Supporting Information

Anchoring Boron Atom to the Specific Tetrahedral Sites of Borosilicate MFI by Imidazolium-based Molecules

Authors: Yufang Ma[a], Lei Wang[a]*, Lei Chen[b], Meikun Shen[c], Xue Yang[d], Tengteng Wang[a], Feixiang Yuan[a], Yu Zhou[b], Jun Wang[b], and Hongjun Zhu[a]*

Affiliations:

[a]School of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing 211800, P. R. China

[b]State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, South Puzhu Rd. 30, Nanjing, 211816, P. R. China

[c]Department of Chemistry and Biochemistry, University of Oregon, 1585 E 13 Ave, Eugene, OR 97403, USA

[d]Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Laboratory of Advanced Materials, and Collaborative Innovation Centre of Chemistry for Energy Materials, Fudan University, Handan Rd. 220, Shanghai, 200433, P. R. China

*Corresponding Author:

L. Wang: l_wang19@njtech.edu.cn, leiw.yz@outlook.com, H. Zhu: zhuhj@njtech.edu.cn

Table of contents

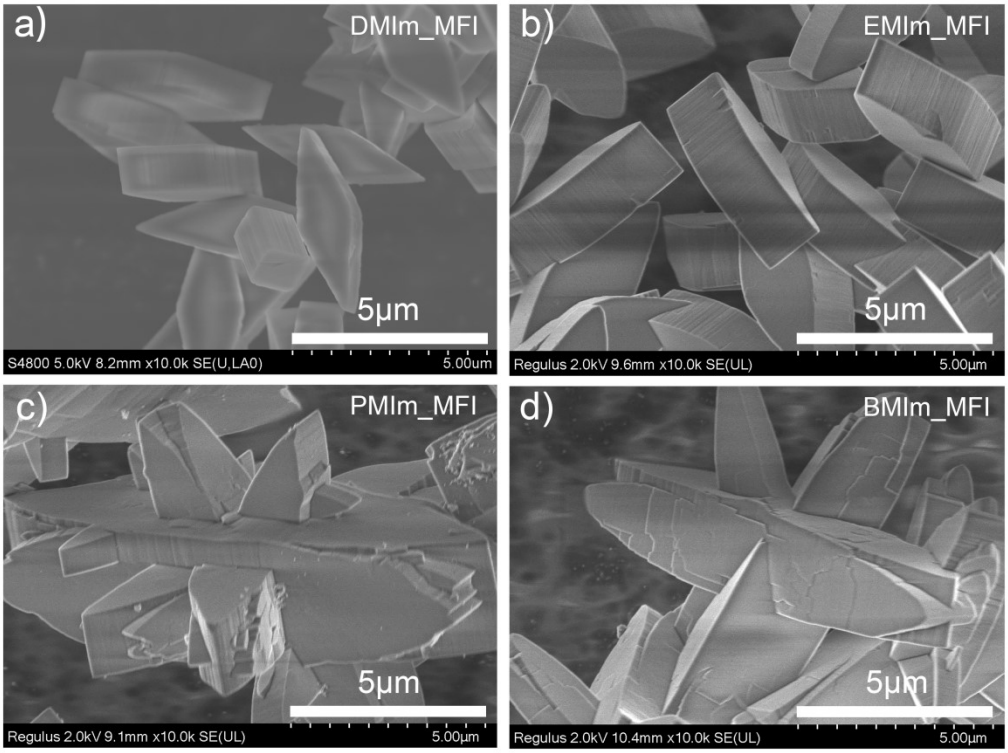


Figure S1. Typical SEM images of as-synthesized borosilicate **MFI** zeolites.

