Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

Cd(II)-nucleobase supramolecular metallo-hydrogels for *in situ* growth of color tunable CdS quantum dots

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Materials

Adenine, guanine, cytosine, thymine and uracil were purchased from Aldrich chemicals. $Cd(NO_3)_2.4H_2O$, $CdCl_2$, $Cd(CH_3COO)_2.2H_2O$,NaCl, KCl, $CaCl_2$, $MnCl_2.4H_2O$, $CuSO_4.5H_2O$, $Zn(NO_3)_2.6H_2O$, sodium hydroxide, nitric acid and sodium sulfide were purchased from Merck, India. Adenosine-5'-monophosphate, Guanosine-5'-monophosphate, Uridine-5'-monophosphate and Adenosine-5'-triphosphate were purchased from SRL chemicals, India. All the chemicals were of analytical grade and were used without any further purification. Milli Q water was used throughout the experiments.

Instrumentation

Transmission electron microscopy (TEM) images were recorded with a Technai G^2 20 Ultra-Twin microscope and a Jeol JEM-2100 microscope at an accelerating voltage of 200 kV. Field emission scanning electron microscopy images were recorded on a Carl Zeiss Supra 55 instrument after coating with gold. Rheological measurements were performed using an Anton Paar Physica MCR 301 rheometer with parallel plate geometry (diameter 50 mm). Powder X-ray diffraction patterns (XRD) of the freeze dried gels were recorded on a Rigaku Smartlab, Automated Multipurpose X-ray diffractometer with Cu Kα source (wavelength of X- rays was 0.154 nm). FTIR spectra were recorded in KBr pellet using Bruker Tensor 27 instrument. Thermogravimetric analysis was performed using a Mettler Toledo thermal analysis system at a heating rate of 5 °C per minute. Fluorescence measurement was performed on a fluoromax-4p fluorometer from Horiba (Model: FM-100).

Synthesis of Cd-thymine and Cd-uracil hydrogels

A stock solution of thymine and uracil (0.2 M) was separately prepared by the addition of solid NaOH to it in small parts under sonication until the nucleobases solubilized and a clear solution was obtained. Similarly, a solution of $Cd(NO_3)_2.4H_2O$ (0.2 M) was prepared by simple dissolution of the metal salt in water.

The metal-nucleobase hybrid hydrogels were formed by the addition of 1.0 mL of $Cd(NO_3)_2.4H_2O$ solution to 1.0 mL of the nucleobase solution. The spontaneous formation of hydrogels was physically ascertained through the inverse-tube method, where no flow of solution was observed.

Electron microscopy studies

The samples for both TEM and FESEM were prepared by diluting the gel samples in water. A small amount of the gel was taken in an Eppendorf tube and after addition of water the gel was crushed using a micropestle. The resulting solution was drop casted on a carbon coated copper grid (for TEM) and glass slides (for FESEM), followed by room temperature drying.

Rheological studies

Rheological investigations were performed using parallel plate geometry of diameter 50 mm. For the measurements, both the hydrogels were first prepared and then a piece of the gel was placed on the plate of the rheometer using a microspatula. The temperature was maintained at 25 °C using an integrated temperature controller from Julabo. Dynamic strain sweep experiments were performed using a constant frequency of 10 rad s^{-1}. The dynamic frequency sweep of the hydrogels was measured as function of frequency in the range of 0.05-100 rad s^{-1} with constant strain value 1%.

Synthesis of blue, white and yellow emitting CdS quantum dots within the Cd-thymine or Cd-uracil gels.

Blue emitting CdS: 0.025 mL (10 mM) Na_2S was added to 1.0 mL of 200 mM deprotonated thymine (or uracil) followed by the addition of 1.0 mL (200 mM) $Cd(NO_3)_2$, which resulted in the formation of a white opaque gel, which when observed under UV lamp showed blue fluorescence.

White emitting CdS: 0.1 mL (10 mM) Na_2S was added to 1.0 mL of 200 mM deprotonated thymine (or uracil) followed by the addition of 1.0 mL (200 mM) $Cd(NO_3)_2$, which resulted in the formation of a nearly white opaque gel, which when observed under UV lamp showed intense white emission.

Yellow emitting CdS: 0.1 mL (or 0.05 mL) (100 mM) Na_2S was added to a 1.0 mL solution of 200 mM deprotonated thymine (or uracil) followed by the addition of 1.0 mL (200 mM) $Cd(NO_3)_2$, which resulted in the formation of a white opaque gel, which when observed under UV lamp showed intense yellow fluorescence.

Effect of temperature on the formation of CdS QDs within gel

The effect of temperature on the formation of yellow emitting CdS QDs within the gel was studied by preparing the gel-QD system at three different temperatures of 5 ^{o}C, 25 ^{o}C and 60 ^{o}C. Briefly, 1.0 mL of thymine (200 mM) was taken in a cuvette of pathlength 10 mm and to it 0.1 mL (100 mM) Na_2S was added and kept at 5 ^{o}C. Separately, a vial containing $Cd(NO_3)_2$ (200 mM) was also placed in the bath at 5 ^{o}C and kept for 30 minutes. After 30 minutes, 1.0 mL of $Cd(NO_3)_2$ (200 mM) was added to the mixture of thymine and Na_2S kept at 5 ^{o}C and emission was recorded by maintaining the temperature of the cuvette holder to 5 ^{o}C. Similarly QD-gel system at 25 ^{o}C and 60 ^{o}C were prepared and emission was recorded.

Sensing of metal ions:

The sensing of metal ions was performed using the white emitting gel. For the sensing experiments, the CdS-gel composite was first diluted with water and homogenized. 2 mL of white emitting gel was prepared in a vial using the above mentioned method. To this gel 2 mL of water was added and the gel was crushed using a micropestle, followed by sonication for proper homogenization. Now, 2 mL of the gel-water mixture was taken in a cuvette using a micropipette and various concentrations of metal ions was added and the emission was recorded.

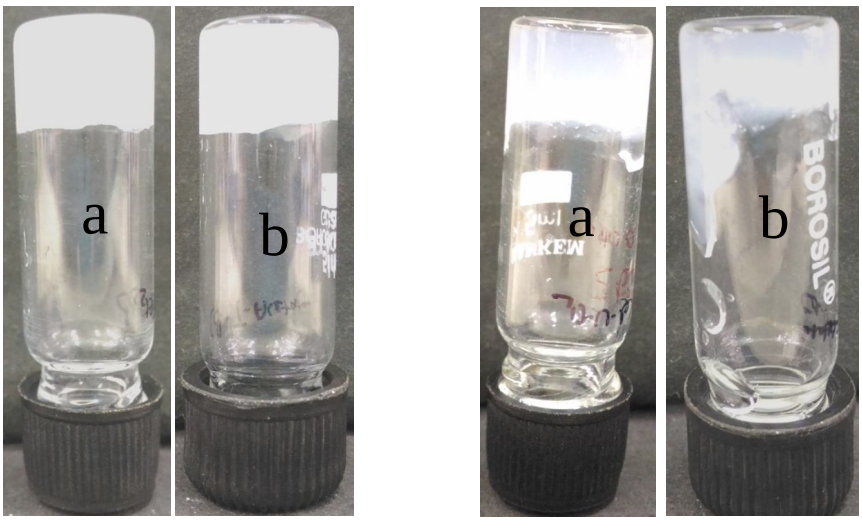


Figure S1. Digital images of Cd-thymine and Cd-uracil hydrogel formed using alkaline thymine and uracil and (a) $CdCl_2$ and (b)$Cd(CH_3COO)_2$.

Figure S2. (a), (b) Digital images of the precipitate formed upon the addition of $Cd(NO_3)_2$ to an alkaline solution of adenine and guanine respectively and (c) digital image of the clear solution obtained upon the interaction of Cd^{2+} ions with alkaline cytosine.

Figure S3. Digital images of the precipitates and clear solutions obtained upon the addition of $Cd(NO_3)_2$ to a neutral solution of (a) AMP, (b) GMP, (c) UMP, (d) ATP.

Figure S4. Digital images of the clear solutions obtained upon the addition of $Cd(NO_3)_2$ to an acidic solution of (a) adenine, (b) guanine, (c) cytosine, (d) thymine and (e) uracil.

