

Hydroxometalates from Anion Exchange Reactions of $[\text{BF}_4]^-$ based Ionic Liquids: Formation of $[\text{M(OH)}_6]^{2-}$ ($\text{M} = \text{Ti, Zr}$) and $[\text{Zr(OH)}_5]^-$

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The hydrolysis reactions of $\text{Ti(O}^{\text{i}}\text{Pr)}_4$ in the presence of different ionic liquids using ethanol as solvent were investigated. The reaction in the presence of $[\text{BMIM}][\text{BF}_4]$ gave rise to the anion exchange reaction product $[\text{BMIM}]_2[\text{Ti(OH)}_6]$ in moderate yield. On the contrary, $\text{Ti}_7\text{O}_4(\text{OEt})_{20}$ was obtained in ionic liquids with other anions. The anion exchange reaction has a broad capacity for group functionalization. It can be used to synthesize both imidazolium and pyridium $[\text{Ti(OH)}_6]^{2-}$ salts. In contrast, under the similar reaction conditions, the reactions of zirconium alcoholate gave rise to $[\text{Zr(OH)}_5]^-$ or $[\text{Zr(OH)}_6]^{2-}$ intermediates depending on the counter cations. Under the solvothermal reaction conditions, $[\text{PF}_6]^-$ based ionic liquids can also undertake the similar anion exchange reactions.

1. Introduction

Ionic liquids as reaction media have recently attracted great interest in the synthesis of inorganic materials¹ because of their distinct properties, such as nonvolatility, nonflammability, high polarity, and the facile isolation of the material.² Much research has been focused on the synthesis of TiO_2 nanomaterials. Hollow TiO_2 microspheres,³ anatase mesoporous TiO_2 nanoparticles,⁴ anatase mesoporous TiO_2 monoliths,⁵ size-controlled anatase TiO_2 nanocrystals,⁶ and rutile TiO_2 nanostructures,⁷ etc., have been synthesized with ease in ionic liquids.

Indeed, the growth of TiO_2 nanostructures in ionic liquids is a complex process. Ionic liquids are normally considered to act as reaction media, template or surfactant.

Dionysiou et al. have pointed out that the use of 1-butyl-3-methyl-imidazolium hexafluorophosphate ($[\text{BMIM}][\text{PF}_6]$) in the synthesis of anatase mesoporous TiO_2 nanoparticles induces controlled hydrolysis of titanium alkoxide, but there was no obvious chemical bond formation between $[\text{BMIM}][\text{PF}_6]$ and titanate.^{4b} However, Liu et al. have found the formation of an ionic liquid-stabilized polyanion complex in the microwave-assisted synthesis of size-controlled anatase TiO_2 nanoparticles using $[\text{BMIM}][\text{BF}_4]$ as media.⁶ Yu et al. have suggested that Ti^{4+} ions are all octahedrally coordinated with the ligands of $[\text{OH}]^-$ and $[\text{Cl}]^-$ through formation of chloride complexes of the type $[\text{Ti(OH)}_m\text{Cl}_n]_2^{2-}$ ($m + n = 6$) in the synthesis of rutile TiO_2 nanorods in $[\text{BMIM}][\text{Cl}]$ with TiCl_4 as precursor.^{7b} Using FTIR, Zhai et al. have confirmed the formation of a bidentate chelating complexation between the carboxylic functional group of 1-methylimidazolium-3-acetate chloride ($[\text{AcMIM}][\text{Cl}]$) and titanate in synthesis of rutile TiO_2 .^{7c} Most recently, Zheng et al. proposed that the interaction between imidazolium cation and TiO_6 octahedra could be a decisive factor for the formation of the rutile phase, which is beneficial for the catenarian nuclei via edge-sharing polycondensation between TiO_6 octahedra because of the mutual π -staking between aromatic rings.⁸ HF and H_2SO_4 were used as additives to inhibit the phase transformation in the hydrothermal synthesis of anatase nanocrystals assisted by ionic liquid.⁹ The synthetical process and the selection of ionic liquids have an important effect on the formation of TiO_2 nanostructures. Compared to the large knowledge on the sol-gel chemistry

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of titanium,¹⁰ the TiO_2 nanostructure formation mechanism in ionic liquids is not clear yet, and no intermediates were separated or identified clearly so far.

Titanium hydroxo complexes, such as $[\text{Ti}(\text{OH})_2]^{2+}$, $[\text{Ti}(\text{OH})_3]^+$, $\text{Ti}(\text{OH})_4$, and $[\text{Ti}(\text{OH})_5]^-$, are considered as intermediates in sol–gel methods synthesis of TiO_2 , and the solution chemistry of these complexes was investigated in detail.¹¹ The pH value of the sol–gel medium is a decisive factor for controlling the final particle size^{11c} and phase.¹² In our present research, we investigate the early hydrolysis stages of $\text{Ti}(\text{O}^{\text{i}}\text{Pr})_4$ in the presence of ionic liquids using EtOH as solvent. We successfully separated $\text{Ti}_7\text{O}_4(\text{OEt})_{20}$ in $[\text{BMIM}]\text{Cl}$ ($\text{BMIM} = 1\text{-butyl-3-methylimidazolium}$), $[\text{BMIM}]\text{Br}$, $[\text{BMIM}]\text{PF}_6^-$, or $[\text{BMIM}]\text{NTf}_2^-$ ($\text{NTf}_2^- = \text{N}(\text{SO}_3\text{CF}_3)_2$), etc. However, we describe here a new imidazolium salt, $[\text{BMIM}]_2[\text{Ti}(\text{OH})_6]$, which was obtained in $[\text{BMIM}]\text{BF}_4^-$ via an anion exchange reaction. In contrast, under similar reaction conditions, the use of zirconium alcoholate gave rise to $[\text{Zr}(\text{OH})_5]^-$ or $[\text{Zr}(\text{OH})_6]^{2-}$ intermediates depending on the counter cations.

