Electronic Supplementary Material (ESI) for New Journal of Chemistry

Columnar Thermotropic Mesophases formed by Dimeric Liquid-Crystalline Ionic Liquids Exhibiting Large Mesophase Ranges

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Synthesis of 1,1'-(1,6-hexanediyl)bis{3-[3,4,5-tris(octyloxy)benzyl]imidazolium} chloride (2-8,6)

Compound **2**-8,6 was produced from **IM-6-IM** and 3,4,5-tris(octyloxy)benzyl chloride in a manner similar to that employed in the synthesis of **2**-8,4, but with a different scale. Yield = 2.22 g (89.6%) as a white solid. ^{1}H NMR (400 MHz): δ = 10.99 (s, 2H), 7.65 (t, 2H), 6.99 (t, 2H), 6.60 (s, 4H), 5.39 (s, 4H), 4.41 (t, 4H), 3.96-3.90 (m, 12H), 2.03 (t, 4H), 1.78-1.68 (m, 12H), 1.51-1.24 (m, 64H), 0.88-0.85 (m, 18H). ^{13}C NMR (100 MHz): δ = 153.9, 139.0, 137.6, 127.7, 122.9, 121.1, 107.6, 73.5, 69.5, 53.9, 49.6, 32.0, 31.9, 30.4, 29.6, 29.5, 29.4, 26.6, 26.2, 22.8, 14.2.

Synthesis of 1,1'-(1,8-octanediyl)bis{3-[3,4,5-tris(octyloxy)benzyl]imidazolium} chloride (2-8,8)

Compound **2**-8,8 was produced from **IM-8-IM** and 3,4,5-tris(octyloxy)benzyl chloride in a manner similar to that employed in the synthesis of **2**-8,4, but with a different scale. Yield = 3.50 g (55.2%) as a white solid. ^{1}H NMR (400 MHz): δ = 10.99 (s, 2H), 7.53 (t, 2H), 7.14 (t, 2H), 6.62 (s, 4H), 5.42 (s, 4H), 4.34 (t, 4H), 3.95-3.89 (m, 12H), 2.02 (t, 4H), 1.79-1.67 (m, 12H), 1.45-1.25 (m, 64H), 0.87-0.84

(m, 18H). ^{13}C NMR (100 MHz): δ = 153.8, 138.9, 137.6, 127.9, 122.5, 121.4, 107.6, 73.5, 69.5, 53.9, 49.9, 32.0, 31.9, 30.4, 29.6, 29.5, 29.4, 27.7, 26.2, 25.4, 22.8, 14.2.

Synthesis of 1,1'-(1,4-butanediyl)bis{3-[3,4,5-tris(dodecyloxy)benzyl]imidazolium} chloride (2-12,4)

Compound **2**-12,4 was produced from **IM-4-IM** and 3,4,5-tris(dodecyloxy)benzyl chloride in a manner similar to that employed in the synthesis of **2**-8,4. Yield = 5.72 g (74.2%) as a white solid. ^{1}H NMR (400 MHz): δ = 10.57 (s, 2H), 7.86 (t, 2H), 7.04 (t, 2H), 6.59 (s, 4H), 5.30 (s, 4H), 4.54 (t, 4H), 3.95-3.90 (m, 12H), 2.18 (t, 4H), 1.80-1.67 (m, 12H), 1.48-1.24 (m, 64H), 0.87-0.84 (m, 18H). ^{13}C NMR (100 MHz): δ = 154.0, 139.1, 137.4, 127.1, 123.1, 121.0, 107.5, 73.6, 69.5, 53.9, 49.6, 32.0, 31.4, 30.4, 29.9, 29.8, 29.7, 29.6, 29.5, 26.3, 26.2, 22.8, 14.2.

Synthesis of 1,1'-(1,6-hexanediyl)bis{3-[3,4,5-tris(dodecyloxy)benzyl]imidazolium} chloride (2-12,6)

Compound **2**-12,6 was produced from **IM-6-IM** and 3,4,5-tris(dodecyloxy)benzyl chloride in a manner similar to that employed in the synthesis of **2**-8,4, but with a different scale. Yield = 2.84 g (90.1%) as a white solid. ^{1}H NMR (400 MHz): δ = 10.88 (s, 2H), 7.73 (t, 2H), 7.09 (t, 2H), 6.60 (s, 4H), 5.37 (s, 4H), 4.40 (t, 4H), 3.94-3.89 (m, 12H), 2.02 (t, 4H), 1.79-1.66 (m, 12H), 1.48-1.23 (m, 64H), 0.87-0.83 (m, 18H). ^{13}C NMR (100 MHz): δ = 153.9, 138.9, 137.8, 127.6, 122.4, 121.0, 107.6, 73.6, 69.6, 54.0, 49.5, 32.0, 30.4, 29.9, 29.8, 29.7, 29.6, 29.5, 29.2, 26.2, 24.5, 22.8, 14.2.

