Supplementary Information

Depletion of Liquid Fragility and Enhancement in Ionic Conductivity in the Glassy Phase of [BmIm][NTf_2] Ionic Liquid under Nano-confinement: PALS and BDS Investigations

Shapath Bhandari[1], Jaideep Mor[1,4], Debasis Sen[2,4], Jitendra Bahadur[2,4], Kanaklata Pandey[3], Dhanadeep Dutta[1,4,*]

[1]Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400 085, India

[2]Solid State Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400 085, India

[3]Radioanalytical Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400 085, India

[4]Homi Bhabha National Institute, Anushaktinagar, Mumbai-400 094, India

*Corresponding author: deep@barc.gov.in, +91 22 2559-4598

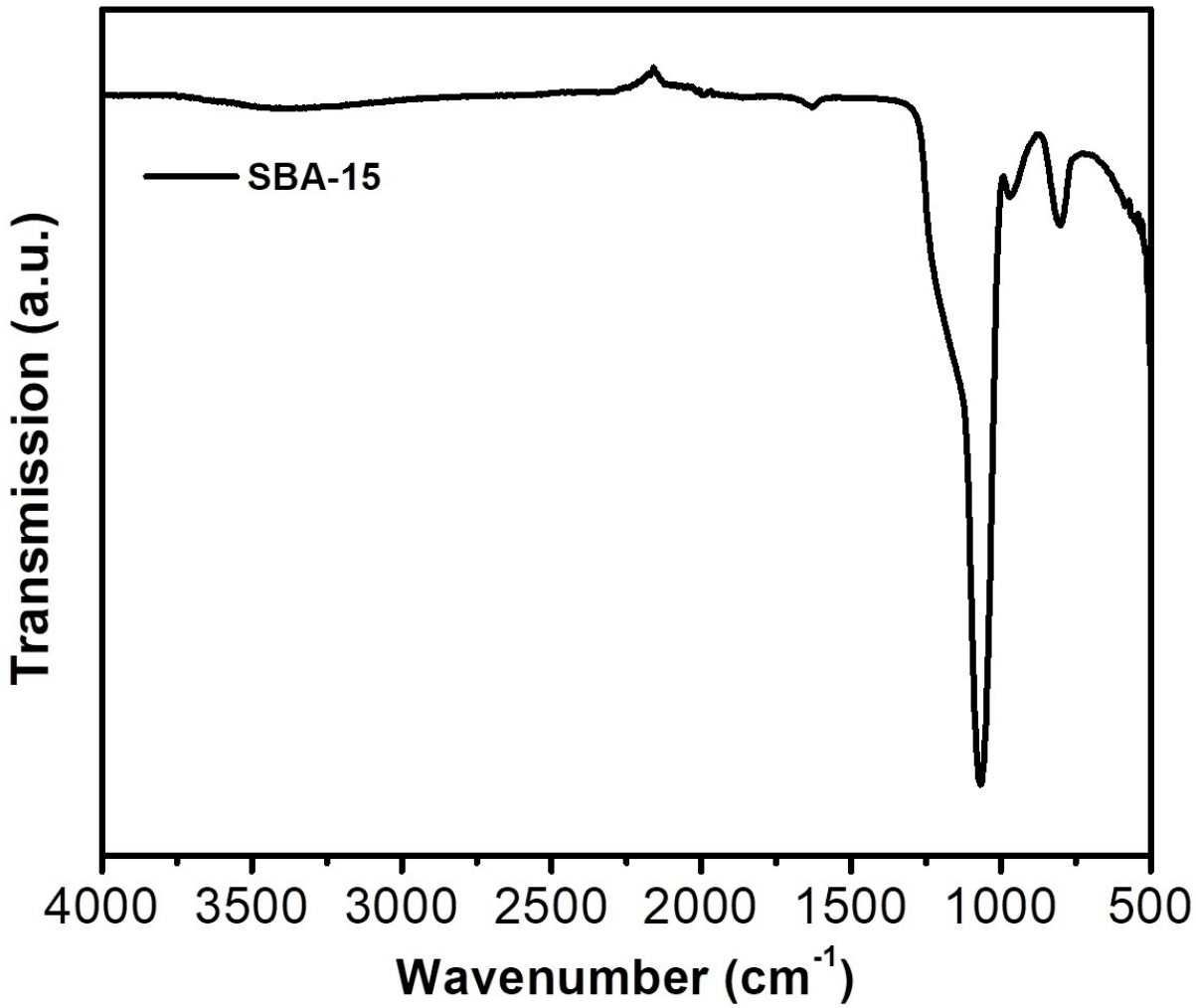


Figure S1: FTIR spectrum of blank SBA-15.

Pore filling calculation from the SAXS data:

Small-angle X-ray scattering experiments measure I(q) at very small scattering vectors (q) or scattering angle (2θ), probing systems with characteristic sizes from a few nanometers to tens of nanometers. Analysis of the scattering profile provides quantitative information about various parameters which give useful information regarding the morphology and correlation of the scatterer in the samples. We know that I(q) is proportional to the contrast factor or square of the difference between the scattering length density of the particle and medium, so we can write,

$$\frac{[I(q)]_S}{[I(q)]_{S+L}} = \frac{(\rho_S)^2}{(\rho_S - \varphi\rho_L)^2} \quad (1)$$

Where, $[I(q)]_S$ and $[I(q)]_{S+L}$ are the scattering intensities corresponding to blank SBA-15 and IL+SBA-15 composite respectively, ρ_S and ρ_L are the scattering length density of blank SBA-15 and pure IL respectively and φ represents the fraction of pore filling.

