Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Tunable emission in lanthanide coordination polymer gels based on a rationally designed blue emissive gelator

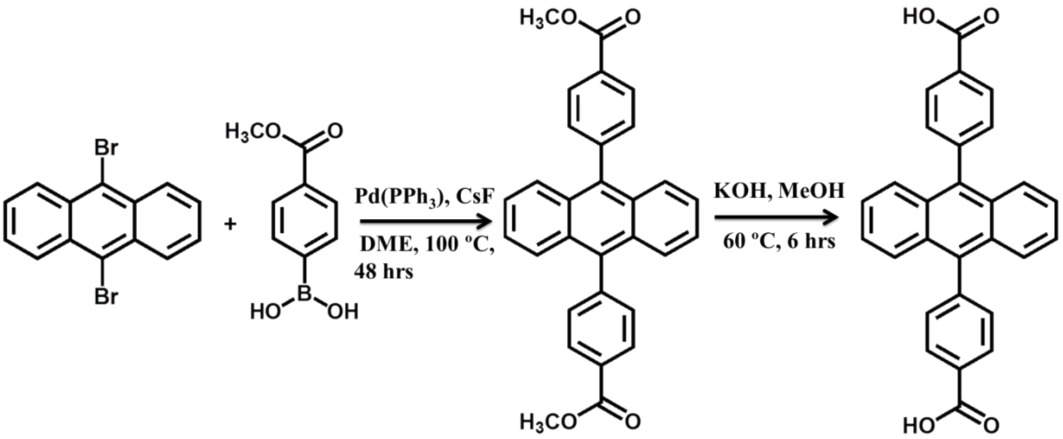
Papri Sutar, Venkata M. Suresh and Tapas Kumar Maji*

Molecular Materials Laboratory, Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560 064, India

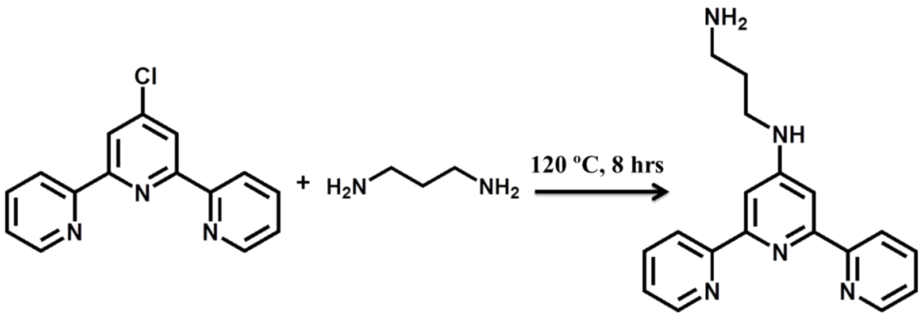
1. Experimental Section.

1.1 Materials and Methods: 9, 10-dibromoanthracene, 4-carboxyphenyl boronic acid, 1,3-diaminopropane, 4′-chloro-2,2′:6′,2″-terpyridine, trichloroisocyanuric acid (TCIC) and triphenylphosphine (PPh_3) were purchased from Sigma-Aldrich chemical Co. Ltd. Solvents were pre-dried using standard procedures before using. For UV-Vis experiments, spectroscopic grade solvents were purchased from Spectrochem. ^1H NMR 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 studies were accomplished using Perkin Elmer Ls 55 Lumeniscence spectrometer. Infrared spectral studies were carried out by making samples with KBr pellets using Bruker FT-IR spectrometer. Powder X-ray diffraction studies were recorded on a Bruker D8 discover instrument using Cu-Kα radiation. Elemental analyses were carried out using a Thermo Scientific Flash 2000 CHN analyzer. Morphology studies were carried out using Lica-S440I field emission scanning electron microscopy (FESEM) by placing samples on silicon wafer under vacuum with accelerating voltage of 10 kV. Transmission electron microscopy (TEM) was performed using JOEL JEM-3010 with accelerating voltage of 300 kV. For this analysis the xerogel was dispersed in ethanol and then drop casted on a carbon coated copper grid.

