

Free ion diffusivity and charge concentration on cross-linked Polymeric Ionic Liquid films doped with sulfonated zwitterion salts and Lithium ions

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1. General Information

All reagents were purchased from Sigma-Aldrich and used without further purification. ¹H and ¹³C NMR experiments were carried out using a Varian INOVA 500 (¹H, 500 MHz and ¹³C, 125 MHz) spectrometer. The chemical shifts are given in delta (δ) values and the coupling constants (J) in Hertz (Hz).

Impedance measurements

Impedance measurements were carried out on samples at several temperatures lying in the range 393 K (20°C) to 453 K (180°C) and frequency window $10^{-1} < f < 10^7$ Hz. **The temperature was firstly and gradually raised and lowered from 20°C to 180°C in steps of 20°C. To ensure the measurements reproducibility the values considered in this work were obtained from the third cycle of temperature scan.** The experiments were performed with 100 mV amplitude, using a Novocontrol broadband dielectric spectrometer (Hundsangen, Germany) integrated by a SR 830 lock-in amplifier with an Alpha dielectric interface. The amplitude of 100 mV was chosen in order to get a linear regime. The membranes were placed between two gold electrodes of 20 mm of diameter coupled to the impedance spectrometer acting as blocking electrodes in a liquid parallel plate cell coupled to the spectrometer and deionized water was incorporated to ensure a fully hydrated state of the samples below 100 °C and in equilibrium with its vapor above 100 °C. The membranes thickness was measured afterwards using a digital micrometer, taking the average of ten measurements at different parts of the surface. During the conductivity measurements, the temperature was kept constant or changed stepwise in all the range of temperatures controlled by a nitrogen jet (QUATRO from Novocontrol) with a temperature error of 0.1 °C, during every single sweep in frequency.

Differential scanning calorimetry: Glass-transition temperatures and melting points were measured by using a Mettler-Toledo differential scanning calorimeter (DSC), model DSC822e. The instrument was calibrated for temperature and heat flow with zinc and indium reference samples provided by Mettler-Toledo. The samples were placed in a 40-μL hermetically sealed aluminum pan with a pinhole in the top. An empty aluminum

pan was used as the reference. Samples were exposed to a flowing N₂ atmosphere. Before the DSC test, each sample was dried at 90–100 °C and 10⁻²-10⁻³ mbar for 4 h, and further *in situ* dried in the differential scanning calorimeter by holding the sample at 130 °C for 120 min as the presence of volatiles, especially water, can affect the glass transition and melting temperatures. Melting transition temperatures were determined by multiple cycles (typically three) involving heating the sample from -50 to 250 °C, followed by cooling from 250 to -50 °C, both at a rate of 5 °C min⁻¹. The melting temperatures were determined at the onset of the transition.

Spectroscopic studies: FTIR spectra were acquired with a MIRacle single-reflection ATR diamond/ZnSe accessory in a JASCO FT/IR-6200 instrument. Raman spectra were obtained in a NRS-3100 equipment (Jasco) with optic microscope and a CCD detector. Samples were exposed to a flowing N₂ atmosphere. Before the spectra were recorded, each sample was dried at 90–100 °C and 10⁻²-10⁻³ mbar for 4 h to remove traces of residual solvent and water.

Thermogravimetric analysis (TGA): the data were recorder in a TG-STDA Mettler Toledo model TGA/SDTA851e/LF/1600 using the following heating program: 1. Heating from 25 °C to a 120 °C at 10 °C/min under N₂ and holding the sample at this temperature for 25 min. 2. Cooling from 120°C to 25°, at 10 °C/min. 3. Measuring the weight loss from 25°C a 700°C at 10 °C/min under N₂.

Viscosity: It was determined with a rotating viscometer (Brookfield R/S-CPS+ Rheometer, USA). Before data were recorded, each sample was dried at 90–100 °C and 10⁻²-10⁻³ mbar for 4 h to remove traces of residual solvent and water.

Preparation of ZIs:LiNTF₂ mixtures (melting protocol): Mixtures of ZIs and LiNTF₂ were prepared the ratios indicated in Table 1. For this purpose, LiNTF₂ and ZIs-1 were mixed together in a mortar till forming a homogeneous solid paste. The resulting mixture was introduced into a glass vial and heated-up to 150 - 160 °C to obtain a melted mixture. Nitrogen was bubbled for 10 min to eliminate dissolved oxygen. The samples were then heated in vacuum at 130-140 °C under high vacuum to eliminate any residual water present.

General procedure for film fabrication: The cross-linked films used in this study were prepared by thermal copolymerisation of the monomeric mixture containing the **ZIs-1-LiNTf₂** mixtures following the composition indicated in Table 2. A typical procedure for the preparation of the samples is described as follows: AIBN was added to a solution formed by the monomeric mixture and the **ZIs-1-LiNTf₂** mixture. Nitrogen was bubbled

for 10 min to eliminate dissolved oxygen. A small part of this solution was pipetted into the narrow space formed between two glass microscopy plates separated by means of two thin lamellas at the ends. The system was introduced into an oven at 65 °C for 24 hours. After polymerization, the two glasses were separated and the film removed and stored in a desiccator. The measured film thickness was very homogeneous even in different points of large samples and from sample to sample.

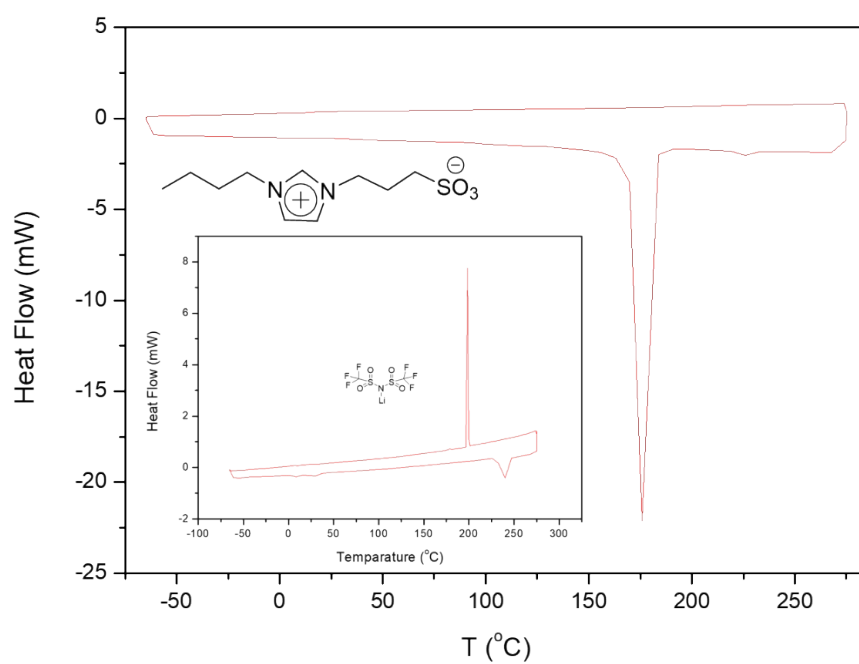


Figure S1. DSC of the zwitterionic salt (3-(1-butyl-1H-imidazol-3-ium-3-yl)propane-1-sulfonate **ZIs-1**. Insert: DSC of LiNTf₂. Conditions: 10 K/min under a nitrogen atmosphere.

