

Supporting Information

Experimental section

Materials

All glassware was stored in a drying oven for several hours at 120 °C prior to use. Compounds including 2,2'-azo-bis(isobutyronitrile) (AIBN), chloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), lithium borohydride (LiBH_4), cholesterol (96%), and n-butylamine were obtained from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). Triethylamine (TEA) and dimethyl formamide (DMF) were purchased from Fisher Scientific (Boston, MA, USA). Polyethylene oxide methyl ether (MW= 2000), 1,4-dioxane (99.8%, extra dry), dichloromethane (DCM) (99.9%, extra dry), methacryloyl chloride (>97%) were purchased from Acros Organics USA. Liquid crystalline monomer, cholesteryl 6-methacryloyloxyhexanoate (C5MA), was prepared according to published work.¹ The RAFT agent S-1-dodecyl-S'-(α, α' -dimethyl- α'' -acetic acid) tricarbonatate (CTA) was synthesized according to a published procedure.² All chemicals used were analytical grade and used without purification. The liquid crystalline brush block copolymer (LCBBC) was synthesized according to our published work.³

Preparation of AuNPs-grafted LCBBC in an organic solvent

To prepare AuNPs-grafted LCBBC, LCBBC (0.15 g, 0.025 mmol) and $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (0.01 g, 0.05 mmol) were dissolved in DMF (10 mL) and stirred in the dark under nitrogen blanket at room temperature for 24 h. Freshly prepared 0.25 M LiBH_4 (1.2 mL, 0.25 mmol) was then added quickly to the solution with vigorous stirring. The reaction mixture immediately turned from yellow to dark purple; violent gas evolution was observed. The solution was stirred for 4 h at room temperature. The reaction mixture was then transferred into dialysis bag (MWCO: 6,000-8,000 Da), followed by dialysis against DMF for 48 h to remove byproducts.

Preparation of LCBBC/AuNPs nanoparticles in ionic liquid

The LCBBC/AuNPs solution was injected dropwise into IL (10 mL), followed by the stirring at $\sim 40^{\circ}\text{C}$ for 3 hours. The solution was transferred into dialysis bag (MWCO: 6,000-8,000 Da), followed by dialysis against THF. The LCBBC/AuNPs NPs were then centrifuged at 11,000 rpm for 10 min, followed by the filtration through 0.45 μm syringe to remove any precipitate. Dry LCBBC/AuNPs nanocomposite, a dark purple colored mesh-like solid, was obtained via freeze-drying.

Preparation of ion gels

To prepare stable solutions and gels, we followed co-solvent aided dissolution method. In this procedure, a pre-weighed nanocomposite was first dissolved in dichloromethane (DCM), a common solvent for both the blocks, with subsequent addition of [BMIM][PF₆] to get the desired concentration. The sample was set aside in a hood for 2 weeks at ambient temperature and DCM was removed by gradual evaporation. Thereafter, the mixture was maintained at $80\pm 5^{\circ}\text{C}$ for 6 hours until constant weight was achieved. In this study the concentration is expressed in wt%. The prepared solutions and ion-gels were stored in air-tight vials and aged for a week at room temperature prior to rheological experiments. All ion gel samples were subjected to vacuum pumping until no further weight loss was detected and were dried in a vacuum oven at 70°C for a day before measurements.

Characterization

The ¹H NMR spectra (Bruker DMX 400 MHz NMR spectrometer) of macromonomer and polymers were recorded in CDCl₃ and the 7.24 ppm peak was used as an internal standard. Molecular weight and polydispersity indices (PDI) of the polymers were determined by gel

permeation chromatography (GPC) by using a Waters 150-C ALC/GPC equipped with Evaporative Light Scattering Detector. THF was used as the eluent with a flow rate of 2.0 mL/min at 40 °C with polystyrene as the standard.

