Electronic Supplementary Material (ESI) for Dalton Transactions

Tb^{3+} sensitization in a *deoxy*cholate organogel matrix: Selective luminescence quenching by an aromatic nitro derivative

Ramesh Kandanelli, Anindya Sarkar and Uday Maitra*

Gelation studies

Gels were prepared by mixing the methanolic solutions (200 µL each) of $Tb(OAc)_3$ and sodium deoxycholate of 5 mM and 15 mM respectively in test tubes of size 10 mm x 75 mm. Immediately after mixing of the solutions the resultant system was a clear solution. But it slowly grew in turbidity forming a translucent gel. It was not homogeneous but sonication of the gel for 8-10 sec converted the gel into sol which led to the gel formation after 5 min.

Following photographs show the process of gelation once stoichiometric amounts (1:3) of methanolic solutions (1 mL each) of $Tb(OAc)_3$ and sodium deoxycholate are mixed in 5 mL culture tube. Final concentrations in the gel: Tb^{3+}-DCh (5/15 mM).

10 sec | 1 min | 2 min | 3 min | 5 min | After Sonication for 8-10 sec | After 5 min

Spectroscopy details

Absorbance was recorded on Perkin Elmer Lamda 35 spectrophotometer. Time delayed fluorescence spectra were recorded on Varian Cary Eclipse spectrophotometer for gel samples and Perkin Elmer LS-50B spectrophotometer was used for solid state samples (xerogels). Phosphorescence mode (delay time 0.2 ms, gate time 3.0 ms, total decay time 20 ms) was used for recording all time delayed emission spectra and all the measurements for the wet gels were done in a 2 mm square cuvette. Absorption spectra were recorded in 1 cm path length quartz cuvettes. For the solid state phosphorescence measurements a round shaped front face accessory (1.6 cm diameter) was used. All the measurements were done at 25 ºC.

Luminescence Studies

Required amount of sensitizer was dissolved in sodium deoxycholate methanolic solutions followed by gel preparation. Gels prepared in test tubes were transferred using accu pipette (200 µL) into cuvettes for performing luminescence experiments.

Tb^{3+} luminescence quenching studies with doping of anthracene and 9-fluorenone in Tb^{3+}-DCh (5/15 mM) gel matrix in presence of 100 µM DHN reveal only about 18% luminescence quenching.

