

Air-stable Photoconductive Films formed from Perylene Bisimide Gelators

Emily R. Draper,^a James J. Walsh,^b Tom O. McDonald,^a Martijn A. Zwijnenburg,^c Petra J. Cameron,^d Alexander J. Cowan,^b Dave J. Adams^{a,*}

^a Department of Chemistry, University of Liverpool, Crown Street, Liverpool, L69 7ZD, U.K.

Email: d.j.adams@liverpool.ac.uk or a.j.cowan@liverpool.ac.uk

^b Stephenson Institute for Renewable Energy, University of Liverpool, Peach Street, Liverpool, L69 7ZF, U.K.

^c Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K.

^d Department of Chemistry, 1 South, University of Bath, Bath, BA2 7AY, U.K.

SUPPORTING INFORMATION

1. Synthesis of PBIs

Typical Synthesis, [N, N'-di(L-valine)-perylene-3,4:9,10-tetracarboxylic acid bisimide] (4).

In a 100 mL Schlenk flask, 0.79 g (1 mmol) of 3,4:9,10-perylenetetracarboxyldianhydride (PTCDA), 0.47 g (2 mmol) of L-valine and 2.80 g (20 mmol) of imidazole were added. These were mixed and purged with nitrogen for 10 minutes. The mixture was then heated to 120 °C under nitrogen and left stirring for 5 hours at this temperature. The reaction was then cooled to 90 °C and 3 mL of deionised water was added. The reaction was left for an hour and then cooled to room temperature before filtering to remove unreacted PTCDA. 50 mL of 2 M HCl was then added to lower the pH to 2-3. The acidified mixture was stirred at 60 °C for 4 hours. The precipitate was then collected by suction-filtration and washed thoroughly with acidified water. The dark red solid was dried overnight in a vacuum oven and then freeze dried to remove any remaining water.

The same method was used to make [N, N'-di(L-alanine)-perylene-3,4:9,10-tetracarboxylic acid bisimide] (1), [N, N'-di(L-histidine)-perylene-3,4:9,10-tetracarboxylic acid bisimide] (2), and [N, N'-di(L-phenylalanine)-perylene-3,4:9,10-tetracarboxylic acid bisimide] (3).

Around 2 μ L of TFA was added to ^1H NMR samples of 2, and ^{13}C NMR samples of 2, 3 and 4 to improve solubility and visibility in NMR.

1: ^1H NMR 400 MHz, (DMSO- d_6 , 25 °C): δ (ppm) = 12.80 (br, 2H; -OH); 8.29 (d, 4 H); 8.21 (d, 4 H); 5.59 (q, 2 H, $J = 7.0$ Hz); 1.68 (q, 6 H, $J = 7.0$ Hz). ^{13}C (100 MHz, DMSO- d_6 , 25 °C): δ (ppm) = 171.2 (COOH); 161.9 (C=O); 134.2, 133.4, 130.7, 127.8, 123.6, 121.8, 119.2 (perylene core C); 48.6 (CH); 14.4 (CH₂). MALDI-TOF MS: calculated 534.11 Da for [C₃₀H₁₈N₂O₈]⁺, found 535.3 Da.

2: ^1H NMR 400 MHz, (DMSO- d_6 and TFA, 25 °C): δ (ppm) = 8.93 (bd, 4 H, $J = 8.3$); 8.56 (bd, 4 H, 8.3 Hz); 7.47 (s, 4 H); 5.85 (t, 2 H); 3.73 (d, 2 H, $J = 15.0$ Hz); 3.45 (d, 2 H, $J = 15.0$ Hz). ^{13}C (100 MHz, DMSO- d_6 and TFA, 25 °C): δ (ppm) = 169.7 (COOH); 162.3 (C=O); 133.9, 131.3, 129.9, 128.3, 125.2, 123.9, 121.8 (perylene core C); 52.6 (CH); 23.7 (CH₂). MALDI-TOF MS: calculated 666.15 Da for [C₃₆H₂₂N₆O₈]⁺, found 665.2 Da.

3: ^1H NMR 400 MHz, (DMSO- d_6 , 25 °C): δ (ppm) = 8.3 (d, 4H); 8.1 (d, 4H); 7.3 (d, 4H, $J = 7.5$ Hz); 7.2 (t, 4H, $J = 7.5$ Hz); 7.1 (t, 2H, $J = 7.5$); 5.9 (t, 2H, $J = 5.3$ Hz); 3.7 (d, 3.5, $J = 5.3$

Hz); 3.5 (d, 2H, $J = 5.3$ Hz). ^{13}C (100 MHz, $\text{DMSO-}d_6$ and TFA, 25 °C): δ (ppm) = 170.6 (COOH); 162.1 (C=O); 133.6, 130.9, 129.1, 125.0, 123.4, 121.6 (perylene core C); 137.9, 128.2, 127.9, 126.4 (aromatic C); 46.6 (CH); 14.4 (CH_2). MALDI-TOF MS: calculated 686.2 Da for $[\text{C}_{42}\text{H}_{26}\text{N}_2\text{O}_8]^+$, found 686.3 Da. HRMS data is shown in Fig. S3.

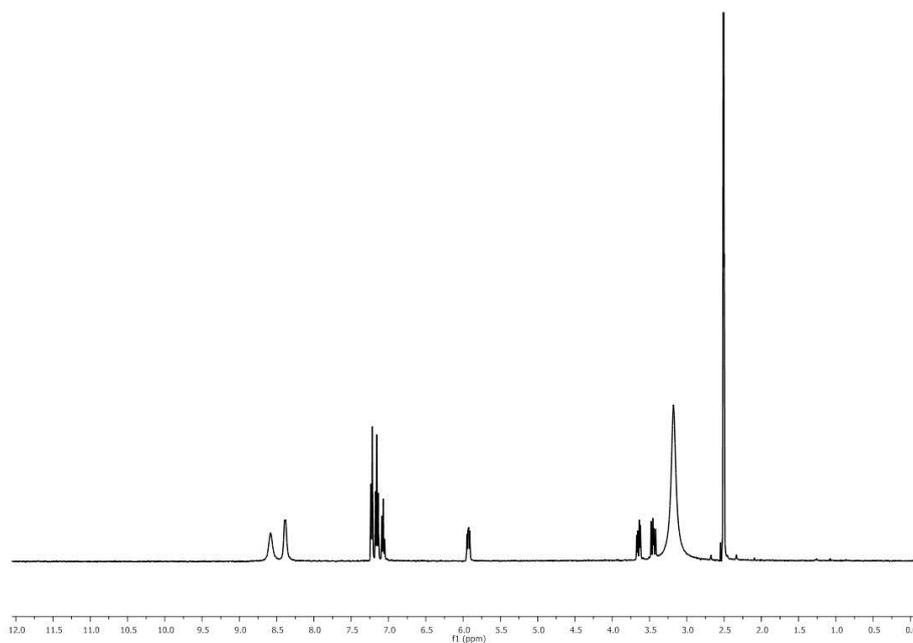


Figure S1. ^1H NMR data (DMSO) for **3**. Peak positions and assignments are included above.

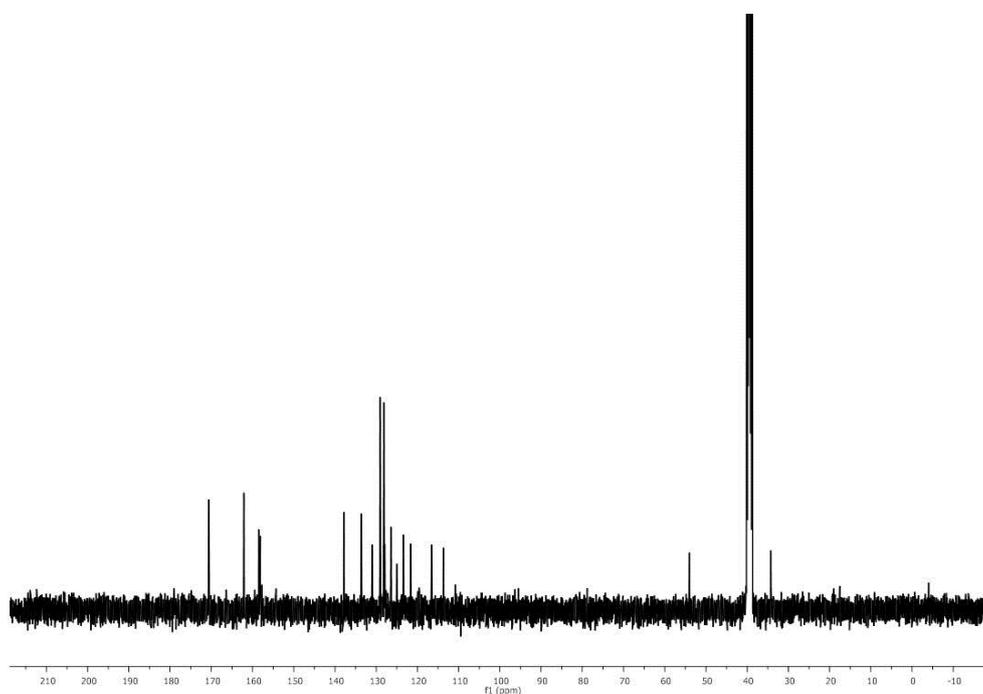


Figure S2. ^{13}C NMR data (DMSO) for **3**. Peak positions and assignments are included above. TFA was added to improve the solubility and hence can also be detected.

Tolerance = 20.0 PPM / DBE: min = -30.0, max = 200.0

Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions

13 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Sample:- PB1-F run in MeOH Cone = 45V

E. Draper / DA

1313M 6 (0.317) AM (Cen,4, 80.00, Ar,5000.0,554.26,0.70,LS 1); Sm (SG, 10x4.00); Cm (5:35)

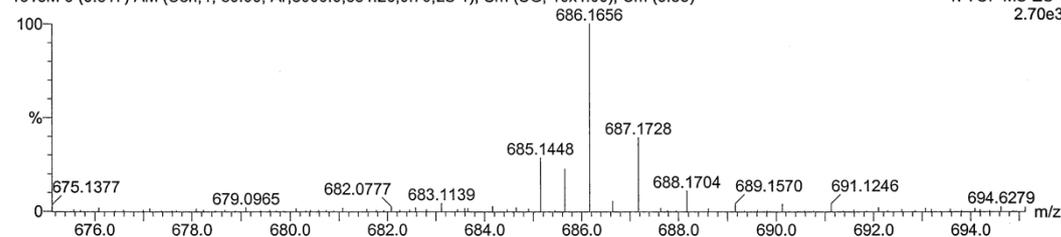
Operator: MM

LCT 21-May-2014 14:27:23

Chemistry Dept. Univ. of Liverpool

1: TOF MS ES-

2.70e3



Minimum: 42.00
Maximum: 100.00

4.0 20.0 -30.0
200.0

Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
686.1656	100.00	686.1689	-3.3	-4.8	31.0	1	C42 H26 N2 O8

Figure S3. High-resolution mass spectroscopy data for **3**.

4: ^1H NMR 400 MHz, (DMSO- d_6 , 25 °C): δ (ppm) = 8.50 (d, 4 H, J = 8.2 Hz); 8.37 (d, 4 H, J = 8.2 Hz); 5.20 (d, 2 H, J = 1.3 Hz); 2.75 (qd, 2 H, J = 7.0, J = 1.3 Hz); 1.29 (d, 6 H, J = 7.0 Hz); 0.81 (d, 6 H, J = 7.0 Hz). ^{13}C (100 MHz, DMSO- d_6 and trifluoroacetic acid (TFA), 25 °C): δ (ppm) = 170.6 (COOH); 162.3 (C=O); 133.4, 130.9, 127.9, 124.8, 123.3, 121.4, 119.3 (perylene core C); 58.1 (CH); 27.0 (CH₂); 19.1 (CH₃); 19.0 (CH₃). MALDI-TOF MS: calculated 590.17 Da for $[\text{C}_{34}\text{H}_{26}\text{N}_2\text{O}_8]^+$, found 590.0 Da. HRMS data is shown in Fig. S6.

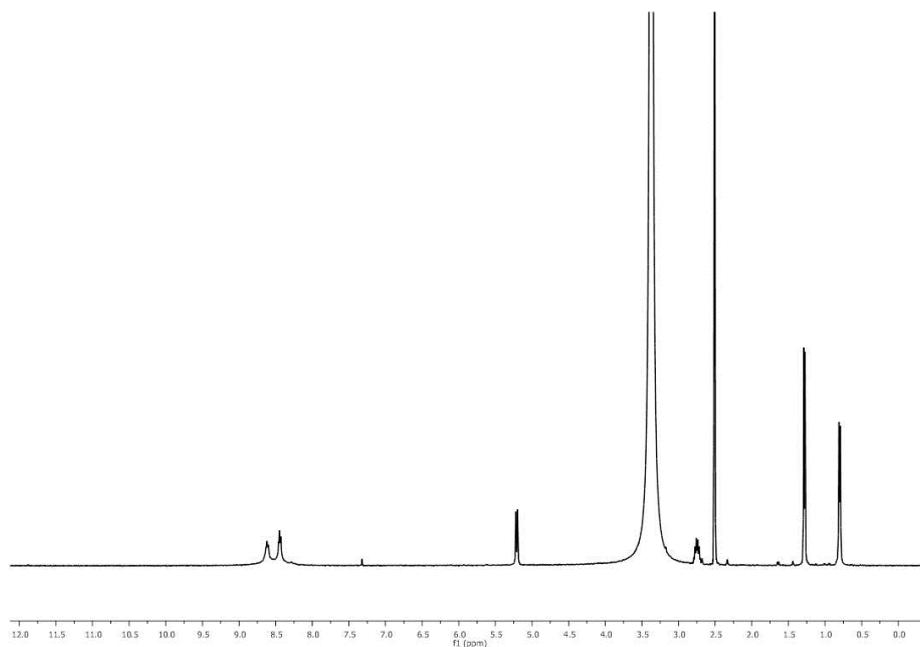


Figure S4. ^1H NMR data (DMSO) for **4**. Peak positions and assignments are included above.