Synthesis of 1,1'-(1,8-octanediyl)bis{3-[3,4,5-tris(dodecyloxy)benzyl]imidazolium} chloride (2-12,8)

Compound **2**-12,8 was produced from **IM-8-IM** and 3,4,5-tris(dodecyloxy)benzyl chloride in a manner similar to that employed in the synthesis of **2**-8,4. Yield = 7.80 g (97%) as a white solid. ^{1}H NMR (400 MHz): δ = 11.06 (s, 2H), 7.51 (t, 2H), 7.13 (t, 2H), 6.62 (s, 4H), 5.42 (s, 4H), 4.34 (t, 4H), 3.95-3.89 (m, 12H), 1.97 (t, 4H), 1.79-1.67 (m, 12H), 1.47-1.24 (m, 64H), 0.87-0.84 (m, 18H). ^{13}C NMR (100 MHz): δ = 153.8, 138.9, 137.7, 127.8, 122.3, 121.3, 107.6, 73.5, 69.5, 53.9, 49.9, 32.0, 30.4, 29.9, 29.8, 29.7, 29.6, 29.5, 27.6, 26.2, 25.3, 22.8, 14.2.

Synthesis of 1,1'-(1,6-hexanediyl)bis{3-[3,4,5-tris(octyloxy)benzyl]imidazolium} tetrafluoroborate (3-8,6**)**

Compound **3**-8,6 was produced from **2**-8,6 and $AgBF_4$ in a manner similar to that employed in the synthesis of **3**-8,4, but with a different scale. Yield = 0.97 g (87.4%) as a white solid. ^{1}H NMR (500 MHz): δ = 8.92 (s, 2H), 7.35 (t, 2H), 7.14 (t, 2H), 6.60 (s, 4H), 5.21 (s, 4H), 4.17 (t, 4H), 3.97-3.90 (m, 12H), 1.90 (t, 4H), 1.80-1.68 (m, 12H), 1.48-1.26 (m, 64H), 0.88-0.84 (m, 18H). ^{13}C NMR (100 MHz): δ = 153.9, 138.9, 135.8, 128.9, 127.6, 122.5, 121.8, 107.5, 73.5, 69.3, 54.1, 49.6, 32.0, 31.9, 30.4, 29.6, 29.5, 29.4, 29.0, 26.2, 24.3, 22.8, 14.2. ESI-MS (methanol, m/z): 1343.9987 (1344.00 calculated [M]+ $C_{74}H_{128}B_2F_8N_4O_6$).

Synthesis of 1,1'-(1,8-octanediyl)bis{3-[3,4,5-tris(octyloxy)benzyl]imidazolium} tetrafluoroborate (3-8,8)

Compound **3**-8,8 was produced from **2**-8,8 and $AgBF_4$ in a manner similar to that employed in the synthesis of **3**-8,4, but with a different scale. Yield = 2.30 g (83.9%) as a white solid. ^{1}H NMR (500 MHz): δ = 8.99 (s, 2H), 7.26 (t, 2H), 7.15 (t, 2H), 6.62 (s, 4H), 5.24 (s, 4H), 4.18 (t, 4H), 3.96-3.90 (m, 12H), 1.97 (t, 4H), 1.80-1.68 (m, 12H), 1.48-1.26 (m, 72H), 0.88-0.84 (m, 18H). ^{13}C NMR (100 MHz): δ = 153.9, 138.9, 136.0, 127.7, 122.1, 121.8, 107.6, 73.5, 69.3, 54.0, 49.9, 32.0, 30.4, 29.6, 29.5,

29.4, 29.2, 27.3, 26.1, 26,2, 24.8, 22.8, 14.2. ESI-MS (methanol, m/z): 1372.0300 (1372.03 calculated [M]+ $C_{76}H_{132}B_2F_8N_4O_6$).

