# **Supporting Information**

# Controlling Surface Chemistry and Mechanical Properties of Metal Ionogels Through Lewis Acidity and Basicity

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## 1. Experimenal

### **Materials and Methods**

1-Methyl-3-octylimidazolium chloride ([omim]Cl), poly(ethylene glycol) diacrylate (average  $M_n = 575$ ), 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone, anhydrous ethyl acetate, anhydrous acetonitrile, and methylimidazole were all purchased from Sigma-Aldrich. Methylimidazole and chlorobutane were distilled under reduced pressure from CaH<sub>2</sub> and stored over activated 4 Å molecular sieves before use. Zinc bis(trifluoromethanesulfonyl)imide and zinc chloride were purchased from Tokyo Chemical Industry UK Ltd.

### Synthesis and Fabrication

1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([bmim][NTf<sub>2</sub>]) was prepared according to an existing literature procedure<sup>1</sup> and characterised by <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR and ion chromatography (IC). 1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([omim][NTf<sub>2</sub>]) was prepared by ion metathesis from commericial [omim]Cl according to the same procedure and purity was as confirmed by <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR and IC.<sup>2</sup> All ionic liquids were dried on a Schlenk line at < 2 x 10<sup>-2</sup> mbar and 70 °C for 24-48 hr before being transferred to an MBraun Glovebox with <0.5 ppm O<sub>2</sub> and <0.5 ppm H<sub>2</sub>O. Metal containing ionic liquids were prepared in the Glovebox by mixing the desired amount of ZnCl<sub>2</sub> or Zn[NTf<sub>2</sub>]<sub>2</sub> with [omim]Cl or [omim][NTf<sub>2</sub>] according to a published procedure.<sup>3</sup> Samples were analysed by XPS to assess purity and speciation. Mixtures of ionic liquid, PEGDA, and photoinitiator were prepared in the same glovebox and removed to ambient air where ionogels were fabricated according to a previously published procedure.<sup>4</sup>

#### Instrumentation

XPS was acquired on a Thermo Scientific K-Alpha monochromated aluminium source (hv = 1486.6 eV) spectrometer. Samples were mounted on a welled copper plate and degassed to  $< 3 \times 10^{-7}$  mbar before being transferred to the analysis chamber, which had a base pressure of  $< 2 \times 10^{-9}$  mbar. A spot size of 400 µm was used for both survey (pass energy = 200 eV, step = 0.5 eV, windown = -10 eV to 1350 eV, scans = 3-5) and high resolution (pass energy = 20 eV, step = 0.1 eV step, scans = 40-70) spectra. A dual-beam flood source was used to charge neutralise samples. Survey spectra were quantified with Avantage 5.951 software, using smart backgrounds and the ALTHERMO1 relative sensitivity factors. High resolution scans were analysed in CasaXPS. For N/O ratios, the average and standard deviation of 5 survey scans from different spots on the ionogel sample surface was measured so that errors reflected surface inhomogeneity, preparation error and measurement error.

Differential surface charging can cause all photoemission peaks to shift to higher binding energies during XPS analysis (photoelectrons are emitted from the sample surface, leaving positive holes). This shifting would complicate chemical state analysis and for this reason we chose to prepare ionogels from [omim]<sup>+</sup> containing ionic liquids because the long-aliphatic chains give an easily identifiable C 1s photoemission with a known binding energy that can be used to adjust the shifting signals to their original positions. Therefore, all [omim]<sup>+</sup> containing ionic liquids and ionogel XP spectra are charge corrected by referencing the aliphatic carbon signal to 285.0 eV.<sup>5</sup> [bmim][NTf<sub>2</sub>] ionic liquids and ionogels are charge corrected by referencing the F 1s signal to that obtained for [omim][NTf<sub>2</sub>], which was 688.8 eV.

Parallel angle resolved XPS (PARXPS) was recorded on a Thermo Scientific Theta Probe monochromated aluminium source (hv = 1486.6 eV) spectrometer. Acquisition parameters were matched to those of the K-Alpha where possible (i.e. 400  $\mu$ m<sup>2</sup> spot size, pass energies, steps) except

survey spectra windows were recorded from -10 eV to 1100 eV to reduce beam exposure time. Samples were mounted on a stainless steel sample plate and data was collected over a 60° angular range in parallel (20-80°), split into 6 channels centred around 25, 35, 45, 55, 65, and 75°. These correlated to 8.2, 7.4, 6.4, 5.2, 3.9, and 2.4 nm information depths (IDs) respectively for organic molecules with inelastic mean free paths (IMFPs) of 3 nm, which were typical of both ionic liquids<sup>6</sup> and PEG with AI K $\alpha$  X-rays.<sup>7</sup> Survey and high resolution spectra were therefore recorded with a large number of scans (45 scans and 120 respectively) to improve data quality. Data was analysed in a similar way to that reported for the K-Alpha. Conventional angle resolved XPS (ARXPS) utilises a sample mounting system that rotates to the desired angle for analysis.<sup>8</sup> Unfortunately, unlike pure ionic liquids and powders, ionogels do not adhere to sample bars or stick to double sided tape. The Theta Probe enables angle-resolved data to be collected without tilting the sample, whish is particularly important when studying the surfaces of soft materials such as ionogels. To examine any instrument effects, [emim]<sup>+</sup> ionogels with 30 wt% PEGDA were prepared, analysed and their N/O ratios were calculated (SI, **Table S2**). The values closely matched the data acquired from the K-alpha instrument, which confirmed that instrument effects (i.e. charge compensation) were negligible.

