Thermophysical Properties of Imidazolium-Based Ionic Liquids: The Effect of Aliphatic versus Aromatic Functionality

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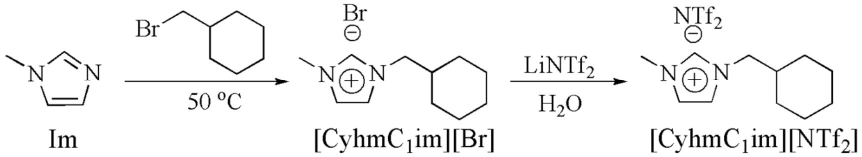
Supporting Information

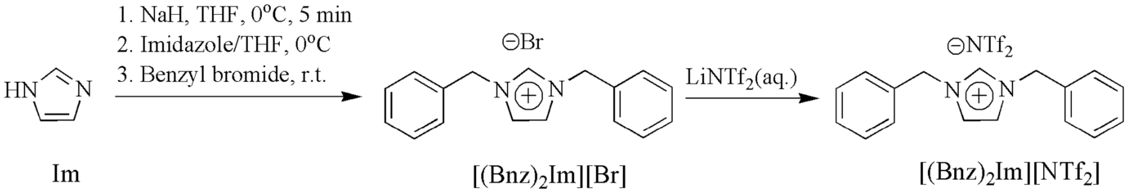
Synthesis of 1-(cyclohexylmethyl)-3-methyl imidazolium bis[(trifluoromethane)sulfonyl]amide ([CyhmC$_1$im][NTf$_2$])



A one-neck round bottom flask, under nitrogen, equipped with a magnetic stirrer and a condenser, was charged with 1-methylimidazole (6.65 g, 81.02 mmol). To this mixture, an excess (1.05 eq.) of (bromomethyl)cyclohexane (15.06 g, 85.07 mmol) was added. The reaction was left under constant stirring at 50 °C, until complete consumption of the 1-methylimidazole. The 1-(cyclohexylmethyl)-3-methylimidazolium bromide formed was then washed three times with 50 mL mixture of hexanes: dichloromethane (4:1 v/v) to remove the unreacted excess of halide. The product was concentrated *in vacuo* on a rotary evaporator. 3 g of activated charcoal and 60 mL of dichloromethane were added to the viscous, colored bromide, and left under stirring for 96 h. The black slurry was then filtered through a gravitational column packed with 10 cm of aluminum oxide (activated, basic, 50-200 micron) and 3 cm of celite 545. The removal of the solvent under reduced pressure afforded [CyhmC$_1$im][Br] as a colorless, viscous liquid at room temperature.

The second stage of synthesis was accomplished via a metathesis reaction.[1] An aqueous solution of lithium bis[(trifluoromethane)sulfonyl]amide (0.98 eq., 20.65 g, 71.91 mmol) was added to the [CyhmC$_1$im][Br] and left to stir overnight. The two-phase system was then repeatedly washed with triple-deionized water until no bromide ions could be detected by the silver nitrate test. The final product, [CyhmC$_1$im][NTf$_2$], a colorless liquid at room temperature, was dried with benzene azeotrope. The residual benzene was removed under vacuum. Yield: 91%.

Synthesis of 1,3-bis(phenylmethyl)-imidazolium bis[(trifluoromethane)sulfonyl]amide ([(Bnz)$_2$im][NTf$_2$])



A three-neck round bottom flask, under nitrogen, equipped with a magnetic stirrer and a condenser, was placed in an ice bath. The container was charged with 40 mL of freshly distilled THF and left under stirring for five minutes. After temperature equilibration, NaH (1.90 g, 79.00 mmol) was added to the flask. The mixture was stirred for another 5 min.

The imidazole (5.38 g, 79.00 mmol) was dissolved in 30 mL of THF and added to the reaction via a pump syringe at a rate of 0.34 mL/min. When the addition was completed, the ice bath was removed and the reaction mixture was further stirred while warming up to room temperature.

A slight excess of benzyl bromide (1.05 eq., 28.37 g, 165.91 mmol) was delivered dropwise to the round-bottom flask at a rate of 0.34 mL/min with an automatic syringe. After the completion of the addition, the reaction was left for 12 h under constant stirring at room temperature while a light yellow slurry was formed.

The slurry was vacuum filtered using anhydrous acetonitrile for rinsing. The liquid obtained was transferred to a one-neck round-bottom flask and evaporated *in vacuo*.

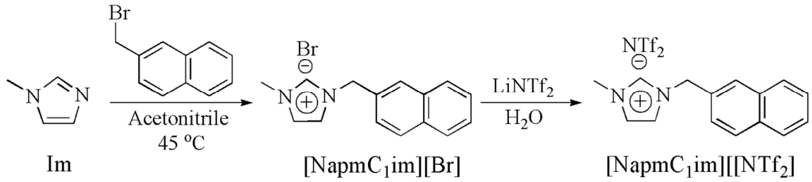
The 1,3-bis(phenylmethyl)-imidazolium bromide formed in this way was washed three times with 50 mL of a 1: 3 (v/v) mixture of acetonitrile and hexanes to remove the excess benzyl bromide. The ionic liquid was concentrated *in vacuo* on a rotary evaporator.

