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Article

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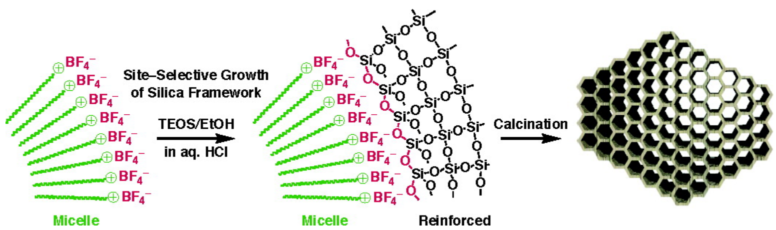

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Tetrafluoroborate Salts as Site-Selective Promoters for Sol−Gel Synthesis of Mesoporous Silica

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Abstract: Tetrafluoroborate ion (BF_4^-) serves as a powerful and better-behaved promoter than fluoride ion (F^-) for hydrolytic condensation of alkoxysilanes, such as tetraethoxy orthosilicate, in aqueous media containing amphiphiles with onium ion headgroups as templates, affording thermally and hydrothermally stable mesoporous silica. According to ^{19}F NMR spectral profiles, BF_4^- is localized on a positive-charged micellar surface, thereby allowing a site-selective growth of the silica framework. The resulting porous silica has an ordered hexagonal structure with a well-developed and thick silicate wall. Even without calcination, the condensation with BF_4^- as the promoter progresses to a large extent to furnish a [Si(OSi-)$_4$]/([HOSi(OSi-)$_3$] + [(HO)$_2$Si(OSi-)$_2$]) ratio of 6.2, which is greater than that of mesoporous silica formed without BF_4^- before (1.5) and even after calcination (3.5) to promote thermal condensation in the solid state.

Introduction

Fluoride ion is known to accelerate protonolysis of alkoxysilanes,[1] for which a hypervalent silicon species Si−F⁻, though proven only in limited cases,[1a,2] has been considered responsible. This method has been applied to the sol−gel synthesis of mesoporous silica, where the hydrolytic condensation of alkoxysilanes, in the presence of amphiphilic templates, is promoted by fluoride salts, such as NaF and NH_4F, to give thermally and hydrothermally stable mesoporous silica.[3] However, in our experience, careful optimization of the molar ratio of fluoride ion to surfactant is crucial to obtain ordered mesoporous structures. In the present paper, we highlight that tetrafluoroborate salts are better-behaved promoters than fluoride salts for the sol−gel synthesis of ordered mesoporous silica. This is based on our serendipitous finding that BF_4^- accelerates an alkoxy group exchange between alkoxysilanes and alcohols under mild conditions. Certain alkoxysilanes are known to be fluorinated by BF_4^- under rather rigorous conditions.[4] However, in general, the fluorine groups in BF_4^- have been considered to possess a much lower affinity than F^- toward silicon species due to the high Lewis acidity of BF_3. On the other hand, in view of the sol−gel synthesis of mesoporous silica, an interesting contrast to be considered between BF_4^- and F^- is that the former is much less hydrophilic and shows a greater ΔG for hydration (-45.4 kcal mol^{-1}) than the latter (-111.1 kcal mol^{-1}).[5] Hence, one may expect that BF_4^- may prefer to be localized on the micellar surface. Here we report a detailed account on the effects of $NaBF_4$ in the sol−gel processing and thermal/hydrothermal properties of resultant mesoporous silica.

Results and Discussion

The alkoxy groups of alkoxysilanes are known to exchange slowly with alcohols at room temperature. We found that the addition of $NaBF_4$ to a CD_3OD solution of tetramethyl orthosilicate (TMOS) results in a notable acceleration of the exchange reaction. An example is shown by the reaction at an initial molar ratio $[NaBF_4]_0/[TMOS]_0$ of 6:100 ($[TMOS]_0 = 0.20$ M) at 25 °C. ^1H NMR spectroscopy of the reaction mixture showed the appearance of a signal due to MeOD at 3.34 ppm, at the expense of the signal due to MeO−Si at 3.55 ppm. The integral ratio of these two signals indicated that the exchange reaction proceeds to 80% in 10 h (Figure 1a), whereas only 6% conversion is attained in the absence of $NaBF_4$ under conditions otherwise identical to those mentioned above (Figure 1e). The observed acceleration effect of $NaBF_4$ appears to be almost comparable to that of NaF (Figure 1b), while other salts, such as NaBr and $NaNO_3$, did not accelerate the exchange reaction (Figure 1c,d).

