Electronic Supplementary Material (ESI) for Chemical Communications.

Self-assembly, Self-sorting, and Electronic Properties of a Diketopyrrolopyrrole Hydrogelator

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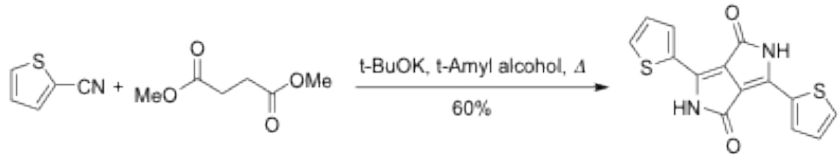
SUPPORTING INFORMATION

Synthesis and Materials

All reagents and solvents were purchased from commercial suppliers and used as received. Solvents were HPLC grade from freshly opened containers and not dried any further. ^{1}H NMR spectra were recorded on a Bruker Avance III HD 500 MHz spectrometer at the University of Liverpool, except that for **CC-002**. ^{13}C NMR spectra were recorded on a Bruker Avance III HD 400 MHz spectrometer at 100 MHz at the University of Liverpool, except that for **CC-002**. ^{1}H and ^{13}C spectra for **CC-002** were recorded on a Bruker Avance III 400 MHz (100 MHz for ^{13}C) spectrometer at the University of Glasgow. Proton and carbon assignments were aided by COSY and HSQC experiments, respectively, where required. Proton spectra are referenced to residual solvent peaks at 7.26 ppm ($CDCl_3$) or 2.50 ppm (DMSO-d_6). Carbon spectra are referenced to residual solvent peaks at 77.16 ppm ($CDCl_3$) or 39.52 ppm (DMSO-d_6). Mass spectra were recorded at the University of Glasgow on a Bruker micrOTOF$_Q$, except that for **BL-001**, which was recorded at the University of Liverpool on an Agilent QTOF 7200. PBI-A was synthesised as previously reported.[1]

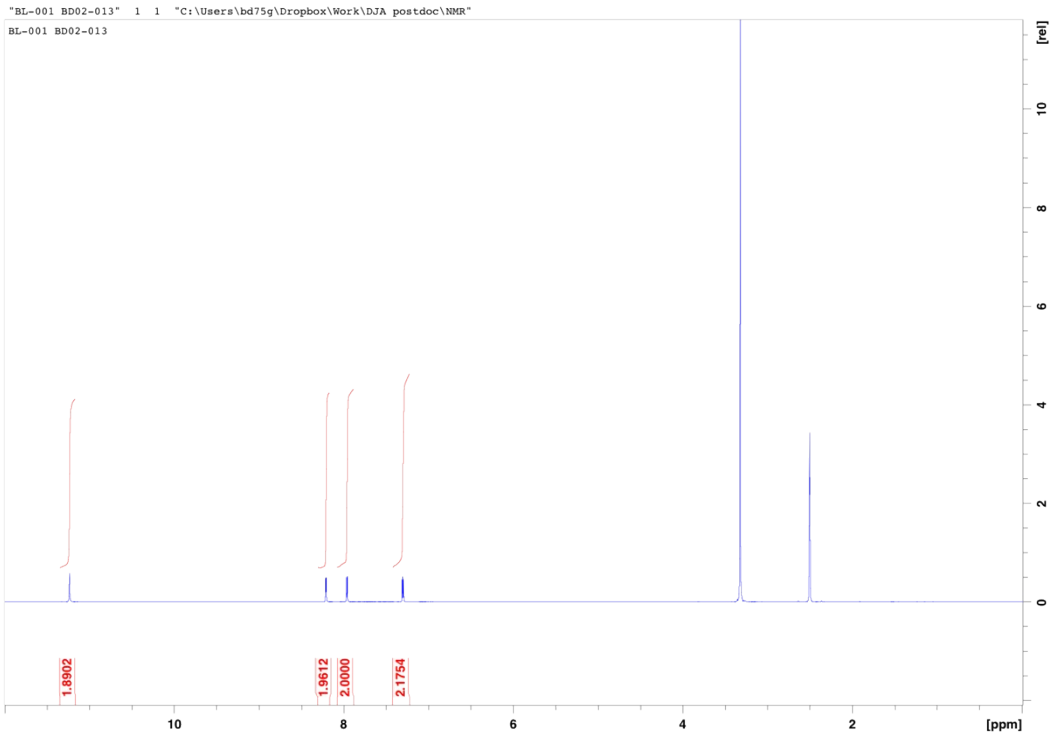
3,6-Di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (BL-001)



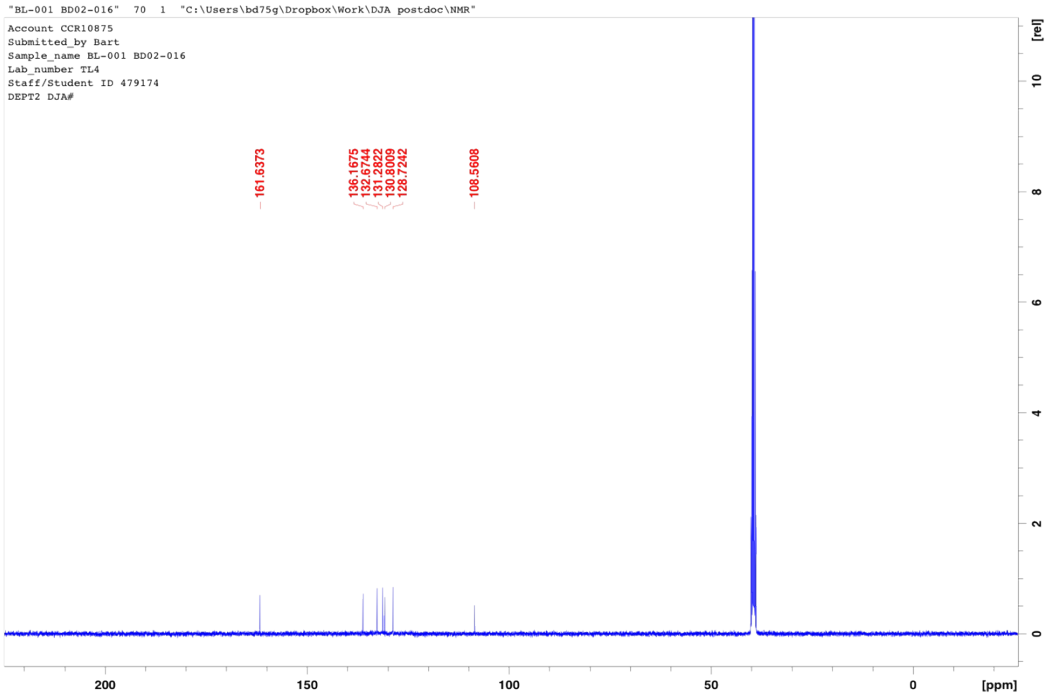
BL-001

Potassium *tert*-butoxide (3.57 eq, 4.00 g) was placed in a 100 mL two-necked flask equipped with a reflux condenser and pressure-equalising dropping funnel and flushed with nitrogen. A solution of thiophene-2-carbonitrile (3 eq, 3.27 g, 2.79 mL) in *tert*-amyl alcohol (25 mL) was added and the mixture heated to 105 °C under positive nitrogen pressure. A solution of dimethyl succinate (9.99 mmol, 1 eq, 1.46 g, 1.30 mL) in *tert*-amyl alcohol (8 mL) was then added in small portions from the dropping funnel over *ca.* 45 minutes. On complete addition, heating was continued for a further two hours. After this time, the temperature was reduced to 65 °C, the mixture diluted with methanol (50 mL), neutralised with glacial acetic acid (*ca.* 4 mL) and then heated at reflux for a further 15 minutes. Upon cooling to room temperature, the mixture was filtered and the filter cake washed with successive portions of hot methanol, hot water, hot methanol, and hot water again. After drying under vacuum at 70 °C overnight, the title compound **BL-001** was obtained as a purple/black solid (1.81 g, 60%). δ_H (500 MHz, ppm, DMSO-d_6) 11.23 (2H, s, NH), 8.21 (2H, dd, *J* 3.75, 1.00 Hz, thiophene-H), 7.96 (2H, dd, *J* 4.97, 1.02 Hz, thiophene-H), 7.30

(2H, dd, *J* 4.85, 3.85 Hz, thiophene-H).[2] ∂_C (100 MHz, ppm, DMSO-d_6) 161.64 (C=O), 136.17, 132.67, 131.28, 130.80, 128.72, 108.56 (aromatic C). MS (CI) m/z: $[M+H]^+$ 301. HRMS (CI) m/z: $[M+H]^+$ calcd for $C_{14}H_9N_2O_2S_2$ 301.0095; found 301.0095.

