Supporting Information

From paramagnetic to superparamagnetic ionic liquid/poly(ionic liquid): the effect of $\pi-\pi$ stacking interaction

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Contents

General experiment

1. Synthesis of the MILs and PMILs

2. NMR analyses of all the compounds


4. GPC of PTMBBDI[Cl]

5. Mass spectra of compounds

6. Raman spectra

7. Thermal and optical property

8. XRD spectra and molecule structure

9. Magnetic behavior

References
**General experiment**

**Materials** 3a,4,7,7a-Tetrahydro-1H-4,7-methanoisoindole-1,3(2H)-dione (98%) was purchased from Huateng Technology; 1,4-dibromobutane (98%) and 1,10-dibromodecane (99%) were purchased from Damas-Beta; 4,4’-biphenol (99%) and N-methyl imidazole (99%) were purchased from Heowns Biochem; potassium iodide (KI) (99%), ethyl vinyl ether (EVE) (98%) and ferroferric oxide (99%, metals basis, 20 nm, spherical) were purchased from Aladdin Industrial. Ionic exchange resin (IRA-400Cl) was purchased from Alfa-Aesar. All of these reagents were used as received without further purification. The Grubbs third generation catalyst (G3) was prepared according to the procedures reported. All the solvents (N,N-Dimethylformamide (DMF), dichloromethane (DCM), tetrahydrofuran (THF), acetone, hydrochloric acid (HCl), petroleum ether, ethyl acetate and methanol) used were purchased from Yuanli Chemical and dried before usage if necessary. All non-aqueous reactions were carried out in oven-dried glassware under nitrogen atmosphere. Column chromatograph was performed on silica gel (200-300 mesh).

**Instrumentation** $^1$H and $^{13}$C NMR spectra were recorded on a VARIAN INOVA 500MHz spectrometer ($^1$H = 500 MHz, $^{13}$C = 126 MHz) and a Bruker AVANCE III 400MHz spectrometer ($^1$H = 400 MHz, $^{13}$C = 101 MHz) at 298 K. Chemical shifts in $^1$H NMR spectra were reported in ppm on the $\delta$ scale from an internal standard of TMS. The following abbreviations were used to explain the multiplicities in $^1$H NMR: s = singlet, d
= doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = doublet of doublet of doublets, m = multiplet, br = broad. Mass spectra were conducted on Bruker-1290 UPLC/micrOTOF-Q II or Bruker-Autoflex tof/tofIII-MALDI-TOF instruments. Raman spectrum was carried out on Renishaw-inVia reflex using a 785 nm excitation wavelength. Polydispersity index (PDI= Mw/Mn) of the synthesized polymers was determined using a gel permeation chromatography (GPC) consisting of a Waters 1515 isocratic HPLC pump, a Waters 2414 refractive index detector and three Waters columns (Styrage HT3, Styrage HT4, Styrage HT5). Freshly DMF with 50 mmol/L bistrifluoromethanesulfonimide lithium (LiTf$_2$N) salt served as the mobile phase and was delivered at a flow rate of 1.0 mL/min. Sample concentrations were ca. 8 mg of polymer/mL of DMF, and the injection volume was 50 μL. At room temperature, X-Ray diffraction data was record on a Rigaku D/MAX-2500 diffractometer, using monochromatic Cu K$_\alpha$ radiation ($\lambda$=1.5418 Å). While, X-Ray diffraction test at liquid nitrogen temperature was carried out on a GANESA 300XL+ system, using monochromatic Cu K$_\alpha$ radiation ($\lambda$=1.5418 Å). XRD spectrum was analyzed by using Jade 6 software, and XRD spectrum simulation was given by Materials Studio 8.0 software. Thermal gravity analysis (TGA) was performed on TA-Q800 and the heating rate was 10 °C/min. The differential scanning calorimetry (DSC) measurement was performed on TA-Q2000. The heating rate of DSC was 10 °C/min and the data adopted came from the second temperature-rise period. Both TGA and DSC measurements were conducted under nitrogen atmosphere. Polarizing optical microscope (POM) observations
were carried out via Nikon ECLIPSE LV100N POL and the heating rate was 1 °C/min when observing. Magnetic properties measurements were performed using a Quantum Design VSM magnetometer utilizing a superconducting quantum interference device (SQUID) method. The samples of MIL and PMIL were measured after putting them in a Teflon capsule directly. DC magnetic susceptibility measurements were performed under applied magnetic fields from 10 kOe while heating from 3K to 300 K, after cooling either in the presence (field cooling, FC) or the absence (zero field cooling, ZFC) of applied field. Magnetization (M) as a function of magnetic field (H) was also measured in the −10 ≤ H (kOe) ≤ 10 range at several temperatures from 3K to 380K.