Taking into consideration the above interesting observations, we investigated hydrolytic condensation of tetraethyl orthosilicate (TEOS) in ethanolic hydrochloric acid in the absence and

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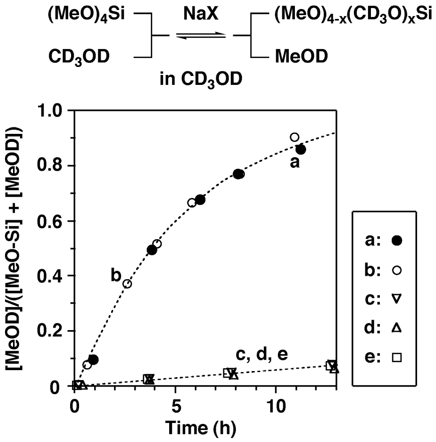


Figure 1. Time-courses of methoxy group exchanges between TMOS (initial concentration = 0.2 M) and CD_3OD in the absence (e) and presence of NaX (X = BF_4 (a), F (b), Br (c), and NO_3 (d)) at $[NaX]_0/[TMOS]_0$ = 6:100 in CD_3OD at 25 °C.

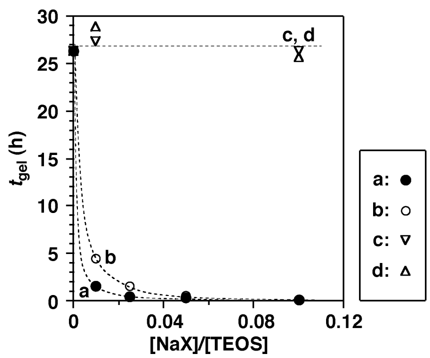


Figure 2. Hydrolytic condensation of TEOS at 25 °C in ethanolic aqueous HCl in the presence of $NaBF_4$ (a), NaF (b), NaBr (c), and $NaNO_3$ (d) at $[TEOS]_0/[H_2O]_0/[HCl]_0/[EtOH]_0$ = 1.0:23:1.0:3.5. Times required to lose fluidity by gelation (t_{gel}).

presence of the above four different sodium salts. Upon addition of $NaBF_4$ to an ethanolic hydrochloric acid solution of TEOS at $[NaBF_4]_0/[TEOS]_0/[H_2O]_0/[HCl]_0/[EtOH]_0$ = 0.01:1.0:23:1.0:3.5, the reaction mixture underwent gelation and completely lost its fluidity in 1.6 h ($=t_{gel}$) at 25 °C as a result of the hydrolytic condensation of TEOS (Figure 2a). Although the addition of NaF to the system also resulted in gelation, the hydrolytic condensation appears to be slower than with $NaBF_4$, where 4.5 h was necessary for complete gelation of the reaction mixture (Figure 2b). Upon incrementally changing the molar ratio, $[NaBF_4]_0/[TEOS]_0$, from 0.01 to 0.025, 0.05, and then 0.1, t_{gel} was significantly reduced to 30, 16, and then 5 min, respectively. On the other hand, as expected from Figure 1, NaBr and $NaNO_3$ under conditions identical to those above did not accelerate the gelation (Figure 2c,d). Thus, $NaBF_4$ is a quite efficient promoter for the hydrolytic condensation of alkoxysilanes. Since the condensation reaction likely involves $F_3B-F-Si(OEt)_4$ as the active species, we investigated, by means of ^{19}F NMR, a mixture of $NaBF_4$ and TEOS in CD_3OD, using NaF as a reference. However, neither BF_4^- nor F^- gave any unique NMR signals, even in the presence of a large excess of TEOS, suggesting that such active hypervalent species are only formed transiently to promote the reaction.[1a,2]

We then investigated effects of $NaBF_4$ on the sol−gel synthesis of mesoporous silica under acidic conditions (Scheme 1) including a surfactant such as 1-cetyl-3-methylimidazolium

