

## Supporting Information

### High aspect ratio, processable coordination polymer gel nanotubes based on an AIE-active LMWG with tunable emission

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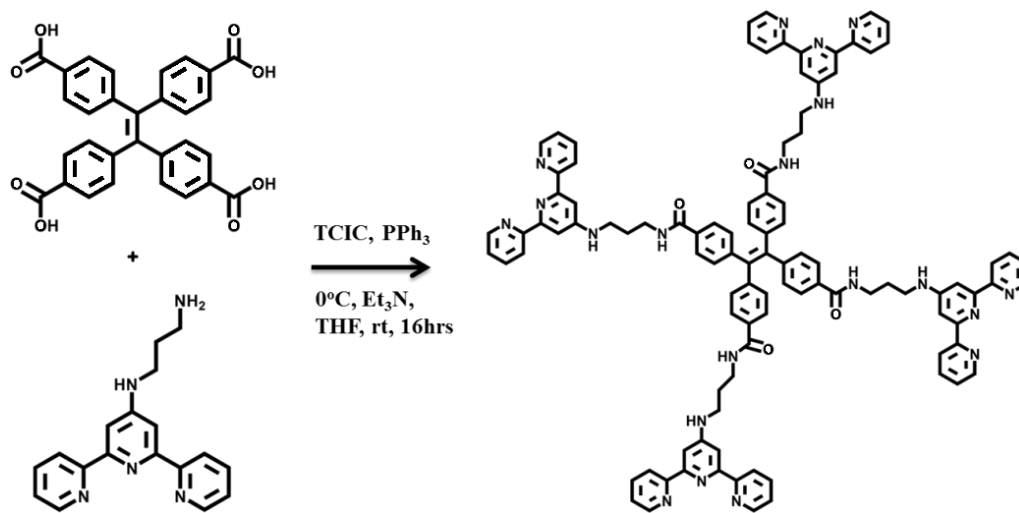
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#### 1. Experimental Section.

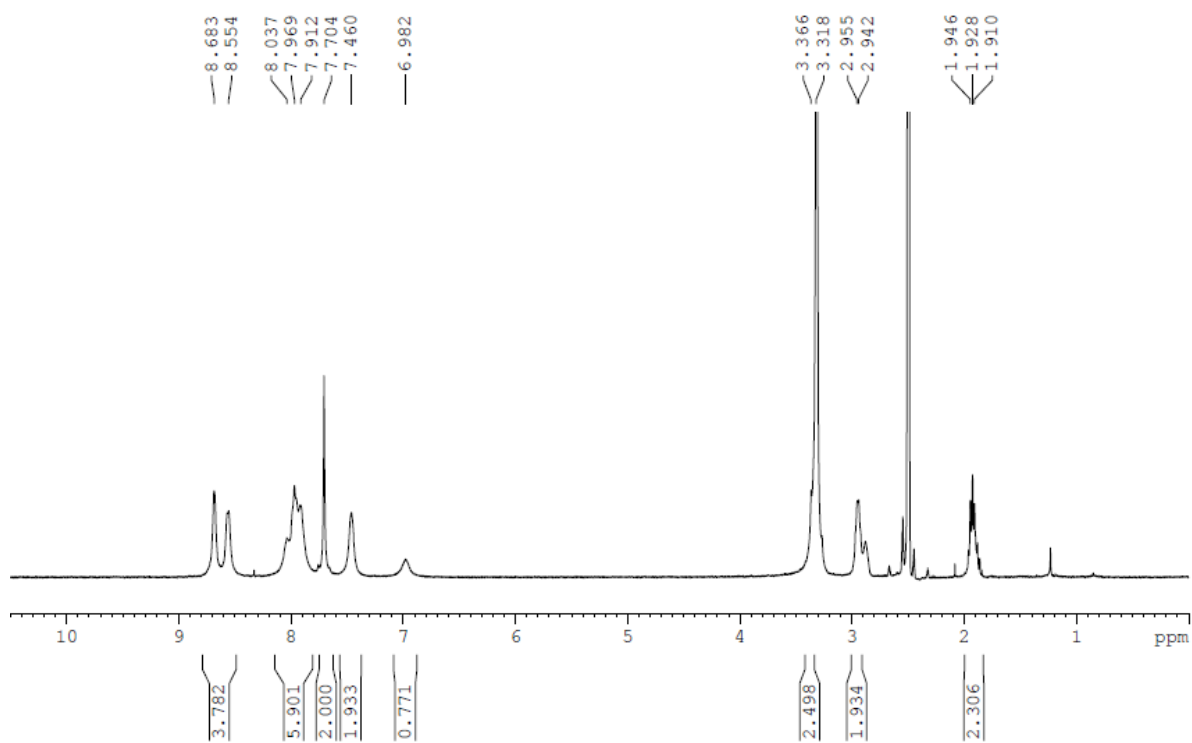
**1.1 Materials and Methods:** Tetraphenylethene, 1,3-diaminopropane, 4'-chloro-2,2':6',2''-terpyridine, trichloroisocyanuric acid (TCIC) and triphenylphosphine (PPh<sub>3</sub>) were purchased from Sigma-Aldrich chemical Co. Ltd. Solvents were pre-dried using standard literature procedures. UV-Vis experiments were carried out with spectroscopic grade solvents purchased from Spectrochem Ltd. <sup>1</sup>H NMR spectrum is recorded on a Bruker AV-400 spectrometer with chemical shifts recorded as ppm and all spectra were calibrated against TMS. UV-Vis spectra were recorded in a Perkin-Elmer lamda 900 spectrometer. Fluorescence measurements were accomplished using Perkin Elmer Ls 55 Luminescence spectrometer. Fourier transform infrared (FTIR) spectra were recorded by making samples with KBr pellets using Bruker FT-IR spectrometer. Rheological measurements were performed using a Physica interfacial rheology system (IRS). Powder X-ray diffraction measurements were carried out on a Bruker D8 discover instrument using Cu-K $\alpha$  radiation. Elemental analyses were carried out using a Thermo Scientific Flash 2000 CHN analyzer. Morphology studies were done using Lica-S440I field emission scanning electron microscopy (FESEM) by placing samples on silicon wafer under vacuum with an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) studies were done

on JOEL JEM-3010 with accelerating voltage of 300 kV. For this analysis the xerogels were dispersed in ethanol and then drop casted on a carbon coated copper grid. The solid state fluorescence quantum yield of **L** solid powder and **L** xerogel was determined by using integrating sphere, an absolute quantum yield measurement and calculated by Horiba Jobin Yvon. Lifetime measurements were carried out on an EPL-405 ps pulsed diode laser (Edinburgh instrument) used as the excitation source ( $\lambda_{\text{ex}} = 405 \text{ nm}$ ).

