Electronic Supporting Information

for

Lanthanide Hydrogels with Tunable Circularly Polarized Luminescence (CPL) via Supramolecular Chirality Induction

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1. General Methods

Optical Measurements: Electronic absorption spectra were recorded on Jasco V-750 UV-Visible Spectrophotometer equipped with a peltier. Circular Dichroism (CD) spectra and temperature-dependent CD spectra were recorded on a Jasco J-815 spectrometer where the sensitivity, time constant and scan rate were chosen appropriately. Fluorescence measurements were carried out on a Jasco FP-8500 spectrofluorometer equipped with a peltier. Circularly polarized luminescence (CPL) measurements were performed with a Jasco CPL-300 spectrometer equipped with a peltier. A scanning speed of 10 nm/min, the excitation slit width of 2000 µM and an emission slit width of 200 µM, integration time (D.I.T) of 30 sec, and with multiple spectral accumulations were employed.

Atomic Force Microscopy (AFM): AFM was done in JPK NANO WIZARD II (in the non-contact mode). Ln(III) and cholate solutions were mixed and sonicated for 1 min. ~20 µL of the gel was immediately transferred on a freshly cleaved mica sheet and lyophilized. This sample was used for AFM imaging of the metastable state. AFM imaging for the gel was done by drop-casting the gel on freshly cleaved mica sheets.

Rheology measurement: Samples were prepared by mixing NaCh (30 mM), Phenanthroline (5 mM) in NaCh and $Eu(NO_3)_3$ (10 mM), then sonicate for ~1 min. Measurement was done in TA Discovery HR3 Rheometer, using a 40 mm parallel plate. Frequency sweep done under 1 Pa stress and Stress sweep done 1 Hz frequency at 25 ^oC.

Materials All chemicals are purchased from Merck (Sigma-Aldrich) and used as such without any further purification. MilliQ water was used as a solvent.

2. Experimental procedures:

Gel Preparation: Samples were prepared by mixing 300 µM of 30 mM aq. NaCh, 200 µM of 5 mM Phenanthroline (solution prepared in 15 mM aq. NaCh) and 500 µM of 10 mM aq. $Eu(NO_3)_3$

solution, to make the final concentration of NaCh-15 mM, Eu(III)-5 mM and phenanthroline-1 mM. Then the solution was sonicated for ~1 min to give red color emitting gel.

A similar method was used for green and yellow colored emitting gel. For green: Tb(III)-5 mM, NaCh-15 mM and phenanthroline-1 mM. For Yellow: Tb(III)-4 mM, Eu(III)-1 mM, NaCh-15 mM and phenanthroline-1 mM.

Kinetics Measurement: Mix NaCh (30 mM), Phenanthroline (5 mM) in NaCh and $Eu(NO_3)_3$ (10 mM) and transfer in the cuvette immediately for the spectroscopic (CD, CPL and PL) measurements.

3. Supporting Figures

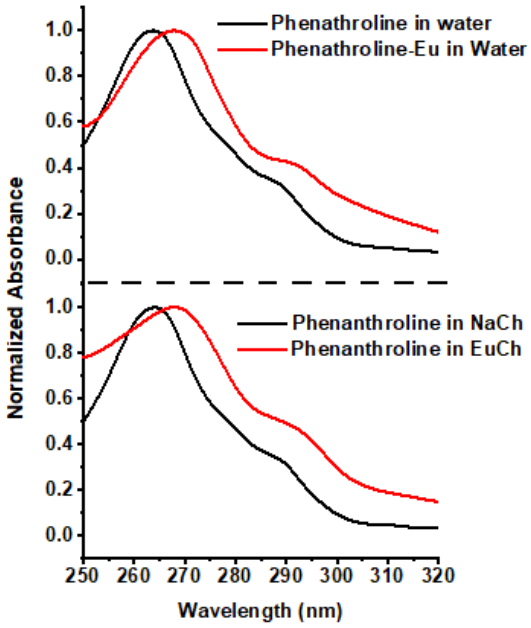

Figure S1: UV-Vis absorption spectra of Phenanthroline with and without Eu(III) in water and NaCh. The 5 nm shift of absorption maxima when Eu(III) is added in each case shows that there is non-covalent interaction between phenanthroline and Eu(III) in water as well as in gel. [**Eu(III)**] = 5 mM, [**Phen**] = 1 mM, [**NaCh**] = 15 mM.