Scheme S1. Synthetic routes for TMBBDI[FeCl₄] and PTMBBDI[FeCl₄].
**Table S1.** The abbreviations and system nomenclatures of all compounds.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>System nomenclature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound 1</td>
<td>2-(4-bromobutyl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoisoindole-1,3(2H)-dione</td>
</tr>
<tr>
<td>Compound 2</td>
<td>2-(4-((4′-hydroxy-[1,1′-biphenyl]-4-yl)oxy)butyl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoisoindole-1,3(2H)-dione</td>
</tr>
<tr>
<td>Compound 3</td>
<td>2-(4-((4′-((10-bromodecyl)oxy)-[1,1′-biphenyl]-4-yl)oxy)butyl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoisoindole-1,3(2H)-dione</td>
</tr>
<tr>
<td>TMBBDI[Cl]</td>
<td>3-(10-((4′-(4-(1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2H-4,7-methanoisoindol-2-yl)butoxy)-[1,1′-biphenyl]-4-yl)oxy)decyl)-1-methyl-1H-imidazol-3-ium chloride</td>
</tr>
<tr>
<td>TMBBDI[FeCl₄]</td>
<td>3-(10-((4′-(4-(1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2H-4,7-methanoisoindol-2-yl)butoxy)-[1,1′-biphenyl]-4-yl)oxy)decyl)-1-methyl-1H-imidazol-3-ium iron(III) chloride</td>
</tr>
<tr>
<td>BTM</td>
<td>2-(10-bromodecyl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoisoindole-1,3(2H)-dione</td>
</tr>
<tr>
<td>HMI[Cl]</td>
<td>3-(10-(1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2H-4,7-methanoisoindol-2-yl)decyl)-1-methyl-1H-imidazol-3-ium chloride</td>
</tr>
<tr>
<td>HMI[FeCl₄]</td>
<td>3-(10-(1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2H-4,7-methanoisoindol-2-yl)decyl)-1-methyl-1H-imidazol-3-ium iron(III) chloride</td>
</tr>
</tbody>
</table>
1. Synthesis of the MILs and PMILs

1.1 Synthesis of compound 1

1,4-Dibromobutane (13.2190 g, 60 mmol) and potassium carbonate (6.9803 g, 50 mmol) were added to a 250 mL round-bottom flask. Then, 3a,4,7,7a-Tetrahydro-1H-4,7-methanoisoindole-1,3(2H)-dione (1.6651 g, 10 mmol) was dissolved in 100 mL DMF, and added to the flask dropwisely. The reaction was stirred for 24 h at room temperature. The resulting mixture was filtrated and the filtrate was evaporated under reduced pressure to remove the solvent. The residue was dissolved in dichloromethane (100 mL) and extracted with water (50 mL×3). The organic layer was collected and dried over MgSO₄. Then the solvent was removed via rotary evaporation. The crude product was purified with column chromatography (silica gel, petroleum ether/ethyl acetate 6/1) to give the compound 1 as a white needle-like powder. (Yield 74%)

\[ ^{1}H \text{ NMR (500 MHz, CDCl}_3) \delta \text{ (ppm)} \] 6.12 (t, \( J = 1.8 \text{ Hz}, 2 \text{H})
3.38 (ddd, \( J = 14.1, 7.0, 4.8 \text{ Hz}, 6 \text{H})
3.29-3.22 (m, 2H)
1.84-1.71 (m, 3H)
1.66-1.51 (m, 3H);

\[ ^{13}C \text{ NMR (126 MHz, CDCl}_3) \delta \text{ (ppm)} \] 177.61, 134.50, 52.26, 45.73, 44.89, 37.29, 32.72, 29.88, 26.42.

