**Supporting Information for**

**Pressure-induced liquid-liquid transition in a family of ionic materials**

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**Synthesis of examined systems.**

Trihexyl(tetradecyl)phosphonium chloride, [P66614]Cl, was kindly provided by Solvay. Trihexyl(tetradecyl)phosphonium bis(oxolato)borate [P666,14][BOB] was bought from Merck, and sodium tricyanomethanide was bought from TCI Chemicals. All other chemicals were purchased from Sigma-Aldrich and used as received.

**[P666,14][TFSI]**. Trihexyl(tetradecyl)phosphonium chloride, [P666,14]Cl (0.010 mol eq.) and lithium bis(trifluoromethanesulfon)imide Li[TFSI] (0.013 mol eq.) were separately dissolved in 25 cm3 deionised water (total 50 cm3) and then combined in a round-bottomed flask (250 cm3), resulting in the formation of a biphasic liquid system; the mixture was left to react (1 h, room temperature, 600 rpm). The aqueous layer was separated, and the organic layer was collected and washed, firstly with deionised water (10 cm3) and then dichloromethane, DCM (10 cm3). Subsequent washes were performed with solution of Li[TFSI] in deionised water until no chloride could be detected with silver nitrate solution. Subsequently, DCM was removed *via* rotary evaporation (30 min, 35 °C) and the ionic liquid was dried under high vacuum (overnight, 70 °C, 10-2 mbar). 1H, 13C, 19F and 31P NMR spectra were recorded in *d6*-DMSO solution.

1H NMR (400 MHz, *d6* -DMSO) δ: 0.83-0.92 (m, 12H), 1.21-1.27 (m, 18H), 1.28-1.35 (m, 14H), 1.35-1.43 (m, 8H), 1.43-1.55 (m, 8H), 2.11-2.23 (m, 8H).

13C NMR (400 MHz, *d6* -DMSO) δ: 13.53, 13.64, 17.28, 17.76, 20.46, 20.50, 20.54, 21.75, 22.07, 28.08, 28.66, 28.74, 28.95, 29.04, 29.06, 29.09, 29.62, 29.77, 29.87, 30.02, 30.34, 31.32, 119.50 (q, CF3).

19F NMR (400 MHz, *d6* -DMSO) δ: -79.00.

31P NMR (400 MHz, *d6* -DMSO) δ: 33.55.

**[P666,14][SCN]**. Trihexyl(tetradcyl)phosphonium chloride [P666,14]Cl (0.010 mol eq.) and K[SCN] (0.013 mol eq.) were separately dissolved in 25 cm3 deionised water (total 50 cm3) and then combined in a round-bottomed flask (250 cm3), resulting in the formation of a biphasic liquid system; the mixture was left to react (1 h, room temperature, 600 rpm). The aqueous layer was separated, and the organic layer was collected and washed, firstly with deionised water (10 cm3) and then dichloromethane, DCM (10 cm3). Subsequent washes were performed with solution of K[SCN] in deionised water until no chloride could be detected with silver nitrate solution. Subsequently, DCM was removed *via* rotary evaporation (30 min, 35 °C) and the ionic liquid was dried under high vacuum (overnight, 70 °C, 10-2 mbar). 1H, 13C and 31P NMR spectra were recorded in *d6*-DMSO solution.

1H NMR (600 MHz, *d6* -DMSO) δ: 0.86-0.94 (m, 12H), 1.23-1.30 (m, 18H), 1.31-1.36 (m, 14H), 1.37-1.44 (m, 8H), 1.45-1.55 (m, 8H), 2.16-2.24 (m, 8H).

13C NMR (600 MHz, *d6* -DMSO) δ: 13.74, 13.80, 17.30, 17.59, 20.42, 20.48, 21.75, 22.04, 28.07, 28.63, 28.67, 28.94, 28.97, 29.01, 29.03, 29.03, 29.65, 29.73, 29.85, 29.95, 30.34, 31.25, 131.07.

31P NMR (600 MHz, *d6* -DMSO) δ: 33.67.

**[P666,14][TCM]**. Trihexyl(tetradecyl)phosphonium chloride [P666,14]Cl (0.010 mol eq.) and sodium tricyanomethanide, Na[TCM] (0.013 mol eq.) were separately dissolved in 25 cm3 deionised water (total 50 cm3) and then combined in a round-bottomed flask (250 cm3), resulting in the formation of a biphasic liquid system; the mixture was left to react (1 h, room temperature, 600 rpm). The aqueous layer was separated, and the organic layer was collected and washed, firstly with deionised water (10 cm3) and then dichloromethane, DCM (10 cm3). Six subsequent washes were performed with solution of Na[TCM] in deionised water until no chloride could be detected with silver nitrate solution. Subsequently, DCM was removed *via* rotary evaporation (30 min, 35 °C) and the ionic liquid was dried under high vacuum (overnight, 70 °C, 10-2 mbar). 1H, 13C and 31P NMR spectra were recorded in *d6*-DMSO solution.