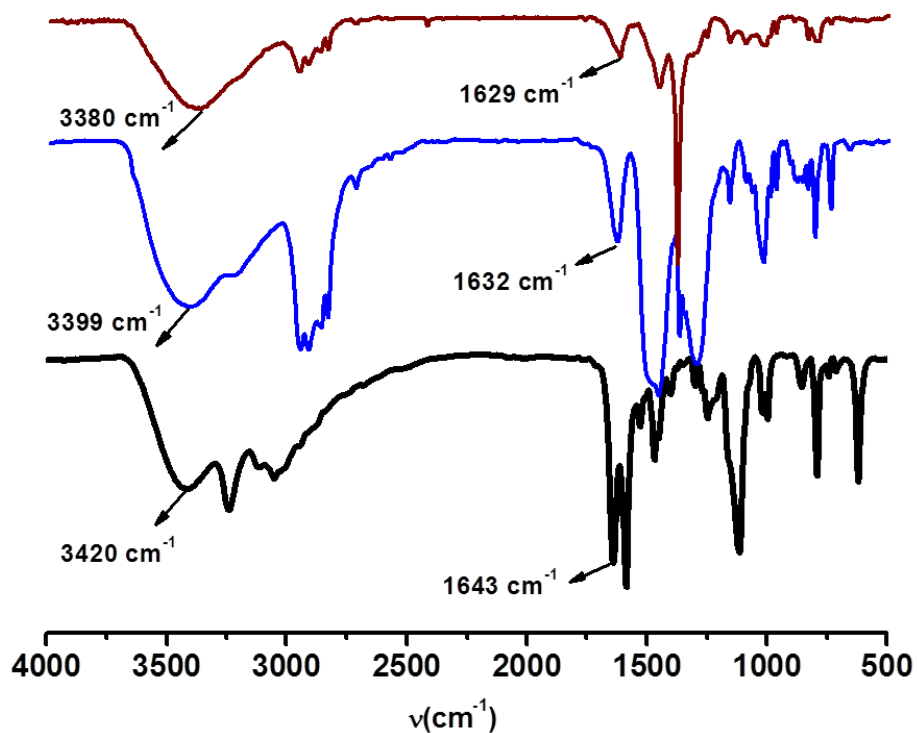
**1.2 Synthesis of ligand (L):** *tetrakis*(4-carboxy)tetraphenylethene and 2,2';6',2''-terpyridin-4'-yl-propane-1,3-diamine are synthesized by the reported procedures,<sup>1</sup> *tetrakis*(4-carboxy)tetraphenylethene (1 eq) is dissolved in tetrahydrofuran (THF) and cooled to 0 °C followed by addition of trichloroisocyanuric acid (TCIC) (4.2 eq) and triphenylphosphine (PPh<sub>3</sub>) (4.2 eq) is added portion wise. The reaction mixture is stirred for 30 minutes at 0 °C under inert atmosphere. To the reaction mixture, a solution of 2,2';6',2''-terpyridin-4'-yl-propane-1,3-diamine (4 eq) and Et<sub>3</sub>N in THF were added under continuous stirring at 0 °C for 15 min and stirred at room temperature for 16 hrs. Precipitates were collected by filtration and washed several times with chloroform and acetone to get **L** in 60 % yield. **L** is dried under vacuum for 6 hrs at room temperature and analysed with <sup>1</sup>H-NMR and HRMS. Elemental analysis calcd. for **L** (C<sub>102</sub>H<sub>88</sub>N<sub>20</sub>O<sub>4</sub>): C, 72.3; H, 5.47; N, 16.54. Found: C, 72.16; H, 5.91; N, 16.28. HRMS (+ESI): *m/z* calculated for C<sub>102</sub>H<sub>88</sub>N<sub>20</sub>O<sub>4</sub>: 1657.9217, found: 1658.72339 [M+H]<sup>+</sup>.



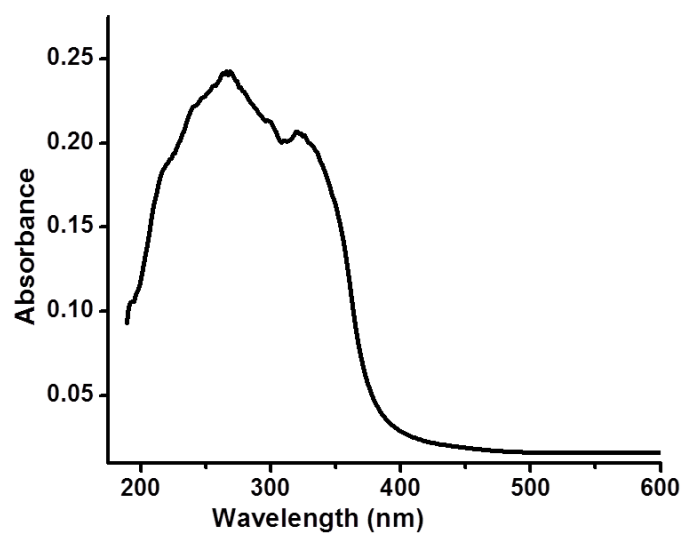
**Fig. S1** Synthetic scheme of **L** using amide coupling strategy.



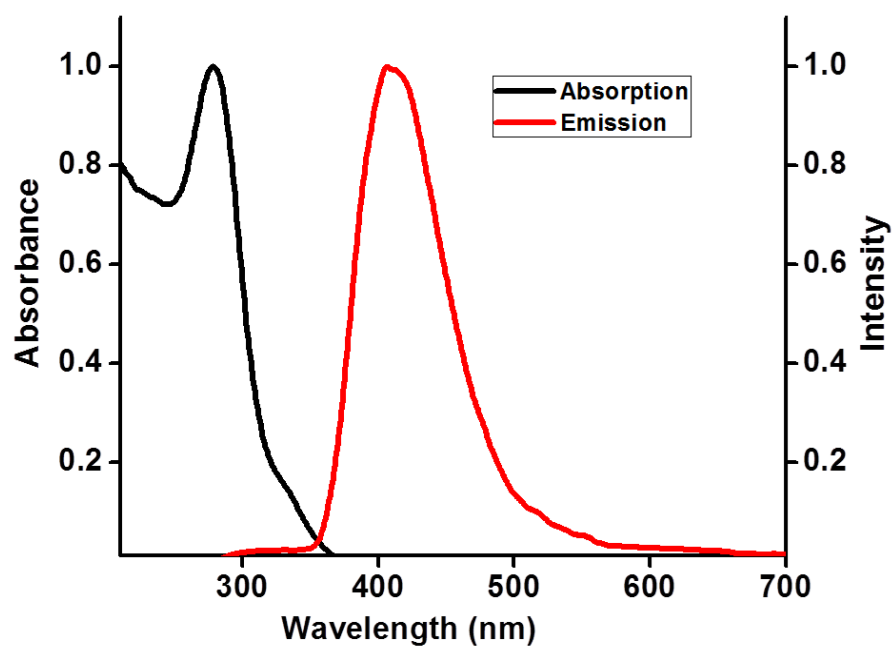
**Fig. S2** <sup>1</sup>H-NMR spectrum of **L** in dmsO-*d*<sup>6</sup> solvent.