1.2 Synthesis of compound 2

4,4′-Biphenol (4.7023 g, 25 mmol), potassium carbonate (6.9803 g, 50 mmol), potassium
iodide (83.0 mg, 0.5 mmol) and catalytic amounts of 18-crown-6 were dissolved in 30 mL of acetone. Then, the mixture had refluxed for 30 minutes. Compound 1 (1.4909 g, 5 mmol) was dissolved in 30 mL acetone, and added to the mixture dropwise. The reaction was refluxed for 24 h. The resulting mixture was transferred into 100 mL of water and acidified with 35% HCl aqueous solution until pH = 5-6. Then, the mixture was extracted with ethyl acetate (50 mL×3). The organic layer was collected and dried over MgSO₄, and the solvents were removed via rotary evaporation. The crude product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate 2/1) to give compound 2 as a white powder. (Yield 50%)

1H NMR (500 MHz, CDCl₃) δ (ppm) 7.42 (ddd, J = 9.5, 5.8, 2.4 Hz, 4H), 6.95-6.85 (m, 4H), 6.11 (t, J = 1.7 Hz, 2H), 3.97 (t, J = 6.1 Hz, 2H), 3.43 (t, J = 7.2 Hz, 2H), 3.40 (m, 2H), 3.26 (dd, J = 2.8, 1.5 Hz, 2H), 1.79-1.71 (m, 3H), 1.70-1.62 (m, 2H), 1.55 (d, J = 8.8 Hz, 1H);

13C NMR (126 MHz, CDCl₃) δ (ppm) 178.18, 157.95, 155.06, 134.49, 133.50, 133.27, 127.86, 127.62, 115.56, 114.78, 67.21, 52.30, 45.81, 44.95, 38.16, 26.67, 24.59.

1.3 Synthesis of compound 3

Compound 2 (403.5 mg, 1 mmol), 1,10-dibromodecane (6.0622 g, 20 mmol) and potassium carbonate (150.0 mg, 1 mmol) were dissolved in 20 mL of acetone at a 100 mL round-bottom flask, which equipped with a spherical condenser. Then, the mixture was refluxed for 24 h. After reaction, the resulting mixture was transferred into ethyl acetate (50 mL) and extracted with water (50 mL×3). The organic layer was collected and
dried over MgSO₄, and the solvents were removed via rotary evaporation. The crude product was purified by column chromatography (silica gel, petroleum ether and petroleum ether/ethyl acetate 2/1) to give the compound 3 as a white powder. (Yield 85%)

1H NMR (500 MHz, CDCl₃) δ (ppm) 7.45 (d, J = 8.6 Hz, 4H), 6.93 (t, J = 9.2 Hz, 4H), 6.11 (s, 2H), 3.98 (q, J = 6.2 Hz, 4H), 3.46-3.36 (m, 6H), 3.28-3.22 (m, 2H), 1.89-1.83 (m, 2H), 1.79 (dd, J = 14.7, 6.9 Hz, 2H), 1.76-1.71 (m, 3H), 1.69-1.61 (m, 2H), 1.54 (d, J = 8.7 Hz, 1H), 1.46 (ddd, J = 18.4, 10.8, 4.9 Hz, 4H), 1.34 (d, J = 21.3 Hz, 6H).

13C NMR (126 MHz, CDCl₃) δ (ppm) 177.87, 158.39, 158.13, 134.62, 133.66, 133.45, 127.81, 114.91, 114.90, 68.21, 67.36, 52.41, 45.91, 45.08, 38.21, 34.18, 32.98, 29.60, 29.51, 29.49, 29.46, 28.90, 28.32, 26.87, 26.20, 24.76.

HRMS (ESI) calculated for C₃₅H₄₄NO₄Br (for [M⁺+Na], based on 100% abundance of ⁷⁹Br), 644.2351; found, 644.2345

