**Supporting information**

# TEMPO-Ionic Liquids as Redox Mediators and Solvents for Li-$O_2$ Batteries

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**The Supporting Information includes:**

1. Synthesis of TEMPOImILs
   1.1. General
   1.2. Synthesis and characterization data
2. Electrochemical characterization
3. Supplementary figures:
   **Figure S1.** TGA and DSC data for TEMPOImIL with n = 8, R = H.
   **Figure S2.** Temperature dependence of ionic conductivities of pure TEMPOImILs with R = H.
   **Figure S3.** Temperature dependence of ionic conductivities of pure TEMPOImILs with R = Me.
   **Figure S4.** Temperature dependence of ionic conductivities of pure TEMPOImILs with n = 4, 6, R = H tested up to 80 °C.
   **Figure S5.** Cyclic voltammogram of TEMPOImIL with n = 4, R = H, 10 cycles.
4. References

# 1. Synthesis of TEMPOImILs

## 1.1. General

4-Hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (4-hydroxy-TEMPO, 97%), 1-methylimidazole (99%), 1,2-dimethylimidazole (97%), 4-dibromobutane (99%), tetra-*n*-butylammonium bromide (≥99%), 1,5-dibromopentane (97%), 1,6-dibromohexane (96%), 1,8-dibromooctane (98%), phenylhydrazine (97%), TEGDME (for cyclic voltammetry, 99%), acetonitrile (99.8%) and LiTFSI for cyclic voltammetry and synthesis (96%) were purchased from Sigma-Aldrich. 1,7-dibromoheptane (95+%) was purchased from Oakwood Chemicals. TEGDME (98+%) and LiTFSI (99.8+%) for the battery tests were purchased from DoDoChem. All solvents used in synthetic procedures were analytical grade. LiTFSI, TEGDME and phenylhydrazine were stored in the glove box. TEGDME was dried with 4Å molecular sieves (Sigma-Aldrich) for at least one week before use. All other chemicals were used as received.

NMR spectra were recorded using an Agilent Technologies NMR spectrometer operating at a frequency of 500.3 MHz for $^{1}$H and 125.7 MHz for $^{13}$C experiments with DMSO-$d_6$ as a solvent. Elemental analysis was performed by the Campbell Microanalytical Laboratory, Department of Chemistry, University of Otago, New Zealand. TGA and DSC curves were obtained simultaneously on Thermal Advantage SDT-Q600 thermal analyzer using alumina crucibles. Experiments were conducted in the temperature range of 25−700 °C at a heating rate of 10 °C min$^{-1}$ under a nitrogen gas flow of 150 mL min$^{-1}$.

## 1.2. Synthesis

TEMPOImILs were synthesized using modified literature methods (Scheme 1).[1-2] NMR spectra ($^{1}$H and $^{13}$C) were obtained by adding phenylhydrazine directly into the NMR tubes prior to acquiring spectra. Spectra, therefore, contain signals corresponding to the reduction product of the nitroxide radical.[3]

*4-(2,2,6,6-tetramethyl-1-oxyl-4-piperidoxyl)butyl bromide (TEMPOLC$_4$Br,* ***2a****)*. To a solution of 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (0.500 g, 0.0029 mol) in toluene (5 mL) was added potassium hydroxide (0.65 g, 0.0116 mol) and tetra-*n*-butylammonium bromide (0.093 g, 0.00029 mol). After stirring for 5 minutes, 1,4-dibromobutane was added, and the mixture was vigorously stirred at room temperature for 24 h. The solvent was then removed on a rotary evaporator, and the mixture was purified using silica column chromatography (2 x 15 cm) eluting with a hexane:dichloromethane mixture using a gradient from 100:0 to 0:100 (by volume). The product was dried under high vacuum to yield 0.34 g (51%) of 4-(2,2,6,6-tetramethyl-1-oxyl-4-piperidoxyl)butyl bromide as a red viscous oil.

TEMPOLC$_n$Br with n = 5–8 (**2b–e**) were obtained as red viscous oils using the same method with the following yields: **2b** – 50%, **2c** – 56%, **2d** – 75%, **2e** – 54%.

TEMPOLC$_4$Br (**2a**). $^{1}$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 1.03 (s, 6H, $CH_3$), 1.07 (s, 6H, $CH_3$), 1.19-1.26 (m, 2H, C(3)$_{Pip}$-H and C(5)$_{Pip}$-H), 1.54-1.61 (m, 2H, -OCH$_2$C<u>H$_2$</u>-), 1.80-1.87 (m, 4H, C(3)$_{Pip}$-H and C(5)$_{Pip}$-H, -C<u>H$_2$</u>CH$_2$Br), 3.39 (t, 2H, $J$ = 6.5 Hz, -OCH$_2$-), 3.49-3.55 (m, 1H, H(4)$_{Pip}$), 3.54 (t, 2H, $J$ = 6.5 Hz, -CH$_2$Br).

TEMPOLC$_5$Br (**2b**). $^{1}$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 1.04 (s, 6H, $CH_3$), 1.08 (s, 6H, $CH_3$), 1.21-1.28 (m, 2H, H(3)$_{Pip}$ and H(5)$_{Pip}$), 1.38-1.52 (m, 4H, -OCH$_2$(C<u>H$_2$</u>)$_2$-), 1.76-1.86 (m, 4H, H(3)$_{Pip}$ and H(5)$_{Pip}$, -C<u>H$_2$</u>CH$_2$Br), 3.37 (t, 2H, $J$ = 6.5 Hz, -OCH$_2$-), 3.39-3.45 (m, 1H, H(4)$_{Pip}$), 3.52 (m, 2H, -CH$_2$Br).

TEMPOLC$_6$Br (**2c**). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 1.04 (s, 6H, $CH_3$), 1.07 (s, 6H, $CH_3$), 1.19-1.26 (m, 2H, H(3)$_{Pip}$ and H(5)$_{Pip}$), 1.26-1.50 (m, 6H, -OCH$_2$(C$\underline{H}_2$)$_3$-), 1.76-1.87 (m, 4H, H(3)$_{Pip}$ and H(5)$_{Pip}$, -C$\underline{H}_2$CH$_2$Br), 3.36 (t, 2H, $J$ = 6.5 Hz, -OCH$_2$-), 3.39-3.45 (m, 1H, H(4)$_{Pip}$), 3.51 (t, 2H, $J$ = 6.5 Hz, -CH$_2$Br).

TEMPOLC$_7$Br (**2d**). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 1.05 (s, 6H, $CH_3$), 1.09 (s, 6H, $CH_3$), 1.19-1.46 (m, 10H, H(3)$_{Pip}$ and H(5)$_{Pip}$, -OCH$_2$(C$\underline{H}_2$)$_4$-), 1.76-1.86 (m, 4H, H(3)$_{Pip}$ and H(5)$_{Pip}$, -C$\underline{H}_2$CH$_2$Br), 3.37 (t, 2H, $J$ = 6.9 Hz, -OCH$_2$-), 3.37-3.43 (m, 1H, H(4)$_{Pip}$), 3.51 (t, 2H, $J$ = 6.9 Hz, -CH$_2$Br).

TEMPOLC$_8$Br (**2e**). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 1.03 (s, 6H, $CH_3$), 1.06 (s, 6H, $CH_3$), 1.19-1.49 (m, 12H, H(3)$_{Pip}$ and H(5)$_{Pip}$, -OCH$_2$(C$\underline{H}_2$)$_5$-), 1.75-1.86 (m, 4H, H(3)$_{Pip}$ and H(5)$_{Pip}$, -C$\underline{H}_2$CH$_2$Br), 3.35 (t, 2H, $J$ = 6.5 Hz, -OCH$_2$-), 3.46-3.52 (m, 1H, H(4)$_{Pip}$), 3.52 (t, 2H, $J$ = 6.5 Hz, -CH$_2$Br).

