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Electronic Supporting Information

Dysprosium electrodeposition from a hexaalkylguanidinium-based ionic liquid

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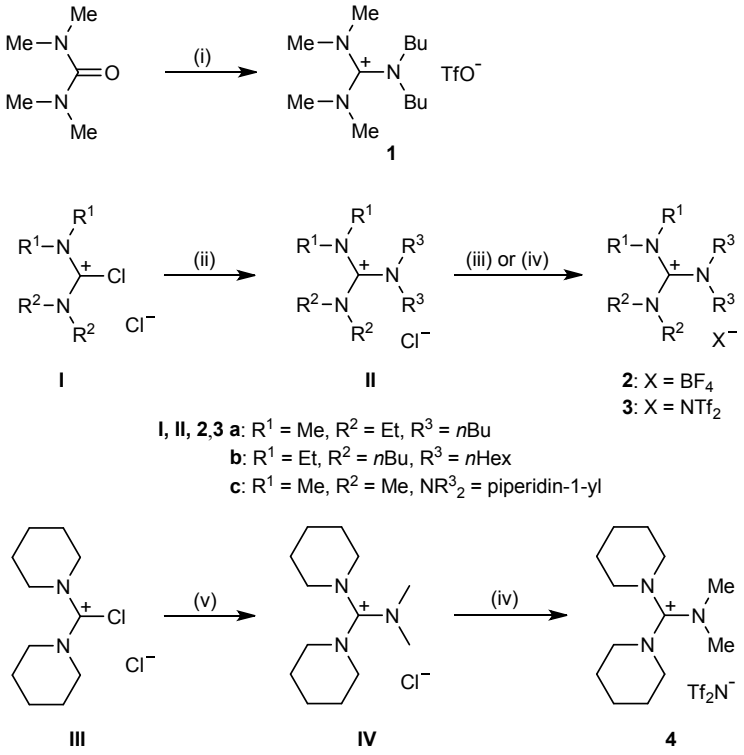
General information

The required guanidinium-based ionic liquids were synthesised along two routes (Scheme 1). The salt $[N_{11}N_{22}N_{44}Gua]OTf$ (**1**) was prepared from tetramethylurea, triflic anhydride and dibutylamine by analogy to a procedure for similar hexaalkylguanidinium triflates.[3] Guanidinium tetrafluoroborate **2b** as well as guanidinium bis(triflyl)imides **3** and **4** were obtained from the corresponding hexaalkylguanidinium chlorides **II** (or **IV**) by anion exchange reactions. The hexaalkylguanidinium chlorides in turn were prepared from tetraalkylchloroformamidinium chlorides **I** (**III**) by an adaptation of the classical procedure.[2]



Scheme 1 Synthesis of guanidinium-based ionic liquids **1**–**4**. (i) 1. $(CF_3SO_2)_2O$; 2. Bu_2NH; (ii) $R^3{}_2NH$, Et_3N, acetonitrile; (iii) $NaBF_4$, CH_2Cl_2; (iv) $LiN(SO_2CF_3)_2$, H_2O; (v) $Me_2N–SiMe_3$, $CHCl_3$. Tf = CF_3SO_2.

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. NMR spectra were recorded on a Bruker DRX 400 spectrometer (^{1}H: 400.13 MHz; ^{13}C: 100.61 MHz; ^{19}F: 376.46 MHz). ^{1}H NMR spectra were referenced to the residual proton signal of the solvent ($\delta(CDCl_3)$ = 7.26 ppm). ^{13}C spectra were referenced to the solvent signal ($\delta(CDCl_3)$ = 77.00 ppm), and ^{19}F spectra to C_6F_6 in $CDCl_3$ ($\delta(C_6F_6)$ = -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 (T_{dec} = temperature of highest decomposition gradient) and differential scanning calorimetry with a Perkin Elmer DSC 7 instrument (T_g = glass transition temperature). Microanalyses were obtained with an Elementar vario MICRO cube instrument.