1.4 Synthesis of TMBBDI[Cl]

Compound 3 (155.7 mg, 0.25 mmol) and catalytic amounts of potassium iodide were dissolved in 20 mL of acetone in a 50 mL round-bottom flask. Then N-methyl imidazole (250 μL, 3.10 mmol) was added to the solution. The mixture was refluxed for 48 h. After reaction, the product was concentrated by rotary evaporation before processing. The concentrated solution was precipitated with excess diethyl ether for three times. After washing with a small amount of water and diethyl ether, a white solid product was given. (Yield 100%)
The solid obtained above (TMBBDI[I]) was dissolved in DMF/water (3:2 v/v). 5g ionic exchange resin (IRA-400Cl) was put into the solution (the resin was washed by DMF and water mixed solution until the washing-solution became colorless) and stirred at room temperature for 12h. After reaction, the product was concentrated through reduced pressure distillation. The concentrated solution was precipitated with excess diethyl ether for three times. After vacuum drying, TMBBDI[Cl] (3-(10-((4'-((4-(1,3-dioxo-3a,4,7,7a-tetrahydro-1H-4,7-methanoisoindol-2(3H)-yl)butoxy)-[1,1'-biphenyl]-4-yl)oxy)decyl)-1-methyl-1H-imidazol-3-ium chloride) was given as a white solid. (Yield 100%)

$^1$H NMR (500 MHz, DMSO-d$_6$) $\delta$ (ppm) 9.29 (s, 1H), 7.80 (s, 1H), 7.73 (s, 1H), 7.49 (d, $J = 8.7$ Hz, 4H), 6.94 (dd, $J = 8.7$, 1.9 Hz, 4H), 6.02 (s, 2H), 4.15 (t, $J = 7.2$ Hz, 2H), 3.95 (q, $J = 6.1$ Hz, 6H), 3.84 (s, 3H), 3.31 (s, 2H), 3.25 (t, $J = 7.0$ Hz, 2H), 3.22 (s, 2H), 1.77 (m, 2H), 1.72-1.66 (m, 2H), 1.60 (m, 2H), 1.55-1.45 (m, 4H), 1.39 (m, 2H), 1.26 (m, 10H).

$^{13}$C NMR $\delta$ (ppm): (126 MHz, DMSO-d$_6$) $\delta$ 178.16, 158.36, 137.17, 135.01, 132.95, 132.87, 127.85, 124.27, 122.94, 115.53, 115.49, 68.15, 67.60, 52.48, 49.46, 45.89, 44.94, 37.98, 36.48, 30.07, 29.75, 29.44, 29.42, 29.38, 29.03, 26.81, 26.20, 26.17, 24.76.

High resolution MALDI-TOF-MS calculated for [C$_{39}$H$_{50}$N$_3$O$_4$]$^+$ (based on 100% abundance of $^{79}$Br): 624.3801, found: 624.4590.

1.5 Synthesis of TMBBDI[FeCl$_4$]

TMBBDI[Cl] (33.0 mg, 0.05 mmol) was dissolved in 6 mL methanol in a 25 mL
round-bottom flask. Equal equivalence FeCl$_3$·6H$_2$O (13.5 mg, 0.05 mmol) was added into the solution and stirred at 45 °C for 24h. After reaction, the product was concentrated by rotary evaporation. The concentrated solution was precipitated with excess diethyl ether for three times. After vacuum drying, TMBBDI[FeCl$_4$] was given as a brown solid. (Yield 100%)

1.6 Synthesis of PTMBBDI[FeCl$_4$]

TMBBDI[Cl] (66.0 mg, 0.10 mmol) was dissolved in a mixed solvent containing 250 µL DMF and 150 µL deionized water under inert atmosphere. G3 catalyst (1.5 mg, 2.00×10$^{-3}$ mmol) was dissolved in 50 µL DMF. Then, the TMBBDI[Cl] was injected into the catalyst solution under an inert atmosphere. The polymerization was conducted for 5h at room temperature. After reaction, ethyl vinyl ether (EVE) 0.5 mL was added into this system to terminate the reaction. The solution was precipitated with excess diethyl ether for three times. After vacuum drying, a brown solid product was given.

$^1$H NMR (500 MHz, CDCl$_3$) δ (ppm) 9.36 (broad, 1H), 7.80 (broad, 1H), 7.74 (broad, 1H), 7.37 (broad, 4H), 6.86 (broad, 4H), 5.27-5.15 (broad, 2H), 4.13 (broad, 2H), 3.84 (broad, 7H), 3.30-2.99 (broad, 6H), 1.73 (broad, 4H), 1.68-1.42 (broad, 6H), 1.33 (broad, 2H), 1.21 (broad, 10H).