2. Results and Discussion

The hydrolysis of $\text{Ti}(\text{O}^{\text{i}}\text{Pr})_4$ in $[\text{BMIM}]\text{Cl}$ was performed using ethanol as solvent under reflux. The hydrolysis product was separated via crystallization. The obtained liquid from the reaction was solved in acetonitrile/EtOAc and filtered. After several days, needle-like crystals precipitated at $-10\text{ }^\circ\text{C}$ and were separated carefully. They were soluble in d^6 -benzene in which no resonance peaks of an imidazolium ring were found by NMR. We had obtained a condensation product of $\text{Ti}(\text{O}^{\text{i}}\text{Pr})_4$ in form of a titanium-oxo-alkoxy cluster ($\text{Ti}_7\text{O}_4(\text{OEt})_{20}$), which was clearly proven by single crystal X-ray diffraction revealing a structure very similar to the one published already.¹³ The yield of $\text{Ti}_7\text{O}_4(\text{OEt})_{20}$ on the basis of $\text{Ti}(\text{O}^{\text{i}}\text{Pr})_4$ was found to be 70%.

To test the generality of our result, we performed the hydrolysis of $\text{Ti}(\text{O}^{\text{i}}\text{Pr})_4$ in other ionic liquids under the similar reaction conditions. The obtained liquids were analyzed by NMR spectra to find that there were no obvious chemical shifts recognizable in NMR spectroscopy except in $[\text{BMIM}]\text{BF}_4^-$, where the resonance peak of the H-2 site on the imidazolium ring was shifted to 8.97 ppm from the ordinary value of 8.47 ppm in other systems (Figure 1). In parallel, the resonance peak of the C-2 site on the imidazolium ring was shifted in ^{13}C NMR from

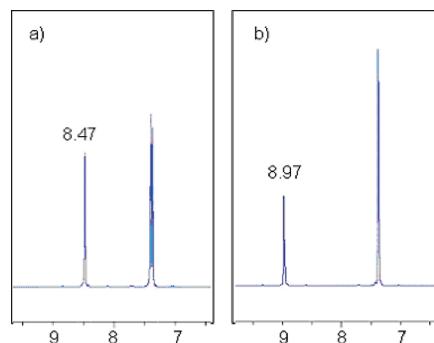


Figure 1. ^1H NMR spectra in CD_3CN . (a) $[\text{BMIM}]\text{BF}_4^-$. (b) The obtained mixture of $[\text{BMIM}]\text{BF}_4^-$ and $\text{Ti}(\text{O}^{\text{i}}\text{Pr})_4$.

Table 1. Hydrolysis Reaction of $\text{Ti}(\text{O}^{\text{i}}\text{Pr})_4$ in $[\text{BMIM}]\text{X}$ to Synthesize $\text{Ti}_7\text{O}_4(\text{OEt})_{20}^a$

entry	X	yield (%)	entry	X	yield (%)
1	Cl^-	70	6	$\text{N}(\text{CN})_2^-$	81
2	Br^-	77	7	SO_3Me^-	55
3	OTs^-	68	8	PF_6^-	48
4	OTf^-	64	9	NTf_2^-	70
5	NCS^-	44	10	SO_4Me^-	66

^a $\text{Ti}(\text{O}^{\text{i}}\text{Pr})_4$ (1 equiv), ionic liquid (2.0 equiv), ethanol as solvent. $\text{Ti}_7\text{O}_4(\text{OEt})_{20}$ was crystallized from acetonitrile/EtOAc.

136.0 to 137.6 (see Supporting Information). This indicates the formation of a new imidazolium compound in $[\text{BMIM}]\text{BF}_4^-$. On the other hand, there were two additional resonance peaks at -129.7 and -143.7 ppm in ^{19}F NMR besides the resonance peak of $[\text{BF}_4]^-$ at -150.4 ppm. And the pH value of the low boiling component diluted with water ($\text{v/v} = 1:1$) was between 3 and 4. These results indicated that $[\text{BF}_4]^-$ was partially decomposed and the formation of a new imidazolium salt had occurred. The products were then separated through crystallization. Table 1 shows the results in detail.

Whereas all other reactions provided $\text{Ti}_7\text{O}_4(\text{OEt})_{20}$ in moderate to high yields, the reaction with $[\text{BMIM}]\text{BF}_4^-$ gave rise to a different product. The assumption of a new imidazolium salt by NMR spectroscopy revealed to be correct as $[\text{BMIM}]_2[\text{Ti}(\text{OH})_6]$ was unambiguously proven by single-crystal X-ray diffraction (Figure 2). The distances from the H-2 site on the imidazolium cation and some oxygen atoms of the hydroxyl groups were found to be 2.197(3), 2.299(3), 2.218(3), and 2.278(3) \AA , respectively. These values indicate hydrogen bridges between the imidazolium cation and the hexa(hydroxo)titanate anion, which was found to consist of a slightly deformed octahedral hydroxyl coordination sphere around the titanium atom.¹⁴ The yield of $[\text{BMIM}]_2[\text{Ti}(\text{OH})_6]$ was calculated to 37%. An anion exchange reaction has given rise to $[\text{BMIM}]_2[\text{Ti}(\text{OH})_6]$ (Scheme 1). So far, the anion $[\text{Ti}(\text{OH})_6]^{2-}$ has been reported as an intermediate, but there is no report about its structure determination by