Scattering length density (ρ) is defined as,

$$\rho = \frac{\sum_{i=1}^{n} b_i}{V_m} \quad (2)$$

where, b_i is the coherent scattering length of the i^{th} atom among the n atoms of the molecule, V_m is the molecular volume.

Molecular volume (V_m) is calculated from the relation, $\frac{M_w}{N_A * d}$ where, M_w is molar mass, N_A is Avogadro number and d is mass density for both SBA-15 and ionic liquid.

The parameter b_i is the coherent scattering length of the atom *i*. X-ray scattering length is given by $Z \times r_e$ where, *Z* is the atomic number of that atom and r_e is the classical electron radius. Putting these values in equation 2 we can get scattering length density (ρ) for both SBA-15 and ionic liquid.

The scattering length density (SLD) depends on photon energy and changes strongly near absorption edge. Although X-ray beam energy (12 keV) is far from the absorption edge of the

constituent atoms (Si, C, O, N), the corrections for photon energy in SLD calculations are incorporated using the available python package (https://github.com/pkienzle/periodictable).

For SBA-15 using bulk density of 1.9 g/cm^3 and X-ray energy of 12 keV we calculated ρ_S to be 1.621×10^{11} cm^2 and for IL using density of 1.44 g/cm^3 we got ρ_L to be 1.252×10^{11} cm^2.

Now, taking the value of the intensities from the SAXS data and putting the ρ values in the given equation, the value of φ comes out to be 0.929.

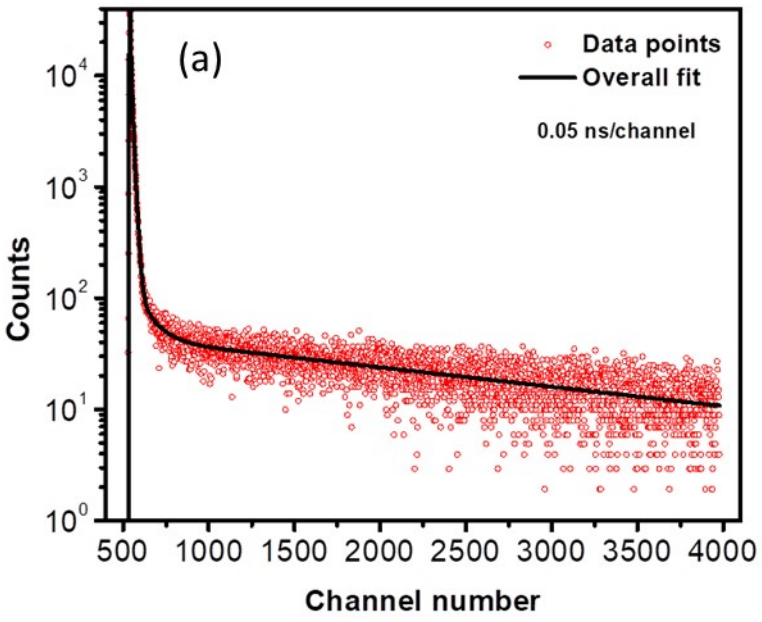
Pore diameter calculation from SAXS data:

Now, for hexagonal lattice, the value of lattice constant (a) can be calculated as,

$$a = \frac{4\pi}{q_{100} \times \sqrt{3}} \qquad (3)$$

where, q_{100} is the peak position corresponding to 100 reflection in SAXS data, which is 0.655 nm^{-1}.

So, putting the values in equation 3, a comes out to be 11.08 nm but this is center-to-center distance between two adjacent cylindrical pores of SBA-15.



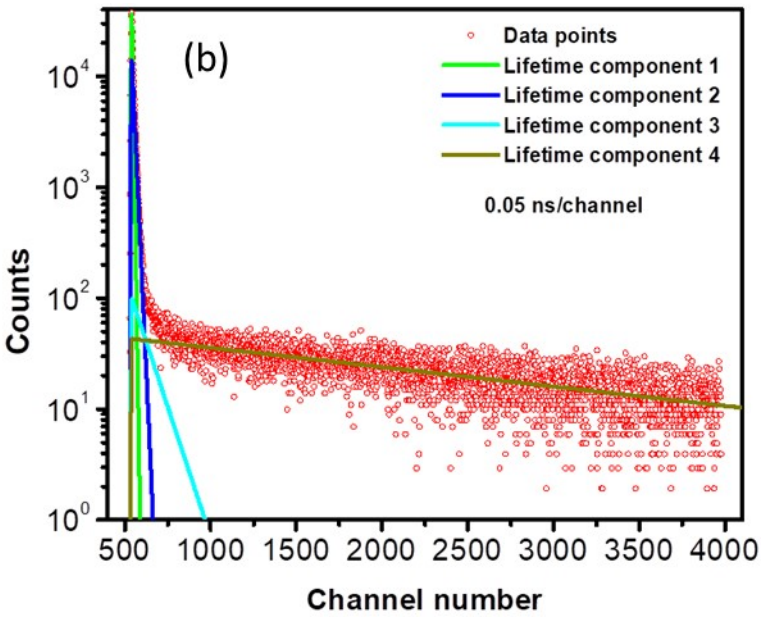


Figure S2: Typical PALS spectrum of (a) blank SBA-15 and (b) corresponding fitting into different lifetime components.