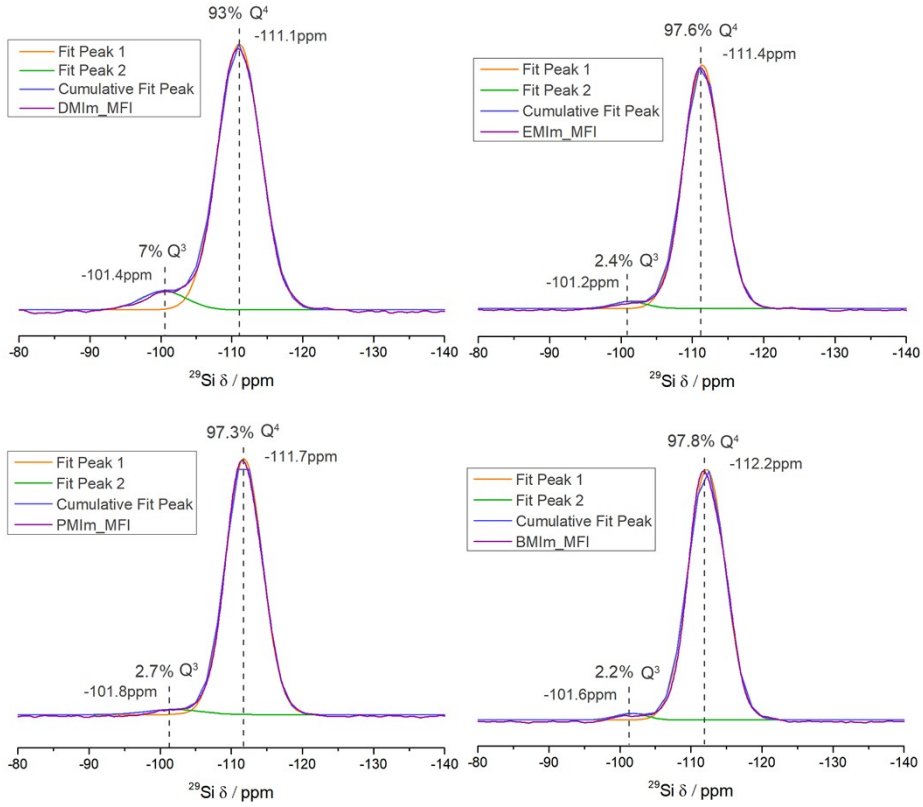


Figure S2. The relative quantity of Q^3 and Q^4 species in the as-synthesized borosilicate **MFI** zeolite.

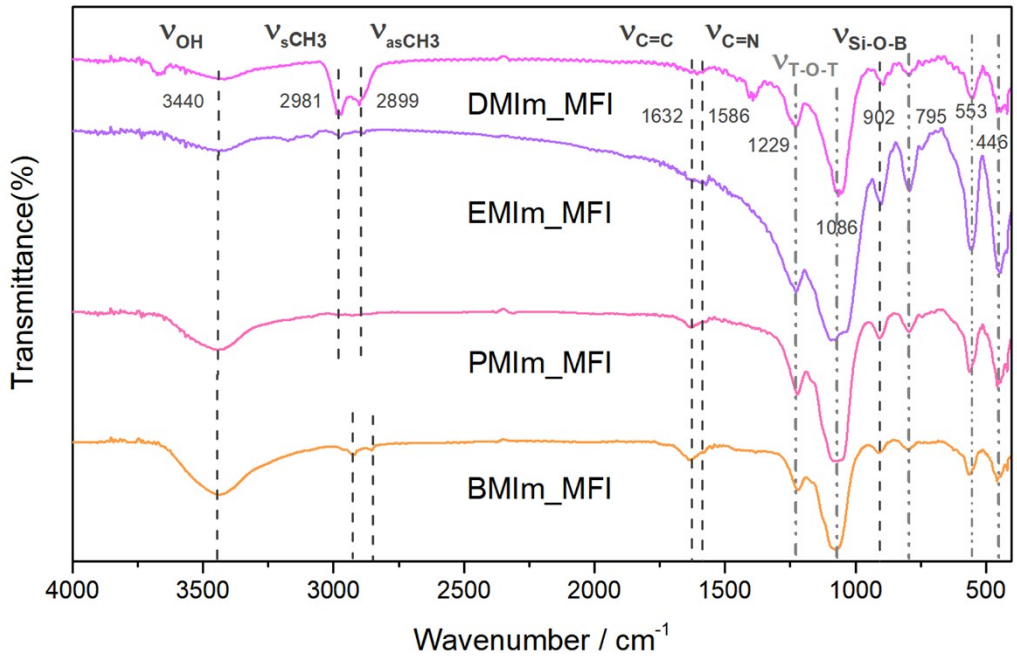


Figure S3. FT-IR spectra of as-synthesized borosilicate **MFI** zeolites.