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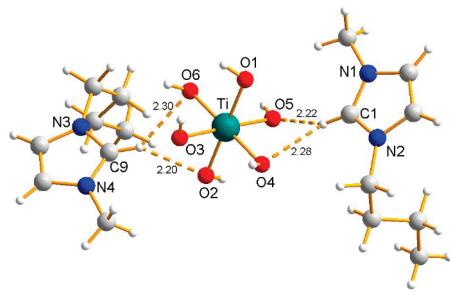
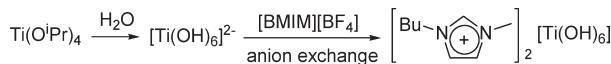


Figure 2. Diamond²⁹ drawing of $[\text{BMIM}]_2[\text{Ti}(\text{OH})_6]$. The quasi octahedral $[\text{Ti}(\text{OH})_6]^{2-}$ is coordinated through hydrogen bridges to the two imidazolium cations.

Scheme 1. Anion Exchange Reaction of $[\text{BMIM}][\text{BF}_4]$ with $\text{Ti}(\text{O}^{\text{i}}\text{Pr})_4$



single crystal X-ray diffraction.¹⁵ The FTIR spectrum of $[\text{BMIM}]_2[\text{Ti}(\text{OH})_6]$ (see Supporting Information, Figure S8; for comparison, FTIR spectrum of $[\text{BMIM}][\text{BF}_4]$ is also shown) exhibits both aromatic and aliphatic C–H stretching in the region 3200 – 2700 cm^{-1} , ring stretching (sym.) at 1570 cm^{-1} , Me C–H stretching at 1455 cm^{-1} , ring stretching (sym.) at 1171 cm^{-1} , C–H in-plane bend at 867 and 775 cm^{-1} , ring bend (asym.) at 618 cm^{-1} , and Ti–O stretching at 525 cm^{-1} . The absorption at 1030 cm^{-1} for B–F stretching in the bulk $[\text{BMIM}][\text{BF}_4]$ had disappeared. Interestingly, there was no obvious absorption at around 3500 cm^{-1} for the O–H stretching. This is possibly due to the blocking induced by the two imidazolium rings. To know if $[\text{BMIM}]_2[\text{Ti}(\text{OH})_6]$ can be transferred to TiO_2 , we carried out the reaction of $\text{Ti}(\text{O}^{\text{i}}\text{Pr})_4$ in the presence of 3 equiv $[\text{BMIM}][\text{BF}_4]$ using ethanol as solvent. After evaporation of the low boiling point components, the clear liquid was cured in an oven at $250\text{ }^\circ\text{C}$ for 4 h. Anatase nanocrystals were obtained successfully. The TEM images are shown in Figure 3, and the PXRD pattern is shown in Figure S1 (see Supporting Information). Ding et al. reported on the microwave assisted synthesis of anatase nanocrystals in $[\text{BMIM}][\text{BF}_4]$, proposing the formation of ionic liquid stabilized poly-anion complexes.⁶ Although the morphologies of TiO_2 powders are not the same, our results make the formation mechanism clear. The formation of $[\text{BMIM}]_2[\text{Ti}(\text{OH})_6]$ plays a key role in the formation of nanocrystals.

Metal-containing ionic liquids have been realized as versatile reaction media, as catalysts, as catalyst precursors, and as reagents for various chemical processes including nanomaterials, which are usually synthesized by the reaction of the halide salts with the corresponding metal halides or by metathesis with alkali salts of metal-based anions, such as $[\text{BMIM}][\text{AlCl}_4]$, $[\text{EMIM}][\text{ZnCl}_3]$,

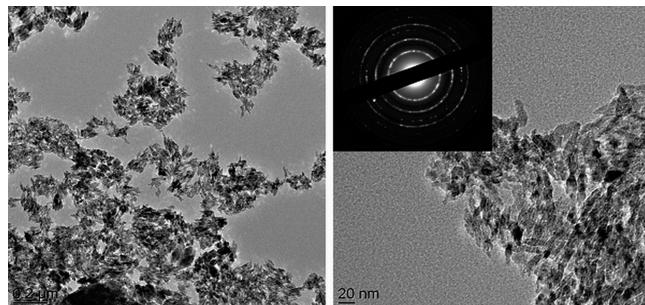


Figure 3. TEM images of anatase nanoparticles; Inset is the selected area electron diffraction pattern.

Table 2. Reaction of $[\text{BF}_4]^-$ Based Ionic Liquids with $\text{Ti}(\text{O}^{\text{i}}\text{Pr})_4$.