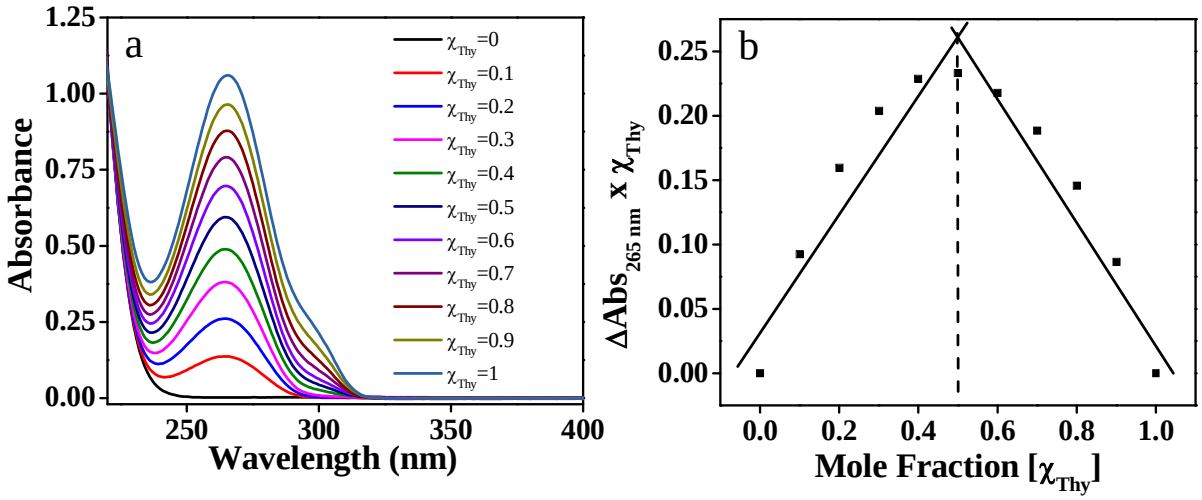


Figure S5.(a) UV-visible spectra of Cd-T complex formed at varying mole fractions of thymine and (b) Job's plot constructed by observing the change in absorbance at 265 nm upon addition of varying mole fractions of thymine to aqueous $Cd(NO_3)_2$ solution.

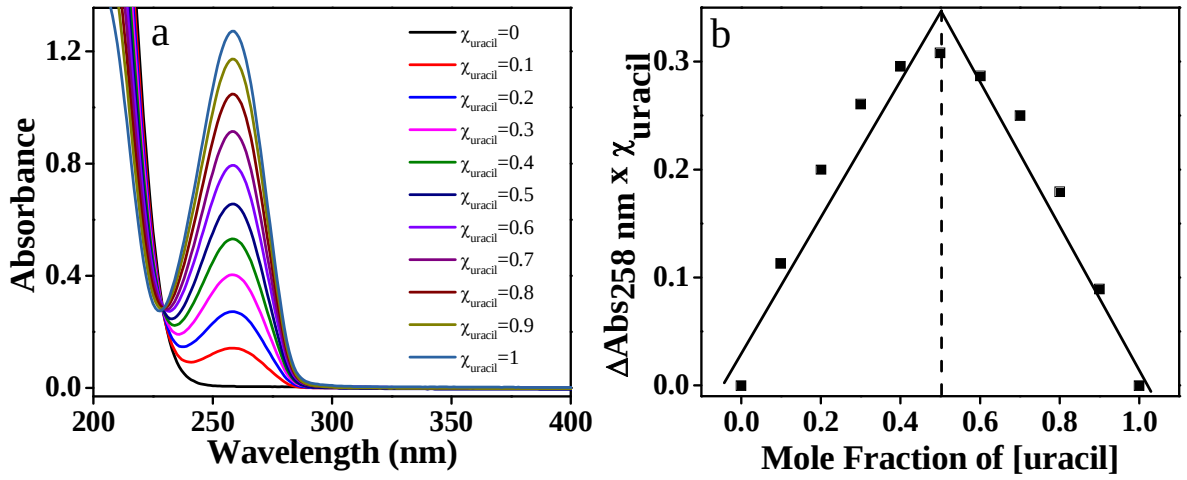


Figure S6.(a) UV-visible spectra of Cd-U complex formed at varying mole fractions of uracil and (b) Job's plot constructed by observing the change in absorbance at 258 nm upon addition of varying mole fractions of uracil to aqueous $Cd(NO_3)_2$ solution.

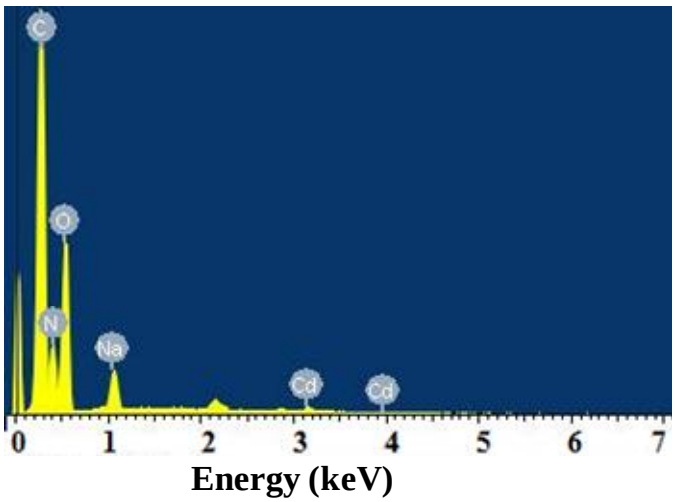


Figure S7. EDX spectrum of Cd-T nanofibers.

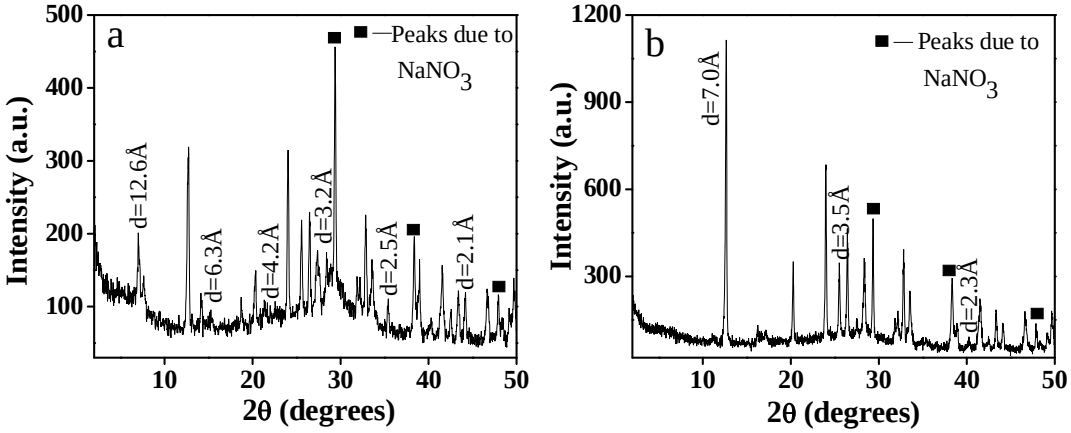


Figure S8. Powder XRD pattern of lyophilized (a) Cd-T hydrogel and (b) Cd-U hydrogel, showing peaks with the corresponding *d*-values.

The powder X-ray diffraction pattern of the freeze dried gels showed a complex pattern of several peaks at 2θ values of 1-50 degrees. For Cd- T gel, periodic reflections at $2\theta = 7.0^0$, 14.2^0, 21.4^0, 28.4^0, 35.4^0 and 43.4^0, corresponding to *d*-spacing of 12.6 Å, 6.3 Å 4.2 Å, 3.1 Å, 2.5 Å and 2.1 Å respectively were observed. These *d*-spacing followed a pattern of 1: 1/2: 1/3: 1/4: 1/5: 1/6, indicating that the hydrogel was organized in a layered pattern, with an inter layer separation of 12.6 Å. Similarly, XRD peaks at $2\theta = 12.7^0$, 25.6^0 and 40.2^0 with a corresponding *d*-spacing of 7.0 Å, 3.5 Å and 2.3 Å respectively were observed for the Cd-U gel in addition to several other peaks. These *d*-values followed a pattern of 1: 1/2: 1/3 suggesting that the hydrogel was arranged in a layered pattern.