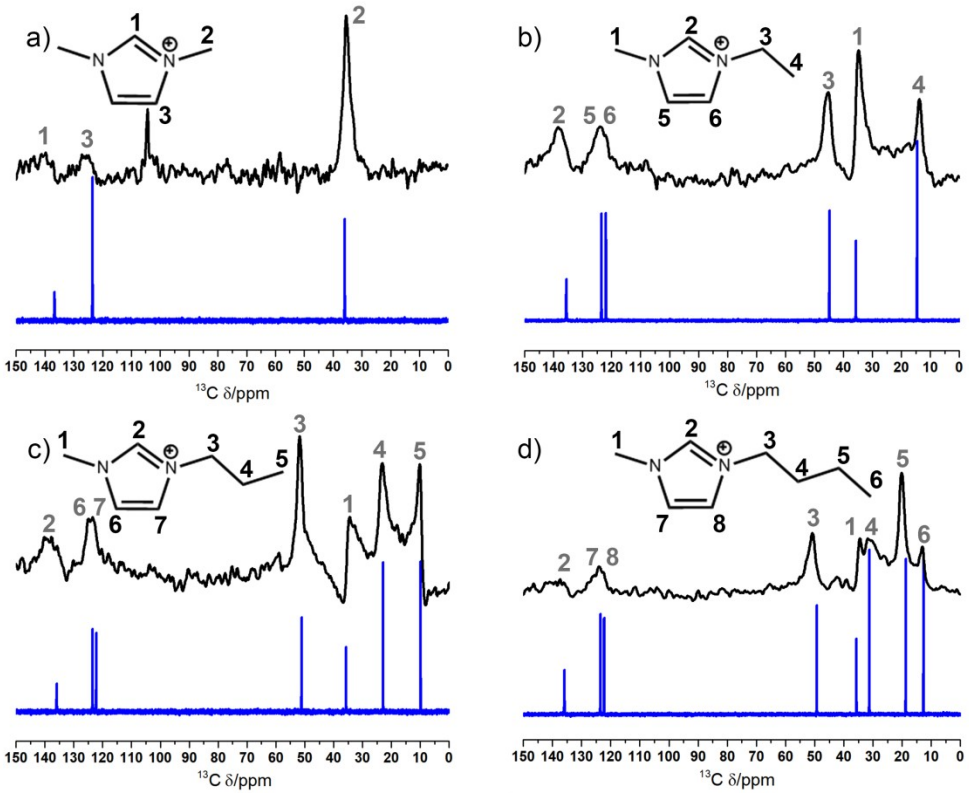


Figure S4. Liquid ^{13}C (bottom: blue) NMR and solid-state ^{1}H→^{13}C CP/MAS NMR (top: black) spectra of different borosilicate **MFI** synthesized using different OSDAs zeolites.

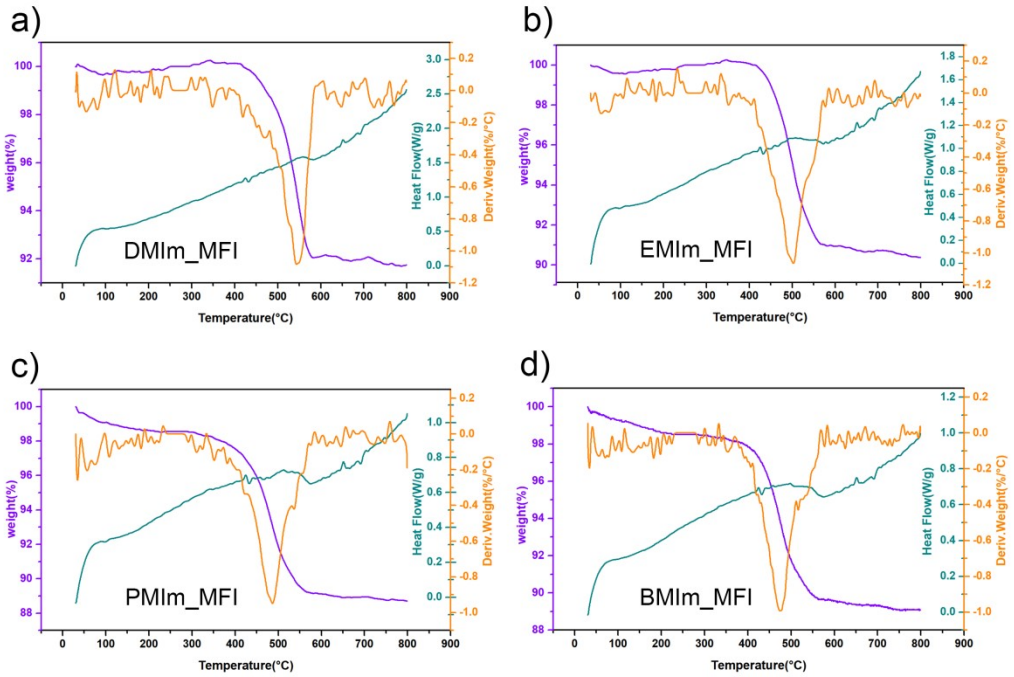


Figure S5. TG-DTA-DSC profiles of as-synthesized borosilicate **MFI** zeolites.

