

## Supporting Information

# **Inducing Thermoreversible Optical Transitions in Urethane-Acrylate Systems via Ionic Liquid Incorporation for Stretchable Smart Devices**

*Terence Yan King Ho<sup>‡</sup>, Ankit<sup>‡</sup>, Benny Febriansyah, Natalia Yantara, Shreyas Pethe, Dino Accoto, Sumod Appukuttan Pullarkat, Nripan Mathews\**

<sup>‡</sup>These authors contributed equally to this work

\*corresponding author - [Nripan@ntu.edu.sg](mailto:Nripan@ntu.edu.sg)

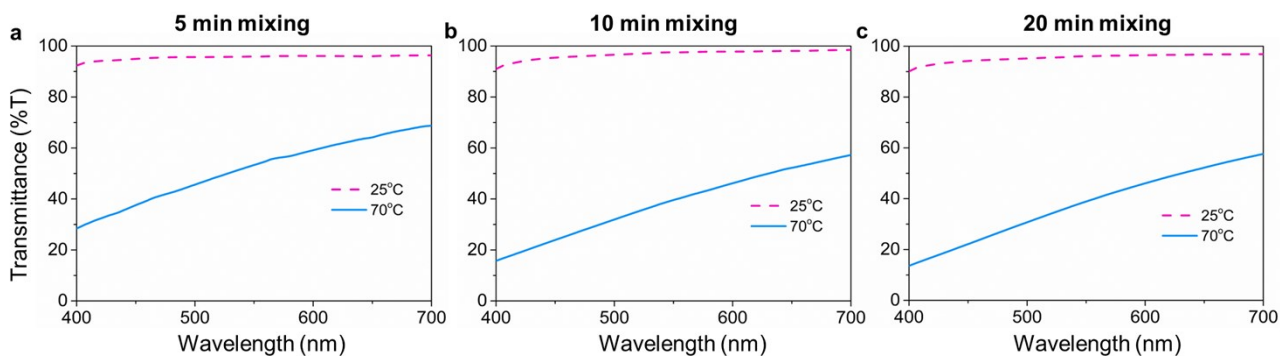


Figure S1. Effect of mixing time of polymer precursor solution on the LCST-driven thermotropic transitions. UV-Vis transmittance for 1-mm thick samples of ILEH-5% at 25°C and 70°C over the complete visible range of spectrum (400 – 700 nm) prepared with different mixing durations of (a) 5 minutes, (b) 10 minutes and (c) 20 minutes. Each sample was degassed for 5 minutes, before ionic liquid was added and mixed for 1 minute.

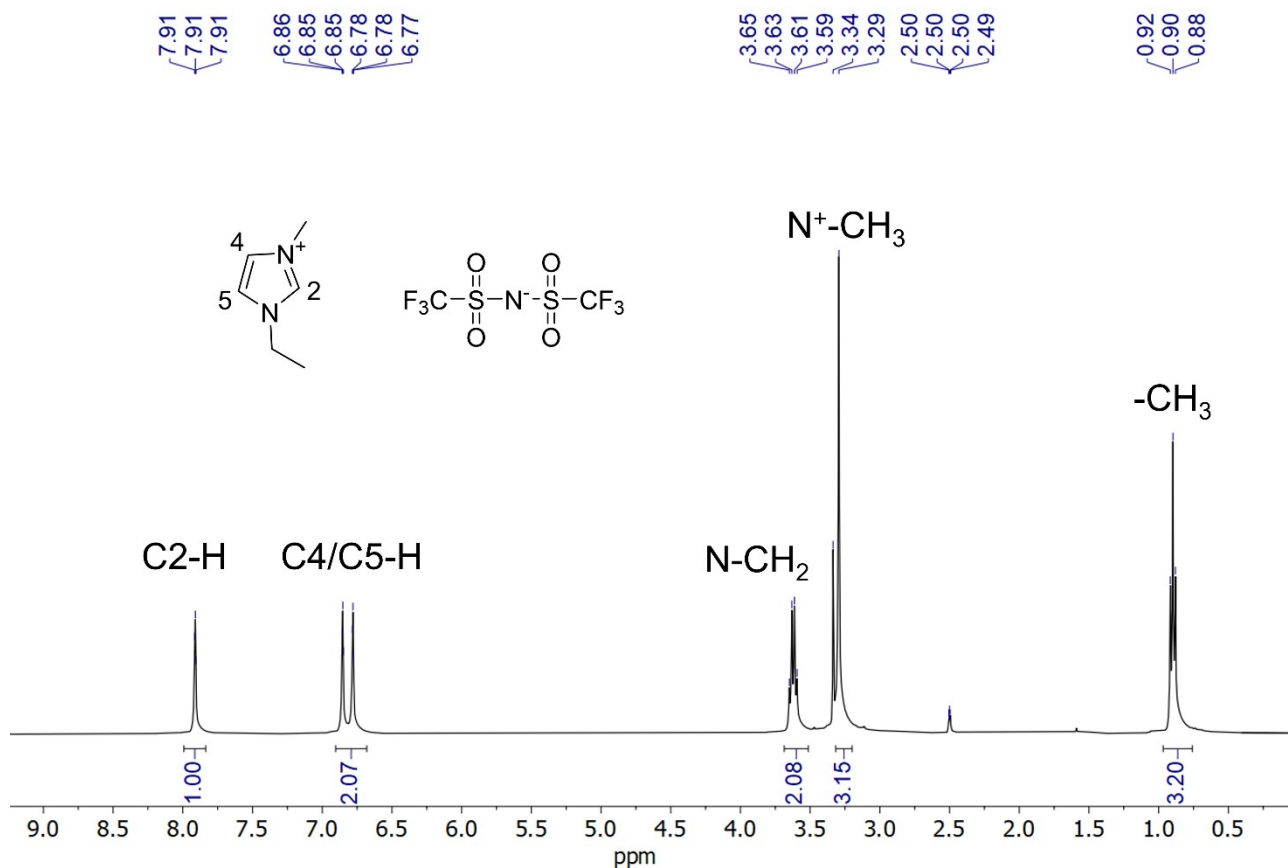


Figure S2.  $^1\text{H}$  NMR spectrum of EMIMTFSI at 25°C. Spectra was taken using the same coaxial technique, with  $\text{DMSO-d}_6$  as the deuterated solvent in the outer tube, and EMIMTFSI as the analyte in the inner tube.