*1-methyl-3-(4-(2,2,6,6-tetramethyl-1-oxyl-4-piperidoxyl)-butyl)imidazolium bromide (TEMPOLC$_4$Im$^{Me}$Br, **3a**)*. To a solution of 1-methylimidazole (0.0673 g, 0.820 mmol) in acetonitrile (1 mL) a solution of 4-(2,2,6,6-tetramethyl-1-oxyl-4-piperidoxyl)butyl bromide (TEMPOLC$_4$Br, **2a**, 0.210 g, 0.683 mmol) in acetonitrile (1 mL) was added. The mixture was stirred at 60 °C for 6 hours. After removing the solvent on a rotary evaporator, the residue was purified by trituration (x3) with sonication in diethyl ether and dried under high vacuum overnight to give 0.170 g (80%) of red viscous oil.

TEMPOLC$_n$Im$^{Me}$Br with n = 5–8 (**3b–e**) and 1,2-dimethyl-3-(4-(2,2,6,6-tetramethyl-1-oxyl-4-piperidoxyl)-alkyl)imidazolium bromides (TEMPOLC$_n$Im$^{(Me)2}$Br, **4a–e**) were obtained similarly. Compounds **3b–e** were isolated as red viscous oils with the yields: **3b** – 42%, **3c** – 79%, **3d** –75%, **3e** – 88%. Compounds **4a–e** were filtered after trituration to give red powders with the following yields: **4a** – 72%, **4b** – 80%, **4c** – 86%, **4d** – 68%, 4e – 45%. $^1$H NMR shifts for compound **3a** matched the literature data.[4] The assignment of the NMR signals was supported by gHSQC and DEPT NMR experiments.

TEMPOLC$_4$Im$^{Me}$Br (**3a**). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 1.03 (s, 6H, $CH_3$), 1.06 (s, 6H, $CH_3$), 1.18-1.26 (m, 2H, H(3)$_{Pip}$ and H(5)$_{Pip}$), 1.39-1.47 (m, 2H, -OCH$_2$C$\underline{H}_2$-), 1.78-1.86 (m, 4H, H(3)$_{Pip}$ and H(5)$_{Pip}$, -C$\underline{H}_2$CH$_2$N<), 3.39 (t, 2H, $J$ = 6.5 Hz, -OCH$_2$-), 3.47-3.54 (m, 1H, H(4)$_{Pip}$), 3.85 (s, 3H, (CH$_3$)$_{Im}$), 4.18 (t, 2H, $J$ = 7.0 Hz, -CH$_2$N<), 7.74 (s, 1H, H(4)$_{Im}$ or H(5)$_{Im}$), 7.77 (s, H(4)$_{Im}$ or H(5)$_{Im}$), 9.15 (s, 1H, H(2)$_{Im}$).

TEMPOLC$_5$Im$^{Me}$Br (**3b**). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 1.03 (s, 6H, $CH_3$), 1.06 (s, 6H, $CH_3$), 1.18-1.30 (m, 4H, H(3)$_{Pip}$ and H(5)$_{Pip}$, -C$\underline{H}_2$CH$_2$CH$_2$N<), 1.45-1.52 (m, 2H, -OCH$_2$C$\underline{H}_2$-), 1.75-1.85 (m, 4H, H(3)$_{Pip}$ and H(5)$_{Pip}$, -C$\underline{H}_2$CH$_2$N<), 3.36 (t, 2H, $J$ = 6.4 Hz, -OCH$_2$-), 3.46-3.53 (m, 1H, H(4)$_{Pip}$), 3.85 (s, 3H, (CH$_3$)$_{Im}$), 4.16 (t, 2H, $J$ = 7.1 Hz, -CH$_2$N<), 7.72 (s, 1H, H(4)$_{Im}$ or H(5)$_{Im}$), 7.78 (s, H(4)$_{Im}$ or H(5)$_{Im}$), 9.15 (s, 1H, H(2)$_{Im}$).

TEMPOLC$_6$Im$^{Me}$Br (**3c**). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 1.04 (s, 6H, $CH_3$), 1.07 (s, 6H, $CH_3$), 1.19-1.35 (m, 6H, H(3)$_{Pip}$ and H(5)$_{Pip}$, -(C$\underline{H}_2$)$_2$CH$_2$CH$_2$N<), 1.41-1.49 (m, 2H, -OCH$_2$C$\underline{H}_2$-), 1.71-1.86 (m, 4H, H(3)$_{Pip}$ and H(5)$_{Pip}$, -C$\underline{H}_2$CH$_2$N<), 3.36 (t, 2H, $J$ = 6.4 Hz, -OCH$_2$-), 3.46-3.53 (m, 1H, H(4)$_{Pip}$), 3.85 (s, 3H, (CH$_3$)$_{Im}$), 4.16 (t, 2H, $J$ = 7.1 Hz, -CH$_2$N<), 7.70-7.72 (m, 1H, C(4)$_{Im}$-H or C(5)$_{Im}$-H), 7.76-7.78 (m, C(4)$_{Im}$-H or C(5)$_{Im}$-H), 9.15 (s, 1H, H(2)$_{Im}$).

TEMPOLC$_7$Im$^{Me}$Br (**3d**). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 1.03 (s, 6H, $CH_3$), 1.06 (s, 6H, $CH_3$), 1.18-1.32 (m, 8H, H(3)$_{Pip}$ and H(5)$_{Pip}$, -(C$\underline{H}_2$)$_3$CH$_2$CH$_2$N<), 1.39-1.47 (m, 2H, -OCH$_2$C$\underline{H}_2$-), 1.71-1.85 (m, 4H, H(3)$_{Pip}$ and H(5)$_{Pip}$, -C$\underline{H}_2$CH$_2$N<), 3.35 (t, 2H, $J$ = 6.6 Hz, -OCH$_2$-), 3.45-3.52 (m, 1H, H(4)$_{Pip}$), 3.85 (s, 3H, (CH$_3$)$_{Im}$), 4.16 (t, 2H, $J$ = 7.2 Hz, -CH$_2$N<), 7.71-7.73 (m, 1H, H(4)$_{Im}$ or H(5)$_{Im}$), 7.78-7.80 (m, H(4)$_{Im}$ or H(5)$_{Im}$), 9.21 (s, 1H, H(2)$_{Im}$).

TEMPOLC$_8$Im$^{Me}$Br (**3e**). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 1.04 (s, 6H, $CH_3$), 1.07 (s, 6H, $CH_3$), 1.19-1.30 (m, 10H, H(3)$_{Pip}$ and H(5)$_{Pip}$, -(C$\underline{H}_2$)$_4$CH$_2$CH$_2$N<), 1.41-1.48 (m, 2H, -OCH$_2$C$\underline{H}_2$-), 1.73-1.86 (m, 4H, H(3)$_{Pip}$ and H(5)$_{Pip}$, -C$\underline{H}_2$CH$_2$N<), 3.35 (t, 2H, $J$ = 6.8 Hz, -OCH$_2$-), 3.46-3.53 (m, 1H, H(4)$_{Pip}$), 3.84 (s, 3H, (CH$_3$)$_{Im}$), 4.14 (t, 2H, $J$ = 7.6 Hz, -CH$_2$N<), 7.70 (s, 1H, H(4)$_{Im}$ or H(5)$_{Im}$), 7.77 (s H(4)$_{Im}$ or H(5)$_{Im}$), 9.15 (s, 1H, H(2)$_{Im}$).

