Supporting Information

Piperidinium ionic liquids as electrolyte solvents for sustained high temperature supercapacitor operation

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General and Materials

Compound **1** was purchased from lolitec Inc. with 99% purity. All other reagents were purchased from Sigma, Aldrich, or Acros and used without further purification. Purity is indicated on the labels. ¹H (500 MHz) and ¹³C (126 MHz) NMR spectra were recorded on Varian INOVA spectrometers. Electrospray mass spectra were obtained on an Agilent 1100 LC/MSD Trap with ESI and APCI sources (LC/MS).

Synthesis of N-methyl-methoxymethyl-piperidinium Bis(trifluoromethylsulfonyl)imide (2)

Bromomethyl methyl ether (Aldrich, technical grade, 90%) (0.2 mol) was added dropwise to a 1.0 M solution of N-methyl-piperidine (Aldrich, 99%) (0.2 mol) and Ethyl Acetate. The reaction was stirred at 50 °C for 12 hours. The solid halide product was recrvstallized 3 times with Dichloromethane (DCM) and Ethyl Acetate. N-methyl-Nmethoxymethyl-piperidinium bromide was obtained as a white solid product in 35% yield. The halide anion was then exchanged for a TFSI anion by dissolving N-methyl-Nmethoxymethyl-piperidinium bromide in 20 mL of DCM and simultaneously dissolving an equimolar amount of LiTFSI salt in 20 mL of deionized water. The two mixtures were combined and stirred at room temperature overnight. The water phase of the mixture was then washed three times with ten mL of DCM. 1 N AqNO₃ was used to confirm the complete elimination of the Bromide anion. The organic layer was dried on MgSO₄ and the solvent was removed under vacuum. N-methyl-N-methoxymethyl-piperidinium TFSI was isolated as a yellow liquid in 27% yield. ¹H-NMR (CD₃OD): δ1.60-1.74 (m, 2 H, CH₂-CH₂-CH₂), 1.84 (m, 4H, CH₂-CH₂), 3.19 (s, 3H, N-CH₃), 3.30-3.37 (m, 4H, CH₂-N-CH₂), 3.62 (s, 3H, O-CH₃), 5.03 (s, 2H, N-CH₂-O) ¹³C-NMR: δ20.81 (2C, CH₂), 22.46 (1C, CH₂), 45.92 (1C, N-CH₃), 49.5 (1C, O-CH₃), 58.96 (2C, CH₂), 61.48 (1C, N-CH₂-O), 117.68, 120.23, 122.78, 125.33 (CF₃); LC/MS: Pos. 144.2 m/z, Neg. 279.9 m/z. NMR's can be found at the end of this document.

Synthesis of N-methyl-N-methoxyethoxyethyl-piperidinium Bis(trifluoromethylsulfonyl)imide (3)

9.00 mmol of N-methylpiperidine was cooled to 0 °C in a dark vessel and flushed with Argon. 1-bromo-methoxyethoxy ethane (9.00 mmol) was added over 30 minutes and the mixture was warmed to room temperature and stirred for 12 hours. The solid halide product was heated to 50 °C overnight while under vacuum to remove left over reactants and N-methyl-N-methoxyethoxyethyl-piperidinium bromide (Acros Organics, 90%)

stabilized with sodium carbonate) was isolated as a brown solid. The halide anion was then exchanged for TFSI using the procedure described above. An orange liquid N-methyl-methoxyethoxyethyl-piperidinium TFSI was obtained. To remove the color impurities, an activated charcoal column was run with sand, silica, and activated charcoal. N-methyl-N-methoxyethoxywthyl-piperidinium TFSI was isolated as a yellow liquid. ¹H-NMR(CD₃OD): δ 1.69 (m, 2H, CH₂-**CH**₂-CH₂), 1.90 (m, 4H, **CH**₂-CH₂-**CH**₂), 3.16 (s, 3H, N-CH₃), 3.40 (s, 3H, O-CH₃), 3.46 (m, 2H, O-CH₂), 3.50 (m, 2H, CH₂-O), 3.55 (m, 2, CH₂-O), 3.60 (m, 4H, CH₂-N-CH₂), 3.9 (m, 2H, CH₂-N); ¹³C-NMR (CDCl₃): δ 19.72 (2C,CH₂), 20.44 (1C, CH₂), 49.27 (1C, N-CH₃), 59.9 (1C, O-CH₃), 62.4 (2C, CH₂), 64.11 (1C, CH₂-O), 70.25 (1C, N-CH₂-CH₂-O), 71.38 (1C, N-CH₂), 115.91, 118.47, 121.03, 123.58 (CF₃); LC/MS: Pos. 202.2 m/z. Neg. 279.9 m/z. NMR's can be found at the end of this document.