Secondary ion mass spectrometry (SIMS) was acquired on an IONTOF ToF-SIMS V equipped with a 25 keV Bi analytical beam.<sup>9</sup> A primary ion beam of  $Bi_{3}^{+}$  was used for a 100  $\mu$ m<sup>2</sup> analysis area and samples were charge neutralised by flooding the surface with low energy electrons (20 eV) during sputtering. An argon cluster  $(Ar_{1000}^+)$  beam operating at 5 keV and 5 nA was used for depth profiling over a 500  $\mu$ m<sup>2</sup> area, and the anlaysis beam was focused in the centre to avoid crater edge effects. For sputtering, an E/n value (i.e. kinetic energy per atom) of 5 eV was chosen for organic ionogels because it is an optimum value that produces normal depth profiles with high sputter yields, without causing significant ion-bombardment damage to organic materials.<sup>10</sup> The sputter beam and primary ion beams were both 45° to the sample surface and the beams were altered during depth profiling. Post data-acquisition crater analysis was attempted for ionogels but changes in temperature and pressure affected surface topology which was too rough for accurate interferometry measurements. The same problem has been encountered for frozen hydrogels.<sup>11</sup> Hence, plots are presented with sputter time, rather than depth (SI, Section 2b). SIMS data was calibrated with 9 masses (H<sup>+</sup>, C<sup>+</sup>, CH<sup>+</sup>, CH<sub>3</sub><sup>+</sup>, C<sub>2</sub>H<sub>3</sub><sup>+</sup>,  $C_3H_5^+$ ,  $C_4H_7^+$ ,  $C_5H_9^+$ ) and the following ions were used to create positive mode depth profiles: 1) metal ions: Zn<sup>+</sup> (*m*/*z* 63.9286) and Co<sup>+</sup> (*m*/*z* 58.9327), 2) ionic liquid: C<sub>12</sub>H<sub>23</sub>N<sub>2</sub><sup>+</sup> (*m*/*z* 195.1856), confirmed by additional fragments C<sub>4</sub>H<sub>7</sub>N<sub>2</sub><sup>+</sup> (*m*/*z* 83.0617), C<sub>5</sub>H<sub>8</sub>N<sub>2</sub><sup>+</sup> (*m*/*z* 96.0675), C<sub>8</sub>H<sub>15</sub>N<sub>2</sub><sup>+</sup> (*m*/*z* 139.1221),  $C_{10}H_{17}N_2^+$  (*m/z* 165.1353),<sup>12,13</sup> 3) PEG:  $C_2H_5O^+$  (*m/z* 45.0340),<sup>14</sup> for which <100 ppm error was used used as an acceptible limit and all signals were normalised to the total counts.

Compressive stress-strain measurements were performed on an Instron 5543 at room temperature with a compression rate of 0.5 mm min<sup>-1</sup> on disc shaped samples (15.5 x 6 mm). Values are reported as the average of three measurements with standard deviation as the error. Ionic liquids [bmim][NTf<sub>2</sub>], [omim][NTf<sub>2</sub>], and [omim]Cl had high viscosities and surface tensions,<sup>15</sup> so ionogel discs were slightly concave on one surface because of the meniscuses present during fabrication. These were left intact to avoid compromising mechanical testing. For this reason, we chose to report high strain data calculated from the region preceding failure, along with low strain data (< 10%). High strain mechanical testing has been shown to correlate to polymer uniformity in PEGDA ionogels.<sup>4</sup> Furthermore, we chose the linear region at high strain, as it was easier to determine (with greater consistency and lower procedural error) for all of our samples. The modulus at high strain was chosen as the most reliable measurement for the maximum mechanical strength that the materials could withstand.

MD simulations were carried out using Amber (2016).<sup>16</sup> [omim]Cl and [omim][NTf<sub>2</sub>], were modelled using the CL&P (Canongia Lopes and Padua) ionic liquid force field,<sup>17,18</sup> and Zn ions were modelled

using parameters developed by Merz.<sup>19</sup> PEGDA with 10 repeating ethylene oxide units was chosen for simplicity as it had the closest MW to PEGDA 575 used in this work. The generalised amber force field (GAFF2)<sup>20</sup> was used to model PEGDA monomers and partial charges were derived from *ab initio* calculations at the HF/6-31G(d) level of theory, followed by a restrained electrostatic potential (RESP) charge fitting procedure.<sup>21</sup> The partial atomic charges of all ionic components were scaled by a factor of 0.8. This was to model the dynamic properties more accurately, as viscosity or diffusivity of ionic liquids in simulations have been proven to be better reproduced if non-unity charges are applied.<sup>22</sup> The scaling of Zn was carried out for consistency, in line with previous studies of other Polymer-IL-metal ion systems.<sup>23</sup> Simulation protocols and analysis details are provided in the supporting information.

Differential scanning calorimetry (DSC) was recorded on a TA Instruments Q2000 DSC, which was linked to a liquid nitrogen cooling system (LCNS). The Q2000 DSC was calibrated by baseline conditioning, Tzero calibration, enthalpy calibration, and temperature calibration (cell constant) before use with sapphire standards, an indium standard, and a zinc standard. Samples of  $\approx$ 10 mg were prepared in Tzero hermetic pans with pinhole lids. The samples were dried at 100 °C before 4 thermal cycles were recorded. The calorimeter was operated under N<sub>2</sub> with a flow rate of 40 mL min<sup>-1</sup> and heating rates of 10 °C min<sup>-1</sup> were used.

Thermogravimetric analysis (TGA) data was measured using a TA Instruments Q500 TGA with Pt pans. Between experiments, the pans were heated to 50 °C in 37% HCl and left to stir for at least 72 hours to remove zinc metal. The pans were then washed in 18.2 M $\Omega$ ·cm Milli-Q ultrapure water, dried, exfoliated in a sand bath, and finally heated at 1000 °C in air to remove organic char. An inert nitrogen purge of 50 mL min<sup>-1</sup> was used with heating rates of 10 °C min<sup>-1</sup>.

