Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic and Assembly Properties of a Water-Soluble Blue Naphthalene Diimide Supplementary Information

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1. General Methods and Materials

Materials: All materials were purchased from Sigma Aldrich and used without modification with the exception of 1,4,5,8-naphthalenetetracarboxylic dianhydride which was purified following the procedure outlined in the experimental section, page S5.

Nuclear Magnetic Resonance (NMR): ^{1}H and ^{13}C spectra were recorded on a Bruker Avance-400 MHz spectrometer at 298 K. Chemical shifts are reported in parts per million (ppm). Multiplicities are reported as: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), multiplet (m), quartet (q), and broad (br).

Cyclic Voltammetry (CV): Electrochemical measurements used an Emstat potentiostat. Measurements were performed in a 40 mL vial with a three-electrode setup. Aqueous (^{i}PrNH)$_2$NDI–V solution (5 mL, 0.25 mg/mL) was placed into a 40 mL vial and the pH was adjusted to the required pH using 1 M HCl and 1 M NaOH. A supporting electrolyte of 0.1 M NaCl at 40% v/v concentration was also used. A glassy carbon disk electrode was used as the working electrode, with a platinum wire as the counter electrode, and Ag/AgCl reference electrode. Measurements were also performed using dichloromethane (^{i}PrNH)$_2$NDI–V solution (5 mL, 0.5 mg/mL) with a supporting electrolyte of 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) with $Ag/AgNO_3$ reference electrode. Electrochemical solutions were purged with N_2 for 5 minutes to deoxygenate the system. The ionization potentials (IP) and electron affinities (EA) were estimated by correlating the oxidation and reduction onsets to the normal hydrogen electrode (NHE), assuming the IP of Fc/Fc^{+} to be 4.80 eV.[1]

UV-Visible Absorption and Emission Spectroscopy (UV/Vis): UV/Vis absorption spectroscopy was carried out using an Agilent Technologies Cary 60 UV-Visible spectrophotometer. UV/Vis emission spectroscopy was carried out using an Agilent Technologies Cary Eclipse fluorescence spectrophotometer. All measurements were recorded at room temperature. Solution UV/Vis experiments run in aqueous solution were done using 40% v/v 0.1 M NaCl adjusted to the required pH using 1 M HCl and 1 M NaOH as a solvent. Absorption measurements were performed using 2 mm quartz cuvettes and emission measurements were performed using 10 mm quartz cuvettes.

Photoluminescence Quantum Yield Determination: The photoluminescence quantum yield (PL QY) of compounds were estimated by using the comparative method proposed by Williams et. al.[2] after slight modification as follows:

$$Q_x = Q_R \frac{A_R F_X}{A_X F_R}\left(\frac{\eta_X}{\eta_R}\right)^2$$

where Q is the PL QY, A is the absorbance of the solution, F is the corrected PL emission intensity, and η is the refractive index of the solution. Subscripts R and X refer to the standard and sample compounds, respectively. Cresyl violet perchlorate[3] (QY 0.56) was used as the reference standard for (^{i}PrNH)$_2$NDI–V in water at pH 10 and in dichloromethane (DCM) and rhodamine B[3] (QY 0.7) was used as the standard for (^{i}PrNH)$_2$NDI–V in DCM with 2.5% v/v trifluoroacetic acid (TFA). To minimize reabsorption effects, the absorbance maxima values of the standard and sample solutions were controlled to be less than 0.1. An excitation wavelength of 550 nm was chosen for

cresyl violet and (^{i}PrNH)$_2$NDI–V in water and DCM and 510 nm was chosen for rhodamine B and (^{i}PrNH)$_2$NDI–V in DCM with 2.5% v/v TFA. Absorption and PL spectra were recorded in ethanol (η = 1.3614) for cresyl violet, methanol (η = 1.3284) for rhodamine B and water at pH 10 (η = 1.3330), DCM (η = 1.4244), and DCM with 2.5% v/v TFA (η = 1.421)[4] for (^{i}PrNH)$_2$NDI–V.

Gelators: Full synthetic details for the 1-ThNap-FF gelator can be found in the literature.[5] All other chemicals were purchased from Sigma Aldrich, Alfa, TCI and Fluorochem.

Stock Solutions: Stock solutions of the gelators 1-ThNap-FF and (^{i}PrNH)$_2$NDI–V (5 or 10 mg/mL) were prepared in Falcon Tubes by suspending 60 mg of material in deionised water and adding 1 M sodium hydroxide solution (one equivalent for 1-ThNap-FF, two equivalents for (^{i}PrNH)$_2$NDI–V) such that the final volume was 6 mL or 12 mL depending on the desired concentration. The solutions were stirred overnight to allow complete dissolution of the material. Next, the pH of each solution was measured and adjusted, if needed, to pH 11 ± 0.1 with either 1 M NaOH or 1 M HCl. For SANS measurements solutions were prepared as described above, with the H_2O and NaOH replaced with D_2O and NaOD.

Gels: Gel samples were prepared in Sterilin vials by the addition of 2 mL of the desired stock solution stock solution to 20 mg of glucono-δ-lactone (GdL). For single component gels the 5 mg/mL 1-ThNap-FF stock solution was used and for the multicomponent gels 1 mL of 10 mg/mL 1-ThNap-FF solution and 1 mL of 10 mg/mL (^{i}PrNH)$_2$NDI–V solution were combined and mixed immediately prior to adding to GdL. The gel solutions were gently shaken three times by hand to ensure complete dissolution of GdL and left to stand quiescently overnight. Rheology data was collected 18 hours after the addition of GdL. For SANS measurements gel samples were prepared with the deuterated gelator solutions and GdL.

pH Measurements: pH measurements were performed using a FC200 pH probe (HANNA Instruments) with a 6 mm x 10 mm conical tip. The accuracy of the pH measurements is quoted as ± 0.1. For monitoring the pH of gelation over time, 2 mL of gelator solution were added to GdL in a Sterilin vial and immersed in a water bath at a controlled temperature. The probe tip was then inserted into the gel with parafilm used to seal the top of the vial/tip. The pH measurements were recorded every 30 seconds for 16 hours until gelation was complete and pH had stabilised.

Rheology: Rheological measurements were carried out using Anton Paar Physica MCR301 and M101 Rheometers. For the frequency and strain sweeps, a cup and vane (ST10-4V8.8/97.5-SN42404) system, with a measuring gap of 1.8 mm at 25°C, was used so that measurements could be directly performed in the 7 mL Sterilin vials. These measurements were performed in triplicate. The average was plotted with error bars calculated by standard deviation.

Frequency sweeps were performed from 1 rad/s to 100 rad/s at a constant strain of 0.5%.

Strain sweeps were performed from 0.1% to 1000% at a frequency of 10 rad/s. This method ensured that 0.5% strain was in the viscoelastic region required for measuring the frequency sweep.

For the time-sweep measurements 2 mL of the stock solutions were added to predetermined masses of GdL. The vial was gently swirled to ensure the complete dissolution of GdL. Next, approximately 1 mL of the gelling solution was poured on the rheometer flat plate and the plate

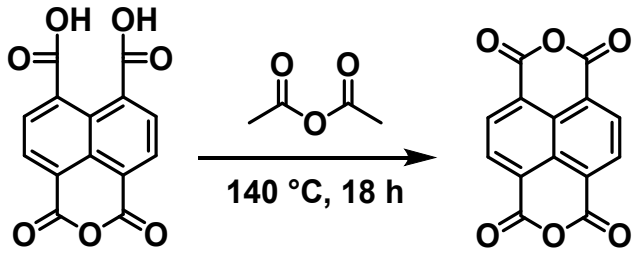
was lowered on top of the solution. The plate was then flooded with mineral oil to prevent evaporation. Time sweep measurements were performed at 25°C using a using a 25 mm sandblasted parallel plate and a measuring gap of 0.9 mm. A constant frequency of 10 rad/s and a strain of 0.5% were applied and the normal force was set to 0 N. The storage modulus (G') and loss modulus (G") were measured over 16 hours.

Small Angle Neutron Scattering (SANS): The solutions were prepared as described above. Samples at low pH were measured in UV spectrophotometer grade quartz cuvettes (Hellma) with a 2 mm path length. These were placed in a temperature-controlled sample rack during the measurements. SANS measurements were performed using the D11 instrument (Institut Laue Langevin, Grenoble, France). A neutron beam, with a fixed wavelength of 6 Å and a divergence of $\Delta\lambda/\lambda = 9\%$, allowed measurements over a large range in Q [$Q = 4\pi\sin(\theta/2)/\lambda$] range of 0.001 to 0.3 $Å^{-1}$, by using three sample-detector distances of 2 m (Coll 4 m), 8 m (Coll 8 m) and 28 m (Coll 28 m).

The data were reduced to 1D scattering curves of intensity vs. Q using Mantid. The electronic background was subtracted, the full detector images for all data were normalized and scattering from the empty cell was subtracted. The scattering from D_2O was also measured and subtracted from the data. Most of the data were radially averaged to produce the 1D curves for each detector position. The instrument-independent data were then fitted to the models discussed in the text using the SasView software package version.[5,6] Fitting parameters are given in Table S1. Data can be found at doi.10.5291/ILL-DATA.9-10-1670.

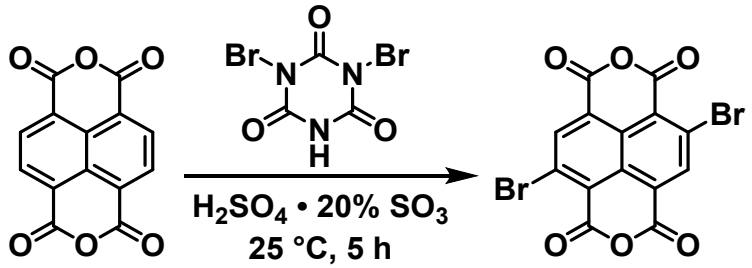
2. Synthetic Procedures

Purification of NTCDA:



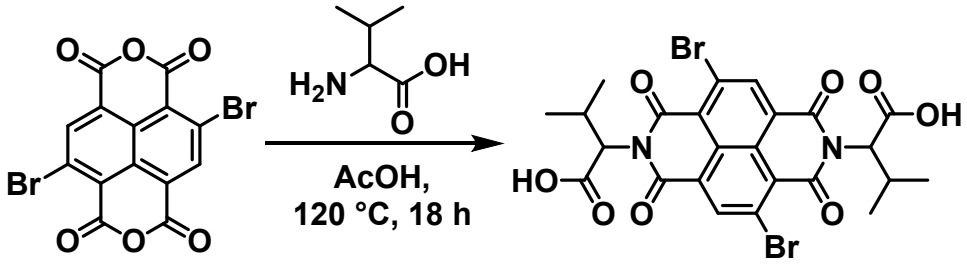
In a 500 mL round bottom flask 21 g of impure NTCDA was suspended in 250 mL acetic anhydride and heated at 140 °C overnight forming a dark brown mixture. The mixture was then vacuum filtered to obtain a brown powder, rinsing with diethyl ether to remove the acetic anhydride. The brown powder was then recrystallized from dimethylformamide to obtain a white powder (12 g, 57% recovery).

Synthesis of Br_2NTCDA:



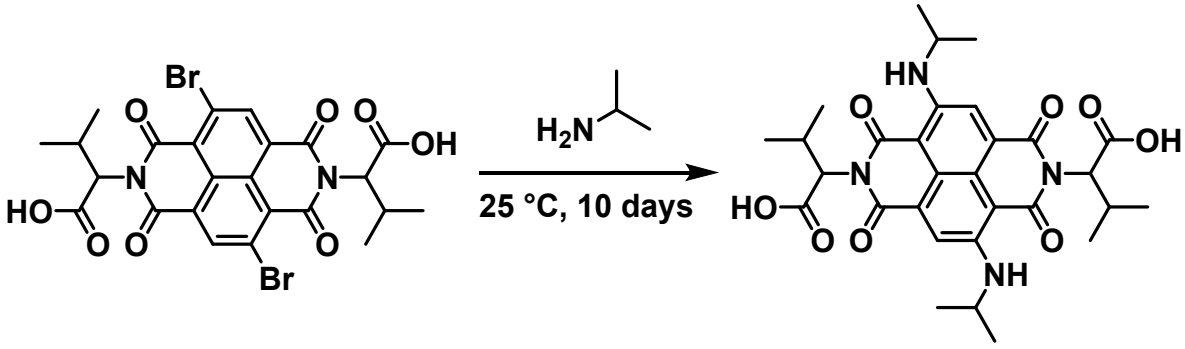
In a 250 mL round bottom flask purified NTCDA (2.68 g, 10.0 mmol, 1.0 eq.) was suspended in 100 mL of fuming H_2SO_4 (20% SO_3). A solution of dibromoisocyanuric acid (2.86 g, 10.0 mmol, 1.0 eq.) was prepared in 50 mL of fuming H_2SO_4 (20% SO_3) and transferred to an addition funnel and then slowly added to the NTCDA suspension over 5 hours. Once the addition was complete the mixture was left to react for one hour and then it was poured over 400 g of ice causing a yellow precipitate to form. The mixture was diluted to 1.5 L with water and left to sit overnight to allow fumes to dissipate. The yellow solid was then obtained *via* vacuum filtration, rinsing with water. The crude yellow solid was suspended in 200 mL of acetonitrile and refluxed for 5 hours. The mixture was then hot filtered to obtain the purified product as a yellow powder (1.22 g, 2.86 mmol, 29%). **^{1}H NMR (400 MHz, DMSO-d_6, ppm):** δ 8.79 (s, 2H).

