## SUPPORTING INFORMATION

## ION CONDUCTING ROMP MONOMERS BASED ON (OXA)NORBORNENES WITH PENDANT IMIDAZOLIUM SALTS CONNECTED VIA OLIGO(OXYETHYLENE) UNITS AND WITH OLIGO(ETHYLENEOXY) TERMINAL MOIETIES

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*Exo,Exo*-Bis(2-(2'-(2''-hydroxyethoxy)ethoxy)ethyl) bicyclo[2.2.1]hept-5-ene-2,3dicarboxylate {NB[C(O)OE<sub>2</sub>OH]<sub>2</sub>, 2b}: General procedure 1 was used to produce a clear oil (3.82 g, 70 %) by using: 1 (2.00 g, 12.2 mmol), tri(ethylene glycol) (50 mL, 374 mmol), and sulfuric acid (0.1 mL, 2 mmol). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 6.21 (s, 2H), 4.23 (m, 4H), 3.79–3.57 (m, 20H), 3.11 (s, 2H), 2.66 (m, 2H), 2.10 (m, 1H), 1.49 (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$ : 173.56, 137.98, 72.62, 70.56, 70.37, 69.07, 63.75, 61.78, 47.27, 45.75, 45.40 (11 signals expected and 11 signals found). HR MS: calc. for C<sub>21</sub>H<sub>35</sub>O<sub>10</sub> [M + H]<sup>+</sup>: m/z 447.2225; found: m/z 447.2214 (error –2.3 ppm); calc. for C<sub>21</sub>H<sub>34</sub>O<sub>10</sub>Na [M + Na]<sup>+</sup>: m/z 469.2044; found: m/z 469.2041 (error 0.6 ppm).

*Exo,Exo*-Bis(2-(2'-(2''-hydroxyethoxy)ethoxy)ethoxy)ethyl) bicyclo[2.2.1]hept-

5-ene-2,3-dicarboxylate {NB[C(O)OE4OH]2, 2c}: General procedure 1 was used to

produce a clear oil (25.3 g, 63 %) by using: **1** (12.3 g, 74.8 mmol), tetra(ethylene glycol) (400 mL, 2.32 mol), and sulfuric acid (0.30 mL, 5.6 mmol). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 6.21 (s, 2H), 4.27 (m, 2H), 4.15 (m, 2H), 3.77 – 3.55 (m, 28H), 3.10 (s, 2H), 2.65 (s, 2H), 2.09 (m, 1H), 1.49 (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$ : 173.53, 137.98, 72.57, 70.67, 70.57, 70.52, 70.38, 69.11, 63.82, 61.75, 47.25, 45.76, 45.37 (13 signals expected and 13 signals found). HR MS: calc. for C<sub>25</sub>H<sub>43</sub>O<sub>12</sub> [M + H]<sup>+</sup>: m/z 535.2749; found: m/z 535.2760 (error 2.1 ppm).

*Exo,Exo-Bis*(2-(2'-(2''-tosyloxyethoxy)ethoxy)ethyl) bicyclo[2.2.1]hept-5-ene-2,3dicarboxylate {NB[C(O)OE<sub>3</sub>OTs]<sub>2</sub>, 3b}: General procedure 2 was used to produce a clear oil (4.13 g, 43%) by using: 2b (5.68 g, 12.7 mmol), TEA (7.0 mL, 50 mmol), DCM (25 mL), and tosyl chloride (7.32 g, 38.4 mmol) in DCM (80 mL). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.79 (d, *J* = 8 Hz, 4H), 7.34 (d, *J* = 8 Hz, 4H), 6.20 (m, 2H), 4.25 (m, 2H), 4.18–4.14 (m, 4H), 4.09 (m, 2H), 3.71 – 3.62 (m, 8H), 3.58 (s, 8H), 3.09 (m, 2H), 2.64 (s, 2H), 2.45 (s, 6H), 2.07 (d, *J* = 9 Hz, 1H), 1.47 (d, *J* = 9 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$ : 173.47, 144.82, 137.94, 133.03, 129.84, 127.97, 70.73, 70.45, 69.22, 69.10, 68.74, 63.73, 47.25, 45.76, 45.34, 21.64 (16 peaks expected and 16 peaks found). High res MS: calc. for C<sub>35</sub>H<sub>47</sub>O<sub>14</sub>S<sub>2</sub>N [M + H]<sup>+</sup>: m/z 755.2402; found: m/z 755.2410 (error 1 ppm); calc. for C<sub>35</sub>H<sub>46</sub>O<sub>14</sub>S<sub>2</sub>Na [M + Na]<sup>+</sup>: m/z 755.2221; found: m/z 772.2688 (error 2.3 ppm); calc. for C<sub>35</sub>H<sub>46</sub>O<sub>14</sub>S<sub>2</sub>K [M + K]<sup>+</sup>: m/z 793.1961; found: m/z 793.2040 (error 10 ppm).

S5

*Exo,Exo-Bis*(2-(2'-(2''-(2'''-tosyloxyethoxy)ethoxy)ethoxy)ethoxy)ethox)) bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate {NB[C(O)OE<sub>4</sub>OTs]<sub>2</sub>, 3c}: General procedure 2 was used to produce a clear oil (5.02 g, 47%) by using: 2c (6.72 g, 12.6 mmol), TEA (7.00 mL, 50.2 mmol), DCM (20 mL) and tosyl chloride (7.06 g, 37.0 mmol) in DCM (80 mL). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.80 (d, *J* = 8 Hz, 4H), 7.34 (d, *J* = 8 Hz, 4H), 6.22–6.18 (m, 2H), 4.27 (m, 2H), 4.18–4.14 (m, 4H), 4.10 (m, 2H), 3.71–3.57 (m, 24H), 3.09 (s, 2H), 2.64 (d, 2H), 2.45 (s, 6H), 2.08 (d, *J* = 9 Hz, 1H), 1.47 (d, *J* = 9 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$ : 173.49, 144.82, 137.95, 132.99, 129.84, 127.97, 70.74, 70.59, 70.53, 70.49, 69.25, 69.05, 68.69, 63.76, 47.22, 45.74, 45.33, 21.65 (18 peaks expected and 18 peaks found). HR MS: calc. for C<sub>39</sub>H<sub>55</sub>O<sub>16</sub>S<sub>2</sub> [M + H]<sup>+</sup>: m/z 843.2926; found: m/z 843.2937 (error 1.4 ppm); calc. for C<sub>39</sub>H<sub>54</sub>O<sub>16</sub>S<sub>2</sub>Na [M + Na]<sup>+</sup>: m/z 865.2745; found: m/z 865.2755 (error 1.1 ppm); calc. for C<sub>39</sub>H<sub>55</sub>O<sub>16</sub>S<sub>2</sub>K [M + K]<sup>+</sup>: m/z 881.2485; found: m/z 881.2502 (error 2.0 ppm).

Exo, Exo-Bis(2-(2'-(2''-(2'''-(2'''-

tosyloxyethoxy)ethoxy)ethoxy)ethoxy)ethoxy)-ethyl) bicyclo[2.2.1]hept-5-ene-2,3dicarboxylate {NB[C(O)OE<sub>6</sub>OTs]<sub>2</sub>, 3e}: General procedure 4 was used to produce a liquid (2.79 g, 82%) by using: 1 (0.37 g, 2.3 mmol), hexa(ethylene glycol) monotosylate (2.04 g, 4.67 mmol), EDCI (0.87 g, 5.6 mmol), DMAP (0.14 g, 1.1 mmol), and DCM (50 mL). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.80 (d, *J* = 8 Hz, 4H), 7.35 (d, *J* = 8 Hz, 4H), 6.20 (s, 2H), 4.32–4.24 (m, 2H), 4.19–4.13 (m, 4H), 4.13–4.06 (m, 2H), 3.80–3.53 (m, 40H), 3.09 (s, 2H), 2.64 (d, *J* = 2 Hz, 2H), 2.45 (s, 6H), 2.08 (d, *J* = 9 Hz, 1H), 1.48 (d, *J* = 9 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  173.47, 144.78, 137.95, 133.02, 129.82, 127.98, 72.49, 70.75, 70.61, 70.57, 70.52, 70.34, 69.24, 69.06, 68.68, 63.76, 61.75, 47.22, 45.75, 45.34, 42.73, 21.65 (22 signals expected and 22 found). HR MS: calc. for  $C_{47}H_{74}O_{20}S_2N$  [M + NH<sub>4</sub>]<sup>+</sup>: m/z 1036.4246; found: m/z 1036.4303 (error –5.5 ppm); calc. for  $C_{47}H_{70}O_{20}S_2Na$  [M + Na]<sup>+</sup>: m/z 1041.3800; found: m/z 1041.3864 (error –6.1 ppm).

Tetra(ethylene glycol) monomethyl ether monotosylate (MeOE<sub>4</sub>OTs, 5c): Tetra(ethylene glycol) monomethyl ether (5.02 g, 24.1 mmol) and THF (1 mL) were combined in a round bottom flask and cooled to 0°C. In a separate container sodium hydroxide (1.02 g, 25.5 mmol) was dissolved in water (1 mL) and added to the glycol solution. Tosyl chloride (4.89 g, 25.6 mmol) dissolved in THF (20 mL) was added dropwise to the reaction mixture. After the tosyl chloride addition was complete, the solution was allowed to warm to room temperature and stirred for 24 h. The organic layer was collected and the aqueous layer was extracted with ether twice. The organic layers were combined and washed with 10% wt sodium hydroxide (x 3), water (x 2), saturated NaCl (x 1), and dried over sodium sulfate. Filtration and removal of the solvent provided the desired product as an oil: 6.41 g (73%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.80 (d, J = 8 Hz, 2H), 7.34 (d, J = 8 Hz, 2H), 4.19 – 4.12 (m, 2H), 3.71 – 3.66 (m, 2H), 3.66 - 3.61 (m, 6H), 3.59 (s, 4H), 3.56 - 3.52 (m, 2H), 3.38 (s, 3H), 2.45 (s, 3H).  $^{13}C$ NMR (126 MHz, CDCl<sub>3</sub>) δ 144.79), 133.01, 129.82, 127.99, 71.93, 70.74, 70.60, 70.59, 70.52, 69.24, 68.68, 59.04, 21.65 (14 peaks expected and 13 peaks found; 2 peaks are believed to be overlapping at 70.52). High res MS: calc. for  $C_{16}H_{27}O_7S [M + H]^+$ : m/z

363.1477; found: m/z 363.1490 (error 3.6 ppm); calc. for C<sub>16</sub>H<sub>30</sub>O<sub>7</sub>SN [M + NH<sub>4</sub>]<sup>+</sup>: m/z 380.1743; found: m/z 380.1754 (error 2.9 ppm).

**Hexa(ethylene glycol) Monotosylate, HOE**<sub>6</sub>**OTs:** General Procedure 3 was used to produce a liquid (8.32 g, 24 %) by using; hexa(ethylene glycol) (22.47 g, 79.59 mmol), tosyl chloride (15.34 g, 80.46 mmol), NaOH (3.20 g, 80.0 mmol), water (10 mL), and THF (40 mL). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.80 (d, J = 8 Hz, 2H), 7.35 (d, J = 8 Hz, 2H), 4.19–4.13 (m, 2H), 3.75–3.56 (m, 22H), 2.45 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 144.77, 132.99, 129.81, 127.96, 72.48, 70.71, 70.59, 70.55, 70.53, 70.52, 70.50, 70.31, 69.26, 68.66, 61.71, 21.63 (17 signals expected and 16 signals found; peak @ 70.59 results from the overlapping of 2 peaks). HR MS: calc. for C<sub>19</sub>H<sub>32</sub>O<sub>9</sub>SNa [M + Na]<sup>+</sup>: m/z 437.1845; found: m/z 437.1837 (error 2 ppm); calc. for C<sub>19</sub>H<sub>32</sub>O<sub>9</sub>SK [M + K]<sup>+</sup>: m/z 475.1404; found: m/z 475.1395 (error 2 ppm).

**1-(2'-Methoxyethyl)imidazole (ImEOMe, 6b):** General procedure 5 was used to produce a yellow tinted liquid (1.08 g, 86 %) by using: imidazole (1.36 g, 20 mmol), sodium hydroxide (0.72 g, 18 mmol), water (25 mL), and 2-chloroethyl methyl ether (0.945 g, 10 mmol) in THF (25 mL). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.52 (s, 1H), 7.05 (s, 1H), 6.97 (s, 1H), 4.09 (t, *J* = 5 Hz, 2H), 3.63 (t, *J* = 5 Hz, 2H), 3.34 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$ : 137.49, 129.30, 119.38, 71.84, 59.02, 47.03 (6 signals expected and 6 signals found). HR MS: calc. for C<sub>6</sub>H<sub>11</sub>N<sub>2</sub>O [M + H]<sup>+</sup>: m/z 127.0866; found: m/z 127.0866 (error 0 ppm).

1-(2'-Methoxyethyl)imidazole (ImEO<sub>2</sub>Me, 6c): The literature procedure <sup>S1</sup> afforded a

yellow liquid (71 %) whose <sup>1</sup>H and <sup>13</sup>C NMR spectra matched the literature report. HR MS: calc. for  $C_8H_{15}N_2O_2$  [M + H]<sup>+</sup>: m/z 171.1134; found: m/z 171.1129 (error 2.9 ppm).