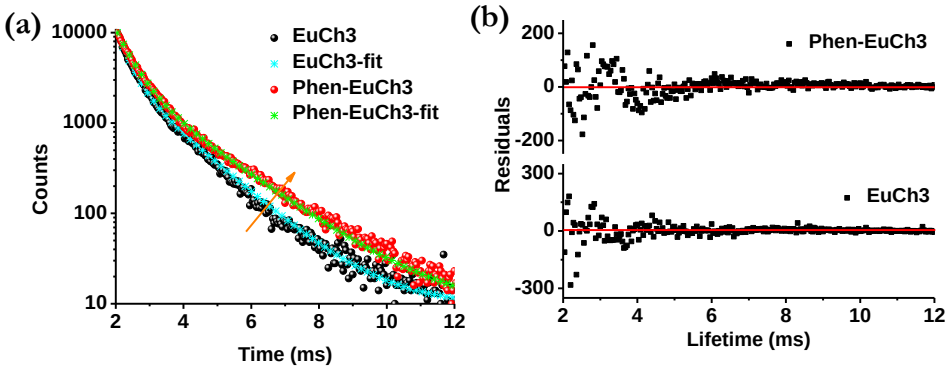

Figure S2: a) Lifetime decay plot, and b) residual curves of Eu(III) with and without phenanthroline (Phen) in **EuCh$_3$** gel ($\lambda_{coll.}$ = 700 nm, $\lambda_{exc.}$ = 298 nm). An increase in Eu(III) luminescence lifetime from 0.15 ms to 0.36 ms in presence of Phen implies sensitization of Eu(III) by Phen.

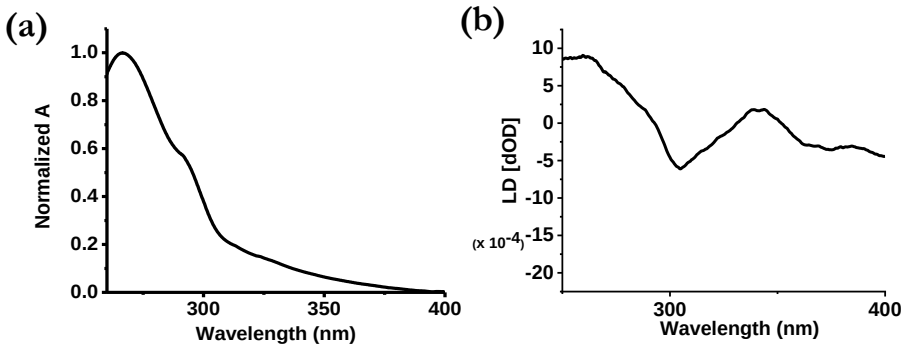

Figure S3: (a) Absorption, and b) LD Spectra of phenanthroline in **EuCh$_3$** gel. The low LD (10^{-4} dOD) of the gel suggest that the LD contribution by the allignment of thr gel fiber on the CD signal of phenanthroline is insignificant.

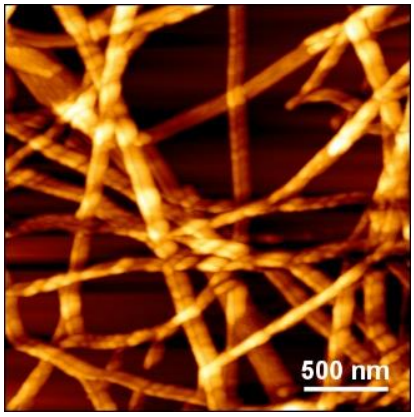

Figure S4: AFM height image of **Phen-EuCh$_3$** gel in Tapping mode. The image shows the three-dimensional cross-linked network of supramolecular fiber.