Synthesis of Br_2NDI–V:



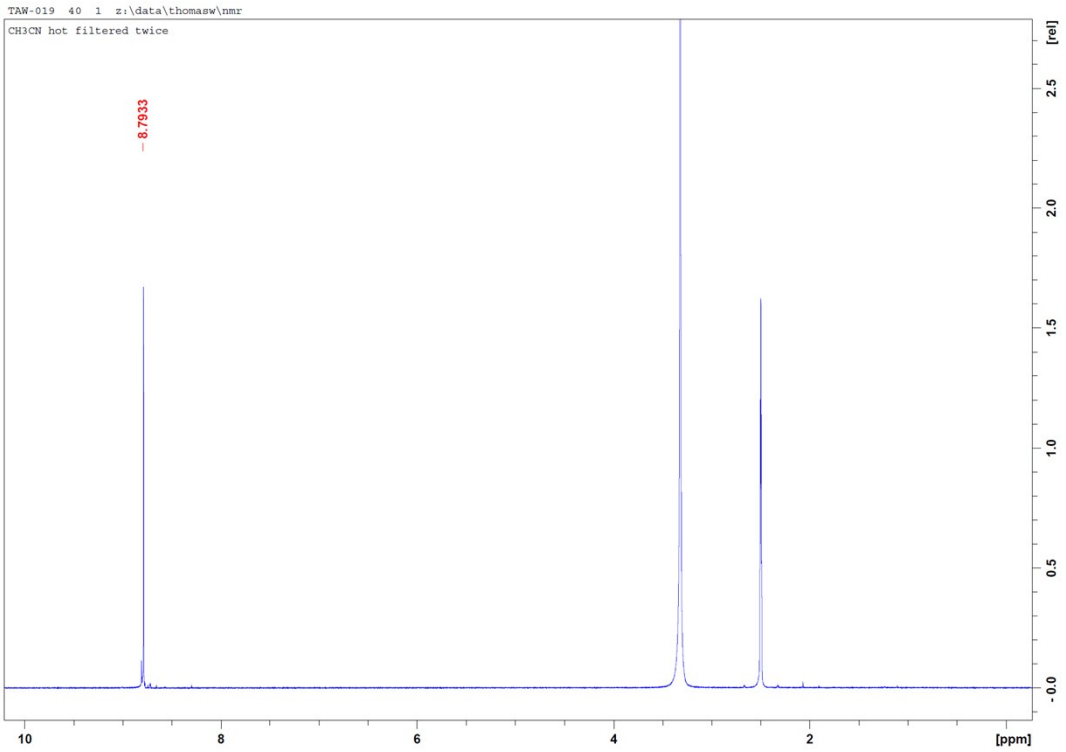
In a 50 mL Schlenk flask Br_2NTCDA (0.50 g, 1.2 mmol, 1.0 eq.) and valine (0.28 g, 2.4 mmol, 2.0 eq.) were combined and purged with N_2 for 15 minutes. Then 10 mL of glacial acetic acid were added and the mixture was heated at 120 °C overnight. After stirring overnight, the mixture was cooled to room temperature and then poured into 100 mL of water at 0 °C causing an orange solid to precipitate. The solid was isolated *via* vacuum filtration rinsing with water. The crude product was obtained as an orange solid (0.56 g, 0.90 mmol, 76%) and used without further purification. **^{1}H NMR (400 MHz, DMSO-d_6, ppm):** δ. 12.88 (br s, 2H), 8.83 (s, 2H), 5.17 (d, 2H, *J*=9.1 Hz), 2.67 (m, 2H), 1.23 (d, 6H, *J*=6.5 Hz), 0.75 (d, 6H, *J*=6.9 Hz); **^{13}C NMR (100 MHz, DMSO-d_6, ppm):** δ 169.9, 160.7, 160.5, 138.2, 128.0, 127.6, 124.9, 123.7, 58.9, 27.1, 22.0, 19.0.

Synthesis of (^{i}PrNH)$_2$NDI–V:

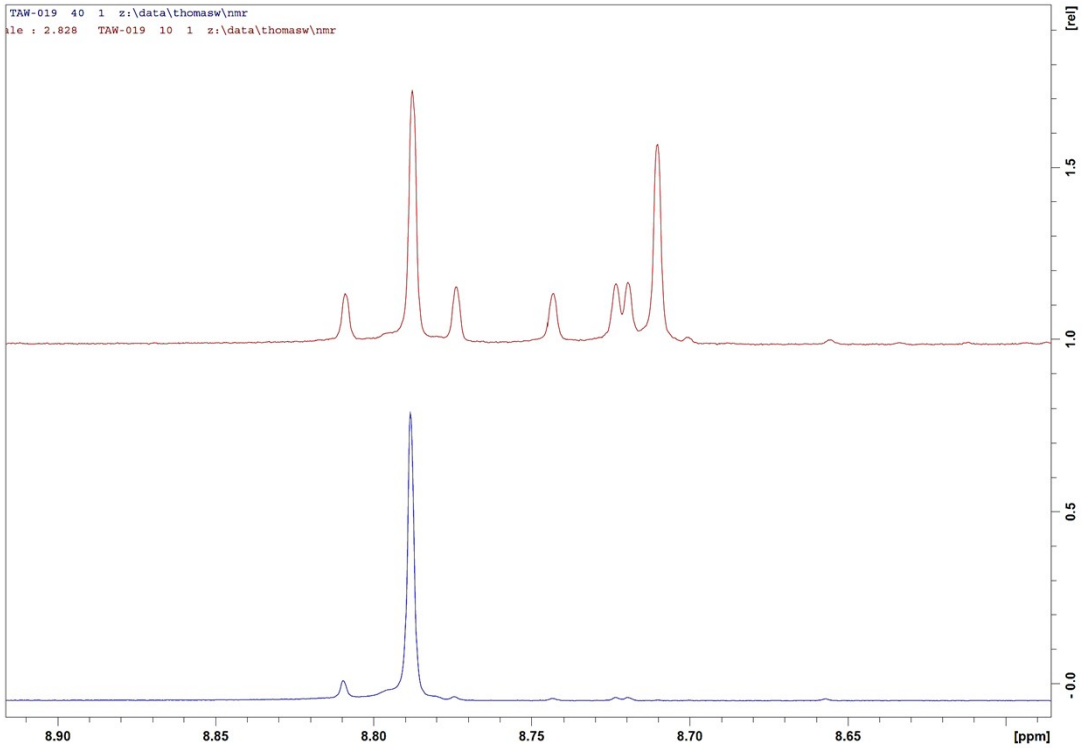


In a 250 mL round bottom flask, Br_2NDI-V (135 mg, 0.22 mmol) was dissolved in 25 mL of degassed isopropylamine forming a reddish mixture. This solution was left to react for 11 days, during which time it turned dark purple. The isopropylamine was removed *via* rotary evaporation and the resulting residue was precipitated with 1 M HCl solution and isolated *via* vacuum filtration. A dark blue solid was obtained and rinsed with water. The crude material was purified *via* column chromatography eluting with 98:2:0.5 CH_2Cl_2/MeOH/TFA solvent mixture. The final product was obtained as a blue solid (100 mg, 0.17 mmol, 80%). **^{1}H NMR (400 MHz, DMSO-d_6, ppm):** δ 12.65 (br s, 2H), 9.19 (d, 2H, *J*=7.5 Hz) 8.12 (s, 2H), 5.19 (d, 2H, *J*=7.3 Hz), 4.16 (m, 2H), 2.70 (m, 2H), 1.35 (d, 6H, *J*=6.2 Hz), 1.34 (d, 6H, *J*=6.3 Hz), 1.23 (2, 6H *J*=6.4 Hz), 0.69 (d, 6H, *J*=6.9 Hz); **^{13}C NMR (100 MHz, DMSO-d_6, ppm):** δ 170.5, 165.3, 162.0, 148.0, 125.1, 120.7, 118.9, 100.4, 57.9, 43.7, 26.8, 22.7, 22.2, 19.0; **HRMS (ESI):** *m/z* 603.2616 (M+Na), calcd. 580.6274.

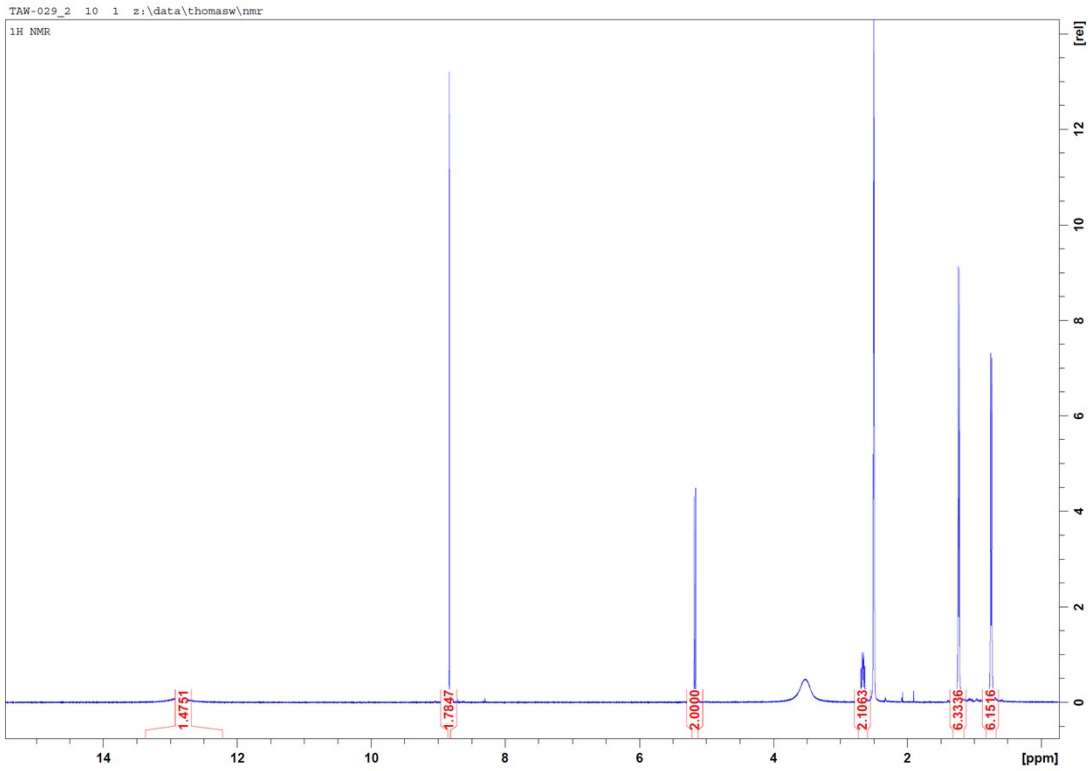
3. Supplementary Figures



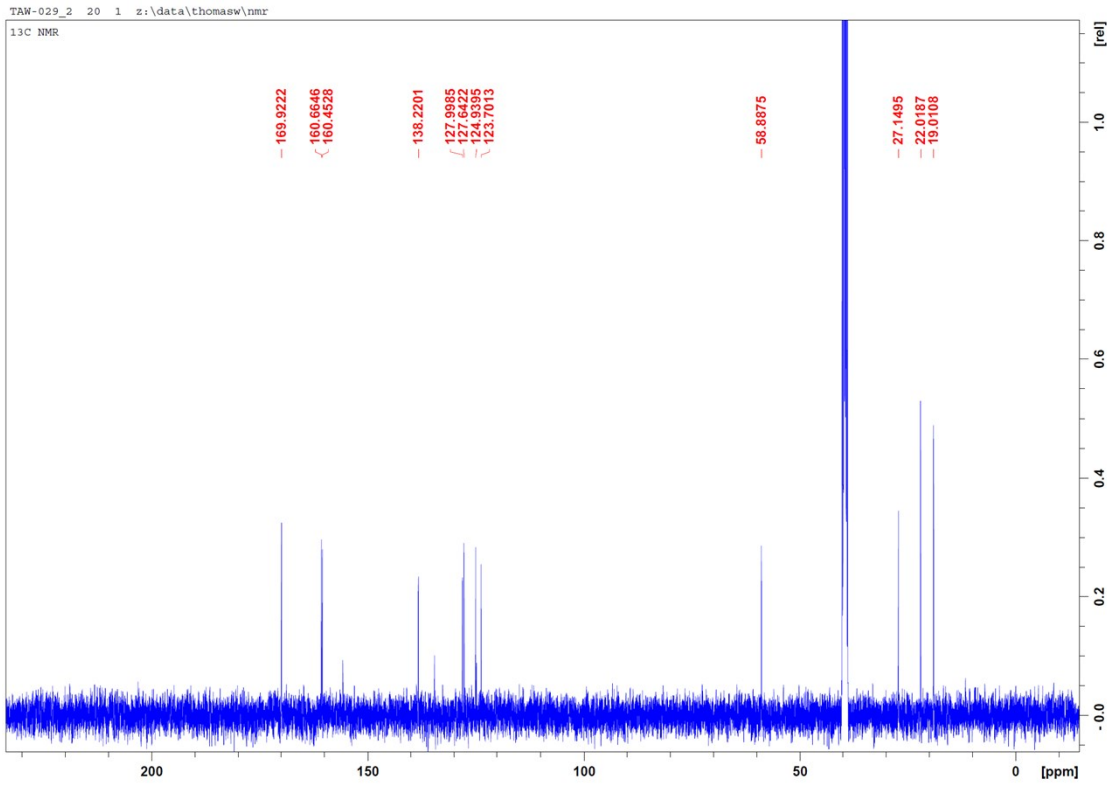
Figures S1: ^{1}H NMR spectrum of Br_2NTCDA in DMSO-d_6.



