

## Supporting Information

### Temperature & pH triggered release characteristics of water / fluorescein from 1-ethyl-3-methylimidazolium ethylsulfate –based ionogels.

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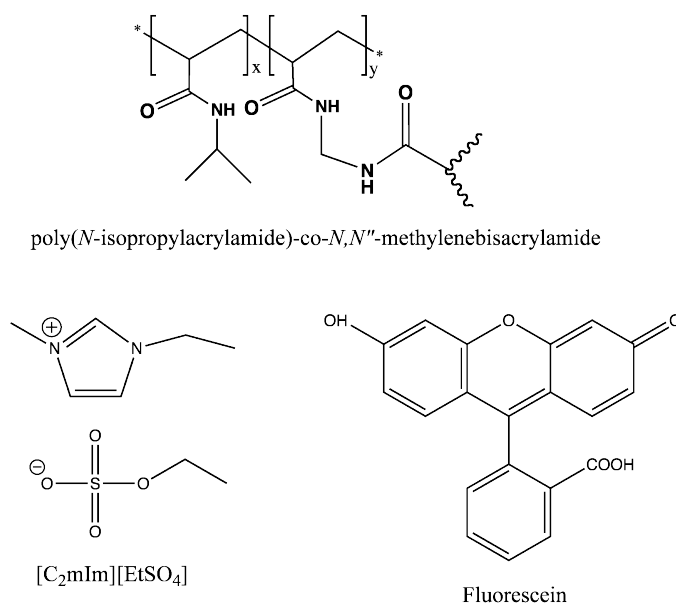
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## I: Chemicals and Materials

*N*-isopropylacrylamide 98% (NIPAAM), *N,N'*-methylenebisacrylamide 99% (MBIS), Aluminum Oxide (activated, basic, Brockmann I), Fluorescein disodium salt, Fluka pH 4, 7 and 9.2 buffer tablets and 2,2-Dimethoxy-2-phenylacetophenone 98% (DMPA) were purchased from Sigma Aldrich®, Ireland and used as received. 1-ethyl methylimidazolium ethylsulfate [C<sub>2</sub>mim][EtSO<sub>4</sub>] was purchased from Sigma Aldrich® Ireland Ltd and purified as outlined below.



**Figure S1:** (top) MBIS crosslinked pNIPAAM, ionic liquid [C<sub>2</sub>mIm][EtSO<sub>4</sub>] and fluorescein in its neutral form.

## II: Experimental

### *IL purification*

Before further analyses, [C<sub>2</sub>mIm][EtSO<sub>4</sub>] was column cleansed using alumina (activated, basic, Brockmann I), with dichloromethane used as the mobile phase, which was subsequently removed under vacuum at 40 °C for 48 hrs at 0.1 Torr<sup>1</sup>. The IL was subsequently stored in an inert atmosphere (N<sub>2</sub>) at room temperature.

<sup>1</sup>H NMR, δ<sub>H</sub> (400 MHz; CD<sub>3</sub>CN): 1.12-1.17 (3H, t, CH<sub>3</sub>), 1.32-1.37 (3H, t, CH<sub>3</sub>), 3.73 (3H, s, CH<sub>3</sub>), 3.9-3.99 (2H, m, CH<sub>2</sub>), 4.04-4.09 (2H, m, CH<sub>2</sub>), 4.69 (H, s, CH), 7.2-7.27 (H, d, CH), 7.32-7.33 (H, d, CH).

### *Preparation of polymer gels*

pNIPAAm ionogels were prepared by mixing 400 mg of NIPAAm monomer (3.53 mmol), 27 mg of MBIS crosslinker (0.176 mmol), 18.1 mg photoinitiator (DMPA (0.07 mmol) (Final molar ratio 100:5:2), with 1200 mg (5.07 mmol, 960 μL) of [C<sub>2</sub>mIm][EtSO<sub>4</sub>] added. The mixture was heated to 30 °C and sonicated for 5 min. until a transparent solution was observed. 200 μL of the monomeric solution was then dispensed into a Teflon mold, 12 mm in radius, and photo-polymerized using a Connecticut® 20 W UV BondWand (365 nm) for 10 mins. A 1 mm diameter punch was then used to isolate the sample area for further analyses.

The control hydrogel experiments were performed in the same manner, by substituting 1.2 g of a 1:1 (v/v) mixture of H<sub>2</sub>O: Ethanol for [C<sub>2</sub>mIm][EtSO<sub>4</sub>].

The fluorescent ionogels were prepared by adding 1.083 mg of Fluorescein disodium salt to the ionogel composition, and polymerised in the same manner as described previously.

#### *Rate of Fluorescein expulsion.*

100 ml of Standard pH solutions were made using Fluka pH 4, 7 and 9.2 buffer tablets (Sigma-Aldrich, Ireland). Ionogels and hydrogels preloaded with 3 mM of fluorescein dye were allowed to swell overnight in the corresponding pH buffered water solution. The swollen gels were then cut in half and placed in solution of the same pH at 40 °C for 1 min (> LCST) and 20 °C (< LCST). The free-standing ionogel membrane was then removed and the resultant solution was stirred for homogeneity. When the sample cooled to room temperature (20 °C), the concentration of fluorescein was measured. Calibration curves can be found in Fig S15 and S16 and emission spectra for the ionogel at pH 4, 7 and 9.2 in Fig S17 and S18 respectively.

### **III: Instrumentation**

#### *Density Measurements*

Densities were measured using a DMA-500 vibrating-tube densiometer from Anton-Paar®. The density meter uses the “oscillating U-tube principle”<sup>2</sup> to determine the density of the liquid. Measurements were performed at atmospheric pressure from 20 to 60 °C for both pure and water-saturated ILs.

#### *Viscosity*

Viscosity measurements were performed at atmospheric pressure in the temperature range 20 to 60 °C on both pure and water-saturated ILs using an Anton-Paar® Viscometer, which employs a rolling ball technique<sup>3</sup>.

#### *Differential Scanning Calorimetry*

Differential Scanning Calorimetry (DSC) was performed using the Perkin Elmer® Pyris 1 Calorimeter. Individual scans were performed in the temperature range from 10 to 50 °C, at a scan rate of 5 °C per minute. Thermal scans below room temperature

were calibrated with the cyclohexane solid-solid transition and melting point at – 87.0 °C and 6.5 °C, respectively. Thermal scans above room temperature were calibrated using indium, tin and zinc with melting points at 156.60, 231.93 and 419.53 °C, respectively. Transition temperatures were taken from the peak maximum of the thermal transition.

#### *Polymer Gel Diameter Measurements*

Each free standing polymerized gel was placed in 5.76 mL de-ionized water at 20 °C for 24 hours before the swelling behavior was recorded. Next, the gels were placed in de-ionized water at 45 °C for 1 minute. This temperature ensures the swollen hydrated ionogels undergo the LCST phase transition (as individually measured using DSC).

De-ionized water was substituted by pH 4, 7 and 9.2 buffer solutions for fluorescence ionogel experiments.

The thickness of the resultant gel samples were calculated using a Mitutoyo® micrometer calibrated to a resolution of 1 µm.

#### *Rheometry*

All measurements were performed on an Anton-Paar® MCR301 rheometer equipped with a steel bottom plate. Initially, all polymerized gels (12 mm diameter) were immersed in deionized water for 24 hours. The swollen gels were then analysed for changes in the loss and storage moduli through the LCST by using a temperature step program. All the swollen gels were analysed in oscillation mode with a parallel plate PP15 tool 15 mm diameter at 0.05 % strain and a frequency of 10 Hz.

The data points were collected every second and the following temperature ramp were applied: Isotherm for 5 min at 20 °C, after which increase to 45 °C (20 °C /min) and isotherm for a total of 9 min thereafter at 45 °C.