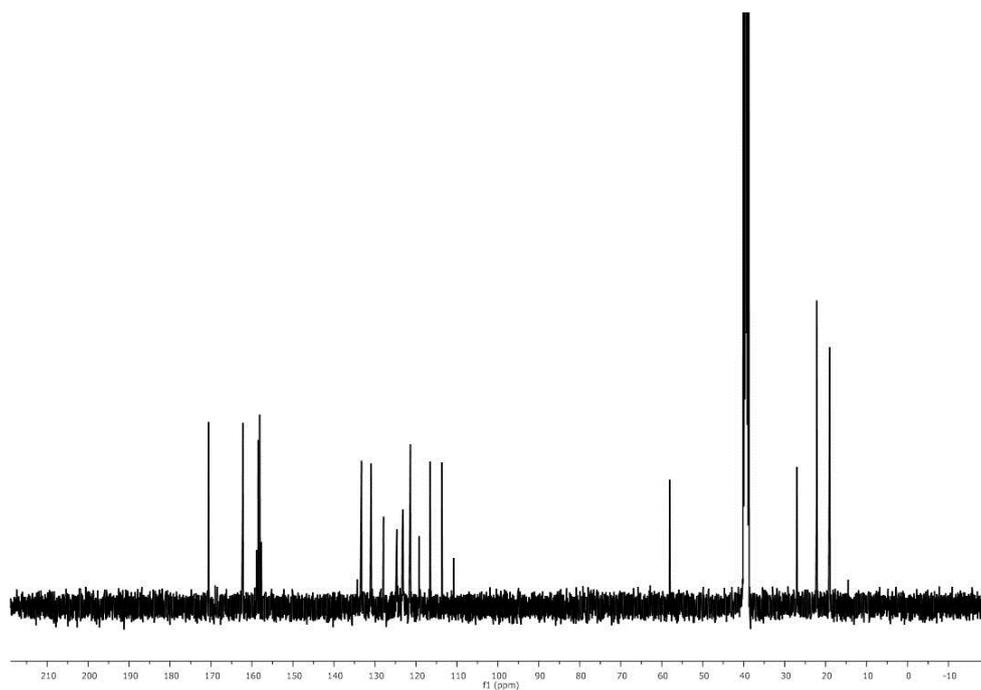


Figure S5. ^{13}C NMR data (DMSO) for **4**. Peak positions and assignments are included above. TFA was added to improve the solubility and hence can also be detected.

Tolerance = 20.0 PPM / DBE: min = -30.0, max = 200.0
 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
 16 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

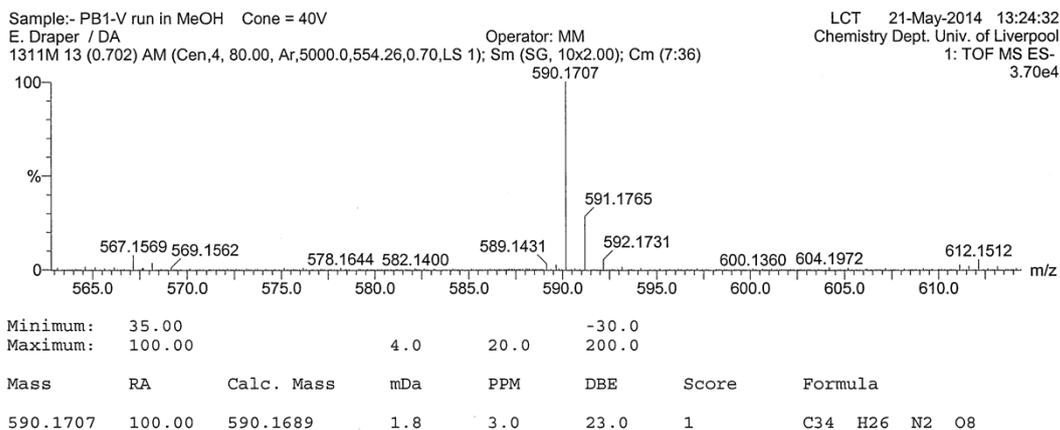


Figure S6. High-resolution mass spectroscopy data for **4**.

2. Analytical Characterisation

Nuclear Magnetic Resonance Spectroscopy (NMR) NMR spectra were recorded using a Bruker DPX-400 spectrometer operating at 400 MHz for ^1H NMR and 100 MHz for ^{13}C , in deuterated DMSO.

Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry (MALDI-TOF) MALDI-TOF mass spectrometry was carried out within the University of Liverpool Biosciences Department using a Waters Micromass M@LDI bench top mass spectrometer with α -cyano-4-hydroxy-cinnamic acid matrix. A saturated solution of the matrix was made up in 50 % acetonitrile, before applying 2 mL to the target followed by a 2 ml of sample followed by a further 2 mL of matrix. The pulse voltages used was 3400 V and the source voltage used was 16,000 V.

3. Preparation of solutions and gels

Preparation of LMWG Solutions The gelator was added to 2 mL of water with an equimolar amount of sodium hydroxide (0.1 M, aqueous) to a concentration of 5 mg/mL. The solution was stirred until all the gelator was dissolved at this high pH.

Hydrogel Formation A pH switch method was used to form the hydrogels. Solutions were prepared as above. The solution was then transferred to a vial containing a pre-weighed amount of glucono- δ -lactone (GdL) and shaken gently. The sample was then left to stand overnight to allow gelation to occur.

Preparation of samples on glass slides Dried solution samples were prepared by dropping 40 μ L of the LMWG onto a glass microscope slide and then leaving overnight to dry in air. Xerogel samples were prepared as described above using GdL, but by gelling inside a 1 mL mould. Once gelation had occurred the gel was then removed from the mould and approximately 0.05 mL of the gel was removed using a scalpel, placed onto a glass microscope slide and allowed to dry in air overnight.

4. Materials Characterisation

Rheological Measurements Dynamic rheological and viscosity measurements were performed using an Anton Paar Physica MCR101 and MCR301 rheometer. A cup and vane measuring system was used to perform frequency and strain sweeps, and a cone and plate measuring system was used to perform viscosity measurements. For frequency and strain tests, 2 mL of the gels were prepared in 7 mL Sterilin vials and left for 24 hours at room temperature before measurements were performed. For viscosity measurements samples were prepared at high pH as previously mentioned. All experiments were performed at 25 °C.

Frequency sweep: Frequency scans were performed from 1 rad/s to 100 rad/s under a strain of 0.5 %. The shear modulus (storage modulus (G') and loss modulus (G'')) were read at 10 rad/s. These measurements were done within the viscoelastic region where G' and G'' were independent of strain amplitude.

Strain sweep: Strain scans were performed from 0.1 % to 100 % with a frequency of 10 rad/s. The critical strain was quoted as the point that G' starts to deviate for linearity and ultimately crosses over the G'' , resulting in gel breakdown. Again this method made sure that 0.5 % strain was in the viscoelastic region required for measuring the frequency sweep.

Viscosity measurements: Viscosity measurements were performed using a cone and plate. The gap distance between the two plates used was 0.1 mm. 1 mL solutions were transferred

onto the plate for measurement. The viscosity of each solution was recorded under the rotation shear rate varying from 1 to 100 s⁻¹. All experiments were conducted at 25 °C.

UV-Vis-NIR Absorption Measurements Solution UV-Vis absorption data was measured using a Thermo Scientific Nanodrop 2000/2000c spectrophotometer. The spectrophotometer was used in cuvette mode where samples were prepared in PMMA plastic cuvettes with a pathlength of 1.0 cm. Aqueous samples were prepared at high pH using equimolar amounts of 0.1 M aqueous NaOH solution to gelator and made up to 2 mL with distilled water. A concentration of 5 mg/mL of a gelator was used for aqueous solutions and a dilution series was made for measurements. Gels were made by the pH switch method and pipetting around 100 µL of the solution whilst still liquid into a cuvette. The open cuvette top was then covered and laid on its side whilst it gelled overnight. This formed a thin layer of gel on one side of the cuvette which could be measured.

Solid UV-Vis-NIR absorption data were obtained using a Shimadzu UV-2550 UV-Vis spectrophotometer running the UV Probe software, version 2.34. Spectra were measured either up to 700 or 1400 nm, with scan speed set to medium and using a slit width of 5.0 nm in transmission mode. Samples were prepared as previously mentioned with GdL. This gel was then transferred onto a glass slide and allowed to dry in air overnight in air to form a thin film xerogel.

For solution UV-Vis-NIR measurements samples were prepared in a sealed degassed quartz cuvette with a pathlength of 1 mm.

Fluorescence Spectroscopy Fluorescence spectra were collected using a Perkin Elmer Fluorescence Spectrometer LS55. Emission and excitation spectra were recorded in 1.0 cm pathlength cuvettes with slit widths of 2.5 nm and 2.5 nm at a scan rate of 100 nm/min. Emission spectra were collected between 200 nm and 800 nm, exciting at 490 nm and 365 nm. Spectra were recorded at pH 11 and pH 3.

X-Ray Diffraction (XRD) Gel samples were prepared *via* the pH switch method and left to dry completely in air and the samples were ground before being measured. LMWG solution samples were also dried in air and ground before being measured.

SEM SEM images were obtained using a Hitachi S-4800 FE-SEM. Gels and solutions at high pH were deposited onto glass cover slips which were stuck onto aluminium SEM stubs and left to dry for 24 hours.

Thermogravimetric analysis (TGA) TGA was carried out on a TA Instruments SDT Q600 TGA machine using a constant air flow of 100 mL/min. Samples were heated to 120 °C with a heating rate 10 °C/min. The samples were kept at 120 °C for 20 minutes to remove any water, then ramped to 200 °C at a heating rate of 10 °C/min.

Photoconductivity Measurements Photoconductivity measurements were performed using a Palmsens³ Potentiostat operating in a two electrode configuration in the absence of a supporting electrolyte. An Applied Photophysics 150 W Xenon arc lamp was used for the 'light' experiments with a spot size of 2 cm². A 365 nm LED (LedEngin Inc, LZ1-10U600) with a light source powered by a TTi QL564P power supply operating at 1.0 W was also used as a light supply. A 10 mL quartz cuvette filled with water was used as an IR filter. Dark experiments were performed in an enclosure in air. Linear sweep measurements were recorded from -4 V to 4 V at a scan rate of 0.05 V/s and a preconditioning step at 0.002 V for 2 seconds. Xerogels were prepared *via* the pH switch method as previously described. Once the gels were formed approximately the same volume of each gel could be placed onto a glass slide between two silver electrodes spaced 3 mm apart. The silver electrodes were made using silver paste which attached copper wires to the glass slide. The gel was then allowed to dry in air overnight to form a xerogel. Epoxy resin glue was placed over the silver electrodes, again this was left to dry overnight. The counter and reference electrode clips were connected to one copper wire and the working on the other copper wire to make a two-electrode experiment. Dried solutions at pH 10 were prepared as previously mentioned but placed between the copper wires on the glass slide. For 'on-off' experiments, a cover was placed over the lamp for 'off' and then removed for 'on'.

Wavelength Response Measurements Samples were prepared on microscope slides between to two silver electrodes as previously mentioned. The light source used was a stabilized 75 W Xenon lamp coupled to a monochromator (OBB Corp., set to 4 nm resolution). Current was measured using a Palmsens³ potentiostat operating with a two using electrode configuration in the absence of a supporting electrolyte. Measurements were ran at 0.05 V/s for 2000 seconds. The light source was switched on at 100 seconds and the current was allowed to reach a plateau so that a change in current could be recorded. The sample was

then put back in the dark and allowed to return to the 'off' state before another measurement was recorded. The intensity of the light at each wavelength was measured using a photodiode so that results could be scaled.

Photochromism A 365 nm LED with a light source powered by a TTi QL564P power supply operating at 1.0 W was used as the light supply. Samples were placed inside the UV-Vis-NIR spectrometer and the light was placed around 5 cm away from the samples whilst spectra were recorded. The incident light intensity on the sample was measured to be approximately 1 mW/cm². Samples were irradiated until intensity of the new peaks plateaued. The lamp was switched off and spectra were taken every minute for the first half an hour, and then 5 minutes until peaks in the spectra had returned to original intensity.

Chemical Reduction of LMWG Chemical reduction of **1** in solution was carried out by adding sodium dithionite. 40 mL of 0.125 mg/mL of LMGW **1** in pH 10 water were added to a 100 mL round bottom flask and sealed with a subaseal. The solution was degassed with argon for 15 minutes. Sodium dithionite was added in 10 mg portions by carefully removing the seal and quickly adding it to the solution and replacing the seal whilst under argon. Samples for UV-Vis-NIR were taken by removing 100 µL of solution with a syringe and placed in a sealed degassed quartz cuvette with a pathlength of 1 mm.

5. Photographs and SEM of the Solutions and Gels

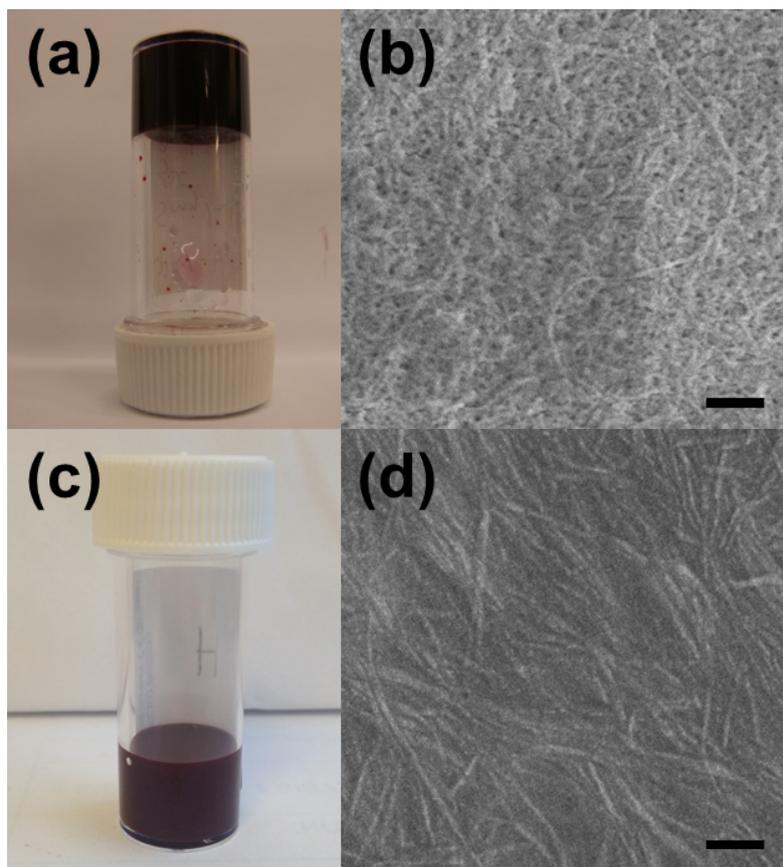


Figure S7. (a) Photograph of a solution of compound **2** at pH 10 at a concentration of 5 mg/mL. (b) SEM image of structures formed in the solution shown in (a). (c) Photograph of a gel formed on acidification of the solution of compound **2** shown in (a). (d) SEM image of structures formed in the gel shown in (c). For (b) and (d), the scale bar represents 2 μm .