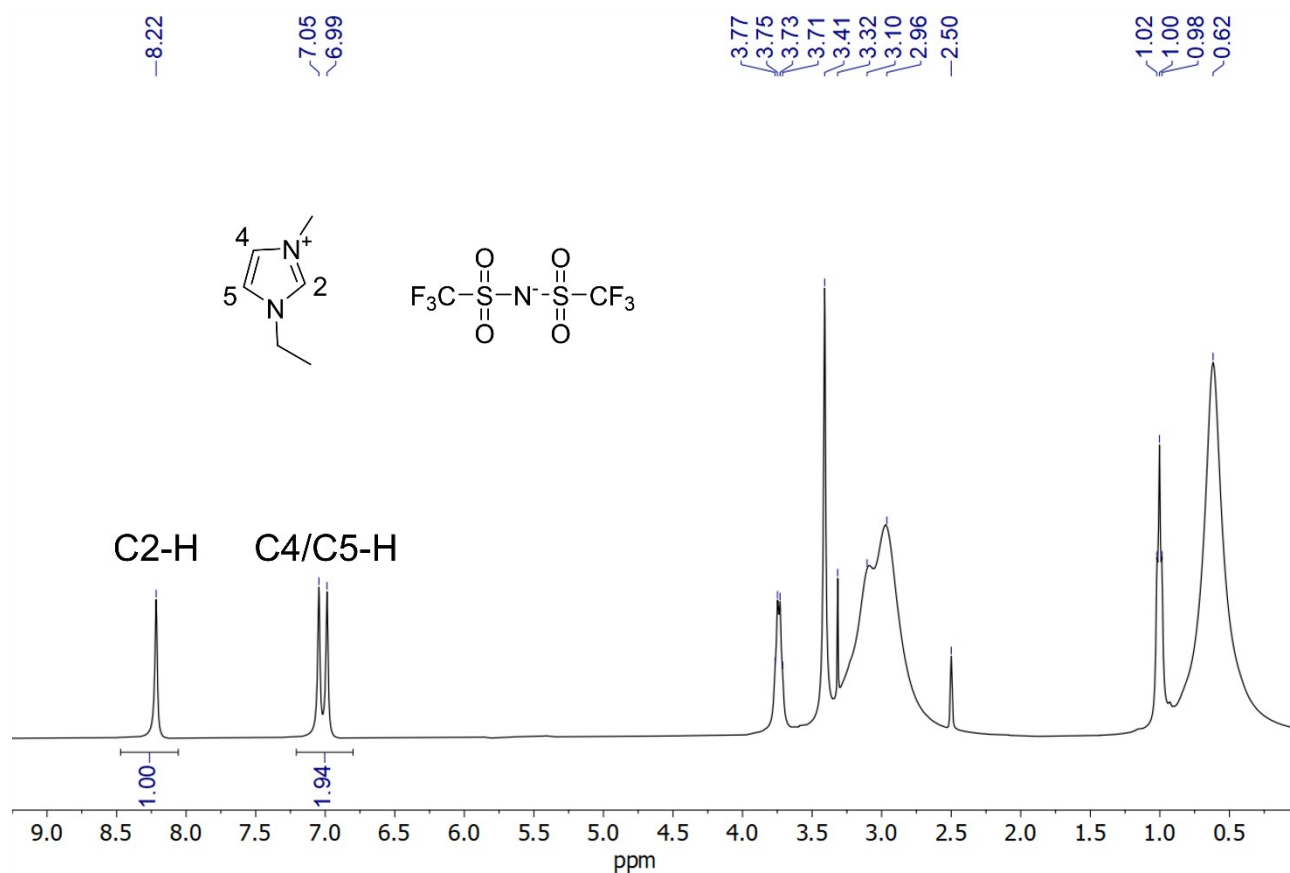


Figure S3. <sup>1</sup>H NMR spectra of CN9018/EMIMTFSI mixture in 1:1 weight ratio at 25°C before heating. Peaks of interest (C2-H & C4/C5-H) belong to the protons on the imidazolium ring of the EMIM<sup>+</sup> cation believed to be responsible for reversible hydrogen bonding. The rest of the peaks belong to the proprietary oligomer CN9018 and the methyl & ethyl group from EMIM<sup>+</sup> cation.