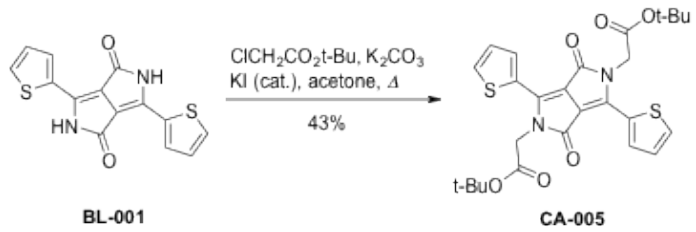


Spectrum 1. ^{1}H NMR spectrum of **BL-001** in DMSO-d_6



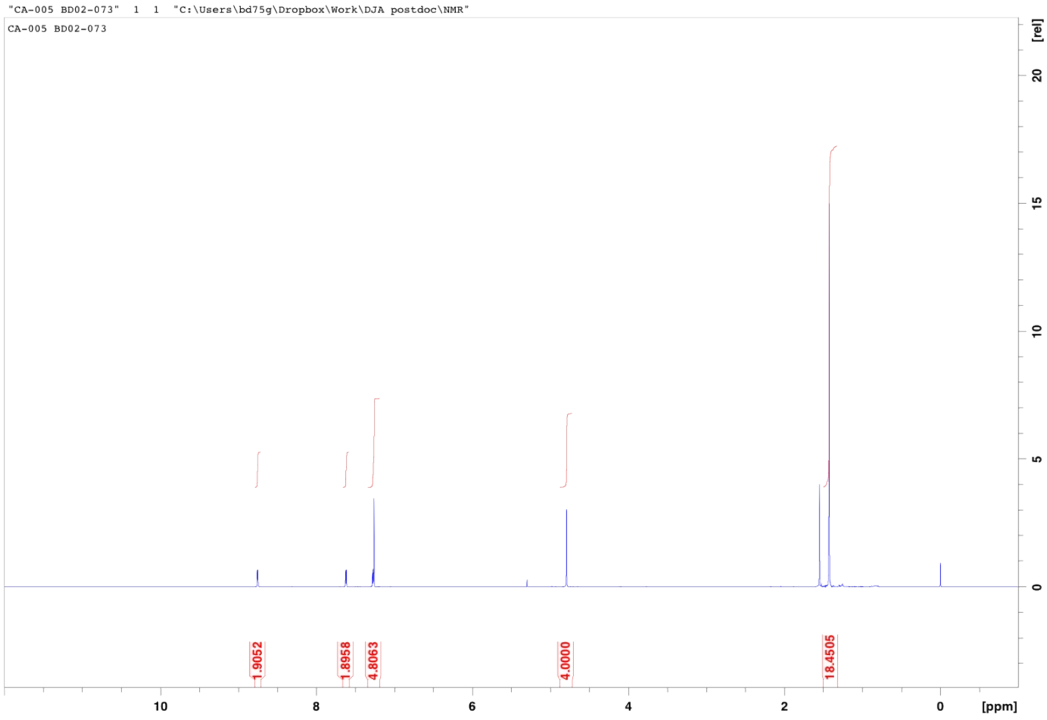
Spectrum 2. ^{13}C NMR spectrum of **BL-001** in DMSO-d_6

Di-*tert*-butyl 2,2'-(1,4-dioxo-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-2,5(1*H*,4*H*)-diyl)diacetate (CA-005)

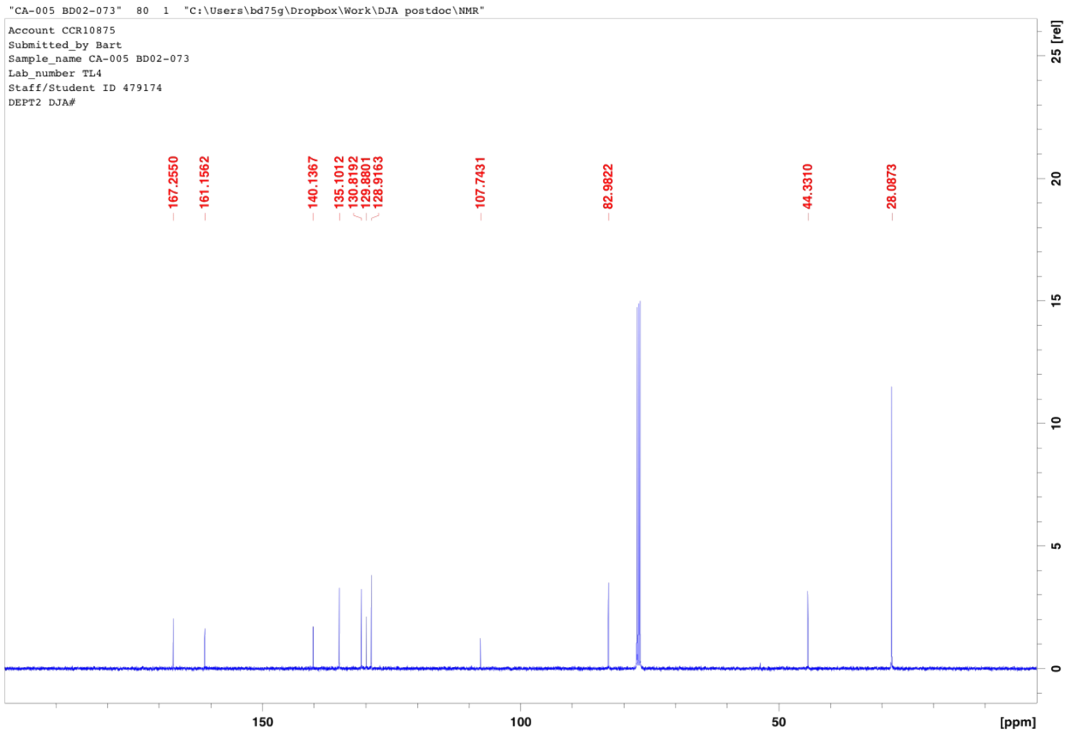


To a suspension of **BL-001** (5.64 g, 18.8 mmol, 1 eq) in acetone (190 mL) was added potassium carbonate (6 eq, 15.6 g), *tert*-butyl chloroacetate (6 eq, 16.1 mL) and potassium iodide (10 mol%, 312 mg) and the mixture was heated at reflux under positive pressure nitrogen atmosphere overnight. After this time, TLC (1:1 ethyl acetate/*n*-hexane) indicated the absence of starting material. The reaction was allowed to cool to ambient temperature and evaporated *in vacuo*. The residue was partitioned between dichloromethane and water, agitated, and the layers separated. The aqueous phase was extracted once with a portion of dichloromethane. The combined organics were washed with brine, dried ($MgSO_4$), filtered, and evaporated to dryness under reduced pressure. Column chromatography on silica gel (wet-loaded, 1:99 ethyl

acetate/dichloromethane, *ca.* 9x8 cm) afforded the title compound **CA-005** as a brown solid (4.28 g, 43%). ∂_H (500 MHz, ppm, $CDCl_3$) 8.75 (2H, dd, *J* 3.88, 0.98 Hz, thiophene-H), 7.62 (2H, dd, *J* 5.00, 1.00 Hz, thiophene-H), 7.27 (2H, dd, *J* 5.00, 3.95 Hz, thiophene-H, partially overlapped by $CDCl_3$ peak), 4.79 (4H, s, CH_2), 1.42 (18H, s, $C(CH_3)_3$). ∂_C (100 MHz, ppm, $CDCl_3$) 167.26, 161.16 (all C=O), 140.14, 135.10, 130.82, 129.88, 128.92, 107.74 (all aromatic-C), 82.98 ($C(CH_3)_3$), 44.33 (CH_2), 28.09 ($C(CH_3)_3$). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{26}H_{28}N_2NaO_6S_2$ 551.1281; found 551.1270.

