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Multifunctional amphiphilic ionic liquid pathway to create water-based magnetic fluids and magnetically-driven mesoporous silica[†]

 Jing Shen, ^{*a} Wen He^b and Tongwen Wang^b

Amphiphilic ionic liquids, 1-alkyl-3-methylimidazolium chloride (C_n mimCl with $n = 10, 12, 14, 16$) were firstly used as modifiers to construct a self-assembly bilayer on the surface of iron oxide nanoparticles for generation of highly stable, water-based magnetic fluids. Subsequently, a magnet-driven mesoporous silica was synthesized by *in situ* self-assembly in the bilayer C_n mimCl-stabilized magnetic fluid using the C_{16} mimCl as template and tetraethylorthosilicate (TEOS) as silicon source *via* a hydrothermal synthesis and following calcination procedure. A systematic study was carried out addressing the influence of the alkyl chain length of C_n mimCl in the primary and secondary layers on the stability of magnetic fluids. The characterization of TEM, XRD, VSM, electrophoresis experiments, TGA and DTA showed that stable water-based magnetic fluids can be synthesized based on the assembly of the well-defined bilayer- C_n mimCl structure with long-chain C_{16} mimCl as secondary layer on the magnetite (Fe_3O_4) nanoparticles. The results of small and wide-angle XRD, TEM, VSM, and N_2 absorption experiments indicated that the nano-scale magnetic Fe_3O_4 particles were inlayed into hexagonal $p6mm$ mesoporous silica (MCM-41 type) framework. Importantly, it was found that the obtained Fe_3O_4 /MCM-41 was an appropriate adsorbent for the adsorption of rhodamine B and methylene blue from their aqueous solution. In addition, the adsorbent could be separated and reclaimed fleetly from the solution under external magnetic field.

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Introduction

The use of ionic liquids has opened new avenues in the synthesis and fabrication of various new materials with advanced properties.^{1–3} Particularly, amphiphilic ionic liquids, composed of a charged hydrophilic imidazolium head group and a hydrophobic 'long tail' domain, can provide not only the amphiphilic properties of conventional surfactants, but also the specificity of typical short-chain room temperature ionic liquids such as low melting point, strong polarity and high resolvability in aqueous solution *etc.* Much work has been made to explore self-organized behaviour of amphiphilic ionic liquids in aqueous and other solvents.^{4–6} For example, Zheng and co-workers measured the micelle formation and the micelle aggregation numbers of amphiphilic ionic liquids in aqueous solution by surface tension, electrical conductivity and fluorescence measurement *etc.*^{7–9} They found that the surface activity of amphiphilic ionic liquids in aqueous solution is

slightly superior to that of the typical cationic surfactants. These self-organized advantages of amphiphilic ionic liquids have been applied to construct ordered mesoporous materials. For instance, ordered mesoporous silica with 2D hexagonal structure was synthesized by using amphiphilic ionic liquids, 1-alkyl-3-methylimidazolium chloride (C_n mimCl, n is number of carbon atoms in alkyl chains), as templates.¹⁰ Zhou *et al.* reported a preparation of supermicroporous lamellar silica through 1-hexadecyl-3-methylimidazolium chloride (C_{16} mimCl) as template.¹¹ Our group has also contributed much effort to successfully synthesize mesoporous silica with high-quality cubic gyroid and 2D hexagonal mesoporous structures by using the C_{16} mimCl as template.¹² More recently, we have employed a C_{16} mimCl-assisted synthesis method to prepare polymer/Pd microspheres and a bimodal porous Pd-decorated silica.¹³ These research results confirmed that C_n mimCl possess a specific templating performance in the synthesis of ordered porous structural materials. However, their potential as modifying agent, especially for the formation of stable C_n -mimCl-functionalized magnetic Fe_3O_4 nanoparticles (NPs) or their multifunctional combination for the fabrication of hybrid porous materials is less commonly known.

The aim of this work is twofold: firstly, it is intended to demonstrate that 1-alkyl-3-methylimidazolium chloride (C_n -mimCl) can serve as a surface functional molecule to construct

^aDepartment of Applied Chemistry, College of Vocational Education, Yunnan Normal University, Kunming 650092, China. E-mail: shenjingbox0225@hotmail.com

^bCollege of Chemistry and Chemical Engineering, Yunnan Normal University, Kunming 650092, China

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a bilayer of C_n mimCl in the surface of magnetic Fe_3O_4 NPs, which can effectively produce a stable water-based magnetic fluid. Secondly, based on the C_n mimCl-based magnetic fluid, a more facile access to prepare magnetically-driven mesoporous silica with magnetic Fe_3O_4 NPs inlayed randomly into ordered hexagonal mesoporous silica framework by using C_{16} mimCl as template and their adsorption properties is presented.

The C_n mimCl-bilayer structure onto Fe_3O_4 NPs is similar to the surfactant-bilayer modified on the surface of iron oxide particles, which has been confirmed to form stable water-based magnetic fluid by effectively overcoming the agglomeration of Fe_3O_4 NPs. The combinations of various surfactants, such as fatty acid/fatty acid,^{14,15} oleate sodium/PEG-4000,¹⁶ oleic acid/succinimide,¹⁷ and oleic acid/sodium dodecyl sulfate¹⁸ etc., have been used as modified bilayer to stabilize Fe_3O_4 NPs in aqueous solution. In our design, the first research goal is to build a C_n mimCl-bilayer on the surface of Fe_3O_4 NPs. We expect that the C_n mimCl should exhibit the strong self-assembly ability on the surface of Fe_3O_4 NPs to form a high charge density and strong hydrophilic surface, which can form stable water-based magnetic fluid.

Recently, significant advances have been achieved in the synthesis of magnetic mesoporous silica materials because of their versatile application such as adsorption and separation,¹⁹ catalysis²⁰ and biological technology.²¹ In the synthesis of these magnetic mesoporous silica materials, the commonly used approach is based on the construction of a core–shell structure, in which magnetite particle services as inner core and a layer mesoporous silica acts as outer shell.²¹ This synthesis procedure is complicated, and it is difficult to accurately control the experimental conditions. It is also impossible to exclude the formation of some irregular pore structures. Thus, the exploitation of a convenient way of homogeneous incorporation of magnetic particles into the framework of mesoporous silica by optimized various methods is still a valuable research issue. Another objective of our research is to demonstrate the supramolecular templating function of C_{16} mimCl for the preparation of highly ordered magnetic mesoporous silica in the prepared Fe_3O_4/C_{16} mimCl/ C_{16} mimCl magnetic fluid. We expect that C_n mimCl can be manipulated in tandem as bilayer modifying agent and templating agent in one system, should provide important guidelines for the multifunctional applications of amphiphilic ionic liquids in the synthesis of various nanostructured materials.

Experimental section

Synthesis of C_n mimCl ($n = 10, 12, 14, 16$)

Amphiphilic ionic liquids, 1-alkyl-3-methylimidazolium chloride (abbreviated as C_n mimCl, n is the number of carbon atoms in alkyl chains, $n = 10, 12, 14, 16$, respectively), were prepared according to a route reported in the literatures.^{13,22} All chemicals were purchased from Acros and used as received. As a typical synthesis of C_{16} mimCl, an excess of 1-hexadecyl chloride (33.41 g, 0.128 mol) was mixed with 1-methylimidazole (10.26 g, 0.125 mol). The mixture was put into a 250 mL flask, refluxed at 90 °C for 24 h, and then cooled to room temperature. The

product was further purified by recrystallization in tetrahydrofuran (THF). After being washed several times with THF, the white crystalline C_{16} mimCl powder was collected by filtration, and dried in air at room temperature. The preparation of the other C_n mimCl was achieved by repeating the above procedure with substitution of the corresponding 1-alkyl chloride for 1-hexadecyl chloride, *i.e.*, 1-decyl chloride for C_{10} mimCl, 1-dodecyl chloride for C_{12} mimCl and 1-tetradecyl chloride for C_{14} mimCl. The structures of the obtained C_n mimCl were identified by IR spectrum (see Fig. S1†).