Rheology measurements

The rheological properties of diblock copolymer solutions and ion-gels were analyzed using the AR-G2 rheometer (TA Instruments, Minimum Torque Oscillation: 0.003 $\mu\text{N}\cdot\text{m}$ and Torque Resolution: 0.1 $\mu\text{N}\cdot\text{m}$) with peltier plate-temperature control. A cone-plate geometry with a diameter, $d = 40.0$ mm, and cone angle (deg: min: sec = 1:59:24), was used for more fluid-like samples with approximately 2 ml of sample added at experimental temperatures. Parallel plate geometry (20 mm diameter) was used for more solid-like samples. Dynamic frequency sweep experiments were performed from 10^{-2} to 10^2 rads^{-1} between 10 and 100 °C while cooling the samples. Dynamic temperature ramp experiments were performed to determine the temperature dependent rheological properties by heating the samples at a rate of 1 °C/min and oscillation frequency (ω) 1 rads^{-1} . Only linear viscoelastic properties were measured for dynamic frequency and temperature ramp experiments and the linear range was determined using strain sweep experiments. Strength of the ion-gels was qualitatively ascertained by running dynamic strain sweeps at oscillation frequency (ω) of 6.283 rads^{-1} . In each experiment 30 minutes conditioning time was allowed for thermal equilibration and to get rid of any shear history introduced while transferring the copolymer solutions to the appropriate geometry.

Ionic conductivity measurements

The ionic conductivity (σ) measurements were carried out in an in-house designed and machined cell using an Agilent 4284A Precision LCR meter. The amplitude of the AC voltage signal was 100 mV and the applied frequency range was 20 Hz to 60000 Hz. The solutions and

gels were heated at 90-100 °C and then filled into the multi-sample cell consisting of two stainless steel blocking electrodes separated by a teflon ring of diameter ($d = 22.2$ mm) and thickness ($L = 2.05$ mm). The cell was calibrated using a 0.1 N aqueous KCl standard solution at 25 °C. Before each conductivity measurement, the sample cell was equilibrated at the testing temperature for 20-30 minutes. Due to the hygroscopic nature of the ionic liquid, all measurements were performed under vacuum to prevent any significant moisture absorption from air. The reported conductivity values for bulk [BMIM][PF₆] and ion-gels were based on the measurements from three repetitions in the temperature dependent experiments.

Thermal analysis

The phase transitions of the LCBBC, LCBBC/AuNPs as well as the ion gels were studied by differential scanning calorimetry (DSC) on TA instrument DSC Q-20 series. The sample was stored in a hermetically sealed alumina pan with another empty pan as reference. Both heating and cooling cycles were carried out at a ramping rate 10 °C/min. Phase transition temperature are determined in either first cooling or second heating cycle scan using TA Universal Analysis software.

Thermal gravimetric analysis (TGA) was performed on Perkin-Elmer TGA-7. The sample was heated from room temperature to 800 °C at a ramping rate of 10 °C/min under an air flow. The results were used to determine the composition of LCBBC/AuNPs

Microstructure Analysis

The freeze-dried sample was further subjected to compression molding process for 1 h to give discoid sheet sample for analysis.

2D WAXS has been used to investigate the liquid crystalline properties of the plain polymer, LCBBC/AuNPs and ion gels. The experiment was performed on Oxford diffraction Xcalibur PX

Ultra with X-ray beam of CuK α radiation ($\lambda = 1.54 \text{ \AA}$) and an Onyx CCD detector. Rectangular samples were prepared by compression molding of powdered samples at 50 °C and subsequently cooled to room temperature in the air. X-ray beam is aligned along the normal the normal to the face or the edge of the film to obtain 2-D diffractogram.

2D SAXS experiments were conducted with X-ray beam ($\lambda = 1.54\text{\AA}$) produced by a CuK α microsource (Bruker). Silver behenate was used for calibration, which has d-spacing of 58.38 \AA . The beam diameter is 1 mm and the scattered intensity is recorded on a gas-wire electronic area (2D) Nanostar detector with a distance of about 150 cm from the sample.

For the sample of the LCBBC/AuNPs solution, cryo-SEM study was performed on FEI Nova NanoSEM 450 with an accelerating voltage of 120 KV. The sample for analysis was prepared by placing a drop of the LCBBC/AuNPs solution on a silicon wafer. The excess of the solution was blotted with filter paper. The samples were then quickly plunged into liquid nitrogen and kept there before imaging. The sample was observed under cryo-SEM without further staining.

For the melt sample of LCBBC/AuNPs nanocomposite, TEM study was performed on Tecnai Biotwin G2 TEM with accelerating voltage of 80 KV. Thin sections with ~ 100 nm thickness were obtained using a Leica Ultracut UCT microtome with a glass knife at -80 °C, and then slowly brought back to room temperature through a freeze-dry process to avoid the absorption of moisture. The thin sections were collected onto 100 mesh TEM grids covered by carbon coated Formvar film, and stained in RuO $_4$ vapor at room temperature for 60 min.