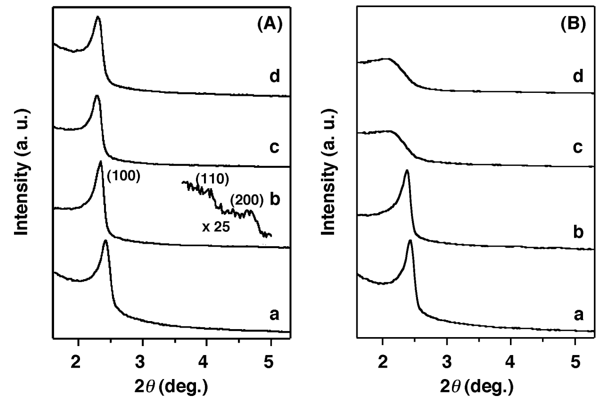


Figure 3. XRD patterns of mesoporous silicates (A) **2**[BF_4] and (B) **2**[F]. Precursor materials **1**[BF_4] and **1**[F] were obtained, respectively, in the presence of $NaBF_4$ and NaF at $[NaX]_0/[CMICl]_0$ = 0.1 (a), 0.5 (b), 1.0 (c), and 2.0 (d). Inset in (A): a magnified XRD pattern in a range 2θ = 3.5−5.0°.

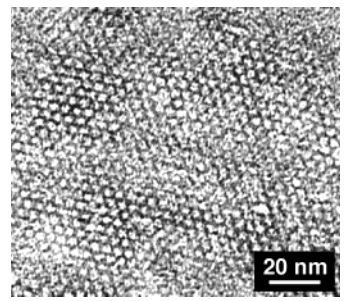
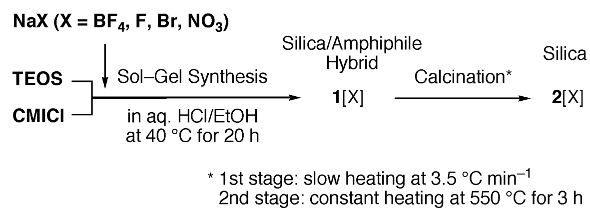


Figure 4. TEM micrograph of calcined material **2**[BF_4]. Precursor material **1**[BF_4] was prepared with CMICl as template in the presence of $NaBF_4$ at $[CMICl]_0/[TEOS]_0/[H_2O]_0/[HCl]_0/[EtOH]_0/[NaBF_4]_0$ = 1.0:3.7:530:32:20:0.50.

Scheme 1



chloride (CMICl) ($[CMICl]_0/[TEOS]_0/[H_2O]_0/[HCl]_0/[EtOH]_0$ = 1.0:3.7:530:32:20).[6] As shown in Figure 3A, the sol−gel reactions in the presence of $NaBF_4$ at $[NaBF_4]_0/[CMICl]_0$ = 0.1 (a), 0.5 (b), 1.0 (c), and 2.0 (d) proceeded to give insoluble precipitates, all of which showed X-ray diffraction (XRD) patterns with (100), (110), and (200) diffraction peaks, typical of hexagonal structures (Figure 3A, only calcined materials **2**[BF_4] are shown). Transmission electron microscopy (TEM) of, e.g., **2**[BF_4] formed at $[NaBF_4]_0/[CMICl]_0$ = 0.5, showed a honeycomb structure, with an interpore distance of 4.4 nm (Figure 4), which is in excellent agreement with that (4.2 nm) estimated from the *d*-spacing of the (100) diffraction (d_{100} = 3.7 nm) using the relationship: interpore distance = $2d_{100}/\sqrt{3}$. In contrast, the sol−gel synthesis with NaF, in place of $NaBF_4$, gave an ordered mesoporous structure only at low $[NaF]_0/[CMICl]_0$ ratios, such as 0.1 (a) and 0.5 (b), while higher $[NaF]_0/[CMICl]_0$ ratios (≥1.0, (c) and (d)) resulted in only broad XRD profiles (Figure 3B).

(6) See Supporting Information.