### *Optical Microscopy*

Optical Microscopy studies were performed using an AIGO® GE-5 digital microscope.

### *Scanning Electron Microscopy*

Ionogel and hydrogel surface areas were imaged using scanning electron microscopy (SEM), performed on a Carl Zeiss EVOLS 15 system at an accelerating voltage of 26.11 kV. Gold Sputtering of all gels was performed on a Polaron® SC7640 Auto/Manual High Resolution Sputter Coater. All gels were coated under the following conditions: Voltage 1.5 kV, 15 mA for 2 minutes at a coating Rate of 5 nm/min. The 10 nm gold coating proved capable of maintaining a saturated ionogel for microscopy imaging.

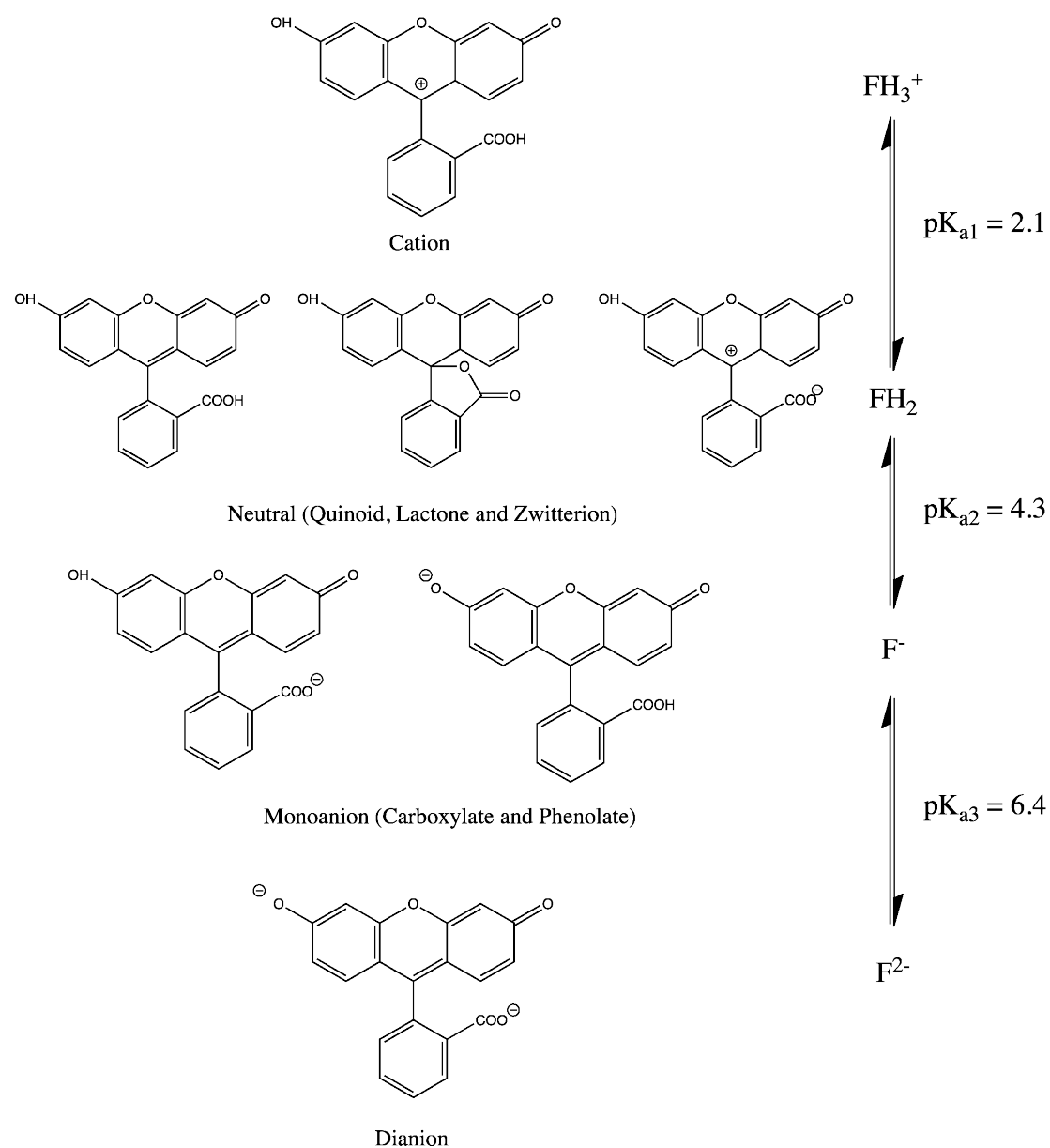
### *UV/Vis Spectroscopy*

UV/Vis transmittance / absorbance spectra were obtained using a Perkin Elmer Lambda 900 UV/Vis/NIR® spectrometer. All spectra were obtained in the wavelength region spanning from 300 to 900 nm at 200 nm/minute, using a 1 nm data interval.

### *Fluorescence Spectroscopy*

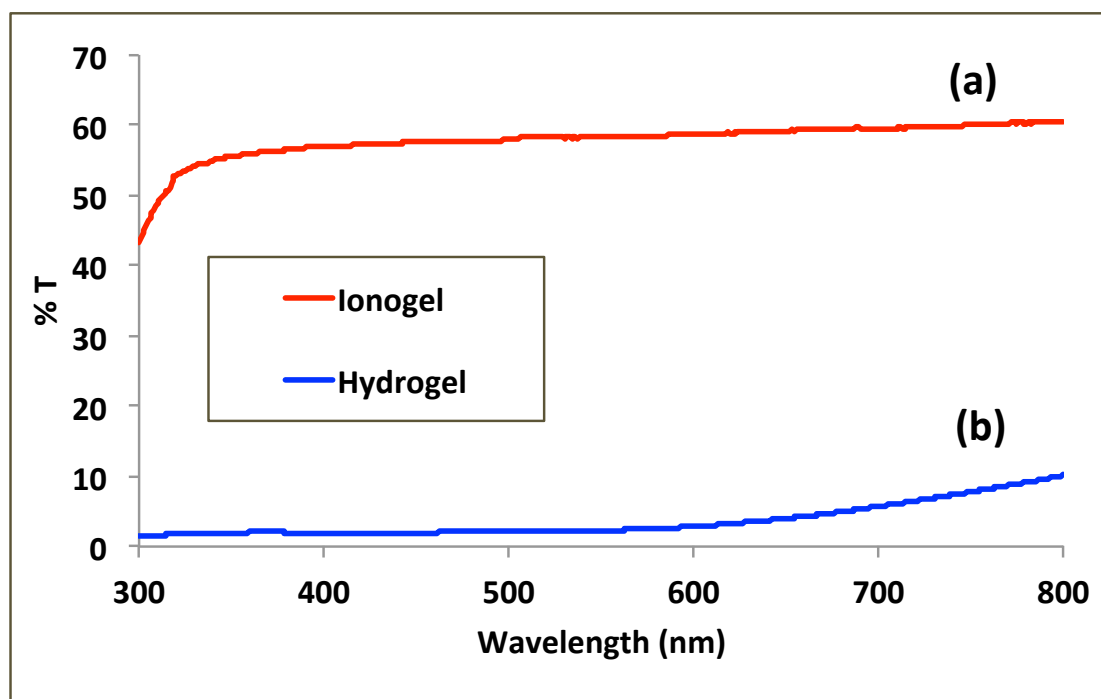
Fluorescence measurements were performed using a Perkin Elmer® LS 50B Luminescence Spectrometer, in the spectral range from 300 to 800 nm, at a scan rate of 100 nm/min.