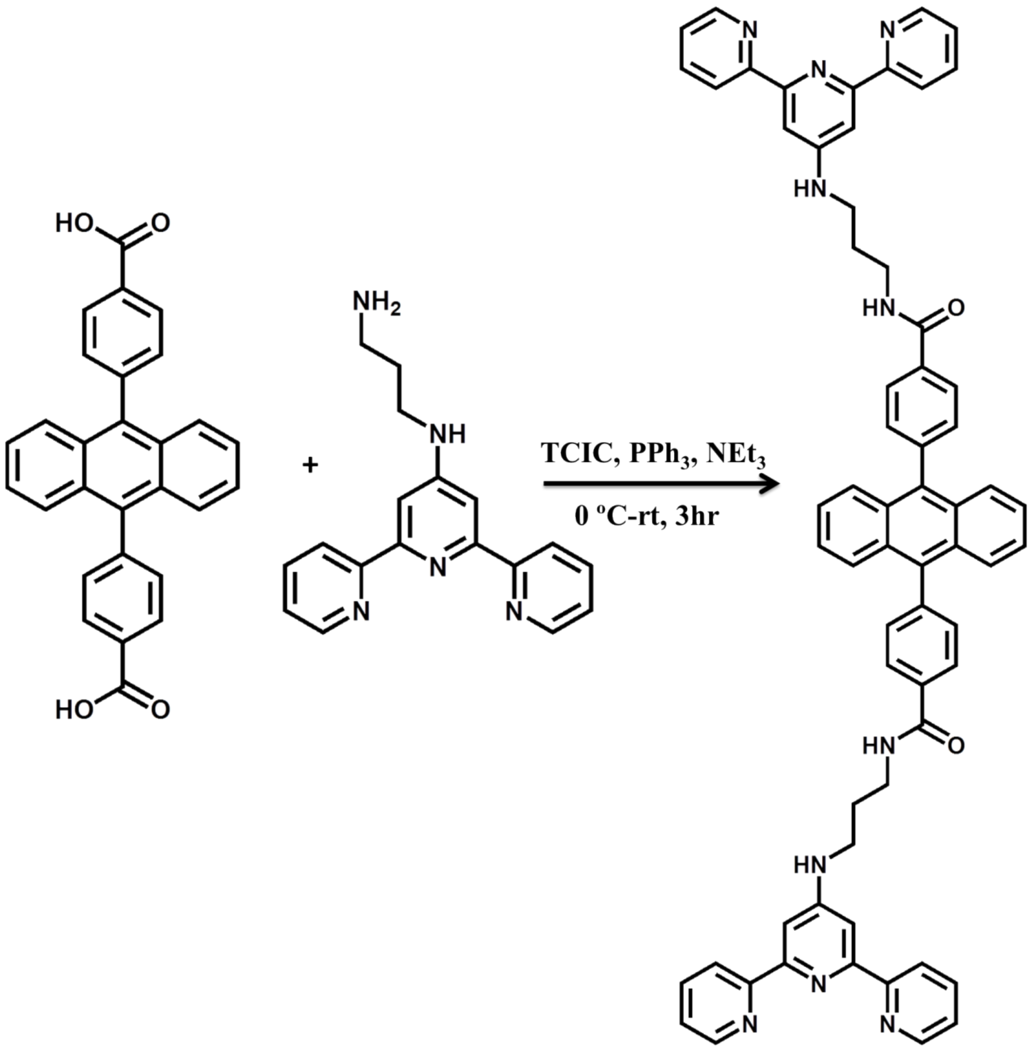
1.2 Synthesis of 9,10-(4-carboxyphenyl)anthracene : 9,10-(4-carboxyphenyl)anthracene was synthesized by slightly modifying the reported procedure.[1] 9,10-dibromoanthracene (740 mg, 2.2 mmol), methyl-4-carboxyphenyl boronic acid (1 g, 5.5 mmol) , CsF (4 g, 2.7 mmol) and $Pd(PPh_3)_4$ (200 mg, 0.17 mmol)) were suspended in 1,2-dimethoxyethane (30 ml). The reaction mixture was refluxed at 100 ºC for 48 hours maintaining the inert condition. After that, the reaction mixture was cooled to room temperature and 100 ml H_2O was added to dissolve the excess CsF, and the organic product was extracted by $CHCl_3$. Pure 9,10-(methyl-4-carboxyphenyl)anthracene was obtained after running the crude product through column using $CHCl_3$/hexane as eluent. Yield: 93 %. The as-prepared 9,10-(methyl-4-carboxyphenyl) anthracene (563 mg, 1.26 mmol) was suspended in MeOH (30 ml). KOH (425 mg, 7.56 mmol)) was added and refluxed for 6 hours at 60 ºC. After cooling to room temperature 6 N HCl was added drop-wise into the reaction mixture. The white precipitate formed was filtered and wash repeatedly by cold water and dried under vacuum. Yield: 96 %. ^{1}H-NMR (400 MHz, $CDCl_3$) δ**:** 8.23 (d, 4H, ArH), 7.62 (m, 4H, ArH), 7.55 (m, 4H, ArH), 7.46 (m, 4H, ArH), 13.11 (br, 2H, COOH). Selected FTIR data (KBr, cm^{-1}): 2986 (b), 2667 (m), 2547 (m), 1688 (s, sh), 1608 (s), 1425 (m), 1291 (m), 769 (m). CHN analysis for $C_{28}H_{18}O_4$: Calc. C, 80.38; H, 4.30%. Expt.: C, 80.85; H, 4.12%.



1.3 Synthesis of 2,2′;6′,2″-terpyridin-4′-yl-propane-1,3-diamine: 2,2′;6′,2″-terpyridin-4′-yl-propane-1,3-diamine was prepared by using reported literature procedure.[2] 4′-chloro-2,2′:6′,2″-terpyridine, (300 mg, 1.12 mmol) was suspended in 1,3-diamino propane (2.16 ml). The reaction mixture was then refluxed at 120 ºC for overnight. After cooling to room temperature, H_2O (25 mL) was added. The white precipitate formed was filtered and further washed with H_2O. The solid was dissolved in dichloromethane and extracted twice with H_2O. The organic layers were combined and dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure to yield a white solid product. Yield: 82%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.53 (d, 2H, ArH), 8.52 (d, 2H, ArH), 7.76 (t, 2H, ArH), 7.60 (s, 2H, ArH), 7.25 (t, 2H, ArH), 5.16 (t, 1H, NH), 3.41 (m, 2H, $NHCH_2$), 2.84 (m, 2H, CH_2), 1.77 (m, 2H, NH_2CH_2). Selected FTIR data (KBr, cm^{-1}): 3340 (b), 2965 (m), 1610-1560 (s), 1464 (m), 1402 (m), 1261 (m), 1094-981 (s), 791 (s). CHN analysis for $C_{18}H_{19}N_5$ Calc.: C, 70.81; H, 6.22; N, 22.95%. Expt.: C, 70.90; H, 6.11; N, 22.83%.



1.4 Synthesis of 9,10-(4-carboxyphenyl)anthracene-di-{[3-([2,2′;6′,2″]-terpyridin-4′-ylamino)-propyl]-amide} (L) : 9,10-(4-carboxyphenyl)anthracene (200 mg, 0.478 mmol) was dissolved in anhydrous THF (20 mL). TCIC (244 mg, 1.05 mmol) and PPh_3 (275 mg, 1.05 mmol) were added into the reaction mixture and stirred at 0 ºC for 40 min under inert condition. 2,2′;6′,2″-terpyridin-4′-yl-propane-1,3-diamine (320 mg, 1.05 mmol) was dissolved in anhydrous THF and Et_3N (293 µl, 2.1 mmol) was added into it. This reaction mixture was drop-wise added into 9,10-(4-carboxyphenyl)anthracene/ TCIC/ PPh_3 solution at 0 ºC and stirred for 45 minutes. After that the reaction mixture was stirred at room temperature for 3 hrs. Precipitates were collected by filtration and washed several times with $CHCl_3$ and dried under reduced pressure. Yield: 88%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.87 (s, 3H, ArH), 8.74 (d, 1H, ArH), 8.30 (m, 1H, ArH), 8.26 (m, 3H, ArH), 8.15 (m, 5H, ArH), 7.79 (s, 3H, ArH), 7.69 (m, 2H, ArH), 2.98 (m, 4H, $NHCH_2$), 1.99 (m, 2H, CH_2). Selected FTIR data (KBr, cm^{-1}): 3436 (m), 3239 (m), 2980- 2888 (m), 2740 (m), 2674 (s), 2493 (m), 1645 (s), 1583 (m), 1472 (m), 1396 (s), 1166 (s), 1135(s), 790 (s).CHN analysis for $C_{64}H_{52}N_{10}O_2$ Calc.: C, 77.41; H, 5.24; N, 14.11%. Expt.: C, 77.53; H, 5.33; N, 14.20%. HRMS (+ESI): *m/z* calculated for $C_{64}H_{52}N_{10}O_2$: 992.4275, found: 993.3209 $[M+H]^+$.