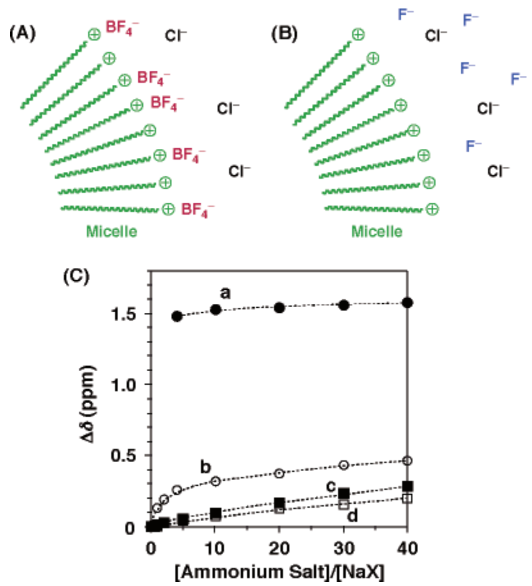


Figure 5. Schematic illustrations for locations of (A) BF_4^- and (B) F^- in water containing surfactant micelles. (C) ^{19}F NMR chemical shift changes of the signals due to BF_4^- and F^- in D_2O solutions of $NaBF_4$ (a) and NaF (b) in the presence of micellar CTACl and those of $NaBF_4$ (c) and NaF (d) in the presence of nonmicellar TMACl at [NaX] = 8.0 mM.

We assume that the above contrasting behaviors of $NaBF_4$ and NaF in the mesostructure formation is due to the difference in hydrophilic natures of these two salts. Namely, less hydrophilic BF_4^- is possibly localized on a micellar surface in aqueous media (Figure 5A) and can promote the silica formation site-selectively around the template micelle. In contrast, F^- is hydrated and may not be selectively localized in proximity to the micellar surface (Figure 5B), so that it would promote the nontemplated silica formation. To support this idea, ^{19}F NMR spectroscopy was conducted at 25 °C on D_2O solutions of $NaBF_4$ and NaF in the presence of varying amounts of onium salts, such as micelle-forming cetyltrimethylammonium chloride (CTACl) and nonmicellar tetramethylammonium chloride (TMACl). Upon mixing of a D_2O solution of CTACl with $NaBF_4$, a white precipitate formed at a [CTACl]/[$NaBF_4$] molar ratio ranging from 0.01 to 3.5 ([$NaBF_4$] = 8.0 mM). The precipitates at [CTACl]/[$NaBF_4$] = 1.0 and 2.0, isolated by filtration, were both identified as chlorine-free $CTABF_4$ by elemental analysis (Calcd for $C_{19}H_{42}BF_4N$: C, 61.45; H, 11.40; B, 2.91; N, 3.77. Found: C, 61.7; H, 11.9; B, 3.0; Cl, <0.02; N, 3.5 and C, 61.5; H, 11.5; B, 3.0; Cl, <0.02; N, 3.5, respectively.) On the other hand, when the [CTACl]/[$NaBF_4$] ratio was further increased, the mixture became homogeneous, without formation of precipitates. The ^{19}F NMR spectrum of a D_2O solution of $NaBF_4$ alone showed a signal due to $^{19}F_4{}^{11}B^-$ at −151.10 ppm (Figure 5C, (a)), along with a minor isotope signal due to $^{19}F_4{}^{10}B^-$ at −151.04 ppm.[6] Upon mixing the solution with CTACl, these signals shifted to, e.g., −149.61 and −149.56 ppm, respectively, at [CTACl]/[$NaBF_4$] = 4.0. However, even upon further incremental changing of [CTACl]/[$NaBF_4$] from 4.0 up to 40.0, these signals hardly showed further downfield shifts, suggesting that the spectral change is nearly saturated, even at [CTACl]/[$NaBF_4$] < 4.0. In contrast, although fluoride ion, upon mixing with CTACl, exhibited a similar downfield shift of the signal (b), the extent was much smaller than that in the case of BF_4^- (a), even at [CTACl]/[NaF] = 40.0. On the other hand, when nonmicellar TMACl was used in place of CTACl, neither BF_4^- (c) nor F^- (d) exhibited a notable downfield shift ($\Delta\delta$ < 0.3 ppm at [TMACl]/[$NaBF_4$] = 40.0). These spectral features, along with the formation of insoluble (hydrophobic) $CTABF_4$, allowed us to conclude that BF_4^-, in contrast with F^-, prefers to be localized in a less hydrophilic environment around the CTACl micelle in aqueous media.

