

Supplementary Information

Characterization and Solution Properties of Quaternary-Ammonium-Salt-Type

Amphiphilic Trimeric Ionic Liquids

Risa Kawai, Shiho Yada, and Tomokazu Yoshimura*

*Department of Chemistry, Faculty of Science, Nara Women's University, Kitaoyanishi-
machi, Nara 630-8506, Japan*

*Corresponding author.

E-mail address: yoshimura@cc.nara-wu.ac.jp (T. Yoshimura)

S1. Synthesis of Quaternary-Ammonium-Salt-Type Amphiphilic Trimeric Ionic Liquids.

The structure of tris(*N*-alkyl-*N*, *N*-dimethyl-2-ammonioethyl)amine tribromide ($3C_n\text{tris-2-Q Br}$), $3C_n\text{tris-2-Q X}$, tris(*N*-alkyl-*N*, *N*-dimethyl-3-ammoniopropyl)amine tribromide ($3C_n\text{tris-3-Q Br}$), $3C_n\text{tris-3-Q X}$, methylalkylbis[3- (dimethylalkylammonio)propyl]ammonium tribromide, ($3C_n\text{lin-3-Q Br}$), and $3C_n\text{lin-3-Q X}$ were determined by ^1H NMR (Bruker Ultrashield 300MHz, Billerica, MA, USA), and elemental analysis (Perkin-Elmer 2400II CHNS/O, Waltham, MA, USA).

S1.1. Tris(*N*-alkyl-*N*, *N*-dimethyl-2-ammonioethyl)amine Tribromide ($3C_n\text{tris-2-Q Br}$).

The yields were as follows: $3C_8\text{tris-2-Q I}$: 38 %, $3C_{10}\text{tris-2-Q I}$: 35 %, $3C_{12}\text{tris-2-Q Br}$: 36 %, $3C_{14}\text{tris-2-Q Br}$: 40 %.

^1H NMR (CDCl_3 , TMS):

$3C_8\text{tris-2-Q I}$. δ 0.883 (t, 18H, $\text{CH}_3-(\text{CH}_2)_{n-1}-\text{N}^+$), 1.27–1.38 (m, 30H, $\text{CH}_3-(\text{CH}_2)_5-\text{CH}_2-\text{CH}_2-\text{N}^+$), 1.78 (m, 6H, $\text{CH}_3-(\text{CH}_2)_5-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.40 (s, 18H, $-\text{N}^+(\text{CH}_3)_2$), 3.48 (t, 6H, $\text{N}-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.64 (t, 6H, $\text{CH}_3-(\text{CH}_2)_5-\text{CH}_2-\text{CH}_2-\text{N}^+$), 4.12 ppm (t, 6H, $\text{N}-\text{CH}_3-\text{CH}_2-\text{N}^+$).

$3C_{10}\text{tris-2-Q I}$. δ 0.882 (t, 18H, $\text{CH}_3-(\text{CH}_2)_9-\text{N}^+$), 1.26–1.38 (m, 3H, $\text{CH}_3-(\text{CH}_2)_7-\text{CH}_2-\text{CH}_2-\text{N}^+$), 1.79 (m, 6H, $\text{CH}_3-(\text{CH}_2)_7-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.40 (s, 18H, $-\text{N}^+(\text{CH}_3)_2$), 3.48 (t, 6H, $\text{N}-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.64 (t, 6H, $\text{CH}_3-(\text{CH}_2)_7-\text{CH}_2-\text{CH}_2-\text{N}^+$), 4.13 ppm (t, 6H, $\text{N}-\text{CH}_3-\text{CH}_2-\text{N}^+$).

$3C_{12}\text{tris-2-Q Br}$. δ 0.882 (t, 18H, $\text{CH}_3-(\text{CH}_2)_{11}-\text{N}^+$), 1.25–1.38 (m, 3H, $\text{CH}_3-(\text{CH}_2)_9-\text{CH}_2-\text{CH}_2-\text{N}^+$), 1.75 (m, 6H, $\text{CH}_3-(\text{CH}_2)_9-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.44 (s, 18H, $-\text{N}^+(\text{CH}_3)_2$), 3.48 (t, 6H, $\text{N}-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.62 (t, 6H, $\text{CH}_3-(\text{CH}_2)_9-\text{CH}_2-\text{CH}_2-\text{N}^+$), 4.06 ppm (t, 6H, $\text{N}-\text{CH}_3-\text{CH}_2-\text{N}^+$).

$3C_{14}\text{tris-2-Q Br}$. δ 0.881 (t, 18H, $\text{CH}_3-(\text{CH}_2)_{13}-\text{N}^+$), 1.25–1.37 (m, 3H, $\text{CH}_3-(\text{CH}_2)_{11}-\text{CH}_2-\text{CH}_2-\text{N}^+$), 1.75 (m, 6H, $\text{CH}_3-(\text{CH}_2)_{11}-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.37 (s, 18H, $-\text{N}^+(\text{CH}_3)_2$), 3.43 (t, 6H, $\text{N}-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.66 (t, 6H, $\text{CH}_3-(\text{CH}_2)_{11}-\text{CH}_2-\text{CH}_2-\text{N}^+$), 4.14 ppm (m, 6H, $\text{N}-\text{CH}_3-\text{CH}_2-\text{N}^+$).

