

Supplementary Information

A self-recovering mechanochromic chiral π -gelator

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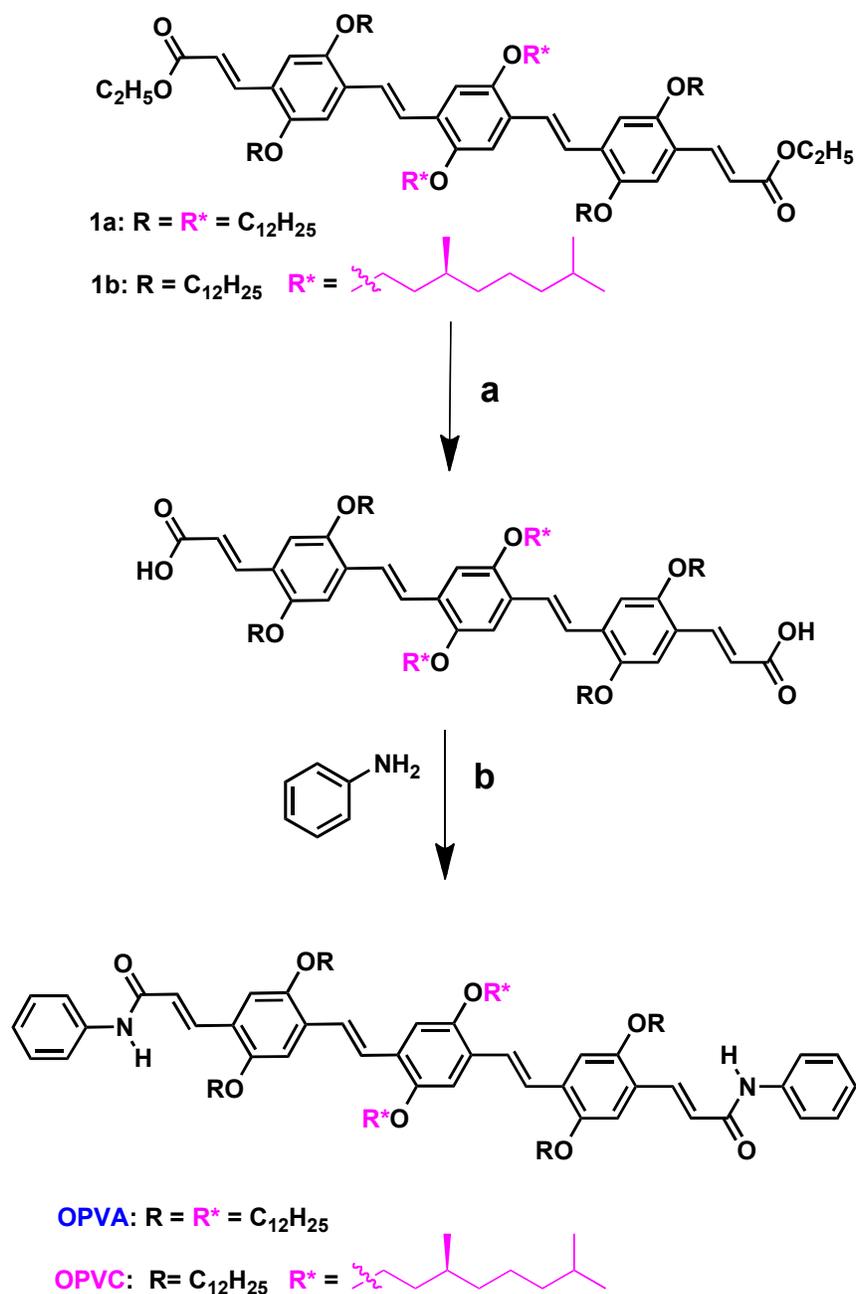
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1. Experimental Section

General Procedures: Unless otherwise stated, all materials and reagents were purchased from commercial suppliers. The solvents and reagents were purified and dried by standard methods prior to use. All melting points were determined on a Mel-Temp-II melting point apparatus and are uncorrected. FT-IR-ATR spectra were recorded on a Shimadzu Nicolet Impact 400D Infrared spectrophotometer. ^1H and ^{13}C NMR spectra were measured on a 500 MHz Bruker Avance DPX spectrometers. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Shimadzu AXIMA-CFR PLUS spectrometer.