#### Information Depths in PARXPS

Information Depths (IDs) were calculated for photoemission signals according to the following equation:

$$ID = \lambda_{in} \cos \alpha \ln \left[ \frac{1}{1 - \left( \frac{P}{100} \right)} \right]$$

Where  $\lambda_{in}$  is the inelastic mean free path (IMFP),  $\alpha$  is the angle of emission with respect to the surface normal, and *P* is the percentage of the photoemission signal, which is set to 95 % in this work. The equation ignores elastic-scattering effect, but values only deviate by 0.54 % from those calculated *via* the Transport Approximation (TA) and are therefore an accurate estimation of ID.<sup>24</sup> IMFP values were calculated for ionic liquids and ionogels using the NIST Electron Effective Attenuation Length Database and the semi-empirical TPP-2M method.<sup>25,26</sup> A band gap energy of 7.4 eV was used<sup>27</sup> for ionic liquids and ionogels and the number of valence electrons (N<sub>v</sub>) were calculated *via* the methods described by Powell and Jablonski in the Database. The photoionoisation asymmetry parameters ( $\beta$ ) selected from the database are shown alongside the calculated IDs and IMFPs (**Table S1**) for the Zn 2p<sub>3/2</sub> and S 2p<sub>3/2</sub> or Cl 2p<sub>3/2</sub> photoemissions, which were chosen because they have the highest and lowest binding energies of all elements in the samples, and therefore represent the extremes of IDs. The compositon of the samples was found to have minimal effects on the IMFP and ID values, but the kinetic energy of the ejected photoelectrons had a significantly larger effect. For this reason, the IDs used in **Figure S2** are those calculated for each angle (25, 35, 45, 55, 65, and 75°) for an IMFP value of 3 nm, which is

an average value for organic samples such as ionic liquids,<sup>28,29</sup> while the values calculated for Zn through the TPP-2M method are used in **Figure 1**.

**Table S1** The IMFP values (nm) calculated using the NIST Electron Effective Attenuation Length Database for ionic liquids and ionogels, with IDs (nm) calculated for the smallest and widest collection angles.

							Informatio / nn	n Depth n
Ionic Liquid	PEGDA / wt%	Photoemission	β	N <sub>v</sub>	IMFP / nm	3σ	25 °	75 °
[omim][NTf <sub>2</sub> ]- <sub>0.33</sub> Zn[NTf <sub>2</sub> ] <sub>2</sub>	0	Zn 2p <sub>3/2</sub>	1.41	538	1.8	5.4	4.9	1.4
		S 2p <sub>3/2</sub>	1.16	538	4.0	12. 0	10.8	3.1
				average:	2.9	8.7	7.9	2.2
[omim]Cl- <sub>0.33</sub> ZnCl <sub>2</sub>	0	Zn 2p <sub>3/2</sub>	1.41	202	1.8	5.4	4.9	1.4
		Cl 2p <sub>3/2</sub>	1.22	202	3.9	11. 8	10.7	3.0
				average:	2.9	8.6	7.8	2.2
[omim][NTf <sub>2</sub> ]- <sub>0.33</sub> Zn[NTf <sub>2</sub> ] <sub>2</sub>	30	Zn 2p <sub>3/2</sub>	1.41	600	1.8	5.4	4.9	1.4
		S 2p <sub>3/2</sub>	1.16	600	4.0	12. 1	10.9	3.1
				average:	2.9	8.7	7.8	2.3
[omim]Cl-0.33ZnCl2	30	Zn 2p <sub>3/2</sub>	1.41	264	1.9	5.6	5.1	1.5
		Cl 2p <sub>3/2</sub>	1.22	264	4.1	12. 2	11.1	3.2
				average:	3.0	8.9	8.1	2.3

## 2. Additional Discussion

#### (a) Metal Ionic Liquid Basicity and Lewis Acidity

Solvents are often compared by solvatochromic methods, such as Kamlet-Taft parameters,<sup>30</sup> or by scales of nucleophilicity/basicity, such as Gutmann acceptor numbers (AN) and donor numbers (DN).<sup>31</sup> Unfortunately, there are no reports of Kamlet-Taft or DN for Zn containing ionic liquids in the literature to the best of our knowledge,<sup>32–34</sup> only Gutman acceptor numbers (AN) which are used to measure the Lewis acidity of metals in ionic liquids.<sup>35</sup> Hence, to determine the relative basicity of ionic liquid with metal ions we have considered the imidazolium N 1s and C<sup>hetero</sup> C 1s B.E.s as measured by XPS. Previous work has shown that XPS B.E.s correlate with both Kamlet-Taft<sup>36</sup> and Gutman DN<sup>32</sup> and can therefore be a reliable indicator of anion basicity. The N 1s B.E. of [omim]Cl-<sub>0.33</sub>ZnCl<sub>2</sub> was 402.0 eV. Compared to that of [omim]Cl, which has an N 1s B.E. of 401.7 eV,<sup>36</sup> this indicated that the [ZnCl<sub>4</sub>]<sup>2</sup> anion had a lower basicity, similar to that of [BF<sub>4</sub>]<sup>-</sup> or [OTf]<sup>-</sup> anions. However, the [omim][NTf<sub>2</sub>]Cl-<sub>0.33</sub>Zn[NTf<sub>2</sub>]<sub>2</sub> cation had an N 1s B.E. of 402.1 eV, which was the same as [omim][NTf2]. Gutman ANs for [omim]Cl-<sub>0.33</sub>ZnCl<sub>2</sub> have been previously published<sup>31</sup> and the metal [ZnCl<sub>4</sub>]<sup>2-</sup> centre was found to be neutral. Although ANs do not exist for [NTf<sub>2</sub>]<sup>-</sup> ionic liquids, Zn 2p B.E.s have been shown to correlate to Gutman ANs,<sup>37</sup> meaning Lewis acidity/basicity can be estimated by XPS. In this work, the B.E. of [omim][NTf<sub>2</sub>]-<sub>0.33</sub>Zn[NTf<sub>2</sub>]<sub>2</sub> Zn 2p<sub>3/2</sub> was 1023.9 eV, which indicated that zinc was highly Lewis acidic.

