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Exploring the bulk-phase structure of ionic liquid mixtures using small-angle neutron scattering

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Supporting Information

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Experimental section

1.1 General considerations

All air-sensitive experimental procedures were performed under an inert atmosphere of nitrogen using standard Schlenk line and glovebox techniques. Toluene was purified with the aid of an Innovative Technologies anhydrous solvent engineering system. Dichloromethane, acetonitrile and hexane were purified by distillation using calcium hydride (for DCM and CH_3CN) and sodium (for hexane) as drying agents. 1-methylimidazole and 1-[D_3]-methylimidazole were dried over calcium hydride and distilled under reduced pressure. Purification of 1-bromoethane and 1-bromododecane was performed by distillation immediately prior to use, in the presence of activated 4 Å molecular sieves under nitrogen (1-bromoethane) or under reduced pressure (1-bromododecane). Deuterium oxide (99.9 % D), [D_5]-ethyl bromide (99.0 % D), and [D_1]-methanol (99.0 % D) were obtained from Aldrich and used without further purification. [D_3]-methyl iodide (99+ % D) was purchased from Acros and used as received. [D_{25}]-dodecyl bromide was provided by the ISIS deuteration facility and used as received. ^{1}H NMR spectra were acquired at 293 K on a JEOL ECX-400 using an operating frequency of 399.78 MHz. Sodium imidazolate and all ionic liquids synthesised are hygroscopic and should be stored under an inert atmosphere.

1.2 Synthesis of protio ILs

1.2.1. Preparation of 1-ethyl-3-methylimidazolium bromide, [C_2mim]Br

This product was prepared according to the literature method.[1] Distilled 1-methylimidazole (91.7 g, 89.0 mL, 1.12 mol) was added dropwise to a flask containing an excess of freshly distilled 1-bromoethane (133.8 g, 92.0 mL, 1.23 mol). The mixture was stirred for 15 min at 50 °C, until the initial turbidity disappeared, and then for 2 h at 70 °C. Upon cooling to 0 °C, a white solid formed, which was ground in a glovebox. The solid was treated with ethyl acetate (20 mL) and stirred at −10 °C for 1 h under nitrogen. After removing the solvent *via* cannula filtration, the white solid was dried *in vacuo* at 60 °C for 6 h (185.7 g, 87% yield). ^{1}H NMR (400 MHz, dmso-d_6, 293 K), δ (ppm): 9.29 (*s*, 1 H), 7.87 (*m*, 1 H), 7.78 (*m*, 1 H), 4.24 (*q*, ^3J = 7.3 Hz, 2 H), 3.90 (*s*, 3 H), 1.44 (*t*, ^3J = 7.3 Hz, 3 H).

1.2.2. Preparation of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C_2mim][Tf_2N]

A solution of [C_2mim]Br (35.0 g, 0.18 mol) in deionised water (150 mL) was treated with a solution of Li[Tf_2N] (53.2 g, 0.18 mol) in deionised water (150 mL). The biphasic system was stirred overnight at room temperature. An aqueous extraction (8 × 50 mL) was performed to remove the lithium halide until no precipitation of AgBr occurred in the aqueous phase upon

addition of $AgNO_3$ solution. The colourless oil was then dried *in vacuo* at 60 °C for 4 days (51.1 g, 71% yield). ^{1}H NMR (400 MHz, acetone-d_6, 293 K), δ (ppm): 8.79 (*s*, 1 H), 7.59 (*s*, 1 H), 7.52 (*s*, 1 H), 4.36 (*q*, ^3J = 7.0 Hz, 2 H), 4.02 (*s*, 3 H), 1.63 (*t*, ^3J = 7.0 Hz, 3 H).

1.2.3. Preparation of 1-dodecyl-3-methylimidazolium bromide, [C_{12}mim]Br

A slight excess of freshly distilled 1-bromododecane (183.7 g, 177.0 mL, 0.73 mol), distilled 1-methylimidazole (56.6 g, 55.0 mL, 0.69 mol) and dry toluene (150 mL) were heated at 60 °C under nitrogen overnight. The homogeneous solution obtained was concentrated under vacuum at 60 °C to give a white solid, which was ground in a glovebox and further dried under vacuum at 60 °C for 7 days (219.0 g, 96% yield). ^{1}H NMR (400 MHz, D_2O, 293 K), δ (ppm): 7.42 (*s*, 1 H), 7.37 (*s*, 1 H), 4.13 (*t*, ^3J = 6.7 Hz, 2 H), 3.83 (*s*, 3 H), 1.85-1.80 (*m*, 2 H), 1.22 (*br s*, 18 H), 0.81 (*t*, ^3J = 5.6 Hz, 3 H).