General procedure for the synthesis of **OPVA** and **OPVC**: The OPV-bisester (**1**) was synthesized according to a known procedure,^{S1} which on hydrolysis using KOH in methanol yielded OPV bisacid (**2**).^{S1c} The final reaction between OPV-bisacid (**2**) and aniline was conducted using a peptide-coupling agent, 1-[bis(dimethylamino)methylene]-1*H*-1,2,3-triazolo[4,5-*b*]pyridinium 3-oxid hexafluorophosphate, (HATU) in the presence of *N,N*-diisopropylethylamine (DIPEA). The OPV acid **2** (0.09 mmol) and aniline (0.4 mmol) were stirred in dry dichloromethane (50 mL) in the presence of DIPEA (0.4 mmol) at 0 °C and HATU (0.4 mmol) was added to the reaction mixture. Reaction was continued to stir for 8 h at room temperature. The reaction mixture was extracted with dichloromethane and washed several times with water, dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. Synthesis and characterisation of **OPVA** has been reported previously.^{S1c}



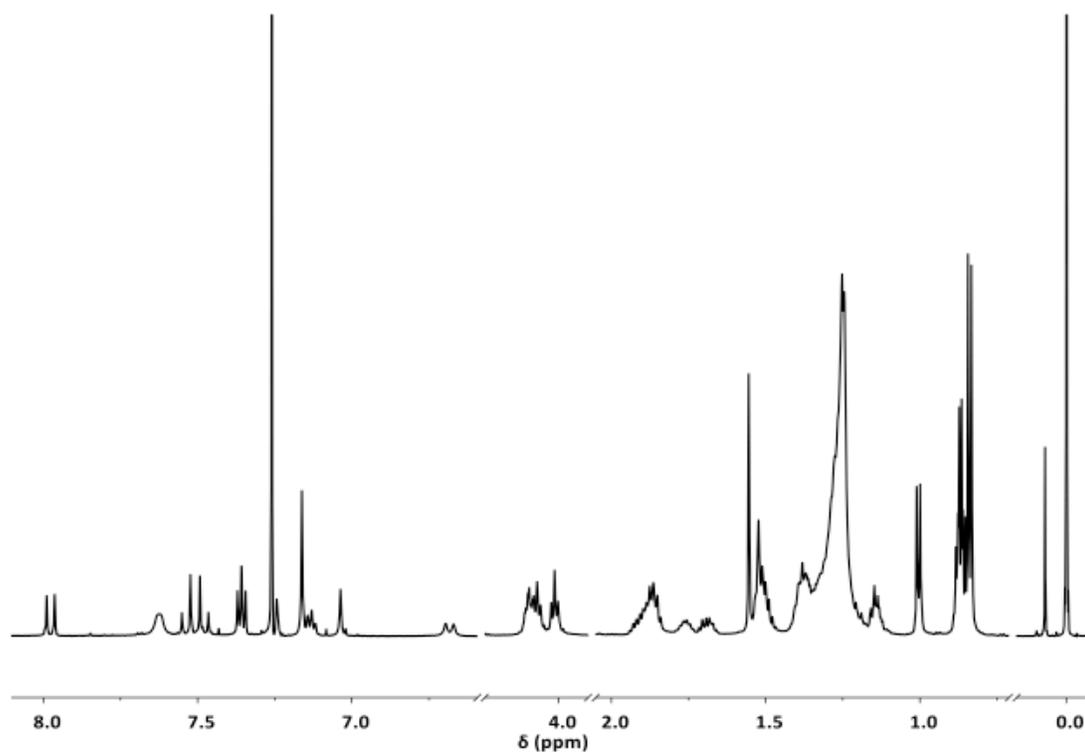
Scheme S1 Reagents and conditions: (a) KOH/MeOH, THF, 60 °C, 5 h, (95%); (b) HATU, DIPEA, dry CH₂Cl₂, 0 °C-rt, 8 h, (**OPVA** 61% and **OPVC** 70%).

Purification by column chromatography (hexane/ CHCl₃, 3:7) over silica gel (230-400 mesh)