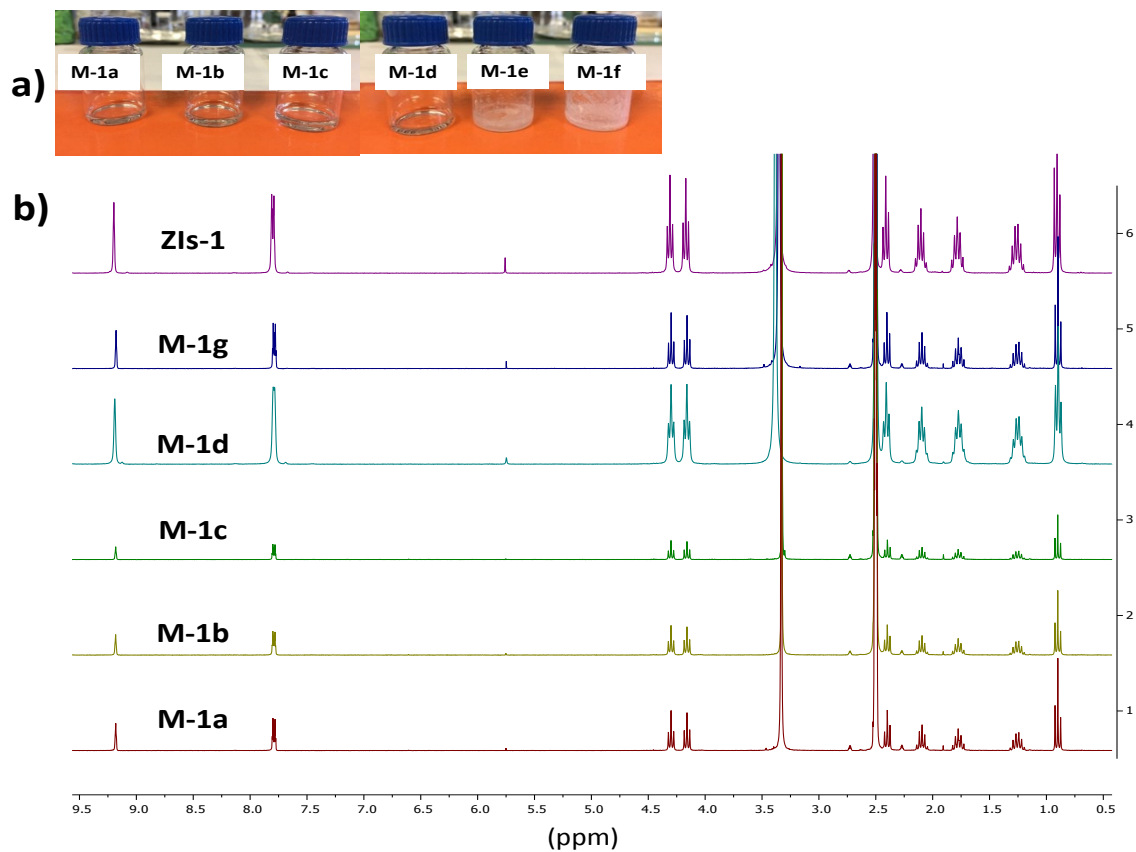


Figure S2. a) Pictures for the different mixtures obtained by mixing **ZIs-1** and LiNTf_2 at different molar ratios (see Table 1 in the main text for composition). b) $^1\text{H-NMR}$ (CD_3SOCD_3) of the some of these mixtures in comparison with pure **ZIs-1**.

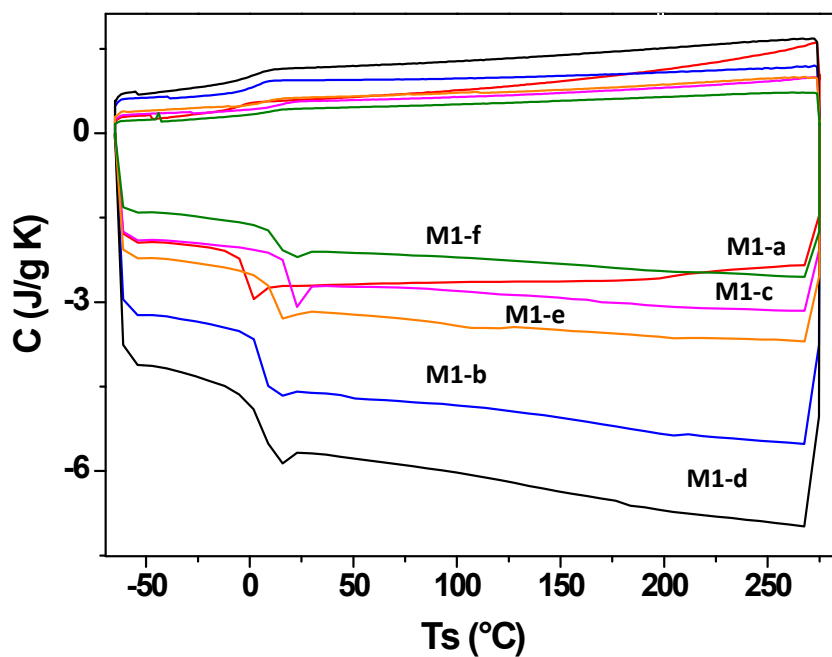
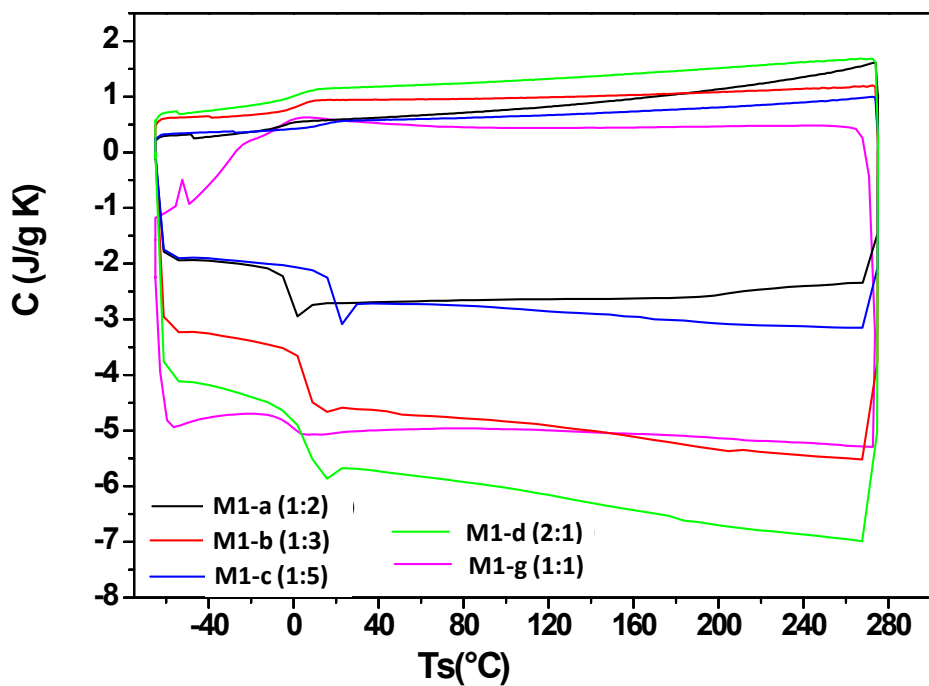