Activated Charcoal Column

To pack a charcoal column first place approximately 0.5 cm of sand at the bottom of the column. Add a 2 cm silica gel layer via wet loading with DCM and pack the gel. Next fill the column approximately ³/₄ full with DCM and add the activated charcoal. Add the activated charcoal slowly while stirring; the activated charcoal is slow to wet and clumps can form if not stirred properly. Do not disturb the silica gel layer with the stirring. Add 10-18 cm of activated charcoal to the column. Pack the column and then wet load your product. Once pack and loaded, run the column using DCM and collect all fractions. Note: activated charcoal packs extremely well, the column will run slowly, do not stir the charcoal or reduce the amount of charcoal used in the column. Best results are achieved if the column if left to run without agitating the column and with the indicated about of charcoal. The column is complete once the collected fractions are clear and no product is detected by TLC.

General Procedure of Thermal Measurements

Before each of the following tests the samples were dried at 80 °C while under vacuum for at least 6 hours. Thermal Gravimetric Analysis (TGA) experiments were completed with TGA Q50 and samples were heated from 20 to 500 °C at a rate of 10 °C min⁻¹. Thermal decomposition point was defined as the temperature were 6% weight loss of the original sample weight was recorded. TGA traces for ionic liquids 1, 2, and 3 can be found at the end of this document.

Thermal transitions were measured using a TA instruments Q100 Differential Scanning Calorimeter from -70 °C to 250 C at a heating rate of 20 °C min⁻¹ and cooling of 5 °C min⁻¹ for three iterations. All samples weighed between 10 to 20 mg. DSC traces for ionic liquids 1, 2, and 3 can be found at the end of this document.

Flammability was tested by placing 0.1 mL of the compound next to an exposed flame for 30 seconds: ignition proved flammability. H-NMR and C-NMR pre- and post-exposure to the flame were then analyzed.



Figure S1. Photographs of the Flammability experiment where N-methyl-N-methoxymethyl-piperidinium TFSI was exposed to an open flame.

Flammability Test Results

lonic liquids 1, 2, and 3 did not catch on fire nor accelerate the fire. When PC was exposed to the flame there were clear indications of acceleration of the flame on the end of the Q-tip. After exposure to the flame, the remaining ionic liquids were analyzed in H-NMR and C-NMR using CD₃Cl. For all three ionic liquids, comparing the H-NMR and the C-NMR from to pre- to post-exposure to the flames, ionic liquid 1 displayed the biggest variability with signals missing in post-exposure H-NMR and C-NMR spectra. This same phenomenon was not seen to the same extent for either electrolyte 2 or 3.



Figure S2. H-NMR spectra comparisons between pre- and post-exposure to a flame for ionic liquids A) 1; B) 2; C) 3.



Figure 3S. H-NMR spectra comparisons between pre- and post-exposure to a flame for ionic liquids A) 1; B) 2; C) 3.

General Procedures for Rheological Measurements

Viscosity was measured on TA Instruments AR 2000 Rheometer. Generally, a 25 mm aluminum plate geometry was used with the gap set to 1000 um. Prior to testing, a preshear at shear a rate of 100 Hz for 10 s followed by a five min equilibrium was performed to eliminate physical memory of the sample. An oscillatory strain sweep was completed between .1 % and 12 % strain at 1 Hz to find the Linear Viscoelastic Region (LVR). Next, a frequency sweep from 0.1 to 12.5 Hz was completed at a strain % within the LVR. The dynamic viscosity was recorded at a specific frequency and strain %.

