Chapter 7

A magnetically responsive one-dimensional mesoporous material functionalized with paramagnetic ionic liquid

Magnetism is generally regarded as intrinsic property of materials and cannot be changed when the material has been synthesized. Magnetic phase transition occurs only when the ordering temperature has been reached by competing with the thermal energy. In this chapter, we show that paramagnetic to ferromagnetic phase transition can be achieved by mesoscopic structural confinement. The imidazolium-based ionic liquids that contain transition metal complex as anions show paramagnetism at room temperature. However, when this kind of paramagnetic ionic liquids are confined into the mesoporous silica template by ultrasonication under vacuum, they become ferromagnetic. This transition was demonstrated by the elevated glass transition temperature and hysteresis in the magnetization curve.
7.1 Introduction

7.1.1 Porous material

Porous materials are of great interests in many applications. A porous medium contains pores with various sizes. According to IUPAC notation, three categories of porous materials can be named based on their pore diameters (Tab. 7.1).

There are many macroporous materials exist in nature with pore size bigger than 50 nm. Many biological reaction and processes rely on these pores because the pore diameter is comparable to the wavelength of the visible light. For example, diatom is one of the largest species around the world (Fig. 7.1a). It is particularly important for the ocean, which contributes more than 45% of the primary production of organic materials. Once they become dead, after millions of years, the silica based cell wall (frustule) turns into an important mineral, the diatomaceous earth, which preserves the shape of the diatom cell (Fig. 7.1b). In recent years, diatomaceous earth receives enormous interests for its significant importance in oil industry, chemical engineering, civil engineering and so on, such as catalytic medium [1], purification filter [2] and even energy storage materials [3].

Microporous materials contain pores with diameters less than 2 nm. They are often used in laboratory for the purpose of trapping, such as ions, gas molecules and bacteria. The common examples include zeolites [4] and metal-organic frameworks [5]. Mesoporous materials are those contain There are many ordered silicon based minerals exist in nature.

Table 7.1 Classification of porous materials based on pore diameters (IUPAC notation).

<table>
<thead>
<tr>
<th>Materials</th>
<th>Macroporous</th>
<th>Mesoporous</th>
<th>Microporous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore size (nm)</td>
<td>&gt; 50</td>
<td>2-50</td>
<td>&lt; 2</td>
</tr>
</tbody>
</table>

Figure 7.1 (a) Optical microscopic image of a diatom cell. (b) Scanning electron microscopic image of diatomaceous earth. (Images are taken from Internet individually)
7.1 Introduction

Figure 7.2 Mean-field prediction of the thermodynamic equilibrium phase structures for conformationally symmetric block-copolymer melts. Phases are labeled as: S (body-centered cubic spheres), C (hexagonal cylinders), G (bicontinuous cubic), L (lamellae). $f_A$ is the volume fraction of component A. (Figure was modified from ref. [6])

7.1.2 Synthesis of mesoporous material using block-copolymer

Copolymer is a kind of polymer that is polymerized with more than two kinds of monomers. The monomers have double-bond or triple-bond that allow cross-linking reaction with one another to form large network. It has of great interest in using as template for fabricating structures in nanoscale.

The packing of molecules follows the thermodynamics, where the energy in the mixing state of block-copolymer is determined by the enthalpy gain and entropy cost. Practically, the molecular weight, volume fraction of the component and the degree of segment incompatibility are three independent parameters that relevant to the final thermodynamically stable morphologies. Figure 7.2 illustrates the transition of the formed nanostructures by mixing polymer A and B as a function of the volume fraction of component A ($f_A$). With increase of $f_A$, a variety of morphologies can be formed, which are body-centered cubic spheres, hexagonal cylinders, bicontinuous cubic and lamellae.

7.2 Concepts

7.2.1 Phase transition of ionic liquid

Ionic liquids receive much attention recently due to their unique properties of strongly polarized charge separation under room temperature. In chapter 1, we have introduced the main difference between ionic liquid and the conventional molten salts, where the former one are composed of large asymmetrical ions that are bonded loosely with each other. Because of that, many ionic liquids are difficult to crystallize simply by cooling, while they form glass instead. In order to obtain their crystal structure, particular technique such as in-situ crystallization method is proposed [7].
Figure 7.3 Characterization of the phase transition process in polymers with differential scanning calorimetry. During warming up, the frozen polymer experiences a sequence of processes. First the chain of polymer starts to be mobile again and glass transition happens. The polymer changes from glass-like solid to rubber-like soft form. Then it might crystallize or directly melting at higher temperature.