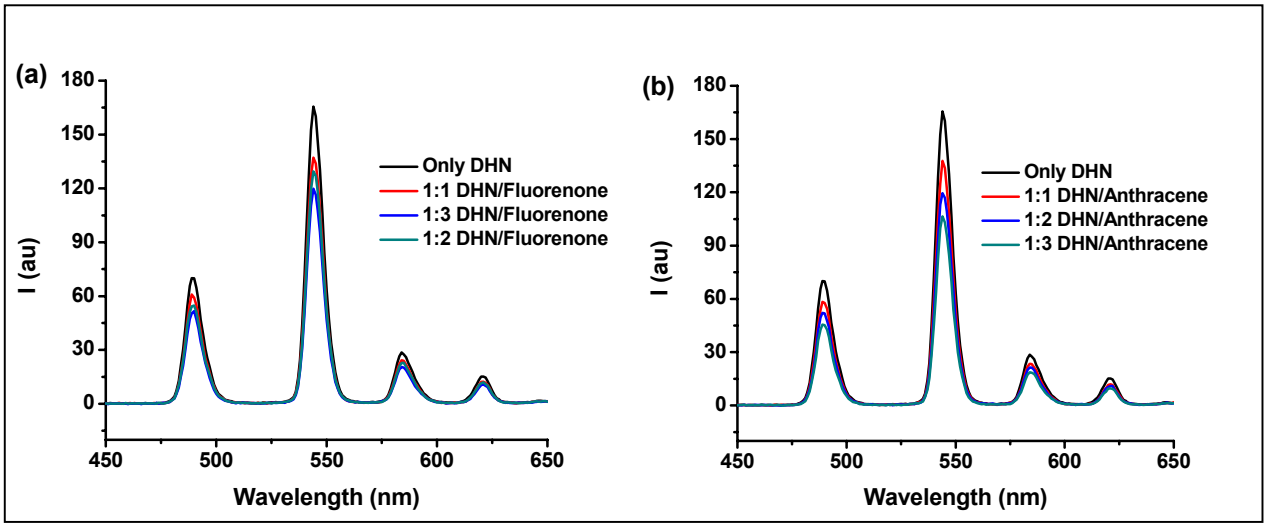


Fig S1 Tb^{3+} luminescence in Tb^{3+}-DCh gels (5/15 mM) in presence of (a) 9-Fluorenone (b) anthracene

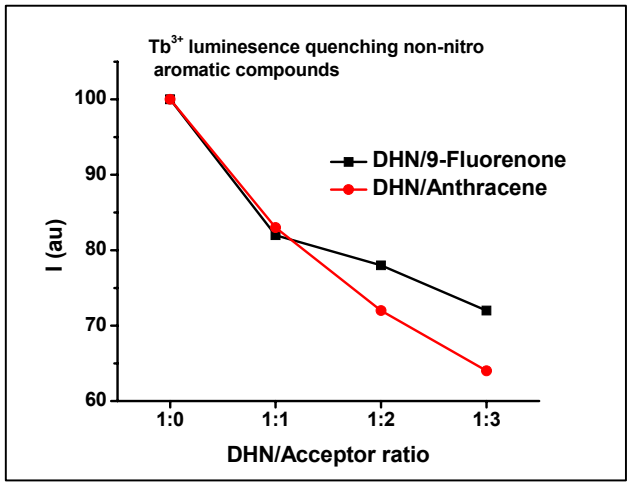


Fig S2a Comparison of Tb^{3+} luminescence intensity (%) quenching by anthracene and 9-fluorenone in Tb^{3+}-DCh (5/15 mM) gels with 100 µM DHN

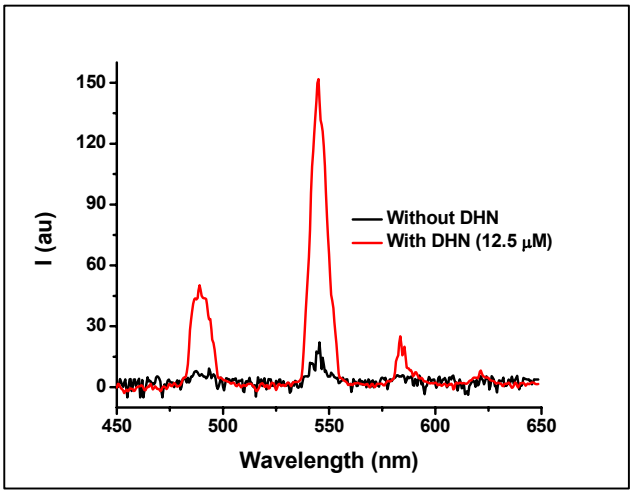


Fig S2b Tb^{3+} luminescence in Tb^{3+}-SDS (5/15 mM) powders

Absorption spectra of the decanted and filtered ethyl acetate solution in which xerogel doped with 12.5 μM DHN was soaked. No bands were observed in the UV-Visible spectra.