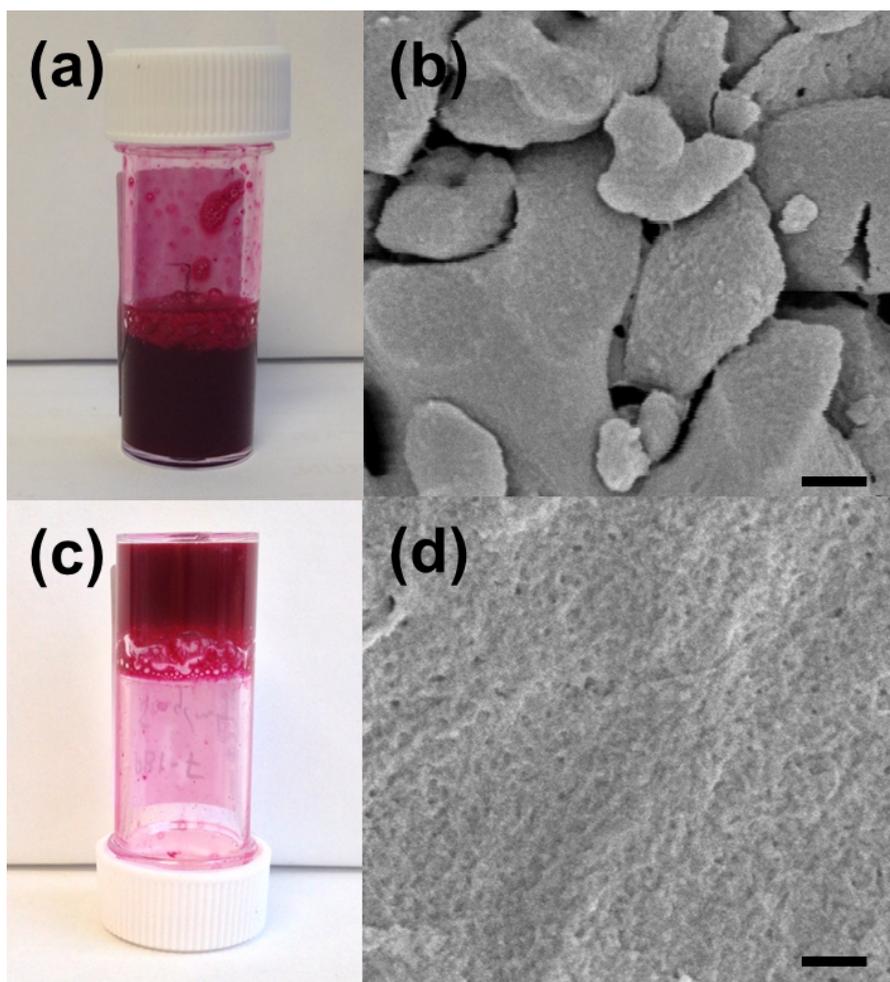


Figure S8. (a) Photograph of a solution of compound **3** at pH 10 at a concentration of 5 mg/mL. (b) SEM image of structures formed in the solution shown in (a). (c) Photograph of a gel formed on acidification of the solution of compound **3** shown in (a). (d) SEM image of structures formed in the gel shown in (c). For (b) and (d), the scale bar represents 2 μm

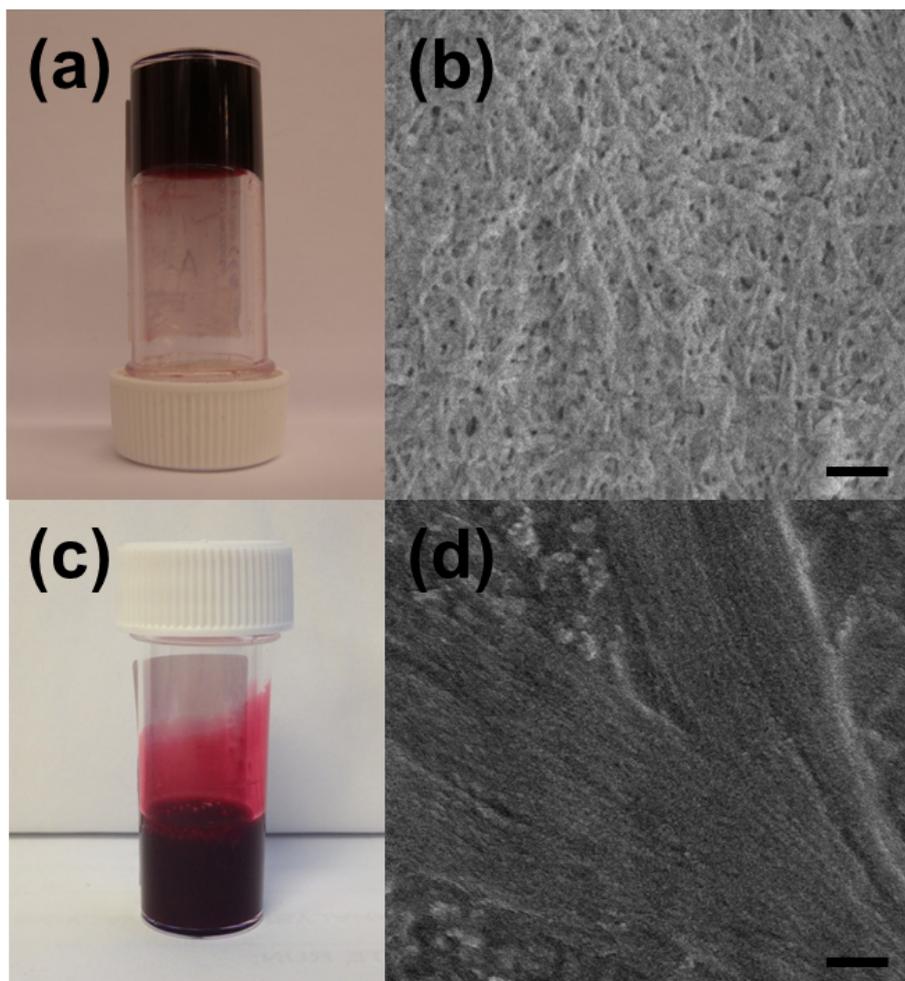


Figure S9. (a) Photograph of a solution of compound **4** at pH 10 at a concentration of 5 mg/mL. (b) SEM image of structures formed in the solution shown in (a). (c) Photograph of a gel formed on acidification of the solution of compound **4** shown in (a). (d) SEM image of structures formed in the gel shown in (c). For (b) and (d), the scale bar represents 2 μm .

6. Viscosity Data

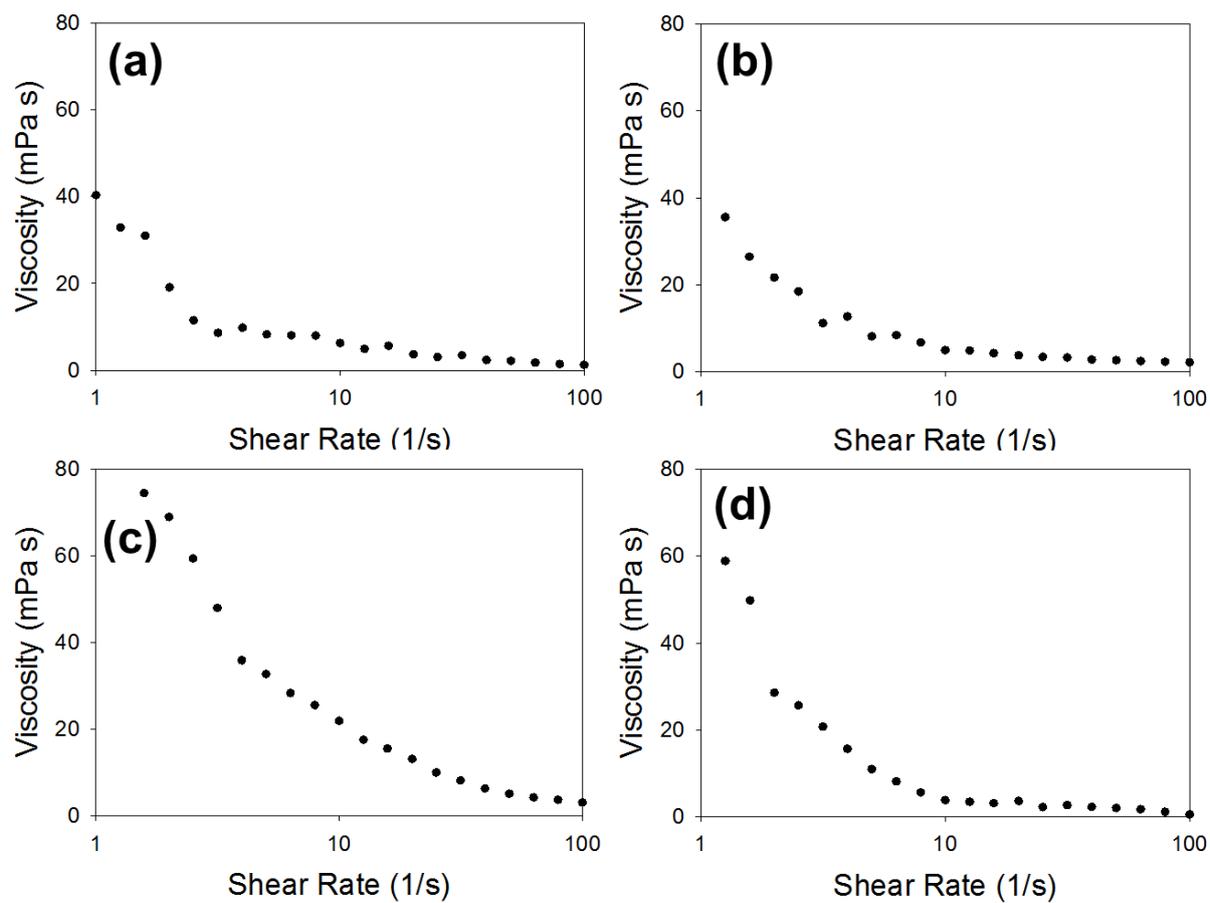


Figure S10. Viscosity measurements of LMWG at pH 10 under increasing shear rate for solutions of (a) **1**, (b) **2**, (c) **3** and (d) **4**