In this method, a Bridgeman type of geometry has been used. Ionic liquid is sealed in a glass tube and frozen by cryogen gas initially. A laser is installed to heat the sample locally. The laser spot melts a small domain and the temperature gradient creates a solid/liquid interface so that the crystal can grow starting there. Laser is moving downward slowly in order to crystallize the ionic liquid of the whole tube. In this way, the glass formation process can be bypassed and single crystal X-ray diffraction measurement can be performed thereafter.

The thermal history also influences the phase transition of ionic liquid. As shown in Figure 1.10 and also reported by others [7], some ionic liquids crystallize during warming up before melting at higher temperature; whereas others experience a glass transition into some rubber-like high viscosity state.

7.2.2 Synthesis of SiO$_2$-based mesoporous template

Prior to the present used mesoporous silica template SBA-15 (Santa Barbara Amorphous No.15) [8], MCM-41 (Mobil Composition of Matter No. 41) was the most famous hexagonally ordered molecular sieve discovered by Mobil Oil Corporation in 1992. The synthesis is based on cetyltrimethylammonium bromide (CTAB) as surfactant template. Due to its smaller size, the pore dimension of the MCM-41 is normally only 2-3 nm. In order to increase the pore size, amphiphilic polymers with larger molecular weight are expected to extend the mesoporous length scale.

The template agent we used for the following synthesis involves using a symmetric triblock copolymer constitutes of poly(ethylene oxide)(PEO) and poly
(propylene oxide) (PPO), namely pluronic P-123. The nominal chemical formula is \( \text{HO(CH}_2\text{CH}_2\text{O)}_{20}\text{(CH}_2\text{CH}(_3)\text{O)}_{70}\text{(CH}_2\text{CH}_2\text{O)}_{20}\text{H} \), which corresponds to a molecular weight of around 5800 g/mol. The silica precursor is tetraethyl orthosilicate (TEOS) with the formula Si(O\text{C}_2\text{H}_5)\text{_4}, which is the ethyl ester of orthosilicic acid Si(OH)\text{_4}.

P-123 has the behavior similar to those hydrocarbon surfactants, which will form micelles when is placed in polar solvent such as water. Depending on the concentration, they are capable of forming spherical or cylindrical micelles. These micelles are used as the backbone to synthesize structured mesoporous materials.

TEOS is the most commonly used crosslinking agent for synthesis of silicon dioxide based on the hydrolysis reaction. When TEOS is reacted with water, the O-R bond in Si(O-R)\text{_4} is attacked by H-OH and converted into Si(OH)\text{_4} and RH. Si(OH)\text{_4} is not stable and will further change to SiO\text{_2}. Depending on the reaction rate and condition, the resulted SiO\text{_2} can be powder, thin film, gel and even highly porous aerogel. This hydrolysis reaction is also called sol-gel reaction.

![Figure 7.4 Constitutions of chemical compounds for the synthesis: P-123 and TEOS.](image)

![Figure 7.5 Schematic illustration of the polymerization process where P-123 block-copolymer aggregates into cylinder morphology at acidic condition.](image)

![Figure 7.6 Sol-gel reaction of silica porous material based on hydrolysis of TEOS.](image)
7.3 Experiments

7.3.1 Synthesis of SBA-15 mesoporous silica

In order to acquire silica gel without aggregating into condensed powder, acidic condition is necessary. The precursors we used are P-123, TEOS, hydrochloric acid (HCl, 37 wt%), and deionized water (DI H$_2$O). The sequences and speed of adding ingredients are the key for successful synthesis. We first dissolved 4 g P-123 into 15 ml HCl and 85 mL DI H$_2$O, forming 1.5 mol/L of solution A.

Afterward, 8.5 g TEOS (98 wt%) was slowly added (drop by drop) to the solution A under vigorous stirring at 2000 rpm. White gel started to form when TEOS was contacted with acidic solution A.

Later on, the as-prepared white gel (with solution) was transferred to a Teflon autoclave and sealed with steal kettle for aging. The kettle was put into oven with the hydrothermal condition at 110 °C for 24 h.

Once the aging was finished, the product was collected by centrifuge. The product was further washed with DI H$_2$O and dried at 60 °C in a form of white powder. At this moment, surfactant P-123 still remained in the product and needed to be removed.

We put the white powder in an Al$_2$O$_3$ crucible and calcinated in a muffle oven in the air at 550 °C for 6 h. The resulted final product was SBA-15 template.

![Figure 7.7 Schematic illustration of the synthesis of SBA-15 silica template based on P-123 surfactants.](image)

7.3.2 Encapsulation of paramagnetic ionic liquid

One gram of SiO$_2$ nanosphere was placed in a two-neck round bottom flask with one neck sealed by rubber cork and the other neck connected to a mechanical pump. The powder was later vacuumed carefully without being blown away.