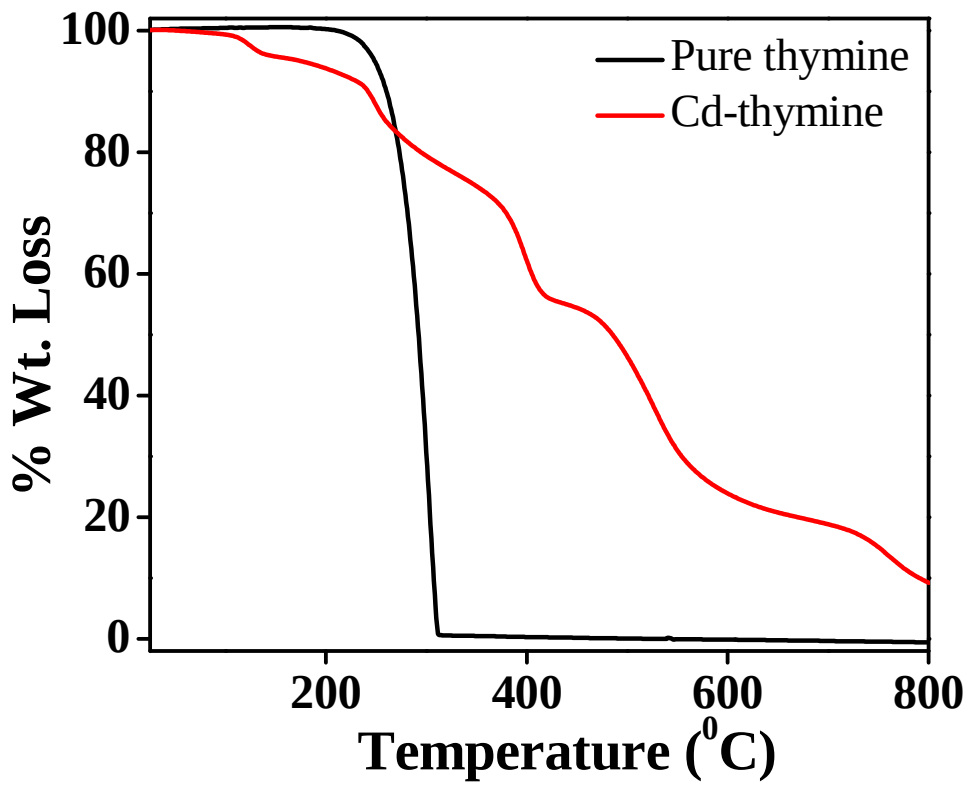


Figure S9. TGA plot of pure thymine and lyophilized Cd-thymine xerogel.

The TGA plot for pure thymine showed complete decomposition of thymine in a single weight loss in the temperature range of 230 °C -310°C. On the other hand, the freeze dried Cd-T hydrogels showed an initial weight loss of about 20% in the temperature range of 25-240 °C, which might be due to the loss of water molecules in the complex. Thereafter continuous decomposition of the material was observed upto a temperature of 740°C. Beyond this temperature the material was stable with a composition of 15%, which might be due to the stability of the metal.

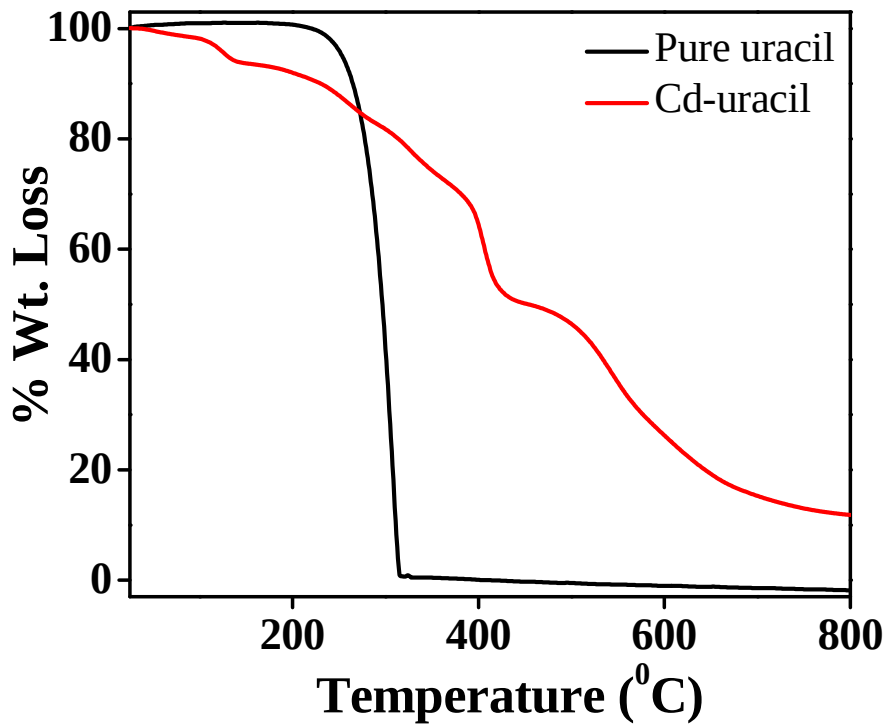


Figure S10. TGA plot of pure uracil and lyophilized Cd-uracil xerogel.

The thermogravimetric analysis for pure uracil showed complete decomposition of uracil in a single weight loss in the temperature range of 230 °C-320 °C. On the other hand, for the Cd-U xerogel, an initial weight loss of 5.5% at 123 °C was observed, probably due to the loss of water molecules in the complex. Two other weight losses in the range of 135-405 °C and 410-700 °C corresponding to the decomposition of the ligands were observed. The material thereafter was stable upto a temperature of 800 °C with a composition of 16%, which might be attributed to the stability of metal.

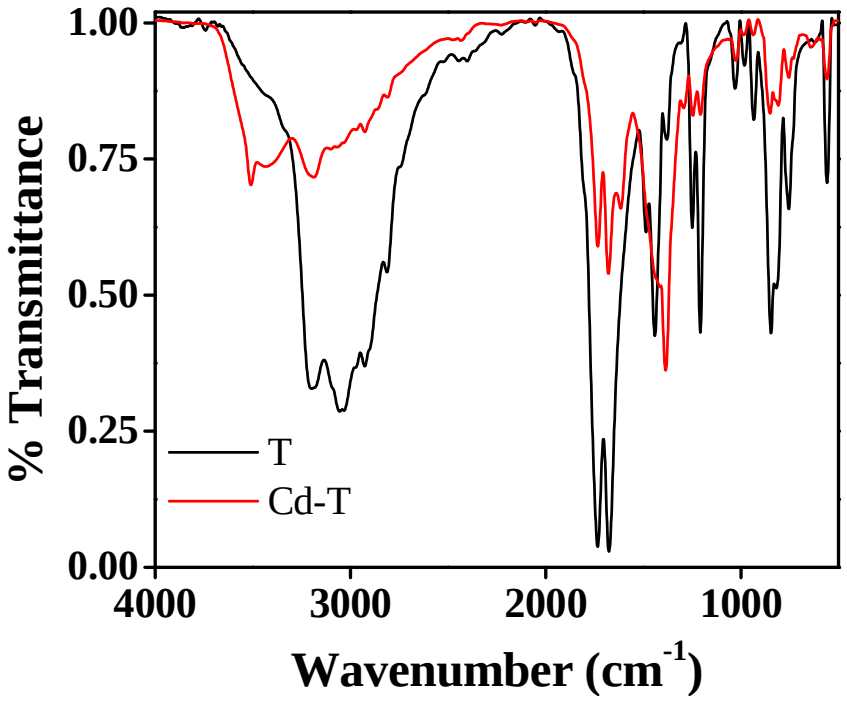


Figure S11. FTIR spectrum of pure thymine and Cd-thymine.