An oscillatory temperature sweep was conducted from 10 to 95 °C with increment of 10 °C and 1 min equilibrium at each temperature with strain and frequency set to 10% and 1 Hz, respectively. Sample were dried at 80 °C overnight while under a vacuum prior to testing.

Newtonian Behavior was tested for ionic liquids 2 and 3 with 1.0 M LiTFSI salt by varying the shear rate from 0.1 Hz to 10 Hz with increments of .1 Hz. At each point the sample was equilibrated for 5 seconds and the viscosity and stress were averaged over 30 seconds. The shear rate versus the viscosity and shear stress (viscosity*shear rate=shear stress) display behaviors of a Newtonian fluid in the described range (See Figure S4).

The average of the complex viscosity for four trials of ionic liquid 2 with 0 M, 0.5 M and 1.0 M with standard deviations were not included in Figure 2 in the manuscript, Figure S5 below contains the average data for ionic liquid 2 with 0 M, 0.5 M, and 1.0 M LiTFSI salt with standard deviation included. The rheometer and method used to collect the complex viscosity was highly repeatable and only slight deviations between the four trials were recorded.

Standard deviation was calculated using the following equation:



Figure S4. Newtonian Behavior of PP1o1TFSI with 1.0 M LiTFSI (left) and PP2o2o1TFSI with 1.0 M LiTFSI (right).



Figure S5. Average viscosity data of 2 with 0 M, 0.5 M, and 1.0 M LiTFSI salt including error bars (N=4).



Figure S6. Complex Viscosity data for ionic liquid 1, 2, and 3 with 0 M LiTFSI salt from Figure 2.



Figure S7. Complex Viscosity data for ionic liquid 1, 2, and 3 with 0.5 M LiTFSI salt from Figure 2.



Figure S8. Complex Viscosity data for ionic liquid 1, 2, and 3 with 1.0 M LiTFSI salt from Figure 2.



Figure S9. Propylene Carbonate (PC) average complex viscosity data with 0 M, 0.5 M, and 1.0 LiTFSI salt additions (N=3).

Conductivity Measurements

Conductivity measurements were performed with a Conductivity Meter (K912, Consort, +/- 0.5% f.s of range for conductivity and +/- 0.3 °C) equipped with a 4- electrode cell to prevent polarization error and fouling of the electrode. 4- electrode probe was calibrated with .01, 0.1 and 1 M KCI Standard Solutions. Testing was completed inside an Argon Glovebox (H₂O <1 ppm, O₂ <0.6 ppm) and a heating block was used to control the temperature, samples were equilibrated for 30 min at each temperature. Samples were dried at 80 °C while under vacuum overnight before testing.

Due to the variability in the heating block controls, the conductivity data were fixed using a power equation to extrapolate exact numbers at specific temperatures. **Figure S6** shows the conductivity data fit to a power curve and **Table S1** displays the fit equations and R^2 values. Only fits of 0.99 were accepted.



Figure S10. Conductivity data fitted utilizing a power curve.

	1 0 M LITFSI	1 1.0 M LITFSI	20 M LITFSI	2 1.0 M LITFSI	30 M LITFSI	3 1.0 M LITFSI	
Eqs	y=0.0037x ^{1.8197}	y=0.0001x ^{2.3441}	y=0.0115x ^{1.539}	y=0.0005x ^{2.1178}	y=0.0209x ^{1.4061}	y=0.0001x ^{2.371}	
R ²	0.99794	0.99891	0.99828	0.99905	0.9956	0.99032	
Table S1. Equations and R ² values from the power fit calculated for the conductivity							
data of 1, 2, and 3 with and without 1.0 M LiTFSI salt additions.							

In **Figure S11** the average data for four conductivity measurements of ionic liquid 2 with and without LiTFSI salt as well standard deviation of both the conductivity and temperature are included to illustrate how the lack of temperature control limits exact comparisons. The raw data are displayed in Table S2 to demonstrate why ionic liquid 2 with 0 M LiTFSI and 1.0 M LiTFSI only have an N of 3 instead of 4.



Figure S11. Averaged conductivity data for ionic liquid 2 with 0 M, 0.5 M, and 1.5 M LiTFSI. Horizontal error bars indicate the deviation of temperature of the ionic liquids. Trials which had large differences between the initial temperature readings were not included in the averages. Vertical error bars indicate the deviation of the conductivity of the ionic liquids. Generally, as the temperature increased, the deviation of the conductivity increased as well.