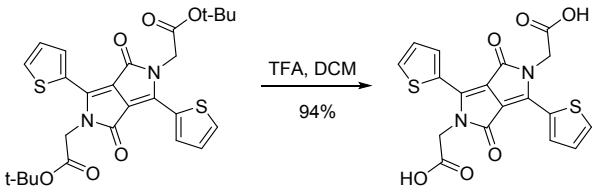


Spectrum 3. ^1H NMR spectrum of **CA-005** in $CDCl_3$



Spectrum 4. ^{13}C NMR spectrum of **CA-005** in $CDCl_3$

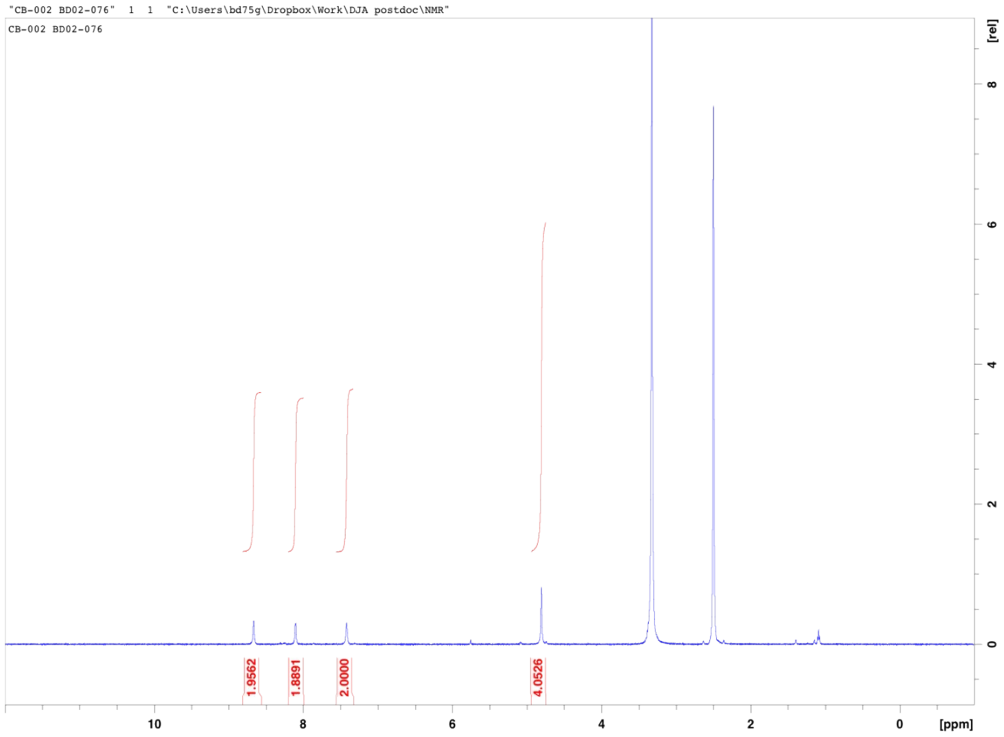
2,2'-(1,4-Dioxo-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-2,5(1*H*,4*H*)-diyl)diacetic acid (CB-002)



CA-005 **CB-002**

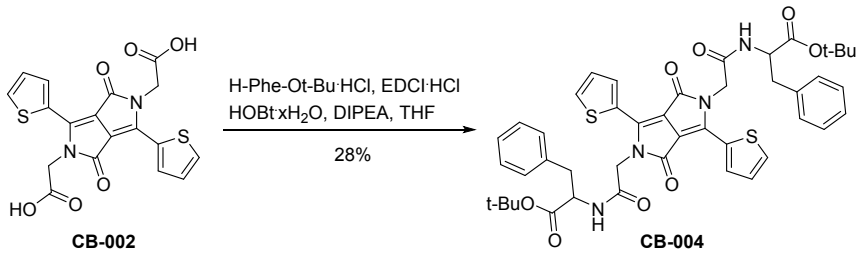
To a solution/suspension of **CA-005** (4.19 g, 7.92 mmol, 1 eq) in dichloromethane (108 mL) was added trifluoroacetic acid (54 mL, *ca.* 45 eq) and the mixture was stirred at ambient temperature overnight. After this time, it was poured into diethyl ether (600 mL), stirred for 15 minutes, filtered, and the solid in the filter washed with diethyl ether. Drying under reduced pressure afforded the title compound **CB-002** as a dark purple solid of sufficient purity (3.10 g, 94% yield, 95% NMR purity: balance diethyl ether and dichloromethane). A ^{13}C spectrum of the compound could not be obtained due to its limited solubility. ∂_H (500 MHz, ppm, DMSO-d_6) 13.40 (2H, br s, COO<u>H</u>), 8.67 (2H, br s, thiophene-<u>H</u>), 8.10 (2H, br d, *J* 3.25 Hz, thiophene-<u>H</u>), 7.42 (2H,

br s, thiophene-H), 4.81 (4H, s, CH_2). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{12}N_2NaO_6S_2$ 439.0029; found 439.0019.



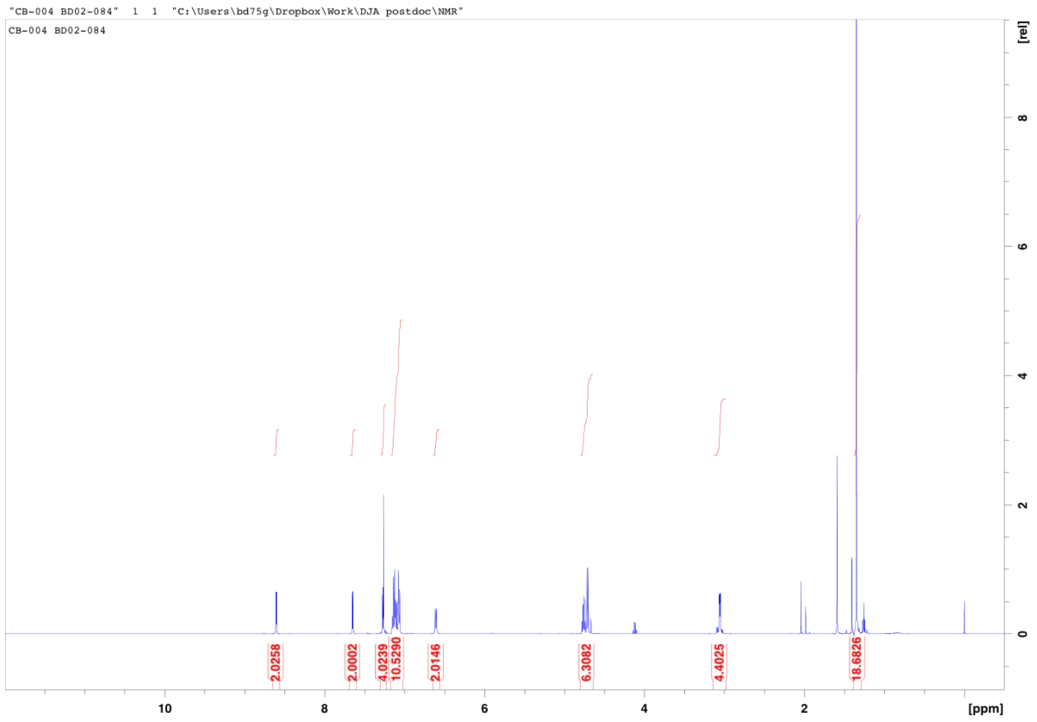
Spectrum 5. ^{1}H NMR spectrum of **CB-002** in DMSO-d_6

Di-*tert*-butyl 2,2'-((2,2'-(1,4-dioxo-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-2,5(1*H*,4*H*)-diyl)*bis*(acetyl))*bis*(azanediyl))*bis*(3-phenylpropanoate) (CB-004)

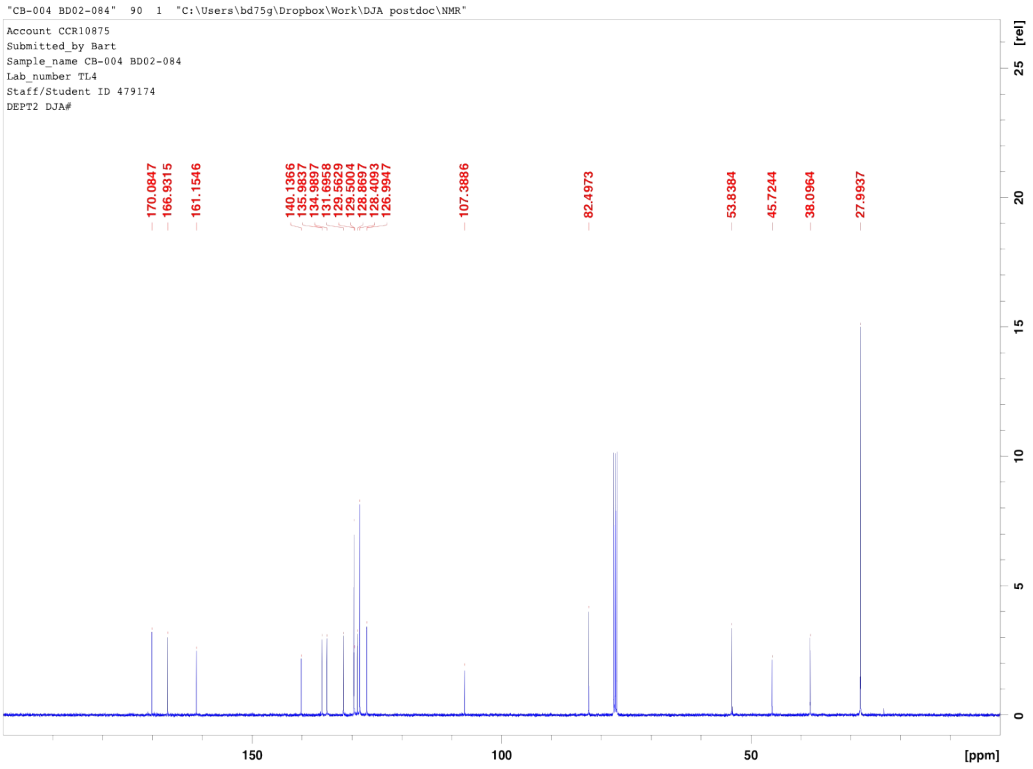


To a suspension of **CB-002** (1.50 g, 3.60 mmol, 1 eq) in THF (50 mL) was added EDCI·HCl (3 eq, 2.07 g), HOBt·xH_2O (3 eq based on 86% purity, 1.70 g), and di*iso*propylethylamine (8 eq, 5.02 mL) and the mixture was stirred for 20 minutes at ambient temperature. Phenylalanine *tert*-butyl ester hydrochloride (2.5 eq, 2.32 g) was then added and the mixture stirred overnight. After this time, it was evaporated *in vacuo*, the residue diluted with dichloromethane, washed in succession with water, 1M HCl (aq), sodium bicarbonate (aq), and brine. Drying ($MgSO_4$), evaporation to dryness and column chromatography on silica gel (wet-loaded, 1:9 ethyl acetate/dichloromethane, *ca.* 12x4 cm) afforded