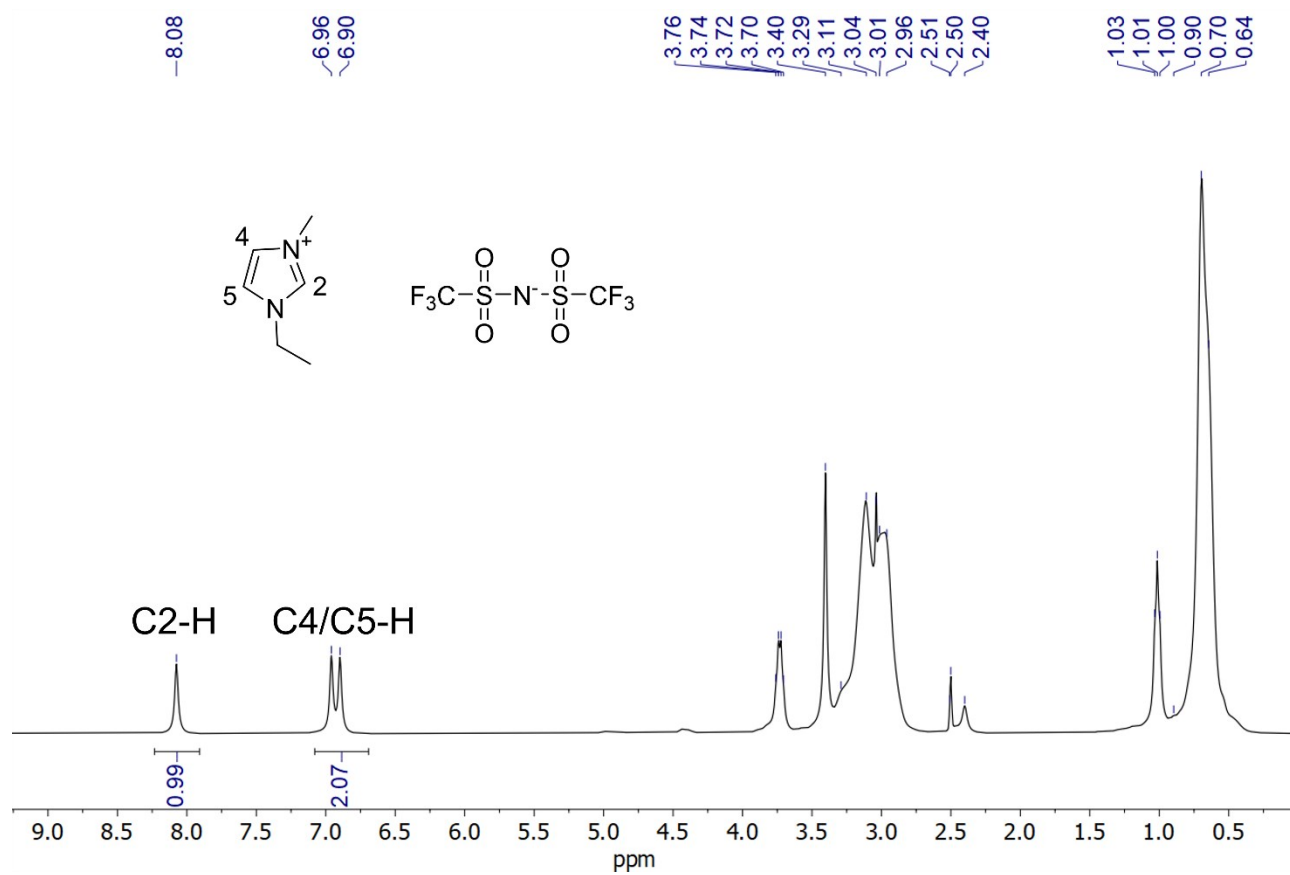


Figure S4.  $^1\text{H}$  NMR spectra of CN9018/EMIMTFSI mixture in 1:1 weight ratio at  $80^\circ\text{C}$ . The peaks of interest (C2-H & C4/C5-H) exhibit an upfield shift due to the decrease in electron density from the breaking of hydrogen bonds at  $80^\circ\text{C}$ . The rest of the peaks show insignificant shifts when heated.

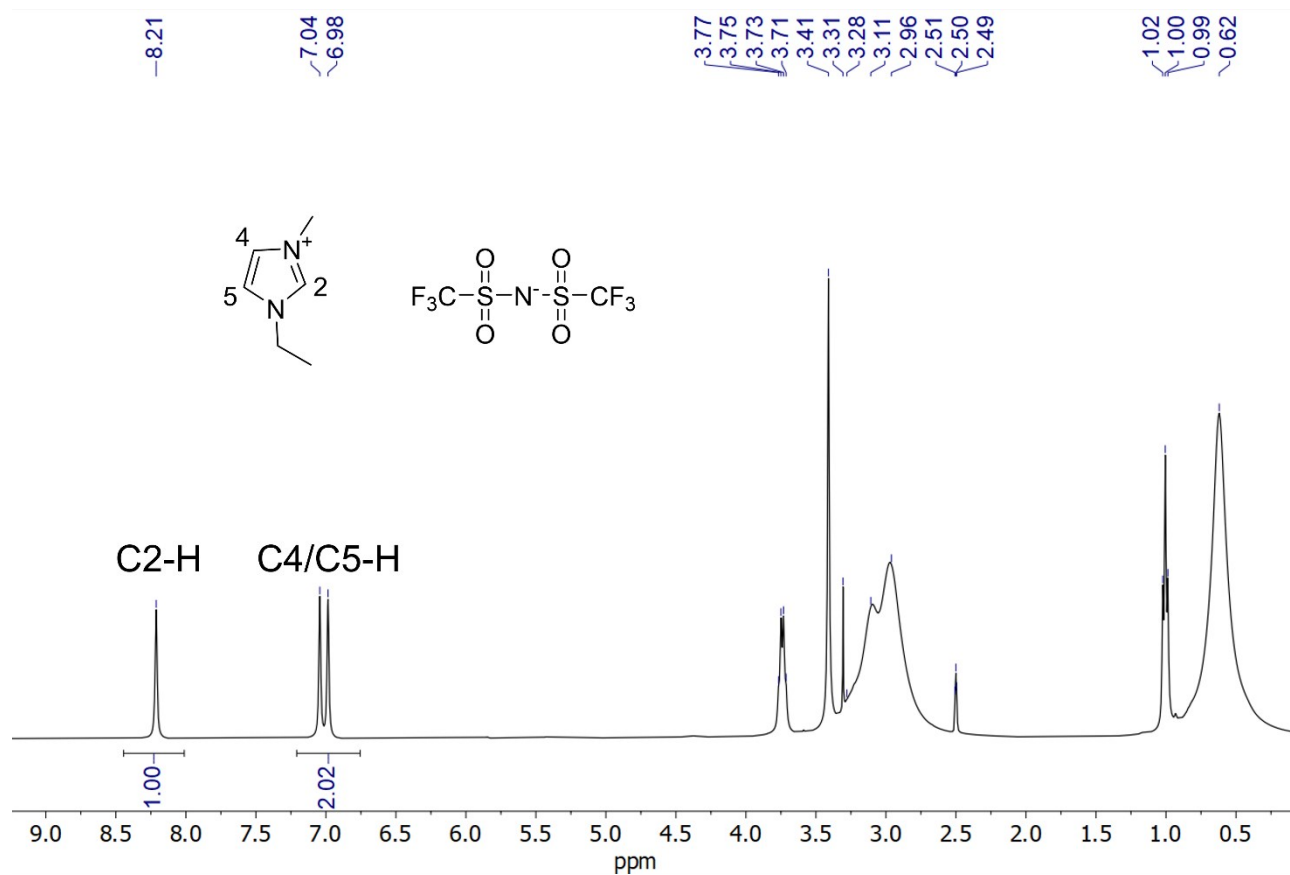


Figure S5.  $^1\text{H}$  NMR spectra of CN9018/EMIMTFSI mixture in 1:1 weight ratio when cooled back to 25°C. The peaks of interest (C2-H & C4/C5-H) exhibit a downfield shift due to the increase in electron density from the reformation of hydrogen bonds at 25°C. This shows reversibility of the hydrogen bonding phenomenon.

