Supplementary Material (ESI) for Chemical Communications

Supporting Information

Trialkylsulfonium dicyanamides – a new family of ionic liquids with very low viscosities†

Dirk Gerhard[a], Samim Cenk Alpaslan[a], Heiner Jakob Gores[b], Marc Uerdingen[c] and Peter Wasserscheid*[a]

Experimental Section

Chemicals

The alkyliodides (Fluka/Aldrich), dialkylsulfides (Aldrich) as well as dry aceton (Acros), sodium dicyanamide (Acros) and trimethylsulfonium iodide (Fluka) applied in this research were purchased from the companies given in brackets. The materials were used without further purification.

Measurements

^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECX 400 MHz spectrometer, in d_6-DMSO.

The viscosity measurements were carried out using an Anton Paar MCR 100 Rheometer under an argon atmosphere at controlled temperature in the range of -20 to 80 °C.

The conductivity was measured using a WTW LF 521 conductivity meter with a LTA 1 measuring cell under argon atmosphere and controlled temperature.

Differential scanning calorimetry (DSC) was carried out using a Netzsch DSC 205 Phoenix under an argon atmosphere with samples hermetically sealed in Al pans and cooled to -140 °C and then reheating at a cooling and heating rate of 10 K/min. The melting points (T_m) were determined from the DSC thermograms during the programmed reheating steps.

Thermogravimetric measurements were conducted on a Netzsch TG 209 with the samples placed in an open Al_2O_3 pan and heated from room temperature up to 450 °C at a heating rate of 10 K/min under an argon atmosphere. The temperature of decomposition (T_{dec}) was determined by using the TG-onset temperature, which is the intersection of the baseline below their decomposition temperature with the tangent to the mass loss versus temperature plots in the TGA experiment.

Thermal stability measurements for trimethylsulfonium dicyanamide were carried out by an isothermal TGA experiment. The sample was heated to the desired temperature with a heating rate of 10 K/min followed by a constant temperature for 12h.

ESI-MS were recorded on a ThermoQuest Finnigan TSQ 7000. The ionic liquids measured are abbreviated as (AB), with A corresponding to the cation and B corresponding to the anion.

UV/Vis spectras were recorded on an Analytik Jena AG Specord 205 using a 2 mm cuvette (neat) and 10 mm cuvette (aqueous solution).

Ionic Chromatography was carried out using a Metrohm IC 761 Compact combined with an auto sampler 831.

General Procedure for the synthesis of trialkylsulfonium dicyanamides

The desired trialkylsulfonium iodides precursors [$R_2R`S$] I were synthesized following the synthetic approach of Paulsson et al.[1] Equimolar amounts of dialkylsulfide and alkyl iodide,

dissolved in dry acetone were stirred in darkness at ambient conditions for several days. All substances were identified by ^{1}H and ^{13}C-NMR after purifying.
Silver dicyanamide was precipitated by mixing aqueous solutions of silver nitrate and sodium dicyanamide (1:1 molar ratio). The white residue was filtered off, washed with water to remove any unreacted reagents and used immediately. An aqueous solution of the iodide was added to aqueous slurry of the excess (1:1.1) silver dicyanamide and the solution was heated to 40 °C with stirring overnight. Silver iodide was removed by filtration before drying the product under reduced pressure of 1 mbar. To ensure complete removal of silver salts from the product, the dried ionic liquid was cooled in a freezer overnight before further filtration. All substances were dried by addition of dry dichloromethane and stirring at 1 mbar and 40 °C overnight. All ionic liquids were obtained as colourless or faint yellow liquids. The halide content was below 3000 ppm for all products.

