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# Supporting information for Bulk nanostructure of the prototypical 'good' and 'poor' solvate ionic liquids [Li(G4)][TFSI] and [Li(G4)][NO<sub>3</sub>].

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## Synthesis of dimethyl diglycolate (2):

To a solution of diglycolic acid (78g, 581.22 mmol) in methanol (450 ml) was added H<sub>2</sub>SO<sub>4</sub> (3mL) slowly. The reaction was left to reflux for 48 h. Methanol was removed under reduced pressure, and the left over liquid was poured onto crushed ice and then extracted with ethyl acetate (5 × 100 mL). The combined organic layers was dried over MgSO<sub>4</sub> and evaporated to give (80 g 84.7%) as colourless liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.72 (s, 6H), 4.20 (s, 4H).

<sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ 51.8, 67.9, 170.0.

# Deuteration of dimethylglycolate (3):

Deuteration of dimethylglycolate was carried out according to a literature procedure.<sup>1</sup> To a cold solution of MeOD (70 mL) sodium (1.3 g) was added under nitrogen atmosphere and continued stirring until dissolves completely. Dimethylglycolate (23.0 g, 141.93 mmol) was added and the solution was stirred. After 3 days the solvent was removed under reduced pressure and replaced by fresh MeOD (70 ml). The stirring was continued and the reaction progress was monitored by <sup>1</sup>H NMR. After 7 days and when no improvement in the deuteration level was noticed, the reaction mixture was poured onto crushed ice and the solution was extracted with dichloromethane (100 mL  $\times$  7). The combined extracts were dried over MgSO<sub>4</sub> and evaporated to give clear liquid (13 g, 55.5%). The deuteration level was calculated by integrating the methyl groups to the residual proton signals of the deuterated methylene groups to give an isotopic purity of 88.5%

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.72 (s, 6H), residual protons 4.17 (s, 0.46H).
<sup>2</sup>H NMR (61.4 MHz, CDCl<sub>3</sub>) δ 4.16 (s).
<sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ 42.4, 51.8, 67.3 (m), 169.9.

## Synthesis of di-ethylene glycol-d<sub>8</sub>(4):

To a cold (0 C°) solution of dimethyl di-glycolate- $d_4$  (16.2 g, 97.56 mmol) in dry THF (200 mL) was added LiAlD<sub>4</sub> (8.0 g, 195.12 moles) in portions over a 2 hours period under a nitrogen atmosphere. The reaction was left to reflux overnight. The reaction was cooled to 0 °C, then ice cold HCl (10 mL 0.5 M) was added slowly over the period of two hours under nitrogen atmosphere. The reaction was left stirring at rt for 2 h, and then was filtered through a 2 cm silica bed. The silica bed was washed with 25% MeOH in ethyl acetate (400 mL). The filtrate was evaporated to give 13.0 g crude product. The crude was further purified by distillation using Kugel Rohr apparatus to give a clear liquid (10.75 g, 96.7%). The deuteration levels were calculated by <sup>1</sup>H NMR spectroscopy by using an external standard (dimethyl sulphone). The overall deuteration level was calculated to be 93.5% D.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  dimethyl sulfone external standard 2.94 (s, 6H), residual protons 3.50 (s, 3.24H), 4.23 (b s, OH).

<sup>2</sup>H NMR (61.4 MHz, CDCl<sub>3</sub>)  $\delta$  3.56 (d, *J* = 8.5 Hz).

 $^{13}$ C NMR (100.6 MHz, CDCl<sub>3</sub>)  $\delta$  42.4, (dimethyl sulfone), 60.4 (m), 71.4 (m).

#### Synthesis of 2-(2-benzyloxy-ethoxy)-ethanol-d<sub>8</sub>(5):

Compound was synthesised according to a literature procedure.<sup>2</sup> A suspension solution of di-ethylene glycol- $d_8$  (2.5 g, 22.0 mmol), Ag<sub>2</sub>O (7.62 g, 33.0 mmol), and benzyl bromide (4.2 g, 4.0 mmol) in dichloromethane (30 mL) was stirred for 1 h. The reaction contents were filtered through a Celite bed and washed with dichloromethane (50 mL). The filtrate was dried over MgSO<sub>4</sub> and evaporated to give a crude residue, which was purified by flash chromatography using 5% MeOH in ethyl acetate to give a colourless viscous liquid (3.6 g, 80%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  2.77 (b s, OH), residual protons 3.58 (m), 3.66 (m), benzyl protons 5.56 (s, 2H), 7.29 (m, 5H).