*N,N-Dibutyl-N',N',N'',N''-tetramethylguanidinium trifluoromethanesulfonate (**1**, [$N_{11}N_{11}N_{44}$Gua]OTf)*

Bis(*N*,*N*,*N*',*N*'-tetramethylamidinio)ether bis(triflate) was prepared from tetramethylurea and triflic anhydride according to published procedures.[1,3] To a suspension of this salt (5.00 g, 9.7 mmol) in dichloromethane (30 mL), cooled at 0 °C, was added dibutylamine (3.3 mL, 19.4 mmol) in CH_2Cl_2 (10 mL) and the mixture was successively stirred at 0 °C for 30 min, at 20 °C for 1 h and at reflux temperature for 2 h. After cooling to room temperature, the solution was concentrated on a rotary evaporator and tetramethylurea was extracted with pentane (10 mL). The lower phase was isolated, diluted with CH_2Cl_2 and washed with dilute aqueous NaOH (0.1 M). The organic phase was dried (Na_2SO_4) and the solvent was evaporated. The desired product was obtained as a light yellow oil; yield: 2.87 g (78%). – T_{dec} = 456 °C, T_g = -73 °C. – ^{1}H NMR ($CDCl_3$): δ = 0.93–0.96 (t, ^3J = 7.3 Hz, 6 H, CH_3CH$_2$), 1.20–1.65 (several m, 8 H, CH$_3$CH_2CH_2CH$_2$N), 2.98 and 3.03 (2 s, each 6 H, NCH$_3$), 3.05–3.20 (m, 4 H, NCH$_2$) ppm. – ^{13}C NMR ($CDCl_3$): δ = 13.7 (CH_3CH$_2$), 20.0 (CH$_3$*C*H$_2$CH$_2$CH$_2$N), 29.6 (CH$_3$CH$_2$*C*H$_2$CH$_2$N), 40.4 (NCH$_3$), 49.3 (NCH$_2$), 163.3 (CN$_3$) ppm. – ^{19}F NMR ($CDCl_3$): δ = -74.7 ppm. – IR (NaCl): ν = 2962 (s), 2936 (s), 2876 (m), 1593 (s), 1568 (s), 1464 (m), 1435 (m), 1411 (m), 1268 (s), 1224 (m), 1150 (s), 1032 (s), 897 (s) cm^{-1}. – MS (CI): *m*/*z* = 228 (100%, [cation]$^+$). – Anal. for $C_{14}H_{30}F_3N_3O_5S$ (377.47): calcd. C 44.55, H 8.01, N 11.13%; found C 44.59, H 8.49, N 11.15%.

*N,N-Dibutyl-N',N'-diethyl-N'',N''-dihexylguanidinium tetrafluoroborate (**2b**, [$N_{22}N_{44}N_{66}$Gua]BF_4)*

