Electronic Supplementary Information

Bis-quaternary ammonium cation based organic ionic plastic crystals: plastic crystal behaviour and ionic liquid properties above melting points

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The synthesis of bis-quaternary ammonium salts

N,N,N′,N′-tetraethyl-N,N′-dimethyl-1,2-ethylenediammonium salts. An amount of 4.40 g (31 mmol) 1-iodomethane was dissolved in 20 ml acetonitrile. Then 2.58 g (15 mmol) N,N,N′,N′-tetraethylethylenediamine was added dropwise into the prepared 1-iodomethane solution. The mixture was stirred at 70 °C for 48 h. Then the solvent was removed under reduced pressure and the solid product was washed with ethyl acetate and dry diethyl ether three times. The product was dried under vacuum at room temperature for more than 24 h to give a white solid: $C_2(N_{2,2,1})_2I$ (6.23g, 91%). ^{1}HNMR (D_2O): 3.80 (s, 4H), 3.51-3.45 (m, 8H), 3.12 (s, 6H), 1.38-1.34 (t, 12H). $C_2(N_{2,2,1})_2$TFSI was obtained by the general anion exchange procedure. $C_2(N_{2,2,1})_2I$

(2.74g, 6 mmol), LiTFSI (5.17 g, 18 mmol) in deionized water (25 mL), $C_2(N_{2,2,1})_2$TFSI was isolated as a white solid (3.89 g, 85%). ^{1}HNMR (DMSO): 3.72 (s, 4H), 3.40-3.25 (m, 8H), 3.02 (s, 6H), 1.29-1.22 (t, 12H). $C_2(N_{2,2,1})_2PF_6$ was obtained via the same procedure as for $C_2(N_{2,2,1})_2$TFSI. $C_2(N_{2,2,1})_2$I (2.74g, 6 mmol) and KPF_6 (3.31 g, 18 mmol) afforded the compound as a white solid $C_2(N_{2,2,1})_2PF_6$ (2.72g, 92%). ^{1}HNMR (DMSO): 3.72 (s, 4H), 3.41-3.24 (m, 8H), 3.01 (s, 6H), 1.30-1.20 (t, 12H).

N,N,N,N′,N′,N′-hexaethyl-1,2-ethylenediammonium salts. The same procedure as for $C_2(N_{2,2,1})_2$I was used. 1-iodoethane (6.39 g, 41 mmol) and N,N,N′,N′-tetraethylethylenediamine (3.45 g, 20 mmol) in acetonitrile (20 mL) produced white solid $C_2(N_{2,2,2})_2$I (9.11g, 94%). ^{1}HNMR (D_2O): 3.68 (s, 4H), 3.45-3.40 (m, 12H), 1.34-1.31 (t, 18H). $C_2(N_{2,2,2})_2$TFSI was obtained by the general anion exchange procedure. $C_2(N_{2,2,2})_2$I (3.87 g, 8 mmol), LiTFSI (6.89 g, 24 mmol) in deionized water (25 mL), $C_2(N_{2,2,2})_2$TFSI was isolated as a white solid (5.75 g, 91%). ^{1}HNMR (DMSO): 3.63 (s, 4H), 3.38-3.30 (m, 12H), 1.25-1.19 (t, 18H). $C_2(N_{2,2,2})_2PF_6$ was obtained by the same procedure as for $C_2(N_{2,2,1})_2PF_6$. $C_2(N_{2,2,2})_2$I (3.87 g, 8 mmol) and KPF_6 (4.42 g, 24 mmol) afforded the compound as a white solid $C_2(N_{2,2,2})_2PF_6$ (3.83 g, 92%). ^{1}HNMR (DMSO): 3.63 (s, 4H), 3.37-3.29 (m, 12H), 1.25-1.18 (t, 18H).

