

# Supplementary Information

Silica based ionogels: interfaces effects with aprotic and protic ionic liquids with lithium  
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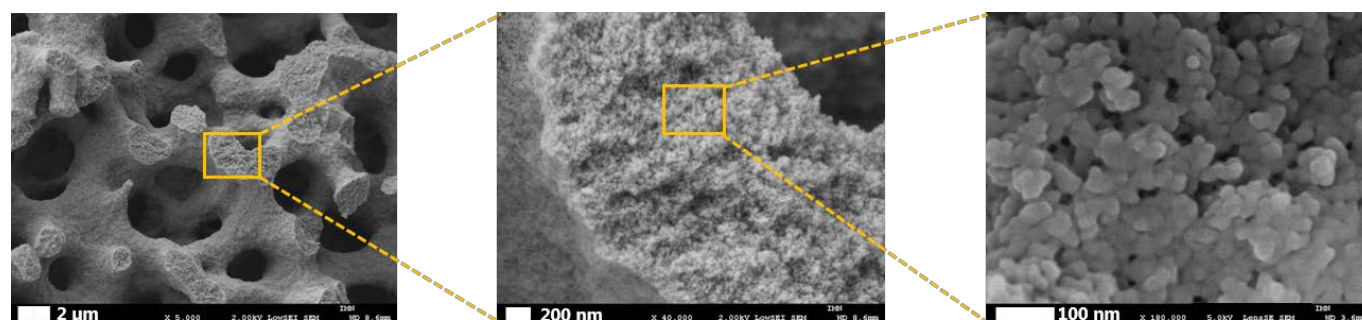


Fig. S1 SEM image of silica monolith

Table S1 Mass fraction and volume of ILs in impregnated silica

| Pyr14TFSI-based ionogels              |            |                                                           | Pyr14-LiTFSI-based ionogels |                                                              |              | PyrH4TFSI-based ionogels                                  |              |                                                              | PyrH4-LiTFSI-based ionogels |                                                              |        |
|---------------------------------------|------------|-----------------------------------------------------------|-----------------------------|--------------------------------------------------------------|--------------|-----------------------------------------------------------|--------------|--------------------------------------------------------------|-----------------------------|--------------------------------------------------------------|--------|
| $\varnothing_{\text{meso (N2)}}$ (nm) | %wt IL     | $V_{\text{total (14)}}$<br>(cm <sup>3</sup> /g of silica) | %wt IL                      | $V_{\text{total (14-Li)}}$<br>(cm <sup>3</sup> /g of silica) | %wt IL       | $V_{\text{total (H4)}}$<br>(cm <sup>3</sup> /g of silica) | %wt IL       | $V_{\text{total (H4-Li)}}$<br>(cm <sup>3</sup> /g of silica) | %wt IL                      | $V_{\text{total (H4-Li)}}$<br>(cm <sup>3</sup> /g of silica) | %wt IL |
| 8.1                                   | 82.5 ± 0.2 | 3.40 ± 0.05                                               | 82.6 ± 0.3                  | 3.32 ± 0.06                                                  | 81.9 ± 0.1   | 3.15 ± 0.01                                               | 82.36 ± 0.02 | 3.24 ± 0.00                                                  |                             |                                                              |        |
| 8.5                                   | 81.9 ± 0.1 | 3.26 ± 0.01                                               | 82.0 ± 0.4                  | 3.19 ± 0.08                                                  | 82.1 ± 0.7   | 3.2 ± 0.1                                                 | 82.4 ± 0.6   | 3.3 ± 0.1                                                    |                             |                                                              |        |
| 9.8                                   | 83.0 ± 0.5 | 3.5 ± 0.1                                                 | 84.0 ± 0.4                  | 3.7 ± 0.1                                                    | 84 ± 1       | 3.6 ± 0.3                                                 | 82.9 ± 0.7   | 3.4 ± 0.1                                                    |                             |                                                              |        |
| 11.2                                  | 82.8 ± 0.1 | 3.47 ± 0.02                                               | 83.1 ± 0.2                  | 3.44 ± 0.05                                                  | 83.7 ± 0.8   | 3.6 ± 0.2                                                 | 83.75 ± 1    | 3.6 ± 0.2                                                    |                             |                                                              |        |
| 12.6                                  | 83.4 ± 0.1 | 3.62 ± 0.04                                               | 83.3 ± 0.3                  | 3.49 ± 0.07                                                  | 83.02 ± 0.05 | 3.41 ± 0.01                                               | 83.2 ± 0.1   | 3.43 ± 0.02                                                  |                             |                                                              |        |
| 16.2                                  | 84.3 ± 0.1 | 3.87 ± 0.02                                               | 84.5 ± 0.2                  | 3.80 ± 0.05                                                  | 84.38 ± 0.01 | 3.770 ± 0.002                                             | 84.44 ± 0.00 | 3.77 ± 0.00                                                  |                             |                                                              |        |