Ionic Liquid 2	2 0 M LITFSI										
Trial 1	Trial 2	Trial 3	Trial 4			Trial 1	Trial 2	Trial 3	Trial 4		
Temperature	3			Standard Deviation	Average Temp.	Conductivity				Standard Deviation	Average Conductivity
С	С	с	С		С	mS/cm	mS/cm	mS/cm	mS/cm		mS/cm
25.7	29.7	29.9	31.1	0.618	30.2	2.24	1.941	1.96	2.98	0.485	2.29
N/A	44.1	44.5	44.7	0.249	44.4	N/A	3.42	3.52	4.84	0.647	3.93
N/A	61.6	62	62.5	0.368	62.0	N/A	5.82	6.08	7.75	0.855	6.55
88.7	79.5	78.4	82.8	1.87	80.2	14.67	9.05	9.33	11.31	1.01	9.90
98.6	101.7	103.6	104.8	1.28	103.4	17.5	14.13	15.75	16.18	0.883	15.35
			Trial 1 is not	included in the stand	lard deviation or	the average					
Ionic Liquid	2 0.5 M LITFS	I									
Trial 1	Trial 2	Trial 3	Trial 4	Standard Deviation	Average Temp.	Trial 1	Trial 2	Trial 3	Trial 4	Standard Deviation	Average Conductivity
С	с	с	С		С	mS/cm	mS/cm	mS/cm	mS/cm		mS/cm
28.7	29.9	28.8	29.7	0.531	29.3	1.39	1.083	1.034	1.641	0.246	1.29
42.1	46	46.3	44.2	1.68	44.7	2.73	2.22	2.2	3.07	0.365	2.56
60.2	63.4	62	62.4	1.16	62.0	5.31	4.13	3.98	5.49	0.678	4.73
80.8	84.2	83.9	84.7	1.53	83.4	9.13	7.38	7.4	9.12	0.868	8.26
98.8	105.7	102.5	103.8	2.52	102.7	13.01	12.1	11.4	12.16	0.571	12.17
			All four trials	are included in the	tandard deviatio	on and averag	e				
Ionic Liquid 2	2 1.0 M LITFSI										
Trial 1	Trial 2	Trial 3	Trial 4	Standard Deviation	Average Temp.	Trial 1	Trial 2	Trial 3	Trial 4	Standard Deviation	Average Conductivity
с	с	с	с		с	mS/cm	mS/cm	mS/cm	mS/cm		mS/cm
28	28.2	27.6	33.2	0.249	27.9	0.695	0.56	0.501	1.115	0.081	0.59
45.9	48.6	47.5	43.3	1.11	47.3	2.01	1.554	1.42	1.83	0.253	1.66
60.4	64.6	62.6	62.8	1.72	62.5	3.64	2.89	2.58	3.83	0.445	3.04
79.4	86.3	85.2	83.8	3.03	83.6	6.52	5.59	5.24	6.8	0.540	5.78
97.2	104.6	106.3	104.5	3.95	102.7	9.91	8.82	8.87	10.11	0.502	9.2
	Trial 4 not included in average or standard deviation: too hot room temperature										

Table S2. Raw conductivity data collected for ionic liquid 2 with 0 M, 0.5 M, and 1.0 M LiTFSI salt.



Figure S12. Conductivity data for ionic liquids 1, 2, and 3 with 0 M LiTFSI salt from Figure 2.



Figure S13. Conductivity data for ionic liquids 1, 2, and 3 with 0.5 M LiTFSI salt from Figure 2.



Figure S14. Conductivity data for ionic liquids 1, 2, and 3 with 1.0 M LiTFSI salt from Figure 2.



Figure S15. Propylene Carbonate (PC) average conductivity data with 0 M, 0.5 M, and 1.0 LiTFSI salt additions (N=3). PC with 0 M LiTFSI displayed low conductivities of 1.0×10^{-3} mS/cm.