Trimethylsulfonium dicyanamide (49.59 g isolated product, 98% yield)

δ_H (400 MHz; d_6-DMSO): 2.85 (9 H, s, $S(CH_3)_3$); δ_C (100 MHz; d_6-DMSO): 26.9 ($S(CH_3)_3$) and 119.7 ($N(CN)_2$); *m/z* (+ES): 77.1 (100%, A^+) and 220.1 (12%, A_2B^+ cluster); *m/z* (-ES): 66.1 (100%, B^-), 209 (63%, AB_2^- cluster), 352.2 (21%, $A_2B_3^-$ cluster) and 495.3 (27%, $A_3B_4^-$ cluster).

Diethylmethylsulfonium dicyanamide (8.23 g isolated product, 95% yield)

δ_H (400 MHz; d_6-DMSO): 1.33 (6 H, t, *J* 7.4 Hz, $S(CH_2CH_3)_2$), 2.85 (3 H, s, SCH_3) and 3.27 (4 H, m, $S(CH_2CH_3)_2$); δ_C (100 MHz; d_6-DMSO): 8.6 ($S(CH_2CH_3)_2$), 26.9 (SCH_3), 34.8 ($S(CH_2CH_3)_2$) and 119.7 ($N(CN)_2$); *m/z* (+ES): 105.0 (100%, A^+) and 276.1 (12%, A_2B^+ cluster); *m/z* (-ES): 66.1 (100%, B^-), 237.2 (80%, AB_2^- cluster) and 408.6 (15%, $A_2B_3^-$ cluster).

Methyldipropylsulfonium dicyanamide (12.35 g isolated product, 98% yield)

δ_H (400 MHz; d_6-DMSO): 1.01 (6 H, t, *J* 7.3, $S(CH_2CH_2CH_3)_2$), 1.75 (4 H, m, $S((CH_2CH_2CH_3)_2$), 2.85 (3 H, s, SCH_3) and 3.27 (4 H, m, $S(CH_2CH_2CH_3)_2$); δ_C (100 MHz; d_6-DMSO): 13.2 ($S(CH_2CH_2CH_3)_2$), 17.6 ($S(CH_2CH_2CH_3)_2$), 22.1 (SCH_3), 42.6 ($S(CH_2CH_2CH_3)_2$) and 119.7 ($N(CN)_2$); *m/z* (+ES): 133.0 (100%, A^+); *m/z* (-ES): 66.1 (100%, B^-), 265.0 (92%, AB_2^- cluster), 464.3 (14%, $A_2B_3^-$ cluster) and 663.6 (13%, $A_3B_4^-$ cluster).

Dibutylmethylsulfonium dicyanamide (8.20 g isolated product, 90% yield)

δ_H (400 MHz; d_6-DMSO): 0.92 (6 H, t, *J* 7.4, $S(CH_2CH_2CH_2CH_3)_2$), 1.42 (4 H, m, $S(CH_2CH_2CH_2CH_3)_2$), 1,72 (4 H, m, 4H, $S((CH_2CH_2CH_2CH_3)_2$), 2.88 (3 H, s, SCH_3) and 3.27 (4 H, m,$S(CH_2CH_2CH_2CH_3)_2$); δ_C (100 MHz; d_6-DMSO): 13.5 ($S(CH_2CH_2CH_2CH_3)_2$), 21.6 ($S(CH_2CH_2CH_2CH_3)_2$), 22.2 ($S(CH_3)$, 25.9 ($S(CH_2CH_2CH_2CH_3)_2$), 37.6 ($S(CH_2CH_2CH_2CH_3)_2$) and 119.6 ($N(CN)_2$); *m/z* (+ES): 160.9 (100%, A^+) and 388.3 (11%, A_2B^- cluster); *m/z* (-ES): 66.1 (55%, B^-) and 293.1 (100%, AB_2^- cluster).

