

Supporting Information

Processable ionogel with thermo-switchable conductivity

Shoujie Shen*^a, Jia Li^a, Qiyu Wu^a, Xingchao Chen^b, Chuao Ma^b, Chan Liu^b, Hongliang Liu*^{b,c}

^a Key Laboratory of Magnetic Molecules and Magnetic Information Materials (Ministry of Education), School of Chemistry and Material Science, Shanxi Normal University, Taiyuan 030031, Shanxi, China

^b School of Chemistry and Chemical Engineering Yantai University, Yantai 264006, P. R. China

^c Shandong Laboratory of Advanced Materials and Green Manufacturing at Yantai, Yantai, 264006, P. R. China

E-mail: shoujie_shen@outlook.com; liuhongliang@ytu.edu.cn

1 Experimental

1.1 Materials

1-Butylimidazole, lithium bis(trifluoromethanesulfonyl)imide (LiNTf₂) were supported by Lanzhou Yulu Fine Chemical Co., Ltd. 4-vinylbenzyl chloride, oxalyl chloride, anhydrous magnesium sulfate (MgSO₄), poly(ethylene glycol) (PEG, M_w ~ 20 000), and methyl tert-butyl ether (MTBE) were purchased from Shanghai Macklin Biochemical Co., Ltd. Acetonitrile, dichloromethane, ethylene glycol dimethacrylate (EGDMA), 2,2-diethoxyacetophenone (DEAP) and ethyl acetate were provided by J&K Scientific. Styrene and 2-methyl-2-[(dodecylsulfanylthiocarbonyl) sulfanyl] propanoic acid (chain transfer agent, CTA) were purchased from Sigma-Aldrich. *n*-Hexane was provided by Beijing Beihua Fine Chemicals Co., Ltd. The LED lights were purchased from Shenzhen Beike Trading Co., Ltd., with a voltage range of 1.9-3.0 V and a current of 20 mA. The UV lamp used for photopolymerization is Princessa PL-LED100F, with a wavelength of 365 nm.

1.2 Synthesis of PS-PEO-PS

The synthesis of PS-PEO-PS triblock copolymer was based on protocol reported by Lodge and co-workers.¹ 1 g CTA and 1.5 g oxalyl chloride were dissolved in 4 mL dichloromethane, then stirred at room temperature for 2 h under argon atmosphere. The product was redissolved in 50 mL dichloromethane after excess reagents were evaporated under vacuum, with addition of 5.5 g PEG. The mixed solution was stirred for 24 h at room temperature. *n*-Hexane was used to precipitate and wash the product for three times to obtain CTA-PEO-CTA macroinitiator (macro-CTA). Then, 1.1 g macro-CTA was dissolved in 3 mL styrene, bubbled with argon for 15 min to remove oxygen. The reversible addition-fragmentation chain transfer (RAFT) polymerization proceeded by heating the reaction mixture at 140 °C for 40 min in a sealed pressure flask. The reaction was stopped using liquid nitrogen. The product was redissolved in 20 mL dichloromethane and dialyzed in dichloromethane for 3 days, subsequently precipitated in *n*-hexane and dried in vacuum to obtain PS-PEO-PS triblock copolymer. ¹H NMR was given in Fig. S1.

1.3 Synthesis of [VBBIm][NTf₂]

[VBBIm][NTf₂] was prepared according to a reported synthesis route.² 4-vinylbenzyl chloride (20.0 g, 0.13 mol) and 1-butyylimidazole (16.2 g, 0.13 mol) were dissolved in 50 mL acetonitrile. The mixed solution was reacted at 45 °C for 24 h under stirring. After reaction, the solution was precipitated in excess MTBE and washed three times to obtain a viscous liquid, 1-(4-vinylbenzyl)-3-butyylimidazolium chloride ([VBBIm]Cl). Yield: 75%. Then 13.5 g [VBBIm]Cl (48 mmol) and 15.2 g LiNTf₂ (53 mmol) were added into 100 mL deionized water, mechanically stirred for 24 h at room temperature for fully reaction. The mixture was extracted by 100 mL ethyl acetate and washed with 50 mL deionized water for three times. The resulting solution was dried with anhydrous MgSO₄ and filtered. A transparent viscous liquid, [VBBIm]NTf₂ was obtained after removing of ethyl acetate by rotary evaporation. Yield: 70%. ¹H NMR was given in Fig. S2.