## IV: Different Prototropic Forms of Fluorescein.

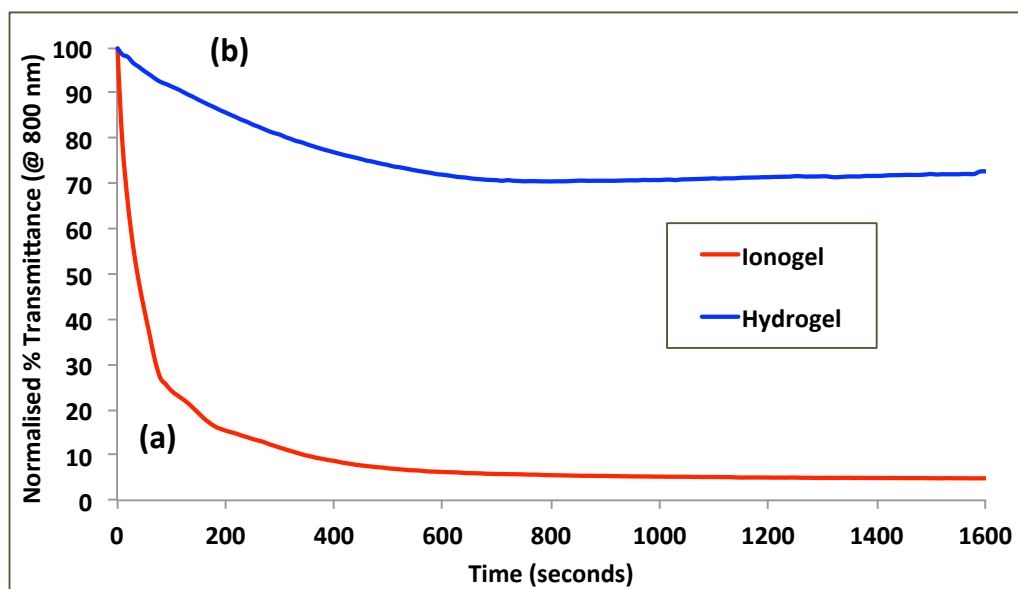


**Fig S2: pH dependence of prototropic forms of fluorescein in aqueous solution [cation ( $\text{FH}_3^+$ ,  $\text{pK}_a = 2.1$ ), neutral ( $\text{FH}_2$ ,  $\text{pK}_a = 4.3$ ), monoanion ( $\text{F}^-$ ,  $\text{pK}_a = 6.4$ ), and dianion ( $\text{F}^{2-}$ )].<sup>4</sup>**

## V: UV-Vis



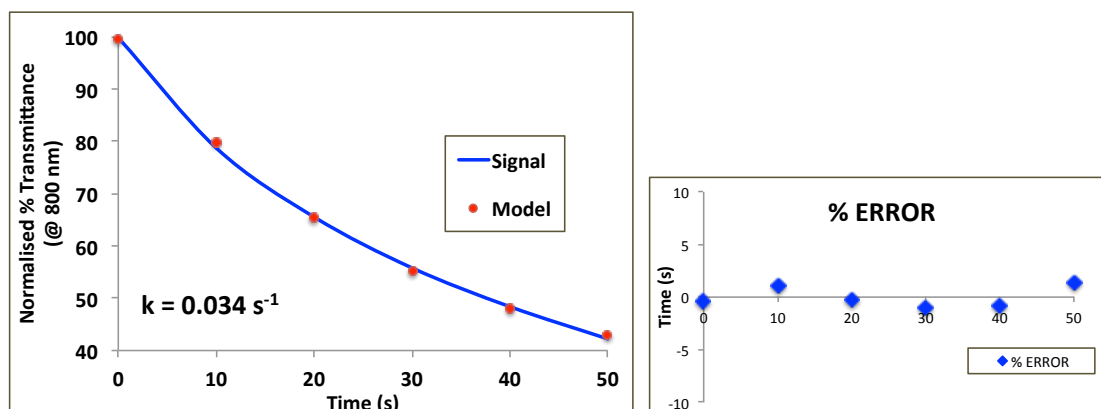
**Figure S3:** Transmittance spectra obtained for (a) Ionogel and (b) Hydrogel after the initial photoinitiation step.



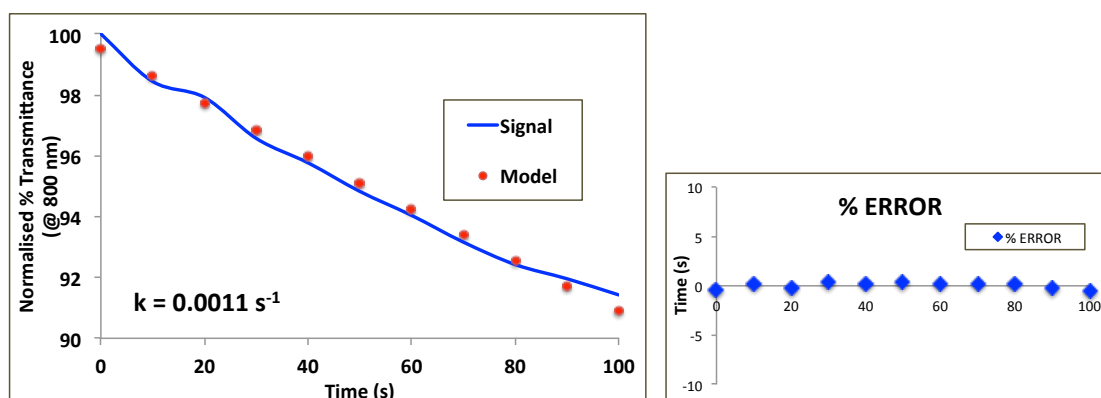
**Figure S4:** Kinetic analysis (@ 20 °C) of the water uptake for (a) Ionogel and (b) Hydrogel after the initial photoinitiation step. As the gel swells it becomes more opaque resulting in decreased transmission at the given wavelength (800 nm)



(a)



(b)



**Figure S5:** Exponential decay analysis used for the determination of rate constants for gel water uptake for (a) the Ionogel and (b) the Hydrogel. As the gel swells it becomes more opaque resulting in decreased transmission at the given wavelength (800 nm). The model was fitted using the SOLVER function in MS Excel® 2011 and the exponential equation,