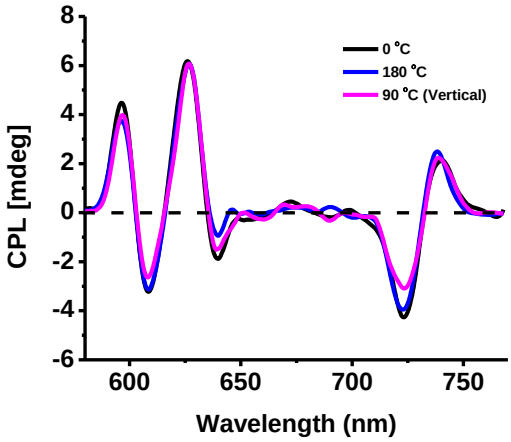

Figure S5: CPL of **Phen-EuCh$_3$** gel at diferent cuvette angles rotation (rotation as Fig2b). The rotation of the sample does not show a significant change in the CPL signal of Eu(III). These shows that the CPL signal observed has no contribution from the LD of the gel fiber orientation.

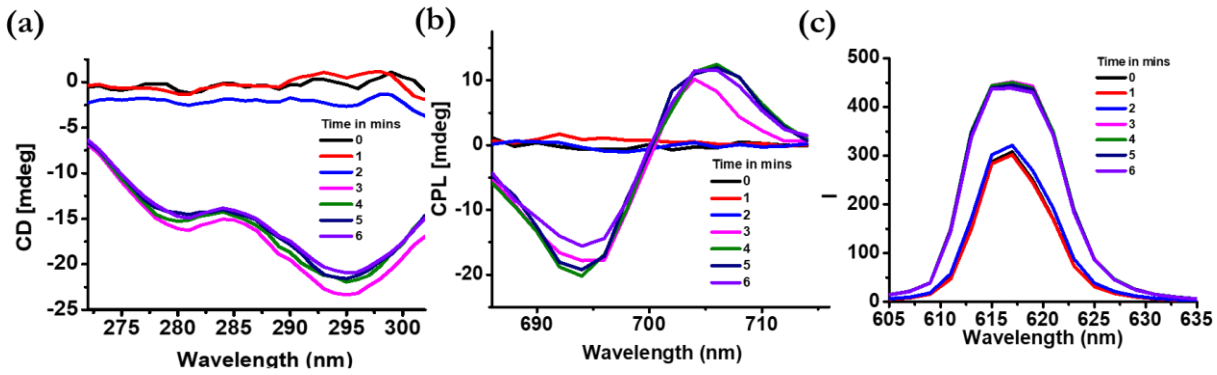

Figure S6: Time-dependent (a) CD, (b) CPL, and (c) PL spectra of **Phen-EuCh$_3$.** The metastable state has no CD or CPL signal but has Eu(III) emission ($\lambda_{exc.}$ = 298 nm). CD and CPL signal was observed only on formation of gel implying the induction of chirality only by the supramolecular gel formation.

