

Electronic Supporting Information

The interfaces of Au(111) and Au(100) in a hexaalkyl-substituted guanidinium ionic liquid: an electrochemical and *in-situ* STM study

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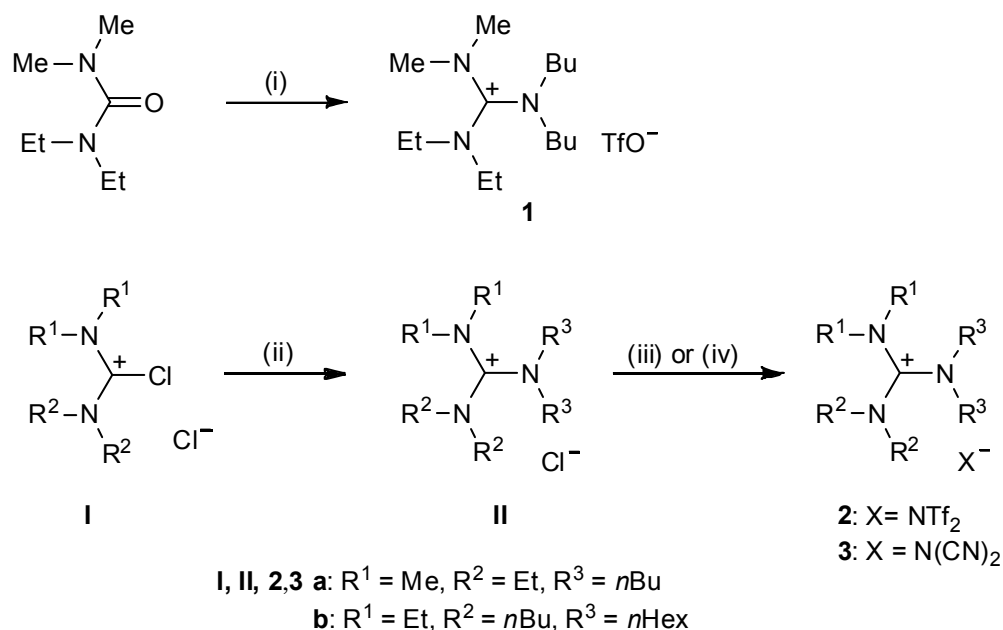
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Synthesis and characterisation of hexaalkylguanidinium-based ionic liquids 1–3

General information

The required guanidinium-based ionic liquids were synthesised on two routes (Scheme 1). *N,N*-Dibutyl-*N',N'*-diethyl-*N'',N''*-dimethylguanidinium trifluoromethanesulfonate ([N₁₁N₂₂N₄₄Gu]OTf, **1**) was prepared chloride-free from *N,N*-diethyl-*N',N'*-dimethylurea, triflic anhydride and dibutylamine as reported.¹ Guanidinium bis(triflyl)amides **2** and guanidinium dicyanamides **3** were obtained from the corresponding hexaalkylguanidinium chlorides **II** by anion exchange reactions. The hexaalkylguanidinium chlorides **II** in turn were prepared from tetraalkylchloroformamidinium chlorides **I** by an adaptation of the classical procedure.²



Scheme 1 Synthesis of guanidinium-based ionic liquids **1–3**. (i) 1. (CF₃SO₂)₂O; 2. Bu₂NH (lit. 1); (ii) R³₂NH, Et₃N, acetonitrile; (iii) LiN(CF₃SO₂)₂, H₂O; (iv) NaN(CN)₂, CH₂Cl₂.

Materials and Methods

Rigorously dried organic solvents were used. All amines were dried with KOH pellets and distilled prior to use. Lithium bis(trifluoromethylsulfonyl)imide (99%) was purchased from Acros Organics and sodium dicyanamide (96%) from Alfa Aesar. Solutions of chloroformamidinium chlorides in acetonitrile were obtained from Professor W. Kantlehner (Hochschule Aalen). NMR spectra were recorded on a Bruker DRX 400 spectrometer (¹H: 400.13 MHz; ¹³C: 100.61 MHz; ¹⁹F: 376.46 MHz). ¹H NMR spectra were referenced to the residual proton signal of the solvent [$\delta(\text{CDCl}_3) = 7.26$ ppm]. ¹³C spectra were referenced to the solvent signal [$\delta(\text{CDCl}_3) = 77.00$ ppm], and ¹⁹F spectra to C₆F₆ in CDCl₃ [$\delta(\text{C}_6\text{F}_6) = -162.9$ ppm]. IR spectra were recorded with a Bruker Vector 22 FTIR spectrometer. Thermogravimetric analysis was performed with a Mettler-Toledo TGA/SDTA 851 instrument and differential scanning calorimetry with a Perkin Elmer DSC 7 instrument (T_{dec} = temperature of highest decomposition gradient, T_{g} = glass transition temperature). Microanalyses were obtained with an Elementar vario MICRO cube instrument.