$$f(t) = Ae^{(-kt)} + z, \text{ where:}$$

$A$  = pre-exponential factor

$k$  = rate constant

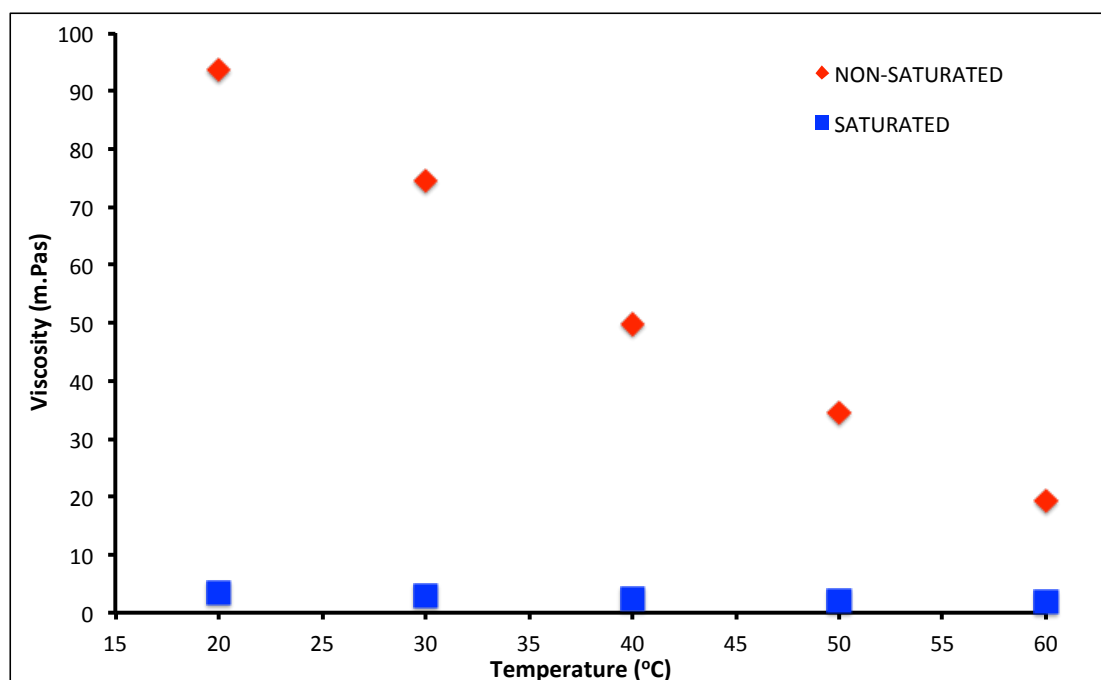
$t$  = time

$z$  = baseline offset.

## VI: Viscosity of [C<sub>2</sub>mIm][EtSO<sub>4</sub>]

Ionic Liquid	Temperature (°C)	NON-SATURATED	SATURATED
		Viscosity (mPa.s)	Viscosity (mPa.s)
[C <sub>2</sub> mIm][EtSO <sub>4</sub> ]	20	93.61	3.43
	30	74.61	3.044
	40	49.71	2.421
	50	34.62	1.99
	60	19.24	1.73

**Table S1:** Viscosity values of non-hydrated and water-saturated mixtures of [C<sub>2</sub>mIm][EtSO<sub>4</sub>] as a function of temperature.



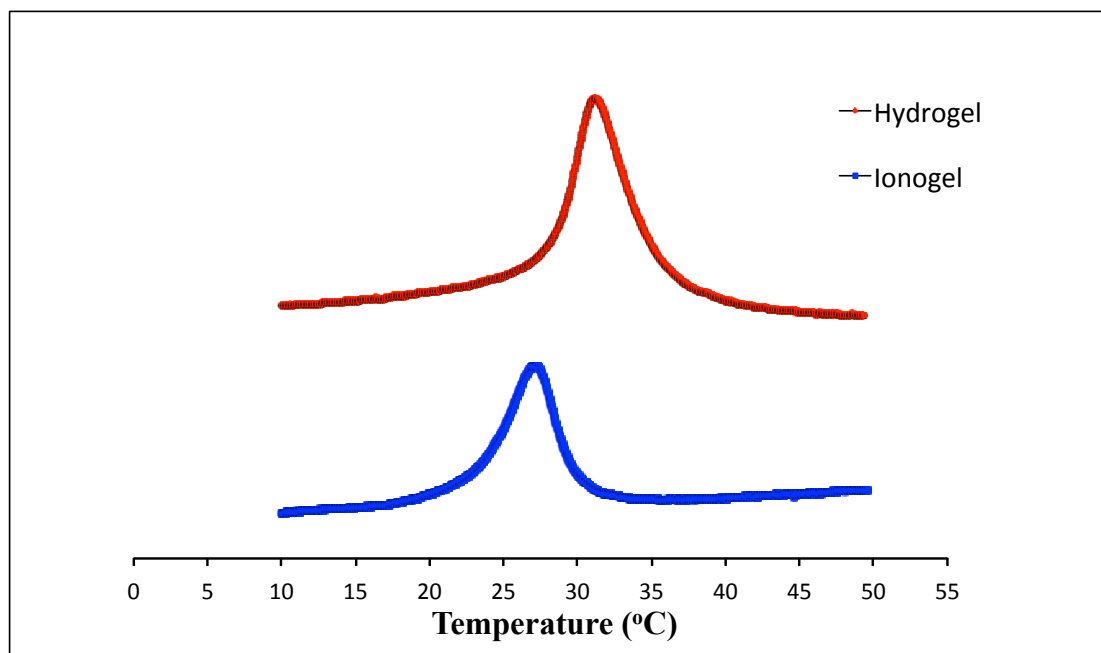
**Figure S6:** Viscosity values of non-hydrated (red) and water-saturated (blue) mixtures of [C<sub>2</sub>mIm][EtSO<sub>4</sub>] as a function of temperature.

## VII: Actuation behavior.

Sample	LCST (°C)	Swollen Diameter/mm (n=3)	% Swelling Increase	Contracted Diameter/mm (n=3)	% Contraction Decrease
Ionogel	26	4.45 (0.09)	28.68	3.05 (0.03)	31.44
Hydrogel	31	3.58 (0.05)	18.59	3.02 (0.09)	21.59

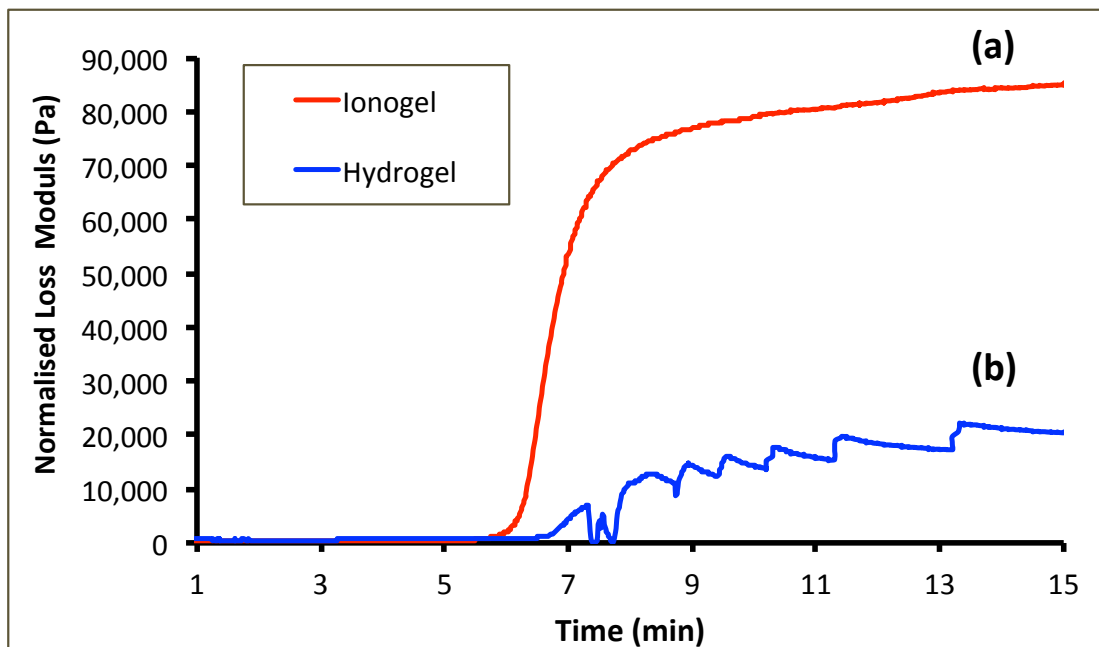
**Table S2:** Summary of the actuation behavior of both gel templates recorded using the digital micrometer. Here the % changes are expressed after the swelling and LCST phase transition behavior, respectively.