N,N,N,N′,N′,N′-hexaethyl-1,3-propanediammonium salts. An amount of 4.59 g (45 mmol) triethylamine was dissolved in 20 ml acetonitrile. Then 4.04 g (20 mmol)

1,3-dibromopropane was added dropwise into the prepared triethylamine solution. The mixture was stirred at 70 °C for 48 h. Then the solvent was removed under reduced pressure and the solid product was washed with ethyl acetate and dry diethyl ether three times. The product was dried under vacuum at 70 °C for more than 24 h to give a white solid: $C_3(N_{2,2,2})_2Br$ (6.96g, 86%). ^{1}HNMR (D_2O): 3.38-3.30 (m, 12H), 3.30-3.24 (t, 4H), 2.14-2.02 (m, 2H), 1.33-1.20 (t, 18H). $C_3(N_{2,2,2})_2TFSI$ was obtained by the general anion exchange procedure. $C_3(N_{2,2,2})_2Br$ (2.83 g, 7 mmol), LiTFSI (6.03 g, 21 mmol) in deionized water (25 mL). The produced $C_3(N_{2,2,2})_2TFSI$ was isolated as a white solid (5.30 g, 94%). ^{1}HNMR (DMSO): 3.30-3.26 (m, 12H), 3.20-3.15 (t, 4H), 1.96-1.88 (m, 2H), 1.21-1.17(m, 18H). $C_3(N_{2,2,2})_2PF_6$ was obtained by the same procedure as for $C_2(N_{2,2,1})_2PF_6$. $C_3(N_{2,2,2})_2Br$ (2.83g, 7 mmol) and KPF_6 (3.87 g, 21 mmol) afforded the compound as a white solid $C_3(N_{2,2,2})_2PF_6$ (3.22 g, 86%). ^{1}HNMR (DMSO): 3.31-3.25 (m, 12H), 3.21-3.13 (t, 4H), 1.98-1.87 (m, 2H), 1.22-1.16 (m, 18H).

N,N,N,N′,N′,N′-hexaethyl-1,4-butanediammonium salts. The same procedure as for $C_3(N_{2,2,2})_2Br$ was used. Triethylamine (4.59 g, 45 mmol) and 1,4-dibromobutane (4.32 g, 20 mmol) in acetonitrile (20 mL) produced white solid $C_4(N_{2,2,2})_2Br$ (7.36g, 88%). ^{1}HNMR (D_2O): 3.37-3.31 (m, 12H), 3.30-3.25 (t, 4H), 2.12-2.04 (m, 2H), 1.29-1.24(m, 18H). $C_4(N_{2,2,2})_2TFSI$ was obtained by the general anion exchange procedure. $C_4(N_{2,2,2})_2Br$ (2.93 g, 7 mmol), LiTFSI (6.03 g, 21 mmol) in deionized water (25 mL). The produced $C_4(N_{2,2,2})_2TFSI$ was isolated as a white solid (5.39 g,

94%). ^{1}HNMR (DMSO): 3.26-3.19 (m, 12H), 3.16-3.10 (t, 4H), 1.65-1.57 (m, 4H), 1.22-1.16 (t, 18H). $C_4(N_{2,2,2})_2PF_6$ was obtained by the same procedure as for $C_2(N_{2,2,1})_2PF_6$. $C_4(N_{2,2,2})_2Br$ (2.93 g, 7 mmol) and KPF_6 (3.87 g, 21 mmol) afforded the compound as a white solid $C_4(N_{2,2,2})_2PF_6$ (3.30 g, 86%). ^{1}HNMR (DMSO): 3.27-3.17 (m, 12H), 3.16-3.09 (t, 4H), 1.67-1.56 (m, 4H), 1.23-1.14 (t, 18H).