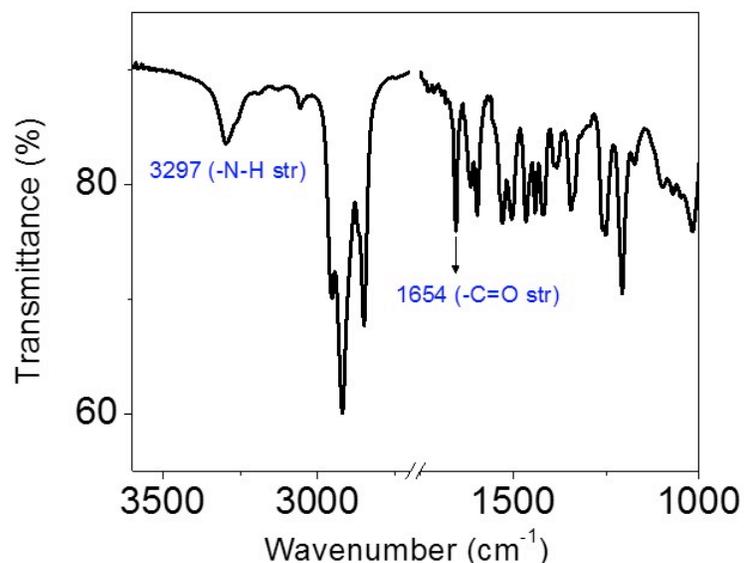
gave **OPVC** as a yellowish orange solid. Yield: 70%; m.p.: 152 ± 2 °C; FT-IR (KBr): $\nu_{max} = 3297,$

2920, 2845, 1654, 1598, 1530, 1506, 1464, 1442, 1420, 1390, 1343, 1261, 1206, 1094, 1013

cm^{-1} ; ^1H NMR (500 MHz, CDCl_3 , TMS, 25 °C): δ = 0.84-0.89 (m, 30H, $-\text{CH}_3$), 1.0-1.88 (m, 100H, $-\text{CH}_2-$), 3.9-4.1 (m, 12H, $-\text{OCH}_2-$), 6.67-6.70 (d, 2H, vinylic- H), 7.04 (s, 2H, Ar- H), 7.10-7.15 (m, 4H, Ar- H), 7.16 (s, 2H, Ar- H), 7.24-7.26 (m, 4H, Ar- H), 7.34-7.37 (t, 4H, Ar- H), 7.47-7.55 (dd, 4H, vinylic- H), 7.63 (br, $-\text{CONH}$), 7.95-8.0 (d, 2H, vinylic- H) ppm; ^{13}C NMR (125 MHz, CDCl_3 , 25 °C): δ = 164.9, 145.5, 143.2, 140.9, 128.1, 127.6, 125.1, 121.2, 118.2, 116.4, 114.1, 68.7, 65.3, 38.8, 37.1, 36.5, 31.2, 29.6, 29.1, 28.3, 27.7, 25.3, 24.1, 22.2, 20.8, 14.2 ppm; MALDI-TOF-MS (matrix: α -cyano-4-hydroxycinnamic acid): mass calcd. for $\text{C}_{108}\text{H}_{168}\text{N}_2\text{O}_8$ $[\text{M}+\text{H}]^+$: m/z = 1621.28, found: 1621.82.



^1H NMR spectrum (500 MHz, 25 °C) of **OPVC** in CDCl_3 .



FT-IR spectrum of **OPVC**.

2. Description of Experimental Techniques

2.1. Spectral Measurements: The film state absorption or reflection spectra were recorded on a Shimadzu UV-Vis spectrophotometer UV-2100 with BaSO₄ as standard. The emission spectra were recorded on a SPEX-Fluorolog F112X spectrofluorimeter using a front face sample holder. In matrix scan experiment, fluorescence spectra were recorded at different excitation wavelengths between 300 and 550 nm. The corresponding emission was collected between 450 and 750 nm. The result was shown as a contour plot based on emission intensity of the spectra at different excitation wavelengths.

2.2. Lifetime and Time Resolved Emission Measurements: Fluorescence lifetimes were measured using an IBH (FluoroCube) time-correlated picosecond single photon counting (TCSPC) system. Samples were excited with a pulsed diode laser (<100 ps pulse duration) at a wavelength of 440 nm (NanoLED-10) with a repetition rate of 1 MHz. The detection system consists of a micro channel plate photomultiplier (5000U-09B, Hamamatsu) with a 38.6 ps response time coupled to a monochromator (5000M) and TCSPC electronics (Data Station Hub including Hub-NL, NanoLED controller and preinstalled Fluorescence Measurement and

Analysis Studio (FMAS) software. The fluorescence lifetime values were determined by deconvoluting the instrument response function with triexponential decay using DAS6 decay analysis software. The quality of the fit has been judged by the fitting parameters such as χ^2 (<1.2) as well as the visual inspection of the residuals. All measurements of solid samples were carried out using a front face sample holder (5000U-04).

2.3. Circular Dichroism (CD) measurements: CD experiments were performed on JASCO 810 spectrometer using quartz plate, equipped with peltier thermostatic cell holders.