PTMBBDI[Cl] (33.0 mg) was dissolved in 6 mL methanol at a 25 mL round-bottom flask. Taking the repeat unit as reference, equal equivalence of FeCl$_3$·6H$_2$O (13.5 mg, 0.05 mmol) was added into the solution and kept the reaction for 24h at 60 °C. After reaction, the product was concentrated by rotary evaporation. The concentrated solution was
precipitated with excess diethyl ether for three times. After vacuum drying, PTMBBDI[FeCl₄] was obtained as a brown solid product.

\[
\begin{align*}
\text{HMI[Br]} & \xrightarrow{\text{IRA-400Cl}} \text{HMI[Cl]} \\
\text{PHMI[Cl]} & \xrightarrow{\text{FeCl₃·6H₂O}} \text{PHMI[FeCl₄]}
\end{align*}
\]

**Scheme S2.** Synthetic route for PHMI[FeCl₄].

1.7 **Synthesis of BTM**

1,10-Dibromodecane (18.0500 g, 60 mmol) and potassium carbonate (6.9803 g, 50 mmol) were added to a 250 mL round-bottom flask. Then, 3a,4,7,7a-tetrahydro-1H-4,7-methanoisoindole-1,3(2H)-dione (1.6651 g, 10 mmol) was
dissolved in 100 mL DMF, and added to the flask dropwisely. The reaction was stirred for 24 h at 60°C. The resulting mixture was filtrated and the filtrate was evaporated under reduced pressure to remove the solvent. The residue was dissolved in dichloromethane (100 mL) and extracted with water (50 mL×3) was added to the solution. The organic layer was collected and dried over MgSO₄, and the solvents were removed via rotary evaporation. The crude product was purified with column chromatography (silica gel, petroleum ether/ethyl acetate 5/1) to give the BTM as a colorless oil product. (Yield 82%)

1H NMR (400 MHz, CDCl₃) δ (ppm) 6.10 (s, 2H), 3.44 – 3.38 (m, 4H), 3.35 – 3.30 (m, 2H), 3.25 (d, J = 1.4 Hz, 2H), 1.91 – 1.81 (m, 2H), 1.74 (d, J = 8.7 Hz, 1H), 1.55 (d, J = 8.7 Hz, 1H), 1.49 – 1.20 (m, 14H).

13C NMR (101 MHz, CDCl₃) δ (ppm) 177.75, 134.39, 52.20, 45.70, 44.88, 38.40, 34.03, 32.80, 29.32, 29.29, 29.04, 28.67, 28.12, 27.76, 26.82.

1.8 Synthesis of HMI[Cl]

BTM (1.1470 g, 3 mmol) was dissolved in 20 mL of THF in a 50 mL round-bottom flask. Then N-methyl imidazole (750 µL, 9.30 mmol) was added to the solution. The mixture was refluxed for 48 h. After reaction, the product was concentrated by rotary evaporation before processing. The concentrated solution was precipitated with excess diethyl ether for three times. Finally, a faint yellow oil product was given. (Yield 100%)

The product obtained above was dissolved in methanol. 10g ionic exchange resin (IRA-400Cl) was put into the solution (the resin was washed by methanol until it became
colorless) and stirred at room temperature for 12h. After reaction, the product was concentrated through reduced pressure distillation. The concentrated solution was precipitated with excess diethyl ether for three times. After vacuum drying, white HMI[Cl] was given. (Yield 100%)

\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \delta (\text{ppm}) 10.85 (s, 1H), 7.29 (s, 1H), 7.22 (s, 1H), 6.08 (s, 2H), 4.31 (t, J = 5.8 Hz, 2H), 4.13 (s, 3H), 3.38 (s, 2H), 3.30 (t, J = 4.9 Hz, 2H), 3.24 (s, 2H), 1.73 (d, J = 7.0 Hz, 1H), 1.53 (d, J = 7.0 Hz, 1H), 1.44 – 1.16 (m, 16H).

\[ \text{C NMR (101 MHz, CDCl}_3\text{)} \delta (\text{ppm}) 177.81, 138.21, 134.39, 123.31, 121.56, 52.21, 50.12, 45.71, 44.87, 38.36, 36.66, 30.26, 29.19, 29.15, 28.92, 28.86, 27.69, 26.74, 26.17.