Density at 30°C: Pyr14TFSI 1.3906 ; Pyr14TFSI + 0.5M LiTFSI 1.4319 ; PyrH4TFSI 1.4326 ; PyrH4TFSI+0.5M LiTFSI 1.4397

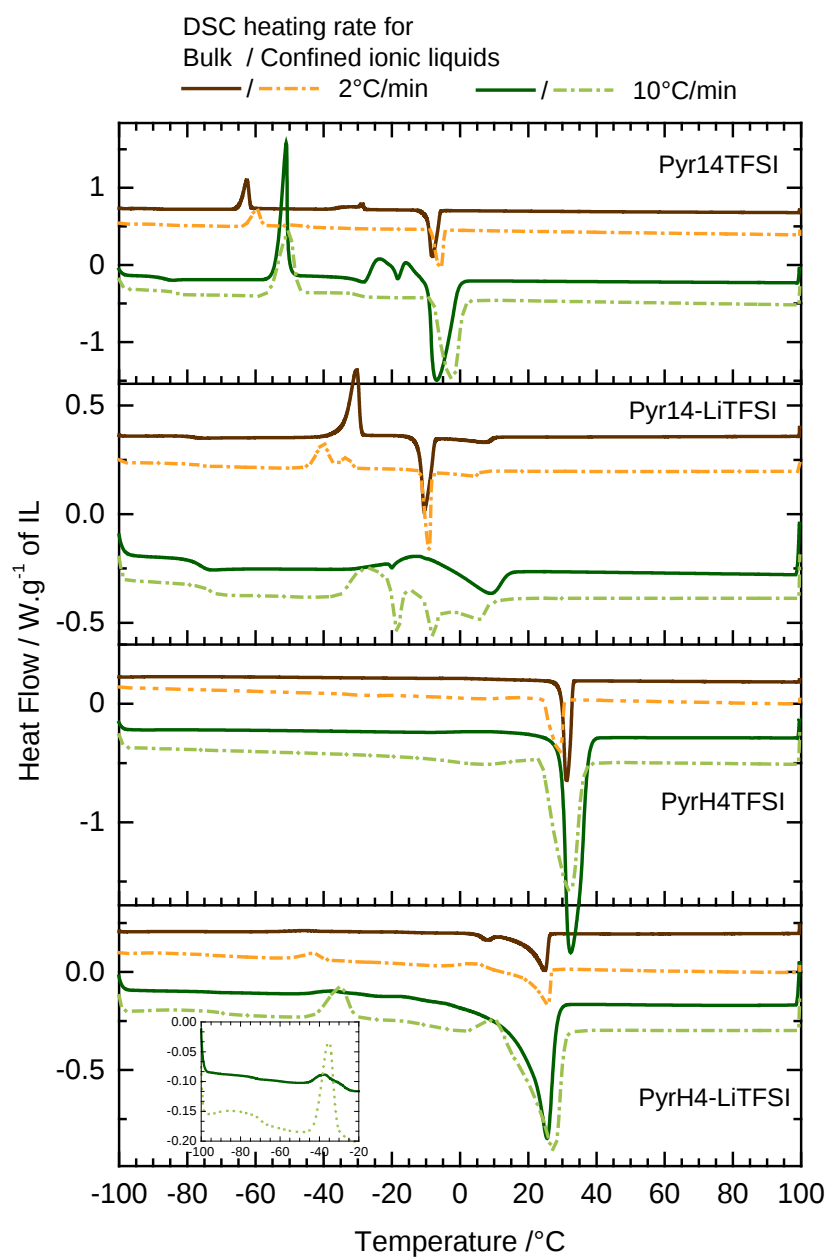


Fig. S2: DSC thermogram of ionic liquids, in bulk state and for a confinement in 11.2 nm meso-porous silica. From top to bottom: Pyr14TFSI, Pyr14-LiTFSI, PyrH4TFSI and PyrH4-LiTFSI. Inset: glass transition of PyrH4-LiTFSI.

