S1. Synthesis

Triethylamine (99.5%) obtained from Carl Roth (Germany) and 1-bromopentane (99%) from Alfa Aesar (Germany) were distilled prior to use. Acetone (99.9%) from Fisher Scientific (Germany) was dried over 4 Å molecular sieves. Triethylphosphine (99%) from Strem (Germany), acetonitrile (HPLC grade) from Th. Geyer (Germany) as well as sodium dicyanamide (>97%) and sodium tricyanomethanide (98%) from IoLiTec (Germany) were used as received. Quaternization reactions were conducted under argon atmosphere. NMR spectra were recorden on an Avance II 400 MHz nuclear magnetic resonance (NMR) spectrometer (Bruker, Germany). Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane (TMS).

S1.1. Triethylpentylammonium bromide [N2225][Br]

For the synthesis of the quaternary ammonium salt 15.0 mLtriethylamine (10.9 g / 108 mmol / 1.3 eq.) and 10.3 mL 1-bromopentane (12.5 g / 83.1 mmol / 1.0 eq.) were dissolved in 150 mL acetonitrile under argon atmosphere. The reaction mixture was stirred for three days at ambient temperature and the solvent and excess reagent removed by rotary evaporation. After further drying for two days in high vacuum 20.3 g of the product (80.6 mmol / 97% yield) were obtained as colorless solid.

^{1}H-NMR (400 MHz, d6-DMSO): δ/ppm = 3.22 (q, $^{3}J_{HH}$ = 7.2 Hz, 6H, N-**C**H_2-CH_3), 3.10 (m, 2H, N-**C**H_2-CH_2), 1.62 – 1.50 (m, 2H, N-CH_2-**C**H_2), 1.39 – 1.21 (m, 4H, N-$(CH_2)_2$-(**C**H_2)$_2$), 1.16 (t, $^{3}J_{HH}$ = 7.2 Hz, 9H, N-CH_2-**C**H_3), 0.88 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H, N-$(CH_2)_4$-**C**H_3).

^{13}C{^{1}H}-NMR (101 MHz, d6-DMSO): δ/ppm = 56.05 (s, N-**C**H_2-CH_2), 52.04 (s, N-**C**H_2-CH_3), 27.99 (s, N-CH_2-**C**H_2), 21.73 (s, N-$(CH_2)_2$-**C**H_2), 20.71 (s, N-$(CH_2)_3$-**C**H_2), 13.84 (s, N-$(CH_2)_4$-**C**H_3), 7.25 (s, N-CH_2-**C**H_3).

S1.2. Triethylpentylammoniumdicyanamide [N2225][DCA]

For the synthesis of the title ionic liquids 9.00 g triethylpentyl ammonium bromide (35.7 mmol / 1.0 eq.) and 4.13 g sodium dicyanamide (46.4 mmol / 1.3 eq.) were dissolved in 200 mL acetone and stirred for 24 hours at ambient temperature. After this the solution was filtered, the solvent was removed by rotary evaporation, and the residue dissolved in 150 mL dichloromethane. The solution was dried over magnesium sulfate, filtered and the solvent removed by rotary evaporation. After drying with stirring for two days on a Schlenk line 8.42 g of the product (35.3 mmol / 99% yield) were obtained as colorless liquid.

^{1}H-NMR (400 MHz, d6-DMSO): δ/ppm = 3.22 (q, $^{3}J_{HH}$ = 7.2 Hz, 6H, N-**C**H_2-CH_3), 3.09 (m, 2H, N-**C**H_2-CH_2), 1.63 – 1.51 (m, 2H, N-CH_2-**C**H_2), 1.40 – 1.23 (m, 4H, N-$(CH_2)_2$-(**C**H_2)$_2$), 1.16 (t, $^{3}J_{HH}$ = 7.2 Hz, 9H, N-CH_2-**C**H_3), 0.88 (t, $^{3}J_{HH}$ = 7.1 Hz, 3H, N-$(CH_2)_4$-**C**H_3).