Synthesis of bilayer C_n mimCl-stabilized magnetic fluids

The bilayer C_n mimCl-stabilized magnetic fluids were synthesized by the chemical coprecipitation of Fe^{2+} and Fe^{3+} salts in 1 : 2 M ratio from a basic aqueous solution containing a small number of C_n mimCl, followed by the modifying process of the primary and secondary C_n mimCl, respectively. In a typical preparation of primary C_{10} mimCl-coated iron oxide particles, 0.86 g of $FeCl_2 \cdot 4H_2O$, 2.35 g of $FeCl_3 \cdot 6H_2O$, and 0.1 g of C_{10} mimCl were dissolved in 40 mL of distilled water at 60 °C under mechanical paddle stirring and N_2 purge. After 10 min, the temperature was raised to 80 °C, followed by 0.5 mL of 33% (w/w) NH_4OH to adjust the pH value of the mixture to 9. After reaction for 10 min, the pH value of the mixture was adjusted again to 13 by adding tetramethylammonium hydroxide dropwise, and then, C_{10} mimCl was further added to the suspension in five 0.2 g amounts over 5 min. The reaction was allowed to proceed for 30 min at 80 °C under constant stirring. Subsequently, the suspension was cooled slowly to room temperature and the precipitates were isolated from the solution by magnetic decantation. The precipitates were further purified with the magnetic decantation and redispersion in water and ethanol for three cycles. The resulted product was coded as Fe_3O_4/C_{10} mimCl. The other primary C_n mimCl-coated iron oxide particles were prepared by repeating above procedure with the corresponding C_n mimCl as primary layer modifier and coded as Fe_3O_4/C_{12} mimCl, Fe_3O_4/C_{14} mimCl and Fe_3O_4/C_{16} mimCl, respectively. For comparison, bare Fe_3O_4 nanoparticles were prepared by above similar procedure without addition of any C_n mimCl.

To prepare stable water-based magnetic fluids, a series of secondary C_n mimCl with similar chemical structures to the primary C_n mimCl were coated on the primary C_n mimCl-coated iron oxide particles. In a typical preparation of Fe_3O_4/C_{10} mimCl/ C_{16} mimCl magnetic fluid, 1 mL of C_{16} mimCl solution (40 g L⁻¹) was firstly added to 20 mL of distilled water. 0.5 g of Fe_3O_4/C_{10} mimCl obtained above was added to the solution under ultrasound at room temperature. After 10 min, C_{16} mimCl solution (40 g L⁻¹) was further added dropwise to the suspension in 1 mL amounts over 5 min under vigorous mechanical paddle stirring until no visible settling and phase separation was observed when the solution was placed over a permanent magnet for a period of 5 min. The sample was coded as Fe_3O_4/C_{10} mimCl/ C_{16} mimCl. The preparations of the other bilayer structures were achieved by repeating the above procedure with corresponding bilayer combination of C_n mimCl as primary and



secondary layers. In order to make subsequent various analyses, a small portion of dried magnetic nanoparticles can be separated from the magnetic fluids by a decantation procedure using a permanent magnet placed next to the bottle to provide a magnetic field of about 0.3 T over 3–4 weeks.

Synthesis of magnetic mesoporous silica

The magnetic mesoporous silica was synthesized by a hydrothermal synthesis procedure in the $\text{Fe}_3\text{O}_4/\text{C}_{16}\text{mimCl}/\text{C}_{16}\text{mimCl}$ fluid using tetraethylorthosilicate (TEOS) as silicon source and $\text{C}_{16}\text{mimCl}$ as template. In a typical synthesis procedure, $\text{C}_{16}\text{mimCl}$ and NaOH were dissolved in the $\text{Fe}_3\text{O}_4/\text{C}_{16}\text{mimCl}/\text{C}_{16}\text{mimCl}$ fluid under mechanical paddle stirring. After homogenization of the mixture, TEOS was added dropwise at room temperature. The molar compositions of the starting mixtures were 1.0 TEOS : x $\text{Fe}_3\text{O}_4/\text{C}_{16}\text{mimCl}/\text{C}_{16}\text{mimCl}$: 0.1 $\text{C}_{16}\text{mimCl}$: 0.45 NaOH : 140 H_2O ($x = 0.025, 0.05, 0.10$, respectively). The resulted mixtures were stirred at room temperature for 60 min, and then transferred into a PTFE-lined steel autoclave and heated at 100 °C for 3 days. After hydrothermal treatment, the mixtures were filtered, washed with deionized water, dried under atmosphere at room temperature, and finally calcined at 550 °C for 5 h with a temperature ramp of 2 °C min⁻¹ under static air conditions to remove the template. The final product, coded as $\text{Fe}_3\text{O}_4/\text{MCM-41}$, was ground into powder for further characterization.

Adsorption experiment

The adsorption experiments were carried out by the adsorption of two dyes, rhodamine B (RhB) and methylene blue (MB), using the prepared $\text{Fe}_3\text{O}_4/\text{MCM-41}$ as adsorbent at room temperature. For comparison, the adsorption experiments of two dyes on the pure mesoporous silica MCM-41 (without Fe_3O_4 NPs) prepared using $\text{C}_{16}\text{mimCl}$ template method which we reported earlier,¹² and on the bare Fe_3O_4 particles synthesized using the same chemical coprecipitation method without adding ionic liquid were also studied at room temperature. In a typical adsorption procedure, $\text{Fe}_3\text{O}_4/\text{MCM-41}$ (0.1 g) was added to the aqueous suspensions (50 mL) of the dye solutions with concentration of x mg L⁻¹ (where $x = 10, 20, 50, 100, 200$, and 400 mg L⁻¹, respectively) under mechanical stirring. At fixed intervals, the precipitates were isolated from the suspensions by magnetic decantation, and the absorbance of the solutions was measured by UV-vis spectrophotometer (SHIMADZU UV-1780) at 554 and 664 nm for RhB and MB solutions, respectively. The decolorization rates of the solutions were calculated according to eqn (1)

$$D\% = (A_0 - A_t) \times 100\% / A_0 \quad (1)$$

where A_0 and A_t are absorbance values of the solution measured before and after the adsorption, respectively. The concentrations of the solutions were also determined by the standard working curves of two corresponding standard dye solutions. The adsorption capacity of $\text{Fe}_3\text{O}_4/\text{MCM-41}$, q_t (mg g⁻¹), at any time t was determined using eqn (2)

$$q_t = (C_0 - C_t)V/m \quad (2)$$

where C_0 and C_t (mg L⁻¹) are the concentrations of the dye at initial time and time t , respectively. V is the volume of solution (L), and m is the amount of $\text{Fe}_3\text{O}_4/\text{MCM-41}$ (g). The experimental data were treated according to Freundlich isotherm equation eqn (3)

$$q_e = K_F C_e^{1/n} \quad (3)$$

where q_e is the equilibrium adsorption capacity (mg g⁻¹); C_e is the equilibrium concentration of dye solution (mg L⁻¹); K_F (mg g⁻¹) and n are empirical constants which reflecting the adsorption capacity and heterogeneity factor, respectively. The linearized form of Freundlich isotherm can be expressed as eqn (4)

$$\log q_e = \log K_F + (1/n)\log C_e \quad (4)$$

Moreover, after the adsorption process, the precipitates were calcined at 550 °C for 5 h to remove the adsorbed dyes. The reusability of the recovered $\text{Fe}_3\text{O}_4/\text{MCM-41}$ adsorbents was also studied by tracking the changes in UV-vis absorption spectrophotograph of the adsorption system under different cycles.