Figure S3. Top: DSC of the different *r.t. liquid mixtures* obtained by mixing **ZIs-1** and **LiNTf₂** at different molar ratios (see Table 1 in the main text for composition). Bottom: DSC of all the mixtures obtained by mixing **ZIs-1** and **LiNTf₂** at different molar ratios (see Table 1 in the main text for composition) after being heated to >200 °C. Curves correspond to the second cycle. Obtained at 10 K/min under a nitrogen atmosphere.

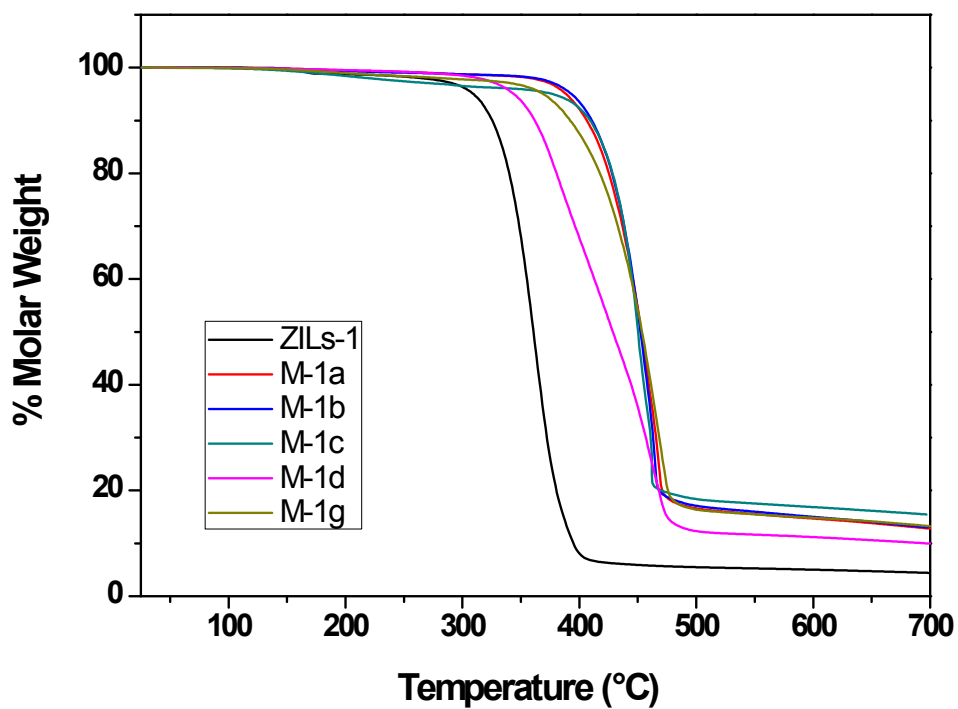
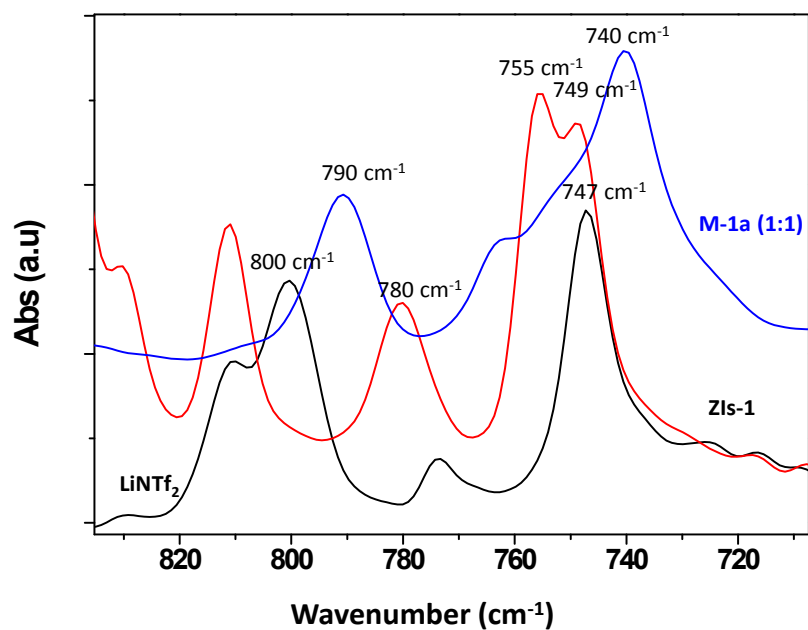


Figure S4. TGA of the mixtures obtained by mixing **ZILs-1** and LiNTf_2 at different molar ratios (see Table 1 in the main text for composition).

a)



b)

