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Anion Exchangeable Layered Silicates Modified with Ionic Liquids on the Interlayer Surface

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Novel layered materials with two-dimensionally arranged anion exchangeable sites in the interlayer space were prepared by immobilization of imidazolium chloride salts (1-butyl (or 1-octyl)-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium chloride, abbreviated as $\mathrm{BimSi(OEt)_3Cl}$ or $\mathrm{OimSi(OEt)_3Cl}$, respectively) containing terminal triethoxysilyl groups onto layered octosilicate via silylation. More than 80% of $\mathrm{SiOH/SiO^-}$ groups on the silicate layers were silylated and they are denoted as Bim-Oct and Oim-Oct. The cation exchangeable sites on octosilicate were stoichiometrically converted to anion exchangeable sites. The confronting arrangement of $\mathrm{SiOH/SiO^-}$ groups on octosilicate is essential for this stoichiometric conversion because the silylation reagents ideally react with the surface $\mathrm{SiOH/SiO^-}$ groups to form bidentate immobilization on octosilicate. The anion exchangeable capacity of the silylated materials is around 2 mmol $\mathrm{g^{-1}}$. The affinity of these materials for $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{I^-}$, and $\mathrm{NO_3^-}$ is quite different from those of conventional anion exchangeable layered double hydroxides (LDHs). Bim-Oct is stable at pH 1.0, which is in clear contrast to the behavior of LDHs. Bim-Oct exhibits a high capacity for sorption of sulfasalazine, a bulky prodrug. The release behavior of the accommodated sulfasalazine is largely dependent on the pH values of simulated gastric and intestinal fluids, suggesting that these novel layered anion exchangers are potentially applicable to drug delivery systems.

Introduction

Inorganic layered materials are quite attractive because of a wide variety of applications, including adsorbents, catalyst supports, porous materials, and building units for nano/meso-structured materials utilizing their unique two-dimensionally confined space.[1] The interactions, especially electrostatic interactions, between layered host materials and guest species strongly affect the reactivity and selectivity of intercalation reactions. Among a large number of layered materials, anion exchangeable layered materials figure prominently in this field and have been studied as hosts or carriers for not only inorganic anions but also drug substances[2] and biological species.[3] Despite the demanding requirement for the creation of such functional materials, there are few kinds of anion exchangeable layered materials. A typical one is layered double hydroxides (LDHs)[4] in which anion exchangeable sites come from substituted trivalent cations in divalent metal hydroxides. Because the property of anion exchangeable sites is limited to the kind of substituting trivalent metal cations, the affinity for various intercalating guest species is almost fixed.[5] In addition, LDHs are unstable in acid media.

Recently, another method of the incorporation of anion exchangeable sites into interlayer spaces has been achieved through the hybridization of cation exchangeable layered clay minerals with calix[4]areneoctols,[6] chitosan,[7] or cationic polyelectrolytes with amine groups.[8] We reported that the color of intercalated anionic dye can be tuned through

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choosing the optimal polyelectrolyte and the reaction pH.[8b] However, because cation sites are generally distributed throughout the whole of the interlayer spaces, the distance and arrangement of anion exchangeable sites cannot be controlled with incorporated polycations. Furthermore, these hybrids possess much lower anion exchange capacity (AEC: 0.2 mequiv/g of host) than that of LDH (2−4.5 mequiv/g of LDH)[4b] because their AEC values rely on the degree of overcompensation of polycations and the degree is limited by steric hindrance of the polymer and repulsion of cations.

Ionic liquids[9,10] have attracted keen interest as "designer solvents",[11] such as ionic conductors,[12,13] as well as solvents for synthesis and catalysis.[14,15] As an anion exchanger, ionic liquids immobilized onto solid supports have received much attention as stationary phases of liquid chromatography[16−18] and catalyst supports.[19−24] Ionic liquids as liquid chromatography stationary phases can separate a wide variety of mixtures, such as nonpolar and polar molecules, cations and anions because of the wide range of properties of the ionic liquids.[18,25] Anionic catalysts on ionic liquids immobilized onto silica supports exhibit high selectivities and activities because of the homogeneous-like state of the catalysts with liquid-state ionic liquids.[21,22] However, silica supports for ionic liquids are so far limited to amorphous ones, such as silica gel,[19a,20a,22a] silica nanoparticles,[21] and mesoporous silica.[19a,23,24,26] Therefore, immobilized ionic liquid molecules are located randomly on such amorphous supports.

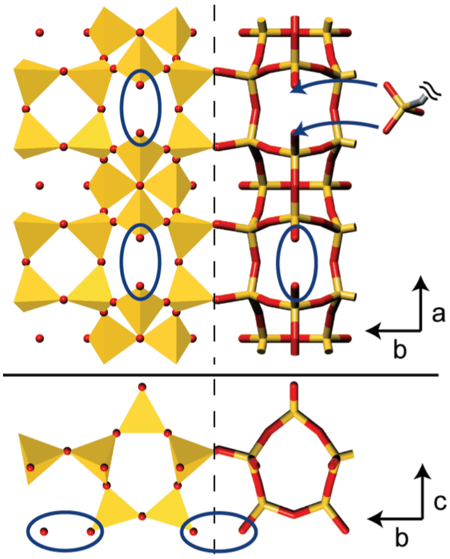

Figure 1. Crystal structure of layered octosilicate. The ellipsoids indicate confronting SiOH/SiO$^-$ groups.

Layered silicates,[27] composed of SiO_4 tetrahedra only, possess SiOH/SiO$^-$ groups on the interlayer surfaces which are reactive for organic modification including silylation.[28−32] In particular, a layered octosilicate[33] ($Na_8[Si_{32}O_{64}(OH)_8 \cdot 32H_2O]$, also known as ilerite or RUB-18) possesses confronting SiOH/SiO$^-$ groups arranged along one axis on the interlayer surfaces (Figure 1).[33b] The confronting groups preferentially induce a bidentate silylation which provides organic groups in a well-arranged manner reflecting the surface structure of the silicate layers.[30] More than 90% of the confronting SiOH/SiO$^-$ groups of octosilicate are silylated with alkoxytrichlorosilanes[30b] and the value is higher than that of another layered silicate kanemite[34] ($NaHSi_2O_5 \cdot 3H_2O$)[29c] though the density of the SiOH/SiO$^-$ groups of kanemite is higher than that of octosilicate. Therefore, octosilicate is an ideal host for immobilization of organic species with optimal arrangement and high density.