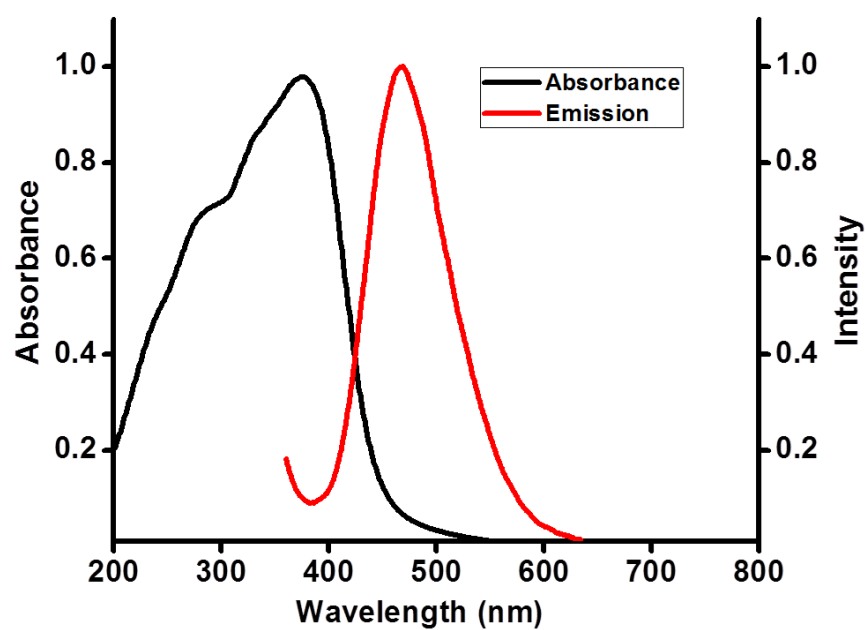
**Fig. S3** FTIR spectra of ligand powder (black), L xerogel (blue) and CPG (wine).



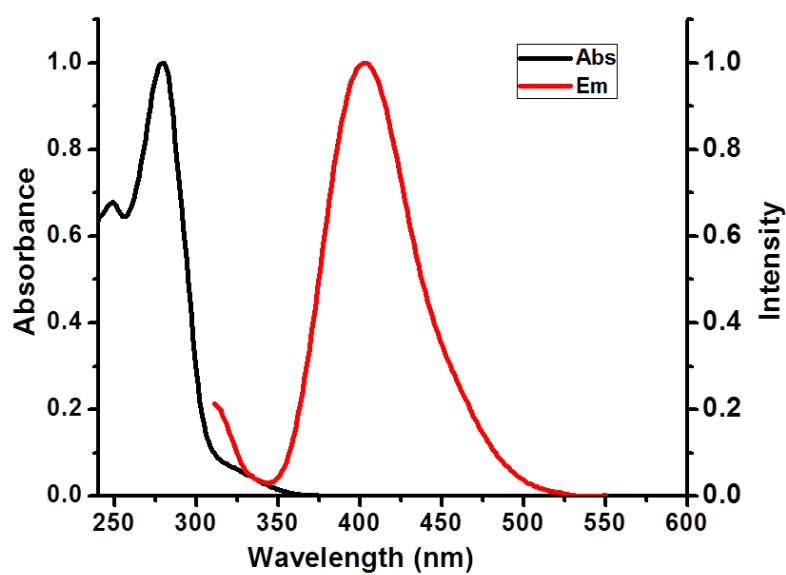
**Fig. S4** Absorption spectrum of L in solid state.



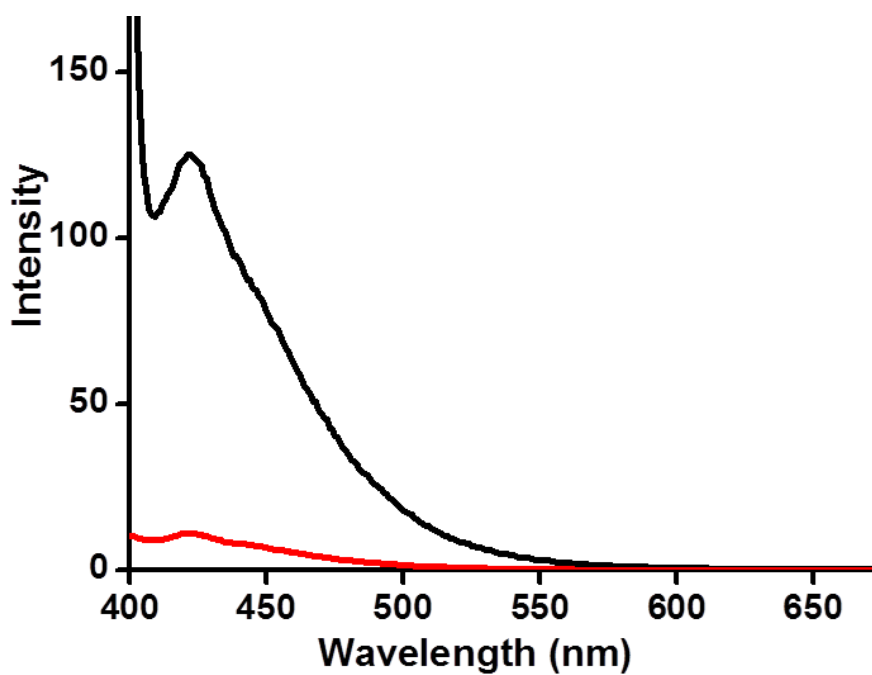
**Fig. S5** Absorbance (black) and emission (red) spectra of TPY in methanol.



