Characterization and functionality of immidazolium ionic liquids modified magnetic nanoparticles

Characterization and functionality of immidazolium ionic liquids-modified magnetic nanoparticles

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Abstract

1,3-dialkylimidazolium-based ionic liquids were chemically synthesized and bonded on the surface of magnetic nanoparticles (MNPs) with easily one-step reaction. The obtained six kinds of ionic liquid-modified MNPs were characterized with transmission electron microscopy, thermogravimetric analysis, magnetization and FTIR, which owned the high adsorption capacity due to the nanometer size and high-density modification with ionic liquids. Functionality of MNPs with ionic liquids greatly influenced the solubility of the MNPs with organic solvents depending on the alkyl chain length and the anions of the ionic liquids. Moreover, the obtained MNPs showed the specific extraction efficiency to organic pollutant, polycyclic aromatic hydrocarbons, while superparamagnetic property of the MNPs facilitated the convenient separation of MNPs from the bulks water samples.

Keywords: Ionic liquid, magnetic nanoparticle, multiple functions, polycyclic aromatic hydrocarbons

1. Introduction

Magnetic nanoparticles (MNPs) have potential application for material science and biomedicine because of their unique superparamagnetism and large surface area. MNPs can be functionalized by modifying their surfaces with various materials to achieve the

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special purposes [1-4]. Coated shell-core MNPs with carbon, alumina, and surfactants have been recently used to preconcentrate inorganic/organic contaminants in environmental and biological samples [5-8]. Ionic liquids, which can be tuned by choosing of the cations and anions independently, exhibited unique physicochemical properties, such as tunable miscibility with water and organic solvents, and have potential applications as electrolyte materials, green solvents, catalysts and separation mediums [9-14]. N,N'-diallylimidazolium-based ionic liquids have also been used as extractant to highly enrich organic pollutants from aqueous samples in microextraction techniques, such as dispersed liquid-liquid microextraction and single drop microextraction, or to functionalize the stationary phase of chromatographic column and solid fiber membranes [15-21]. MNPs coated with ionic liquid was applied to preconcentrate polycyclic aromatic hydrocarbons (PAHs) in water samples through forming mixed hemimicelles on the surface of MNPs. However, it has been noted the coating of ionic liquid is noncovalent, which means that ionic liquid is more easily desorbed from surface and preconcentration of organic pollutants is strongly affected by the extraction parameters. In this work, a novel kind of modified MNPs with N,N`-dialkylimidazolium-based ionic liquids containing different alkyl chain lengths and inorganic anions were synthesized by covalent bonding. The functionalization of the resultant MNPs were confirmed by transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and Fourier transform infrared spectra (FTIR). Although the naked and modified MNPs had similar saturation magnetizations, the obvious differences of solubility in water and organic solvents were observed. The modified MNPs were used to preconcentration the trace level of carcinogenic PAHs in environmental water samples. To the best of our knowledge, this is the first work about application of the chemically bonded ionic liquid-modified MNPs for detecting carcinogenic organic pollutants in environmental water samples.

2. Experimental

3-(2-Imidazolin-1-yl) propyltriethoxysilane was purchased from Sigma-Aldrich. 1-Chlorohexane, 1-chlorooctane and 1-chlorodecane were purchased from Tokyo Chemical Industry Co., Ltd (Japan). $NaPF_6$, $FeCl_3·6H_2O$ and $FeCl_2·4H_2O$ were purchased from Wako Pure Chemical Industries, Ltd. PAHs standards were purchased from Supelco (USA). Organic solvents are HPLC grade. A Milli-Q water purification system (USA) was used to prepare ultrapure water.