N,N,N,N′,N′,N′-hexaethyl-1,6-hexanediammonium salts. The same procedure as for $C_3(N_{2,2,2})_2Br$ was used. Triethylamine (4.59 g, 45 mmol) and 1,6-dibromohexane (4.88 g, 20 mmol) in acetonitrile (20 mL) produced white solid $C_6(N_{2,2,2})_2Br$ (8.3 g, 93%). ^{1}HNMR (D_2O): 3.38-3.30 (m, 12H), 3.25-3.16 (t, 4H), 1.75-1.61 (m, 4H), 1.40-1.36 (m, 4H), 1.31-1.20 (t, 18H). $C_6(N_{2,2,2})_2TFSI$ was obtained by the general anion exchange procedure. $C_6(N_{2,2,2})_2Br$ (3.12 g, 7 mmol), LiTFSI (6.03 g, 21 mmol) in deionized water (25 mL). The produced $C_6(N_{2,2,2})_2TFSI$ was isolated as a white solid (4.97 g, 84%). ^{1}HNMR (DMSO): 3.26-3.18 (m, 12H), 3.11-3.08 (t, 4H), 1.64-1.54 (m, 4H), 1.35-1.31 (m, 4H),1.19-1.14 (t, 18H). $C_6(N_{2,2,2})_2PF_6$ was obtained by the same procedure as for $C_2(N_{2,2,1})_2PF_6$. $C_6(N_{2,2,2})_2Br$ (3.12 g, 7 mmol) and KPF_6 (3.87 g, 21 mmol) afforded the compound as a white solid $C_6(N_{2,2,2})_2PF_6$ (3.51 g, 87%). ^{1}HNMR (DMSO): 3.27-3.18 (m, 12H), 3.13-3.05 (t, 4H), 1.63-1.52 (m, 4H), 1.39-1.28 (m, 4H),1.22-1.11 (t, 18H).

N,N,N′,N′-Tetraethyl-N,N′-dipropyl-1,2-ethylenediammonium salts. The same procedure as for $C_2(N_{2,2,1})_2I$ was used. 1-iodopropane (6.97 g, 41 mmol) and

N,N,N′,N′-Tetraethylethylenediamine (3.45 g, 20 mmol) in acetonitrile (20 mL) produced white solid $C_2(N_{2,2,3})_2I$ (9.69 g, 93%). ^{1}HNMR (D_2O): 3.69 (s, 4H), 3.47-3.40 (m, 8H), 3.32-3.26 (t, 4H), 1.78-1.68 (m, 4H), 1.35-1.29 (t, 12H), 1.00-0.94 (t, 6H). $C_2(N_{2,2,3})_2$TFSI was obtained by the general anion exchange procedure. $C_2(N_{2,2,3})_2I$ (3.07 g, 6 mmol), LiTFSI (5.17 g, 18 mmol) in deionized water (25 mL), $C_2(N_{2,2,3})_2$TFSI was isolated as a white solid (4.37 g, 89%). ^{1}HNMR (DMSO): 3.65(s, 4H), 3.39-3.30(m, 8H), 3.14-3.10(t, 4H), 1.65-1.55(m, 4H), 1.25-1.20(t, 12H), 0.98-0.90(t, 6H).

N,N,N′,N′-Tetraethyl-N,N′-dibutyl-1,2-ethylenediammonium salts. The same procedure as for $C_2(N_{2,2,1})_2I$ was used. 1-iodobutane (7.54 g, 41 mmol) and N,N,N′,N′-Tetraethylethylenediamine (3.45 g, 20 mmol) in acetonitrile (20 mL) produced white solid $C_2(N_{2,2,4})_2I$ (10.05 g, 93%). ^{1}HNMR (D_2O): 3.70 (s, 4H), 3.49-3.42 (m, 8H), 3.38-3.32 (t, 4H), 1.75-1.65 (m, 4H), 1.43-1.37 (m, 4H), 1.36-1.31(t, 12H), 0.98-0.94 (t, 6H). $C_2(N_{2,2,4})_2$TFSI was obtained by the general anion exchange procedure. $C_2(N_{2,2,4})_2I$ (3.24 g, 6 mmol), LiTFSI (5.17 g, 18 mmol) in deionized water (25 mL). The produced $C_2(N_{2,2,4})_2$TFSI was isolated as a white solid (4.82 g, 95%). ^{1}HNMR (DMSO): 3.65(s, 4H), 3.39-3.30(m, 8H), 3.28-3.20 (t, 4H), 1.64-1.53 (m, 4H), 1.38-1.28 (m, 4H), 1.26-1.20(t, 12H), 0.99-0.93 (t, 6H).