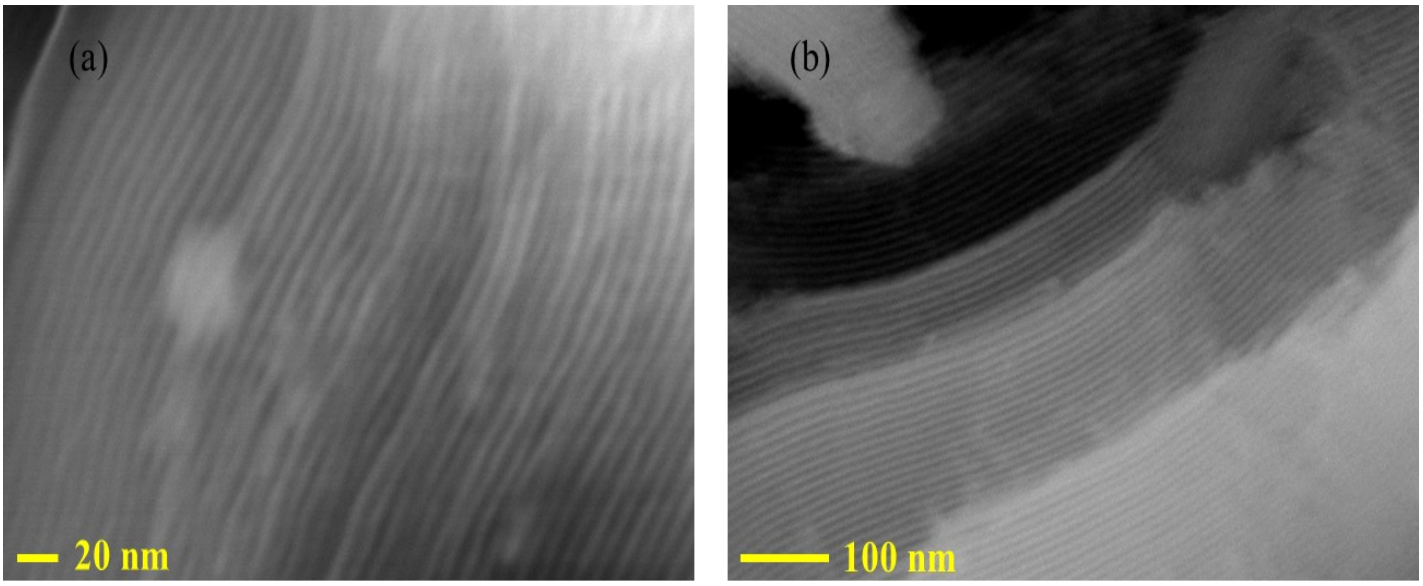


Figure S3: Magnified FESEM images of blank (a) SBA-15 and (b) IL+SBA-15 composite. The sharp hexagonal structure of SBA-15 is visible in both cases.

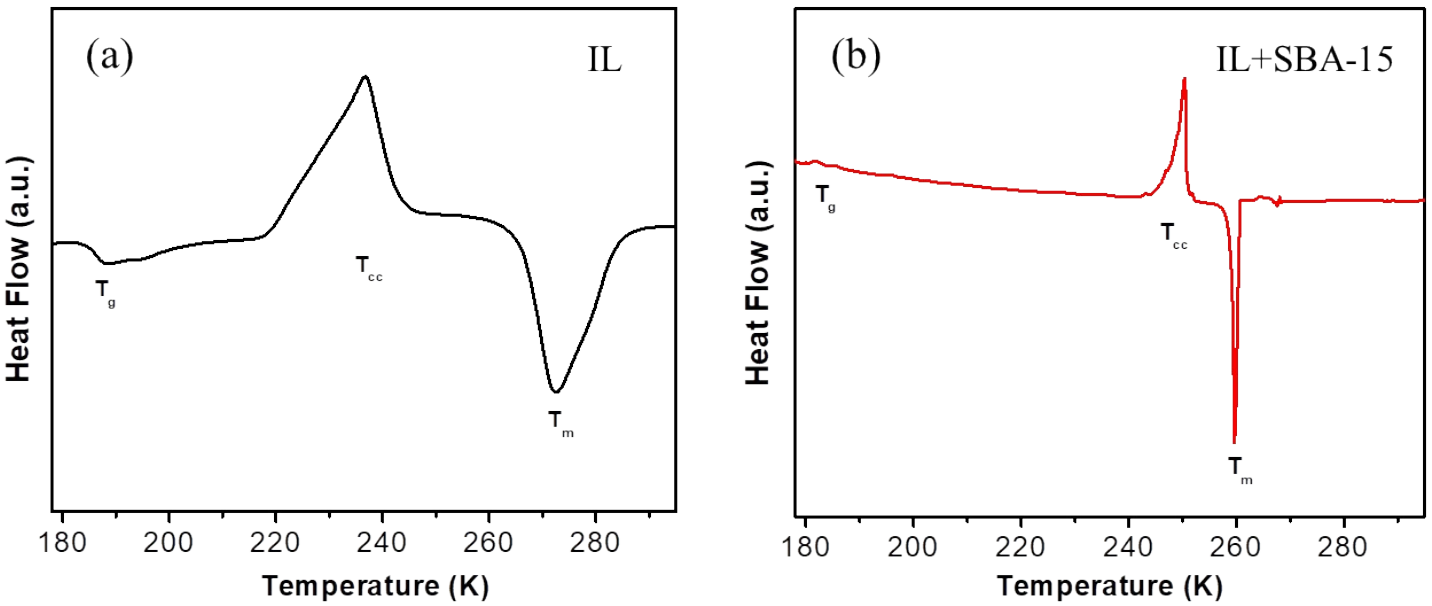


Figure S4: (a) Differential scanning calorimetry (DSC) profiles for bulk IL and (b) IL+SBA-15 composite systems obtained at a heating rate of 10 K/min (T_g, T_{cc} and T_m are glass transition, cold crystallization and melting temperatures respectively).