the title compound **CB-004** as a purple solid which was not purified any further (834 mg, 28% yield, 98% NMR purity: balance ethyl acetate). ∂_H (500 MHz, ppm, $CDCl_3$) 8.60 (2H, dd, *J* 3.98, 1.12 Hz, thiophene-H), 7.65 (2H, dd, *J* 5.08, 1.02 Hz, thiophene-H), 7.27 (2H, dd, *J* 4.95, 4.00 Hz, thiophene-H, partially overlapped by $CDCl_3$ signal), 7.15-7.06 (10H, m, C_6H_5), 6.61 (2H, d, *J* 7.60 Hz, NH), 4.76 (2H, dt, *J* 7.63, 6.16 Hz, CH*), 4.71 (4H, dd, *J* 24.98, 17.18 Hz, NCH_2), 3.06 (4H, dd, *J* 5.90, 2.30 Hz, $PhCH_2$), 1.35 (18H, s, $C(CH_3)_3$). ∂_C (100 MHz, ppm, $CDCl_3$) 170.08, 166.93, 161.15 (all C=O), 140.14, 135.98, 134.99, 131.70, 129.56, 129.50, 128.87, 128.41, 126.99, 107.39 (all aromatic-C), 82.50 ($C(CH_3)_3$), 53.84 (C*), 45.72 (NCH_2), 38.10 ($PhCH_2$), 27.99 ($C(CH_3)_3$). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{44}H_{46}N_4NaO_8S_2$ 845.2649; found 845.2632.

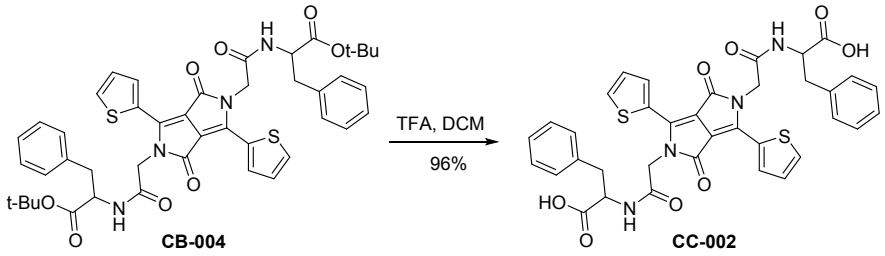


Spectrum 6. ^1H NMR spectrum of **CB-004** in $CDCl_3$



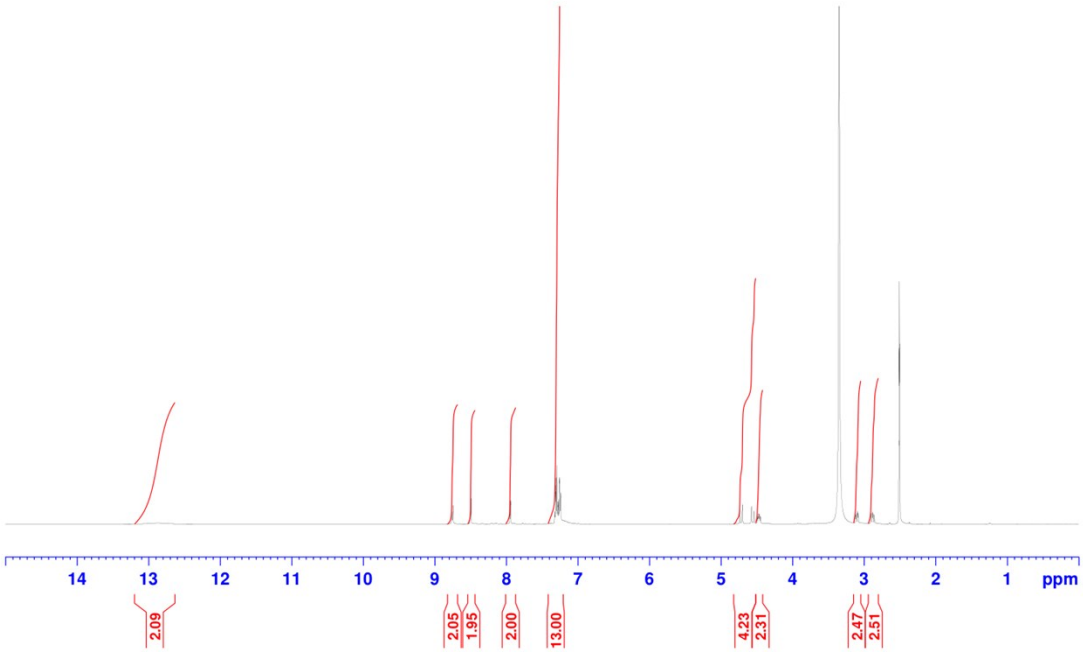
Spectrum 7. ^{13}C NMR spectrum of **CB-004** in $CDCl_3$

2,2'-((2,2'-(1,4-Dioxo-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-2,5(1*H*,4*H*)-diyl)bis(acetyl))bis(azanediyl))bis(3-phenylpropanoic acid) (CC-002) (DPP-1)

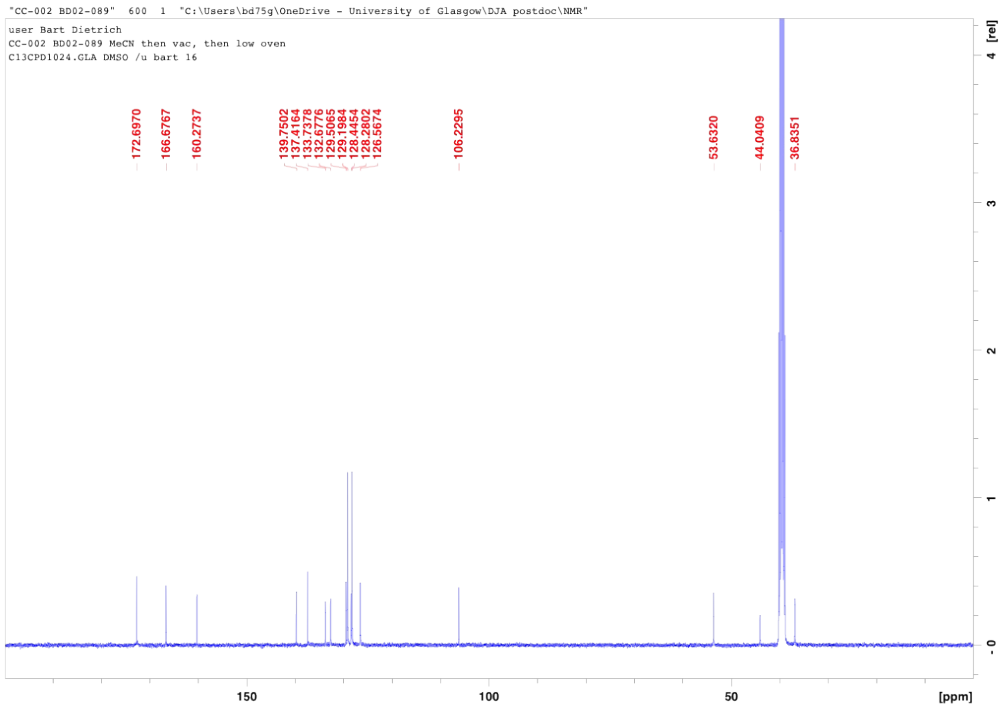


To a solution of **CB-004** (746 mg, 0.906 mmol, 1 eq) in dichloromethane (40 mL) was added trifluoroacetic acid (20 mL, *ca.* 300 eq) and the mixture was stirred overnight. After this time, it was poured into diethyl ether (500 mL), stirred for 15 minutes and filtered. The solid in the filter was washed with diethyl ether and dried under vacuum, affording the title compound **CC-002** as a dark purple solid (616 mg, 96%). δ_H (400 MHz, ppm, DMSO-d_6) 12.87 (2H, br s, COOH), 8.75 (2H, d, *J* 8.20 Hz, thiophene-H), 8.50 (2H, dd, *J* 3.88, 1.12 Hz, thiophene-H), 7.95 (2H, dd, *J* 5.03, 1.08 Hz, thiophene-H), 7.32-7.24 (12H, m,