<sup>2</sup>H NMR (61.4 MHz, CDCl<sub>3</sub>)  $\delta$  3.11 (m).

<sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ 60.9 (m), 60.4 (m), 68.5 (m), 69.0 (m), 72.0 (m), 73.0 (s), 127.6 (s), 127.7 (s, 2 x C), 128.3 (s, 2 x C).

ESI-MS: [M<sup>+Na</sup>] 227. Mass distribution 39.9%, *d*<sub>8</sub>; 36.3%, *d*<sub>7</sub>; 12.4%, *d*<sub>6</sub>; 1.3%, *d*<sub>5</sub>.

# Synthesis of 2-(4-methyl-phenylsulfonyl(2-benzyloxy-ethoxy)-ethanol-d<sub>8</sub>(6):

To a solution of 2-(2-benzyloxy-ethoxy)-ethanol- $d_8$  (4.0 g, 19.59 mmol) and triethylamine (1.98 g, 19.59 mmol) in DCM (50 mL) was added *para*-toluene sulfonyl chloride (3.72 g, 19.59 mmol). The reaction mixture was left stirring at rt for overnight under a nitrogen atmosphere. The reaction mixture was diluted with DCM (50 mL) then partitioned with DCM (3 × 50 mL). The combined organic extracts were dried over MgSO<sub>4</sub> and evaporated to give residue, which is further purified by flash column chromatography using as solvent system of 30% ethyl acetate in petroleum ether to give a colourless white solid (6.2 g, 88%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  2.44 (s, 3H), residual protons 3.54 (m, 0.009H), 3.58 (m, 0.114H), 3.67 (m, 0.118H), benzyl protons 4.53 (s, 2H), 7.33 (m, 7H), 7.79 (d, J = 8.14Hz, 2H).

<sup>2</sup>H NMR (61.4 MHz, CDCl<sub>3</sub>) δ 3.57 (m, 6D), 4.13 (m, 2D).

<sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ 21.7, 73.4, 127.6, 127.67, 127.9, 128.3, 129.7, 133.0, 138.0, 144.0.

<sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) {<sup>1</sup>H} and {<sup>2</sup>H} decoupled  $\delta$  21.7, 67.8, 68.5, 68.57, 69.8, 73.3, 73.4, 127.6, 127.67, 127.9, 128.3, 129.7, 133.0, 138.0, 144.0.

#### Synthesis of 1,15-diphenyl-2,5,8,11,14,-pentaoxapentadecane-d<sub>16</sub>(7):

A solution of mono-bn-diethylene glycol (2.71 g, 13.28 mmol), 1-*para*-touene sulfonyl-2-(2-benzyl-ethoxy)ethane (4.76 g, 13.28 mmol), KOH powder (6.0 g, 107.14 mmol) and tetrabutylammonium bromide (0.59 g, 0.0018 mol) in THF (100 mL) was stirred at rt for 4 days under nitrogen. The reaction mixture was passed through a Celite bed and the bed was washed with dichloromethane (50 mL). The filterate was evaporated to give a pale yellow colour residue, which was purified by flash column chromatography using as solvent system of 40% ethylacetate in hexane to give a colourless viscous liquid (4.0 g, 77%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  residual protons 3.61 (m, 0.6H), benzyl protons 4.56 (s, 4H), 7.35 (m, 10H). <sup>2</sup>H NMR (61.4 MHz, CDCl<sub>3</sub>)  $\delta$  3.61 (s).

<sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ 68.5 (m), 69.6 (m), 73.0 (s), 127.3 (s), 127.5 (s, 2 x C), 128.4 (s), 138.1 (s).