2.4. Transmission Electron Microscopy (TEM): TEM was performed on a FEI, TECNAI 30 G2 S-TWIN microscope with an accelerating voltage of 100 kV. Samples for TEM analysis were prepared on carbon-coated copper grids without staining. The samples were prepared by solution drop casting and kept in a desiccator under vacuum for overnight.

2.5. Fluorescent Microscopy: Fluorescent microscopic images were recorded on a Leica DM2500 fluorescence microscope.

2.6. Differential Scanning Calorimetry (DSC): DSC was performed using a Perkin-Elmer Pyris 6 DSC instrument in sealed aluminum pans under nitrogen flow, at a heat/cooling rate of 10 °C/min.

2.7 X-Ray Diffraction (XRD): OPVC and OPVA gels were coated on a quartz plate and the solvent was slowly evaporated. X-ray diffractogram of the dried films was recorded on a Phillips diffractometer using Ni filtered Cu K α radiation.

3. Supplementary Figures

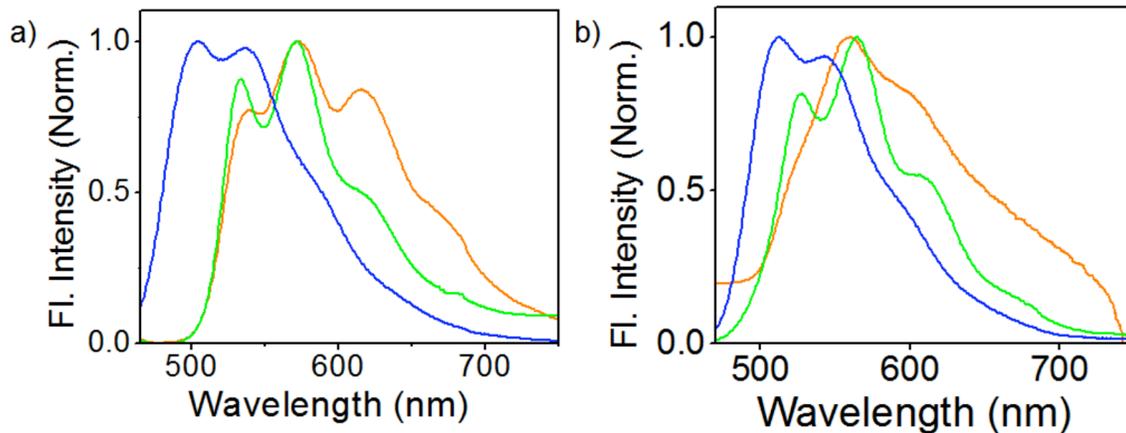


Fig. S1 Normalized emission spectra in *n*-decane at 80 °C (—), room temperature (—) and xerogel (—) of (a) **OPVC** ($\lambda_{\text{ex}} = 440$ nm, $c = 1.3$ mM) and (b) **OPVA** ($\lambda_{\text{ex}} = 440$ nm, $c = 1.3$ mM).