From the viewpoint of the highest utilization of ionic liquids on solid supports, it is extremely important to select and/or design supports possessing a high surface area, high accessibility, confined space, and controllability of immobilized sites;[23] and all these requirements can be provided by well-defined layered silicates. The distance

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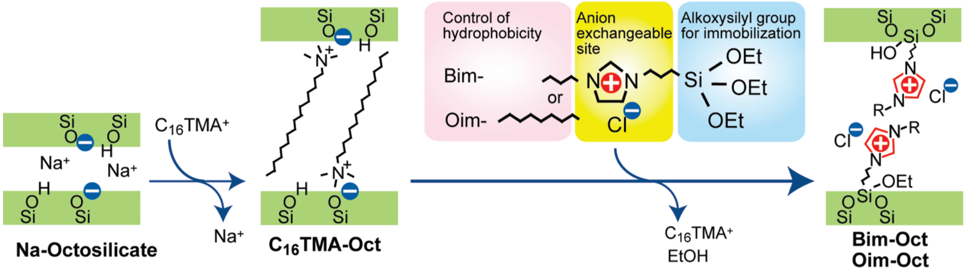

Figure 2. Synthetic pathway of anion exchangeable layered silicates. The first step is the intercalation of hexadecyltrimethylammonium ions for the expansion of the interlayer distance. The second step is immobilization of triethoxysilyl-terminated imidazolium salts with butyl or octyl groups.

of immobilized sites can be controlled by choosing the kind of layered silicates and modifying agents. Hybridization of layered materials and ionic liquids has been reported for a few cases; ionic liquids are intercalated into clays such as montmorillonite[35,36] and kaolinite.[37] However, these studies have not focused on the control of layer charge and covalent immobilization. From the viewpoint of the layered materials, well-designed anion exchangeable sites are quite essential for developing advanced functional nanomaterials. Consequently, the immobilization of ionic liquids in the interlayer space of layered silicates can satisfy all the requirements described above because the structure of the ionic liquids is diverse and the hydrophilicity/hydrophobicity is controllable.

Here, we report the synthesis of anion exchangeable layered silicate via immobilization of ionic liquids onto the interlayer surfaces of octosilicate (Figure 2). We utilized ionic liquids containing three specific functional groups as follows; (i) butyl or octyl group attached on the imidazolium group for the control of hydrophobicity, (ii) triethoxysilyl group for immobilization, and (iii) imidazolium group for bridging both the alkyl chain and triethoxysilylpropyl group (Figure 2). Because of two quaternized nitrogens, imidazolium groups are more useful for bridging two functional groups than trimethylammonium groups, which are also used conventionally.[38,39] In addition, imidazolium groups can form metal complexes, and in particular, complexes with Pd or Ir species are useful as catalysts for cross-coupling reactions.[23,40] We can expect that the cation exchangeable sites of the SiOH/SiO^- groups can be converted to anion exchangeable sites of the imidazolium salts via silylation. The derivatized layered hybrids should have the following expected properties, such as a relatively high AEC, high durability in acid solution, and controllability of the affinity for guest species. Finally, we investigated the possibility of using the derivatives as a drug-delivery carrier for an anti-inflammatory prodrug, sulfasalazine,[41] in oral administration, which needs high capacity, accessibility, and durability in gastric fluid, because oral administration needs high dosage, and sulfasalazine is metabolized into the active form in the colon.

Experimental Section

1. Materials. Layered Na-octosilicate ($Na_8[Si_{32}O_{64}(OH)_8 \cdot 32H_2O]$) was synthesized according to previous reports.[30] Na-Octosilicate (3.0 g) was dispersed in an aqueous solution (0.1 mol L^{-1}, 100 mL) of hexadecyltrimethylammonium chloride (C_{16}TMACl, Tokyo Chemical Industry Co.). The mixture was stirred at room temperature for 1 day and then centrifuged to remove the supernatant. This procedure was repeated three times in total. The resulting slurry was washed with water and air-dried at room temperature to obtain the intermediate product (C_{16}TMA-Oct) for silylation.[30]

The silylating reagent was synthesized according to a previously reported method.[21] All reactions were performed under a nitrogen atmosphere using a vacuum line and Schlenk technique. A mixture of 3-(2-imidazolin-1-yl)propyltriethoxysilane (denoted as ImSi, Gelest, Inc.) and 3 equiv. of alkyl chloride (1-chlorobutane or 1-chlorooctane, Aldrich) was stirred at 70 °C for 1 day. The mixture was washed with *n*-hexane (100 mL) five times. The mixture was evaporated under a reduced pressure at room temperature for 2 h, and then at 70 °C for 3 h. 1-Butyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium chloride (BimSi$(OEt)_3$Cl) and 1-octyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium chloride (OimSi$(OEt)_3$Cl) were obtained as orange-colored waxy solids. The physical state of BimSi$(OEt)_3$Cl and OimSi$(OEt)_3$Cl depends on the amount of water in the system. BimSi$(OEt)_3$Cl and OimSi$(OEt)_3$Cl, dried in vacuum and obtained as waxy solids, rapidly change to viscous liquids at ambient atmosphere by the absorption of water vapor. These viscous liquids can be transformed again to waxy solids by drying in vacuum. These ionic liquids were identified by ^{1}H, ^{13}C, and ^{29}Si NMR as well as mass spectroscopy (all the data are shown in the Supporting Information.).

2. Immobilization of Ionic Liquids onto C_{16}TMA-Oct. Silylation of C_{16}TMA-Oct was performed under a N_2 atmosphere. Toluene (100 mL; anhydrous, Wako Pure Chemical Industries, Ltd.) and BimSi$(OEt)_3$Cl (3.7 g) or OimSi$(OEt)_3$Cl (4.2 g) was added to C_{16}TMA-Oct (1.0 g), which was dried in vacuum at 120 °C for 2 h beforehand. The amount of added ionic liquids equals to 2.5 equiv. of SiOH/SiO^- groups of C_{16}TMA-Oct. The mixtures were stirred at 70 °C for 1 day. After being cooled at room temperature, they were centrifuged and washed with acetonitrile, acetone, and *n*-hexane three times for each solvent with 100 mL. The products were dried under reduced pressure at room temperature for 1 day to yield silylated derivatives denoted as

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Bim-Oct (with a butyl group) and Oim-Oct (with an octyl group) as white powders.