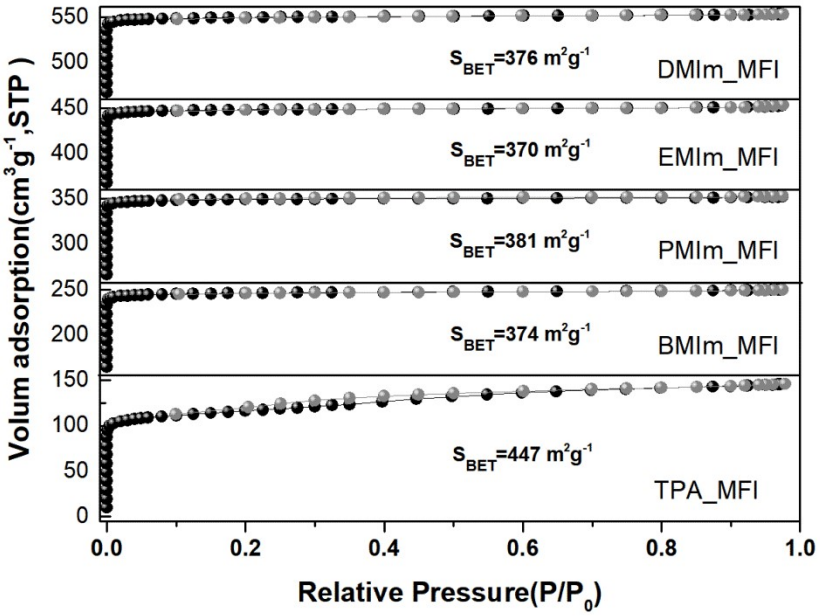


Figure S6. N_2 adsorption-desorption isotherms of calcined borosilicate **MFI** zeolites.

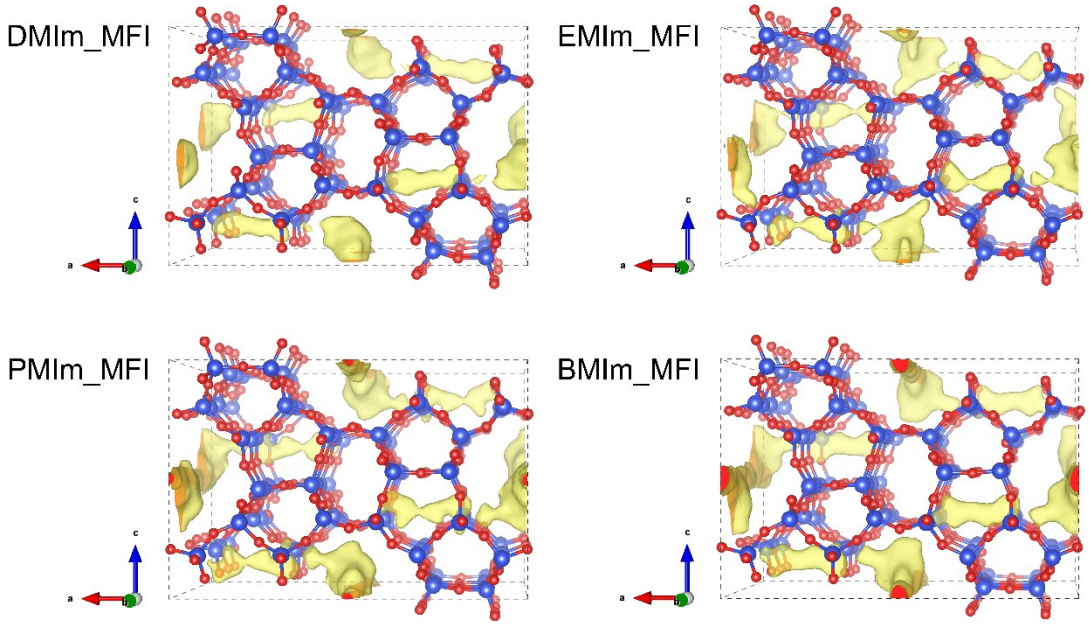


Figure S7. Electron density map of as-synthesized borosilicate **MFI** zeolites.