Synthesis of 1,1'-(1,4-butanediyl)bis{3-[3,4,5-tris(dodecyloxy)benzyl]imidazolium} tetrafluoroborate (3-12,4)

Compound **3**-12,4 was produced from **2**-12,4 and $AgBF_4$ in a manner similar to that employed in the synthesis of **3**-8,4, but with a different scale. Yield = 2.14 g (64.8%) as a white solid. ^{1}H NMR (500 MHz): δ = 8.82 (s, 2H), 7.40 (t, 2H), 7.10 (t, 2H), 6.57 (s, 4H), 5.17 (s, 4H), 4.23 (t, 4H), 3.96-3.90 (m, 12H), 1.99 (t, 4H), 1.80-1.68 (m, 12H), 1.48-1.25 (m, 112H), 0.88-0.85 (m, 18H). ^{13}C NMR (100 MHz): δ = 154.0, 139.0, 135.6, 127.2, 122.8, 121.7, 107.5, 73.6, 54.2, 49.3, 32.0, 30.4, 29.9, 29.8, 29.7, 29.6, 29.5, 26.2, 22.8, 14.2. ESI-MS (methanol, m/z): 1352.3416 (1352.34 calculated [M]+ $C_{96}H_{172}B_2F_8N_4O_6$).

Synthesis of 1,1'-(1,6-hexanediyl)bis{3-[3,4,5-tris(dodecyloxy)benzyl]imidazolium} tetrafluoroborate (3-12,6)

Compound **3**-12,6 was produced from **2**-12,6 and $AgBF_4$ in a manner similar to that employed in the synthesis of **3**-8,4, but with a different scale. Yield = 1.21g (85.9%) as a white solid. ^{1}H NMR (500 MHz): δ = 8.91 (s, 2H), 7.33 (t, 2H), 7.12 (t , 2H), 6.59 (s, 4H), 5.20 (s, 4H), 4.16 (t, 4H), 3.95-3.89 (m, 12H), 1.89 (t, 4H), 1.76-1.67 (m, 12H), 1.46-1.24 (m, 112H), 0.86 (m, 18H). ^{13}C NMR (100 MHz): δ = 153.9, 139.0, 135.9, 127.5, 122.4, 121.8, 107.5, 73.5, 69.4, 54.1, 49.7, 32.0, 30.5, 29.9, 29.8, 29.7, 29.6, 29.5, 28.9, 26.3, 26.2, 24.3, 22.8, 14.2. ESI-MS (methanol, m/z): 1680.3729 (1680.37 calculated [M]+ $C_{98}H_{176}B_2F_8N_4O_6$).

Synthesis of 1,1'-(1,8-octanediyl)bis{3-[3,4,5-tris(dodecyloxy)benzyl]imidazolium} tetrafluoroborate (3-12,8)

Compound **3**-12,8 was produced from **2**-12,8 and $AgBF_4$ in a manner similar to that employed in the synthesis of **3**-8,4. Yield = 2.81 g (82.4%) as a white solid. ^{1}H NMR (500 MHz): δ = 9.03 (s, 2H), 7.25 (t, 2H), 7.15 (t , 2H), 6.61 (s, 4H), 5.25 (s, 4H), 4.18 (t, 4H), 3.96-3.90 (m, 12H), 1.89 (t, 4H), 1.79-1.68 (m, 12H), 1.48-1.25 (m, 120H), 0.88-0.85 (m, 18H). ^{13}C NMR (100 MHz): δ = 153.9, 138.9, 136.1, 127.7, 122.0, 121.8, 107.6, 73.5, 69.4, 54.0, 49.9, 32.0, 30.4, 29.9, 29.8, 29.7, 29.6, 29.5, 29.2, 27.2, 26.2, 24.8, 22.8, 14.2. ESI-MS (methanol, m/z): 1708.4042 (1708.40 calculated [M]+ $C_{100}H_{180}B_2F_8N_4O_6$).