Characterization

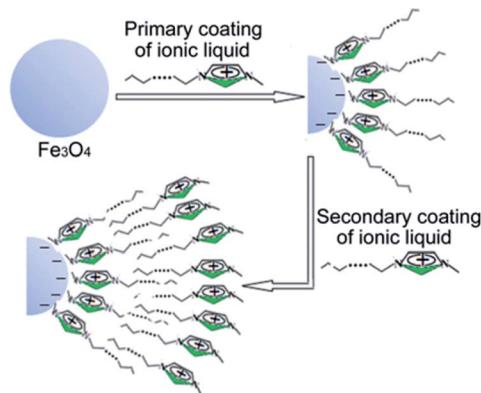
Small- and wide-angle X-ray diffraction (XRD) patterns were measured on a TTR III powder X-ray diffractometer using Cu K α radiation (wavelength 0.154 nm) at a rate of 0.05° 2 θ s⁻¹ and operated at 40 kV and 30 mA. Transmission electron microscopy (TEM) images were taken on a JEM-2100 electron microscope at an acceleration voltage of 200 kV. The specimens for TEM were prepared by dropping a small drop of the solutions onto a carbon-coated copper grid. Electrophoresis experiments were performed on a Nanjing Sangli DYL-3 electrophoresis apparatus with 15 V of external voltage. The magnetization of the samples was measured by a vibrating sample magnetometer (VSM 7407) at room temperature. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed with a ZRY-1P thermal analysis system. Nitrogen sorption experiments were conducted using a Micromeritics Tristar 3000 automated gas adsorption analyzer. A TENSOR27 Fourier transform infrared (FT-IR) spectrometer was employed for recording IR spectra.

Results and discussion

Synthesis and characterization of C_nmimCl bilayer assembled onto Fe_3O_4 particles

As schematically depicted in Scheme 1, the strategy to prepare the hydrophilic magnetic Fe_3O_4 NPs with ionic liquid C_nmimCl bilayer as shell involves the first synthesis of Fe_3O_4 NPs, followed by coating magnetite NPs with C_nmimCl ($n = 10, 12, 14, 16$) as inner layer and outer layers, respectively. The Fe_3O_4 NPs were synthesized based on the well-established coprecipitation method using Fe^{2+} and Fe^{3+} salts from a basic aqueous solution.²³ We found that during the precipitation process, the size





Scheme 1 Schematic diagram of the synthesis procedure of $\text{Fe}_3\text{O}_4/\text{C}_n\text{mimCl}/\text{C}_n\text{mimCl}$ particle using C_nmimCl as bilayer modifier.

of Fe_3O_4 NPs can be easily controlled with the initial presence of a small quantity of C_nmimCl (2.5 g L^{-1}). Before coating primary C_nmimCl , the pH value of the suspension was adjusted to 13 by adding TMAOH, which led to negatively charged iron oxide particles.²⁴ The precipitated Fe_3O_4 NPs were first coated with a primary layer of C_nmimCl adsorbed to the iron oxide surfaces through an electrostatic attraction between the negatively charged Fe_3O_4 NPs and the positively charged imidazole heads of C_nmimCl . For example, the particles coated with monolayer $\text{C}_{10}\text{mimCl}$ were unstable and settled from the aqueous solution in a few minutes due to its hydrocarbon chains extending from the particle surface (Fig. S2a†). These particles were attracted by placing a magnet near the glass bottle, demonstrating that the particles possess magnetic properties (Fig. S2b†). Compared with the frequently-used surfactants such as fatty acids that are sparingly soluble in water and their solubility was enhanced by the presence of acetone,¹⁵ C_nmimCl is highly soluble in water because of its special hydrophilic imidazole head. The excellent solubility of C_nmimCl in water provide the possibility of direct interactions between individual molecules of C_nmimCl and Fe_3O_4 particle, which is especially important for limiting the growth of Fe_3O_4 particle and preventing the agglomeration of the particles. Moreover, it was found that a drop by drop and slow adding way for the C_nmimCl aqueous solution is especially important for preventing the micelle formation of C_nmimCl in the dispersion. For example, the cmc of $\text{C}_{16}\text{mimCl}$ at 298 K was reported to be 1.21 mM ,²⁵ and the concentration of one drop of the $\text{C}_{16}\text{mimCl}$ aqueous solution in the suspension is about 0.043 mM , which is well below the cmc of $\text{C}_{16}\text{mimCl}$. Hence, this adding way is favourable to coat the individual $\text{C}_{16}\text{mimCl}$ molecule onto Fe_3O_4 particles efficiently.

To prepare stable water-based magnetic fluids, C_nmimCl was secondly coated on the $\text{Fe}_3\text{O}_4/\text{C}_n\text{mimCl}$ particles to form $\text{Fe}_3\text{O}_4/\text{C}_n\text{mimCl}/\text{C}_n\text{mimCl}$ particles. As shown in Fig. S2c,† $\text{Fe}_3\text{O}_4/\text{C}_{10}\text{mimCl}/\text{C}_{16}\text{mimCl}$ colloidal suspension exhibited a remarkable stability as evidenced by a lack of observable precipitation over periods of more than 12 months. The zeta potential (ζ) of the $\text{Fe}_3\text{O}_4/\text{C}_{10}\text{mimCl}/\text{C}_{16}\text{mimCl}$ colloidal suspension was found to be approximately $+40 \text{ mV}$ measured by electrophoresis experiments. These results imply a hypothetical structure of the exposure of imidazole head groups of the secondary layer

$\text{C}_{16}\text{mimCl}$ molecules toward the surrounding solution, and their hydrophobic long alkyl chain extending or inserting into the fence of alkyl chain of $\text{Fe}_3\text{O}_4/\text{C}_{10}\text{mimCl}/\text{C}_{16}\text{mimCl}$ by means of a hydrophobic interaction. The exposure of imidazole head groups in the surface of $\text{Fe}_3\text{O}_4/\text{C}_{10}\text{mimCl}/\text{C}_{16}\text{mimCl}$ provided high charge density and strong hydrophilic surfaces, resulting in the formation of stable and water-based magnetic fluid. We observed the formation of similar stable water-based magnetic fluids for $\text{Fe}_3\text{O}_4/\text{C}_{12}\text{mimCl}/\text{C}_{16}\text{mimCl}$, $\text{Fe}_3\text{O}_4/\text{C}_{14}\text{mimCl}/\text{C}_{16}\text{mimCl}$ and $\text{Fe}_3\text{O}_4/\text{C}_{16}\text{mimCl}/\text{C}_{16}\text{mimCl}$.

Fig. 1A and B show the typical TEM images of ionic liquid bilayer-stabilized $\text{Fe}_3\text{O}_4/\text{C}_{10}\text{mimCl}/\text{C}_{16}\text{mimCl}$ and $\text{Fe}_3\text{O}_4/\text{C}_{16}\text{mimCl}/\text{C}_{16}\text{mimCl}$ particles, respectively. It is clear that both magnetic oxides formed a well-dispersed quasi spherical morphology with clear boundary and mean diameter of approximately 10.5 and 10.1 nm. Electron diffractions (the insets in Fig. 1A and B) measured from a large zone present a series of rings that can be indexed to the magnetite structure, which is consistent with the results obtained from wide-angle XRD patterns described in Fig. S3.†

