Supporting information for

Confined Supramolecular Polymer in Water with Exceptional Stability, Photoluminescence and Chiroptical Properties

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Materials and methods: Reagents and solvents were purchased from commercials sources and purified by standard protocols as reported in the literature.[1] Spectroscopy grade solvents were used for all physical and spectroscopy studies. UV-Vis experiments were performed in a JASCO V-750 UV-visible spectrometer. Fluorescence spectra were recorded in a Horiba FluoroMax-3 spectrophotometer. TEM images were captured in JEOL-2010EX instrument operating at an accelerating voltage of 200 KV. The energy dispersive X-ray (EDAX) spectroscopy was performed on the same TEM instrument equipped with an EDAX detector (Oxford LINK-ISIS 300) for elemental composition analysis. Fluorescence microscopy images were collected using an inverted fluorescence microscope from Olympus, Tokyo, Japan (Olympus IX73). Multicell DSC from TA instrument was used to examine the thermodynamic properties. Dynamic Light Scattering (DLS) measurements were carried out in a Malvern instrument at a scattering angle of 173°. Circular dichroism (CD) spectra were recorded in a JASCO J-810 spectropolarimeter. Circularly polarized luminescence (CPL) experiments were carried out on a Jasco CPL-300 spectrophotometer having digital integration time (D.I.T) fixed at 4.0 seconds with multiple spectral accumulations.

Synthesis and characterization: Synthesis and characterization of (*S*, *S*)-NDI-1 has been reported by us elsewhere.[2]

Preparation of SPNR-1/SPNR-2: DSPE-PEG (4mg) and NDI-1 (1 mg for SPNR-1 and 0.1 mg for SPNR-2) were dissolved in 300 μL of tetrahydrofuran (THF) and sonicated for 10 min to produce a homogeneous solution. The obtained deep red solution was injected dropwise into a vial containing 2 ml of distilled water over a period of 15 min with constant stirring. Once the THF solution was completely injected into water, the mixed dispersion was sonicated for 30 minutes. After that, the dispersion was stirred overnight at 50 °C in an oil bath to remove residual THF. Subsequently it was subjected to dialysis against water for 2 days in a dialysis bag with molecular weight cutoff of 2000 gm/ mole. Then the solution was passed through a 0.45 μm syringe filter and the obtained transparent dispersion was stored at 4 °C for further use.

Calculation of encapsulation efficiency: As the UV-Vis spectra obtained from the SPNR-1/SPNR-2 match with the J-aggregated NDI-1 spectrum in decane, we have used the molar extinction co-efficient (ε) of NDI-1 in decane to estimate the amount of NDI-1 in SPNRs. The molar extinction co-efficient (ε) of NDI-1 (at 554 nm) in decane was estimated to be 13342 $M^{-1}cm^{-1}$ from the concentration dependent absorption spectra (Fig. S4). Using this value, absorption intensity of SPNR-1/ SPNR-2 at 554 nm and NDI-1/ lipid ratio from the feed, the encapsulation efficiency was estimated and reported in Table S1.

Entry	Amount of NDI-1	Final solution volume	NDI-1 conc. (theoretical)	NDI-1 conc. (estimated from ε)	Encapsulation efficiency
SPNR-1	1.0 mg	2.25 mL	0.3956 mM	0.34 mM	86%
SPNR-2	0.1 mg	2.35 mL	0.0378 mM	0.031	82%

Table S1 Estimation of encapsulation efficiency of NDI-1 in SPNR-1 and SPNR-2.

Sample preparations for various physical studies:

UV/Vis, PL, CD, CPL and DLS experiments:

SPNR-1/SPNR-2 dispersion in water was prepared as per the procedure described above and directly used for these experiments. Temperature, cuvette path length and other experimental parameters have been reported in the respective figure captions.

Microscopy experiments

For TEM experiments, aqueous dispersion of SPNR-1 or SPNR-2 was drop-casted on a carbon coated copper grid and dried in the air for 24 h before imaging. For fluorescence microscopy, 20 μL of the required solution was casted on a clean glass slide and dried before imaging. AFM image was captured in a Bruker Innova-S 2 instrument in the tapping mode. Aqueous dispersion of SPNR-1 was spin-coated on a freshly cleaned mica surface and dried in air for 24 before the experiment.

