

Electronic Supplementary Information  
for:

**Characterisation of hydration water in Nafion membrane**

Stewart F. Parker\* and Shrey Shah, ISIS Facility, STFC Rutherford Appleton Laboratory,  
Chilton, Didcot, Oxon, OX11 0QX, UK.

**Contents**

<b>S1</b> - Phase diagram of TFSA. $n$ H <sub>2</sub> O .....	<b>2</b>
<b>S2</b> - Infrared and INS spectra of Nafion dried 180 °C .....	<b>3</b>
<b>S3</b> - Infrared and INS spectra of Nafion dried in a glove box .....	<b>3</b>
<b>S4</b> - Infrared and INS spectra of Nafion dried over P <sub>2</sub> O <sub>5</sub> .....	<b>4</b>
<b>S5</b> - Infrared and INS spectra of Nafion dried over MgCl <sub>2</sub> .....	<b>4</b>
<b>S6</b> - Infrared and INS spectra of Nafion as received.....	<b>5</b>
<b>S7</b> - Infrared and INS spectra of Nafion soaked in water.....	<b>5</b>
<b>S8</b> – Solid state infrared and INS spectra of TFSA .....	<b>6</b>
<b>S9</b> - Infrared spectra of liquid and solid TFSA.....	<b>6</b>
<b>S10</b> - Solid state infrared and INS spectra of TFSA.0.5H <sub>2</sub> O .....	<b>7</b>
<b>S11</b> - Spectra of liquid and solid TFSA.0.5H <sub>2</sub> O .....	<b>7</b>
<b>S12</b> - Solid state infrared, FT-Raman and INS spectra of TFSA.H <sub>2</sub> O .....	<b>8</b>
<b>S13</b> - Infrared spectra of liquid and solid TFSA.H <sub>2</sub> O.....	<b>8</b>
<b>S14</b> - Solid state infrared and INS spectra of TFSA.2H <sub>2</sub> O .....	<b>9</b>
<b>S15</b> - Spectra of liquid and solid TFSA.2H <sub>2</sub> O .....	<b>9</b>
<b>S16</b> - Solid state infrared and INS spectra of TFSA.4H <sub>2</sub> O .....	<b>10</b>
<b>S17</b> - Spectra of liquid and solid TFSA.4H <sub>2</sub> O .....	<b>10</b>
<b>S18</b> - Solid state infrared and INS spectra of TFSA.5H <sub>2</sub> O .....	<b>11</b>
<b>S19</b> - Spectra of liquid and solid TFSA.5H <sub>2</sub> O .....	<b>11</b>