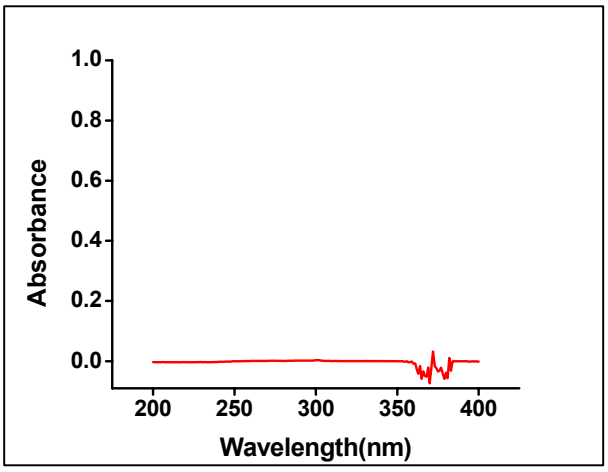


Fig S3 shows absorption spectra of EtOAc

Solid state luminescence studies

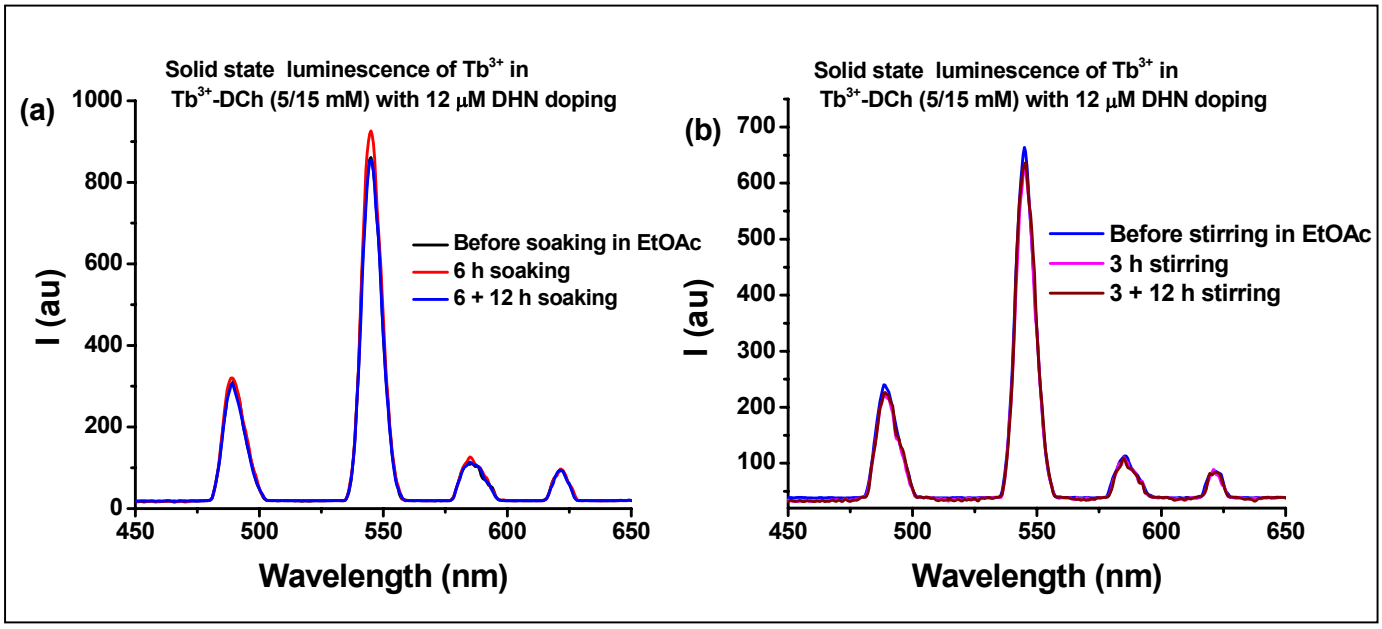
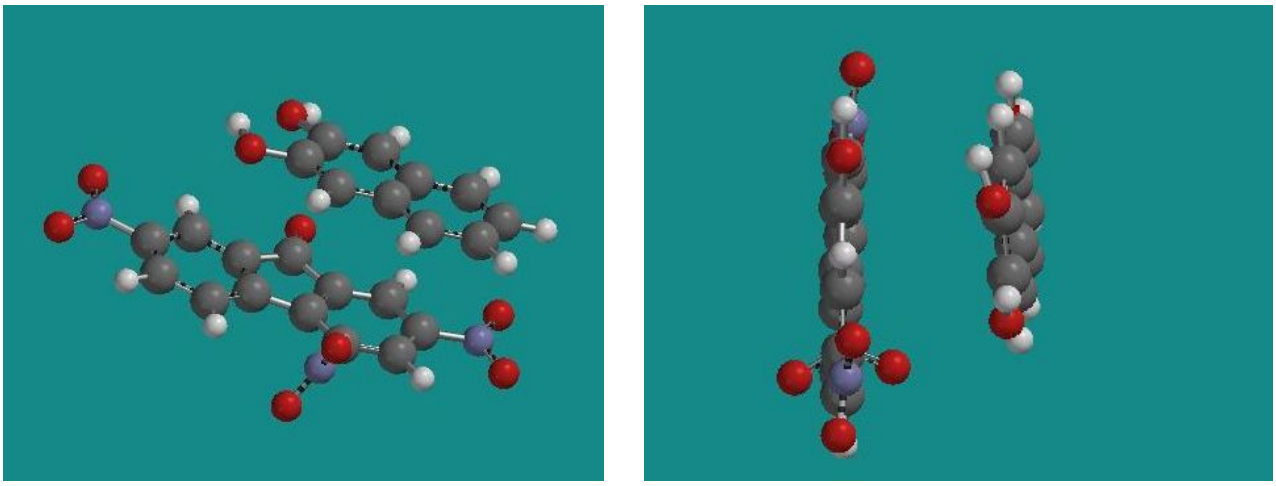