TEMPOLC$_4$Im$^{(Me)2}$Br (**4a**). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 1.04 (s, 6H, $CH_3$), 1.07 (s, 6H, $CH_3$), 1.19-1.26 (m, 2H, H(3)$_{Pip}$ and H(5)$_{Pip}$), 1.42-1.50 (m, 2H, -OCH$_2$C$\underline{H}_2$-), 1.69-1.78 (m, 2H, -C$\underline{H}_2$CH$_2$N<), 1.81-1.87 (m, 2H, H(3)$_{Pip}$ and H(5)$_{Pip}$), 2.58 (s, 3H, C(2)$_{Im}$CH$_3$), 3.40 (t, 2H, $J$ = 6.3 Hz, -OCH$_2$-), 3.48-3.55 (m, 1H, H(4)$_{Pip}$), 3.75 (s, 3H, N(1)$_{Im}$CH$_3$), 4.13 (t, 2H, $J$ = 7.4 Hz, -CH$_2$N<), 7.62-7.65 (m, 1H, H(4)$_{Im}$ or H(5)$_{Im}$), 7.65-7.67 (m, 1H, H(4)$_{Im}$ or H(5)$_{Im}$).

TEMPOLC$_5$Im$^{(Me)2}$Br (**4b**). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 1.04 (s, 6H, $CH_3$), 1.07 (s, 6H, $CH_3$), 1.19-1.34 (m, 4H, H(3)$_{Pip}$ and H(5)$_{Pip}$, -C$\underline{H}_2$CH$_2$CH$_2$N<), 1.46-1.52 (m, 2H, -OCH$_2$C$\underline{H}_2$-), 1.68-1.76 (m, 2H, -C$\underline{H}_2$CH$_2$N<), 1.79-1.86 (m, 2H, H(3)$_{Pip}$ and H(5)$_{Pip}$), 2.58 (s, 3H, C(2)$_{Im}$CH$_3$), 3.36 (t, 2H, $J$ = 6.5 Hz, -OCH$_2$-), 3.45-3.54 (m, 1H, H(4)$_{Pip}$), 3.75 (s, 3H, N(1)$_{Im}$CH$_3$), 4.10 (t, 2H, $J$ = 7.3 Hz, -CH$_2$N<), 7.62-7.65 (m, 1H, H(4)$_{Im}$ or H(5)$_{Im}$), 7.65-7.67 (m, 1H, H(4)$_{Im}$ or H(5)$_{Im}$).

TEMPOLC$_6$Im$^{(Me)2}$Br (**4c**). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 1.05 (s, 6H, $CH_3$), 1.09 (s, 6H, $CH_3$), 1.22-1.37 (m, 6H, H(3)$_{Pip}$ and H(5)$_{Pip}$, -(C$\underline{H}_2$)$_2$CH$_2$CH$_2$N<), 1.44-1.52 (m, 2H, -OCH$_2$C$\underline{H}_2$-), 1.65-1.73 (m, 2H, -C$\underline{H}_2$CH$_2$N<), 1.81-1.87 (m, 2H, H(3)$_{Pip}$ and H(5)$_{Pip}$), 2.55 (s, 3H, C(2)$_{Im}$CH$_3$), 3.37 (t, 2H, $J$ = 6.4 Hz, -OCH$_2$-), 3.47-3.56 (m, 1H, H(4)$_{Pip}$), 3.72 (s, 3H, N(1)$_{Im}$CH$_3$), 4.06 (t, 2H, $J$ = 7.4 Hz, -CH$_2$N<), 7.62-7.65 (m, 1H, H(4)$_{Im}$ or H(5)$_{Im}$), 7.65-7.67 (m, 1H, H(4)$_{Im}$ or H(5)$_{Im}$).

TEMPOLC$_7$Im$^{(Me)2}$Br (**4d**). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 1.03 (s, 6H, $CH_3$), 1.07 (s, 6H, $CH_3$), 1.19-1.34 (m, 8H, H(3)$_{Pip}$ and H(5)$_{Pip}$, -(C$\underline{H}_2$)$_3$CH$_2$CH$_2$N<), 1.40-1.48 (m, 2H, -OCH$_2$C$\underline{H}_2$-), 1.65-1.73 (m, 2H, -C$\underline{H}_2$CH$_2$N<), 1.80-1.86 (m, 2H, H(3)$_{Pip}$ and H(5)$_{Pip}$), 2.57 (s, 3H, C(2)$_{Im}$CH$_3$), 3.35 (t, 2H, $J$ = 6.6 Hz, -OCH$_2$-), 3.45-3.53 (m, 1H, H(4)$_{Pip}$), 3.74 (s, 3H, N(1)$_{Im}$CH$_3$), 4.09 (t, 2H, $J$ = 7.3 Hz, -CH$_2$N<), 7.61-7.64 (m, 1H, H(4)$_{Im}$ or H(5)$_{Im}$), 7.64-7.67 (m, 1H, H(4)$_{Im}$ or H(5)$_{Im}$).

TEMPOLC$_8$Im$^{(Me)2}$Br (**4e**). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 1.04 (s, 6H, $CH_3$), 1.08 (s, 6H, $CH_3$), 1.19-1.33 (m, 10H, H(3)$_{Pip}$ and H(5)$_{Pip}$, -(C$\underline{H}_2$)$_4$CH$_2$CH$_2$N<), 1.41-1.49 (m, 2H, -OCH$_2$C$\underline{H}_2$-), 1.65-1.73 (m, 2H, -C$\underline{H}_2$CH$_2$N<), 1.81-1.87 (m, 2H, H(3)$_{Pip}$ and H(5)$_{Pip}$), 2.54-2.59 (m, 3H, C(2)$_{Im}$CH$_3$), 3.36 (t, 2H, $J$ = 6.5 Hz, -OCH$_2$-), 3.46-3.54 (m, 1H, H(4)$_{Pip}$), 3.72-3.76 (m, 3H, N(1)$_{Im}$CH$_3$), 4.08 (t, 2H, $J$ = 7.6 Hz, -CH$_2$N<), 7.60-7.67 (m, 2H, H(4)$_{Im}$ and H(5)$_{Im}$).

*1-Methyl-3-(4-(2,2,6,6-tetramethyl-1-oxyl-4-piperidoxyl)-butyl)imidazolium bis(trifluoromethane)sulfonimide (TEMPOLC$_4$Im$^{Me}$TFSI,* ***5a****).* To a solution of TEMPOLC$_4$Im$^{Me}$Br (**3a**, 0.690 g, 1.77 mmol) in water (2.5 mL) at 70 °C, was added a solution of LiTFSI (0.508 g, 1.77 mmol) in water (2.5 mL) at 70 °C. The oil that immediately formed was extracted with dichloromethane (3 x 1 mL). The combined organic fractions were washed with water (3 x 5

mL). A silver(I) nitrate test indicated the absence of bromide ions in the final solution. The solution was concentrated using a rotary evaporator and purified by column chromatography on silica (2 x 15cm) eluting with chloroform followed by ethyl acetate:methanol using a gradient from 10:0 to 10:1 (by volume). Compound 5a was dried at 90–100 °C under high vacuum with stirring for 2 hours to give a red viscous oil (0.808 g, 79%). It was stored in a glove box under an inert atmosphere.

TEMPOLC$_n$Im$^{Me}$TFSI with n = 5–8 (**5b–e**) and 1,2-dimethyl-3-(4-(2,2,6,6-tetramethyl-1-oxyl-4-piperidoxyl)-alkyl)imidazolium bis(trifluoromethane)sulfonimides (TEMPOLC$_n$Im$^{(Me)2}$TFSI, **6a–e**) were synthesized likewise to give red viscous oils, yields: **5b** – 91%, **5c** – 97%, **5d** – 93%, **5e** – 79%; **6b** – 93%, **6c** – 95%, **6d** – 90%, **6e** – 93%. Compound **6a** was isolated in the form of red powder (91%). $^1$H NMR signals for compound **6b** matched the literature data.[5] The assignment of the NMR shifts was supported by gHSQC and DEPT NMR data.