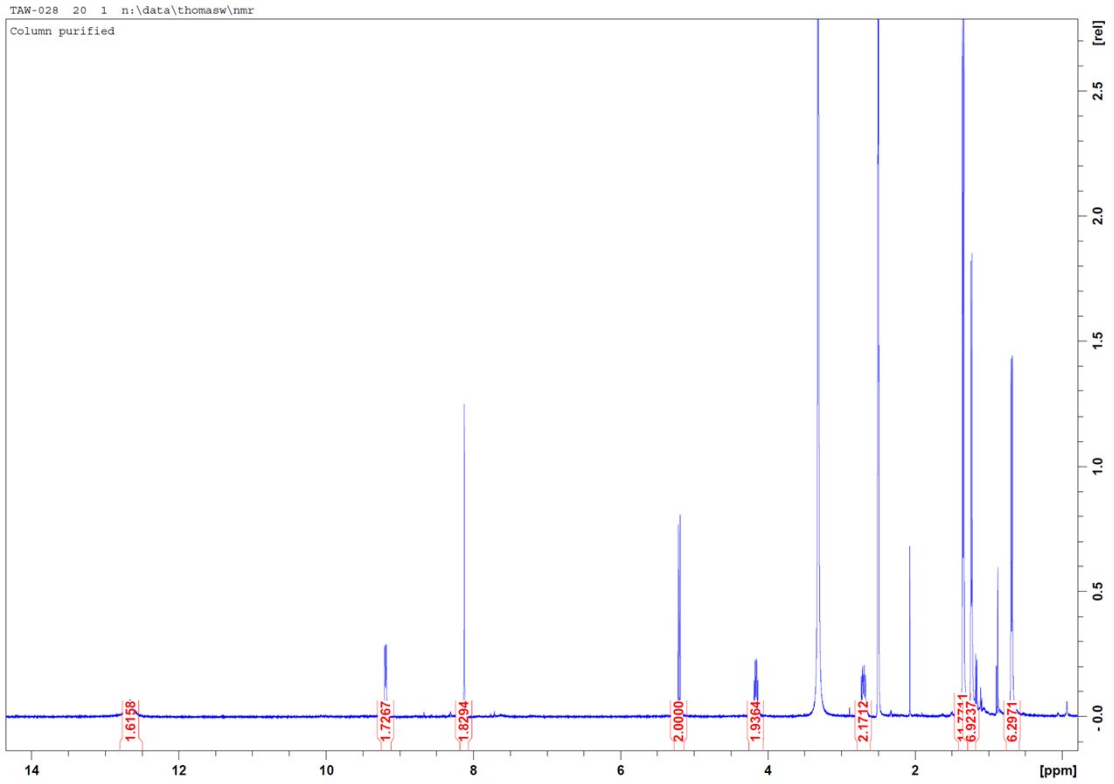
Figures S2: ^{1}H NMR spectrum of Br_2NTCDA in DMSO-d_6 before (top) and after (bottom) washing with acetonitrile.



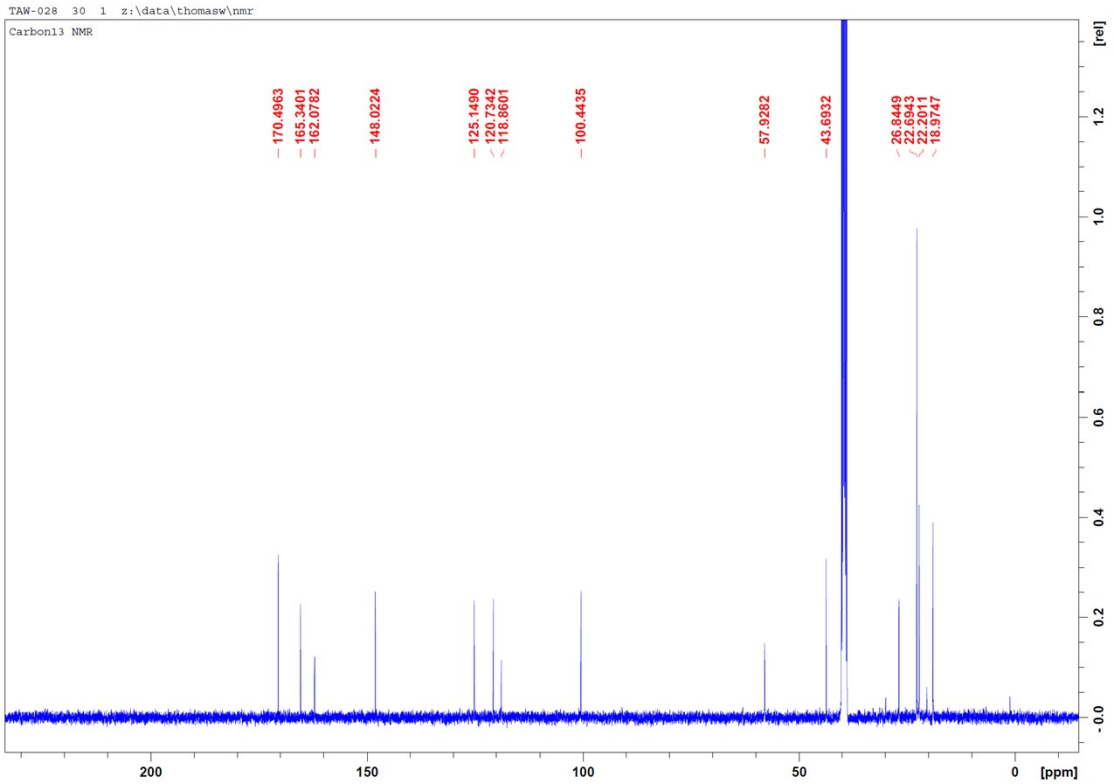
Figures S3: ^{1}H NMR spectrum of $Br_2NDI–V$ in DMSO-d_6.



Figures S4: ^{13}C NMR spectrum of $Br_2NDI–V$ in DMSO-d_6.



Figures S5: ^{1}H NMR spectrum of (^{i}PrNH)$_2$NDI–V in DMSO-d$_6$.



Figures S6: ^{13}C NMR spectrum of (^{i}PrNH)$_2$NDI–V in DMSO-d$_6$.

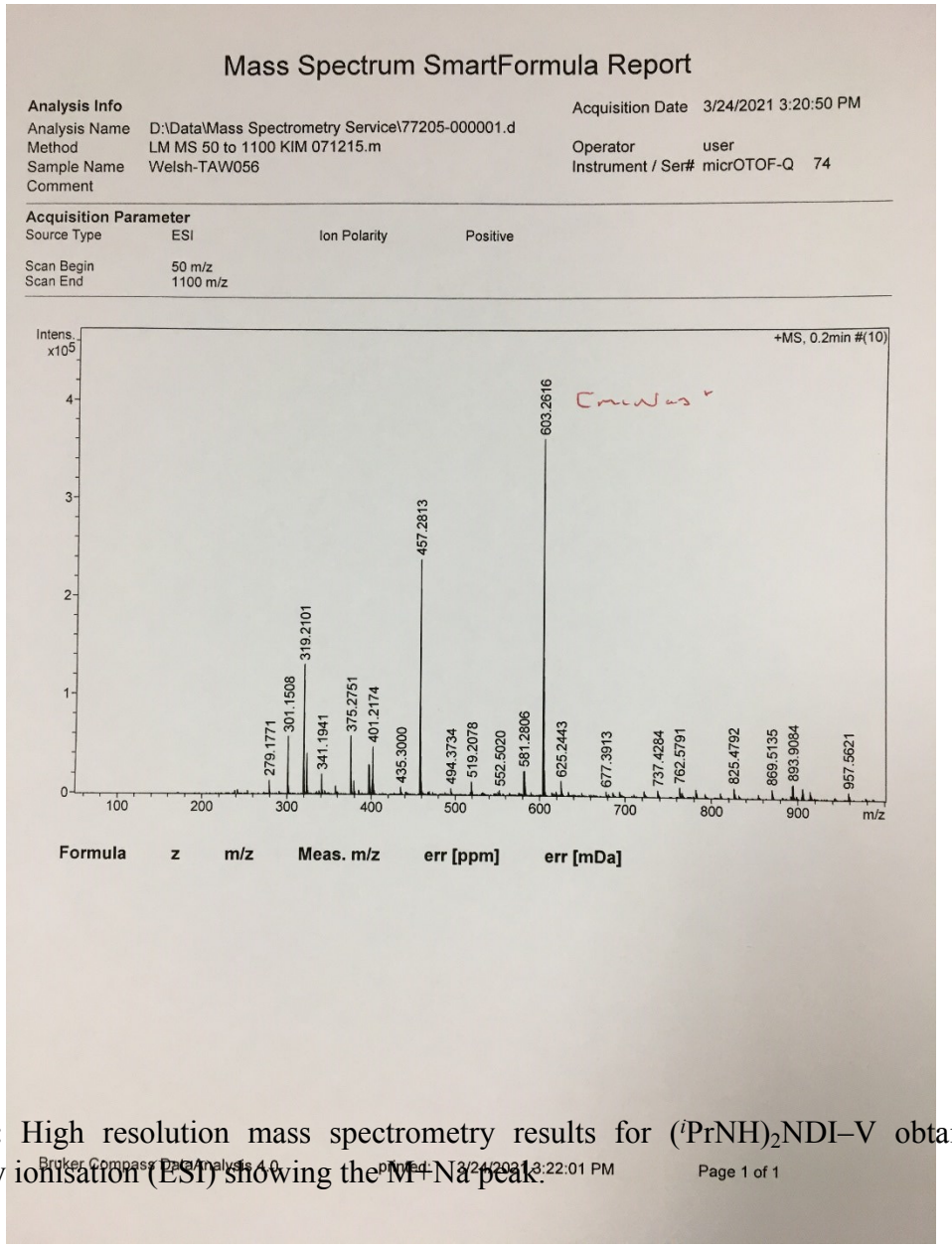


Figure S7: High resolution mass spectrometry results for (^{i}PrNH)$_2$NDI–V obtained using electrospray ionisation (ESI) showing the M+Na peak.

Cyclic Voltammetry

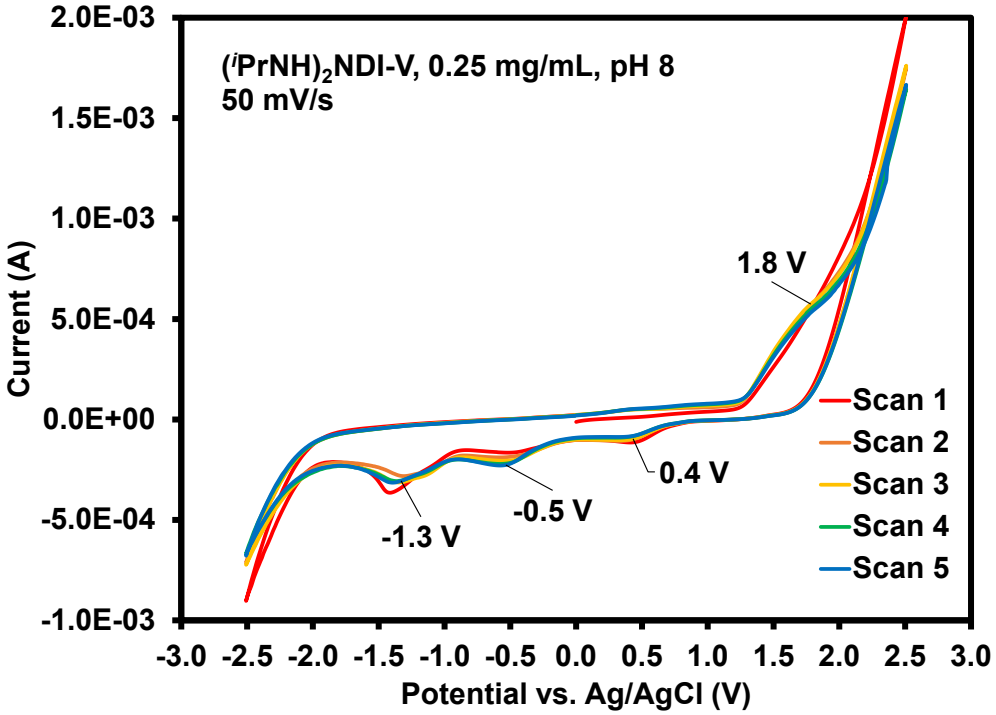


Figure S8: Cyclic voltammogram of (^{i}PrNH)$_2$NDI–V in water with 40% v/v 0.1 M NaCl as an electrolyte and pH adjusted to 8 with 1 M NaOH measured at 50 mV/s.