#### (b) SIMS Sputter Depths

Sputter rates vary in different organic materials<sup>38</sup> and rates can even change as an interface is approached because surface binding energies are affected by underlying material.<sup>39</sup> Furthermore, the sputtering yield depends on the density, MW<sup>40</sup> and the degree of cross-linking for polymeric materials.<sup>41</sup> This is a problem for multicomponent materials which results in distorted depth profiles.<sup>42</sup> For ionogels, the change from surface ionic liquid to cross-linked PEGDA/ionic liquid undoubtedly resulted in a change in sputter rate; however, the observed trends were still valid and the only effect would be compression of the depth profile plot as the ionic liquid is removed and the cross-linked PEGDA/ionic liquid layer is reached. For an estimate of crater depth, the equation reported by Seah<sup>41</sup> and the experimental parameters used in this work were applied to inorganic SiO<sub>2</sub> and organic PMMA as examples (Note: the equation was validated by comparison to experimental data obtained for these samples) of low and high sputter yields materials. The theoretical sputter rate of SiO<sub>2</sub> would be 3.56 nm/s, giving a total depth of 4,277 nm over 1200 s, and 37.3 nm/s for PMMA, giving a depth of 44,694 nm. A factor of 10 is relatively small in comparison to other publications that report differences of 100 or 100,000 times.<sup>41,43</sup>

## 3. Additional Data



**Figure S1** (a) XPS N/O ratios for [omim]Cl with 5-40% PEGDA (black circles) and [omim][NTf<sub>2</sub>] with 0-40 wt% PEGDA (green squares), and (b) expansion of [omim][NTf<sub>2</sub>] data with N/O ratios of [emim][NTf<sub>2</sub>] 0-40 wt% PEGDA<sup>4</sup> (green triangles) for comparison.

Table S2 Comparison of N/O ratios for [emim] <sup>+</sup>	ionogels with 30 wt% PEGDA measured using Thern	no
K-alpha and Thermo Theta probe instruments.		

		N/O Ratio				
Ionogel	PEGDA / wt%	K-alpha <sup>4</sup>	Theta Probe			
[emim][OAc]	30 wt%	0.11	0.13			
[emim][EtSO <sub>4</sub> ]	30 wt%	0.25	0.33			
[emim][OTf]	30 wt%	0.59	0.63			
[emim][NTf <sub>2</sub> ]	30 wt%	0.65	0.66			

Table S3	Atomic	compositions	determined	by 2	XPS	for	[omim][NTf <sub>2</sub> ]	ionogels	with	PEGDA	polymers
from 0-4	0 wt%.										

	۸+	Atomic Composition / at%									
	A	Atomic Composition / at/8									
PEGDA / %	С	Ν	0	F	S	N/O					
0	48.5	10.1	13.7	20.5	6.9	0.74					
5	49.2	9.1	13.3	20.1	8.4	0.69					
10	50.6	9.0	13.0	19.0	8.4	0.70					
20	50.8	8.7	13.6	18.9	8.0	0.64					
30	54.9	7.9	12.5	16.0	8.7	0.63					
40	53.7	8.5	16.6	14.9	7.1	0.51					

	Atomi	c Compo	sition	/ at%	
PEGDA / %	С	Ν	0	CI	N/O
0	81.7	11.2	0.0	7.1	-
5	79.8	12.1	0.7	7.4	16.58
10	79.6	12.1	0.9	7.3	13.43
20	79.3	12.2	1.2	7.3	10.20
30	81.4	11.1	1.1	6.4	10.05
40	79.4	11.7	1.8	7.1	6.50

Table S5 Comparison of N/O ratios for [Rmim][NTf<sub>2</sub>] ionogels with 30 wt% PEGDA.

Ionogel	PEGDA / wt%	N/O Ratio
[emim][NTf <sub>2</sub> ]	30 wt%	0.66
[bmim][NTf <sub>2</sub> ]	30 wt%	0.62
[omim][NTf <sub>2</sub> ]	30 wt%	0.63
Average		0.637 ± 0.017

**Table S6** Atomic compositions (at%) of the five areas analysed during XPS quantification of  $[omim]Cl_{0.33}ZnCl_2$  with 30 wt% PEGDA ionogel.

		Are	ea (400 µ	m²)			
	1	2	3	4	5	Average	Error
C 1s	76.83	72.72	73.46	73.43	72.98	73.88	1.50
N 1s	10.71	10.41	10.14	10.04	10.23	10.31	0.24
O 1s	1.42	0.73	0.49	0.88	0.90	0.88	0.31
Cl 2p	8.99	13.18	13.18	12.97	13.10	12.28	1.65
Zn 2p3/2	2.04	2.96	2.74	2.68	2.79	2.64	0.32

**Table S7** Atomic compositions (at%) of the five areas analysed during XPS quantification of $[omim][NTf_2]_{-0.33}Zn[NTf_2]_2$  with 30 wt% PEGDA ionogel.

		Are	ea (400 µ	m²)			
	1	2	3	4	5	Average	Error
C 1s	53.53	53.85	54.17	54.76	53.15	53.89	0.50
N 1s	9.14	9.07	8.67	8.96	9.31	9.03	0.19
O 1s	12.02	11.98	12.69	12.12	11.92	12.15	0.26
F 1s	16.20	16.01	15.78	15.39	16.34	15.94	0.31
S 2p	9.11	9.08	8.68	8.75	9.28	8.98	0.21
Zn 2p3/2	0.00	0.00	0.00	0.03	0.00	0.01	0.01



**Figure S2** PARXPS survey scans for (a)  $[\text{omim}]Cl_{0.33}ZnCl_2$  (b)  $[\text{omim}][NTf_2]_{0.33}Zn[NTf_2]_2$  (c)  $[\text{omim}]Cl_{0.33}ZnCl2$  with 30 wt% PEGDA (d)  $[\text{omim}][NTf_2]_{0.33}Zn[NTf_2] + 30\%$  PEGDA, showing 2.4 nm (red), 3.9 nm (orange), 5.2 nm (green), 6.4 nm (blue), 7.4 nm (brown), and 8.2 nm (black) depths.



Figure S3 N/Zn ratios for [omim]Cl-<sub>0.33</sub>ZnCl<sub>2</sub> (red) and the corresponding 30% PEGDA ionogel.

**Table S8** Summary of PARXPS parameters for Zn in ionic liquids and 30 wt% PEGDA ionogels. FWHM and binding energies are shown for the Zn  $2p_{3/2}$  photoemission.