## VIII: Thermal Behavior



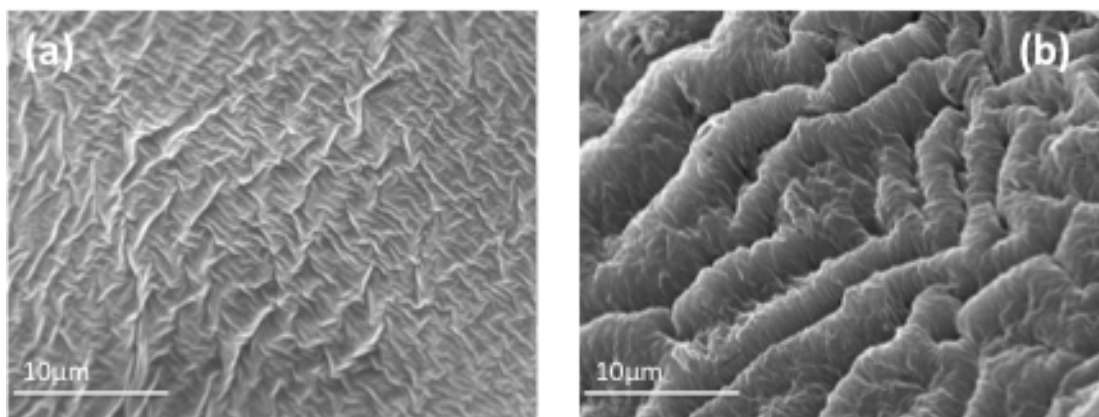
**Figure S7:** DSC temperature profiles obtained for the pNIPAAm LCST transition of Ionogel (26 °C) and Hydrogel (31 °C).

## IX: Mechanical data

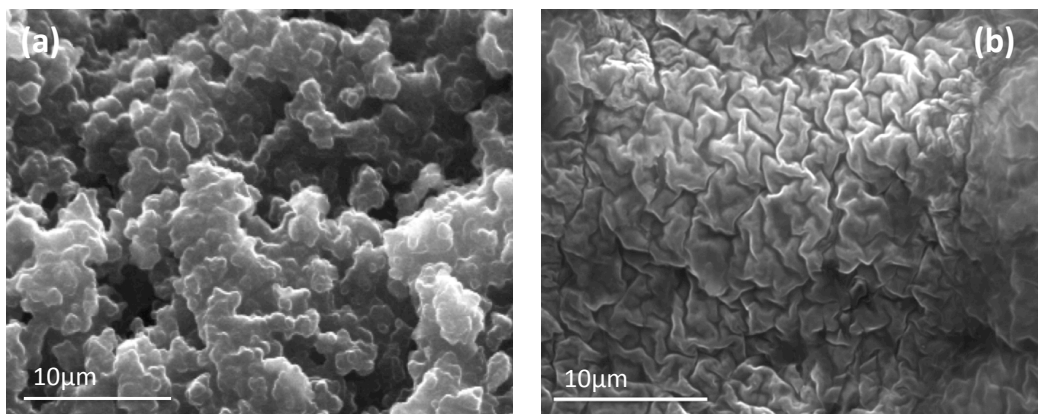


**Figure S8:** Loss moduli as a function of LCST phase transition for (a) [C<sub>2</sub>mIm][EtSO<sub>4</sub>] Ionogel and (b) hydrogel (heated from 20°C to 45°C @ 20°C / min, starting after 5 minutes).

## X: SEM

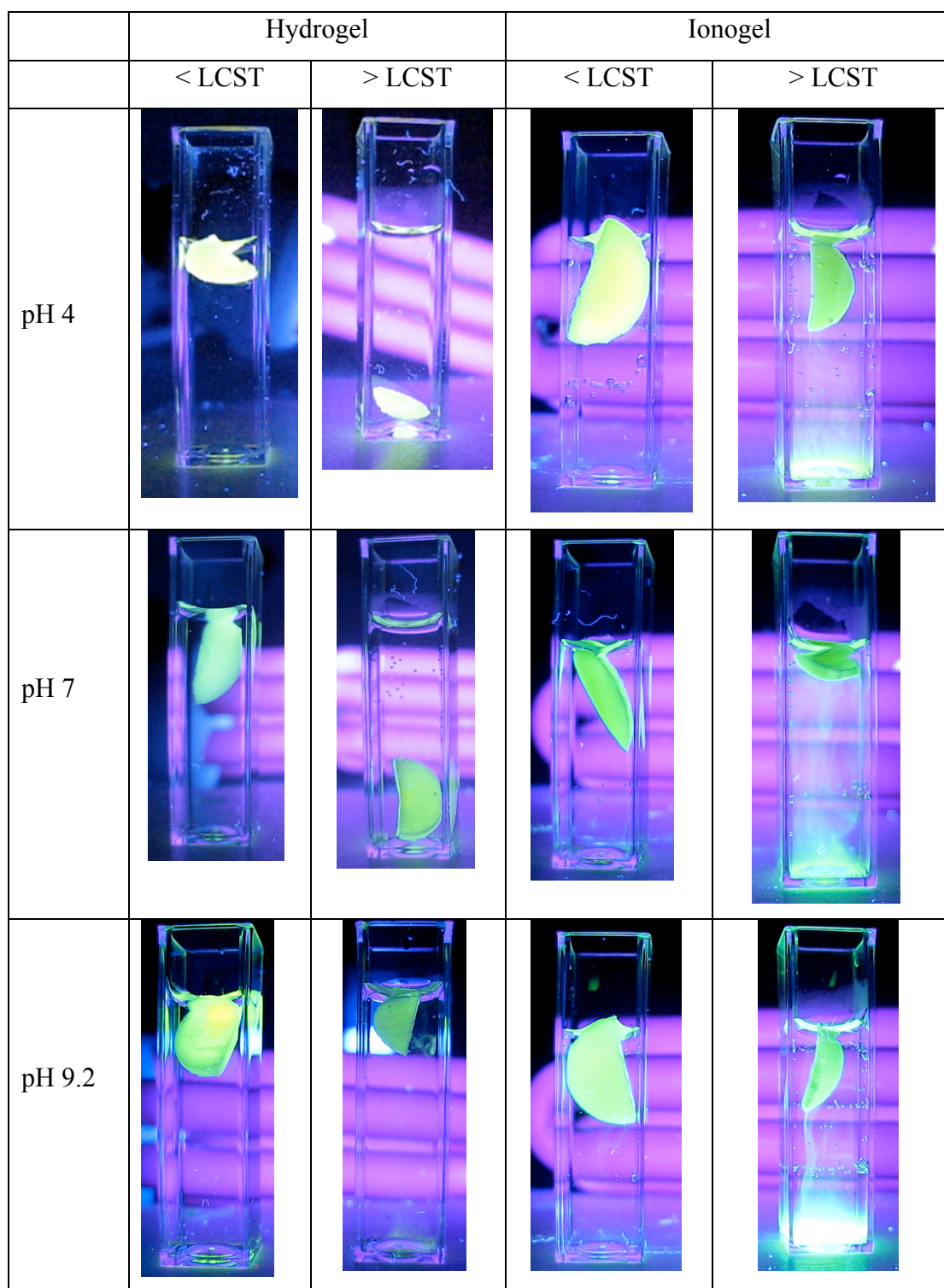


**Figure S9:** SEM Images of pNIPAAm control hydrogel, (a) after polymerisation (non-hydrated) and (b) after hydration in de-ionised water for 24 hours.