Cyclic voltammetry measurements

Cyclic voltammetry for ion gels was performed inside a 0.1 M Lithium trifluoromethanesulfonate/Propylene carbonate electrolyte solution. A three electrode cell containing ion gel film deposited ITO coated glass ($7\times 50\times 0.7$ mm, sheet resistance =5-15

ohms/sq) as working electrode, blank ITO coated glass (7×50×0.7mm, sheet resistance =5-15 ohms/sq) as counter electrode and a silver wire as the pseudo reference electrode was used. Potential was scanned between -2 and +2 V for 2 cycles at a scan rate of 50 mV/s.

References

1. I. W. Hamley, V. Castelletto, P. Parras, Z. B. Lu, C. T. Imrie and T. Itoh, *Soft Matter* 2005, **1**, 355-363
2. J. Lai, D. Filla and R. Shea, *Macromolecules* 2002, **35**, 6754-6756
3. C.T. Nguyen, T.H. Tran, X. Lu and R.M. Kasi, *Polym. Chem.* 2014, **5**, 2774-2783

Table S1. Molecular characterization of as-synthesized LCBBC

Polymer	M _n (g/mol)		Weight fraction ^c (%)		Conversion ^d (%)
	GPC ^b	PDI	PMA-g-PEO	PC5MA	
PMA-g-PEO-thioester	29 150	1.21	100	-	82
LCBBC-thioester	38 420	1.31	70	30	90
LCBBC ^a	38 540	1.35	70	30	95 ^e

^a LCBBC was obtained from reduction of LCBBC-thioester by *n*-butylamine in THF, ^b Determined by GPC calibrated at 40 °C with THF as the mobile phase with polystyrene standards, ^c The ratio of the integrals of peaks by ¹H-NMR spectra at 5.33 ppm (olefin group in cholesteryl moiety) and 3.64 ppm (PEO repeating unit) is used to calculate the weight fraction of the LCBBC, ^d Conversion of monomer to polymer was determined using ¹H- NMR analysis, ^e Conversion of reduction was determined using UV-visible spectra.