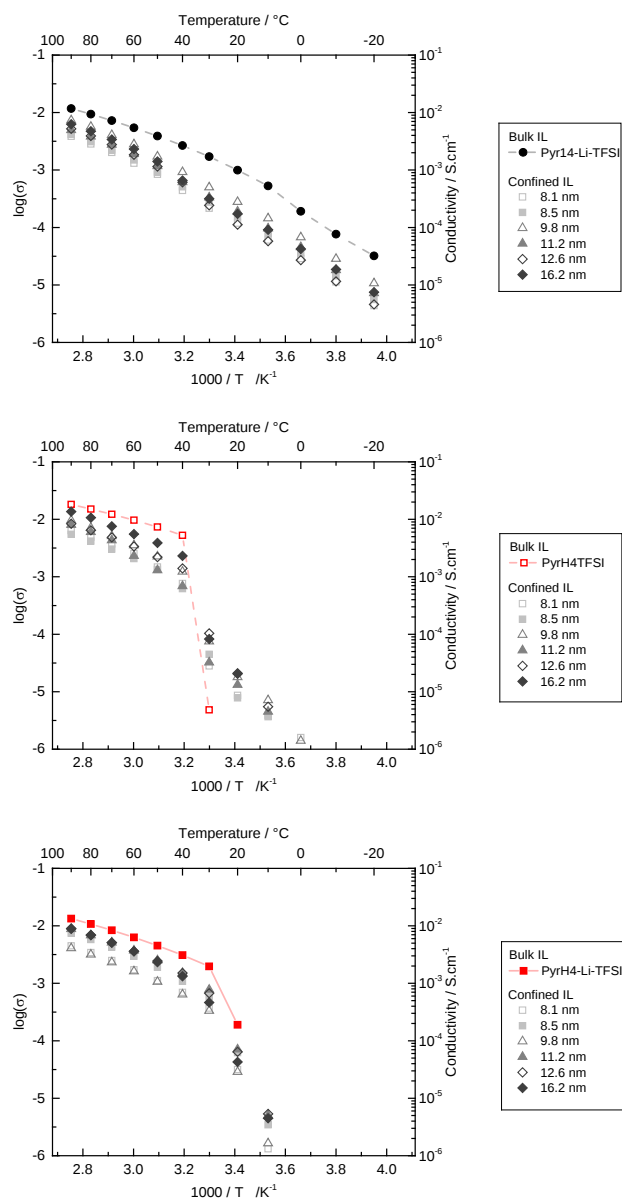


Fig. S3: Conductivity of Pyr14TFSI, PyrH4TFSI and PyrH4-Li-TFSI bulk ionic liquids and ionogels.