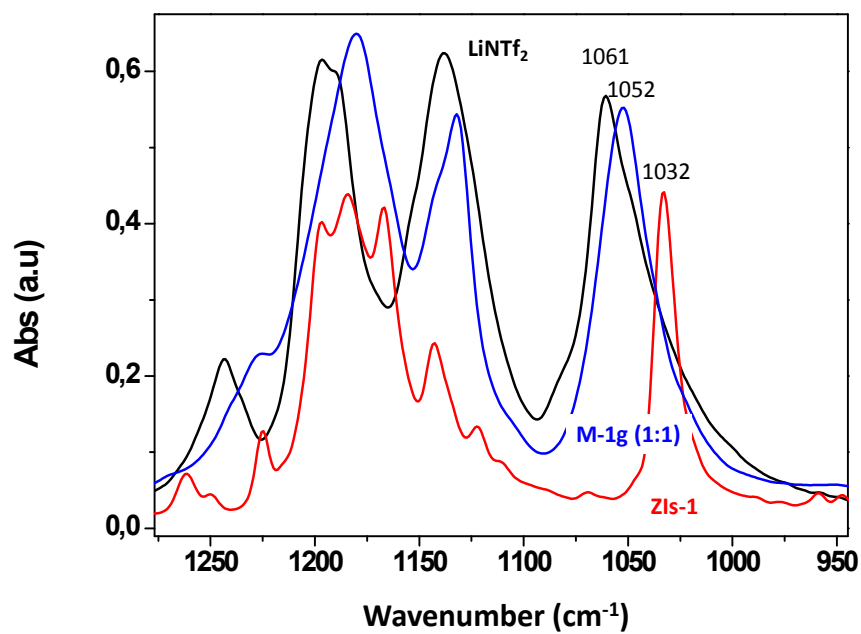
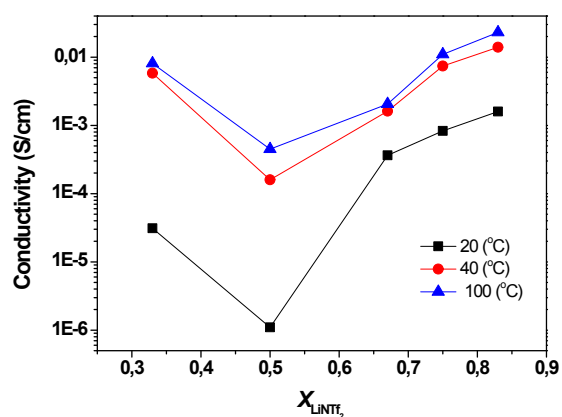
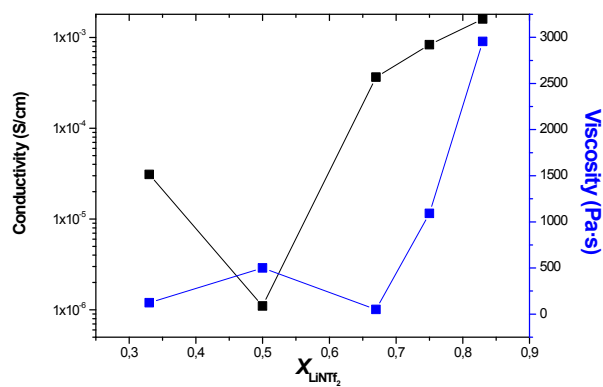


Figure S5. Selected region of the ATR-FT-IR of LiINTf₂, ZIs-1 and M-1g (equimolecular mixture of LiINTf₂ and ZIs-1).

a)



b) T=25



T= 100

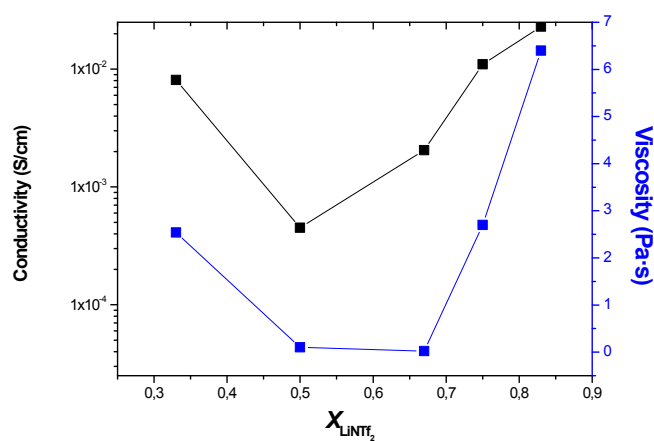


Figure S6. a) Effect of the mole fraction of $LiNTf_2$ on the ionic conductivity at 20, 40 and 100 °C for the different molar mixtures **ZIs-1**: $LiNTf_2$. b) Comparison of conductivity and viscosity at 25 and 100 °C for the different molar mixtures **ZIs-1**: $LiNTf_2$.

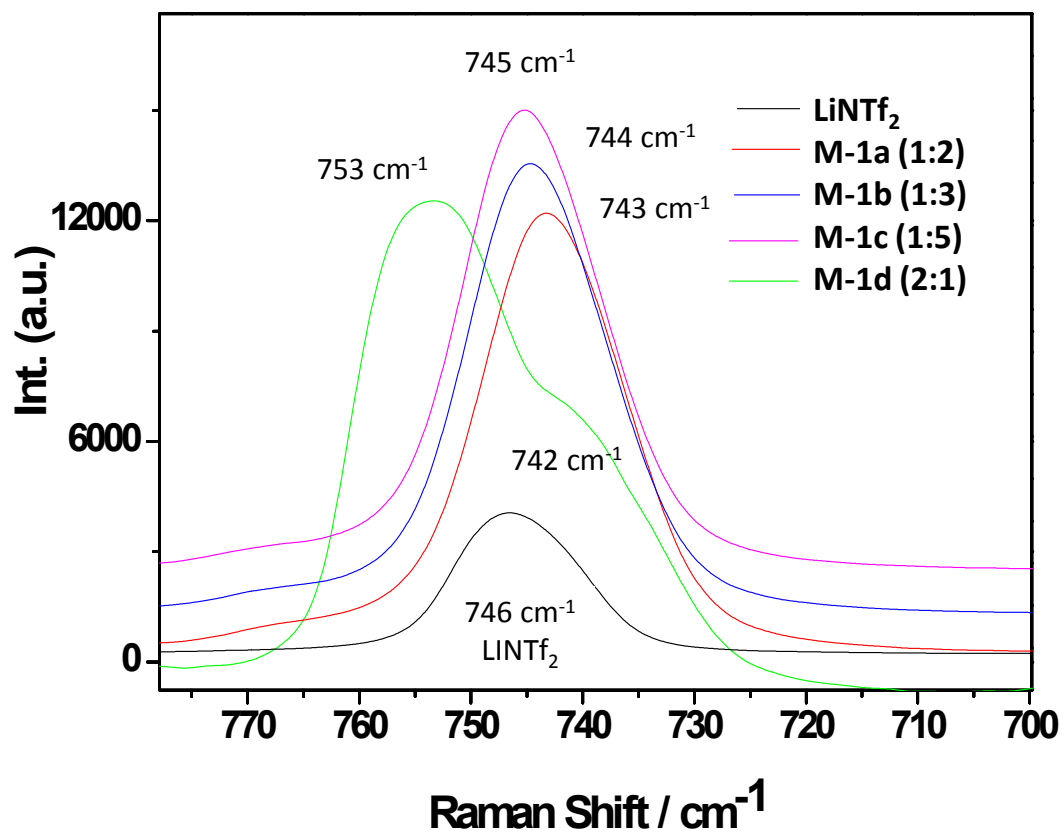


Figure S7. Selected region of the Raman spectra of the different **ZIs-1:LiNTf₂** molar mixtures in comparison with LiNTf₂.