$C_6\underline{H}_5$ and N$\underline{H}$), 4.72 (2H, d, *J* 18.06, NC$\underline{H}_a$H$_b$), 4.56 (2H, d, *J* 18.06, NCH$_a\underline{H}_b$), 4.49-4.45 (2H, m, C$\underline{H}$*), 3.10 (2H, dd, *J* 13.76, 4.60 Hz, PhC$\underline{H}_a$H$_b$), 2.88 (2H, dd, *J* 13.73, 9.68 Hz, PhCH$_a\underline{H}_b$). δ_C (100 MHz, ppm, DMSO-d$_6$) 172.70, 166.68, 160.27 (all $\underline{C}$=O), 139.75, 137.42, 133.74, 132.68, 129.51, 129.20, 128.44, 128.28, 126.57, 106.23 (all aromatic-$\underline{C}$), 53.63 ($\underline{C}$*), 44.04 (N$\underline{C}$H$_2$), 36.84 (Ph$\underline{C}$H$_2$). No mass spectrum could be obtained as the molecular ion was of insufficient intensity for accurate mass measurement under all available ionisation modes (EI, ESI, CI, FAB).



Spectrum 8. ^{1}H NMR spectrum of **CC-002 (DPP-1)** in DMSO-d$_6$



Spectrum 9. NMR spectrum of **CC-002 (DPP-1)** in DMSO-d_6

Procedures and Instruments

Preparation of LMWG Solutions

The **DPP-1** gelator was added to 2 mL of water with 1 molar equivalent of sodium hydroxide (0.1 M, aqueous) to a concentration of 5 mg/mL. The solution was stirred until all the gelator had dissolved. The solution of **PBI-A** was prepared in the same way.

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 5 mg/mL of glucono-δ-lactone (GdL) and shaken gently until the GdL had visibly dissolved. The sample was then left to stand overnight to allow gelation to occur.

In multi-component systems samples were prepared at 10 mg/mL then 1 mL of each gelator solution was added together to give a 5 mg/mL **DPP-1** + 5 mg/mL **PBI-A** solution. 10 mg/mL of GdL was then used for gelation.

Rheological Measurements

Dynamic rheological and viscosity measurements were performed using an Anton Paar Physica MCR101 rheometer. For frequency and strain sweeps gels were prepared in 7 mL Sterilin bijous and measured using a vane and cup geometry. A cone and plate measuring system was used to perform viscosity

and shear alignment measurements. A parallel plate measuring system was used for time sweeps. For time sweeps, the gels were prepared in a vial. GdL was added to the vial and then this mixture was immediately transferred onto the bottom plate. All experiments were performed at 25 °C.

Strain sweeps: Strain sweep experiments were performed from a strain of 0.1 % -1000 % at a frequency of 10 rad/s. The breaking point was determined by the % strain at which G′ and G″ deviated from linearity. Measurements were performed in triplicate at 25 °C.

Frequency sweeps: Frequency sweeps were measured from 0.1 to 100 rad/s. Measurements were performed in triplicate at 25 °C. G′ and G″ are quoted at 10 rad/s.

Time sweeps: Time sweeps were performed with a sandblasted 50 mm plate with a plate gap of 0.8 mm. Tests were performed at an angular frequency of 10 rad s^{-1} and with a strain of 0.5 %. The plates were flooded with mineral oil to prevent the sample from drying.

Dynamic viscosity measurements: Viscosity measurements were performed using a 50 mm cone geometry. 1 mL of solution was poured onto the bottom plate and the solution was allowed to equilibrate to 25 °C.

Shear aligning: Shear aligning experiments were performed using a 25 mm cone geometry with a piece of glass secured to the bottom plate. A constant shear rate of 10 s^{-1} was applied to the samples and a viscosity measurement recorded every 30 seconds. For shear aligned solutions these measurements were done for 16 hours.

pH and pK_a Measurements

A FC200 pH probe (HANNA instruments) with a 6 mm x 10 mm conical tip was used for pH measurements. The stated accuracy of the pH measurements is ±0.1. For pH measurement during gelation with GdL pH was recorded every minute until a gel was formed. The temperature was maintained at 25 °C during the titration by using a circulating water bath. pK_a determination was done by adding aliquots of 5 µL of a 0.1 M HCl (aq) solution to the gelator at high pH. The pH was allowed to equilibrate for 5 minutes before the pH was measured and the next aliquot was added. The pK_a was determined by where the pH plateaued.

Nuclear Magnetic Resonance Spectroscopy

The NMR time series were collected on a Bruker Avance II 400 MHz wide bore spectrometer. All measurements were performed off lock in H_2O at 298 K. ^1H

spectra were acquired with the double-echo W5 WATERGATE sequence of Liu et al. (Bruker pulse program library ZGGPW5). The delay between successive pulses in the selective pulse train was set at 125 μs corresponding to a 4000 Hz separation between the null points. 8 scans were acquired with a signal acquisition time of 2 s and a relaxation delay of 8.1 s, giving a total acquisition time of 80 seconds. Integrals of gelators **DPP-1** and **PBI-A** were obtained relative to sodium methanesulfonate (1 mM) added as an internal chemical shift reference.

Photoconductivity Measurements

Photoconductivity measurements were performed using an Autolab Potentiostat operating in a two-electrode configuration in the absence of a supporting electrolyte. Experiments were performed in an enclosure in air inside a Faraday cage. 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. A 3 mm spacing was achieved by cutting out a 3 mm x 3 mm square in Scotch tape as a mask on a glass microscope slide. 10 μL solution or gel could then be placed in the mask and left to dry. Once the material had dried, the Scotch tape could be removed and silver electrodes placed either side of the sample. The silver electrodes were prepared using silver paste (Electrodag 1514) which attached copper wires to the glass slide. 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 electrode to the other copper wire to make a two-electrode experiment.

For directional dependence measurements, silver electrodes were placed 3 mm apart with and against the alignment of the samples, this was determined using the optical microscope to place the electrodes.

For the measurements under iodine, the above samples were measured for the before measurement and then placed in a petri dish with approx. 100 mg of iodine crystals. The petri dish was the sealed with Parafilm and the samples were left for 20 minutes. The samples were then immediately measured. The samples were then left for around ten minutes in air and then again measured, by this time the iodine had left the films and the current returned to normal.

Photoresponse Measurements were performed using an Autolab Potentiostat operating in a two-electrode configuration in the absence of a supporting electrolyte. 365 nm, 400nm, 450 nm, 470 nm, 528 nm, 590 nm and 628 nm LEDs (LedEngin Inc, LZ1-10U600) powered by a TTi QL564P power supply operating at 3.9 V were used as a light supply. 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. The current recorded at 4 V was then used for the photoresponse value at each wavelength.

Optical Microscopy under Cross-Polarised Light

Optical microscope images were collected using a Nikon Eclipse LV100 microscope with a Nikon TU Plan ELWD 50x/0.60 lens attached to an Infinity2-1C camera, under cross-polarised light. Samples for optical microscopy were prepared on glass microscope slides and allowed to dry for 24 hours before imaging.

Scanning Electron Microscopy

Samples were prepared for SEM by placing a small amount of material onto a glass cover slip. The samples were allowed to fully dry for 24 hours in air. The glass slip was then attached to a 15 mm aluminium screw-in-stub by a carbon tab. Samples were then measured in deceleration mode at 2 kV at a height of 3 mm.

UV-Vis Absorption Spectroscopy

Solution UV-Vis absorption data was measured using a Thermo Scientific Nanodrop 2000/2000c spectrophotometer. The spectrophotometer was used in cuvette mode and samples were prepared in PMMA plastic cuvettes with a pathlength of 1.0 cm.

Solid UV-vis absorption spectra were recorded using a Shimadzu UV-2550 UV−Vis spectrophotometer running the UV Probe software, version 2.34 with a slit width of 5 nm fitted with an integrating sphere attachment. Samples were dried on microscope slides overnight before being measured.

Fibre Distribution Measurements Measurement of fibre widths were performed using ImageJ image analysis software. Images used for measurements were collected by SEM. A total of 90 measurements on each image were used to create the distribution curves.