The magnetization curves of bare Fe_3O_4 , $\text{Fe}_3\text{O}_4/\text{C}_{10}\text{mimCl}$, $\text{Fe}_3\text{O}_4/\text{C}_{10}\text{mimCl}/\text{C}_{16}\text{mimCl}$ (Fig. 2A) and bare Fe_3O_4 , $\text{Fe}_3\text{O}_4/\text{C}_{16}\text{mimCl}$, $\text{Fe}_3\text{O}_4/\text{C}_{16}\text{mimCl}/\text{C}_{16}\text{mimCl}$ (Fig. 2B) displayed a typical magnetization "S" curve, where no reduced remanence and coercivity were observed, revealing the superparamagnetic nature of these magnetic particles. The saturation magnetization (M_s) of 74.2, 65.1 and 55.1 emu g⁻¹ was determined for bare Fe_3O_4 , $\text{Fe}_3\text{O}_4/\text{C}_{10}\text{mimCl}$ and $\text{Fe}_3\text{O}_4/\text{C}_{10}\text{mimCl}/\text{C}_{16}\text{mimCl}$,

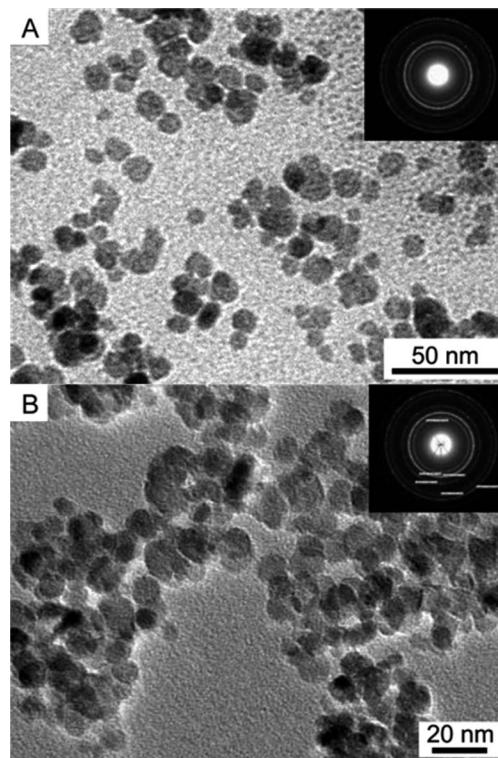


Fig. 1 TEM images of (A) ionic liquid bilayer-stabilized $\text{Fe}_3\text{O}_4/\text{C}_{10}\text{mimCl}/\text{C}_{16}\text{mimCl}$ and (B) $\text{Fe}_3\text{O}_4/\text{C}_{16}\text{mimCl}/\text{C}_{16}\text{mimCl}$ particles. The insets show the corresponding electron diffraction images.



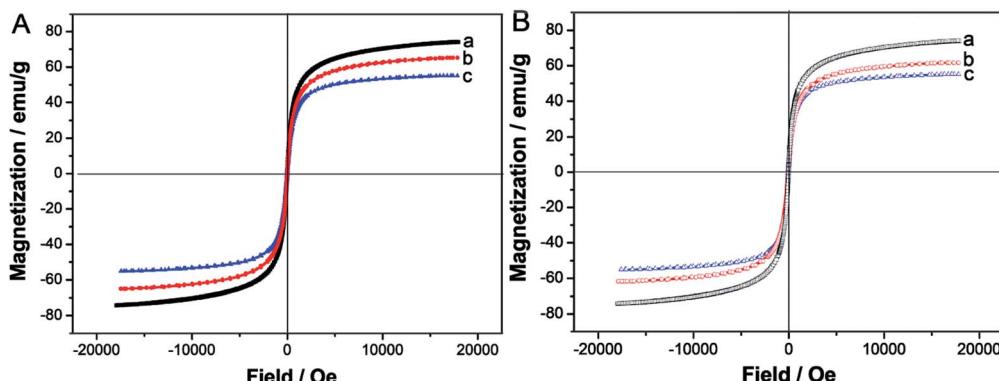


Fig. 2 (A) Magnetization curves of (a) bare Fe_3O_4 , (b) $\text{Fe}_3\text{O}_4/\text{C}_{10}\text{mimCl}$, (c) $\text{Fe}_3\text{O}_4/\text{C}_{10}\text{mimCl}/\text{C}_{16}\text{mimCl}$, and (B) magnetization curves of (a) bare Fe_3O_4 , (b) $\text{Fe}_3\text{O}_4/\text{C}_{16}\text{mimCl}$, (c) $\text{Fe}_3\text{O}_4/\text{C}_{16}\text{mimCl}/\text{C}_{16}\text{mimCl}$.

respectively. The similar results of the gradual reducing M_s from 74.2 to 61.8 and 55.0 emu g^{-1} can be observed for bare Fe_3O_4 , $\text{Fe}_3\text{O}_4/\text{C}_{16}\text{mimCl}$ and $\text{Fe}_3\text{O}_4/\text{C}_{16}\text{mimCl}/\text{C}_{16}\text{mimCl}$ (see Fig. 2B). Obviously, the coating of primary $\text{C}_{10}\text{mimCl}$ (or $\text{C}_{16}\text{mimCl}$) layer onto Fe_3O_4 NPs led to a significant decrease in the values of M_s , and the coating of secondary $\text{C}_{16}\text{mimCl}$ layer onto $\text{Fe}_3\text{O}_4/\text{C}_{10}\text{mimCl}$ (or $\text{Fe}_3\text{O}_4/\text{C}_{16}\text{mimCl}$) particles showed lower value of M_s , *i.e.* $M_s(\text{Fe}_3\text{O}_4) > M_s(\text{Fe}_3\text{O}_4/\text{C}_{10}\text{mimCl}) > M_s(\text{Fe}_3\text{O}_4/\text{C}_{10}\text{mimCl}/\text{C}_{16}\text{mimCl})$. These phenomena can be attributed to the detachment from dipole coupling due to the introduction of nonmagnetic species (C_nmimCl) on the surface of Fe_3O_4 particles.^{26,27}

To demonstrate the existence of C_nmimCl bilayer on the surface of iron oxide NPs, thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed for the samples dried at room temperature. Fig. 3A and B present the

typical TGA and DTA curves of $\text{Fe}_3\text{O}_4/\text{C}_{10}\text{mimCl}$ and $\text{Fe}_3\text{O}_4/\text{C}_{10}\text{mimCl}/\text{C}_{16}\text{mimCl}$, respectively. As can be seen in Fig. 3A (TGA curves), at the temperature below 150 °C, both samples exhibited a small decrease step with a percentage weight loss of about 4.0% and 3.6% owing to the removal of adsorbed water in the samples. For the monolayer $\text{C}_{10}\text{mimCl}$ -coated particles ($\text{Fe}_3\text{O}_4/\text{C}_{10}\text{mimCl}$), a well-defined percentage weight loss of about 4.5% was detected over a temperature range of 170–400 °C. The weight loss should be assigned to desorption and subsequent combustion of the monolayer $\text{C}_{10}\text{mimCl}$ on the surface of particles. For the bilayer $\text{C}_{10}\text{mimCl}/\text{C}_{16}\text{mimCl}$ -coated particles ($\text{Fe}_3\text{O}_4/\text{C}_{10}\text{mimCl}/\text{C}_{16}\text{mimCl}$), a more significant percentage weight loss of about 12.7% was observed between 170 and 450 °C. The difference of weight loss between $\text{Fe}_3\text{O}_4/\text{C}_{10}\text{mimCl}$ and $\text{Fe}_3\text{O}_4/\text{C}_{10}\text{mimCl}/\text{C}_{16}\text{mimCl}$ can be attributed to the removal of the secondary $\text{C}_{16}\text{mimCl}$ shell layer. The DTA

