-26.

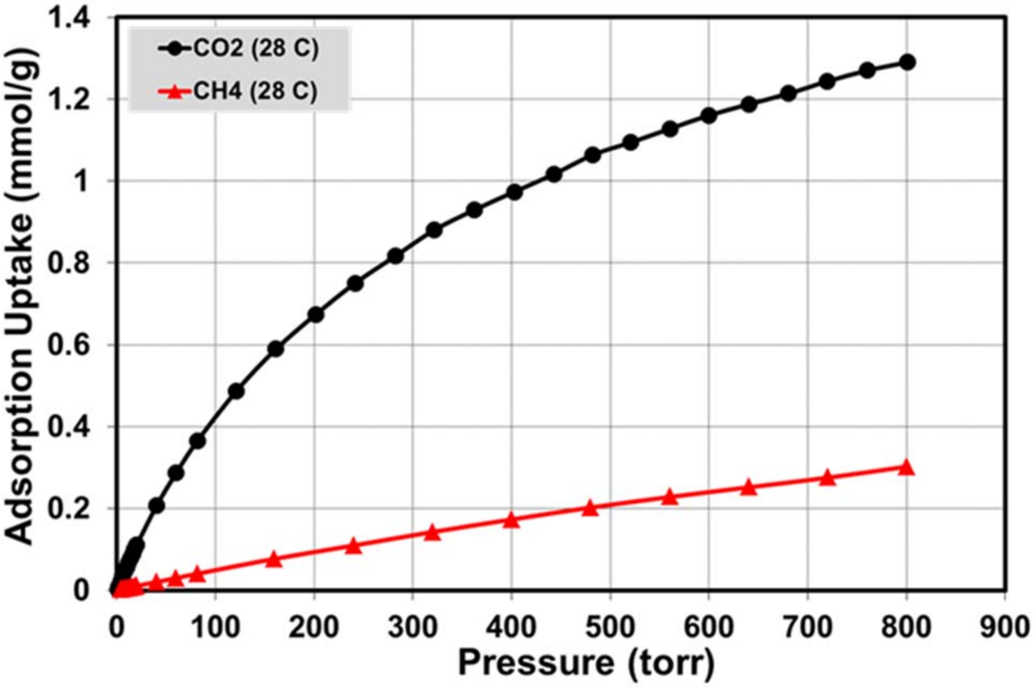


**Figure S7** $CO_2$ and $CH_4$ sorption isotherms at 301 K for EMM-26 prepared in fluoride media.

## References

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2. W. Wan, J. Sun, J. Su, S. Hovmöller and X. Zou, *J. App. Crystallogr.* 2013, **46**, 1863–1873.
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4. de Vos Burchart, E. Ph.D. Thesis, Technical University of Delft, The Netherlands, 1992; Table I, Chapter XII.
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