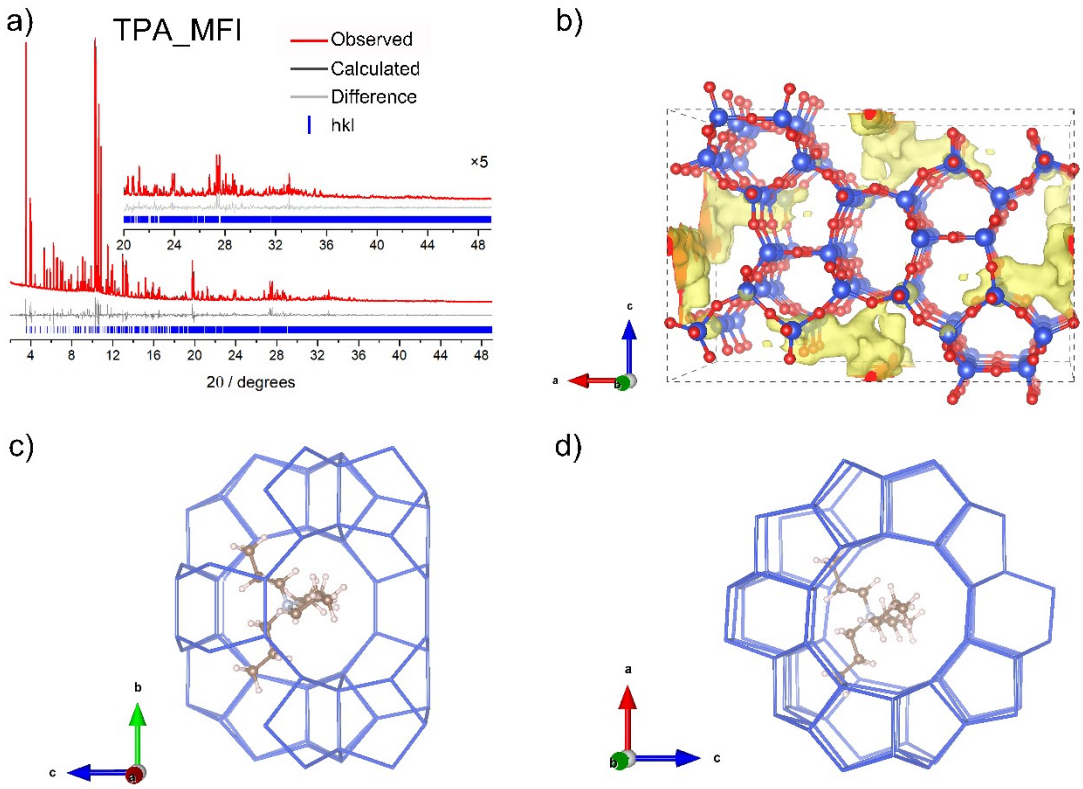


Figure S8. a) Rietveld refinement profiles of borosilicate **MFI** zeolite synthesized by TPA^+ cation, b) Electron density map of TPA directed borosilicate **MFI** zeolite. c) Projection viewed along the [100] direction, and d) the projection viewed along the [010] direction, respectively.