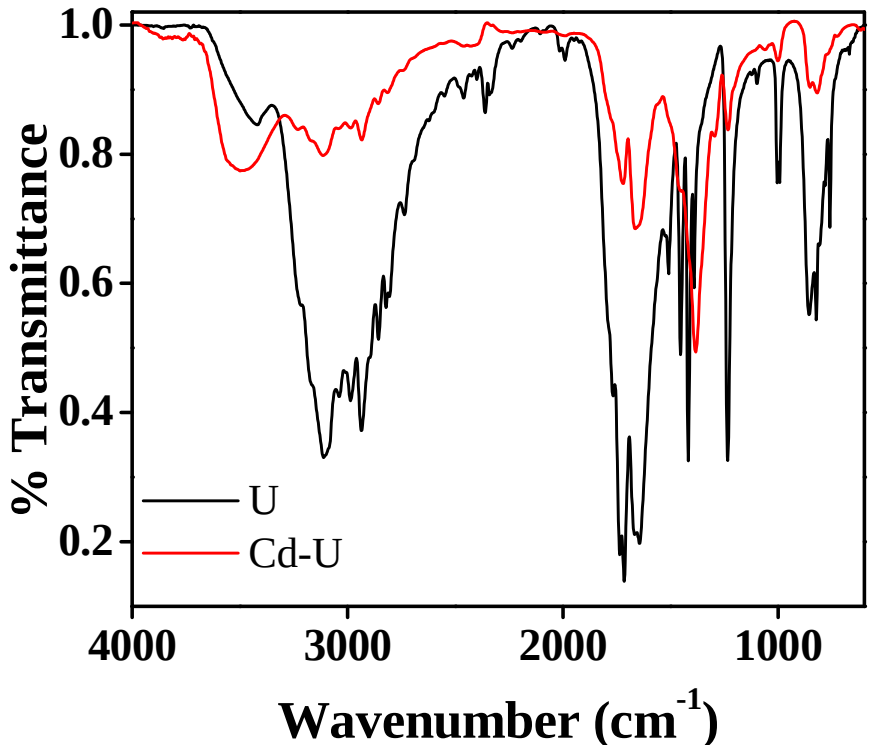


Figure S12. FTIR spectrum of pure uracil and Cd-uracil.

Elemental composition of the Cd-U metallogel

	C (%)	N (%)	H (%)
Experimental	12.47	13.63	1.64
Theoretical	12.52	14.60	1.82

Table S1. Experimental and theoretical elemental composition of the Cd-U metallo-hydrogel, indicating the formation of the complex $[Cd(U)(NO_3)_2(H_2O)_2]$ upon the interaction of Cd^{2+} ions to aqueous alkaline uracil.

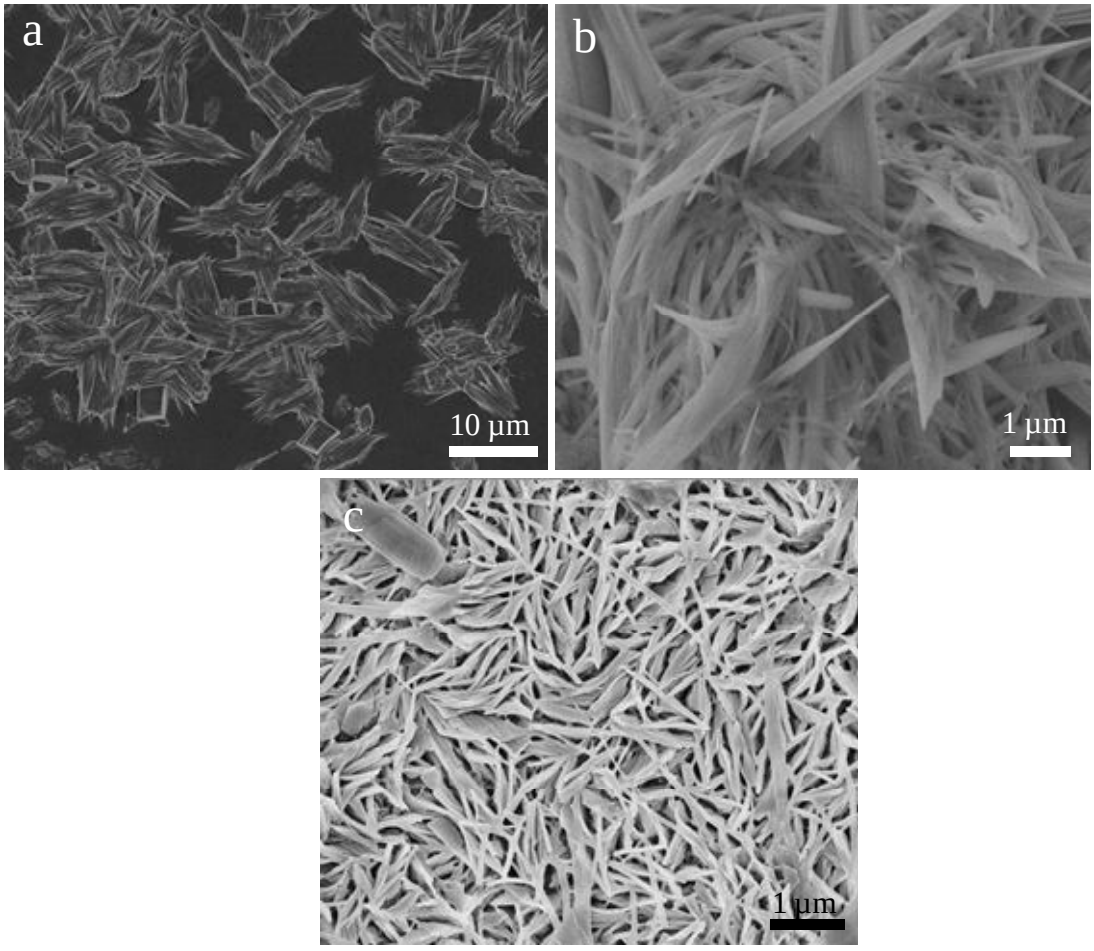


Figure S13. (a), (b) and (c) FESEM images of (a) Cd-A precipitate, (b) Cd-G precipitate and (c) Cd-C clear solution.