1.2.4. Preparation of 1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C_{12}mim][Tf_2N]

A solution of [C_{12}mim]Br (58.1 g, 0.18 mol) and deionised water (150 mL) was treated with Li[Tf_2N] (50.9 g, 0.18 mol) in deionised water (150 mL). The biphasic system was stirred overnight at room temperature. The IL phase was separated and thoroughly washed with deionised water (8 × 70 mL). Efficient removal of halides was tested by addition of a solution of $AgNO_3$ in deionised water to an aliquot of the aqueous phase from the previous wash. The pale yellow oil was then dried *in vacuo* at 60 °C for 4 days (80.6 g, 86% yield). ^{1}H NMR (400 MHz, acetone-d_6, 293 K), δ (ppm): 8.78 (*s*, 1 H), 7.56 (*m*, 1 H), 7.50 (*s*, 1 H), 4.28 (*t*, ^3J = 7.0 Hz, 2 H), 3.99 (*s*, 3 H), 2.00-1.93 (*m*, 2 H), 1.30 (*br s*, 18 H), 0.92 (*t*, ^3J = 6.6 Hz, 3 H).

1.3. Synthesis of precursors for the deuteration chemistry

1.3.1. Preparation of sodium imidazolate

Deprotonation of imidazole was performed following a literature method with some modifications.[2] A suspension of sodium hydride (2.05 g, 85.4 mmol) in dry acetonitrile (150 mL) was cooled in an ice bath under a nitrogen atmosphere. Imidazole (5.53 g, 81.2 mmol) was ground into a fine powder and slowly added over a course of 3 hours. A gentle effervescence of hydrogen occurred during addition. After 24 hours of stirring, the solvent was removed *in vacuo*. Due to the high hygroscopicity of the product, the work-up must be performed under nitrogen. The white solid was washed with dry hexane (4 × 30 mL) and dried at 100 °C under reduced pressure for 1-2 hours (6.93 g, 95% yield). ^{1}H NMR (400 MHz, D_2O, 293 K), δ (ppm): 7.78 (*s*, 1 H), 7.14 (*s*, 2 H).

1.3.2. Preparation of 1-[D_3]-methylimidazole

Methylation of sodium imidazolate was carried out following a literature method with some modifications.[2] Finely ground sodium imidazolate (28.00 g, 0.31 mol) was suspended in dry

acetonitrile (350 mL) under nitrogen and cooled down in an ice/salt bath to −15 °C. To this, [D_3]-methyl iodide (45.18 g, 19.4 mL, 0.31 mol) was added dropwise over a course of 3 hours, during which time a yellow colour evolved. The resulting mixture was stirred at −15 °C for 3-5 additional hours and then allowed to warm to room temperature. After 3 days of stirring, the solvent was removed *in vacuo* to give an orange residue, which was then extracted with dry DCM (6 × 100 mL) *via* cannula transfer. A yellowish oil was obtained after removal of the dichloromethane under reduced pressure. The product was purified by vacuum distillation. The colourless liquid obtained (19.4 g, ~17 mL, 73% yield) was stored at 4 °C under nitrogen. The degree of deuteration on the methyl group was quantitative. ^{1}H NMR (400 MHz, dmso-d_6, 293 K), δ (ppm): 7.60 (*s*, 1 H), 7.15 (*s*, 1 H), 6.91 (*s*, 1 H).

1.4. Synthesis of chain-deuterated ILs

1.4.1. Synthesis of [D_5]-1-ethyl-3-methylimidazolium bromide, [C_2mim-d_5]Br

Distilled 1-methylimidazole (3.55 g, 3.44 mL, 43.2 mmol) was added dropwise to a 10 mol% excess of [D_5]-ethyl bromide (5.42 g, 3.55 mL, 47.6 mmol). The mixture was stirred at 50 °C for 15 min, and then for 2 h at 70 °C. Upon cooling to room temperature a white solid formed, which was ground in a glovebox. The solid was treated with ethyl acetate (20 mL) and stirred at −10 °C for 1 h under nitrogen. After the solvent was removed *via* cannula, the white solid was dried *in vacuo* at room temperature for 2 h followed by 60 °C for 8 h (7.85 g, 93% yield). The degree of deuteration on the ethyl group was quantitative. ^{1}H NMR (400 MHz, dmso-d_6, 293 K), δ (ppm): 9.28 (*s*, 1 H), 7.84 (*m*, 1 H), 7.75 (*m*, 1 H), 3.86 (*s*, 3 H).