**1-(2'-(2''-(2'''-Methoxyethoxy)ethoxy)ethyl)imidazole** (ImEO<sub>3</sub>Me, 6d): General procedure 5 was used to produce a clear oil (6.76 g, 76 %) by using: imidazole (2.83 g, 41.6 mmol), sodium hydroxide (1.88 g, 47.0 mmol), water (3 mL), and **5b** (14.38 g, 45.17 mmol) in THF (20 mL). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.53 (s, 1H), 7.04 (s, 1H), 6.99 (s, 1H), 4.11 (t, J = 5 Hz, 2H), 3.77–3.72 (m, 2H), 3.64–3.58 (m, 6H), 3.56–3.52 (m, 2H), 3.38 (s, 3H); this closely matched the literature report.<sup>S2 13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ: 137.56, 129.27, 119.41, 71.94, 70.72, 70.61, 70.59, 70.56, 59.05, 47.05 (10 signals expected and 10 signals found). HR MS: calc. for C<sub>10</sub>H<sub>19</sub>O<sub>3</sub>N<sub>2</sub> [M + H]<sup>+</sup>: m/z 215.1390; found: m/z 215.1397 (error 3 ppm).

**1-(2',5',8',11'-Tetraoxatridecan-13'-yl)imidazole (ImEO<sub>4</sub>Me, 6e):** General procedure 5 was used to produce a clear oil (4.32 g, 94 %) by using: imidazole (2.76 g, 40.5 mmol), sodium hydroxide (1.53 g, 38.3 mmol), water (5 mL) and **5c** (6.46 g, 17.8 mmol) in THF (60 mL). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.53 (s, 1H), 7.04 (s, 1H), 7.00 (s, 1H), 4.11 (t, *J* = 5 Hz, 2H), 3.74 (t, *J* = 5 Hz, 2H), 3.69–3.53 (m, 12H), 3.37 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ: 137.52, 129.24, 119.40, 71.93, 70.70, 70.61, 70.56, 70.54, 70.52, 59.00, 47.03 (12 signals expected and 11 signals found; it is believed that two peaks overlap at 70.61). HR MS: calc. for  $C_{12}H_{23}O_4N_2$  [M + H]<sup>+</sup>: m/z 259.1652; found: m/z 259.1665 (error 5.0 ppm).

*Exo,Exo*-NB[C(O)OEIm<sup>+</sup>EOMe]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> (8b): General procedure 6 was used to produce an oil (4.85 g, 52 %) by using: 4 (3.55g, 8.96 mmol), 6b (4.42 g, 35.0 mmol)

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and LiTFSI (6.20 g, 21.6 mmol). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  9.12 (t, *J* = 2 Hz, 2H), 7.73 (dt, *J* = 4, 2 Hz, 4H), 6.19 (t, *J* = 2 Hz, 2H), 4.48–4.36 (m, 6H), 4.36–4.31 (m, 4H), 4.22–4.12 (m, 2H), 3.68–3.61 (m, 4H), 3.22 (s, 6H), 2.92–2.88 (m, 2H), 2.58 (d, *J* = 2 Hz, 2H), 1.67 (d, *J* = 9 Hz, 1H), 1.28 (dt, *J* = 9, 2 Hz, 1H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ 172.90, 138.16, 137.27, 123.27, 123.00, 119.9 (q, *J* = 323 Hz), 69.97, 62.69, 58.49, 49.21, 48.41, 46.93, 45.53, 45.16. (14 signals expected and 14 signals found). HR MS: calc. for C<sub>27</sub>H<sub>36</sub>O<sub>10</sub>N<sub>5</sub>S<sub>2</sub>F<sub>6</sub> [M – TFSI]<sup>+</sup>: m/z 768.1808; found: m/z 768.1792 (error –2.1 ppm); calc. for C<sub>25</sub>H<sub>36</sub>O<sub>6</sub>N<sub>4</sub> [M – 2TFSI]<sup>+2</sup>: m/z 244.1312; found: m/z 244.1288 (error – 9.8 ppm). T<sub>q</sub> (DSC) = –39 °C. Conductivity at 25 °C = 2.42 X 10<sup>-5</sup> S/cm.

*Exo*,*Exo*-NB[C(O)OEIm<sup>+</sup>EO<sub>2</sub>Me]<sub>2</sub> (TFSI)<sub>2</sub> (8c): General procedure 6 was used to produce an oil (4.94 g, 52%) by using: 4 (3.30 g, 8.34 mmol), 6c (5.00 g, 29.37 mmol), and LiTFSI (6.00 g, 20.9 mmol). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ : 8.82 (s, 2H), 7.54 (s, 2H), 7.50 (s, 2H), 6.25 (s, 2H), 4.46 (m, 8H), 4.41–4.36 (m, 4H), 3.90–3.83 (m, 4H), 3.65 (s, 4H), 3.55 (s, 4H), 3.36 (s, 6H), 3.08 (s, 2H), 2.72 (s, 2H), 1.82 (m, 1H), 1.49 (m, 1H). <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ : 173.84, 138.21, 136.74, 123.91, 122.78, 120.22 (q, J = 323 Hz), 71.92, 70.57, 68.68, 62.80, 58.89, 50.40, 49.23, 47.80, 45.92, 45.49 (16 signals expected and 16 major signals found; additionally, minor signals were observed for most carbon signals, this is due to an equilibrium between hydrogen bonded and non-hydrogen bonded ethyleneoxy-imidazolium moieties in CD<sub>2</sub>Cl<sub>2</sub>; see text for explanation). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  172.95, 138.17, 137.27, 123.31, 122.98, 119.91 (q, J = 323 Hz), 71.49, 69.77, 68.55, 62.78, 58.49, 49.34, 48.44, 46.94, 45.56, 45.17 (16 signals expected and 16 signals found). HR MS: calc. for C<sub>31</sub>H<sub>44</sub>O<sub>12</sub>N<sub>5</sub>S<sub>2</sub>F<sub>6</sub>

 $[M - TFSI]^+$ : m/z 856.2327; found: m/z 856.2312 (error -1.8 ppm); calc. for C<sub>29</sub>H<sub>44</sub>O<sub>8</sub>N<sub>4</sub> (M - 2 TFSI)<sup>+2</sup>: m/z 288.1580; found: m/z 288.1576 (error -1.4 ppm). T<sub>g</sub> (DSC) = -45 °C. Conductivity at 25 °C = 2.95 X 10<sup>-5</sup> S/cm.

*Exo,Exo*-NB[C(O)OEIm<sup>+</sup>EO<sub>3</sub>Me]<sub>2</sub> (TFSI)<sub>2</sub> (8d): General procedure 6 was used to produce an oil (7.57 g, 59%) by using: 4 (4.15 g, 10.5 mmol), 6d (4.97 g, 23.12 mmol), and LiTFSI (6.50 g, 22.6 mmol). <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$ : 9.16 (s, 2H), 7.79 (m, 4H), 6.29–6.19 (m, 2H), 4.54–4.41 (m, 6H), 4.41–4.33 (m, 4H), 4.22 (m, 2H), 3.81–3.75 (m, 4H), 3.59–3.53 (m, 4H), 3.53–3.46 (m, 8H), 3.43 (m, 4H), 3.24 (s, 6H), 2.98–2.92 (m, 2H), 2.63 (d, 2H), 1.72 (d, J = 9 Hz, 1H), 1.32 (d, J = 9 Hz, 1H). <sup>13</sup>C NMR (126 MHz, DMSO- $d_6$ )  $\delta$ : 172.99, 138.21, 137.28, 123.41, 122.96, 119.94 (J = 323 Hz), 71.71, 70.01, 69.98, 69.93, 68.59, 62.80, 58.51, 49.31, 48.43, 46.97, 45.58, 45.20 (17 signals expected and 17 signals found). HR MS: calc. for C<sub>35</sub>H<sub>52</sub>O<sub>14</sub>N<sub>5</sub>S<sub>2</sub>F<sub>6</sub> [M – TFSI]<sup>+</sup>: m/z 944.2851; found: m/z 944.2840 (error –1.1 ppm); calc. for C<sub>33</sub>H<sub>52</sub>O<sub>10</sub>N<sub>4</sub> [M – 2TFSI]<sup>+2</sup>: m/z 332.1836; found: m/z 332.1840 (error 1 ppm). T<sub>g</sub> (DSC) = –50 °C. Conductivity at 25 °C = 7.10 x 10<sup>-5</sup> S/cm.

*Exo,Exo*-NB[C(O)OEIm<sup>+</sup>EO<sub>4</sub>Me]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> (8e): General procedure 6 was used to produce an oil (2.38 g, 70%) by using: 4 (1.03 g, 2.60 mmol), **6e** (1.90 g, 7.37 mmol) and LiTFSI (1.86 g, 6.48 mmol). <sup>1</sup>H NMR (500 MHz, DMSO-*d<sub>6</sub>*) δ 9.14 (s, 2H), 7.78 (m, 4H), 6.23 (m, 2H), 4.46 (m, 6H), 4.41–4.35 (m, 4H), 4.22 (m, 2H), 3.79 (t, *J* = 4 Hz, 4H), 3.60–3.53 (m, 4H), 3.53–3.47 (m, 16H), 3.43 (t, *J* = 4 Hz, 4H), 3.24 (s, 3H), 3.23 (s, 3H), 2.95 (m, 2H), 2.63 (d, 2H), 1.72 (d, *J* = 9 Hz, 1H), 1.32 (d, *J* = 9 Hz, 1H). <sup>13</sup>C NMR (126 MHz, DMSO-*d<sub>6</sub>*) δ 172.98, 138.22, 137.30, 123.41, 122.97, 119.95 (q, *J* = 323 Hz),

71.72, 70.19, 70.17, 70.03, 70.00, 69.98, 69.97, 68.60, 62.81, 58.49, 49.35, 48.44, 46.98, 45.59, 45.21 (20 signals expected and 20 signals found). HR MS: calc. for  $C_{41}H_{60}O_{20}N_6S_4F_{12}Na$  [M + Na]<sup>+</sup>: m/z 1335.2446; found: m/z 1335.2462 (error 1.2 ppm); calc. for  $C_{39}H_{60}O_{16}N_5S_2F_6$  [M – TFSI]<sup>+</sup>: m/z 1032.3375; found: m/z 1032.3392 (error 1.1 ppm); calc. for  $C_{37}H_{60}O_{12}N_4$  [M – 2TFSI]<sup>+2</sup>: m/z 376.2098; found: m/z 376.2111 (error 3.3 ppm). T<sub>g</sub> (DSC) = -42 °C. Conductivity at 25°C = 3.88 x 10<sup>-5</sup> S/cm.

*Exo,Exo*-NB[C(O)OE<sub>2</sub>Im<sup>+</sup>Bu]<sub>2</sub> (TFSI)<sub>2</sub> (8f): General procedure 6 was used to produce an oil (1.28 g, 52%) by using 3a (1.45 g, 2.18 mmol), 6a (1.55 g, 12.5 mmol) and LiTFSI (2.36 g, 8.22 mmol). <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.10 (s, 2H), 7.78 (t, J = 2 Hz, 2H), 7.71 (t, J = 2 Hz, 2H), 6.23 (t, J = 2 Hz, 1H), 4.36–4.29 (m, 4H), 4.20–4.07 (m, 6H), 3.95–3.90 (m, 2H), 3.78–3.71 (m, 4H), 3.57 (t, J = 5 Hz, 4H), 2.96–2.91 (m, 2H), 2.54 (d, J = 2 Hz, 2H), 1.89 (d, J = 9 Hz, 1H), 1.75 (p, J = 8 Hz, 4H), 1.32 (d, J = 9 Hz, 1H), 1.28–1.18 (m, 4H), 0.88 (t, J = 8 Hz, 6H). <sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ )  $\delta$  173.21, 138.22, 136.74, 123.23, 122.66, 119.91 (q, J = 323 Hz), 68.45, 63.69, 49.20, 49.02, 46.99, 45.55, 45.22, 31.80, 19.20, 13.68 (16 signals expected and 16 signals found). HR MS: calc. for  $C_{41}H_{60}O_{20}N_6S_4F_{12}Na [M + Na]^+$ : m/z 1335.2446; found: m/z 1335.2462 (error 1.2 ppm); calc. for  $C_{33}H_{48}O_{10}N_5S_2F_6$  [M - TFSI]<sup>+</sup>: m/z 852.2741; found: m/z 852.2743 (error 0.2 ppm); calc. for  $C_{31}H_{48}O_6N_4$  [M – 2TFSI]<sup>+2</sup>: m/z 286.1781; found: m/z 286.1791 (error 3.3 ppm).  $T_g$  (DSC) = -47 °C. Conductivity at 25 °C = 7.75 x 10<sup>-5</sup> S/cm. Exo, Exo-NB[C(O)OE<sub>2</sub>Im<sup>+</sup>EOMe]<sub>2</sub> (TFSI)<sub>2</sub> (8g): General procedure 6 was used to produce an oil (2.54 g, 73%) by using **3a** (2.03 g, 3.05 mmol), **6b** (1.53 g, 12.2 mmol) and LiTFSI (2.28 g, 7.94 mmol). <sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>) δ 9.04 (s, 2H), 7.78 (s,

4H), 6.27 (s, 2H), 4.62–4.54 (m, 8H), 4.27 (m, 2H), 4.12 (m, 2H), 3.97 (t, J = 5 Hz, 4H), 3.83 (t, J = 5 Hz, 4H), 3.74 (t, J = 5 Hz, 4H), 3.36 (s, 6H), 3.06 (s, 2H), 2.66 (d, J = 2 Hz, 2H), 2.08 (d, J = 8 Hz, 1H), 1.41 (d, J = 8.5 Hz, 1H). <sup>13</sup>C NMR (126 MHz, acetone- $d_6$ )  $\delta$ 174.01, 138.80, 137.70, 123.95, 123.77, 121.07 (q, J = 320 Hz), 70.81, 69.68, 69.44, 64.38, 59.00, 50.64, 50.60, 47.99, 46.46, 45.94 (16 peaks expected and 16 peaks found). HR MS: calc. for C<sub>29</sub>H<sub>44</sub>O<sub>8</sub>N<sub>4</sub> [M – 2TFSI]<sup>+2</sup>: m/z 288.1574; found: m/z 288.1596 (error 7.5 ppm); calc. for C<sub>31</sub>H<sub>44</sub>O<sub>12</sub>N<sub>5</sub>S<sub>2</sub>F<sub>6</sub> [M – TFSI]<sup>+</sup>: m/z 856.2327; found: m/z 856.2356 (error 3.4 ppm); T<sub>g</sub> (DSC) = -39 °C. Conductivity at 25 °C = 4.80 x 10<sup>-5</sup> S/cm.