TEMPOLC$_4$Im$^{Me}$TFSI (**5a**). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 1.06 (s, 6H, $CH_3$), 1.09 (s, 6H, $CH_3$), 1.21-1.29 (m, 2H, H(3)$_{Pip}$ and H(5)$_{Pip}$), 1.41-1.49 (m, 2H, -OCH$_2$C$\underline{H}_2$-), 1.78-1.88 (m, 4H, H(3)$_{Pip}$ and H(5)$_{Pip}$, -C$\underline{H}_2$CH$_2$N<), 3.40 (t, 2H, $J$ = 6.3 Hz, -OCH$_2$-), 3.49-3.56 (m, 1H, H(4)$_{Pip}$), 3.83 (s, 3H, (CH$_3$)$_{Im}$), 4.15 (t, 2H, $J$ = 7.1 Hz, -CH$_2$N<), 7.66 (s, 1H, H(4)$_{Im}$ or H(5)$_{Im}$), 7.72 (s, H(4)$_{Im}$ or H(5)$_{Im}$), 9.05 (s, 1H, H(2)$_{Im}$). $^{13}$C NMR (DMSO-$d_6$, 126 MHz): $\delta$ 20.7 ((CH$_3$)$_{Pip}$), 26.4 (-C$\underline{H}_2$CH$_2$N<), 26.9 (-OCH$_2$C$\underline{H}_2$-), 32.6 ((CH$_3$)$_{Pip}$), 35.9 ((CH$_3$)$_{Im}$), 44.8 (C(3)$_{Pip}$, C(5)$_{Pip}$), 48.9 (-CH$_2$N<), 58.1 (C(2)$_{Pip}$, C(6)$_{Pip}$), 66.6 (-OCH$_2$-), 70.2 (C(4)$_{Pip}$), 119.7 (q, CF$_3$, $J$ = 322 Hz), 122.4, 123.8 (C(4)$_{Im}$, C(5)$_{Im}$), 136.7 (C(2)$_{Im}$). Anal. Calcd for $C_{19}H_{31}F_6N_4O_6S_2$: C 38.71, H 5.30, N 9.50. Found: C 38.42, H 5.29, N 9.48.

TEMPOLC$_5$Im$^{Me}$TFSI (**5b**). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 1.03 (s, 6H, $CH_3$), 1.06 (s, 6H, $CH_3$), 1.18-1.30 (m, 4H, H(3)$_{Pip}$ and H(5)$_{Pip}$, -C$\underline{H}_2$CH$_2$CH$_2$N<), 1.45-1.52 (m, 2H, -OCH$_2$C$\underline{H}_2$-), 1.75-1.85 (m, 4H, H(3)$_{Pip}$ and H(5)$_{Pip}$, -C$\underline{H}_2$CH$_2$N<), 3.36 (t, 2H, $J$ = 6.5 Hz, -OCH$_2$-), 3.46-3.53 (m, 1H, H(4)$_{Pip}$), 3.84 (s, 3H, (CH$_3$)$_{Im}$), 4.15 (t, 2H, $J$ = 7.0 Hz, -CH$_2$N<), 7.69 (s, 1H, H(4)$_{Im}$ or H(5)$_{Im}$), 7.75 (s, H(4)$_{Im}$ or H(5)$_{Im}$), 9.09 (s, 1H, H(2)$_{Im}$). $^{13}$C NMR (DMSO-$d_6$, 126 MHz): $\delta$ 20.8 ((CH$_3$)$_{Pip}$), 22.6 (-C$\underline{H}_2$(CH$_2$)$_2$N<), 29.2 (-C$\underline{H}_2$CH$_2$N<), 29.5 (-OCH$_2$C$\underline{H}_2$-), 32.6 ((CH$_3$)$_{Pip}$), 35.9 ((CH$_3$)$_{Im}$), 44.9 (C(3)$_{Pip}$, C(5)$_{Pip}$), 49.0 (-CH$_2$N<), 58.2 (C(2)$_{Pip}$, C(6)$_{Pip}$), 67.1 (-OCH$_2$-), 70.3 (C(4)$_{Pip}$), 119.8 (q, CF$_3$, $J$ = 322 Hz), 122.4, 123.7 (C(4)$_{Im}$, C(5)$_{Im}$), 136.6 (C(2)$_{Im}$). Anal. Calcd for $C_{20}H_{33}F_6N_4O_6S_2 \cdot 0.5H_2O$: C 39.21, H 5.59, N 9.15. Found: C 39.03, H 5.48, N 9.27.

TEMPOLC$_6$Im$^{Me}$TFSI (**5c**). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 1.05 (s, 6H, $CH_3$), 1.09 (s, 6H, $CH_3$), 1.20-1.36 (m, 6H, H(3)$_{Pip}$ and H(5)$_{Pip}$, -(C$\underline{H}_2$)$_2$CH$_2$CH$_2$N<), 1.43-1.51 (m, 2H, -OCH$_2$C$\underline{H}_2$-), 1.73-1.87 (m, 4H, H(3)$_{Pip}$ and H(5)$_{Pip}$, -C$\underline{H}_2$CH$_2$N<), 3.36 (t, 2H, $J$ = 6.6 Hz, -OCH$_2$-), 3.46-3.53 (m, 1H, H(4)$_{Pip}$), 3.83 (s, 3H, (CH$_3$)$_{Im}$), 4.12 (t, 2H, $J$ = 7.1 Hz, -CH$_2$N<), 7.67 (s, 1H, H(4)$_{Im}$ or H(5)$_{Im}$), 7.73 (s, H(4)$_{Im}$ or H(5)$_{Im}$), 9.07 (s, 1H, H(2)$_{Im}$). $^{13}$C NMR (DMSO-$d_6$, 126 MHz): $\delta$ 20.8 ((CH$_3$)$_{Pip}$), 25.4, 25.6 (-(C$\underline{H}_2$)$_2$(CH$_2$)$_2$N<), 29.6 (-C$\underline{H}_2$CH$_2$N<), 29.7 (-OCH$_2$C$\underline{H}_2$-), 32.6 ((CH$_3$)$_{Pip}$), 35.9 ((CH$_3$)$_{Im}$), 44.9 (C(3)$_{Pip}$, C(5)$_{Pip}$), 49.0 (-CH$_2$N<), 58.2 (C(2)$_{Pip}$, C(6)$_{Pip}$), 67.3 (-OCH$_2$-), 70.2 (C(4)$_{Pip}$), 119.8 (q, CF$_3$, $J$ = 321 Hz), 122.4, 123.7 (C(4)$_{Im}$, C(5)$_{Im}$), 136.6 (C(2)$_{Im}$). Anal. Calcd for $C_{21}H_{35}F_6N_4O_6S_2 \cdot H_2O$: C 39.68, H 5.87, N 8.81. Found: C 39.45, H 5.55, N 8.97.