1.9 Synthesis of HMI[FeCl₄]

HMI[Cl] (84.0 mg, 0.2 mmol) was dissolved in 6 mL methanol in a 25 mL round-bottom flask. Equal equivalence FeCl₃·6H₂O (54.0 mg, 0.2 mmol) was added into the solution and stirred at 45 °C for 24h. After reaction, the product was concentrated by rotary evaporation. The concentrated solution was precipitated with excess diethyl ether for three times. After vacuum drying, HMI[FeCl₄] was given as a brown ropy liquid. (Yield 100%)

1.10 Synthesis of PHMI[FeCl₄]

HMI[Cl] (84.0 mg, 0.2 mmol) was dissolved in 200 μL dichloromethane. G3 catalyst (2.9 mg, 4.00×10⁻³ mmol) was dissolved in 100 μL dichloromethane. Then, the HMI[Cl] was injected into the catalyst solution. And, the polymerization was conducted for 0.5h at room temperature. After reaction, ethyl vinyl ether (EVE) 0.5 mL was added into this
system to terminate the reaction. The solution was precipitated with excess diethyl ether for three times. After vacuum drying, a brown solid product was given.

The obtained PHMI[Cl] was dissolved in 15 mL methanol at a 50 mL round-bottom flask. Take the repeat unit as reference, equal equivalence of FeCl$_3$·6H$_2$O (54.0 mg, 0.2 mmol) was added into the solution and kept the reaction for 24h at 60 °C. After reaction, the product was concentrated by rotary evaporation. The concentrated solution was precipitated with excess diethyl ether for three times. After vacuum drying, PHMI[FeCl$_4$] was obtained as a brown solid product.
2 NMR analyses of all the compounds

2.1 Preparation of magnetic monomer TMBBDI[FeCl₄]

Briefly, compound 1 was prepared from 3a,4,7,7a-Tetrahydro-1H-4,7-methanoisoindole-1,3(2H)-dione and 1,4-dibromobutane. To introduce a mesogenic unit, compound 1 and 4,4'-biphenol were reacted by a S_N2 reaction. Then the compound 3 could also be obtained by a S_N2 reaction from compound 2 and 1,10-dibromodecane. Through a quaternization with 1-methylimidazole under potassium iodide and the ion exchange reaction using chloride ion exchange resin, compound 3 could translate into TMBBDI[Cl]. This polymerizable monomer was characterized by NMR and the spectra were given below. Other intermediate products involved in the process of synthesis were unambiguously characterized by ^1H and ^13C NMR and the results were also given. The signals of all the protons and carbon nuclei were completely interpreted reasonably. The cation of TMBBDI[Cl] ([C_{39}H_{50}N_{3}O_{4}]^+) was also verified by MALDI-TOF-MS which showed a m/z of 624.4590, close to the calculated value 624.3801.

2.2 Preparation of magnetic polymer PTMBBDI[FeCl₄]

In this paper, magnetic polymer TMBBDI[FeCl₄] was prepared by the post-modification method of PTMBBDI[Cl] to avoid the catalyst poisoning via direct polymerization of
TMBBDI[FeCl₄].

From the –¹H NMR test result, all the signals showed typically broad peaks of polymer. Compared with the monomer TMBBDI[Cl], the signal at 6.03 ppm which assigned to the double bond in the norbornene disappeared, and new broad peaks at the range of 5.21-5.60 ppm were assigned to the protons from the double bond in the polymer main chain. The degree of polymerization (DP) could be calculated from –¹H NMR by comparing the double bond signals in before and after the polymerization and the value was 50.

**Figure S1.** –¹H NMR of compound 1 in CDCl₃.
Figure S2. $^1$H NMR of compound 2 in CDCl$_3$.

Figure S3. $^1$H NMR of compound 3 in CDCl$_3$. 
Figure S4. $^1$H NMR of TMBBDI[Cl] in DMSO-$d_6$.

Figure S5. $^{13}$C NMR of compound 1 in CDCl$_3$. 
Figure S6. $^{13}$C NMR of compound 2 in CDCl$_3$.

Figure S7. $^{13}$C NMR of compound 3 in CDCl$_3$. 
**Figure S8.** $^{13}$C NMR of TMBBDI[Cl] in DMSO-$d_6$.