*Exo,Exo*-NB[C(O)OE<sub>2</sub>Im<sup>+</sup>EO<sub>2</sub>Me]<sub>2</sub> (TFSI)<sub>2</sub> (8h): General procedure 6 was used to produce an oil (1.54 g, 58%) by using **3a** (1.43 g, 2.15 mmol), **6c** (1.54 g, 12.2 mmol) and LiTFSI (1.75 g, 6.10 mmol). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  9.08 (s, 2H), 7.76 (t, *J* = 2 Hz, 2H), 7.73 (t, *J* = 2 Hz, 2H), 6.26 (t, *J* = 2 Hz, 2H), 4.37 (m, 8H), 4.16 (m, 2H), 3.96 (m, 2H), 3.78 (t, *J* = 4 Hz, 8H), 3.59 (t, *J* = 4 Hz, 4H), 3.57–3.52 (m, 4H), 3.44–3.39 (m, 4H), 3.22 (s, 6H), 2.99–2.94 (m, 2H), 2.58 (d, *J* = 2 Hz, 2H), 1.91 (d, *J* = 9 Hz, 1H), 1.35 (d, *J* = 9 Hz, 1H). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  173.26, 138.24, 137.09, 123.02, 123.00, 119.93 (q, *J* = 323 Hz), 71.52, 69.82, 68.56, 68.53, 68.47, 63.70, 58.52, 49.30, 49.21, 47.01, 45.57, 45.24 (18 signals expected and 18 signals found). HR MS: calc. for C<sub>35</sub>H<sub>52</sub>O<sub>14</sub>N<sub>5</sub>S<sub>2</sub>F<sub>6</sub> [M – TFSI]<sup>+</sup>: m/z 344.2851; found: m/z 342.1838 (error 0.6 ppm). T<sub>q</sub> (DSC) = -49 °C. Conductivity at 25 °C = 7.72 x 10<sup>-5</sup> S/cm.

*Exo,Exo*-NB[C(O)OE<sub>2</sub>Im<sup>+</sup>EO<sub>3</sub>Me]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> (8i): General procedure 6 was used to produce an oil (2.45 g, 75%) by using **3a** (1.67 g, 2.50 mmol), **6d** (1.85 g, 9.10 mmol) and LiTFSI (1.85 g, 6.46 mmol). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.81 (s, 2H), 7.52 (s, 2H), 7.42 (s, 2H), 6.29–6.16 (m, 2H), 4.37 (m, 8H), 4.20–4.15 (m, 3H), 3.84 (m, 8H), 3.67 (m, 8H), 3.64–3.60 (m, 8H), 3.55 (m, 4H), 3.36 (s, 6H), 3.08 (s, 2H), 2.65 (s, 2H), 2.03 (d, *J* = 9 Hz, 1H), 1.49 (d, *J* = 9 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  173.55, 137.95, 136.33, 123.18, 122.76, 119.80 (q, J = 321 Hz), 77.23, 71.80, 70.29, 70.21, 69.04, 68.55, 68.52, 63.55, 58.87, 49.79, 47.37, 45.67, 45.34 (20 signals expected and 19 signals found; peak @ 70.21 is considered to be 2 overlapping peaks). HR MS: calc. for C<sub>37</sub>H<sub>60</sub>O<sub>12</sub> [M – 2TFSI]<sup>+2</sup> : m/z 376.2098 second isotope peak; found: m/z 376.2082 (error –4.4 ppm). T<sub>q</sub> (DSC) = –54 °C. Conductivity at 25 °C = 5.39 x 10<sup>-5</sup> S/cm.

*Exo,Exo*-NB[C(O)OE<sub>2</sub>Im<sup>+</sup>EO<sub>4</sub>Me]<sub>2</sub> (TFSI')<sub>2</sub> (8j): General procedure 6 was used to produce an oil (3.43 g, 50%) by using **3a** (3.28 g, 4.92 mmol), **6e** (3.17 g, 12.3 mmol) and LiTFSI (4.70 g, 16.4 mmol). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.84 (s, 2H), 7.53 (s, 2H), 7.45 (s, 2H), 6.23 (s, 2H), 4.38 (s, 8H), 4.18 (s, 4H), 3.91–3.81 (m, 8H), 3.74–3.58 (m, 24H), 3.56–3.50 (m, 4H), 3.34 (s, 6H), 3.08 (s, 2H), 2.65 (s, 2H), 2.03 (d, *J* = 9 Hz, 1H), 1.49 (d, *J* = 9 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  173.55, 137.96, 136.47, 123.18, 122.81, 119.83 (q, J = 319 Hz), 71.85, 70.43, 70.36, 70.32, 70.27, 70.23, 69.04, 68.58, 68.55, 63.56, 58.86, 49.84, 49.81, 47.38, 45.67, 45.35 (22 signals expected and 22 signals found). HR MS: calc. for C<sub>43</sub>H<sub>68</sub>O<sub>18</sub>N<sub>5</sub>S<sub>2</sub>F<sub>6</sub> [M – TFSI]<sup>+</sup>: m/z 1120.3899; found: m/z 1120.3860 (error –3.5 ppm); calc. for C<sub>41</sub>H<sub>68</sub>O<sub>14</sub>N<sub>4</sub> [M – 2TFSI]<sup>+2</sup>: m/z 420.2361;

found: m/z 420.2351 (error –2.4 ppm).  $T_g$  (DSC) = –57 °C. Conductivity at 25 °C = 6.26 x 10<sup>-5</sup> S/cm.

*Exo*,*Exo*-NB[C(O)OE<sub>3</sub>Im<sup>+</sup>Bu]<sub>2</sub> (TFSI)<sub>2</sub> (8k): General procedure 6 was used to produce an oil (1.99 g, 61 %) by using **3b** (2.01 g, 2.66 mmol), **6a** (0.800 g, 6.44 mmol) and LiTFSI (1.91 g, 6.65 mmol). <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  9.13 (s, 2H), 7.80 (t, J = 2Hz, 2H), 7.75 (t, J = 2 Hz, 2H), 6.24 (t, J = 2 Hz, 2H), 4.38–4.31 (m, 4H), 4.22–4.12 (m, 6H), 3.99–3.94 (m, 2H), 3.81–3.74 (m, 4H), 3.55–3.50 (m, 12H), 2.99 (s, 2H), 2.58 (d, J = 2 Hz, 2H), 1.96–1.94 (m, 1H), 1.77 (quin, J = 8 Hz, 4H), 1.35–1.33 (m, 1H), 1.25 (h, J = 8 Hz, 4H), 0.91 (t, J = 8 Hz, 6H). <sup>13</sup>C NMR (126 MHz, DMSO- $d_6$ )  $\delta$  173.30, 138.22, 136.75, 123.25, 122.67, 119.93 (q, J = 323 Hz), 69.97, 69.92, 68.61, 68.56, 63.90, 49.27, 49.02, 46.96, 45.60, 45.18, 31.81, 19.21, 13.70 (19 signals expected and 19 found). HR MS: calc. for  $C_{37}H_{56}O_{12}N_5S_2F_6$  [M – TFSI]<sup>+</sup>: m/z 940.3266; found: m/z 940.3186 (error -8.5 ppm).  $T_q$  (DSC) = -47 °C. Conductivity at 25 °C = 7.66 x 10<sup>-5</sup> S/cm. Exo, Exo-NB[C(O)OE<sub>3</sub>Im<sup>+</sup>EOMe]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> (8I): General procedure 6 was used to produce an oil (0.86 g, 50 %) by using **3b** (1.06 g, 1.41 mmol), **6b** (0.712 g, 5.65 mmol) and LiTFSI (1.05 g, 3.66 mmol). <sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>) δ 9.04 (s, 2H), 7.80 (s, 2H), 7.76 (s, 2H), 6.25 (s, 2H), 4.57 (s, 8H), 4.27 (m, 2H), 4.11 (m, 2H), 3.96 (m, 4H), 3.84 (m, 4H), 3.73-3.60 (m, 12H), 3.37 (s, 6H), 3.06 (s, 2H), 2.63 (s, 2H), 2.10 (m, 1H), 1.40 (m, 1H). <sup>13</sup>C NMR (126 MHz, acetone- $d_6$ )  $\delta$  173.07, 137.84, 136.73, 123.04, 122.81, 120.13 (q, J = 323 Hz), 70.10, 69.89, 68.71, 68.55, 63.64, 58.07, 49.71, 49.65, 46.93, 45.57, 44.89 (18 signals expected and 17 signals found; peak @ 70.10 ppm is considered to be two peaks overlapping). HR MS: calc. for  $C_{35}H_{52}O_{14}N_5S_2F_6$  [M –

TFSI]<sup>+</sup>: m/z 944.2851; found: m/z 944.2853 (error 0.3 ppm); calc. for  $C_{33}H_{52}O_{10}N_4$  [M – 2 TFSI]<sup>+2</sup>: m/z 332.1836; found: m/z 332.1849 (error 3.7 ppm). T<sub>g</sub> (DSC) = -43 °C. Conductivity at 25 °C = 6.54 x 10<sup>-5</sup> S/cm.

*Exo*,*Exo*-NB[C(O)OE<sub>3</sub>Im<sup>+</sup>EO<sub>2</sub>Me]<sub>2</sub> (TFSI')<sub>2</sub> (8m): General procedure 6 was used to produce an oil (0.93 g, 61%) by using **3b** (0.884 g, 1.17 mmol), **6c** (0.898 g, 5.27 mmol) and LiTFSI (0.90 g, 3.1 mmol). <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$  9.06 (s, 2H), 7.79 (s, 4H), 6.25 (s, 2H), 4.56 (s, 8H), 4.31–4.24 (m, 2H), 4.15–4.07 (m, 2H), 3.96 (m, 8H), 3.73–3.60 (m, 16H), 3.53–3.48 (m, 4H), 3.31 (s, 6H), 3.05 (s, 2H), 2.63 (s, 2H), 2.10 (d, J = 9 Hz, 1H), 1.40 (d, J = 9 Hz, 1H). <sup>13</sup>C NMR (126 MHz, acetone- $d_6$ )  $\delta$  173.06, 137.84, 136.82, 122.92, 122.88, 120.12 (q, J = 323 Hz), 71.54, 70.11, 70.09, 69.94, 68.71, 68.57, 68.46, 63.64, 57.93, 49.73, 49.70, 46.93, 45.57, 44.88 (20 peaks expected and 20 peaks found). HR MS: calc. for C<sub>39</sub>H<sub>60</sub>O<sub>16</sub>N<sub>5</sub>S<sub>2</sub>F<sub>6</sub> [M – TFSI]<sup>+</sup>: m/z 1032.3375; found: m/z 1032.3372 (error –0.3 ppm); calc. for C<sub>37</sub>H<sub>60</sub>O<sub>12</sub>N<sub>4</sub> [M – 2TFSI]<sup>+</sup>: m/z 376.2098; found: m/z 376.2113 (error 3.9 ppm). T<sub>g</sub> (DSC) = –47 °C. Conductivity at 25 °C = 8.95 x 10<sup>-5</sup> S/cm.

*Exo,Exo*-NB[C(O)OE<sub>3</sub>Im<sup>+</sup>EO<sub>3</sub>Me]<sub>2</sub> (TFSI)<sub>2</sub> (8n): General procedure 6 was used to produce an oil (1.27 g, 48%) by using **3b** (1.42 g, 1.88 mmol), **6d** (1.01 g, 4.70 mmol) and LiTFSI (1.35 g, 4.70 mmol). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  9.08 (s, 2H), 7.75 (dt, J = 9, 2 Hz, 4H), 6.24 (t, J = 2 Hz, 2H), 4.37 (t, J = 4 Hz, 8H), 4.16 (m, 2H), 3.97 (m, 2H), 3.81–3.75 (m, 8H), 3.55 (m, 12H), 3.53–3.48 (m, 12H), 3.43 (m, 4H), 3.24 (s, 6H), 3.02–2.96 (m, 2H), 2.59 (d, J = 2 Hz, 2H), 1.95 (d, J = 9 Hz, 1H), 1.35 (d, J = 9 Hz, 1H). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  173.34, 138.23, 137.05, 123.08, 122.99, 119.95 (g, J = 9

323 Hz), 71.71, 70.03, 69.99, 69.97, 69.94, 68.64, 68.62, 68.58, 63.92, 58.50, 49.26, 46.97, 45.60, 45.18 (22 signals expected and 20 found). HR MS: calc. for  $C_{43}H_{68}O_{18}N_5S_2F_6$  [M – TFSI]<sup>+</sup>: m/z 1120.3899; found: m/z 1120.3946 (error 4.1 ppm); calc. for  $C_{41}H_{68}O_{14}N_4$  [M – 2TFSI]<sup>+2</sup>: m/z 420.2361; found: m/z 420.2381 (error 4.8 ppm).  $T_g$  (DSC) = -46 °C. Conductivity at 25 °C = 8.93 x 10<sup>-5</sup> S/cm.