Synthesis of 1,1'-(1,8-octanediyl)bis{3-[3,4,5-tris(octyloxy)benzyl]imidazolium} bis(trifluoro-methylsulfonyl)imide (4-8,8)

Compound **4**-8,8 was produced from **2**-8,8 and $LiTf_2N$ in a manner similar to that employed in the synthesis of **4**-8,4. Yield = 0.71 g (80.6%) as a very viscous liquid. $AgBF_4$ test shows no Cl^- existing. ^{1}H NMR (500 MHz): δ = 8.86 (s, 2H), 7.30 (t, 2H), 7.17 (t, 2H), 6.55 (s, 4H), 5.17 (s, 4H), 4.16 (t, 4H), 3.94-3.91 (m, 12H), 1.86 (t, 4H), 1.80-1.68 (m, 12H), 1.48-1.26 (m, 120H), 0.88-0.84 (m, 18H). ^{13}C NMR (100 MHz): δ = 154.0, 138.9, 135.3, 127.2, 122.5, 122.0, 121.5, 107.4, 73.6, 69.3, 54.1, 50.2, 32.0, 31.9, 30.4, 29.6, 29.5, 29.4, 27.7, 22.8, 14.2.

Synthesis of 1,1'-(1,4-butanediyl)bis{3-[3,4,5-tris(dodecyloxy)-benzyl]imidazolium} bis(trifluoromethylsulfonyl)imide (4-12,4)

Compound **4**-12,4 was produced from **2**-12,4 and $LiTf_2N$ in a manner similar to that employed in the synthesis of **4**-8,4. Yield = 0.87 g (85.4%) as a white solid. $AgBF_4$ test shows no Cl^- existing. ^{1}H NMR (500 MHz): δ = 8.82 (s, 2H), 7.41 (t, 2H), 7.11 (t, 2H), 6.52 (s, 4H), 5.14 (s, 4H), 4.26 (t, 4H), 3.94-3.90 (m, 12H), 2.02 (t, 4H), 1.80-1.68 (m, 12H), 1.46-1.24 (m, 120H), 0.88-0.84 (m, 18H). ^{13}C NMR (100 MHz):

δ = 154.1, 139.2, 135.2, 126.7, 123.0, 122.0, 121.4, 107.5, 73.6, 69.4, 54.4, 49.4, 32.0, 32.0, 30.4, 29.9, 29.8, 29.7, 29.5, 29.4, 27.2, 26.2, 22.8, 22.8, 14.2.

Synthesis of 1,1'-(1,8-octanediyl)bis{3-[3,4,5-tris(dodecyloxy)benzyl]imidazolium} bis(tri-fluoromethylsulfonyl)imide (4-12,8**)**

Compound **4**-12,8 was produced from **2**-12,8 and $LiTf_2N$ in a manner similar to that employed in the synthesis of **4**-8,4. Yield = 0.86 g (81.1%) as a white solid. $AgBF_4$ test shows no Cl^- existing. ^1H NMR (500 MHz): δ = 8.88 (s, 2H), 7.29 (t, 2H), 7.15 (t , 2H), 6.55 (s, 4H), 5.18 (s, 4H), 4.17 (t, 4H), 3.94-3.91 (m, 12H), 1.87 (t, 4H), 1.80-1.68 (m, 12H), 1.46-1.24 (m, 120H), 0.88-0.84 (m, 18H). ^{13}C NMR (100 MHz): δ = 154.0, 139.1, 135.4, 127.1, 122.4, 121.9, 121.5, 121.4, 118.3, 107.5, 73.6, 69.4, 54.0, 50.2, 32.0, 32.0, 30.4, 29.9, 29.8, 29.8, 29.8, 29.7, 29.5, 29.5, 29.4, 27.6, 22.8, 22.8, 14.2.

Synthesis of 1-methyl-3-[3,4,5-tris(octyloxy)benzyl]imidazolium chloride (5-8**)**

The compound was produced according to the previous paper.[S1] ^1H NMR (500 MHz): δ = 0.86 (t, 9H), 1.26-1.49 (m, 30H), 1.69-1.81 (m, 6H), 3.94 (t, 6H), 4.06 (s, 3H), 5.39 (s, 2H), 6.61 (s, 2H), 7.046 (t, 1H), 7.049 (t, 1H), 11.23 (s, 1H). ^{13}C NMR (100 MHz): δ = 14.2, 22.8, 26.2, 29.4, 29.5, 29.6, 30.4, 31.9, 32.0, 36.8, 54.1, 69.6, 73.6, 107.7, 121.1, 123.0, 127.4, 154.0.