Determination of fluorescence quantum yield

Fluorescence quantum yields[3] of SPNR-1/SPNR-2 in aqueous medium were determined by absolute methods in solution phase using a Horiba Quanta Phi integrated sphere system attached with a Horiba Jobin Yvon Fluoromax-4 spectrophotometer. To confirm the authenticity of the obtained results, two known dye molecules (Rhodamine-B and Rhodamine-6G) were tested and obtained values were found to be comparable with that of the literature reports.

CPL measurements

Circularly polarized luminescence (CPL) measurements were carried out using the JASCO CPL-300 setup which is equipped with a double prism linearly polarizing monochromator to avoid linear polarization effects and thus the resultant CPL signal is exempted from any undesired linear dichroism signals. CPL was evaluated using the difference between left and right circularly polarized radiation intensities emitted by the sample which was itself carried out by the JASCO Spectral Manager Suite supplied from the instrument. During the measurements, digital integration time (D.I.T) was kept fixed at 4.0 seconds with multiple spectral accumulations (3) at a scanning speed of 50 nm/ min to avoid unwanted noise. Samples were excited at 500 nm (similar to that of fluorescence experiments) in cuvettes of 0.1 cm path lengths and excitation/emission slit widths were maintained at 2000 mm each and the instrument was calibrated with standard D and L-camphor solutions in ethanol (0.4% W/V) prior to measuring actual samples.

Probing time dependent growth of SPNR

For understanding the growth of supramolecular polymers inside lipid confinement, time dependent UV-Vis experiments were performed. 0.1 mg of NDI-1 and 4.0 mg of DSPS-PEG were dissolved together in 300 μL of THF by sonication for 10 min. The obtained deep red solution was then injected dropwise into a vial containing 2 ml of distilled water while constant stirring. Once the addition was complete,

the UV-Vis spectra of the resultant solution was monitored as a function of time (in a 1.0 cm UV cuvette without any lid at 2 minutes of interval) at 50 ^{o}C while being stirred constantly. Then the absorbance intensity at the J-band (554 nm) was plotted against time to get an idea about the growth of the supramolecular polymers inside lipid confinement.

Additional figures:

Fig. S1 Images of (*left*)- SPNR-2 in H_2O and (*right*)-the vial in which a solution of NDI-1 in THF (0.1 mg in 300 µL) was injected to water (2700 µL) in the absence of the lipid.

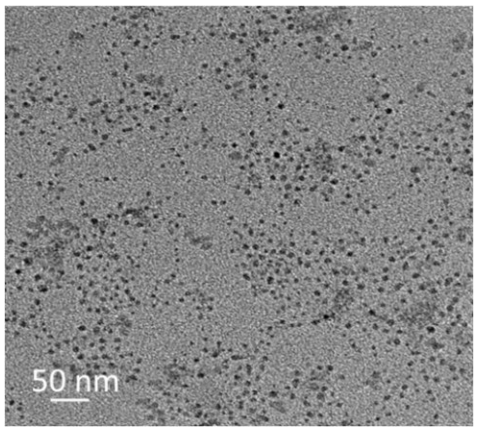

Fig. S2 TEM image of aqueous aggregates of DSPE-PEG (c = 2 mg/ mL).