#### Synthesis of tetraethylene glycol-d<sub>16</sub>(8):

A solution of 1,15-diphenyl-2,5,8,11,14,-pentaoxapentadecane- $d_{16}$  (3.25 g, 8.32 mol) in methanol (25 mL) was bubbled for 5 minutes with N<sub>2</sub> gas. To this solution Pd/C (320 mg, 10% w/w) was added and the reaction mixture was bubbled for five minutes with H<sub>2</sub> gas. A 1L H<sub>2</sub> gas balloon was attached to the reaction flask which was then sealed and the reaction was stirred for 2 h. The reaction mixture was filtered through a 10 cm Celite bed which was then washed with methanol (50 mL). The solvent was evaporated to give a clear pale yellow liquid (1.86 g, 99%)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  residual protons 3.57 (m), 3.64 (m), 3.86 (s, OH).

<sup>2</sup>H NMR (61.4 MHz, CDCl<sub>3</sub>) δ 3.60 (m).

<sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>)  $\delta$  60.7 (m), 69.4 (m), 71.9 (m).

<sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) {<sup>1</sup>H} and {<sup>2</sup>H} decoupled  $\delta$  60.7, 69.0, 69.6, 71.9.

ESI-MS: [M<sup>+Na</sup>] 233.

# Synthesis of 1,15-dimethyl-2,5,8,11,14,-pentaoxapentadecane-d<sub>22</sub>(9):

A solution of tetraethylene glycol- $d_{16}$  (2.0 g, 8.84 mmol), iodomethane- $d_3$  (3.84 g, 26.52 mmol), KOH powder (5.0 g, 89.28 mmol) and tetrabutylammonium bromide (0.59 g, 1.88 mmol) in THF (100 mL) was stirred at rt for 4 days under nitrogen. The reaction mixture was passed through a Celite bed, and the bed was washed with dichloromethane (50 mL). The filtrate was evaporated to give a pale yellow colour residue, which was purified by flash column chromatography using as solvent system of 100% ethylacetate to give a colourless viscous liquid (1.36 g, 63%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  residual protons 3.60 (m).

<sup>2</sup>H NMR (61.4 MHz, CDCl<sub>3</sub>) δ 3.33 (s), 3.52 (m), 3.61(m).

<sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ 58.2 (m), 69.6 (m), 71.2 (m).

<sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) {<sup>1</sup>H} and {<sup>2</sup>H} decoupled  $\delta$  58.0, 69.6 (m), 69.9, 70.0, 70.9.

ESI-MS: [M<sup>+Na</sup>] 267. Mass distribution 72.4%, *d*<sub>22</sub>; 22.9%, *d*<sub>21</sub>; 4.6%, *d*<sub>20</sub>.

#### Synthesis of 1,15-dimethyl-2,5,8,11,14,-pentaoxapentadecane-d<sub>16</sub> (10):

A solution of tetraethylene glycol- $d_{16}$  (2.0 g, 8.18 mmol), iodomethane (3.48 g, 24.54 mmol), KOH powder (5.0 g, 89.28 mmol) and tetrabutylammonium bromide (0.59 g, 1.88 mmol) in THF (100 mL) was stirred at rt for 4 days under nitrogen. The reaction mixture was passed through a Celite bed, and the bed was washed with dichloromethane (50 mL). The filtrate was evaporated to give a pale yellow colour residue, which was purified by flash column chromatography using as solvent system of 100% ethylacetate to give colourless viscous liquid (1.35 g, 70%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  residual protons 3.36 (s, 6H), residual protons 3.61 (m, 0.061H).

<sup>2</sup>H NMR (61.4 MHz, CDCl<sub>3</sub>) δ 3.49 (m), 3.61(m).

<sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>)  $\delta$  59.0 (s), 69.9 (m), 71.2 (m).

<sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) {<sup>1</sup>H} and {<sup>2</sup>H} decoupled  $\delta$  59.0, 69.59, 69.96, 69.71, 69.97, 70.09, 71.8. ESI-MS: (M<sup>+Na</sup>) 261. Mass distribution 54.1%,  $d_{16}$ ; 33.5%,  $d_{15}$ ; 12.4 %,  $d_{14}$ .