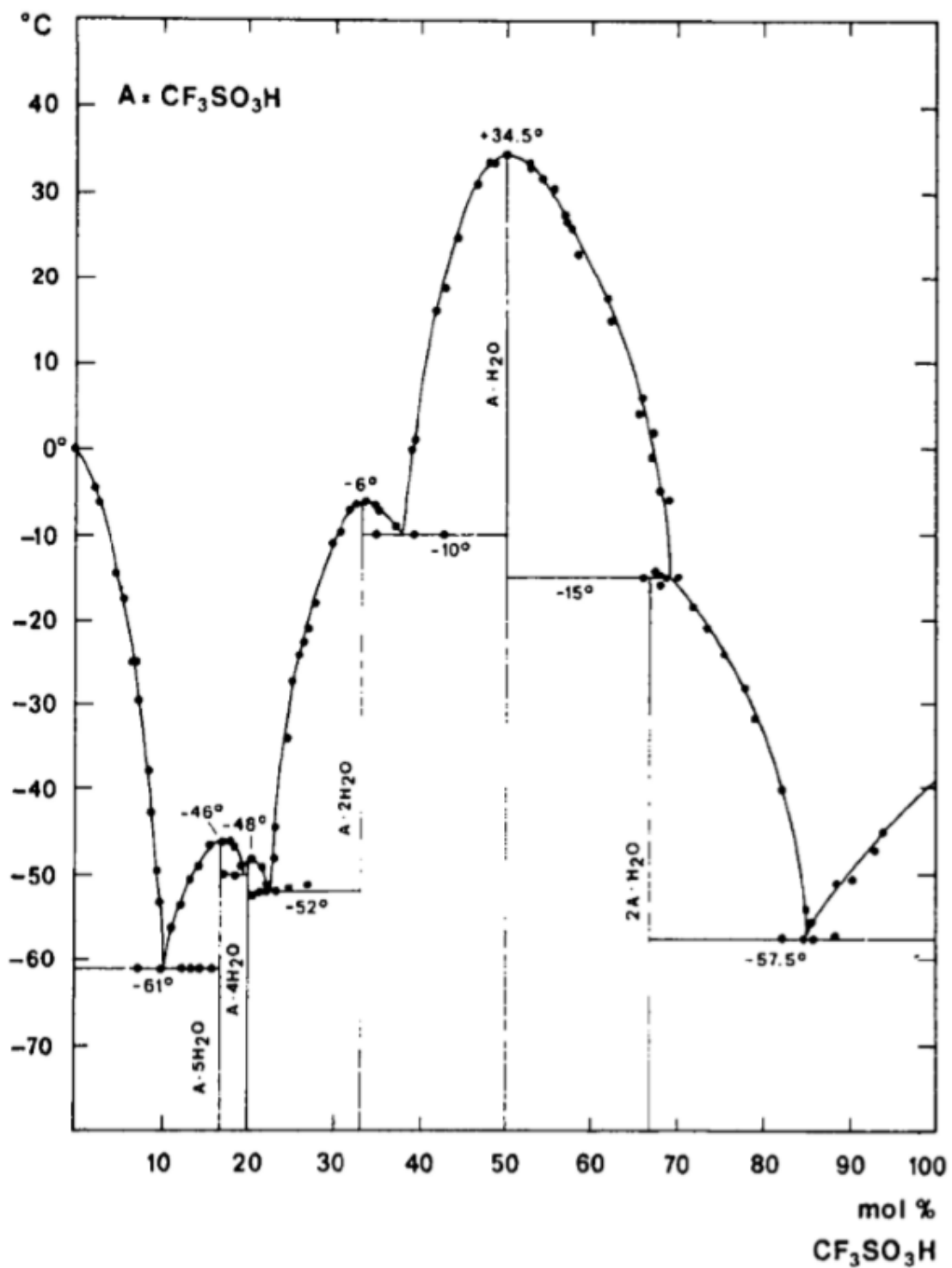
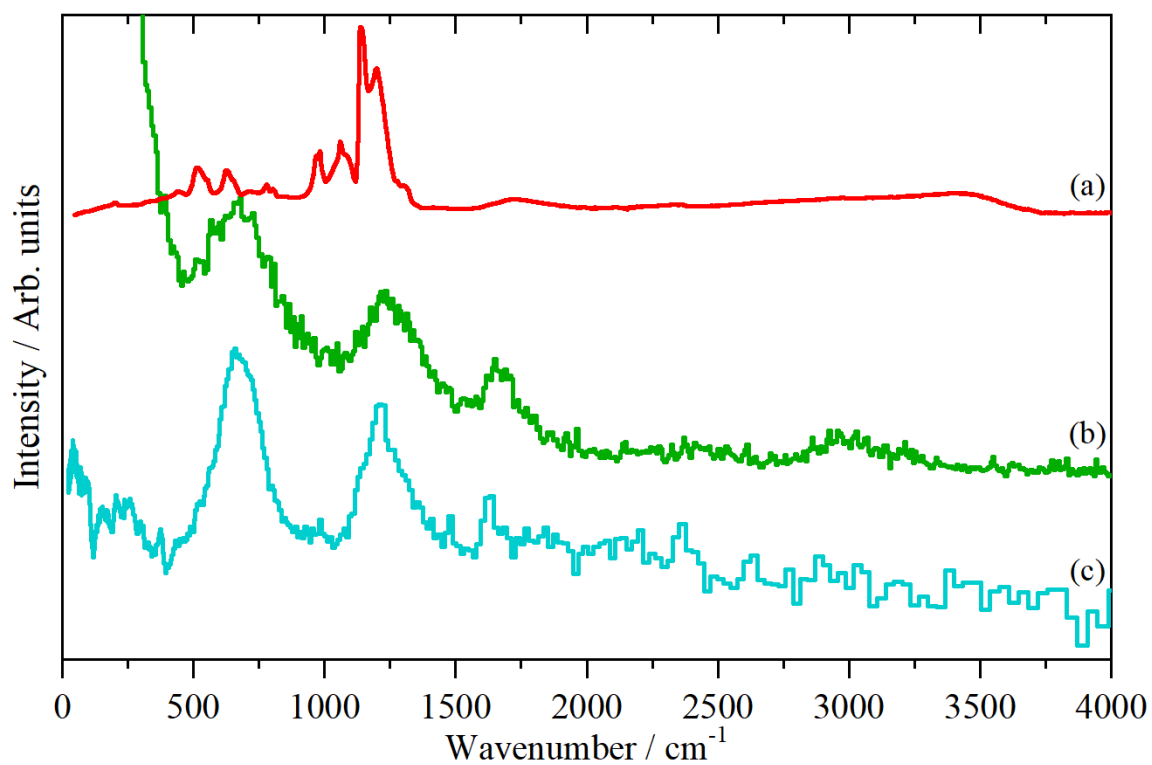
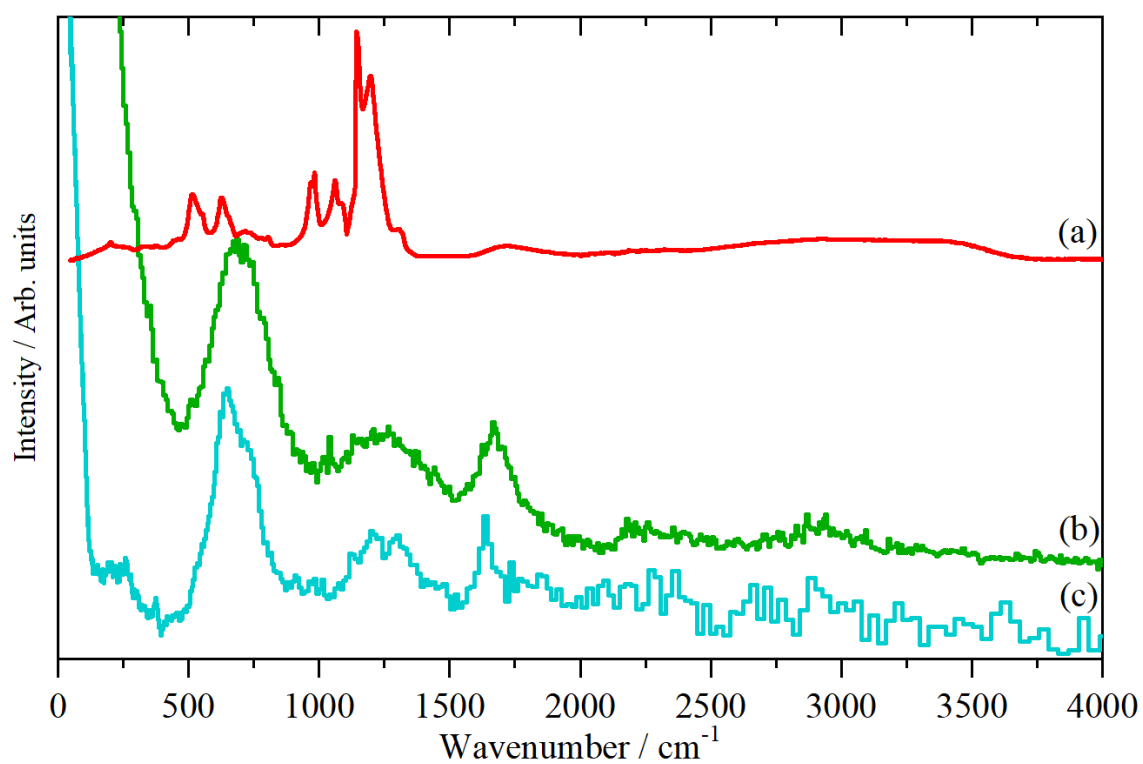


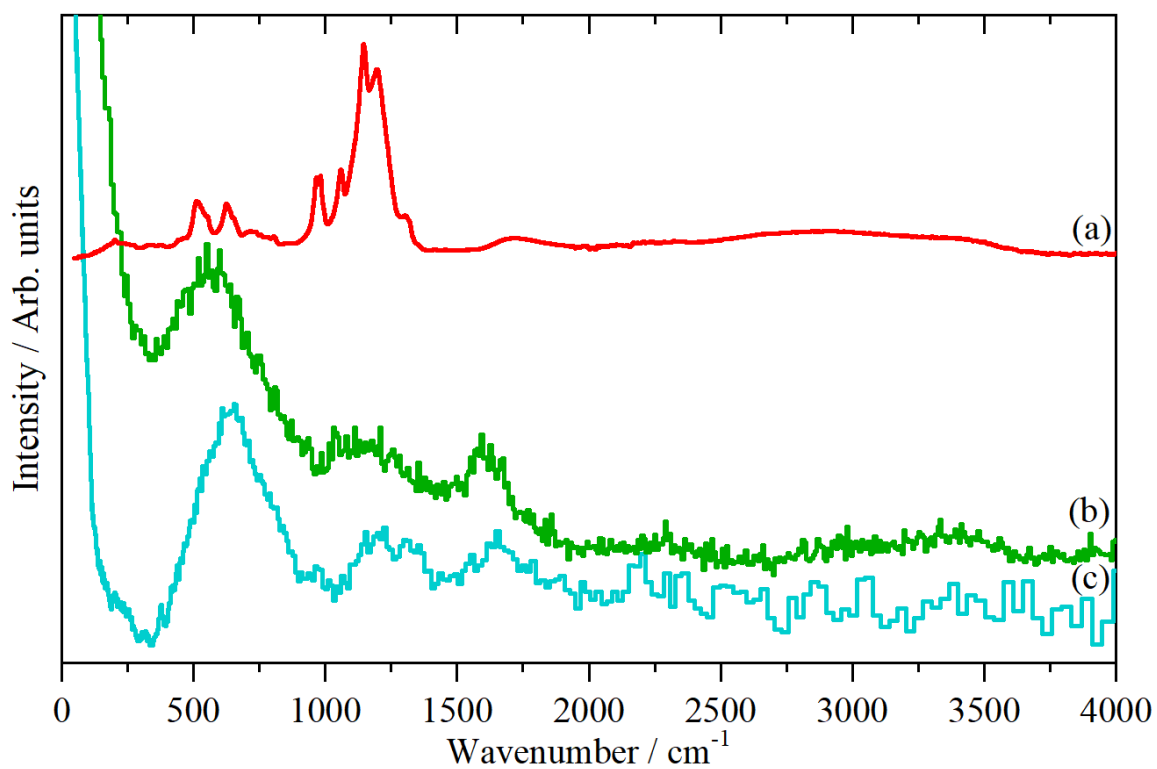
Fig. S1 Phase diagram of  $\text{TFSA} \cdot n\text{H}_2\text{O}$ . Reproduced from: R. Delaplane, J. Lundgren and I. Olovsson, *Acta Cryst.* B31 (1975) 2208–2213 (doi: 10.1107/S056774087500725X) with permission of the International Union of Crystallography.