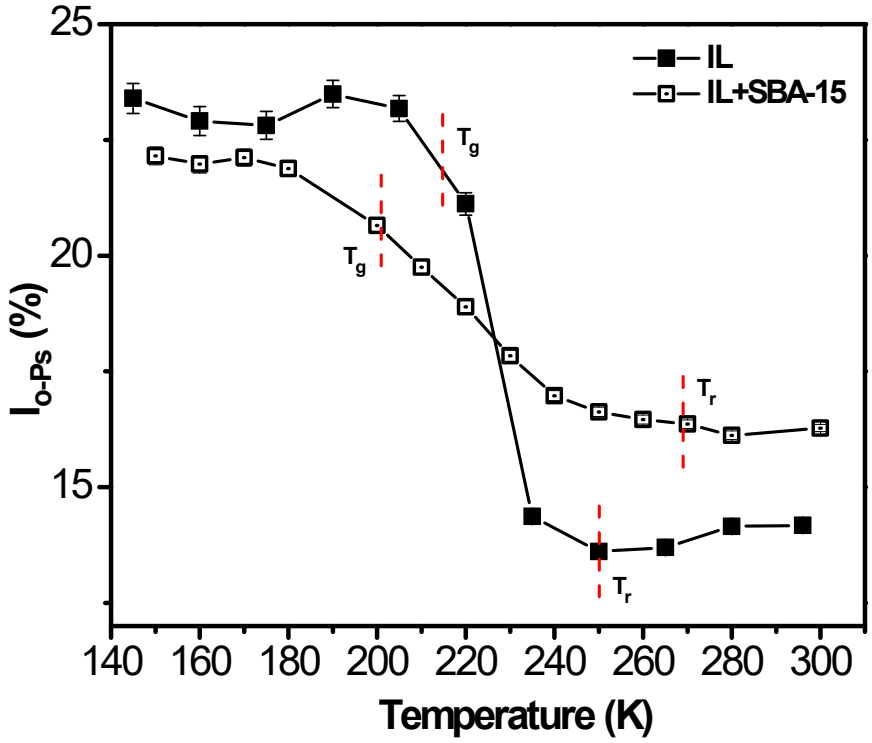
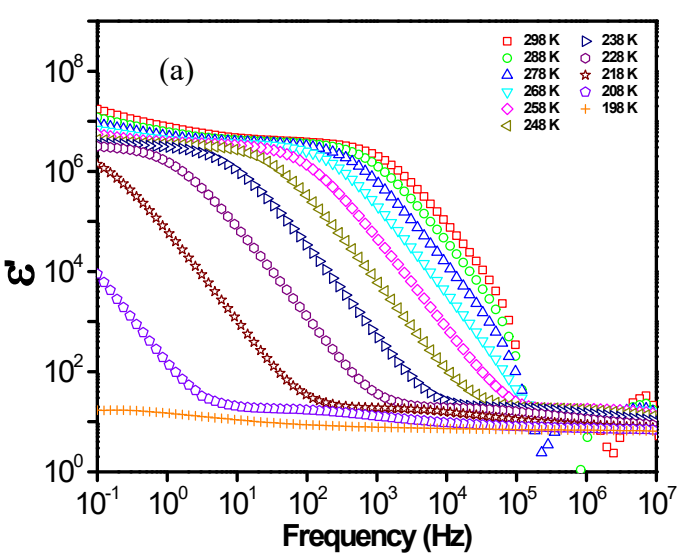
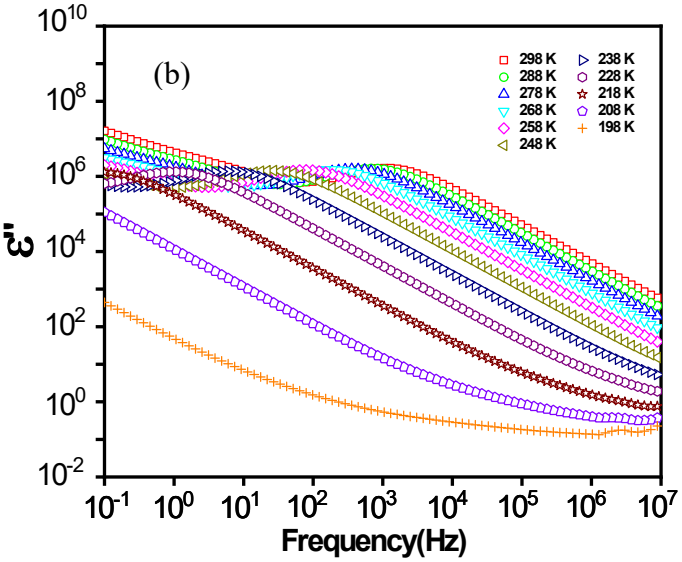
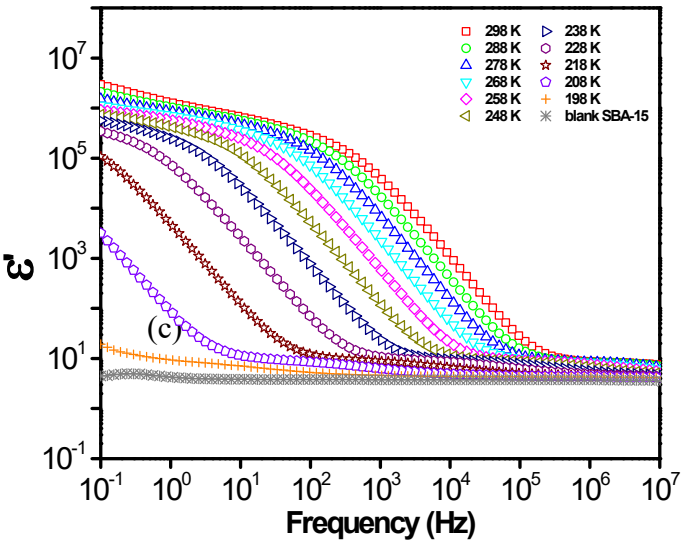