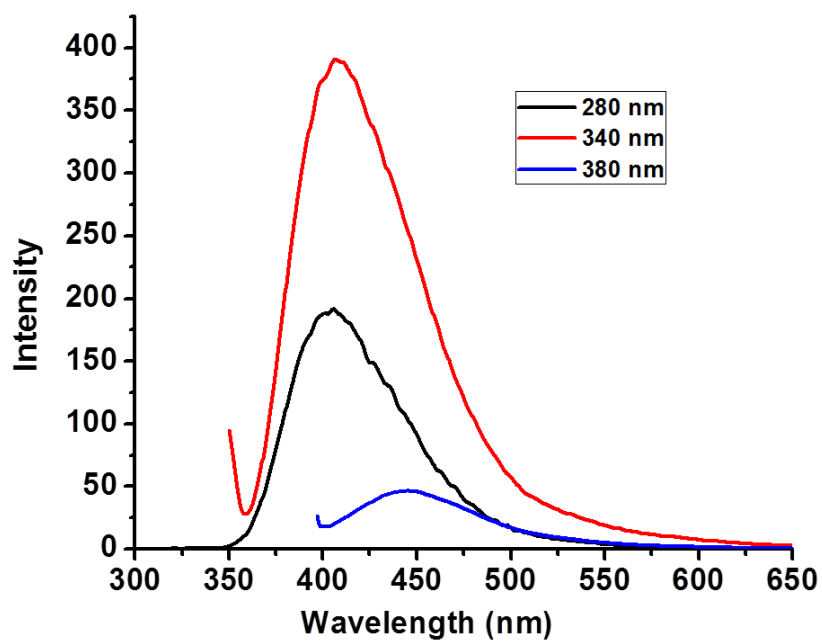
**Fig. S6** Absorbance (black) and emission (red) spectra of *tetrakis*(4-carboxy)tetraphenylethene in solid state.



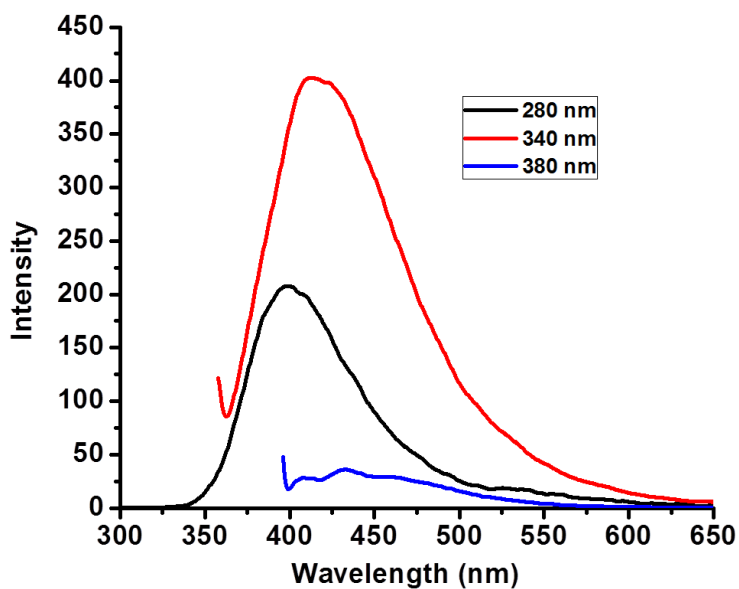
**Fig. S7** UV/Vis absorption (black) and emission spectrum (red, exc: 280 nm) of methanol solution of **L** ( $3 \times 10^{-5}$  M) at 298 K.



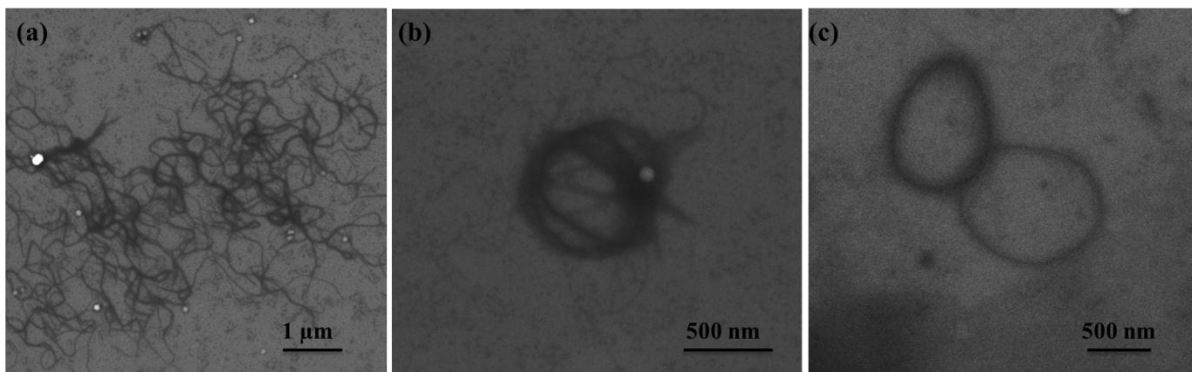
**Fig. S8** Emission spectra of methanol solution of **L** ( $3 \times 10^{-5}$  M) excited at 350 nm (black) and 390 nm (red) showing no TPE based emission.



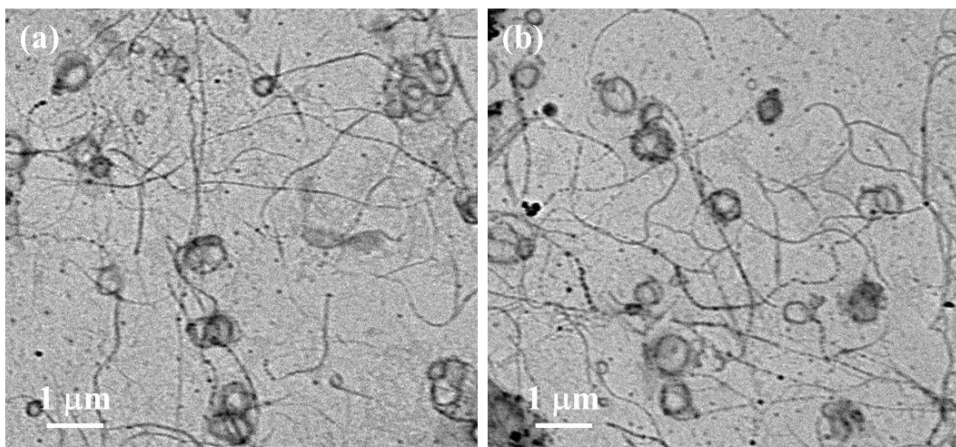
**Fig. S9** Emission spectra of L in DMF ( $3 \times 10^{-5}$  M) at different excitation wavelengths.