1H NMR (600 MHz, *d6* -DMSO) δ: 0.84-0.93 (m, 12H), 1.21-1.28 (m, 18H), 1.30-1.35 (m, 14H), 1.35-1.42 (m, 8H), 1.43-1.54 (m, 8H), 2.14-2.23 (m, 8H).

13C NMR (600 MHz, *d6* -DMSO) δ: 13.70, 13.76, 17.28, 17.69, 20.38, 20.45, 21.75, 21.98, 28.07, 28.61, 28.65, 28.91, 28.97, 29.01, 29.03, 29.05, 29.65, 29.71, 29.85, 29.95, 30.34, 31.20, 160.28.

31P NMR (600 MHz, *d6* -DMSO) δ: 33.67.

**[P666,14][BF4]**. Trihexyl(tetradecyl)phosphonium chloride [P666,14]Cl (0.010 mol eq.) and sodium tetrafluoroborate, Na[BF4] (0.013 mol eq.) were separately dissolved in 25 cm3 deionised water (total 50 cm3) and then combined in a round-bottomed flask (250 cm3), resulting in the formation of a biphasic liquid system; the mixture was left to react (1 h, room temperature, 600 rpm). The aqueous layer was separated, and the organic layer was collected and washed, firstly with deionised water (10 cm3) and then dichloromethane, DCM (10 cm3). Subsequent washes were performed with solution of Na[BF4] in deionised water until no chloride could be detected with silver nitrate solution. Subsequently, DCM was removed *via* rotary evaporation (30 min, 35 °C) and the ionic liquid was dried under high vacuum (overnight, 70 °C, 10-2 mbar). 1H, 13C, 11B and 31P NMR spectra were recorded in *d6*-DMSO solution.

1H NMR (600 MHz, *d6* -DMSO) δ: 0.89-0.96 (m, 12H), 1.25-1.32 (m, 18H), 1.32-1.38 (m, 14H), 1.39-1.47 (m, 8H), 1.47-1.56 (m, 8H), 2.17-2.26 (m, 8H).

13C NMR (600 MHz, *d6* -DMSO) δ: 13.75, 13.83, 17.30, 17.61, 20.47, 20.50, 21.77, 22.06, 28.07, 28.63, 28.70, 28.94, 28.99, 29.01, 29.03, 29.05, 29.65, 29.75, 29.88, 29.98, 30.36, 31.28.

11B NMR (600 MHz, *d6* -DMSO) δ: -1.26.

19F NMR (600 MHz, *d6* -DMSO) δ: -148.42.

31P NMR (600 MHz, *d6* -DMSO) δ: 33.70.

**[P666,14][TAU]**. Trihexyl(tetradecyl)phosphonium chloride [P666,14]Cl was converted to [P666,14][OH] (solution in methanol) following a literature procedure.[[1]](#endnote-1) [P666,14][TAU] was synthesised following a modified literature procedure.[[2]](#endnote-2) Taurine (0.012 mol eq.) was dissolved in 35 cm3 of deionised water and [P666,14][OH] (0.015 mol eq., solution in methanol) was added. The solution was stirred for 2 h at ambient temperature and the water-methanol mixture was removed *via* rotary evaporation (3 h, 30-80 °C). Crude product was dissolved in 50 ml of dry acetonitrile and stored in the fridge (5 °C) overnight. The excess taurine crystallised and was filtered off. Acetonitrile was removed *via* rotary evaporation (30 min, 60 °C) and the ionic liquid was dried under high vacuum (overnight, 70 °C, 10-2 mbar). 1H, 13C, 11B and 31P NMR spectra were recorded in *d6*-DMSO solution.