*Exo*,*Exo*-NB[C(0)OE<sub>3</sub>Im<sup>+</sup>EO<sub>4</sub>Me]<sub>2</sub> (TFSI)<sub>2</sub> (80): General procedure 6 was used to produce an oil (0.60 g, 61%) by using **3b** (0.503 g, 0.667 mmol), **6e** (0.430 g, 1.66 mmol) and LiTFSI (0.479 g, 1.67 mmol). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 9.08 (s, 2H), 7.75 (m, 4H), 6.24 (t, J = 2 Hz, 2H), 4.37 (t, J = 5 Hz, 8H), 4.16 (m, 2H), 3.97 (m, 2H), 3.78 (m, 8H), 3.60–3.46 (m, 32H), 3.43 (m, 4H), 3.24 (s, 3H), 3.23 (s, 3H) 3.02–2.97 (m, 2H), 2.59 (d, J = 2 Hz, 2H), 1.95 (d, J = 9 Hz, 1H), 1.35 (d, J = 9 Hz, 1H). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>) δ 173.33, 138.24, 137.08, 123.08, 123.00, 119.95 (q, J = 323 Hz), 71.72, 70.21, 70.18, 70.06, 70.04, 70.01, 69.99, 69.94, 68.65, 68.62, 68.59, 63.92, 58.51, 58.49, 49.30, 49.26, 46.97, 45.61, 45.19 (24 signals expected and 25 signals found). HR MS: calc. for C<sub>47</sub>H<sub>76</sub>O<sub>20</sub>N<sub>5</sub>S<sub>2</sub>F<sub>6</sub> [M – TFSI]<sup>+</sup>: m/z 1208.4424; found: m/z 1208.4537 (error 9.4 ppm); calc. for C<sub>45</sub>H<sub>76</sub>O<sub>16</sub>N<sub>4</sub> [M – 2TFSI]<sup>+2</sup>: m/z 464.2623; found: m/z 464.2667 (error 9.6 ppm). T<sub>g</sub> (DSC) = -45 °C. Conductivity at 25 °C = 7.94 x 10<sup>-5</sup> S/cm.

*Exo,Exo*-NB[C(O)OE<sub>4</sub>Im<sup>+</sup>Bu]<sub>2</sub> (TFSI)<sub>2</sub> (8p): General procedure 6 was used to produce an oil (1.72 g, 54%) by using 3c (2.04 g, 2.42 mmol), 6a (0.751 g, 6.05 mmol) and LiTFSI (1.74 g, 6.05 mmol). <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  9.13 (s, 2H), 7.79 (t, *J* = 2 Hz, 2H), 7.76 (t, *J* = 2 Hz, 2H), 6.23 (t, *J* = 2 Hz, 2H), 4.38–4.32 (m, 4H), 4.22–4.13 (m, 6H), 3.98 (m, 2H), 3.80–3.74 (m, 4H), 3.61–3.53 (m, 8H), 3.50 (m, 12H), 3.00–2.97 (m, 2H), 2.58 (d, J = 2 Hz, 2H), 1.95 (m, 1H), 1.78 (quin, J = 7 Hz, 4H), 1.34 (m, 1H), 1.26 (sex, J = 7 Hz, 4H), 0.91 (t, J = 7 Hz, 6H). <sup>13</sup>C NMR (126 MHz, DMSO- $d_6$ )  $\delta$  173.33, 138.24, 136.76, 123.29, 122.67, 119.95 (q, J = 323 Hz), 70.17, 70.12, 70.04, 69.97, 68.63, 68.54, 63.94, 49.27, 49.03, 46.96, 45.59, 45.17, 31.81, 19.21, 13.70 (21 signals expected and 21 signals found). HR MS: calc. for C<sub>41</sub>H<sub>64</sub>O<sub>14</sub>N<sub>5</sub>S<sub>2</sub>F<sub>6</sub> [M – TFSI]<sup>+1</sup>: m/z 1028.3790; found: m/z 1028.3810 (error 1.9 ppm); calc. for C<sub>39</sub>H<sub>64</sub>O<sub>10</sub>N<sub>4</sub> [M – 2 TFSI] ]<sup>+2</sup>: m/z 374.2306; found: m/z 374.2315 (error 2 ppm). T<sub>g</sub> (DSC) = –45 °C. Conductivity at 25 °C = 6.82 x 10<sup>-5</sup> S/cm.

*Exo*, *Exo*-NB[C(O)OE<sub>4</sub>Im<sup>+</sup>EOMe]<sub>2</sub> (TFSI)<sub>2</sub> (8q): General procedure 6 was used to produce an oil (1.25 g, 43%) by using 3c (1.88 g, 2.23 mmol), 6b (1.51 g, 12.0 mmol) and LiTFSI (2.09 g, 7.28 mmol). <sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>)  $\delta$  9.02 (s, 2H), 7.77 (s, 2H), 7.72 (s, 2H), 6.24 (t, *J* = 2 Hz, 2H), 4.53 (m, 8H), 4.25 (m, 2H), 4.09 (m, 2H), 3.95–3.91 (m, 4H), 3.84–3.80 (m, 4H), 3.68 (m, 8H), 3.62 (m, 12H), 3.36 (s, 6H), 3.06 – 3.02 (m, 2H), 2.58 (d, *J* = 2 Hz, 2H), 2.08 (d, *J* = 9 Hz, 1H), 1.38 (d, *J* = 9 Hz, 1H). <sup>13</sup>C NMR (126 MHz, acetone-*d*<sub>6</sub>)  $\delta$  173.13, 137.85, 136.77, 123.03, 122.72, 120.08 (q, J = 323 Hz), 70.25, 70.13, 70.12, 70.09, 69.88, 68.67, 68.46, 63.69, 58.08, 49.66, 49.59, 46.89, 45.53, 44.86 (20 peaks expected and 20 peaks found). HR MS: calc. for C<sub>39</sub>H<sub>60</sub>O<sub>16</sub>N<sub>5</sub>S<sub>2</sub>F<sub>6</sub> [M – TFSI]<sup>+</sup>: m/z 1032.3375; found: m/z 1032.3376 (error 0.08 ppm); calc. for C<sub>37</sub>H<sub>60</sub>O<sub>12</sub>N<sub>4</sub> [M – 2TFSI]<sup>+2</sup>: m/z 376.2098; found: m/z 376.2117 (error 4.7 ppm). T<sub>g</sub> (DSC) = -43 °C. Conductivity at 25 °C = 6.51 x 10<sup>-5</sup> S/cm.

*Exo*, *Exo*-NB[C(O)OE<sub>4</sub>Im<sup>+</sup>EO<sub>2</sub>Me]<sub>2</sub> (TFSI)<sub>2</sub> (8r): General procedure 6 was used to produce an oil (1.73 g, 45%) by using 3c (2.29 g, 2.71 mmol), 6c (0.856 g, 6.79 mmol) and LiTFSI (1.95 g, 6.79 mmol). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  9.08 (s, 2H), 7.75 (m, 4H), 6.24 (t, *J* = 2 Hz, 2H), 4.37 (t, *J* = 5 Hz, 8H), 4.17 (m, 2H), 4.03–3.95 (m, 2H), 3.78 (t, *J* = 5 Hz, 8H), 3.59–3.53 (m, 12H), 3.53–3.47 (m, 12H), 3.44–3.40 (m, 4H), 3.22 (s, 6H), 3.02–2.96 (m, 2H), 2.59 (d, *J* = 2 Hz, 2H), 1.96 (d, *J* = 9 Hz, 1H), 1.34 (d, *J* = 9 Hz, 1H). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  173.34, 138.24, 137.09, 123.07, 122.98, 119.95 (q, *J* = 323 Hz), 71.53, 70.17, 70.11, 70.04, 69.83, 69.83, 68.62, 68.58, 63.95, 58.51, 49.30, 49.28, 46.95, 45.59, 45.17 (22 signals expected and 21 signals found). HR MS: calc. for C<sub>43</sub>H<sub>68</sub>O<sub>18</sub>N<sub>5</sub>S<sub>2</sub>F<sub>6</sub> [M – TFSI]<sup>+</sup>: m/z 1120.3899; found: m/z 1120.3891 (error –0.8 ppm); calc. for C<sub>41</sub>H<sub>68</sub>O<sub>14</sub>N<sub>4</sub> [M – 2TFSI]<sup>+2</sup>: m/z 420.2361; found: m/z 420.2374 (error 3.2 ppm). T<sub>0</sub> (DSC) = –46 °C. Conductivity at 25 °C = 9.57 x 10<sup>-5</sup> S/cm.

*Exo,Exo*-NB[C(O)OE<sub>4</sub>Im<sup>+</sup>EO<sub>3</sub>Me]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> (8s): General procedure 6 was used to produce an oil (2.07 g, 67%) by using **3c** (1.76 g, 2.09 mmol), **6d** (1.15 g, 5.39 mmol) and LiTFSI (1.58 g, 5.50 mmol). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  9.07 (s, 2H), 7.75 (m, 4H), 6.24 (t, *J* = 2 Hz, 2H), 4.37 (t, *J* = 5 Hz, 8H), 4.20–4.13 (m, 2H), 3.98 (m, 2H), 3.82–3.75 (m, 8H), 3.59–3.54 (m, 13H), 3.54–3.47 (m, 21H), 3.43 (m, 4H), 3.24 (s, 6H), 3.01–2.97 (m, 2H), 2.58 (d, *J* = 2 Hz, 2H), 1.95 (d, *J* = 9 Hz, 1H), 1.34 (d, *J* = 9 Hz, 1H). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  173.33, 138.24, 137.06, 123.06, 123.03, 119.95 (q, *J* = 323 Hz), 71.72, 70.17, 70.12, 70.04, 70.00, 69.98, 68.62, 68.59, 63.94, 58.52, 49.26, 46.96, 45.60, 45.18 (24 signals expected and 20 signals found). HR MS: calc. for C<sub>47</sub>H<sub>76</sub>O<sub>20</sub>N<sub>5</sub>S<sub>2</sub>F<sub>6</sub> [M – TFSI]<sup>+</sup>: m/z 1208.4424; found: m/z 1208.4441 (error 1.4 ppm);

calc. for  $C_{45}H_{76}O_{16}N_4 [M - 2TFSI]^{+2}$ : m/z 464.2623; found: m/z 464.2651 (error 6.0 ppm). T<sub>g</sub> (DSC) = -45 °C. Conductivity at 25 °C = 7.90 x 10<sup>-5</sup> S/cm.

*Exo*,*Exo*-NB[C(O)OE<sub>4</sub>Im<sup>+</sup>EO<sub>4</sub>Me]<sub>2</sub> (TFSI)<sub>2</sub> (8t): General procedure 6 was used to produce an oil (1.08 g, 27%) by using **3c** (2.11 g, 2.50 mmol), **6e** (2.15 g, 8.31 mmol) and LiTFSI (1.79 g, 6.23 mmol). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 9.09 (s, 2H), 7.78–7.72 (m, 4H), 6.24 (m, 2H), 4.37 (m, 8H), 4.16 (m, 2H), 3.98 (m, 2H), 3.82–3.74 (m, 8H), 3.59–3.53 (m, 12H), 3.50 (m, 28H), 3.43 (m, 4H), 3.24 (s, 6H), 3.01 – 2.96 (m, 2H), 2.58 (m, 2H), 1.95 (d, *J* = 9 Hz, 1H), 1.34 (d, *J* = 9 Hz, 1H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 173.36, 138.20, 136.97, 122.99, 122.96, 119.88 (q, J = 323), 71.66, 70.14, 70.12, 70.06, 69.98, 69.97, 69.95, 69.94, 68.57, 68.52, 63.93, 58.47, 58.44, 49.22, 46.93, 45.55, 45.12 (26 signals expected and 23 signals found; peaks in the ethyleneoxy region suspected to be overlapping). HR MS: calc. for C<sub>53</sub>H<sub>84</sub>O<sub>26</sub>N<sub>6</sub>S<sub>4</sub>F<sub>12</sub>Na [M + Na]<sup>+</sup>: m/z 1599.4019; found: m/z 1599.3942 (error –4.8 ppm); calc. for C<sub>51</sub>H<sub>84</sub>O<sub>22</sub>N<sub>5</sub>S<sub>2</sub>F<sub>6</sub> [M – TFSI]<sup>+</sup>: m/z 1296.4948; found: m/z 1296.4889 (error –4.6 ppm). HR MS: calc. for C<sub>49</sub>H<sub>84</sub>O<sub>18</sub>N<sub>4</sub> [M - 2TFSI]<sup>+2</sup>: m/z 508.2885; found: m/z 508.2869 (error –3.2 ppm). T<sub>g</sub> (DSC) = –47 °C. Conductivity at 25 °C = 6.99 x 10<sup>-5</sup> S/cm.