^{13}C{^{1}H}-NMR (101 MHz, d6-DMSO): δ/ppm = 119.16 (s, $N(CN)_2$), 56.10 (s, N-**C**H_2-CH_2), 52.07 (s, N-**C**H_2-CH_3), 28.02 (s, N-CH_2-**C**H_2), 21.77 (s, N-$(CH_2)_2$-**C**H_2), 20.72 (s, N-$(CH_2)_3$-**C**H_2), 13.86 (s, N-$(CH_2)_4$-**C**H_3), 7.22 (s, N-CH_2-**C**H_3).

S1.3. Triethylpentylammoniumtricyanomethanide[N2225][TCM]

For the synthesis of the title ionic liquids 9.00 g triethylpentyl ammonium bromide (35.7 mmol / 1.0 eq.) and 5.25 g sodium tricyanomethanide (46.4 mmol / 1.3 eq.) were dissolved in 200 mL acetone and stirred for 24 hours at ambient temperature. After this the solution was filtered, the solvent was removed by rotary evaporation, and the residue dissolved in 150 mL dichloromethane. The solution was dried over magnesium sulfate, filtered and the solvent removed by rotary evaporation. After drying with stirring for two days on a Schlenk line 9.18 g of the product (35.0 mmol / 98% yield) were obtained as colorless liquid.

^{1}H-NMR (400 MHz, d6-DMSO): δ/ppm = 3.21 (q, $^{3}J_{HH}$ = 7.2 Hz, 6H, N-**CH_2**-CH_3), 3.09 (m, 2H, N-**CH_2**-CH_2), 1.63 – 1.50 (m, 2H, N-CH_2-**CH_2**), 1.40 – 1.21 (m, 4H, N-$(CH_2)_2$-**$(CH_2)_2$**), 1.16 (t, $^{3}J_{HH}$ = 7.2 Hz, 9H, N-CH_2-**CH_3**), 0.89 (t, $^{3}J_{HH}$ = 7.1 Hz, 3H, N-$(CH_2)_4$-**CH_3**).

^{13}C{^{1}H}-NMR (101 MHz, d6-DMSO): δ/ppm = 120.60 (s, C(**CN**)$_3$), 56.08 (s, N-**CH_2**-CH_2), 52.05 (s, N-**CH_2**-CH_3), 28.01 (s, N-CH_2-**CH_2**), 21.76 (s, N-$(CH_2)_2$-**CH_2**), 20.71 (s, N-$(CH_2)_3$-**CH_2**), 13.83 (s, N-$(CH_2)_4$-**CH_3**), 7.19 (s, N-CH_2-**CH_3**).

S.1.4. Triethylpentyl phosphonium bromide [P2225][Br]

For the synthesis of the quaternary phosphonium salt 12.5 mL triethyphosphine (10 g / 84.6 mmol / 1.0 eq.)and 13.6 mL 1-bromopentane (16.6 g / 110 mmol / 1.2 eq.) were dissolved in 150 mL acetonitrile under argon atmosphere. The reaction mixture was stirred for three days at ambient temperature and the solvent and excess reagent removed by rotary evaporation. After further drying for two days in high vacuum 23.3 g of the product (82.9 mmol / 98% yield) were obtained as colorless solid.

^{1}H-NMR (400 MHz, d6-DMSO): δ/ppm = 2.36 – 2.20 (m, 8H, P-CH_2), 1.55 – 1.41 (m, 2H, P-CH_2-**CH_2**), 1.41 – 1.24 (m, 4H, P-$(CH_2)_2$-(**CH_2**)$_2$), 1.11 (dt, $^{3}J_{PH}$ = 18.0 Hz, $^{3}J_{HH}$ = 7.7 Hz, 9H, P-CH_2-**CH_3**), 0.86 (t, $^{3}J_{HH}$ = 7.0 Hz, 3H, P-$(CH_2)_4$-**CH_3**).