3. Sorption of Anionic Dye into Bim-Oct or Oim-Oct by Anion Exchange. The sorption isotherms were obtained by the following procedure. Bim-Oct or Oim-Oct (2.5 mg) was dispersed into 2.0 mL of an aqueous solution of Orange II (4-[(2-hydroxy-1-naphthyl)azo]benzenesulfonic acid, monosodium salt; Tokyo Chemical Industry Co.) with various concentrations (0.50−8.0 mM), and the mixtures were shaken at 25 °C for 2 days.[42] The solids were separated by centrifugation at 9700 × *g* (12000 rpm) for 5 min. The supernatants were diluted with deionized water and analyzed with a UV−vis spectrometer. The amount of Orange II loaded into the samples was calculated from the concentration of the dye in the supernatants by measuring the absorbance at 485 nm with a calibration curve. For the characterization of the exchanged products by powder XRD, Bim-Oct and Oim-Oct (0.15 g) were treated with 200 mL of the solution of Orange II (2.75 mM) for 1 day in the same manner.

4. Anion Exchange with Various Inorganic Anions. A solution containing four anions was prepared by dissolving NaCl, NaBr, NaI, and $NaNO_3$ (25 mM, respectively) into deionized water.[43] Bim-Oct or Oim-Oct (0.10 g) was dispersed into the solution, and stirred for 2 days at room temperature. After centrifugation for the removal of the supernatant, the slurry was washed with water four times.[44] The solid was dried for 1 day under reduced pressure at room temperature, and white powders were obtained from Bim-Oct and Oim-Oct that are denoted as Bim-Oct_A and Oim-Oct_A, respectively.

5. Sorption and Release of Prodrug in Bim-Oct. Bim-Oct (50 mg) was dispersed into an aqueous solution (1 L, 40.0 μM) of sulfasalazine (2-hydroxy-5-[[4-[(2-pyridinylamino)sulfonyl]phenyl]-azo] benzoic acid; Sigma) and stirred at 25 °C for 1 day. After filtration and drying for 1 day at room temperature under reduced pressure, yellow colored powders were obtained. The sorbed amount of sulfasalazine was determined by the decrease in the absorbance at 360 nm of the residual solution with a calibration curve. An in vitro release experiment was performed in a simulated gastric fluid (aqueous solution of HCl at pH 1.2) and an intestinal fluid (Ringer's solution at pH 7.4).[45] The sulfasalazine-loaded sample (10 mg) was dispersed into the simulated fluids (100 mL), and stirred (200 rpm) at 37 °C. To determine the time course of the release behavior of sulfasalazine, a part of the suspension (1.6 mL) was centrifuged at 9700 × *g* (12000 rpm) for 5 min, and the concentration of sulfasalazine in the supernatant was measured by the variation of the absorbance at 360 nm. After the measurement, the precipitates and supernatants were returned to the suspensions.

6. Characterization. Powder X-ray diffraction (XRD) measurements were performed on a Rigaku Rint-Ultima III powder diffractometer with a radiation of CuKα (λ = 0.15418 nm) by using parallel beam geometry equipped with a parabolic multilayer solar slit. Solid-state ^{13}C CP/MAS NMR spectra were recorded on a JEOL JNM-CMX-400 spectrometer at a resonance frequency of 100.5 MHz and a recycle delay of 5 s. The samples were put into a 5 mm zirconia rotor and spun at 8 kHz. Solid-state ^{29}Si MAS NMR spectra were also recorded on the same spectrometer at a resonance frequency of 79.42 MHz with a 45° pulse and a recycle delay of 200 s with a 7.5 mm zirconia rotor by spinning at 5 kHz. It was confirmed that the signals were fully relaxed under these conditions so that quantitative analysis was possible.[30b] The ^{13}C and ^{29}Si chemical shifts were externally referenced to hexamethylbenzene at 17.4 ppm ($-\underline{C}H_3$) and poly(dimethylsiloxane) at −33.8 ppm, respectively. The amounts of organic constituents were determined by CHN analysis (Perkin-Elmer, 2400 Series II). The halogen contents were measured by ion chromatography with an SX-Elements microanalyzer YS-10 (Yanaco New Science Inc.). Thermogravimetry (TG) measurements were carried out with a Rigaku Thermo Plus 2 instrument under a dry air flow at a heating rate of 10 °C min^{-1}. The scanning electron microscopy (SEM) images were obtained by using a JEOL JSM-6500F microscope at an accelerating voltage of 15 kV. UV−vis absorption spectra were measured with a JASCO V-530 UV/vis spectrophotometer. Raman spectra were obtained with a Renishaw inVia Reflex Raman Microscope.

Results and Discussion

1. Immobilization of Ionic Liquids onto Layered Octosilicate. The presence of imidazolium groups on octosilicate was confirmed by the ^{13}C CP/MAS NMR spectra (see the Supporting Information, Figure S1). All signals (158.9, 59.3, 49.2−48.7, 30.0, 21.6, 21.2, 20.3, 14.4, and 10.9 ppm) in the ^{13}C CP/MAS NMR spectrum of Bim-Oct are assignable to $BimSi(OEt)_{3-x}$ (x = 1−3) cation. In the ^{13}C CP/MAS NMR spectrum of Oim-Oct, all of the observed signals (159.1, 59.4, 52.5−49.0, 32.8, 30.1, 28.1, 27.4, 23.5, 18.5, 14.9, 12.6, and 10.2 ppm) are attributed to the $Oim(OEt)_{3-x}$ cation. No peaks assignable to C_{16}TMA cation were observed. Therefore, C_{16}TMA cations were completely removed from Bim-Oct and Oim-Oct during the silylation with ethoxy-terminated imidazolium cations.