7. Powder X-Ray Diffraction

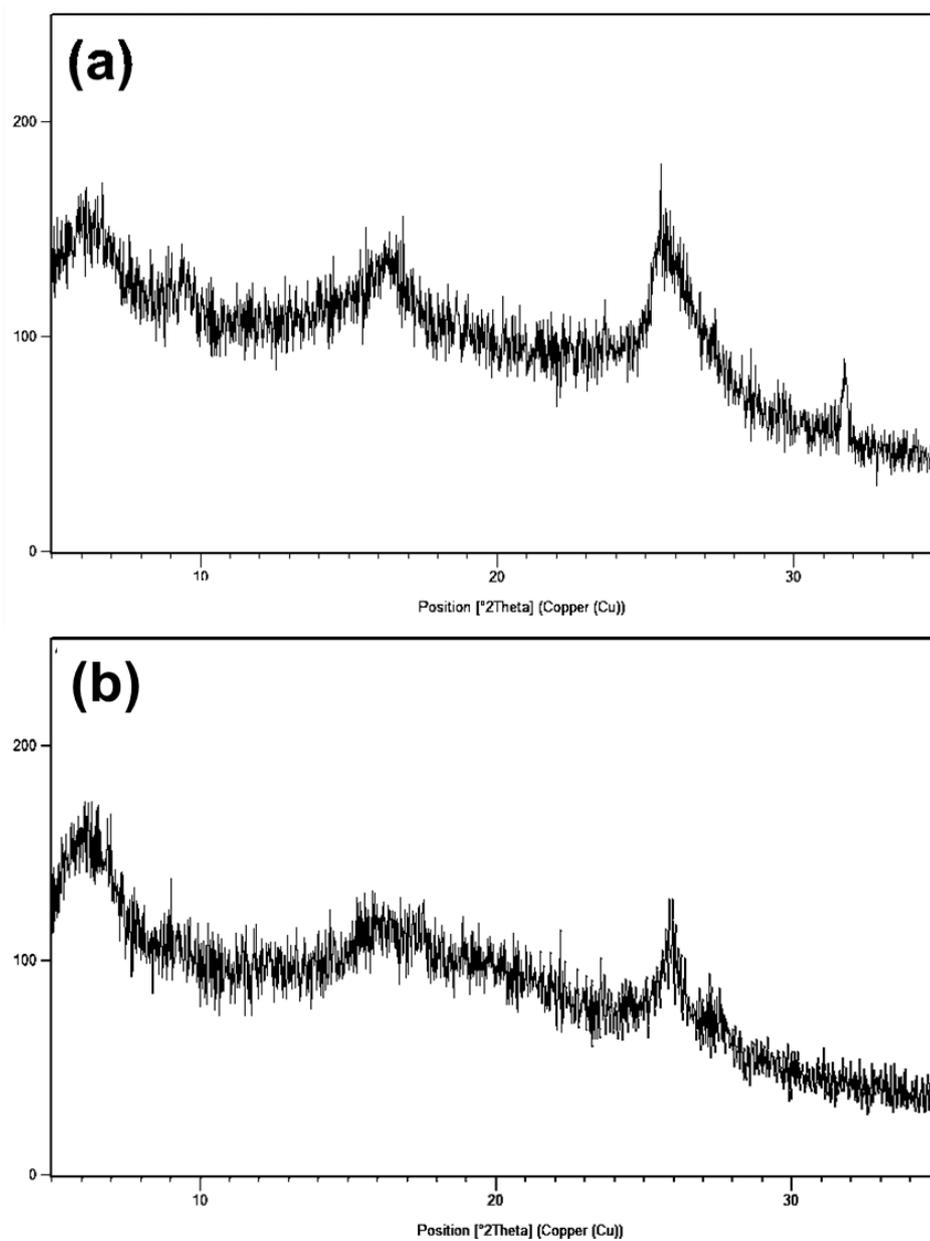


Figure S11. XRD patterns of **1** (a) dried solution (b) xerogel

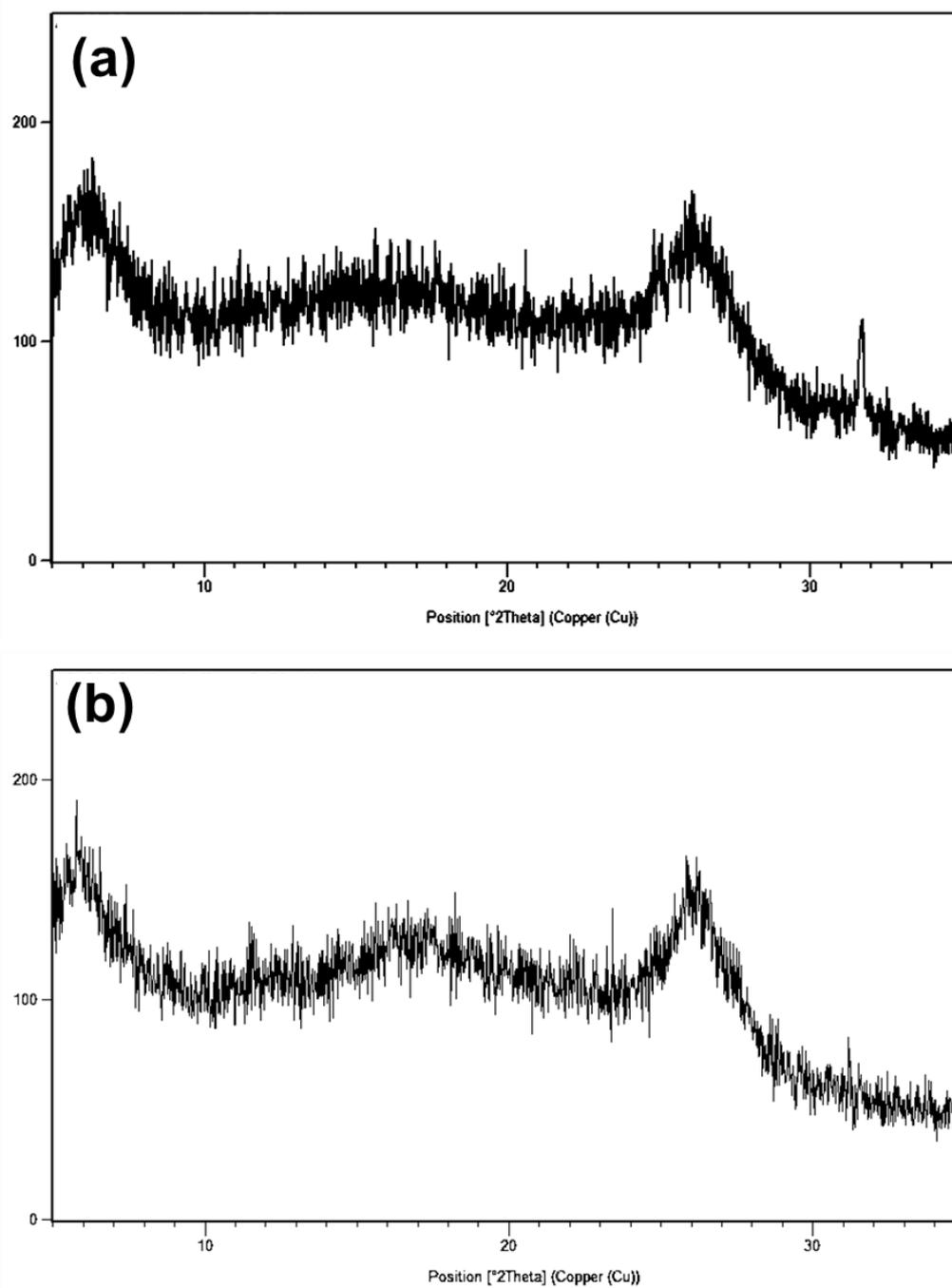


Figure S12. XRD patterns of 2 (a) dried solution (b) xerogel

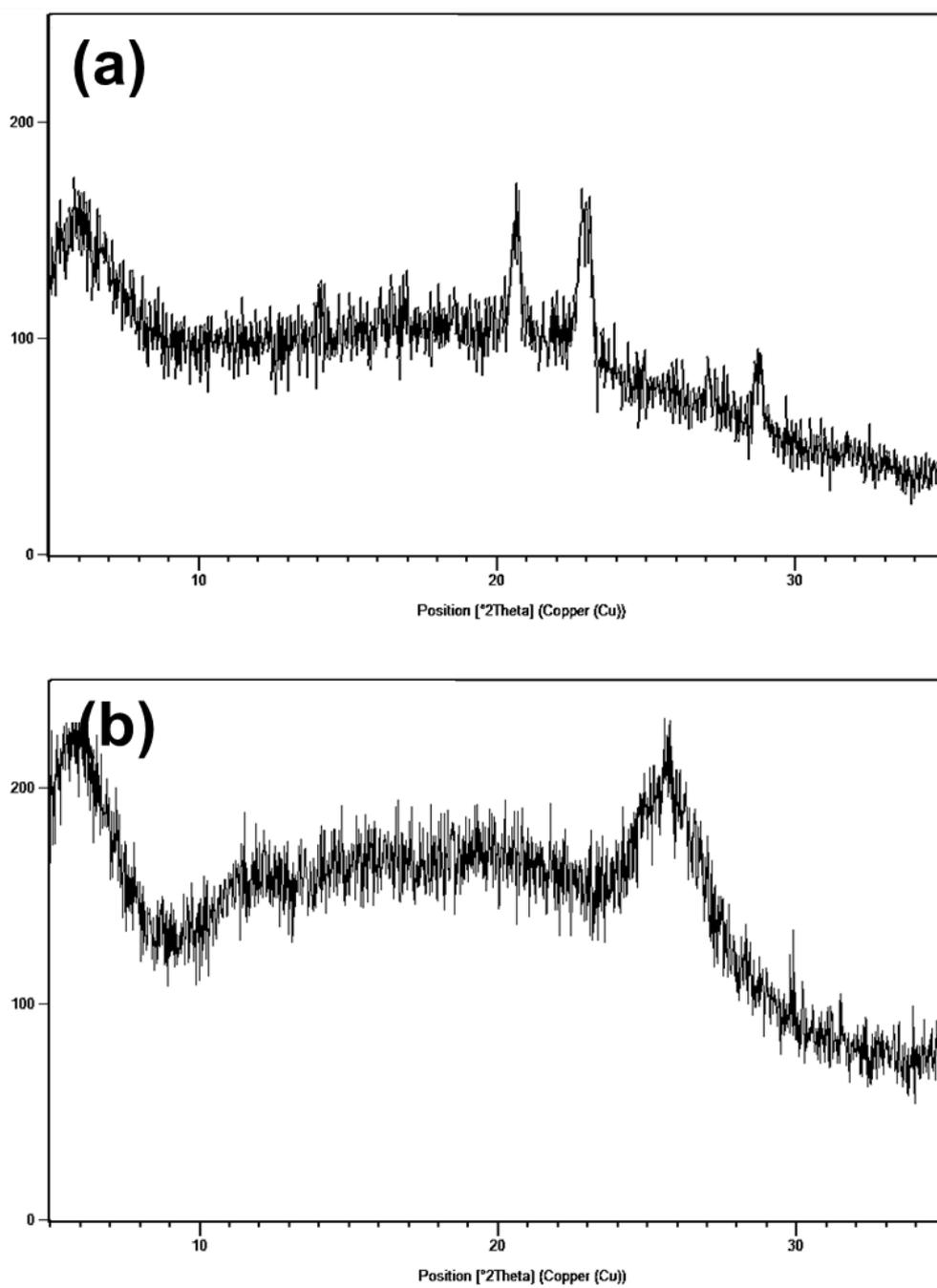


Figure S13. XRD patterns of **3** (a) dried solution (b) xerogel

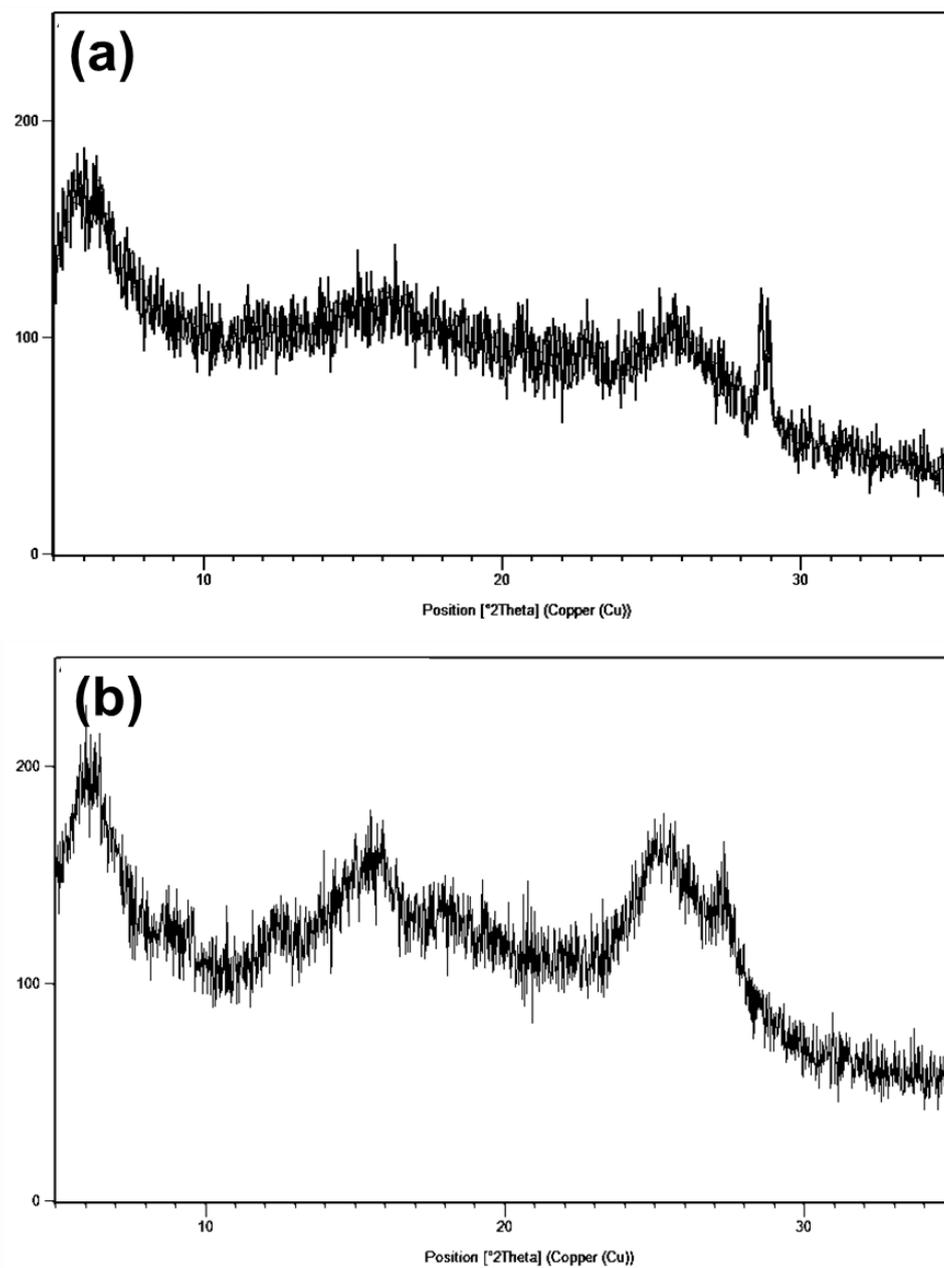


Figure S14. XRD patterns of 4 (a) dried solution (b) xerogel

8. Rheology Data

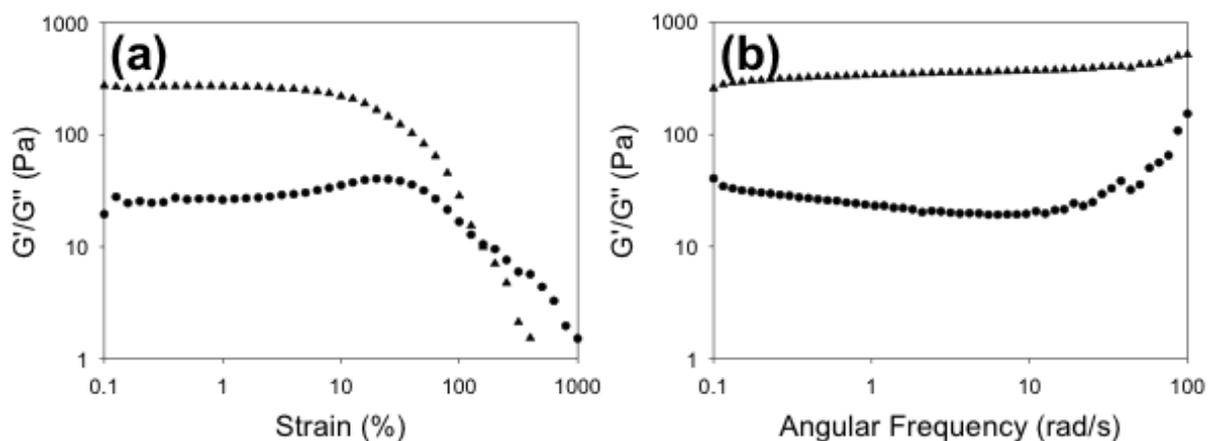


Figure S15. Graphs showing G' (triangle) and G'' (circle) for **1** gels during (a) strain sweep and (b) frequency sweep at 0.5 % strain