3 g of activated charcoal and 75 mL of acetonitrile were added to the flask and left under stirring for 72 h. The black slurry formed was then filtered through a gravitational column packed with 10 cm of aluminum oxide (activated, basic, 50-200 micron) and 3 cm of celite 545.

The removal of the acetonitrile under reduced pressure afforded [(Bnz)$_2$im][Br] as a colorless, viscous liquid at room temperature.

The second stage of synthesis was accomplished *via* a metathesis reaction.[1] An aqueous solution of lithium bis[(trifluoromethane)sulfonyl]amide (22.68 g, 79.00 mmol) was added to the ionic liquid and left to stir for 12 h. The two-phase system was then repeatedly washed with triple-deionized water until no bromide ions could be detected by the silver-nitrate test. The final product, [(Bnz)$_2$im][NTf$_2$], was dried with benzene azeotrope. The residual benzene was removed under vacuum. Yield: 90%.

Synthesis of 1-methyl-3-(2-naphthylmethyl)imidazolium bis[(trifluoromethane)sulfonyl]amide ([NapmC$_1$im][NTf$_2$])



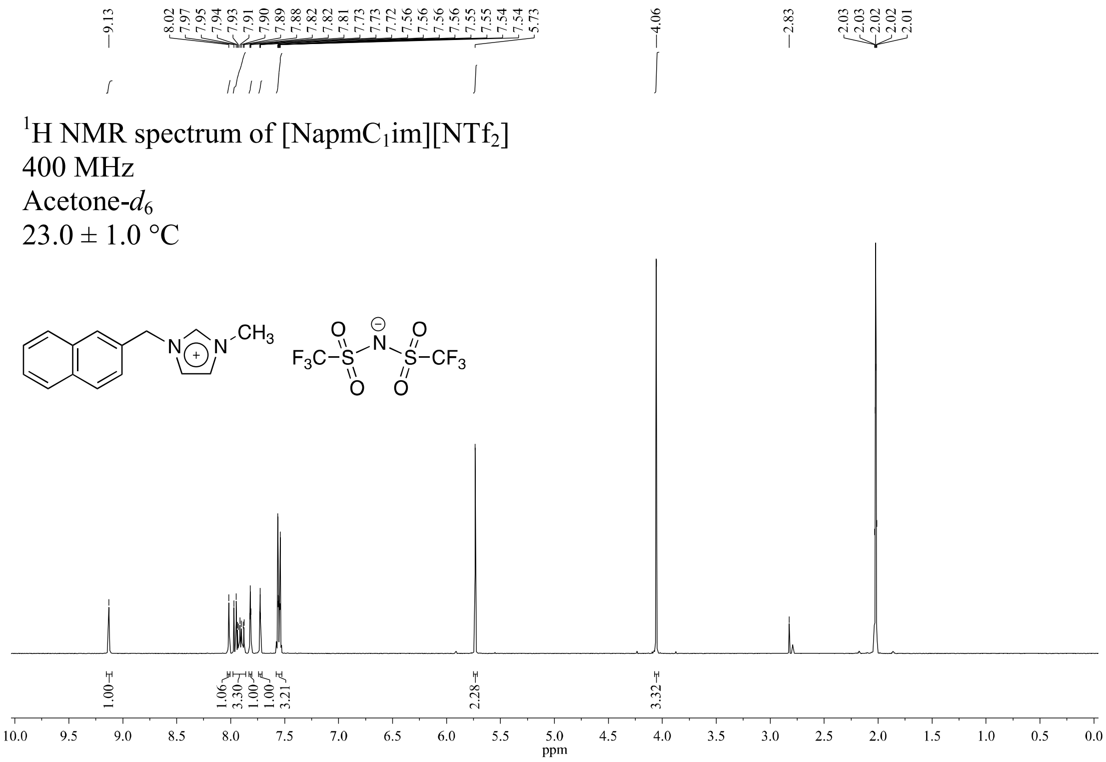
A two-neck round bottom flask, under nitrogen, equipped with a magnetic stirrer and a condenser, was charged with anhydrous acetonitrile (40 mL) and a slight excess (1.02 eq.) of 1-(bromomethyl)naphthalene (23.06 g, 104.29 mmol). The flask was placed in an oil bath regulated at 45 °C and stirred until the complete dissolution of the solid bromide. To this mixture, 1-methylimidazole (8.39 g, 102.24 mmol) was added in a single round. The reaction was left for 24 h under constant stirring, while a light-brown liquid was produced. The 1-methyl-3-(2-naphthylmethyl)imidazolium bromide formed was then washed three times with 50 mL mixture of hexanes: acetonitrile (4:1 v/v) to remove the unreacted excess of halide. The product was concentrated *in vacuo* on a rotary evaporator. 3 g of activated charcoal and 60 mL of acetonitrile were added to the viscous, colored bromide, and left under stirring for 72 hours. The black slurry was then filtered through a gravitational column packed with 10 cm of aluminum oxide (activated, basic, 50-200 micron) and 3 cm of celite 545. The solvent used was 500 mL of acetonitrile. The removal of the acetonitrile under reduced pressure afforded [NapmC$_1$im][Br] as a white, solid product at room temperature. (Caution: when drying the product on the Schlenk line, the manifold should not be open more than 5% of its capacity for 24 hours. If fully open, a thick rich foam instantaneously forms that can compromise the vacuum line.)