entry	reactant	product	yields (%)
1	$\text{Oct}-\text{N}^+ \left[\begin{array}{c} \text{C} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{C} \end{array} \right] \text{N}^- [\text{BF}_4]$	$\left[\text{Oct}-\text{N}^+ \left[\begin{array}{c} \text{C} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{C} \end{array} \right] \text{N}^- \right]_2 [\text{Ti}(\text{OH})_6]$	83
2	$\text{Dod}-\text{N}^+ \left[\begin{array}{c} \text{C} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{C} \end{array} \right] \text{N}^- [\text{BF}_4]$	$\left[\text{Dod}-\text{N}^+ \left[\begin{array}{c} \text{C} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{C} \end{array} \right] \text{N}^- \right]_2 [\text{Ti}(\text{OH})_6]$	82
3	$\text{C}_2\text{H}_4-\text{N}^+ \left[\begin{array}{c} \text{C} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{C} \end{array} \right] \text{N}^- [\text{BF}_4]$	$\left[\text{C}_2\text{H}_4-\text{N}^+ \left[\begin{array}{c} \text{C} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{C} \end{array} \right] \text{N}^- \right]_2 [\text{Ti}(\text{OH})_6]$	43
4	$\text{HO}-\text{CH}_2-\text{N}^+ \left[\begin{array}{c} \text{C} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{C} \end{array} \right] \text{N}^- [\text{BF}_4]$	$\left[\text{HO}-\text{CH}_2-\text{N}^+ \left[\begin{array}{c} \text{C} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{C} \end{array} \right] \text{N}^- \right]_2 [\text{Ti}(\text{OH})_6]$	57
5	$\text{C}_6\text{H}_5-\text{N}^+ \left[\begin{array}{c} \text{C} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{C} \end{array} \right] \text{N}^- [\text{BF}_4]$	$\left[\text{C}_6\text{H}_5-\text{N}^+ \left[\begin{array}{c} \text{C} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{C} \end{array} \right] \text{N}^- \right]_2 [\text{Ti}(\text{OH})_6]$	45
6	$\text{C}_6\text{H}_5-\text{N}^+ \left[\begin{array}{c} \text{C} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{C} \end{array} \right] \text{N}^- [\text{BF}_4]$	$\left[\text{C}_6\text{H}_5-\text{N}^+ \left[\begin{array}{c} \text{C} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{C} \end{array} \right] \text{N}^- \right]_2 [\text{Ti}(\text{OH})_6]$	57

^a The reaction conditions: ionic liquid (2 equiv), $\text{Ti}(\text{O}^{\text{i}}\text{Pr})_4$ (1 equiv), EtOH as solvent. The product was separated by crystallization.

$[\text{BMIM}][\text{FeCl}_4]$, $[\text{RR'IM}][\text{SbF}_6]$, $[\text{RR'IM}][\text{BF}_6]$, and so on.¹⁶ Although it is well-known that $[\text{BF}_4]^-$ based ionic liquids are apt to hydrolyze, there is no report about their anion exchange reaction to form another ionic liquid.¹⁷ Whereas only the anion $[\text{BF}_4]^-$ could be used for the preparation and isolation of $[\text{Ti}(\text{OH})_6]^{2-}$, we extended our search for other cations. The results are shown in Table 2. The substitution of the initial butyl by octyl or dodecyl successfully gave rise to the $[\text{RMIM}]_2[\text{Ti}(\text{OH})_6]$ ($\text{R}=\text{octyl}$ or dodecyl) in excellent yields (Table 2, entry 1, 2). The substitution of butyl by an unsaturated vinyl also provided the product in a yield of 43% (Table 2, entry 3). More interestingly, the substitution of butyl by 2-hydroxyethyl provided the product in a yield of 57% (Table 2, entry 4), which might be functionalized further. Its single crystal X-ray diffraction structure is shown in Figure 4. In this structure, the doubly charged $[\text{Ti}(\text{OH})_6]^{2-}$ anion, which is situated on a center of symmetry, is coordinated by a hydroxyl group of a side chain. This is clearly different from $[\text{BMIM}]_2[\text{Ti}(\text{OH})_6]$ (see Figure 1), in which the hydrogen bridge is of the type C–H \cdots O and not of O–H \cdots O. This anion exchange reaction with $[\text{BF}_4]^-$ anions is also suitable for pyridium based ionic liquids. $[\text{RPM}]_2[\text{Ti}(\text{OH})_6]$ were synthesized in good yields

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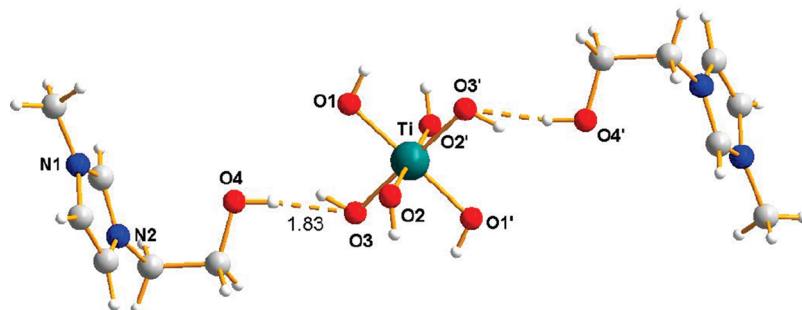


Figure 4. Diamond²⁹ drawing: $[\text{HOEtMIM}]_2[\text{Ti}(\text{OH})_6]$. In this structure the centrosymmetric $[\text{Ti}(\text{OH})_6]^{2-}$ anion is coordinated through $\text{O}-\text{H}\cdots\text{O}$ bonds.

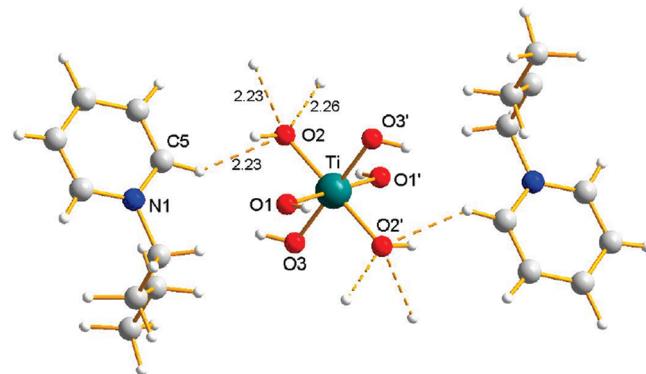


Figure 5. Diamond²⁹ drawing of $[\text{BMP}]_2[\text{Ti}(\text{OH})_6]$. In this structure the centrosymmetric $[\text{Ti}(\text{OH})_6]^{2-}$ anion is coordinated through $\text{C}-\text{H}\cdots\text{O}$ bonds.