Ethyldimethylsulfonium dicyanamide (5.01 g isolated product, 95% yield)

δ_H (400 MHz; d_6-DMSO): 1.33 (3 H, t, *J* 7.4, SCH_2CH_3), 2.85 (6 H, s, $S(CH_3)_2$) and 3.27 (2 H, q, *J* 7.4, SCH_2CH_3); δ_C (100 MHz, d_6-DMSO): 8.6 (SCH_2CH_3), 26.9 ($S(CH_3)_2$), 36.9 (SCH_2CH_3) and 119.7 ($N(CN)_2$); *m/z* (+ES): 91.1 (100%, A^+) and 248.1 (7%, A_2B^+ cluster); m/z (ES): = 66.1 (100%, B^-), 223.1 (78%, AB_2^- cluster), 380.2 (10%, $A_2B_3^-$ cluster) and 537.4 (15%, $A_3B_4^-$ cluster).

Triethylsulfonium dicyanamide (6.57 g isolated product, 94% yield)

δ_H (400 MHz; d_6-DMSO): 1.31 (9 H, t, *J* 7.3, $S(CH_2CH_3)_3$) and 3.27 (6 H, q, *J* 7.3, $S(CH_2CH_3)_3$); δ_C (100 MHz, d_6-DMSO): 8.6 ($S(CH_2CH_3)_3$), 31.9 ($S(CH_2CH_3)_3$) and 119.7 ($N(CN)_2$); *m/z* (+ES): 119 (100%, A^+); *m/z* (-ES): 66.1 (100%, B^-), 251.1 (75%, AB_2^- cluster) and 436.3 (7%, $A_2B_3^-$ cluster).

Ethyldipropylsulfonium dicyanamide (6.00 g isolated product, 96% yield)

δ_H (400 MHz; d_6-DMSO): 1.02 (6 H, t, *J* 7.4, $S(CH_2CH_2CH_3)_2$), 1.35 (3 H, t, *J* 7.3, SCH_2CH_3), 1.76 (4 H, m, $S(CH_2CH_2CH_3)_2$, 3.22-3.27 (6 H, m, $S(CH_2CH_2CH_3)_2$), and SCH_2CH_3); δ_C (100 MHz, d_6-DMSO): 9.0 (SCH_2CH_3), 13.2 ($S(CH_2CH_2CH_3)_2$), 17.6 ($S(CH_2CH_2CH_3)_2$), 33.4 (SCH_2CH_3), 42.1 ($S(CH_2CH_2CH_3)_2$), and 119.7 ($N(CN)_2$); *m/z* (+ES): 147.0 (100%, A^+); *m/z* (-ES): 66.1 (100%, B^-), 279.0 (82%, AB_2^- cluster), 492.4 (7%, $A_2B_3^-$ cluster) and 705.0 (8%, $A_3B_4^-$ cluster).

Dibutylethylsulfoniumdicyanamide (6.39 g isolated product, 92% yield)

δ_H (400 MHz; d_6-DMSO): 0.93 (6 H, t, *J* 7.4, $S(CH_2CH_2CH_2CH_3)_2$), 1.35 (2 H, t, *J* 7.3, $S(CH_2CH_3)$), 1.45 (4 H, m, $S(CH_2CH_2CH_2CH_3)_2$) and 3.28-3.38 (m, 7 H, $S(CH_2CH_3)$ and $S(CH_2CH_2CH_2CH_3)_2$); δ_C (100 MHz, d_6-DMSO): 9.0 ($S(CH_2CH_3)$, 13.8 ($S(CH_2CH_2CH_2CH_3)_2$), 21.7 ($S(CH_2CH_2CH_2CH_3)_2$), 25.9 ($S(CH_2CH_2CH_2CH_3)_2$), 33.3 ($S(CH_2CH_3)$, 37.8 ($S(CH_2CH_2CH_2CH_3)_2$) and 119.6 ($N(CN)_2$); *m/z* (+ES): 175 (100%, A^+); *m/z* (-ES): 66.1 (100%,B^-), 307.2 (80%, AB_2^- cluster).