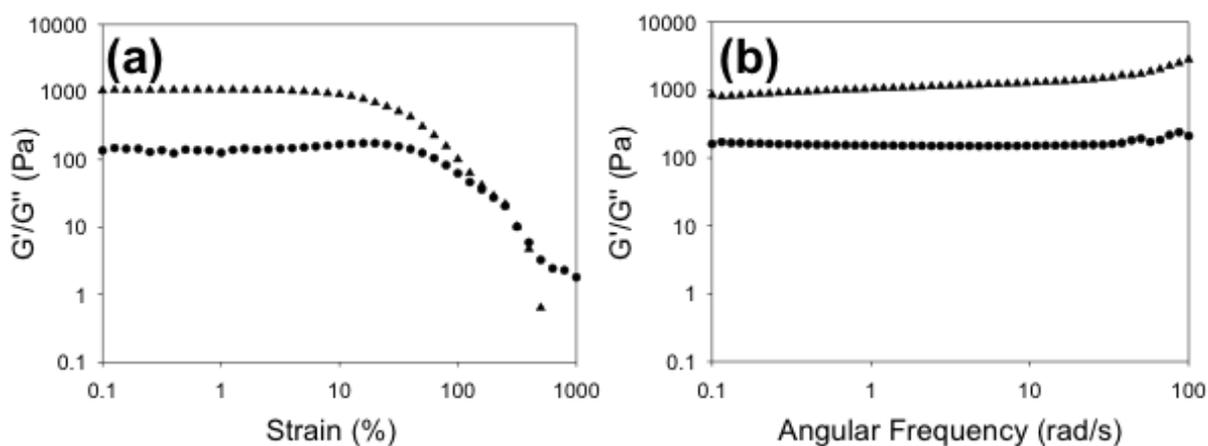


Figure S16. Graphs showing G' (triangle) and G'' (circle) for **2** gels during (a) strain sweep and (b) frequency sweep at 0.5 % strain

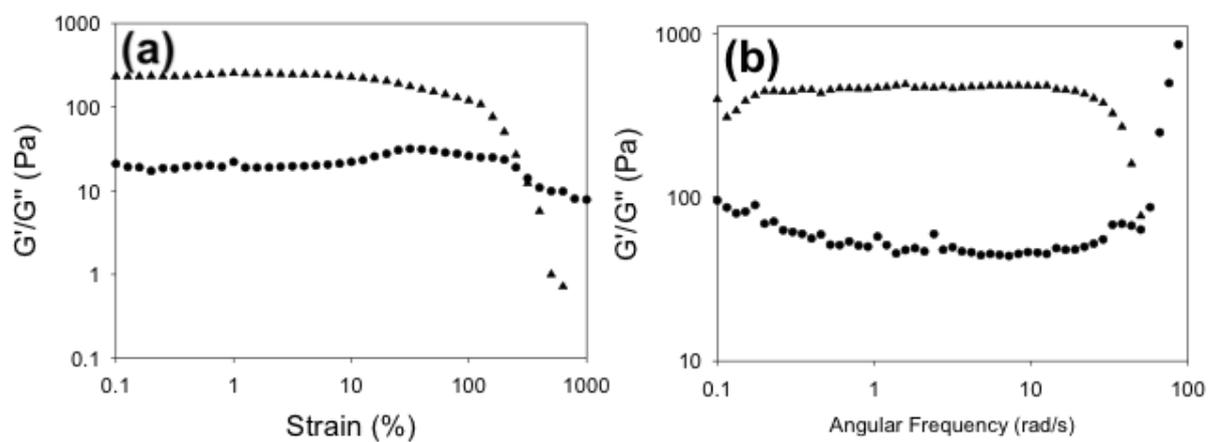


Figure S17. Graphs showing G' (triangle) and G'' (circle) for 3 gels during (a) strain sweep and (b) frequency sweep at 0.5 % strain

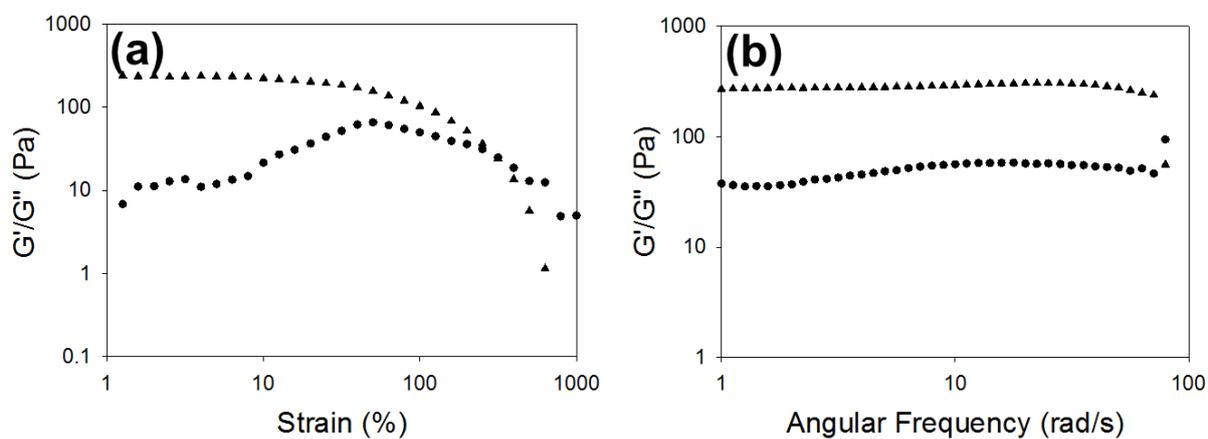


Figure S18. Graphs showing G' (triangle) and G'' (circle) for 4 gels during (a) strain sweep and (b) frequency sweep at 0.5 % strain

9. UV-vis and Fluorescence

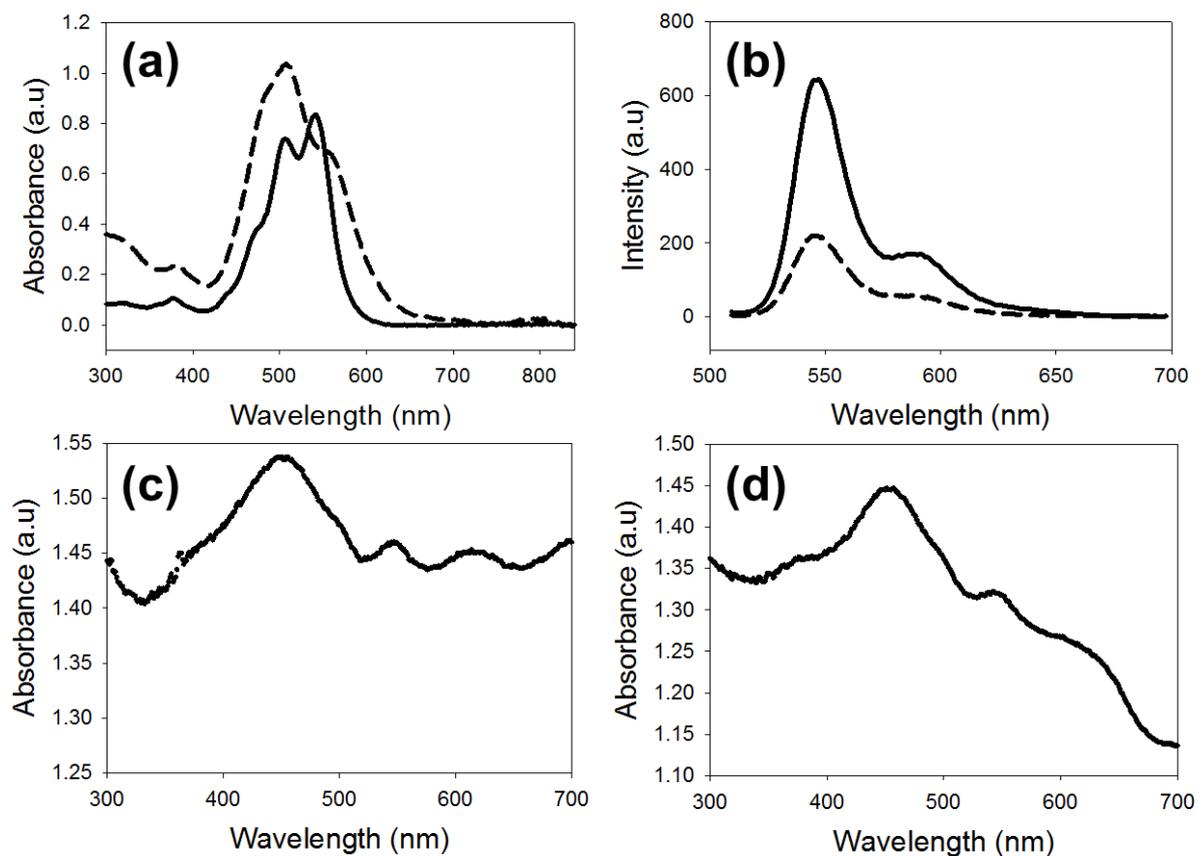


Figure S19. (a) UV-Vis spectra showing absorbance of **2** in solution (solid line) and as a gel (dashed line) (b) Fluorescence spectra of **2** at 470 nm in solution at pH 10 (solid line) and pH 3 (dashed line) (c) UV-Vis spectrum of **2** xerogel (d) UV-Vis spectrum of **2** dried solution

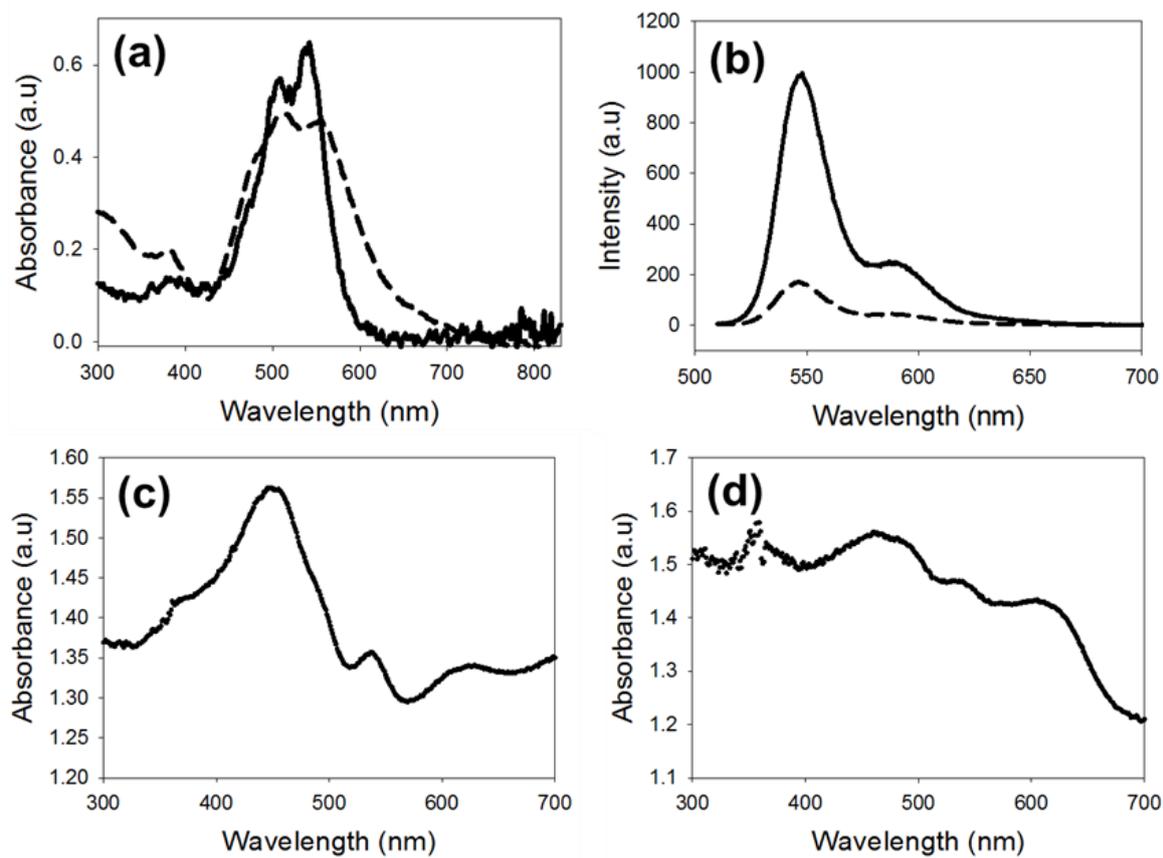


Figure S20. (a) UV-Vis spectra showing absorbance of **3** in solution (solid line) and as a gel (dashed line) (b) Fluorescence spectra of **3** at 470 nm in solution at pH 10 (solid line) and pH 3 (dashed line) (c) UV-Vis spectrum of **3** xerogel (d) UV-Vis spectrum of **3** dried solution