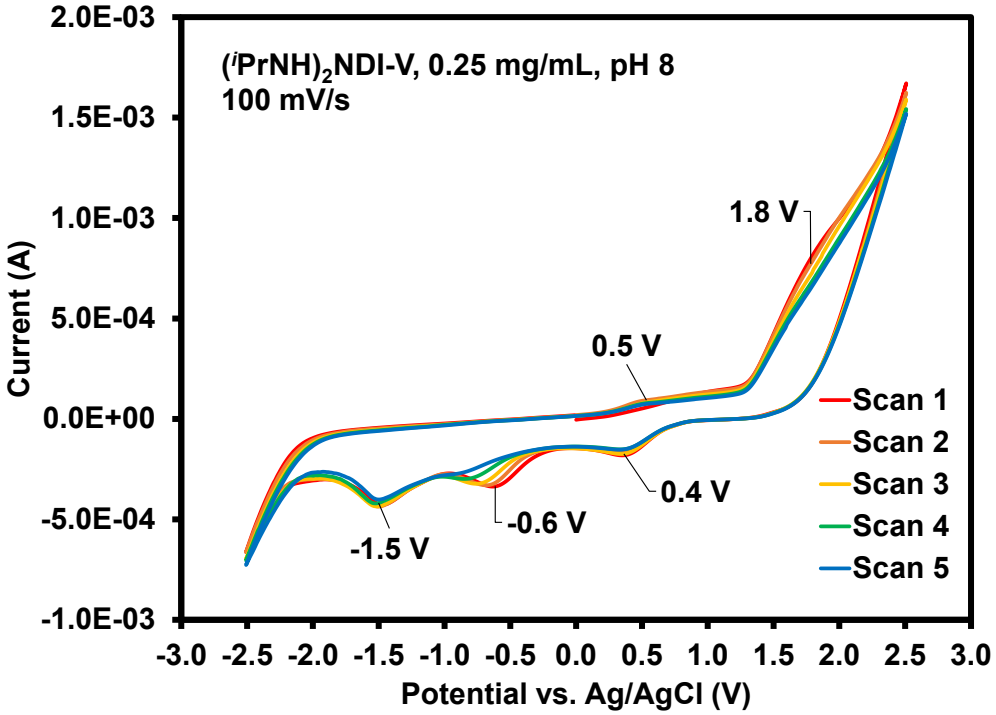


Figure S9: Cyclic voltammogram of (^{i}PrNH)$_2$NDI–V in water with 40% v/v 0.1 M NaCl as an electrolyte and pH-adjusted to 8 with 1 M NaOH measured at 100 mV/s.

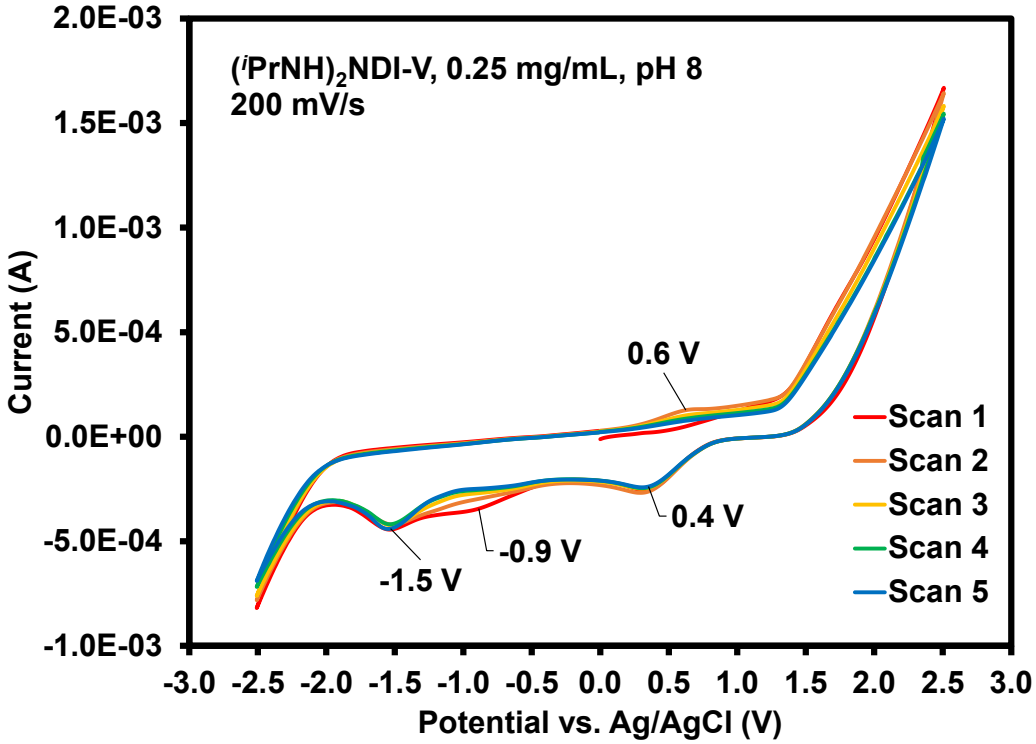


Figure S10: Cyclic voltammogram of (^{i}PrNH)$_2$NDI–V in water with 40% v/v 0.1 M NaCl as an electrolyte and pH-adjusted to 8 with 1 M NaOH measured at 200 mV/s.

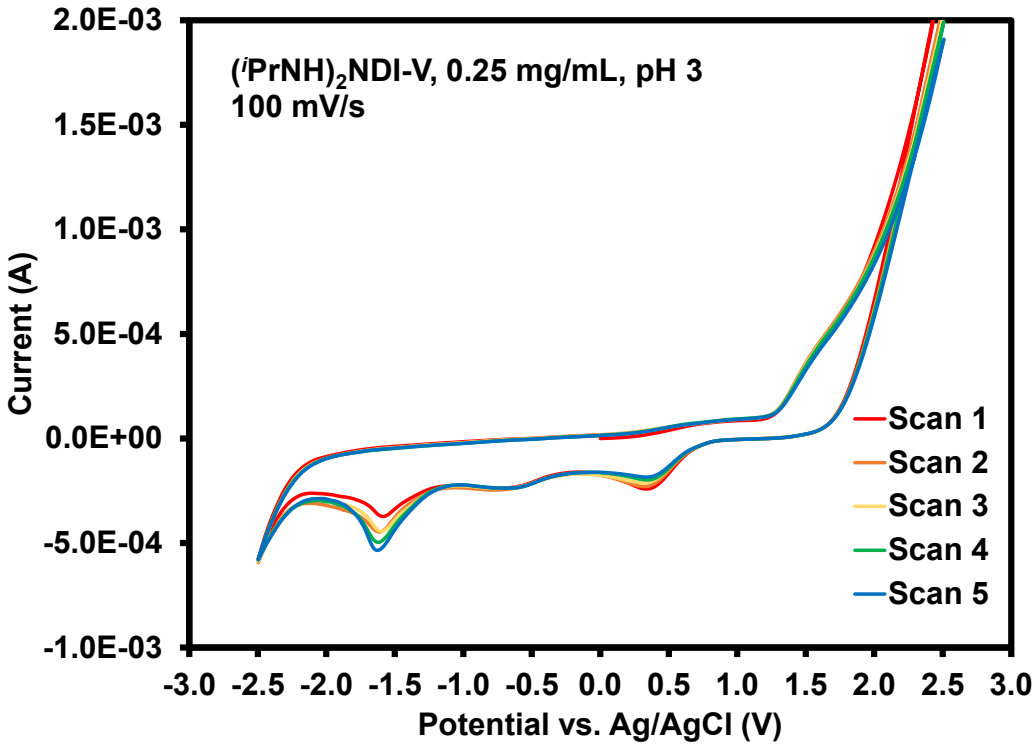


Figure S11: Cyclic voltammogram of (^{i}PrNH)$_2$NDI–V in water with 40% v/v 0.1 M NaCl as an electrolyte and pH-adjusted to 3 with 1 M HCl and 1 M NaOH measured at 100 mV/s.

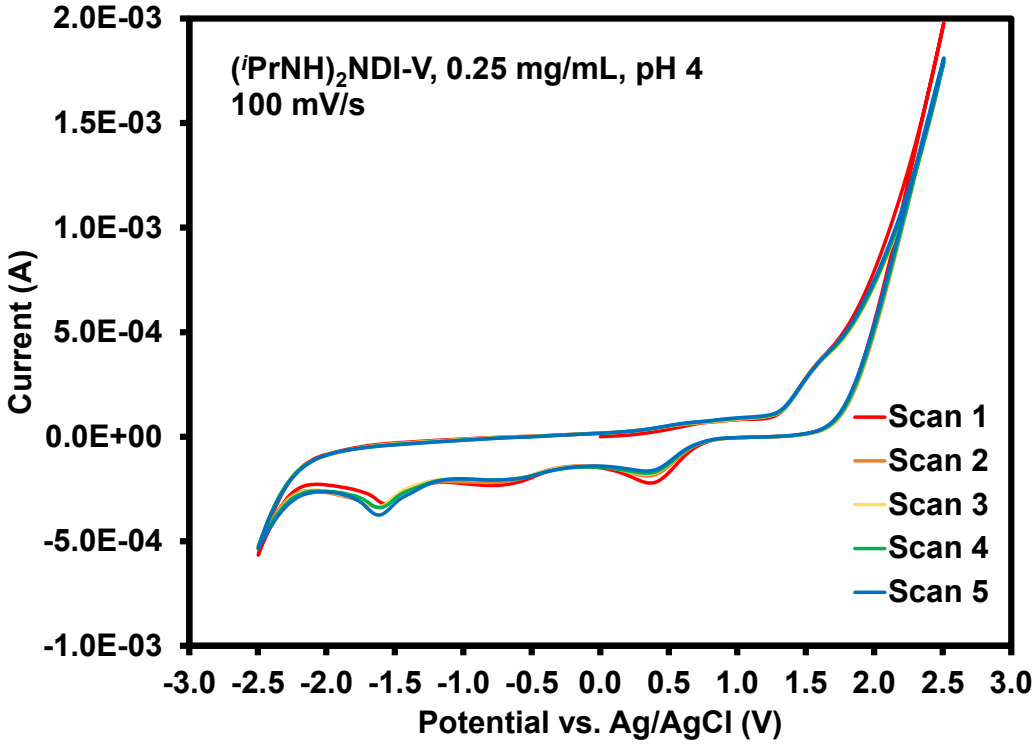


Figure S12: Cyclic voltammogram of (^{i}PrNH)$_2$NDI–V in water with 40% v/v 0.1 M NaCl as an electrolyte and pH-adjusted to 4 with 1 M HCl and 1 M NaOH measured at 100 mV/s.

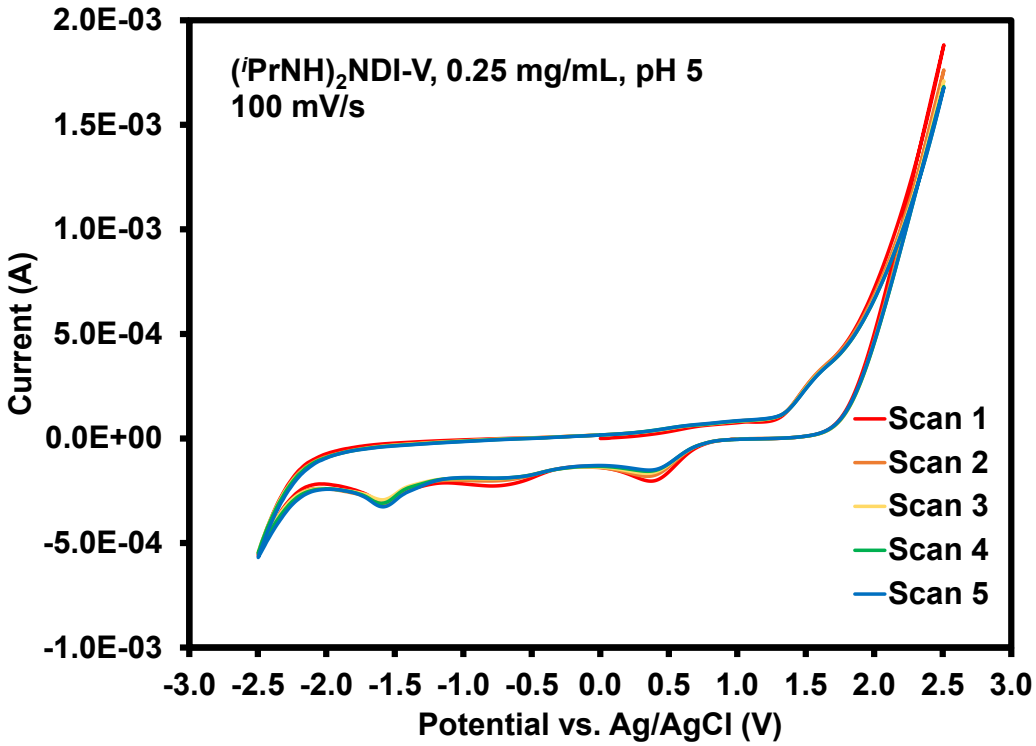


Figure S13: Cyclic voltammogram of (^{i}PrNH)$_2$NDI–V in water with 40% v/v 0.1 M NaCl as an electrolyte and pH-adjusted to 5 with 1 M HCl and 1 M NaOH measured at 100 mV/s.

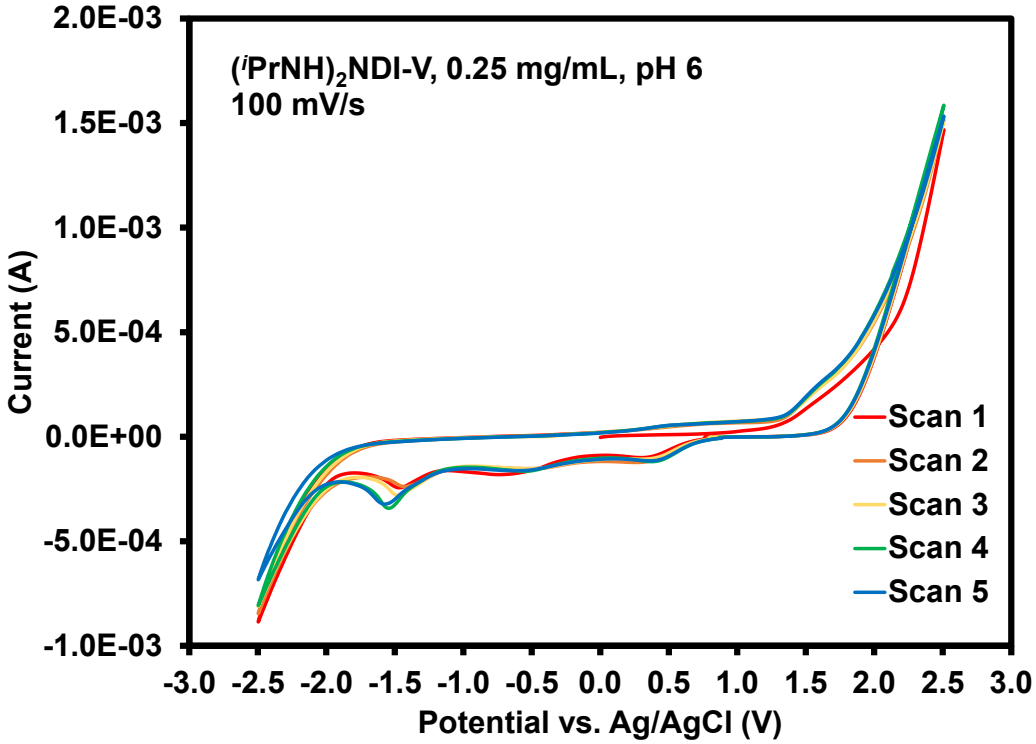


Figure S14: Cyclic voltammogram of (^{i}PrNH)$_2$NDI–V in water with 40% v/v 0.1 M NaCl as an electrolyte and pH-adjusted to 6 with 1 M HCl and 1 M NaOH measured at 100 mV/s.