Ionic Liquid	PEGDA/ wt%	Depth / nm	Zn / at%	FWHM / eV	Binding Energy / eV
[omim]Cl- <sub>0.33</sub> ZnCl <sub>2</sub>	0	4.9	1.75	1.2	1022.1
	0	1.4	0.85	1.3	1021.9
	30	5.1	2.07	1.3	1022.1
	30	1.5	0.54	1.3	1022.0
[omim][NTf <sub>2</sub> ]Cl- <sub>0.33</sub> Zn[NTf <sub>2</sub> ] <sub>2</sub>	0	4.9	1.12	1.6	1023.8
	0	1.4	0.76	1.5	1023.8
	30	4.9	0	-	-
	30	1.4	0	-	-

**Table S9** Binding energies of ionic liquid and ionogel photoemission signals from XPS (top section) and PARXPS (bottom section). Highest intensity peaks are show (i.e.  $2p_{3/2}$ ) and all [omim]<sup>+</sup> samples are charge corrected by setting the aliphatic component to 285.0 eV.<sup>44</sup> [emim][NTf<sub>2</sub>] and [bmim][NTf<sub>2</sub>] ionogels are referenced to the N 1s value obtained for corrected [omim][NTf<sub>2</sub>] at 402.1 eV.

		C 1s				N	1s			S 2p	Cl 2p	Zn 2p
Ionic Liquid	PEGDA / wt%	Caliphatic	Chetero	C <sup>2</sup>	CF3	Cation	Anion	0 1s	F 1s	3/2	3/2	3/2
[omim][NTf <sub>2</sub> ]	0	285.0	286.7	287.6	292.9	402.1	399.4	532.7	688.8	169.0		
[emim][NTf <sub>2</sub> ]	30	285.4	286.7	287.6	293.0	402.1	399.5	532.7	688.9	169.0		
[bmim][NTf <sub>2</sub> ]	30	285.2	286.7	287.6	292.9	402.1	399.5	532.7	688.8	169.0		
[omim][NTf <sub>2</sub> ]	30	285.0	286.7	287.6	292.9	402.1	399.5	532.7	688.9	169.0		
[omim]Cl	30	285.0	286.2	287.1		401.7		532.7				
[omim][NTf <sub>2</sub> ]- <sub>0.33</sub> Zn[NTf <sub>2</sub> ] <sub>2</sub>	0	285.0	286.8	287.6	293.3	402.2	400.0	533.3	689.2	169.8		1023.9
[omim]Cl- <sub>0.33</sub> ZnCl <sub>2</sub>	0	285.0	286.2	287.1		401.7					198.2	1022.1
[omim][NTf <sub>2</sub> ]- <sub>0.33</sub> Zn[NTf <sub>2</sub> ] <sub>2</sub>	30	285.0	286.7	287.6	292.9	402.0	399.5	532.6	688.8	168.9		1022.8
[omim]Cl- <sub>0.33</sub> ZnCl <sub>2</sub>	30	285.0	286.2	287.9		401.4		532.6			189.1	1022.4
[omim][NTf <sub>2</sub> ]	30	285.0	286.7	287.6	292.9	402.1	399.4	532.7	688.8	169.0		
[omim][NTf <sub>2</sub> ]- 0.33Zn[NTf <sub>2</sub> ] <sub>2</sub>	0	285.0	286.7	287.5	293.3	402.1	399.9	533.2	689.0	169.5		1023.8



**Figure S4** SIMS Mass spectra of (a)  $[omim][NTf_2]$  ionic liquid and (b)  $[omim][NTf_2]$  ionogel with 30 wt% PEGDA, showing the appearance of  $C_2H_5O^+$  (m/z 45) in the ionogel.



**Figure S5** SIMS depth profiles of  $[omim][NTf_2]_{-0.33}Co[NTf_2]_2$  with 30 wt% PEGDA, showing the  $[omim]^+$  cation (red), PEGDA (black), and cobalt (dark blue), with Co<sup>+</sup> depth profile overlaid from the  $[omim][NTf_2]_{-0.33}Co[NTf_2]_2$  ionic liquid (pale blue).



**Figure S6** Plots of compressive stress against compressive strain for ionogels of (a) [bmim][NTf<sub>2</sub>], (b) [omim][NTf<sub>2</sub>], and (c) [omim]Cl with PEGDA concentrations of 10% (black), 20% (red), 30% (blue), and 40% (green). (d) Compressive stress-strain plots for zinc containing 30 wt% ionogels of [omim]Cl- $_{0.33}$ ZnCl<sub>2</sub> (red) and [omim][NTf<sub>2</sub>]- $_{0.33}$ Zn[NTf<sub>2</sub>]<sub>2</sub> (black).

lonic Liquid	PEGDA / wt%	Compressive Modulus (low strain) / MPa	Compressive Modulus (high strain) / MPa	Failure Stress / MPa	Failure Strain / %
[bmim][NTf2]	10 wt%	0.24 ± 0.034	0.76 ± 0.13	$0.15 \pm 0.02$	43.50 ± 3.63
	20 wt%	0.83 ± 0.050	$2.09 \pm 0.05$	0.75 ± 0.13	47.27 ± 4.12
	30 wt%	$1.23 \pm 0.13$	4.36 ± 0.10	$0.61 \pm 0.10$	37.51 ± 7.17
	40 wt%	2.37 ± 0.48	10.18 ± 0.76	$1.67 \pm 0.21$	39.08 ± 1.26
[omim]Cl	10 wt%	$0.029 \pm 0.0051$	1.94 ± 0.77	-	-
	20 wt%	0.015 ± 0.0011	$0.64 \pm 0.13$	$0.09 \pm 0.01$	61.36 ± 0.71
	30 wt%	0.065 ± 0.0077	$1.32 \pm 0.20$	$0.24 \pm 0.01$	58.39 ± 2.77
	40 wt%	0.11 ± 0.0057	1.83 ± 0.81	0.57 ± 0.04	76.32 ± 0.89
[omim][NTf2]	10 wt%	0.16 ± 0.037	$0.71 \pm 0.03$	$0.13 \pm 0.01$	43.37 ± 3.61
	20 wt%	0.89 ± 0.093	2.39 ± 0.35	$0.40 \pm 0.08$	33.47 ± 3.77
	30 wt%	1.71 ± 0.20	4.66 ± 0.20	$0.64 \pm 0.08$	33.33 ± 4.90
	40 wt%	2.24 ± 0.69	10.58 ± 0.95	2.09 ± 0.04	47.42 ± 2.64
[omim]Cl + ZnCl2	30 wt%	0.15 ± 0.02	2.60 ± 0.16	$0.64 \pm 0.06$	74.58 ± 5.16
[omim][NTf2] + Zn(NTf2)2	30 wt%	0.77 ± 0.14	2.99 ± 0.39	0.87 ± 0.28	52.65 ± 1.68