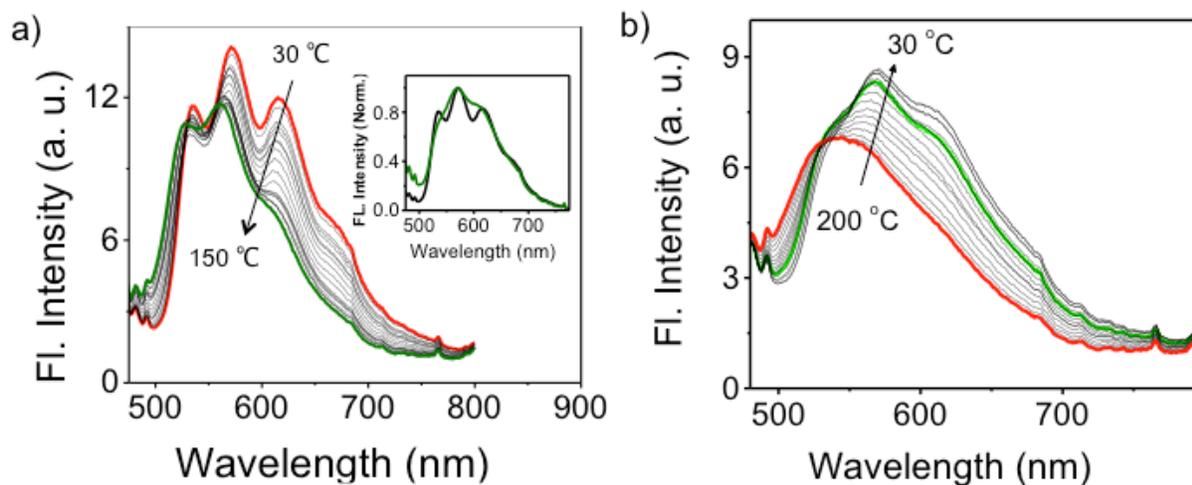


Fig. S2 (a) Variable temperature fluorescence spectra of **OPVC** ($\lambda_{\text{ex}} = 440$ nm) xerogel by changing from 30 to 150 °C; inset shows normalized fluorescence spectra at 30 °C before (—) and after (—) thermal annealing. (b) Variable temperature spectra of **OPVC** xerogel by varying temperature from 200 (—) to 30 °C (—).

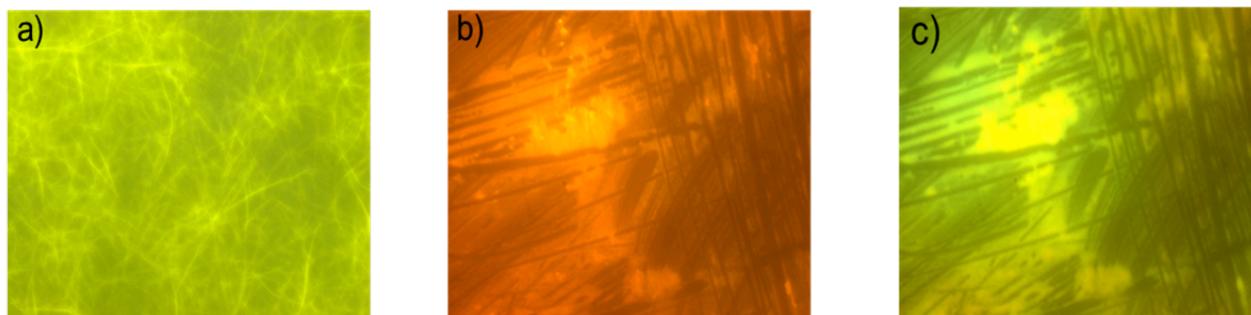


Fig. S3 Fluorescence microscopy images of **OPVC** (a) *n*-decane xerogel, (b) sheared and (c) self-recovered (over time).

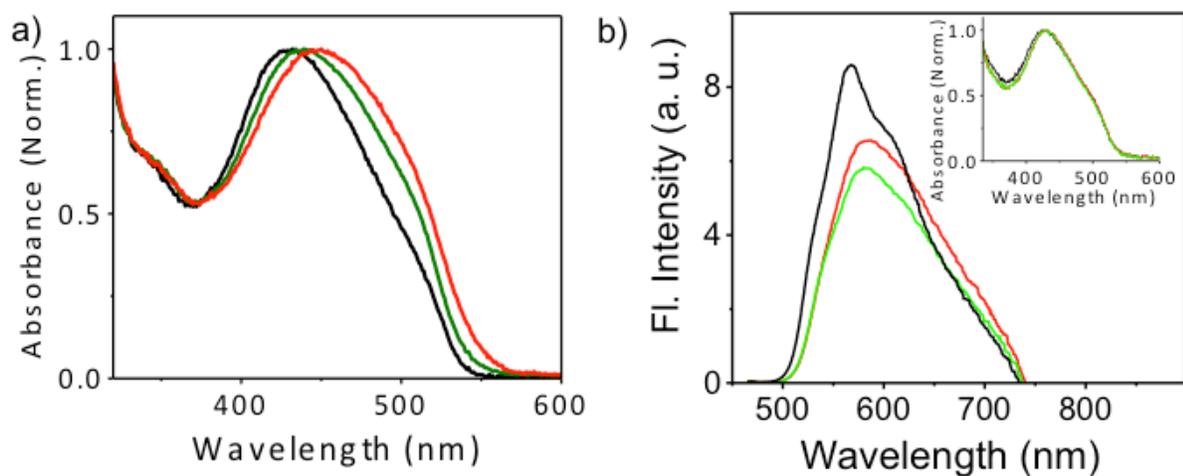


Fig. S4 (a) Absorption spectra of **OPVC** xerogel before shearing (—), after shearing (—) and after self-recovery (—). (b) Effect of shearing on **OPVA** xerogel emission before shearing (—), after shearing (—) and after 1 h (—). Inset shows corresponding changes in absorption spectra.