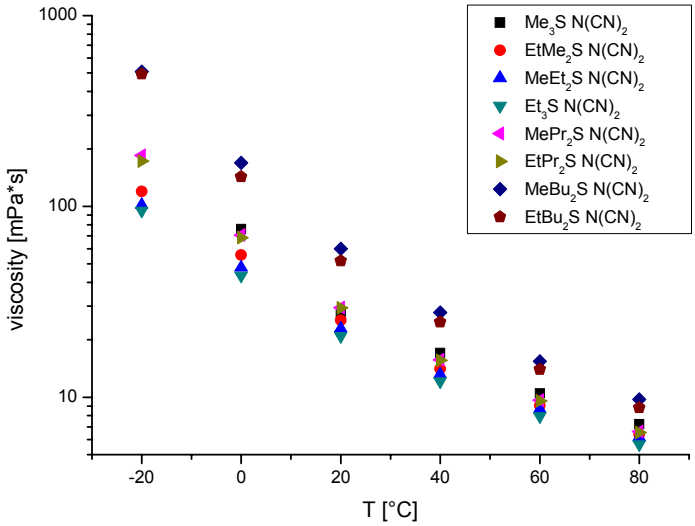


Figure S1: Temperature dependency of viscosity

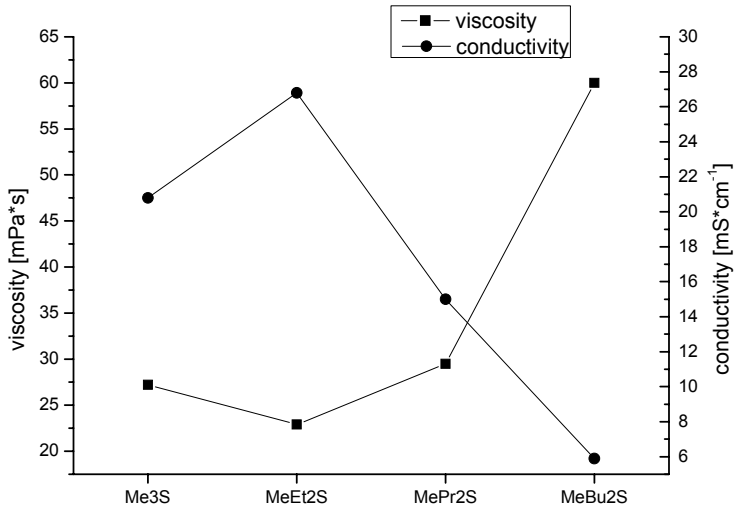


Figure S2: Viscosity/conductivity of ionic liquids at 20 °C (R` = Me)

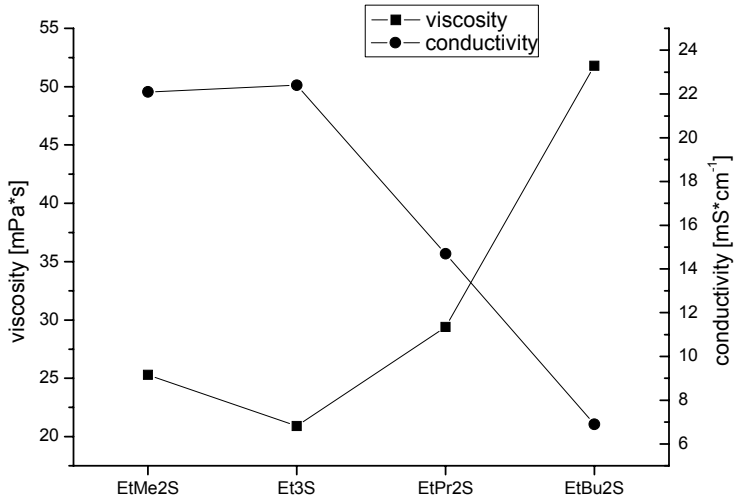


Figure S3: Viscosity/conductivity of ionic liquids at 20 °C (R `= Et)