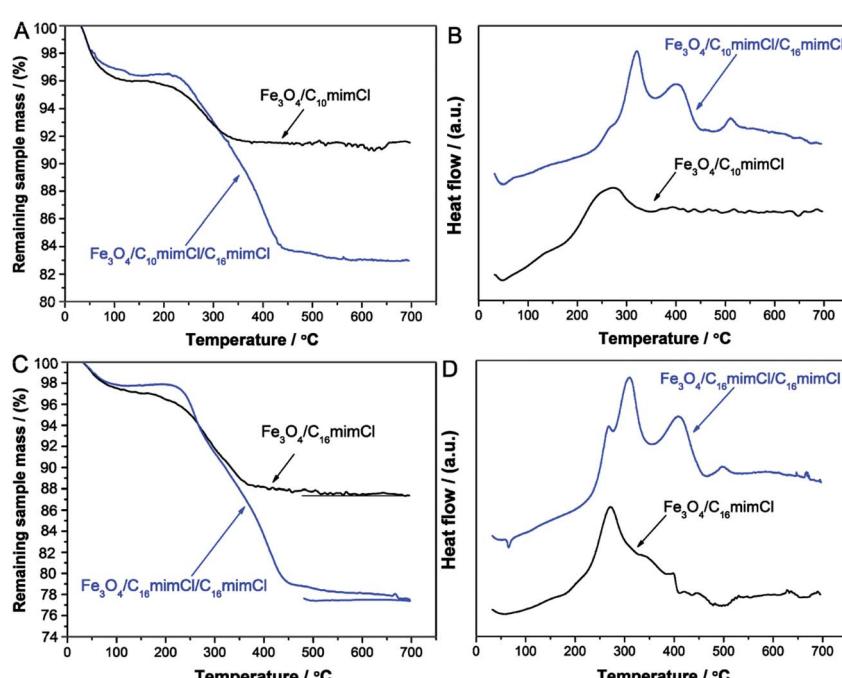


Fig. 3 (A) TGA and (B) DTA curves of $\text{Fe}_3\text{O}_4/\text{C}_{10}\text{mimCl}$ and $\text{Fe}_3\text{O}_4/\text{C}_{10}\text{mimCl}/\text{C}_{16}\text{mimCl}$. (C) TGA and (D) DTA curves of $\text{Fe}_3\text{O}_4/\text{C}_{16}\text{mimCl}$ and $\text{Fe}_3\text{O}_4/\text{C}_{16}\text{mimCl}/\text{C}_{16}\text{mimCl}$.

Table 1 Coverage parameters of the monolayer and secondary layer C_n mimCl on Fe_3O_4 particle surface

Sample	wt ^a % (adsorbed water)	wt ^a % (C_n mimCl onto Fe_3O_4 NPs)	wt% (out layer C_n mimCl)	wt _{out} ^b (weight of out layer C_n mimCl on per g Fe_3O_4) (g)	N_{out}^c (number of out layer C_n mimCl molecules on each particle)
Fe_3O_4/C_{10} mimCl	4.0	4.5	4.5	0.05	316
Fe_3O_4/C_{10} mimCl/ C_{16} mimCl	3.6	12.7	8.2	0.098	469
Fe_3O_4/C_{16} mimCl	2.8	9.2	9.2	0.105	501
Fe_3O_4/C_{16} mimCl/ C_{16} mimCl	2.2	19.2	10	0.127	608

^a The mass percent content of component was determined on the basis of the results of TGA. ^b $wt_{out} = wt\% \text{ (out)} / wt\% Fe_3O_4$, where the mass percent content of Fe_3O_4 was calculated by a formula that subtracts the mass percent of C_n mimCl and corresponding adsorbed water. ^c $N_{out} = N_1/N_2$, where $N_1 = wt_{out} \times N_A/M_{out}$ is the number of C_n mimCl molecules per g Fe_3O_4 , with N_A being the Avogadro constant and M_{out} being the molar mass of out layer C_n mimCl, and $N_2 = V_1/V_2$ is the number of Fe_3O_4 particles per g Fe_3O_4 , with $V_1 = 1/\rho$ and $V_2 = 4\pi R_1^3/3$ (or $V_2 = 4\pi R_2^3/3$) being the volume per g Fe_3O_4 and the volume per particle, respectively, where ρ is the density of Fe_3O_4 (5.18 g cm⁻³) and R_1 is the radius of Fe_3O_4 particle, and $R_2 = R_1 + l$, with l being the length of primary layer C_n mimCl.

curve (Fig. 3B) of Fe_3O_4/C_{10} mimCl exhibited one well-defined exothermic peak in the temperature range of 200–350 °C, corresponding to decomposition of the monolayer C_{10} mimCl on the surface of particles, while The DTA curve of Fe_3O_4/C_{10} mimCl/ C_{16} mimCl (Fig. 3B) displayed two distinguishable exothermic peaks between 250 and 450 °C, which might be due to the decomposition of the outer layer (the secondary layer) C_{16} mimCl and the inner layer (the primary layer) C_{10} mimCl, respectively. A small exothermic peak at around 500–600 °C is possibly due to the structural transformation from magnetite to hematite when the temperature of magnetite NPs was exceeded 400 °C.²⁸ These observations can be easily explained in terms of the different molecular weights and boiling points of C_{10} mimCl and C_{16} mimCl molecules. Moreover, the two exothermic peaks taken place at different temperature can be assigned to the difference of interactions, such as electrostatic attraction between C_{10} mimCl and magnetite NPs, and hydrophobic interaction between the alkyl chain of C_{10} mimCl and C_{16} mimCl. The similar results can be observed in Fig. 3C for Fe_3O_4/C_{16} mimCl (weight loss of about 9.2%) and Fe_3O_4/C_{16} mimCl/ C_{16} mimCl (weight loss of about 19.2%), and Fig. 3D for Fe_3O_4/C_{16} mimCl with one exothermic peak and for Fe_3O_4/C_{16} mimCl/ C_{16} mimCl with two exothermic peaks. These results revealed the existence of two different molecular layers coated on the iron oxide surface. Analogous to our results, Shen *et al.* observed the significant difference in the weight loss for monolayer and bilayer fatty acid surfactant-coated magnetite particles.¹⁵

We calculated further the coverage parameters of the monolayer C_n mimCl and the secondary layer C_n mimCl on the Fe_3O_4 particle surface, respectively, in terms of the above TGA results. In these calculations, Fe_3O_4 particle was regard as spherical shape with mean diameter D of 10 nm on the basis of the results of TEM (Fig. 1). The surface areas of the spheres were determined with diameters D and $D + 2l$ for the monolayer and secondary coating of surfactants, respectively,¹⁵ with l being the chain length of the primary surfactant. For example, the surfactant with chain length of C_{10} was estimated to be *ca.* 1.415 nm based on the method proposed by Shaw.²⁹ Table 1 lists the coverage parameters of the monolayer and secondary layer C_n mimCl assembled with C_{10} mimCl and C_{16} mimCl on Fe_3O_4