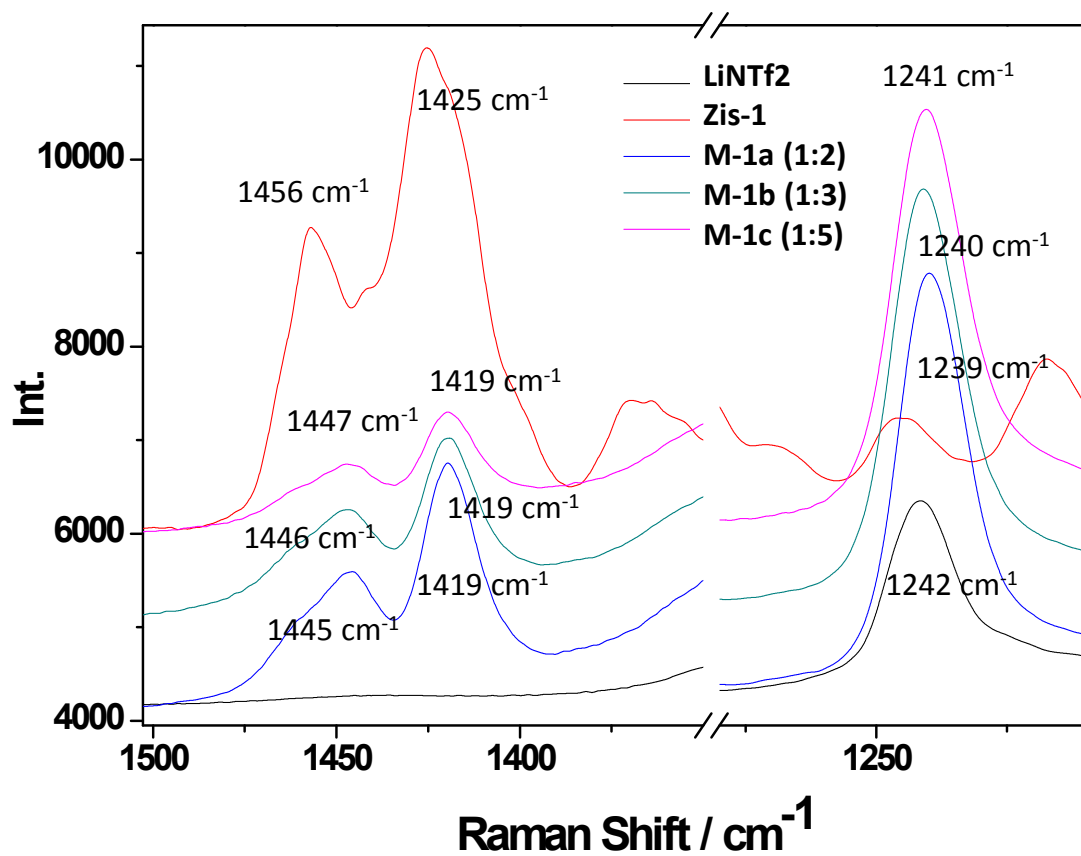


Figure S8. Selected region of the Raman spectra of the different **ZIs-1:LiNTf₂** molar mixtures in comparison with **LiNTf₂** and **ZIs-1**.

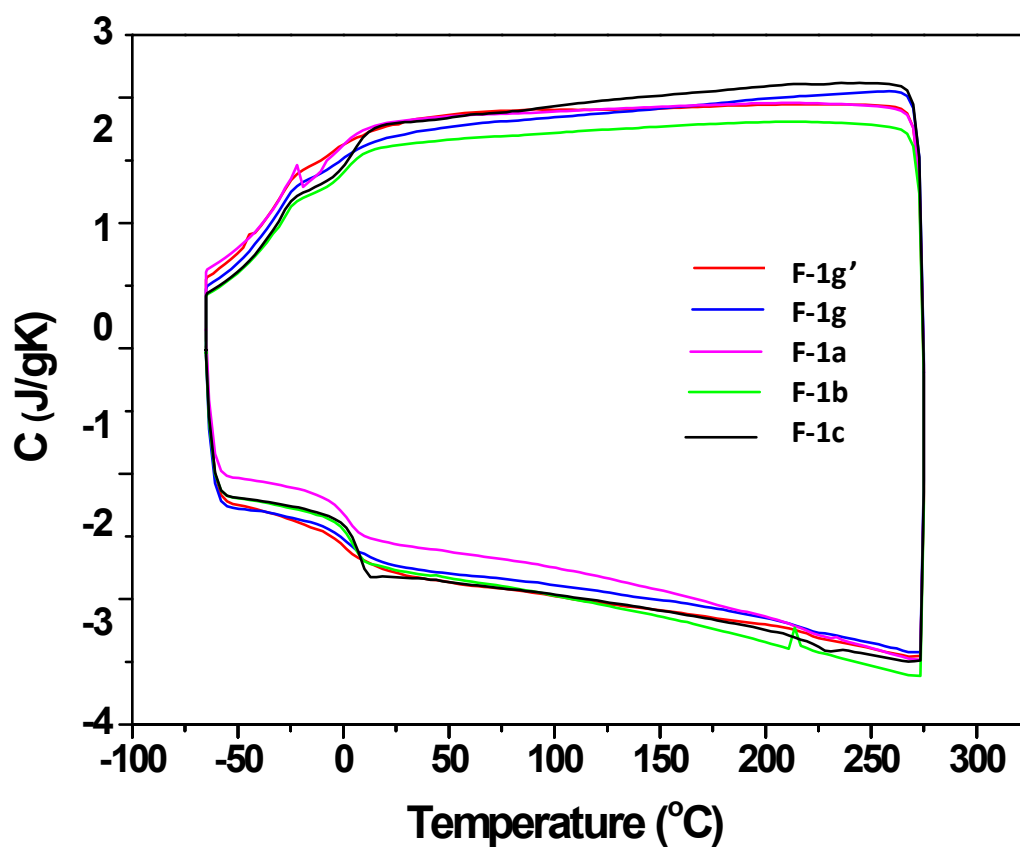


Figure S9. DSC for the films prepared (see Table 2 in the main text for composition). Cycle 2. Obtained at 10 K/min under a nitrogen atmosphere.