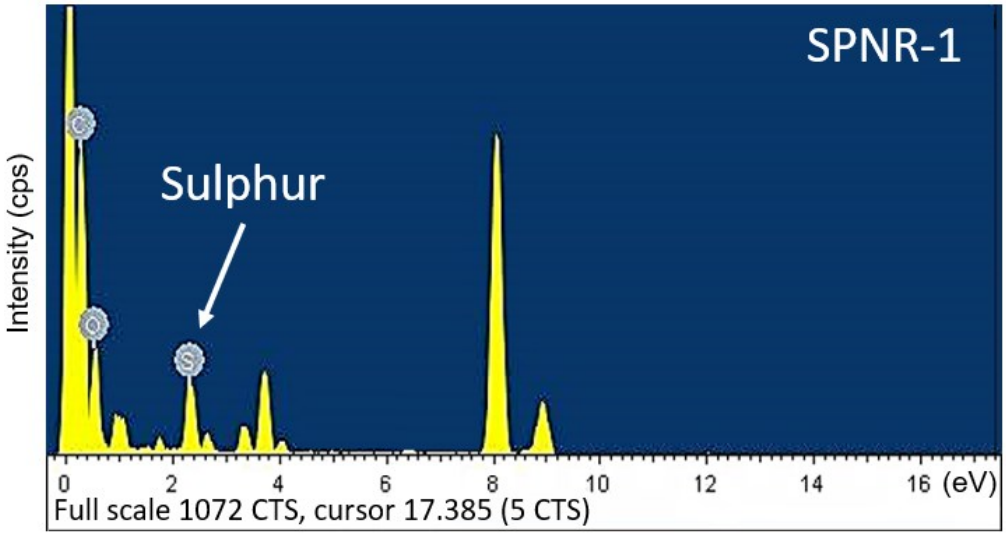

Fig. S3 EDAX profile of SPNR-1 showing the presence of sulphur inside the nanoparticles.[4]

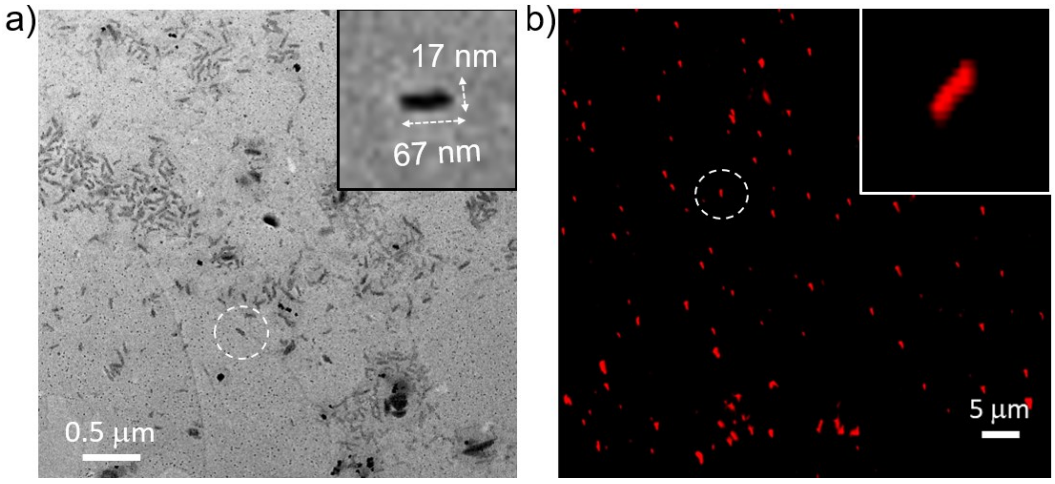

Fig. S4 (a) TEM and (b) fluorescence microscopy images of SPNR-2; insets show zoomed image of the rod marked in circle.