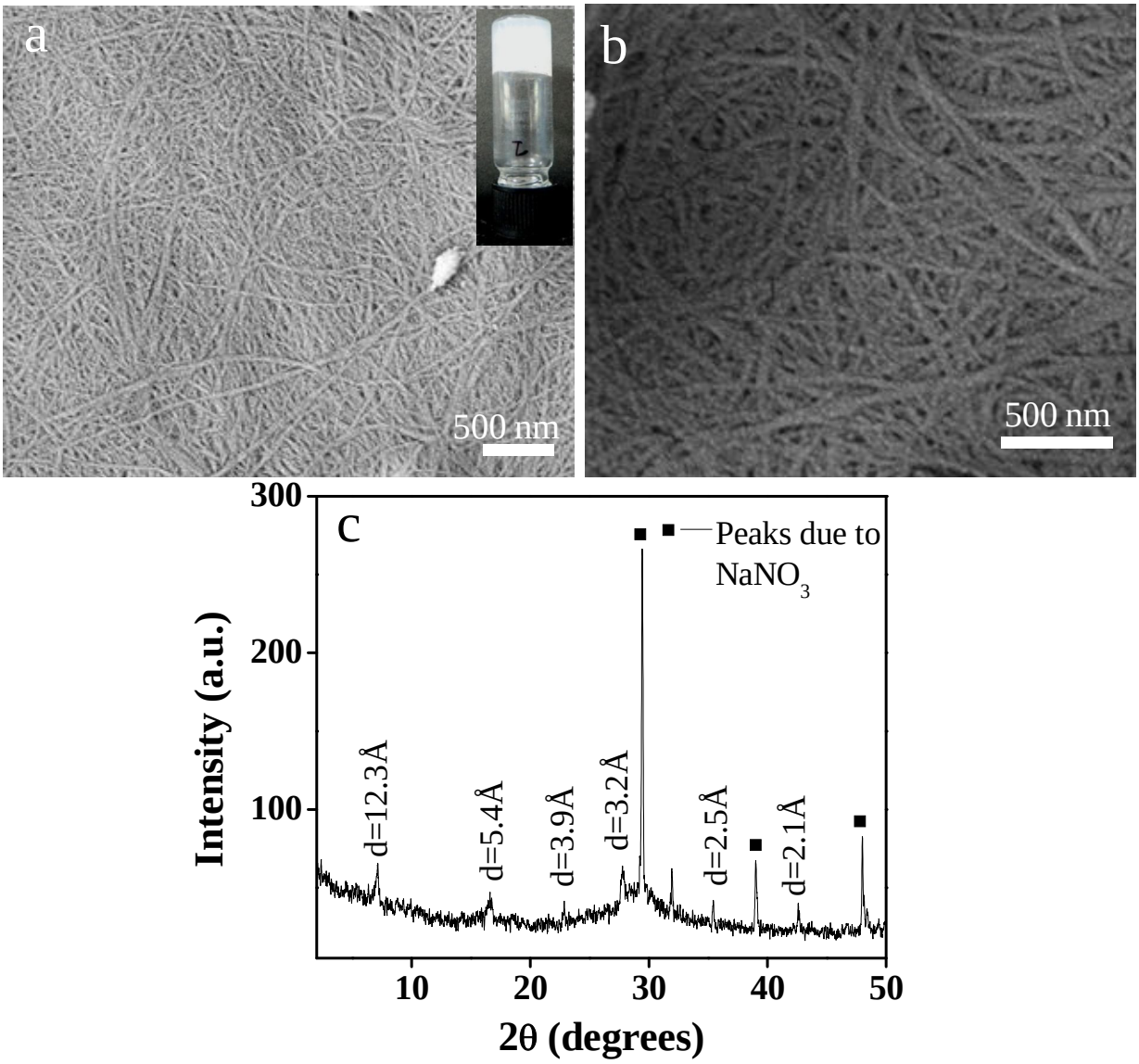


Figure S14. (a) FESEM image of the nanofibers formed within the Cd-T-U hydrogel; *inset:* Digital image of the hydrogel, (b) Higher magnification SEM image of the Cd-T-U hydrogel, showing the formation of nanofibers and (c) Powder X-ray diffraction pattern of the lyophilized Cd-T-U xerogels, showing peaks with corresponding *d*-values.

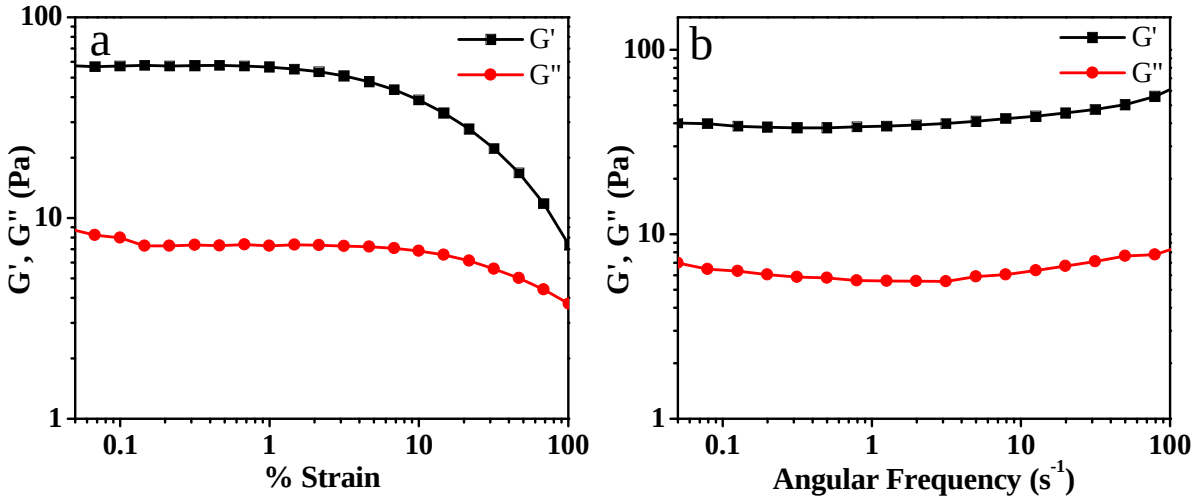


Figure S15. (a) Strain sweep rheological investigation of Cd-T-U hydrogel and (b) Frequency sweep rheological experiment for the Cd-T-U hydrogel at a fixed strain of 1%.

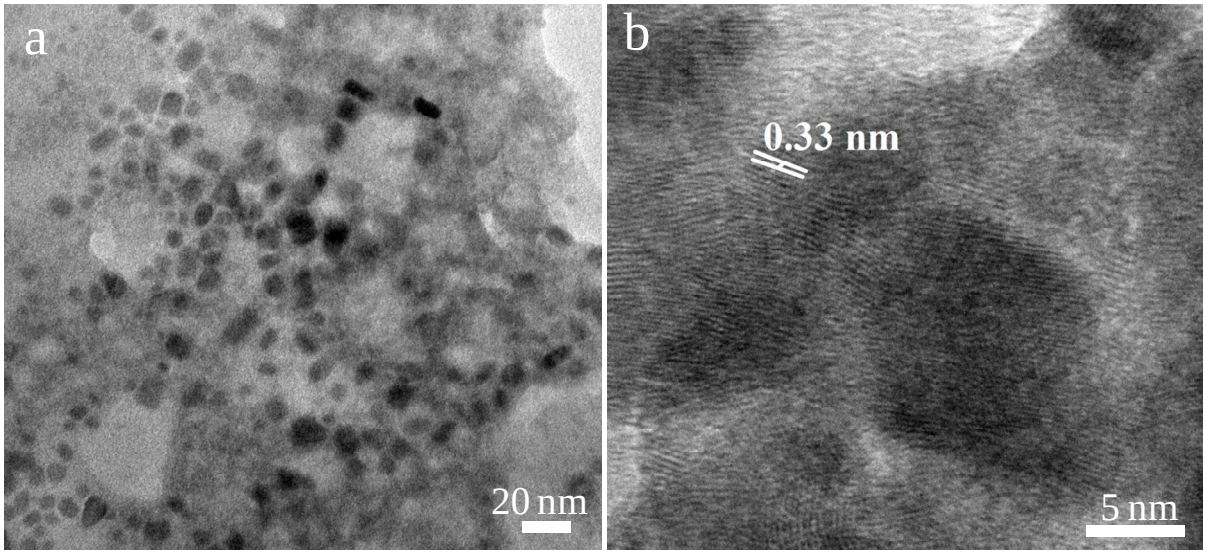


Figure S16. (a) TEM image and (b) HRTEM image of CdS nanoparticles formed within the Cd-U hydrogel.

Stability of CdS QDs within the hydrogel with time:

The stability of the CdS QDs formed within both the Cd-T and Cd-U hydrogels was investigated by time dependent fluorescence studies. It was observed that the emission intensity of the CdS nanoparticles in both the gels decreased with time, together with a slight red shift in emission maximum (Fig. S15). The TEM studies of the CdS QDs within the gels indicated that the initially formed CdS QDs agglomerated with time to form larger particles (Fig. S16 and S17). This agglomeration of the CdS QDs with time might lead to a decrease in the emission intensity of the nanoparticles together with a slight shift towards the red region.

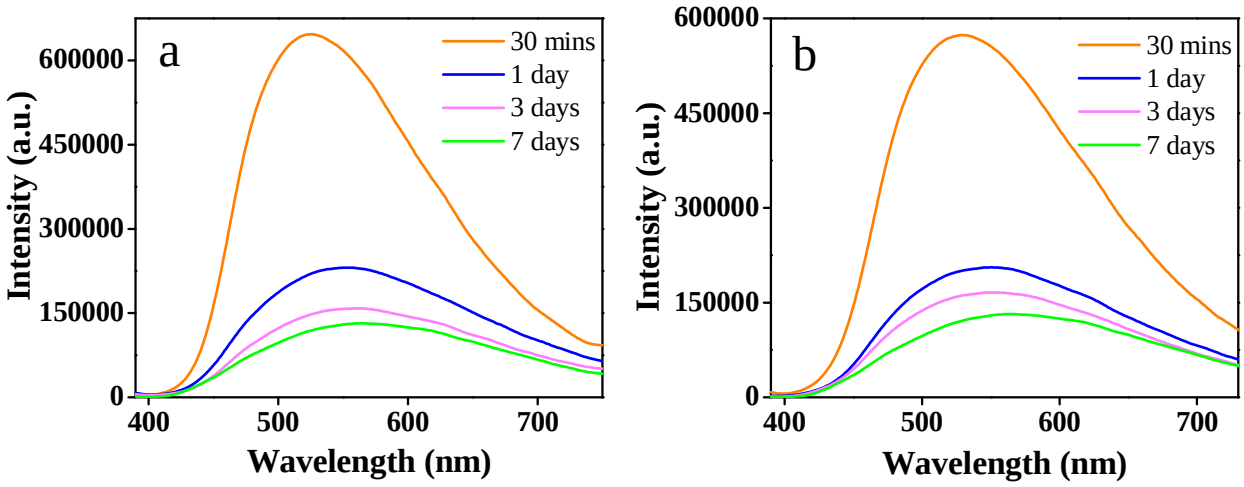


Figure S17. Time dependent fluorescence emission spectrum for the CdS quantum dots generated within (a) Cd-T hydrogel and (b) Cd-U hydrogel.