*Exo,Exo*-NB[C(O)OE<sub>5</sub>Im<sup>+</sup>EO<sub>2</sub>Me]<sub>2</sub> (TFSΓ)<sub>2</sub> (8u): General procedure 6 was used to produce an oil (0.91 g, 35 %) by using **3d** (1.62 g, 1.73 mmol), **6c** (0.65 g, 5.2 mmol) and LiTFSI (1.25 g, 4.35 mmol). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 9.08 (s, 2H), 7.76–7.75 (m, 4H), 6.24 (s, 2H), 4.37 (t, *J* = 5 Hz, 8H), 4.20–4.12 (m, 2H), 4.00–3.97 (m, 2H), 3.83–3.74 (m, 8H), 3.58–3.49 (m, 32 H), 3.43–3.40 (m, 4H), 3.22 (s, 6H), 3.02–2.94 (m, 2H), 2.60–2.59 (m, 2H), 1.97–1.95 (m, 1H), 1.35–1.33 (m, 1H). <sup>13</sup>C NMR (126 MHz,

DMSO-*d*<sub>6</sub>)  $\delta$  173.33, 138.23, 137.09, 123.06, 122.97, 119.93 (q, J = 323 Hz), 71.53, 70.22, 70.17, 70.14, 70.04, 69.98, 69.83, 68.61, 68.58, 63.95, 58.52, 49.29, 46.94, 45.59, 45.17 (24 signals expected and 21 signals found, 3 signals expected to be overlapping in ethyleneoxy region). HR MS: calc. for C<sub>45</sub>H<sub>76</sub>O<sub>16</sub>N<sub>4</sub> [M - 2TFSI]<sup>+2</sup>: m/z 464.2623; found: m/z 464.2609 (error –3.0 ppm). T<sub>g</sub> (DSC) = –46 °C. Conductivity at 25 °C = 7.22 x 10<sup>-5</sup> S/cm.

*Exo*,*Exo*-NB[C(O)OE<sub>6</sub>Im<sup>+</sup>EO<sub>2</sub>Me]<sub>2</sub> (TFSI)<sub>2</sub> (8v): General procedure 6 was used to produce an oil (1.03 g, 81 %) by using **3e** (0.813 g, 0.798 mmol), **6c** (0.340 g, 2.00 mmol) and LiTFSI (0.580 g, 2.02 mmol). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  9.08 (s, 2H), 7.76–7.74 (m, 4H), 6.24 (t, *J* = 2 Hz, 2H), 4.37 (t, *J* = 5 Hz, 8H), 4.18–4.14 (m, 2H), 4.01–3.96 (m, 2H), 3.82–3.73 (m, 8H), 3.58–3.54 (m, 12H), 3.51–3.48 (m, 28H), 3.43–3.41 (m, 4H), 3.22 (s, 6H), 3.02–2.98 (m, 2H), 2.61–2.60 (m, 2H), 1.97–1.95 (m, 1H), 1.35–1.33 (m, 1H). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  173.33, 138.23, 137.09, 123.07, 122.97, 119.93 (q, J = 323 Hz), 71.53, 70.24, 70.20, 70.17, 70.14, 70.04, 69.98, 69.83, 68.60, 63.96, 58.53, 49.29, 46.94, 45.58, 45.17 (26 signals expected and 21 signals found, signals expected to be overlapping in ethyleneoxy region). HR MS: calc. for C<sub>53</sub>H<sub>84</sub>O<sub>26</sub>N<sub>6</sub>S<sub>4</sub>F<sub>12</sub>K [M + K]<sup>+1</sup>: m/z 1599.4024; found: m/z 1599.3987 (error 2.3 ppm); calc. for C<sub>53</sub>H<sub>84</sub>O<sub>26</sub>N<sub>7</sub>S<sub>4</sub>F<sub>12</sub>K [M + K]<sup>+1</sup>: m/z 1615.3764; found: m/z 1615.3721 (error 2.7 ppm); calc. for C<sub>53</sub>H<sub>88</sub>O<sub>26</sub>N<sub>7</sub>S<sub>4</sub>F<sub>12</sub> [M + NH<sub>4</sub>]<sup>+1</sup>: m/z 1594.4470; found: m/z 1594.4405 (error 4.1 ppm). T<sub>g</sub> (DSC) = –54 °C. Conductivity at 25 °C = 9.27 x 10<sup>-5</sup> S/cm.

## Effect of other bulky anions on the RT conductivity

BARF and TPFB both take advantage of a negatively charged boron atom that has its charge highly dispersed over four aromatic rings substituted with electron withdrawing substituents. AOT was selected due to its non-symmetrical nature and because it is actually a mixture of eight stereoisomers at three chiral centers and hence was expected to lower  $T_gs$  and in turn raise conductivities. DDS was chosen to compare its sulfate moiety to the sulfonate group in AOT. The syntheses were actually anion exchanges, as noted in **Scheme S1**.



General Procedure 7, two-armed norbornene imidazoliums with various anions. Exo, Exo-NB[C(O)OE<sub>4</sub>Im<sup>+</sup>EO<sub>2</sub>Me]<sub>2</sub> (BARF)<sub>2</sub> (9r): To a flask containing acetone (10 mL) was added 7r (0.312 g, 0.264 mmol) and NaBARF (0.584 g, 0.649 mmol) with magnetic stirring under nitrogen. The reaction mixture was held at reflux for 20 h, after which solvent was removed by rotary evaporation. The remaining material was taken up in DCM and filtered. The solvent was removed by rotary evaporation and the desired product was collected as a viscous oil (0.676 g, 99%). <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$ 9.09 (s, 2H), 7.76–7.75 (m, 4H), 7.67 (s, 8H), 7.62 (s, 16H), 6.21 (t, J = 2 Hz, 2H), 4.37 (t, J = 5 Hz, 8H), 4.20-4.14 (m, 2H), 4.00-3.96 (m, 2H), 3.81-3.75 (m, 8H), 3.59-3.46(m, 24H), 3.42-3.38 (m, 4H), 3.20 (s, 6H), 3.00-2.96 (m, 2H), 2.58 (d, J = 2 Hz, 2H), 1.95 (d, J = 9 Hz, 1H), 1.33 (d, J = 9 Hz, 1H). <sup>13</sup>C NMR (126 MHz, DMSO- $d_6$ )  $\delta$  173.32, 161.42 (q, J = 50 Hz), 138.19, 137.10, 134.50, 128.96 (qq, J = 32, 3 Hz), 127.69, 124.45 (d, J = 273 Hz), 123.03 (d, J = 10 Hz), 121.19, 118.05, 71.53, 70.17, 70.11, 70.05, 69.97, 69.82, 68.63, 68.59, 63.93, 58.46, 55.34, 49.30, 46.95, 45.58, 45.15, 31.08 (27 signals expected and 27 signals found). HR MS: calc. for C<sub>73</sub>H<sub>80</sub>BN<sub>4</sub>O<sub>14</sub>F<sub>24</sub>  $[M - BARF]^+$ : m/z 1703.5381; found: m/z 1703.5376 (error -0.3 ppm). T<sub>a</sub> (DSC) = -26, -6 °C. Conductivity at 25 °C =  $3.19 \times 10^{-8}$  S/cm.

*Exo,Exo*-NB[C(O)OE<sub>4</sub>Im<sup>+</sup>EO<sub>2</sub>Me]<sub>2</sub> (TPFB<sup>-</sup>)<sub>2</sub> (10r): By General Procedure 7 7r (0.129 g, 0.109 mmol) and lithium tetrakis(pentafluorophenyl)boron (0.584 g, 0.670 mmol) led to an oil (0.225 g, 95%). <sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>) δ 9.14 (s, 2H), 7.83–7.81 (m, 4H), 6.21 (s, 2H), 4.59 (s, 8H), 4.33–4.22 (m, 2H), 4.12–4.10 (m, 2H), 3.96 (s, 8H), 3.74–3.57 (m, 28H), 3.29 (s, 6H), 3.04 (s, 2H), 2.60 (s, 2H), 1.38 (s, 1H), 1.23 (s, 1H). <sup>13</sup>C

NMR (126 MHz, acetone- $d_6$ )  $\delta$  173.08, 148.17 (d, J = 238 Hz), 137.75, 137.18 (tt, J = 247, 14 Hz), 136.98, 124.16, 122.95, 122.80, 71.55, 70.26, 70.16, 70.13, 70.10, 69.95, 68.69, 68.52, 68.50, 63.62, 57.83, 49.74, 49.72, 46.91, 45.54, 44.84 (25 signals expected and 24 signals found, two aromatic signals overlapping due to splitting of aryl C-F signals). HR MS: calc. for  $C_{65}H_{68}BF_{20}N_4O_{14}$  [M - TPFB]<sup>+</sup>: m/z 1519.4506; found: m/z 1519.4415 (error 6.0 ppm); calc. for  $C_{89}H_{68}B_2F_{40}N_4O_{14}Na$  [M + Na]<sup>+</sup>: m/z 2221.4177; found: m/z 2221.4037 (error 6.3 ppm). T<sub>g</sub> (DSC) = -27 °C. Conductivity at 25 °C not measured.

*Exo*,*Exo*-NB[C(O)OEIm<sup>+</sup>Bu]<sub>2</sub> (AOT)<sub>2</sub> (11a): By General Procedure 7 7a (A = Br) (1.21 g, 1.88 mmol) and dioctyl sulfosuccinate sodium salt (AOT, 2.10 g, 4.72 mmol) yielded an oil (1.36 g, 55%). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  9.24–9.17 (m, 2H), 7.87–7.74 (m, 4H), 6.22 (m, 2H), 4.48–4.42 (m, 8H), 4.23–4.19 (m, 8H), 3.95–3.83 (m, 20H), 3.65 (dd, *J* = 12, 4 Hz, 4H), 2.96–2.91 (m, 6H), 2.89 (s, 2H), 2.82 (d, *J* = 4 Hz, 3H), 2.79 (d, *J* = 4 Hz, 2H), 2.62 (d, *J* = 2 Hz, 2H), 1.77 (p, *J* = 8 Hz, 6H), 1.70 (d, *J* = 9 Hz, 2H), 1.50 (bs, 10H), 1.41–1.13 (m, 30H), 0.94–0.79 (m, 22H). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  172.92, 171.48, 168.83, 138.18, 137.05, 136.78, 123.23, 122.99, 122.63, 66.65, 66.58, 66.55, 66.51, 62.78, 61.89, 59.74, 52.12, 49.08, 48.94, 48.46, 46.94, 45.56, 45.20, 38.64, 38.59, 38.56, 34.55, 31.86, 30.20, 30.08, 30.02, 28.80, 23.65, 23.62, 23.47, 23.44, 22.88, 22.85, 19.25, 19.19, 14.37, 14.35, 13.74, 11.27, 11.24, 11.20 (34 signals expected considering a single isomer of AOT, but AOT contains eight stereoisomers at three chiral centers, 46 signals found with many appearing to overlap). HR MS: calc. for C<sub>67</sub>H<sub>114</sub>N<sub>4</sub>O<sub>18</sub>S<sub>2</sub>Na [M + Na]<sup>+</sup>: m/z 1349.7467; found: m/z 1349.7467 (error 0 ppm); calc.

for  $C_{47}H_{77}N_4O_{11}S$  [M - AOT]<sup>+</sup>: m/z 905.5310; found: m/z 905.5312 (error 0.2 ppm). T<sub>g</sub> (DSC) = -25 °C. Conductivity at 25 °C = 2.57 x 10<sup>-9</sup> S/cm.

*Exo,Exo*-NB[C(O)OEIm<sup>+</sup>Bu]<sub>2</sub> (DDS<sup>-</sup>)<sub>2</sub> (12a): By General Procedure 7 7a (A = Br) (0.78 g, 1.2 mmol) and dodecyl sodium sulfate (DDS) (0.88 g, 3.1 mmol) afforded a viscous oil (0.96 g, 83%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  9.28 (t, *J* = 2 Hz, 2H), 7.85–7.81 (m, 4H), 6.20 (t, *J* = 2 Hz, 2H), 4.42–4.40 (m, 4H), 4.21–4.17 (m, 8H), 3.65 (t, *J* = 7 Hz, 2H), 2.92–2.91 (m, 2H), 2.60 (d, *J* = 1.8 Hz, 2H), 1.82–1.64 (m, 8H), 1.50–1.39 (m, 4H), 1.22 (s, 30H), 0.93–0.80 (m, 24H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  172.92, 138.16, 137.03, 123.21, 122.96, 65.95, 62.77, 59.70, 49.06, 48.45, 46.92, 45.54, 31.81, 31.74, 29.52, 29.51, 29.47, 29.23, 29.16, 25.97, 22.54, 19.16, 14.40, 13.74 (24 peaks expected and 24 peaks found). HR MS: calc. for C<sub>27</sub>H<sub>40</sub>N<sub>4</sub>O<sub>4</sub> [M – 2 DDS]<sup>+2</sup>: m/z 242.1519; found: m/z 242.1534 (error –6.2 ppm). T<sub>g</sub> (DSC) = 5 °C. Conductivity at 25 °C = 1.24 x 10<sup>-10</sup> S/cm.

*Exo*-NBC(O)OE<sub>4</sub>Im<sup>+</sup>EOMe TFSI<sup>-</sup> (15b): 15b (2.96g, 84%) was synthesized via General Procedure 8 using 1-(2'-methoxyethyl)imidazole (6b) in the final quaternization. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN)  $\delta$  8.58 (s, 1H), 7.46 (t, *J* = 6, 1H), 7.40 (t, *J* = 6, 1H), 6.14 (m, 2H), 4.30 (m, 5H), 4.19 (m, 2H), 3.60 (t, *J* = 4, 2H), 3.70 (t, *J* = 6, 2H), 3.64 (t, *J* = 6, 2H), 3.52-3.65 (m, 10H), 3.00 (bs, 1H), 2.91 (bs, 1H), 2.29 (m, obscured by H<sub>2</sub>O), 1.87 (m, 1H), 1.49 (d, *J* = 8, 1H), 1.33 (m, 2H). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  9.09 (s, 1H), 7.74 (bs, 2H), 6.15 (m, 2H), 4.37 (t, *J* = 4, 4H), 4.15 (m, 2H), 3.78 (t, *J* = 4, 2H), 3.68 (t, *J* = 6, 2H), 3.61 (t, *J* = 6, 2H), 3.45-3.67 (m, 8H), 3.27 (s, 3H), 2.97 (bs, 1H), 2.89 (bs, 1H), 2.17 (m, 1H), 1.81 (m, 1H) 1.40 (d, *J* = 8, 1H), 1.28 (m, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  175.25, 137.92, 136.82, 135.63, 123.38, 122.72, 119.52 (q, *J* = 322), 69.75, 100.50 (m) = 0.50 (m) = 0.50

69.74, 69.71, 69.60, 69.56, 68.37, 68.17, 63.25, 48.79, 46.10, 45.91, 42.48, 41.09, 35.75, 30.68, 29.93 (23 signals expected and 23 signals found). HR MS: calcd. for  $C_{22}H_{35}N_2O_6$  (M – TFSI)<sup>+</sup> m/z 432.2490, found m/z 423.2493, (error 0.7 ppm). DSC (5.0 °C/min): T<sub>a</sub> -65 °C. Conductivity at 25 °C = 2.07 x 10<sup>-4</sup> S/cm.