Supplementary Figures

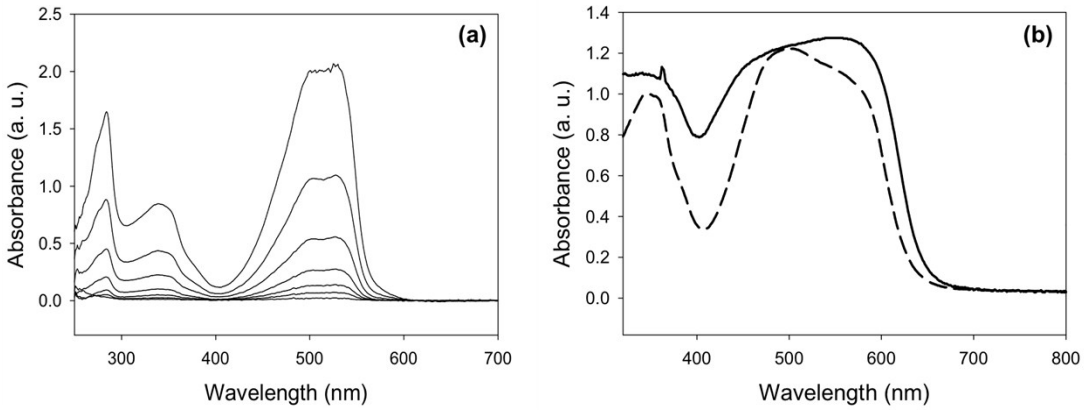


Figure S1. (a) Solution UV-vis absorption spectra of **DPP-1** diluted in pH 9 water from 0.08 mg/mL to 0.0006 mg/mL (b) Solid UV-vis absorption spectra of a xerogel of **DPP-1** (solid line) and the dried solution of **DPP-1** (dashed line).

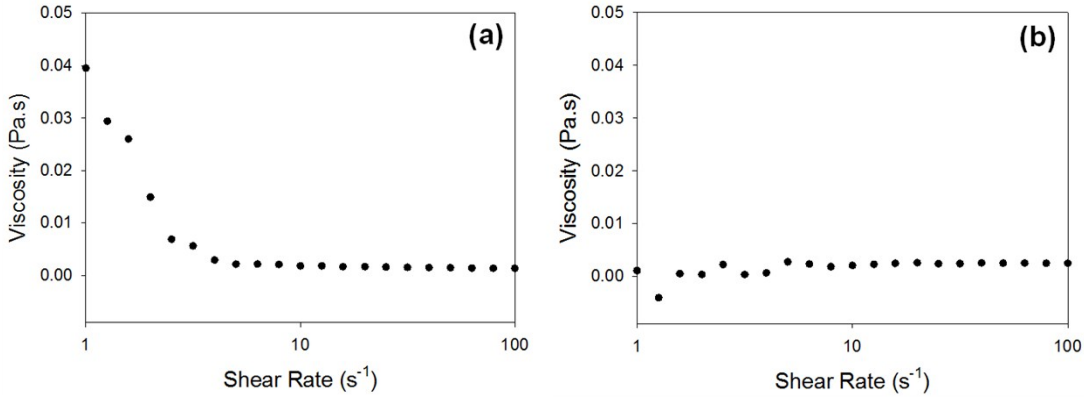


Figure S2. Dynamic viscosity plot of a solution of **DPP-1** at 5 mg/mL using (a) 1 equivalent of NaOH and (b) using 2 equivalents of NaOH.

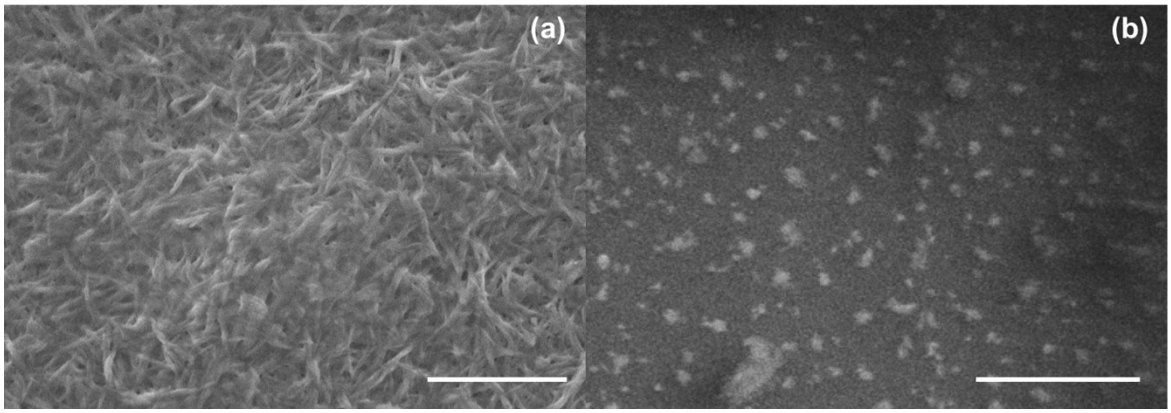


Figure S3. SEM images of **DPP-1** as a (a) xerogel and (b) dried solution. Both scale bars represent 1 μm.

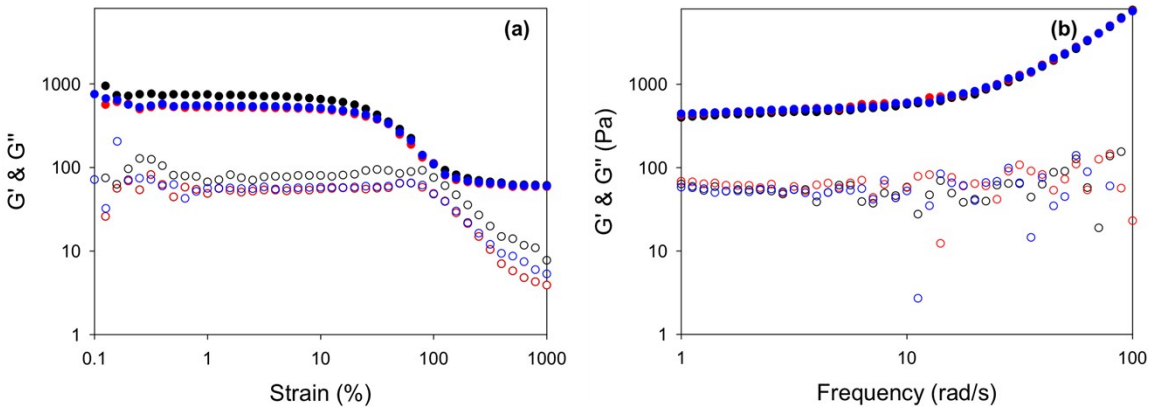


Figure S4. Dynamic rheological measurements performed on a 5 mg/mL gel of **DPP-1** with 5 mg/mL of GdL. (a) Strain sweeps from 0.1 - 1000 % strain. (b) Frequency sweeps performed from 1- 100 rad/s. All tests were performed at 25 ˚C. Full shapes represent G´ and open shapes represent G˝. Different colours of data are for repeat measurements.

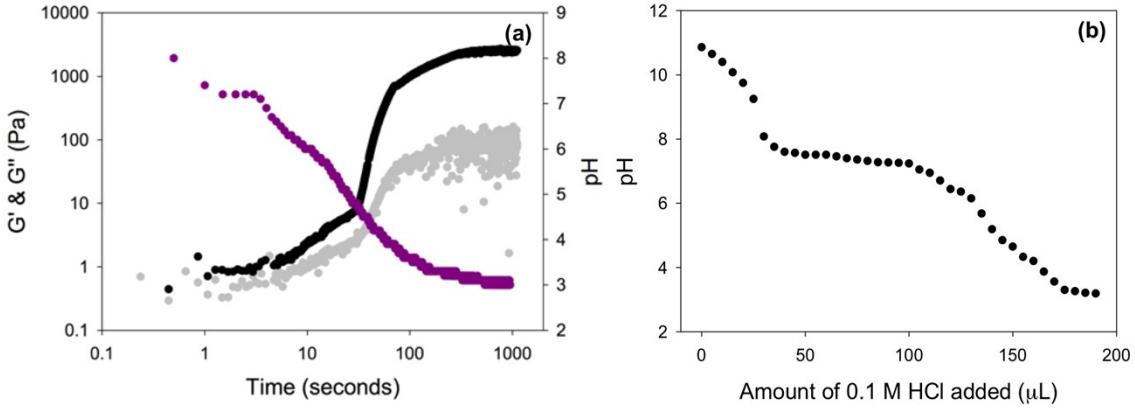


Figure S5 (a) Monitoring gelation of DPP-1 with the development of G' (black data) and G" (grey data) over time with the decrease in pH (purple data) (b) pK_a determination of **DPP-1** with the slow addition of 0.1 M HCl.