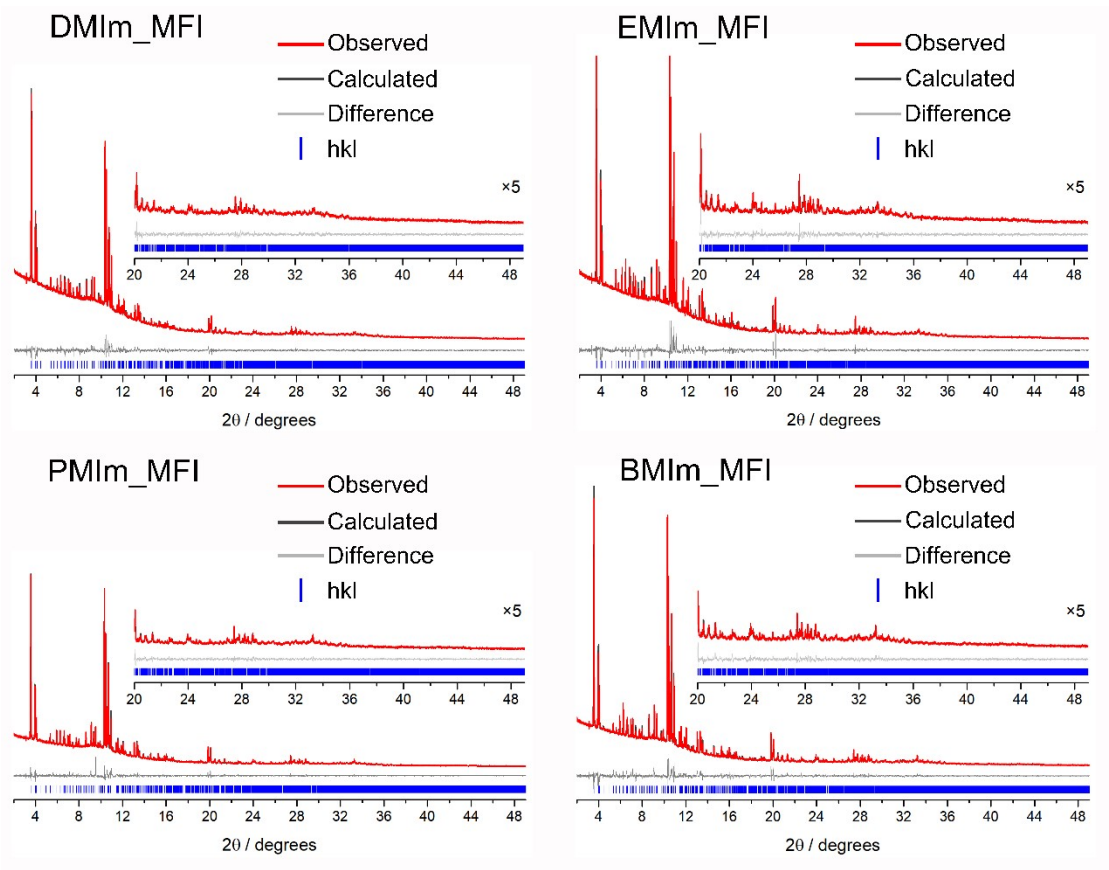


Figure S9. Rietveld refinement profiles of as-synthesized borosilicate **MFI** zeolites.

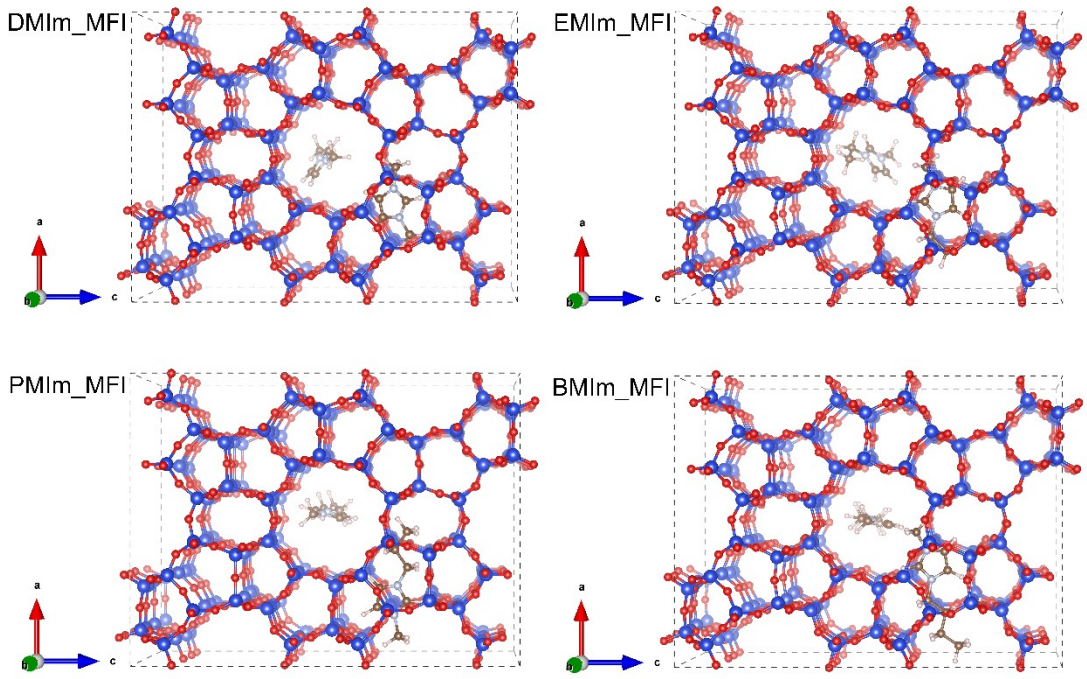
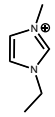
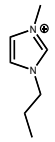
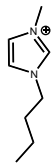


Figure S10. The distribution of OSDAs in the as-synthesized borosilicate **MFI** framework.