TEMPOLC$_7$Im$^{Me}$TFSI (**5d**). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 1.04 (s, 6H, $CH_3$), 1.08 (s, 6H, $CH_3$), 1.18-1.34 (m, 8H, H(3)$_{Pip}$ and H(5)$_{Pip}$, -(C$\underline{H}_2$)$_3$CH$_2$CH$_2$N<), 1.41-1.49 (m, 2H, -OCH$_2$C$\underline{H}_2$-), 1.71-1.87 (m, 4H, H(3)$_{Pip}$ and H(5)$_{Pip}$, -C$\underline{H}_2$CH$_2$N<), 3.36 (t, 2H, $J$ = 6.6 Hz, -

$OCH_2$-), 3.46-3.53 (m, 1H, $H(4)_{Pip}$), 3.84 (s, 3H, $(CH_3)_{Im}$), 4.16 (t, 2H, $J$ = 7.0 Hz, -$CH_2$N<), 7.67 (s, 1H, $H(4)_{Im}$ or $H(5)_{Im}$), 7.74 (s, $H(4)_{Im}$ or $H(5)_{Im}$), 9.07 (s, 1H, $H(2)_{Im}$). $^{13}$C NMR (DMSO-$d_6$, 126 MHz): $\delta$ 20.8 ($(CH_3)_{Pip}$), 25.7, 25.8, 28.5 (-$\underline{C}H_2(CH_2)_2$N<, -O$(CH_2)_2\underline{C}H_2$-, -$\underline{C}H_2(CH_2)_3$N<), 29.6 (-$\underline{C}H_2CH_2$N<), 29.8 (-$OCH_2\underline{C}H_2$-), 32.6 ($(CH_3)_{Pip}$), 35.9 ($(CH_3)_{Im}$), 44.9 ($C(3)_{Pip}$, $C(5)_{Pip}$), 49.0 (-$CH_2$N<), 58.1 ($C(2)_{Pip}$, $C(6)_{Pip}$), 67.4 (-$OCH_2$-), 70.2 ($C(4)_{Pip}$), 119.8 (q, $CF_3$, $J$ = 322 Hz), 122.4, 123.7 ($C(4)_{Im}$, $C(5)_{Im}$), 136.6 ($C(2)_{Im}$). Anal. Calcd for $C_{22}H_{37}F_6N_4O_6S_2$: C 41.83, H 5.90, N 8.87. Found: C 41.79, H 5.92, N 8.63.

TEMPOLC$_8$Im$^{Me}$TFSI (**5e**). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 1.03 (s, 6H, $CH_3$), 1.06 (s, 6H, $CH_3$), 1.18-1.32 (m, 10H, $H(3)_{Pip}$ and $H(5)_{Pip}$, -$(C\underline{H}_2)_4CH_2CH_2$N<), 1.40-1.48 (m, 2H, -$OCH_2C\underline{H}_2$-), 1.73-1.85 (m, 4H, $H(3)_{Pip}$ and $H(5)_{Pip}$, -$C\underline{H}_2CH_2$N<), , 3.35 (t, 2H, $J$ = 6.5 Hz, -$OCH_2$-), 3.45-3.54 (m, 1H, $H(4)_{Pip}$), 3.84 (s, 3H, $(CH_3)_{Im}$), 4.14 (t, 2H, $J$ = 7.0 Hz, -$CH_2$N<), 7.69 (s, 1H, $H(4)_{Im}$ or $H(5)_{Im}$), 7.75 (s, $H(4)_{Im}$ or $H(5)_{Im}$), 9.09 (s, 1H, $H(2)_{Im}$). $^{13}$C NMR (DMSO-$d_6$, 126 MHz): $\delta$ 20.8 ($(CH_3)_{Pip}$), 25.7, 25.9 (-$(\underline{C}H_2)_2(CH_2)_4$N<), 28.6, 28.9 (-$\underline{C}H_2(CH_2)_2$N<, -O$(CH_2)_2\underline{C}H_2$-), 29.6 (-$\underline{C}H_2CH_2$N<), 29.9 (-$OCH_2\underline{C}H_2$-), 32.5 ($(CH_3)_{Pip}$), 35.9 ($(CH_3)_{Im}$), 44.9 ($C(3)_{Pip}$, $C(5)_{Pip}$), 49.0 (-$CH_2$N<), 58.1 ($C(2)_{Pip}$, $C(6)_{Pip}$), 67.38 (-$OCH_2$-), 70.1 ($C(4)_{Pip}$), 119.7 (q, $CF_3$, $J$ = 322 Hz), 122.4, 123.8 ($C(4)_{Im}$, $C(5)_{Im}$), 136.6 ($C(2)_{Im}$). Anal. Calcd for $C_{23}H_{39}F_6N_4O_6S_2$: C 42.78, H 6.09, N 8.68. Found: C 42.63, H 5.99, N 8.74.

TEMPOLC$_4$Im$^{(Me)2}$TFSI (**6a**). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 1.05 (s, 6H, $CH_3$), 1.08 (s, 6H, $CH_3$), 1.20-1.28 (m, 2H, $H(3)_{Pip}$ and $H(5)_{Pip}$), 1.43-1.51 (m, 2H, -$OCH_2C\underline{H}_2$-), 1.71-1.78 (m, 2H, -$C\underline{H}_2CH_2$N<), 1.82-1.88 (m, 2H, $H(3)_{Pip}$ and $H(5)_{Pip}$), 2.55 (s, 3H, $C(2)_{Im}CH_3$), 3.41 (t, 2H, $J$ = 6.2 Hz, -$OCH_2$-), 3.49-3.56 (m, 1H, $H(4)_{Pip}$), 3.73 (s, 3H, $N(1)_{Im}CH_3$), 4.11 (t, 2H, $J$ = 7.2 Hz, -$CH_2$N<), 7.57-7.60 (m, 1H, $H(4)_{Im}$ or $H(5)_{Im}$), 7.60-7.63 (m, 1H, $H(4)_{Im}$ or $H(5)_{Im}$). $^{13}$C NMR (DMSO-$d_6$, 126 MHz): $\delta$ 9.2 ($C(2)_{Im}\underline{C}H_3$), 20.7 ($(CH_3)_{Pip}$), 26.4 (-$\underline{C}H_2CH_2$N<), 26.7 (-$OCH_2\underline{C}H_2$-), 32.7 ($(CH_3)_{Pip}$), 34.8 ($N(1)_{Im}CH_3$), 44.9 ($C(3)_{Pip}$, $C(5)_{Pip}$), 47.6 (-$CH_2$N<), 58.2 ($C(2)_{Pip}$, $C(6)_{Pip}$), 66.8 (-$OCH_2$-), 70.3 ($C(4)_{Pip}$), 119.8 (q, $CF_3$, $J$ = 322 Hz), 121.0, 122.5 ($C(4)_{Im}$, $C(5)_{Im}$), 144.2 ($C(2)_{Im}$). Anal. Calcd for $C_{20}H_{33}F_6N_4O_6S_2\cdot H_2O$: C 38.64, H 5.67, N 9.01. Found: C 38.39, H 5.55, N 8.78.

TEMPOLC$_5$Im$^{(Me)2}$TFSI (**6b**). $^{13}$C NMR (DMSO-$d_6$, 126 MHz): $\delta$ 9.2 ($C(2)_{Im}\underline{C}H_3$), 20.8 ($(CH_3)_{Pip}$), 22.8 (-$\underline{C}H_2(CH_2)_2$N<), 29.2 (-$\underline{C}H_2CH_2$N<), 29.3 (-$OCH_2\underline{C}H_2$-), 32.6 ($(CH_3)_{Pip}$), 34.8 ($N(1)_{Im}CH_3$), 44.9 ($C(3)_{Pip}$, $C(5)_{Pip}$), 47.7 (-$CH_2$N<), 58.2 ($C(2)_{Pip}$, $C(6)_{Pip}$), 67.2 (-$OCH_2$-), 70.3 ($C(4)_{Pip}$), 119.7 (q, $CF_3$, $J$ = 322 Hz), 121.0, 122.4 ($C(4)_{Im}$, $C(5)_{Im}$), 144.1 ($C(2)_{Im}$). Anal. Calcd for $C_{21}H_{35}F_6N_4O_6S_2\cdot 1.5H_2O$: C 39.12, H 5.94, N 8.69. Found: C 39.42, H 5.74, N 8.26.