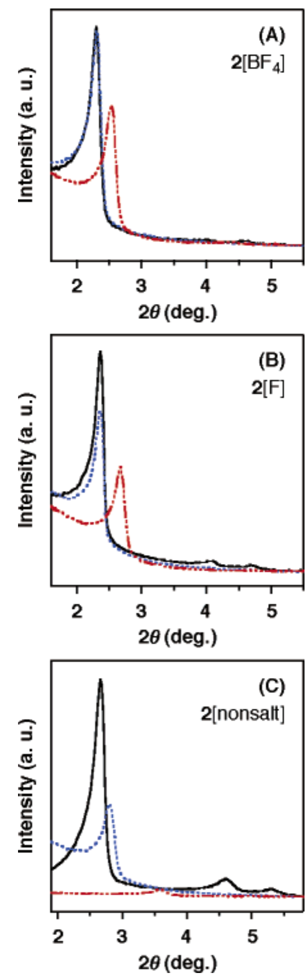


Figure 6. XRD patterns of calcined materials (A) **2**[BF_4], (B) **2**[F], and (C) **2**[nonsalt] before (solid black curves) and after being heated in air at 900 °C for 3 h (broken red curves) or in water at 100 °C for 32 h (broken blue curves).

We found that mesoporous silica **2**[BF_4], prepared by this accelerated sol−gel synthesis with BF_4^-, is thermally and hydrothermally stable, even more so than that synthesized with F^- (**2**[F]). For example, upon heating at 900 °C for 3 h, reference mesoporous silica **2**[nonsalt], formed without any salt addition, lost the majority of its hexagonal structure, as observed by XRD (Figure 6C; from solid black to broken red curves), where the %-survival value, as evaluated from a decrease in intensity of the (100) diffraction peak, was only 4% (Figure 7A). In sharp contrast, **2**[BF_4] preserved its hexagonal structure to a greater extent with a %-survival value of 65% (Figure 7A). This value is also definitely higher than that of **2**[F] (49%) (Figures 6B and 7A). On the other hand, **2**[Br] and **2**[NO_3], obtained with NaBr and $NaNO_3$, respectively, lost their hexagonal structures considerably, where the %-survival values were only as low as 19 and 9% (Figure 7A). Upon being heated in water at 100 °C

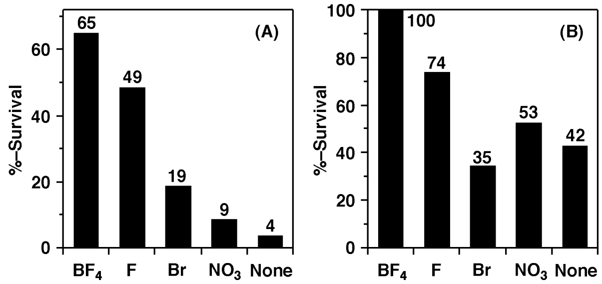


Figure 7. Stabilities of calcined materials **2**[X] on (A) thermal (900 °C, 3 h) and (B) hydrothermal (100 °C in water, 32 h) treatments. Precursor materials, **1**[X], were obtained with CMICl as the template in the absence (none) and presence of NaX (X = BF_4, F, Br, and NO_3) at $[NaX]_0/[CMICl]_0$ = 0.5. %-Survival values were given by $I/I_0 \times 100$, where I_0 and I are intensities of (100) diffraction before and after the treatments, respectively.

Table 1. Structural Properties of Mesoporous Silicates

	d_{100} (nm)[a]	pore diameter (nm)	wall thickness (nm)[b]	surface area ($m^2\ g^{-1}$)	$Q^4/(Q^3 + Q^2)$ uncalcined[c]	$Q^4/(Q^3 + Q^2)$ calcined
2[BF_4]	3.77	2.1	2.3	810	6.2	7.6
2[F]	3.71	2.1	2.2	860	4.8	5.6
2[Br]	3.29	2.1	1.7	1480	1.5	3.7
2[nonsalt]	3.29	2.1	1.7	1260	1.5	3.5

[a] *d*-spacings of (100) diffraction in XRD. [b] Wall thickness = [interpore distance] − [pore diameter]. [c] Evaluated by ^{29}Si MAS NMR spectroscopy of uncalcined **1**[X].