**Figure S9.** $^1$H NMR of PTMBBDI[Cl] in DMSO-$d_6$. 
2.3 Preparation of reference magnetic polymer PHMI[FeCl₄]

PHMI[FeCl₄] was prepared as reference in this paper. Compared with magnetic polymer PTMMBDI[FeCl₄], the structure of PHMI[FeCl₄] didn’t contain biphenyl units, which could insured that the physics behaviors cannot affect by the π–π stacking interaction. From the ¹H NMR test result, the signals of intermediates and polymer were reasonably assigned. Compared with the PTMMBDI[Cl] (Figure S4), the signals of biphenyl units were disappeared. Also, the integration areas between 1 to 4 ppm were decreased assigned to the space between norbornene and biphenyl removed. In order to exclude the impact of molecule weight, degree of polymerization was also controlled to 50.

![Chemical structure of BTM in CDCl₃](image)

**Figure S10.** ¹H NMR of BTM in CDCl₃.
Figure S11. $^1$H NMR of HMI[Cl] in CDCl$_3$.

Figure S12. $^{13}$C NMR of BTM in CDCl$_3$. 
Figure S13. $^{13}$C NMR of HMI[Cl] in CDCl$_3$.

Figure S14. $^1$H NMR of PHMI[Cl] in CDCl$_3$. 
3 Kinetics for TMBBDI[Cl] polymerization

TMBBDI[Cl] (99.1 mg, 0.15 mmol) was dissolved in a mixed solvent containing 375 μL DMF and 225 μL deionized water under inert atmosphere. G3 catalyst (2.2 mg, 3.00×10⁻³ mmol) was dissolved in 50 μL DMF. Then, the TMBBDI[Cl] was injected into the catalyst solution under an inert atmosphere. Samples were taken at different interval times and added to a vial containing 0.5 mL EVE to terminate the reaction. The solution was precipitated with excess diethyl ether for three times and the conversion rate was analyzed via ¹H NMR.

Kinetic studies were operated by taking samples at different intervals. As calculated from the area of double bond of both monomer and polymer, the conversion of TMBBDI[Cl] was obtained, and thus the DP at different intervals was calculated. As shown in Figure S15, the DP of PTMBBDI[Cl] increased linearly with the extension of reaction time, which certified the living polymerization of TMBBDI[Cl] catalyzed by G3 catalyst.

![Figure S15. Polymerization kinetics of PTMBBDI[Cl].](image)

Figure S15. Polymerization kinetics of PTMBBDI[Cl].
4 GPC of PTMBBDI[Cl]

Gel Permeation Chromatography (GPC) characterization of the polyelectrolyte was also operated via the strategy reported by Matyjaszewski’s group. As shown in Figure S16, the peak was mainly symmetric with a PDI was 1.26 and a molecular weight ($M_n$) was 57.2 kDa.

Figure S16. GPC trace of PTMBBDI[Cl].
5 Mass spectra of compounds

Figure S17. HRMS of [compound 3+Na⁺] (Calcd m/z: 644.24, found m/z: 644.23).

Figure S18. MALDI-TOF-MS of [TMBBDI]⁺ with a HCCA matrix (Calcd m/z: 624.38, found m/z: 624.46).
6 Raman spectra

Magnetic monomer and magnetic polymer were prepared by complexing Cl-containing poly(ionic liquid)s with FeCl$_3$ and precipitated in diethyl ether until the solution was colorless for further purification. Magnetic anion FeCl$_4^-$ can be observed from Raman spectra as shown in Figure 1c. The 785 nm laser was used as the excitation source in order to avoid fluorescence from impurities. The sharp peaks appeared at 334 cm$^{-1}$ in the spectra were assigned to the symmetric Fe-Cl bond stretching vibrations of FeCl$_4^-$. The peaks at 134 cm$^{-1}$ in the spectrum were assigned to the Fe-Cl bond bending vibrations. Thus, it can be confirmed that the tested samples contain FeCl$_4^-$ anions.