TEMPOLC$_6$Im$^{(Me)2}$TFSI (**6c**). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 1.06 (s, 6H, $CH_3$), 1.10 (s, 6H, $CH_3$), 1.22-1.37 (m, 6H, $H(3)_{Pip}$ and $H(5)_{Pip}$, -$(C\underline{H}_2)_2CH_2CH_2$N<), 1.43-1.51 (m, 2H, -$OCH_2C\underline{H}_2$-), 1.65-1.73 (m, 2H, -$C\underline{H}_2CH_2$N<), 1.82-1.88 (m, 2H, $H(3)_{Pip}$ and $H(5)_{Pip}$), 2.55 (s, 3H, $C(2)_{Im}CH_3$), 3.37 (t, 2H, $J$ = 6.7 Hz, -$OCH_2$-), 3.47-3.56 (m, 1H, $H(4)_{Pip}$), 3.72 (s, 3H, $N(1)_{Im}CH_3$), 4.06 (t, 2H, $J$ = 7.1 Hz, -$CH_2$N<), 7.56-7.59 (m, 1H, $H(4)_{Im}$ or $H(5)_{Im}$), 7.59-7.62 (m, 1H, $H(4)_{Im}$ or $H(5)_{Im}$). $^{13}$C NMR (DMSO-$d_6$, 126 MHz): $\delta$ 9.2 ($C(2)_{Im}\underline{C}H_3$), 20.8 ($(CH_3)_{Pip}$), 25.5, 25.7 (-$(\underline{C}H_2)_2(CH_2)_2$N<), 29.3 (-$\underline{C}H_2CH_2$N<), 29.7 (-$OCH_2\underline{C}H_2$-), 32.6 ($(CH_3)_{Pip}$), 34.8 ($N(1)_{Im}CH_3$), 44.9 ($C(3)_{Pip}$, $C(5)_{Pip}$), 47.7 (-$CH_2$N<), 58.1 ($C(2)_{Pip}$, $C(6)_{Pip}$), 67.3 (-$OCH_2$-), 70.2 ($C(4)_{Pip}$), 119.8 (q, $CF_3$, $J$ = 322 Hz), 121.0, 122.4 ($C(4)_{Im}$, $C(5)_{Im}$), 144.2 ($C(2)_{Im}$). Anal. Calcd for $C_{22}H_{37}F_6N_4O_6S_2$: C 41.83, H 5.90, N 8.87. Found: C 41.64, H 5.88, N 8.57.

TEMPOLC$_7$Im$^{(Me)2}$TFSI (**6d**). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 1.05 (s, 6H, $CH_3$), 1.08 (s, 6H, $CH_3$), 1.21-1.32 (m, 8H, $H(3)_{Pip}$ and $H(5)_{Pip}$, -$(C\underline{H}_2)_3CH_2CH_2$N<), 1.42-1.49 (m, 2H, -$OCH_2C\underline{H}_2$-), 1.65-1.74 (m, 2H, -$C\underline{H}_2CH_2$N<), 1.82-1.87 (m, 2H, $H(3)_{Pip}$ and $H(5)_{Pip}$), 2.55 (s,

3H, $C(2)_{Im}CH_3$), 3.36 (t, 2H, *J* = 6.7 Hz, -$OCH_2$-), 3.47-3.56 (m, 1H, $H(4)_{Pip}$), 3.72 (s, 3H, $N(1)_{Im}CH_3$), 4.07 (t, 2H, *J* = 7.3 Hz, -$CH_2$N<), 7.57-7.60 (m, 1H, $H(4)_{Im}$ or $H(5)_{Im}$), 7.60-7.63 (m, 1H, $H(4)_{Im}$ or $H(5)_{Im}$). $^{13}$C NMR (DMSO-$d_6$, 126 MHz): $\delta$9.2 ($C(2)_{Im}\underline{C}H_3$), 20.8 ($(CH_3)_{Pip}$), 25.79, 25.81 (-$\underline{C}H_2(CH_2)_2$N<, -$O(CH_2)_2\underline{C}H_2$-), 28.6 (-$\underline{C}H_2(CH_2)_3$N<), 29.3 (-$\underline{C}H_2CH_2$N<), 29.8 (-$OCH_2\underline{C}H_2$-), 32.6 ($(CH_3)_{Pip}$), 34.8 ($N(1)_{Im}CH_3$), 44.9 ($C(3)_{Pip}$, $C(5)_{Pip}$), 47.7 (-$CH_2$N<), 58.1 ($C(2)_{Pip}$, $C(6)_{Pip}$), 67.4 (-$OCH_2$-), 70.1 ($C(4)_{Pip}$), 119.8 (q, $CF_3$, *J* = 322 Hz), 121.0, 122.4 ($C(4)_{Im}$, $C(5)_{Im}$), 144.2 ($C(2)_{Im}$). Anal. Calcd for $C_{23}H_{39}F_6N_4O_6S_2$: C 42.78, H 6.09, N 8.68. Found: C 42.94, H 6.03, N 8.37.

TEMPOL$C_8$Im$^{(Me)2}$TFSI (**6e**). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta$ 1.07 (s, 6H, $CH_3$), 1.11 (s, 6H, $CH_3$), 1.21-1.34 (m, 10H, $H(3)_{Pip}$ and $H(5)_{Pip}$, -$(C\underline{H}_2)_4CH_2CH_2$N<), 1.43-1.52 (m, 2H, -$OCH_2C\underline{H}_2$-), 1.65-1.73 (m, 2H, -$C\underline{H}_2CH_2$N<), 1.83-1.89 (m, 2H, $H(3)_{Pip}$ and $H(5)_{Pip}$), 2.53 (s, 3H, $C(2)_{Im}CH_3$), 3.38 (t, 2H, *J* = 6.3 Hz, -$OCH_2$-), 3.48-3.56 (m, 1H, $H(4)_{Pip}$), 3.71 (s, 3H, $N(1)_{Im}CH_3$), 4.05 (t, 2H, *J* = 7.3 Hz, -$CH_2$N<), 7.54-7.57 (m, 1H, $H(4)_{Im}$ or $H(5)_{Im}$), 7.57-7.60 (m, 1H, $H(4)_{Im}$ or $H(5)_{Im}$). $^{13}$C NMR (DMSO-$d_6$, 126 MHz): $\delta$ 9.14 ($C(2)_{Im}$-$\underline{C}H_3$), 20.81 ($(CH_3)_{Pip}$), 25.81, 25.93 (-$(\underline{C}H_2)_2(CH_2)_4$N<), 28.74, 28.99 (-$\underline{C}H_2(CH_2)_2$N<, -$O(CH_2)_2\underline{C}H_2$-), 29.36 (-$\underline{C}H_2CH_2$N<), 29.93 (-$OCH_2\underline{C}H_2$-), 32.57 ($(CH_3)_{Pip}$), 34.74 ($N(1)_{Im}CH_3$), 44.96 ($C(3)_{Pip}$, $C(5)_{Pip}$), 47.74 (-$CH_2$N<), 58.15 ($C(2)_{Pip}$, $C(6)_{Pip}$), 67.48 (-$OCH_2$-), 70.18 ($C(4)_{Pip}$), 119.79 (q, $CF_3$, *J* = 322 Hz), 121.08, 122.42 ($C(4)_{Im}$, $C(5)_{Im}$), 144.13 ($C(2)_{Im}$). Anal. Calcd for $C_{24}H_{41}F_6N_4O_6S_2 \cdot 1.66H_2O$: C 41.80, H 6.48, N 8.12. Found: C 42.06, H 6.24, N 7.80.