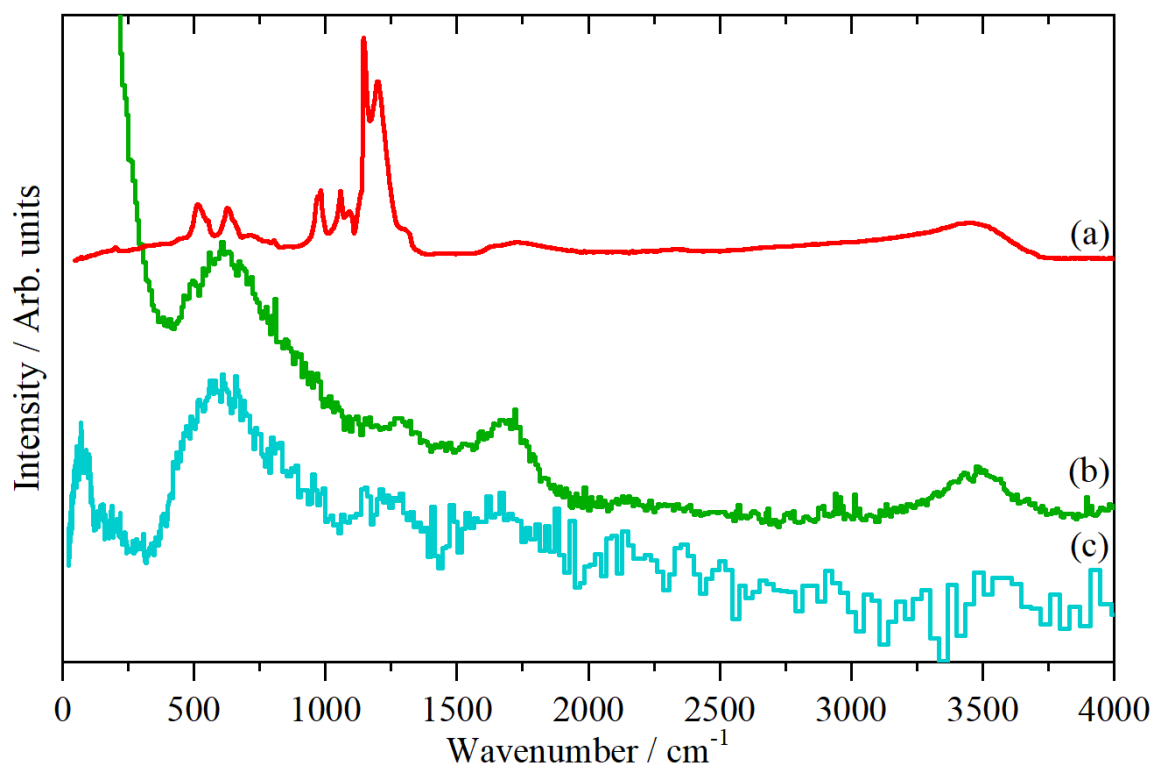
**Fig. S2** Infrared (a) and INS ((b) MAPS and (c) TOSCA) of Nafion dried in a vacuum oven at 180 °C for two days.



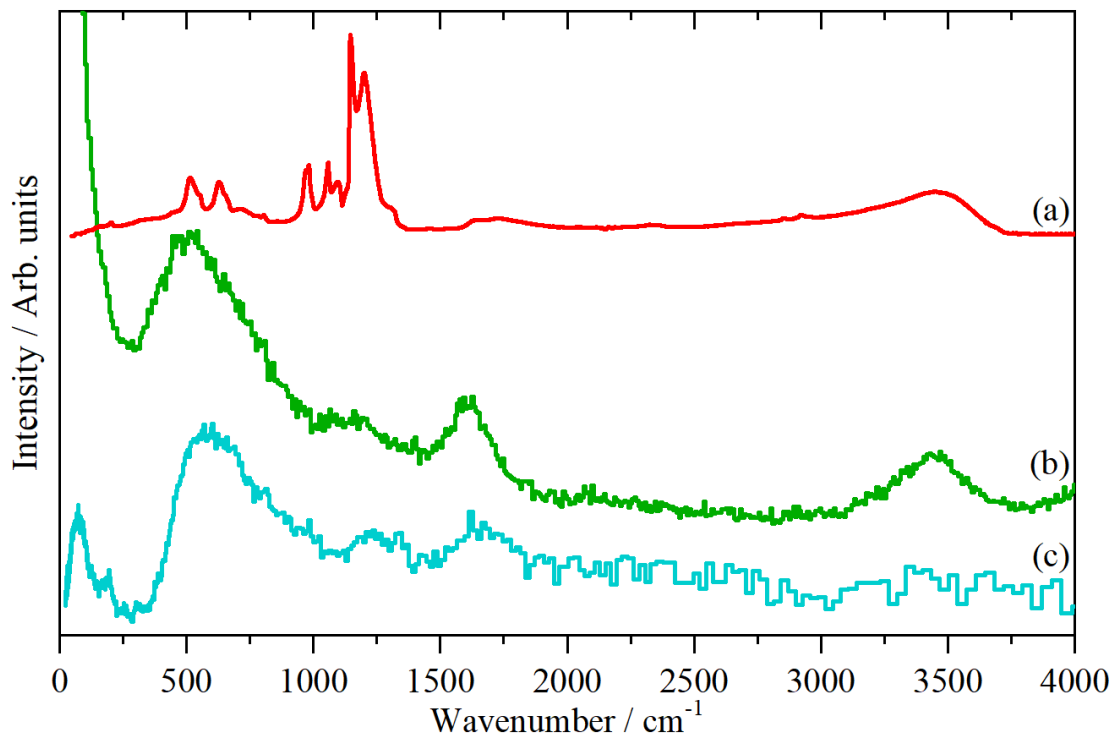
**Fig. S3** Infrared (a) and INS ((b) MAPS and (c) TOSCA) of Nafion dried in a glove box at room temperature for seven days.