^{13}C{^{1}H}-NMR (101 MHz, d6-DMSO): δ/ppm = 32.19 (d, $^{3}J_{CP}$ = 15.0 Hz, P-$(CH_2)_2$-**CH_2**), 21.30 (s, P-$(CH_2)_3$-**CH_2**), 20.17 (d, $^{2}J_{CP}$ = 4.4 Hz, P-CH_2-**CH_2**), 16.79 (d, $^{1}J_{CP}$ = 47.5 Hz, P-**CH_2**-CH_2), 13.59 (s, P-$(CH_2)_4$-**CH_3**), 10.65 (d, $^{1}J_{CP}$ = 48.7 Hz, P-**CH_2**-CH_3), 5.25 (d, $^{2}J_{CP}$ = 5.4 Hz, P-CH_2-**CH_3**).

^{31}P{^{1}H}-NMR (162 MHz, d6-DMSO): δ/ppm = 38.88 (s).

S1.5. Triethylpentyl phosphonium dicyanamide [P2225][DCA]

For the synthesis of the title ionic liquids 9.00 g triethylpentyl phosphonium bromide (33.4 mmol / 1.0 eq.) and 3.87 g sodium dicyanamide (43.4 mmol / 1.3 eq.) were dissolved in 200 mL acetone and stirred for 24 hours at ambient temperature. After this the solution was filtered, the solvent was removed by rotary evaporation, and the residue dissolved in 150 mL dichloromethane. The solution was dried over magnesium sulfate, filtered and the solvent removed by rotary evaporation. After drying with stirring for two days on a Schlenk line 8.44 g of the product (33.1 mmol / 99% yield) were obtained as colorless liquid.

^{1}H-NMR (400 MHz, d6-DMSO): δ/ppm = 2.28 – 2.12 (m, 8H, P-CH_2), 1.55 – 1.42 (m, 2H, P-CH_2-**CH_2**), 1.42 – 1.26 (m, 4H, P-$(CH_2)_2$-(**CH_2**)$_2$), 1.13 (dt, $^{3}J_{PH}$ = 18.0 Hz, $^{3}J_{HH}$ = 7.6 Hz, 9H, P-CH_2-**CH_3**), 0.88 (t, $^{3}J_{HH}$ = 7.0 Hz, 3H, P-$(CH_2)_4$-**CH_3**).

^{13}C{^{1}H}-NMR (101 MHz, d6-DMSO): δ/ppm = 119.14 (s, $N(CN)_2$), 32.33 (d, $^{3}J_{CP}$ = 15.0 Hz, P-$(CH_2)_2$-**CH_2**), 21.44 (s, P-$(CH_2)_3$-**CH_2**), 20.23 (d, $^{2}J_{CP}$ = 4.4 Hz, P-CH_2-**CH_2**), 16.46 (d, $^{1}J_{CP}$ = 47.4 Hz, P-**CH_2**-CH_2), 13.72 (s, P-$(CH_2)_4$-**CH_3**), 10.63 (d, $^{1}J_{CP}$ = 48.9 Hz, P-**CH_2**-CH_3), 5.25 (d, $^{2}J_{CP}$ = 5.3 Hz, P-CH_2-**CH_3**).

^{31}P{^{1}H}-NMR (162 MHz, d6-DMSO): δ/ppm = 38.93 (s).

S1.6. Triethylpentyl phosphonium tricyanomethanid [P2225][TCM]

For the synthesis of the title ionic liquids 9.00 g triethylpentyl phosphonium bromide (33.4 mmol / 1.0 eq.) and 4.90 g sodium dicyanamide (43.4 mmol / 1.3 eq.) were dissolved in 200 mL acetone and stirred for 24 hours at ambient temperature. After this the solution was filtered, the solvent was removed by rotary evaporation, and the residue dissolved in 150 mL dichloromethane. The solution was dried over magnesium sulfate, filtered and the solvent removed by rotary evaporation. After drying with stirring for two days on a Schlenk line 9.14 g of the product (32.7 mmol / 98% yield) were obtained as colorless liquid.

^{1}H-NMR (400 MHz, d6-DMSO): δ/ppm = 2.26 – 2.1i0 (m, 8H, P-CH_2), 1.55 – 1.42 (m, 2H, P-CH_2-z**CH_2**), 1.42 – 1.28zz (m, 4H, P-$(CH_2)_2$-(**CH_2**)$_2$), 1.11 (dt, $^{3}J_{PH}$ = 18.0 Hz, $^{3}J_{HH}$ = 7.8 Hz, 9H, P-CH_2-**CH_3**), 0.88 (t, $^{3}J_{HH}$ = 7.1 Hz, 3H, P-$(CH_2)_4$-**CH_3**).