#### Synthesis of 1,15-dimethyl-2,5,8,11,14,-pentaoxapentadecane-d6 (11):



A solution of tetraethylene glycol (4.0 g, 19.04 mmol), iodomethane- $d_3$  (8.27 g, 57.12 mmol), KOH powder (5.0 g, 89.28 mmol) and tetrabutylammonium bromide (0.59 g, 1.88 mmol) in THF (100 mL) was stirred at rt for 4 days under nitrogen. The reaction mixture was passed through a Celite bed, and the bed was washed

with dichloromethane (50 mL). The filtrate was evaporated to give a pale yellow colour residue, which was purified by flash column chromatography using as solvent system of 100% ethylacetate to give a colourless viscous liquid (3.0 g, 65%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.52 (m, 4H), 3.63 (m, 12H).

<sup>2</sup>H NMR (61.4 MHz, CDCl<sub>3</sub>) δ 3.27 (s, 6D).

<sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>)  $\delta$  59.0 (s), 69.9 (m), 71.2 (m).

<sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) {<sup>1</sup>H} and {<sup>2</sup>H} decoupled  $\delta$  58.0 (m), 70.43, 70.47, 70.49, 71.7. ESI-MS: [M<sup>+Na</sup>] 251.



Figure S1: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) of tetraethylene glycol methylether-d<sub>6</sub> (11).





Figure S5: <sup>2</sup>H NMR (CDCl<sub>3</sub>, 102.6 MHz) of tetraethylene glycol methylether- $d_{16}$  (10).



<sup>200</sup> 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm **Figure S7:** <sup>13</sup>C {<sup>1</sup>H} and {<sup>2</sup>H} decoupled (100.6 MHz) NMR of tetraethylene glycolmethyl ether- $d_{16}(10)$ .



**Figure S9**: <sup>2</sup>H NMR (CDCl<sub>3</sub>, 102.6 MHz) of tetraethylene glycol methylether- $d_{22}$  (9).



Figure S11: <sup>13</sup>C {<sup>1</sup>H} and {<sup>2</sup>H} decoupled (100.6 MHz) NMR of tetraethylene glycolmethyl ether- $d_{22}(9)$ .





**Figure S13**: <sup>2</sup>H NMR (CDCl<sub>3</sub>, 102.6 MHz) of tetraethylene glycol- $d_{16}$  (**8**).



<sup>200</sup> 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm **Figure S14**: <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz) of tetraethylene glycol- $d_{16}$  (**8**).



200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm Figure S15: <sup>13</sup>C {<sup>1</sup>H} and {<sup>2</sup>H} decoupled (100.6 MHz) NMR of tetraethylene glycol- $d_{16}$ (8).



**Figure S17**: <sup>2</sup>H NMR (CDCl<sub>3</sub>, 102.6 MHz) of 1,15-diphenyl-2,5,8,11,14,-pentaoxapentadecane- $d_{16}$  (7).



**Figure S18**: <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz) of 1,15-diphenyl-2,5,8,11,14,-pentaoxapentadecane- $d_{16}$  (7).





**Figure S20**: <sup>2</sup>H NMR (CDCl<sub>3</sub>, 100.6 MHz) of 2-(4-methyl-phenylsulfonyl(2-benzyloxy-ethoxy)-ethanol- $d_8$  (6).



Figure S21: <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz) of 2-(4-methyl-phenylsulfonyl(2-benzyloxy-ethoxy)-ethanol- $d_8$  (6).



Figure S22: <sup>13</sup>C NMR {<sup>1</sup>H} and {<sup>2</sup>H} decoupled (CDCl<sub>3</sub>, 100.6 MHz) of 2-(4-methyl-phenylsulfonyl(2-benzyloxy-ethoxy)-ethanol- $d_8$  (6).



**Figure S23**. SDF plots for Li<sup>+</sup> cations around (left to right) G4 O<sub>1</sub>, G4 O<sub>2</sub> and G4 O<sub>3</sub> atoms (highlighted by green circles) in [Li(G4)][TFSI], distances used corresponding to the first peak in the corresponding Li $\cdots$ O<sub>2</sub>  $g_{ij}(\mathbf{r})$ .



**Figure S24**. SDF plots for Li<sup>+</sup> cations around (left to right) G4 O<sub>1</sub>, G4 O<sub>2</sub> and G4 O<sub>3</sub> atoms (highlighted by green circles) in [Li(G4)][NO<sub>3</sub>], distances used corresponding to the first peak in the corresponding Li $\cdots$ O<sub>2</sub> g<sub>ij</sub>(r).

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