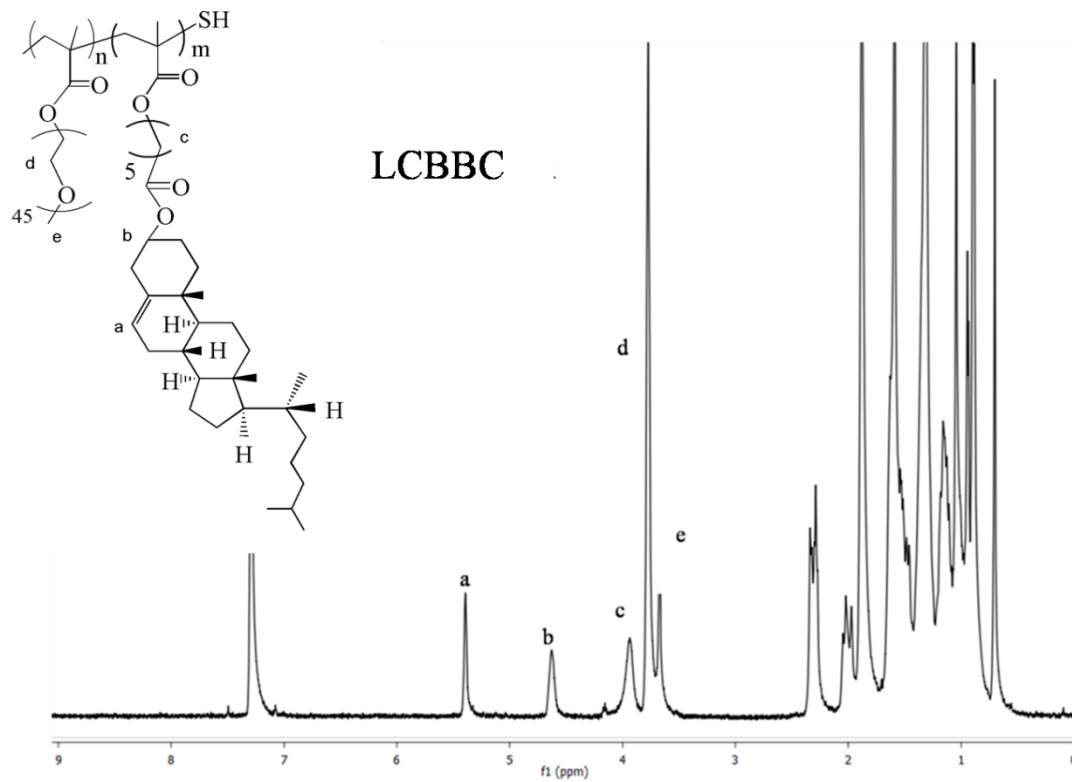


Figure S1: ¹H-NMR spectra of as-prepared LCBBC in CDCl₃ at room temperature.

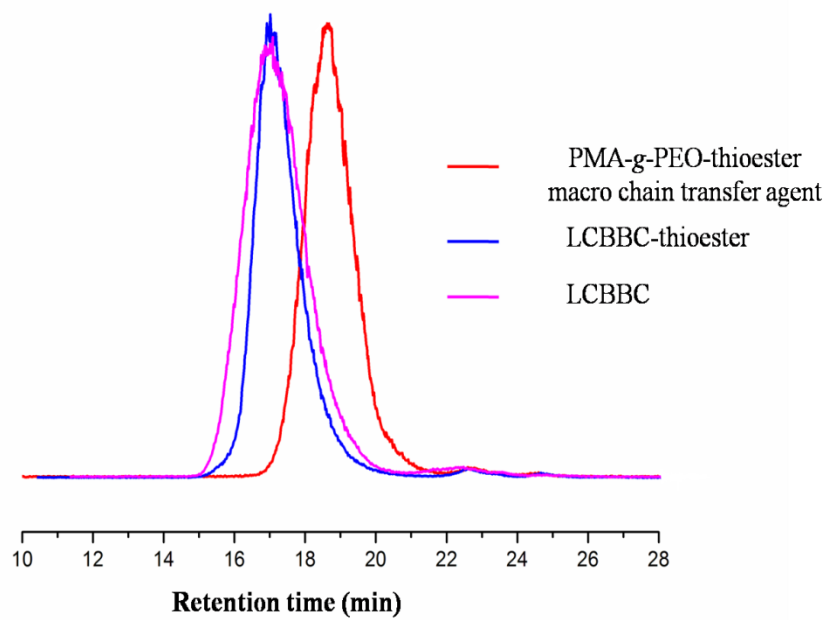


Figure S2. GPC traces of the prepared LCBBC

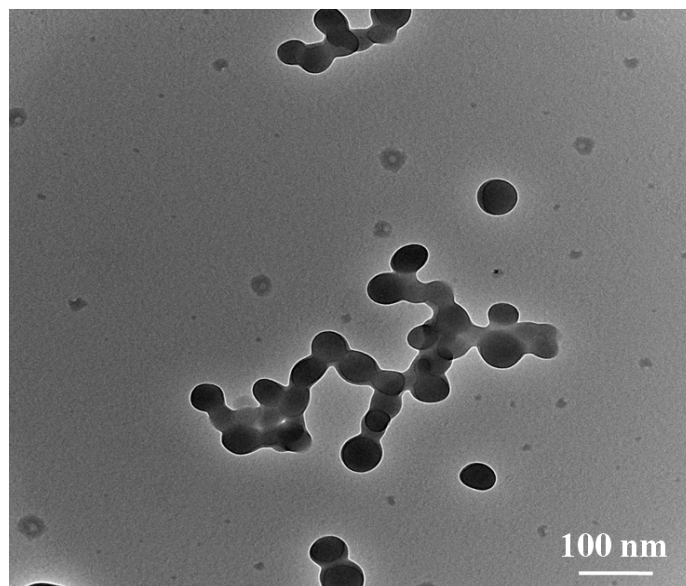
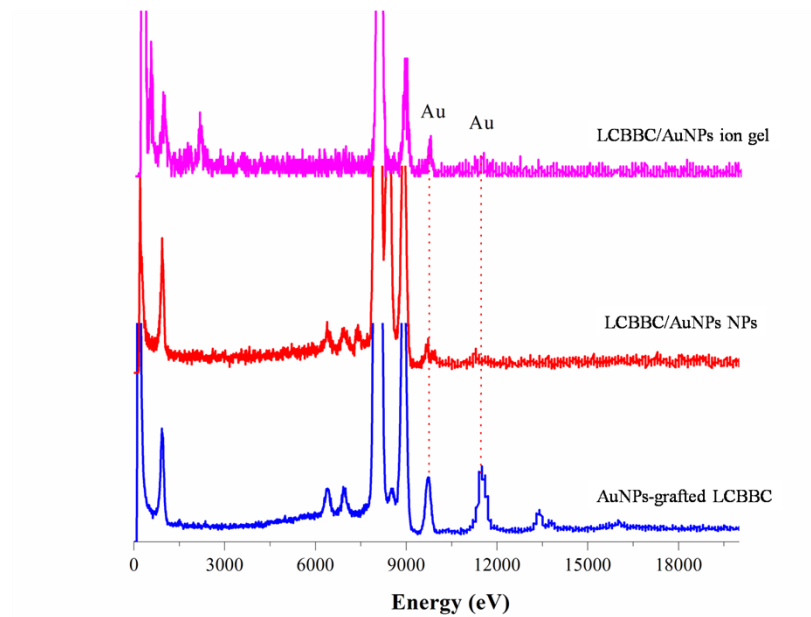