N,N,N′,N′-Tetraethyl-N,N′-dihexyl-1,2-ethylenediammonium salts. The same procedure as for $C_2(N_{2,2,1})_2I$ was used. 1-Iodohexane (8.69 g, 41 mmol) and

N,N,N′,N′-tetraethylethylenediamine (3.45 g, 20 mmol) in acetonitrile (20 mL) produced white solid $C_2(N_{2,2,6})_2I$ (10.99g, 92%). ^{1}HNMR (D_2O): 3.73(s, 4H), 3.53-3.44 (m, 8H), 3.42-3.43 (t, 4H), 1.80-1.69 (m, 4H), 1.41-1.35 (m, 4H), 1.32-1.29 (t, 8H), 1.27-1.24 (t, 12H), 0.98-0.91 (t, 6H). $C_2(N_{2,2,6})_2$TFSI was obtained by the general anion exchange procedure. $C_2(N_{2,2,6})_2I$ (3.58 g, 6.0 mmol), LiTFSI (5.17 g, 18.0 mmol) in deionized water (25 mL). The produced $C_2(N_{2,2,6})_2$TFSI was isolated as a white solid (5.09g, 94%).^{1}HNMR (DMSO): 3.64(s, 4H), 3.37-3.33 (m, 8H), 3.26-3.22 (t, 4H), 1.63-1.56 (m, 4H), 1.36-1.31 (m, 4H), 1.29-1.26 (t, 8H), 1.24-1.21 (t, 12H), 0.91-0.85 (t, 6H).

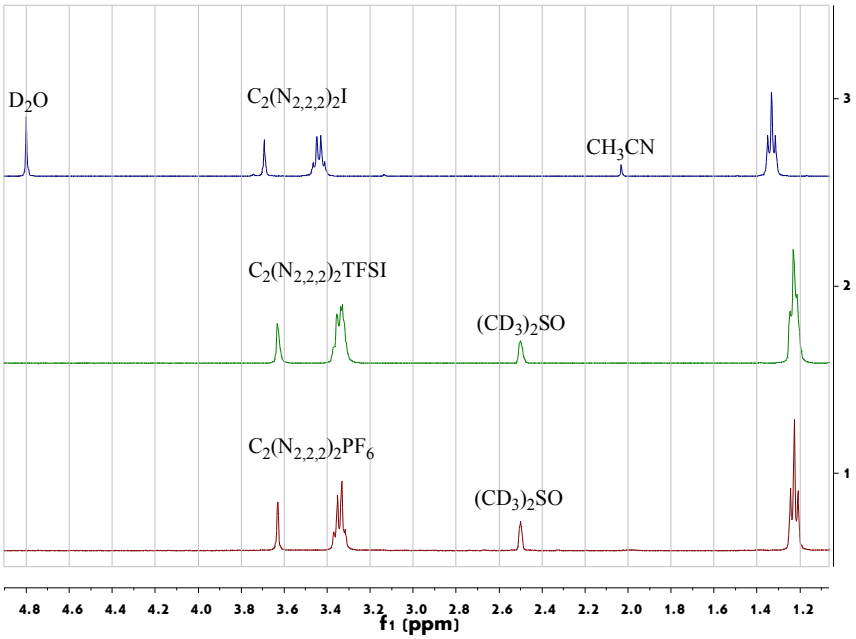

Fig S1. ^{1}H NMR spectrum of $C_2(N_{2,2,2})_2I$, $C_2(N_{2,2,2})_2$TFSI and $C_2(N_{2,2,2})_2PF_6$ in D_2O, $(CD_3)_2SO$ and $(CD_3)_2SO$, respectively.