(Table 1, entry 5, 6, R = butyl or octyl). The structure of $[\text{BPM}]_2[\text{Ti}(\text{OH})_6]$ (BPM = *N*-butyl-pyridium) was identified by the single crystal X-ray diffraction (Figure 5). There is a multiple hydrogen bonding between the pyridium cation and the hexahydroxotitanate, of which only one type is shown in the Figure 4. However, under the similar reaction conditions, we could not separate hydroxotitanate from the reaction of $\text{Ti}(\text{O}^{\text{i}}\text{Pr})_4$ in the presence of $[\text{Bu}_4\text{N}][\text{BF}_4]$ or $[\text{Bu}_4\text{P}][\text{BF}_4]$.

The hydrolysis reactions of $\text{Ti}(\text{O}^{\text{i}}\text{Pr})_4$ in $[\text{BF}_4]^-$ based ionic liquids were different to the reactions in other anion ionic liquids. Formally, tetrafluoroborate was replaced by the double anion $[\text{Ti}(\text{OH})_6]^{2-}$. The hydrolysis of $\text{Ti}(\text{O}^{\text{i}}\text{Pr})_4$ in $[\text{BMIM}][\text{Cl}]$ or $[\text{BMIM}][\text{Br}]$ did not produce $[\text{BMIM}]_2[\text{Ti}(\text{OH})_6]$; this could be because of the halide being a coordinating anion, which can form $[\text{Ti}(\text{OR})_n(\text{OH})_{4-n}\text{X}_m]^{m-}$ to inhibit the formation of $[\text{Ti}(\text{OH})_6]^{2-}$. For the uncoordinating anions, such as $[\text{OTf}]^-$, $[\text{PF}_6]^-$, and $[\text{NTf}_2]^-$, the counterionic liquids seem to be thermochemically more stable than $[\text{BMIM}]_2[\text{Ti}(\text{OH})_6]$. However, under more serious solvothermal conditions, $[\text{BMIM}][\text{PF}_6]$ undertook the anion exchange reaction to form $[\text{BMIM}]_2[\text{Ti}(\text{OH})_6]$ as well at 210 °C in an autoclave. In contrast, the reactions in the presence of other ionic liquids, such as $[\text{BMIM}][\text{Cl}]$, $[\text{BMIM}][\text{Br}]$, $[\text{BMIM}][\text{SO}_4\text{Me}]$, $[\text{BMIM}][\text{OTf}]$, or $[\text{BMIM}][\text{NTf}_2]$, etc., only afforded anatase nanoparticles. The details of the anatase nanoparticles synthesis are reported elsewhere.¹⁸ In these

anion exchange reactions, $[\text{BF}_4]^-$ or $[\text{PF}_6]^-$ was found to be partially decomposed, which may play the driving force in the anion exchange reactions.

Consecutively, we carried out the hydrolysis reaction of $\text{Zr}(\text{OPr})_4$ in $[\text{EMIM}][\text{BF}_4]$ (EMIM = 1-ethyl-3-methyl imidazolium) under similar reaction conditions to $\text{Ti}(\text{O}^{\text{i}}\text{Pr})_4$. After refluxing four hours in EtOH, white solids precipitated. They were crystallized from $\text{CH}_3\text{CN}/\text{DMSO}$ to give rise to needle-like crystals. NMR spectroscopy revealed that again an imidazolium salt had been formed. The structure determined by the X-ray structure determination is shown in Figure 6. Interestingly, it contains seven-coordinate $\text{Zr}(\text{IV})$ centers which are part of a C_2 -symmetric sigmoid chain. The polymeric $\{[\text{Zr}(\text{OH})_5]^- \}_\infty$ in the lattice is made of four hydroxyl-bridges and three terminal OH-groups on each zirconium atom. The sigmoid chains are in parallel arrangements forming a supermolecular architecture held together by $[\text{EMIM}]$ cations. Unfortunately, the cations are disordered in the structure. Occasionally, the crystals in ethanol (consisting less 0.1% water) were kept at room temperature. After several weeks, some block-like crystals were formed. The crystal was determined as $[\text{EMIM}]_2[\text{Zr}_2(\text{OH})_{10}] \cdot 2\text{H}_2\text{O}$ by the X-ray structure determination (Figure 7). This indicates that the polymeric $\{[\text{Zr}(\text{OH})_5]^- \}_\infty$ can be partially decomposed by water to form $\{[\text{Zr}_2(\text{OH})_{10}]^{2-} \cdot 2\text{H}_2\text{O}\}$. Recently, Rao et al. reported a similar infinite chain of PbBr_3 in $[\text{EMIM}][\text{PbBr}_3]$.¹⁹ The reaction described before was extended to $[\text{BMIM}][\text{BF}_4]$ (B and V stand for butyl and vinyl) and $[\text{BVIM}][\text{BF}_4]$ to give rise to the anion exchange products as well (Scheme 2). A C_2 -symmetric sigmoid polymeric $\{[\text{Zr}(\text{OH})_5]^- \}_\infty$ was resolved in the single crystal of $[\text{BMIM}]_2\{[\text{Zr}(\text{OH})_5]^- \}_\infty$ again. In contrast, a six-coordinated $\text{Zr}(\text{IV})$ cation in $[\text{BVIM}]_2[\text{Zr}(\text{OH})_6]$ was obtained as shown in Figure 8. So far, the formation of $[\text{Zr}(\text{OH})_5]^-$ and $[\text{Zr}(\text{OH})_6]^{2-}$ has only been observed at very high hydroxide concentrations, for example, in 1–10 M NaOH ,²⁰ and there is no report about their structure determination by the single crystal X-ray diffraction. Dinuclear, trinuclear, and tetra-nuclear zirconium hydroxo complexes with $\text{Zr}-\text{O}(\text{H})-\text{Zr}$ bridges have been reported in the literature, such