Elemental analysis:

$3C_8\text{tris-2-Q I}$. Calcd. for $\text{C}_{38}\text{H}_{81}\text{N}_4\text{I}_3$: C, 38.33; H, 8.42; N, 7.55. Found: C, 38.68; H, 9.78; N, 7.64.

$3C_{10}\text{tris-2-Q I}$. Calcd. for $\text{C}_{42}\text{H}_{93}\text{N}_4\text{I}_3$: C, 48.74; H, 9.06; N, 5.41. Found: C, 48.65; H, 9.24; N, 5.81.

$3C_{12}\text{tris-2-Q Br}$. Calcd. for $\text{C}_{48}\text{H}_{105}\text{N}_4\text{Br}_3$: C, 58.94; H, 10.82; N, 5.73. Found: C, 58.35; H, 11.03; N, 5.70.

$3C_{14}\text{tris-2-Q Br}$. Calcd. for $\text{C}_{54}\text{H}_{117}\text{N}_4\text{Br}_3 \cdot 2\text{H}_2\text{O}$: C, 59.05; H, 11.11; N, 5.10. Found: C, 59.04; H, 11.33; N, 5.44.

S1. 2. Tris(*N*-alkyl-*N*, *N*-dimethyl-3-ammoniopropyl)amine Tribromide ($3C_n\text{tris-3-Q Br}$).

The yields were as follows: $3C_8\text{tris-3-Q Br}$: 48 %, $3C_{10}\text{tris-3-Q Br}$: 92 %, $3C_{12}\text{tris-3-Q Br}$: 86 %, $3C_{14}\text{tris-3-Q Br}$: 86 %.

^1H NMR (CDCl_3 , TMS):

$3C_8\text{tris-3-Q Br}$. δ 0.878 (t, 9H, $\text{CH}_3-(\text{CH}_2)_{11}-\text{N}^+$), 1.27–1.36 (m, 30H, $\text{CH}_3-(\text{CH}_2)_9-\text{CH}_2-\text{CH}_2-\text{N}^+$), 1.75

(m, 6H, $\text{CH}_3-(\text{CH}_2)_7-\text{CH}_2-\text{CH}_2-\text{N}^+$), 2.29 (m 6H, $\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}^+$), 2.86 (t, 6H, $\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.34 (s, 18H, $-\text{N}^+(\text{CH}_3)_2$), 3.54 (t, 6H, $\text{CH}_3-(\text{CH}_2)_9-\text{CH}_2-\text{CH}_2-\text{N}^+$), 4.07 ppm (t, 6H, $\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}^+$).

$3\text{C}_{10}\text{tris-3-Q Br}$. δ 0.880 (t, 9H, $\text{CH}_3-(\text{CH}_2)_{11}-\text{N}^+$), 1.26–1.36 (m, 42H, $\text{CH}_3-(\text{CH}_2)_9-\text{CH}_2-\text{CH}_2-\text{N}^+$), 1.75 (m, 6H, $\text{CH}_3-(\text{CH}_2)_7-\text{CH}_2-\text{CH}_2-\text{N}^+$), 2.28 (m 6H, $\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}^+$), 2.88 (t, 6H, $\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.35 (s, 18H, $-\text{N}^+(\text{CH}_3)_2$), 3.53 (t, 6H, $\text{CH}_3-(\text{CH}_2)_9-\text{CH}_2-\text{CH}_2-\text{N}^+$), 4.08 ppm (t, 6H, $\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}^+$).

$3\text{C}_{12}\text{tris-3-Q Br}$. δ 0.880 (t, 9H, $\text{CH}_3-(\text{CH}_2)_{11}-\text{N}^+$), 1.26–1.36 (m, 54H, $\text{CH}_3-(\text{CH}_2)_9-\text{CH}_2-\text{CH}_2-\text{N}^+$), 1.74 (m, 6H, $\text{CH}_3-(\text{CH}_2)_7-\text{CH}_2-\text{CH}_2-\text{N}^+$), 2.18 (m 6H, $\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}^+$), 2.72 (t, 6H, $\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.34 (s, 18H, $-\text{N}^+(\text{CH}_3)_2$), 3.54 (t, 6H, $\text{CH}_3-(\text{CH}_2)_9-\text{CH}_2-\text{CH}_2-\text{N}^+$), 4.06 ppm (t, 6H, $\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}^+$).