Synthesis of 1-methyl-3-[3,4,5-tris(decyloxy)benzyl]imidazolium chloride (5-10**)**

The compound was produced in a manner similar to that employed in the synthesis of 1-methyl-3-[3,4,5-tris(dodecyloxy)benzyl]imidazolium chloride (**5**-12) reported before.[S1] The difference is that 1-bromodecane was used as instead. ^1H NMR (500 MHz): δ = 0.86 (t, 9H), 1.26-1.49 (m, 42H), 1.69-1.81 (m, 6H), 3.94 (t, 6H), 4.06 (s,

3H), 5.39 (s, 2H), 6.61 (s, 2H), 7.046 (t, 1H), 7.049 (t, 1H), 11.24 (s, 1H). ^{13}C NMR (100 MHz): δ = 14.2, 22.8, 26.2, 29.5, 29.7, 29.8, 30.4, 32.0, 36.8, 54.1, 69.6, 73.6, 107.7, 121.1, 122.6, 127.4, 130.1, 139.1, 154.0.

Synthesis of 1-methyl-3-[3,4,5-tris(dodecyloxy)benzyl]imidazolium chloride (5-12)

The compound was produced according to the previous paper.[S1] ^{1}H NMR (500 MHz): δ = 0.86 (t, 9H), 1.26-1.49 (m, 54H), 1.69-1.81 (m, 6H), 3.94 (t, 6H), 4.06 (s, 3H), 5.39 (s, 2H), 6.61 (s, 2H), 7.03 (t, 1H), 7.06 (t, 1H), 11.29 (s, 1H). ^{13}C NMR (100 MHz): δ = 14.2, 22.8, 26.2, 29.5, 29.7, 29.8, 30.4, 32.0, 36.7, 53.9, 69.5, 73.5, 107.6, 121.4, 123.0, 127.7, 138.4, 139.0, 153.9.

Synthesis of 1-Methyl-3-[3,4,5-tris(tetradecyloxy)benzyl]imidazolium chloride (5-14)

The compound was produced in a manner similar to that employed in the synthesis of **5**-12 reported before.[S1] The difference is that 1-bromotetradecane was used as instead. ^{1}H NMR (400 MHz): δ = 0.86 (t, 9H), 1.24-1.48 (m, 54H), 1.67-1.88 (m, 6H), 3.93 (t, 6H), 4.07 (s, 3H), 5.40 (s, 2H), 6.62 (s, 2H), 7.08 (t, 1H), 7.13 (t, 1H), 11.07 (s, 1H). ^{13}C NMR (100 MHz): δ = 14.2, 22.8, 26.2, 29.5, 29.7, 29.8, 30.4, 32.0, 36.8, 54.0, 69.6, 73.6, 107.7, 121.2, 122.7, 127.4, 138.9, 154.0.

Synthesis of 1-methyl-3-[3,4,5-tris(octyloxy)benzyl]imidazolium tetrafluoroborate (6-8)

The compound was produced according to the previous paper.[S1] ^{1}H NMR (500 MHz): δ = 0.86 (t, 9H), 1.26-1.49 (m, 30H), 1.69-1.81 (m, 6H), 3.94-3.90 (m, 9H), 5.17 (s, 2H), 6.58 (s, 2H), 7.14 (t, 1H), 7.17 (t, 1H), 8.84 (s, 1H). ^{13}C NMR (100 MHz): δ =

14.2, 22.8, 26.2, 29.4, 29.5, 29.6, 30.4, 31.9, 32.0, 36.5, 54.0, 69.4, 73.5, 107.5, 121.7, 123.3, 127.4, 136.8, 139.0, 154.0.

Synthesis of 1-methyl-3-[3,4,5-tris(decyloxy)benzyl]imidazolium tetrafluoroborate (6-10)

The compound was produced in a manner similar to that employed in the synthesis of **6**-8 or **3**-8,4. ^{1}H NMR (500 MHz): δ = 0.86 (t, 9H), 1.26-1.49 (m, 42H), 1.69-1.81 (m, 6H), 3.94-3.90 (m, 9H), 5.18 (s, 2H), 6.58 (s, 2H), 7.11 (t, 1H), 7.14 (t, 1H), 8.93 (s, 1H). ^{13}C NMR (100 MHz): δ = 14.2, 22.8, 26.2, 29.4, 29.5, 29.7, 29.8, 30.4, 32.0, 36.6, 54.2, 69.5, 73.6, 107.6, 121.7, 123.1, 127.1, 137.0, 139.2, 154.0.

