

*Electronic Supporting Information (ESI)*

**Novel PEG-Functionalized Ionic Liquids for Cellulose Dissolution and Saccharification**

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**<sup>1</sup>H and <sup>13</sup>C MR of New Ionic Liquids**

*1,1'-(3,6,9-Trioxaundecane-1,1-diyl)bis(triethylammonium-N-yl) diacetate (1, [TEG-(Et<sub>3</sub>N)<sub>2</sub>][OAc]<sub>2</sub>). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, [ppm]) δ = 1.34 (18H, t, 2×(CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N, J = 6.0 Hz), 1.87 (6H, s, 2×CH<sub>3</sub>COO<sup>-</sup>), 3.50 (12H, m, 2×(CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N), 3.62 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>N), 3.68-3.72 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>N), 3.96 (2H, t, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>N, J = 6.0 Hz). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, [ppm]) δ = 7.69, 25.32, 53.64, 56.85, 64.26, 70.12, 70.33, 176.37.*

*(2, [PEG200-(Et<sub>3</sub>N)<sub>2</sub>][OAc]<sub>2</sub>). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, [ppm]) δ = 1.35 (18H, t, 2×(CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N, J = 3.9 Hz), 1.90 (6H, s, 2×CH<sub>3</sub>COO<sup>-</sup>), 3.45-3.50 (12H, m, (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N), 3.62 (18H, m, NCH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OCH<sub>2</sub>CH<sub>2</sub>N), 3.93 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OCH<sub>2</sub>CH<sub>2</sub>N). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, [ppm]) δ = 7.72, 11.59, 24.62, 47.50, 53.82, 56.80, 64.48, 70.34, 176.68.*

*(3, [PEG300-(Et<sub>3</sub>N)<sub>2</sub>][OAc]<sub>2</sub>). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, [ppm]) δ = 1.36 (18H, t, 2×(CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N, J = 4.5 Hz), 1.91 (6H, s, 2×CH<sub>3</sub>COO<sup>-</sup>), 3.50 (12H, m, (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N), 3.62 (20H, m, NCH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OCH<sub>2</sub>CH<sub>2</sub>N), 3.73 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OCH<sub>2</sub>CH<sub>2</sub>N), 3.94 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OCH<sub>2</sub>CH<sub>2</sub>N). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, [ppm]) δ = 7.86, 25.42, 53.90, 56.97, 64.69, 70.42, 70.51, 176.75.*

*(4, [PEG400-(Et<sub>3</sub>N)<sub>2</sub>][OAc]<sub>2</sub>). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, [ppm]) δ = 1.39 (18H, t, 2×(CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N, J = 6.9 Hz), 1.94 (6H, s, 2×CH<sub>3</sub>COO<sup>-</sup>), 3.50-3.54 (12H, m, (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N), 3.66 (34H, m, NCH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OCH<sub>2</sub>CH<sub>2</sub>N), 3.79 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OCH<sub>2</sub>CH<sub>2</sub>N), 3.95 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OCH<sub>2</sub>CH<sub>2</sub>N). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, [ppm]) δ = 7.79, 25.33, 53.81, 56.90, 64.69, 70.23, 70.47, 176.62.*

*(5, [PEG600-(Et<sub>3</sub>N)<sub>2</sub>][OAc]<sub>2</sub>). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, [ppm]) δ = 1.36 (18H, t, 2×(CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N, J = 7.2 Hz), 1.93 (6H, s, 2×CH<sub>3</sub>COO<sup>-</sup>), 3.40-3.56 (12H, m, (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N), 3.61-3.64 (52H, m, NCH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OCH<sub>2</sub>CH<sub>2</sub>N), 3.78 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OCH<sub>2</sub>CH<sub>2</sub>N), 3.93 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OCH<sub>2</sub>CH<sub>2</sub>N). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, [ppm]) δ = 7.60, 7.79, 11.70, 47.57, 52.15, 52.41, 53.81, 56.86, 64.67, 69.71, 70.22, 70.33, 70.49, 176.52.*

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(6, [PEG400-(Et<sub>3</sub>N)<sub>2</sub>]Cl<sub>2</sub>). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, [ppm]) δ = 1.39 (18H, t, 2×(CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N, J = 9.0 Hz), 3.54-3.59 (12H, m, (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N), 3.62-3.64 (35H, m, NCH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OCH<sub>2</sub>CH<sub>2</sub>N), 3.71-3.76 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OCH<sub>2</sub>CH<sub>2</sub>N), 3.96 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OCH<sub>2</sub>CH<sub>2</sub>N). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, [ppm]) δ = 8.08, 54.10, 57.13, 64.58, 70.27, 70.43, 71.29.