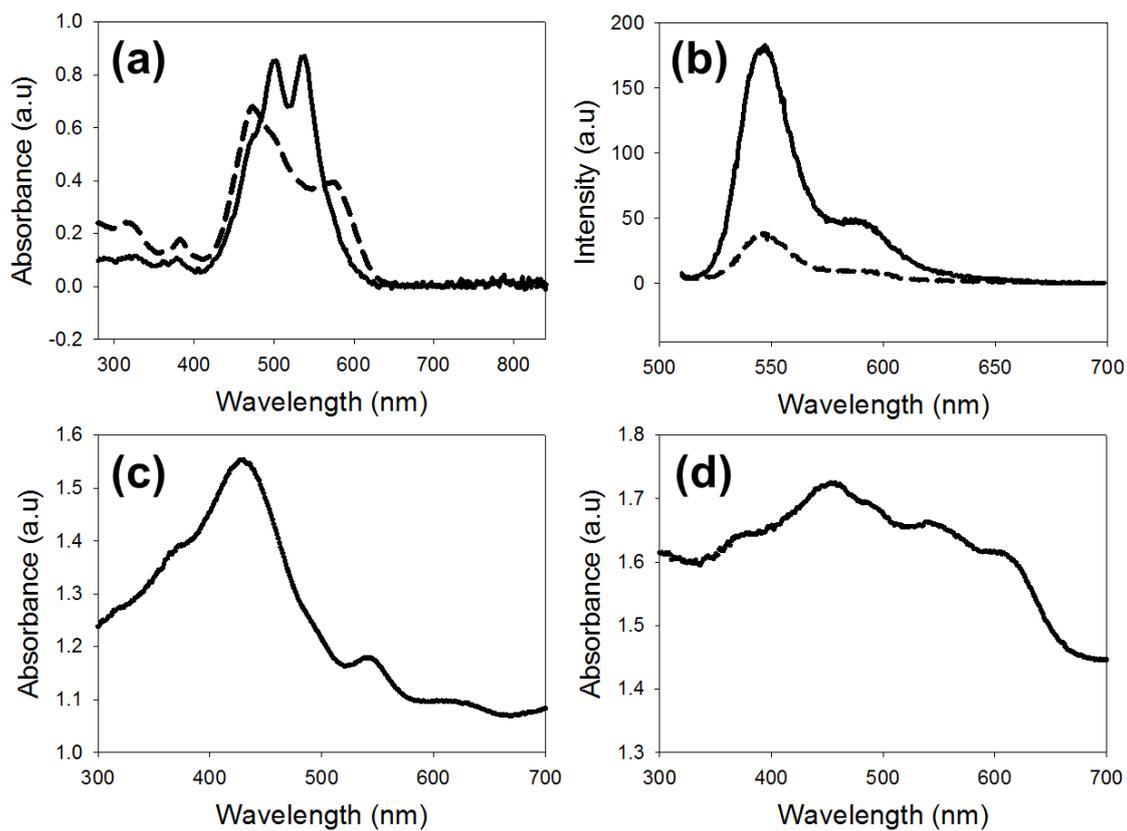


Figure S21. (a) UV-Vis spectra showing absorbance of **4** in solution (solid line) and as a gel (dashed line) (b) Fluorescence spectra of **4** at 470 nm in solution at pH 10 (solid line) and pH 3 (dashed line) (c) UV-Vis spectrum of **4** xerogel (d) UV-Vis spectrum of **4** dried solution

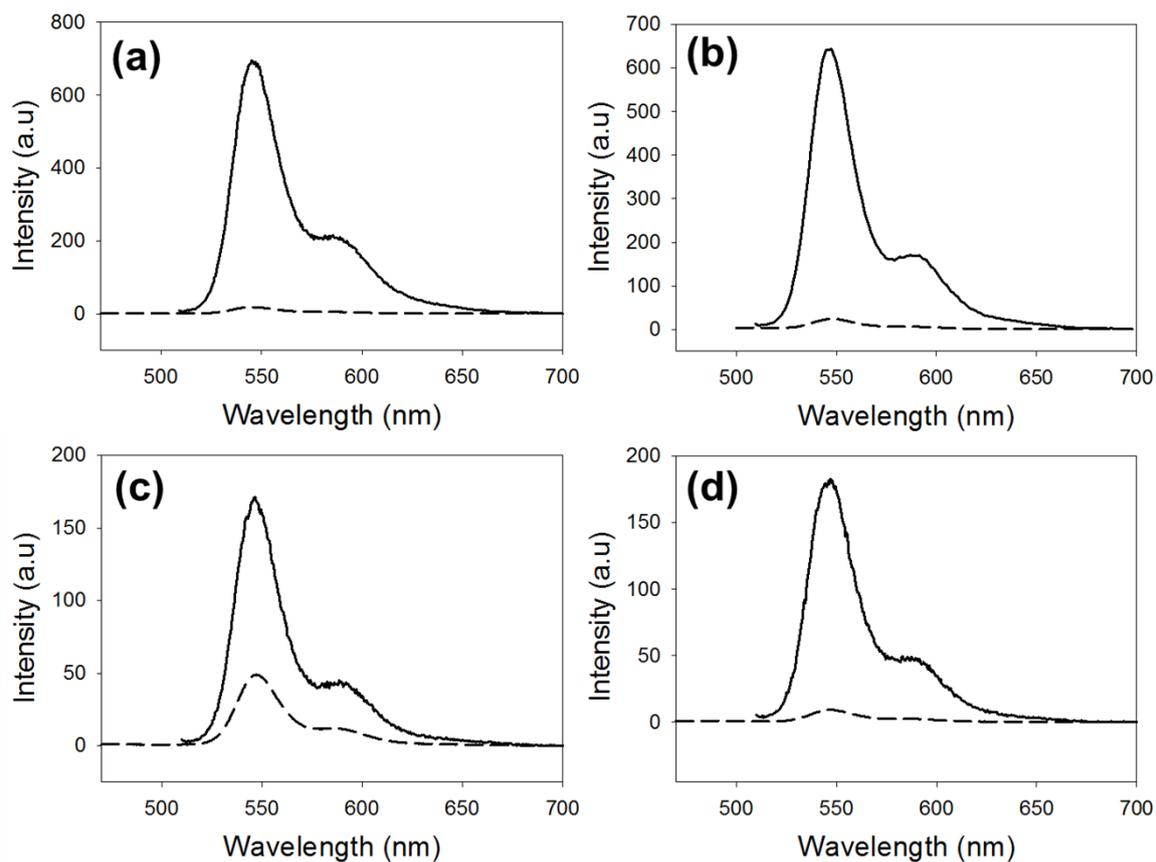


Figure S22. Fluorescence spectra of LMWG solutions at pH 10 excited at 365 nm (dashed line) and 490 nm (solid line) for (a) **1**, (b) **2**, (c) **3** and (d) **4**

10. Film Morphology

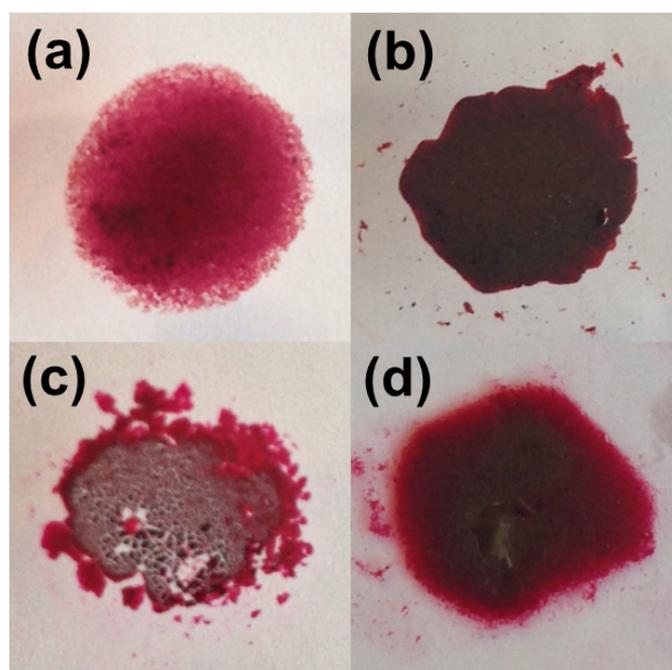


Figure S23. Photographs showing example xerogels on glass slides (a) **1** (b) **2** (c) **3** and (d) **4**

11. Conductivity

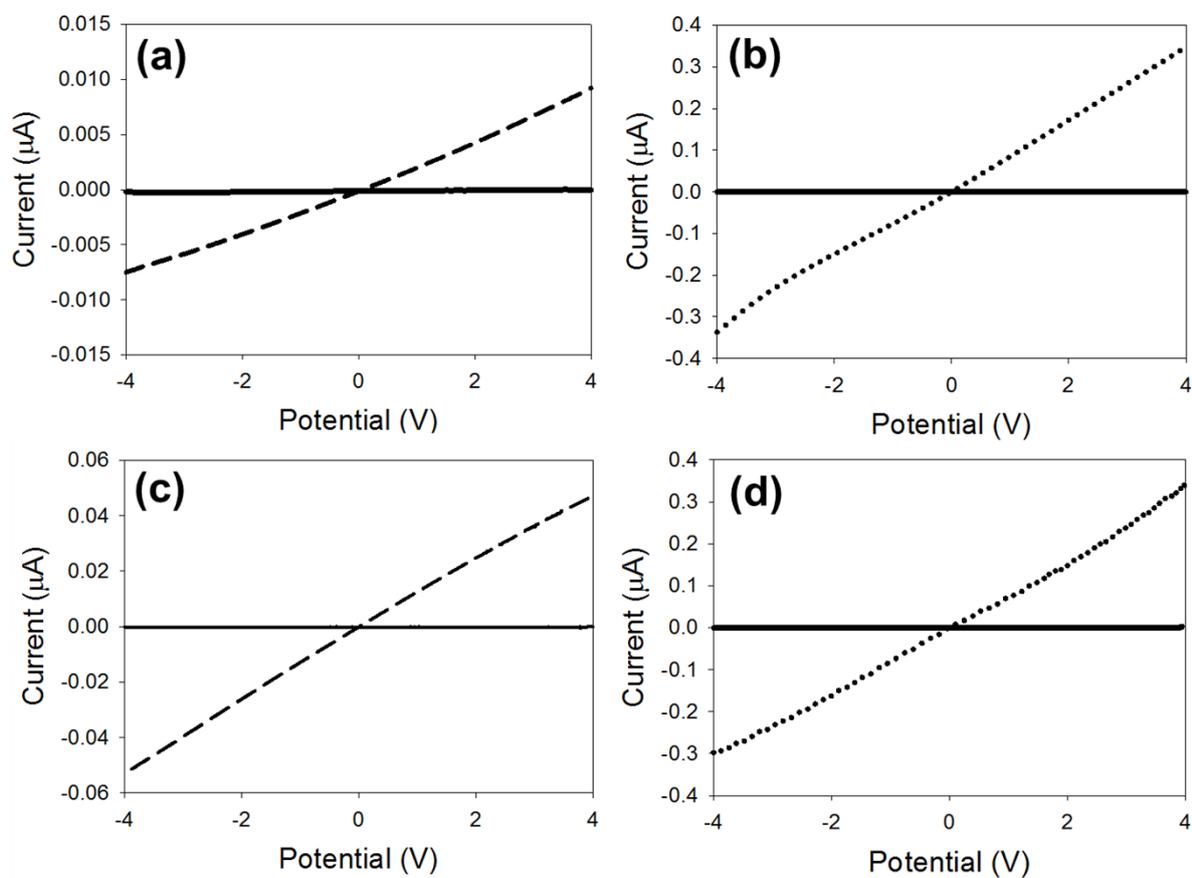


Figure S24. I-V curves in the light and the dark for **1** (a) xerogel under 365 nm LED (b) dried solution under 365 nm LED (c) xerogel under 150 W Xenon lamp and (d) dried solution under 150 W Xenon lamp. Solid line represents measurements in the dark. Dashed and dotted lines represent measurements in the light

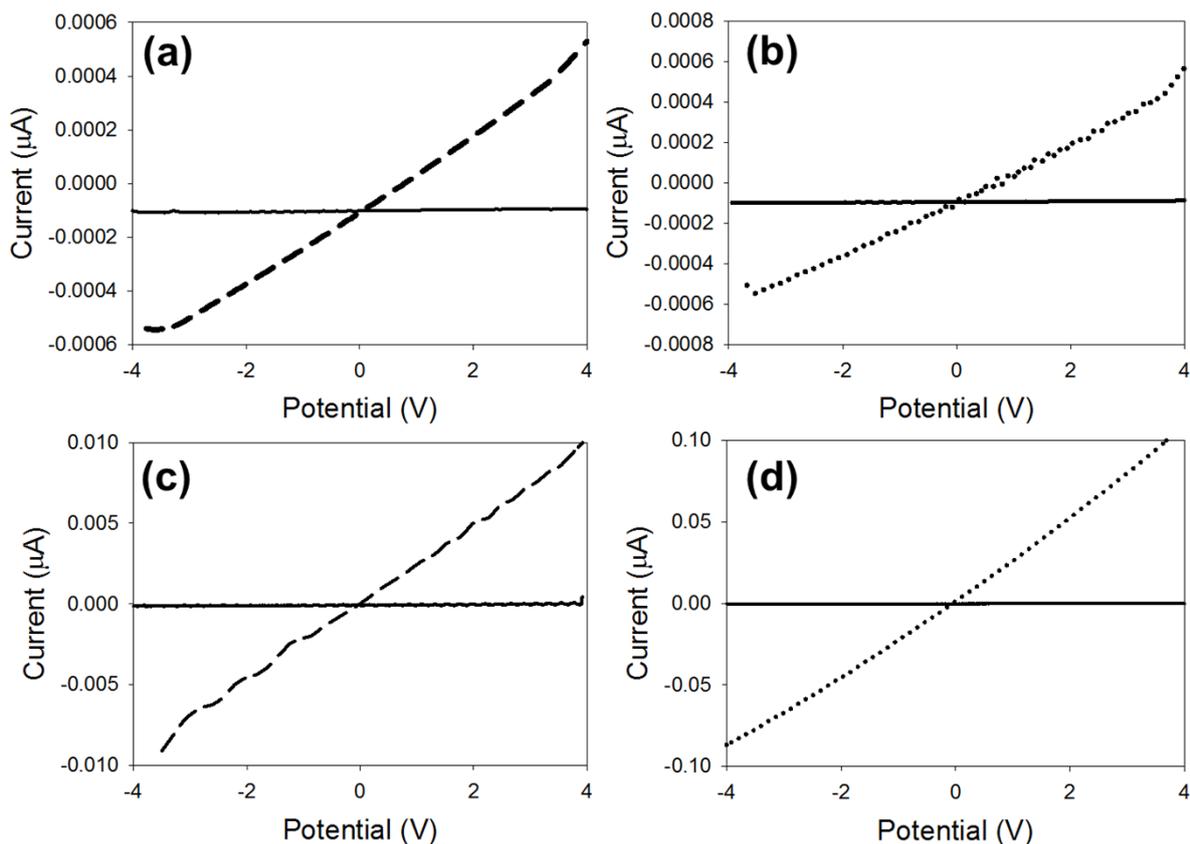


Figure S25. I-V curves in the light and the dark for **2** (a) xerogel under 365 nm LED (b) dried solution under 365 nm LED (c) xerogel under 150 W Xenon lamp and (d) dried solution under 150 W Xenon lamp. Solid line represents measurements in the dark. Dashed and dotted lines represent measurements in the light