$3\text{C}_{14}\text{tris-3-Q Br}$. δ 0.880 (t, 9H, $\text{CH}_3-(\text{CH}_2)_{11}-\text{N}^+$), 1.25–1.36 (m, 66H, $\text{CH}_3-(\text{CH}_2)_9-\text{CH}_2-\text{CH}_2-\text{N}^+$), 1.60 (m, 6H, $\text{CH}_3-(\text{CH}_2)_7-\text{CH}_2-\text{CH}_2-\text{N}^+$), 2.22 (m 6H, $\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}^+$), 2.78 (t, 6H, $\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.34 (s, 18H, $-\text{N}^+(\text{CH}_3)_2$), 3.54 (t, 6H, $\text{CH}_3-(\text{CH}_2)_9-\text{CH}_2-\text{CH}_2-\text{N}^+$), 4.07 ppm (t, 6H, $\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}^+$).

Elemental analysis:

$3\text{C}_8\text{tris-3-Q Br}$. Calcd. for $\text{C}_{39}\text{H}_{87}\text{N}_4\text{Br}_3 \cdot 3\text{H}_2\text{O}$: C, 51.71; H, 10.35; N, 6.18. Found : C, 51.82; H, 11.14; N, 6.19. $3\text{C}_{10}\text{tris-3-Q Br}$. Calcd. for $\text{C}_{45}\text{H}_{99}\text{N}_4\text{Br}_3 \cdot 2\text{H}_2\text{O}$: C, 55.60; H, 10.68; N, 5.76. Found : C, 55.31; H, 11.35; N, 5.78. $3\text{C}_{12}\text{tris-3-Q Br}$. Calcd. for $\text{C}_{51}\text{H}_{111}\text{N}_4\text{Br}_3 \cdot 2\text{H}_2\text{O}$: C, 58.00; H, 10.97; N, 5.30. Found : C, 57.85; H, 11.56; N, 5.30. $3\text{C}_{14}\text{tris-3-Q Br}$. Calcd. for $\text{C}_{57}\text{H}_{123}\text{N}_4\text{Br}_3 \cdot 2\text{H}_2\text{O}$: C, 60.03; H, 11.23; N, 4.91. Found : C, 60.05; H, 11.78; N, 4.94.

SI. 3. Methylalkylbis[3-(dimethylalkylammonio)propyl]ammonium Tribromide ($3\text{C}_n\text{lin-3-Q Br}$).

The yields were as follows: $3\text{C}_8\text{lin-3-Q Br}$: 86 %, $3\text{C}_{10}\text{lin-3-Q Br}$: 94 %, $3\text{C}_{12}\text{lin-3-Q Br}$: 70 %, $3\text{C}_{14}\text{lin-3-Q Br}$: 93 %.¹H NMR (CDCl_3 , TMS):

$3\text{C}_8\text{lin-3-Q Br}$. δ 0.882 (t, 9H, $\text{CH}_3-(\text{CH}_2)_{13}-\text{N}^+$), 1.26–1.33 (m, 30H, $\text{CH}_3-(\text{CH}_2)_5-\text{CH}_2-\text{CH}_2-\text{N}^+$), 1.80 (m, 6H, $\text{CH}_3-(\text{CH}_2)_{11}-\text{CH}_2-\text{CH}_2-\text{N}^+$), 2.63 (m, 4H, $\text{N}^+-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.42 (s, 15H, $-\text{N}^+(\text{CH}_3)_2$, $(\text{CH}_3)_2\text{N}^+-(\text{CH}_2)_3-\text{N}^+-\text{CH}_3$), 3.49 (m, 6H, $\text{CH}_3-(\text{CH}_2)_{11}-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.92 ppm (m, 8H, $\text{N}^+-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}^+$).

$3\text{C}_{10}\text{lin-3-Q Br}$. δ 0.879 (t, 9H, $\text{CH}_3-(\text{CH}_2)_{13}-\text{N}^+$), 1.26–1.36 (m, 42H, $\text{CH}_3-(\text{CH}_2)_7-\text{CH}_2-\text{CH}_2-\text{N}^+$), 1.81 (m, 6H, $\text{CH}_3-(\text{CH}_2)_{11}-\text{CH}_2-\text{CH}_2-\text{N}^+$), 2.69 (m, 4H, $\text{N}^+-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.42 (s, 15H, $-\text{N}^+(\text{CH}_3)_2$, $(\text{CH}_3)_2\text{N}^+-(\text{CH}_2)_3-\text{N}^+-\text{CH}_3$), 3.51 (m, 6H, $\text{CH}_3-(\text{CH}_2)_{11}-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.87 ppm (m, 8H, $\text{N}^+-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}^+$).

$3\text{C}_{12}\text{lin-3-Q Br}$. δ 0.883 (t, 9H, $\text{CH}_3-(\text{CH}_2)_{13}-\text{N}^+$), 1.26–1.36 (m, 54H, $\text{CH}_3-(\text{CH}_2)_9-\text{CH}_2-\text{CH}_2-\text{N}^+$), 1.80 (m, 6H, $\text{CH}_3-(\text{CH}_2)_{11}-\text{CH}_2-\text{CH}_2-\text{N}^+$), 2.78 (m, 4H, $\text{N}^+-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.41 (s, 15H, $-\text{N}^+(\text{CH}_3)_2$,

$(\text{CH}_3)_2\text{N}^+(\text{CH}_2)_3\text{N}^+\text{CH}_3$, 3.51 (m, 6H, $\text{CH}_3-(\text{CH}_2)_{11}-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.91 ppm (m, 8H, $\text{N}^+-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}^+$).