**Table S10** Compressive modulus of cross-linked PEGDA ionogels at low strain ( $\approx$  10%) and high strain (before fracturing), failure stress, and failure strain.



## 4. PARXPS High Resolution Scans

**Figure S7** PARXPS data for [omim]Cl- $_{0.33}$ ZnCl<sub>2</sub> showing 25 ° (black) and 75 ° (red) emission angles. Scans (a-d) show background subtracted data and scan (e) shows background subtracted and area normalised data (C 1s scans are normalised to  $C^{hetero}$  areas).



**Figure S8** PARXPS data for  $[omim][NTf_2]_{-0.33}Zn[NTf_2]_2$  showing 25 ° (black) and 75 ° (red) emission angles. Scans (a-f) show background subtracted data and scans (g-h) show background subtracted and area normalised data (C 1s scans are normalised to *C*<sup>hetero</sup> areas; N 1s scans are normalised to imidazolium N areas).



**Figure S9** PARXPS data for [omim]Cl- $_{0.33}$ ZnCl<sub>2</sub> with 30 wt% PEGDA, showing 25 ° (black) and 75 ° (red) emission angles. Scans (a-e) show background subtracted data and scan (d) shows background subtracted and area normalised data (C 1s scans are normalised to  $C^{hetero}$  areas).



**Figure S10** PARXPS data for  $[omim][NTf_2]_{0.33}Zn[NTf_2]_2$  with 30 wt% PEGDA, showing 25 ° (black) and 75 ° (red) emission angles. Scans (a-g) show background subtracted data and scans (h-f) show background subtracted and area normalised data (C 1s scans are normalised to  $C^{hetero}$  areas; N 1s scans

are normalised to imidazolium N areas). Note: (g) is a repeat from a separate sample to validate the result.



## 5. XPS Survey and High Resolution Scans

Figure S11 (a) Survey and (b-e) high resolution XP spectra for [omim]Cl with 5 wt% PEGDA.



Figure S12 (a) Survey and (b-e) high resolution XP spectra for [omim]Cl with 10 wt% PEGDA.



Figure S13 (a) Survey and (b-e) high resolution XP spectra for [omim]Cl with 20 wt% PEGDA.



Figure S14 (a) Survey and (b-e) high resolution XP spectra for [omim]Cl with 30 wt% PEGDA.



Figure S15 (a) Survey and (b-e) high resolution XP spectra for [omim]Cl with 40 wt% PEGDA.



Figure S16 (a) Survey and (b-e) high resolution XP spectra for [omim]Cl-0.33ZnCl<sub>2</sub> with 30 wt% PEGDA.



Figure S17 (a) Survey and (b-e) high resolution XP spectra for [omim]Cl-<sub>0.33</sub>ZnCl<sub>2</sub>.



Figure S18 (a) Survey and (b-f) high resolution XP spectra for [omim][NTf<sub>2</sub>] with 5 wt% PEGDA.



Figure S19 (a) Survey and (b-f) high resolution XP spectra for [omim][NTf<sub>2</sub>] with 10 wt% PEGDA.



Figure S20 (a) Survey and (b-f) high resolution XP spectra for [omim][NTf<sub>2</sub>] with 20 wt% PEGDA.



Figure S21 (a) Survey and (b-f) high resolution XP spectra for [omim][NTf<sub>2</sub>] with 30 wt% PEGDA.



Figure S22 (a) Survey and (b-f) high resolution XP spectra for [omim][NTf<sub>2</sub>] with 40 wt% PEGDA.



**Figure S23** (a) Survey and (b-f) high resolution XP spectra for the bulk of an ionogel composed of  $[omim][NTf_2] \chi 0.33 Zn[NTf_2]_2$  with 30 wt% PEGDA.



**Figure S24** (a) Survey and (b-g) high resolution XP spectra for the surface of an ionogel composed of  $[\text{omim}][\text{NTf}_2] \chi 0.33 \text{ Zn}[\text{NTf}_2]_2$  with 30 wt% PEGDA. Note: Zn 2p scan was recorded over 20 mins.



Figure S25 (a) Survey and (b-g) high resolution XP spectra for  $[omim][NTf_2]_{-0.33}Zn[NTf_2]_2$  ionic liquid.

## 6. Molecular Dynamics Simulations

Each of the six systems investigated consisted of a constant number of ions with increasing number of PEGDA monomers (**Table S11**). For comparison, the PEGDA/Zn<sup>+</sup> ratio of  $[omim][NTf_2]_{-0.33}Zn[NTf_2]_2$  with 30 wt% PEGDA was approximately 1.1.

All molecular dynamics (MD) simulations were carried out under periodic boundary conditions using Amber (2016).<sup>16</sup> The particle mesh Ewald (PME) method was employed for long-range electrostatics interactions and a 1.2 nm cut-off was employed for non-bonded interactions.<sup>45</sup> SHAKE was employed for all bonds containing hydrogen atoms.<sup>46</sup>

IL/PEGDA	30	10	6	30	10	6
Zn/PEGDA	5	1.7	1	0	0	0
[omim]⁺	300	300	300	300	300	300
Cl <sup>-</sup> /[NTf <sub>2</sub> ] <sup>-</sup>	400	400	400	300	300	300
Zn <sup>2+</sup>	50	50	50	0	0	0
PEGDA	10	30	50	10	30	50

 Table S11 Numbers of molecules present in each simulation.