*Exo*-NBC(O)OE<sub>4</sub>Im<sup>+</sup>EO<sub>2</sub>Me TFSI<sup>-</sup> (15c): 15c (2.92g, 79%) was synthesized via General Procedure 8 using 6c in the final quaternization. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN)  $\delta$  8.65 (s, 1H), 7.45 (m, 2H), 6.14 (m, 2H), 4.29 (t, *J* = 5, 4H), 4.18 (q, *J* = 5, 2H), 3.79 (t, *J* = 5, 4H), 3.7 – 3.45 (m, 14H), 3.28 (s, 3H), 2.99 (s, 1H), 2.90 (s, 1H), 2.19 (m, obscured by water peak), 1.86 (m, 1H), 1.46 (d, *J* = 10, 1H), 1.33 (m, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  175.62, 138.29, 137.05, 136.00, 123.05, 122.90, 119.90 (q, *J* = 322), 72.73, 70.10, 70.02, 69.98, 69.95, 68.75, 68.52, 63.62, 60.62, 58.46, 55.27, 49.23, 49.14, 46.48, 46.28, 42.85, 41.47, 30.30 (25 signals expected and 25 signals found). HR MS: calcd. for C<sub>24</sub>H<sub>39</sub>N<sub>2</sub>O<sub>7</sub> (M - TFSI)<sup>+</sup> m/z 467.2757, found m/z 467.2752 (error 1 ppm). DSC (5.0 °C/min): T<sub>g</sub> -69 °C. Conductivity at 25 °C = 4.39 x 10<sup>-4</sup> S/cm.

*Exo*-NBC(O)OE<sub>4</sub>Im<sup>+</sup>EO<sub>3</sub>Me TFSI<sup>-</sup> (15d): 15d (2.81g, 71%) was synthesized via General Procedure 8 using 1-(2'-(2"-(2"'-methoxyethoxy)ethoxy)ethoxy)ethyl)imidazole (6d) in the final quaternization. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.09 (s, 1H), 7.74 (bs, 2H), 6.15 (m, 2H), 4.36 (t, J = 4, 4H), 4.15 (m, 2H), 3.78 (t, J = 6, 2H), 3.60 (t, J = 6, 2H), 3.40-3.58 (m, 18H), 3.23 (s, 3H), 2.97 (bs, 1H), 2.89 (bs, 1H), 2.17 (m, 1H), 1.81 (dt, J = 6, 1H) 1.40 (d, J = 8, 1H), 1.28 (m, 2H). <sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ )  $\delta$  175.24, 137.92, 136.62, 135.62, 122.61, 119.51 (q, J = 323), 71.28, 69.75, 69.72, 69.63, 69.61, 69.57, 69.55, 68.37, 68.18, 68.16, 63.24, 58.07, 54.91, 48.83, 46.10, 45.90, 44.09, 42.47, 41.08,

29.93 (27 signals expected and 26 signals found). HR MS calcd. for  $C_{26}H_{43}N_2O_8$  (M - TFSI)<sup>+</sup> m/z 511.3011, found m/z 511.3014 (error 0.5 ppm). DSC (5.0 °C/min): T<sub>g</sub> -56 °C. Conductivity at 25 °C = 2.79 x 10<sup>-4</sup> S/cm.

*Exo*,*Exo*-ONB[C(O)OE<sub>4</sub>Im<sup>+</sup>EOMe]<sub>2</sub> (TFSI')<sub>2</sub> (18b): General Procedure 9 using 17b (1.5 g, 1.8 mmol) and 1-(2'-methoxyethyl)imidazole (6b, 1 g, 6 mmol) afforded the product as a pale yellow oil (1.7 g, 72%). <sup>1</sup>H-NMR (acetone- $d_6$ , 400 MHz):  $\delta$  2.85 (s, 2H), 3.29 (s, 6H), 3.49 (t, J = 4Hz, 4H), 3.59-3.68 (m, 24H), 3.90-3.94 (q, J = 4 Hz, 8H), 4.09-4.30 (m, 4H), 4.52 (t, J = 4Hz, 8H), 5.20 (s, 2H), 6.51 (s, 2H), 7.75 (d, 4H), 9.03 (s, 2H). <sup>13</sup>C-NMR (acetone- $d_6$ , 101 MHz):  $\delta$  46.6, 49.6, 49.6, 57.9, 63.9, 68.5, 68.6, 69.9, 70.0, 70.2, 70.3, 71.52 80.5, 120.1 (q, J = 323 Hz), 122.8, 122.9, 136.6, 136.9, 171.5 (19 peaks observed, theory: 19). HR MS: m/z 680.1076 (M + 2 Na)<sup>+2</sup>, calc. for (C<sub>40</sub>H<sub>58</sub>F<sub>12</sub>N<sub>6</sub>Na<sub>2</sub>O<sub>21</sub>S<sub>4</sub>)<sup>+2</sup> m/z 680.1065 (error 1.6 ppm); m/z 966.2921 [M - TFSI - C<sub>4</sub>H<sub>4</sub>O (furan)]<sup>+</sup>, calc. for C<sub>34</sub>H<sub>54</sub>F<sub>6</sub>N<sub>5</sub>O<sub>16</sub>S<sub>2</sub> m/z 966.2906 (error 1.5 ppm); m/z 1034.3204 (M - TFSI)<sub>+</sub>, calc. for C<sub>38</sub>H<sub>58</sub>F<sub>12</sub>N<sub>6</sub>NaO<sub>21</sub>S<sub>4</sub> m/z 1337.2238 (error 1.3 ppm). T<sub>g</sub> (DSC) = -42 °C Conductivity at 25 °C = 1.2 x 10<sup>-4</sup> S/cm.

*Exo,Exo*-ONB[C(O)OE<sub>4</sub>Im<sup>+</sup>EO<sub>2</sub>Me]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> (18c): General Procedure 9 using ditosylate 17b (2.02 g, 2.4 mmol) and 1-(2'-(2"-methoxyethoxy)ethyl)imidazole (6c, 1.12 g, 6 mmol) yielded the product as a pale yellow oil (2.02 g, 60%). <sup>1</sup>H-NMR (acetone- $d_6$ , 400 MHz):  $\delta$  2.85 (s, 2H), 3.29 (s, 6H), 3.49 (t, J = 4Hz, 4H), 3.59-3.68 (m, 24H), 3.90-3.94 (q, J = 4 Hz, 8H), 4.09-4.30 (m, 4H), 4.52 (t, J = 4Hz, 8H), 5.20 (s, 2H), 6.51 (s, 2H), 7.75 (d, 4H), 9.03 (s, 2H). <sup>13</sup>C-NMR (acetone- $d_6$ , 101 MHz):  $\delta$  46.6, 49.6, 49.6,

57.9, 63.9, 68.50, 68.6, 69.9, 70.0, 70.2, 70.3, 71.5, 80.5, 120.1 (q, J = 323 Hz), 122.8, 122.9, 136.6, 136.9, 171.5 (20 peaks observed, theory: 21). HR MS: m/z 724.1376 (M + 2 Na)<sup>+2</sup>, calc. for C<sub>44</sub>H<sub>66</sub>F<sub>12</sub>N<sub>6</sub>Na<sub>2</sub>O<sub>23</sub>S<sub>4</sub> m/z 724.1327 (error 6.7 ppm); m/z 1054.3468 [M - TFSI - C<sub>4</sub>H<sub>4</sub>O (furan)]<sup>+</sup>, calc. for C<sub>38</sub>H<sub>62</sub>F<sub>6</sub>N<sub>5</sub>O<sub>18</sub>S<sub>2</sub> m/z 1054.3430 (error 3.6 ppm); m/z 1123.3774 (M + H - TFSI)<sup>+</sup>, calc. for C<sub>42</sub>H<sub>67</sub>F<sub>6</sub>N<sub>5</sub>O<sub>19</sub>S<sub>2</sub> m/z 1123.3770 (error 0.3 ppm); m/z 1425.2805 (M + Na)<sup>+</sup>, calc. for C<sub>44</sub>H<sub>66</sub>F<sub>12</sub>N<sub>6</sub>NaO<sub>23</sub>S<sub>4</sub> m/z 1425.2763 (error 2.9 ppm). T<sub>g</sub> (DSC) = -44 °C Conductivity at 25 °C = 7.9 x 10<sup>-5</sup> S/cm.

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Compound Lab	bel RT	Mass	Abund	±	Formula	Tgt Mass	(ppm)
Cpd 1: C17	H26 O8 0.14	358.163	21845	52	C17 H26 O8	358.1628	0.76
Compound Label	RT	Algorithm		Mass			
Cpd 1: C17 H26 O8	0.142	Find By Form	ula	358.163	3		
x10 6 Cpd 1: C1	7 H26 O8: +E	SI EIC(89.540	1, 90.5	480, 107.	5745, 112.5299	) Scan Frag=	125.0V tp_set
1 0.1420							1
4-							
3							
2-							
1	$\mathbf{A}$						
0.1 0.2	2 0.3 0.4 0	0.5 0.6 0.7	0.8 0.	9 1 1	1 1.2 1.3 1	4 1.5 1.6 1	7 1.8 1.9
		Cour	nts vs.	Ăcquisitio	n Time (min)		.,
MS Spectrum	7 H26 O8. +E	SI Scop (0.103	26-0-28	01 min 1	2 econe) Frage	1250V to set 1	10017 n1 pei
x10 5 CPU 1. CT	359.17	05	50-0.20	or min, i	Z scans) Frag-	125.0V tp_56t_	10017_p1_esi
2-	(M+H	)+					
1.5-							
1							
			li.				
0.5-				1			
O line har		humanation on him human	humber			1 1	
200	300	400 500 Cour	60 nts vs.	0 70 Mass-to-C	0 800 Charge (m/z)	900 1000	1100
m/z Cá	alc m/z	Diff(ppm)	z	Abund	Formula		Ion
359.1705	359.17	1.14		228136	C17 H27 O8		(M+H)+
359.3366				5304			
360.1741	360.1735	1.78		45706	C17 H27 O8		(M+H)+
361.1728	361.1756	-7.81		10007	C17 H27 O8		(M+H)+
376.1961	376.1966	-1.27	1	34891	C17 H30 N O8		(M+NH4)+
377.2005	377.1999	1.51	1	6870	C17 H30 N O8		(M+NH4)+
378.1926	378.2021	-24.94	1	2479	C17 H30 N O8		(M+NH4)+
381.1521	381.152	0.32	1	221096	C17 H26 Na O	8	(M+Na)+
382.155	382.1554	-1.09	1	41029	C17 H26 Na O	8	(M+Na)+
383,1557	383,1576	-4.86	1	8217	C17 H26 Na O	8	(M+Na)+

Figure S1. HR MS of norbornene diol  $NB[C(O)OE_2OH]_2$  (2a).

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**Figure S2.** HR MS of norbornene diol  $NB[C(O)OE_3OH]_2$  (**2b**).



Figure S3.	HR MS of norbornene diol NB[C(O)OE <sub>4</sub> OH] <sub>2</sub> ( <b>2c</b> ).	

558.2614

559.2637

558.2603

559.2627

1.97

1.9

1

1

70128

14824

C25 H42 Na O12

C25 H42 Na O12

(M+Na)+

(M+Na)+



685.2151	685.2175	-3.5	1	19977	C31 H42 N O12 S2	(M+NH4)+
686.2125	686.2151	-3.7	1	9221	C31 H42 N O12 S2	(M+NH4)+
689.1681	689.1697	-2.28	1	52542	C31 H38 Na O12 S2	(M+Na)+
690.1704	690.1729	-3.58	1	18416	C31 H38 Na O12 S2	(M+Na)+
691.1683	691.1705	-3.1	1	8480	C31 H38 Na O12 S2	(M+Na)+

Figure S4. HR MS of norbornene ditosylate NB[C(O)OE<sub>2</sub>OTs]<sub>2</sub> (3a).



//3.2/13	//3.2699	1.83		55774	C35 H50 N 014 S2	(M+NH4)+
774.2698	774.2681	2.27		25417	C35 H50 N O14 S2	(M+NH4)+
775.2696	775.2694	0.32		7502	C35 H50 N O14 S2	(M+NH4)+
777.2239	777.2221	2.29		76459	C35 H46 Na O14 S2	(M+Na)+
778.2265	778.2254	1.41	1	30384	C35 H46 Na O14 S2	(M+Na)+
779.2249	779.2235	1.83	1	14040	C35 H46 Na O14 S2	(M+Na)+
780.2273	780.2248	3.16	1	4102	C35 H46 Na O14 S2	(M+Na)+
793.204	793.1961	9.97	1	3145	C35 H46 K O14 S2	(M+K)+

Figure S5a. HR MS of norbornene ditosylate NB[C(O)OE<sub>3</sub>OTs]<sub>2</sub> (3b).



Figure S5b. HR MS of norbornene ditosylate NB[C(O)OE<sub>3</sub>OTs]<sub>2</sub> (3b).