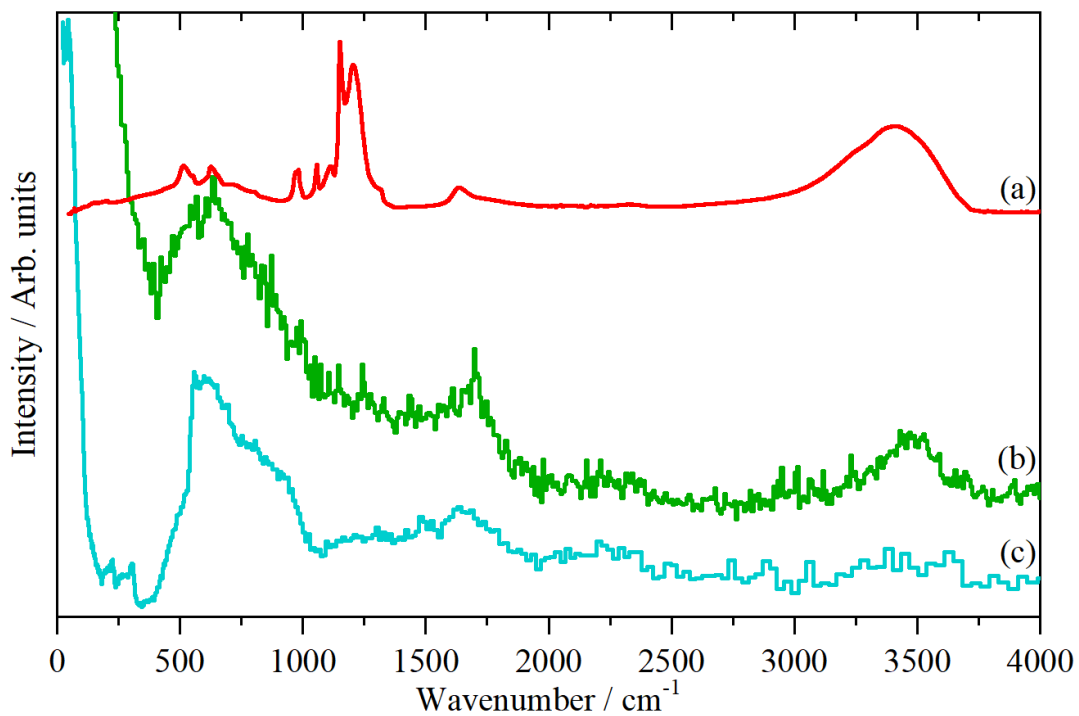
**Fig. S4** Infrared (a) and INS ((b) MAPS and (c) TOSCA) of Nafion dried over P<sub>2</sub>O<sub>5</sub> for 6 days.



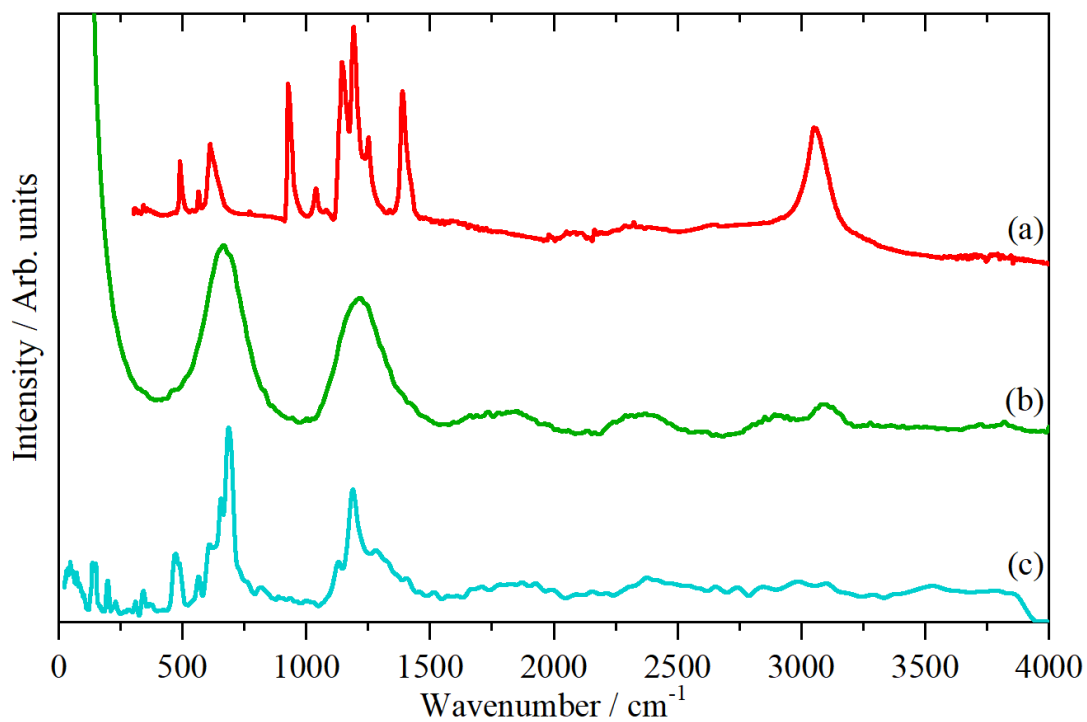
**Fig. S5** Infrared (a) and INS ((b) MAPS and (c) TOSCA) of Nafion dried over MgCl<sub>2</sub> for 6 days.



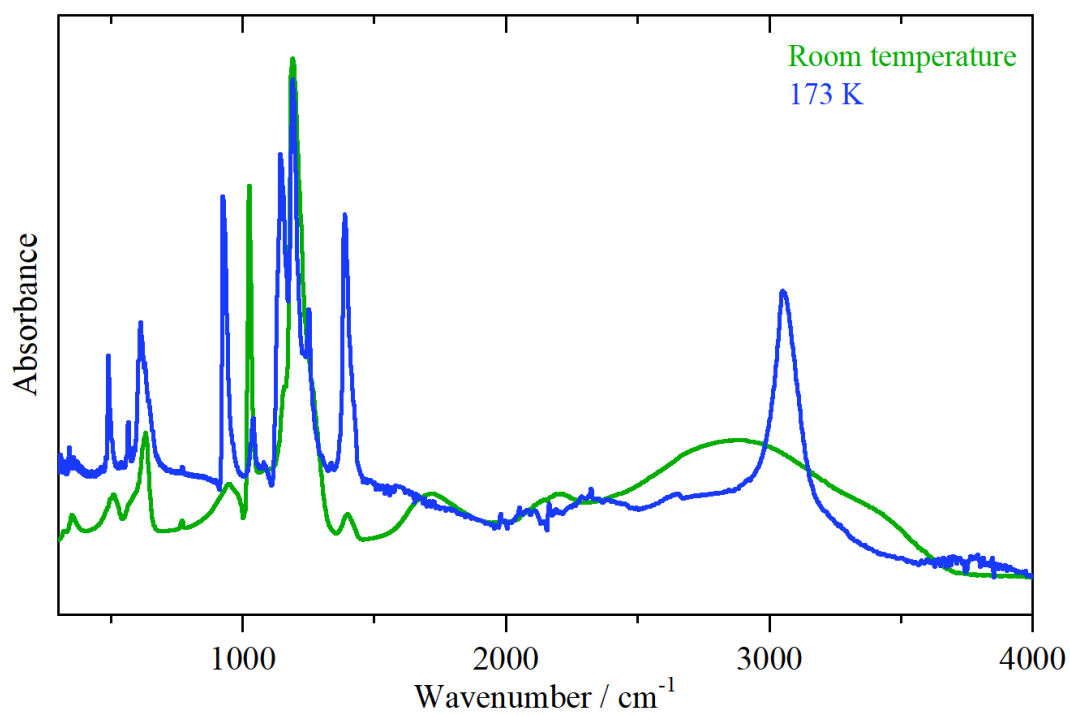
**Fig. S6** Infrared (a) and INS ((b) MAPS and (c) TOSCA) of Nafion as received.