N,N-Dibutyl-*N',N'*-diethyl-*N'',N''*-dimethylguanidinium chloride (**IIa**)

To a solution of *N,N*-diethyl-*N',N'*-dimethylchloroformamidinium chloride (**Ia**) (3.98 g, 20.0 mmol) in dry acetonitrile (25 mL) was added a solution of dibutylamine (2.59 g, 3.40 mL, 20.0 mmol) and triethylamine (2.12 g, 2.92 mL, 21.0 mmol) in dry diethyl ether (10 mL). The mixture was stirred for 12 h, the precipitated ammonium salt was filtered off, and the volatiles were evaporated at 70 mbar/40 °C. In order to destroy remaining ammonium salt(s), 0.1 M aqueous NaOH was added to the residue until the pH was slightly basic. Water and triethylamine were removed by vacuum distillation, and the residue was dissolved in a mixture of dry acetonitrile and diethylether and filtered. After evaporation of the solvents, the solid residue was washed with several portions of diethyl ether for the purpose of decolorisation. The product so obtained was kept at 60 °C/0.001 mbar for 6 h. White powder (4.05 g, 70% yield); m.p. 79 °C, T_g -42 °C, T_{dec} 292 °C. ^1H NMR (CDCl_3): δ = 0.87 (t, 6 H, $\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.12–1.70 (several m, 14 H, NCH_2CH_3 , $\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 3.07/3.09 (2 s, 3 H each, NCH_3), 2.95–3.40 (m, 8 H, NCH_2) ppm. ^{13}C NMR (CDCl_3): δ = 12.84, 13.16, 13.51, 13.56 ($(\text{CH}_2)_n\text{CH}_3$); 19.80, 19.96, 29.47, 29.73 ($\text{CH}_2(\text{CH}_2)_2\text{CH}_3$); 40.65, 40.86 (NCH_3); 43.62, 44.03 (NCH_2CH_3); 49.06, 49.64 (NCH_2 -butyl); 163.19 (CN_3) ppm. IR (KBr): ν = 2958 (m), 2931 (m), 2871 (m), 1582 (s), 1541 (s), 1458 (m), 1417 (m), 1281 (vs), 1221 (m), 1112 (s), 1070 (s) cm^{-1} . Anal. calcd for $\text{C}_{15}\text{H}_{34}\text{ClN}_3$ (291.90): C 61.72, H 11.74, N 14.40%; found: C 61.23, H 11.67, N 14.16%.

***N,N*-Dibutyl-*N',N'*-diethyl-*N'',N''*-dihexylguanidinium chloride (**Ib**)**

Prepared according to the procedure for **Ia** from *N,N*-dibutyl-*N',N'*-diethylchloroformamidinium chloride (**Ib**) (14.16 g, 50.0 mmol) in acetonitrile (35 mL), dihexylamine (9.27 g, 11.7 mL, 50.0 mmol) and triethylamine (5.06 g, 7.03 mL, 50.0 mmol) in dry diethyl ether (10 mL). White powder (17.7 g, 82% yield); m.p. 71 °C, T_g -10 °C, T_{dec} 280 °C. ^1H NMR (CDCl_3): δ = 0.86 (t, 6 H, $\text{C}_5\text{H}_{11}\text{CH}_3$), 0.90–0.95 (2 t, 6 H, $\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.20–1.75 (several m, 30 H, $\text{CH}_2(\text{CH}_2)_4\text{CH}_3$, NCH_2CH_3 und $\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 3.00–3.53 (several m, 12 H, NCH_2) ppm. ^{13}C NMR (CDCl_3): δ = 13.10, 13.12, 13.61, 13.81, 13.83, (CH_3); 20.04, 20.05, 22.42, 22.44, 26.49, 26.55, 27.48, 27.52, 29.57, 29.63, 31.21, 31.26 ($(\text{CH}_2)_n\text{CH}_3$, $n = 2,4$); 44.18, 44.22 (NCH_2 -ethyl); 49.53, 49.79, 49.77 (NCH_2 -butyl, -hexyl); 163.80 (CN_3) ppm. IR (KBr): ν = 2959 (s), 2929 (s), 2869 (m), 1537 (s), 1458 (m), 1358 (m), 1235 (vs), 1188 (m) cm^{-1} . Anal. calcd for $\text{C}_{25}\text{H}_{54}\text{ClN}_3$ (432.17): C 69.48, H 12.59, N 9.72%; found: C 69.58, H 12.28, N 9.56%.