HO
O
NH2
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TCIC, PPh3, NEt3
0 ºC-rt, 3hr
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HN
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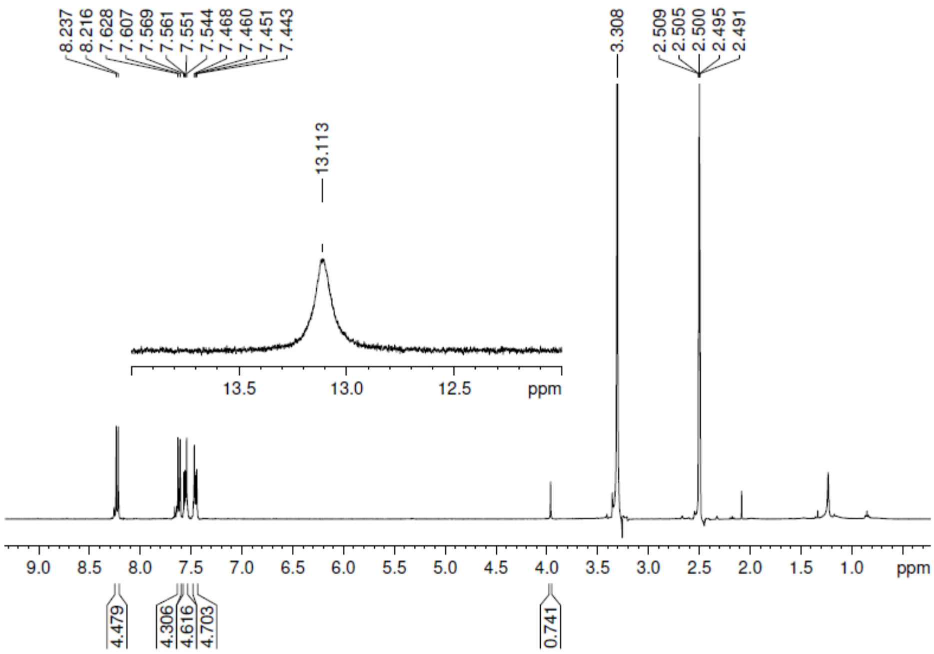

Fig. S1 [1]H-NMR spectra of 9,10-(4-carboxyphenyl)anthracene in $CDCl_3$ solvent.

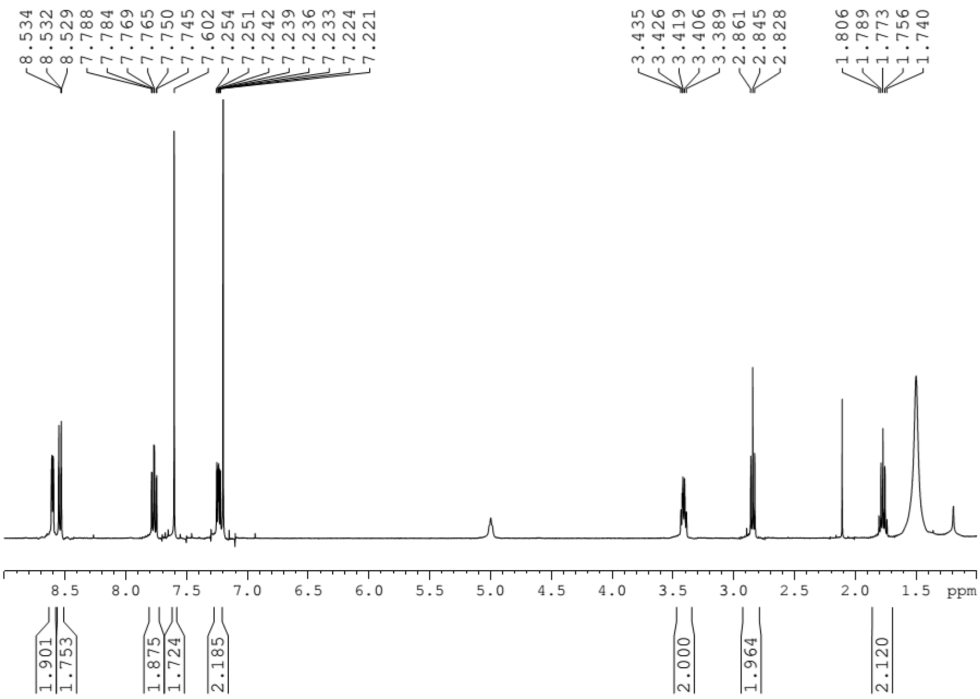

Fig. S2 [1]H-NMR spectra of 2,2′;6′,2″-terpyridin-4′-yl-propane-1,3-diamine in $CDCl_3$ solvent.