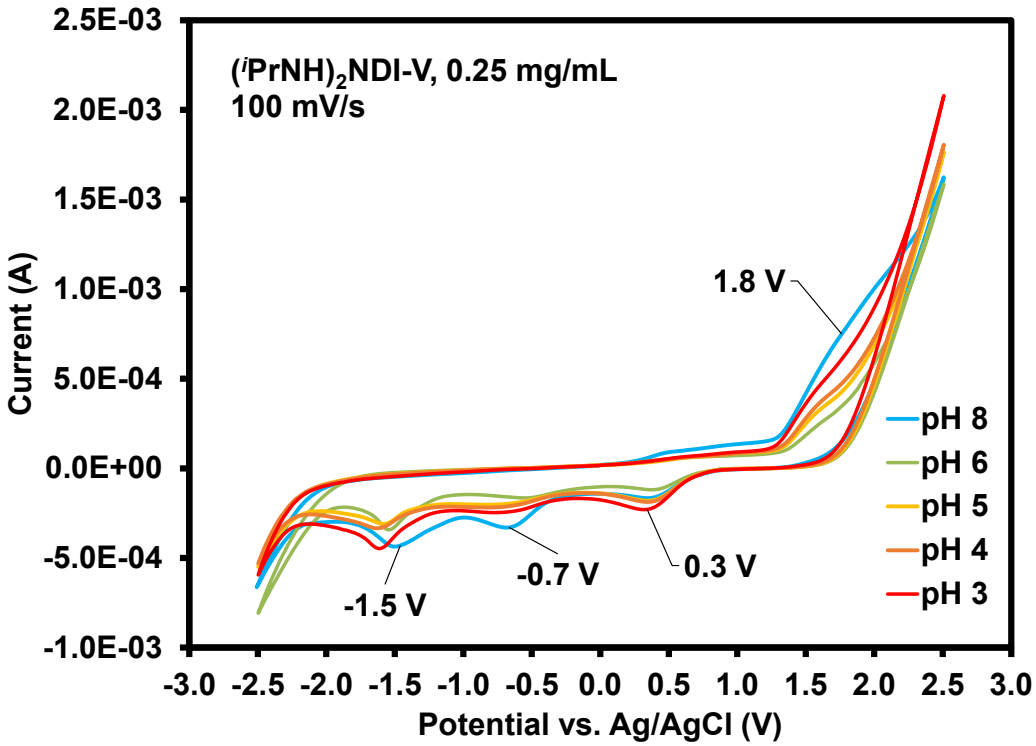


Figure S15: Cyclic voltammogram of (^{i}PrNH)$_2$NDI–V in water with 40% v/v 0.1 M NaCl as an electrolyte and pH-adjusted to various pH values with 1 M HCl and 1 M NaOH at 100 mV/s.

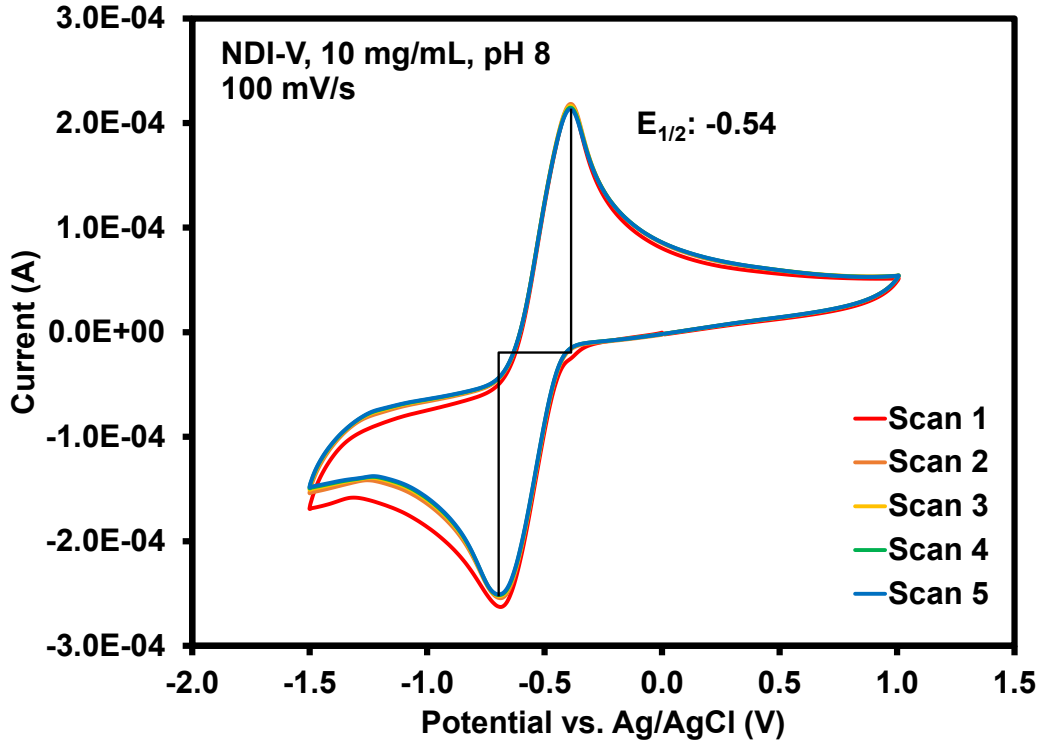


Figure S16: Cyclic voltammogram of NDI–V in water with 40% v/v 0.1 M NaCl as an electrolyte and pH-adjusted to 8 with 1 M HCl and 1 M NaOH measured at 100 mV/s.

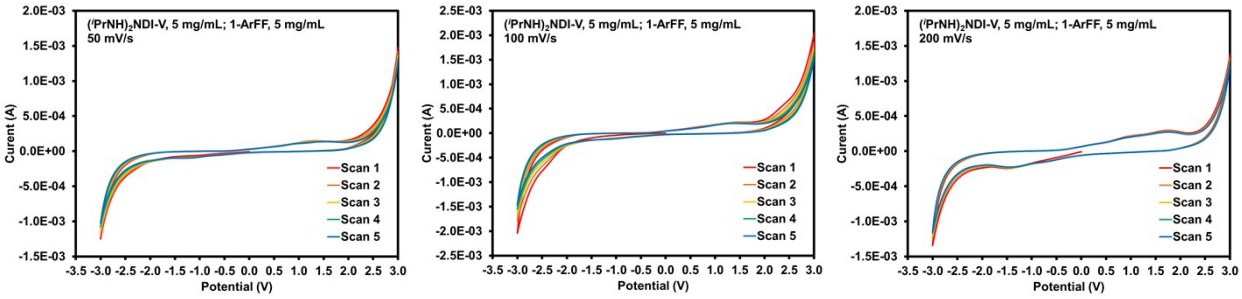


Figure S17: Cyclic voltammograms of (^{i}PrNH)$_2$NDI–V at 5 mg/mL in hydrogel made with 1-ThNap-FF at 5 mg/mL and triggered with GdL at 10 mg/mL measured at various scan rates.

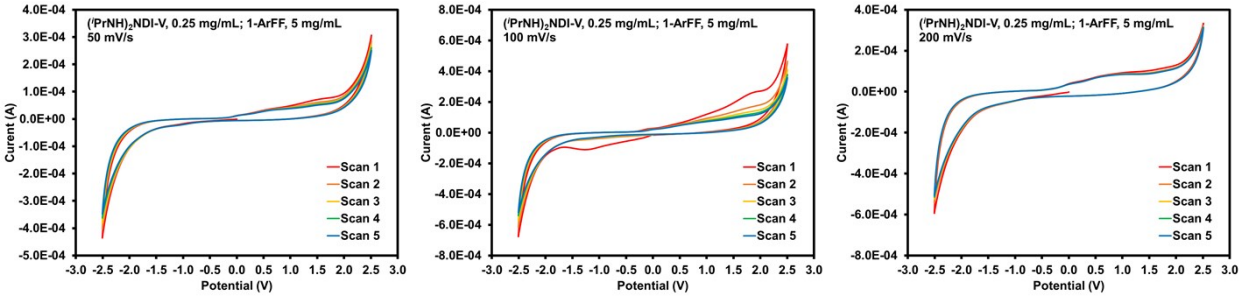


Figure S18: Cyclic voltammograms of (^{i}PrNH)$_2$NDI–V at 0.25 mg/mL in hydrogel made with 1-ThNap-FF at 5 mg/mL and triggered with GdL at 10 mg/mL measured at various scan rates.

Optical Spectroscopy

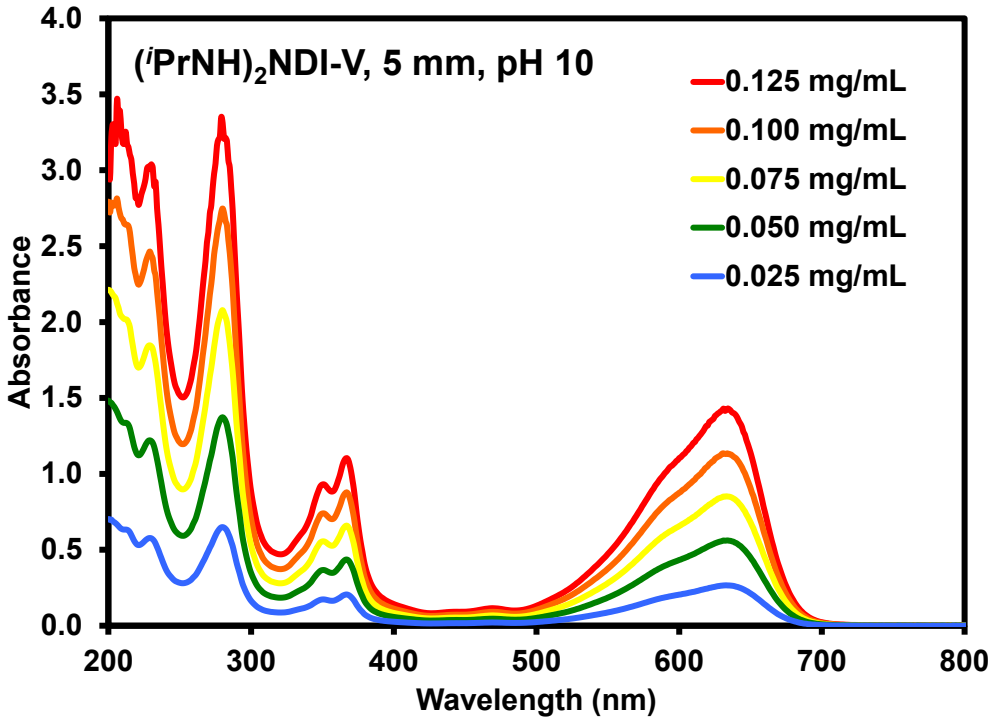


Figure S19: Optical absorption profile for (^{i}PrNH)$_2$NDI–V in water with 40% v/v 0.1 M NaCl and pH-adjusted to 10 with 1 M NaOH measured in 5 mm quartz cuvettes at various concentrations.

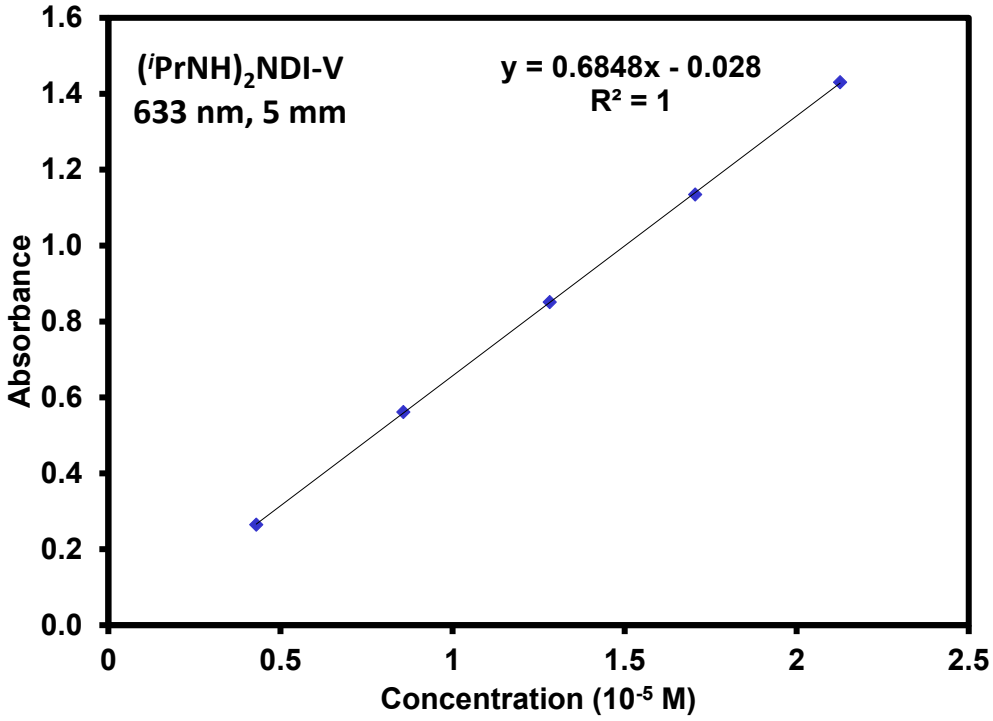


Figure S20: Absorbance versus concentration plot at 633 nm for (^{i}PrNH)$_2$NDI–V in water with 40% v/v 0.1 M NaCl and pH-adjusted to 10 with 1 M NaOH measured in 5 mm quartz cuvettes.