1.4.2. Synthesis of [D_5]-1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C_2mim-d_5][Tf_2N]

A solution of [C_2mim-d_5]Br (7.75 g, 39.5 mmol) in deionised water (7 mL) was treated with a solution of Li[Tf_2N] (11.34 g, 39.5 mmol) in deionised water (8 mL). The biphasic system was stirred overnight at room temperature, under nitrogen. The ionic liquid phase was separated and the aqueous phase extracted with dichloromethane (3 × 10 mL). The combined organic phases were washed with deionised water until no precipitation of AgBr occurred in the aqueous phase upon addition of $AgNO_3$ solution. The organic layer was then dried *in vacuo* at 60 °C for 8 h to yield a colourless oil (12.96 g, 83% yield). The degree of deuteration on the ethyl group remained unchanged during the metathesis step. ^{1}H NMR (400 MHz, acetone-d_6, 293 K), δ (ppm): 8.97 (*s*, 1 H), 7.74 (*m*, 1 H), 7.67 (*m*, 1 H), 4.04 (*s*, 3 H).

1.4.3. Synthesis of [D_8]-1-ethyl-3-methylimidazolium bromide, [C_2mim-d_8]Br

This product was prepared according to the literature method.[1] [D_3]-methylimidazole (3.8 g, 44.6 mmol) was added dropwise to [D_5]-ethyl bromide (5.6 g, 3.7 mL, 49.6 mmol). The mixture was stirred for 15-20 min at 50 °C, until the initial turbidity disappeared, and then for

2 h at 70 °C. Upon cooling, a yellowish solid was obtained, which was ground in a glovebox. The solid was treated with ethyl acetate (15 mL) and stirred at −10 °C for 1 h 30 min under nitrogen. After removing the solvent *via* cannula filtration, the white solid was dried *in vacuo* at 60 °C for 6 h (7.5 g, 85% yield). The degree of deuteration on the alkyl groups was quantitative. ^{1}H NMR (400 MHz, dmso-d_6, 293 K), δ (ppm): 9.29 (*s*, 1 H), 7.87 (*m*, 1 H), 7.78 (*m*, 1 H).

1.4.4. Synthesis of [D_8]-1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C_2mim-d_8][Tf_2N]

The preparation of this product was carried out using the reported procedure.[1] [D_8]-1-ethyl-3-methylimidazolium bromide (7.4 g, 37.4 mmol) and lithium bis(trifluoromethylsulfonyl)imide (11.9 g, 41.5 mmol) were stirred for 24 h at room temperature in deionised water (15 mL). The biphasic system was treated with ethyl acetate (30 mL), the layers were separated, and the aqueous phase was extracted with ethyl acetate (15 mL). The solvent of the combined organic layers was removed *in vacuo*, and the crude was partitioned between ethyl acetate (10 mL) and deionised water (20 mL). The organic phase was thoroughly washed with deionised water (7 × 10 mL). Efficient removal of halides was tested by addition of a solution of $AgNO_3$ in deionised water to an aliquot of the aqueous phase from the previous wash. The organic phase was dried at 60 °C *in vacuo* for 4 h (10.0 g, 67% yield). The degree of deuteration on the alkyl groups remained unchanged during the metathesis step. ^{1}H NMR (400 MHz, acetone-d_6, 293 K), δ (ppm): 8.79 (*s*, 1 H), 7.59 (*s*, 1 H), 7.52 (*s*, 1 H).

1.4.5. Synthesis of [D_{25}]-1-dodecyl-3-methylimidazolium bromide, [C_{12}mim-d_{25}]Br

[D_{25}]-1-bromododecane (5.0 g, 18.2 mmol), 3 mol% excess of distilled 1-methylimidazole (1.54 g, 1.5 mL, 18.8 mmol) and dry toluene (4 mL) were heated at 60 °C under nitrogen overnight. The homogeneous solution obtained was concentrated and dried under vacuum at 60 °C for 6 h. Once the liquid was cooled to room temperature a white solid was formed (6.05 g, 95% yield). The degree of deuteration on the dodecyl group was quantitative. ^{1}H NMR (400 MHz, acetone-d_6, 293 K), δ (ppm): 8.45 (*s*, 1 H), 8.43 (*s*, 1 H), 4.80 (*s*, 3 H).