The magnetic iron oxide nanoparticles (MNPs) were synthesized by the Massart's method with minor changes (Scheme 1) [22]. Six kind of (3-triethoxysilylpropyl)-4,5-dihydroimidazolium (TIM) ionic liquids (1-hexyl-3-TIM

chloride (HTIMCl), 1-octyl-3-TIM chloride (OTIMCl), 1-decyl-3-TIM chloride (DTIMCl), 1-hexyl-3-TIM hexafluorophosphate (HTIMPF$_6$), 1-octyl-3-TIM hexafluorophosphate (OTIMPF$_6$), 1-decyl-3-TIM hexafluorophosphate (DTIMPF$_6$)) were synthesized (Table 1). The synthesis method was as below (Scheme 1): a mixture of 3-(2-imidazolin-1-yl) propyltriethoxysilane and 1-chloroalkane was stirred at 120 ℃ for 8 h. Then the mixture was cooled to room temperature to afford 1-alkyl-3-(3-triethoxysilylpropyl)-4, 5-dihydroimidazolium chloride as an orange oil. To a solution of 1-alkyl-3-(3-triethoxysilylpropyl)-4, 5-dihydroimidazolium chloride in CH$_3$CN was added NaPF$_6$ at room temperature. After stirring for 5 min, the reaction mixture was filtrated, and the volatile were evaporated off to afford 1-alkyl-3-(3-triethoxysilylpropyl)-4, 5-dihydroimidazolium hexafluorophosphate. The resultants were colourless powders when alkyl were hexyl and decyl with melting point of 131-132 ℃ and 123-124 ℃, respectively, while the resultant was an orange oil when the alkyl was octyl. The obtained ionic liquids were confirmed by FTIR, H-NMR and C-NMR. The ionic liquid-functional MNPs were obtained through adding a solution of the desired functionalized ionic liquid and 28% aqueous NH$_3$. After mechanical stirring for 36 h at room temperature, the ionic liquid-functionalized MNPs were magnetically separated, washed with EtOH and concentrated to dryness under reduced pressure (less than 1 mmHg) to give the desired product as black powders. The ionic liquid-modified MNPs are designated as MNP-X, where X is the abbreviation of the ionic liquid (Table 1).

Morphologies were observed by TEM (JEM-2010, Tokyo, Japan) and HRTEM images were obtained using the same transmission electron microscope. Thermogravimetric analysis (TGA) was done with a TG/DTA 6200 (SII Nano Technology, Tokyo, Japan). X-ray powder diffraction (XRD) was carried out on a Rigaku x-ray RINT2200 (Ultima, Tokyo, Japan) diffractometer with Cu K$_\alpha$ radiation (λ= 0.1542 nm). Magnetic properties were measured with a SQUID magnetometer (Quantum Design MPMS). FTIR were taken in KBr pressed pellets with a suitable ratio of MNP to KBr on a FTIR-8700 (shimadzu, Kyoto, Japan).

The functional MNPs were added to the filtered river water sample to enrich the organic pollutants, polycyclic aromatic hydrocarbons (PAHs), under the sonication effect. After that an NdFeB magnet was then utilized to collect the MNPs from samples, and then the enriched PAHs were eluted with hexane. 1 mL final solution was obtained after concentrating the elution solution and transferring the solvent to acetonitrile, analyzed with HPLC [23].

3. Results and Discussion

The structures of the ILs, MNPs and the functional MNPs were confirmed by the FTIR spectra (Figure 1, H-NMR and C-NMR spectra can be obtained from the support information). The peaks in the naked Fe_3O_4 and MNP-DTIMPF$_6$ at 558 cm^{-1} were due to the Fe-O group and the peaks in DTIMPF$_6$ and MNP-DTIMPF$_6$ at 850 cm^{-1}, 1654 cm^{-1} and 2931 cm^{-1} were due to the –P-F, -C=N- and C-H groups, respectively. These results demonstrated the successful bonding of DTIMPF$_6$ to the naked MNPs by covalent bonds. The peaks in the MNP-DTIMPF$_6$ at 2360 cm^{-1} might be due to the –C=O of CO_2 absorbed on the surface of MNP-DTIMPF$_6$.

TEM images showed the naked MNPs (Figure 2a) and a representative ionic liquid-modified MNPs (MNP-DTIMPF$_6$; Figure 2b, 2c) were quasi-spheres with a mean diameter of about 12 nm. The naked and modified MNPs showed no differences in shape or size. No changes on shape and size of the MNPs were observed after treatment with the water samples. Our modified MNPs differed from coated shell-core structure MNPs, which had a thick coated shell [4-7]. Elemental analysis data showed that the carbon contents of ionic liquid-modified MNPs ranged from 4.25 to 7.15 % depending on the alkyl chain length, whereas the carbon content of naked Fe_3O_4 was 0 % (Table 2). The N and H contents of naked Fe_3O_4 might come from air and water absorbed on the surface of MNPs.