High res MS: calc. for  $C_{39}H_{54}O_{16}S_2$  [M]+: m/z 842.2853; found: m/z 842.2865 (error 1.4 ppm)

**Figure S6.** HR MS of norbornene ditosylate  $NB[C(O)OE_4OTs]_2$  (**3c**).


Figure S7. HR MS of norbornene ditosylate NB[C(O)OE<sub>5</sub>OTs]<sub>2</sub> (3d).



Figure S8. HR MS of norbornene ditosylate NB[C(O)OE<sub>6</sub>OTs]<sub>2</sub> (3e).



HR MS: calc. for  $C_{13}H_{16}Br_2O_4$  fragment  $[M - C_2H_4Br_2 + H]^+$ : m/z 209.0814; found: m/z 209.0795 (error -9.1 ppm). Calc. for  $C_{13}H_{18}Br_2O_4(M + H)^+$  m/z 397.9551; there is an unlabeled peak that seems to correspond to this ion.

Figure S9. HR MS of norbornene dibromide NB[C(O)OEBr]<sub>2</sub> (4).



HR MS: calc. for  $C_{17}H_{28}O_8S [M + NH_4]^+$ : m/z 410.1843; found: m/z 410.1836 (error 2 ppm).

Figure S10. HR MS of penta(ethylene glycol) monotosylate HOE<sub>5</sub>OTs.



HR MS: calc. for  $C_{19}H_{32}O_9S [M + Na]^+$ : m/z 459.1659; found: m/z 459.1661 (error -0.4 ppm).

Figure S11. HR MS of hexa(ethylene glycol) monotosylate HOE<sub>6</sub>OTs.



	313.0513	313.0507	1.97	1	281	C12 H18 K O5 S	(M+K)+	
								-
F	Figure S12.	HR MS	of di(ethvle	ene	e alvcol	) monomethyl	ether monotosyla	ate MeOE

33153

4580

297.0774

298.0806

297.0767

298.0799

2.44

2.19 1

1

**Figure S12.** HR MS of di(ethylene glycol) monomethyl ether monotosylate MeOE<sub>2</sub>OTs (**5a**).

C12 H18 Na O5 S

C12 H18 Na O5 S

(M+Na)+

(M+Na)+



**Figure S13.** HR MS of tetra(ethylene glycol) monomethyl ether monotosylate MeOE<sub>4</sub>OTs (**5c**).



## **MS Spectrum Peak List**

m/z	Calc m/z	Diff(ppm)	Abund	Formula	Ion
121.049			1133		
123.0552			18688		
124.0396			46032		
125.0453			3483		
125.1073	125.1073	0.13	226033	C7 H13 N2	(M+H)+
125.2078			4854		
126.1101	126.1102	-0.43	17925	C7 H13 N2	(M+H)+
127.0158			24365		
127.1114	127.113	-12.34	1316	C7 H13 N2	(M+H)+
129.0465			1223		

Figure S14. HR MS of N-substituted imidazole ImBu (6a).



Figure S15. HR MS of N-substituted imidazole ImEOMe (6b).



m/z	Calc m/z	Diff(ppm)	Abund	Formula	Ion
167.1226			7320		
168.1223			1198		
169.1378			5888		
171.1129	171.1128	0.46	473125	C8 H15 N2 O2	(M+H)+
171.2295			15173		
171.2723			2854		
171.3567			1176		
172.1167	172.1157	5.48	43251	C8 H15 N2 O2	(M+H)+
173.11	173.1178	-45.39	5163	C8 H15 N2 O2	(M+H)+
175.0907			3202		

Figure S16. HR MS of N-substituted imidazole ImEO<sub>2</sub>Me (6c).



Figure S17. HR MS of N-substituted imidazole ImEO<sub>3</sub>Me (6d).



Figure S18. HR MS of N-substituted imidazole ImEO<sub>4</sub>Me (6e).



**Figure S19.** HR MS of norbornene di(imidazolium) bis(TFSI) NB[C(O)OEIm<sup>+</sup>Bu]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> (**8a**).



**Figure S20a.** HR MS of norbornene di(imidazolium) bis(TFSI) NB[C(O)OEIm<sup>+</sup>EOCH<sub>3</sub>]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> (**8b**).



**Figure S20b.** HR MS of norbornene di(imidazolium) bis(TFSI) NB[C(O)OEIm<sup>+</sup>EOCH<sub>3</sub>]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> (**8b**).



**Figure S21.** HR MS of norbornene di(imidazolium) bis(TFSI) NB[C(O)OEIm<sup>+</sup>EO<sub>2</sub>CH<sub>3</sub>]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> (**8c**).



MS S	pectrum	Peak	List
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m/z	Calc m/z	Diff(ppm)	Z	Abund	Formula	Ion
332.184	332.1836	1.21	2	112160	C33 H52 N4 O10	M+2
332.6862	332.6852	3.1	2	41584	C33 H52 N4 O10	M+2
333.1854	333.1866	-3.36	2	11027	C33 H52 N4 O10	M+2
361.2347				439541		
361.401				11664		
362.2372				83564		
363.2393				13055		
365.1365				18306		
366.1404				3985		
687.3642	687.3576	9.61	1	187	C33 H52 N4 Na O10	(M+Na)+

**Figure S22a.** HR MS of norbornene di(imidazolium) bis(TFSI) NB[C(O)OEIm<sup>+</sup>EO<sub>3</sub>CH<sub>3</sub>]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> (**8d**).



**Figure S22b.** HR MS of norbornene di(imidazolium) bis(TFSI) NB[C(O)OEIm<sup>+</sup>EO<sub>3</sub>CH<sub>3</sub>]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> (**8d**).



**Figure S23a.** HR MS of norbornene di(imidazolium) bis(TFSI) NB[C(O)OEIm<sup>+</sup>EO<sub>4</sub>CH<sub>3</sub>]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> (**8e**).



**Figure S23b.** HR MS of norbornene di(imidazolium) bis(TFSI) NB[C(O)OEIm<sup>+</sup>EO<sub>4</sub>CH<sub>3</sub>]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> (**8e**).



280 300 320 340 360 380 400 420 440 460 480 500 520 540 560 580 600 Counts vs. Mass-to-Charge (m/z)

HR MS: calc. for  $C_{35}H_{48}O_{14}N_4$  [M – 2TFSI]<sup>+2</sup>: m/z 286.1781; found: m/z 286.1791 (error 3.3 ppm).

**Figure S24a.** HR MS of norbornene di(imidazolium) bis(TFSI) NB[C(O)OE<sub>2</sub>Im<sup>+</sup>Bu]<sub>2</sub> (TFSI)<sub>2</sub> (**8f**).



**Figure S24b.** HR MS of norbornene di(imidazolium) bis(TFSI) NB[C(O)OE<sub>2</sub>Im<sup>+</sup>Bu]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> (**8**f).



**Figure S25.** HR MS of norbornene di(imidazolium) bis(TFSI) NB[C(O)OE<sub>2</sub>Im<sup>+</sup>EOCH<sub>3</sub>]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> (**8g**).



**Figure S26a.** HR MS of norbornene di(imidazolium) bis(TFSI)  $NB[C(O)OE_2Im^+EO_2CH_3]_2$  (TFSI)<sub>2</sub> (**8h**).



**Figure S26b.** HR MS of norbornene di(imidazolium) bis(TFSI)  $NB[C(O)OE_2Im^+EO_2CH_3]_2$  (TFSI)<sub>2</sub> (**8h**).



 370.3791			3732		
376.7097	376.7114	-4.7	67104	C37 H60 N4 O12	M+2
376.8815			1579		
377.211	377.2128	-4.67	17672	C37 H60 N4 O12	M+2
377.7119	377.7141	-6	3795	C37 H60 N4 O12	M+2
378.2163			1818		

**Figure S27.** HR MS of norbornene di(imidazolium) bis(TFSI) NB[C(O)OE<sub>2</sub>Im<sup>+</sup>EO<sub>3</sub>CH<sub>3</sub>]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> (**8i**).



**Figure S28.** HR MS of norbornene di(imidazolium) bis(TFSI) NB[C(O)OE<sub>2</sub>Im<sup>+</sup>EO<sub>4</sub>CH<sub>3</sub>]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> (**8j**).



**Figure S29.** DSC trace (second heating) of norbornene di(imidazolium) bis(TFSI)  $NB[C(O)OE_2Im^+EO_4CH_3]_2$  (TFSI)<sub>2</sub> (**8j**).



HR MS: calc. for  $C_{39}H_{56}O_{16}N_5S_2F_6$  [M – TFSI]<sup>+</sup>: m/z 940.3266; found: m/z 940.3186 (error -8.5 ppm).

**Figure S30.** HR MS of norbornene di(imidazolium) bis(TFSI) NB[C(O)OE<sub>3</sub>Im<sup>+</sup>Bu]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> (**8k**).



High res MS +2 peak: calc. for  $C_{33}H_{52}O_{10}N_4$  [M]+: m/z 664.3683; found: m/z 664.3696 (error 1.8 ppm)

**Figure S31a.** HR MS of norbornene di(imidazolium) bis(TFSI) NB[C(O)OE<sub>3</sub>Im<sup>+</sup>EOCH<sub>3</sub>]<sub>2</sub> (TFSI)<sub>2</sub> (8I).



High res MS +1 peak: calc. for  $C_{35}H_{52}O_{14}N_5S_2F_6$  [M]+: m/z 944.2856; found: m/z 944.2853 (error -0.3 ppm)

**Figure S31b.** HR MS of norbornene di(imidazolium) bis(TFSI) NB[C(O)OE<sub>3</sub>Im<sup>+</sup>EOCH<sub>3</sub>]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> (**8I**).



**Figure S32a.** HR MS of norbornene di(imidazolium) bis(TFSI) NB[C(O)OE<sub>3</sub>Im<sup>+</sup>EO<sub>2</sub>CH<sub>3</sub>]<sub>2</sub> (TFSI)<sub>2</sub> (**8m**).





		_	
MS Sp	ectrum	Pea	k l ist

m/z	Calc m/z	Diff(ppm)	Abund	Formula	Ion
375.2981			2654		
376.2113	376.2098	3.85	399225	C37 H60 N4 O12	M+2
376.3791			11632		
376.4508			2664		
376.7126	376.7114	3.06	173624	C37 H60 N4 O12	M+2
376.8809			5227		
377.2138	377.2128	2.73	45906	C37 H60 N4 O12	M+2
377.7156	377.7141	3.87	9287	C37 H60 N4 O12	M+2
378.2147	378.2154	-1.93	2806	C37 H60 N4 O12	M+2
380.3318			2499		

**Figure S32b.** HR MS of norbornene di(imidazolium) bis(TFSI)  $NB[C(O)OE_3Im^+EO_2CH_3]_2$  (TFSI)<sub>2</sub> (**8m**).



HR MS: calc. for  $C_{45}H_{68}O_{22}N_6S_4F_{12}$  [M - TFSI]<sup>+</sup>: m/z 1120.3899; found: m/z 1120.3946 (error 4.1 ppm). HR MS: calc. for  $C_{45}H_{68}O_{22}N_6S_4F_{12}$  [M - 2TFSI]<sup>+2</sup>: m/z 420.2361; found: m/z 420.2381 (error 4.8 ppm)

**Figure S33.** HR MS of norbornene di(imidazolium) bis(TFSI) NB[C(O)OE<sub>3</sub>Im<sup>+</sup>EO<sub>3</sub>CH<sub>3</sub>]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> (**8n**).



9.6 ppm)

**Figure S34.** HR MS of norbornene di(imidazolium) bis(TFSI) NB[C(O)OE<sub>3</sub>Im<sup>+</sup>EO<sub>4</sub>CH<sub>3</sub>]<sub>2</sub> (TFSI)<sub>2</sub> (**80**).



HR MS: calc. for  $C_{43}H_{64}O_{18}N_4$  [M – 2TFSI]<sup>+2</sup>: m/z 374.2306; found: m/z 374.2315 (error 2 ppm).

**Figure S35.** HR MS of norbornene di(imidazolium) bis(TFSI) NB[C(O)OE<sub>4</sub>Im<sup>+</sup>Bu]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> (**8p**).


**Figure S36a.** HR MS of norbornene di(imidazolium) bis(TFSI) NB[C(O)OE<sub>4</sub>Im<sup>+</sup>EOCH<sub>3</sub>]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> (**8q**).



Compound Label RT Algorithm Mass



m/z	Calc m/z	Diff(ppm)	Abund	Formula	Ion
371.3177			3832		
372.1033			1355		
376.2116	376.2098	4.71	175451	C37 H60 N4 O12	M+2
376.3819			3681		
376.7131	376.7114	4.54	74314	C37 H60 N4 O12	M+2
376.8822			1689		
377.2145	377.2128	4.46	20157	C37 H60 N4 O12	M+2
377.716	377.7141	4.92	4124	C37 H60 N4 O12	M+2
378.2088			1646		
380.3313			2073		

**Figure S36b.** HR MS of norbornene di(imidazolium) bis(TFSI) NB[C(O)OE<sub>4</sub>Im<sup>+</sup>EOCH<sub>3</sub>]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> (**8q**).



HR MS: calc. for  $C_{45}H_{68}O_{22}N_5S_2F_6$  [M - TFSI]<sup>+</sup>: m/z 1120.3899; found: m/z 1120.3891 (error -0.8 ppm). HR MS: calc. for  $C_{45}H_{68}O_{22}N_4$  [M - 2TFSI]<sup>+2</sup>: m/z 420.2361; found: m/z 420.2374 (error 3.2 ppm)

**Figure S37.** HR MS of norbornene di(imidazolium) bis(TFSI) NB[C(O)OE<sub>4</sub>Im<sup>+</sup>EO<sub>2</sub>CH<sub>3</sub>]<sub>2</sub> (TFSI)<sub>2</sub> (**8r**).