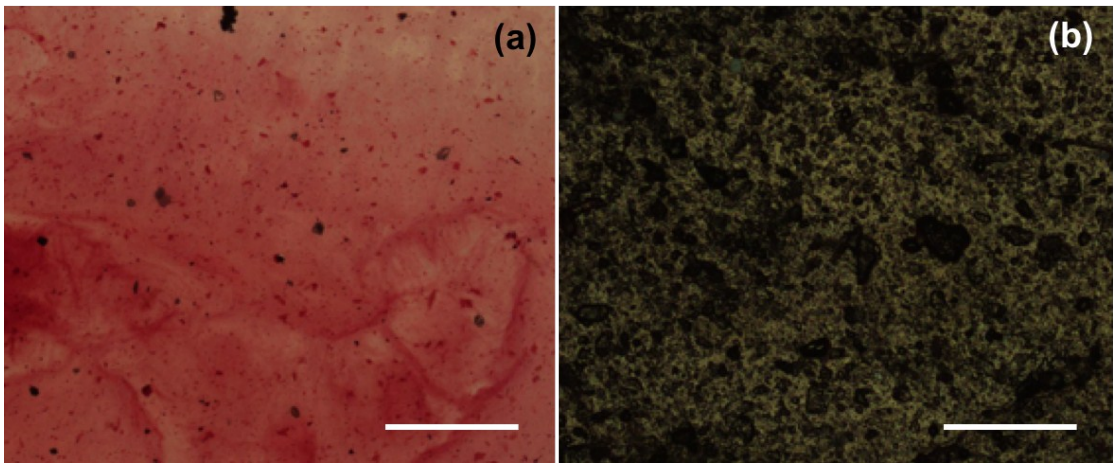


Figure S6. Microscope images taken under cross-polarised light of (a) the dried solution and (b) the xerogel. Scale bars represent 0.1 mm.

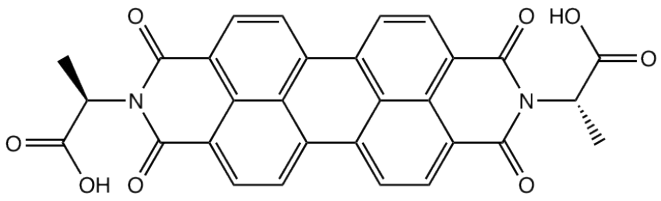


Figure S7. Chemical structure of **PBI-A** LMWG

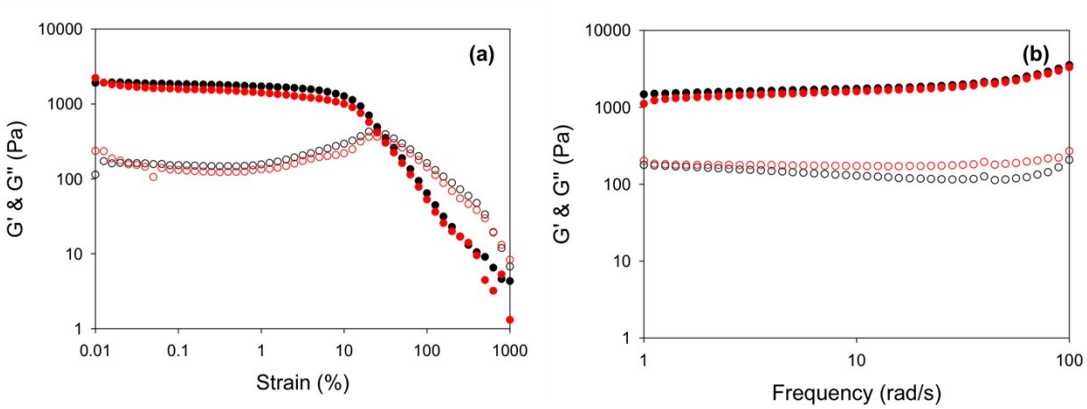


Figure S8. Rheological test of self-sorted **DPP-1 + PBI-A** gels at a total concentration of 5 mg/mL at 25 °C (a) Strain sweep performed at 10 rad s-1 (b) Frequency sweeps at a strain of 0.5 % strain. Full shapes represent G´ and open shapes represent G˝. Different colours of data are for repeat measurements.

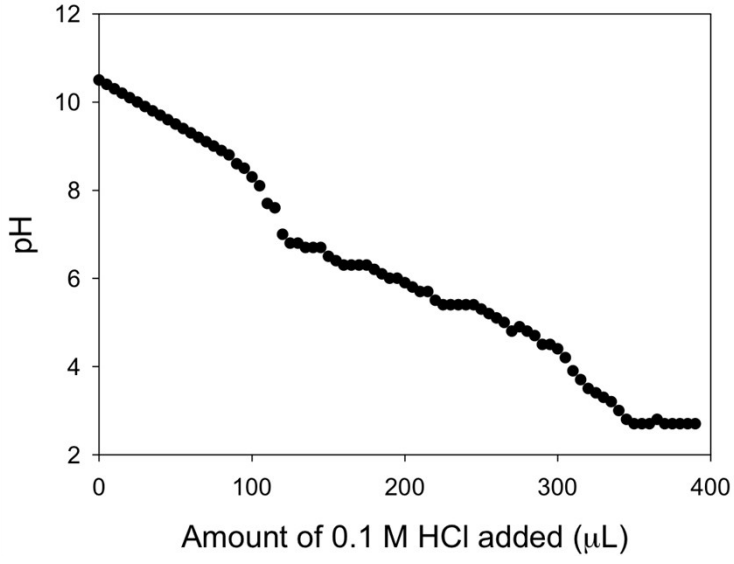


Figure S9. pH titration of **DPP-1** + **PBI-A** with the slow addition of 0.1 M HCl showing plateaus at around 7.2 (pK_a **DPP-1**) and at 5.9 (**PBI-A** pK_a-1) and 5.4 (pK_a 2 **PBI-A**).

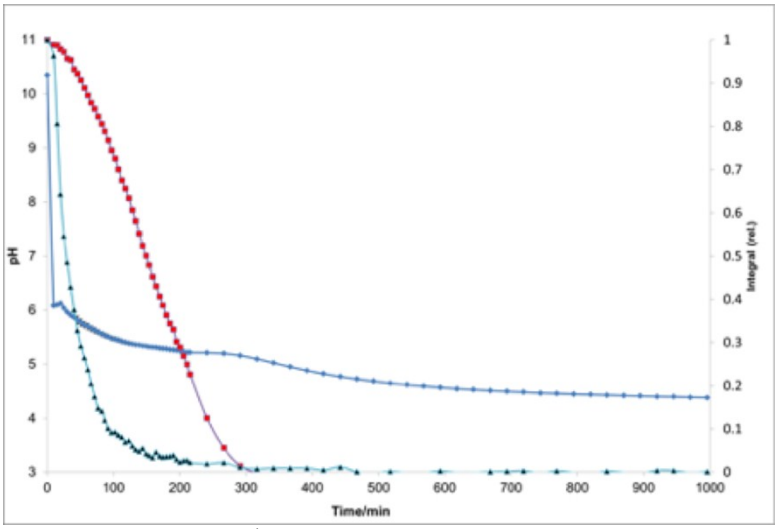


Figure S10. Monitoring gelation by ^{1}H NMR spectroscopy by the disappearance of the gelators over time. Red data is the C$\underline{H}_3$ from **PBI-A** and green data is the C$\underline{H}_2$ from **DPP-1.** Blue data is the pH. The data show the **DPP-1** assembling before the **PBI-A**, suggesting self-sorting of the two gelators.

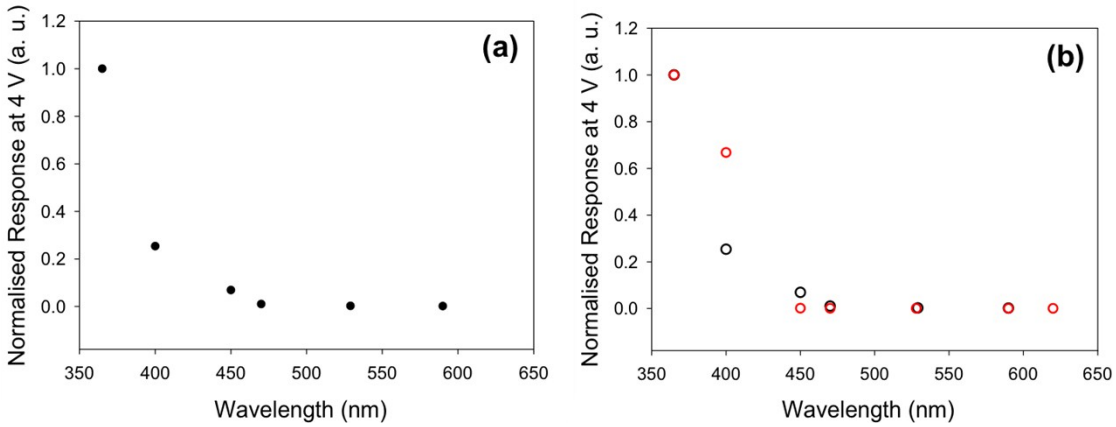


Figure S11. Conductivity normalised to response at 365 nm wavelength dependence at 4 V of (a) **DPP-1** + **PBI-A** xerogel (b) **DPP-1** + **PBI-A** xerogel (black data) compared with **PBI-A** xerogel alone (red data).