^{13}C{^{1}H}-NMR (101 MHz, d6-DMSO): δ/ppm = 120.58 (s, C(**CN**)$_3$), 32.33 (d, $^{3}J_{CP}$ = 14.8 Hz, P-$(CH_2)_2$-**CH_2**), 21.45 (s, P-$(CH_2)_3$-**CH_2**), 20.23 (d, $^{2}J_{CP}$ = 4.5 Hz, P-CH_2-**CH_2**), 16.45 (d, $^{1}J_{CP}$ = 47.5 Hz, P-**CH_2**-CH_2), 13.71 (s, P-$(CH_2)_4$-**CH_3**), 10.62 (d, $^{1}J_{CP}$ = 48.9 Hz, P-**CH_2**-CH_3), 5.22 (d, $^{2}J_{CP}$ = 5.3 Hz, P-CH_2-**CH_3**).

^{31}P{^{1}H}-NMR (162 MHz, d6-DMSO): δ/ppm = 38.95 (s).

S2. Physicochemical Characterization

S2.1 Density

Experimental values of the ionic liquids' densities are given in Table S1. The linear fitting parameter according to equation (S1) are given Table S2.

$$\rho = n - m \cdot T \quad \text{(S1)}$$

Table S1: Experimental T-dependent values of the ionic liquids' density ρ.

T/ K	Density ρ/ g mL^{-1}.			
	[N2225][DCA]	[N2225][TCM]	[P2225][DCA]	[P2225][TCM]
298.15	0.9832	0.9589	1.0064	0.9703
308.15	0.9775	0.9530	1.0008	0.9645
318.15	0.9716	0.9472	0.9950	0.9584
328.15	0.9661	0.9415	0.9897	0.9524
338.15	0.9607	0.9353	0.9839	0.9465
348.15	0.9552	0.9301	0.9785	0.9407
358.15	0.9498	0.9245	0.9730	0.9352
368.15	0.9446	0.9190	0.9675	0.9291

Table S2: Linear fitting parameters$a$ and b for the ionic liquids' densities according to equation (S1).

Ionic liquid	n / g mL^{-1}	m / 10^{-4}g mL^{-1}K^{-1}	R^2
[N2225][DCA]	1.147 ± 0.001	5.515 ± 0.037	0.99973
[N2225][TCM]	1.129 ± 0.001	5.709 ± 0.041	0.99969
[P2225][DCA]	1.172 ± 0.001	5.559 ± 0.023	0.99989
[P2225][TCM]	1.146 ± 0.001	5.882 ± 0.028	0.99986

S2.2. Viscosity

Experimental values of the ionic liquids' viscosity η at different temperatures are given in Table S3. The fitting parameters for the Vogel-Fulcher-Tammann equation are given in the main manuscript.

Table S3: Experimental T-dependent viscosity values of the investigated ionic liquids.

T/ K	Viscosity η / mPa s			
	[N2225][DCA]	[N2225][TCM]	[P2225][DCA]	[P2225][TCM]
298.15	196.7	63.03	141.3	39.81
303.15	147.5	50.05	110.4	32.37
308.15	113.6	40.72	88.24	26.72
313.15	89.24	33.65	71.50	22.38
318.15	71.52	28.27	58.84	18.98
323.15	58.10	24.00	48.95	16.31
328.15	48.02	20.65	41.14	14.13
333.15	40.19	17.94	34.90	12.30
338.15	34.03	15.73	29.67	10.82
343.15	29.15	13.92	25.65	9.60
348.15	25.27	12.42	22.59	8.57
353.15	22.07	11.15	19.74	7.70
358.15	19.44	10.08	17.53	6.94
363.15	17.25	9.16	15.67	6.28
368.15	15.43	8.38	14.03	5.70
373.15	13.87	7.70	12.68	5.22
378.15	12.57	7.11	11.38	4.80

S2.3. Specific Conductivity

Experimental values for the specific conductivityκ obtained by impedance spectroscopy are given in Table S4. The fitting parameter according to the VFT equation are summarized in Table S5.

