Supporting Information

Ion Specific, Odd-Even Glass Transition Temperatures and Conductivities in

Precise Network Polymerized Ionic Liquids

Chengtian Shen, Qiujie Zhao and Christopher M. Evans

Experimental Methods

Materials:

1,4-dibromobutane (99%), 1,5-dibromopentane (97%), 1,6-dibromohexane (98%), 1,7dibromoheptane (97%), 1,8-dibromooctane (98%), 1,9-dibromononane (97%), 1,10dibromodecane (97%), 1,11-dibromoundecane (\geq 98%), 1,12-dibromododecane (98%), bis(trifluoromethylsulfonyl)imide lithium salt (LiTFSI, 99.95%), sodium tetrafluoroborate (NaBF₄, 98%), and methanol (MeOH, ACS grade) were purchased from Sigma Aldrich and used without further purification. Tris(2-dimethylaminoethyl)amine (Me₆TREN, 99+%) was purchased from Alfa Aesar and used without further purification.

Synthesis of Br network polymerized ionic liquid (n-PIL) with different linker length (C_xBr)

To synthesize a sheet (3.5 cm × 3.5 cm × 0.17 mm) of ammonium n-PIL with different linker size (x = 4 - 12), tris(2-dimethylaminoethyl)amine (2 equiv., 0.96 mmol) and the corresponding dibromo compound (3 equiv., 1.44 mmol) were first combined in a small 5 mL vial. The amount of each component needs to be measured with high accuracy (< 0.1 wt% difference from theoretical mass with consideration of reactant purities) to ensure high conversion during the polymerization. The solution was thoroughly mixed by a vortexer and degassed by sonication. The monomer solution was then transferred into a glass mold with Kapton tape (150 µm thick) as the spacer. A thin layer of vacuum grease was applied on top of the Kapton tape to provide an air-tight seal for the reaction. Another glass slide was then used as a top cover of the mold and a 2 kg weight was placed to apply pressure. After the network was cured at 80 °C for 16 hours, it was carefully peeled off of the glass slide and placed on top of a Teflon[®] sheet to prevent sticking onto other objects.

Ion exchange of Br networks to TFSI networks

To synthesize AmC_xTFSI n-PIL, the AmC_xBr n-PILs were swelled in MeOH for 30 mins. The wet network was then immersed into a LiTFSI (9 equiv., 25.9 mmol) MeOH solution (50 mL) for 48 hours with minimal stirring. The network was then washed (> 3 times) by soaking in fresh MeOH for 1 hour each time to remove access LiTFSI salt and LiBr salt until conductivity of final wash solution is less than 0.5 μ S/cm. The resulting AmC_xTFSI networks were dried in a vacuum oven overnight at 100 °C and quickly transferred into the glovebox for storage and further use.

Ion exchange of Br networks to BF4 networks

To synthesize AmC_xBF_4 networks, the C_x Br networks were swelled in MeOH/H₂O (v/v 80:20) for 30 mins. The network was then immersed into a sodium tetrafluoroborate (NaBF₄, 9 equiv., 25.9 mmol) MeOH/H₂O (v/v 80:20) solution (50 mL) overnight with minimal stirring. The wet network was then washed three times by soaking in MeOH/H₂O (v/v 80:20) for 1 hour each time to remove access NaBF₄ salt and NaBr salt (conductivity of final wash solution < 0.5 μ S/cm). The resulting AmC_xBF₄ networks were dried in a vacuum oven overnight at 100 °C and quickly transferred into the glovebox for storage and further use.

Structural characterization

¹³C solid state nuclear magnetic resonance of the AmC_xBr n-PILs was measured using a Varian Unity Inova instrument (UI300WB, 300 MHz) via direct polarization magic angle spinning (DPMAS) at 10 kHz spanning frequency, 5600 scans, 5 sec cycle delays ($d_1 = 5$ s). A pseudo T1 measurement was done with $d_1 = 1,5$, 10 and 20 s to ensure 5 s is sufficient for all ¹³C nuclei to relax.

Elemental analysis was done by submitting AmC_xTFSI and AmC_xBF_4 n-PILs to the Microanalysis Laboratory at the School of Chemical Sciences at University of Illinois, Urbana-Champaign. For CHN analysis, a PerkinElmer 2400 Series II was used, and for Br and F analysis, Thermo Scientific Orion Ion Selective Electrodes were used. All n-PIL samples were prepared in the glove box and packed under argon to minimize the influence of moisture during transfer.