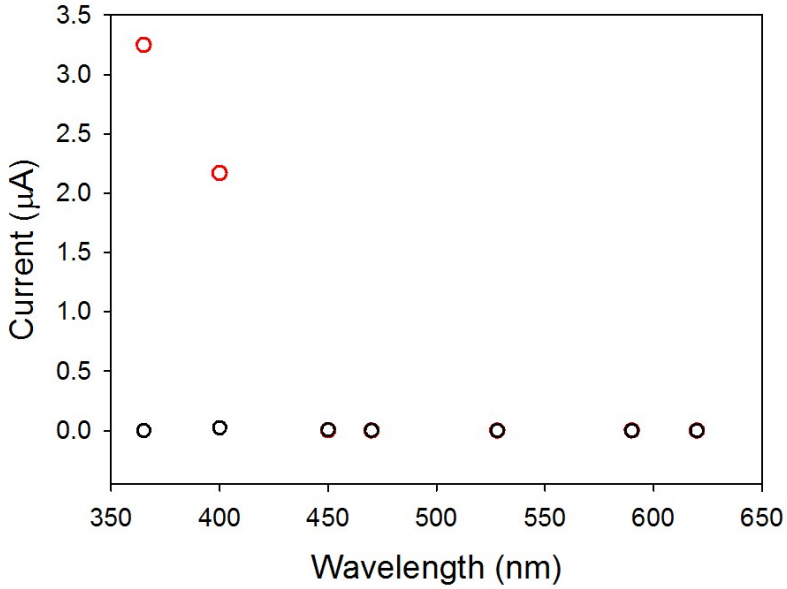


Figure S12. Conductivity not normalised to response at 365 nm wavelength dependence at 4 V of **DPP-1** + **PBI-A** xerogel (black data) and **PBI-A** xerogel alone (red data).

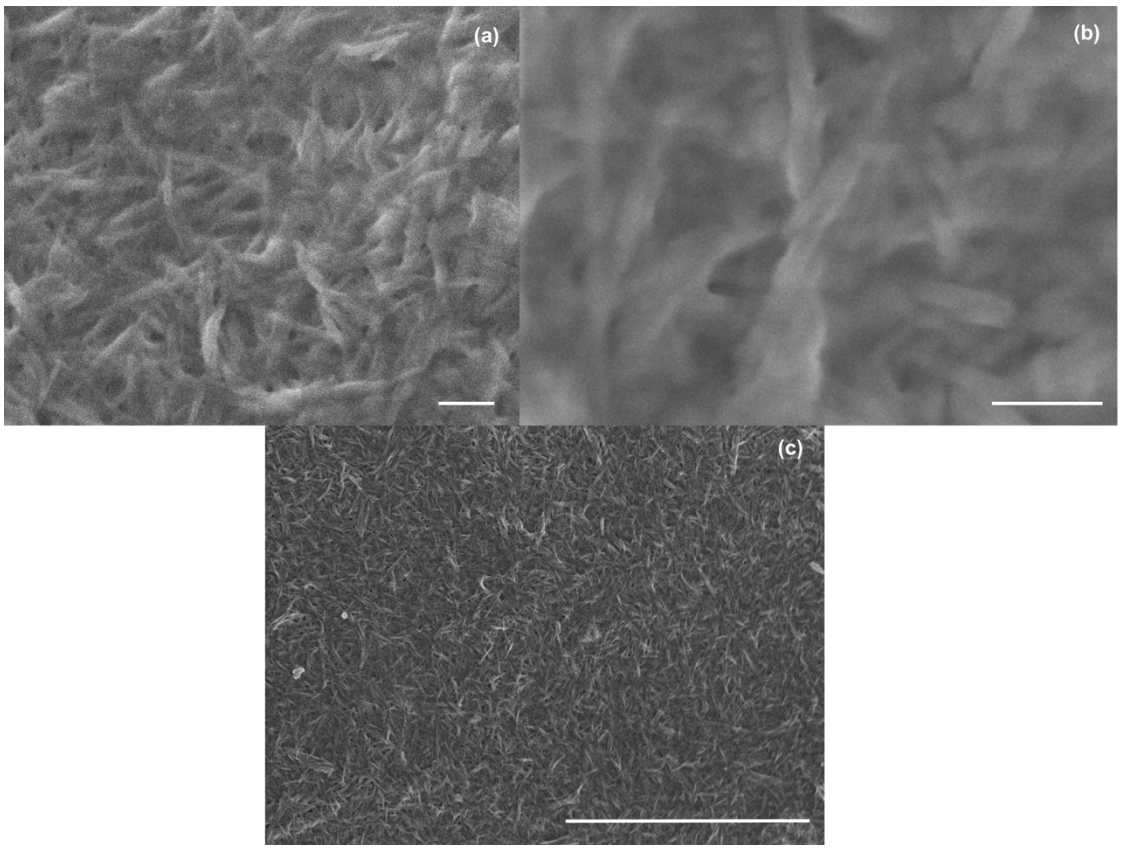


Figure S13. SEM images of **PBI-A + DPP-1** xerogel showing some twisting of the fibres and no phase separation upon drying. Both (a) and (b) scale bars represent 200 nm and (c) scale bar is 5 µm.

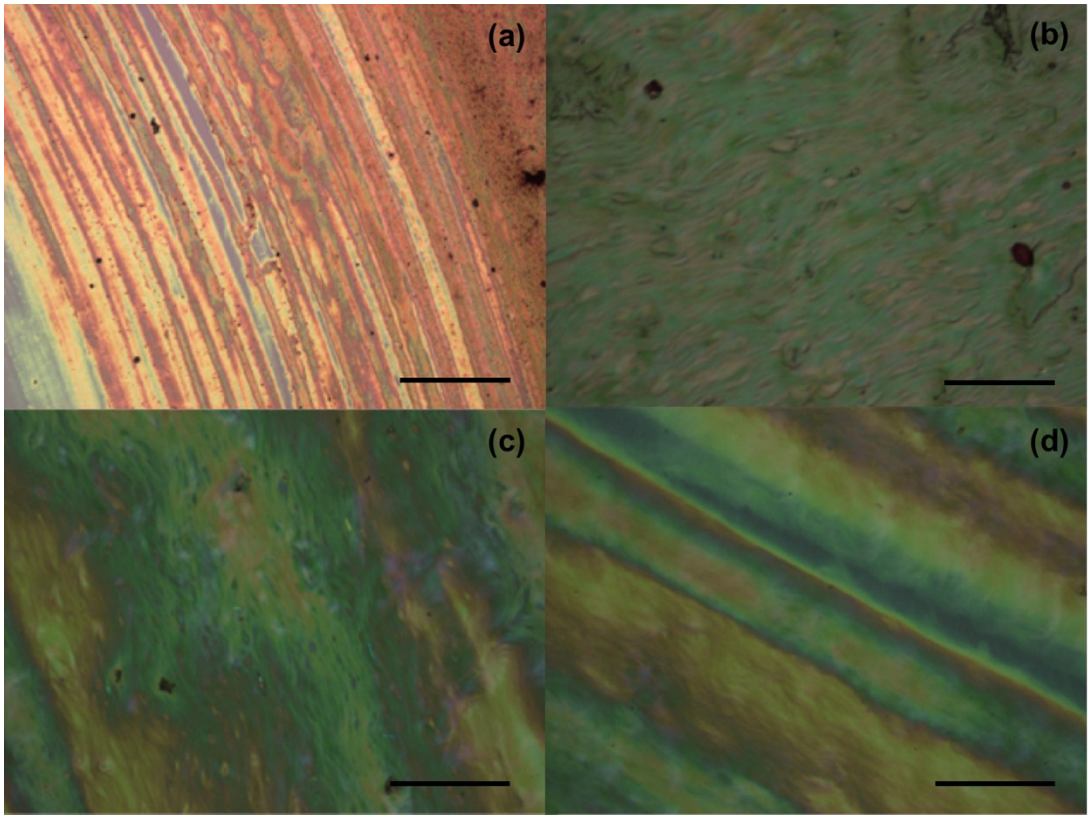


Figure S14. Different images of shear aligned solution of **DPP-1** taken under cross-polarised light showing aligned structures. Scale bar for (a) is 0.2 mm, scale bars for (b), (c) and (d) are 50 μm.

References

1. E. R. Draper, J. J. Walsh, T. O. McDonald, M. A. Zwijnenburg, P. J. Cameron, A. J. Cowan and D. J. Adams, *J. Mat. Chem. C*, 2014, **2**, 5570-5575.
2. Y. Zou, D. Gendron, R. Badrou-Aïch, A. Najari, Y. Tao and M. Leclerc, *Macromolecules*, 2009, **42**, 2891-2894.