$3\text{C}_{14}\text{lin-3-Q Br}$. δ 0.881 (t, 9H, $\text{CH}_3-(\text{CH}_2)_{13}-\text{N}^+$), 1.26–1.35 (m, 66H, $\text{CH}_3-(\text{CH}_2)_{11}-\text{CH}_2-\text{CH}_2-\text{N}^+$), 1.80 (m, 6H, $\text{CH}_3-(\text{CH}_2)_{11}-\text{CH}_2-\text{CH}_2-\text{N}^+$), 2.79 (m, 4H, $\text{N}^+-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.44 (s, 15H, $-\text{N}^+(\text{CH}_3)_2$, $(\text{CH}_3)_2\text{N}^+(\text{CH}_2)_3\text{N}^+\text{CH}_3$), 3.48 (m, 6H, $\text{CH}_3-(\text{CH}_2)_{11}-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.91 ppm (m, 8H, $\text{N}^+-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}^+$).

Elemental analysis:

$3\text{C}_8\text{lin-3-Q Br}$. Calcd. for $\text{C}_{35}\text{H}_{78}\text{N}_3\text{Br}_3$: C, 53.84; H, 10.07; N, 5.38. Found : C, 53.77; H, 10.58; N, 5.39.

$3\text{C}_{10}\text{lin-3-Q Br}$. Calcd. for $\text{C}_{41}\text{H}_{90}\text{N}_3\text{Br}_3$: C, 56.94; H, 10.49; N, 4.86. Found : C, 56.40; H, 10.82; N, 4.90.

$3\text{C}_{12}\text{lin-3-Q Br}$. Calcd. for $\text{C}_{47}\text{H}_{102}\text{N}_3\text{Br}_3 \cdot \text{H}_2\text{O}$: C, 58.37; H, 10.84; N, 4.35. Found : C, 58.08; H, 11.23; N, 4.35.

SI. 4. Tris(N-alkyl-N, N-dimethyl-2-ammoniomethyl)amine Bis(trifluoromethanesulfonyl)amide ($3\text{C}_n\text{tris-2-Q NTf}_2$).

The yields were as follows: $3\text{C}_8\text{tris-2-Q NTf}_2$: 56 %, $3\text{C}_{10}\text{tris-2-Q NTf}_2$: 92 %, $3\text{C}_{12}\text{tris-2-Q NTf}_2$: 83 %, $3\text{C}_{14}\text{tris-2-Q NTf}_2$: 97 %.

$^1\text{H NMR}$ (CDCl_3 , TMS):

$3\text{C}_8\text{tris-2-Q NTf}_2$. δ 0.878 (t, 9H, $\text{CH}_3-(\text{CH}_2)_7-\text{N}^+$), 1.26–1.33 (m, 30H, $\text{CH}_3-(\text{CH}_2)_5-\text{CH}_2-\text{CH}_2-\text{N}^+$), 1.72 (m, 6H, $\text{CH}_3-(\text{CH}_2)_5-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.08 (s, 18H, $-\text{N}^+(\text{CH}_3)_2$), 3.13 (t, 6H, $\text{N}-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.27–3.32 (m 6H, $\text{CH}_3-(\text{CH}_2)_5-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.52 ppm (t, 6H, $\text{N}-\text{CH}_3-\text{CH}_2-\text{N}^+$).

$3\text{C}_{10}\text{tris-2-Q NTf}_2$. δ 0.878 (t, 9H, $\text{CH}_3-(\text{CH}_2)_9-\text{N}^+$), 1.26–1.33 (m, 42H, $\text{CH}_3-(\text{CH}_2)_7-\text{CH}_2-\text{CH}_2-\text{N}^+$), 1.72 (m, 6H, $\text{CH}_3-(\text{CH}_2)_7-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.07 (s, 18H, $-\text{N}^+(\text{CH}_3)_2$), 3.14 (t, 6H, $\text{N}-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.27–3.30 (m 6H, $\text{CH}_3-(\text{CH}_2)_7-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.56 ppm (t, 6H, $\text{N}-\text{CH}_3-\text{CH}_2-\text{N}^+$).

$3\text{C}_{12}\text{tris-2-Q NTf}_2$. δ 0.878 (t, 9H, $\text{CH}_3-(\text{CH}_2)_{11}-\text{N}^+$), 1.25–1.33 (m, 54H, $\text{CH}_3-(\text{CH}_2)_9-\text{CH}_2-\text{CH}_2-\text{N}^+$), 1.72 (m, 6H, $\text{CH}_3-(\text{CH}_2)_9-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.08 (s, 18H, $-\text{N}^+(\text{CH}_3)_2$), 3.13 (t, 6H, $\text{N}-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.26–3.30 (m 6H, $\text{CH}_3-(\text{CH}_2)_9-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.53 ppm (t, 6H, $\text{N}-\text{CH}_3-\text{CH}_2-\text{N}^+$).