Figure S5: The o-Ps *pick-off* annihilation intensity ($I_{o\text{-}Ps}$) vs temperature plot for both bulk IL and confined IL (IL+SBA-15 composite).


(a)
298 K
288 K
278 K
268 K
258 K
248 K
238 K
228 K
218 K
208 K
198 K
ε'
Frequency (Hz)


(b)
298 K
288 K
278 K
268 K
258 K
248 K
238 K
228 K
218 K
208 K
198 K
ε''
Frequency(Hz)


(c)
298 K
288 K
278 K
268 K
258 K
248 K
238 K
228 K
218 K
208 K
198 K
blank SBA-15
ε'
Frequency (Hz)

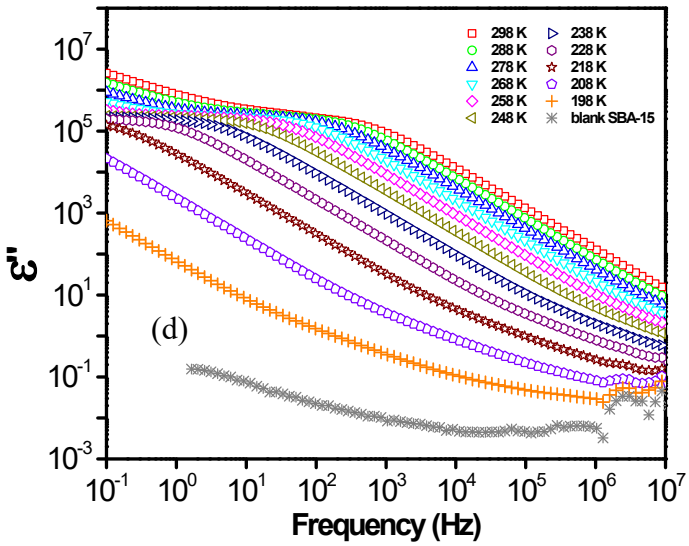

(d)
298 K
288 K
278 K
268 K
258 K
248 K
238 K
228 K
218 K
208 K
198 K
blank SBA-15
ε''
Frequency (Hz)

Figure S6: Dielectric spectra of bulk IL [(a) & (b)] and IL+SBA-15 [(c) & (d)]. The real parts of the permittivity are shown in (a) & (c) and the imaginary parts are shown in (b) & (d). Data for blank SBA-15 are shown at 258 K.