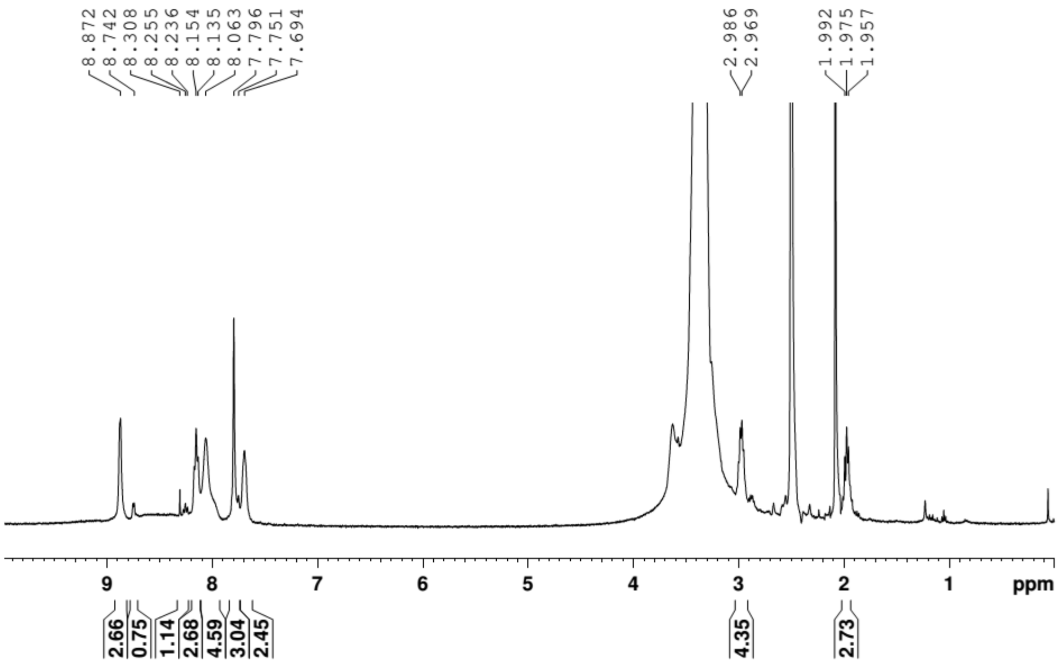

Fig. S3 ^{1}H-NMR spectra of **L** in DMSO-d^6 solvent.

1.5 Synthesis of ligand gel: 1×10^{-3} M ligand solution in 1:1 $CHCl_3$/THF mixture is heated at 90 ºC for few minutes to form a viscous liquid which on cooling results in opaque gel. The formation of gel is confirmed by inversion-test method. Selected IR data (KBr, cm^{-1}): 3424 (m), 3233 (s), 2968- 2831 (s), 2722 (s), 1638 (s), 1583 (s), 1461 (s), 1376 (s), 1166 (m), 973 (m), 841 (s), 792 (s).

1.6 Synthesis of coordination polymer gels (TbL and EuL): Solution of **L** (1×10^{-3} M) in $CHCl_3$/ THF (1:1) is mixed with solution of $Tb(NO_3)_3.6H_2O$ or $Eu(NO_3)_3.6H_2O$ (1×10^{-3} M, in THF) in 1:1 volumetric ratio. The mixture is heated at 90 ºC for 3 minutes to prepare a viscous solution which eventually results stable opaque gel upon cooling. Selected IR data (KBr, cm^{-1}): For **TbL** xerogel : 3400 (b), 2964- 2916 (m), 1624 (s), 1479 (s), 1383 (s), 1263 (s), 1103- 1019 (s), 804 (s). For **EuL** xerogel: 3400 (b), 2976- 2836 (m), 1630 (m), 1464 (m), 1166 (m), 972 (m), 839 (m). CHN analysis : Calculated values for **TbL**: C, 58.33; H, 4.59; N, 12.28%. Found: C, 58.42; H, 4.67; N, 12.32%. Predicted formula: [Tb(L)(NO_3)$_3$.2THF]. Calculated values for **EuL**: C, 58.57; H, 4.61; N, 12.33%. Found: C, 58.62; H, 4.70; N, 12.29%. Predicted formula: [Eu(L)(NO_3)$_3$.2THF].

1.7 Synthesis of TbEu1 and TbEu2: First (1×10^{-3} M) and (1.2×10^{-3} M) solutions of $Tb(NO_3)_3.6H_2O$ and $Eu(NO_3)_3.6H_2O$ are prepared by dissolving the metal salts in THF. After that 250 µl solution of $Tb(NO_3)_3.6H_2O$ and 250 µl solution of $Eu(NO_3)_3.6H_2O$ are added into 500 µl solution of L (1×10^{-3} M). The mixture is heated at 90 ºC for few minutes to form viscous solution which is eventually converted to stable gel (**TbEu1**) after cooling. **TbEu2** is prepared in a similar way. First (1×10^{-3} M) and (2×10^{-3} M) solution of $Tb(NO_3)_3.6H_2O$ and $Eu(NO_3)_3.6H_2O$ are prepared in THF. After that 250 µl solution of $Tb(NO_3)_3.6H_2O$ and 250 µl solution of $Eu(NO_3)_3.6H_2O$ are added into 500 µl solution of L (1×10^{-3} M) and the mixture is heated at 90 ºC for few minutes. The viscous solution formed is cooled and forms **TbEu2** coordination polymer gel. Selected FTIR data of **TbEu2** (KBr, cm^{-1}): 3421 (b), 2948- 2829 (m), 1628 (s), 1460 (m), 1161 (m), 974-838 (m), 735 (m).

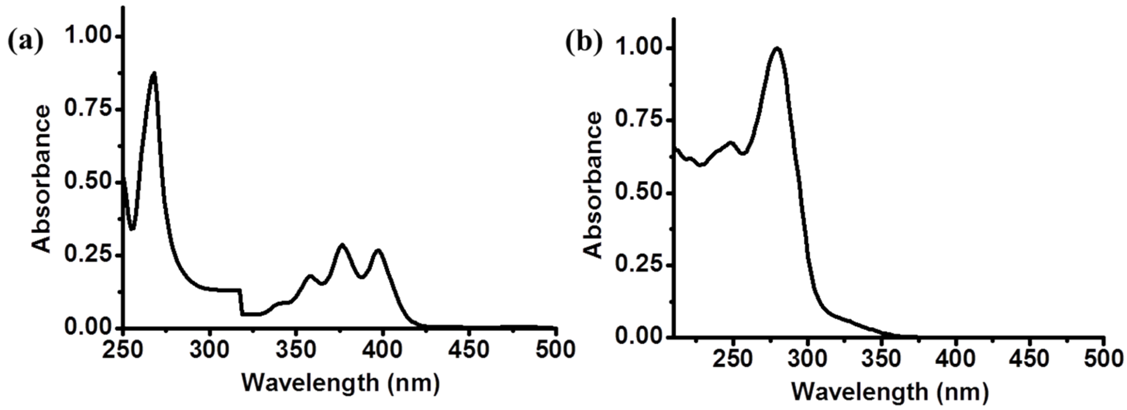

Fig. S4 (a) Absorption spectra of 9,10-(4-carboxyphenyl)anthracene in DMSO and (b) absorption spectra of 2,2′;6′,2″-terpyridin-4′-yl-propane-1,3-diamine in MeOH.