## 2. Electrochemical characterization

Cyclic voltammetry and electrochemical impedance spectroscopy were performed using a CHI660D electrochemical workstation. Cyclic voltammetry was conducted in a conventional three-electrode cell. Glassy carbon (Ø 3 mm), platinum wire and non-aqueous $Ag/Ag^+$ were used as a working, counter and a reference electrode, respectively. The $Ag/Ag^+$ reference electrode consisted of a silver wire immersed in 0.1 M LiTFSI (or 0.5 M TBATFSI) and 0.01 M $AgNO_3$ in TEGDME and conductivity to the bulk solution was maintained via a Vycor frit. The $Ag/Ag^+$ reference electrode was calibrated against a $Li/Li^+$ reference electrode. $Li/Li^+$ reference electrodes were fabricated by wrapping Li foil (1x1 $cm^2$) around a nickel wire. The potential of $Ag/Ag^+$ with 0.1 M LiTFSI or 0.5 M TBATFSI in TEGDME was 3.55 V or 3.66 V vs $Li/Li^+$, respectively. Cyclic voltammetry experiments were performed in TEGDME with 0.1 M LiTFSI or 0.5 M TBATFSI and 10 mmol of TEMPOImILs at a scan rate of 100 mV/s. The glassy carbon working electrode was polished, washed and dried prior to use as well as between different measurements. Experiments were conducted under $O_2$ atmosphere. The saturation of the gas was achieved by bubbling dry gas for 10 min. EIS spectra were collected in the frequency range 100 kHz to 1 Hz with an amplitude of an AC voltage of 5 mV. The tests were performed by soaking two stainless steel blocking electrodes in the pure TEMPOImILs samples. The system was sealed in a glove box. Samples were kept at each test temperature for 30 min prior to each measurement to reach thermal equilibrium.

Galvanostatic discharge−charge tests were carried out on a Neware battery testing system. A two-electrode Swagelok-type cell with an air hole (0.785 $cm^2$) on the cathode side was used. The cells were assembled in an argon-filled glove box with water and oxygen levels of less than 0.1 ppm and rested for 1 hour at 60 °C prior to being purged with oxygen. Lithium metal (16 mm), carbon nanotubes (12 mm) and glass fiber (18 mm) were used as an anode, cathode and separator, respectively. To prepare CNT cathodes, a mixture of CNTs:PTFE (9:1 by weight) in *i*-$PrOH/H_2O$ was stirred for 18 h, casted on pre-cut glass fiber membranes and dried. The loading of the cathode material was ~0.5 mg $cm^{-2}$. The electrolyte was prepared by dissolving 0.5 M LiTFSI in TEMPOImILs.