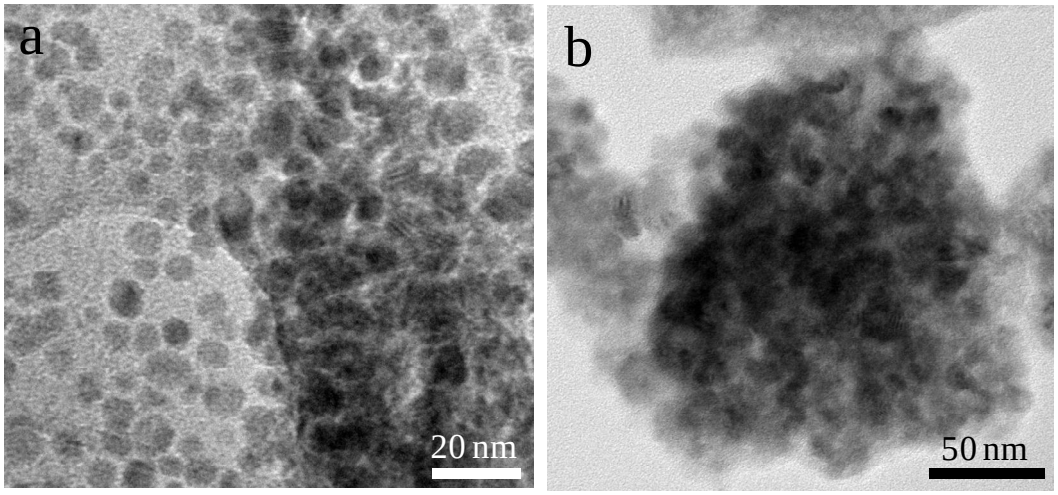


Figure S18.TEM images of CdS QDs formed within the Cd-T hydrogel (a) fresh and (b) after 7 days.

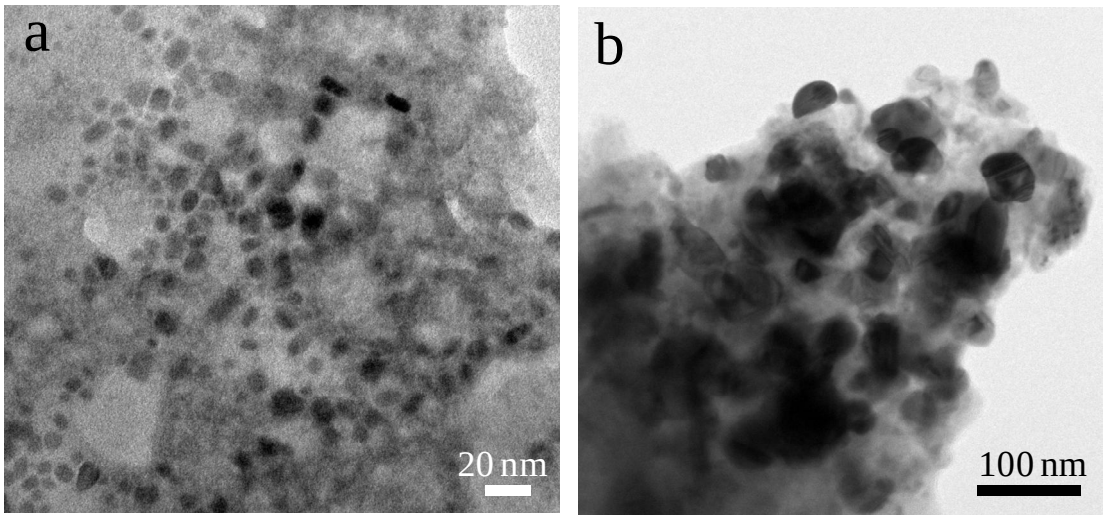


Figure S19.TEM images of CdS QDs formed within the Cd-U hydrogel (a) fresh and (b) after 7 days showing agglomeration.

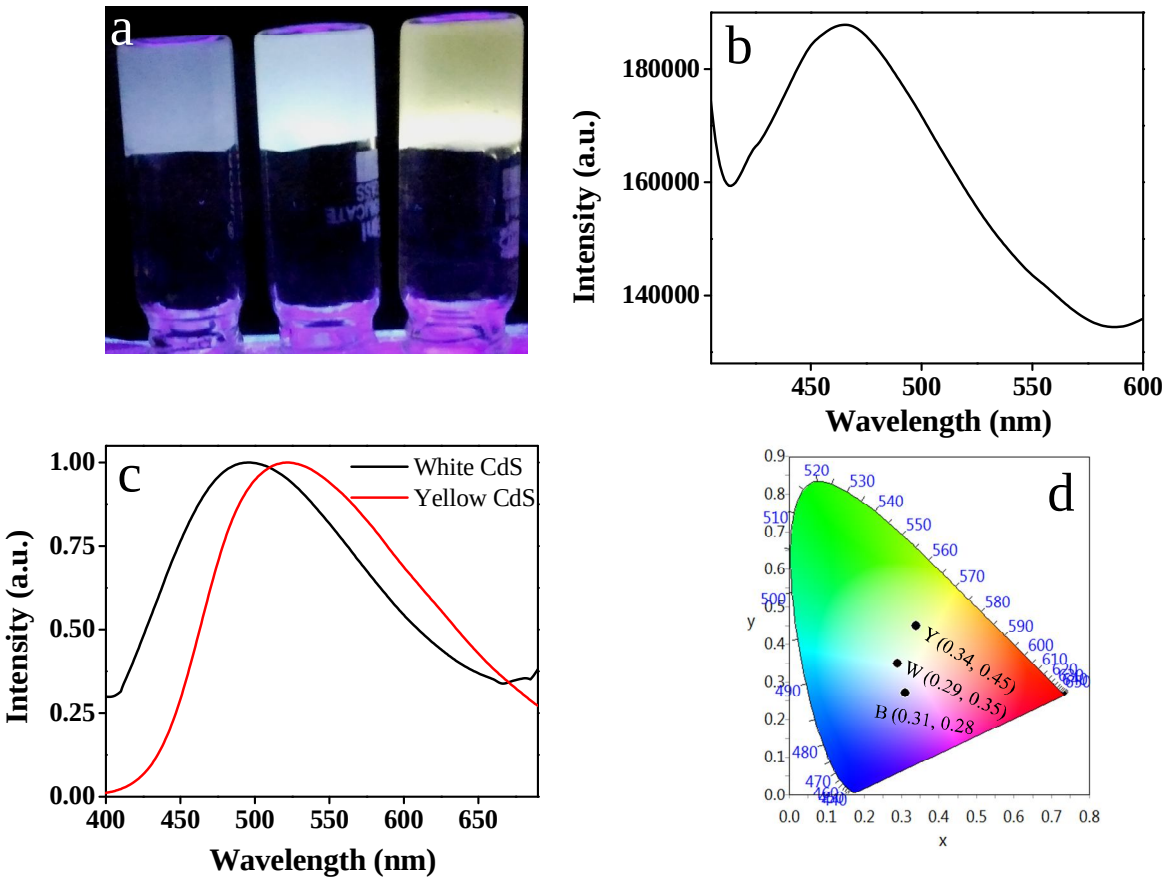
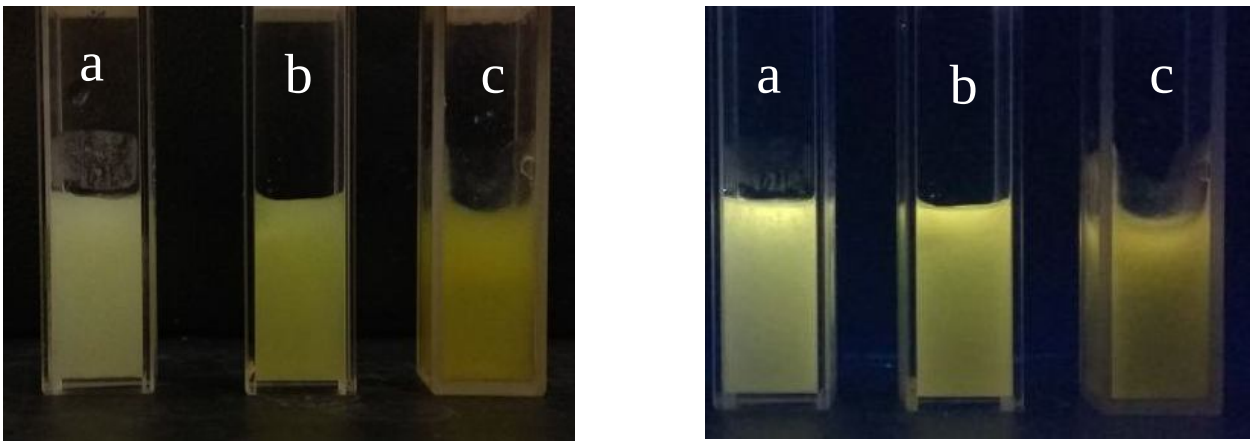