1.4.6. Synthesis of [D_{25}]-1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C_{12}mim-d_{25}][Tf_2N]

A solution of [C_{12}mim-d_{25}]Br (6.05 g, 17.0 mmol) in water (12 mL) was treated with Li[Tf_2N] (4.87 g, 17.0 mmol) in deionised water (12 mL). The biphasic system was stirred overnight at room temperature under nitrogen. The ionic liquid phase was separated and the aqueous phase extracted with dichloromethane (3 × 20 mL). The combined organic layers were washed with deionised water until no precipitation of AgBr occurred in the aqueous phase upon addition of $AgNO_3$ solution. The organic layer was then dried *in vacuo* at 60 °C for 7 h

to yield a colourless oil (8.91 g, 94% yield). The degree of deuteration on the dodecyl group remained unchanged during the metathesis step. ^{1}H NMR (400 MHz, acetone-d_6, 293 K), δ (ppm): 9.01 (*s*, 1 H), 7.76 (*m*, 1 H), 7.70 (*m*, 1 H), 4.05 (*s*, 3 H).

1.4.7. Synthesis of [D_{28}]-1-dodecyl-3-methylimidazolium bromide, [C_{12}mim-d_{28}]Br

[D_{25}]-1-bromododecane (2.98 g, 2.5 mL, 10.9 mmol), an excess of distilled 1-[D_3]-methylimidazole (0.99 g, 0.88 mL, 11.7 mmol) and dry toluene (2.5 mL) were heated at 60 °C under nitrogen overnight. The solvent was then removed under vacuum and the product was further dried at 60 °C for 5-8 hours to give a white gel. The sample was left in an ice/NaCl bath overnight to promote precipitation. The white solid obtained was ground in a glovebox and further dried under vacuum for 2 hours (3.62 g, 93% yield). The degree of deuteration on the alkyl groups was quantitative. ^{1}H NMR (400 MHz, D_2O, 293 K), δ (ppm): 7.42 (*s*, 1 H), 7.37 (*s*, 1 H).

1.4.8. Synthesis of [D_{28}]-1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C_{12}mim-d_{28}][Tf_2N]

A solution of [C_{12}mim-d_{28}]Br (3.46 g, 9.6 mmol) and water (10 mL) was treated with Li[Tf_2N] (2.81 g, 9.8 mmol) in deionised water (10 mL). The biphasic system was stirred overnight at room temperature. After this time, the IL phase was separated and the aqueous phase extracted with DCM (3 × 15 mL). The organic layers were combined and thoroughly washed with deionised water (8 × 30 mL). Efficient removal of halides was tested by addition of a solution of $AgNO_3$ in deionised water to an aliquot of the aqueous phase from the previous wash. The organic layer was then dried *in vacuo* at 60 °C for 8 hours to give a colourless oil (4.88 g, 90% yield). The degree of deuteration on the alkyl groups remained unchanged during the metathesis step. ^{1}H NMR (400 MHz, acetone-d_6, 293 K), δ (ppm): 8.78 (*s*, 1 H), 7.56 (*m*, 1 H), 7.50 (*s*, 1 H).

1.5. Synthesis of perdeuterated ILs

1.5.1. Synthesis of [D_{11}]-1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C_2mim-d_{11}][Tf_2N]

This product was prepared following a literature method.[1] [D_8]-1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (4.9 g, 12.2 mmol) was dissolved in [D_1]-methanol (24.4 g, 30 mL, 0.7 mol), treated with caesium hydroxide monohydrate (0.6 g, 3.6 mmol) and stirred for 24 h at 50 °C under nitrogen. The mixture was neutralised with an 80% aqueous solution of bis(trifluoromethylsulfonyl)imide, and the solvent was removed *in vacuo*. The residue was partitioned between dichloromethane (25 mL) and deuterium oxide (15 mL). The layers were separated and the aqueous layer was extracted with dichloromethane (25 mL). The combined organic layers were washed with deuterium oxide (3 × 15 mL), and the solvent