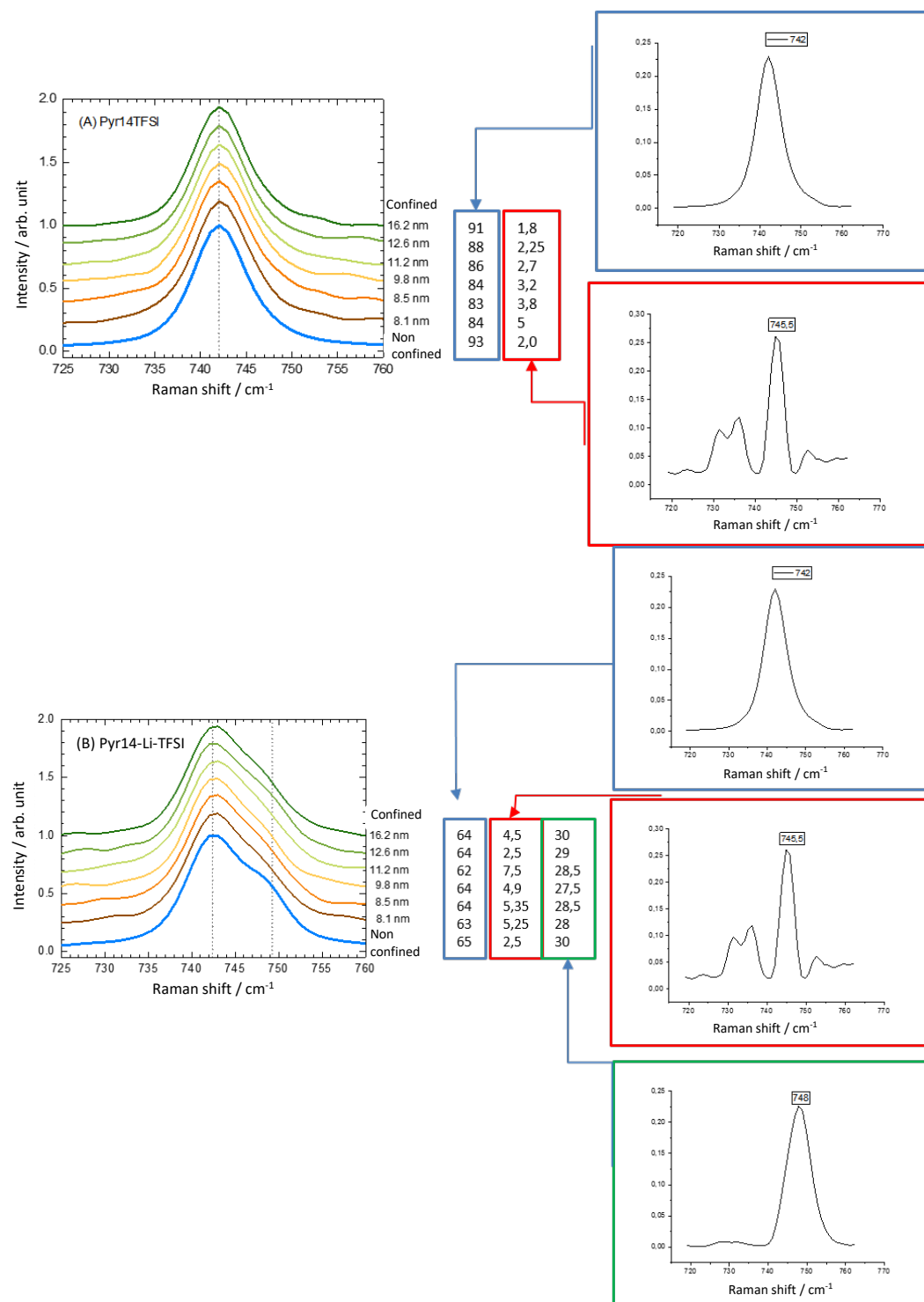


Fig. S4:-BPSS. Examples of BPSS algorithm application, for Pyr14TFSI bulk and confined (A) without  $\text{Li}^+$  and (B) with 0.5 M of  $\text{Li}^+$ . The weight of each source is noted in column, in front of mesopore sizes.

Table S2: Fitting parameters obtained for non-confined and confined Pyr14-LiTFSI (named by meso-pore size). \*fixed parameters

