# Electronic Supplementary Information

# Self-assembly of Peptide-based Multi-colour Gels triggered by Up-converting Rare Earth Nanoparticles

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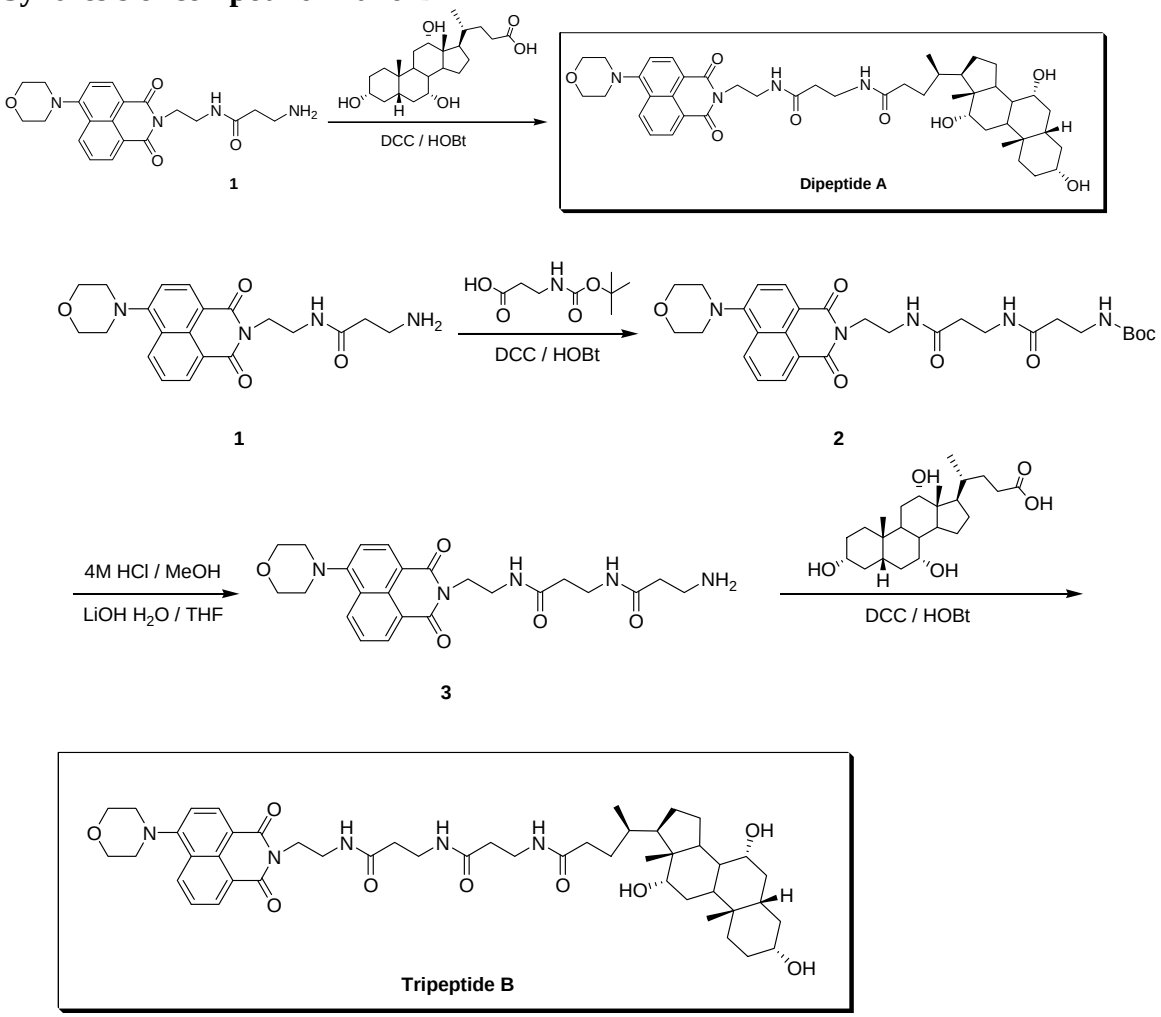
## Experimental Section