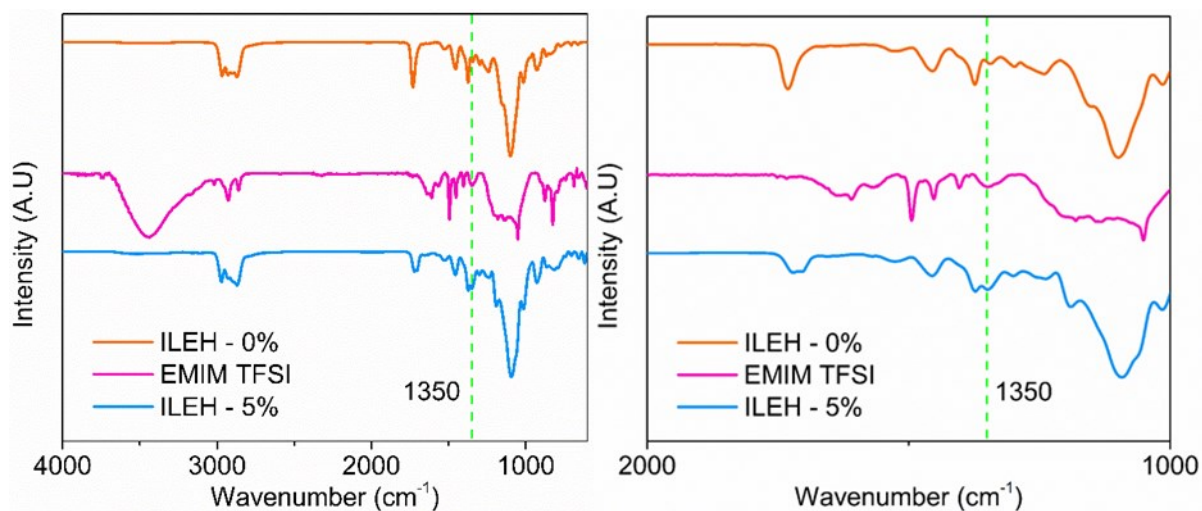


Figure S6. FTIR spectra of ILEH – 0%, ILEH – 5% and EMIMTFSI. The presence of characteristic peak at 1350 cm<sup>-1</sup> (green dotted line) belonging to sulfonyl group (S=O) from EMIMTFSI was observed in ILEH – 5%, and absent in ILEH – 0%, confirming the incorporation of EMIMTFSI in the synthesised gels. Zoomed in spectra from wavenumbers 2000 – 1000 cm<sup>-1</sup> on the right.

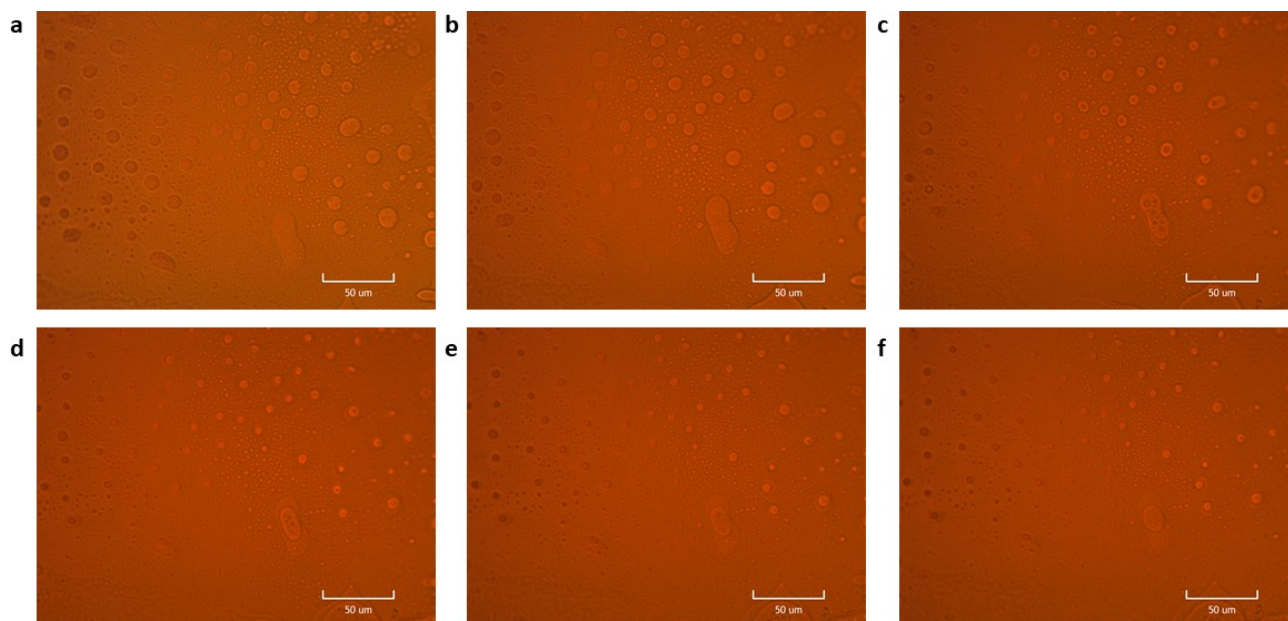


Figure S7. Timelapse of ILEH-5% being heated captured using optical microscopy at a) 0, b) 30, c) 60, d) 90, e) 120, and f) 150 seconds timestamps. The heat was continuously supplied at the 0 second mark, and heat supply was subsequently removed at the 150 second mark. Formation of small globules are observed to be shrinking away from their boundary. This visually shows the breaking of hydrogen bonds between EMIMTFSI and the polymer network, resulting in EMIMTFSI-EMIMTFSI interactions to dominate, leading to the coalescence of smaller globules (as seen from c-f).