**Fig. S10** Emission spectra of L in EtOH ( $3 \times 10^{-5}$  M) at different excitation wavelengths.

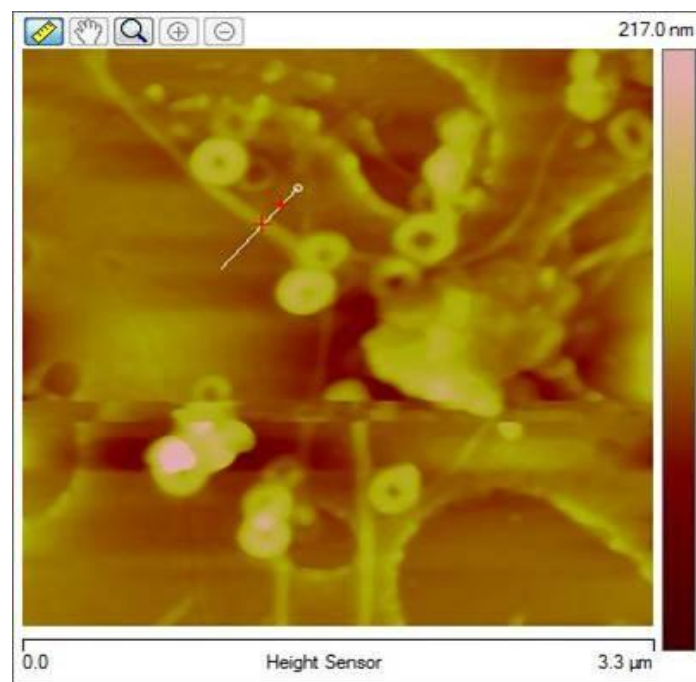


**Fig. S11** FESEM images of **L** xerogel showing (a) nanofibers and (b), (c) coiling of nanostructures with nanoring formation.

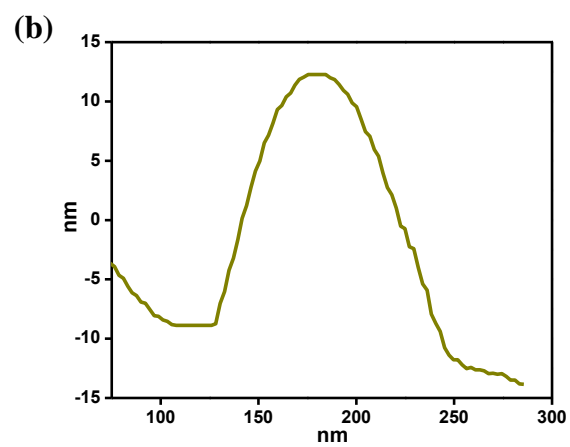
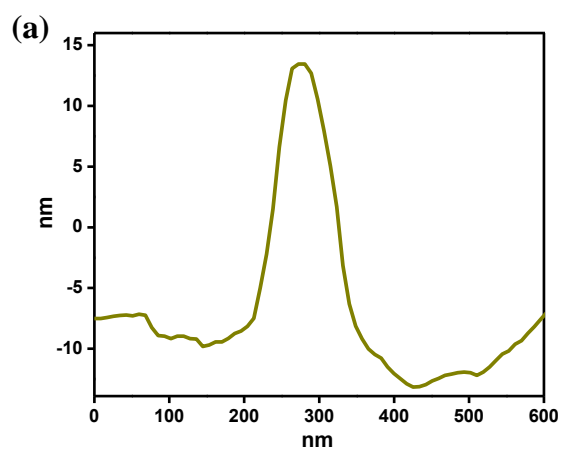


**Fig. S12** TEM images of **L** xerogel showing nanofibers and coiling of nanostructures with nanoring formation.





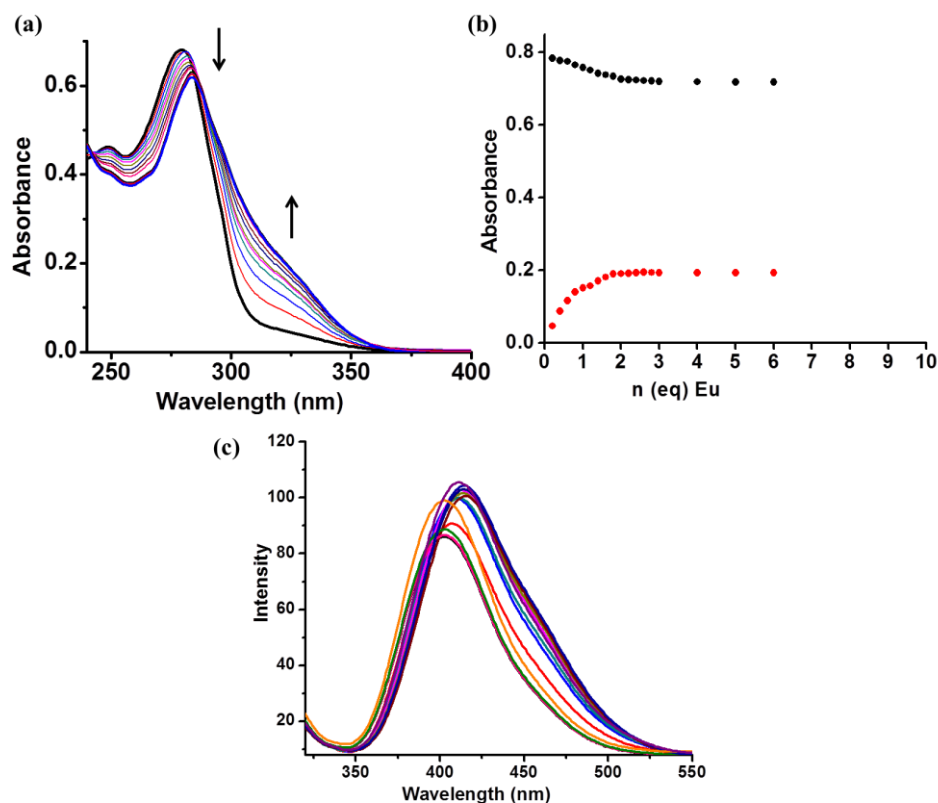
**Fig. S13** AFM image of L xerogel showing (a) nanofibers and nanorings.