![Figure 7.8 Illustration of the vacuum encapsulation process, where paramagnetic ionic liquid molecules are absorbed within the pores of the SBA-15 silica template.](image)
Then, about 20 ml of BMIM[FeCl₄] paramagnetic ionic liquid (PIL) was syringe-injected into the flask to fully immerse the powder. In this step, it is better to avoid direct drop of PIL on the powder in order to prevent splashing powder everywhere on the wall of flask.

Afterwards, the flask was put in an ultrasonic bath and heated in silicone oil at 120-170 °C for 12-48 h. Ultrasonication was maintained during the heating process to facilitate the diffusion of PIL molecule into the pore of SBA-15.

The encapsulation process was terminated by stopping ultrasonication and heating. After the flask was cooled down back to room temperature,

7.3.3 Synthesis of SiO₂ nanospheres as comparison

SiO₂ nanospheres were synthesized for comparison purpose. Basic environment (pH > 12) was required for the deposition of SiO₂ nanosphere. We prepared the medium with ammonia (NH₃-H₂O), ethanol (EtOH) and DI H₂O. To aim particle size of 80 nm, the molar ratio between TEOS and DI H₂O is 1 : 2, so that the usage of TEOS, NH₃-H₂O and DI H₂O respect to 60 mL EtOH were 12 mmol, 60 mmol and 120 mmol, respectively. Since all precursors are in liquid form at room temperature, the volumes for TEOS and NH₃-H₂O (25 wt%) were 1 mL, 4 mL, respectively.

The mixture was sealed in a 100 ml round bottom flask with rubber cork and magnetic stirred at room temperature for 96 h at 600 rpm. Afterward, the stirring was stopped and the deposition was further grown with Ostwald ripening process for 30 h. Later, the white deposition was separated by centrifuge and dried in the oven. In the end, the powder was calcined in the air at 550 °C for 12 h.

Identical method was used for encapsulation attempt. In the end, the obtained sample was collected for the magnetic measurement.

7.3.4 Transmission electron microscopy

Transmission electron microscope (TEM) was used to characterize the morphology and pore size of the calcined SBA-15 including different sample orientations. TEM specimens were prepared as follows. SBA-15 powders were first dispersed in absolute ethanol, followed by drooping one droplet onto a piece of TEM copper grid and naturally dried. Specimens were analyzed using JEOL JEM2010 microscopes with LaB6 filament at 200 kV. The images were collected by Gatan Erlangshen CCD camera.

Figure 7.9a shows well-ordered hexagonal arrays of mesopores. We analyzed the TEM image with the Digital Micrograph software and it shows that the distance between mesopores is estimated to be 5 nm (Fig. 7.9b).
Figure 7.9 (a) Transmission electron microscopic image of calcinated SBA-15 mesoporous silica with cylinder structure. Yellow line indicates the part where the pore size was determined. (b) The pore size profile of the sample shown in the TEM image. The average pore size is around 5 nm. (c) TEM images of overlapped two particles, showing hexagonal pore configuration. (d) Low resolution TEM image shows the size of a single particle. (Images was taken by Dr. Bin Chen from University of Groningen.)

7.3.5 Raman spectra of PIL and PIL@SBA-15

To study the mechanism of magnetic interaction between neighbouring magnetic centers, we performed the Raman spectroscopy measurement. The Raman signal was excited by a Cobolt Samba 25 diode pumped solid-state green lasers with wavelength of 532 nm. The laser light was passed through two pinholes and a line filter. Then, the light was focused on sample carried by a silicon wafer through a microscope with maximum ×100 objective lens. The laser power at the sample was about 0.4 mW.

Scattered light was collected at about 30° from the excitation beam, collimated, passed through a superholographic notch filter, and sent into a spectrometer (ANDOR, model: SR-500i-D1-R). The light was dispersed via 600 to 1800 lines/mm grating and detected via a Peltier-cooled CCD (ANDOR, model: DV420A-OE). Spectral positions and intensity were calibrated referring to the spectrum of Si before the measurement of ionic liquid samples. The signal was
subtracted from the background. Sometimes there will be some spike peak due to “cosmic rays”. We repeatedly took the background until there were no spikes. The collection time was 30 s.