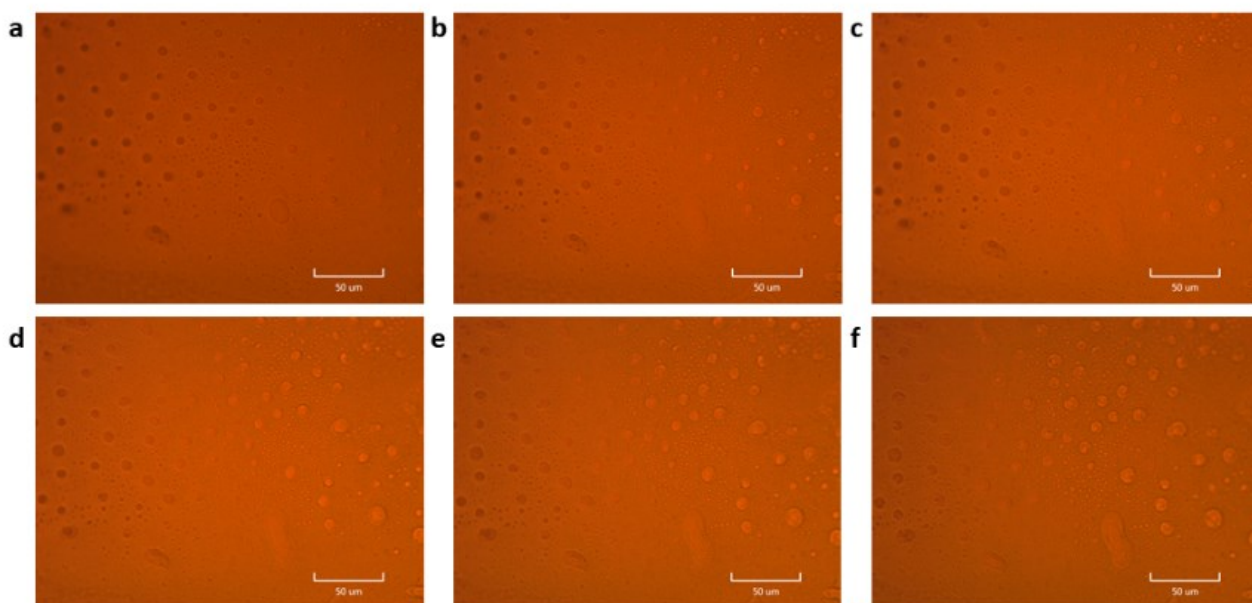


Figure S8. Continuation from Figure S7, timelapse of ILEH-5% being cooled at a) 180, b) 210, c) 240, d) 270, e) 300, f) 330 seconds timestamps. The smaller globules that were formed slowly re-expands and joins back with its morphological boundary, leading to its disappearance. This visually shows the reformation of hydrogen bonds between EMIMTFSI and polymer network.



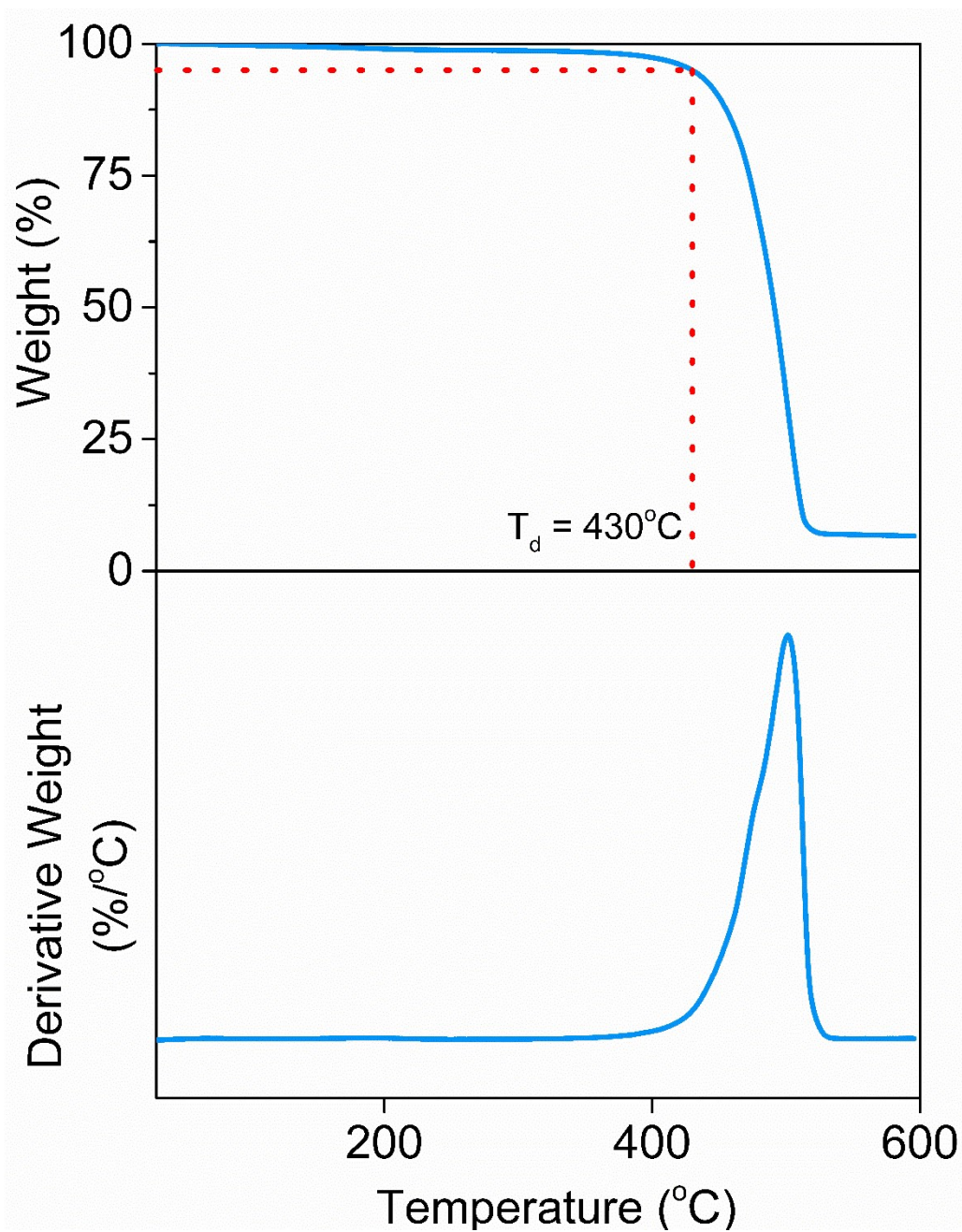


Figure S9. Thermogravimetric analysis of EMIMTFSI shows great thermal stability of ionic liquid EMIMTFSI, with degradation temperature ( $T_d$ ) of 430°C.