The simulation protocol was:

- 1. Initial configurations were generated using the PACKMOL program.
- 2. Energy minimisation were performed.
- 3. All systems were slowly heated to 600 K, in the NVT ensemble over 5 ns to remove possible energy hotspots in the initial configurations. Temperature was controlled using the Langevin thermostat ( $\gamma = 1.0 \text{ ps}^{-1}$ ).<sup>47</sup> This was followed by a short (1 ns) simulation in the NPT ensemble to correct densities. Temperature was controlled using the Langevin thermostat with a collision frequency of  $\gamma = 1.0 \text{ ps}^{-1}$  and pressure was maintained using a Berendsen barostat<sup>48</sup> (t = 1.0 ps<sup>-1</sup>). A 2 fs time step was employed for all simulations.
- 4. The systems were then cooled to 378 K in the NVT ensemble over 1ns using the same settings as above.
- 5. Each system was then subjected to 100 ns runs in the NPT ensemble at 378 K, with the last 50 ns used as the production run and analysed. Temperature was again controlled using the Langevin thermostat with a collision frequency of  $\gamma = 1.0 \text{ ps}^{-1}$  and pressure was controlled using a Berendsen barostat (t = 1.0 ps<sup>-1</sup>). A 2 fs time step was employed for all simulations.

Analysis of trajectories has been carried out using CPPTRAJ<sup>49</sup> and TRAVIS (version 200504-hf2).<sup>50,51</sup> The average end-to-end distance (R) and the average radius of gyration ( $R_g$ ) were calculated for each PEGDA/Zn<sup>+</sup> ratio.  $R_g$  is defined as the square root of the sum of squared distances of all atoms from the centre of mass of the system:

$$R_g = \sqrt{\frac{1}{M} \sum_{i} m_i (r_i - r_{cm})^2}$$

Where M is the total mass of the monomer chain,  $m_i$  is the mass of atom i,  $r_i$  is the position of atom i, and  $r_{CM}$  is the position of the centre of mass of the monomer chains. Hydrogen atoms were excluded when calculating  $R_g$ . Solvent accessible surface areas (SASA) were determined using the Connelly method<sup>52</sup> as implemented in CPPTRAJ.



**Figure S26** Snapshots from  $[omim][NTf_2]_{0.33}Zn[NTf_2]_2$  with PEGDA/Zn 1 at different times throughout the simulation.

#### Radial distribution functions g(r)

For alkyl-alkyl and alkyl-PEGDA RDFs the alkyl chains are divided in to three progressively longer lengths where each carbon atom is labelled 1-8 from the nitrogen bound  $-CH_2$ - carbon to the terminal  $-CH_3$ : C<sub>7</sub>-C<sub>8</sub>, C<sub>5</sub>-C<sub>8</sub> and C<sub>3</sub>-C<sub>8</sub>.



**Figure S27** (a) Zn-O([NTf<sub>2</sub>]<sup>-</sup>), (b) Zn-N([NTf<sub>2</sub>]<sup>-</sup>), (c) Zn-O(PEGDA: 2-12), and (d) Zn-O(PEGDA: 1,13) RDFs for PEGDA/Zn<sup>2+</sup> 0.2 (purple), 0.6 (blue), and 1.0 (green) in [omim][NTf<sub>2</sub>]-<sub>0.33</sub>Zn[NTf<sub>2</sub>]<sub>2</sub>.



**Figure S28** (a-c) Zn-O(PEGDA) and (d-e) Zn-Cl<sup>-</sup> RDFs for PEGDA/Zn<sup>2+</sup> 0.2 (purple), 0.6 (blue), and 1.0 (green) in [omim]Cl- $_{0.33}$ ZnCl<sub>2</sub>. (a) Zn-O(PEGDA) for Zn interaction with O (2-12) in the PEGDA chain, (b) expansion of the first maximum for (a), and (c) a close up of the first maximum for the Zn-O interactions with the terminal O atoms (1 and 13). (d) RDF for Zn-Cl<sup>-</sup> sites, and (e) expansion of the Zn-Cl<sup>-</sup> first maximum of (d).



**Figure S29** (a-c)  $[\text{omim}]^+$ -O(PEGDA: 2-12) RDFs for imidazolium ring protons (a) H<sup>2</sup>-O, (b) H<sup>4</sup>-O, and (c) H<sup>5</sup>-O in  $[\text{omim}]Cl_{-0.33}ZnCl_2$ . (d-f)  $[\text{omim}]^+$ -O(PEGDA: 2-12) RDFs for imidazolium ring protons (a) H<sup>2</sup>-O, (b) H<sup>4</sup>-O, and (c) H<sup>5</sup>-O in  $[\text{omim}][\text{NTf}_2]_{-0.33}Zn[\text{NTf}_2]_2$ , for PEGDA/Zn<sup>2+</sup> 0.2 (purple), 0.6 (blue) and 1.0 (green).



**Figure S30** (a-c)  $[\text{omim}]^+$ -Cl RDFs for imidazolium ring protons (a) H<sup>2</sup>-Cl<sup>-</sup>, (b) H<sup>4</sup>-Cl<sup>-</sup>, and (c) H<sup>5</sup>-Cl<sup>-</sup> in  $[\text{omim}]Cl_{0.33}ZnCl_2$ . (d-f)  $[\text{omim}]^+$ -O( $[\text{NTf}_2]^-$ ) RDFs for imidazolium ring protons (a) H<sup>2</sup>-O, (b) H<sup>4</sup>-O, and (c) H<sup>5</sup>-O in  $[\text{omim}][\text{NTf}_2]_{-0.33}Zn[\text{NTf}_2]_2$  for PEGDA/Zn<sup>2+</sup> 0.2 (purple), 0.6 (blue) and 1.0 (green).