$3\text{C}_{14}\text{tris-2-Q NTf}_2$. δ 0.878 (t, 9H, $\text{CH}_3-(\text{CH}_2)_{13}-\text{N}^+$), 1.25–1.33 (m, 66H, $\text{CH}_3-(\text{CH}_2)_{11}-\text{CH}_2-\text{CH}_2-\text{N}^+$), 1.72 (m, 6H, $\text{CH}_3-(\text{CH}_2)_{11}-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.09 (s, 18H, $-\text{N}^+(\text{CH}_3)_2$), 3.13 (t, 6H, $\text{N}-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.27–3.33 (m 6H, $\text{CH}_3-(\text{CH}_2)_{11}-\text{CH}_2-\text{CH}_2-\text{N}^+$), 3.57 ppm (t, 6H, $\text{N}-\text{CH}_3-\text{CH}_2-\text{N}^+$).

Elemental analysis:

$3\text{C}_8\text{tris-2-Q NTf}_2$. Calcd. for $\text{C}_{42}\text{H}_{81}\text{N}_7\text{O}_{12}\text{F}_{18}\text{S}_6$: C, 35.76; H, 5.79; N, 6.95. Found : C, 35.66; H, 5.75; N, 6.91.

$3\text{C}_8\text{tris-2-Q NTf}_2$. Calcd. for $\text{C}_{42}\text{H}_{81}\text{N}_7\text{F}_{18}\text{O}_{12}\text{S}_6$: C, 35.76; H, 5.79; N, 6.95. Found : C, 35.66; H, 5.75; N, 6.91.

$3\text{C}_{10}\text{tris-2-Q NTf}_2$. Calcd. for $\text{C}_{48}\text{H}_{93}\text{N}_7\text{F}_{18}\text{O}_{18}\text{S}_6$: C, 38.57; H, 6.27; N, 6.56. Found : C, 39.10; H, 6.81; N,

6.58.

3C₁₂tris-2-Q NTf₂. Calcd. for C₅₄H₁₀₅N₇F₁₈O₁₂S₆: C, 41.08; H, 6.70; N, 6.21. Found : C, 41.29; H, 7.46; N, 6.25.

3C₁₄tris-2-Q NTf₂. Calcd. for C₆₀H₁₁₇N₇F₁₈O₁₂S₆: C, 43.57; H, 7.92; N, 6.59. Found : C, 43.73; H, 8.01; N, 6.62.

S1. 5. Tris(N-alkyl-N, N-dimethyl-3-ammoniopropyl)amine X [X : Trifluoromethanesulfonate, Bis(trifluoromethanesulfonyl)amide, Bis(fluorosulfonyl)amide, Bis(trifluoromethanesulfonyl)amide] (3C_ntris-3-Q X, X = PF₆, OTf, FSA, NTf₂).

The yields were as follows: 3C₁₂tris-3-Q PF₆: 58 %, 3C₁₂tris-3-Q OTf: 73 %, 3C₁₂tris-3-Q FSA: 87 %. 3C₈tris-3-Q NTf₂: 90 %, 3C₁₀tris-3-Q NTf₂: 92 %, 3C₁₂tris-3-Q NTf₂: 87 %, 3C₁₄tris-3-Q NTf₂: 93 %.

¹H NMR (CDCl₃, TMS):

3C₁₂tris-3-Q PF₆. δ 0.872 (t, 9H, CH₃-(CH₂)₁₁-N⁺), 1.25–1.34 (m, 54H, CH₃-(CH₂)₉-CH₂-CH₂-N⁺), 1.73 (m, 6H, CH₃-(CH₂)₉-CH₂-CH₂-N⁺), 2.07 (m 6H, N-CH₂-CH₂-CH₂-N⁺), 2.70 (t, 6H, N-CH₂-CH₂-CH₂-N⁺), 3.06 (s, 18H, -N⁺(CH₃)₂), 3.26–3.30 (m, 6H, CH₃-(CH₂)₉-CH₂-CH₂-N⁺), 3.52–3.53 ppm (m, 6H, N-CH₂-CH₂-CH₂-N⁺).

3C₁₂tris-3-Q OTf. δ 0.880 (t, 9H, CH₃-(CH₂)₁₁-N⁺), 1.25–1.33 (m, 54H, CH₃-(CH₂)₉-CH₂-CH₂-N⁺), 1.71 (m, 6H, CH₃-(CH₂)₉-CH₂-CH₂-N⁺), 2.11 (m 6H, N-CH₂-CH₂-CH₂-N⁺), 2.69 (t, 6H, N-CH₂-CH₂-CH₂-N⁺), 3.13 (s, 18H, -N⁺(CH₃)₂), 3.30–3.36 (m, 6H, CH₃-(CH₂)₉-CH₂-CH₂-N⁺), 3.57–3.63 ppm (m, 6H, N-CH₂-CH₂-CH₂-N⁺).