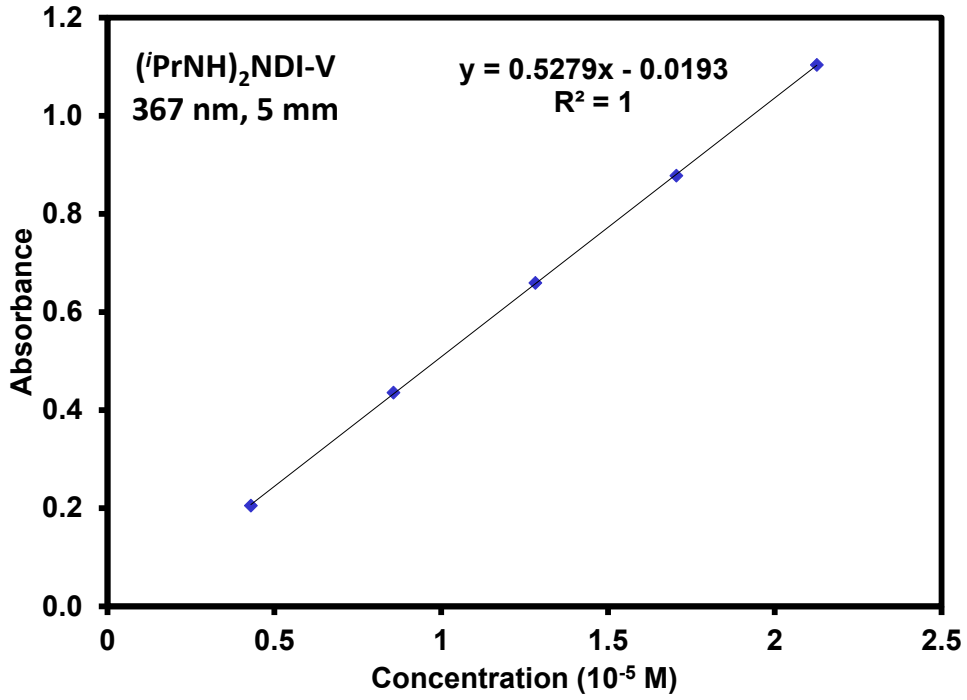


Figure S21: Absorbance versus concentration plot at 367 nm for (^{i}PrNH)$_2$NDI–V in water with 40% v/v 0.1 M NaCl and pH-adjusted to 10 with 1 M NaOH measured in 5 mm quartz cuvettes.

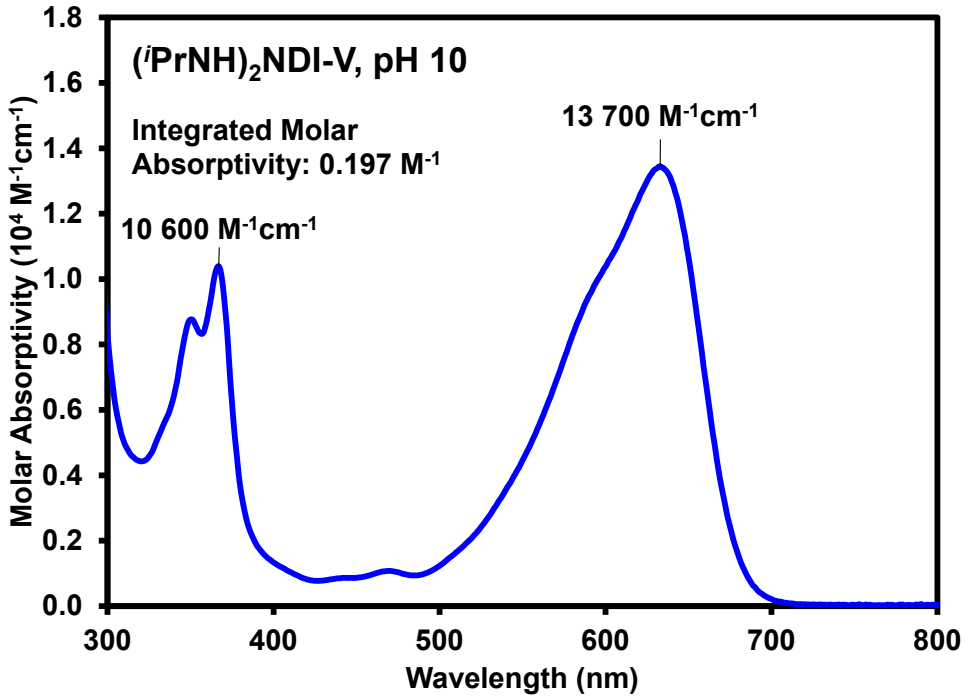


Figure S22: Absorption profile for (^{i}PrNH)$_2$NDI–V in water with 40% v/v 0.1 M NaCl as an electrolyte and pH-adjusted to 10 with 1 M NaOH showing molar absorptivity coefficients at 367 nm and 633 nm as well as the integrated molar absorptivity.

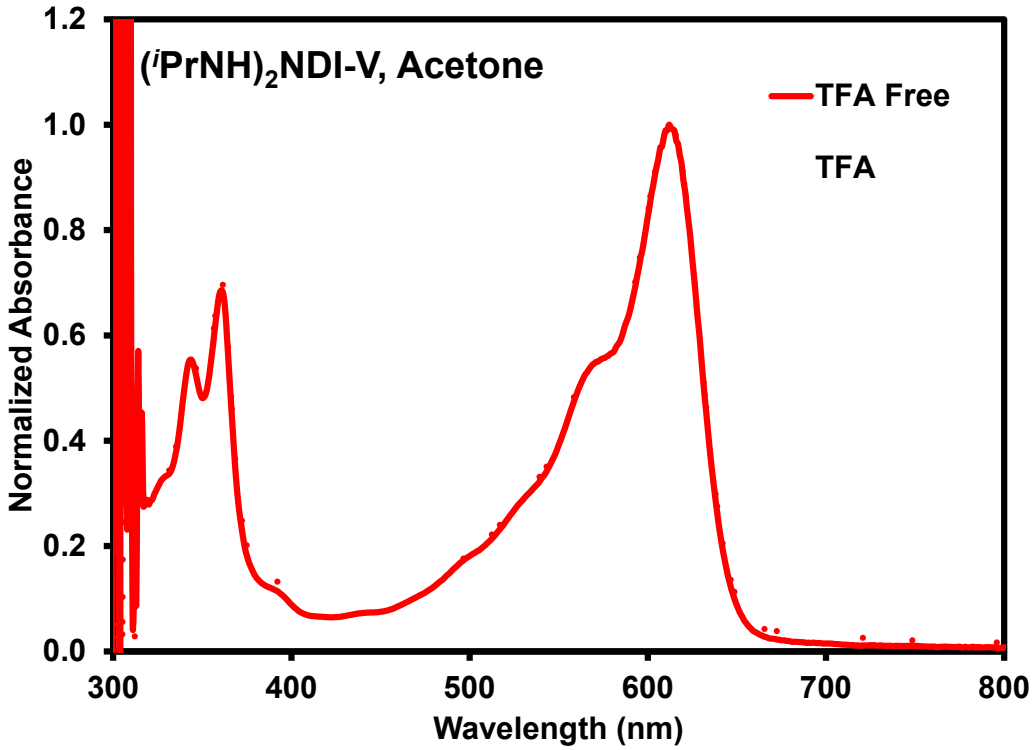


Figure S23: Normalized absorption profile for (^{i}PrNH)$_2$NDI–V in acetone with and without a 2.5% v/v TFA aliquot measured in 2 mm quartz cuvettes.

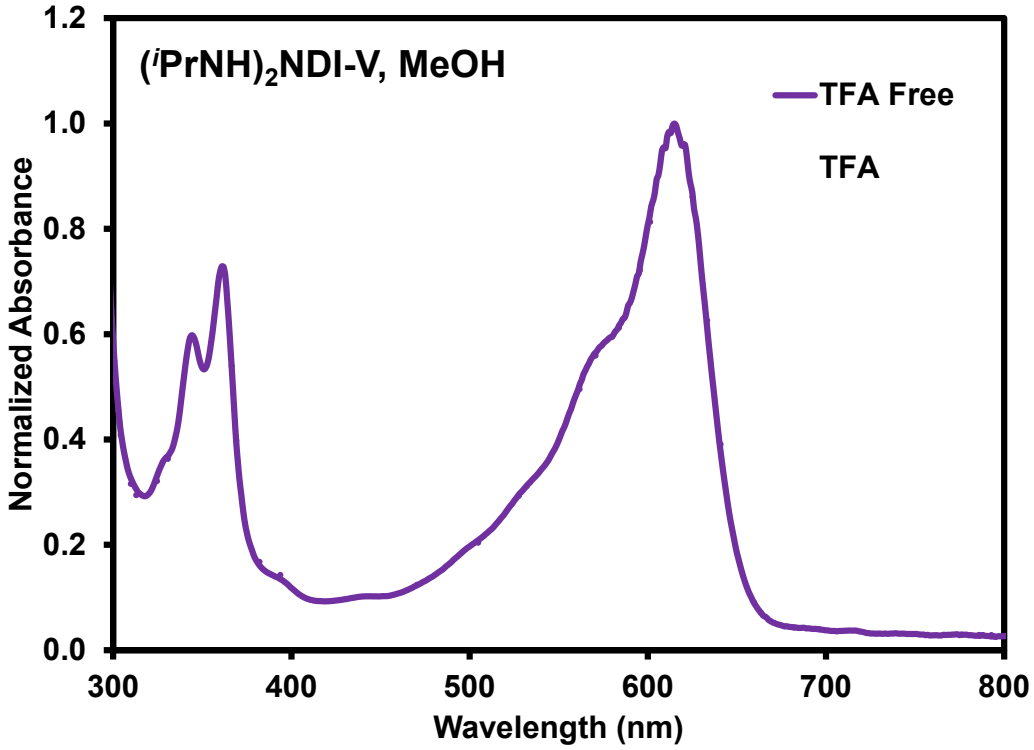


Figure S24: Normalized absorption profile for (^{i}PrNH)$_2$NDI–V in methanol with and without a 2.5% v/v TFA aliquot measured in 2 mm quartz cuvettes.

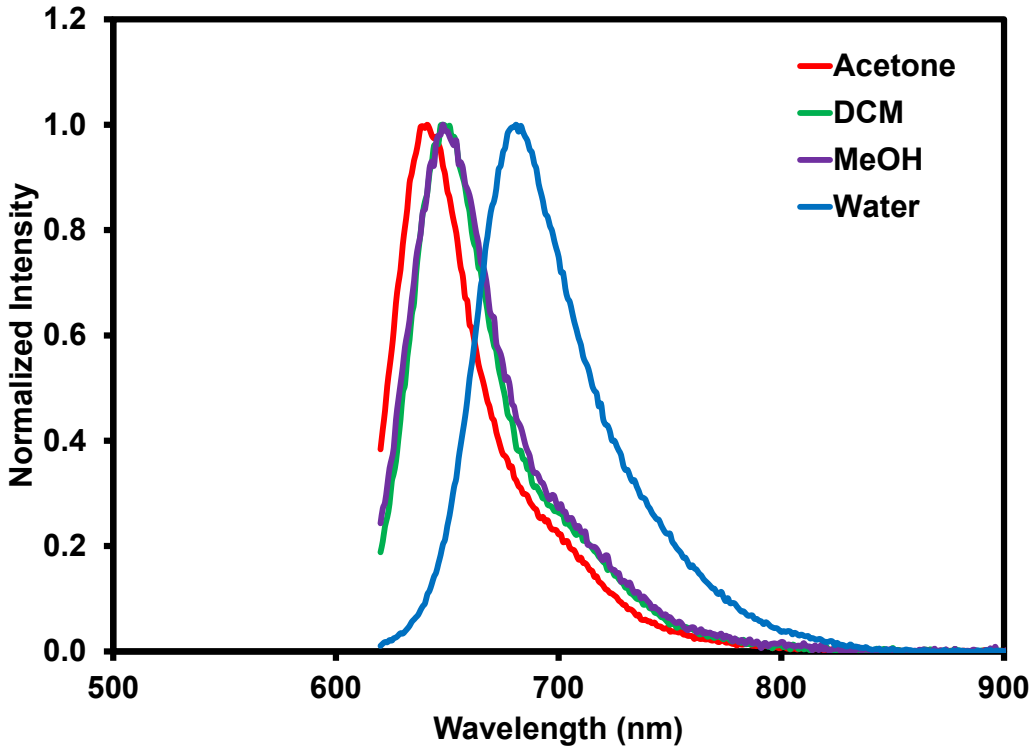


Figure S25: Normalized emission profiles for (^{i}PrNH)$_2$NDI–V in various solvents with excitation at 600 nm.