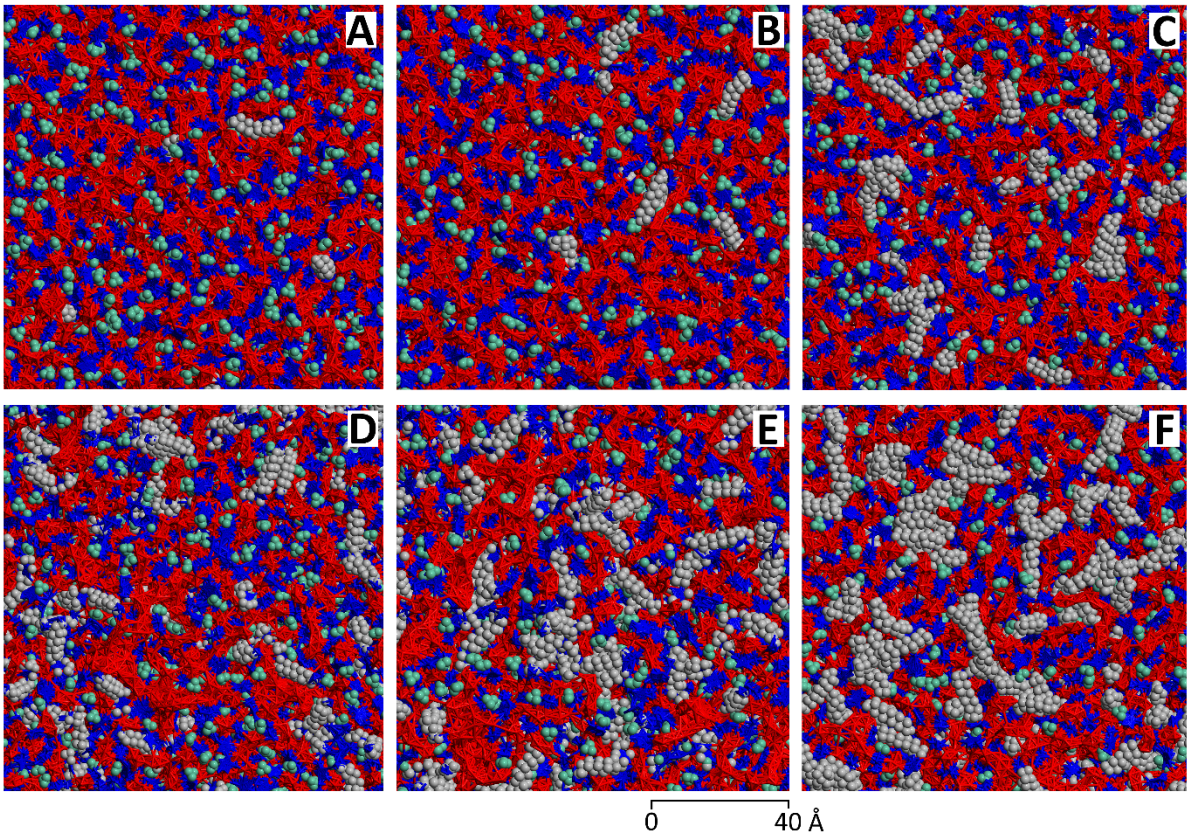
was removed *in vacuo*. The resulting colourless oil was dried *in vacuo* at 60 °C for 6 h (4.6 g, 93% yield). The ^{1}H NMR spectrum in CD_2Cl_2 in the presence of hexamethylbenzene as an internal reference revealed a degree of deuteration of 87% on the C^2 position of the aromatic ring, and 94% on the C^4 and C^5 positions. The degree of deuteration on the alkyl groups remained unchanged during the ring deuteration step.