Table S1. Phase diagram of different OSDAs.

	OH^-/T Si/B	0.38	0.37	0.36	0.34	0.33	0.31
	5	TON+quartz	TON+quartz	TON+quartz	TON+quartz	TON+quartz	TON+quartz
	10	TON+quartz	TON+quartz	TON+quartz	TON+quartz	TON+quartz	TON+quartz
	15	TON	TON	MFI	MFI	Multiphase	Multiphase
	20	TON	TON+quartz	TON+quartz	TON+quartz	TON+quartz	TON+quartz
	25	TON	TON+quartz	TON	TON	TON+quartz	TON
	50	TON	TON	TON	TON+quartz	TON+quartz	TON+quartz
	5	TON+MFI	TON+MFI	TON+MFI	TON+MFI	TON	MFI
	10	MFI+quartz	Multiphase	Multiphase	Multiphase	TON+MFI	Multiphase
	15	MFI	TON+MFI	MFI	TON+MFI	TON+MFI	TON+MFI
	20	TON+quartz	TON+quartz	MFI+quartz	TON	TON	TON+quartz
	25	TON+quartz	TON+quartz	TON+quartz	TON+quartz	TON+quartz	TON+quartz
	50	TON	TON+quartz	TON	TON	TON+quartz	TON
	5	MFI+TON	MFI+quartz	MFI	MFI+TON	MFI+quartz	MFI
	10	MFI+TON	MFI+quartz	MFI+quartz	MFI+quartz	MFI+quartz	MFI+quartz
	15	TON+MFI	MFI+TON	MFI	MFI+TON	MFI+TON	MFI+TON
	20	MFI	MFI	MFI	MFI	MFI	MFI
	25	TON+quartz	TON+quartz	MFI+quartz	MFI+quartz	MFI+quartz	TON+quartz
	50	MFI+quartz	MFI+quartz	MFI+quartz	TON+quartz	TON+quartz	MFI+quartz
	5	MFI+ANA	MFI+ANA	MFI+ANA	MFI+ANA	MFI	MFI+quartz
	10	TON+MFI	TON+MFI	TON+MFI	MFI	MFI+TON	MFI+quartz
	15	MFI+quartz	MFI+quartz	MFI	MFI+quartz	MFI+TON	TON
	20	MFI+quartz	MFI+quartz	MFI+quartz	TON+quartz	TON+quartz	TON+quartz
	25	TON+MFI	Multiphase	MFI	MFI	MFI+TON	TON+MFI
	50	TON+quartz	TON+quartz	TON+quartz	TON	TON+quartz	TON

Note：The gel composition is 1 SiO_2 : *x* B_2O_3 : *y* NaOH : 0.18 OSDA : 84 H_2O ($0.02 \le x \le 0.20$; $0.31 \le y \le 0.38$), where OSDA used: 1, 3-dimethylimidazole , 1-ethyl-3-methylimidazole , 1-propyl-3-methylimidazole, 1-butyl-3-methylimidazole , respectively.

Table S2. General composition of different borosilicate **MFI** zeolites.

Entry	General Composition	Number of OSDA/u.c.	Compensate by OSDA	Si/B Ratio [a]
DMIm_MFI	$\|Na_{0.22}(C_5H_9N_2)_{5.58}\|[B_{6.29}Si_{89.71}O_{192}]$	5.58	89%	14.26
EMIm_MFI	$\|Na_{0.56}(C_6H_{11}N_2)_{4.39}(H_2O)_{8.77}\|[B_{4.95}Si_{91.05}O_{192}]$	4.39	89%	18.39
PMIm_MFI	$\|Na_{0.04}(C_7H_{13}N_2)_{6.25}(H_2O)_{0.30}\|[B_{6.29}Si_{89.71}O_{192}]$	6.25	99%	14.26
BMIm_MFI	$\|Na_{0.42}(C_8H_{15}N_2)_{4.06}(H_2O)_{1.30}\|[B_{4.48}Si_{91.52}O_{192}]$	4.06	91%	20.42

Note: [a] The Si/B ratio was determined by ICP results.