**General Methods.** All starting materials were obtained from commercial supplies and used as received. Di-tert-butyl dicarbonate (97%) and cholic acid (98%) were provided from Alfa Aesar. Dicylohexylcarbodiimide (99%) was obtained from Acros. β-Alanine (98.5%), 4-Bromo-1, 8-naphthalic anhydride(95%), 1-Hydroxybenzotriazole (95%) and Ethane-1, 2-diamine anhydrous (99%) were supplied from Sinopharm Chemical Reagent Co., Ltd. (Shanghai). Oleic acid was obtained from Alfa Aesar. Rare earth chlorides ($LnCl_3$, Ln: Y, Yb, Er, Tm) were prepared by dissolving the corresponding oxides ($Y_2O_3$, $Yb_2O_3$, $Er_2O_3$, and $Tm_2O_3$ from Beijing Lansu Co. China) in 10% hydrochloric solution and then evaporating the water completely. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Mercuryplus, at 400 and 100 MHz, respectively. Proton chemical shifts are reported in parts per million downfield from tetramethylsilane. Matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) mass was recorded on an AXIMA-CFRPLVS mass spectrometer (Shimadzu). ESI-MS data were recorded on a Waters Quattro Micro API LC-MS-MS spectrometer (Waters, USA). Element analysis was carried out on a VARIOEL3 apparatus (ELEMENTAR). Melting points were determined on a hot-plate melting point apparatus XT4-100A without corrected.

## Synthesis of compound A and B




**Scheme S1** Synthesis of the gelators

### General procedure

**N-(2-ethylcarbamoyl-ethyl)-carbamic acid-cholylimide-4-morpholin-1, 8-naphthalimide Compound (A).** To a solution of cholic acid (2.06 g, 5.04 mmol) in dry THF (50 mL) was added compound **1**[1] (2.0 g, 5.04 mmol), 1-hydroxybenzotriazole (HOBt) (0.68 g, 5.04 mmol) and $Et_3N$ (0.65 mL, 5.04 mmol) in THF (100 mL) and followed by a THF (20 mL) solution of dicylohexylcarbodiimide (DCC) (1.25 g, 6.05 mmol) after 10 minutes. The reaction mixture was stirred for 48 hours at room temperature and the dicyclohexyl urea formed was filtered. After the solvent was removed, the residue was purified by column chromatography ($SiO_2$; $CHCl_3$ / MeOH = 100:1-50:1) to give compound **A** (1.8 g, 45.3%) as a yellow solid. Mp: 227-229 ºC. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.66 (s, 3H), 0.89 (s, 3H), 0.96-0.97 (d, $J$ = 6.4, 3H), 1.09-2.39 (m, 27H), 2.65 (br, s, 1H), 3.27-3.29 (t, $J$ = 4.4, 4H), 3.43-4.46 (t, $J$ = 6.4, 4H), 3.64-3.66 (d, $J$ = 5.2, 2H), 3.83 (br, s, 1H), 3.94 (br, s, 1H),

4.02-4.04 (t, *J* = 4.0, 4H), 4.36-4.39 (t, *J* = 5.2, 2H), 6.80 (br, s, 2H), 7.23-7.25 (d, *J* = 8.0, 1H), 7.69-7.73 (d, *J* = 7.6, 1H), 8.41-8.43 (d, *J* = 8.4, 1H), 8.50-8.52 (d, *J* = 8.0, 1H), 8.56-8.58 (d, *J* = 7.2, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 12.5, 17.5, 22.5, 23.2, 26.6, 28.3, 29.3, 30.5, 31.6, 31.8, 34.6, 34.7, 35.4, 35.5, 35.7, 39.3, 39.6, 39.9, 41.5, 41.9, 46.5, 53.5, 53.8, 67.0, 68.4, 71.9, 73.0, 115.1, 122.9, 125.9, 126.1, 130.0, 130.5, 131.5, 132.9, 156.0, 164.6, 165.0. MALDI-TOF-MS calcd for $C_{45}H_{62}N_4O_8$: 786.46; found: 787.47$[M+H]^+$. Anal. calcd for $C_{45}H_{62}N_4O_8$: C 68.68, H 7.94, N 7.12; found: C 68.80, H 8.01, N 7.08.