| Fitted component | Parameter          | Pyr14-LiTFSI | 8.1 nm | 8.5 nm | 9.8 nm | 11.2 nm | 12.6 nm | 16.2 nm |
|------------------|--------------------|--------------|--------|--------|--------|---------|---------|---------|
|                  | $y_0$              | 0.016        | 0.009  | 0.005  | 0.008  | 0.008   | 0.005   | 0.007   |
| C1               | $x_c^*$            | 741.8        | 741.7  | 741.7  | 741.7  | 741.7   | 741.7   | 741.7   |
|                  | A                  | 2.24         | 0.63   | 0.53   | 0.55   | 0.80    | 0.57    | 0.66    |
|                  | $6 < \omega < 8$   | 6.56         | 6.67   | 6.67   | 6.33   | 7.69    | 6.66    | 6.39    |
|                  | $\mu^*$            | 0.68         | 0.68   | 0.68   | 0.68   | 0.68    | 0.68    | 0.68    |
|                  |                    |              |        |        |        |         |         |         |
| C2               | $x_c^*$            | 743          | 743    | 743    | 743    | 743.01  | 743     | 743     |
|                  | A                  | 1.44         | 1.23   | 1.06   | 1.2    | 1.2     | 0.67    | 1.41    |
|                  | $6 < \omega < 9$   | 7.50         | 7.77   | 7.77   | 7.73   | 7.78    | 7.77    | 8.00    |
|                  | $\mu^*$            | 0.74         | 0.74   | 0.74   | 0.74   | 0.74    | 0.74    | 0.74    |
|                  |                    |              |        |        |        |         |         |         |
| C3               | $x_c^*$            | 748.3        | 748.3  | 748.3  | 748.3  | 748.3   | 748.3   | 748.3   |
|                  | A                  | 1.28         | 0.45   | 0.39   | 0.36   | 0.51    | 0.37    | 0.50    |
|                  | $6 < \omega < 7.2$ | 7.14         | 7      | 7      | 6.2    | 7.2     | 7       | 7       |
|                  | $\mu^*$            | 0            | 0      | 0      | 0      | 0       | 0       | 0       |
|                  |                    |              |        |        |        |         |         |         |

$$y = y_0 + A \times \left[ \mu \frac{2}{\pi} \frac{\omega}{4(x - x_c)^2 + \omega^2} + (1 - \mu) \frac{\sqrt{4 \ln 2}}{\omega \sqrt{\pi}} \exp\left(-\frac{4 \ln 2}{\omega^2}(x - x_c)^2\right) \right]$$

With  $y_0$  : offset,  $x_c$  : peak centre,  $A$  : peak area,  $\mu$  : profil shape factor (% of Lorentzian) and  $\omega$  : FWHM.

Table S3: Fitting parameters obtained for non-confined and confined PyrH4-LiTFSI (named by meso-pore size). \*fixed parameters

| Fitted component | Parameter      | PyrH4-LiTFSI | 8.1 nm   | 8.5 nm   | 9.8 nm   | 11.2 nm  | 12.6 nm  | 16.2 nm  |
|------------------|----------------|--------------|----------|----------|----------|----------|----------|----------|
| C1               | $\gamma_0$     | 0.007        | 0.004    | 0.004    | 0.004    | 0.005    | 0.0034   | 0.004    |
|                  | $xc^*$         | 743.06       | 743.06   | 743.06   | 743.06   | 743.06   | 743.06   | 743.06   |
|                  | A              | 1.98         | 0.44     | 0.76     | 0.95     | 0.86     | 0.41     | 1.11     |
|                  | $\omega < 8$   | 7.75         | 7.75     | 7.75     | 7.75     | 7.75     | 7.75     | 7.75     |
|                  | $\mu^*$        | 0.68         | 0.68     | 0.68     | 0.68     | 0.68     | 0.68     | 0.68     |
| C2               | $xc^*$         | 745          | 745      | 745      | 745      | 745      | 745      | 745      |
|                  | A              | 1.72         | 0.33     | 0.47     | 0.57     | 0.41     | 0.59     | 0.57     |
|                  | $\omega < 7$   | <u>7</u>     | <u>7</u> | <u>7</u> | <u>7</u> | <u>7</u> | <u>7</u> | <u>7</u> |
|                  | $\mu^*$        | 0.74         | 0.74     | 0.74     | 0.74     | 0.74     | 0.74     | 0.74     |
| C3               | $xc^*$         | 748.72       | 748.72   | 748.72   | 748.72   | 748.72   | 748.72   | 748.72   |
|                  | A              | 0.60         | 0.03     | 0.19     | 0.3      | 0.25     | 0.16     | 0.34     |
|                  | $\omega < 6.2$ | <u>6</u>     | <u>6</u> | <u>6</u> | <u>6</u> | <u>6</u> | <u>6</u> | <u>6</u> |
|                  | $\mu^*$        | 0            | 0        | 0        | 0        | 0        | 0        | 0        |