Synthesis of 1-methyl-3-[3,4,5-tris(dodecyloxy)benzyl]imidazolium tetrafluoroborate (6-12)

The compound was produced according to the previous paper.[S1] ^{1}H NMR (500 MHz): δ = 0.86 (t, *J* = 6.8 Hz, 9H), 1.26-1.49 (m, 54H), 1.69-1.81 (m, 6H), 3.94-3.90 (m, 9H), 5.17 (s, 2H), 6.58 (s, 2H), 7.12 (s, 1H), 7.14 (s, 1H), 8.90 (s, 1H). ^{13}C NMR (100 MHz): δ = 14.2, 22.8, 26.2, 29.5, 29.6, 29.7, 29.8, 30.4, 32.0, 36.5, 54.1, 69.5, 73.5, 107.6, 121.7, 123.2, 127.2, 137.0, 139.1, 154.0.

Synthesis of 1-methyl-3-[3,4,5-tris(tetradecyloxy)benzyl]imidazolium tetrafluoroborate (6-14)

The compound was produced in a manner similar to that employed in the synthesis of **6**-8 or **3**-8,4. ^{1}H NMR (500 MHz): δ = 0.87 (t, 9H), 1.24-1.48 (m, 54H), 1.68-1.79 (m, 6H), 3.94-3.90 (m, 9H), 5.17 (s, 2H), 6.59 (s, 2H), 7.16 (s, 1H), 7.18 (s, 1H), 8.84 (s, 1H). ^{13}C NMR (100 MHz): δ = 14.22, 22.79, 26.24, 29.5, 29.6, 29.7, 29.8, 29.9, 30.4, 32.0, 36.5, 54.0, 69.4, 73.5, 107.5, 121.8, 123.3, 127.4, 136.7, 139.0, 154.0.

Synthesis of 1-methyl-3-[3,4,5-tris(octyloxy)benzyl]imidazolium bis(trifluoromethylsulfonyl)imide (7-8)

The compound was produced according to the previous paper.[S2] ^{1}H NMR (500 MHz): δ = 0.86 (t, 9H), 1.26-1.49 (m, 30H), 1.69-1.81 (m, 6H), 3.93-3.90 (m, 9H), 5.28 (s, 2H), 6.55 (s, 2H), 7.15 (s, 1H), 7.17 (s, 1H), 8.82 (s, 1H). ^{13}C NMR (100 MHz): δ = 14.2, 22.7, 22.8, 26.1, 26.2, 29.3, 29.4, 29.6, 30.4, 31.9, 32.0, 36.6, 54.2, 69.4, 73.6, 107.6, 121.9, 123.4, 126.8, 136.3, 139.3, 154.1.

Synthesis of 1-methyl-3-[3,4,5-tris(decyloxy)benzyl]imidazolium bis(trifluoromethylsulfonyl)imide (7-10)

The compound was produced in a manner similar to that employed in the synthesis of **7**-8 or **4**-8,4. ^{1}H NMR (500 MHz): δ = 0.86 (t, 9H), 1.26-1.49 (m, 42H), 1.69-1.81 (m, 6H), 3.93-3.90 (m, 9H), 5.18 (s, 2H), 6.55 (s, 2H), 7.14 (s, 1H), 7.16 (s, 1H), 8.84 (s, 1H). ^{13}C NMR (100 MHz): δ = 14.2, 22.8, 26.1, 26.2, 29.4, 29.5, 29.7, 29.8, 30.4, 32.0, 36.7, 54.3, 69.5, 73.6, 107.7, 121.9, 123.3, 126.7, 136.4, 139.3, 154.1.

Synthesis of 1-methyl-3-[3,4,5-tris(dodecyloxy)benzyl]imidazolium bis(trifluoromethylsulfonyl)imide (7-12)

The compound was produced according to the previous paper.[S1] ^{1}H NMR (500 MHz): δ = 0.87 (t, 9H), 1.25-1.46 (m, 54H), 1.69-1.81 (m, 6H), 3.95-3.92 (m, 9H), 5.19 (s, 2H), 6.56 (s, 2H), 7.16 (t, 1H), 7.18 (t, 1H), 8.83 (s, 1H). ^{13}C NMR (100 MHz): δ = 14.2, 22.8, 26.2, 29.4, 29.5, 29.7, 29.8, 32.0, 36.6, 54.2, 69.4, 73.6, 107.6, 121.9, 123.4, 126.8, 136.3, 139.2, 154.1.