***N,N*-Dibutyl-*N',N'*-diethyl-*N'',N''*-dimethylguanidinium bis(trifluoromethylsulfonyl)-imide (**2a**, [$\text{N}_{11}\text{N}_{22}\text{N}_{44}\text{Gu}$]NTf₂)**

To a solution of guanidinium chloride **IIa** (4.00 g, 13.7 mmol) in water (30 mL) was added a solution of $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ (3.94 g, 13.7 mmol) in water (15 mL). Two layers were formed instantly. The reaction mixture was kept stirring at 70 °C for 30 min. After cooling, dichloromethane (30 mL) was added and the organic phase was extracted with water until the test on Cl^- in the water phase was negative. The CH_2Cl_2 phase was dried (Na_2SO_4), the solvent was evaporated, and the residue was dried at 80 °C/0.001 mbar for 6 h. If necessary, a CH_2Cl_2 solution of the ionic liquid was treated with activated carbon by stirring overnight. A slight decoloration of the ionic liquid by treatment with activated carbon in CH_2Cl_2 for 12 h was achieved. Yellow oil (6.40 g, 87% yield); T_g -68 °C, T_{dec} 448 °C. ^1H NMR (CDCl_3): δ = 0.95 (t, 6 H, $\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.16–1.72 (several m, 14 H, NCH_2CH_3 , $\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 2.985/2.987 (2 s, 3 H each, NCH_3), 2.99–3.34 (2 m, 8 H, NCH_2) ppm. ^{13}C NMR (CDCl_3): δ = 12.62, 12.96, 13.54, 13.59 ($(\text{CH}_2)_n\text{CH}_3$); 19.89, 20.01, 29.43, 29.69 ($\text{CH}_2(\text{CH}_2)_2\text{CH}_3$); 40.36, 40.47 (NCH_3); 43.46, 44.00 (NCH_2CH_3); 49.11, 49.82 (NCH_2 -butyl); 163.49 (CN_3) ppm. ^{19}F NMR (CDCl_3): δ □ = -79.7 ppm. IR (NaCl): ν = 2965 (m), 2938 (m), 1578 (s), 1545 (s), 1461 (m), 1421 (m), 1352 (vs), 1139 (s), 1058 (s) cm^{-1} . Anal. calcd for $\text{C}_{17}\text{H}_{34}\text{F}_6\text{N}_4\text{O}_4\text{S}_2$ (536.60): C 38.05, H 6.39, N 10.44%; found C 38.03, H 6.33, N 10.43%.

***N,N*-Dibutyl-*N',N'*-diethyl-*N'',N''*-dihexylguanidinium bis(trifluoromethylsulfonyl)imide (2b, $\text{N}_{22}\text{N}_{44}\text{N}_{66}\text{Gu}[\text{NTf}_2]$):** Prepared from guanidinium chloride **IIb** (6.00 g, 13.88 mmol) and $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ (3.98 g, 13.88 mmol) in water (60 mL) as described for **2a**. Light-yellow oil (8.57 g, 91% yield); T_g -3 °C, T_{dec} 460 °C. ^1H NMR (CDCl_3): δ = 0.89 (t, 6 H, CH_3), 0.92–0.97 (2 t, 6 H, CH_3), 1.22 (t, 6 H, NCH_2CH_3), 1.22–1.77 (several m, 24 H, $\text{CH}_2(\text{CH}_2)_4\text{CH}_3$, $\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 2.97–3.42 (several m, 12 H, NCH_2) ppm. ^{13}C NMR (CDCl_3): δ = 12.74, 12.76, 13.56, 13.58, 13.85, 13.87 (CH_3); 19.99, 20.02, 22.45, 22.48, 26.46, 26.50, 27.40, 27.42, 29.46, 29.53, 31.20, 31.25 ($(\text{CH}_2)_n\text{CH}_3$, $n = 2,4$); 43.82, 43.85 (NCH_2 -ethyl); 49.37, 49.46, 49.62, 49.64 (NCH_2 -butyl, -hexyl); 163.82 (CN_3) ppm. ^{19}F NMR (CDCl_3): δ = -79.6 ppm. IR (NaCl): ν = 2962 (s), 2935 (s), 2873 (m), 1539 (s), 1463 (m), 1440 (m), 1353 (vs), 1227 (m), 1194 (s), 1058 (s) cm^{-1} . Anal. calcd for $\text{C}_{27}\text{H}_{54}\text{F}_6\text{N}_4\text{O}_4\text{S}_2$ (676.86): C 47.91, H 8.04, N 8.28%; found C 47.91, H 8.30, N 8.26%.