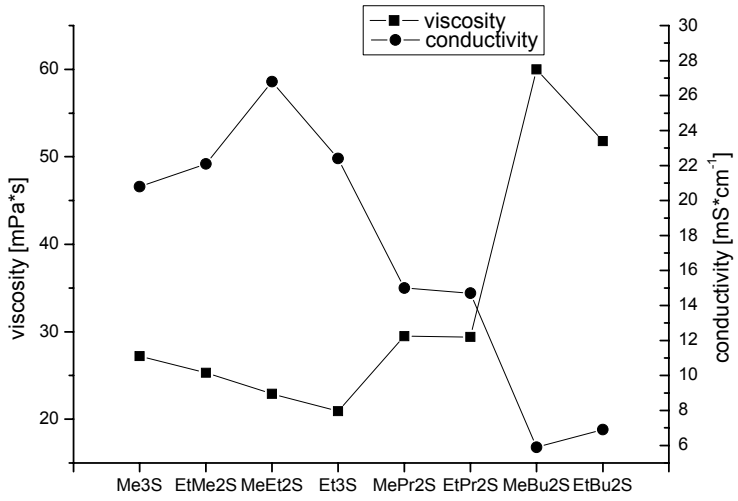


Figure S4: Viscosity/conductivity of ionic liquids at 20 °C

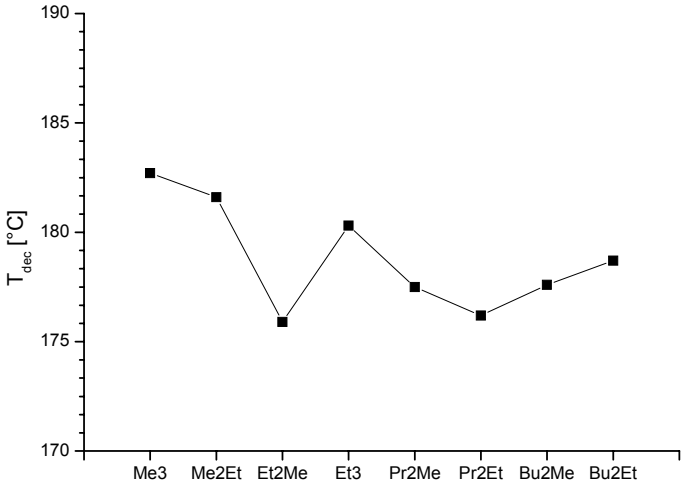


Figure S4: Temperature of decomposition

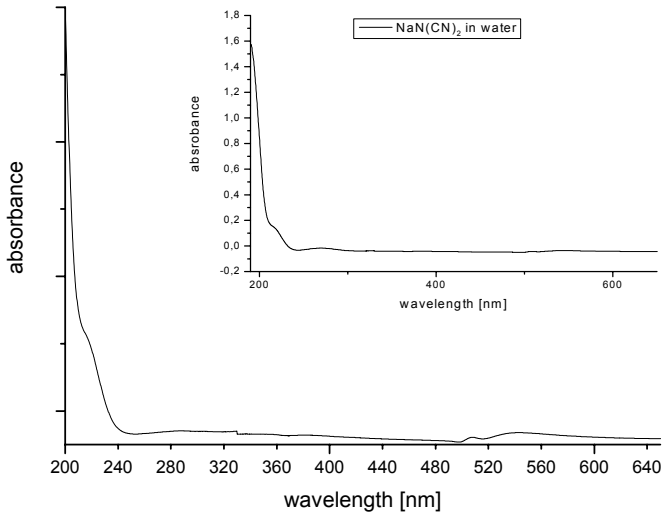


Figure S5: UV/Vis-absorbance of Trimethylsulfonium dicyanamide and sodium dicyanamide in water