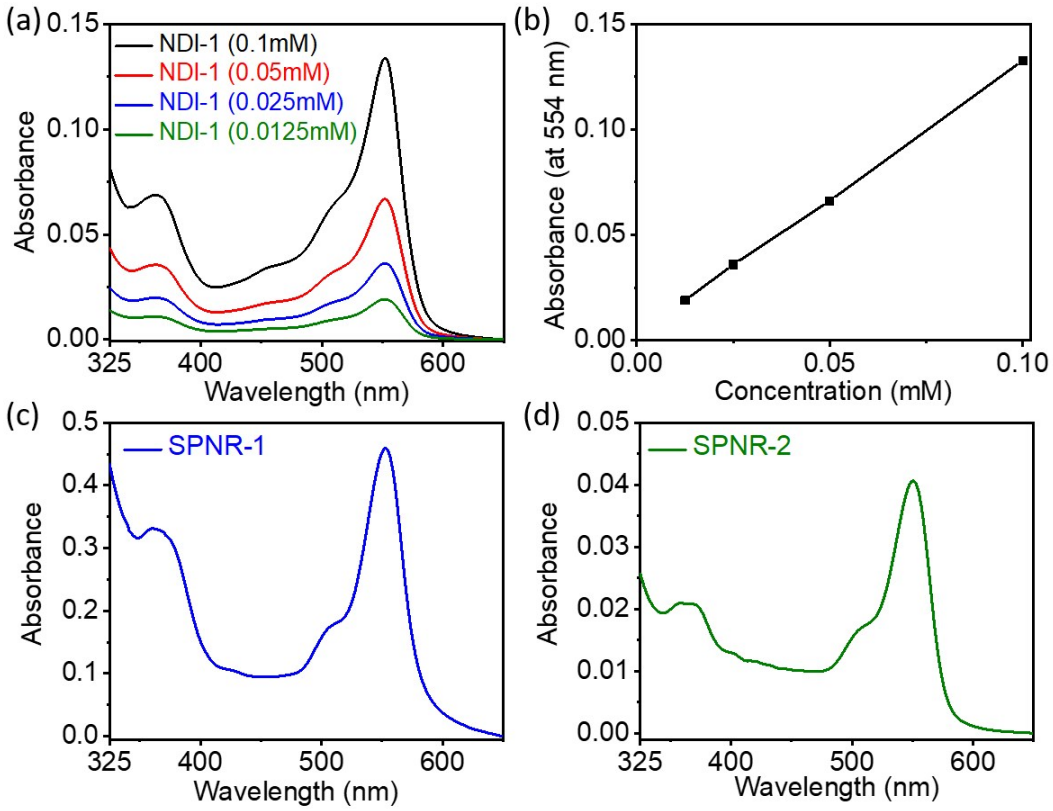

Fig. S5 (a) Concentration dependent UV-Vis spectra of NDI-1 in decane (l = 0.1 cm, T = 25 °C) and (b) corresponding absorbance (554 nm) vs. concentration plot; (c) and (d) depicts the UV-Vis spectra of the as prepared SPNR-1 and SPNR-2 dispersions in water (l = 0.1 cm, T = 25 °C).

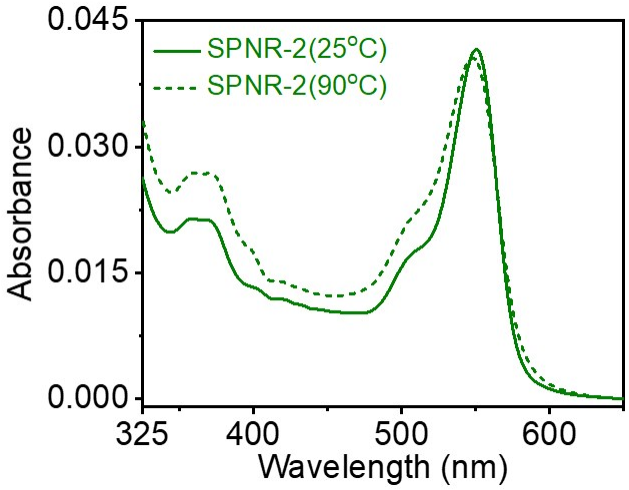

Fig. S6 Temperature dependent UV-Vis spectra of SPNR-2 dispersion in water (l = 0.1 cm).

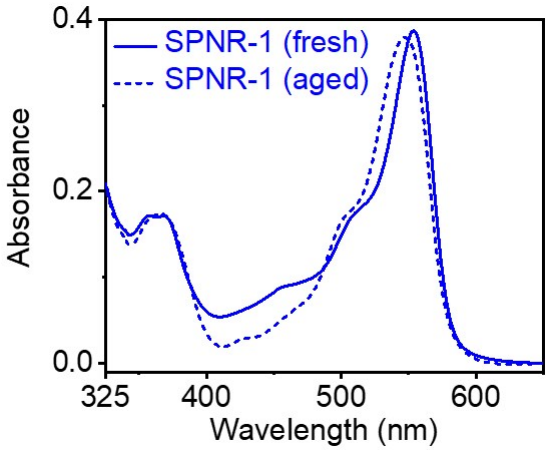

Fig. S7 UV-Vis spectra of fresh and aged (six months) SPNR-1 dispersion in water (l = 0.1 cm, T = 25 °C).