for 32 h, **2**[BF_4] also showed a high hydrothermal stability, without any loss of the hexagonal structure (Figures 6A and 7B: from solid black to broken blue curves), whereas **2**[F] obviously lost the structural regularity (%-survival value = 74%) (Figures 6B and 7B). As expected, **2**[Br] and **2**[NO_3], as well as **2**[nonsalt] (%-survival value = 42%), underwent a serious structural disordering under the above hydrothermal conditions, where the %-survival values were 35 and 53%, respectively (Figure 7B). In relation to these observations, when an onium ion surfactant bearing BF_4^- as counteranion was used, reinforced silica was obtained without external addition of $NaBF_4$. For example, in water at 100 °C for 32 h, the mesoporous silica templated by 1-cetyl-3-methylimidazolium tetrafluoroborate ($CMIBF_4$) hardly lost the hexagonal structure (%-survival value = 96%).[6]

Some structural properties of mesoporous silicates are summarized in Table 1. Elemental analysis showed that calcined material **2**[BF_4] is boron- and fluorine-free (found: B, <0.05; F, <0.002; Si, 42). N_2 adsorption/desorption isotherms indicated that the pore diameters of **2**[BF_4], **2**[F], **2**[Br], and **2**[nonsalt] are all 2.1 nm. On the other hand, the interpore distances, as estimated by the XRD analysis, suggested that the silica walls of **2**[BF_4] and **2**[F] were 2.2 and 2.1 nm thick, which were much thicker than those of **2**[Br] and **2**[nonsalt] (1.7 nm). In conformity with this observation, the surface areas of **2**[BF_4] and **2**[F] in the N_2 adsorption were 810 and 860 $m^2\ g^{-1}$, which are smaller by 30−55% than those of **2**[Br] and **2**[nonsalt]. On the other hand, ^{29}Si MAS NMR spectroscopy of uncalcined **1**[BF_4], obtained directly from the sol−gel reaction system, showed a major signal at −110 ppm due to $Si(OSi\text{-})_4$ (Q^4), whereas signals at −100 and −90 ppm due to $HOSi(OSi\text{-})_3$ (Q^3) and $(HO)_2Si(OSi\text{-})_2$ (Q^2), respectively, were negligibly small.[6] The integral ratio of the signals $Q^4/(Q^3 + Q^2)$ was calculated to be 6.2, which is much greater than those of **1**[Br] (1.5) and **1**[nonsalt] (1.5) and even higher than that of **1**(F) (4.8). It is known that the content of Q^4 is increased on calcination as the result of thermal-induced condensation. In fact, the $Q^4/(Q^3 + Q^2)$ ratio of **1**[nonsalt], after the initial programmed heating at 3.5 °C min^{-1}, followed by constant heating for 3 h at 550 °C, was increased to 3.5, which is, however, still lower than that of uncalcined **1**[BF_4] and much lower than that after the calcination (7.6). Thus, as-synthesized **1**[BF_4] already possesses a well-developed silicate framework. Such a high degree of condensation and the thick silicate framework (Table 1) both are likely responsible for the high thermal and hydrothermal stabilities of the mesoporous silica.[7] That the site-selective hydrolytic condensation of TEOS promoted by BF_4^- enables the formation of highly condensed silica without spoiling the mesostructural integrity of the material takes great advantage of BF_4^- over F^-.

Conclusions

We have demonstrated that BF_4^- is a powerful and better-behaved promoter than F^- for hydrolytic condensation of alkoxysilanes, such as TEOS, in aqueous media. BF_4^- is less hydrophilic than F^- and localized more selectively on a micellar surface so that it can site-selectively accelerate the hydrolytic condensation of TEOS, affording ordered mesoporous silica with a highly condensed and thick silicate wall. This phenomenon is reminiscent of biological mineralization, which is triggered by the adsorption of minerals on organic surfaces. Considering an increasing interest in organic/inorganic hybrids,[8] the site-selective growth of silicate framework with BF_4^-, reported herein, is considered quite important for the fabrication of nanocomposite materials with functional organic domains in ordered inorganic frameworks.

Supporting Information Available: Experimental details; ^{19}F NMR spectra of D_2O solutions of $NaBF_4$ and NaF in the presence of onium salts; ^{29}Si MAS NMR spectra of uncalcined **1**[BF_4], **1**[F], and **1**[nonsalt]; XRD patterns of calcined mesoporous silica, obtained with $CMIBF_4$ as template, before and after being heated in water at 100 °C for 32 h. This material is available free of charge via the Internet at http://pubs.acs.org.

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