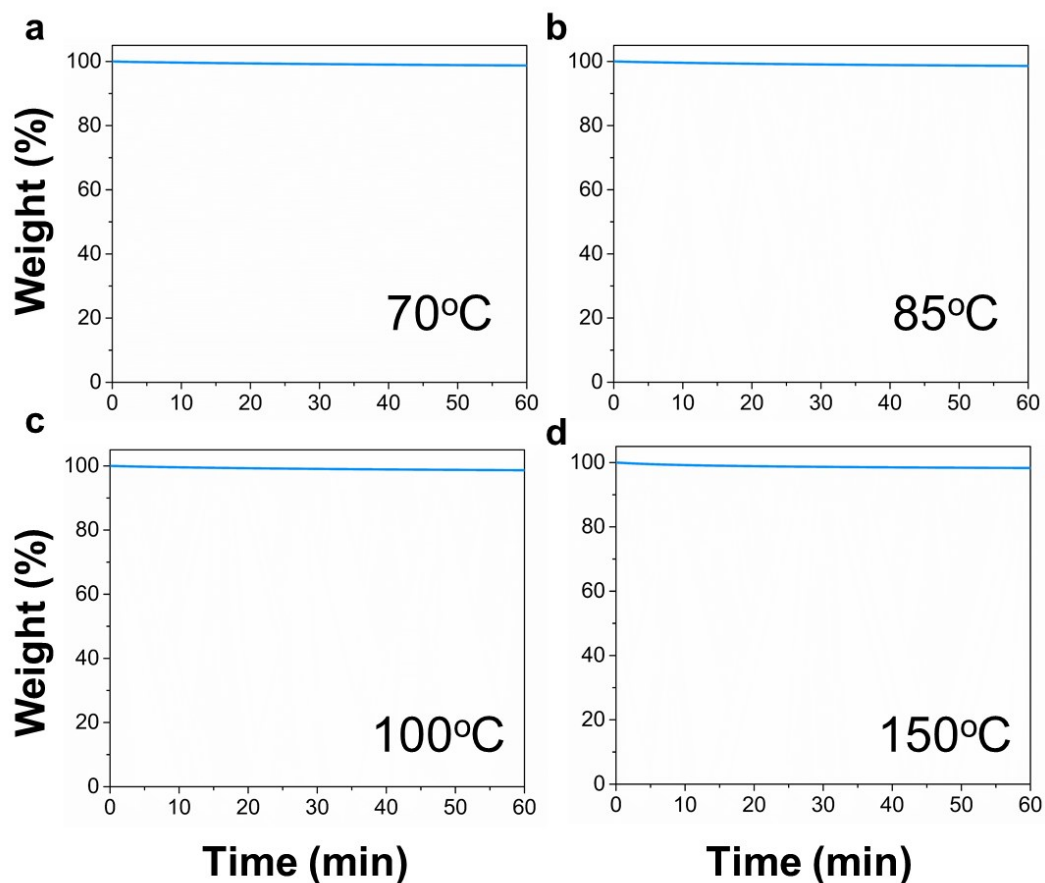


Figure S10. Isothermal TGA graphs of ILEH-5% at (a) 70°C, (b) 85°C, (c) 100°C and (d) 150°C.

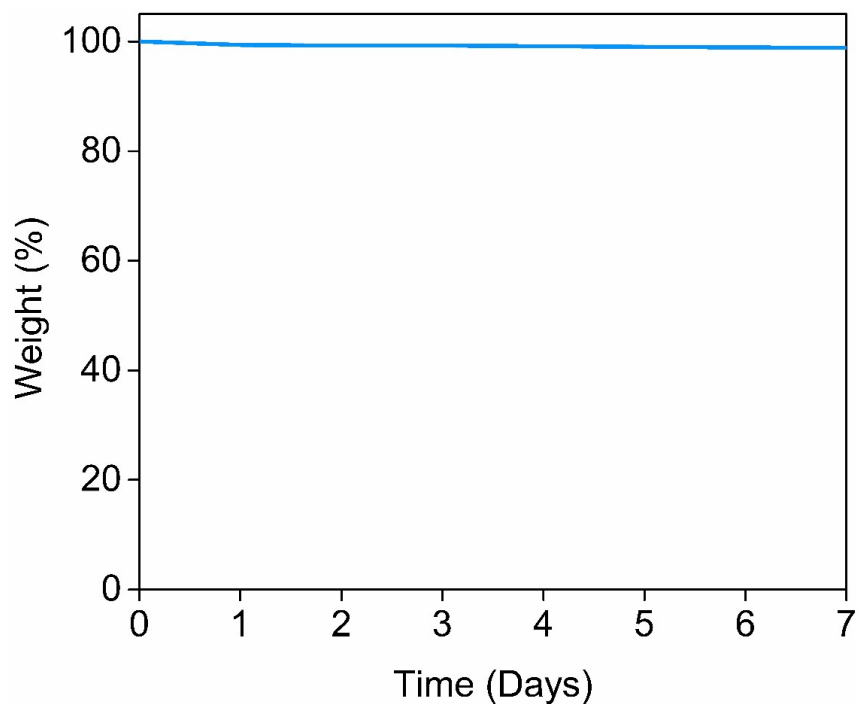


Figure S11. Ambient stability of ILEH-20% sample kept in the open at room temperature ( $\sim 25^\circ\text{C}$ ) and relative humidity of 50 – 60% for a week. Negligible changes to weight were observed, highlighting its ambient stability.