3C₁₂tris-3-Q FSA. δ 0.880 (t, 9H, CH₃-(CH₂)₁₁-N⁺), 1.26–1.36 (m, 54H, CH₃-(CH₂)₉-CH₂-CH₂-N⁺), 1.73 (m, 6H, CH₃-(CH₂)₉-CH₂-CH₂-N⁺), 2.01 (m 6H, N-CH₂-CH₂-CH₂-N⁺), 2.67 (t, 6H, N-CH₂-CH₂-CH₂-N⁺), 3.06 (s, 18H, -N⁺(CH₃)₂), 3.23–3.28 (m, 6H, CH₃-(CH₂)₉-CH₂-CH₂-N⁺), 3.35–3.41 ppm (m, 6H, N-CH₂-CH₂-CH₂-N⁺).

3C₈tris-3-Q NTf₂. δ 0.879 (t, 9H, CH₃-(CH₂)₇-N⁺), 1.27–1.34 (m, 30H, CH₃-(CH₂)₅-CH₂-CH₂-N⁺), 1.72 (m, 6H, CH₃-(CH₂)₅-CH₂-CH₂-N⁺), 2.23 (m 6H, N-CH₂-CH₂-CH₂-N⁺), 3.07 (s, 18H, -N⁺(CH₃)₂), 3.26 (t, 6H, CH₃-(CH₂)₅-CH₂-CH₂-N⁺), 3.44 ppm (t, 12H, N-CH₂-CH₂-CH₂-N⁺).

3C₁₀tris-3-Q NTf₂. δ 0.879 (t, 9H, CH₃-(CH₂)₉-N⁺), 1.26–1.34 (m, 42H, CH₃-(CH₂)₇-CH₂-CH₂-N⁺), 1.71 (m, 6H, CH₃-(CH₂)₇-CH₂-CH₂-N⁺), 2.06 (m 6H, N-CH₂-CH₂-CH₂-N⁺), 3.07 (s, 18H, -N⁺(CH₃)₂), 3.28 (t, 6H, CH₃-(CH₂)₇-CH₂-CH₂-N⁺), 3.41 ppm (t, 12H, N-CH₂-CH₂-CH₂-N⁺).

3C₁₂tris-3-Q NTf₂. δ 0.878 (t, 9H, CH₃-(CH₂)₁₁-N⁺), 1.26–1.33 (m, 54H, CH₃-(CH₂)₉-CH₂-CH₂-N⁺), 1.72 (m, 6H, CH₃-(CH₂)₉-CH₂-CH₂-N⁺), 2.37 (m 6H, N-CH₂-CH₂-CH₂-N⁺), 3.07 (s, 18H, -N⁺(CH₃)₂), 3.26 (t, 6H, CH₃-(CH₂)₉-CH₂-CH₂-N⁺), 3.46 ppm (t, 12H, N-CH₂-CH₂-CH₂-N⁺).

3C₁₄tris-3-Q NTf₂. δ 0.878 (t, 9H, CH₃-(CH₂)₁₃-N⁺), 1.25–1.34 (m, 66H, CH₃-(CH₂)₁₁-CH₂-CH₂-N⁺), 1.71 (m, 6H, CH₃-(CH₂)₁₁-CH₂-CH₂-N⁺), 2.17 (m 6H, N-CH₂-CH₂-CH₂-N⁺), 2.96 (m 6H, N-CH₂-CH₂-

CH₂-N⁺), 3.06 (s, 18H, -N⁺(CH₃)₂), 3.26 (t, 6H, CH₃-(CH₂)₁₁-CH₂-CH₂-N⁺), 3.43 ppm (t, 6H, N-CH₂-CH₂-CH₂-N⁺).

Elemental analysis:

3C₁₂tris-3-Q PF₆. Calcd. for C₅₁H₁₁₁N₄F₁₈P₃ : C, 50.40; H, 9.21; N, 4.61. Found : C, 50.71; H, 9.48; N, 4.73.

3C₁₂tris-3-Q OTf. Calcd. for C₅₄H₁₁₁N₄F₉O₉S₃ : C, 52.83; H, 9.11; N, 4.56. Found : C, 52.26; H, 9.40; N, 4.57. 3C₁₂tris-3-Q FSA. Calcd. for C₅₁H₁₁₁N₇F₆O₁₂S₆ : C, 46.38; H, 8.47; N, 7.42. Found : C, 46.12; H, 10.02; N, 7.55.

3C₈tris-3-Q NTf₂. Calcd. for C₄₅H₈₇N₇F₁₈O₁₂S₆: C, 37.21; H, 6.04; N, 6.75. Found : C, 37.44; H, 6.23; N, 6.60. 3C₁₀tris-3-Q NTf₂. Calcd. for C₅₁H₉₉N₇F₁₈O₁₂S₆: C, 39.86; H, 6.49; N, 6.38. Found : C, 39.20; H, 6.44; N, 6.45. 3C₁₂tris-3-Q NTf₂. Calcd. for C₅₇H₁₁₁N₇F₁₈O₁₂S₆: C, 42.24; H, 6.90; N, 6.05. Found : C, 42.05; H, 7.09; N, 6.12. 3C₁₄tris-3-Q NTf₂. Calcd. for C₆₃H₁₂₃N₇F₁₈O₁₂S₆·H₂O: C, 43.46; H, 7.35; N, 5.63. Found : C, 42.58; H, 7.52; N, 5.76.