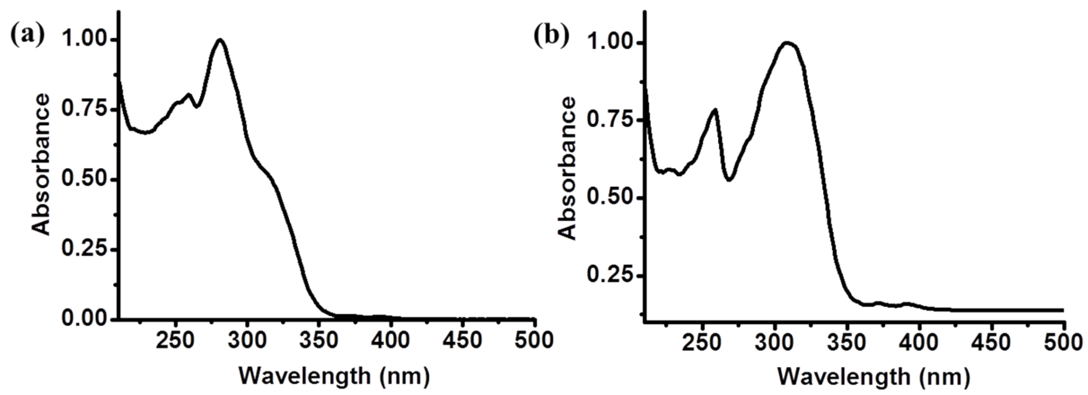

Fig. S5 (a) Absorption spectra of **L** in MeOH and (b) Absorption spectra of **L** after subtracting the absorption spectra of 2,2′;6′,2″-terpyridin-4′-yl-propane-1,3-diamine which shows peak at 310 nm indicating π-π* transition of **ant** core.

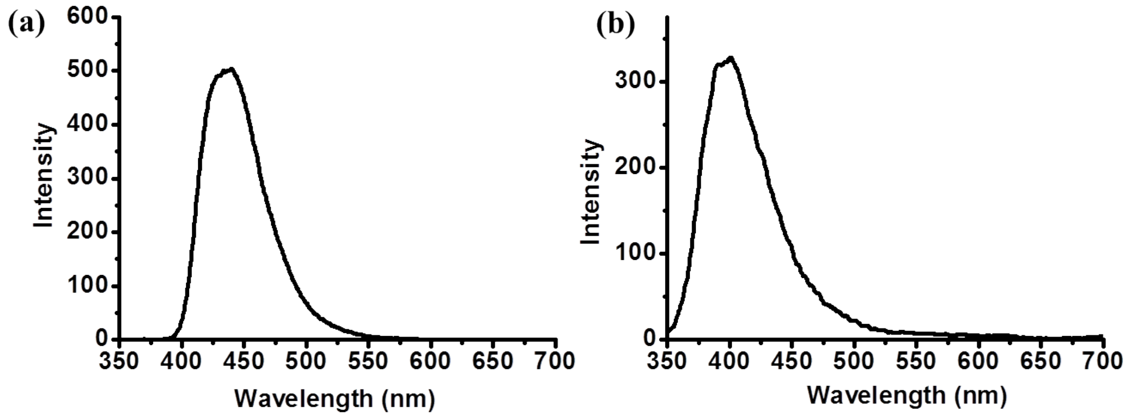

Fig. S6 (a) Emission spectra of 9,10-(4-carboxyphenyl)anthracene in DMSO (10^{-4} M) and (b) 2,2′;6′,2″-terpyridin-4′-yl-propane-1,3-diamine in MeOH (10^{-4} M).

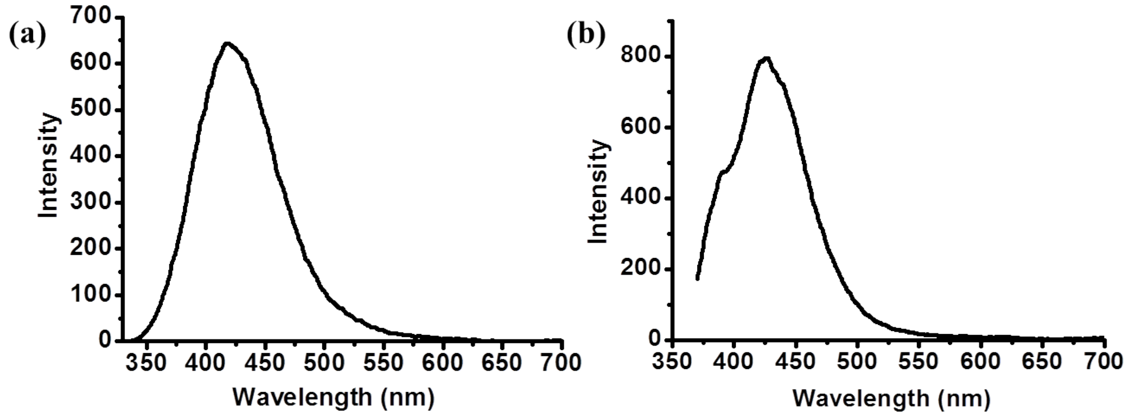

Fig. S7 (a) Emission spectra of **L** in MeOH (10^{-4} M) and (b) Combined emission spectra of 9,10-(4-carboxyphenyl)anthracene and 2,2′;6′,2″-terpyridin-4′-yl-propane-1,3-diamine . This indicates emission is originating from both **ant** and **tpy**.

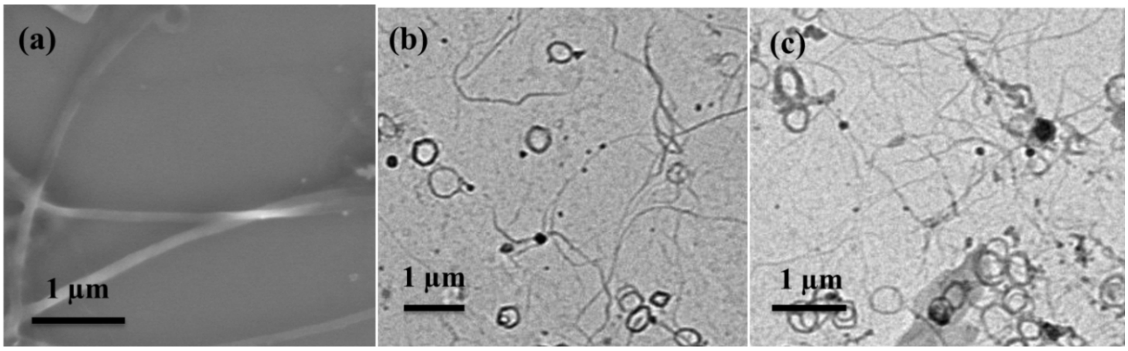

Fig. S8 (a) FESEM image of **L** xerogel, (b) and (c) TEM images of **L** xerogel showing the presence of nanofibers and nanorings.