**N-(2-ethylcarbamoyl-ethyl)-ethylcarbamoyl-carbamic acid tert-butyl ester-4-morpholin-1, 8-naphthalimide (2)** A mixture of **1** (1.0 g, 2.52 mmol), 3-*t*-butoxycarbonylamino-propionic acid (0.57 g, 3.02 mmol), dicylohexylcarbodiimide (DCC) (0.62 g, 3.02 mmol), 1-hydroxybenzotriazole (HOBt) (0.41 g, 3.02 mmol) and $Et_3N$ (0.40 mL, 3.02 mmol) in $CH_2Cl_2$ (100 mL) was stirred for 48 h under nitrogen atmosphere. The reaction mixture was concentrated *in vacuo* to give crude compound, which was purified by column chromatography ($SiO_2$; $CHCl_3$ / MeOH = 50:1-5:1) to give **2** (1.1 g, 76.9%) as a yellow solid. Mp: 209-211ºC. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.42 (s, 9H), 2.27-2.29 (t, *J* = 5.2, 2H), 2.35-2.37 (t, *J* = 5.2, 2H), 3.27-3.30 (t, *J* = 4.4, 4H), 3.37-3.45 (m, 4H), 3.65-3.69 (dd, *J* = 5.6, 2H), 4.02-4.04 (t, *J* = 4.4, 4H), 4.38-4.41 (t, *J* = 5.2, 2H), 5.29 (br, s, 1H), 6.62 (br, s, 1H), 6.74 (br, s, 1H), 7.23-7.25 (d, *J* = 8.0, 1H), 7.70-7.74 (t, *J* = 7.2, 1H), 8.43-8.45 (d, *J* = 8.8, 1H), 8.51-8.53(d, *J* = 8.0, 1H), 8.57-8.59(d, *J* = 7.2, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 28.4, 35.6, 35.8, 36.4, 36.9, 39.3, 39.9, 45.8, 53.5, 67.0, 115.0, 116.6, 122.9, 126.0, 126.2, 130.0, 130.6, 131.5, 132.9, 156.1, 164.7, 165.2, 171.6, 172.2. MS (ESI) calcd for $C_{29}H_{37}N_5O_7$: 567.27; found: 568.4$[M+H]^+$. Anal. calcd for $C_{29}H_{37}N_5O_7$: C 61.36, H 6.57, N 12.34; found: C 61.29, H 6.52, N 12.41.

**N-ethyl-3-(2-ethylcarbamoyl)-propionamide-4-morpholin-1, 8-naphthalimide (3)** To the mixture of **2** (1.0 g, 1.76 mmol) in MeOH (80 mL), 4M HCl (10.0 mL, 40 mmol) in MeOH was added dropwise at temperature of 0 ºC. The reaction mixture was allowed to room temperature for 24 h, followed by dropwise addition of 4M LiOH (20.0 mL, 80 mmol, THF/$H_2O$). The aqueous phase was extracted with $CHCl_3$ for three times. The $CHCl_3$ extracts were pooled, washed with water, dried over anhydrous $Na_2SO_4$ and evaporated *in vacuo*. The crude compound was purified by column chromatography ($SiO_2$; $CHCl_3$ / MeOH = 5:1-2:1) to give **3** (0.60 g, 73.2%) as a yellow solid. Mp:147-149 ºC. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.87 (br, s, 2H), 2.27-2.33 (m, 4H), 2.96-2.99 (t, *J* = 5.6, 2H), 3.27-3.29 (t, *J* = 4.4, 4H), 3.40-3.45

(dd, *J* = 6.0, 2H), 3.63-3.67 (dd, *J* = 5.2, 2H), 4.02-4.04 (t, *J* = 4.4, 4H), 4.36-4.39 (t, *J* = 5.2, 2H), 6.67 (br, s, 1H), 7.22-7.24 (d, *J* = 8.0, 1H), 7.69-7.73 (t, *J* = 7.6, 1H), 8.42-8.44 (d, *J* = 8.4, 1H), 8.51-8.53 (d, *J* = 8.0, 1H), 8.57-8.59 (d, *J* = 7.2, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* 35.6, 36.0, 38.4 39.1, 39.2, 39.7, 46.2, 53.5, 67.0, 115.0, 116.6, 122.9, 125.9, 126.2, 130.0, 130.5, 131.5, 132.9, 156.1, 164.6, 165.1, 172.2, 172.3. MS (ESI) calcd for $C_{24}H_{29}N_5O_5$: 467.22; Found: 468.3$[M+H]^+$. Anal. calcd for $C_{24}H_{29}N_5O_5$: C 61.66, H 6.25, N 14.98; found: C 61.78, H 6.31, N 15.02.