S1. 6. Methylalkylbis[3-(dimethylalkylammonio)propyl]ammonium bis(trifluoromethanesulfonyl)amide (3C_nlin-3-Q NTf₂).

The yields were as follows: 3C₈lin-3-Q NTf₂: 90 %, 3C₁₀lin-3-Q NTf₂: 95 %, 3C₁₂lin-3-Q NTf₂: 89 %, 3C₁₄lin-3-Q NTf₂: 93 %.

¹H NMR (CDCl₃, TMS):

3C₈lin-3-Q NTf₂. δ 0.859 (t, 9H, CH₃-(CH₂)₇-N⁺), 1.26–1.34 (m, 30H, CH₃-(CH₂)₅-CH₂-CH₂-N⁺), 1.74 (m, 6H, CH₃-(CH₂)₅-CH₂-CH₂-N⁺), 2.35 (m, 4H, N⁺-CH₂-CH₂-CH₂-N⁺), 3.11 (s, 12H, -N⁺(CH₃)₂), 3.27 (s, 3H, (CH₃)₂N⁺-(CH₂)₃-N⁺-CH₃), 3.35 (m, 6H, CH₃-(CH₂)₅-CH₂-CH₂-N⁺), 3.48 ppm (t, 8H, N⁺-CH₂-CH₂-CH₂-N⁺).

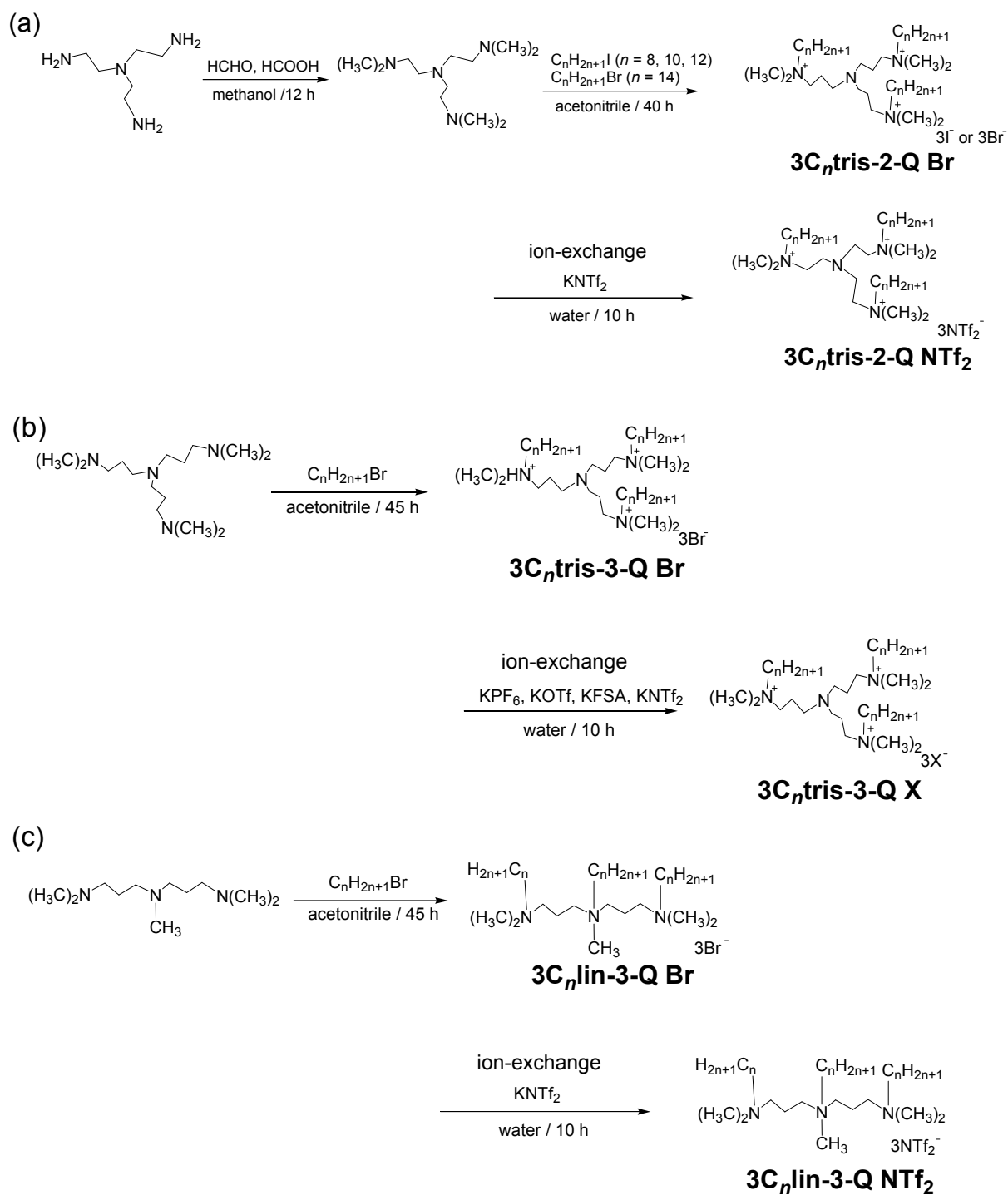
3C₁₀lin-3-Q NTf₂. δ 0.880 (t, 9H, CH₃-(CH₂)₉-N⁺), 1.26–1.32 (m, 42H, CH₃-(CH₂)₇-CH₂-CH₂-N⁺), 1.70 (m, 6H, CH₃-(CH₂)₇-CH₂-CH₂-N⁺), 2.50 (m, 4H, N⁺-CH₂-CH₂-CH₂-N⁺), 3.40 (s, 12H, -N⁺(CH₃)₂), 3.48 (s, 3H, (CH₃)₂N⁺-(CH₂)₃-N⁺-CH₃), 3.37 (m, 6H, CH₃-(CH₂)₇-CH₂-CH₂-N⁺), 3.72 ppm (m, 8H, N⁺-CH₂-CH₂-CH₂-N⁺).