**Fig. S14** AFM cross-sectional analysis of **L** xerogel showing the height of (a) nanofibers and (b) nanorings.

### **1.3 Titration of L with Eu(III) ion in methanol:**

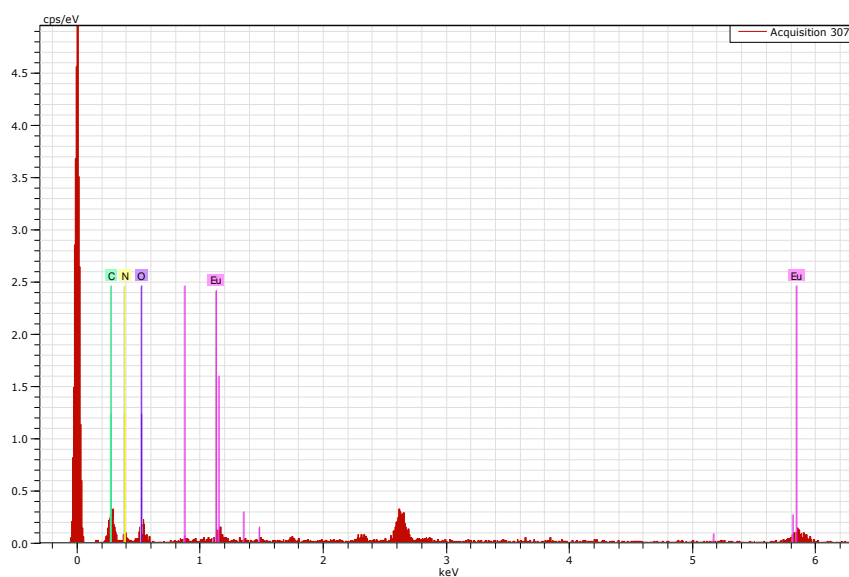
Fig. S15 shows changes in absorbance spectra of **L** ( $3 \times 10^{-5}$  M), on incremental addition of 10  $\mu$ L of Eu(III) solution ( $10^{-3}$  M) which is equivalent to 0.3 eq of Eu(III) ion the absorbance maxima at 280 nm is shifted bathochromically with a concomitant increase in the band centered at 320 nm suggesting clear binding of metal ion with ligand and is consistent with the literature reports.<sup>1c</sup> The results of the titration are plotted along with Jobs plot which indeed suggest a 1:2 (L/Eu) complex formation (Fig. S15). The emission spectrum of **L** is shown in Fig. S15. Excitation of **L** at 280 nm shows weak fluorescence centered at 410 nm assigned to TPY unit of **L** and no emission bands corresponding to Eu(III) were observed on incremental addition of Eu(III) solution. Slight changes in shift in emission at 410 nm may be attributed to the conformational changes in TPY on metal ion binding. It is worth mentioning that no TPE centered emission is observed may be due to the non-radiative decay of TPE emission at dilutions.



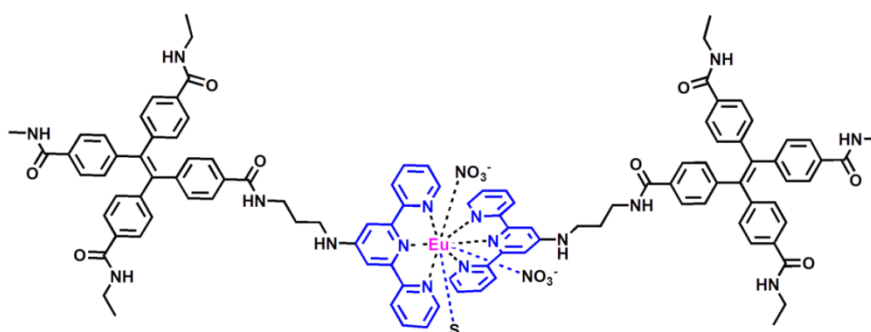
**Fig. S15** Changes in (a) absorption spectra of **L** ( $3 \times 10^{-5}$  M) in methanol upon titrating with equivalents of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  at 298 K and (b) binding isotherms for UV/Vis absorption spectra (black:280 nm and red:320 nm). (c) Changes in emission spectra on addition of incremental amounts of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ . Arrows indicate the changes in absorption spectrum on addition of amounts of Eu(III) ion to the **L** solution.

**1.4 Synthesis of L gel:**  $7 \times 10^{-3}$  M ligand solution in 1:2  $\text{CHCl}_3/\text{THF}$  mixture is heated at 90 °C for few minutes to dissolve which on cooling results in immediate opaque gel formation. Gel is observed to be stable upon inversion. Selected IR data of xerogel ( $\text{KBr}$ ,  $\text{cm}^{-1}$ ): 3399 (b), 3228 (w), 2946-2822 (m), 1632 (m), 1464 (s), 1301 (m), 1166 (m), 1023 (m), 806 (m). CHN analysis: Calculated values for  $(\text{C}_{102}\text{H}_{88}\text{N}_{20}\text{O}_4)(\text{C}_4\text{H}_8\text{O})_2$ : C;73.29, H; 5.82, N; 15.55. Found: C; 72.57, H; 5.87, N; 15.39. Predicted formula: **L**·2THF·0.5H<sub>2</sub>O.

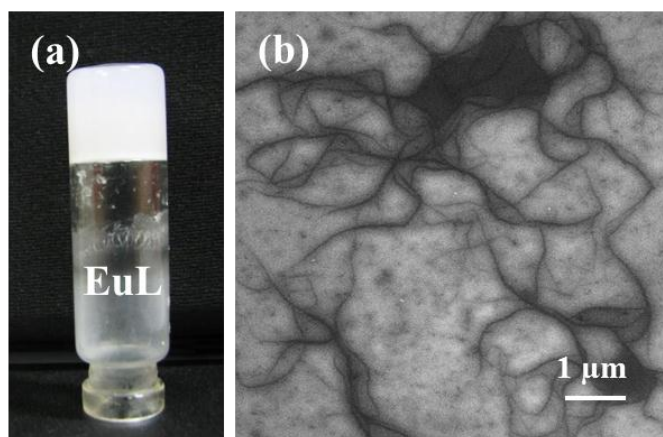
**1.5 Synthesis of CPG:** Solution of **L** ( $7 \times 10^{-3}$  M) in  $\text{CHCl}_3/\text{THF}$  (1:2) is mixed with solution of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  ( $1.4 \times 10^{-2}$  M) in THF and heated at  $90^\circ\text{C}$  for few minutes. Formation of viscous liquid is observed initially which on cooling to room temperature yields a stable opaque gel. Selected IR data for xerogel ( $\text{KBr}$ ,  $\text{cm}^{-1}$ ): 3379 (b), 3211 (w), 2963-2829 (m), 1629 (m), 1461 (s), 1382 (m), 1172 (w), 1108 (w), 1016 (w), 801 (m). CHN analysis : Found: C, 53.51; H, 4.35; N, 14.98. Predicted formula:  $[\text{Eu}_2\text{L} \cdot 6(\text{NO}_3) \cdot 2\text{THF}]$ .