**N-(2-ethylcarbamoyl)-propionamide-3-choylethylimide-4-morpholin-1,8-naphthalimide Compound (B)** To a solution of cholic acid (1.31 g, 3.21 mmol) in dry THF (40 mL) was added compound **3** (1.5 g, 3.21 mmol), 1-hydroxybenzotriazole (HOBt) (0.43 g, 3.21 mmol) and $Et_3N$ (0.42 mL, 3.21 mmol) in THF (80 mL) and followed a THF solution (10 mL) of DCC (0.8 g, 3.85 mmol) after 10 minutes. The reaction mixture was stirred for 48 hours at room temperature and the dicyclohexyl urea formed was filtered. The solvent was removed and the residue was purified by column chromatography ($SiO_2$; $CHCl_3$ / MeOH = 100:1-30:1) to give compound **B** (1.2 g, 43.5%) as a yellow solid. Mp: 165-167 ºC. $^1$H NMR (400 MHz, $CDCl_3$): *δ* 0.65 (s, 3H), 0.87 (s, 3H), 0.98-0.99 (d, *J* = 6.0, 3H), 1.20-2.53 (m, 30H), 3.26-3.28 (t, *J* = 4.4, 4H), 3.41-3.52 (m, 6H), 3.63-3.64 (d, *J* = 4.8, 2H), 3.81 (br, s, 1H), 3.93 (br, s, 1H), 4.02-4.04 (t, *J* = 4.4, 4H), 4.34-4.36 (t, *J* = 4.4, 2H), 7.09 (br, s, 2H), 7.21-7.23 (d, *J* = 8.0, 1H), 7.67-7.71 (t, *J* = 8.4, 1H), 8.38-8.40 (d, *J* = 8.4, 1H), 8.47-8.49 (d, *J* = 8.0, 1H), 8.53-8.54 (d, *J* = 7.2, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* 12.4, 17.5, 22.5, 26.6, 27.6, 34.7, 35.3, 35.8, 38.9, 39.6, 39.8, 41.5, 41.9, 46.0, 46.4, 53.4, 67.0, 71.8, 72.9, 115.1, 116.5, 122.9, 125.9, 130.5, 131.4, 156.0, 164.6, 165.0, 172.3. MALDI-TOF-MS calcd for $C_{48}H_{67}N_5O_9$: 857.49. Found: 858.33$[M+H]^+$ . Anal. calcd for $C_{48}H_{67}N_5O_9$: C 67.19, H 7.87, N 8.16; found: C 67.49, H 7.92, N 8.08.

**Synthesis of oleic acid-capped - UCNPs.**

Various UCNPs were prepared by a modified hydrothermal process**.** [2] In a typical synthesis, NaOH (1.2 g, 30 mmol), water (9 mL), ethanol (15 mL) and oleic acid (20 mL) were mixed under agitation to form a homogeneous solution. Then 0.6 mmol (total amounts) of rare-earth chloride (1.2 mL, 0.5 mol/L $LnCl_3$, UCNPs-Red, Ln: 78 mol% Y + 20 mol% Yb + 2 mol % Er; UCNPs-Green: 73 mol % Y + 25 mol % Yb + 2 mol % Er; UCNPs-Blue: 79 mol % Y + 20 mol % Yb + 1 mol %Tm)[3] aqueous solution was added under magnetic stirring. Subsequently, 1.0 M aqueous NaF solution (4 mL) was added dropwise to the above solution.

The mixture was agitated for about 10 min, then transferred to a 50 mL autoclave, sealed, and hydrothermally treated at 160 °C for 8 h. The system was cooled to room-temperature naturally, and the products were deposited at the bottom of the vessel. Cyclohexane was used to dissolve and collect the products. The products were subsequently deposited by adding ethanol to the sample-containing cyclohexane solution. The resulting mixture was then centrifuged to give powder. Pure powders could be obtained by purifying the samples with ethanol several times to remove oleic acid, sodium oleic, and other remnants.