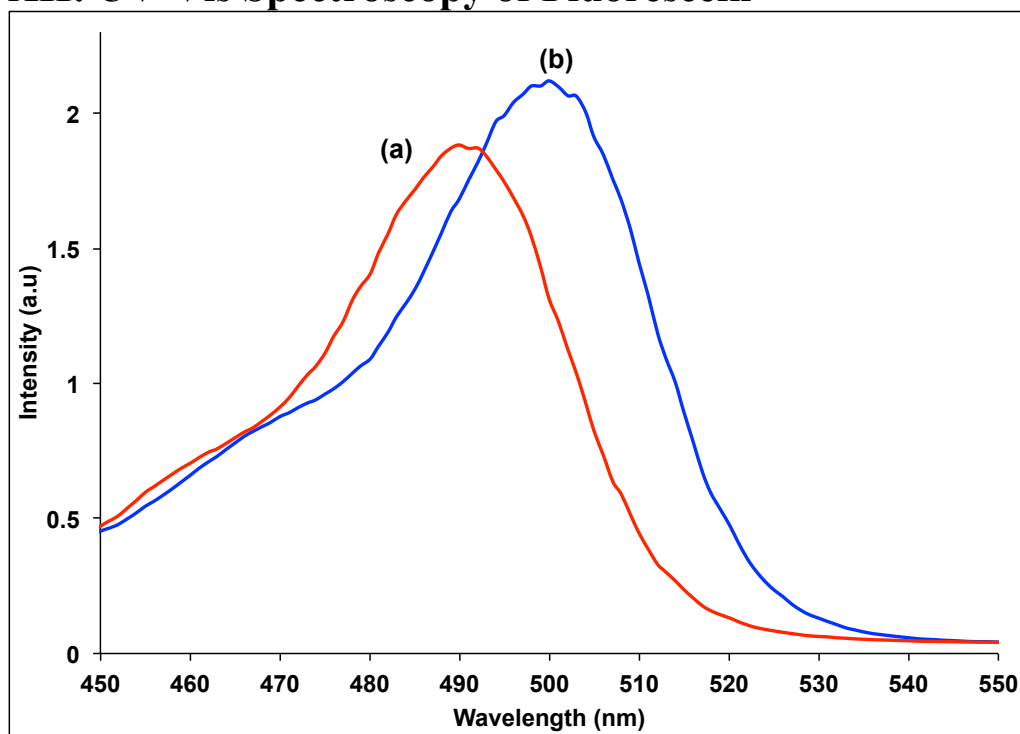
**Figure S10:** Scanning Electron Microscopy images of (a) Ionogel after polymerisation (non-hydrated) and (b) after hydration in de-ionised water for 24 hours.

## XI: Video Details

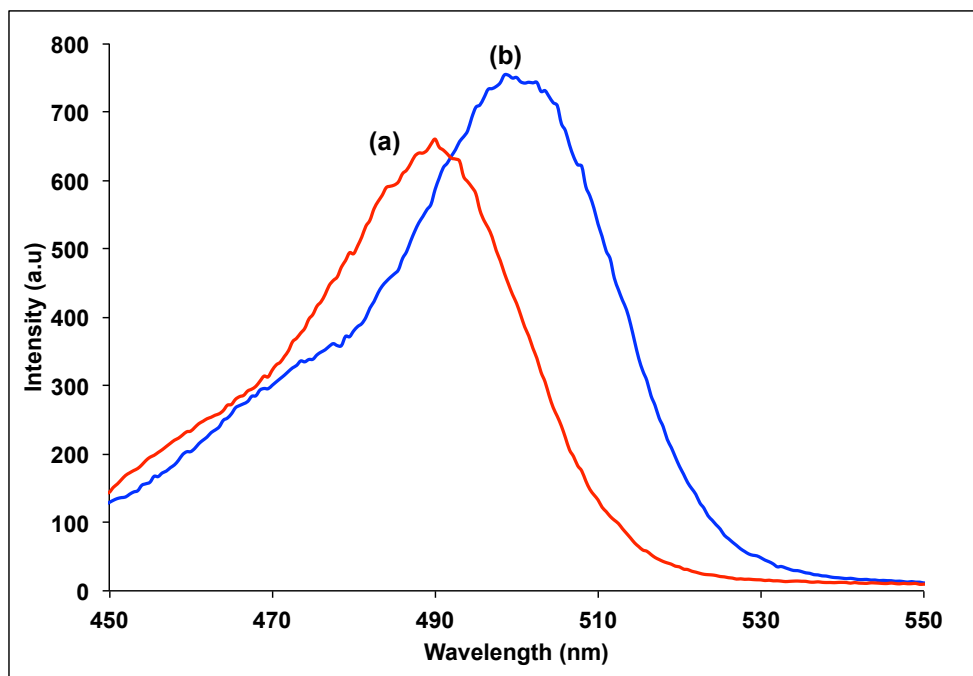


**Fig S11:** Video capture of release of fluorescein from free-standing hydrogel and Ionogel membranes after 1 min, at pH 4.0, 7.0 and 9.2, for  $T < LCST$  (20 °C) and  $T > LCST$  (40 °C). The full videos can be viewed at: <http://tinyurl.com/bhnrfo> (Hydrogel) and <http://tinyurl.com/bha479p> (Ionogel).

## XII: UV-Vis Spectroscopy of Fluorescein



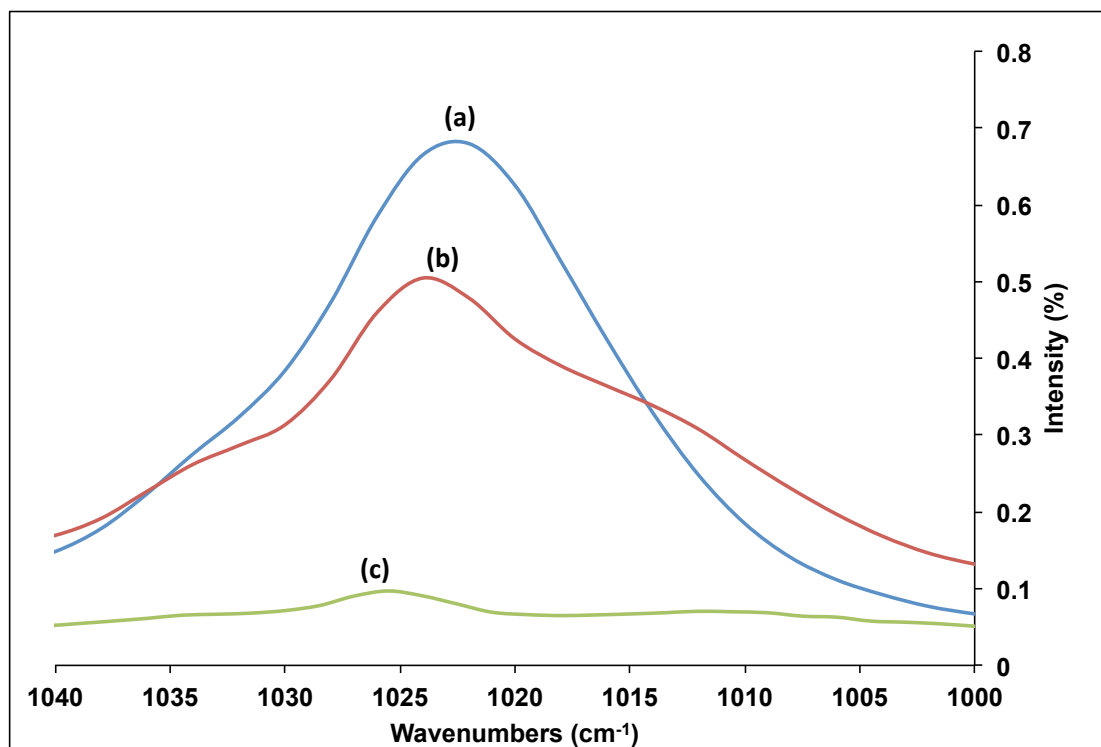
**Figure S12:** Absorbance spectra of fluorescein in (a) pH 7 buffer and (b) (1:1, v/v) IL/pH 7 buffer mixture.



