

Electronic Supplementary Information

Thermo- and Electro- Dual Responsive Poly(ionic Liquid) Electrolyte Based Smart Windows

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Materials. N-isopropylacrylamide (NIPAM) was purchased from Aladdin Reagents Co. (Shanghai, China). 4,4'-Bipyridine was purchased from Alfa. 1-Vinylimidazole, 1-methylimidazole, ammonium persulfate, tetramethylethylenediamine and allyl bromide were purchased from Acros. 1-Bromoethane, 1-bromobutane, 1-bromohexane, 1-bromooctane, ethyl alcohol, diethyl ether, acetonitrile and ethyl acetate were purchased from Shanghai Chemical Reagents Co. (Shanghai, China) and used as received. All the monomers were passed through a column of neutral alumina to remove the inhibitor before use. Deionized water was utilized throughout all the experiments.

**Synthesis of 3-butyl-1-vinylimidazolium bromide ([BVIm][Br]),
3-ethyl-methyl-imidazolium bromide ([EMIm][Br]),
3-butyl-1-methyl-imidazolium bromide ([BMIm][Br]),
3-hexyl-1-methyl-imidazolium bromide ([HMIm][Br]),
3-octyl-1-methyl-imidazolium bromide ([OMIm][Br]) and diallyl viologen (DAV)**

[BVIm][Br] was synthesized according to the method previously reported.¹ A mixture containing 1-vinylimidazole (3.00 g, 0.032 mol) and equivalent mole ratio of 1-bromoethane (5.18 g, 0.032 mol) was stirred at 25 °C for 3 days. The synthesized compound was purified with diethyl ether three times, and then dried under vacuum at 30 °C. Colorless viscous liquid (yield: 92%). ¹HNMR (400 MHz, D₂O) δ(ppm): 7.78 (s, 1H), 7.60 (d, 1H), 7.11 (d, 1H), 5.75 (d, 2H), 5.40 (t, 1H), 4.25 (t, 2H), 1.86 (m, 2H), 1.35 (m, 2H), 0.70 (t, 3H).

[EMIm][Br], [BMIm][Br], [HMIm][Br], and [OMIm][Br] were synthesized and purified follow the method applied for [BVIm][Br].

[EMIm][Br]. ¹HNMR (400 MHz, D₂O) δ(ppm): 7.78 (m, 2H), 7.60 (d, 1H), 1.75 (m, 2H), 0.80 (t, 3H).

[BMIm][Br]. ¹HNMR (400 MHz, D₂O) δ(ppm): 7.50 (m, 2H), 7.10 (s, 1H), 7.32 (m, 1H), 4.25 (t, 2H), 1.90 (m, 2H), 0.90 (t, 3H).

[HMIm][Br]. ¹HNMR (400 MHz, D₂O) δ(ppm): 7.58 (m, 2H), 7.10 (d, 1H), 4.21 (t, 2H), 3.95 (d, 3H), 1.80 (t, 2H), 1.35 (m, 6H), 0.80 (t, 3H).

[OMIm][Br]. ¹HNMR (400 MHz, D₂O) δ(ppm): 7.40 (m, 2H), 7.20 (d, 1H), 4.25 (t, 2H), 3.95 (d, 3H), 1.90 (t, 2H), 1.45 (m, 10H), 0.90 (t, 3H).

Diallyl viologen (DAV) was synthesized follow the method reported.² A mixture containing 4,4'-bipyridine (1.0 g, 6.41 mmol) and allyl bromide (0.8 g, 12.90 mmol) (1:2, molar ratio) dissolved in a 10 mL acetonitrile was stirred at 0 °C for 4 h. The resultant raw product was purified by evaporating the acetonitrile to yield yellow precipitate. The precipitate was washed three times with diethyl ether and then dried under vacuum at 25 °C (yield: 79%). ¹HNMR (400 MHz, D₂O) δ(ppm): 9.20 (d, 4H), 8.51 (d, 4H), 6.25 (m, 2H), 5.60 (m, 4H), 5.35 (m, 4H).