HR MS: calc. for  $C_{49}H_{76}O_{24}N_5S_2F_6$  [M – TFSI]<sup>+</sup>: m/z 1208.4424; found: m/z 1208.4441 (error 1.4 ppm). HR MS: calc. for  $C_{49}H_{76}O_{24}N_4$  [M – 2TFSI]<sup>+2</sup>: m/z 464.2623; found: m/z 464.2651 (error 6.0 ppm).

**Figure S38.** HR MS of norbornene di(imidazolium) bis(TFSI) NB[C(O)OE<sub>4</sub>Im<sup>+</sup>EO<sub>3</sub>CH<sub>3</sub>]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> (8s).



**Figure S39a.** HR MS of norbornene di(imidazolium) bis(TFSI)  $NB[C(O)OE_4Im^+EO_4CH_3]_2$  (TFSI)<sub>2</sub> (**8t**).



**Figure S39b.** HR MS of norbornene di(imidazolium) bis(TFSI) NB[OE<sub>4</sub>ImEO<sub>4</sub>CH<sub>3</sub><sup>+</sup>]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> (8t).





HR MS: calc. for  $C_{49}H_{76}O_{24}N_6S_4F_{12}$  [M - 21FSI]<sup>2</sup>: m/z 464.2623; found: m/z 464.2609 (error – 3.0 ppm).

**Figure S40.** HR MS of norbornene di(imidazolium) bis(TFSI) NB[C(O)OE<sub>5</sub>Im<sup>+</sup>EO<sub>2</sub>Me]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> (**8u**).





0.2

HR MS: calc. for  $C_{53}H_{84}O_{26}N_6S_4F_{12}$  [M + Na]<sup>+1</sup>: m/z 1599.4024; found: m/z 1599.3987 (error 2.3 ppm).

**Figure S41.** HR MS of norbornene di(imidazolium) bis(TFSI) NB[C(O)OE<sub>6</sub>Im<sup>+</sup>EO<sub>2</sub>Me]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> (**8v**).



**Figure S42.** HR MS of norbornene di(imidazolium) ditosylate NB[C(O)OE<sub>4</sub>Im<sup>+</sup>EO<sub>2</sub>Me]<sub>2</sub> (Tos<sup>-</sup>)<sub>2</sub> (**7r**).

### Discussion of Relationship Between RT Conductivity and T<sub>g</sub>

We conclude that a long oxyethylene linkage between the norbornene and the imidazolium cation is desirable, so that steric crowding between the two arms can be reduced and additional intramolecular interactions can be achieved. The ethyleneoxy tail units also then can wrap around the cation for a stabilizing effect. This hypothesis can also serve as an explanation as to why for X = 1 in Figure S43 the RT conductivity is a smooth function of T<sub>g</sub> as Y varies: the highest conductivity for the lowest T<sub>g</sub>. In this case the conductivity is controlled by  $T_g$ . However, for X = 2, 3, and 4 the relationships are different. We surmise that when X = 1 the steric crowding at the two cations prevents the terminal ethyleneoxy chain from interacting effectively with the imidazolium unit. But once a spacer of at least two oxyethylene units (X  $\ge$  2) is employed, the terminal di(ethyleneoxy) tail can arch back to stabilize the less hindered cations and moreover the tether itself can interact with the cation. This complexation of the cation promotes release of the anion, thus increasing the number of charge carriers, and affording increased conductivity; however, the effect on  $T_g$  is more complex, because interactions of the tether and terminal ethyleneoxy units with the cation are competitive and result in restricted conformations that raise T<sub>g</sub>. However, as Y increases the charge density is diluted, reducing conductivity, so that for X > 1 the maximum RT conductivity is observed at Y=2, regardless of the value of X.

**Figure S44** shows the effect of variation of the tether length X at constant terminal unit length Y. Consistent with the above discussion for the butyl and Y = 1 cases the RT conductivity follows T<sub>g</sub> in the conventionally expected manner. However,

this dramatically changes for Y > 1. The RT conductivity for Y = 2 displays significant scatter and for Y = 3 the RT conductivity is more or less linear with  $T_g$ ! For Y = 4 a maximum is observed in the plot. For all cases, Y = 1 to 4 the maximum RT conductivities are observed with X = 3 or 4. These results are interpreted as representing competition between the tether and terminal moieties for complexation of the cation and the conformational complexity that evolves with the changing structures. Complexation of either segment would result in loss of conformational freedom and thus increase  $T_g$  above the otherwise expected value.





### Solvent Effects on Chemical Shifts of N,N'-Dimethylimiazolium TFSI

To aid in the understanding the NMR results for the monomers in various solvents, dimethylimidazolium TFSI was studied in ether, glyme, diglyme, triglyme, and tetraglyme (**Figure S45**) by <sup>1</sup>H NMR (**Figure S46**). Dimethylimidazolium TFSI was dissolved in each of the solvents to form 0.27 mM solutions. A sealed capillary containing chloroform-*d* served as an external standard ( $\delta = 7.26$  ppm). As the number of oxygen atoms in the solvent increased, the proton peaks of the imidazolium unit were steadily shifted upfield. H<sub>1</sub> was used for analysis because its chemical shift change was greatest and because it is the most acidic hydrogen. The shifting of imidazolium protons upfield indicates the degree to which hydrogen bonding is occurring between the acidic protons of the imidazolium ring and oxygen atoms of the solvent. Figure S47 shows the dependence of the chemical shift on the concentration of ether oxygen atoms, supporting this interpretation.



**Figure S45.** Ethereal solvents used to probe intermolecular interactions between the N,N'-dimethylimidazolium cation and ethyleneoxy units.



**Figure S46.** Partial <sup>1</sup>H NMR (500 MHz) spectra of dimethyl imidazolium TFSI (0.27 mM) in: A) ether, B) glyme, C) diglyme, D) triglyme, E) tetraglyme.



**Figure S47.** Chemical shift of  $H_1$  of dimethyl imidazolium TFSI vs. oxygen content of the solvent; fit to a logarithmic trend line to guide the eye.

### NB[(EO)<sub>4</sub>Im(EO)<sub>2</sub>CH<sub>3</sub> BARF]<sub>2</sub>



HR MS: calc. for  $C_{105}H_{92}B_2N_4O_{14}F_{48}$  [M - BARF]<sup>+</sup>: m/z 1703.5375; found: m/z 1703.5376 (error -0.06 ppm)



**Figure S48.** HR MS of norbornene di(imidazolium) bis(BARF) NB[C(O)OE<sub>4</sub>Im<sup>+</sup>EO<sub>2</sub>Me]<sub>2</sub> (BARF<sup>-</sup>)<sub>2</sub> (**9r**).



# NB[(EO)<sub>4</sub>Im(EO)<sub>2</sub> TPFB]<sub>2</sub>

HR MS: calc. for  $C_{65}H_{68}BF_{20}N_4O_{14}$  [M - TPFB]<sup>+</sup>: m/z 1519.4506; found: m/z 1519.4415 (error 6.0 ppm)

Figure S49. HR MS of norbornene di(imidazolium) bis(TFPB) NB[C(O)OE<sub>4</sub>Im<sup>+</sup>EO<sub>2</sub>Me]<sub>2</sub> (TFPB<sup>-</sup>)<sub>2</sub> (10r).



ppm)  $(e_{67}\pi_{114}\pi_{4}O_{18}S_2 [w_1 + m_3] \cdot m_2 + 1549.7462, 100 m_0 \cdot m_2 + 1549.7467 (e_{15})$ 



**Figure S50.** HR MS of norbornene di(imidazolium) bis(AOT) NB[C(O)OEIm<sup>+</sup>Bu]<sub>2</sub> (AOT<sup>-</sup>)<sub>2</sub> (**11a**).



HR MS: calc. for  $C_{47}H_{82}N_4O_{12}S_2$  [M – 2 DDS]<sup>+2</sup>: m/z 242.1520; found: m/z 242.1534 (error – 5.8 ppm)

**Figure S51.** HR MS of norbornene di(imidazolium) bis(DDS) NB[C(O)OEIm<sup>+</sup>Bu]<sub>2</sub> (DDS<sup>-</sup>)<sub>2</sub> (**12a**).

			T <sub>g</sub> *	Conductivity
Cpd.	Anion	Name	(°C)	@ 25 °C (S/cm)
8r	TFSI	$NB[C(O)OE_4Im^+EO_2Me]_2 (TFSI)_2$	–46 °C	9.57 x 10 <sup>-5</sup>
9r	BARF	$NB[C(O)OE_4Im^+EO_2Me]_2(BARF)_2$	–26, –6 °C	3.19 x 10 <sup>-8</sup>
10r	TPFB	$NB[C(O)OE_4Im^+EO_2Me]_2 (TPFB^-)_2$	–27 °C	N/A
8a	TFSI	NB[C(O)OEIm <sup>+</sup> Bu] <sub>2</sub> (TFSI <sup>-</sup> ) <sub>2</sub>	_44 °C	3.07 x 10 <sup>-5</sup>
11a	AOT	NB[C(O)OEIm <sup>+</sup> Bu] <sub>2</sub> (AOT <sup>-</sup> ) <sub>2</sub>	–25 °C	2.57 x 10 <sup>-9</sup>
12a	DSS	NB[C(O)OEIm <sup>+</sup> Bu] <sub>2</sub> (DDS <sup>-</sup> ) <sub>2</sub>	5 °C	1.24 x 10 <sup>-10</sup>

Table S1. Glass transition temperatures and room temperature conductivities of 8r, 9r, 10r, 8a, 11a and 12a.

\* Determined by DSC at 10 °C/min during the second heating scan. The midpoint of the change in heat capacity was defined as the glass transition temperature.

**Table S1** lists T<sub>g</sub> and RT conductivity values for these monomer salts. The T<sub>g</sub>s of **9r** and **10r** with the boron anions are approximately 20 °C higher than their TFSI counterpart **8r** and RT conductivities are nearly three orders of magnitude lower. The increased T<sub>g</sub> values yield a medium less favorable for mass transport of these large anions. Considering the similar T<sub>g</sub> value of **9r** and **10r** alongside the low RT conductivity of **9r** and the cost of NaTPFB (~ \$1/2 mg), its conductivity was not measured since more material is required. For the sulfonate **11a** and sulfate **12a**, T<sub>g</sub> values are nearly 20 and 50 °C higher and RT conductivities range from four to five orders of magnitude lower than their TFSI counterpart **8a**. The T<sub>g</sub> increase in **9r** and **10r** is likely in part due to the large and rigidly confined aromatic rings. The anions of **11a** and **12a**, however, contain flexible hydrocarbon chains, so the lower conductivity in these systems is attributed mainly to the lack of charge delocalization in the sulfonate

and sulfate anions, leading to tighter ion pairs and fewer free anions and a lower dielectric constant.



Figure S52. HR MS of norbornene monotosylate NBC(O)OE<sub>4</sub>OTs (14).



Figure S53. HR MS of monomer NBC(O)OE<sub>4</sub>ImMe<sup>+</sup> TFSI<sup>-</sup> (15a).



Figure S54. HR MS for monomer NBC(O)OE<sub>4</sub>Im<sup>+</sup>EOMe TFSI<sup>-</sup> (15b).



**Figure S55.** HRMS for monomer NBC(O)OE<sub>4</sub>Im<sup>+</sup>EO<sub>2</sub>Me TFSI<sup>-</sup> (15c).



**Figure S56.** DSC trace for the monomer NBC(O)OE<sub>4</sub>Im<sup>+</sup>EO<sub>2</sub>Me TFSI<sup>-</sup> (**15c**) with a T<sub>g</sub> of -69  $^{\circ}$ C. Second heating cycle shown.



**Figure S57.** HR MS of norbornene mono(imidazolium) TFSI NBC(O)OE<sub>4</sub>Im<sup>+</sup>EO<sub>3</sub>Me TFSI<sup>-</sup> (15d).



**Figure S58a.** HR MS of oxaorbornene di(imidazolium) bis(TFSI) ONB[C(O)OE<sub>3</sub>Im<sup>+</sup>EOMe]<sub>2</sub> (TFSI)<sub>2</sub> (18a).



Figure S58b. HR MS of oxaorbornene di(imidazolium) bis(TFSI)  $ONB[C(O)OE_3Im^+EOMe]_2$  (TFSI<sup>-</sup>)<sub>2</sub> (18a).



**Figure S59.** DSC trace of oxaorbornene di(imidazolium) bis(TFSI) ONB[C(O)OE<sub>3</sub>Im<sup>+</sup>EOMe]<sub>2</sub> (TFSI<sup>-</sup>)<sub>2</sub> **(18a**) (red curve labelled HG AM 29 001).



**Figure S60a.** HR MS of oxaorbornene di(imidazolium) bis(TFSI) ONB[C(O)OE<sub>4</sub>Im<sup>+</sup>EOMe]<sub>2</sub> (TFSI)<sub>2</sub> (18b).



**Figure S60b.** HR MS of oxaorbornene di(imidazolium) bis(TFSI)  $ONB[C(O)OE_4Im^+EOMe]_2$  (TFSI<sup>-</sup>)<sub>2</sub> (**18b**).



 $ONB[C(O)OE_4Im^+EO_2Me]_2 (TFSI^-)_2$  (18c).



Figure S61b. HR MS of oxaorbornene di(imidazolium) bis(TFSI)  $ONB[C(O)OE_4Im^+EO_2Me]_2$  (TFSI<sup>-</sup>)<sub>2</sub> (18c).

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