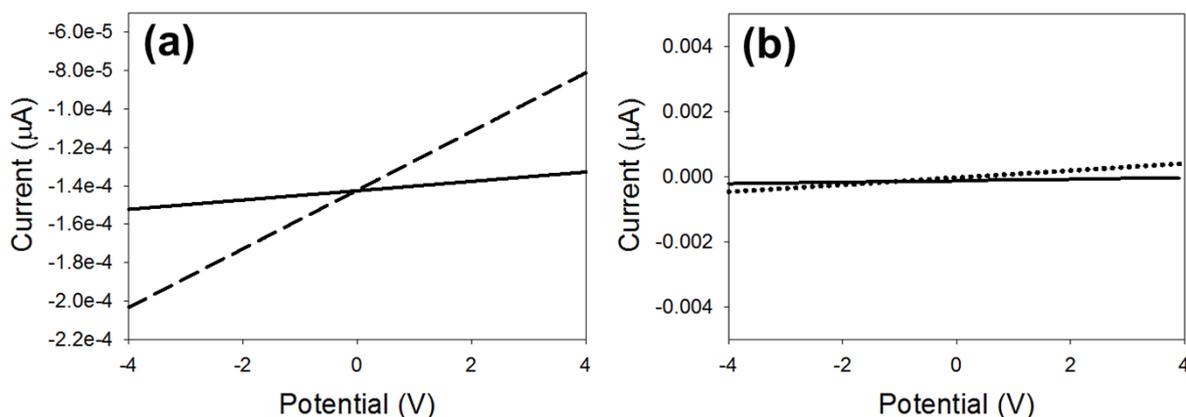


Figure S26. I-V curves in the light and the dark for **3** (a) xerogel under 150 W Xenon lamp and (b) dried solution under 150 W Xenon lamp. Solid line represents measurements in the dark. Dashed and dotted lines represent measurements in the light

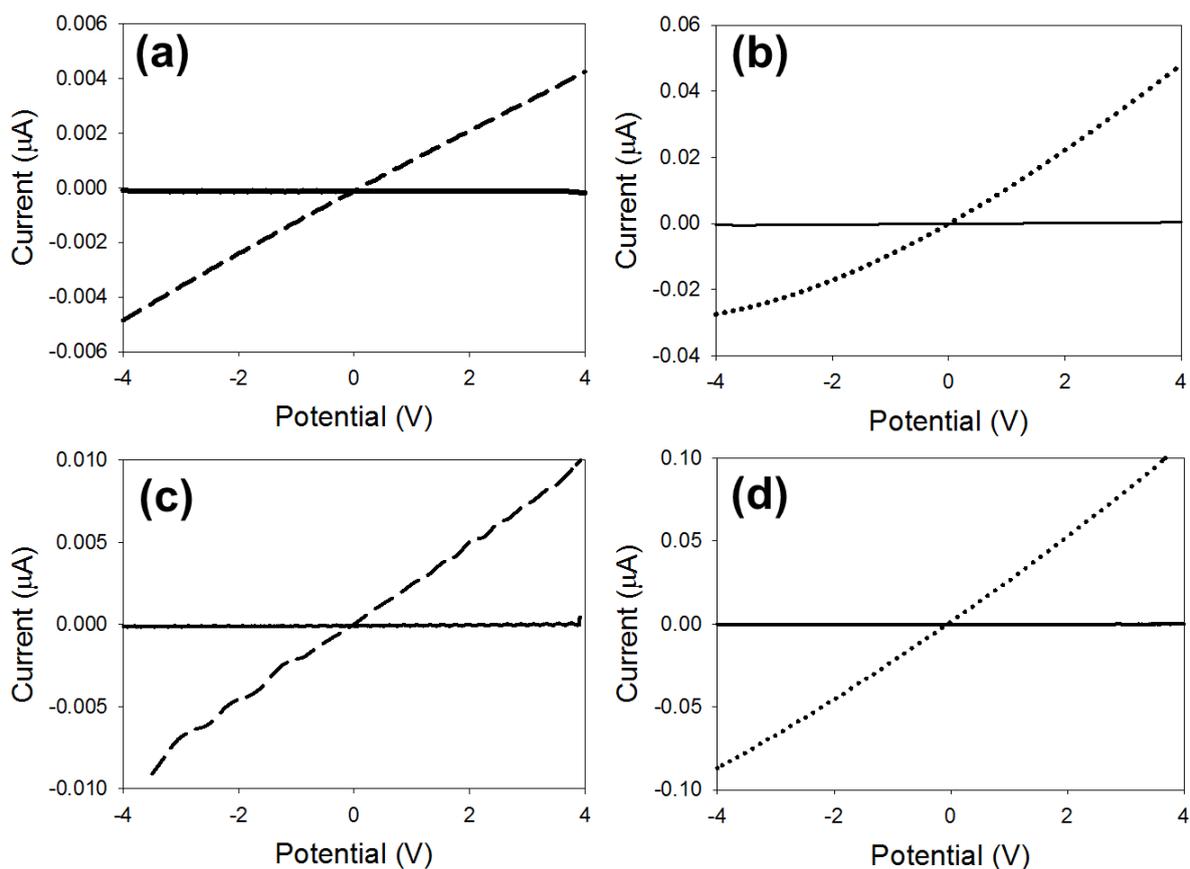


Figure S27. I-V curves in the light and the dark for **4** (a) xerogel under 365 nm LED (b) dried solution under 365 nm LED (c) xerogel under 150 W Xenon lamp and (d) dried solution under 150 W Xenon lamp. Solid line represents measurements in the dark. Dashed and dotted lines represent measurements in the light

12. Wavelength Response

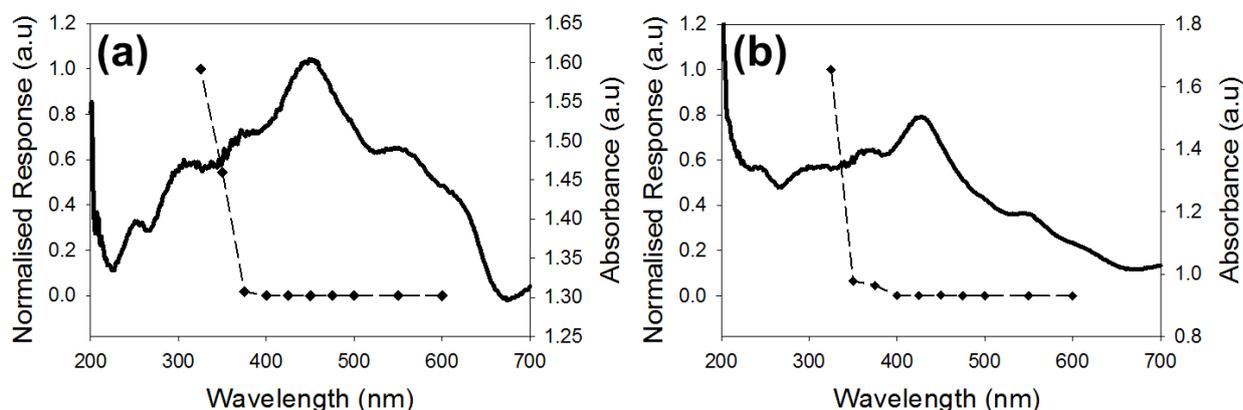


Figure S28. UV-Vis spectra (solid line) showing absorbance of **1** as a (a) xerogel (b) dried LMWG solution with change in current at different wavelengths of light (circles). Wavelengths below 320 nm were not studied as the output of our lamp and optics decreases rapidly at very short wavelengths.

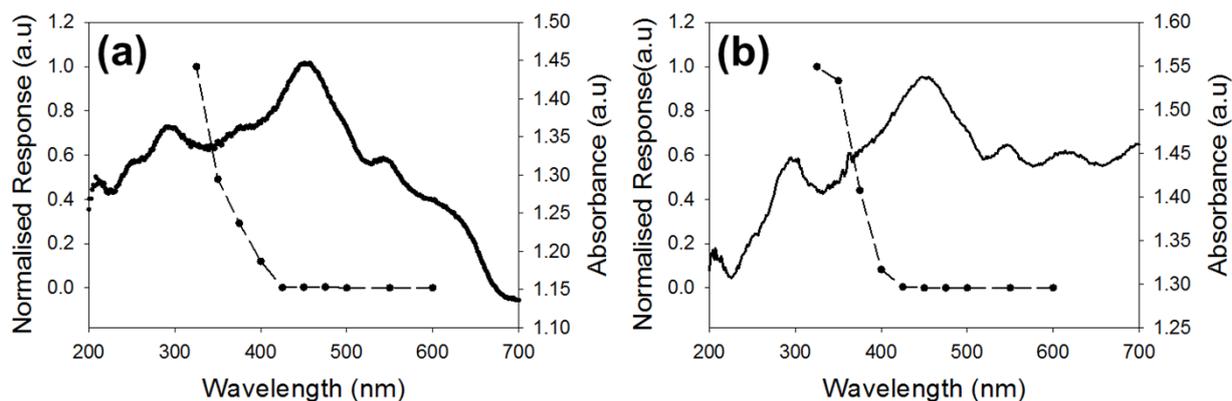


Figure S29. UV-Vis spectra (solid line) showing absorbance of **2** as a (a) xerogel (b) dried LMWG solution with change in current at different wavelengths of light (circles). Wavelengths below 320 nm were not studied as the output of our lamp and optics decreases rapidly at very short wavelengths.

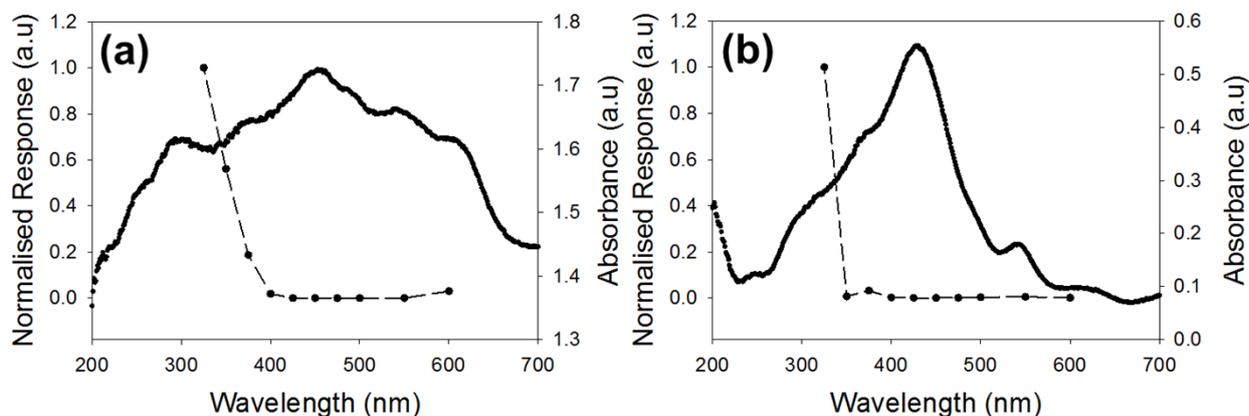


Figure S30. UV-Vis spectra (solid line) showing absorbance of **4** as a (a) xerogel (b) dried LMWG solution with change in current at different wavelengths of light (circles). Wavelengths below 320 nm were not studied as the output of our lamp and optics decreases rapidly at very short wavelengths.

13. Growth and Decay of Photoconductivity

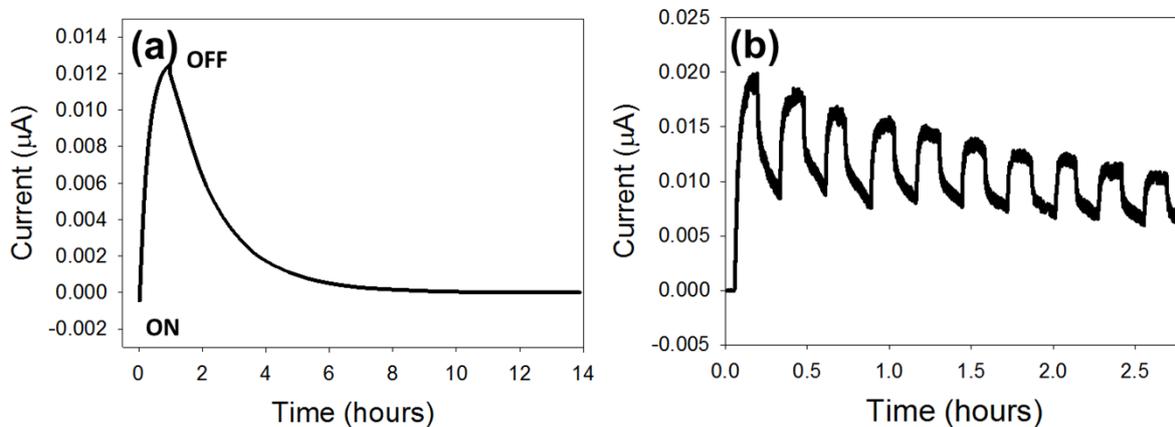


Figure S31. Xerogel of **1** (a) showing the change in conductivity when a 365 nm LED is turned on and off allowing conductivity to return back to off state (b) Showing light on for 500 seconds and off for 500 seconds cycles