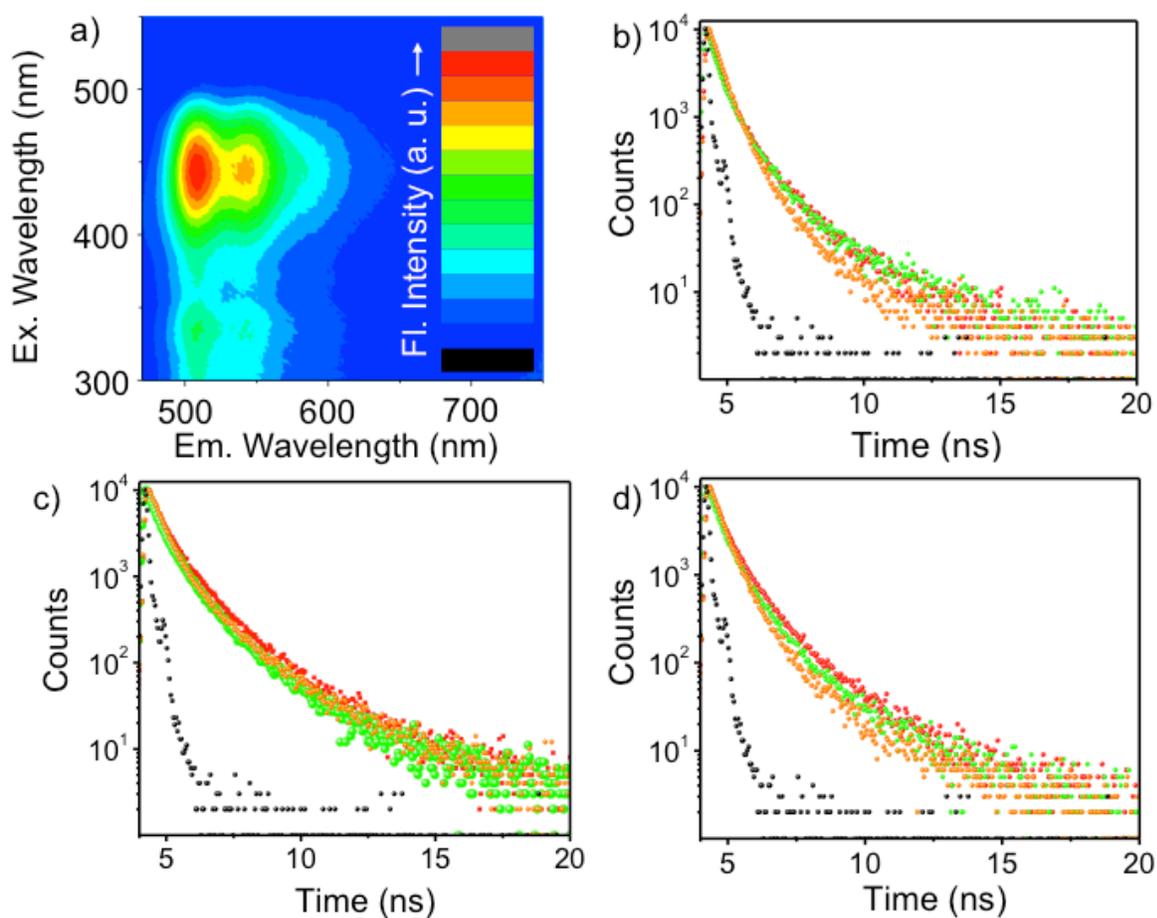


Fig. S5 Contour map of the observed fluorescence intensity (red maximum and blue minimum) of **OPVC** as a function of the fluorescence excitation and emission wavelength (matrix scan) of (a) *n*-decane solution (1×10^{-6} M). Lifetime decay profiles collected at (b) 535 nm, (c) 570 nm and (d) 620 nm of xerogel (orange), sheared (red) and recovered (green) **OPVC** aggregates. Prompt (black), $\lambda_{\text{ex}} = 440$ nm.