As reported previously,[30b] the ^{29}Si MAS NMR spectrum of C_{16}TMA-Oct (Figure 3a) shows two narrow signals at −100 ppm and −110 ppm, corresponding to the $Q^3(\underline{Si}(OSi)_3OH/O^-)$ and $Q^4(\underline{Si}(OSi)_4)$ units with an integral ratio of 1:1, which is the same as that of pristine Na-Octosilicate. The ^{29}Si MAS NMR spectrum of Bim-Oct (Figure 3b) indicates broad Q^3 (−102 ppm) and Q^4 (−111 ppm) signals with the integral ratio (Q^3:Q^4) of 18:182. Therefore, 82% of the $SiOH/SiO^-$ groups in C_{16}TMA-Oct were silylated and converted to Q^4 units. The spectrum also shows new signals at −50, −57, and −66 ppm, which are attributed to the T^1, T^2, and T^3 sites of grafted $Bim\underline{Si}\equiv$ groups with the integral ratio of T^1:T^2:T^3 = 7:44:20. No signal assignable to the T^0 environment was observed. The Si species with T^2 units are dominant in the immobilized silylation reagent, which is in accordance with the bidentate grafting of confronting $SiOH/SiO^-$ groups.[30a,b,33b] Because the $SiOH/SiO^-$ groups are highly silylated, the imidazolium groups are probably located on the silicate layers in an ordered arrangement reflecting the confronting $SiOH/SiO^-$ groups arranged along one axis. The ^{29}Si MAS NMR spectrum of Oim-Oct (Figure 3c) shows similar signals (T^1:T^2:T^3:Q^3:Q^4 = 9:36:21:17:183). It should be noted that the presence of T^3 units in Bim-Oct

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(42) We have confirmed that the sorption and desorption of Orange II reached equilibrium at 6 h and 2 days, respectively.

(43) The amount of added NaCl was slightly decreased because of the presence of Cl^- in the interlayer of Bim-Oct or Oim-Oct. The total amount of Cl^- was set at 25 mM.

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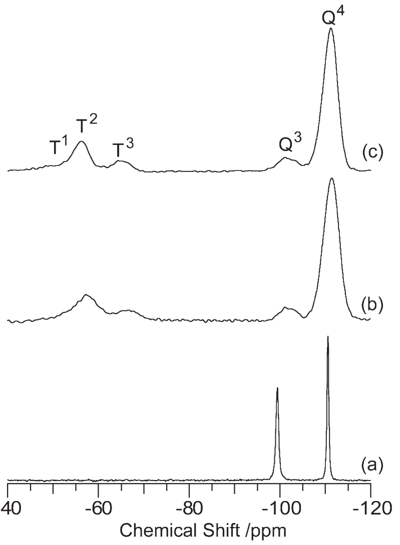

Figure 3. ^{29}Si MAS NMR spectra of (a) C_{16}TMA-Oct, (b) Bim-Oct, and (c) Oim-Oct.

and Oim-Oct indicates the condensation that occurs between the ethoxy groups of the coupling agents. This condensation may be caused by contamination with water because of the hygroscopic property of BimSi(OEt)$_3$Cl and OimSi(OEt)$_3$Cl, as described in the Experimental Section.

For comparison, C_{16}TMA-Oct was allowed to react with a nonionic ImSi (3-(2-imidazolin-1-yl)propyltriethoxysilane, before quaternization). The ^{29}Si MAS NMR spectrum of the product (imidazol-Oct) showed the integral ratio of Q^3:Q^4 = 86:114 (Supporting Information, Figure S2), indicating the low reactivity of the nonionic reagent. The electrostatic interaction between the SiO$^-$ and cationic imidazolium groups probably enhances the intercalation of BimSi(OEt)$_3$Cl and OimSi(OEt)$_3$Cl into the anionic interlayer space of the silicate hosts. Actually, it was found that the C_{16}TMA cations remained in imidazol-Oct after the reaction, which was confirmed by the ^{13}C CP/MAS NMR spectrum (Supporting Information, Figure S3).

In addition, we investigated the hydrolysis behavior of the triethoxy groups of BimSi(OEt)$_3$Cl and OimSi(OEt)$_3$Cl without the addition of any acid.[46] The ethoxy groups were partially (about 10 and 30%, respectively) hydrolyzed after stirring for 1 day at room temperature, whereas MeSi(OEt)$_3$ was not hydrolyzed under the same condition. It is highly possible for BimSi(OEt)$_3$Cl and OimSi(OEt)$_3$Cl, which are hygroscopic (see experiment 2), to adsorb water, and the adsorbed water (weak acid) may hydrolyze the ethoxy groups. Thus, imidazolium chloride groups are effective not only for the creation of anion exchangeable sites, but also for hydrolysis of the ethoxy groups and the following siloxane bond formation leading to the immobilization of imidazolium groups.

We investigated the effect of the density and ordering of silanol groups on the surface of the silicate layer by using another layered silicate of kanemite. Kanemite consists of only SiO$_4$ tetrahedra with a Q^3 environment.[34] The density of the SiOH/SiO$^-$ groups on the interlayer surface of kanemite (5.6 groups nm^{-2}) is higher than that of octosilicate (3.7 groups nm^{-2}) when they are calculated on the basis of their crystal structures.[33b,34] Immobilization of BimSi(OEt)$_3$Cl onto kanemite was performed in the same manner as that onto octosilicate (The procedure is described in the Supporting Information.). The sample is denoted as Bim-kane. The ^{29}Si MAS NMR spectrum of Bim-kane (see the Supporting Information, Figure S4) shows the signals assignable to the T^1, T^2, T^3, Q^3, and Q^4 environments with the integral ratio of 8:18:9:37:63 (This ratio is normalized as $Q^3 + Q^4 = 100$). The spectrum of C_{16}TMA-kanemite before silylation shows the Q^3 and Q^4 signals with the integral ratio of 92:8.[47] Therefore, ca. 55% (63 − 8 = 55) of the SiOH/SiO$^-$ groups were silylated. The amount of imidazolium groups immobilized onto Bim-kane is 1.4 groups nm^{-2} and the data are calculated from the CHN and TG data (see the Supporting Information, Table S1). In spite of the higher density of the SiOH/SiO$^-$ groups of kanemite than octosilicate, the silylation ratio (55%) as well as the density of immobilized imidazolium groups (1.4 groups nm^{-2}) of Bim-kane were lower than those of Bim-Oct (83%, 1.8 groups nm^{-2}). Similar phenomena were previously reported for silylation with trichlorosilane groups.[29c] In the case of the immobilization of octoxytrichlorosilanes onto octosilicate, more than 90% of the SiOH/SiO$^-$ groups were silylated.[30a] On the other hand, in the case of the immobilization of octyltrichlorosilanes onto kanemite, the ratio of silylated SiOH/SiO$^-$ groups was 65%.[29c] The lower degree of silylation of kanemite should come from the excessive number of SiOH/SiO$^-$ groups and their closeness: the full silylation reaction is very difficult because of both the steric hindrance of the silylation reagents and their condensation. Because the confronting SiOH/SiO$^-$ groups on octosilicate are effective for bidentate immobilization, the use of octosilicate is very advantageous for the ordered arrangement of ionic liquids with high density on the crystalline interlayer surfaces.