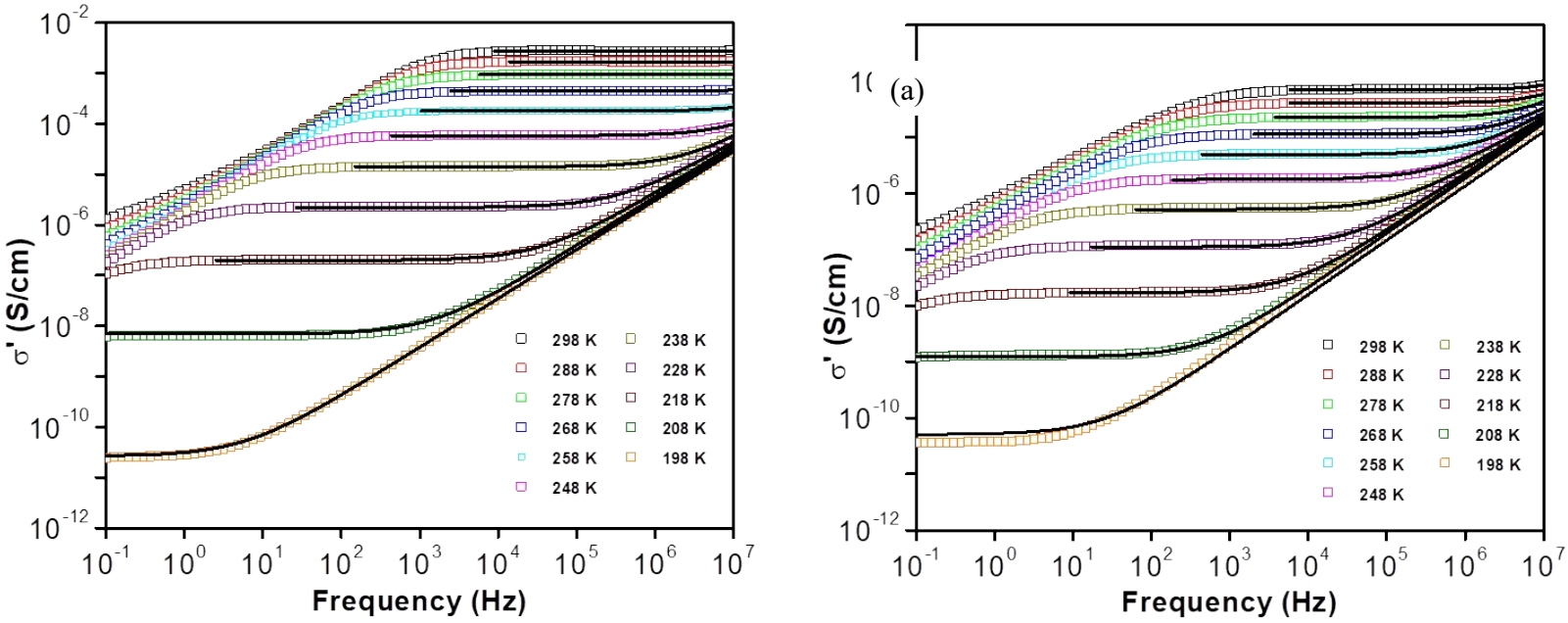
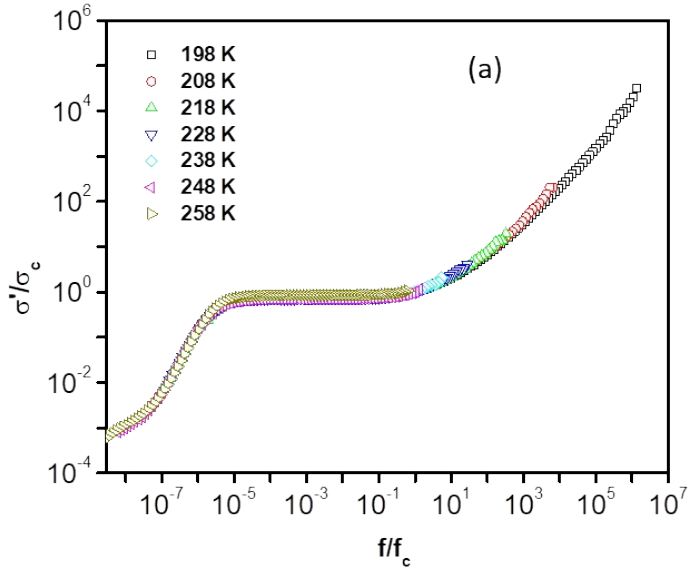
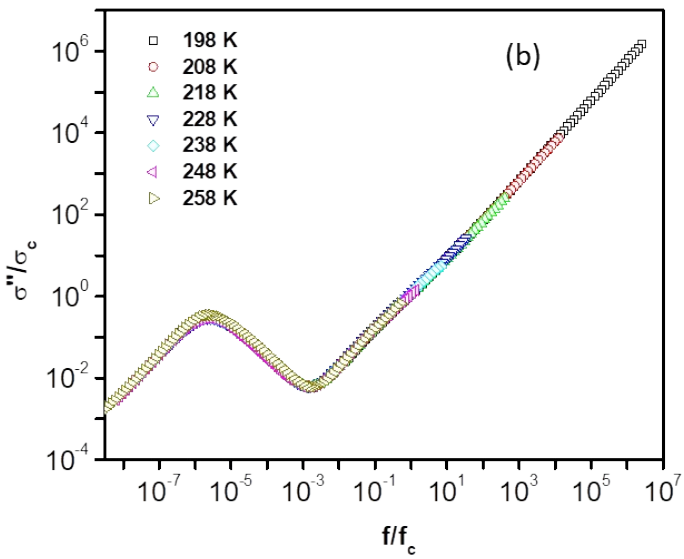
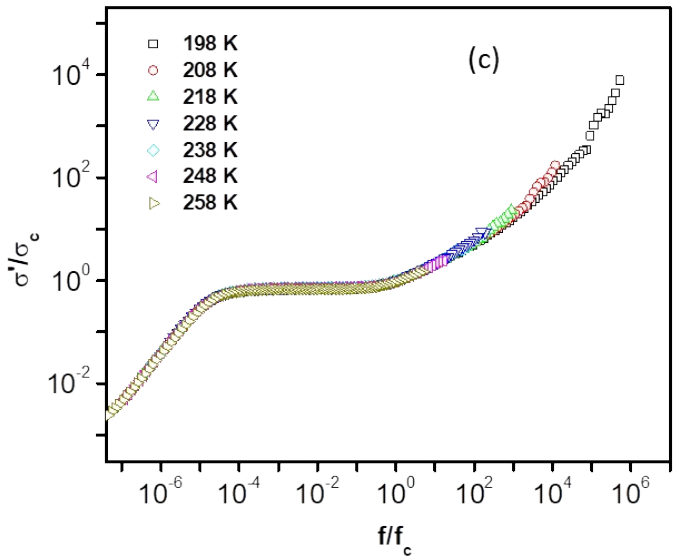


Figure S7: The fitting of real part of conductivity (σ′) using Jonscher's power law for (a) IL and (b) IL+SBA-15 at different temperature. The solid lines show fitting curve.