## 3. Supplementary Figures

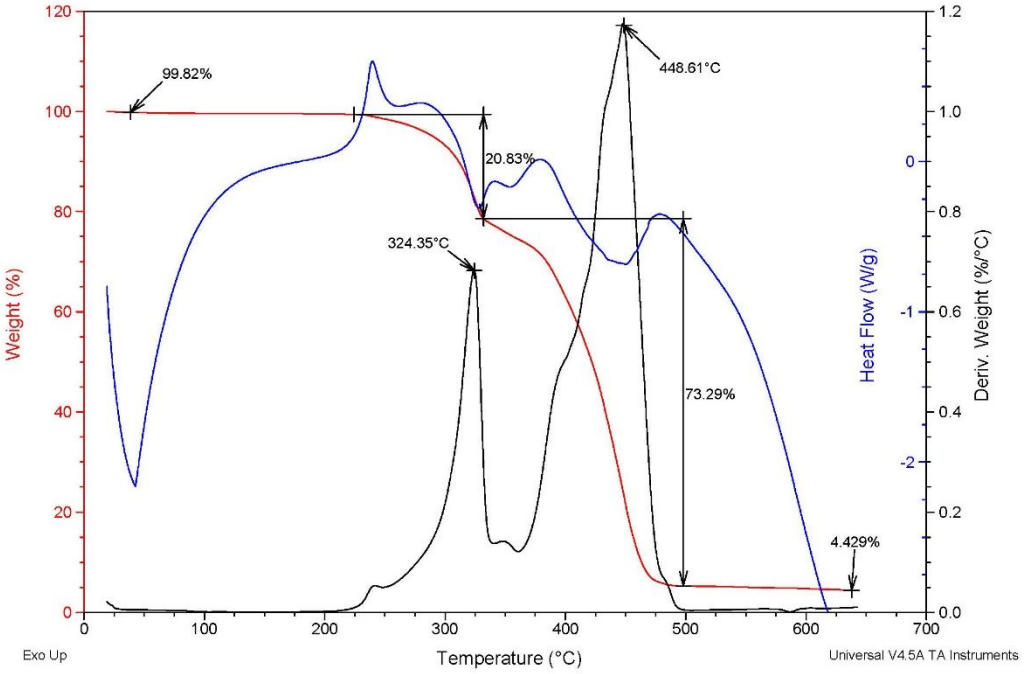


**Figure S1.** TGA and DSC data for TEMPOImIL with n = 8, R = H.

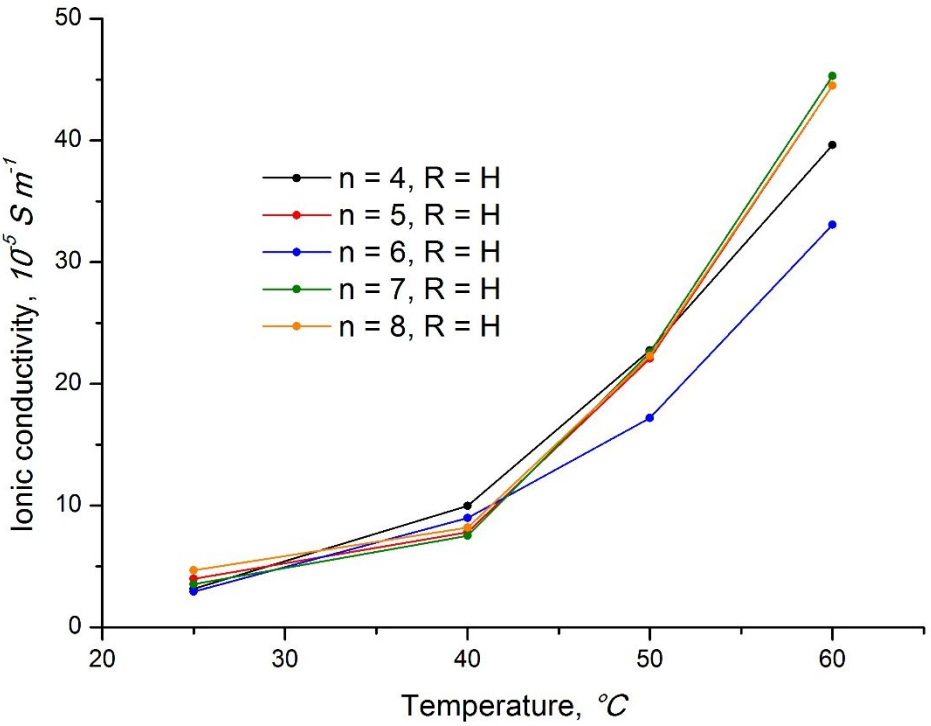


**Figure S2.** Temperature dependence of ionic conductivities of pure TEMPOImILs (R = H).

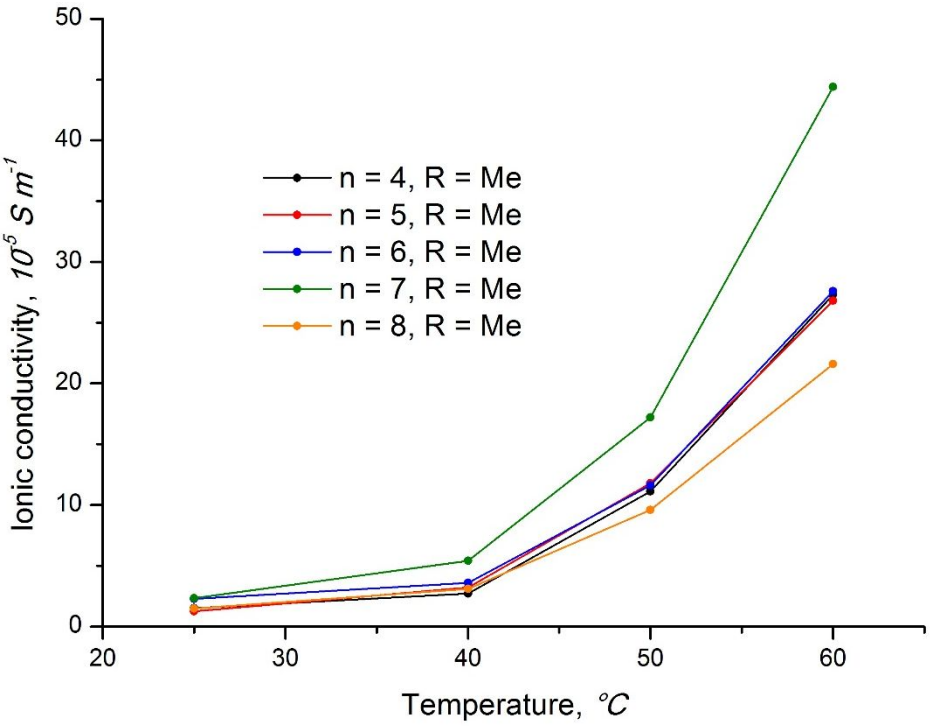


**Figure S3.** Temperature dependence of ionic conductivities of pure TEMPOImILs (R = Me).

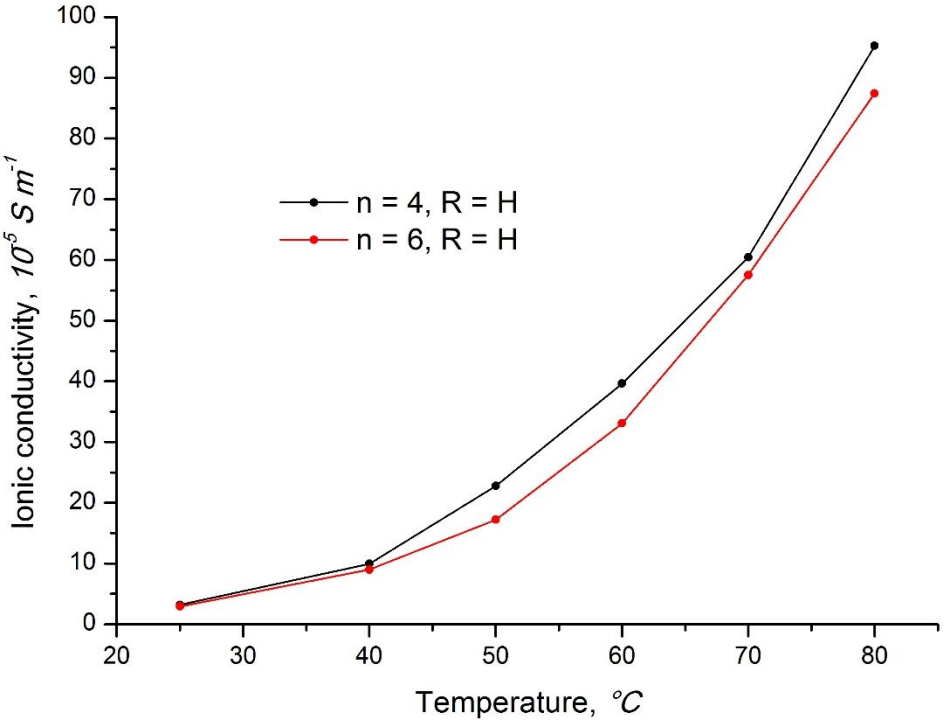


**Figure S4.** Temperature dependence of ionic conductivities of pure TEMPOImILs (n = 4, 6, R = H) up to 80 °C.

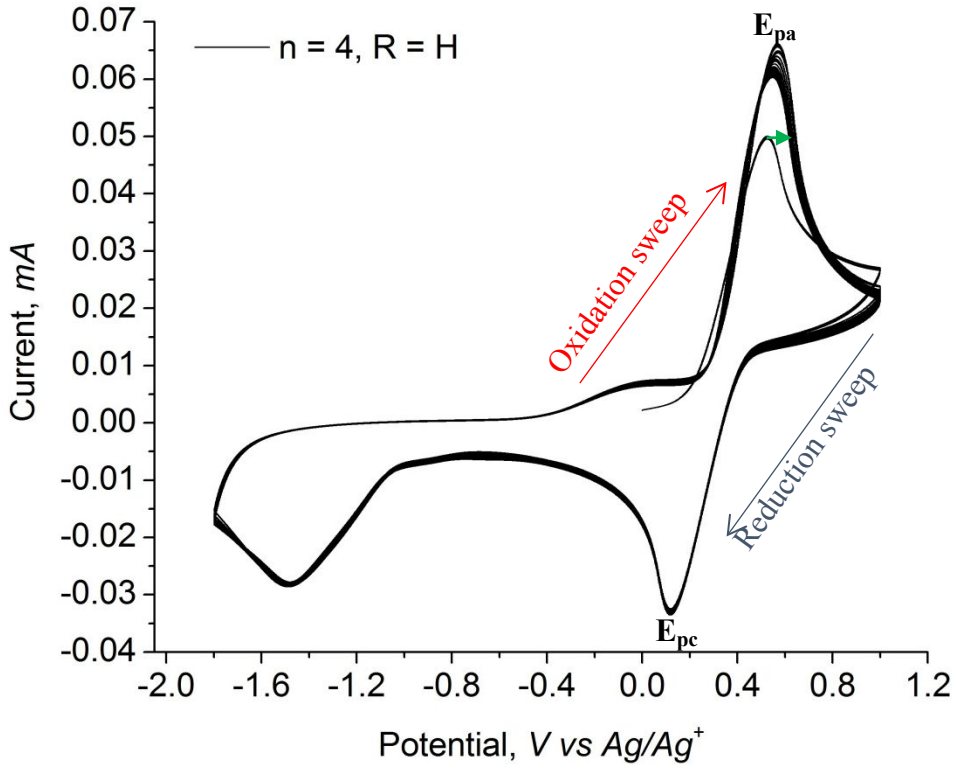


**Figure S5.** Cyclic voltammogram of TEMPOImIL with n = 4, R = H, 10 cycles. The effect of TEMPOImILs on the OER is visible upon prolonged cycling (Fig. S5). After the first cycle, the anodic peak $\mathbf{E_{pa}}$ related to the oxidation of the nitroxide group shifts to higher potential values and increases in intensity due to interaction with $Li_2O_2$ deposited during the ORR, while the corresponding cathodic peak $\mathbf{E_{pc}}$ remains the same, which means that $Li_2O_2$ was fully removed by the oxidised form of the redox mediator ($RM^+$), proving the efficiency of TEMPOImILs as charge RMs.[6]

## 4. References


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