Table S4: Experimental values for the specific conductivity of the investigated ionic liquids.

T / K	Specific conductivity κ / mS cm^{-1}			
	[N2225][DCA]	[N2225][TCM]	[P2225][DCA]	[P2225][TCM]
298.15	2.065	3.687	2.286	4.730
303.15	2.705	4.608	2.885	5.687
308.15	3.476	5.610	3.620	6.786
313.15	4.360	6.750	4.422	7.953
318.15	5.365	8.014	5.330	9.227
323.15	6.522	9.376	6.377	10.622
328.15	7.816	10.86	7.523	12.095
333.15	9.254	12.46	8.809	13.66
338.15	10.85	14.15	10.21	15.31
343.15	12.59	15.92	11.72	17.08
348.15	14.45	17.78	13.40	18.92
353.15	16.39	19.75	15.14	20.86
358.15	18.49	21.84	16.98	22.87
363.15	20.71	23.99	19.00	24.97
368.15	23.05	26.20	21.10	27.04
373.15	25.50	28.49	23.34	29.25

Table S5: VFT fitting parametersκ_0, B_κ and$T_{0,\kappa}$for the specific conductivity κ of the investigated ionic liquids including coefficient of determination R^2.

Ionic liquid	κ_0/ mS cm^{-1}	B_κ / K	$T_{0,\kappa}$ / K	R^2
[N2225][DCA]	890.9 ± 23.0	–641.7 ± 7.9	192.55 ± 0.9	0.99999
[N2225][TCM]	591.9 ± 9.5	–566.0 ± 5.0	186.62 ± 0.7	>0.99999
[P2225][DCA]	1233.3 ± 32.4	–805.4 ± 9.1	170.16 ± 1.0	>0.99999
[P2225][TCM]	635.9 ± 12.9	–621.0 ± 6.9	170.16 ± 1.0	>0.99999

S2.4. Molar conductivity

Calculated values of the ionic liquids' molar conductivity Λ_M at different temperatures are given in Table S6. The fitting parameters for the VFT equation are given in the main manuscript.

Table S6: Calculated values of the ionic liquids'molar conductivities at different temperatures.

T / K	Molar conductivity Λ_M / S $cm^2 mol^{-1}$			
	[N2225][DCA]	[N2225][TCM]	[P2225][DCA]	[P2225][TCM]
298.15	0.501	1.017	0.580	1.372
303.15	0.658	1.275	0.734	1.654
308.15	0.848	1.557	0.924	1.980
313.15	1.066	1.878	1.132	2.328
318.15	1.316	2.237	1.368	2.709
323.15	1.604	2.625	1.641	3.128
328.15	1.928	3.051	1.941	3.573
333.15	2.289	3.510	2.279	4.047
338.15	2.693	3.998	2.648	4.551
343.15	3.132	4.513	3.050	5.092
348.15	3.606	5.055	3.497	5.658
353.15	4.102	5.631	3.962	6.257
358.15	4.641	6.246	4.457	6.883
363.15	5.214	6.882	5.001	7.538
368.15	5.819	7.540	5.570	8.188
373.15	6.455	8.225	6.177	8.888

S2.5. Cation self-diffusion coefficients

Experimental values of the ionic liquids'' cation self-diffusion coefficients D_{S+} at different temperatures are given in Table S7. The fitting parameters for the VFT equation are given in the main manuscript.