Synthesis of P(NIPAM-DAV) IL gels

A precursor mixture containing NIPAM (0.2 g, 1.77 mmol) and diallyl-viologen (crosslinker agent, 1.0 wt% of NIPAM), ammonium persulfate (1.0 wt%, initiator) and tetramethylethylenediamine (TEMED) (1.0 wt%, crosslinking accelerator) was stirred in 1.5 mL ionic liquid solvent (methylimidazolium bromide (MIm)/H₂O (0/1 to 0.8/0.2, weight ratio)). The mixture was degassed with N₂ and reacted at 20 °C for 0.5 h in an ampoule tube. After the completion of the polymerization, the homogeneous solution yielded the P(NIPAM-DAV) IL gels.

Synthesis of P(NIPAM-BVIm-DAV) gels

The P(NIPAM-BVIm-DAV) gels were prepared via the polymerization of a mixture containing N-isopropylacrylamide (1.0-0.5, molar ratio), [BMIm][Br] (0.0-0.5, molar ratio), diallyl-viologen as the crosslinker (1.0 wt% of the monomers), ammonium persulfate (1.0 wt%, as a initiator) and tetramethylethylenediamine (1.0

wt%, as the crosslinking accelerator). The mixture was stirred in a deionized water (0.16 g/mL, relative to the weight of monomer) and reacted at 20 °C for 0.5 h in an ampoule tube under nitrogen atmosphere. The P(NIPAM-BVIm-DAV) gels were obtained after the completion of the polymerization.

Preparation of P(NIPAM-DAV) gel or P(NIPAM-BVIm-DAV) gel based TEDs

To fabricate a TE device, the prepared homogeneous polymer gels were cut into the desired shape and transferred onto the target ITO glass. Then, the gel was sandwiched with a second ITO glass, and firmly sealed by 100 µm thick double-sided tape.³

Characterization

¹HNMR measurements were tested on UNITY INOVA 400MHz nuclear magnetic resonance instrument at room temperature using D₂O as the solvent. Fourier transform infrared (FT-IR) spectra were conducted on a Varian CP3800 spectrometer at a resolution of 4 cm⁻¹ in the range of 4000-400 cm⁻¹. The transmittance of the TEDs was recorded on UV-vis absorption spectra from 20 to 55 °C at 550 nm using a TU-1800 SPC spectrophotometer with the heating rate at 1 °C min⁻¹. The current-voltage measurements were performed on Autolab PGSTAT 302N electrochemical workstation.

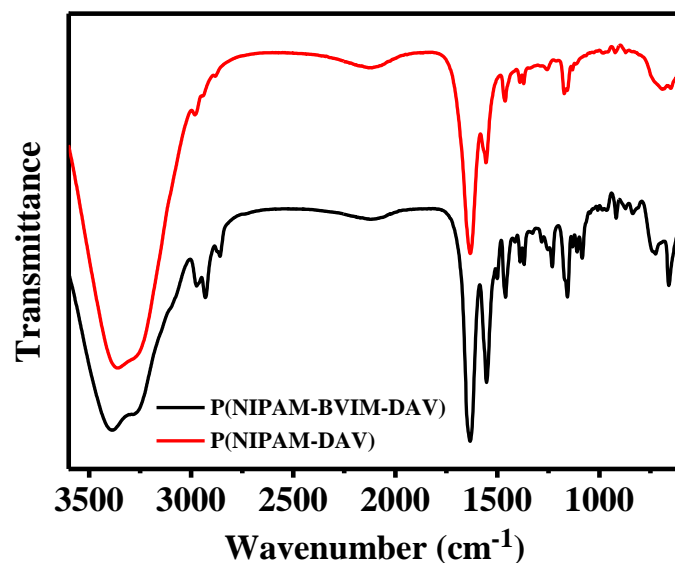


Fig. S1 FT-IR spectra of the P(NIPAM-DAV) IL gels (red line) and P(NIPAM-BVIm-DAV) (black line) gels.