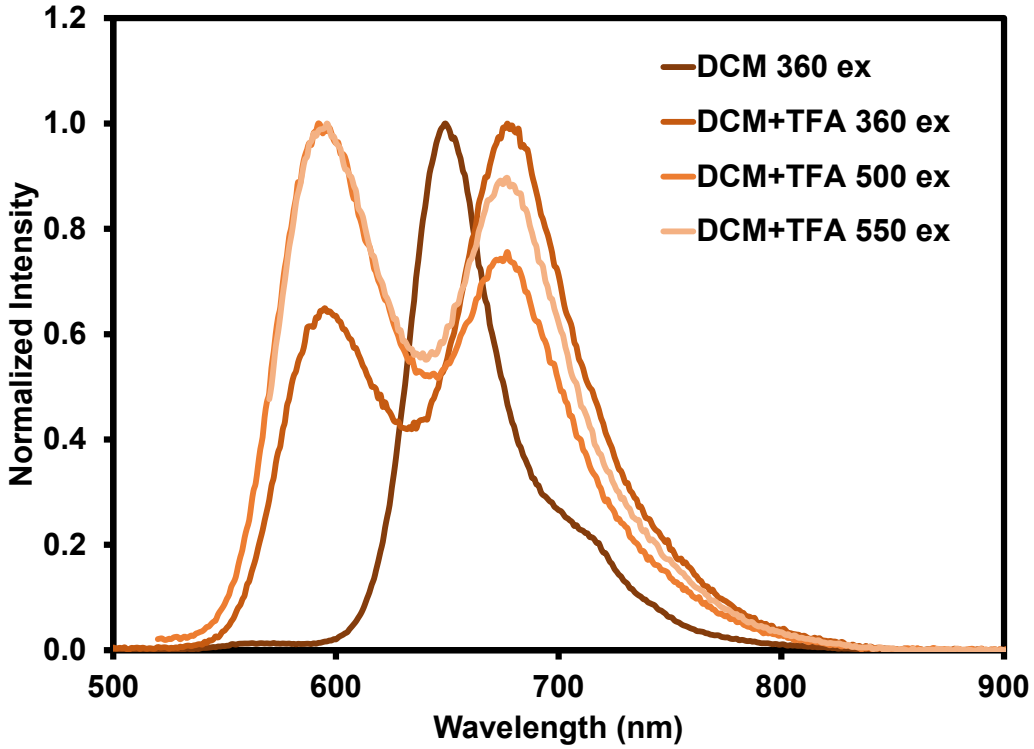


Figure S26: Normalized emission profiles for (^{i}PrNH)$_2$NDI–V in DCM with different excitation wavelengths (see legend).

Rheology

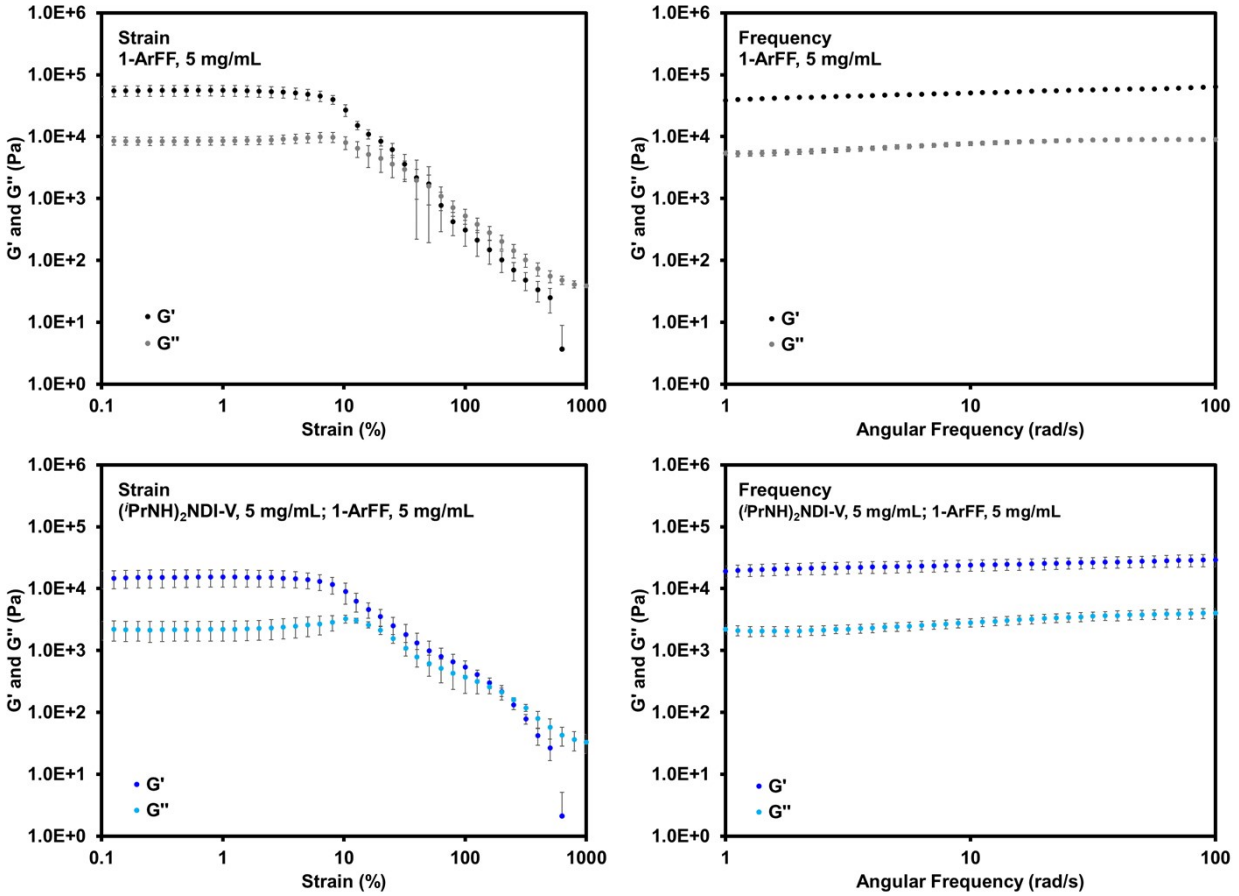


Figure S27: Strain and frequency plots for single component (top) and blend (bottom) gels. Each measurement was performed in triplicate and the average values with standard deviation error bars are displayed.

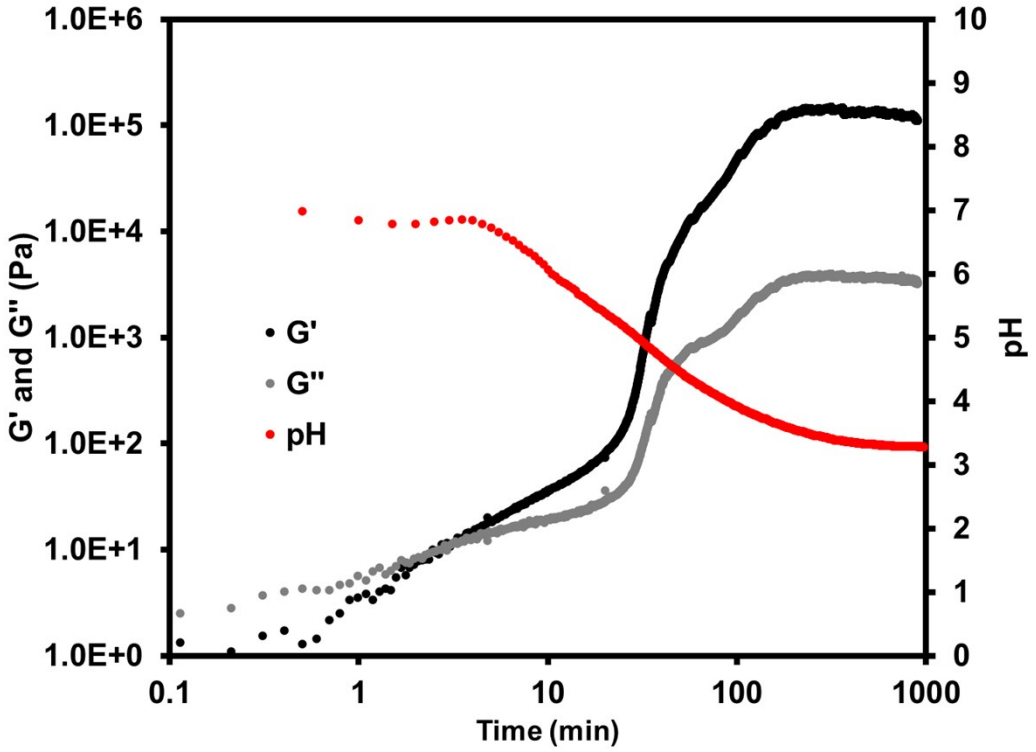


Figure S28: Time-sweep rheological and pH data for single-component 1-ThNap-FF gel.

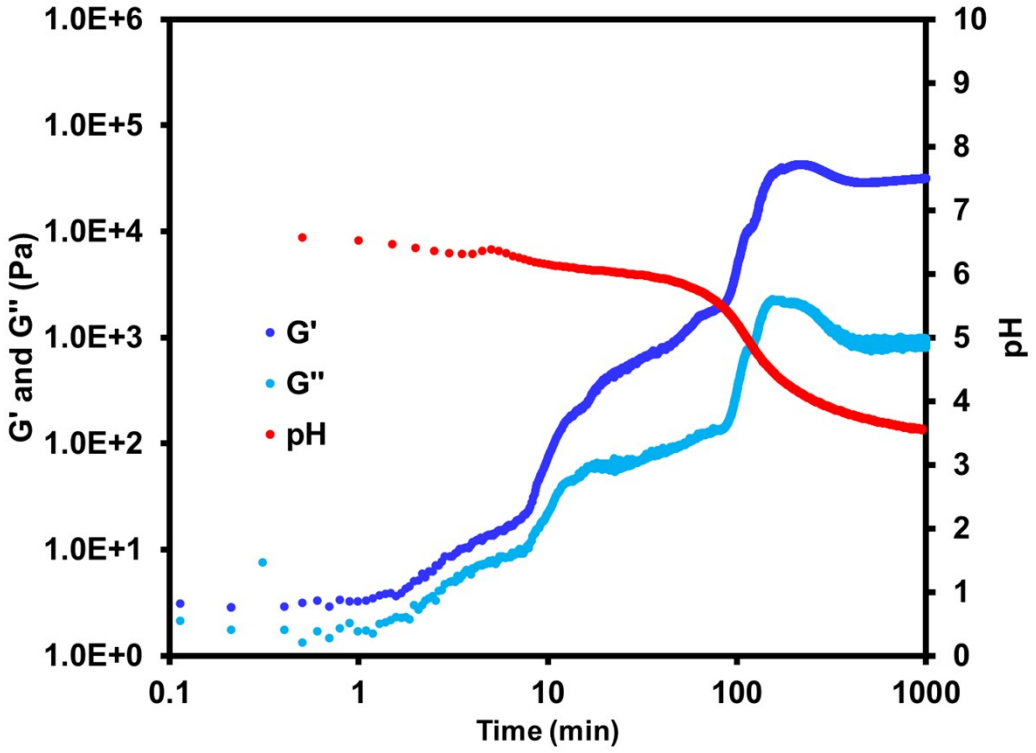


Figure S29: Time-sweep rheological and pH data for multicomponent 1-ThNap-FF + (^{i}PrNH)$_2$NDI–V gel.

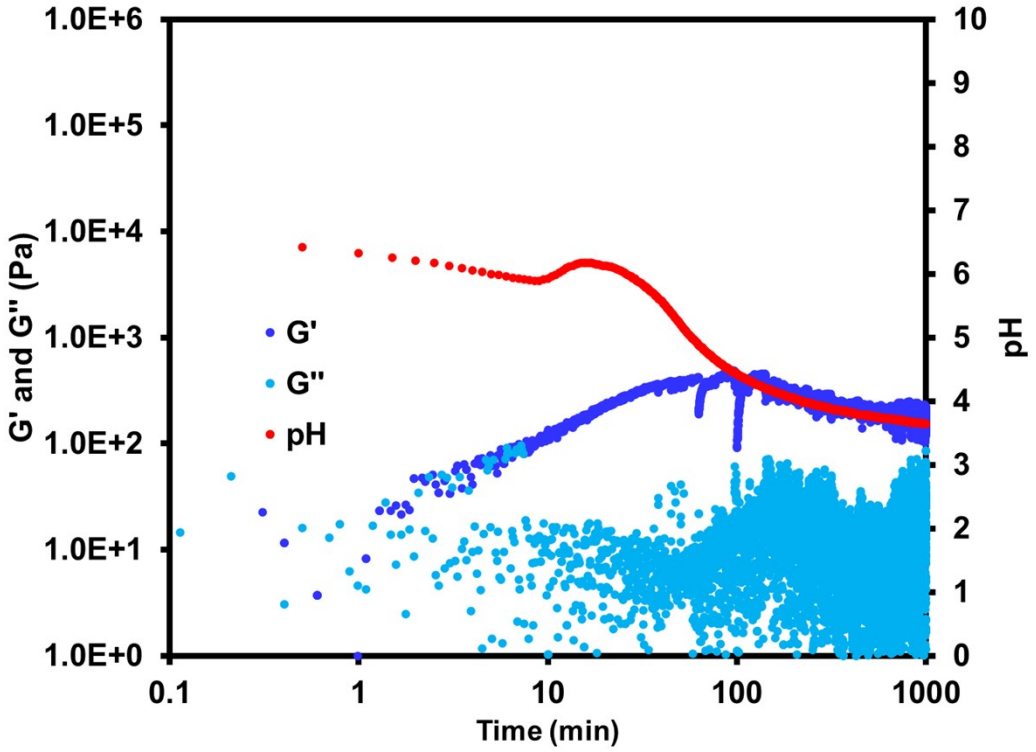


Figure S30: Time-sweep rheological and pH data for single-component (^{i}PrNH)$_2$NDI–V solution. Rheological data was obtained using a cup and vane rather than the parallel plate used for gels.