Figure S20. (a) Digital image of the CdS quantum dot incorporated Cd-U gel showing blue, white and yellow color under UV lamp (λ_{ex}=365 nm) depending upon the concentration of Na_2S. (b) Emission spectra of the blue emitting quantum dot incorporated Cd-U gel. (c) Normalized emission spectra of the white and yellow emitting quantum dot incorporated Cd-U gel and (d) Chromaticity plot for the CdS incorporated Cd-U gel; B-blue emitting, W-white emitting, Y-yellow emitting.

The fluorescence emission spectrum for the blue emitting CdS QDs incorporated in the Cd-U hydrogel showed a maximum at 465 nm. On the other hand for the white emitting gel a broad spectrum covering the entire visible region with emission maximum at 497 nm was observed. The yellow emitting CdS quantum dots incorporated hydrogel showed a broad spectrum with maxima at 524 nm. The CIE (Commission international de d'Eclairage) chromaticity coordinates for blue emitting QDs (0.31, 0.28) appeared in the blue region. On the other hand, while the CIE coordinates for the yellow emitting CdS QDs (0.34, 0.45) appeared in the yellowish-green region, the CIE coordinates for the white emitting gel were (0.29, 0.35).



Under daylight Under UV light

Figure S21. Digital images of the CdS-gel composite formed using thymine as ligand at different temperatures under daylight and under UV light with an excitation wavelength of 365 nm; (a) 5 °C, (b) 25 °C and (c) 60 °C.

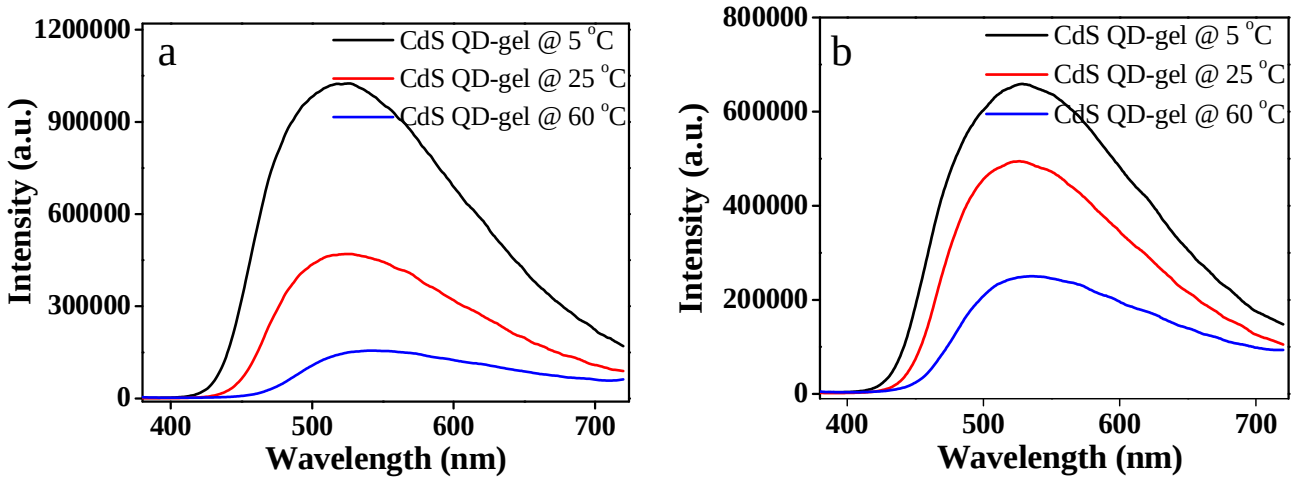


Figure S22. Fluorescence emission spectrum of CdS QD-gel composite synthesized at5 °C, 25 °C and 60 °C after 5 minutes at the respective temperatures of synthesis and (b) after 1 hour at 25 °C respectively.

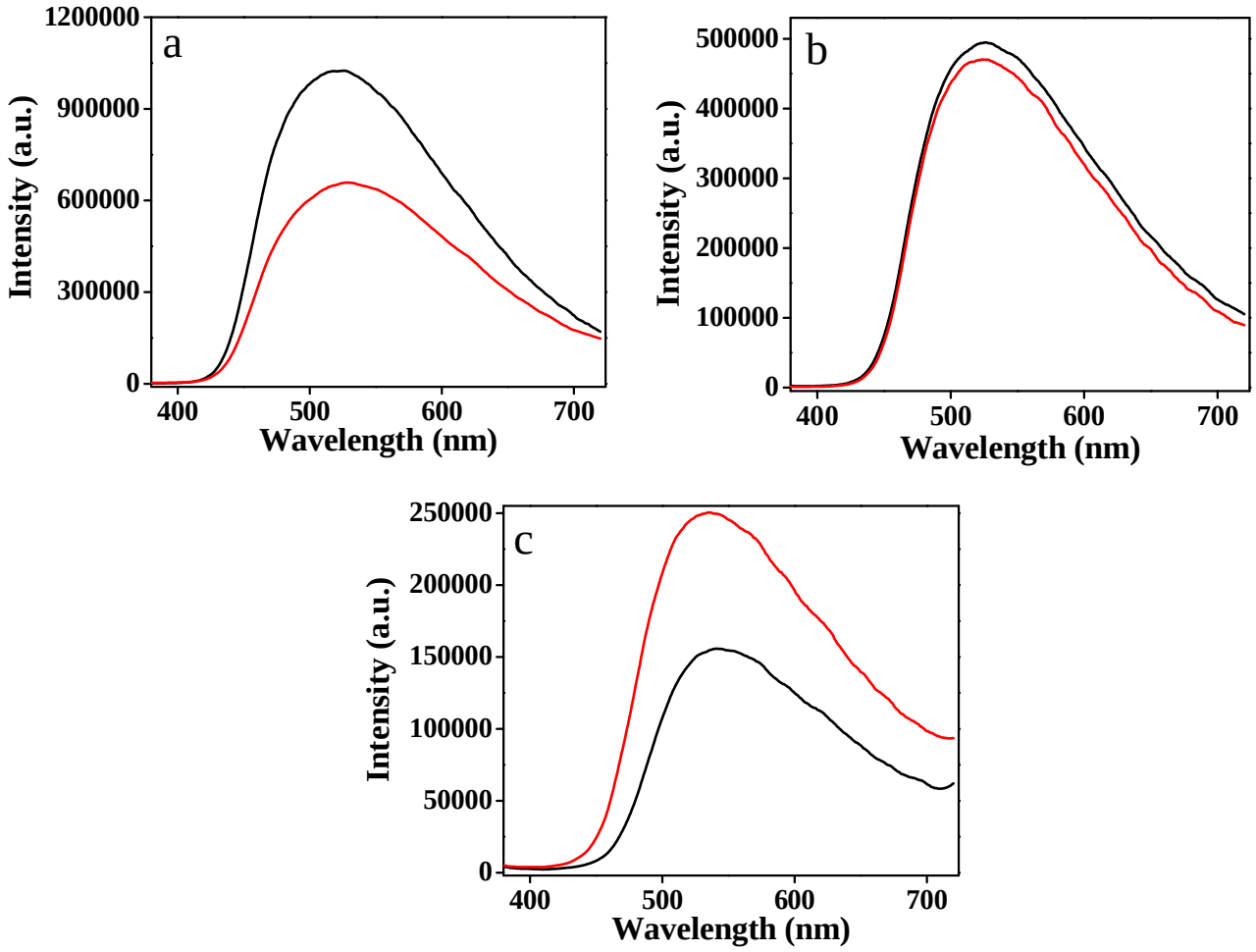


Figure S23. Fluorescence emission spectrum of CdS QD-gel composite synthesized at (a)5 $^{\circ}$C, (b) 25 $^{\circ}$C and (c) 60 $^{\circ}$C; ***black line***: emission recorded at respective temperatures after 5 minutes and ***red line***: emission spectrum recorded after 60 minutes at 25 ^{o}C.