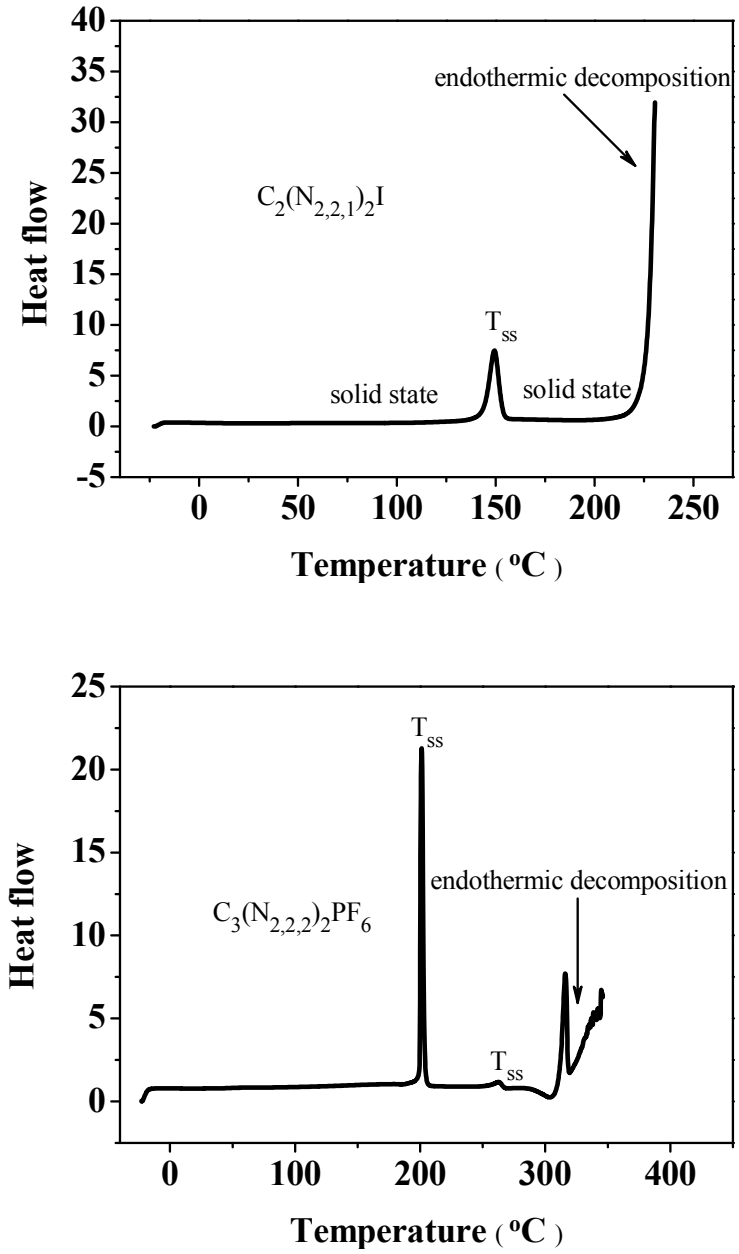

Fig S2. Differential scanning calorimetric trace (DSC) for the $C_2(N_{2,2,1})_2I$ and $C_3(N_{2,2,2})_2PF_6$ under N_2 atmosphere. Heating rate: 10 °C min^{-1}.