The C/N molar ratios of Bim-Oct and Oim-Oct (5.3 and 7.3, respectively,Table 1) are less than the calculated ratios (5.8 and 7.8) based on the amount of residual ethoxy groups evaluated from the integral ratio of the peaks of T^1, T^2, and T^3 in the ^{29}Si MAS NMR spectra (see ref 48 for the details of the calculation.). This difference

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(46) The hydrolysis was investigated without any acid. Water was added to BimSi(OEt)$_3$, OimSi(OEt)$_3$, or methyltriethoxysilane. The amount of water was adjusted to be 2 equiv. of ethoxy groups in these reagents. The mixture was stirred for 1 d at room temperature. The ratio of hydrolyzed triethoxysilyl groups was determined from the integral ratio of signals due to T^0 and T^1 in ^{29}Si NMR.

(47) Takahashi, N.; Tamura, H.; Mochizuki, D.; Kimura, T.; Kuroda, K. *Langmuir* **2007**, *23*, 10765–10771.

(48) The immobilized silylating reagents with T^1, T^2, and T^3 have residual two, one, and zero OEt (or OH) group(s), respectively. The T^1:T^2:T^3 ratios were 7:44:20 and 9:36:21 for Bim-Oct and Oim-Oct, respectively. On the basis of these ratios, the amouts of residual OEt (or OH) groups of Bim-Oct and Oim-Oct are 0.82 and 0.83 per one silylating reagent, respectively. If all the ethoxy groups remained without hydrolysis, one immobilized group has carbon numbers of 11.6 (= 0.82 × 2 + 10) and 15.7 (= 0.83 × 2 + 14) for Bim-Oct and Oim-Oct, and the C/N ratios of 5.8 and 7.8, respectively.

Table 1. Composition of the Silylated Samples

sample	C (mass %)	N (mass %)	Cl (mass %)	SiO_2 (mass %)[a]	C/N	Cl/N	imidazolium/silanol group[b]
Bim-Oct	23.8	5.3	6.2	57	5.3	0.46	0.49
Oim-Oct	30.4	4.9	5.8	51	7.3	0.47	0.52

[a] Residual amount after heating of the sample at 900 °C by TG. [b] The ratio of imidazolium group per one SiOH(or SiO^-) group.

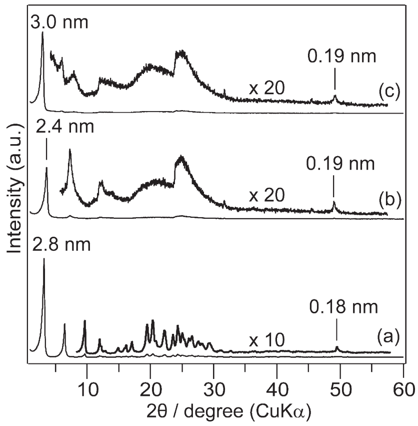

Figure 4. XRD patterns of (a) C_{16}TMA-Oct, (b) Bim-Oct, and (c) Oim-Oct.

indicates partial hydrolysis of the ethoxy groups. The ratios of imidazolium groups per silylated $SiOH/SiO^-$ groups in Bim-Oct and Oim-Oct were 0.49 and 0.52, respectively, which was calculated from the C/N/Si ratio. Therefore, one silylating reagent reacted with about two $SiOH/SiO^-$ groups. From the elemental analysis and crystal structure of the octosilicate layer, the densities of the immobilized imidazolium groups are 1.8 and 1.9 groups nm^{-2} for Bim-Oct and Oim-Oct, respectively. The Cl/N ratios of Bim-Oct and Oim-Oct were 0.46 and 0.47, respectively (Table 1). This is because one imidazolium salt originally contains two nitrogens (Figure 2), such that the Cl^- anions and imidazolium cations are present with almost a 1:1 ratio in the interlayer region. In addition, on the basis of the results of ^{13}C CP/MAS NMR, the C_{16}TMA cations were completely removed. Taking the charge balance in the interlayer region into account, it is obvious that the unsilylated SiO^- sites are not paired with imidazolium cations, and that probably these are present as not SiO^- anions, but SiOH.

The powder XRD peaks at 2.4, 1.2, and 0.73 nm, assignable to (001), (002), and (003) diffraction peaks, were observed for Bim-Oct (Figure 4b). The basal spacing of 2.4 nm is lower than that of C_{16}TMA-Oct (2.8 nm, Figure 4a). The thickness of the silicate layer of octosilicate is 0.74 nm as estimated from the *d*-spacing of the protonated octosilicate.[30c] On the basis of molecular modeling,[49] the full length of the immobilized butylimidazolium group from the alkyl chain terminal group to the silicon is ca. 1.4 nm if the alkyl chain takes an all-trans conformation. The sum of the thickness of the silicate layer and the estimated length of the butylimidazolium group (0.7 nm + 1.4 nm = 2.1 nm) is less than the *d*-value of 2.4 nm. Therefore, the arrangement of the immobilized organic groups in the interlayer is estimated to be a bilayer rather than a monolayer. In the case of a monolayer on a Si/SiO_2 substrate, the thickness of the immobilized $BimSi(OEt)_3Cl$ is estimated to be 0.8 nm by ellipsometry.[50] The *d*-spacing of 2.4 nm agrees well with the sum of the thicknesses of the silicate layer and two monolayers of the $BimSi(OEt)_{3-x}$ group (0.7 nm + 0.8 nm × 2 = 2.3 nm). The XRD pattern of Oim-Oct also exhibits similar peaks with *d*-spacings of 3.0, 1.5, and 1.1 nm (Figure 4c), where the larger spacings can be attributed to the longer alkyl chain length compared with the Bim-Oct case.