***N,N*-Dibutyl-*N',N'*-diethyl-*N'',N''*-dimethylguanidinium dicyanamide (3a, $[\text{N}_{11}\text{N}_{22}\text{N}_{44}]\text{N}(\text{CN})_2$)**

To a solution of guanidinium chloride **IIa** (4.75 g, 16.3 mmol) in dichloromethane (25 mL) sodium dicyanamide (2.11 g, 1.4 equiv) was added, and the mixture was stirred at 22 °C for 24 h.

The precipitate was filtered off, and the mother liquid was stirred with activated carbon for several hours. After filtration the solvent was evaporated and the remaining ionic liquid was dried at 80 °C/0.001 mbar for 6 h. Yellow oil (4.57 g, 87% yield); T_g -60 °C, T_{dec} 371 °C. ^1H NMR (CDCl_3): δ = 0.93–0.98 (2 t, 6 H, $\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.21–1.70 (several m, 14 H, NCH_2CH_3 , $\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 3.031/3.036 (2 s, 3 H each, NCH_3), 3.01–3.35 (several m, 8 H, NCH_2) ppm. ^{13}C NMR (CDCl_3): δ = 12.80, 13.11, 13.65, 13.71 ($(\text{CH}_2)_n\text{CH}_3$); 19.96, 20.10, 29.48, 29.71 ($\text{CH}_2(\text{CH}_2)_2\text{CH}_3$); 40.38, 40.55 (NCH_3); 43.50, 44.14 (NCH_2CH_3); 49.13, 49.70 (NCH_2 -butyl); 119.94 (CN, anion), 163.40 (CN_3) ppm. IR (NaCl): ν = 2961 (s), 2875 (s), 2222 (s), 2187 (m), 2127 (s), 1580 (s), 1549 (s), 1460 (m), 1421 (m), 1382 (w), 1302 (m) cm^{-1} . Anal. calcd for $\text{C}_{17}\text{H}_{34}\text{N}_6$ (322.49): C 63.31, H 10.63, N 26.06%; found: C 63.42, H 10.67, N 26.02%.

***N,N*-Dibutyl-*N'*,*N'*-diethyl-*N''*,*N''*-dihexylguanidinium dicyanamide (3b,
[$\text{N}_{22}\text{N}_{44}\text{N}_{66}$] $\text{N}(\text{CN})_2$)**

Prepared from guanidinium chloride **Ib** (2.78 g, 6.44 mmol) and $\text{NaN}(\text{CN})_2$ (0.83 g, 9.02 mmol) in CH_2Cl_2 (20 mL) as described for **3a**. Light-yellow oil (2.75 g, 93% yield); T_g -57 °C, T_{dec} 373 °C. ^1H NMR (CDCl_3): δ = 0.89 (t, 6 H, CH_3), 0.95–0.99 (2 t, 6 H, CH_3), 1.26 (t, 6 H, NCH_2CH_3), 1.25–1.80 (several m, 24 H, $\text{CH}_2(\text{CH}_2)_4\text{CH}_3$, und $\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 3.01–3.45 (several m, 12 H, NCH_2) ppm. ^{13}C NMR (CDCl_3): δ = 12.91, 12.92, 13.64, 13.67, 13.88, 13.90 (CH_3); 20.06, 20.08, 22.47, 22.48, 26.50, 26.56, 27.44, 27.49, 29.50, 29.59, 31.23, 31.26 ($(\text{CH}_2)_n\text{CH}_3$, $n = 2, 4$); 43.87, 43.90 (NCH_2 -ethyl); 49.41, 49.47, 49.65 (NCH_2 -butyl, -hexyl); 119.98 (CN, anion), 163.84 (CN_3) ppm. IR (NaCl): ν = 2933 (s), 2873 (s), 2222 (s), 2187 (m), 2126 (s), 1538 (s), 1456 (m), 1380 (m), 1302 (m) cm^{-1} . Anal. calcd for $\text{C}_{27}\text{H}_{54}\text{N}_6$ (462.75): C 70.08, H 11.76, N 18.16%; found: C 70.07, H 11.53, N 18.05%.

Literature

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