Thermogravimetric analysis (TGA) of naked MNPs detected no significant peaks (Figure 3). There was a 3 % weight loss as the temperature increased from 100 ℃ to 700 ℃, which might be due to a loss of absorbed water. In contrast, the functionalized MNPs lost weight in two steps. The first step occurred over the range 100-250 ℃, and might also be due to the loss of absorbed water. The second step consisted of a weight loss of about 5 % over the range 250-450 ℃, and might be due to the burning of bonded ionic liquids. At higher temperatures of 450-700 ℃, the weight remained constant, implying the presence of only Fe_3O_4 left within the temperature range.

The XRD patterns of naked Fe_3O_4 and a representative modified MNP (MNP-DTIMPF$_6$; Figure 4) had six characteristic peaks (2θ = 30.1, 35.5, 43.1, 53.4, 57.0 and 62.6 °), corresponding to the Miller indices (220), (311), (400), (422), (511) and (440), respectively. The same peaks were observed for all the modified MNPs. These peaks were in agreement with those in the Mineral Powder Diffraction File Data Book (International Center for Diffraction Data, No. 19-629), indicating that the MNPs were

pure Fe_3O_4 with a spinel structure. Also, the binding process did not result in a phase change of the modified MNPs. Plots of magnetization versus magnetic field (M-H loop) at 25 ℃, obtained with a superconducting interference device (SQUID), showed very weak hysteresis in both naked Fe_3O_4 and MNP-DTIMPF$_6$ nanoparticles (Figure 5), indicating that the modified MNPs were superparamagnetic. The saturation magnetization (M) of modified MNPs (60.8 to 63.2 emu g^{-1}) was only slightly less than that of naked Fe_3O_4 nanoparticles (65.8 emu g^{-1}), indicating that it was little affected by modification of the surface of MNPs. Superparamagnetism of ionic liquid-modified MNPs was an advantage because it prevented the aggregation of MNPs, so that MNPs can be dispersed into a solution again after removal of an external magnet.

The solubility of MNPs strongly depended on the alkyl chain length and anions of the ionic liquid. Modification of MNPs with 1-butyl-3-TIM chloride greatly increased their solubility in water and polar organic solvents [24]. In the present work, the modified MNPs were not soluble in water regardless of the alkyl chain and anions, although they could be dispersed ultrasonically. However, they were soluble and stable in polar organic solvents (*e.g.*, MeOH, EtOH and CH_2Cl_2) to varying degrees depending on the solvent. In strong polar solvents like MeOH and EtOH, the modified MNPs with chloride as anion were more soluble than those with PF$_6^-$ as anion. The solubility decreased with increasing alkyl chain length: hexyl>octyl>decyl. On the other hand, in CH_2Cl_2, a weak polar solvent, the modified MNPs with PF$_6^-$ as anion were more soluble, with solubility increasing with increasing chain length: decyl>octyl>hexyl. Strangely, MNP-OTIMPF$_6$ has highest solubility in both strong and weak polar solvents (Figure 6). Its unexpected high solubility in organic solvent might be related in some way to its low melting point (OTIMPF$_6$ was orange-colored liquid while HTIMPF$_6$ and DTIMPF$_6$ were colorless powder). Neither naked MNP nor modified MNPs were soluble in nonpolar organic solvents, such as hexane.

PAHs were designated as the priority monitoring pollutants due to their potential carcinogenic or mutagenic properties. In the present work, ten PAHs with 4~6 fused rings (fluoranthene (Flu), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthrene (BbF), benzo[*k*]fluoranthrene (BkF), benzo[*a*]pyrene (BaP), dibenz[*a,h*]anthracene (DBA), benzo[*g,h,i*]perylene (BgPe) and indeno[1,2,3-*cd*]pyrene (IDP) were selected as target to examine the functionality of the MNPs. The results of the spiked river water samples with PAHs standards were compared with the original water samples. Recoveries of PAHs from spiked water samples with ionic liquid-modified MNPs were much higher