The second stage of synthesis was accomplished via a metathesis reaction.[1] An aqueous solution of lithium bis[(trifluoromethane)sulfonyl]amide (0.98 eq., 26.64 g, 92.80 mmol) was added to the [NapmC$_1$im][Br] and left to stir overnight. The two-phase system was then repeatedly washed with triple-deionized water until no bromide ions could be detected by the silver nitrate test. The final product, [NapmC$_1$im][NTf$_2$], a colorless liquid at room temperature, was dried with benzene azeotrope. The residual benzene was removed under vacuum. After extended drying the product solidifies. Yield: 73%.

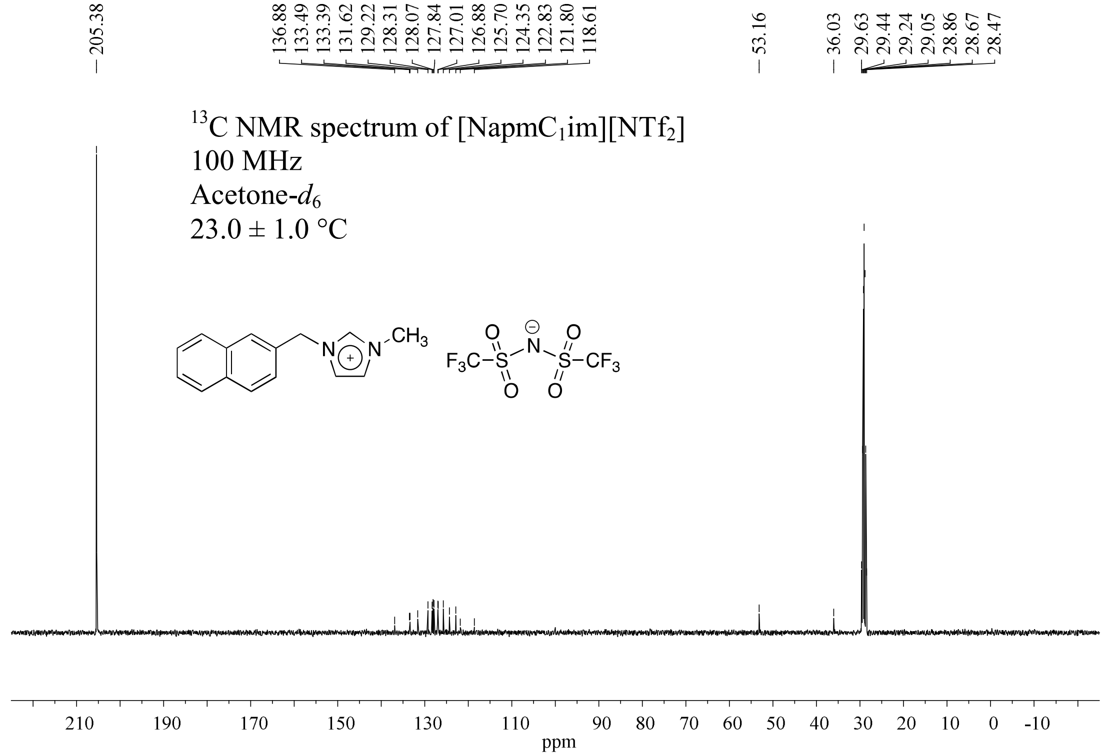
References

(1) Bonhôte, P.; Dias, A.-P.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. *Inorg. Chem.* **1996**, *35*, 1168–1178.

^{1}H NMR (400 MHz, Acetone-d_6) δ: 9.13 (s, 1H), 8.02 (bs, 1H), 7.95-7.88 (m, 3H), 7.82 (t, J = 1.79 Hz, 1H), 7.73 (t, J = 1.76 Hz, 1H), 7.56-7.54 (m, 3H), 5.73 (s, 2H), 4.06 (s, 3H)
^{13}C NMR (100 MHz, Acetone-d_6) δ: 136.9, 133.5, 133.4, 131.6, 129.2, 128.3, 128.1, 127.8, 127.0, 126.9, 125.7, 124.4, 122.8, 120.2 (q, $^{1}J_{C\text{-}F}$ =320.8), 53.2, 36.0
^{19}F NMR (375 MHz, Acetone-d_6) δ: -79.8



^{1}H NMR spectrum of [NapmC$_1$im][NTf$_2$]
400 MHz
Acetone-d_6
23.0 ± 1.0 °C



^{13}C NMR spectrum of [NapmC$_1$im][NTf$_2$]
100 MHz
Acetone-d_6
23.0 ± 1.0 °C

^{19}F NMR spectrum of [NapmC$_1$im][NTf$_2$]
375 MHz
Acetone-d_6
23.0 ± 1.0 °C