Supporting Information

Unexpected Self-assemble, Photoluminescence Behavior, and Film-Forming Properties of Polysiloxane-Based Imidazolium Ionic Liquids Prepared by One-Pot Thiol–ene Reaction

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Experimental

Materials
2,2-Dimethoxy-2-phenylacetophenone (DMPA) was purchased from Aladdin Co. (China) and used as received. 3-Mercaptopropylmethyldimethoxysilane (MPDMS) and Dimethoxydimethylsilane were purchased from Diamond Advanced Material of Chemical Inc. (China) and distilled before use. 1-methylimidazole (98%), allyl bromide, 4-bromobutene, and 5-bromo-1-pentene were provided by Sigma–Aldrich and used as received. Tetrahydrofuran (THF) and toluene were purified according to routine procedure and distilled over sodium before use. PMMS was synthesized according to the previous report.¹

Characterization and measurements
The thiol-ene reaction was irradiated by UV on a Spectroline Model SB–100P/FA lamp (365 nm, 100 w). UV intensity is 4500μW/cm² at a distance of 38 cm. ¹H NMR spectra was recorded on a Bruker AVANCE 400 spectrometer at 25 °C using CDCl₃ as solvent and without tetramethylsilane (TMS) as an interior label. Fourier transform infrared spectra (FT-IR) were recorded on a Bruker TENSOR27 infrared spectrophotometer with KBr pellet technique within the 4000-400 cm⁻¹ region. Luminescence (excitation and emission) spectra of the samples were determined with a Hitachi F-4500 fluorescence spectrophotometer using a monochromated Xe lamp as an excitation source; excitation and emission slits were 5 and 5 nm, respectively. Contact angle was recorded on a Dataphysics OCA-20 contact angle analyzer with distilled water as the test liquid. Scanning electronic microscopy (SEM) images were obtained with Hitachi S-4800 (7 kV). The samples were cut and coated with a thin layer of gold before the investigation. The samples of aggregation behaviors for TEM
were prepared by spreading a drop of aggregate toluene solution on a copper grid followed by air drying at room temperature before the measurement on a JEM-1011 (100 kV) electron microscopy.

**General procedures to synthesize vinyl-functionalized ILs**

Vinyl functionalized **ILs** were synthesized using classical procedure according to the literatures. Considering **NL1** as an example, 1 equiv. of 1-methylimidazole was added dropwise to 1.1 equiv. of allyl bromide in toluene as shown in Scheme 1. Then, the mixture was stirred at 110 °C for 48h. Toluene was removed by using a separatory funnel. In addition, more toluene were used to wash the crude product to remove the unreactants. **NL1** was finally obtained after drying under vacuum.

Data of ILs:

**NL1:** $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 4.04$, 3H; 4.95, 2H; 5.34-5.38, 2H; 5.89-6.00, 1H; 7.47, 1H; 7.65, 1H; 10.13, 1H.

$^{13}$C NMR (CD$_3$OD, 100 MHz): $\delta = 36.55$, 51.57, 122.12, 123.77, 129.82, 136.48, 162.20. Yield: 95%.

**NL2:** $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 2.58$-$2.65$, 2H; 4.03, 3H; 4.39-4.41, 2H; 4.99-5.05, 2H; 5.66-5.80, 1H; 7.26-$7.58$, 2H; 10.20, 1H.

$^{13}$C NMR (CD$_3$OD, 100 MHz): $\delta = 33.98$, 36.33, 48.64, 119.13, 122.29, 123.35, 132.02, 136.47. Yield: 93%.

**NL3:** $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 1.93$-$2.08$, 4H; 4.05, 3H; 4.27-4.30, 2H; 4.96-5.01, 2H; 5.63-5.76, 1H; 7.48, 1H; 7.61, 1H; 10.28, 1H.
\[^{13}\text{C}\] NMR (CD\(_2\)OD, 100 MHz): δ = 29.61, 29.95, 36.46, 48.97, 116.03, 122.17, 123.64, 135.91, 136.46. Yield: 90%.

### 2.4 General procedures to synthesize IL-functionalized polysiloxane (PNLs) by thiol–ene reaction

The synthetic routes for functionalized PMMS (PNLs) are illustrated in Scheme 1. A series of IL-functionalized PMMS (PNLs) (Table 1) were prepared following the similar route. Considering PNL1-1 as an example, 0.20 g (1 mmol) NL1, 0.04 g (0.15 mmol) DMPA, and 1.28 g PMMS were dissolved in dry THF/CH\(_3\)OH vessel. The vessels were placed under UV light irradiation (365 nm, 100 W) with gentle stirring for 15 min at room temperature. Toluene was added to remove DMPA and redundant reactants. PNL1-1 was obtained after solvent evaporation at low pressure, followed by vacuum drying at 60 °C for 24 h. Gel permeation chromatography (GPC) data are listed in Table 1.

**Data of PNL1-1:**

\(^1\text{H}\) NMR (CD\(_3\)OD, 400 MHz): δ = 0.11-0.16, 0.64-0.70, 1.65, 2.23-2.28, 2.55-2.57, 4.11-4.13, 4.50-4.52, 7.41-7.80, 9.90; \[^{13}\text{C}\] NMR (CD\(_3\)OD, 100 MHz): -1.36, 15.80, 23.19, 27.14, 29.05, 34.04, 36.62, 57.00, 122.46, 127.67, 136.72. Yield: 85%.

**Data of PNL2-4:**

\(^1\text{H}\) NMR (CD\(_3\)OD, 400 MHz): δ = 0.11, 0.61-0.67, 1.65, 2.23-2.28, 2.55-2.57, 4.11-4.14, 4.34-4.38, 7.55-7.60, 8.05-8.08; \[^{13}\text{C}\] NMR (CD\(_3\)OD, 100 MHz): 136.80; 124.02; 122.58; 121.14; 118.57; 50.10; 49.01; 48.23; 36.15; 34.18; 29.62; 27.63; 1.02. Yield: 92%.

**Data of PNL3-4:**
$^1$H NMR (CD$_3$OD, 400 MHz): $\delta = 0.11-0.20, 0.62-0.70, 1.64-1.70, 2.03-2.18, 2.53-2.56, 2.68-2.80, 4.10-4.14, 4.47-4.49, 7.46, 7.62, 9.39-9.56$; $^{13}$C NMR (CD$_3$OD, 100 MHz): 10.80, 23.00, 27.78, 29.76, 34.04, 36.07, 79.15, 122.60, 123.89, 136.74. Yield: 88%.

Figure S1. FTIR spectra of PMMS, NL1, and PNL1-3.
Figure S2. $^1$H-NMR of PMMS, NL1, and PNL1-4.

Figure S3. (a) Emission spectra of PNL1s in solid film state, and (b) excitation spectra of PNL1s in solid film state.
Reference