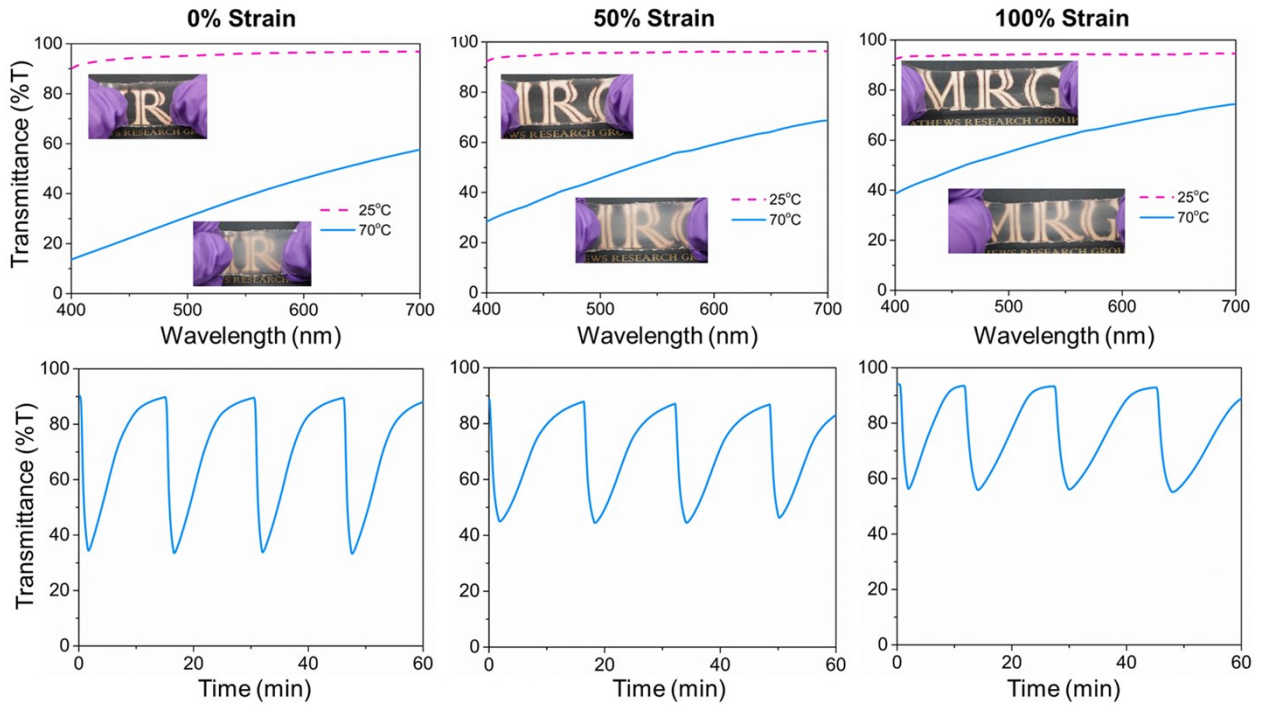


Fig. S12. UV-Vis transmittance for 1-mm thick ILEH-5% samples stretched to 0, 50 and 100% strain. (Top) UV-Vis transmittance of samples at 25°C and 70°C over the complete visible range spectrum (400 – 700 nm) with inset images of the sample at corresponding temperatures and (bottom) cyclic heating-cooling tests of samples at wavelength of 500 nm between 25°C and 70°C for 1 hour.

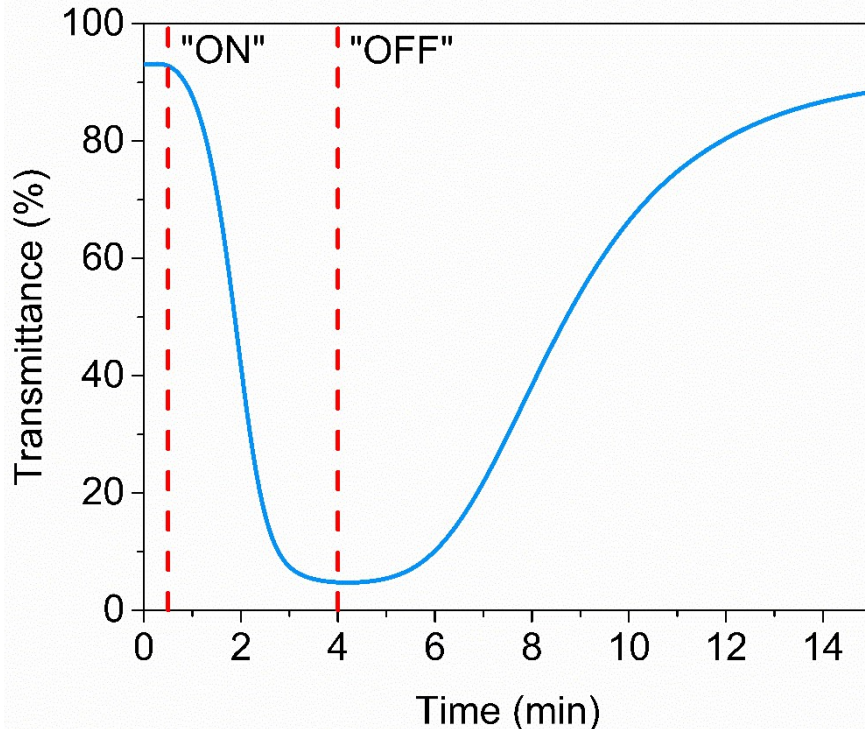


Fig S13. Thermal-induced optical response in ILEH-5%. Heater was switched on at 0.5-minute mark and switched off at the 4-minute mark when the sample had reached 80°C. Quick response to thermal stimulus is demonstrated here in our ILEH-5%, with almost immediate drop in transmittance value upon application of thermal stimulus.