Figure 7.10 shows the Raman spectra of difference polarization angles. We noticed that there were two characteristic peaks at wavenumber around 150 cm\(^{-1}\) and 350 cm\(^{-1}\). They belong to the vibrational modes of FeCl\(_4\)\(^-\) ion. The high wavenumber peaks are due to the **stretching modes**, with symmetric and asymmetric vibration modes at 331 cm\(^{-1}\) and 390 cm\(^{-1}\), respectively. The peaks at 116 cm\(^{-1}\) and 166 cm\(^{-1}\) are related to the **bending mode** of the Fe-Cl bond [9].

Interestingly, the relative intensity between bending and stretching modes changes with respect to the linear polarization angle. When the analyzer is aligned with the laser polarization, the maximum Raman scattering is observed for stretching mode. Rotating the polarizer leads to the ratio between the crossed intensity over aligned intensity (**depolarization ratio**) approaches zero. However, while intensity of the peaks corresponding to the stretching mode extinguishes, the intensity of the bending mode peaks enhances.

For isotropic samples, the Raman spectra are not sensitive to the orientation of the polarized light. Normally, liquids are regarded as isotropic, hence should be weak polarization dependence. However, here we found that paramagnetic ionic liquids are very sensitive to the polarized light, with depolarization ratio almost equals to zero. This discovery indicates that ionic liquids show some properties that only crystals have even with quite low viscosity.

![Figure 7.10 Raman spectra taken with linear polarized incident light. The crossed angles between the analyzer and the Raman scattered light are labeled on the right. Peaks corresponding to different vibration modes are indicated with dash lines.](image)
7.4 Results and discussion

7.4.1 Magnetic susceptibility measurement

In chapter 1 and 4, we have discussed the paramagnetic nature of PIL. Magnetic susceptibility of pristine BMIM[FeCl₄] follows Curie’s law with weak antiferromagnetic interaction below 80 K (Fig. 4.10b). However, BMIM[FeCl₄]@SBA-15 sample reveals evidences of magnetic ordering. The inverse magnetic susceptibility shows deviation downwards from the Curie-Weiss law (Fig. 7.11b), which is indicative of the onset of a net magnetic moment below some critical temperatures [10].

![Figure 7.11](image)

**Figure 7.11** (a) Normal and (b) Inverted magnetic susceptibility of BMIM[FeCl₄]. The purple line shows the linear fitting to the high temperature region.

7.4.2 Magnetization curve of PIL@SBA-15

In order to confirm the emergence of ferromagnetic state at low temperature, we measured the magnetization curve of PIL@SBA-15 at 20 K. Over the applied magnetic field range from -2 T to 2 T, it shows a non-linear field dependency, which is significantly different from the pristine PIL (Fig. 7.12a).

We further demonstrated the emergence of ferromagnetism was due to SBA-15 mesoporous, rather than side reaction with SiO₂. By applying the identical method of encapsulation to SiO₂ nanosphere, we are not able to repeat the observation of hysteresis at same temperature (Fig. 7.12b). This control experiment strongly confirmed the indispensable prerequisite of SBA-15 in inducing ferromagnetism in BMIM[FeCl₄].
7.4 Results and discussion

Figure 7.12 The magnetization curve of PIL@SBA-15 (a) and PIL+SiO$_2$ nanosphere (b), where the former one shows non-linear field dependence of the magnetization. The inset shows the hysteresis loop after subtracting the linear paramagnetic background at high $B$ field.

7.4.3 Magnetization curve of the precursors

To exclude the possible reason that ferromagnetic impurities cause the magnetic response after encapsulation, we measured the magnetization curves of the precursors prior to the encapsulation process. Figure 7.13 shows three magnetization curves measured at 20 K. The ones of FeCl$_3$ and BMIM[FeCl$_4$] are almost identical to each other, demonstrating that the paramagnetic nature of ionic liquid is conveyed by Fe$^{3+}$ in FeCl$_4^-$ anion. In addition, no hysteresis was found to the best of experiment resolution, which eliminated the possibility of ferromagnetic impurity contamination from the results. On the other hand, SBA-15 silica template shows weaker diamagnetic behavior that cannot contribute much to the magnetization of encapsulated product.

To exclude the possibility of BMIM[FeCl$_4$] degradation during heating and form ferromagnetic impurity, we measured the PIL heated in the air at 120 °C and sample showed identical behavior as Figure 7.13b.

Figure 7.13 Magnetization curve of anhydrous FeCl$_3$ (a), as-synthesized BMIM[FeCl$_4$] (b) and SBA-15 silica template (c) at 20 K.
7.4.4 Low temperature differential scanning calorimetry

Phase transitions of PIL after encapsulated in SBA-15 nanopores can be reflected in the differential scanning calorimetry measurement. We determined that the melting temperature $T_m$ of pure BMIM[FeBr$_4$] is about 0 °C. After encapsulation, $T_m$ of the composite material PIL@SBA-15 increases to 35 °C. This indicates that the new form of PIL possesses a much better thermal stability (Fig. 7.14).