(7, [PEG400-(Et-Im)<sub>2</sub>][OAc]<sub>2</sub>). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, [ppm]) δ = 1.56 (6H, t, 2×CH<sub>3</sub>CH<sub>2</sub>N, J = 9.0 Hz), 1.95 (6H, s, 2×CH<sub>3</sub>COO<sup>-</sup>), 3.63 (26H, m, NCH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OCH<sub>2</sub>CH<sub>2</sub>N), 3.86 (4H, t, NCH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OCH<sub>2</sub>CH<sub>2</sub>N, J = 6.0), 4.36 (4H, q, 2×CH<sub>3</sub>CH<sub>2</sub>N, J = 9.0 Hz), 4.58 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OCH<sub>2</sub>CH<sub>2</sub>N), 7.66 (2H, m, 2×NCHCHN). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, [ppm]) δ = 15.43, 25.20, 44.71, 49.19, 69.22, 70.08, 70.13, 70.27, 70.34, 120.91, 121.39, 123.32, 138.54, 177.50.

(8, [PEG400-(Et-Pip)<sub>2</sub>][OAc]<sub>2</sub>). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, [ppm]) δ = 1.36 (6H, t, 2×CH<sub>3</sub>CH<sub>2</sub>N, J = 6.0 Hz), 1.75 (4H, m, 2×CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 1.89 (4H, m, 2×CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 1.96 (6H, s, 2×CH<sub>3</sub>COO<sup>-</sup>), 3.49-3.60 (8H, m, 2×CH<sub>3</sub>CH<sub>2</sub>N, 2×CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 3.62-3.64 (27H, m, NCH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OCH<sub>2</sub>CH<sub>2</sub>N), 3.78 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OCH<sub>2</sub>CH<sub>2</sub>N), 3.94 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OCH<sub>2</sub>CH<sub>2</sub>N). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, [ppm]) δ = 7.14, 7.52, 19.68, 19.81, 20.85, 24.16, 25.70, 52.84, 54.50, 54.85, 57.71, 58.03, 58.31, 59.15, 64.39, 68.82, 70.20, 70.31, 70.47, 176.32.

(9, [PEG600-(Et-Pip)<sub>2</sub>][OAc]<sub>2</sub>). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, [ppm]) δ = 1.35 36 (6H, t, 2×CH<sub>3</sub>CH<sub>2</sub>N, J = 9.0 Hz), 1.73 (4H, m, 2×CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 1.88 (4H, m, 2×CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 1.95 6H, s, 2×CH<sub>3</sub>COO<sup>-</sup>), 3.42-3.57 (8H, m, 2×CH<sub>3</sub>CH<sub>2</sub>N, 2×CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 3.61-3.64 (43H, m, NCH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OCH<sub>2</sub>CH<sub>2</sub>N), 3.69-3.75 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OCH<sub>2</sub>CH<sub>2</sub>N), 3.93 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OCH<sub>2</sub>CH<sub>2</sub>N). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, [ppm]) δ = 7.07, 7.47, 19.61, 19.77, 20.86, 23.88, 24.00, 25.47, 54.61, 54.70, 57.82, 58.16, 59.29, 64.28, 68.55, 70.18, 70.27, 70.44, 176.43.

Triethyl (2-(2-methoxyethoxy)ethoxy)ethylammonium acetate (10, [Me(OEt)<sub>3</sub>-Et<sub>3</sub>N][OAc]). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, [ppm]) δ = 1.36 (9H, t, (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N, J = 7.2 Hz), 1.90 (3H, s, CH<sub>3</sub>COO<sup>-</sup>), 3.36 (3H, s, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.51 (6H, m, (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N), 3.61 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.66 (6H, m, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.71 (2H, t, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>, J = 4.4 Hz). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, [ppm]) δ = 7.63, 25.04, 53.70, 55.16, 56.74, 58.12, 58.75, 64.48, 70.13, 71.67, 176.52.