Supercapacitor Fabrication

The supercapacitors were fabricated using a method previously described by our laboratory. Activated Carbon (AC) working electrodes were fabricated using a standard method: 75 wt% AC, 15 wt% acetylene black (AB), and 10 wt% poly(vinylidene upride) binder in N-methyl-pyrrolidinone solvent were ground together in a mortar. AC and AB were dried at 80 and 120 C in a vacuum oven, respectively. The generated mixture was then coated on stainless steel sheets (1.58 cm diameter). All electrodes produced had approximately 1 to 2 mg of active material after drying under vacuum at 80 °C overnight. Coin cells were assembled using CR2032 coin cells (MTI Co.) and were comprised of a spring, two identical electrodes (by weight) and two Celgard 480 membrane separators. During assembly, the separators were soaked in the ionic liquid electrolyte at 60 °C for 15 minutes. Once thoroughly soaked, the bottom of a coin cell was fitted with a spring, one electrode, and the separators were placed on top, followed by the second electrode and the cap. The cell was then crimped shut and left to rest at room temperature for 12 hours prior to testing.

Electrochemical Measurements

All electrochemical measurements were performed on VerSTAT Battery Tester. A cyclic voltammogram was run on the coin cells to determine the electrochemical window for charge discharge cycling experiments. Multiple scans at different scan rates ranging from 100 mV/s to 20 mV/s were run on coin cells containing PC, electrolytes 1 and 2. A non-faradaic region (no oxidation and reduction peaks) between 0-2.5 V was observed for all the three electrolytes. This voltage range chosen as the potential window for all charge discharge cycling experiments.

For the charge discharge cycling, a current density of 1 A/g was chosen for all experiments and the cells were cycled between 0-2.5V. The discharge capacitance was calculated from the following equation:

$$C_s = 2I_{const}/(m * (dV/dt))$$

Where I = constant current applied in A, in our experiments, dV/dt = slope of discharge curve, m = mass of each electrode in g

Energy and power density calculations

Charge discharge cycle experiments were carried out at different current densities (1, 2, 5 and 10 A/g) both at 100 degrees and room temperature for propylene carbonate and electrolyte 2. Energy density (Wh/kg) and power density (W/kg) were calculated using the following equations:

$$E = \frac{1}{8} C_S \Delta V^2$$
$$P = \frac{E}{\Delta t}$$

Where ΔV is the window potential (V) and Δt is the discharge time.

Figure S16 shows five charge discharge cycles of PC and electrolyte 2 at various current densities 2, 5 and 10 A/g at a window potential of 0-2.5V.



Figure S16. Charge discharge cycles of PC and electrolyte at different current densities: a) 25 °C b) 100 °C.

Computational Calculations

The binding energies (BE) were determined as follows:

$$BE = E^{CP}(CA) - E_{min}(C) - E_{min}(A) + \Delta ZPVE$$
(S1)

Where $E^{CP}(CA)$ is the counter-poise corrected energy of the cation-anion pair, $E_{\min}(C)$ and $E_{\min}(A)$ are the minimum energies of the cation and anion respectively, and $\Delta ZPVE$ is the change in zero-point vibrational energy between the separated ions and the ion pair. The counter-poise corrected energy is used to avoid basis-set superposition error (BSSE). All structures were optimized at the B3LYP/6-31G(d) level of theory and the resulting geometries were used to calculate energies at the B3LYP/6-311G(d,p) level of theory. This level of theory has been found to give reliable results when compared to previous studies. Using the [C₁mpyr][CI], conf 1 optimized geometry from literature (E. I. Izgorodina, U. L. Bernard, and D. R. MacFarlane, *J. Phys. Chem. A.*, 2009, **113**, 7064-7072), we calculated a BE of -94.55 kcal mol⁻¹ as compared to the reported value of -95.22 kcal mol⁻¹ which was found at the MP2/aug-cc-pVTZ level of theory. All calculations were performed with Gaussian 16. Calculations used a polarizable continuum model (PCM) with ε =15.2 to simulate the environmental effects unless labeled differently. Higher dielectric constant leads to weaker binding energies.