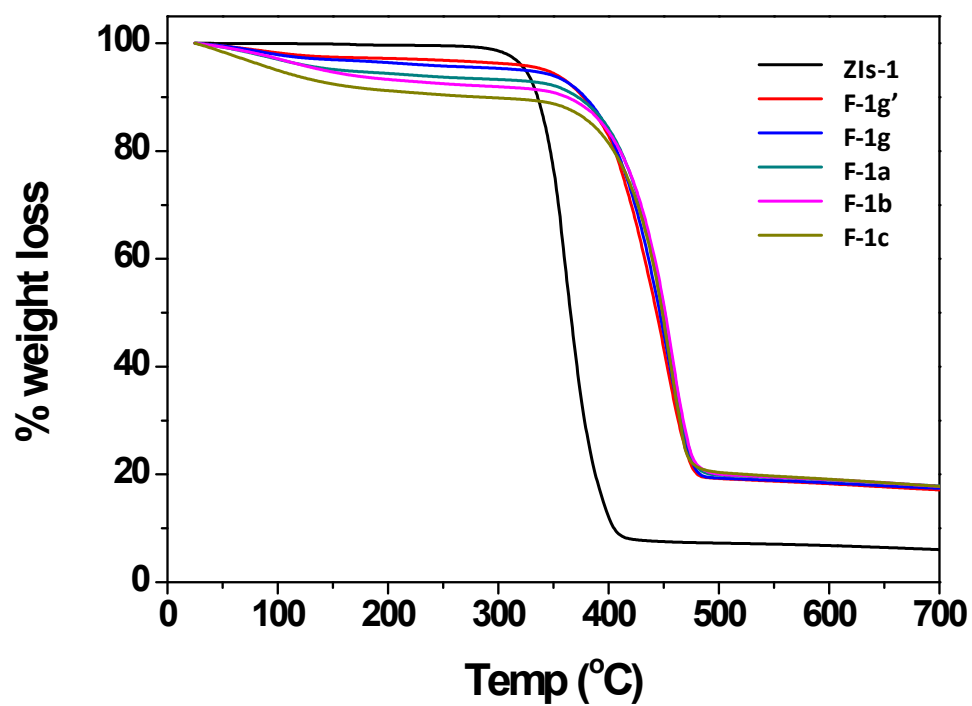


Figure S10. TGA of all films prepared in comparison with **ZIs-1** (see Table 2 in the main text for composition).

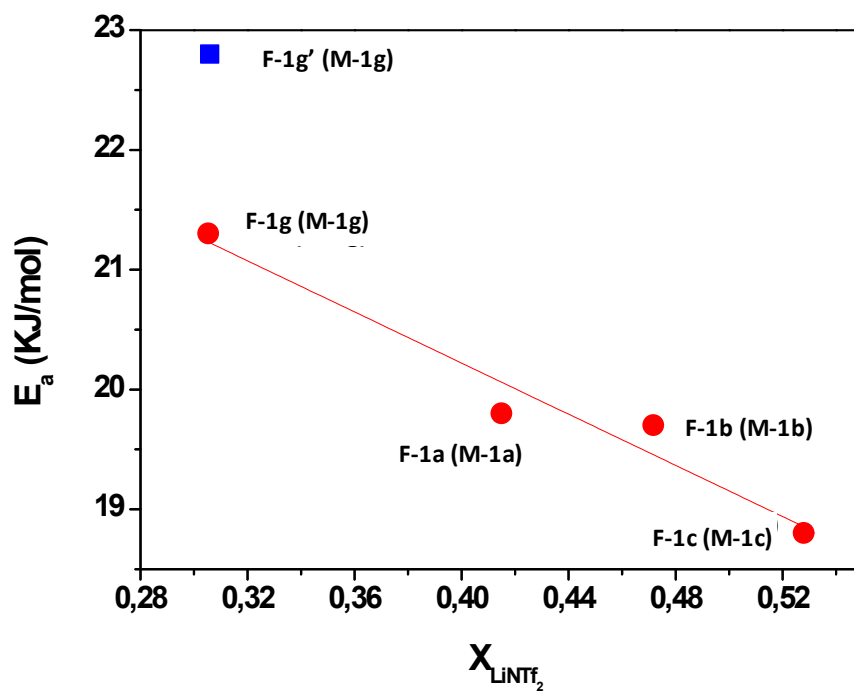


Figure S11. Activation Energy vs composition of the mixture used (see Table 2 in the main text for composition).