than those of the naked Fe_3O_4, clearly demonstrating the extraction ability of imidazolium-based ionic liquids of the modified MNPs to PAHs. Ionic liquid-modified MNPs with hexafluorophosphate anion had much higher recoveries than MNPs with chloride anion when the alkyl was hexyl, while they had similar recoveries when the alkyl was octyl or decyl. In general, recoveries of PAHs were higher for MNPs with PF_6^- anion than that with Cl^- anion. π-π and hydrophobic interactions between PAHs and N,N'-dialkylimidazolium-based ionic liquids were presented [19]. The main interaction should be π-π interaction when the alkyl is hexyl. The anions greatly affected the property of N,N'-dialkylimidazolium-based ionic liquid. However, the property of ionic liquid gradually depended on the cation with increasing of alkyl chain length and hydrophobic interaction played an important role to preconcentration. Hence, a better detection efficiency might be improved if MNPs were modified with ionic liquids with longer alkyl chain, *e.g.* octadecyl, and PF_6^- or more hydrophobic anions were provided. As a demonstration, MNP-DTIMPF$_6$ was found to efficiently preconcentrate several PAHs (Flu, Pyr, BaA, Chr, BbF, BkF and BaP) from a river water sample (Figure 7). A similar chromatogram was obtained with the river water sample spiked with PAH standard solutions, confirming the detections.

4. Conclusion

1-alkyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium anion ionic liquids were synthesized and successfully bonded to the MNPs. Measurement of IR, NMR, TGA, TEM and elemental analysis confirmed the structures. XRD and MPMS analysis illustrated the Fe_3O_4 core of the MNPs with superparamagnetism. Functionality of MNPs with ionic liquids greatly influenced their solubility in organic solvents and facilitated the specific extraction capability to organic pollutants.

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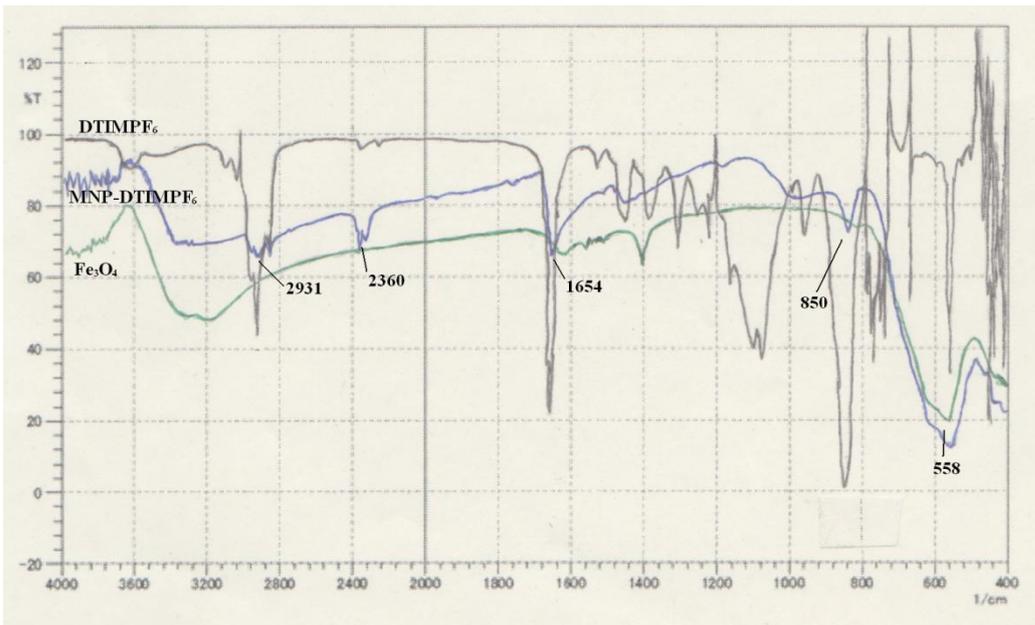
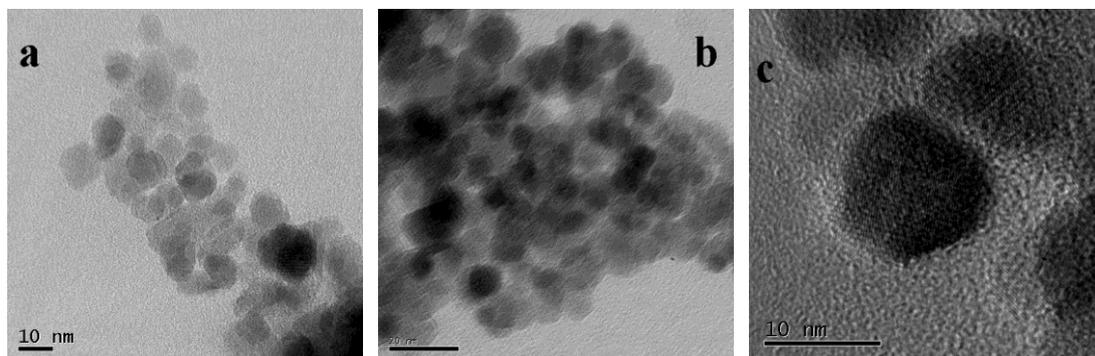Figure 1: IR spectra of Fe_3O_4, $DTIMPF_6$ and $MNP-DTIMPF_6$