Synthesis of 1-methyl-3-[3,4,5-tris(tetradecyloxy)benzyl]imidazolium

bis(trifluoromethylsulfonyl)imide (7-14)

The compound was produced in a manner similar to that employed in the synthesis of **7**-8 or **4**-8,4. ^{1}H NMR (500 MHz): δ = 0.87 (t, 9H), 1.25-1.46 (m, 54H), 1.68-1.80 (m, 6H), 3.95-3.91 (9H), 5.19 (s, 2H), 6.57 (s, 2H), 7.17 (t, 1H), 7.19 (t, 1H), 8.95 (s, 1H). ^{13}C NMR (100 MHz): 14.2, 22.8, 26.2, 29.5, 29.7, 29.8, 30.4, 32.0, 36.6, 54.2, 69.4, 73.6, 107.6, 121.9, 123.4, 126.9, 136.4, 139.2, 154.1.

Table S1: Elemental analytical data for all compounds

	Calculated (Found)/%			
Compound	**C**	**H**	**N**	***x*H$_2$O†**
2-8,4	68.86 (68.90)	10.34 (10.09)	4.46 (4.67)	2.4
2-8,6	69.03 (68.72)	10.43 (10.18)	4.35 (4.32)	2.6
2-8,8	69.48 (69.32)	10.51 (10.29)	4.26 (4.49)	2.5
2-12,4	73.06 (73.33)	11.19 (11.03)	3.55 (3.27)	1.6
2-12,6	72.81 (72.69)	11.25 (10.95)	3.47 (3.55)	2.1
2-12,8	73.01 (72.96)	11.30 (11.18)	3.41 (3.58)	2.2
3-8,4	65.74 (65.89)	9.50 (9.49)	4.26 (3.98)	–
3-8,6	66.16 (66.30)	9.60 (9.65)	4.17 (4.26)	–
3-8,8	66.56 (66.68)	9.70 (9.69)	4.09 (4.13)	–
3-12,4	69.79 (69.89)	10.49 (10.49)	3.39 (3.36)	–
3-12,6	70.06 (70.10)	10.56 (10.52)	3.33 (3.41)	–
3-12,8	70.31 (70.57)	10.62 (10.51)	3.28 (3.17)	–
4-8,4	53.64 (53.68)	7.34 (7.37)	4.94 (4.97)	–
4-8,8	54.65 (54.29)	7.57 (7.54)	4.78 (4.80)	–
4-12,4	58.91 (59.23)	8.50 (8.55)	4.12 (4.13)	–
4-12-8	59.63 (59.44)	8.66 (8.61)	4.01 (4.09)	–
5-8	70.00 (69.95)	10.37 (10.41)	4.72 (4.75)	0.4
5-10	72.30 (72.44)	10.86 (10.96)	4.11 (4.10)	0.2
5-12	73.42 (73.32)	11.25 (11.25)	3.64 (3.56)	0.4
5-14	74.94 (74.95)	11.56 (11.60)	3.30 (3.25)	0.2
6-8	64.30 (64.90)	9.40 (9.40)	4.40 (4.30)	–
6-10	67.21 (67.23)	10.01 (9.94)	3.92 (3.86)	–
6-12	69.15 (69.49)	10.47 (10.47)	3.51 (3.44)	–
6-14	70.72 (70.70)	10.84 (10.79)	3.17 (3.14)	–

7-8	53.03 (53.07)	7.34 (7.27)	5.01 (4.90)	–
7-10	56.00 (55.99)	7.98 (7.89)	4.56 (4.50)	–
7-12	58.48 (58.56)	8.39 (8.51)	4.18 (4.13)	–
7-14	60.58 (60.51)	8.97 (8.99)	3.85 (3.84)	–

† The water content of all compounds was measured by Karl Fischer and it was found that the chlorides easily absorb water from the air. The lower values for compounds **5**-*n* shows the effect of drying under vacuum. Where non-zero values are given for *x* (degree of hydration), the values of *x* were obtained by Karl Fischer titration.

Reference:

S1. M. Yoshio, T. Mukai, H. Ohno and T. Kato, *J. Am. Chem. Soc.,* 2004, **126**, 994.

S2. M. Yoshio, T. Ichikawa, H. Shimura, T. Kagata, A. Hamasaki, T. Mukai, H. Ohno and T. Kato, *Bull. Chem. Soc. Jpn.,* 2007, **80**, 1836.