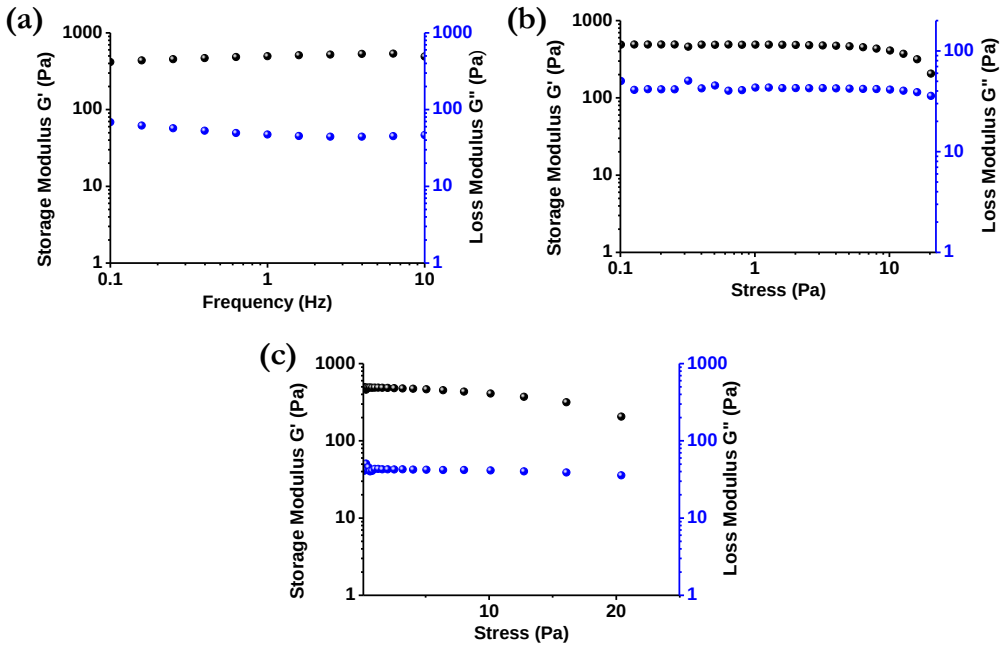

Figure S7: Rheological studies of **Phen-EuCh$_3$** gels. a) Frequency sweep with constant stress amplitude. b) Stress amplitude sweep with constant frequency in logarithmic scale, and c) linear scale . Frequency sweep is done under 1 Pa stress and Stress sweep is done 1 Hz frequency at 25 ^{o}C.

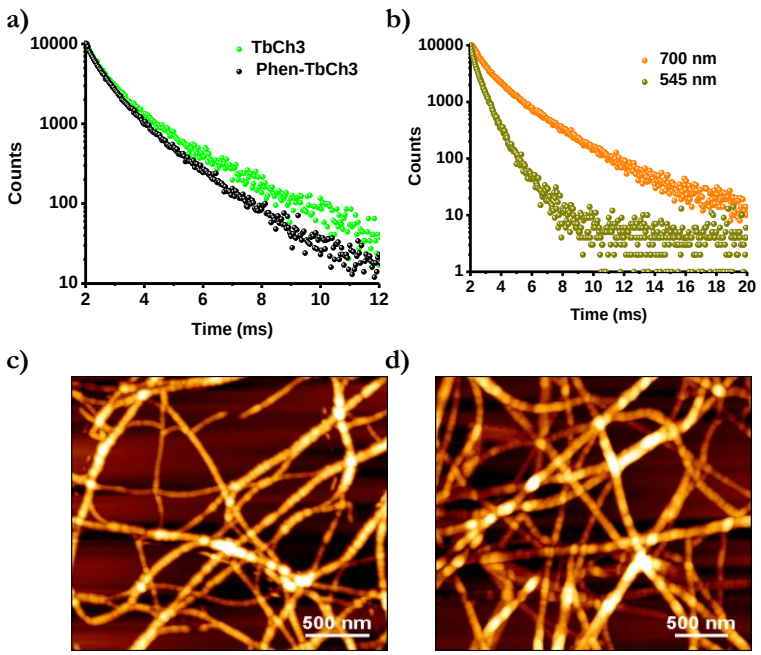

Figure S8: (a) Fluorescence lifetime decay of Tb(III) with and without phenanthroline, (b) Fluorescence lifetime decay of Eu(III) ($\lambda_{coll.}$ = 700 nm, $\lambda_{exc.}$ = 298 nm) and Tb(III) ($\lambda_{coll.}$ = 545 nm, $\lambda_{exc.}$ = 298 nm) in Yellow color emitting gel, (c) AFM image of gel green-emitting gel (**Phen-TbCh$_3$** gel) (d) AFM image of yellow emitting gel (**Phen-TbCh$_3$-EuCh$_3$** gel).

Note: The lifetime data shows the senstisation of Tb(III) by Phen.