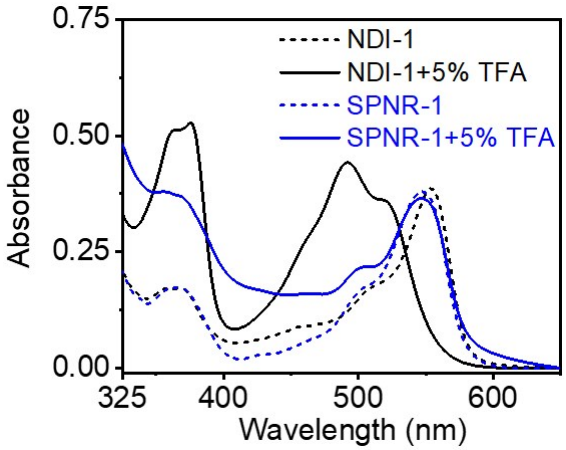

Fig. S8 UV-Vis spectra of NDI-1 in decane (black, c = 0.35 mM) and SPNR-1 in water (blue) in the presence (solid) or absence (dashed) of 5% (v/ v) TFA (l = 0.1 cm, T = 25 °C).

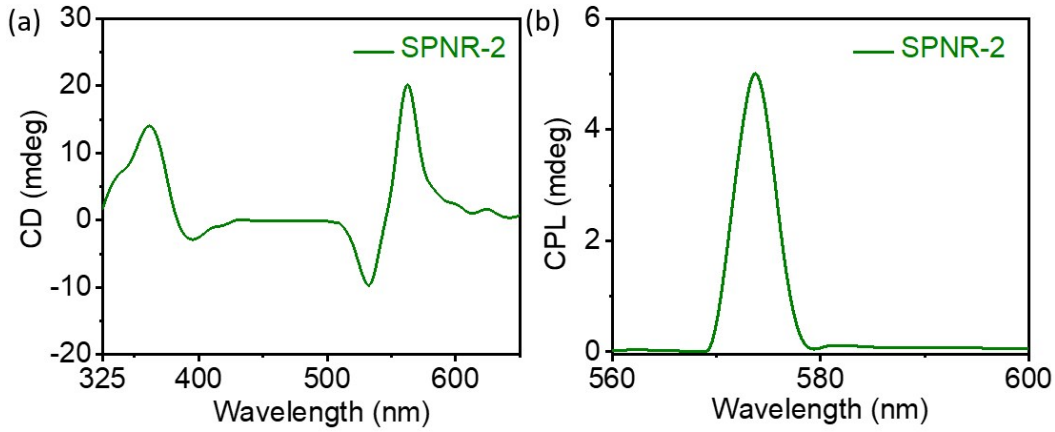

Fig. S9 (a) CD and (b) CPL spectra of SPNR-2 at 25 °C (l = 1.0 cm and 0.1 cm, respectively).

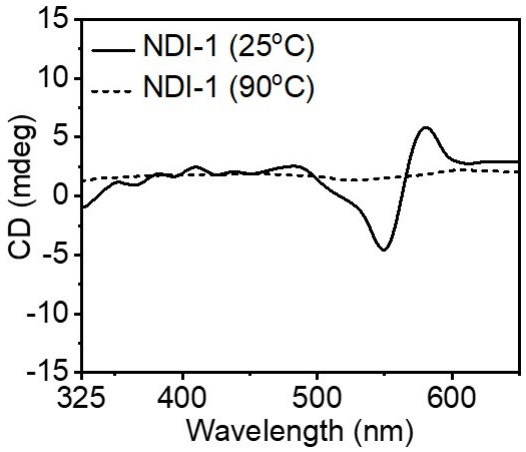

Fig. S10 Temperature dependent CD spectra of NDI-1 in decane (*c* = 0.35 mM, *l* = 0.1 cm).