1.4 Preparation of the Ionogel

To fabricate ionogel, 0.7 g [VBBIm][NTf₂], 0.6 g [MMI][NTf₂], EGDMA (3 mol% of [VBBIm][NTf₂]), DEAP (1 mol% of [VBBIm][NTf₂]) and 0.2 g PS-PEO-PS were dissolved in 4 mL dichloromethane and stirred for 1 h to form a homogenous solution. The viscosity of the physical precursor was tuned by controlled evaporation of dichloromethane. The physically cross-linked ionogel was self-assembled under vacuum overnight prior to polymerization. Subsequently, the physical-co-chemical ionogel was formed after exposed under UV for 60 min to prompt the in-situ polymerization of [VBBIm][NTf₂].

1.5 Versatile Processability of the Ionogel

The ionogel can be fabricated by various methods including spray coating and 3D printing. First, we prepared the pre-gel solutions for spray coating by dissolving a certain weight of mixed ILs and corresponding ratios of PS-PEO-PS, EGDMA and 2,2-diethoxyacetophenone in dichloromethane. For spray coating, the viscosity of pre-gel solution was around 10⁻¹ Pa s with the concentration of about 1 g mL⁻¹. The pre-gel solution was sprayed onto 0.03 mm stainless copper mask plate substrates to form a homogeneous film. After dried for a day, we used a UV flashlight to cure the ionogel.

The conductive coating of ionogel was obtained after curing for 60 min. The substrates with ionogel coating are conductive and have the ability to light up LEDs. We connect the red, green, and blue LED lights to form patterns of petals, leaves, and flower stalks respectively. Each pattern is then further connected with the ionogel to form a circuit. When fingers press on the ionogel connecting different patterns, the ionogel will become more conductive under body temperature, thus lighting up the corresponding pattern.

1.6 Conductivity Test

The concentration of [MMI][NTf₂] can affect the conductivity of the ionogels. The ionogel samples with thickness of 0.65 mm, length of 40 mm, and width of 10 mm were placed between two electrodes, and the conductivity was tested using AC impedance on an electrochemical workstation (CHI660E). We have evaluated the conductivity variations of the ionogels during the heating and cooling processes, spanning a temperature range from -20 °C to 40 °C, with intervals of 5 °C. During the testing process, the temperature was controlled by using a temperature control unit (TPC 160U, TC-U). In this work, concentrations were chosen from 10 wt% to 44 wt% for [MMI][NTf₂]. When the concentration of [MMI][NTf₂] is 10%, the conductivity is $5.5 \times 10^{-3} \text{ S m}^{-1}$. At a concentration of 25 wt%, the conductivity is $3.3 \times 10^{-2} \text{ S m}^{-1}$; at a concentration of 36%, the conductivity is $6.4 \times 10^{-2} \text{ S m}^{-1}$; at a concentration of 40%, the conductivity is 1.06 S m^{-1} ; and at a concentration of 44%, the conductivity is 0.45 S m^{-1} .

1.7 Thermo-responsive Conductivity Test

The thermo-responsive conductivity of this unique material is totally reversible. Conductivity of the ionogel can reversibly switch between low conductivity (about 0.009 S m^{-1}) to high conductivity (about 0.11 S m^{-1}) for at least ten cycles. No significant changes in the values were observed during cycling, indicating no structural damage during freezing and heating cycles.

1.8 Tensile Tests

Tensile tests were conducted for ionogels with different mass fractions of [MMI][NTF₂]. More specifically, physical precursor of different mass fractions of [MMI][NTF₂] was transferred into a rectangular-shaped silicon rubber mould. Following UV light irradiation at room temperature, the desired ionogel sheets were obtained through the chemical crosslinking. Tensile tests were conducted on ionogel samples with dimensions of 20 mm × 5 mm × 2 mm using an electronic tensile testing machine equipped with a 100-N load cell, at a stretching rate of 100 mm min⁻¹. Based on the conductivity and mechanical properties, we selected a mass fraction of 40 wt% for [MMI][NTF₂] as the optimal ratio for the ionogel.

1.9 Characterization

Differential scanning calorimetry (DSC) was carried out on a TA Instrument (DSC 300) with a scan rate of 5 °C min⁻¹ under dry nitrogen environment. Thermal gravimetric analysis (TGA) measurement was performed on a Mettler TGA2 via scanning a temperature range from room temperature up to 800 °C (20 °C min⁻¹) under dry nitrogen environment. DMA experiments were performed on a TA Q800 instrument in “multi-frequency-strain” mode. The samples were measured from -100 °C to 60 °C under a nitrogen atmosphere, at a heating rate of 5 °C min⁻¹ and frequency of 1 Hz.