N,*N*-Dibutyl-*N*',*N*'-diethyl-*N*'',*N*''-dihexylguanidinium chloride (**IIb**) was prepared from *N*,*N*-dibutyl-*N*',*N*'-diethylchloroformamidinium chloride[2] (**Ib**) as described.[4] Salt **IIb** (5.0 g, 11.6 mmol) was dissolved in dichloromethane (20 mL), sodium tetrafluoroborate (1.8 g, 16.7 mmol) was added, and the suspension was stirred at room temperature for 24 h. The precipitate was filtered off and washed with dichloromethane. The combined organic phases were dried (Na_2SO_4), stirred over charcoal for 15 min and filtered. The solvent was removed on a rotary evaporator, and the product was dried for 8 h at 80 °C/0.05 mbar in a Kugelrohr apparatus. The product was obtained as a colourless oil; yield: 4.9 g (88%). – T_{dec} = 462 °C, T_g = -71 °C. – ^{1}H NMR ($CDCl_3$): δ = 0.84–0.98 (several overlapping t, 12 H, 4 CH$_3$ of Hex and Bu), 1.18–1.78 (several m and t, 30 H, NCH$_2$CH_3, NCH$_2$(CH_2)$_2$CH$_3$ and NCH$_2$(CH_2)$_4$CH$_3$), 2.98–3.44 (several m, 12 H, NCH$_2$) ppm. – ^{13}C NMR ($CDCl_3$): δ = 12.76, 12.77, 13.60, 13.63, 13.87 and 13.88 (CH$_3$); 19.99, 20.03, 22.46, 22.48, 26.47, 26.51, 27.36, 27.38, 29.44, 29.49, 31.23 and 31.28 ((*C*H$_2$)$_2$CH$_3$ and (*C*H$_2$)$_4$CH$_3$); 43.80 and 43.83 (N*C*H$_2$CH$_3$); 49.32, 49.40, 49.56 and 49.58 (NCH$_2$ of Hex and Bu); 163.9 (CN$_3$) ppm. – IR (NaCl): ν = 2958 (s), 2933 (s), 2873 (m), 1539 (s), 1460 (m), 1440 (m), 1380 (m), 1311 (m), 1056 (s), 792 (w) cm^{-1}. – MS (CI): *m*/*z* = 396

(100%, [cation]$^+$). – Anal. for $C_{25}H_{54}BF_4N_3$ (483.52): calcd. C 62.10, H 11.26, N 8.69%; found C 61.96, H 12.07, N 8.75%.

*N,N-Dibutyl-N',N'-diethyl-N'',N''-dimethylguanidinium bis(trifluoromethylsulfonyl)imide (**3a**, $[N_{11}N_{22}N_{44}Gua]TFSI$)*

The synthesis and spectroscopic/analytical characterisation of this room-temperature ionic liquid has been published.[4]

*N,N,N',N'-Tetramethyl-N'',N''-pentamethyleneguanidinium bis(trifluoromethylsulfonyl)imide (**3c**, $[N_{11}N_{11}N_{pip}Gua]TFSI$) N-((dimethylamino)(piperidin-1-yl)methylene)-N-methylmethanaminium chloride*

The synthesis and spectroscopic/analytical characterisation of this room-temperature ionic liquid has been published.[5]

*N,N-Dimethyl-N',N'-pentamethylene-N'',N''-pentamethylene-guanidinium bis(trifluoromethylsulfonyl)imide (**4**, $[N_{11}N_{pip}N_{pip}Gua]TFSI$)*

a) *1-(Chloro(piperidin-1-yl)methylene)piperidin-1-ium chloride* (**III**). 1,1-Carbonyldipiperidine (3.3 g, 16.6 mmol) dissolved in dry CH_2Cl_2 (10 mL) was added dropwise to a solution of freshly distilled oxalyl chloride (1.6 mL, 18.3 mmol) in dry CH_2Cl_2 (20 mL) under an argon atmosphere. The solution was heated at reflux for 9 h (evolution of CO and CO_2), then the solvent was evaporated at 15 mbar. The remaining solid was washed with several portions of dry diethyl ether until the washing ether was colourless (removal of excess oxalyl chloride, unreacted urea and coloured impurities). After drying for 3 h at 20 °C/0.05 mbar, the product was obtained as a yellow moisture-sensitive powder; yield: 4.0 g (95%). – ^{1}H NMR ($CDCl_3$): δ = 1.75–1.90 (m, 6 H, 3-H_{pip}, 4-H_{pip}, 5-H_{pip}), 3.95-4.05 (m 4 H, 2-H_{pip}, 6-H_{pip}) ppm.