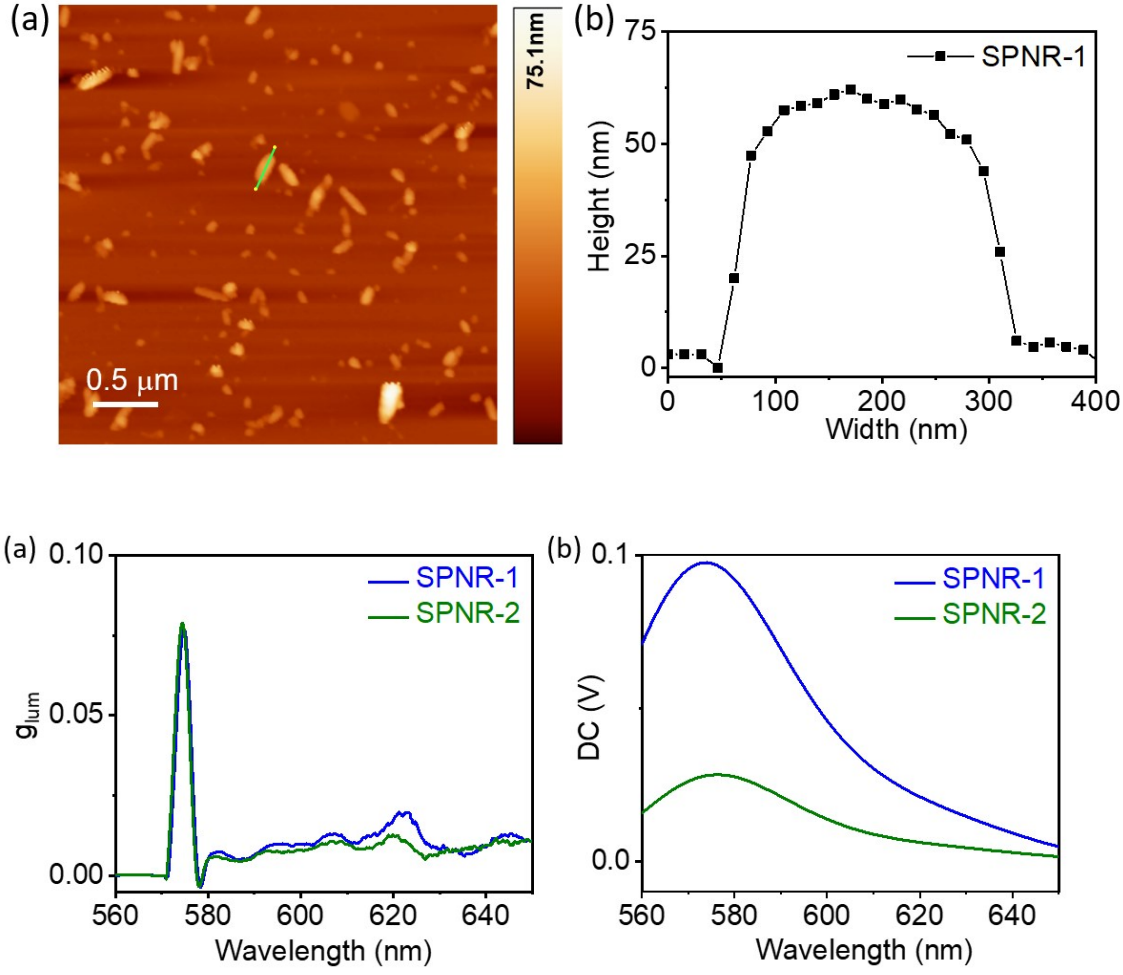

Fig. S11 (a) AFM image and (b) corresponding height profile diagram of SPNR-1.

Fig. S12 (a) Variation of g_{lum} as a function of wavelength for SPNR-1 and SPNR-2. The spectrum was derived from the CPL spectra using inbuilt instrument software; (b) Plot of DC (V) vs. wavelength during CPL measurements.