Fig S4: Solid state luminescence of Tb^{3+}-DCh (5/15 mM) xerogels with 12.5 μM DHN after (a) soaking and (b) stirring in EtOAc

Two batches of xerogels of Tb^{3+}-DCh (5/15 mM) were prepared and checked for luminescence. Though they showed different luminescent intensities there was no leaching of DHN from the gel fibers after soaking (Fig S4a) or stirring in EtOAc (Fig S4b). After initial luminescence study of xerogels one of them was soaked in EtOAc for 6 h and the other was stirred for 3 h. After

decanting and removing the solvent from both of the xerogels their luminescence intensity did not alter significantly compared to their pre-processed spectra. The luminescence did not change either even on overnight (12 h) soaking or stirring in EtOAc.

Spartan molecular modeling



Energy minimization studies of DHN-TNF complex, from two different views. Hartree Fock method was used to calculate the energy (527 kJ mol^{-1}) of the complex. Color code: Carbons (grey), Nitrogens (purple), Oxygens (red) and Hydrogens (white).

Scanning Electron Microscopy

After the gel was prepared in the test tube (10 mm x 75 mm), 10 μL of the sample was placed on the SEM sample holder after a fresh carbon tape was placed on it. Sample was air dried for an overnight (12-14 h) period then dried under vacuum for 4-5 hours. Gold coating was performed prior to the imaging was done.

Transmission Electron Microscopy

Thin films of the gels were made on the surface of carbon coated copper grids by dipping the grids inside the gel. Grids were then allowed to air dry for 6-8 hours. Then they were stained with 1% aqueous uranyl acetate solution and dried in the dessicator for 4-5 hours under high vacuum before recording the TEM images.

Atomic Force Microscopy

10 μL of the gel sample was placed on a freshly cleaved mica surface. Sample was allowed to air dry for an overnight period (12-14 h). Later the sample was dried under high vacuum for 5-6 hrs. AFM measurements were carried out in contact mode setting. Error signal images which reveal bunching of micro fibers into macro fibrils are shown in **Fig S4**.