**Figure S31** (a-c) Alkyl-alkyl RDFs for [omim]Cl- $_{0.33}$ ZnCl<sub>2</sub> for PEGDA/Zn<sup>2+</sup> 0.2 (a), 0.6 (b) and 1.0 (c). (d-f) alkyl-alkyl RDFs for [omim][NTf<sub>2</sub>]- $_{0.33}$ Zn[NTf<sub>2</sub>]<sub>2</sub> for PEGDA/Zn<sup>2+</sup> 0.2 (d), 0.6 (e) and 1.0 (f), showing averaged site-site interaction for C<sub>7</sub>-C<sub>8</sub> (light blue), C<sub>5</sub>-C<sub>8</sub> (green), and C<sub>3</sub>-C<sub>8</sub> (purple).



**Figure S32** (a-c) Alkyl-PEGDA RDFs for  $[\text{omim}]Cl_{-0.33}ZnCl_2$  for PEGDA/Zn<sup>2+</sup> 0.2 (a), 0.6 (b) and 1.0 (c). (d-f) alkyl-PEGDA RDFs for  $[\text{omim}][NTf_2]_{-0.33}Zn[NTf_2]_2$  for PEGDA/Zn<sup>2+</sup> 0.2 (d), 0.6 (e) and 1.0 (f), showing averaged site-site interaction for C<sub>7</sub>-C<sub>8</sub> (light blue), C<sub>5</sub>-C<sub>8</sub> (green), and C<sub>3</sub>-C<sub>8</sub> (purple).



**Figure S33** Representative examples of R (a, b),  $R_g$  (c, d), and SASA (e, f) of several PEGDA monomers (0.2 PEGDA/Zn<sup>+</sup>) in [omim]Cl<sub>-0.33</sub>ZnCl<sub>2</sub> (a, c, e) and [omim][NTf<sub>2</sub>]-<sub>0.33</sub>Zn[NTf<sub>2</sub>]<sub>2</sub> (b, d, f) ionic liquids.

## 7. Thermal Analysis

			Thermal parameters / °C		
	χZn[A]₂	PEGDA / %	T <sub>g</sub> 1	T <sub>g</sub> 2	T <sub>onset</sub>
[omim]Cl	0	0	-61.4		239
	0.33	0	-55.7		293
	0	30	-30.0		239
	0.1	30	-30.0		256
	0.33	30	-38.7	-18.2	333
	washe	d polymer	-25.3		
[omim][NTf <sub>2</sub> ]	0	0	-86.0ª		408
	0.33	0	-62.7		363
	0	30	-49.5		388
	0.05	30			234
	0.2	30	-36.8		215
	0.33	30	-12.3		235
	washed polymer		-24.2		

**Table S12** Glass transitions  $(T_g)$  measured by DSC and onset temperatures  $(T_{onset})$  measured by TGA for the ionic liquids and ionogels reported in this section.

<sup>a</sup>Reference <sup>53</sup>



**Figure S34** DSC of the ionic liquid [omim]Cl at 10 °C min<sup>-1</sup> (the first two cycles and last cycle are omitted for clarity).



**Figure S35** DSC of the ionic liquid  $[omim]Cl_{-0.33}ZnCl_2$  at 10 °C min<sup>-1</sup> (the first two cycles and last cycle are omitted for clarity).



**Figure S36** DSC of the ionic liquid  $[omim][NTf_2]_{-0.33}Zn[NTf_2]_2$  at 10 °C min<sup>-1</sup> (the first two cycles and last cycle are omitted for clarity). Note: a relatively large enthalpic relaxation peak appears after the glass transition.



**Figure S37** DSC of the ionogel [omim]Cl with 30% PEGDA at 10 °C min<sup>-1</sup> (the first two cycles and last cycle are omitted for clarity).



**Figure S38** DSC of the ionogel  $[omim][NTf_2]$  with 30% PEGDA at 10 °C min<sup>-1</sup> (the first two cycles and last cycle are omitted for clarity).



**Figure S39** DSC of the ionogel [omim]Cl- $_{0.33}$ ZnCl<sub>2</sub> with 30% PEGDA at 10 °C min<sup>-1</sup> (the first two cycles and last cycle are omitted for clarity).



**Figure S40** DSC of the ionogel [omim]Cl- $_{0.1}$ ZnCl<sub>2</sub> with 30% PEGDA at 10 °C min<sup>-1</sup> (the first two cycles and last cycle are omitted for clarity).



**Figure S41** DSC of the ionogel  $[omim][NTf_2]_{-0.33}Zn[NTf_2]_2$  with 30% PEGDA at 10 °C min<sup>-1</sup> (the first two cycles and last cycle are omitted for clarity).



**Figure S42** DSC of the ionogel  $[omim][NTf_2]_{-0.2}Zn[NTf_2]_2$  with 30% PEGDA at 10 °C min<sup>-1</sup> (the first two cycles and last cycle are omitted for clarity).



**Figure S43** DSC at 10 °C min<sup>-1</sup> of the polymer isolated from the [omim]Cl with 30% PEGDA ionogel by removing the ionic liquid with MeOH (10-20 mg of ionogel stirred in 50 mL MeOH for 24 hr).



**Figure S44** DSC at 10 °C min<sup>-1</sup> of the polymer isolated from the  $[omim][NTf_2]$  with 30% PEGDA ionogel by removing the ionic liquid with MeOH (10-20 mg of ionogel stirred in 50 mL MeOH for 24 hr).



**Figure S45** TGA curves for [omim]Cl and [omim]Cl- $\chi$ ZnCl<sub>2</sub> ionogels at 10 °C min<sup>-1</sup> in an N<sub>2</sub> atmosphere.



**Figure S46** TGA curves for  $[omim][NTf_2]$  and  $[omim][NTf_2]_{-0.33}Zn[NTf_2]_2$  ionogels at 10 °C min<sup>-1</sup> in an N<sub>2</sub> atmosphere.



**Figure S47** TGA curves for  $[omim][NTf_2]$  and  $[omim][NTf_2]-\chi Zn[NTf_2]_2$  ionogels at 10 °C min<sup>-1</sup> in an N<sub>2</sub> atmosphere.

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