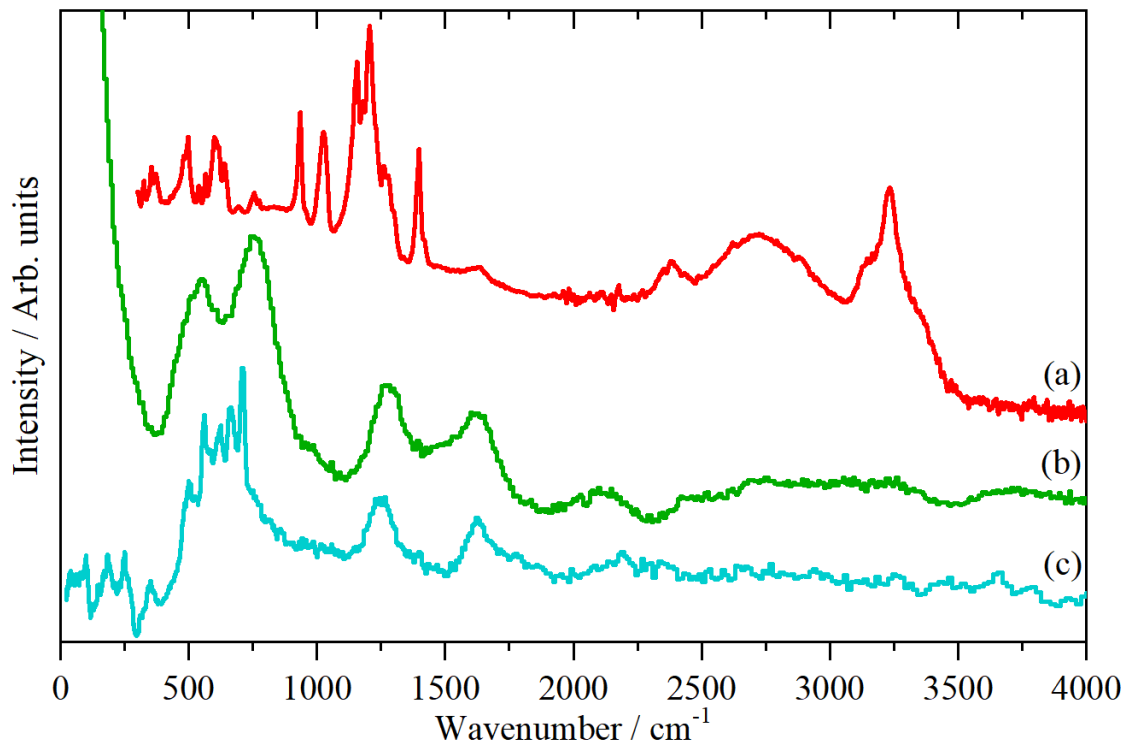
**Fig. S7** Infrared (a) and INS ((b) MAPS and (c) TOSCA) of Nafion soaked in distilled water for three days.



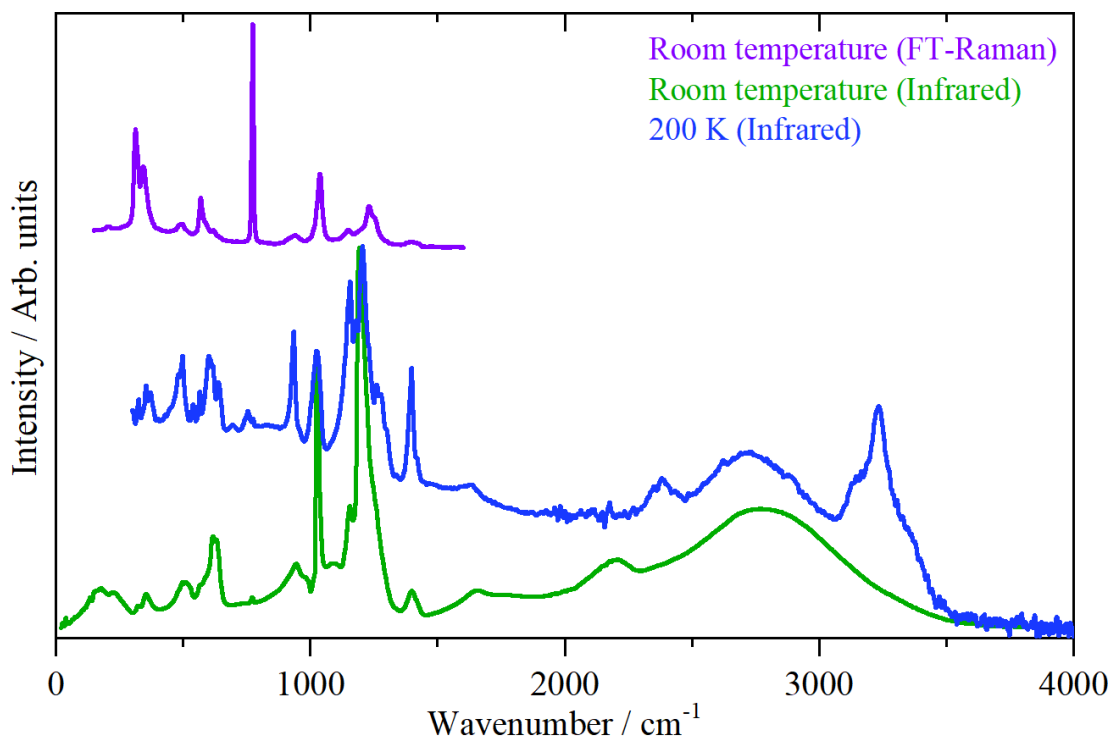
**Fig. S8** Solid state infrared (a) and INS ((b) MAPS and (c) TOSCA) of TFSA.



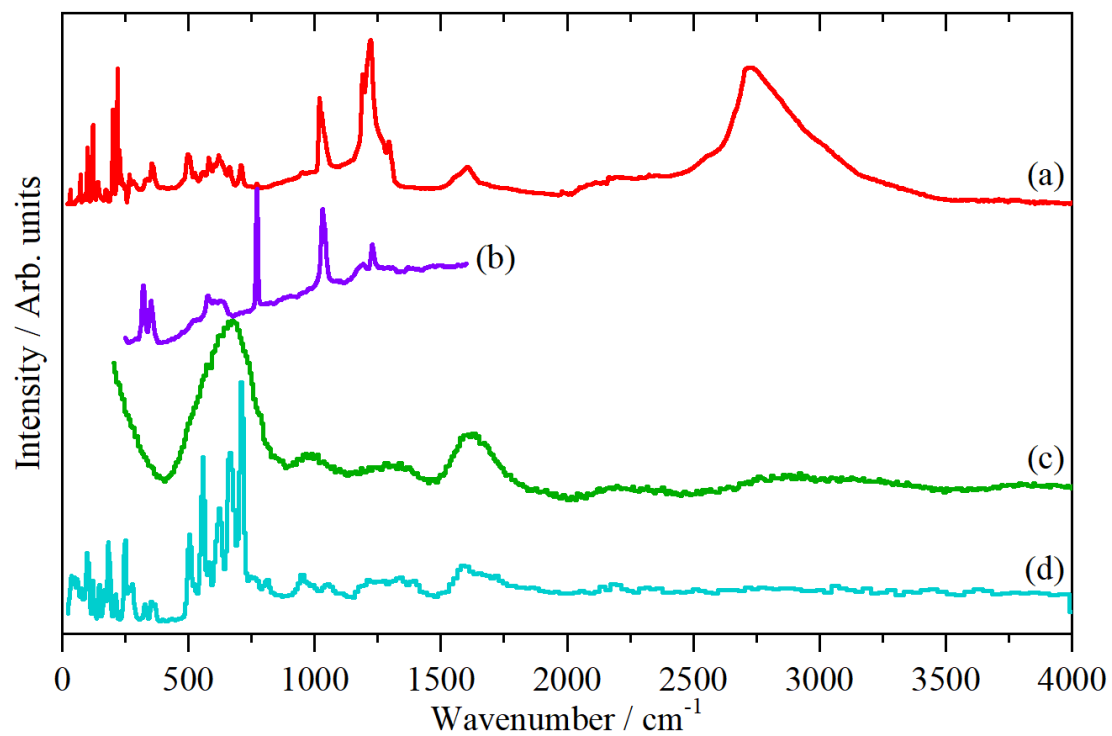
**Fig. S9** Infrared spectra of liquid (room temperature, green) and solid (173 K, blue) TFSA.