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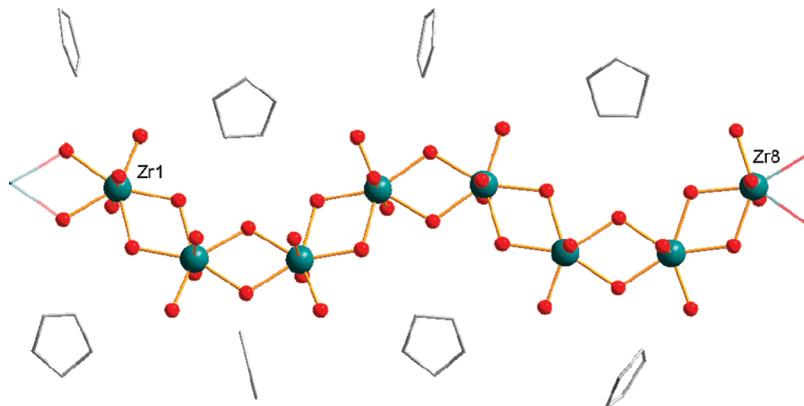


Figure 6. Diamond²⁹ drawing of $[\text{EMIM}]_\infty\{[\text{Zr}(\text{OH})_5]^- \}_\infty$. Only the rings are given for the imidazolium part because of the badly dissolved cations. Each zirconium atom is in a quasi pentagonal bipyramidal oxygen (hydroxyl) coordination sphere.

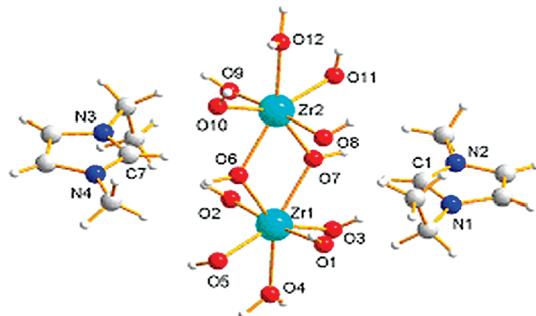
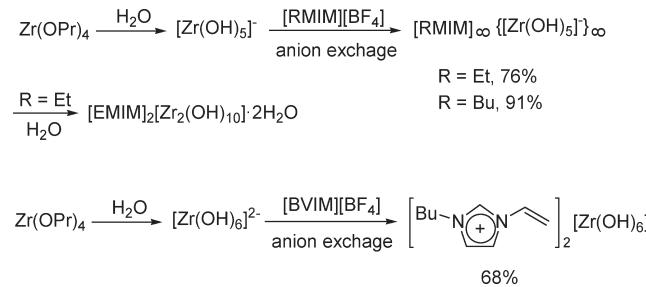


Figure 7. Diamond²⁹ drawing of $[\text{EMIM}]_2[\text{Zr}_2(\text{OH})_{10}] \cdot 2\text{H}_2\text{O}$. The $[\text{Zr}_2(\text{OH})_{10}] \cdot 2\text{H}_2\text{O}^{2-}$ anion is built of two pentagonal bipyramidal ZrO_7 entities bridged by two (OH) groups.

Scheme 2. Anion Exchange Reaction of $[\text{RMIM}][\text{BF}_4]$ with $\text{Zr}(\text{OPr})_4$



as $[(\text{C}_5\text{H}_5)_2\text{Zr}(\text{NO}_3)_2(\text{OH})]_2$,²¹ $[(\text{C}_5\text{H}_5)_2\text{Zr}(\text{OCOCF}_3)(\text{OH})]_2$,²² $[(\text{C}_5\text{H}_5)_2\text{Zr}_2(\text{OH})_2(\text{H}_2\text{O})_6][\text{CF}_3\text{SO}_3]_4$, $[(\text{C}_5\text{H}_5)_2\text{Zr}_2(\text{OH})_2(\text{H}_2\text{O})_6][\text{ClO}_4]_4$,²³ $[\text{Zr}_3(\text{O})(\text{OH})_3(\text{C}_6\text{H}_5\text{COO})_3(\text{C}_5\text{H}_5)_3][\text{C}_6\text{H}_5\text{COO}]$,²⁴ $[\text{Zr}_3(\text{OH})_4]^{4+}$, $[\text{Zr}_4(\text{OH})_8]^{8+}$,²⁵ etc.

In comparison, the reaction of $\text{Zr}(\text{OPr})_4$ in the presence of other ionic liquids with different anions under the similar reaction conditions, such as $[\text{BMIM}][\text{Cl}]$, $[\text{BMIM}][\text{PF}_6]$ or $[\text{BMIM}][\text{NTf}_2]$, did not afford the anion exchange product. As found in the titanium case, under the solvothermal conditions, the reaction in the presence of

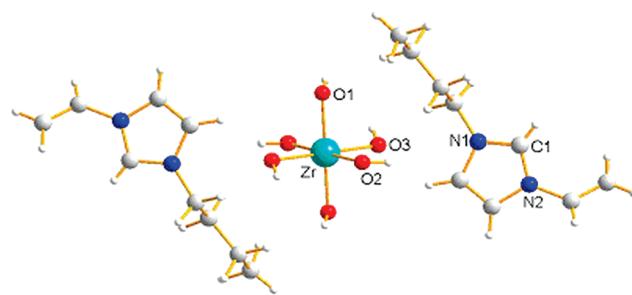


Figure 8. Diamond²⁹ drawing of $[\text{BVIM}]_2[\text{Zr}(\text{OH})_6]$. The $[\text{Zr}(\text{OH})_6]^{2-}$ anion has no closer contacts to further hydrogen atoms in the crystals.