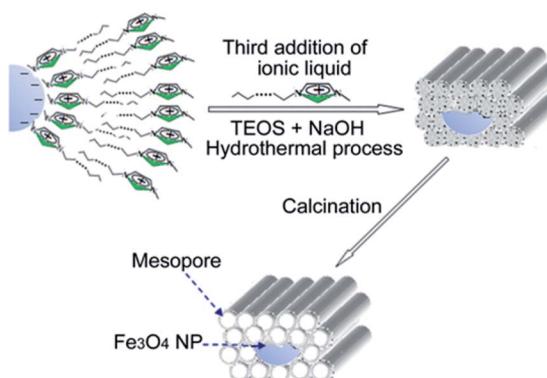
particle surface. It is clear that the increase in the number of carbon atoms of the monolayer layer ionic liquid molecule from 10 to 16 increased the weight percent of the ionic liquid from 4.5 to 9.2, and the number of the ionic liquid molecules on each particle increased from 316 to 501. Meanwhile, the number of the C_{16} mimCl molecules in secondary layer on each particle increased from 469 to 608. These results demonstrated that the long-chain C_{16} mimCl has stronger anchoring capacity on the iron oxide surface. The molecule number of 608 on each particle is close to that of the saturated fatty acids (*e.g.* myristic acid) adhered to iron oxide particle by a densely packed pattern.¹⁴ We observed that the long-chain C_{16} mimCl exhibited a stronger assembly capability than that of the short-chain C_{10} mimCl for the secondary layer construction. The phenomenon can be explained on the basis of a competition between affinity of the imidazole head groups of C_n mimCl for water and hydrophobic interaction between hydrocarbon tails of the primary and secondary C_n mimCl. It was known that the positively charged imidazole head groups possess intense hydrophilic properties.² The shorter the hydrocarbon tail of C_n mimCl is, the stronger the hydrophilic ability of C_n mimCl has. Hence, as the short-chain C_{10} mimCl was used as the secondary layer stabilizer, a highly affinity of water might make its molecules to have a tendency to remain in aqueous solution, resulting in a loose array of molecules on the particle surface. We found that the construction of Fe_3O_4/C_{10} mimCl/ C_{10} mimCl, Fe_3O_4/C_{12} mimCl/ C_{10} mimCl, Fe_3O_4/C_{14} mimCl/ C_{10} mimCl and Fe_3O_4/C_{16} mimCl/ C_{10} mimCl cannot produce stable magnetic fluids, and their particles settled from the aqueous solution in a few minutes. When the carbon atom number of the secondary layer C_n mimCl increases to 16, the hydrophobic interaction is evidently enhanced, leading to a significant increase in the assembly capability on the particle coated with the primary layer C_n mimCl. The bilayer C_n mimCl-coated Fe_3O_4 NPs, such as Fe_3O_4/C_{16} mimCl/ C_{16} mimCl, having close-packed imidazole head-groups exposing to the surrounding solution would provide a highly charge-density and strongly hydrophilic surface. The special structure surface can prevent the particles not only from aggregating but also from oxidizing through the electrostatic and steric repulsions between the particles, leading to the highly stable, water-based magnetic fluids.



Characterization of $C_{16}\text{mimCl}$ -based magnetic mesoporous silica

As shown in the Scheme 2, in the above synthesized $\text{Fe}_3\text{O}_4/C_{16}\text{mim}/C_{16}\text{mim}$ magnetic fluid, a magnetic mesoporous silica was synthesized by a hydrothermal synthesis using $C_{16}\text{mimCl}$ as template and TEOS as silicon source. Fig. 4 shows small-angle XRD patterns of the calcined samples prepared from reaction mixtures with an initial molar ratio $n(\text{Fe}_3\text{O}_4/C_{16}\text{mimCl}/C_{16}\text{mimCl})/n(\text{TEOS})$ of 0.025, 0.05 and 0.10, respectively. It is seen that very similar diffraction patterns with three well-resolved characteristic peaks attributed to (100), (110) and (200) planes of $p6mm$ hexagonal structure (with reciprocal spacing, $1/d_{hkl}$, ratios of $31/2$, 2 , $71/2$) were detected for two samples (Fig. 4a and b). These well-defined reflections peaks are in good agreement with the peaks of patterns from the siliceous MCM-41 prepared using quaternary ammonium ion surfactants,³⁰ which suggests that the presence of magnetic particles with $n(\text{Fe}_3\text{O}_4/C_{16}\text{mimCl}/C_{16}\text{mimCl})/n(\text{TEOS})$ of 0.025 and 0.05 did not destroy the ordered array of mesoporous cannelles. However, when the molar ratio was increased to 0.10 (Fig. 4c), only one well-resolved diffraction peak (100) in the 2θ range between 2 and 8 was detected, indicating that the ordered degree of mesopores is reduced. This is probably owing to the overfull addition of $\text{Fe}_3\text{O}_4/C_{16}\text{mimCl}/C_{16}\text{mimCl}$ particles, disrupting the charge density matching between the silicon species and $C_{16}\text{mimCl}$ liquid crystal phase, finally, leading to the partial breakdown of long-range ordered mesoporous silica structure. Generally, when guest species are loaded in the mesopores, the intensity of their XRD lines decreases.³¹

TEM images recorded along [100] (Fig. 5A) and [001] (Fig. 5B) directions for the calcined sample with $n(\text{Fe}_3\text{O}_4/C_{16}\text{mimCl}/C_{16}\text{mimCl})/n(\text{TEOS})$ of 0.05 showed ordered hexagonal arrangement of mesopore channels as well as dark quasi spherical Fe_3O_4 NPs. These Fe_3O_4 NPs were enwrapped by the ordered mesoporous silica channels and distributed randomly throughout the mesoporous silica matrix. The TEM images provided a direct and conclusive evidence of the coexistence of Fe_3O_4 NPs and well-defined ordered mesoporous silica. Wide-angle XRD pattern (Fig. S4A†) of this sample measured at 2θ of $20\text{--}80^\circ$ presented some distinguishable weak Bragg peaks



Scheme 2 Schematic diagram of prepared route of magnetic mesoporous silica using $C_{16}\text{mimCl}$ as template and TEOS as silicon source in the $\text{Fe}_3\text{O}_4/C_{16}\text{mimCl}/C_{16}\text{mimCl}$ magnetic fluid.

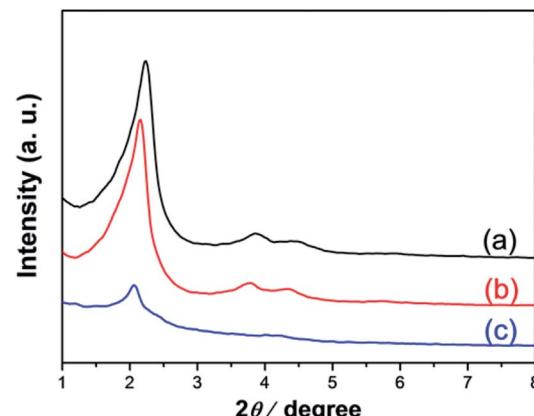


Fig. 4 Small-angle XRD patterns of calcined samples prepared using $C_{16}\text{mimCl}$ as template in the $\text{Fe}_3\text{O}_4/C_{16}\text{mimCl}/C_{16}\text{mimCl}$ magnetic fluid with an initial molar ratio $n(\text{Fe}_3\text{O}_4/C_{16}\text{mimCl}/C_{16}\text{mimCl})/n(\text{TEOS})$ of (a) 0.025, (b) 0.05 and (c) 0.10.

that can be assigned to magnetite crystalline phase (JCPDS card no. 28-0491), which further confirms the existence of magnetite Fe_3O_4 NPs in the sample. A gradual protuberance at low angle can be attributed to amorphous silica of the pore walls.³² Magnetization curve of this sample shown in Fig. S4B† exhibited also a typical magnetization “S” curve without obvious remanence and coercivity, revealing the superparamagnetic feature of the magnetic mesoporous silica.

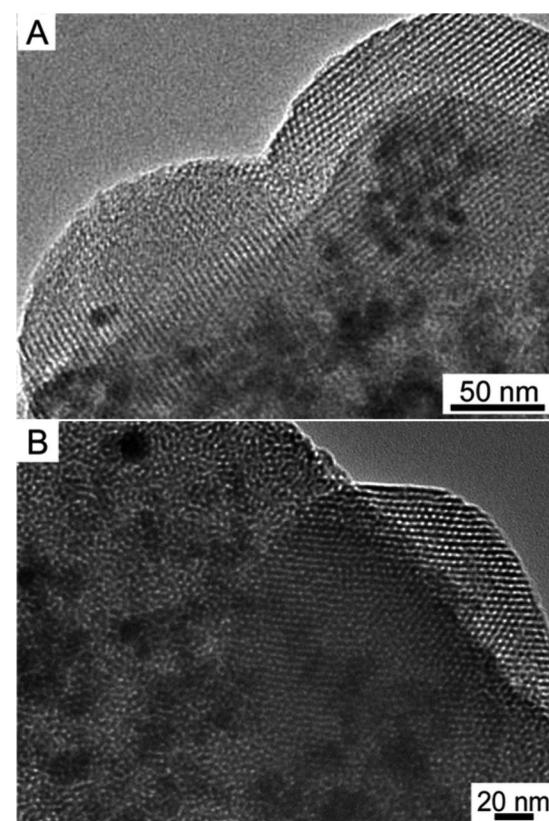


Fig. 5 TEM images recorded along the (A) [100] and (B) [001] directions of calcined sample prepared using $C_{16}\text{mimCl}$ as template in the $\text{Fe}_3\text{O}_4/C_{16}\text{mimCl}/C_{16}\text{mimCl}$ magnetic fluid.