Figure S3: Cryo-SEM image of plain LCBBC nanoparticles in IL

(A)



(B)

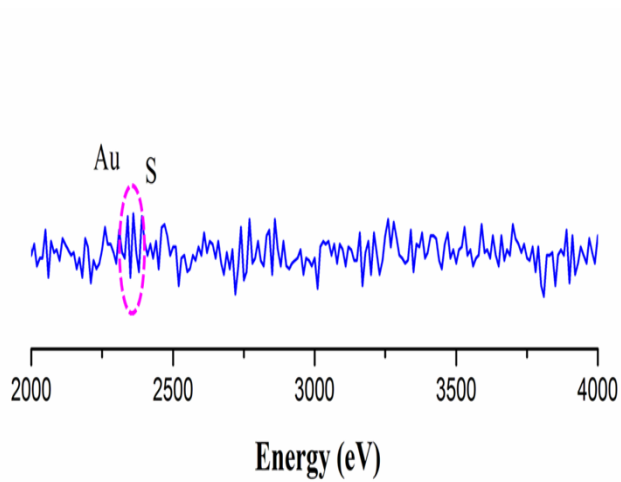


Figure S4: EDX spectroscopy of (A) AuNPs within AuNPs-grafted LCBBC, LCBBC/AuNPs NPs in IL, and LCBBC/AuNPs ion gel; (B) Zoom-in LCBBC/AuNPs nanocomposite