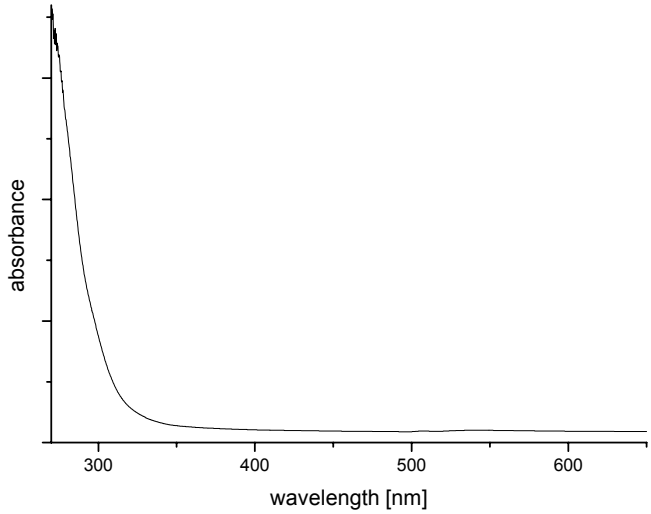


Figure S6: UV/Vis-absorbance of neat Trimethylsulfonium dicyanamide

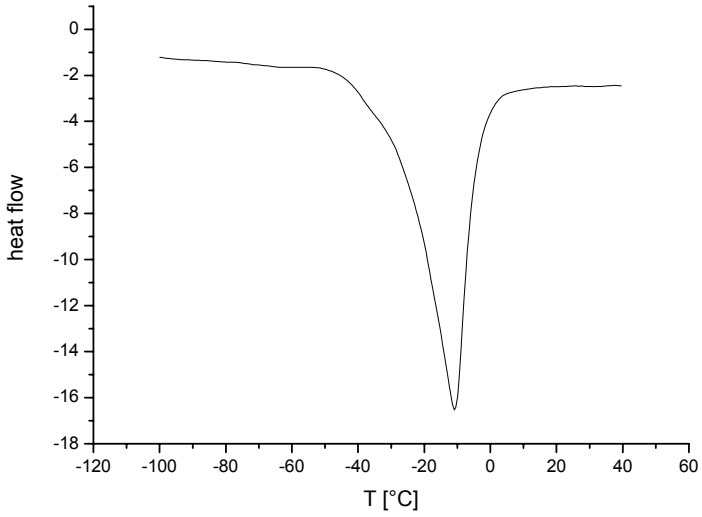
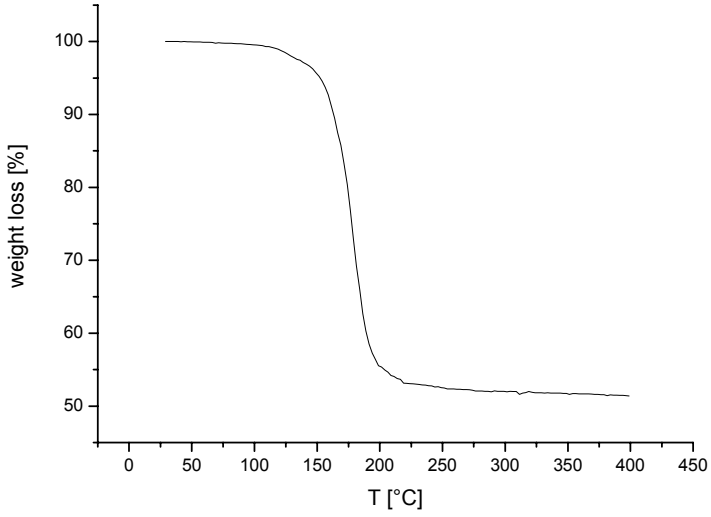


Figure S8: DSC of Ethyldimethylsulfonium dicyanamide



Graph 7: TGA of Trimethylsulfonium dicyanamide

[1] H. Paulsson, M. Berggrund, E. Svantesson, A. Hagfeldt, L. Kloo, *Solar Energy Materials and Solar Cells*, **2004**, *82*, 345.