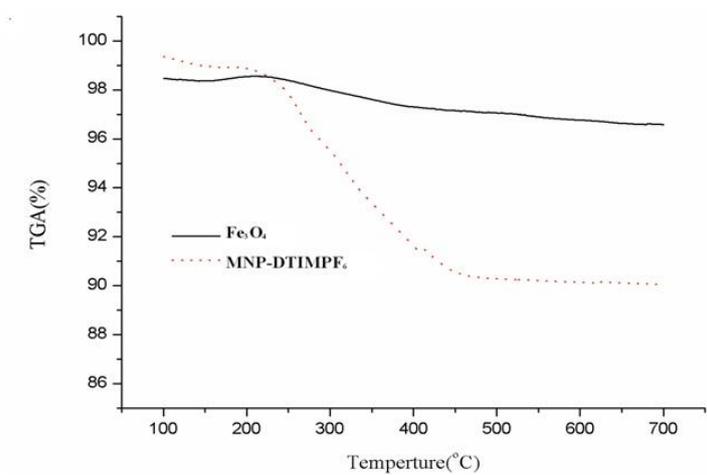Figure 2: a) TEM of Fe$_3$O$_4$, b) TEM of MNP-DTIMPF$_6$, c) HRTEM of MNP-DTIMPF$_6$
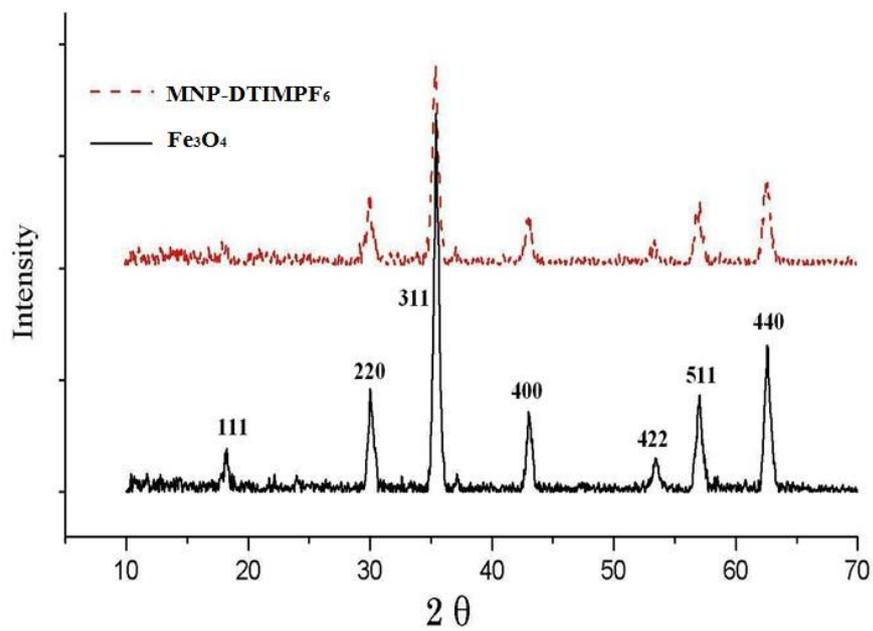
Figure 3: TGA of Fe_3O_4 and MNP-DTIMPF$_6$