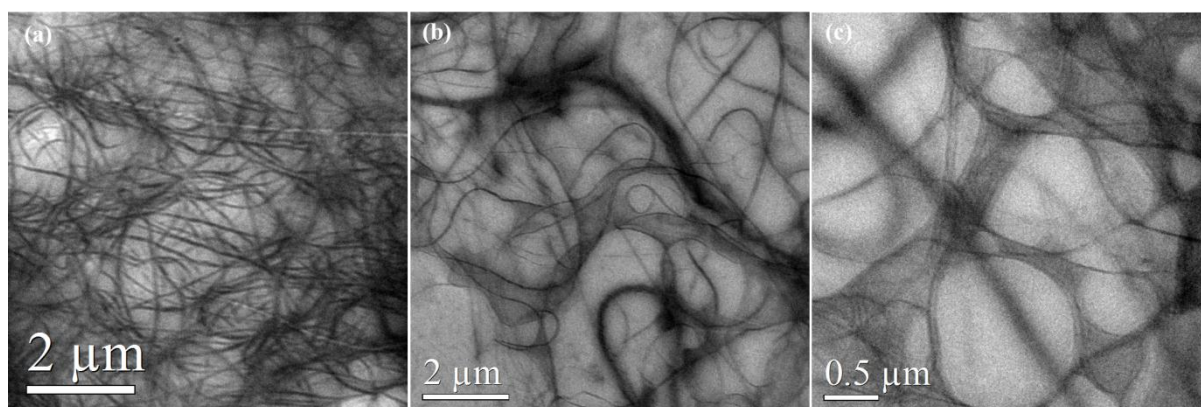
**Fig. S16** EDAX of CPG showing the presence of Eu(III) ion.



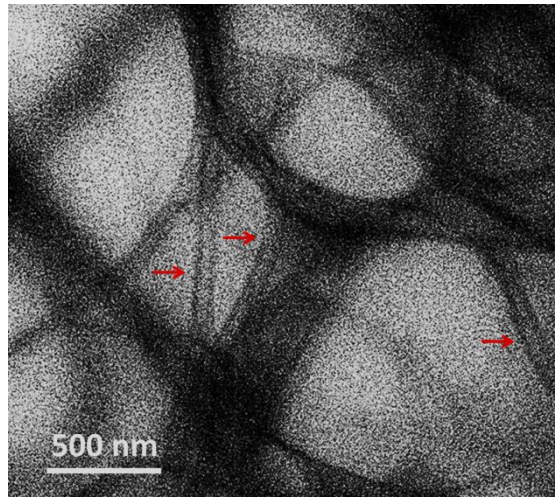
**Fig. S17** Probable Coordination environment around the Eu(III) center showing the orthogonal orientation of TPY units in CPG.



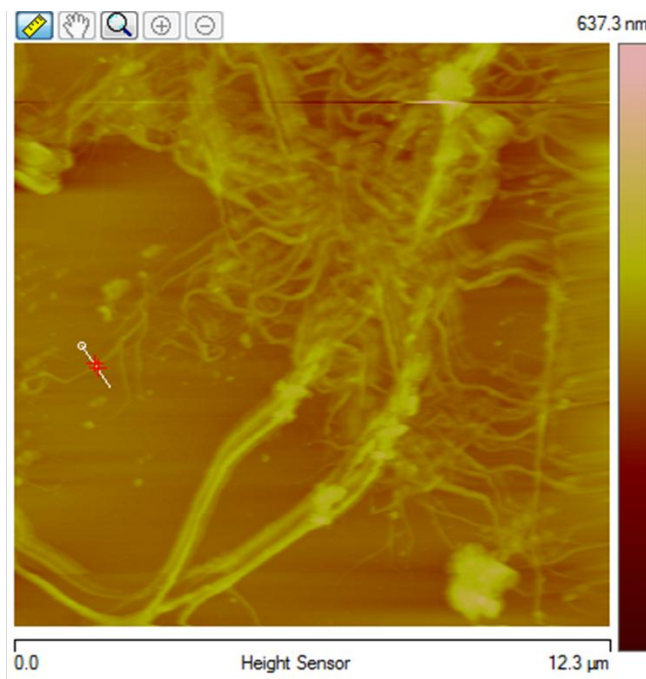
**Fig. S18** (a) Daylight image of CPG on inversion and (b) its FESEM image.



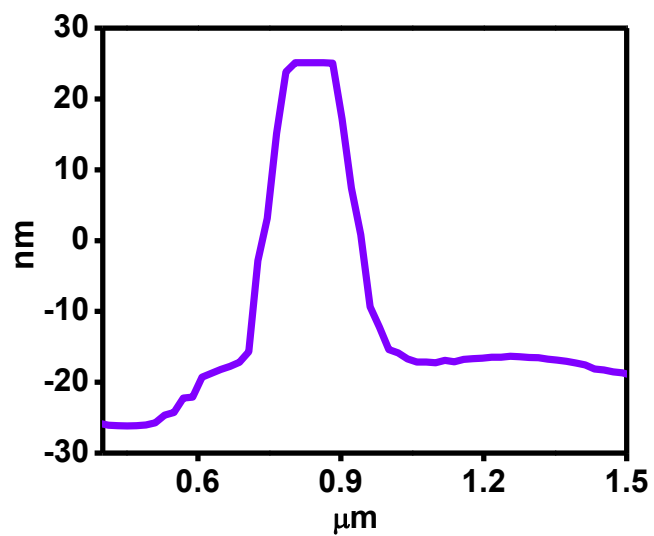
**Fig. S19** TEM images of CPG showing nanotubular structures.



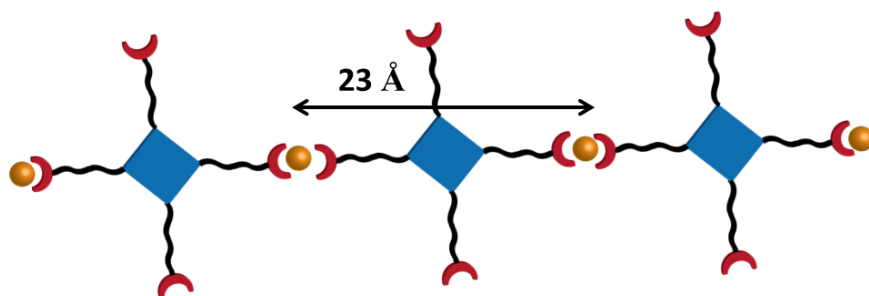
**Fig. S20** TEM image of CPG showing nanotubular structures.