Table S7: Experimental values for the cation self-diffusion coefficients $D_{S+}$of the ionic liquids

T / K	Cation self-diffusion coefficient D_{S+} / $m^2 s^{-1}$			
	[N2225][DCA]	[N2225][TCM]	[P2225][DCA]	[P2225][TCM]
278.15	1.23×10^{-12}	4.65×10^{-12}	2.03×10^{-12}	7.98×10^{-12}
283.15	1.92×10^{-12}	6.73×10^{-12}	2.87×10^{-12}	1.07×10^{-11}
288.15	2.88×10^{-12}	9.37×10^{-12}	3.98×10^{-12}	1.40×10^{-11}
293.15	4.25×10^{-12}	1.27×10^{-11}	5.40×10^{-12}	1.79×10^{-11}
298.15	5.89×10^{-12}	1.68×10^{-11}	7.18×10^{-12}	2.26×10^{-11}
303.15	8.06×10^{-12}	2.16×10^{-11}	9.40×10^{-12}	2.82×10^{-11}
308.15	1.08×10^{-11}	2.74×10^{-11}	1.21×10^{-11}	3.44×10^{-11}
313.15	1.41×10^{-11}	3.40×10^{-11}	1.54×10^{-11}	4.17×10^{-11}
318.15	1.81×10^{-11}	4.17×10^{-11}	1.92×10^{-11}	4.97×10^{-11}
323.15	2.27×10^{-11}	5.00×10^{-11}	2.36×10^{-11}	5.90×10^{-11}
328.15	2.81×10^{-11}	5.96×10^{-11}	2.87×10^{-11}	6.91×10^{-11}
333.15	3.42×10^{-11}	7.01×10^{-11}	3.46×10^{-11}	8.01×10^{-11}
338.15	4.12×10^{-11}	8.17×10^{-11}	4.11×10^{-11}	9.17×10^{-11}
343.15	4.89×10^{-11}	9.45×10^{-11}	4.87×10^{-11}	1.05×10^{-10}
348.15	5.79×10^{-11}	1.08×10^{-10}	5.67×10^{-11}	1.19×10^{-10}
353.15	6.72×10^{-11}	1.23×10^{-10}	6.58×10^{-11}	1.34×10^{-10}
358.15	7.82×10^{-11}	1.39×10^{-10}	7.61×10^{-11}	1.50×10^{-10}
363.15	9.01×10^{-11}	1.56×10^{-10}	8.77×10^{-11}	1.67×10^{-10}

S2.6. Walden Relation

Experimental values of the viscosity and molar conductivity were analyzed using the Walden relation according to equation (S2). The obtained linear fitting parameters are given in Table S8.

$$\log\left(\frac{\Lambda_M}{S \cdot cm^2 \cdot mol^{-1}}\right) = \log(C) + t \cdot \log\left(\frac{0.1\ Pa \cdot s}{\eta}\right) \qquad (S2)$$

Table S8: Linear fitting parameters $\log(C)$ and t according to the Walden relation (equation (S2)) including coefficient of determination R^2.

Ionic liquid	$\log(C)$/ 10^{-1}	t / 1	R^2
[N2225][DCA]	–0.198 ± 0.006	0.965 ± 0.001	0.99998
[N2225][TCM]	–1.952 ± 0.013	0.994 ± 0.002	0.99996
[P2225][DCA]	–0.899 ± 0.009	0.979 ± 0.002	0.99996
[P2225][TCM]	–2.319 ± 0.010	0.922 ± 0.001	0.99998

S2.7. Stokes–Einstein Relation

Experimental values of the viscosity and the cation self-diffusion coefficients were analyzed using the Stokes–Einstein relation according to equation (S3). The obtained linear fitting parameters are given in Table S9.

$$\log\left(\frac{D_{S+}}{\mathrm{m^2 s^{-1}}} \cdot \frac{T^{-1}}{\mathrm{K^{-1}}}\right) = a + u \cdot \log(\eta^{-1}/(\mathrm{mPa\ s})^{-1}) \qquad \text{(S3)}$$

Table S9: Linear fitting parameters a and u according to the Stokes–Einstein relation (equation (S3)) including coefficient of determination R^2.

Ionic liquid	a/ 1	u / 1	R^2
[N2225][DCA]	−11.324 ± 0.002	1.038 ± 0.001	0.99998
[N2225][TCM]	−11.355 ± 0.001	1.055 ± 0.001	0.99999
[P2225][DCA]	−11.374 ± 0.004	1.044 ± 0.002	0.99994
[P2225][TCM]	−11.554 ± 0.002	0.979 ± 0.002	0.99997