3C₁₂lin-3-Q NTf₂. δ 0.882 (t, 9H, CH₃-(CH₂)₁₁-N⁺), 1.26–1.35 (m, 54H, CH₃-(CH₂)₉-CH₂-CH₂-N⁺), 1.72 (m, 6H, CH₃-(CH₂)₉-CH₂-CH₂-N⁺), 2.61 (m, 4H, N⁺-CH₂-CH₂-CH₂-N⁺), 3.40 (s, 12H, -N⁺(CH₃)₂), 3.48 (s, 3H, (CH₃)₂N⁺-(CH₂)₃-N⁺-CH₃), 3.48 (m, 6H, CH₃-(CH₂)₉-CH₂-CH₂-N⁺), 3.93 ppm (t, 8H, N⁺-CH₂-CH₂-CH₂-N⁺).

3C₁₄lin-3-Q NTf₂. δ 0.879 (t, 9H, CH₃-(CH₂)₁₃-N⁺), 1.26–1.33 (m, 66H, CH₃-(CH₂)₁₁-CH₂-CH₂-N⁺), 1.72 (m, 6H, CH₃-(CH₂)₁₁-CH₂-CH₂-N⁺), 2.62 (m, 4H, N⁺-CH₂-CH₂-CH₂-N⁺), 3.41 (s, 12H, -N⁺(CH₃)₂), 3.48 (s, 3H, (CH₃)₂N⁺-(CH₂)₃-N⁺-CH₃), 3.48 (m, 6H, CH₃-(CH₂)₁₁-CH₂-CH₂-N⁺), 3.94 ppm (m, 8H, N⁺-CH₂-CH₂-CH₂-N⁺).

Elemental analysis:

3C₈lin-3-Q NTf₂. Calcd. for C₄₁H₇₈N₆F₁₈O₁₂S₆: C, 35.65; H, 5.69; N, 6.08. Found : C, 35.77; H, 5.87; N, 6.22. 3C₁₀lin-3-Q NTf₂. Calcd. for C₄₇H₉₀N₆F₁₈O₁₂S₆: C, 38.52; H, 6.19; N, 5.73. Found : C, 38.94; H, 6.25; N, 5.79. 3C₁₂lin-3-Q NTf₂. Calcd. for C₅₃H₁₀₂N₆F₁₈O₁₂S₆: C, 41.08; H, 6.63; N, 5.42. Found : C, 41.80; H, 6.82; N, 5.45. 3C₁₄lin-3-Q NTf₂. Calcd. for C₅₉H₁₁₄N₆F₁₈O₁₂S₆: C, 43.37; H, 7.03; N, 5.14. Found : C, 43.89; H, 7.41; N, 5.21.



Scheme S1 Synthetic schemes of quaternary ammonium salt-type trimeric amphiphilic compounds: (a) 3C_ntris-2-Q NTf₂, (b) 3C_ntris-3-Q X, and (c) 3C_nlin-3-Q NTf₂.

S2. Melting point.

Table S1 Values of melting point obtained from DSC for amphiphilic compounds $3C_n\text{tris-}s\text{-Q X}$ and

Compound	$n = 8$	10	12	14
$3C_n\text{tris-}2\text{-Q NTf}_2$	4.4	50.1	48.6	31.3
$3C_n\text{tris-}3\text{-Q PF}_6$			85.5	
$3C_n\text{tris-}3\text{-Q OTf}$			161.6	
$3C_n\text{tris-}3\text{-Q FSA}$			28.5	
$3C_n\text{tris-}3\text{-Q NTf}_2$	-0.7	0.6	-3.8	-9.1
$3C_n\text{lin-}3\text{-Q NTf}_2$	-19.9	-5.2	46.6	62.3
$3C_n\text{lin-}s\text{-Q NTf}_2$.				