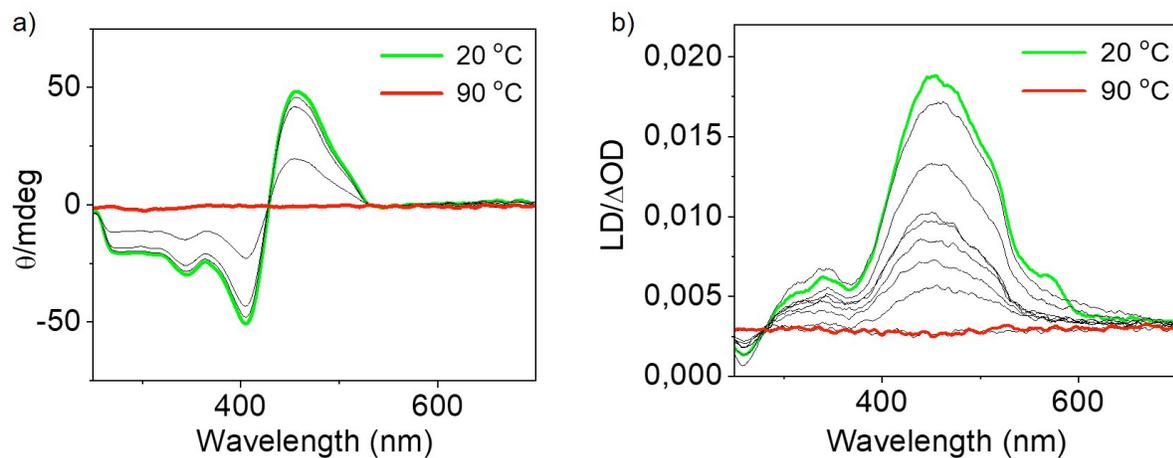


Fig. S6 a) CD and b) LD spectra of OPVC in *n*-decane upon varying the temperature from 90 to 20 °C ($c = 5 \times 10^{-5}$ M, $l = 1$ mm).

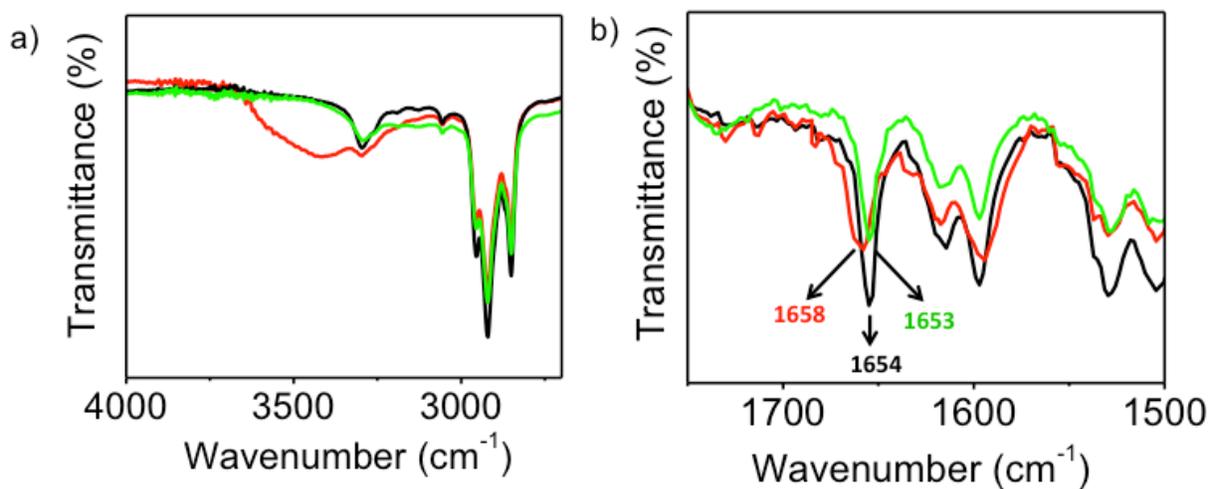


Fig. S7 Changes in FT-IR spectra (a) amide II (N-H stretching) and (b) amide I (C=O stretching) bands of OPVC xerogel (—), sheared (—) and self-recovered (—).