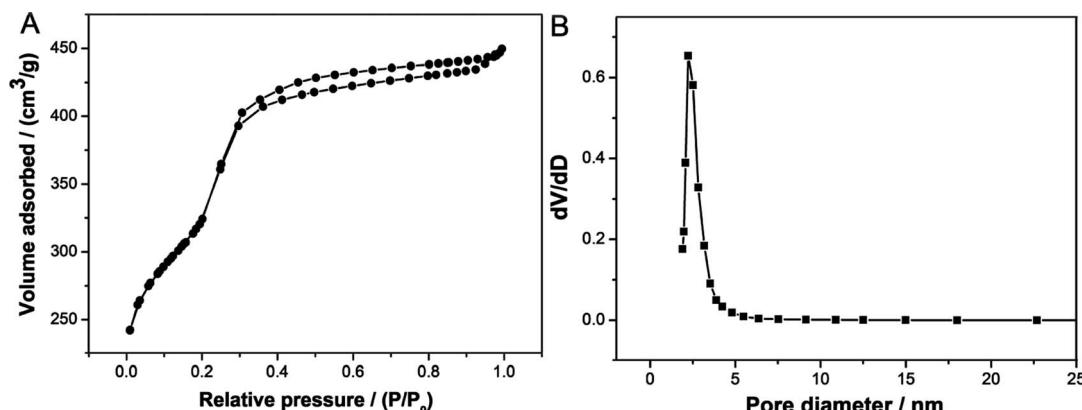


Fig. 6 (A) N₂ adsorption–desorption isotherm of calcined sample prepared using C₁₆mimCl as template in the Fe₃O₄/C₁₆mimCl/C₁₆mimCl magnetic fluid, and (B) its BJH pore size distribution.

Nitrogen physisorption isotherm (Fig. 6A) of this sample displayed a type IV adsorption isotherm with an obvious hysteresis loop at a relatively high p/p_0 values according to IUPAC,³³ indicating the presence of open pores. A steep increasing occurs at a relative pressure $0.30 < p/p_0 < 0.43$, which is due to the filling of mesoporous walls by capillary condensation. In the previous publication,¹² the hysteresis phenomenon was observed and attributable to the filling of a secondary pore structure, which resulted from grain boundaries, creating small cavities between adjacent ordered regions. In this sample, the Fe₃O₄ NPs can be regarded as grain, and its boundaries might create small cavities, therefore, resulting in the visible hysteresis loop. Pore size distribution calculated by BJH model (Fig. 6B) showed a narrow pore size distribution with the mean size of about 2.5 nm, which is in agreement with the value from TEM images. The BET surface area and total pore volume are 915 m² g⁻¹ and 0.78 cm³ g⁻¹, respectively.

Adsorption of magnetic mesoporous silica

To evaluate the adsorption properties of the prepared Fe₃O₄/MCM-41, we employed rhodamine B (RhB) and methylene blue (MB) solutions as model systems at room temperature. Fig. 7 shows the time-dependent decolorization rates of two dye solutions measured at different initial concentrations after adsorption using the Fe₃O₄/MCM-41 as adsorbent. It is clear that the decolorization rates of both solutions increased fast and reached a nearly plateau slope (about 90%) within 10 min except for MB with initial concentration of 200 mg L⁻¹. Fig. 8 shows the effect of contact time on the adsorption capacity of the Fe₃O₄/MCM-41 in RhB (Fig. 8A) and MB (Fig. 8B) solutions with different initial concentrations of 20, 50, 100, 200 and 400 mg L⁻¹, respectively. The two dyes were adsorbed rapidly in the initial 5 min. After that, the adsorption capacity did not change with increasing of the contact time, indicating the adsorption equilibrium was approached. For adsorption of RhB, the adsorption capacity of the Fe₃O₄/MCM-41 in RhB solutions with different initial concentrations of 20, 50, 100, 200 and 400 mg L⁻¹ at equilibrium (30 min) can reach 9.74, 24.4, 48.8, 98.0 and 196 mg g⁻¹, respectively (Fig. 8A). Compared with

the maximum adsorption capacity ($q_m = 196$ mg g⁻¹) of the Fe₃O₄/MCM-41, the pure mesoporous silica MCM-41 had higher adsorption capacity ($q_m = 393$ mg g⁻¹), which is exactly two times that of the Fe₃O₄/MCM-41. The reason is probably that the specific surface area (1200 m² g⁻¹)¹² of the pure MCM-41 is

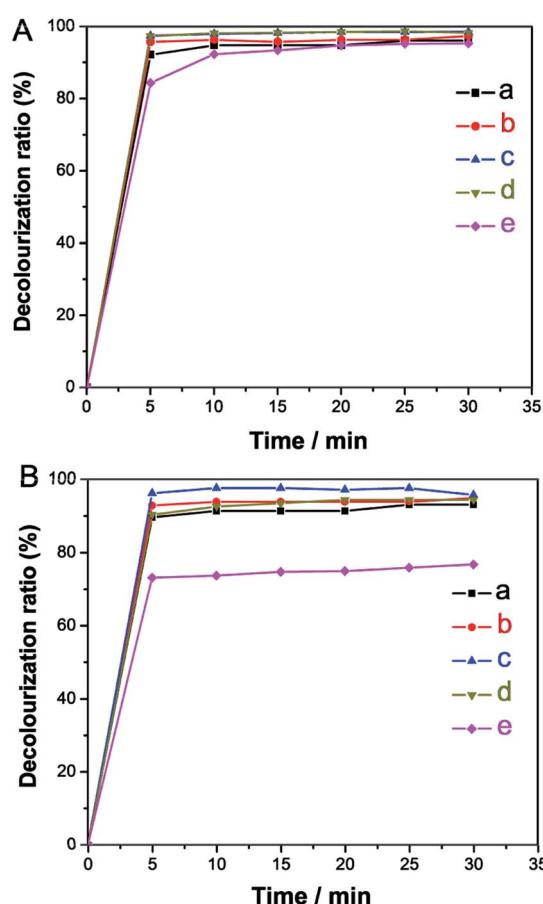


Fig. 7 Decolorization rates of (A) rhodamine B and (B) methylene blue solutions after adsorption using Fe₃O₄/MCM-41 as adsorbent and magnetic separation at different time interval. The initial concentrations of solutions for rhodamine B: (a) 20, (b) 50, (c) 100, (d) 200 (e) 400 mg L⁻¹, and for methylene blue: (a) 10, (b) 20, (c) 50, (d) 100 (e) 200 mg L⁻¹.