Triethyl (2-methoxyethoxy)ethylammonium acetate (11, [Me(OEt)<sub>2</sub>-Et<sub>3</sub>N][OAc]). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, [ppm]) δ = 1.37 (9H, t, (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N, J = 7.2 Hz), 1.91 (3H, s, CH<sub>3</sub>COO<sup>-</sup>), 3.35 (3H, s, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.53 (8H, m, (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N and NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.65 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.77 (2H, t, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>, J = 4.4 Hz).

N-ethyl N-(2-(2-methoxyethoxy)ethoxy)ethylpiperidinium acetate (12, [Me(OEt)<sub>3</sub>-Et-Pip][OAc]). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, [ppm]) δ = 1.36 (3H, t, CH<sub>3</sub>CH<sub>2</sub>N, J = 6.0 Hz), 1.75 (2H, t, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N, J = 3.0 Hz), 1.89 (4H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 1.93 (3H, s, CH<sub>3</sub>COO<sup>-</sup>), 3.36 (3H, s, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.52 (4H, m, CH<sub>3</sub>CH<sub>2</sub>N, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 3.60-3.72 (8H, m, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.77 (2H, m, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.95 (2H, t, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>, J = 6.0 Hz). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, [ppm]) δ = 7.01, 7.40, 19.56, 19.70, 20.73, 24.05, 24.41, 25.63, 54.34, 54.75, 57.71, 57.96, 58.25, 58.77, 59.07, 64.26, 68.70, 70.11, 71.69, 176.34.

N-ethyl N-(2-methoxyethoxy)ethylpiperidinium acetate (13, [Me(OEt)<sub>2</sub>-Et-Pip][OAc]). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, [ppm]) δ = 1.36 (3H, t, CH<sub>3</sub>CH<sub>2</sub>N, J = 7.2 Hz), 1.76 (2H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 1.90 (4H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 1.95 (3H, s, CH<sub>3</sub>COO<sup>-</sup>), 3.35 (3H, s, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.50-3.56 (4H, m, CH<sub>3</sub>CH<sub>2</sub>N, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 3.62-3.78 (4H, m, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.82 (2H, m, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.94 3.95 (2H, m, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, [ppm]) δ =

7.07, 7.45, 19.63, 19.77, 20.73, 24.45, 52.74, 54.37, 57.67, 57.90, 58.78, 58.98, 64.35, 70.29, 71.50, 77.00, 77.43, 77.64, 77.85, 176.25.

*N*-(2-(2-methoxyethoxy)ethoxy)ethyl *N*-methylpiperidinium dimethylphosphate (**14**, [TEGM-Me-Pip][Me<sub>2</sub>PO<sub>4</sub>]). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, [ppm]) δ = 1.71 (2H, t, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N, *J* = 3.0 Hz), 1.90 (4H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 3.36 (3H, s, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.51-3.54 (2H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 3.56 (3H, s, CH<sub>3</sub>N), 3.59 (6H, s, POCH<sub>3</sub>), 3.61-3.80 (8H, m, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.91 (2H, m, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 3.98 (2H, m, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, [ppm]) δ = 20.25, 20.47, 20.74, 20.83, 22.06, 22.33, 22.86, 44.16, 48.66, 52.48, 52.56, 53.58, 58.97, 62.00, 62.33, 62.52, 64.83, 70.21, 70.34, 71.85.

Tetra-*n*-butylphosphonium acetate (**15**, [Bu<sub>4</sub>P][OAc]). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, [ppm]) δ = 0.98 (12H, t, 4 × CH<sub>3</sub>-, *J* = 5.2 Hz), 1.46-1.60 (16H, m, 4 × CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 1.93 (3H, s, CH<sub>3</sub>COO<sup>-</sup>), 2.36-2.46 (8H, m, 4 × CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, [ppm]) δ = 13.42, 18.28, 18.90, 23.73, 23.79, 23.84, 24.04, 25.56, 176.60.