To exclude the presence of iron-based metal oxides, the Raman spectra of Fe$_2$O$_3$ and Fe$_3$O$_4$ were tested. Their characteristic peaks are located at 226, 295, 409 and 497 cm$^{-1}$ for Fe$_2$O$_3$ and 696 cm$^{-1}$ for Fe$_3$O$_4$. 
7 Thermal and optical property

After the structural confirmation, we measured the thermal properties and optical properties of the poly(ionic liquid)s. Thermal gravity analysis (TGA) data showed that all of the magnetic compounds decomposed at about 300 °C. Figure S21 showed the differential scanning calorimetry (DSC) measurements of magnetic monomer and polymer. It was confirmed three small broad peaks in DSC profiles on the heating scan of
the measurement. And the three peaks were assigned to glass transition temperature \((T_g)\), liquid crystal transition temperature \((T_i)\) and melting temperature \((T_m)\). Compared with polymer, the small molecule magnetic ionic liquid TMBBDI[FeCl\(_4\)] had much lower transition temperature. The melting temperature was 29 °C corresponding to the macro-phenomena that the TMBBDI[FeCl\(_4\)] shows a molten state at room temperature. While the transition temperature of polymer increased obviously owing to the rigidity main chain and high molecule weight. In consequence, at the temperature ranges, 20-30°C for TMBBDI[FeCl\(_4\)] and 95-133°C for PTMBBDI[FeCl\(_4\)] respectively, materials showed typical mesomorphic phenomena. In contrast, samples containing no biphenyl showed only typical thermal transition, a melting peak at -26 °C of HMI[FeCl\(_4\)] and glass transition temperature at 12°C of PHMI[FeCl\(_4\)].

Polarizing optical microscope observation was conducted in the transition ranges after DSC measurements. With temperature increasing at a 1 K/min speed, a blue paillette of TMBBDI[FeCl\(_4\)] was observed in a temperature range 28-36°C associated with blue phases which were types of liquid crystal phases that appeared in a temperature range between a chiral nematic phase and an isotropic liquid phase (Figure S22). The blue phase temperature was a little higher than the melting point measured by DSC might be generated by hysteresis.\(^7\)\(^-\)\(^9\) Similar textures were also been record when observed PTMBBDI[FeCl\(_4\)] (Figure S22) while much weaker. The range of a blue phase was higher than monomer and appeared in 93-120°C which was consistent with the DSC results.
Figure S20. TGA diagrams of TMBBDI[FeCl₄], PTMBBDI[FeCl₄], HMI[FeCl₄] and PHMI[FeCl₄].

Figure S21. DSC diagrams of (A) TMBBDI[FeCl₄], (B) PTMBBDI[FeCl₄], (C) HMI[FeCl₄] and (D) PHMI[FeCl₄] with a heating rate of 10 °C/min.
Figure S22. Polarized optical micrographs of TMBBDI[FeCl₄] (A) dark field at 19 °C; (B) blue phase texture at 30 °C; and PTMBBDI[FeCl₄] (C) dark field at 71 °C; (D) blue phase texture at 116 °C.

8 XRD spectra and molecule Structure

When the XRD spectrum of TMBBDI[FeCl₄] was expressed by the momentum transfer vector (q) (Figure S23) which q satisfies the equation $q = (4\pi/\lambda) \sin \theta$,¹⁰ the first three diffraction peaks approximately had 1: 2: 3 relationships, which were in agreement with q to 3q. It implied that a characteristic lamellar structure was developed.¹¹
Figure S23. X-ray diffraction patterns (room temperature) of TMBBDI[FeCl₄] expressed by the momentum transfer vector (q).

According to the result got through the XRD date, it was given an approximate molecular arrangement in Figure S24. It should be a single layer structure.
Figure S24. Possible molecular arrangement of TMBBDI[FeCl₄].
**Figure S25.** X-ray diffraction pattern (room temperature) of PTMBBDI[FeCl₄].

**Figure S26.** X-ray diffraction pattern (room temperature) of HMI[FeCl₄].
Figure S27. X-ray diffraction pattern (room temperature) of PHMI[FeCl$_4$].

9 Magnetic behavior

Figure S28. Enlarged M-H curves of (a), (b) TMBBDI[FeCl$_4$] and (c), (d) PTMBBDI[FeCl$_4$] at 300K and 380K.
**Figure S29.** Enlarged M-H curves of ferric oxide doped styrene at different temperature (iron content was the same as TMBBDI[FeCl₄], 6.79%).

**Figure S30.** Temperature dependence of $\chi^*_g T$ for (A) HMI[FeCl₄] and (B) HMI[FeCl₄] at an applied magnetic field of 10k Oe.

**Figure S31.** Time dependence of $\chi^*_g T$ for TMBBDI[FeCl₄] (solid circle) and HMI[FeCl₄] (open circle) at an applied magnetic field of 500 Oe.
References