Thermal characterization

All DSC samples were prepared in the glove box and packed under argon to minimize the influence of moisture. The T_{gs} of the n-PILs were measured using a DSC (Q2500, TA instruments) from

-50 °C to 100 °C at a heating/cooling rate of 10 °C/min for AmC_xTFSI n-PILs and 50 °C to 200 °C for C_xBF₄ n-PILs. The half point of ΔC_p was used to determine the T_g s of the samples.

The thermal stability of the n-PILs were measured using a TGA (Q50, TA instruments) from 20 °C to 600 °C at a heating rate of 10 °C/min. Degradation temperature (T_d)s are defined as the temperature where 5 wt.% of sample is lost.

Ionic conductivity measurements

The ionic conductivities of n-PILs were measured using electrochemical impedance spectroscopy (EIS). Inside the glovebox, a 5 mm diameter circular disk was punched from the synthesized network sheet and placed between two polished stainless-steel electrodes with one layer of Kapton[®] tape as the spacer. Then it was placed in a sample holder (Bio-logic CESH) and connected to a Bio-logic SP300 potentiostat outside the glovebox. The sample was under constant nitrogen flow throughout the measurement. The sample was first heated to T_g +90K and equilibrated for at least 2 hours. Then the impedance spectra were collected from T_g +90K to T_g +10K with a 5K temperature interval and a 30-minute equilibration time before each measurement. The thickness was checked before and after the measurement to ensure no significant deformation of the network. The impedance data was processed to make a plot of real (σ ') and imaginary (σ '') conductivities versus frequency. The network ionic conductivity was taken as the real conductivity where *tan* $\delta = \sigma'/\sigma''$ is at a maximum.

X-ray Scattering

The morphologies of n-PILs were characterized using transmission wide-angle X-ray scattering (WAXS). The WAXS setup is composed of a Xenocs GeniX3D Cu Kα X-ray source (1.54Å) and a Pilatus 2D detector. A rod beam stop was placed in front of the detector to attenuate the primary

beam. The sample-to-detector distance was first calibrated with silver behenate powder. Then all n-PILs samples were lined up on the sample holder and the scattering patterns were collected with 30-minute exposure time on each sample at ambient condition (~20 °C). The 2D diffraction data were radially averaged using FIT2D software and the intensity was plotted as a function of scattering vector q.

Figures and Tables



Figure S1. (Left) A 4 mm diameter AmC₁₀Br network swollen in MeOH, (Middle) a 4 mm diameter network swollen



in DI water and (Right) a dry 4mm diameter network as comparison.

Figure S2. (Blue) ¹³C NMR of Me₆TREN in DMSO-d₆, ¹³C Solid state NMR of (Green) C₁₂ dibromo starting material and (Red) AmC₁₂Br n-PIL.

Covalently crosslinked networks are not soluble in any solvent, making them difficult to characterize. As shown in the NMR data of the starting materials and resulting Br network (Figure S1), peak 1 and peak α merge to form peak **a** which represents the methylene carbons adjacent to

ammonium center. Peak **3** shifts down field after the quaternization of tethered tertiary amine and forms peak **b** in combination with peak **2**. Peak **c** represents aliphatic carbons in between ammonium junctions therefore has similar chemical shift compare to peak β .

Table S1. Elemental Analysis data for AmC_xTFSI n-PILs

	Ne	etwork Ele		ment	Theoretical wt%		Actual	wt%
	AmC₄TFSI AmC₅TFSI			Br	0.0 %		0.3	%
				F	29.6 %		29.4	%
				С	25.	0 %	25.4	%
				Н	3.7 %		3.6	%
				N	8.5 %		8.1	%
				Br	0.0 %		0.3	%
				F	29.1 %		29.2	2 %
				С		26.0 %		5%
				Н 3.9%		3.9	%	
				N 8.3 %		8.3	%	
			Br		0.0 %		0.5	%
			F		28.6 %		31.3 %	
	Am	C ₆ TFSI	С		27.1 %		27.7	%
			Н		4.0 %		4.0	%
				N	8.2 %		8.1	%
				Br O) %	0.9	%
			F		28.1 %		28.2	2 %
	Am	C ₇ TFSI	С		28.1 %		28.7	/ %
			Н		4.2 %		4.4	%
			N		8.0 %		8.0	%
			Br		0.0 %		1.8	%
			F		27.6%		32.1	L %
	Am	C ₈ TFSI	С		29.1 %		29.9 %	
			Н		4.4 %		4.4 %	
				N	7.9 %		7.7	%
	Br			0.0	%	0.	8 %	
AmC₀TFSI		F		27.1 %		29.8 %		
		С		30.02 %		30.4 %		
		Н		4.6 %		4.6 %		
		N		7.8 %		7.8 %		
			Br		0.0 %		0.7 %	
AmC ₁₀ TFSI		F		26.7 %		28.9 %		
		С		30.9 %		31.2 %		