The melting temperature of ionic liquids is the combination effect of the electrostatic Coulomb interaction, hydrogen bonding and van der Waals forces. SBA-15 templates offer atomically thin one-dimensional channels that restrict the ionic orientation [11]. The enhancement of the inter-molecular interaction increases the stability of the encapsulated PIL.

![Graph](image1.png)

**Figure 7.14** Low temperature differential scanning calorimetry curve for BMIM[FeCl$_4$] before (in blue) and after (in red) encapsulated into SBA-15 template.

7.4.5 Raman spectrum of PIL@SBA-15

![Graph](image2.png)

**Figure 7.15** Raman spectrum of PIL@SBA-15 taken without polarizer. The sample shows strong photoluminescence and the fringes at low wavenumbers are due to the interference of light.
We attempted to resolve the change of molecular vibrations after encapsulated in SBA-15, however, due to the strong photoluminescence (PL) of mesoporous SiO₂, we are not able to recognize the peaks of PIL from the strongly enhanced background. The PL signal of SiO₂ nanotubes has been reported by others [12, 13].

### 7.4.6 Plausible explanation of one-dimensional ferromagnetism

Because of high uniaxial magnetic anisotropy, one-dimensional (1D) magnets are attracted growing interests in information storage area. 1D magnets are often based on organic molecules [14, 15]. Single chain magnets of inorganic compounds promise to have stronger exchange interaction. However, The inorganic supramolecules are easily aggregated and form 3D structure.

Considering the distances between two nearest magnetic centers (Fe³⁺) are in the order of 10 Å, pristine BMIM[FeCl₄] show no magnetic exchange interaction and behaves as paramagnet. However, a similar molecule 1-ethyl-3-methylimidazolium tetrachloroferrate (EMIM[FeCl₄]) shows antiferromagnetism below 4 K, which is due to the Fe-Cl–Cl-Fe super-exchange pathway [16]. Because of the smaller chain length of the organic cation (from butyl- to ethyl-), the antiferromagnetic interaction is stronger in EMIM[FeCl₄] and can be measured at relatively high temperature. There has been study of pressure-induced three-dimensional long-range magnetic ordering in EMIM[FeCl₄] under high pressure. It was found that under intermediate pressure (0.3 GPa < P < 1 GPa), the sample showed ferromagnetism; while above or below the pressure, the sample showed antiferromagnetism [9].

It is worth noting that the surface of SiO₂ is terminated by -OH group, which could react with FeCl₄⁻. In the end, FeCl₄⁻ will be reduced to Fe²⁺Cl₃⁻ (Fig. 7.16a). However, Fe²⁺Cl₃⁻ is not stable and behaves as a Lewis base. It is very likely that Fe²⁺Cl₃⁻ will bond with Fe₃⁺Cl₄⁻ to form a dimer in order to lower the negative charge (Fig. 7.16b). Formation of dimer Fe₂Cl₇⁻, a discrete form of FeₓCl₇, with both Fe³⁺ and Fe²⁺ is the building block of the 1D ferromagnetic chain. To our knowledge, same single chain ferromagnetism has also been reported for (H₂melamine)₂[FeCl₅]Cl [17].

Fe³⁺ has the high-spin state, with the crystal field of both t₂g and e₈ orbitals half-occupied. Mediated by the Cl⁻, the electron of Fe³⁺ can hop to Fe²⁺ with the spin direction preserved. This is due to the **Hund rule** (first), and Pauling exclusion principle. This indirect exchange interaction is called the **double-exchange** mechanism and couples the spin of two Fe ions with different valence states (Fig. 7.16c).
7.5 Summary

Encapsulation of paramagnetic ions inside nanostructures is capable of inducing long range magnetic ordering. The BMIM[FeCl₄] encapsulated SBA-15 silica template with pore size of 5 nm shows hints of ferromagnetic ordering at low temperature. The ferromagnetic state has been evidenced by the magnetic susceptibility measurement, which shows deviation from the Curie’s law for paramagnetism. Magnetization curve at 20 K shows hysteresis loop after subtracting the paramagnetic background. Low temperature DSC measurement further supports the enhanced inter-molecular interaction with increased melting temperature. Possibilities of ferromagnetic impurity contamination are excluded, where precursors show no divergence from the linear field dependence of magnetization. We ascribed the emergent magnetic ordering as a result of double-exchange mediated through Fe³⁺–Cl–Fe²⁺, resulted in one-dimensional ferromagnetic chain.
7.6 References