Cation-Anion Pair	BSSE Correction		Binding Energy
	(KCal mol ⁻)	(KCAI MOI	(KCal mol ⁻)
PP111-TFSI	5.380	-0.323	-11,443
PP1o1-TFSI	4.872	-0.253	-11.497
PP2o2o1-TFSI	5.521	-0.123	-9.872
Li-TFSI Config1	3.404	-0.003	-10.218
Li-TFSI Config2	5.101	-0.007	-11.024
Li-TFSI Config3	5.333	-0.026	-14.105
Li-TFSI Config1	3.315	0.018	-7.476
(ε=51.1)			
Li-TFSI Config2	5.079	-0.010	-6.645
(ε=51.1)			
Li-TFSI Config3	5.246	-0.018	-8.890
(ε=51.1)			
Li-TFSI Config1	3.188	-0.011	-6.728
(ε=78.4)		0.004	0.040
LI-TFSI Config2	5.079	-0.004	-6.019
(8=78.4)	0.044	0.040	7 1 1 0
	0.241	-0.016	-1.142
(ε=/8.4)	20.024	2 271	22.054
LIF	29.934	2.371	-22.004

Table S3. Calculated binding energies, basis set superposition errors (BSSE), and zero-point vibrational energy corrections (Δ ZPVE)

Comparison to Published Works Table S4. Comparison of ionic liquid 1 physical properties to literature values.

Ionic Liquid 1	a) σ (mS/cm)	b) η (Pa.s)	c) T _d (°C)	d) T _m (°C)	e) T _c
This manuscript	1.40	0.14	386	19	-23
Ref. 29	1.51	.117	N/A	8.7	N/A
Ref. 31	2.9 ¹	.141	385 ²	N/A	N/A

a). conductivity at 25 °C. b). complex viscosity at 25 °C. c) Thermal degradation at 6 % weight loss. d) Glass transition temperature. ^{1.} Conductivity was measured using a CHI660A electrochemical workstation with a coin cell equipped with two platinum electrodes. ^{2.} Degradation was defined at 10 % weight loss with a heating rate of 10 °C/min.

Table S5. Comparison of ionic liquid 2 physical properties to literature values.

Ionic Liquid 2	a) σ (mS/cm)	b) η (Pa.s)	c) T _d (°C)	d) T _g (°C)
This Manuscript	2.29	0.08	288	N/A
Ref. 34	2.2 ¹	N/A	>420 ²	-79.2 ³

a). conductivity at 25 °C. b). complex viscosity at 25 °C. c) Thermal degradation at 6 % weight loss. d) Glass transition temperature. ^{1.} Conductivity was measured using a CHI604B electrochemical workstation with a coin cell equipped with two stainless steel electrodes. ^{2.} Degradation was defined at the initial weight loss with a heating rate of 5 °C/min. ^{3.} Differential Scanning Calorimetry was used at a heating rate of 5 °C/min from -100 °C to 0 °C.

Table 00. Comparison of forme inquid o physical properties to interature values.							
Ionic Liquid 3	a) σ (mS/cm)	b) η (Pa.s)	c) T _d (°C)	d) T _g (°C)			
This manuscript	2.00	0.14	356	N/A			
Ref. 35	~2 ¹ ; 17 at 97 °C	N/A	413.4 ²	N/A			
Dof 38	1 62 ³ 10 at 80 °C	0.0834	3325	80			

Table S6. Comparison of ionic liquid 3 physical properties to literature values.

Ref. 38 1.62^3 ; 10 at 80 °C 0.083^4 332^5 -80a). conductivity at 25 °C. b). complex viscosity at 25 °C. c) Thermal degradation at 6 %weight loss. d) Glass transition temperature. ^{1.} Conductivity was measured using aBiologic VSP-219electrochemical workstation with a coin cell equipped with twoplatinum electrodes. ^{2.} Authors did not define thermal degradation or the method used. ^{3.}SensION + EC71Benchtop meter. ^{4.} Gemini Rotonetic Drive 2 cone and platerheometer. ^{5.} Differential Scanning Calorimetry heating rate of 5 K/min from 183.13 K to323.15 K. T_d is defined as 5 % weight loss.

H-NMR's:











Figure S19. ¹H NMR of 3 in CDCl₃.



Figure S20. ¹³C NMR of 3 in CDCl₃.