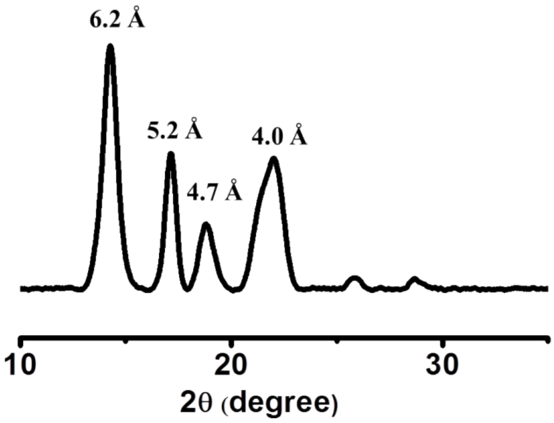

Fig. S9 Powder X-ray diffraction pattern of **L** xerogel with corresponding *d*- spacing values.

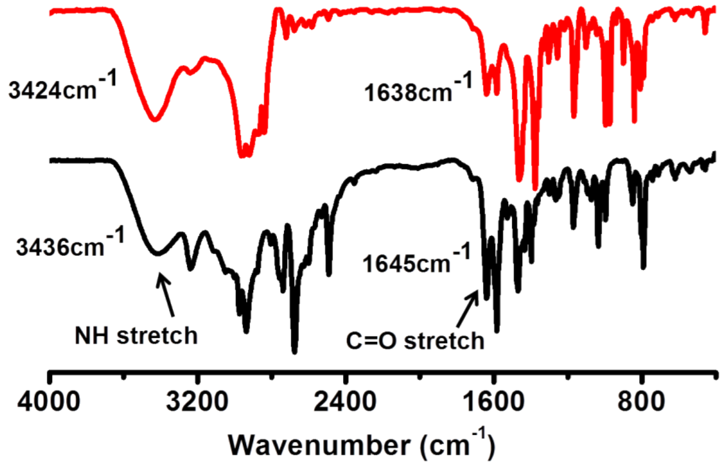

Fig. S10 Comparison of FTIR of **L** (black) and **L** xerogel (red).

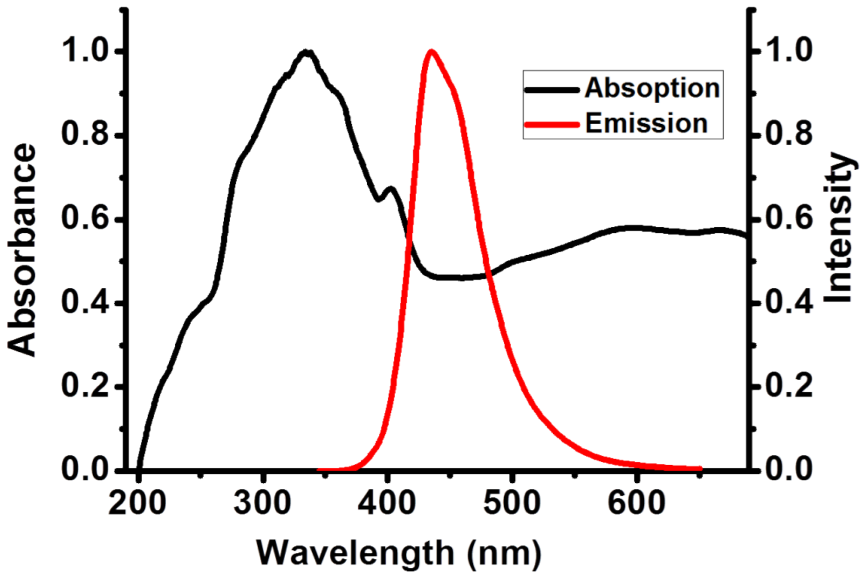

Fig. S11 Solid state absorption (black) and emission (red) spectra of **L** xerogel.

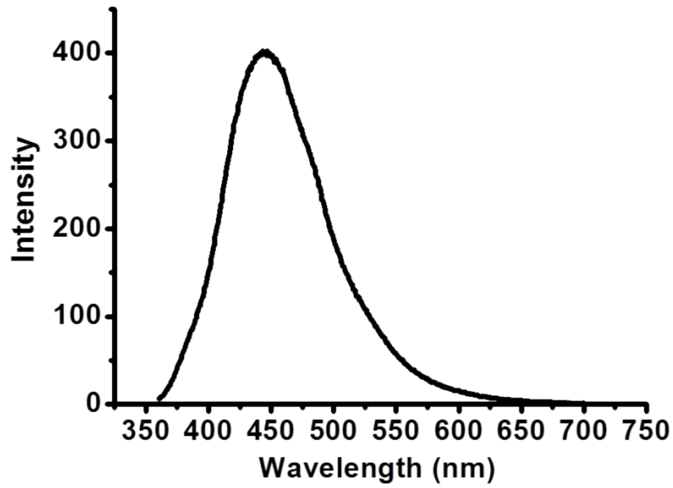

Fig. S12 Emission spectra of **L** gel coated quartz substrate.