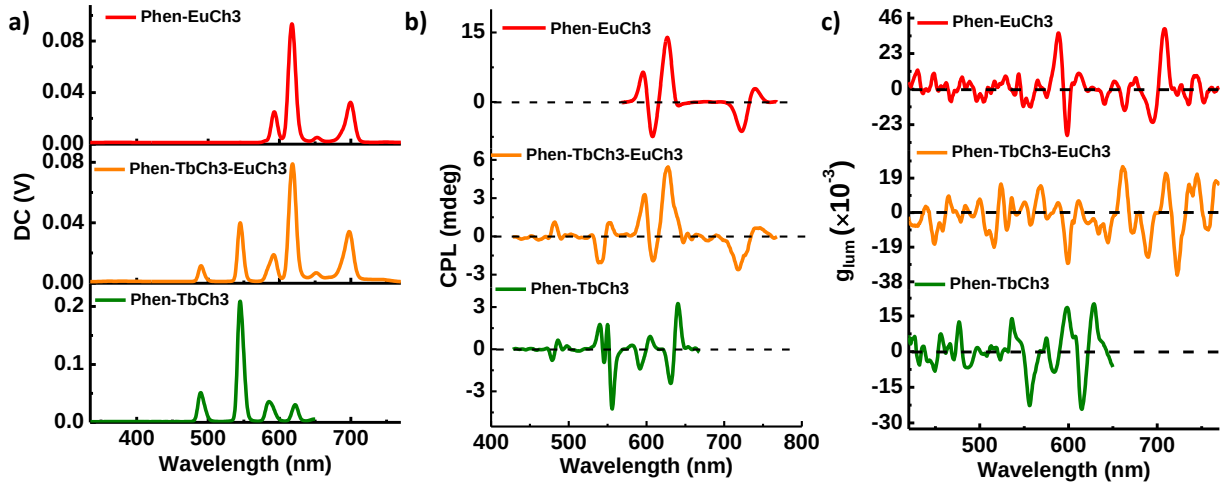

Figure S9: (a) DC signal, (b) CPL signal, and (c) g_{lum} signal of Red (**Phen-EuCh3**), Yellow (**Phen-TbCh3-EuCh3**) and Green color (**Phen-TbCh3**) emitting gel.

Table S1. Luminescent lifetime of Eu (III) ($\lambda_{coll.}$ = 700 nm) and Tb (III) ($\lambda_{coll.}$ = 545 nm) in different gels. Note: The percentage of the smaller component in each sample is very small, 1-2 percent and it is not possible to assign them with particular Eu population with certainty. This small fraction of Eu population might just be due to the heterogeneity of supramolecular gel system.

Sample ($\lambda_{exc.}$ = 298 nm	**τ_1 (ms)**	**Relative component**	**τ_2 (ms)**	**Relative component**	**τ_{ave}(ms)**	***x^2***
$EuCh_3$ ($\lambda_{coll.}$ = 700 nm)	0.14	0.99	1.01	0.01	0.15	0.99
Phen-$EuCh_3$ ($\lambda_{coll.}$ = 700 nm)	0.35	0.98	1.08	0.02	0.36	0.99
$TbCh_3$ ($\lambda_{coll.}$ = 545 nm)	0.32	0.99	1.19	0.01	0.33	0.99
Phen-$TbCh_3$ ($\lambda_{coll.}$ = 545 nm)	0.39	0.98	1.53	0.02	0.41	0.99
Phen-$EuCh_3$- $TbCh_3$ ($\lambda_{coll.}$ = 545 nm)	0.15	0.99	0.65	0.01	0.15	0.99
Phen-$EuCh_3$- $TbCh_3$ ($\lambda_{coll.}$ = 700 nm)	0.72	0.93	2.39	0.07	0.84	0.99

Table S2. The table includes the specific Eu(III) emission transitions, their corresponding wavelengths, and the associated g_{lum} values.

System	Emission wavelength (nm)	Transitions	g_{lum} value ($\times 10^{-2}$)	Quantum yield
Phen-EuCh3	593	$^5D_0$-$^7F_1$	1.3	20%
	617	$^5D_0$-$^7F_2$	0.4	
	698	$^5D_0$-$^7F_4$	-1.6	
Phen-TbCh3	490	$^5D_4$-$^7F_6$	-0.5	27%
	544	$^5D_4$-$^7F_5$	0.4	
	584	$^5D_4$-$^7F_4$	-0.8	
	622	$^5D_4$-$^7F_3$	-0.01	