2. Figures

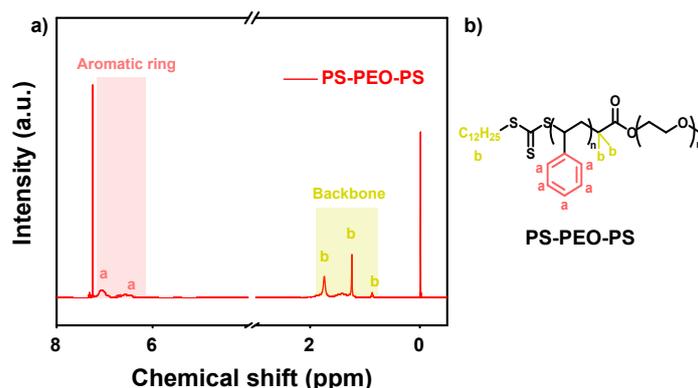


Fig. S1 (a) ¹H NMR spectrum and (b) molecular structure of PS-PEO-PS. The deuterated solvent used here is chloroform-d.

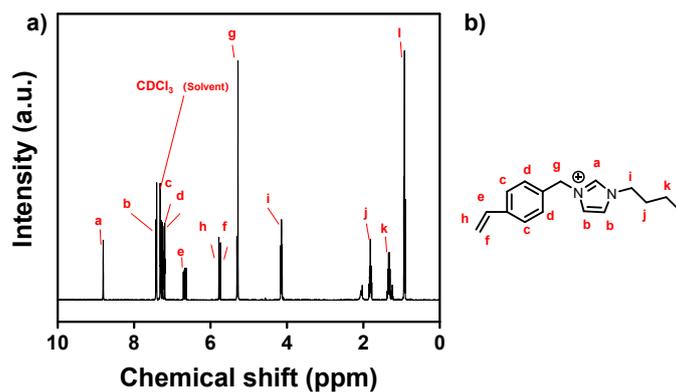


Fig. S2 (a) ^1H NMR spectrum and (b) corresponding molecular structure of [VBBIIm][NTf₂]. The deuterated solvent used here is chloroform-d.

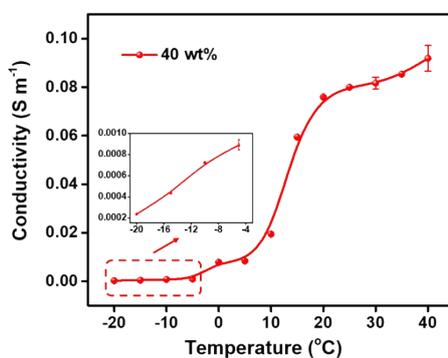


Fig. S3 Conductivity of the ionogel with 40% of [MMI][NTf₂] as a function of temperature.

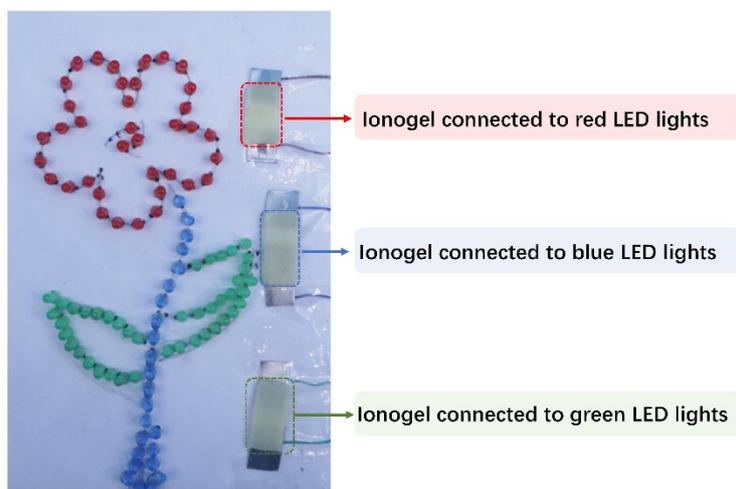


Fig. S4 The circuit diagram with ionogels and flowers in series.

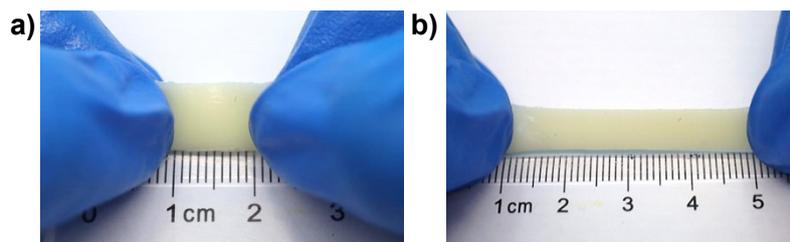


Fig. S5 The ionogel can withstand stretching.

References:

1. Y. He, P. G. Boswell, P. Bühlmann and T. P. Lodge, *J. Phys. Chem. B.*, 2007, **111**, 4645–4652.
2. H. He, M. Zhong, B. Adzima, D. Luebke, H. Nulwala and K. Matyjaszewski, *J. Am. Chem. Soc.*, 2013, **135**, 4227–4230.