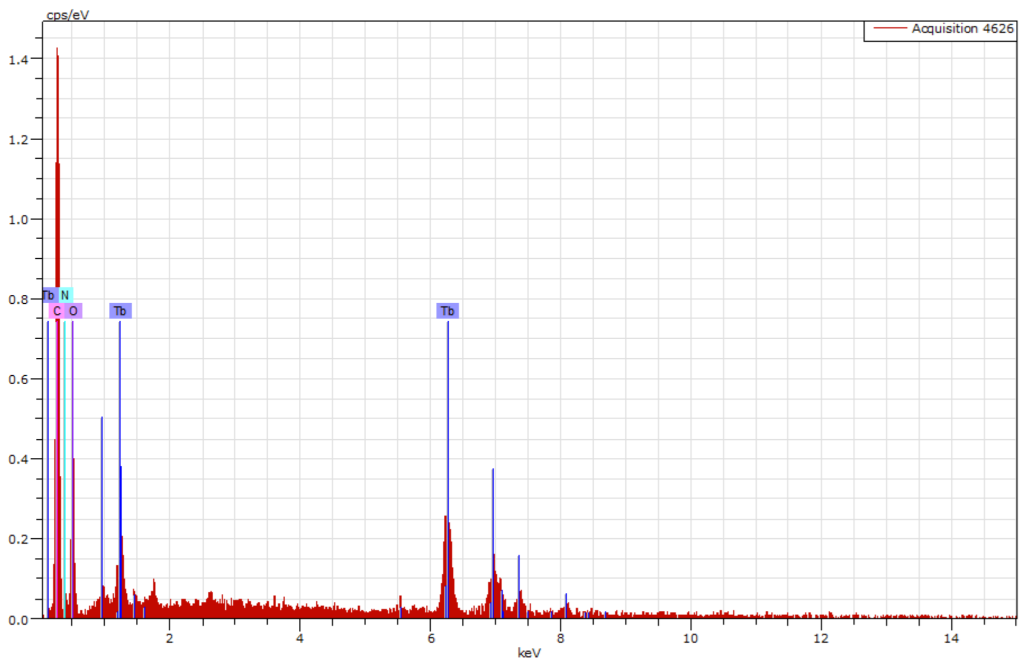

Fig. S13 EDXS of **TbL** showing the presence of Tb^{III} in xerogel.

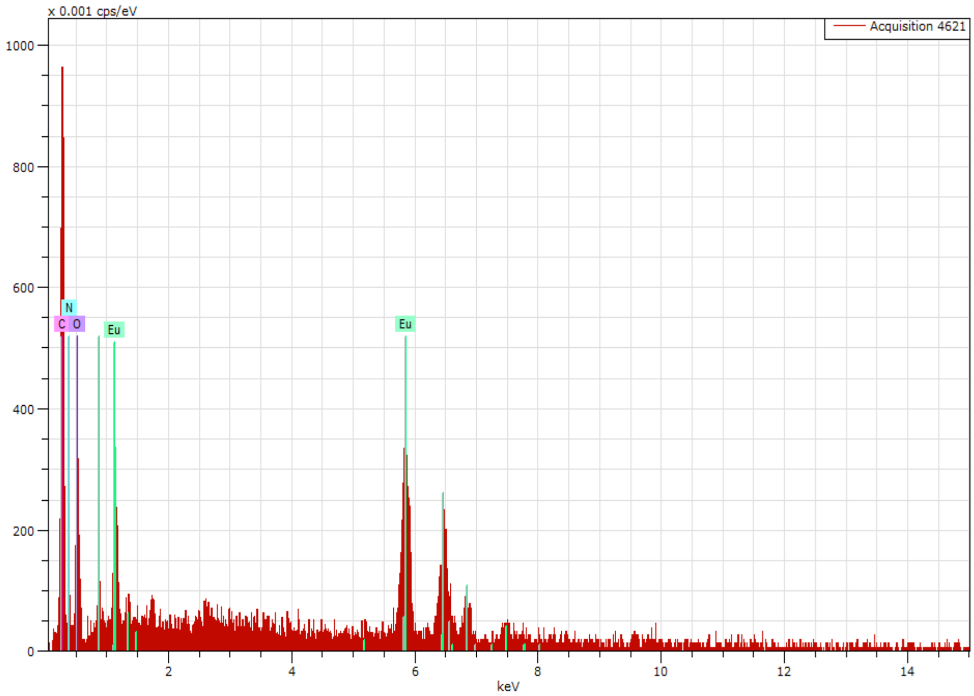

Fig. S14 EDXS of **EuL** showing the presence of Eu^{III} in xerogel.

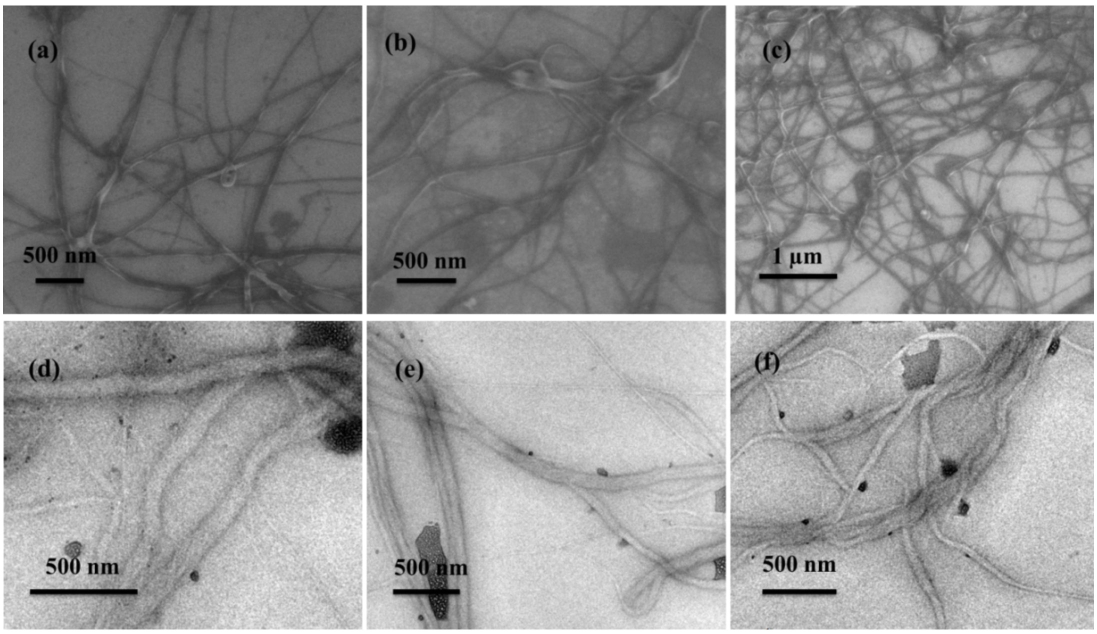

Fig. S15 (a), (b), (c) FESEM images of **TbL** xerogel and (d), (e), (f) TEM images of **TbL** xerogel showing the presence of coiled-nanofiber morphology.