**Figure S13:** Absorbance spectra of fluorescein in (a) pH 9.2 buffer and (b) (1:1, v/v) IL/pH 9.2 buffer mixture.

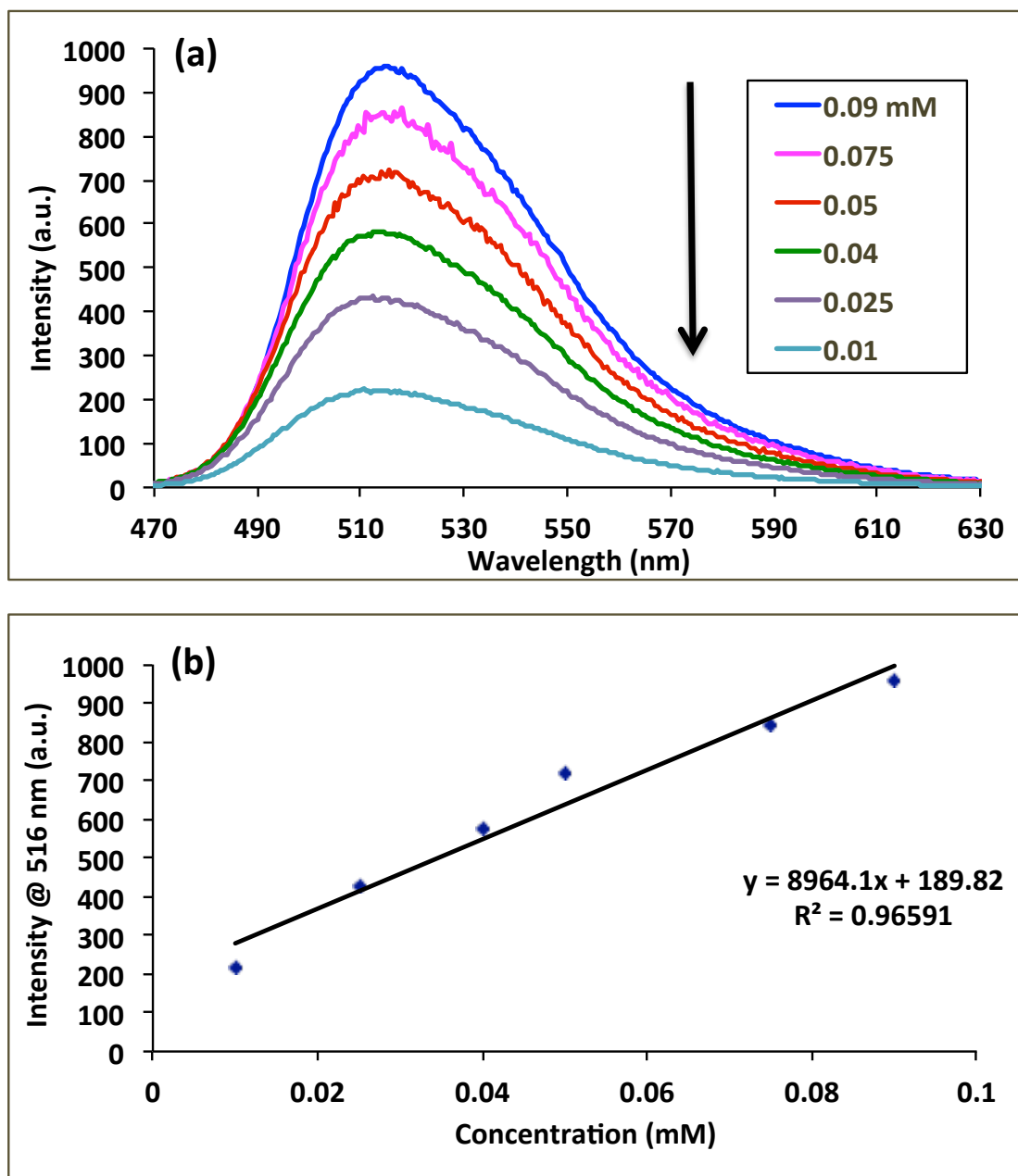


### XIII: Raman Spectroscopy

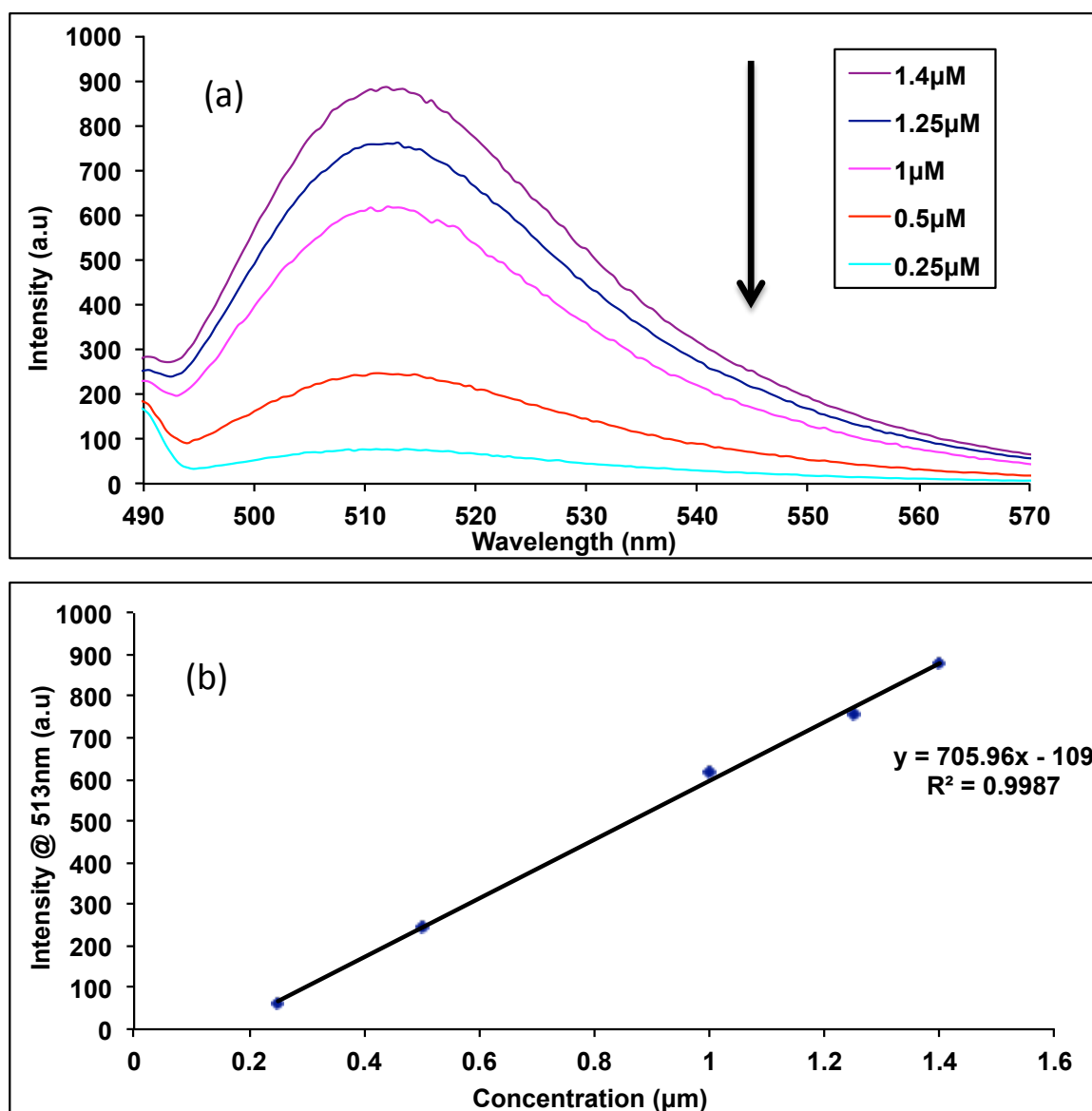


**Figure S14:** Raman spectra of symmetrical  $-\text{SO}_3^-$  stretch found in (a)  $[\text{C}_2\text{mIm}][\text{EtSO}_4]$ , (b) a 1:1 (v/v) IL at pH 4 containing Fluorescein and (c) a sample of the solution expelled from the ionogel above the LCST <sup>5</sup>.