198 K
208 K
218 K
228 K
238 K
248 K
258 K
(a)
σ'/σc
f/fc


198 K
208 K
218 K
228 K
238 K
248 K
258 K
(b)
σ''/σc
f/fc


198 K
208 K
218 K
228 K
238 K
248 K
258 K
(c)
σ'/σc
f/fc

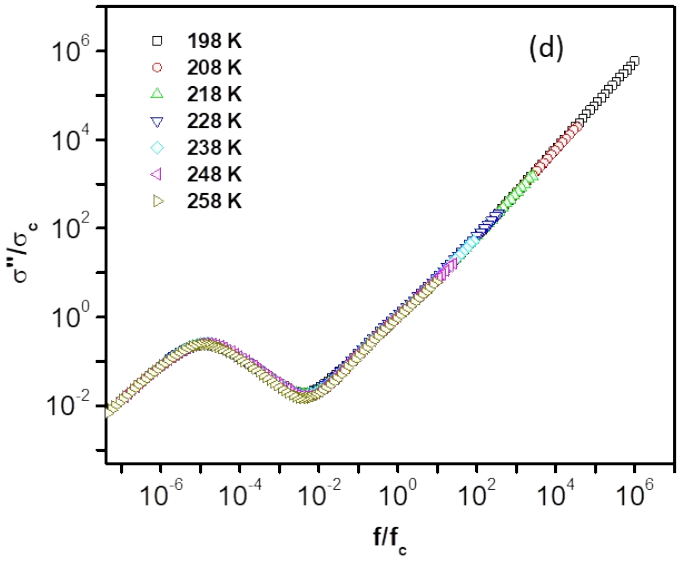
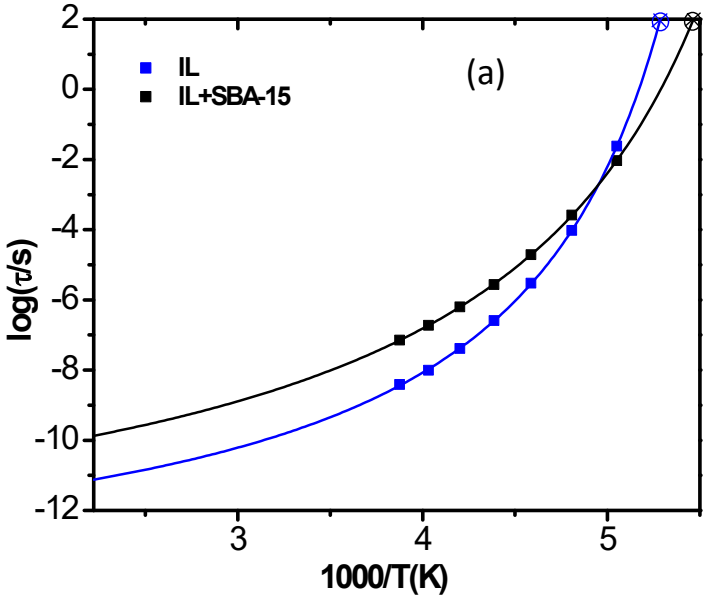

198 K
208 K
218 K
228 K
238 K
248 K
258 K
(d)
σ''/σc
f/fc

Figure S8: Plot of σ′ and σ″ vs. frequency after scaling with respect to σ_c and f_c at different temperatures for IL [(a) & (b)] and IL+SBA-15 [(c) & (d)] respectively.


IL
IL+SBA-15
(a)
log(τ/s)
1000/T(K)
2
0
-2
-4
-6
-8
-10
-12
3
4
5

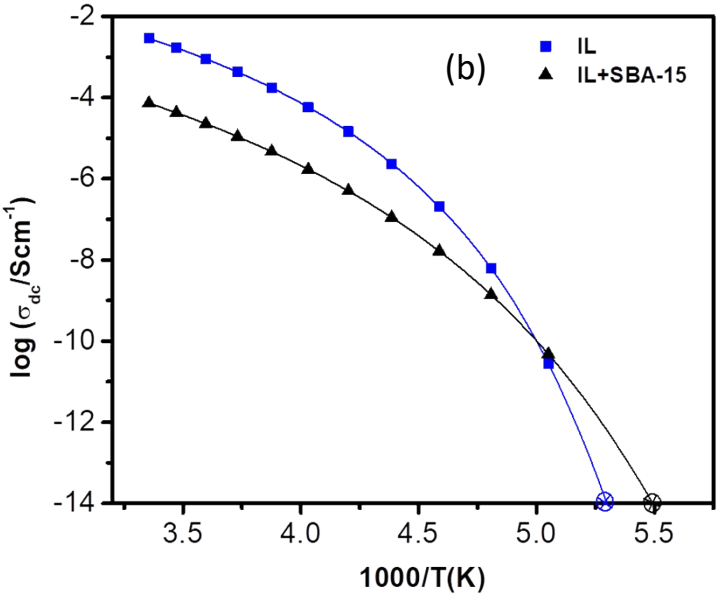

IL
IL+SBA-15
(b)
log (σdc/Scm-1)
1000/T(K)
-2
-4
-6
-8
-10
-12
-14
3.5
4.0
4.5
5.0
5.5

Figure S9: The variation of (a) relaxation time and (b) dc conductivity of IL and IL+SBA-15 with temperature. The marked points on the ordinate for both the relaxation time and dc conductivity plots represent glass transition temperature (T_g) for both bulk IL and IL+SBA-15.