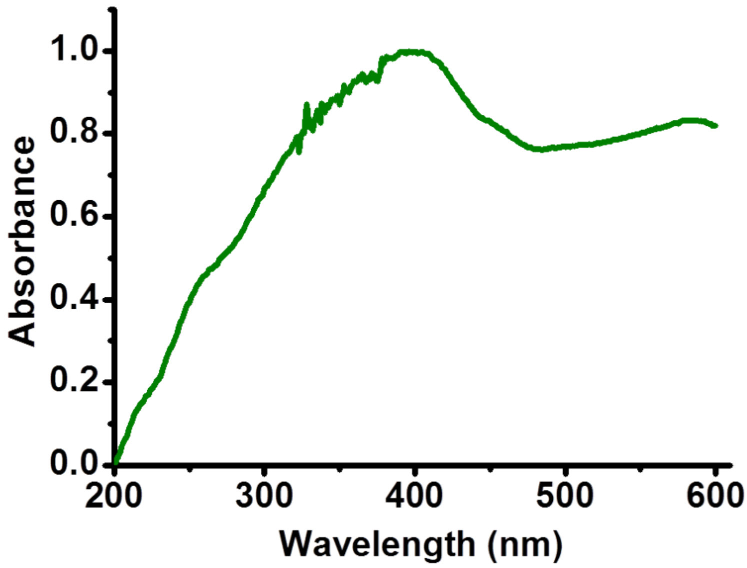

Fig. S16 Solid state absorption spectra of **TbL** xerogel.

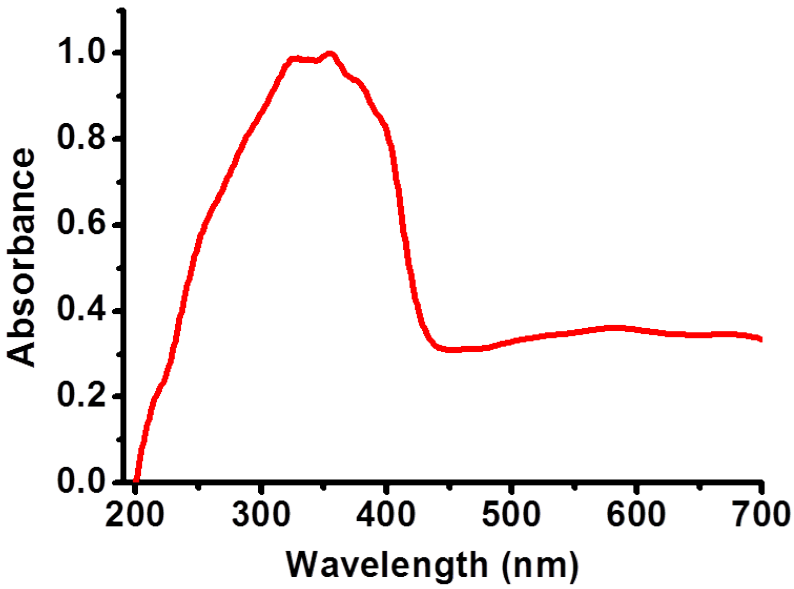

Fig. S17 Solid state absorption spectra of **EuL** xerogel.

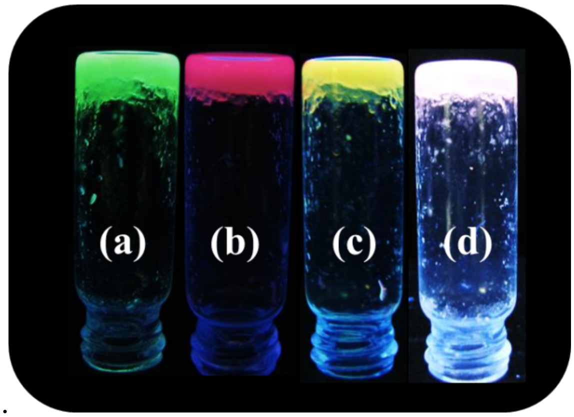

Fig. S18 Photograph of (a) **TbL**, (b) **EuL**, (c) **TbEu1** and (d) **TbEu2** gels under UV light showing green, pink, yellow and white emission respectively.

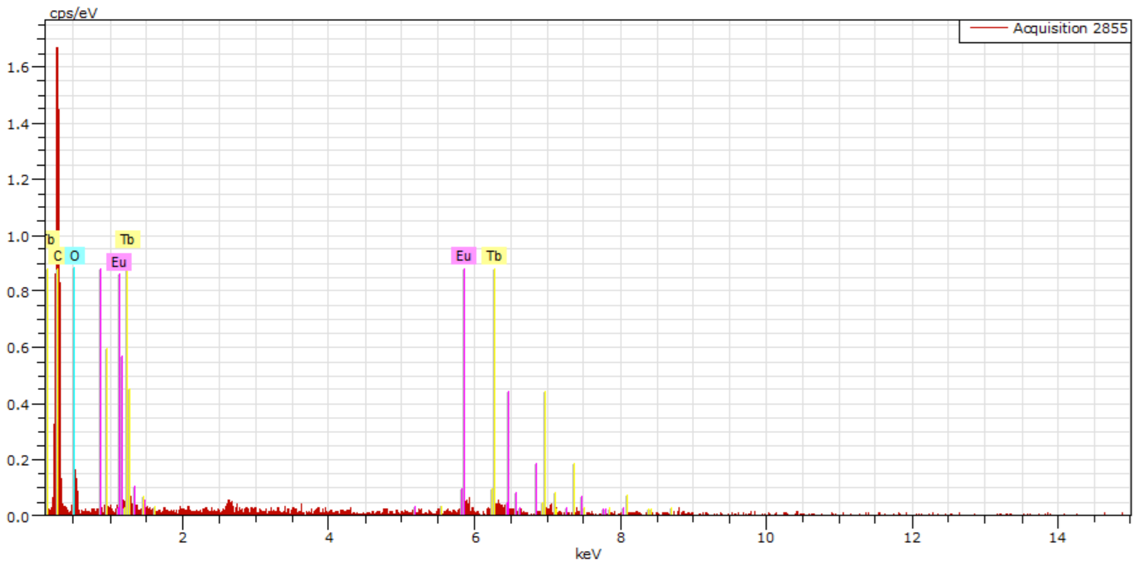

Fig. S19 EDXS of **TbEu2** showing the presence of both Tb^{III} and Eu^{III} in xerogel.

References:

1. (a) S. Ma, D. Sun, P. M. Forster, D. Yuan, W. Zhuang, Y.-S. Chen, J. B. Parise and H.-C. Zhou, *Inorg. Chem.*, 2009, **48**, 4616-4618; (b) D. Shi, Y. Ren, H. Jiang, J. Lu and X. Cheng, *Dalton Trans.*, 2013, **42**, 484-491.
2. 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**, 7208-7212.