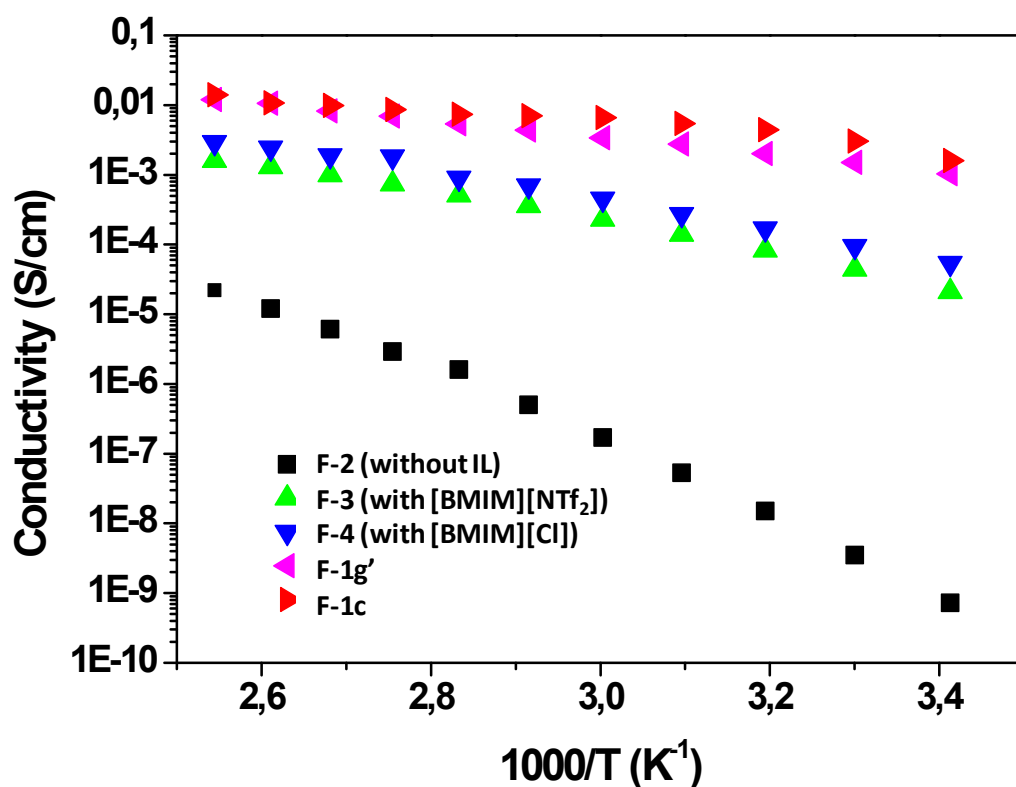


Figure S12. A comparative study of conductivity versus temperature for different PILs with similar crosslinking and doped with either [BMIM][Cl] or [BMIM][NTf₂] (B. Altava, V. Compañ, A. Andrio, L. F. del Castillo, S. Mollá, M. I. Burguete, E. García-Verdugo and S. V. Luis, *Polymer*, 2015, **72**, 69 and A. Garcia-Bernabé, A. Rivera, A. Granados, S. V. Luis and V. Compañ, *Electrochim. Acta*, 2016, **213**, 887) and “ion gels” **F-1g'** and **F-1c** from this work. **F-2:** ca. 90 % wt of **IL-1** and 10 % wt TMPTMA in the monomeric mixture (without IL). **F-3:** ca. 90 % wt of **IL-1**, 10 % wt TMPTMA in the monomeric mixture, ca. 50 % [BMIM][NTf₂] in the film; **F-4:** ca. 90 % wt of **IL-1** and 10 wt % TMPTMA in the monomeric mixture, ca. 50 % [BMIM][NTf₂] in the film.

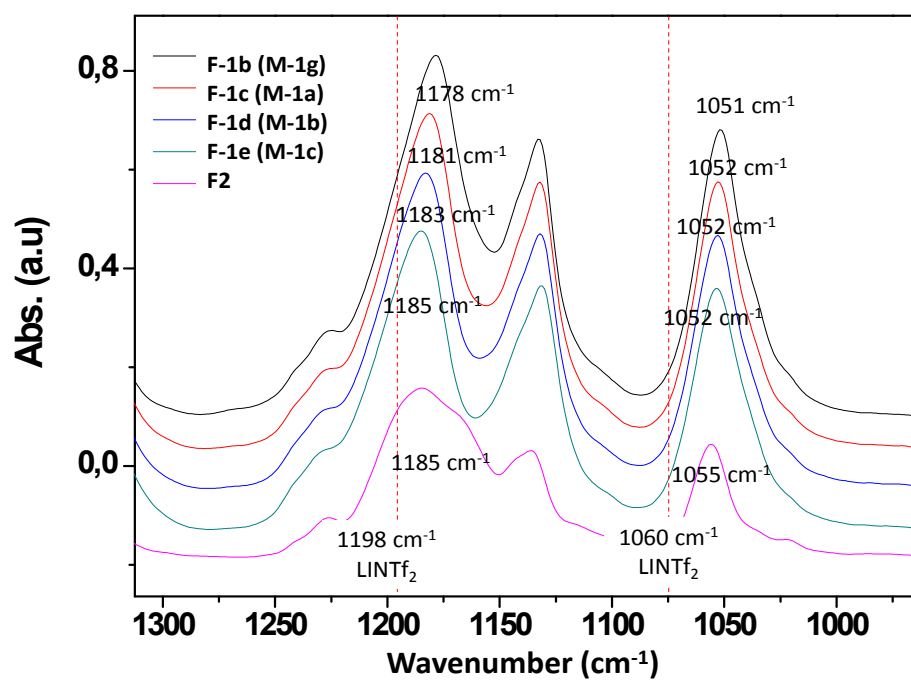


Figure S13. Selected region of the ATR-FT-IR of the some of the films doped with different **ZIs-1**:LiNTf₂ mixtures (see Table 2 in the main text for composition) in comparison with **F-2** (film without doping).

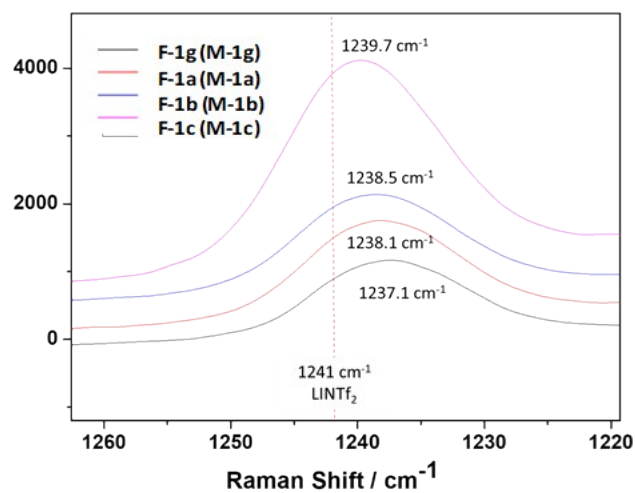
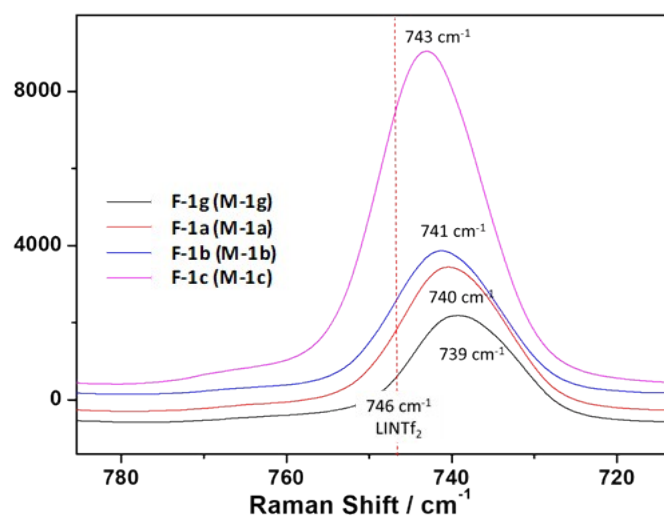


Figure S14. Selected region of the Raman spectra of the some of the films doped with different **ZIs-1:LiNTf₂** mixtures (see Table 2 in the main text for composition).