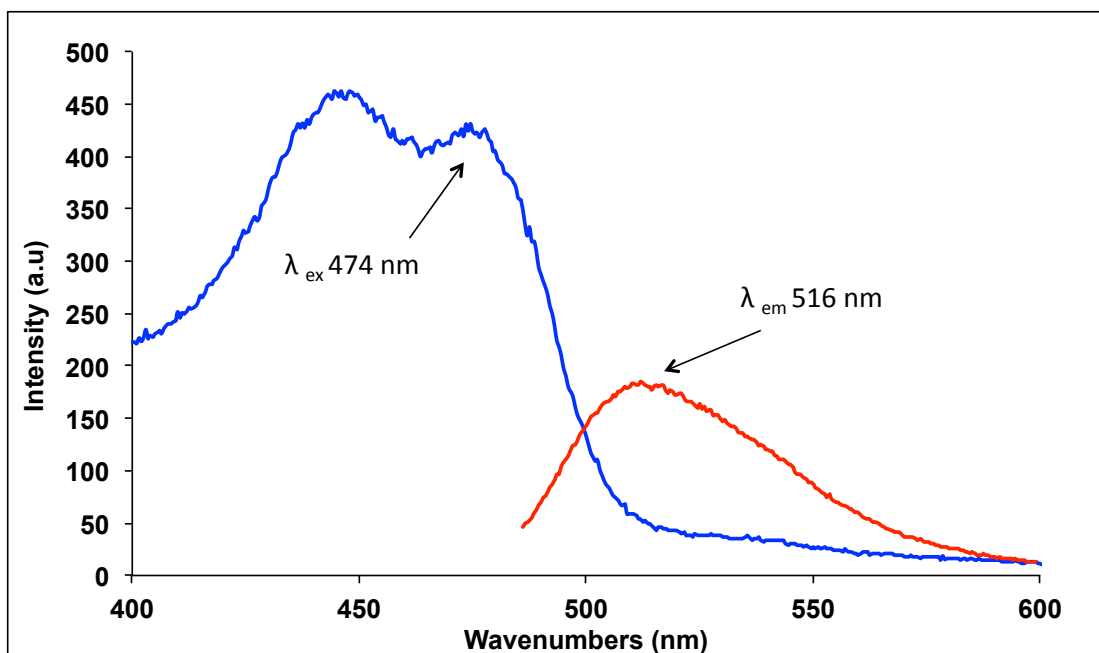
## XIV: Fluorescence spectroscopy.



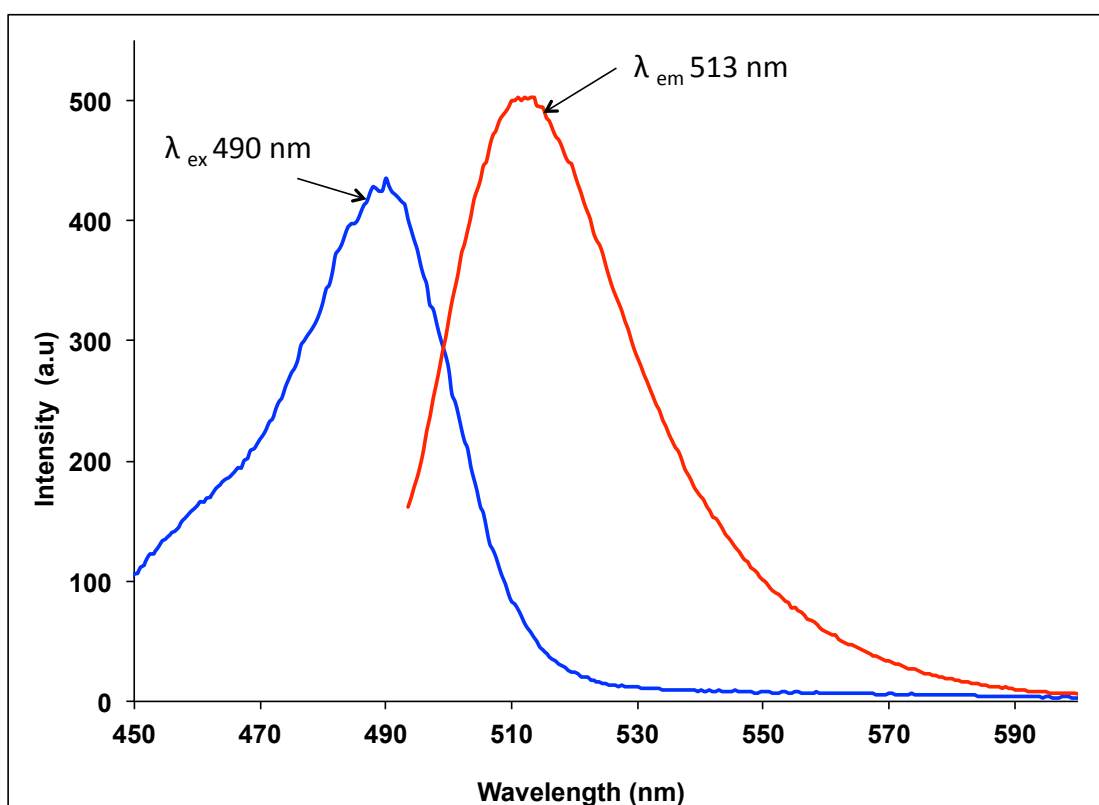
**Figure S15:** (a) Emission spectra of 0.01 – 0.09 mM fluorescein in pH 4 buffer solution (excitation wavelength = 460 nm) and, (b) the calibration plot, taken at emission wavelength = 516 nm.



**Figure S16:** (a) Emission spectra of 0.25 – 1.4 μM fluorescein in pH 7 buffer solution (excitation wavelength = 490 nm) and, (b) the calibration plot, taken at emission wavelength = 513 nm.



**Figure S17:** Excitation and emission spectra for fluorescein obtained from the bathing solution for the ionogel membrane at pH 4 ( $T > LCST$ ) after 1 min.



**Figure S18:** Excitation and emission spectra obtained for fluorescein obtained from the bathing solution for the ionogel membrane at pH 7 ( $T > LCST$ ) after 1 min. pH 9.2 yielded the same excitation and emission values. Spectra not shown for clarity.

**Table S3:** Concentration of released fluorescein (mM) for free standing Hydrogel and Ionogel membranes (n = 3) above the LCST (40 °C). Standard deviation is presented in brackets.

	pH 4	pH 7	pH 9.2
Hydrogel			
1	-	0.0082	0.1981
2	-	0.0082	0.1971
3	-	0.0081	0.1957
<b>Average</b>	-	<b>0.0082</b> <b>(4.97 x 10<sup>-5</sup>)</b>	<b>0.1970</b> <b>(1.20 x 10<sup>-3</sup>)</b>
Ionogel			
1	0.3025	0.3329	0.4845
2	0.3025	0.3616	0.5589
3	0.3020	0.3584	0.5712
<b>Average</b>	<b>0.3023</b> <b>(2.96 x 10<sup>-4</sup>)</b>	<b>0.3510</b> <b>(1.57 x 10<sup>-2</sup>)</b>	<b>0.5382</b> <b>(4.49 x 10<sup>-2</sup>)</b>

## XV: References

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