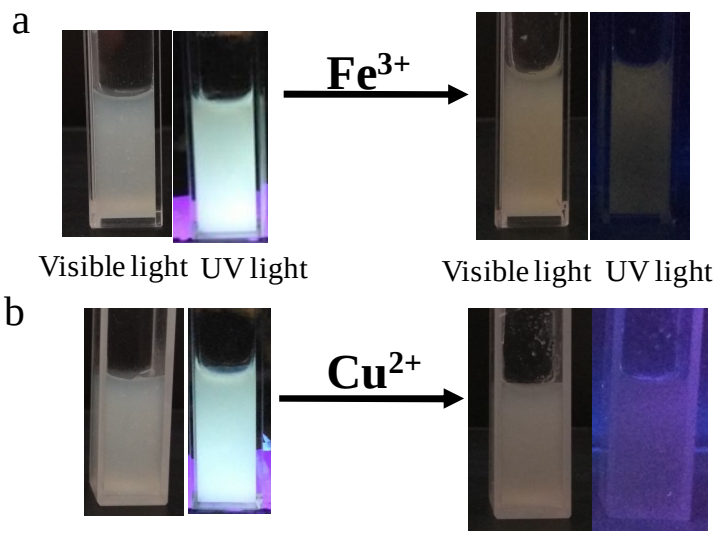


Figure S24. Digital images of the gel dispersed in water under visible and UV light before and after addition of (a) Fe^{3+} ions and (b) Cu^{2+} ions.

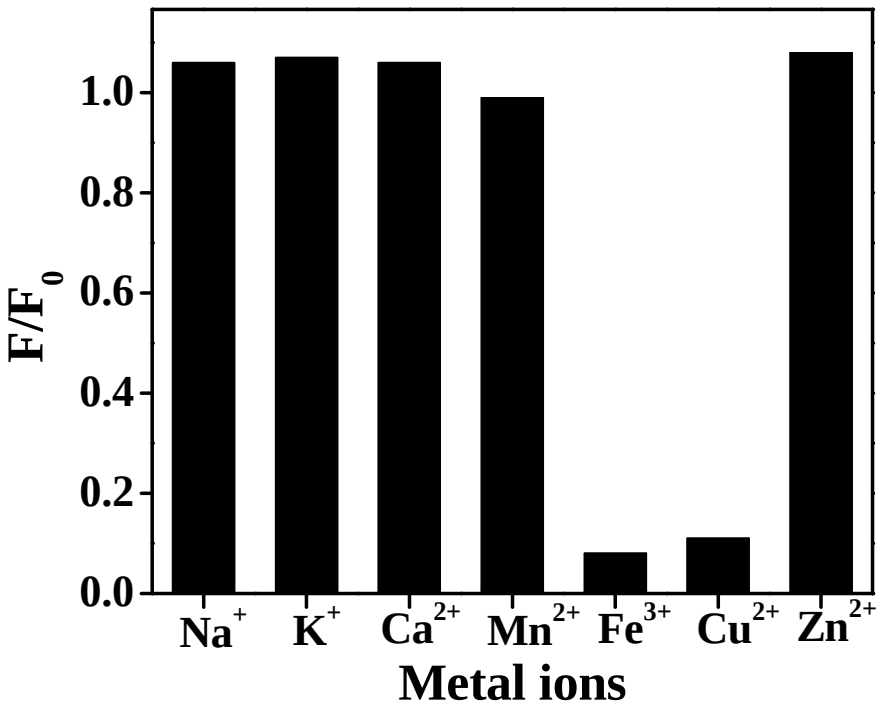


Figure S25. Selectivity studies of the white light emitting CdS-gel system for sensing of metal ions. The sensing was selective for Fe^{3+} and Cu^{2+} ions among the tested metal ions.

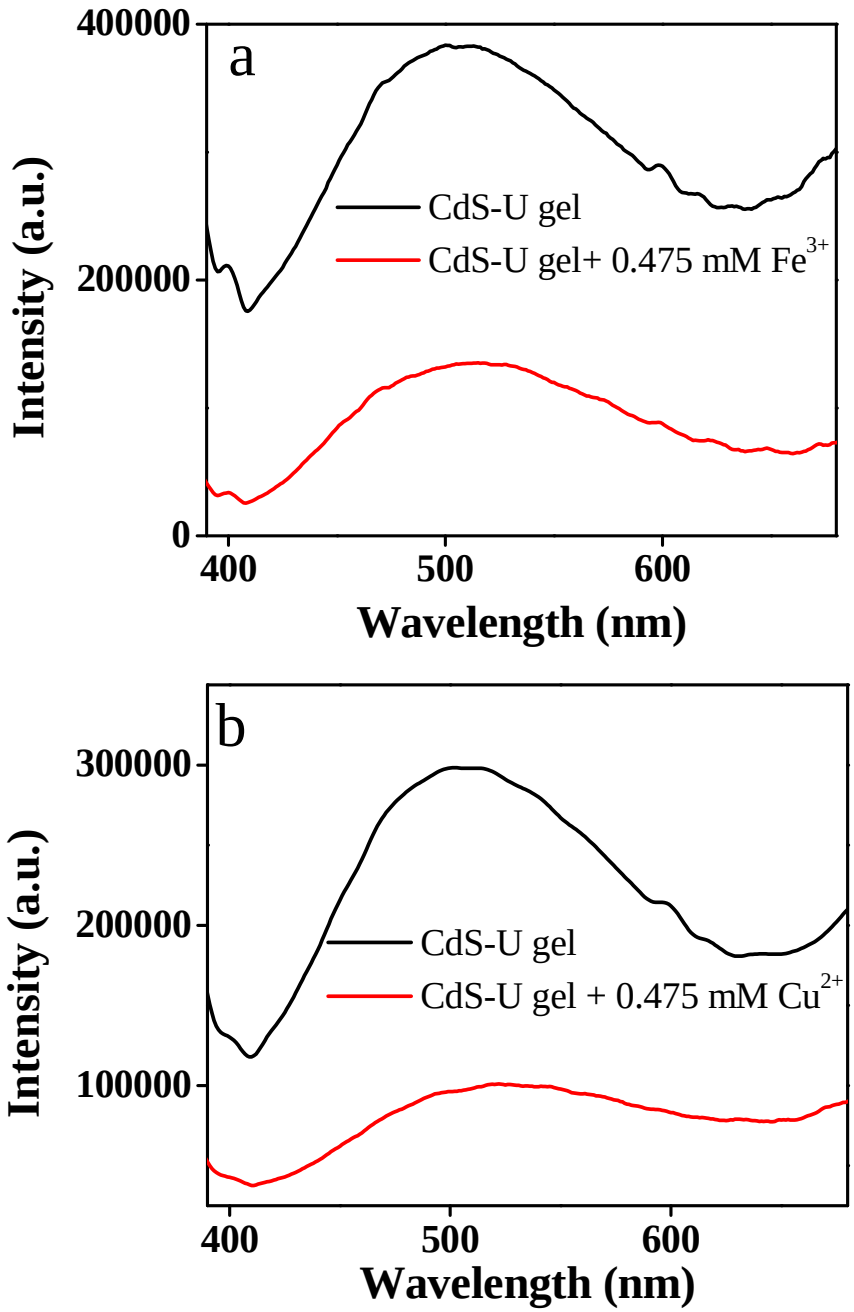


Figure S26. Emission spectrum of CdS-gel system synthesized using uracil as ligand, (a) before and after addition of 0.475 mM Fe^{3+} ions and (b) before and after addition of 0.475 mM Cu^{2+} ions.