1.5.2. Synthesis of [D_{31}]-1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C_{12}mim-d_{31}][Tf_2N]

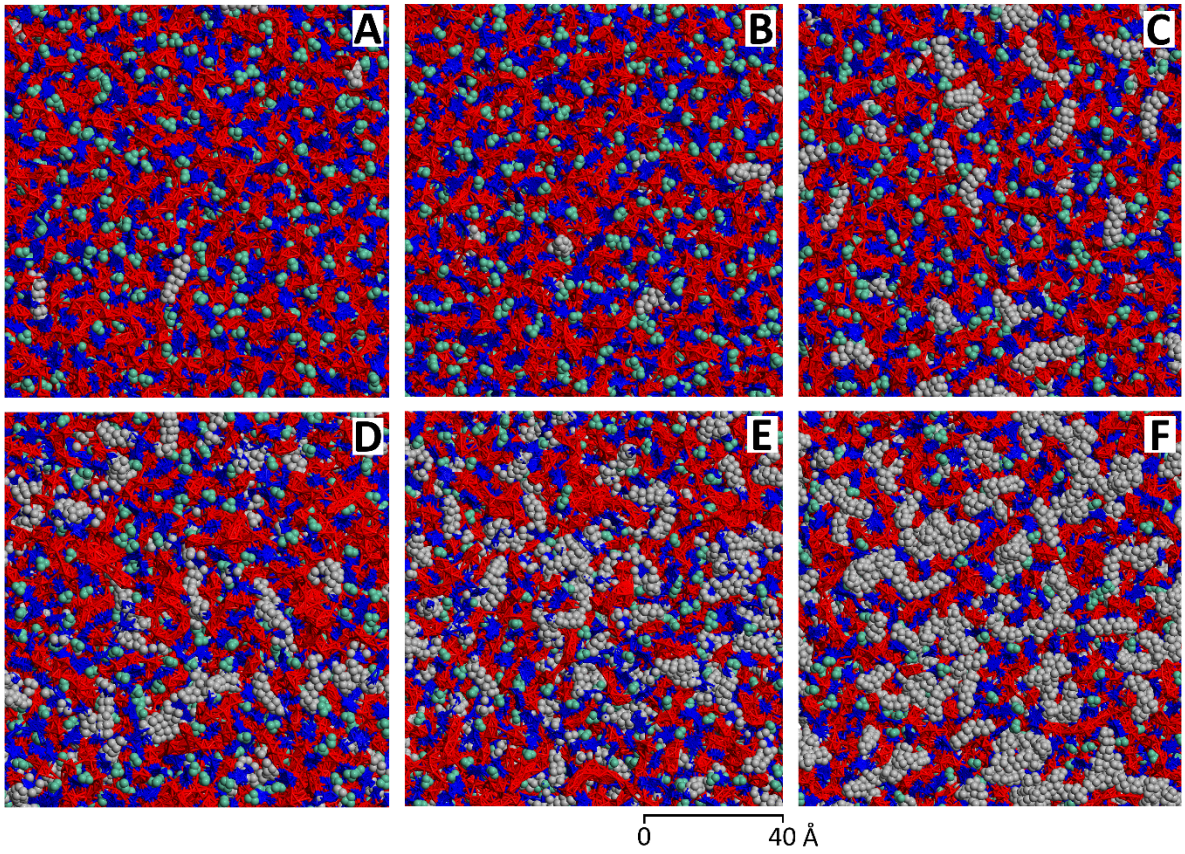
This product was prepared following a literature method for the ring deuteration of its [C_2mim] analogue.[1] [D_{28}]-1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (5.85 g, 10.5 mmol) was dissolved in [D_1]-methanol (21.2 g, 26 mL, 0.64 mol), treated with caesium hydroxide monohydrate (0.52 g, 3.1 mmol) and stirred for 24 h at 50 °C under nitrogen. The mixture was neutralised with 1:3 v/v H[Tf_2N]/D_2O (where H[Tf_2N] is a commercially available 80% aqueous solution of bis(trifluoromethylsulfonyl)imide), and the solvent was removed *in vacuo*. The residue was partitioned between dichloromethane (20 mL) and deuterium oxide (20 mL). The layers were separated and the aqueous phase was extracted with dichloromethane (15 mL). The combined organic layers were washed with deuterium oxide (3 × 15 mL), and the solvent was subsequently removed *in vacuo*. The resulting colourless oil was dried *in vacuo* at 60 °C for 6 h (5.52 g, 94% yield). The ^{1}H NMR spectrum in CD_2Cl_2 in the presence of hexamethylbenzene as an internal reference revealed a degree of deuteration of 94% on the C^2 position of the aromatic ring, and 95% on the C^4 and C^5 positions. The degree of deuteration on the alkyl groups remained unchanged during the ring deuteration step. Following this methodology, we have observed that the degree of deuteration on the C^2 position can vary within the range 84-94%.

1.3 Snapshots from MD simulations

Representative snapshots of the simulation boxes from the equilibrated MD simulations are shown below.



Snapshots from simulations at 300K. Panels A to F show x = 0.01, 0.04, 0.16, 0.24, 0.32 and 0.42 respectively.



Snapshots from simulations at 500K. Panels A to F show x = 0.01, 0.04, 0.16, 0.24, 0.32 and 0.42 respectively.

1. R. Giernoth and D. Bankmann, *Eur. J. Org. Chem.*, 2008, 2881-2886.
2. M. Bergtrup and P. Larsen, *Acta Chem. Scandin.*, **1990**, *44*, 1050-1057.