$[\text{BMIM}][\text{PF}_6]$ produced the anion exchange reaction product as well. Recently, $[\text{BF}_4]^-$ based ionic liquids were used as additive in ethylene glycol to synthesize monoclinic ZrO_2 nanowires. The authors suggested that the formation of $\text{Zr}(\text{OCH}_2\text{CH}_2\text{O})\text{F}_2$ solid gel.²⁶ However, our results may lead to a different explanation.

3. Conclusion

In summary, we carried out the hydrolysis reaction of $\text{Ti}(\text{O}^i\text{Pr})_4$ in $[\text{BMIM}][\text{X}]$ with ethanol as solvent. We found that most of the tested ionic liquids mediated the hydrolysis of $\text{Ti}(\text{O}^i\text{Pr})_4$ to give rise to $\text{Ti}_7\text{O}_4(\text{OEt})_{20}$ in good yields. One exception is the reaction in $[\text{BMIM}][\text{BF}_4]$, in which an isolable and structurally characterized dianion $[\text{Ti}(\text{OH})_6]^{2-}$ replaced the $[\text{BF}_4]^-$ anion. This reaction has a broad capacity for group functionalization on the cation side. It can be used to synthesize both imidazolium and pyridium $[\text{Ti}(\text{OH})_6]$ salts. In contrast to titanium, zirconium alcoholate gives rise to more complex results. The reaction of $[\text{EMIM}][\text{BF}_4]$ gave rise to seven-coordinated $\text{Zr}(\text{IV})$ product $[\text{EMIM}]_\infty\{[\text{Zr}(\text{OH})_5]^- \}_\infty$, in which the anion forms a C_2 -symmetric sigmoid polymeric chain $\{[\text{Zr}(\text{OH})_5]^- \}_\infty$ held together by $\text{Zr}–\text{O}(\text{H})–\text{Zr}$ bridges. It can be partially decomposed by H_2O to form $[\text{EMIM}]_2[\text{Zr}_2(\text{OH})_{10}] \cdot 2\text{H}_2\text{O}$. On the other hand, the reaction of $[\text{BVIM}][\text{BF}_4]$ gave rise to six-coordinating $\text{Zr}(\text{IV})$ product $[\text{BVIM}]_2[\text{Zr}(\text{OH})_6]$ with an isolated $[\text{Zr}(\text{OH})_6]^{2-}$ anion in good yield. Under the solvothermal conditions, $[\text{PF}_6]^-$

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based ionic liquids can also carry out the anion exchange reaction. It is worth noting that our results may improve the understanding of the nanostructure formation mechanism in ionic liquids. Ionic liquids do not only act as media, surfactant or template, but may reveal side reactions (as shown here for $[\text{BF}_4]^-$ and $[\text{PF}_6]^-$) that play a key role in the formation of nanostructures.

4. Experimental Section

General Information. All chemicals were used as received without any additional purification step. Ionic liquids were synthesized according literature method²⁷ or bought from IoLiTec GmbH. Melting points were determined using MPA120 EZ-Melt Automated Melting Point Apparatus (Stanford Research Systems, Inc.). NMR spectra were recorded using a Bruker DRX 300 NMR spectrometer. FTIR were carried out in Bruker IFS 66 V spectrometer. X-ray structure determination: The data were collected at 153 k on a BrukerAXS X8Apex CCD diffractometer operating with graphite-monochromatized Mo K α radiation. Frames of 0.5° oscillation were exposed, deriving data in the θ range of 2 to 27° with a completeness of $\sim 97\%$. Structure solution and full least-squares refinement with anisotropic thermal parameters of all non-hydrogen atoms were performed using SHELX.²⁸ Elemental analyses were performed with the elemental analyzer vario EI III of Elementar Analyse sensysteme GmbH. Titanium has been analyzed with ICP-AES (Ultima 2 der Firma Horiba Jobin Yvon at $\lambda = 336, 121$ nm). Powder X-ray diffraction (XRD) spectra was collected on a Bruker AXS D8 powder diffractometer unit, using Cu K α radiation ($\lambda = 0.154$ nm), operating at 40 kV and 40 mA. Transmission electron microscope (TEM) was measured with a JEM-3010 electron microscope. Elemental analyses, as well as the pertinent spectroscopic data (NMR, IR) of all products not mentioned below, especially those containing zirconium, are assembled in the Supporting Information.