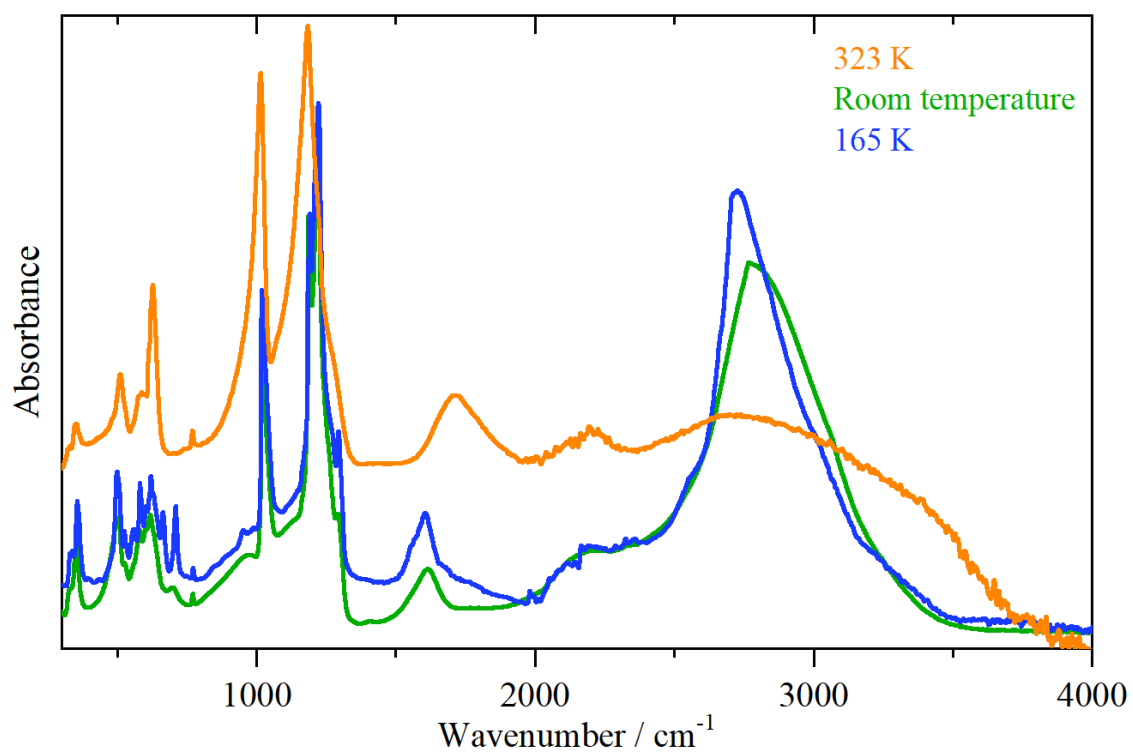
**Fig. S10** Solid state infrared (a) and INS ((b) MAPS and (c) TOSCA) of TFSA.0.5H<sub>2</sub>O.



**Fig. S11** Spectra of liquid (room temperature, FT-Raman violet, infrared green) and solid (200 K, infrared blue) TFSA.0.5H<sub>2</sub>O.