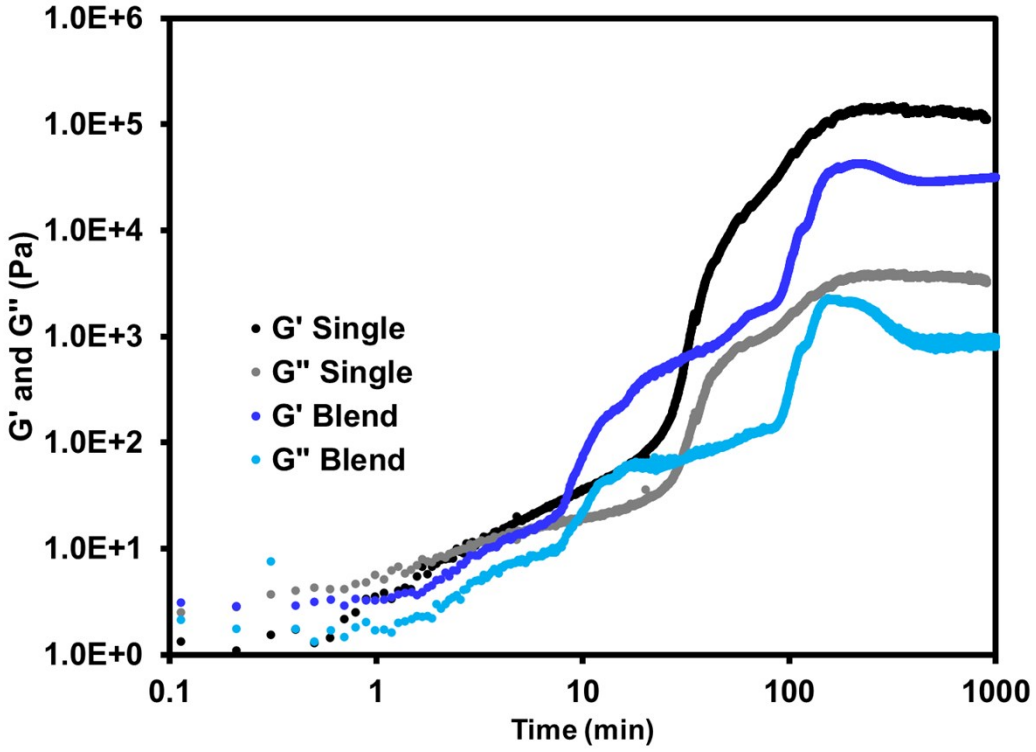


Figure S31: A comparison of the time sweep rheological data for both single and blend gels.

Small Angle Neutron Scattering (SANS)

(^{i}PrNH)$_2$NDI–V best fits to a power law alone. The scattering intensity is lower than for the other samples.

1-ThNap-FF best fits to a flexible cylinder combined with a power law.

(^{i}PrNH)$_2$NDI–V + 1-ThNap-FF best fits to a flexible cylinder combined with a power law, but polydispersity is needed in the radius to obtain a reasonable fit.

The fitting of the below data is not perfect (higher χ^2 than desired) showing that the structures present cannot be explained perfectly by the fits in the fitting programme. The fits look suitable by eye and so the structures can be assumed to be not far off the models used. This shows that something more complicated is going on, or something that cannot be captured by the models.

Table S1: Summary of fits to the SANS data for the single component (^{i}PrNH)$_2$NDI–V solution, single component 1-ThNap-FF gel, and blend 1-ThNap-FF + (^{i}PrNH)$_2$NDI–V gel. For all of the below, the SLD would be about 3×10^{-6} A^{-2}.

	(^{i}PrNH)$_2$NDI–V	**1-ThNap-FF**	**(^{i}PrNH)$_2$NDI–V + 1-ThNap-FF**
Background (cm^{-1})	0.0003*	0.0015*	0.004*
Scale (power law)	$8.60\times10^{-7} \pm 4.18\times10^{-8}$	$2.47\times10^{-5} \pm 7.16\times10^{-7}$	$2.74\times10^{-5} \pm 2.13\times10^{-6}$
Power Law	3.57 ± 0.002	2.41 ± 0.01	2.83 ± 0.02
Scale (flexible cylinder)		$3.57\times10^{-3} \pm 6.6\times10^{-4}$	$1.76\times10^{-3} \pm 2.15\times10^{-5}$
Length (Å)		450 ± 2	5000*
Kuhn Length (Å)			23 ± 0.4
Radius (Å)		33 ± 1	50 ± 0.1 (polydispersity = 0.2)
χ^2	73.7	22.7	29.8

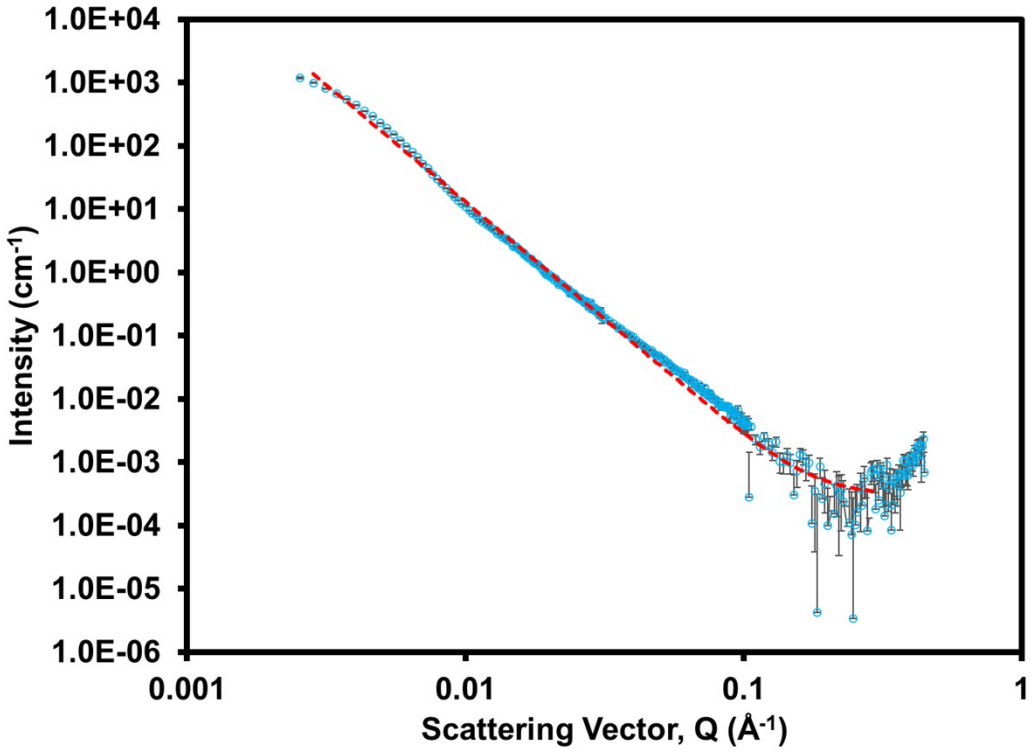


Figure S32: SANS for the single-component (^{i}PrNH)$_2$NDI–V solution with circles to represent SANS data and red dashed line to illustrate the fit.

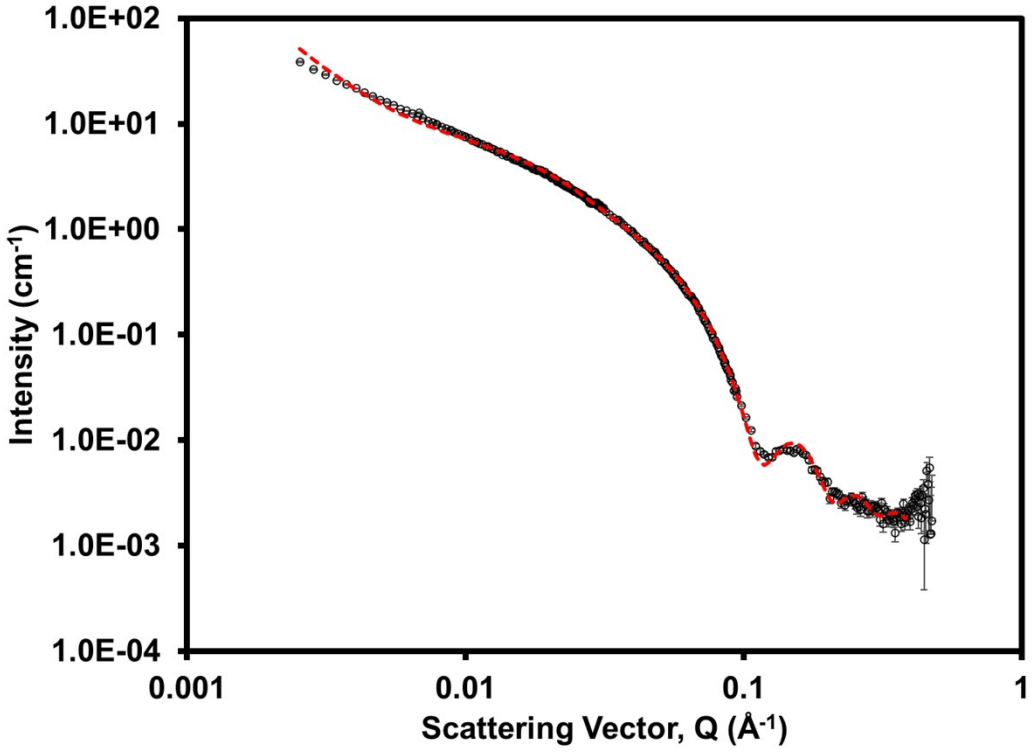


Figure S33: SANS for the single-component 1-ThNap-FF gel with circles to represent SANS data and red dashed line to illustrate the fit.

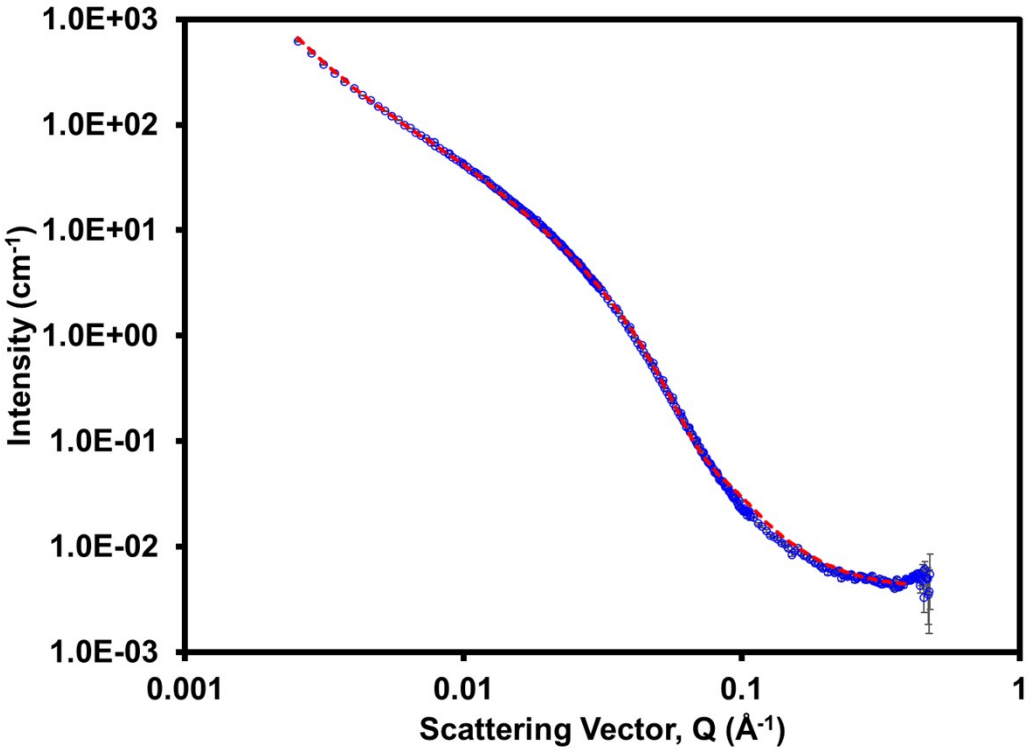


Figure S34: SANS for the multicomponent (^{i}PrNH)$_2$NDI–V + 1-ThNap-FF gel with circles to represent SANS data and red dashed line to illustrate the fit.

References

1 J. Pommerehne, H. Vestweber, W. Guss, R. F. Mahrt, H. Bässler, M. Porsch and J. Daub, *Adv. Mater.*, 1995, **7**, 551–554.

2 A. T. R. Williams, S. A. Winfield and J. N. Miller, *Analyst*, 1983, **108**, 1067–1071.

3 A. M. Brouwer, *Pure Appl. Chem.*, 2011, **83**, 2213–2228.

4 W. Heller, *J. Phys. Chem.*, 1965, **69**, 1123–1129.

5 M. C. Nolan, A. M. F. Caparrós, B. Dietrich, M. Barrow, E. R. Cross, M. Bleuel, S. M. King and D. J. Adams, *Soft Matter*, 2017, **13**, 8426–8432.

6 SasView, SasView, https://sasview.github.io/, (accessed 16 April 2021).