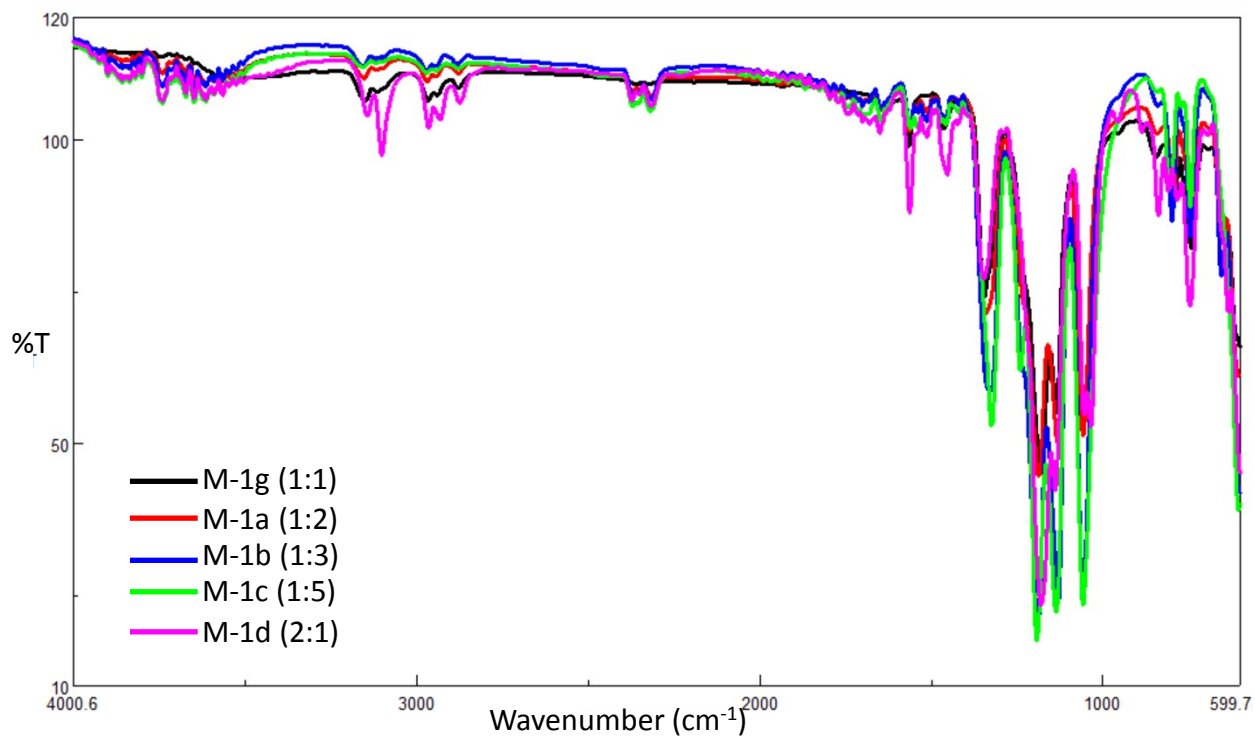


Figure S15. Comparison of ATR-FT-IR spectra of the different ZIs-1:LiNTf₂ molar mixtures as prepared using the melting protocol.

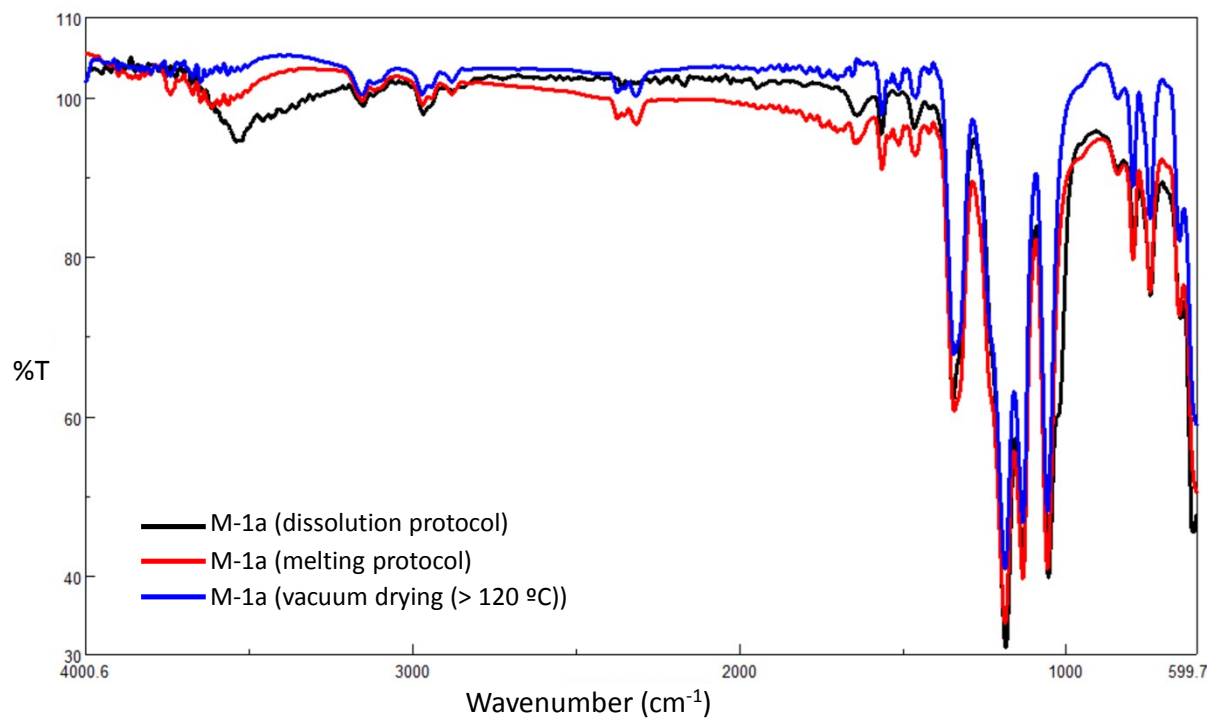


Figure S16. Comparison of ATR-FT-IR spectra of **ZIs-1:LiNTf₂ 1:2** molar mixtures as prepared using the dissolution protocol (black line) and the melting protocol (red line) as well as a sample after thorough vacuum drying (> 120 °C) (blue line).