In the XRD patterns of Bim-Oct and Oim-Oct, the peaks observed at ca. 49° are attributed to the (400) lattice plane of Na-Octosilicate[30] as in C_{16}TMA-Oct (Figure 4a). The (400) lattice plane of Na-Octosilicate is perpendicular to the silicate layer. Therefore, the structural regularity of the crystalline silicate layers is retained after silylation. On the other hand, the *d*-values (0.19 nm) of these peaks in Bim-Oct and Oim-Oct are slightly larger than that of C_{16}TMA-Oct (0.18 nm). This difference may be ascribable to the distortion in the silicate framework by forming new siloxane networks. The same distortion was previously reported for the cases of the silylated samples of C_{16}TMA-Oct with dialkoxydichlorosilanes[30a] or alkoxytrichlorosilanes.[30b]

SEM images of Na-Octosilicate and C_{16}TMA-Oct showed square, platelike morphologies of 2−5 μm in lateral size (Figure 5a, b). These square morphologies reflect the crystal structure of Na-Octosilicate (*I*4$_1$/*amd*).[33b] The morphology of Bim-Oct was a square plate having bending, distortion, and wrinkles on the surface (Figure 5c). In the SEM image of Oim-Oct (Figure 5d), the wrinkles become more apparent compared with that of Bim-Oct. This suggests the progress of a stacking disordering of silicate layers of Oim-Oct during the silylation reaction. These morphological changes have not been observed for the cases of silylated octosilicate with other reagents.[30,31] C_{16}TMA-Oct (Figure 4a) and samples silylated with alkoxytrichlorosilanes[30b] or dialkoxydichlorosilanes[30a] showed many sharp peaks at the higher 2θ region of the XRD patterns. However, Bim-Oct and Oim-Oct showed only broadened peaks at 25° and a small peak at 49°. The disappearance of the sharp peaks can be attributed to the disordering in the layer structure.

We analyzed Bim-Oct by Raman spectroscopy for the investigation of the state of the immobilized organic groups in the interlayer. The Raman spectrum of Bim-Oct

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(49) The structurally optimized calculation was performed with Discover Module, MS Modeling Version 4.4; Accelrys Inc.: San Diego, CA, 2008.

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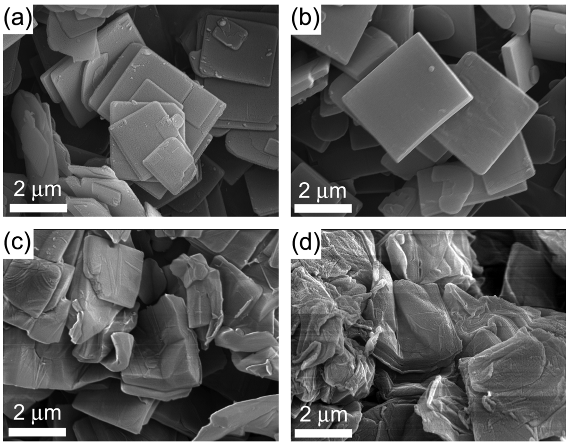

Figure 5. SEM images of (a) Na-Octosilicate, (b) C_{16}TMA-Oct, (c) Bim-Oct, and (d) Oim-Oct.

(see the Supporting Information, Figure S5) revealed bands due to the $CH_3CH_2\underline{C}H_2\text{-}\underline{C}H_2N$ bond at 692, 597, 487 cm^{-1},[51] which are assignable to a gauche−trans (GT) form. The bands due to this GT form are predominantly observed in the spectrum of 1-butyl-3-methyl-imidazolium chloride in the liquid state.[51] Thus we infer that the butyl imidazolium groups in the interlayer are liquid-like. In general, ionic liquids are known as attractive lubricant additives because of the reduction in the friction between the self-assembled monolayers.[52] The bending and distortion of the Bim-Oct and Oim-Oct layers (see Figure 5c,d) can be explained by assuming the liquidlike state of imidazolium groups.

2. Anion Exchange. Because imidazolium cations are successfully immobilized onto the interlayer surface with nonimmobilized Cl^- in the ratio of 1:1, these imidazolium chloride groups are expected to act as anion exchangeable sites. Anion exchange reactions of Bim-Oct and Oim-Oct with anionic dye of Orange II and inorganic anions (Cl^-, Br^-, I^-, and NO_3^-) were investigated.

After stirring in an aqueous solution of Orange II, the color of the Bim-Oct and Oim-Oct changed from white to red. The XRD patterns of the samples after sorption of Orange II showed peaks with *d*-spacings at 3.5 nm for the samples from Bim-Oct, and 4.1 nm from Oim-Oct (see the Supporting Information, Figure S6), suggesting the successful intercalation of Orange II molecules. The amounts of Cl^- in the products were zero for both Bim-Oct and Oim-Oct after the sorption.

The sorption isotherm of Orange II into Bim-Oct (Figure 6) indicates a significant increase at low concentration of up to ca. 1 mM and a plateau at ca. 2 mM. The sorption isotherm of Oim-Oct also indicates a similar curve with a significant increase until ca. 1 mM, and the following plateau above ca. 2 mM. In the Giles classification of solution sorption isotherms,[53] this type of sorption isotherm is classified as an H curve, which is a special case of the L curve (Langmuir type). The origin of the H curve comes from the high affinity between solutes and adsorbents. Therefore, the shape of the isotherm supports the idea that the driving force for the sorption of Orange II into Bim-Oct or Oim-Oct is an electrostatic one between the cationic imidazolium groups and anionic Orange II. The saturated amounts of sorbed Orange II were 2.0 mmol g^{-1} for Bim-Oct and 1.8 mmol g^{-1} for Oim-Oct, respectively. These values are in good agreement with the amounts of imidazolium groups in Bim-Oct and Oim-Oct (1.9 and 1.7 mmol g^{-1}; CHN analysis and TG data, Table 1). Therefore, almost all of the imidazolium groups can act as anion exchange sites in the interlayer.

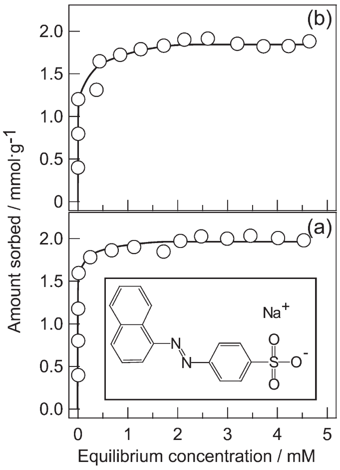

Figure 6. Sorption isotherms of Orange II into (a) Bim-Oct and (b) Oim-Oct. Inset: structural formula of Orange II.