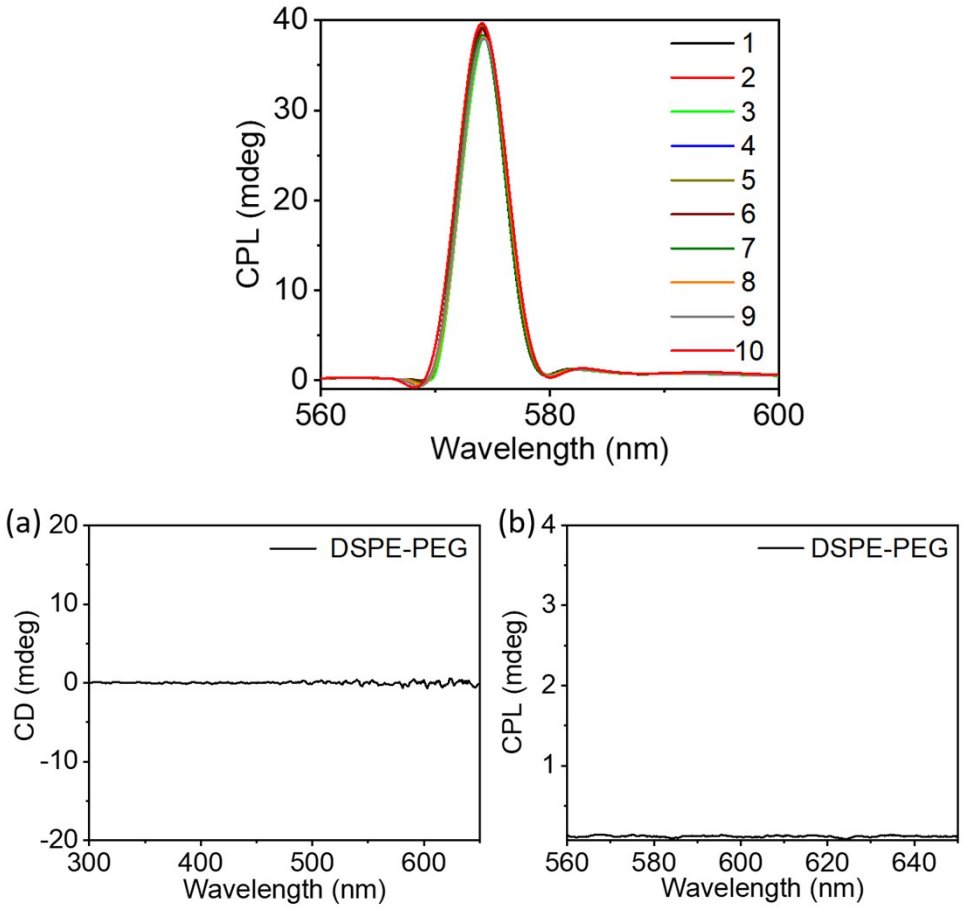

Fig. S13 CPL spectra of SPNR-1 at 25 °C (repeated 10 times to check the reproducibility, *l* = 0.1 cm). Numbers inside the figure the run number of the experiment.

Fig. S14 (a) CD and (b) CPL spectra of DSPE-PEG in water at 25 °C (*c* = 2 mg/mL, *l* = 0.1 cm).

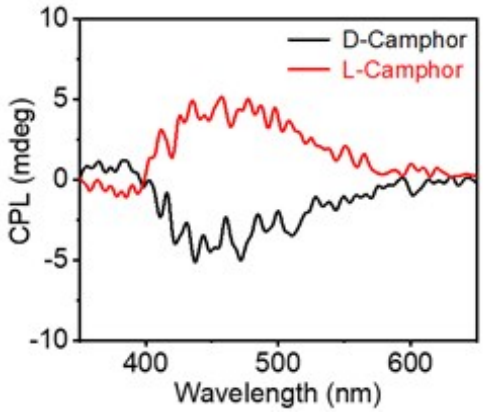

Fig. S15 CPL spectra of D-Camphor and L-Camphor (standard samples) in ethanol (*c* = 4 mg/mL, *l* = 0.1 cm) at 25 ^{o}C showing expected spectral behaviour.

References:

1. D. Perrin, W. L. F. Armarego, D. R. Perrin*, Purification of Laboratory Chemicals*, 2nd ed., Pergamon, Oxford, 1980.

2. A. Mukherjee and S. Ghosh, Chem. Eur. J., 2020, **26**, 12874.

3. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy (2nd ed.)*, Kluwer Academic/Plenum Publishers, New York 1999.

4. M. Scimeca, S. Bischetti, H. K. Lamsira, R. Bonfiglio and E. Bonanno, *Eur. J. Histochem.*, 2018, **62**, 89.