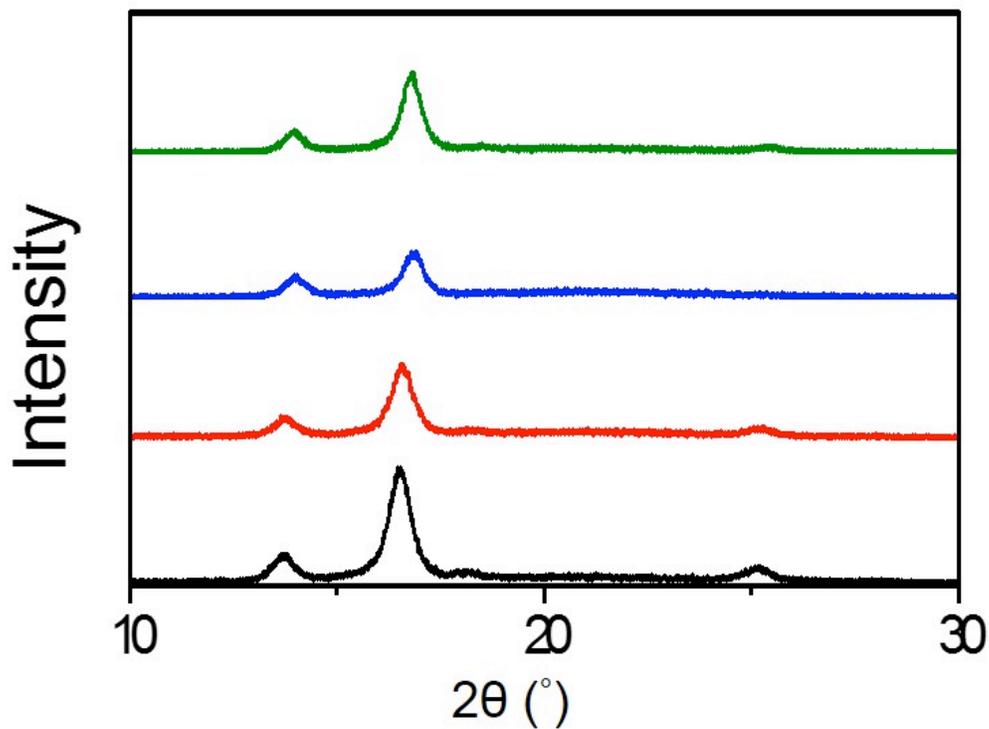


Fig. S8 XRD pattern of OPVC xerogel (—), sheared (—), annealed at 140 °C for 1 h (—), and solvent recovered xerogel (—).

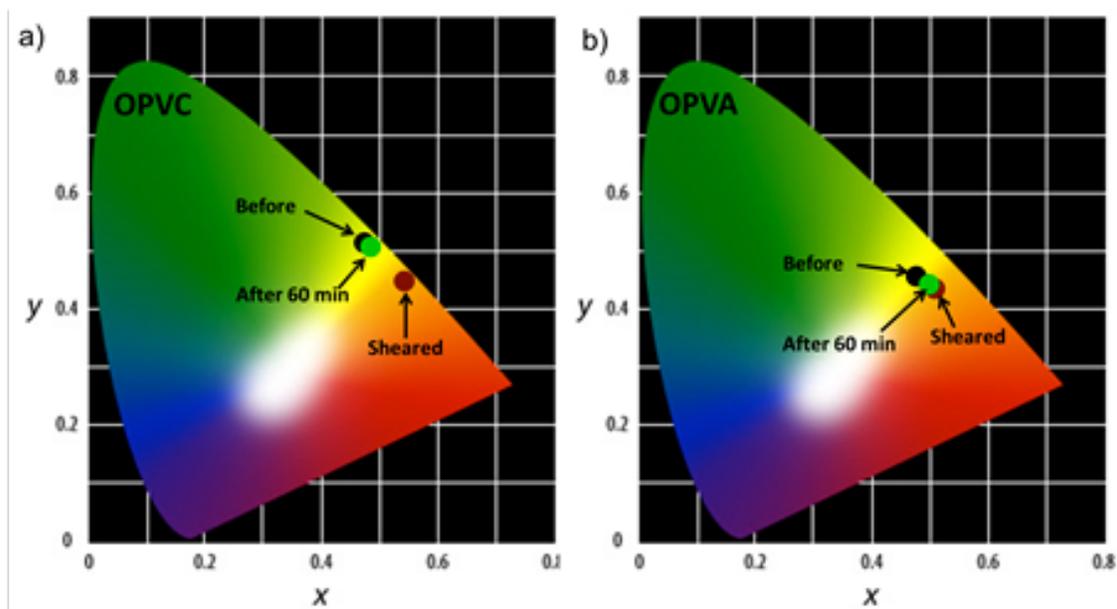


Fig. S9 1931 CIE coordinate values of emission from (a) OPVC (b) OPVA xerogel before and after shearing and recovery after 1 h.

4. Supplementary Information References

S1. (a) V. K. Praveen, S. J. George, R. Varghese, C. Vijayakumar and A. Ajayaghosh, *J. Am. Chem. Soc.*, 2006, **128**, 7542; (b) A. Ajayaghosh, V. K. Praveen, S. Srinivasan and R. Varghese, *Adv. Mater.*, 2007, **19**, 411; (c) K. K. Kartha, V. K. Praveen, S. S. Babu, C. Sandeep and A. Ajayaghosh, *Chem. –Asian J.*, 2015, **10**, 2250.