**Fig. S21** AFM image of CPG nanotubes.



**Fig. S22** AFM cross-sectional analysis of CPG showing the height of nanotubes.

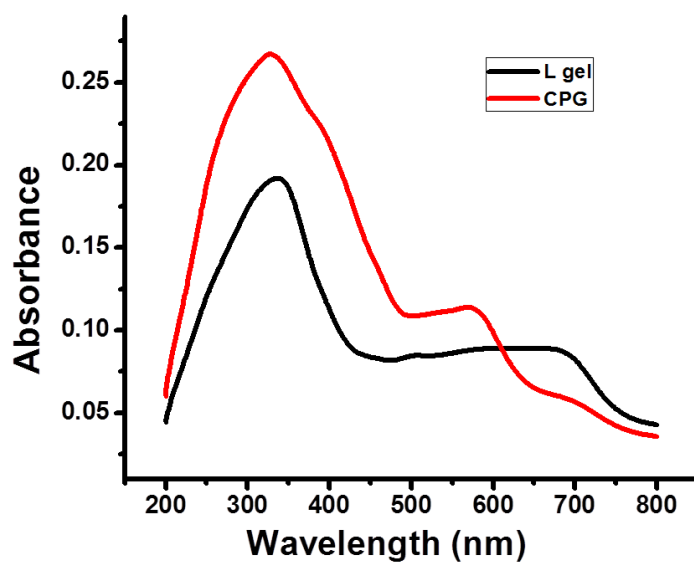


**Fig. S23** Proposed coordination of Eu(III) to the TPY units in CPG.

**Table 1.** Unit cell parameters of CPG<sup>a</sup>, Indexed using CRYSFIRE powder indexing system using Taup (TP) program<sup>2</sup>

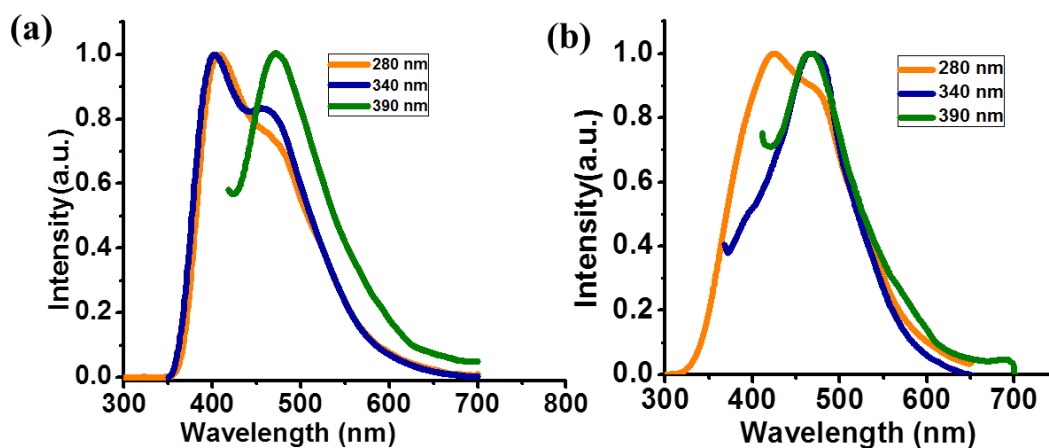
<i>h</i>	<i>k</i>	<i>l</i>	$2\theta$	<i>D</i> (exptl)	<i>D</i> (cald)	max. dev.
0	1	0	4.0277	21.92022	22.32656	.417E-04
0	2	1	8.8255	10.01158	10.09515	.907E-04
0	3	2	14.0302	6.30717	6.29857	.143E-03
0	2	4	16.9468	5.22768	5.22488	.172E-03
0	0	5	18.7555	4.72743	4.72996	.190E-03
1	0	0	21.7445	4.08388	4.08574	.218E-03
1	4	2	28.0661	28.0661	3.17574	.277E-03
1	3	8	39.4929	2.27995	2.27989	.374E-03

<sup>a</sup> $V = 2157.35$  (Å<sup>3</sup>). Phase = orthorhombic. Parameters :  $a = 4.08574$  Å,  $b = 22.3266$  Å,  $c = 23.6498$  Å ;  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ , and  $\gamma = 90^\circ$ .

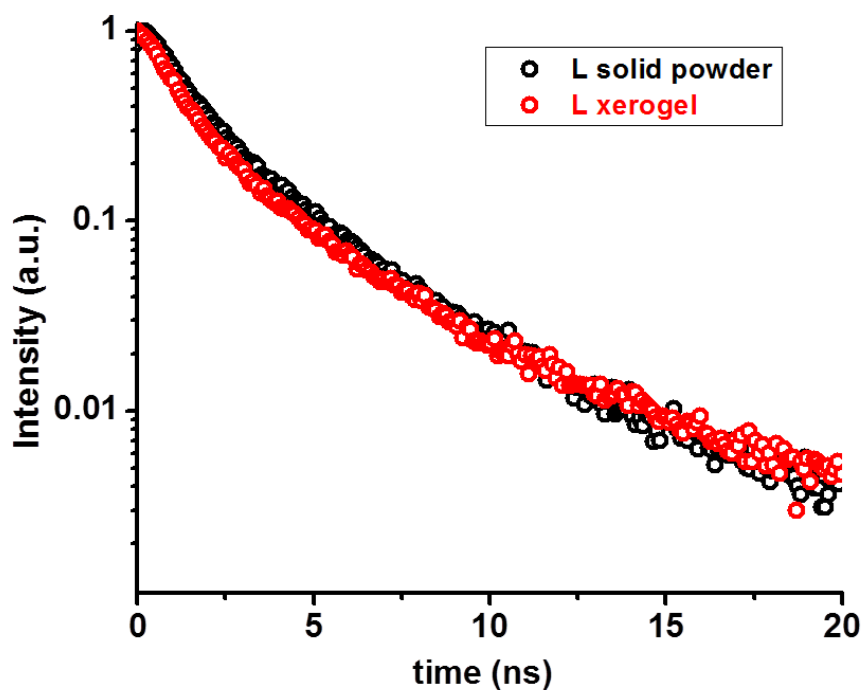


**Fig. S24** Absorption spectra of L xerogel (black) and CPG xerogel (red).





**Fig. S25** Emission spectra at different excitation wavelengths (280, 340 and 390 nm) for (a) L solid powder and (b) L xerogel.



**Fig. S26** Time resolved fluorescence life-time of L solid powder (black) and L xerogel (red).

## References

1. (a) N. B. Shustova, B. D. McCarthy and M. Dinca, *J. Am. Chem. Soc.*, 2011, **133**, 20126; (b) O. Kotova, R. Daly, C. M. G. dos Santos, M. Boese, P. E. Kruger, J. J. Boland and T. Gunnlaugsson, *Angew. Chem. Int. Ed.*, 2012, **51**, 7208; (c) R. D. Rodrigues, I. M. A. Barros and E. L. S. Lima, *Tetrahedron Lett.*, 2005, **46**, 5945.
2. D. Taupin, *J. Appl. Cryst.*, 1973, **6**, 380.