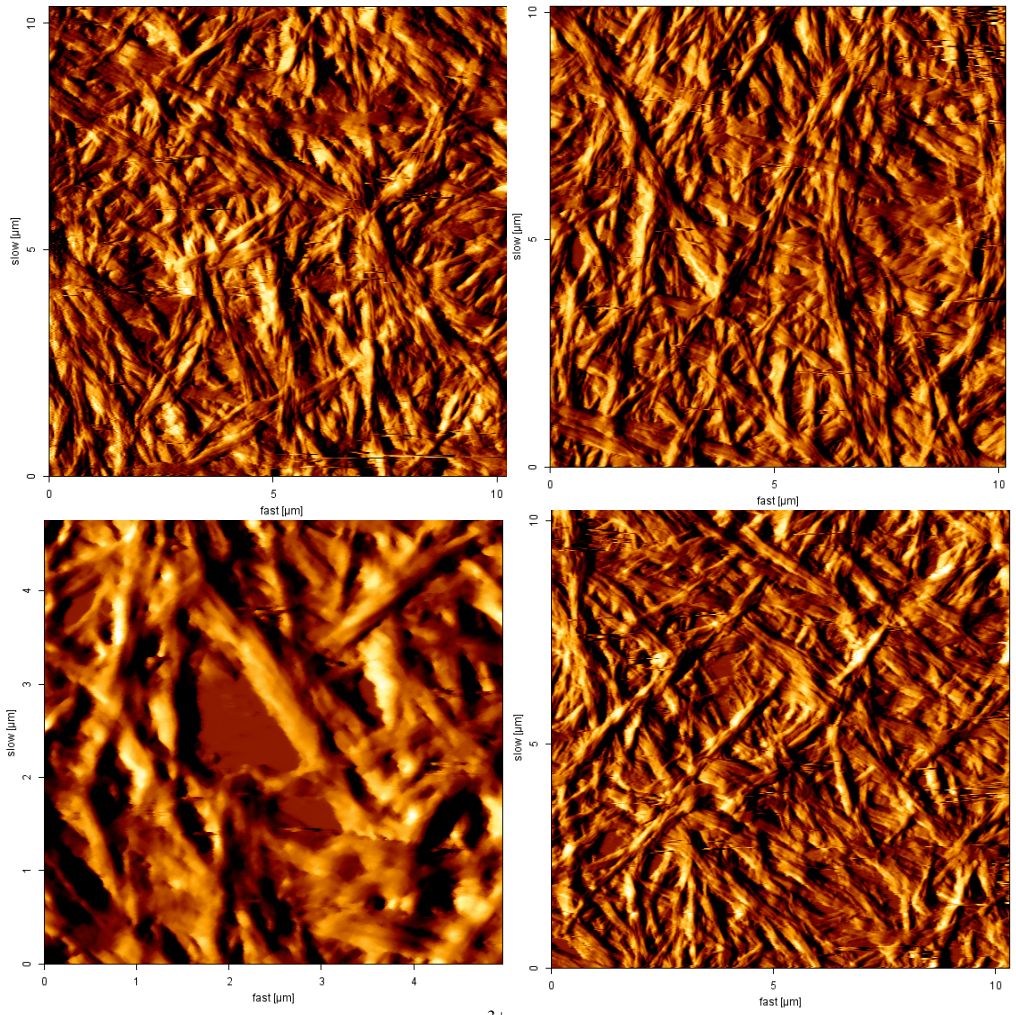


Fig S5 AFM Error signal images of Tb^{3+}-DCh (2.5/7.5 mM) xerogels on mica surface

Rheology

Dynamic rheological measurements were performed on the gels on an AR 1000 rheometer (TA instruments) using a plate-plate geometry. Only the rotor was serrated with a diameter of 20 mm which was used for all the measurements. Temperature of the plate was maintained at 18 ºC (± 0.1 ºC) since methanol was the solvent. The gels were made in 15 mL culture tubes (with flat bottom) and then scooped onto the plate. Geometry gap of 400 μm was set after 5 min of loading the sample. The solvent evaporation was minimized by placing a metallic cover as a solvent trap.