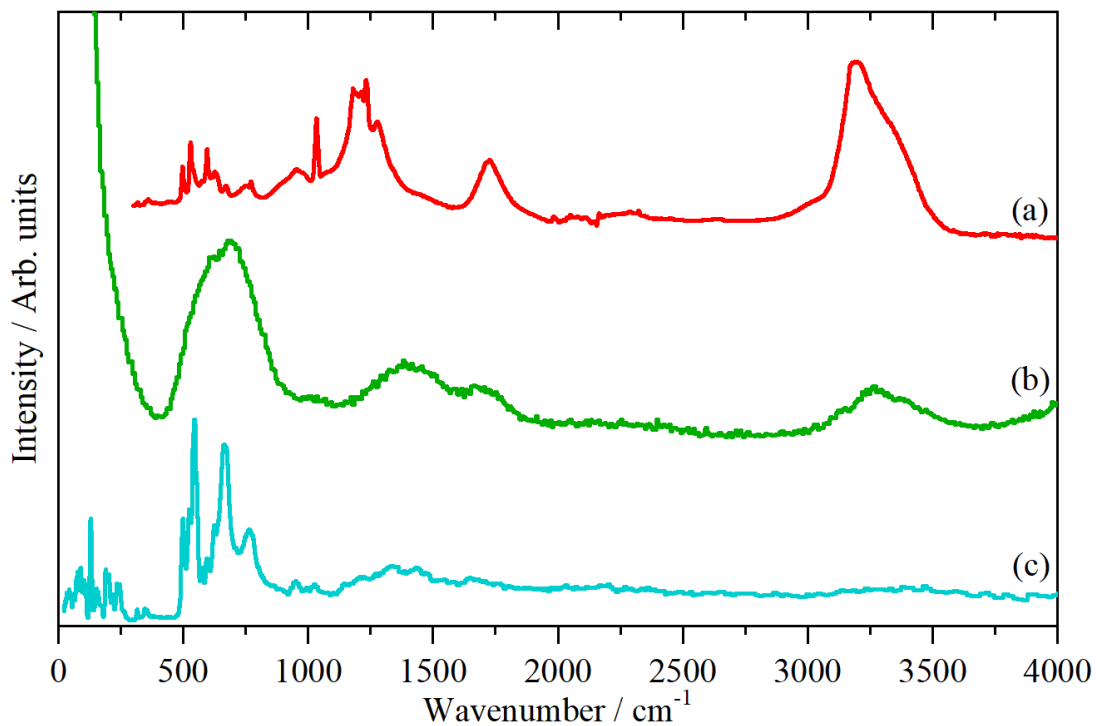


**Fig. S12** Solid state infrared (a), (b) FT-Raman and INS ((c) MAPS and (d) TOSCA) spectra of TFSA.H<sub>2</sub>O.

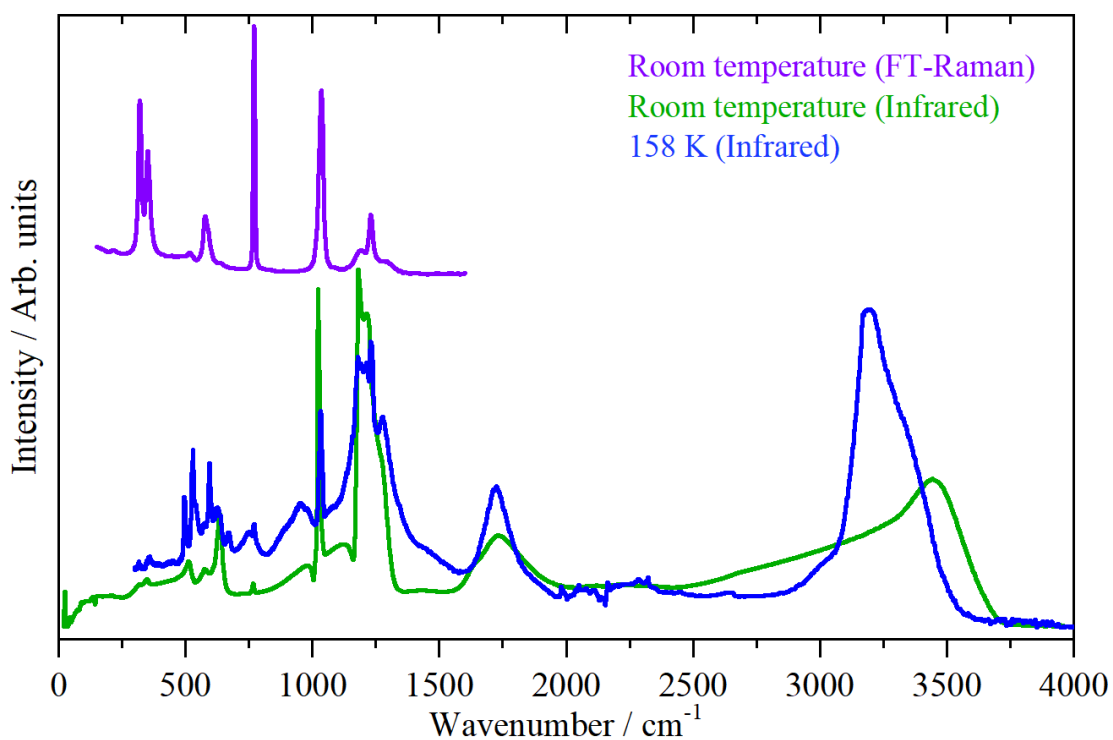


**Fig. S13** Infrared spectra of liquid (323 K, orange) and solid (room temperature, green and 165 K, blue) TFSA.H<sub>2</sub>O.

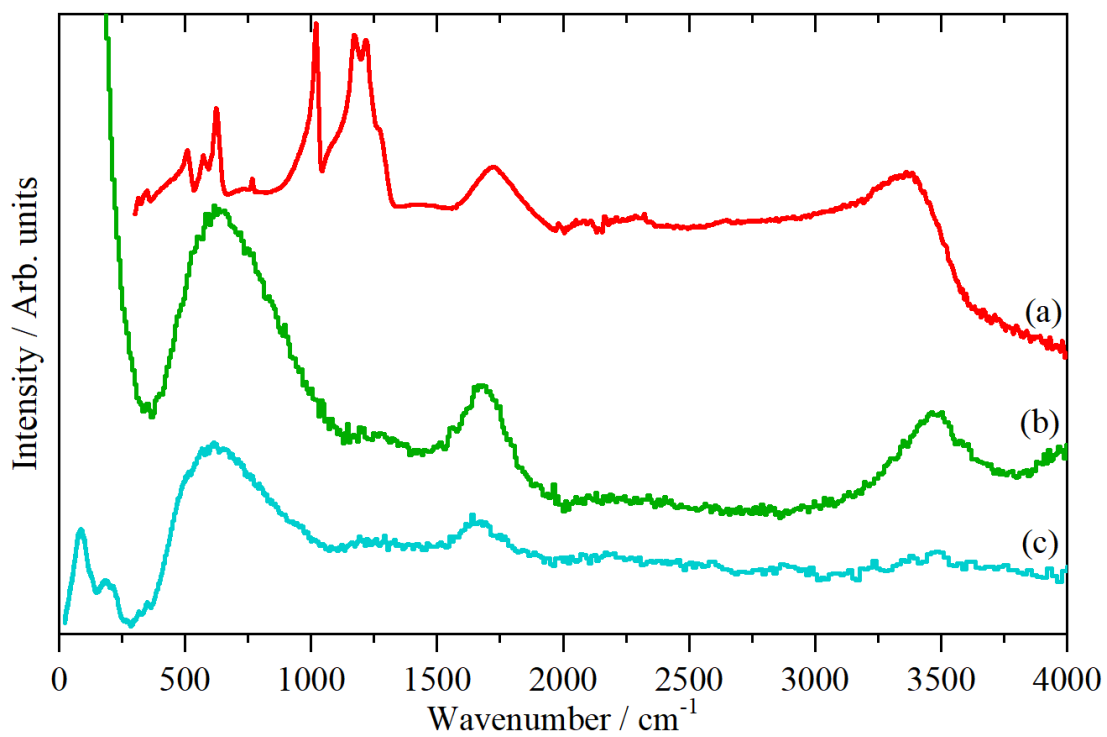




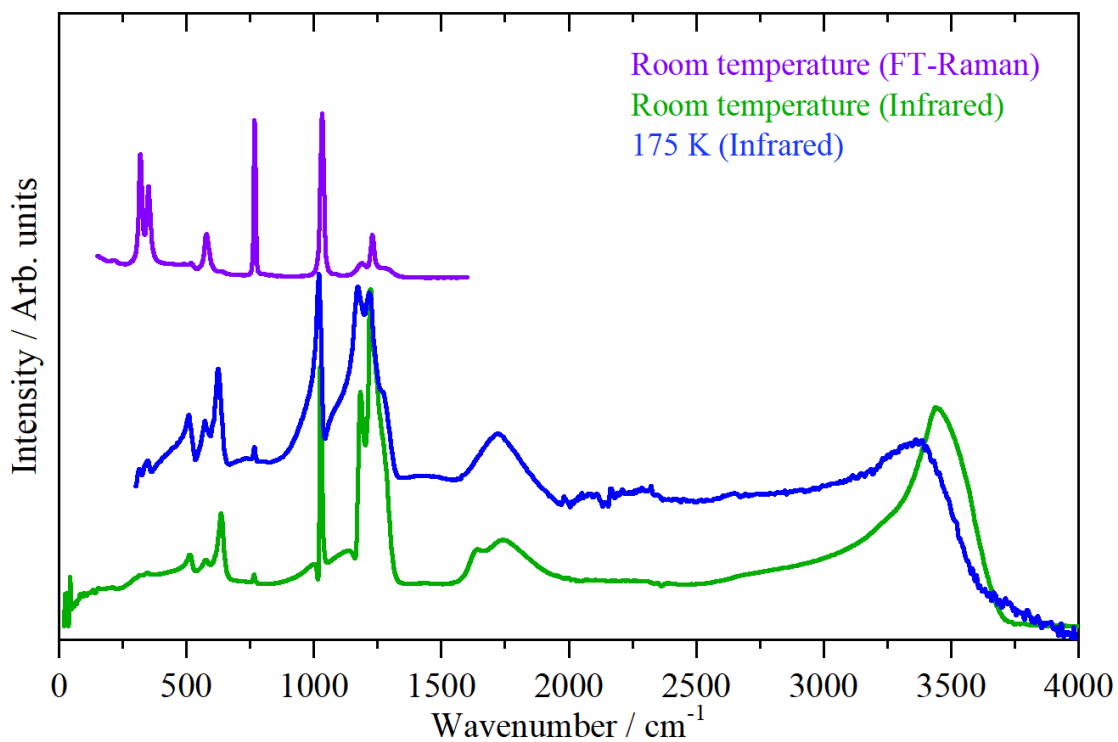
**Fig. S14** Solid state infrared (a) and INS ((b) MAPS and (c) TOSCA) spectra of TFSA.2H<sub>2</sub>O.