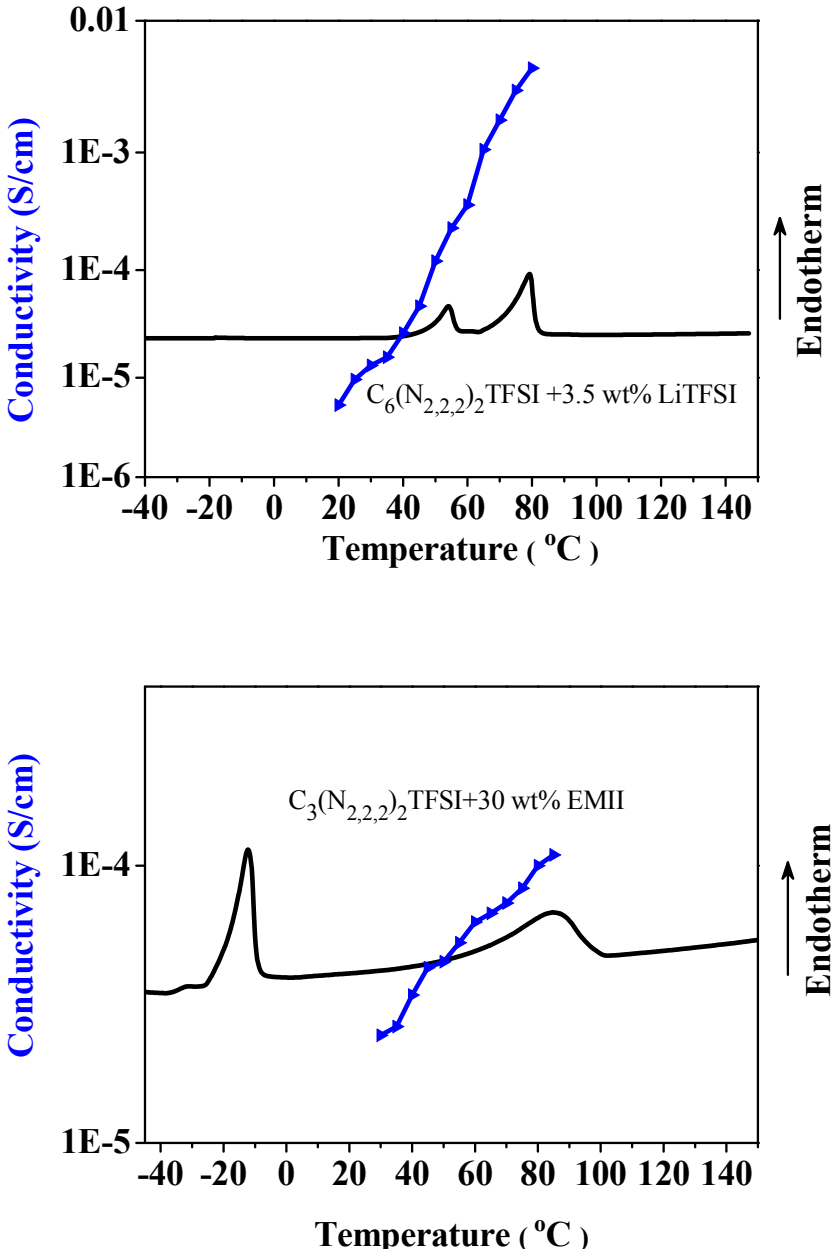

Fig S3. Differential scanning calorimetric trace and the conductivity-temperature plot for $C_6(N_{2,2,2})_2TFSI$ +3.5 wt % LiTFSI and $C_3(N_{2,2,2})_2TFSI$ + 30 wt % EMII.

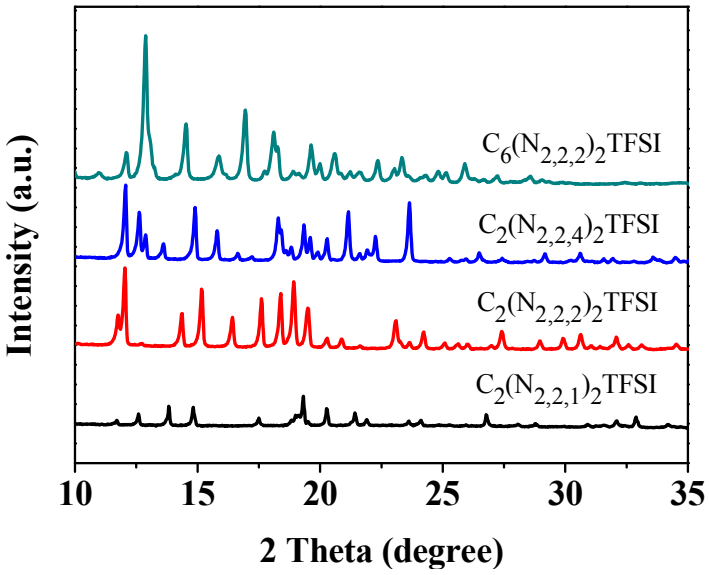

Fig S4. XRD patterns of the $C_2(N_{2,2,1})_2TFSI$, $C_2(N_{2,2,2})_2TFSI$, $C_2(N_{2,2,4})_2TFSI$ and $C_6(N_{2,2,2})_2TFSI$ measured at room temperature.