Figure 4: X-ray diffraction patterns of Fe_3O_4 and MNP-DTIMPF$_6$ (Miller indices of the peaks are indicated).
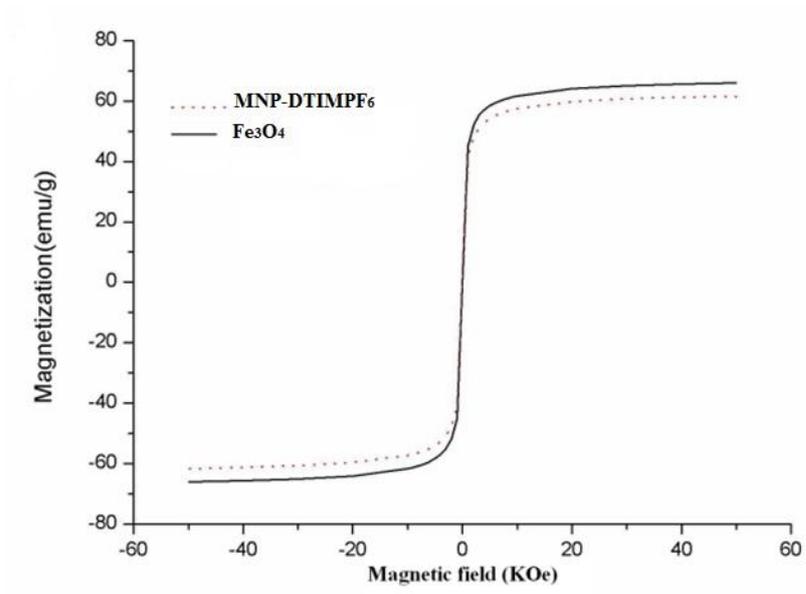
Figure 5: Magnetization *vs.* magnetic field for Fe_3O_4 and MNP-DTIMPF$_6$ at 25℃.

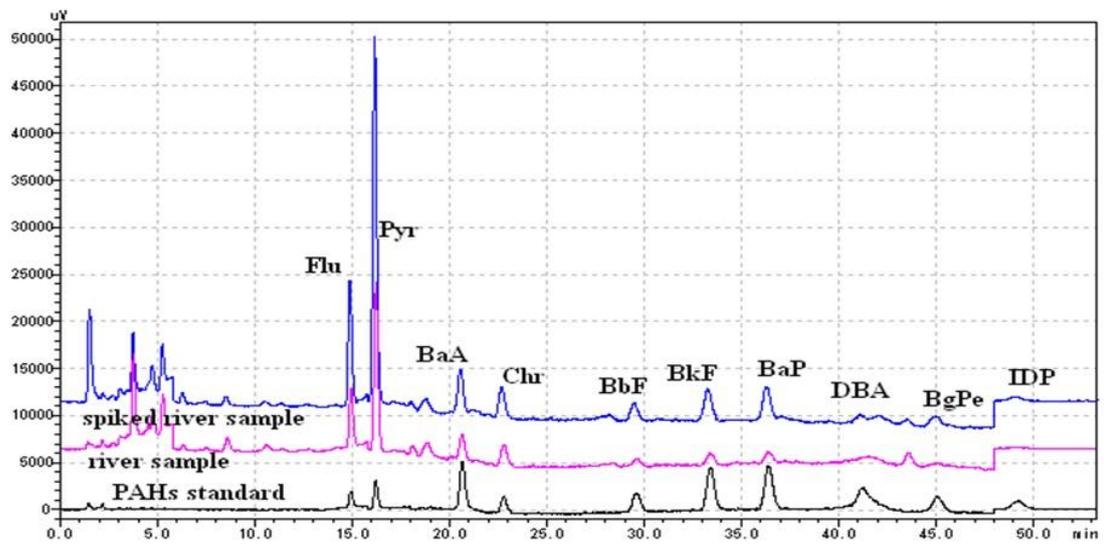Figure 6: Solubility of the naked and modified MNPs in methanol and CH$_2$Cl$_2$,