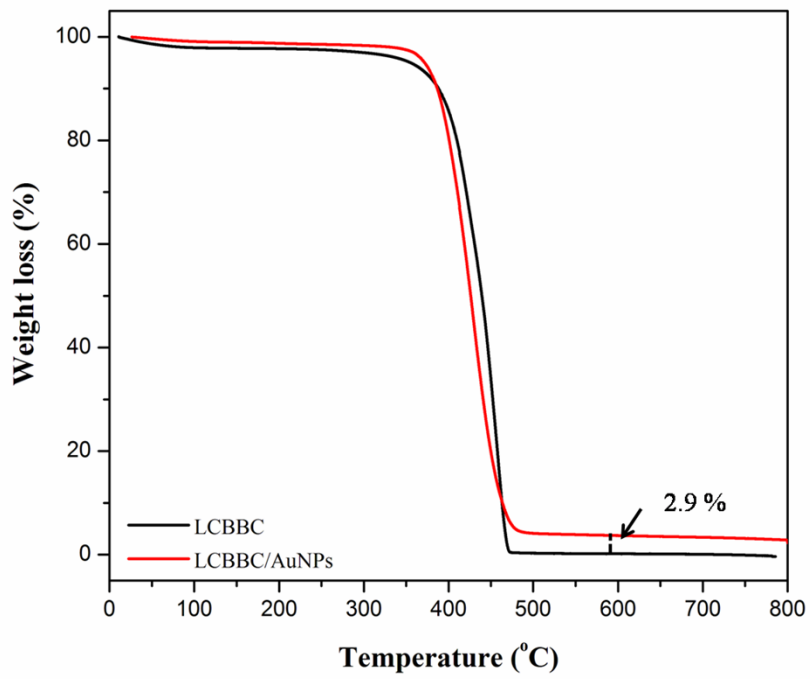


Figure S5: TGA traces of plain LCBBC and LCBBC/AuNPs ion gels

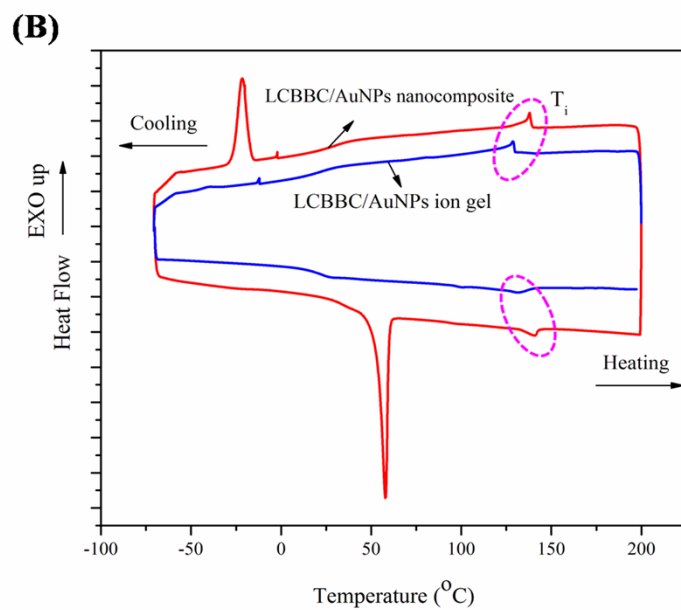
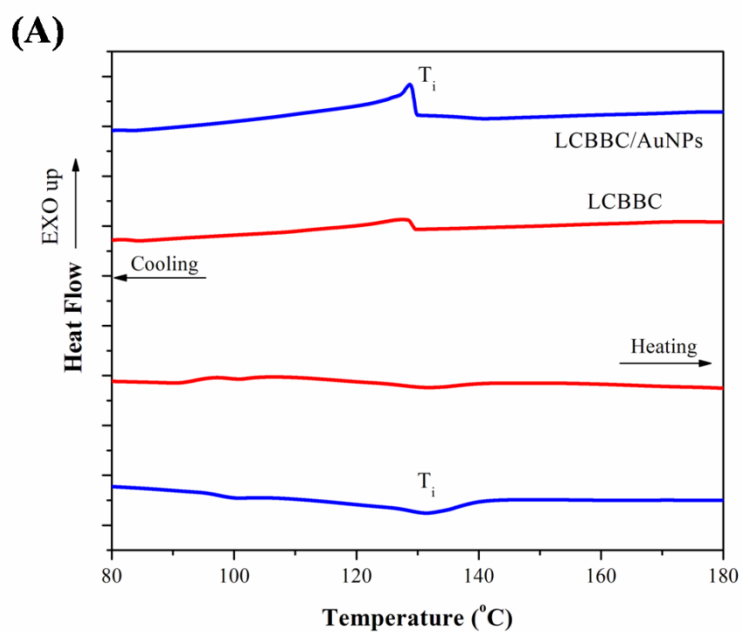


Figure S6: DSC traces of (A) Plain LCBBC and LCBBC/AuNPs nanocomposite, and (B) LCBBC/AuNPs nanocomposite and LCBBC/AuNPs ion gel at ramping rate of 10 $^{\circ}\text{C}/\text{min}$ in the second heating and cooling cycle.