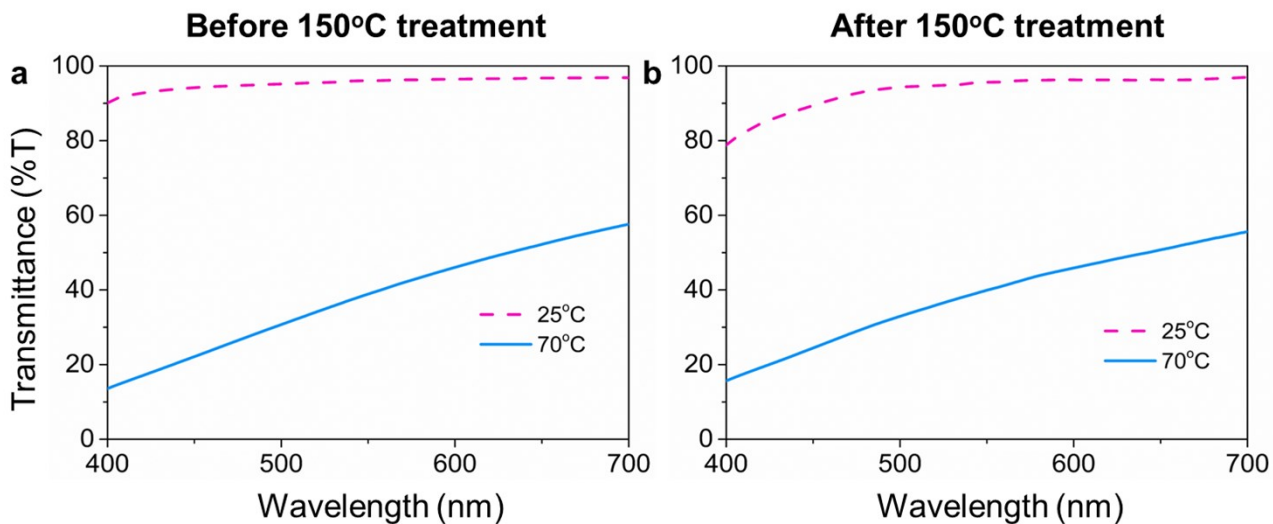


Figure S14. UV-Vis transmittance of 1-mm thick ILEH-5% samples at 25°C and 70°C over the complete visible spectrum range (400 – 700 nm) (a) before and (b) after being subjected to high temperature of 150°C for 1 hour.

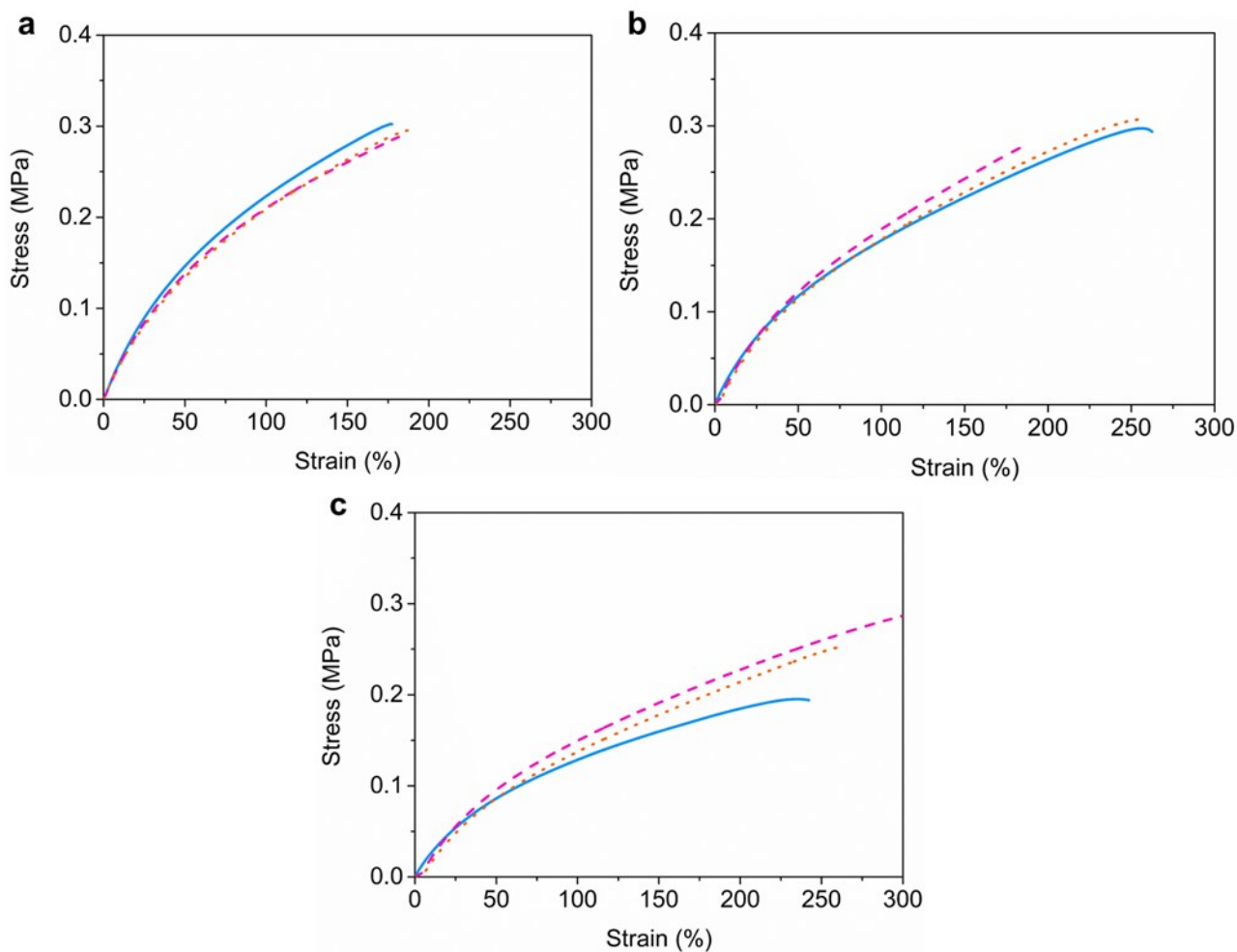


Figure S15. Stress-strain curves of (a) ILEH-0%, (b) ILEH-5%, (c) ILEH-20%. Mechanical tests were performed on three different samples for each formulation. With increasing amount of EMIMTFSI added to our gels, we observe both the softening effect (lower Young's modulus) and increase in ultimate strain at break.