Table S3. Physical sorption details of calcined zeolites.

Entry	BET surface area [a] / m^2g^{-1}	Langmuir Surface area [b] / m^2g^{-1}	Single point surface area[c] at $p/p_0 = 0.02$/ m^2g^{-1}	Total pore volume [d]/ $cm^3 g^{-1}$	Micropore volume [d]/$cm^3 g^{-1}$
DMIm_MFI	374	394	373	0.15	0.14
EMIm_MFI	381	399	380	0.15	0.14
PMIm_MFI	370	390	369	0.15	0.14
BMIm_MFI	376	396	376	0.15	0.14
TPA_MFI	447	491	445	0.23	0.16

Note: [a]Calculated by the BET method; [b]Calculated by the Langmuir method; [c] Single point adsorption total pore volume of pores less than 79 nm width at $p/p_0 = 0.98$. [d] Calculated by the *t*-plot method.

Table S4. Rietveld refinement profiles of as-made borosilicate **MFI** zeolites.

	DMIm_MFI	EMIm_MFI	PMIm_MFI	BMIm_MFI	TPA_MFI
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	***Pnma***	***Pnma***	***Pnma***	***Pnma***	***Pnma***
Chemical Formula	$\|Na_{0.22}(C_5H_9N_2)_{5.58}\|$ $[B_{6.29}Si_{89.71}O_{192}]$	$\|Na_{0.56}(C_6H_{11}N_2)_{4.39}(H_2O)_{8.77}\|[B_{4.95}Si_{91.05}O_{192}]$	$\|Na_{0.04}(C_7H_{13}N_2)_{6.25}(H_2O)_{0.30}\|[B_{6.29}Si_{89.71}O_{192}]$	$\|Na_{0.42}(C_8H_{15}N_2)_{4.06}(H_2O)_{1.30}\|[B_{4.48}Si_{91.52}O_{192}]$	$\|Na_{2.34}(C_{12}H_{29}NO)_{4.72}(H2O)_{0.68}\|[B_{0.7}Si_{93.71}O_{192}]$
Formula Weight	6042.36	6092.65	6475.63	6464.29	7277.65
OSDA/u.c.	5.58	4.39	6.25	4.06	4.72
2*θ* range refinement/º	2-49	2-49	2-49	2-49	2-49
Refinement method	Rietveld	Rietveld	Rietveld	Rietveld	Rietveld
Detector	MYTHEN 1K	MYTHEN 1K	MYTHEN 1K	MYTHEN 1K	MYTHEN 1K
Sample holder	spinning 0.5 mm capillary	spinning 0.5 mm capillary	spinning 0.5 mm capillary	spinning 0.5 mm capillary	spinning 0.5 mm capillary
Wavelength / Å	0.6887	0.6887	0.6887	0.6887	0.6887
2*θ* Zero shift / º	-0.006441	-0.002867	-0.001228	-0.003094	-0.005006
Number of parameters	208	207	198	206	198
Number of *hkl*s	5017	5063	5102	5113	5198
a / Å	19.9106(11)	19.9543(10)	19.9892(3)	19.9997(10)	20.0445(2)
***b* / Å**	19.6572(11)	19.7136(9)	19.7610(3)	19.7849(10)	19.9204(2)
***c* / Å**	13.2495(7)	13.2726(6)	13.3066(3)	13.3278(6)	13.3984(1)
***V* / Å^3**	5185.7	5221.1	5256.20	5273.7	5349.89
Rwp/Rp/Rexp (%)	2.41 / 1.71 / 1.61	3.38 / 2.18 / 1.58	4.76 / 3.11 / 2.18	3.61 / 2.46 / 1.87	6.92 / 4.75 / 1.97
GoF	1.49	2.14	2.01	1.92	3.51
CSD number	2119319	2119320	2119321	2119318	2121437

Table S5. Boron enriched T sites in the reported borosilicates.

Framework type code	Boron enriched T sites	Composite building units
MVY (MCM-70)	T4	4-MR
SEW (SSZ-82)	T10 T11	4-MR
EWS (EMM-26)	T4 T6 T7	4-MR
ATS (SSZ-55)	T1	4-MR
IFW (SSZ-87)	T7 T8	4-MR
SFN (SSZ-59)	T6 T7	4-MR