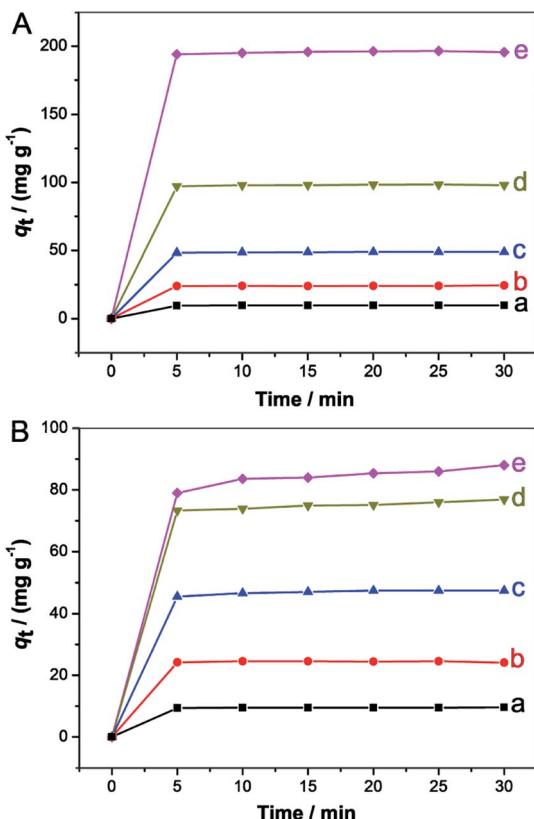


Fig. 8 Adsorbed capacity of $\text{Fe}_3\text{O}_4/\text{MCM-41}$ as a function of contact time for (A) RhB and (B) MB at different initial concentrations of (a) 20, (b) 50, (c) 100, (d) 200 (e) 400 mg L^{-1} at room temperature.

higher than that of the $\text{Fe}_3\text{O}_4/\text{MCM-41}$ ($915 \text{ m}^2 \text{ g}^{-1}$). However, the pure mesoporous silica MCM-41 can only be recovered from the solution by centrifugation, while the $\text{Fe}_3\text{O}_4/\text{MCM-41}$ can be easily recovered by magnetic separation technology. The q_m of the bare Fe_3O_4 particles prepared using the same chemical coprecipitation method without adding ionic liquid was found to be 7.5 mg g^{-1} , which is lower than that of the $\text{Fe}_3\text{O}_4/\text{MCM-41}$. This may be attributed to the fact that the $\text{Fe}_3\text{O}_4/\text{MCM-41}$ has adequate mesoporous channels.

Similarly, for adsorption of MB, the adsorption capacity of the $\text{Fe}_3\text{O}_4/\text{MCM-41}$ in MB solutions with different initial concentrations of 20, 50, 100, 200 and 400 mg L^{-1} at equilibrium (30 min) was found to be 9.62, 24.1, 47.5, 76.9 and 88.0 mg g^{-1} , respectively (Fig. 8B). It is clear that when the initial concentration of dyes is less than 100 mg L^{-1} , the adsorption capacity of the $\text{Fe}_3\text{O}_4/\text{MCM-41}$ for both dye solutions is close. However, when the initial concentration of dyes was increased from 200 to 400 mg L^{-1} , the adsorption capacity of the $\text{Fe}_3\text{O}_4/\text{MCM-41}$ increased from 98.0 to 196 mg g^{-1} for RhB solution, while for MB solution, the value increased slowly from 76.9 to 88.0 mg g^{-1} . It can be seen that for both dye solutions with high concentration ($\geq 200 \text{ mg g}^{-1}$), the $\text{Fe}_3\text{O}_4/\text{MCM-41}$ is more beneficial for adsorption of RhB than MB. This phenomenon may be attributed to the fact the $\text{Fe}_3\text{O}_4/\text{MCM-41}$ is more likely to adsorb RhB with larger molecular structure because of the special mesoporous structure of the $\text{Fe}_3\text{O}_4/\text{MCM-41}$. It was also

Table 2 Recycling of the adsorbents

Dye	Cycle	Decolorization rates (%)
Rhodamine B	1	95
	2	88.5
	3	82.1
	4	72.2
Methylene blue	1	93
	2	87.6
	3	80.5
	4	73.7

found that for the adsorption of MB, the q_m of 97.5, 88.0 and 5.50 mg g^{-1} was determined for pure MCM-41, $\text{Fe}_3\text{O}_4/\text{MCM-41}$ and bare Fe_3O_4 particles, respectively, which showed a similar trend with that of the adsorption of RhB.

The well-defined linear relations (see Fig. S5†), fitted by Freundlich isotherm equation were observed for RhB solution in the range of $20\text{--}400 \text{ mg L}^{-1}$ and for MB solution in the range of $10\text{--}100 \text{ mg L}^{-1}$ adsorbed on the $\text{Fe}_3\text{O}_4/\text{MCM-41}$. The obtained values of K_F and $1/n$ were found to be 20 mg g^{-1} and 1.074 for RhB, and 11 mg g^{-1} and 0.957 for MB, respectively. Obviously, the adsorption capacity of the $\text{Fe}_3\text{O}_4/\text{MCM-41}$ to RhB is higher than that of MB.

These results of adsorption analyses imply that the $\text{Fe}_3\text{O}_4/\text{MCM-41}$ has luxuriant mesoporous channels and high surface area, and can be potentially used as an adsorbent in liquid-phase processes. It is well-known that silicon-based MCM-41 mesopores have abundant and negatively charged surface silicon hydroxyl groups, which can adsorb the positively charged cationic dye, such as RhB or MB, by means of an electrostatic adsorption.

The magnetic separability of the dye-adsorbed $\text{Fe}_3\text{O}_4/\text{MCM-41}$ adsorbents was tested by placing a conventional laboratory magnet near the small beaker containing the mixtures of two dye solutions (100 mg L^{-1}) and the adsorbent powder. As shown in Fig. S6,† after a certain time interval, the powder was attracted by the magnet (on the right), and the colour of the powder changed from grey to orange-red (Fig. S6A†) and grey to blue (Fig. S6B†) for RhB-adsorbed and MB-adsorbed $\text{Fe}_3\text{O}_4/\text{MCM-41}$, respectively. The clear solution could be decanted off or removed by pipette. These simple experiments confirmed that the $\text{Fe}_3\text{O}_4/\text{MCM-41}$ is magnetic and can be used as a magnetic adsorbent to remove dyes in liquid-phase.

The regeneration of the $\text{Fe}_3\text{O}_4/\text{MCM-41}$ was conducted by calcination of the dye-adsorbed $\text{Fe}_3\text{O}_4/\text{MCM-41}$ powder at $550 \text{ }^\circ\text{C}$ for 5 h to remove the dyes from the pores. The reclaimed powder can be used as an adsorbent again. Table 2 shows the decolorization rates of RhB and MB solutions (100 mg L^{-1}) after four cycles. After the three cycles, the decolorization rates of both dye solutions can be maintained at more than 80%. However, after the fourth cycle, the decolorization rates were reduced to about 70%. The phenomenon may be caused by partial collapse of the mesoporous structure of the adsorbent after several cycles.



Conclusions

In summary, amphiphilic 1-alkyl-3-methylimidazolium chloride (C_n mimCl) can serve as a surface functional molecule to construct bilayer C_n mimCl structure in the surface of magnetic Fe_3O_4 nanoparticles. It was found that C_n mimCl ($n = 10, 12, 14, 16$) can be used to assemble the primer layer, and long chain C_{16} mimCl is favourable for the construction of the secondary layer. The bilayer C_n mimCl-based Fe_3O_4 particles provide a highly charge-density and strongly hydrophilic surface, leading to the highly stable, water-based magnetic fluids. Moreover, in the C_n mimCl-based magnetic fluid, a magnetically-driven mesoporous silica with magnetic Fe_3O_4 NPs inlayed randomly into ordered hexagonal mesoporous silica (MCM-41 type) framework can be prepared by using C_{16} mimCl as template. Furthermore, the obtained Fe_3O_4 /MCM-41 with high surface area of up to $915\text{ m}^2\text{ g}^{-1}$ exhibited enhanced decolorization rates (about 95%) within 5 min for the rhodamine B and methylene blue from their aqueous solutions (100 mg L^{-1}). This work may provide a new approach for the development of multifunctional amphiphilic ionic liquid in the practical nanomaterial applications.

Conflicts of interest

There are no conflicts to declare.

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