General Procedure of the Synthesis of $\text{Ti}_7\text{O}_4(\text{OEt})_{20}$ in $[\text{BMIM}][\text{X}]$. $\text{Ti}(\text{O}^i\text{Pr})_4$ (2.84 g, 10 mmol) was added dropwise to the solution of $[\text{BMIM}][\text{Cl}]$ (3.49 g, 20 mmol) and ethanol (11.4 g) under magnetic stirring at room temperature in an open flask (relative humidity $\approx 45\%$). After the mixture was stirred for 1 h at room temperature to obtain a turbid solution, the temperature was raised up to reflux, and the precipitates were solved to obtain a clear liquid. We continued stirring for 4 h and distilled off the low boiling component to give rise to a biphasic liquid. The liquid was solved in CH_3CN and EtOAc under reflux, filtered, and kept at a fridge to grow crystals (-10 °C). After several days, needle-like crystals precipitated. The mother liquid was decanted, and the product was washed several times with acetonitrile/EtOAc (v/v, 1:1). The product was dried under vacuum to give rise to 1.30 g $\text{Ti}_7\text{O}_4(\text{OEt})_{20}$ in 70% yield. ^1H NMR (300 Hz, C_6D_6): $\delta = 1.10\text{--}2.10$ (m, 60 H), 4.49–5.35 (m, 40 H). ^{13}C NMR (300 Hz, C_6D_6): $\delta = 18.3, 18.6, 18.8, 18.9, 19.0, 19.35, 19.41, 19.49, 19.51, 65.9, 70.2, 70.5, 70.7, 71.2, 71.3, 71.5, 71.6, 72.2$. The product has been identified with single crystal X-ray diffraction. The reactions of $\text{Ti}(\text{O}^i\text{Pr})_4$ in other ionic liquids (see Table 1) were similar to this procedure.

General Procedure of the Synthesis of Hexa(hydroxo)titanate Salts. $\text{Ti}(\text{O}^i\text{Pr})_4$ (2.84 g, 10 mmol) was added dropwise to the

solution of $[\text{BMIM}][\text{BF}_4]$ (4.52 g, 20 mmol) and ethanol (11.4 g) under magnetic stirring at room temperature in an open flask (relative humidity $\approx 45\%$). After the mixture was stirred for 1 h at room temperature to obtain a turbid solution, the temperature was raised up to reflux, and the precipitates were solved to obtain a clear liquid. We continued stirring for 4 h and distilled off the low boiling component to give rise to a clear liquid. The liquid was solved in CH_3CN and EtOAc under reflux, filtered and kept in a fridge to grow crystal (-10 °C). After several days, the product was collected via filter and washed with $\text{EtOAc}/\text{CH}_3\text{CN}$ (v/v, 1:1) to give rise to 1.55 g of $[\text{BMIM}]_2[\text{Ti}(\text{OH})_6]$ in 37% yield. Colorless needle-like crystal, mp: 176–177 °C. IR: 525, 618, 775, 867, 1165, 1455, 2960, 3100 (cm^{-1}). ^1H NMR (300 Hz, CD_3CN): $\delta = 0.91$ (t, $J = 7.2$ Hz, 6H), 1.29 (m, 4H), 1.79 (m, 4H), 2.45 (br, OH), 3.87 (s, 6H), 4.18 (t, $J = 7.2$ Hz, 4H), 7.34–7.39 (m, 4H), 9.18 (s, 2H). ^{13}C NMR (300 Hz, CD_3CN): $\delta = 12.7, 19.0, 31.7, 35.6, 49.0, 121.8, 123.4, 137.6$. Anal. Calcd for $\text{C}_{16}\text{H}_{36}\text{N}_4\text{O}_6\text{Ti}\cdot\text{H}_2\text{O}$: C, 43.05; H, 8.58; N, 12.55; Found C: 42.99, H: 6.75; N, 12.50. The product has been identified with single-crystal X-ray diffraction. The synthesis of other hexa(hydroxo)titanate salts (Table 2) was similar to this procedure.

Synthesis of TiO_2 Nanoparticles. $\text{Ti}(\text{O}^i\text{Pr})_4$ (1.89 g, 6.67 mmol) was added dropwise to the solution of $[\text{BMIM}][\text{BF}_4]$ (4.52 g, 20 mmol) and ethanol (8 g) under magnetic stirring at room temperature in an open flask (relative humidity $\approx 45\%$). After stirring for 1 h at room temperature to obtain a turbid solution, the temperature was raised up to reflux, and the precipitates were solved to obtain a clear liquid. We continued stirring for 4 h and distilled off the low boiling component to give rise to a clear liquid. The flask with the clear liquid was then transferred to an oven. The temperature was raised up at the rate of 5 °C/min to 250 °C and kept at 250 °C for four hours. It was cooled down gradually to room temperature in the oven. The precipitated solids were separated via centrifugation and washed with EtOH for 6 times. The solids were further extracted with CH_3CN for two days with a Soxhlet extractor. Finally, the products were separated via centrifugation and dried in the air. The products were identified as anatase nanoparticles with PXRD and TEM.

General Solvothermal Synthesis Procedure. $\text{Ti}(\text{O}^i\text{Pr})_4$ was added dropwise to the solution of $[\text{BMIM}][\text{PF}_6]$ (20 mmol) in ethanol (26 g, 2% water) in a 250 mL of Teflon flask under magnetic stirring. The flask was put into an autoclave, and the temperature was raised up at the ramp rate of 4.4 °C/min to 210 °C. The whole solvothermal procession took 12 h. It was cooled down gradually to room temperature in the autoclave. The low boiling point components were rotationally evaporated under low vacuum. The anion exchange reaction products were then separated via crystallization. The product was identified as $[\text{BMIM}]_2[\text{Ti}(\text{OH})_6]$ with single crystal X-ray diffraction. Under the same solvothermal reactions conditions, the reaction of $\text{Zr}(\text{O}^i\text{Pr})_4$ with $[\text{BMIM}][\text{PF}_6]$ showed the anion exchange reaction as well. The product has the similar NMR spectra with $[\text{BMIM}]_{\infty}\{[\text{Zr}(\text{OH})_5]\}_{\infty}$. It was not further identified with single crystal X-ray diffraction.

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Supporting Information Available: Experimental procedures, analytical data of new compounds, crystallographic data, NMR spectra, PXRD pattern, and TEM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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