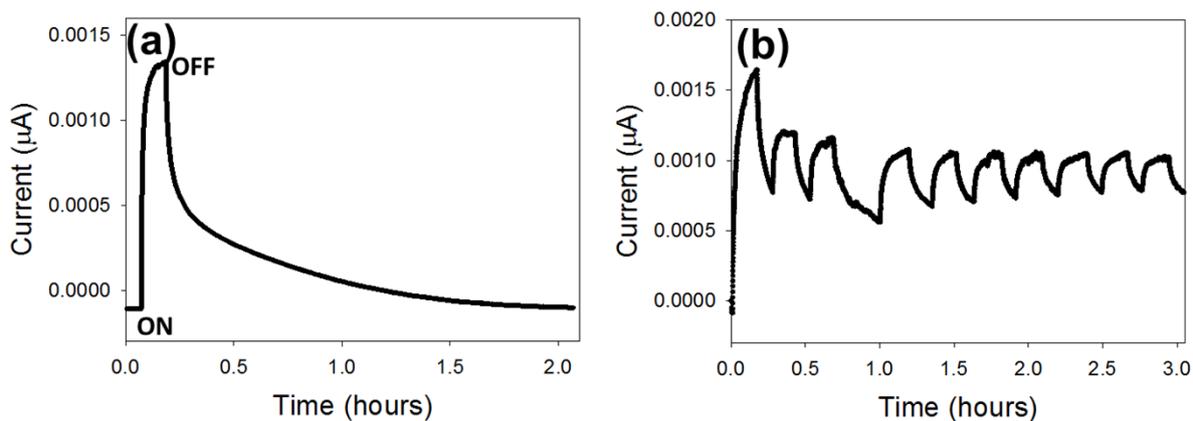


Figure S32. Dried solution of **2** (a) showing the change in conductivity when a 365 nm LED is turned on and off allowing conductivity to return back to off state (b) Showing light on for 500 seconds and off for 500 seconds cycles

14. Photochromism

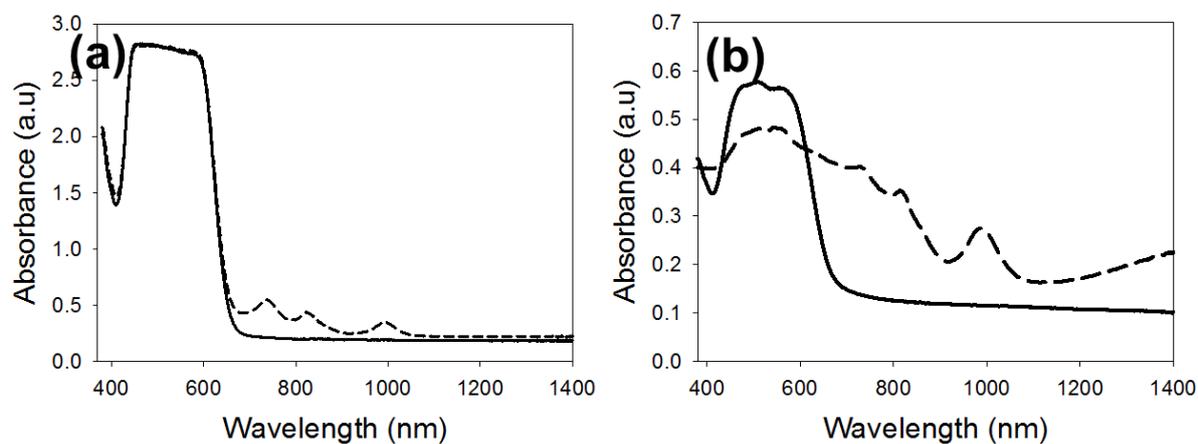


Figure S33. UV-Vis spectra of **1** as a (a) xerogel and (b) dried solution in the dark (solid line) and after around 30 minutes of irradiation with a 365 nm LED (dashed line)

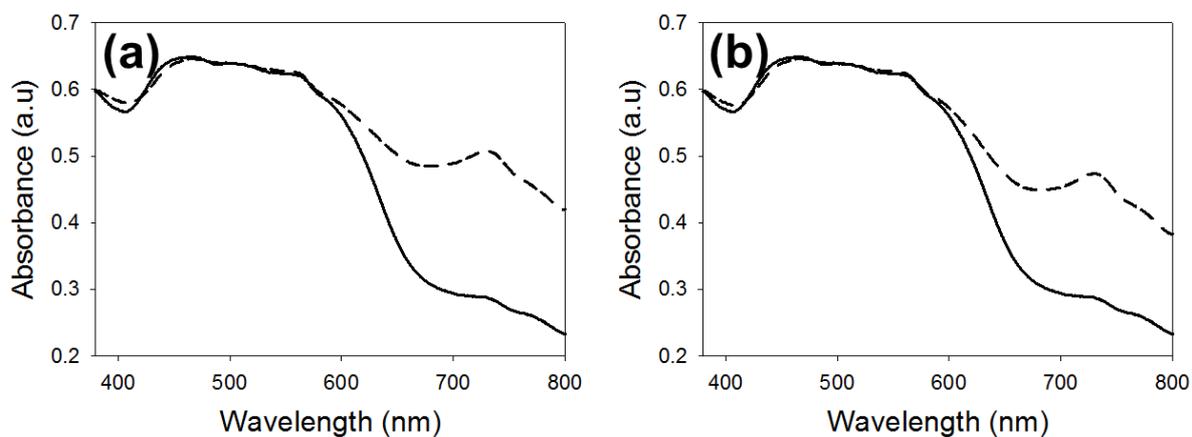


Figure S34. UV-Vis spectra of **3** as a (a) xerogel and (b) dried solution in the dark (solid line) and after around 30 minutes of irradiation with a 365 nm LED (dashed line)

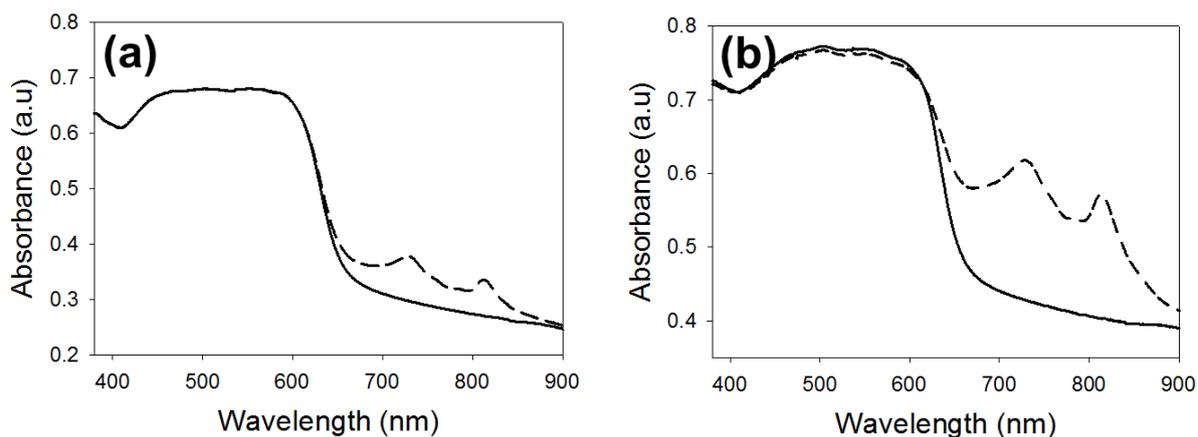


Figure S35. UV-Vis spectra of **4** as a (a) xerogel and (b) dried solution in the dark (solid line) and after around 30 minutes of irradiation with a 365 nm LED (dashed line)

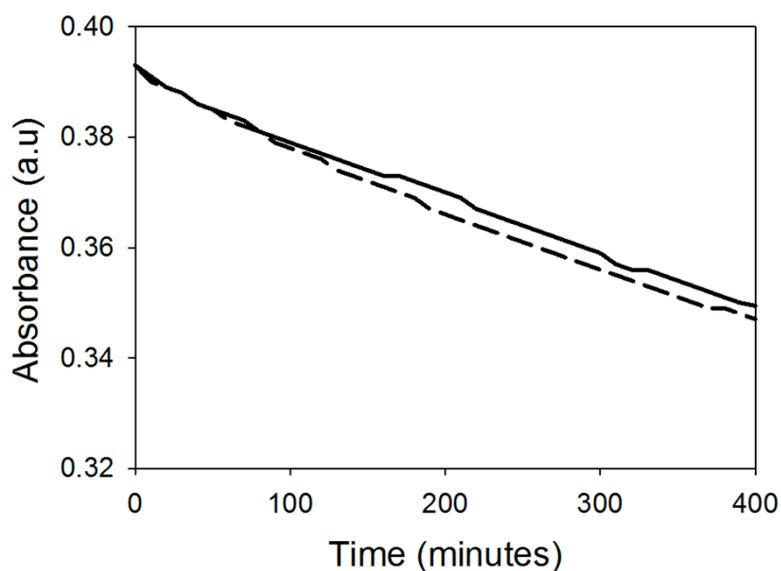


Figure S36. Graph showing change in absorbance at 730 nm of xerogel **1** after the 365 nm LED was turned off in air (dashed line) and under argon (solid line) for 400 minutes

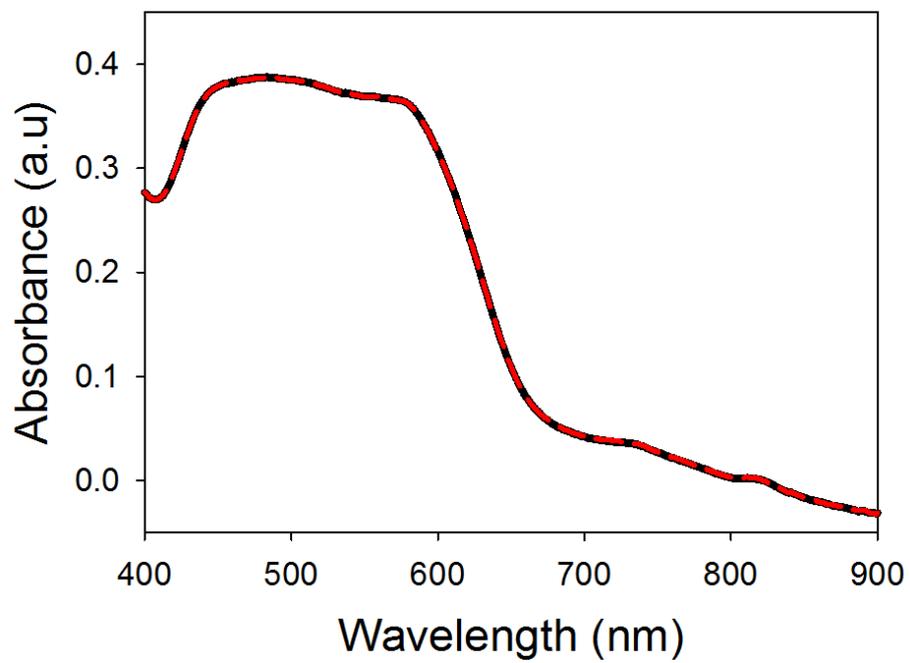


Figure S37. UV-Vis spectra showing the absorbance of xerogel **1** in the dark (solid line) and after 45 minutes irradiation under a 465 nm LED (dashed red line)

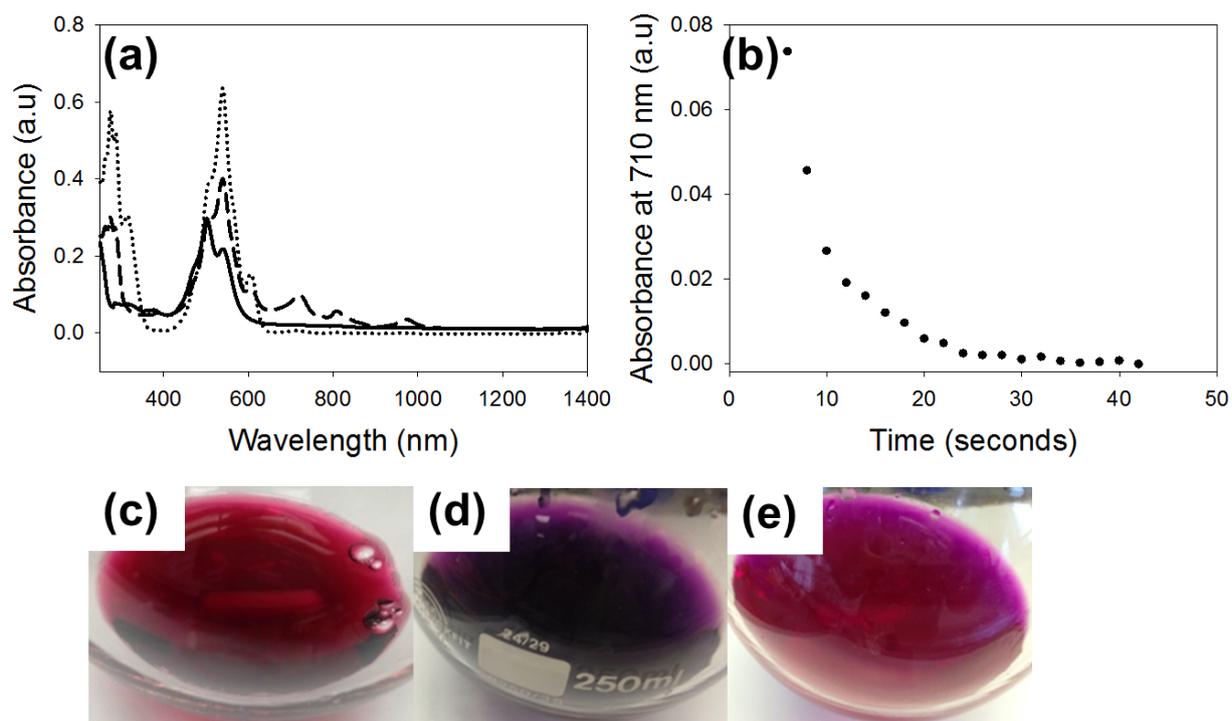


Figure S38. (a) UV-Vis showing absorbance of **1** in solution after with various amounts of sodium dithionite added. Solid line represents before sodium dithionite was added (photograph (c)), dashed line is after 20 mg of sodium dithionite was added (photograph (d)) and the dotted line is after 40 mg of sodium dithionite was added (photograph (e)) (b) Change of absorbance in the peak in UV-Vis at 710 nm of the dashed line after being exposed to air.