Figure 7: Chromatograms of PAHs standard, river water sample and spiked river water

sample

Table 1: Ionic liquids synthesized for this study

| Abbrev.	Ionic liquid	M [g mol^{-1}]
HTIMCl	1-hexyl-3-TIM chloride*	504
OTIMCl	1-octyl-3-TIM chloride	532
DTIMCl	1-decyl-3-TIM chloride	560
HTIMPF$_6$	1-hexyl-3-TIM hexafluorophosphate	395
OTIMPF$_6$	1-octyl-3-TIM hexafluorophosphate	423
DTIMPF$_6$	1-decyl-3-TIM hexafluorophosphate	451

TIM: (3-triethoxysilylpropyl)-4,5-dihydroimidazolium

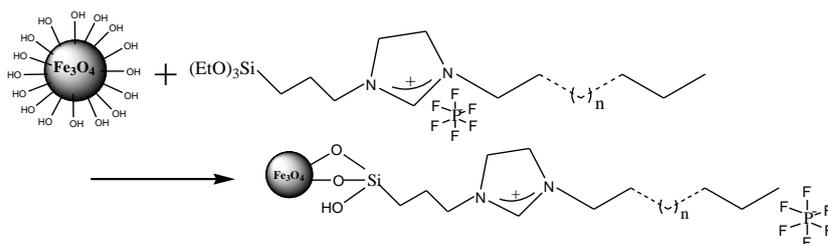Table 2: Results of elemental analysis and TGA of MNPs

MNPs	Elemental analysis (%)			TGA(%)
	C	H	N	A
Fe_3O_4	0.00	0.60	0.43	
MNP-HTIMPF$_6$	4.25	1.08	0.89	4.8
MNP-OTIMPF$_6$	5.42	1.28	1.33	4.5
MNP-DTIMPF$_6$	6.35	1.45	0.98	6.5
MNP-HTIMCl	4.54	1.10	0.99	4.8
MNP-OTIMCl	4.99	1.17	0.97	4.6
MNP-DTIMCl	7.15	1.55	1.09	8.5

(1) $2Fe^{3+} + Fe^{2+} + 8OH^- \longrightarrow Fe_3O_4$

(2)
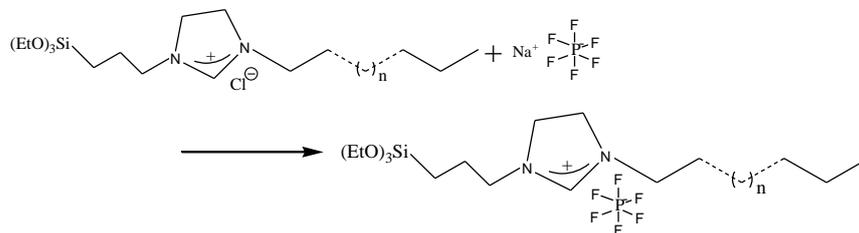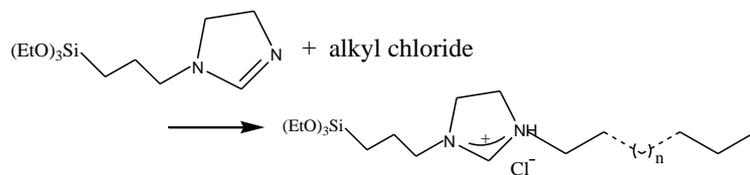
(3)
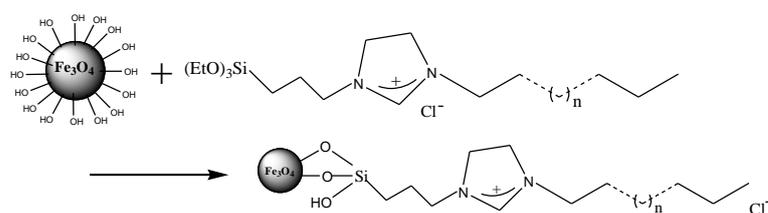
Scheme 1. Synthesis of ionic liquid-modified MNPs (alkyl=hexyl, octyl and decyl)