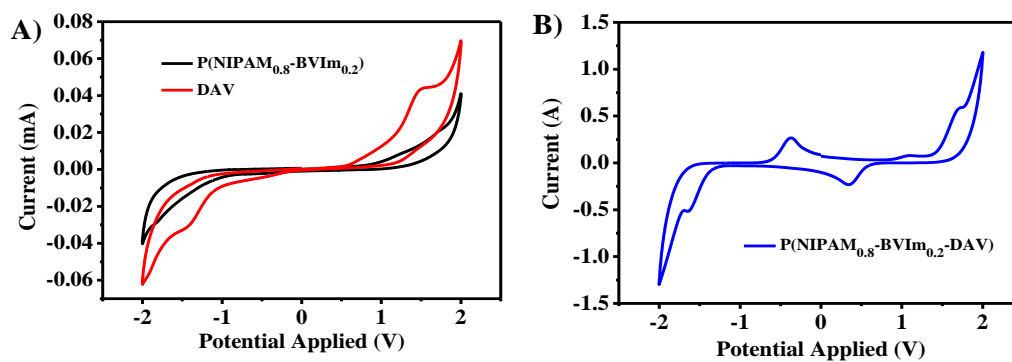


Fig. S2. A) Cyclic voltammogram of diallyl-viologen (DAV) and P(NIPAM_{0.8}-BVIm_{0.2}); B) Cyclic voltammogram of the P(NIPAM_{0.8}-BVIm_{0.2}-DAV) gel at a potential sweep rate of 20 mV s⁻¹ using two ITO-coated glasses as the working and counter electrode, respectively.

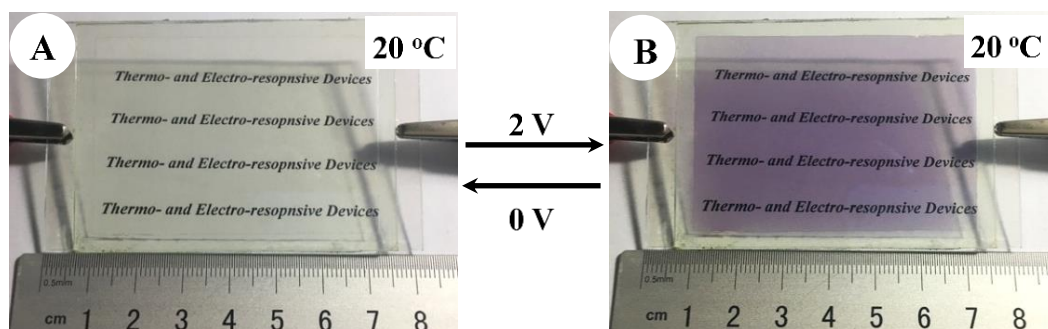


Fig. S3 Photographs of P(NIPAM_{0.8}-BVIm_{0.2}-DAV) gel based TEDs A) at transparent and colorless; and B) transparent and purple colored states. The reduction and oxidation processes were performed by applying 2.0 and 0.0 V, respectively.

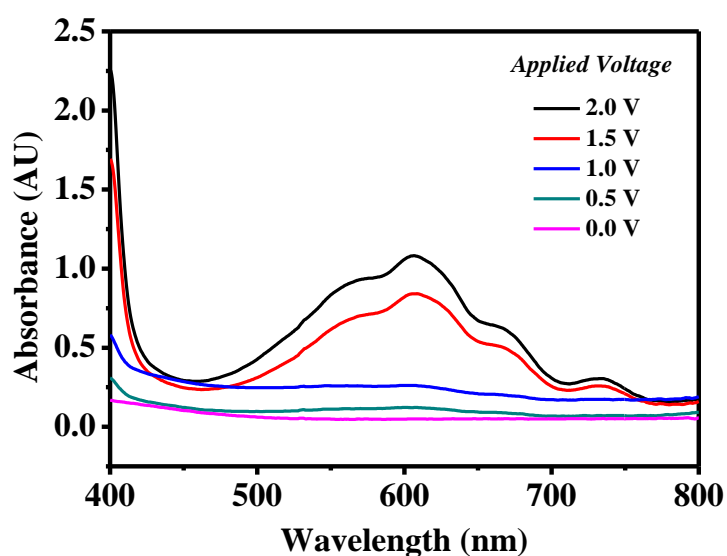


Fig. S4 UV-vis absorption spectra of P(NIPAM_{0.8}-BVIm_{0.2}-DAV) gel based TEDs at various applied voltages.

References

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