In general, pristine octosilicate possesses $SiOH/SiO^-$ groups on the interlayer surface with an ordered arrangement, which act as cation exchangeable sites. The maximum cation exchange capacity of octosilicate is equal to the amount of $SiOH/SiO^-$ groups. As described above, two confronting $SiOH/SiO^-$ groups are capped with about one silylating reagent with a bidentate immobilization capability. The silylating reagent is composed of one set of imidazolium cations and Cl^- anions. All Cl^- anions can be exchanged with the anionic dye. As a result, two cation exchangeable sites of the $SiOH/SiO^-$ groups were converted to one anion exchangeable site. The confronting arrangement of $SiOH/SiO^-$ groups must be necessary for this stoichiometric conversion of the exchangeable sites because the bidentate immobilization of silylation reagents is specific for octosilicate. In fact, the $SiOH/SiO^-$ groups of kanemite are not fully silylated, as described above.

We compared the AEC values of Bim-Oct and Oim-Oct with those of other layered inorganic anion exchangeable materials. A hybrid of chitosan intercalated montmorillonite possesses an anion exchange property because of the presence of the excess NH_3^+ sites of chitosan.[7] The maximum AEC is 0.57 mequiv g^{-1} (gram in this case is based on the weight of not the hybrid but the starting clay). Fluoromica accommodating polyelectrolytes in the interlayer by overcompensation also shows anion exchange reactions.

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Table 2. Molar Ratios of Various Sorbed Anions to Imidazolium Cations[a]

sample	Cl^-/Im	Br^-/Im	I^-/Im	NO_3^-/Im[b]
Bim-Oct_A	0.05	0.06	0.27	0.51
Oim-Oct_A	0.04	0.08	0.53	0.33

[a] Im: Imidazolium cation immobilized in Bim-Oct or Oim-Oct. [b] The ratio of NO_3^-/Im was calculated from the nitrogen contents excluding the contents of imidazolium groups.

The sorbed amount of anionic dyes into the hybrids is 0.2 mequiv (g of clay)$^{-1}$ at the maximum.[8a] Because these values of AEC are based on the weight of the pristine clays, their AEC values based on the total amount of hybrids are lower than these values. Despite the fact that Bim-Oct and Oim-Oct comprise not only an inorganic framework but also organic species; the exchange capacities of Bim-Oct and Oim-Oct (2.0 and 1.8 mmol g^{-1}) are higher than those of conventional hybrids, and close to those of LDHs (2−4.5 mequiv g^{-1}).[4b] Thus, both Bim-Oct and Oim-Oct possess relatively high AEC values, which is attributed to the high density of SiOH/SiO^- groups on the silicate layer of octosilicate.

We also investigated the time course of the sorption of Orange II into Bim-Oct and Oim-Oct in 2.75 mM solutions (see the Supporting Information, Figure S7). The amounts sorbed by Bim-Oct and Oim-Oct reached an equilibrium at 30 and 180 min, respectively. This difference in the sorption behavior may be explained by the low accessibility of Orange II ions into the interlayer of Oim-Oct because of the more hydrophobic longer alkyl chain. Therefore, this result suggests that the sorption of anionic guests into these anion exchangers can be controlled by adjusting the alkyl chain length of the anchored imidazolium cations. In fact, Bim-Oct was dispersed rapidly into water, unlike Oim-Oct, which required stirring to achieve dispersion (see a video of this process on the Web).

Next, we investigated the sorption behavior of various inorganic anions (Cl^-, Br^-, I^-, and NO_3^-) into Bim-Oct and Oim-Oct. Table 2 shows the molar ratios of each anion sorbed to the imidazolium cations. In the case of Bim-Oct, the order of the amounts of sorbed anions was: $NO_3^- > I^- > Br^- \approx Cl^-$. When Oim-Oct was used as the sorbent, the order was: $I^- > NO_3^- > Br^- \approx Cl^-$. The orders of Bim-Oct and Oim-Oct were quite different from those of LDHs ($Br^- > Cl^- > NO_3^- > I^-$) in the case of sorption of mixed anions.[54] It was reported that the amount of anions sorbed onto imidazolium groups immobilized on silica gel depends on the Hofmeister anion series which is related to the size and degree of hydration: $NO_3^- > I^- > Br^- > Cl^-$.[16] The order of the affinity of Bim-Oct for anions has a good agreement with this order. This trend can be explained by considering that the cationic sites of alkyl imidazolium groups are more hydrophobic and less acceptable for hydrated anions than cationic sites on LDHs. Oim-Oct showed a similar order to that of Bim-Oct. We think that the difference in the order for iodide and nitrate ($I^- > NO_3^-$) may be caused by a lower accessibility for the slightly bulky NO_3^- into the interlayer space with the longer octyl chain.

3. Sorption and Controlled Release of Prodrug Depending on pH. Sulfasalazine is metabolized through splitting into mesalamine and sulfapyridine by azo-reduction bacteria in the colon.[41] Therefore, a delivery support for sulfasalazine needs durability in gastric acid. LDH is not usable for this kind of prodrug release because LDH is soluble in acid solution. To prove the usability of Bim-Oct in low-pH solutions, the durability of Bim-Oct in hydrochloric acid at pH 1.0 was investigated (see experimental details in the Supporting Information). After stirring for 50 h, only 2.9% of silicon was dissolved into the solution, as confirmed by ICP. The XRD pattern of the precipitate showed a peak at 0.19 nm ((400) lattice plane) which is similar to that before the acid treatment (see the Supporting Information, Figure S8), indicating the retention of the structural regularity of the crystalline silicate layers. This durability can be explained by the stability of the silicate frameworks of layered octosilicate.

To investigate the potential of Bim-Oct for application as an intelligent drug carrier, the sorption and release behavior of sulfasalazine into/from the layered solids was studied. After the sorption, the *d*-value of the sample became 2.9 nm (see the Supporting Information, Figure S9), which is larger than that of Bim-Oct (2.4 nm, Figure 4b). It is suggested that the sulfasalazine molecules were successfully intercalated into the interlayer of Bim-Oct. No peaks assignable to crystalline sulfasalazine were observed in the pattern of Bim-Oct after the sorption, suggesting that the sulfasalazine molecules are not in a crystal state but well-dispersed in the interlayer.