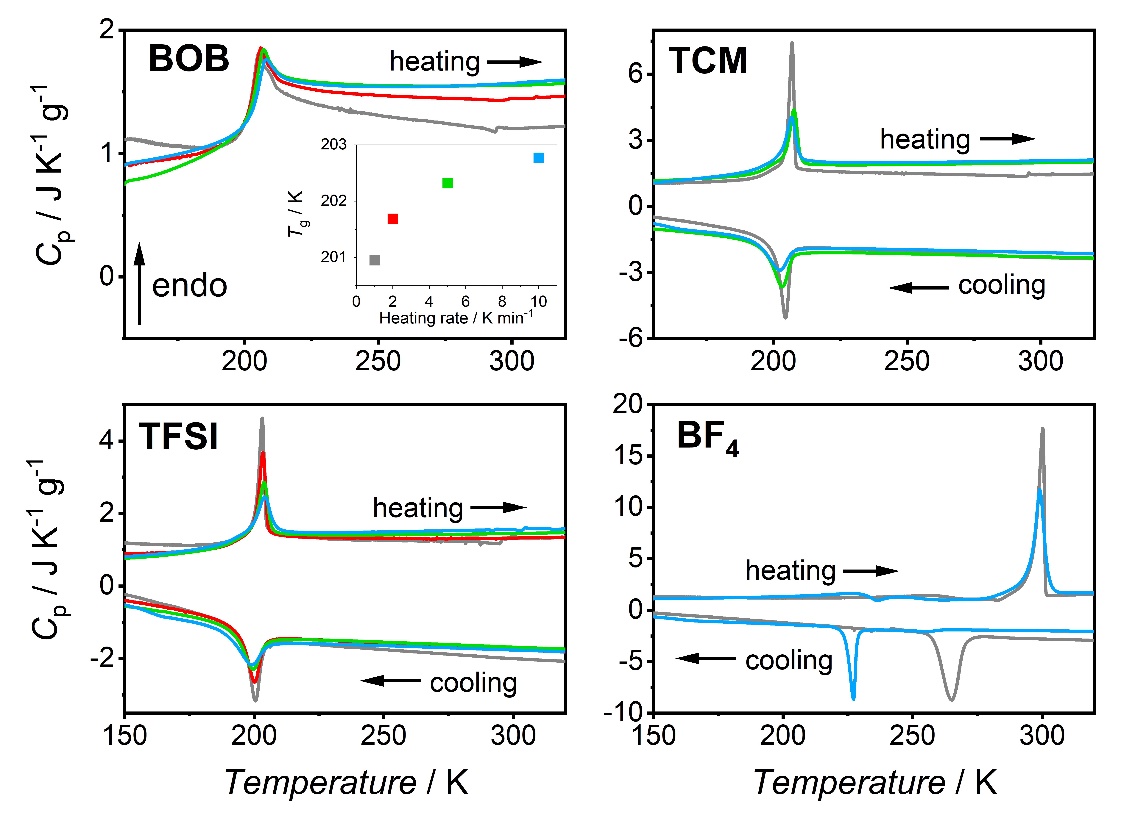
1H NMR (600 MHz, *d6* -DMSO) δ: 0.83-0.92 (m, 12H) 1.19-1.28 (m, 18H), 1.28-1.35 (m, 14H), 1.35-1.44 (m, 8H), 1.44-1.54 (m, 8H), 2.20-2.30 (m, 8H), 2.47-2.53 (t, 2H), 2.77-2.83 (t, 2H).

13C NMR (600 MHz, *d6* -DMSO) δ: 13.61, 13.66, 17.31, 17.63, 20.56, 20.58, 21.75, 22.03, 28.13, 28.68, 28.96, 28.98, 29.02, 29.04, 29.66, 29.76, 29.92, 30.02 30.37, 31.26, 38.52, 54.76.

31P NMR (600 MHz, *d6* -DMSO) δ: 33.53.

Prior to the measurements, the samples were dried under vacuum at 90 ℃ for 24h. The water content of the samples, detected using the Karl Fischer method, is around 500 and 300 ppm before and after drying, respectively.

**Calorimetric data with different scanning rate**



**Figure S1.** Heat capacity measured on different heating and cooling rate:10 (blue), 5 (green), 2 (red), and 1 (gray) K/min for [P666,14]-based ionic liquids. Inset presents the change of glass transition temperature with the heating rate for [P666,14][BOB].

**Ambient pressure dielectric measurements**



**Figure S2**. ε′ as a function of temperature at fix frequency (*f*=1MHz) during cooling (blue) and heating (red) with a rate of 1K/min for [P66614] [BOB], [P66614] [TCM], [P66614] [TFSI], and [P66614] [BF4]. The light blue and light red curves in the graph of [P66614] [BF4] denote the cooling and heating processes with a rate of 5K/min, respectively.



**Figure S3.** Stickel analysis of studied samples. Arrows indicate the LLT.



**Figure S4.** The dc-conductivity of [P666,14]-based ionic liquids as a function of temperature.

**Density results**



**Figure S5.** Temperature dependence of specific volume for[P666,14][TCM] and [P666,14][TFSI]. The data for [P666,14][TFSI] were taken from ref. [[3]](#endnote-3).

1. J. L. Ferguson, J. D. Holbrey, S. Ng, N. V. Plechkova, K. R. Seddon, A. A. Tomaszowska and D. F. Wassell, *Pure Appl. Chem*., 2012, **84**, 723–744 [↑](#endnote-ref-1)
2. Brett F. Goodrich, Juan C. de la Fuente, Burcu E. Gurkan, Zulema K. Lopez, Erica A. Price, Yong Huang, and Joan F. Brennecke\*, *J. Phys. Chem. B*, **115**, 29, 9140–9150 (**2011)** [↑](#endnote-ref-2)
3. Klomfar, J.; Souckova, M.; Patek, J. Low Temperature Densities from (218 to 364) K and up to 50 MPa in Pressure and Surface Tension for Trihexyl(tetradecyl)phosphonium Bis(trifluoromethylsulfonyl)imide and Dicyanamide and 1‐Hexyl-3-methylimidazolium Hexafluorophosphate *J. Chem. Eng. Data* **59**(7), 2263-2274, 2014 [↑](#endnote-ref-3)