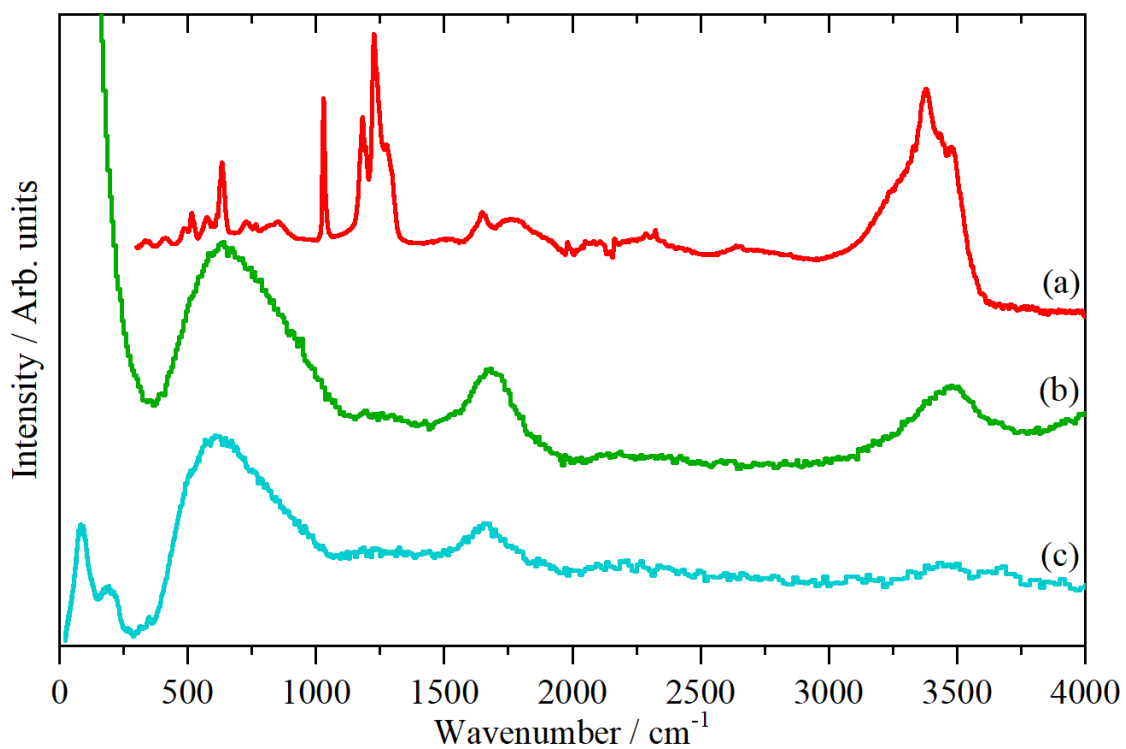
**Fig. S15** Spectra of liquid (room temperature, FT-Raman violet, infrared green) and solid (158 K, infrared blue) TFSA.2H<sub>2</sub>O.



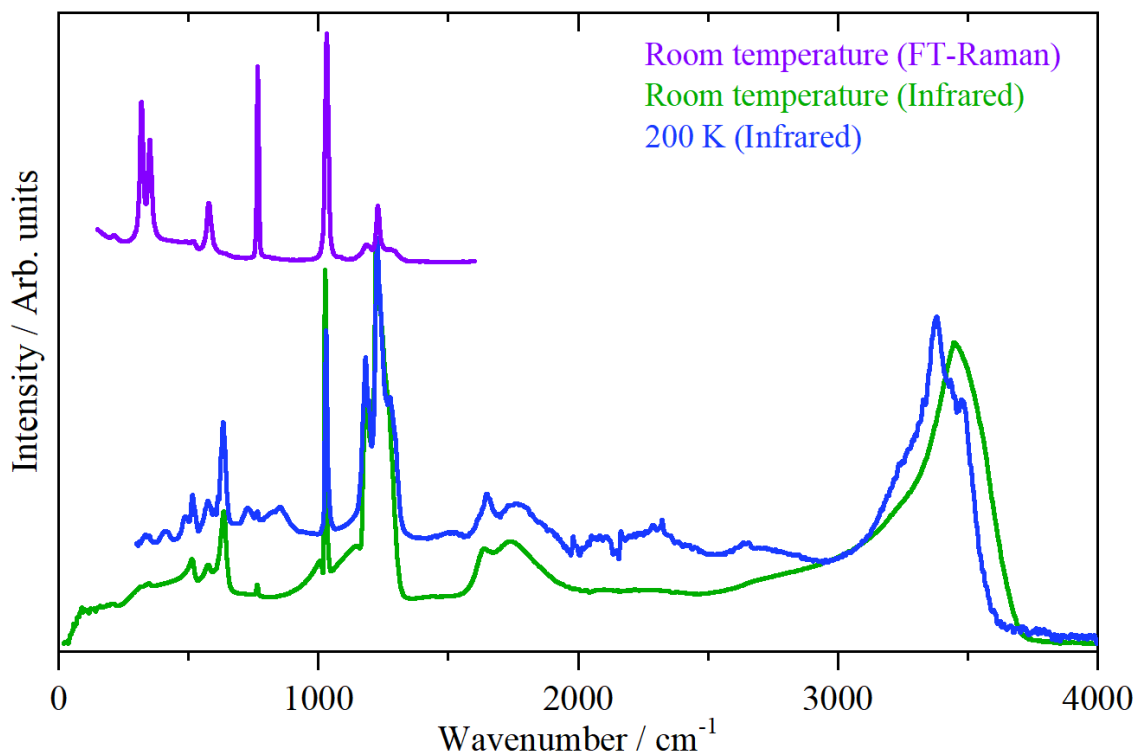
**Fig. S16** Solid state infrared (a) and INS ((b) MAPS and (c) TOSCA) spectra of TFSA.4H<sub>2</sub>O.



**Fig. S17** Spectra of liquid (room temperature, FT-Raman violet, infrared green) and solid (158 K, infrared blue) TFSA.4H<sub>2</sub>O.



**Fig. S18** Solid state infrared (a) and INS ((b) MAPS and (c) TOSCA) spectra of TFSA.5H<sub>2</sub>O.



**Fig. S19** Spectra of liquid (room temperature, FT-Raman violet, infrared green) and solid (200 K, infrared blue) TFSA.5H<sub>2</sub>O.