Typically, a dose of drugs for oral administration needs a high amount. For example, a daily dose of sulfasalazine is usually 2−4 g for adults.[55] Therefore, supports for oral-administration drugs demand high efficiency of sorption.[56] The amount of sulfasalazine sorbed into Bim-Oct was 0.75 mmol g^{-1} (30 wt %) determined by the concentration of residual solution of sulfasalazine. This amount is comparable to the case of certain polymeric supports such as calcium-alginate-chitosan gel (45 wt % at maximum)[57] and polymer microcapsules (72 wt % at maximum) including sulfasalazine crystals on the surface.[56] Lee et al. reported that mesoporous silica nanoparticles functionalized with trimethylammonium groups (MSN-TA) can accommodate sulfasalazine.[45] The amount loaded was 0.0428 mmol g^{-1} at maximum from an aqueous solution in spite of the high surface area of mesoporous silica (ca. 1000 m^2 g^{-1}). It is remarkable that Bim-Oct can intercalate more than a ten times larger amount of sulfasalazine than MSN-TA. This difference can be explained by the amount of anion exchangeable

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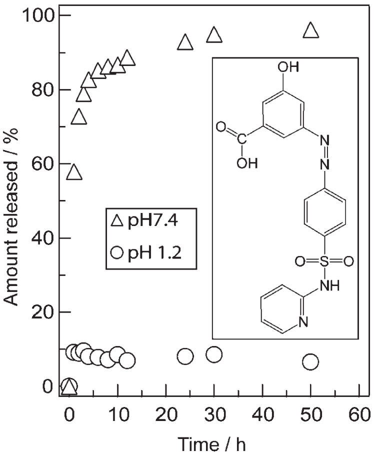

Figure 7. Release behavior of sulfasalazine sorbed on Bim-Oct at pH 7.4 and 1.2. Inset: structural formula of sulfasalazine.

sites. AEC, determined by sorption of Orange II, of MSN-TA (about 0.17 mmol g^{-1}) is much lower than that of Bim-Oct (2.0 mmol g^{-1}). In addition, bulky guest molecules tend to be stuck around the mesopore entrance.[58] In contrast, all surfaces of the layered structure can be used for the sorption of guest molecules. The interlayer space is flexible for a wide variety of guest molecules with different sizes because of the expansion of the interlayer.

The release of the prodrug was conducted in two simulated fluids of gastric acid at pH 1.2 and intestinal fluid at pH 7.4 (Figure 7). At the strong acidic condition (pH 1.2), only 9% of the sorbed sulfasalazine was released from the Bim-Oct after 50 h. In contrast, at pH 7.4, the rate of released sulfasalazine was increased by up to 83% after stirring for 4 h, 90% after 24 h; and finally, almost all the sulfasalazine (up to 96%) was released from the interlayer after 50 h. This contrast with the pH can be explained by the solubility of sulfasalazine, which is almost insoluble into water at low pH and soluble at neutral solution.[57] In the case of MSN-TA,[45] a released amount of sulfasalazine was only ca. 60% at pH 7.4 after 20 h by using the sample with the higher loading of sulfasalazine (0.0428 mmol g^{-1}). In the exceptional case, the released amount reached 90% by using a sample with very low loading (0.0005 mmol g^{-1}). In addition, the amount released was decreased with higher loadings of sulfasalazine in polymer microcapsules.[56] In contrast, Bim-Oct indicated a higher released amount (ca. 90%) at pH 7.4 after 20 h in spite of the very high loading of sulfasalazine. In general, both the size and connectivity of mesopores affect the drug-release rate.[59,60] Larger pores and 3D connected pores are advantageous for high rates of release because of the high accessibility.[59] It is easily inferred that layered structures have high accessibility because guest molecules can be released from all end-facets. Therefore, the larger released amount is probably caused by the higher accessibility of the layered structure. Thus, Bim-Oct shows high durability in acid solutions, high capacity for sulfasalazine, and high accessibility. These properties should be very valuable for their application in drug-delivery systems (DDSs) for prodrugs in oral administration.

Conclusion

The functions of layered octosilicate are significantly changed and designed by the creation of two-dimensionally arranged anion exchangeable sites in the interlayer surface. Cation exchangeable sites of the SiOH/SiO$^-$ groups on octosilicate are stoichiometrically converted to anion exchangeable sites. Octosilicate is very suitable for the creation of highly and closely ordered imidazolium groups because of the presence of ordered SiOH/SiO$^-$ groups on the crystalline silicate layers. The properties of these layered materials can be summarized as follows. (i) The AECs are higher than those of conventional clay−polymer hybrids. In addition, the sorption rate of anionic dye was controllable by changing the alkyl chain length. (ii) The affinity for guest species is completely different from LDH, and it is remarkable that the affinity for inorganic anions was varied by changing the length of the alkyl chain. (iii) The application of the derivatized silicates in DDS for oral administration should also be focused on because of their high accessibility, capacity, and durability. Ionic liquids immobilized onto solid supports have also been used for single-site heterogeneous catalysts.[23] Utilizing the crystal structure of the host layered silicates, the density and distance of the immobilized functional groups can be deliberately controlled at the angstrom level in two-dimensionally confined spaces, yielding more intelligent catalytic systems. Therefore, the hybridization of layered silicates and a wide variety of designed ionic liquids will create a new pathway for various practical applications, such as catalysts, green solvents, and ionic conductors, thereby contributing to the expansion of the material science field.

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Supporting Information Available: Spectral data of synthesized ionic liquids; ^{13}C CP/MAS NMR spectra of the products; ^{29}Si- and ^{13}C CP/MAS NMR spectra of imidazol-Oct; procedure for the synthesis of Bim-kane; ^{29}Si MAS NMR spectrum of Bim-kane; composition of Bim-kane; Raman spectrum of Bim-Oct; XRD patterns of Bim-Oct and Oim-Oct intercalating Orange II; sorption behavior of Orange II into the products; experimental procedure for the investigation of the durability of Bim-Oct in an acid solution; XRD pattern of Bim-Oct after the acid treatment; and XRD pattern of Bim-Oct sorbed sulfasalazine (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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