Table S1: Best fitted values of fragility parameter (B) and Vogel temperature (T_0) from VFT fitting:

	IL		**IL+SBA-15**	
	B (K)	T_0 (K)	B (K)	T_0 (K)
From relaxation (τ)	878.3±30.5	162.8±0.9	1084.9±22.0	147.9±0.7
From dc conductivity (σ_{dc})	922.9±17.1	161.4±0.4	1245.5±36.1	141.9±1.2

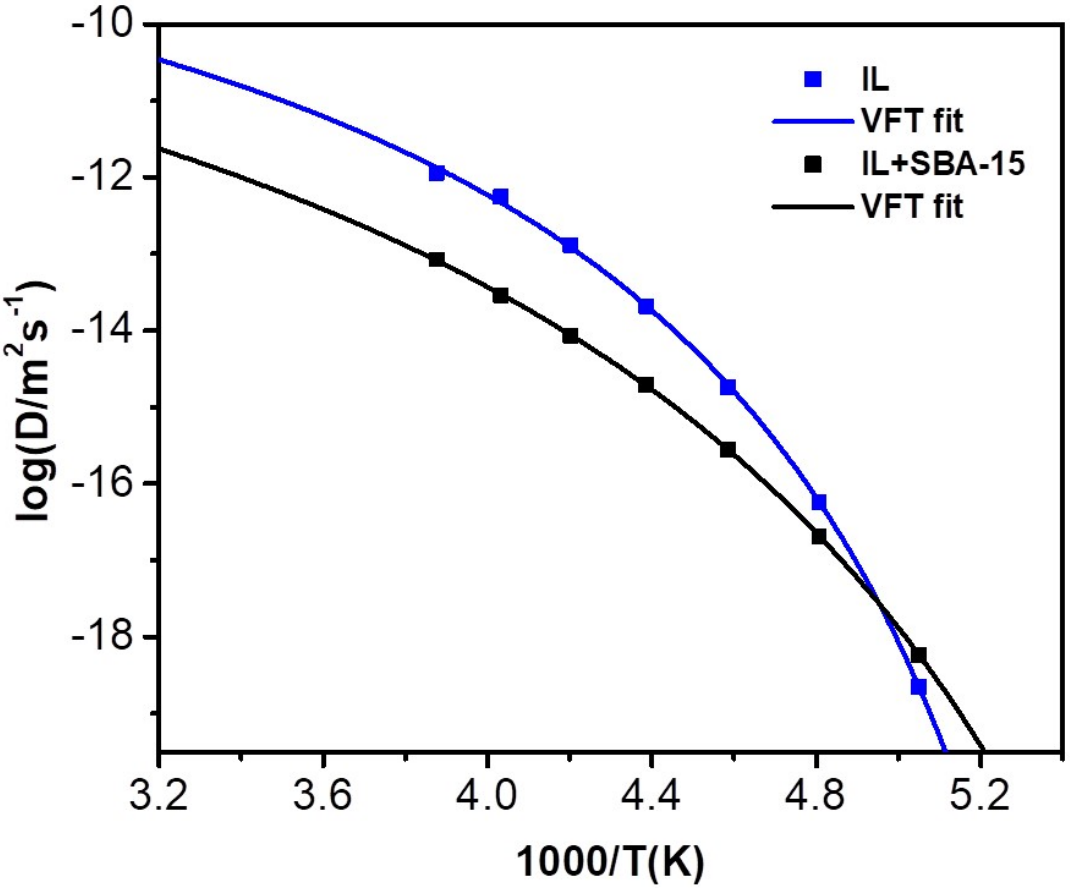


Figure S10: Temperature dependence of diffusion coefficients (*D*) as determined from Einstein-Smoluchowski equation with the help of BDS measurement. The lines here indicate VFT fit of diffusivity data.

Table S2: Best fitting parameters obtained from the fitting of experimental conductivity data of bulk IL using Jonscher's power law formula.

Temperature (K)	σ_{dc} (x 10^{-7} Scm^{-1})	A (x 10^{-15})	n	R^2(%)
298	27500	-	-	-
288	16900	-	-	-
278	9328.07	-	-	-
268	4445.21	2.13	1.4264	99.20
258	1798.28	169.05	1.1816	99.14
248	581.11	2597.52	1.0280	99.55
238	140.04	5498.00	0.9867	99.14
228	21.92	13085.10	0.9285	99.95
218	1.97	9361.24	0.9415	99.99
208	6.93×10^{-2}	5889.50	0.9640	99.99
198	2.67×10^{-4}	4709.86	0.9678	99.99

Table S3: Best fitting parameters obtained from the fitting of experimental conductivity data of IL+SBA-15 composite using Jonscher's power law formula.

Temperature (K)	σ_{dc} (x 10^{-7} Scm^{-1})	A (x 10^{-15})	n	R^2(%)
298	710.19	0.857	1.4610	99.14
288	406.75	18.71	1.2835	99.90
278	226.62	207.77	1.1424	99.90
268	112.76	1377.9	1.0289	99.91
258	48.55	4501.96	0.9555	99.93
248	17.61	6813.92	0.9270	99.96
238	5.14	6135.20	0.9299	99.96
228	1.10	4569.98	0.9450	99.96
218	1.68×10^{-1}	2956.46	0.9703	99.99
208	1.21×10^{-2}	2379.37	0.9824	99.99
198	5.07×10^{-4}	2101.91	0.9881	99.99