Н	4.7 %	4.7 %
N	7.6 %	7.6 %

Network	Element	Theoretical wt%	Actual wt%
	Br	0.0 %	1.8 %
	F	26.3 %	28.0 %
AmC ₁₁ TFSI	C	31.8 %	32.5 %
	Н	4.9 %	4.9 %
	N	7.5 %	7.5 %
	Br	0.0 %	0.8 %
	F	25.8 %	26.9 %
AmC ₁₂ TFSI	C	32.7 %	32.9 %
	Н	5.0 %	5.0 %
	N	7.4 %	7.3 %

 Table S2. Elemental analysis data of AmC_xBF₄ n-PILs

Network	Element	Theoretical wt%	Actual wt%
	Br	0.0 %	3.1 %
	F	39.7 %	34.4 %
AmC ₄ BF ₄	С	37.6 %	36.7 %
	Н	7.4 %	7.3 %
	N	9.7 %	8.9 %
	Br	0.0 %	1.1 %
	F	38.3 %	36.2 %
AmC₅BF₄	С	39.3 %	39.1 %
	Н	7.6 %	3.7 %
	N	9.4 %	9.2 %
	Br	0.0 %	0.7 %
	F	37.0 %	34.9 %
AmC ₆ BF ₄	С	40.9 %	40.2 %
	Н	7.8 %	7.8 %
	N	9.1 %	8.6 %
	Br	0.0 %	0.5 %
	F	35.7 %	35.0 %
AmC ₇ BF ₄	С	42.3 %	41.3 %
	Н	8.1 %	8.0 %
	N	8.8 %	8.4 %
	Br	0.0 %	0.84 %
AmC ₈ BF ₄	F	34.6 %	30.2 %
	С	43.7 %	42.7 %

Н	8.3 %	5.3 %
N	8.5 %	8.0 %

Network	Element	Theoretical wt%	Actual wt%
	Br	0.0 %	0.6 %
	F	33.5 %	30.6 %
AmC ₉ BF₄	С	45.0 %	44.3 %
	Н	8.5 %	8.5 %
	N	8.2 %	8.1 %
	Br	0.0 %	0.7 %
	F	32.5 %	30.4 %
AmC ₁₀ BF ₄	С	46.3 %	45.1 %
	Н	8.6 %	8.5 %
	N	8.0 %	7.7 %
	Br	0.0 %	0.5 %
	F	31.6 %	34.0 %
AmC ₁₁ BF ₄	С	47.4 %	46.5 %
	Н	8.8 %	8.7 %
	N	7.8 %	7.7 %
	Br	0.0 %	0.6 %
	F	30.7 %	33.2 %
AmC ₁₂ BF ₄	С	48.5 %	47.7 %
	н	8.9 %	8.9 %
	N	7.5 %	7.5 %



Figure S3. (a-b.) TGA curves of AmC_xTFSI and AmC_xBF_4 n-PILs up to 600 °C. (c.) T_ds plotted with respect to the length of carbon spacer.



Figure S4. Ionic conductivity of AmC₉TFSI n-PIL at 90 °C, which is a representative data for conductivity measurements for all Am n-PILs. DC conductivity is determined at $tan(\delta)$ maximum.



Figure S5. Conductivity data from two independently synthesized AmCxTFSI n-PILs.

Table S3. T_g and D from independently prepared AmCxTFSI n-PILs. D is calculated by fitting conductivity data with VFT equation.

n-PIL sample	T_g (K) Batch 1	T_g (K) Batch 2	D Batch 1	D Batch 2
C₄ TFSI	321	319	6.1	6.4
C₅ TFSI	275	277	5.4	5.2
C ₆ TFSI	293	291	5.8	6.8
C ₇ TFSI	276	275	5.1	5.1
C ₈ TFSI	281	283	5.0	5.2
C ₉ TFSI	274	275	5.0	5.0