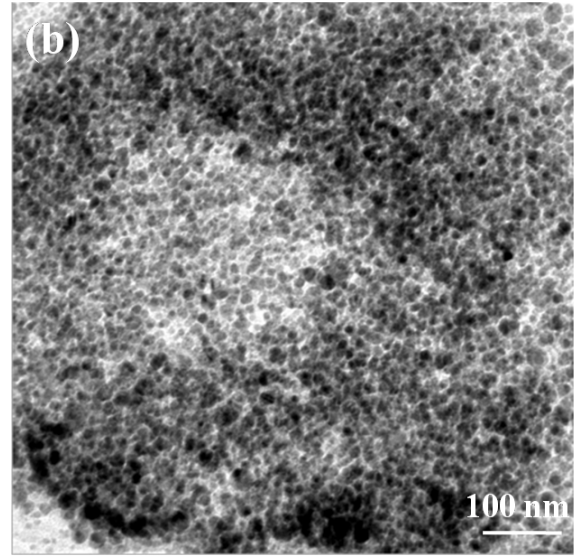
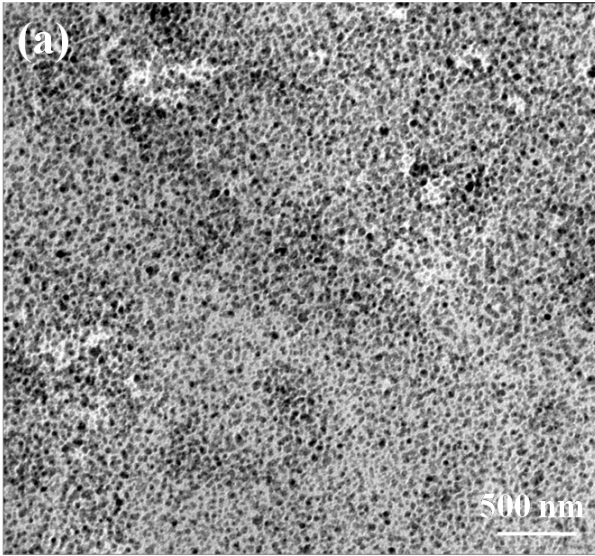


Figure S7. TEM images of compression molding LCBBC/AuNPs nanocomposite. The ultrathin cross-section sample was prepared by cryomicrotomy and stained with RuO_4 .

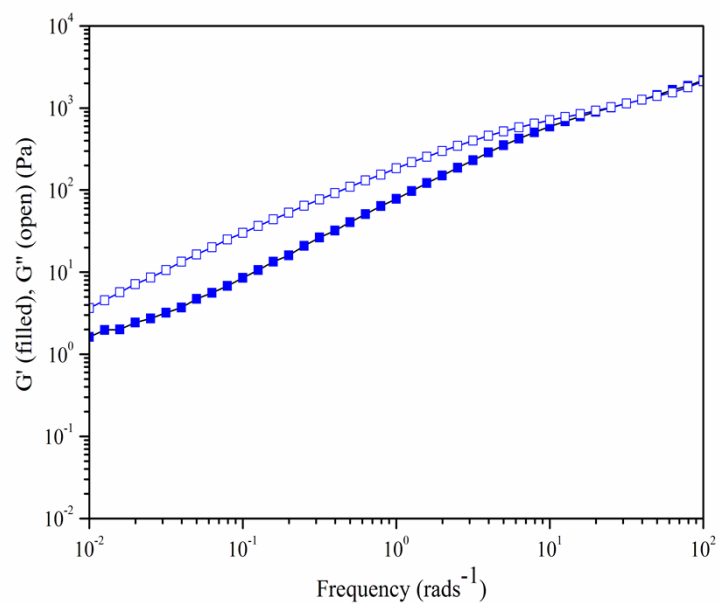


Figure S8: Dynamic frequency sweep at 3 wt% concentration of LCBBC/AuNPs ion gel at 25 °C

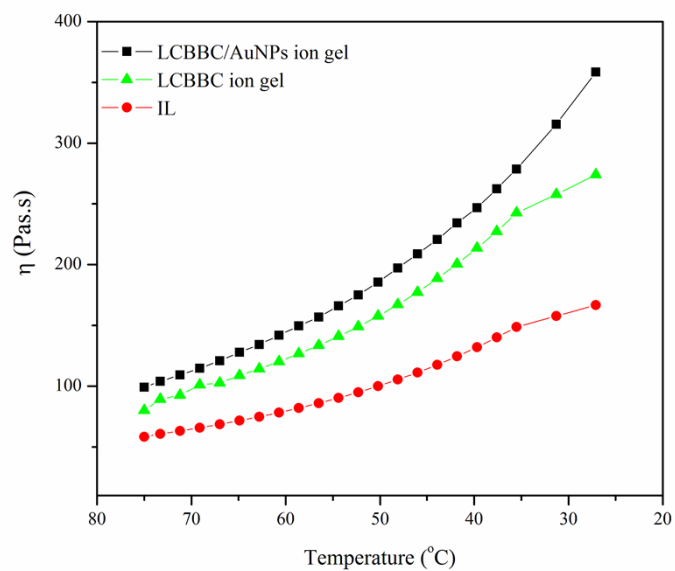


Figure S9. Viscosity vs temperature of bulk IL and 5 wt% ion gel