b) *N-(Di(piperidin-1-yl)methylene)-N-methylmethanaminium chloride* (**IV**). A solution of salt **III** (1.1 g, 4.5 mmol) in dry chloroform (10 mL) was cooled at 0 °C. A solution of dimethyl(trimethylsilyl)amine (0.8 mL, 4.95 mmol) in dry $CHCl_3$ (5 mL) was added in small portions under an argon atmosphere and the reaction mixture was refluxed for 1.5 h. After cooling, the volatile components were evaporated on a rotary evaporator (40 °C/40 mbar). The remaining solid was recrystallised from dry ethyl acetate/dimethylformamide (2:1, v/v). The colourless hygroscopic crystals were dried for 8 h at 80 °C/0.05 mbar. Yield: 0.9 g (79%); m. p. 205 °C. – TGA: T_{dec} = 322 °C. – ^{1}H NMR ($CDCl_3$): δ = 1.55–1.75 (m, 12 H, 3-H_{pip}, 4-H_{pip}, 5-H_{pip}), 3.04 (s, 6 H, NCH_3), 3.20–3.40 (m, 8 H, 2-H_{pip}, 6-H_{pip}) ppm. – ^{13}C NMR ($CDCl_3$): δ = 23.2 (C-4_{pip}), 25.0 and 25.1 (C-3_{pip}, C-5_{pip}), 40.9 (NCH_3), 50.1 and 50.2 (C-2_{pip}, C-6_{pip}), 162.3 (CN_3) ppm. – IR (ATR): ν = 2936 (m), 2854 (m), 1577 (s), 1552 (s), 1446 (m), 1416 (m), 1379 (m), 1283 (m), 1258 (m), 862 (m) cm^{-1}. – Anal. for $C_{13}H_{26}ClN_3 \times 0.5H_2O$ (259.81 + 9.00): calcd. C 58.08, H, 10.12, N 15.63%; found C 58.25, H 10.35, N 15.75%.

c) *Anion exchange, synthesis of **4**:* Solutions of salt **IV** (0.60 g, 2.3 mmol) and of lithium bis(trifluoromethylsulfonyl)imide (0.70 g, 2.3 mmol) in deionised water (5 mL each) were combined, whereby two phases appeared instantly. After stirring the mixture at 70 °C for 30 min, it was cooled to room temperature and dichloromethane (20 mL) was added. The organic phase was separated and washed with several portions of deionised water until a test on chloride ions in the rinsing water ($AgNO_3$) was negative. The organic phase was dried with Na_2SO_4, stirred over charcoal for 15 min and filtered. The solvent was removed on a rotary evaporator, and the product was dried for 8 h at 120 °C/0.05 mbar in a Kugelrohr apparatus. The product was obtained as a colourless oil; yield: 1.0 g (86%). – T_{dec} = 461 °C, T_g = -62 °C. – ^{1}H NMR ($CDCl_3$): δ = 1.63–1.78 (m, 12 H, 3-H_{pip}, 4-H_{pip}, 5-H_{pip}), 2.99 (s, 6 H, NCH_3), 3.20–3.35 (m, 8 H, 2-H_{pip}, 6-H_{pip}) ppm. – ^{13}C NMR ($CDCl_3$): δ = 23.4 (4-C_{pip}), 25.0 and 25.2 (3-C_{pip}, 5-C_{pip}); 40.6 (NCH_3), 50.17 and 50.18 (2-C_{pip}, 6-C_{pip}), 118.6 and 121.1 (CF_3), 162.5 (CN_3) ppm. – ^{19}F NMR ($CDCl_3$): δ = -75.2 ppm. – IR (NaCl): ν = 2946 (s), 2868 (s), 1560 (s), 1449 (s), 1428 (s), 1350 (s), 1285 (s), 1259 (s), 1187 (s), 1135 (s), 1057 (s), 1015 (m), 920 (m), 872 (m) cm^{-1}. – MS (CI): *m*/*z* = 224 (100%, [cation]$^+$). – Anal. for $C_{15}H_{26}F_6N_4O_4S_2$ (504.51): calcd. C 35.71, H 5.19, N 11.11%; found C 35.68, H 5.20, N 11.19%.

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