**Techniques:** UV-visible spectra were recorded on an UV-vis 2550 spectroscope (Shimadzu). Fourier transform infrared (FT-IR) spectra were performed using an IRPRESTIGE-21 spectroscope (Shimadzu) with KBr pellets. TEM was recorded on a JEOL JEM-2011 and a JEOL JEM-2100F apparatus, operating at 200 KV and fitted with an EDX analysis accessory. The sample was prepared by putting the gel on a carbon-coated copper grid stained with phosphotungstic acid (2.0 wt% aqueous) and freeze dried for 48 h. X-ray diffraction (XRD) measurements were made with a Bruker D4 X-ray diffractometer using Cu Kα radiation ($\lambda$ = 0.15418 nm). Thermogravimetric analysis (TGA) curves were recorded on a DTG-60H (Shimadzu) at a heating rate of 10 °C/min. CLSM experiments were performed on an OLYMPUS IX81 confocal laser scanning microscope equipped with a 60x oil-immersion objective lens. Excitation at 405 nm was carried out with a semiconductor laser. Emission was collected from 450 to 550 nm. An organogel spot was prepared on a dish for CLSM observation. Sonication treatment of a sol was performed in a KQ-500DB ultrasonic cleaner (max. power, 500 W, 40 KHz, Kunshang Ultrasound Instrument Co, Ltd., China). Freezing dry was performed in a FDU-1200 Freeze Dryer (Tokyo Rikakikai, Japan) with the trap temperature of -45 ºC.

Rheological measurements were carried out on freshly prepared gels using a controlled stress rheometer (MCR301, Anton Paar, Austria). Parallel plate geometry of 25 mm diameter and 0.3 mm gap was employed throughout dynamic oscillatory work. The following tests were performed: increasing amplitude of oscillation up to 100% apparent strain shear (kept a frequency of 1 $rads^{-1}$) and frequency sweeps at 25 ºC (from 62.8-0.25 $rads^{-1}$, 0.1% strain).

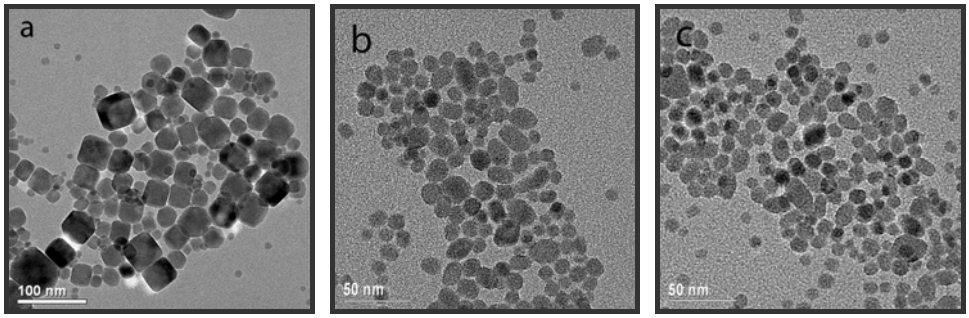



**Figure S1** TEM images of UCNPs; (a) α-$NaYF_4$: 20 mol%Yb, 2 mol%Er (UCNPs-red); (b) α-$NaYF_4$: 25 mol%Yb, 2 mol%Er (UCNPs-green); (c) α-$NaYF_4$: 21 mol%Yb, 1 mol%Tm (UCNPs-blue).

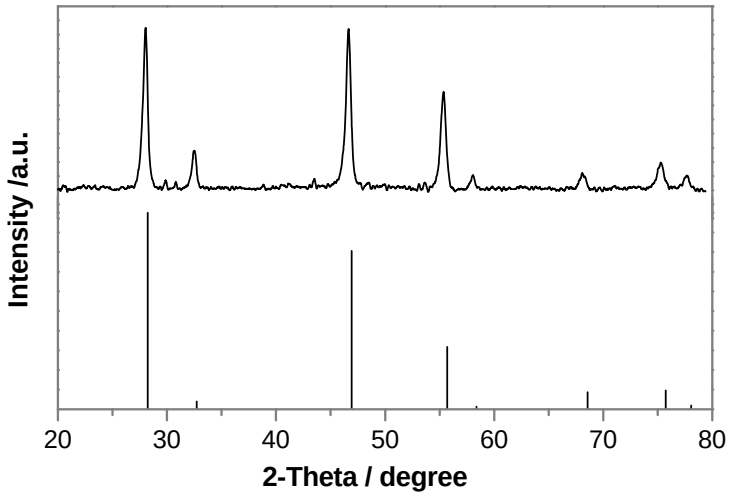



**Figure S2** XRD patterns of the as prepared UCNPs-red. The standard patterns of cublic (JCPDS card 77-2042) phase of $NaYF_4$ is also supplied. These samples have the dominant cubic phase.

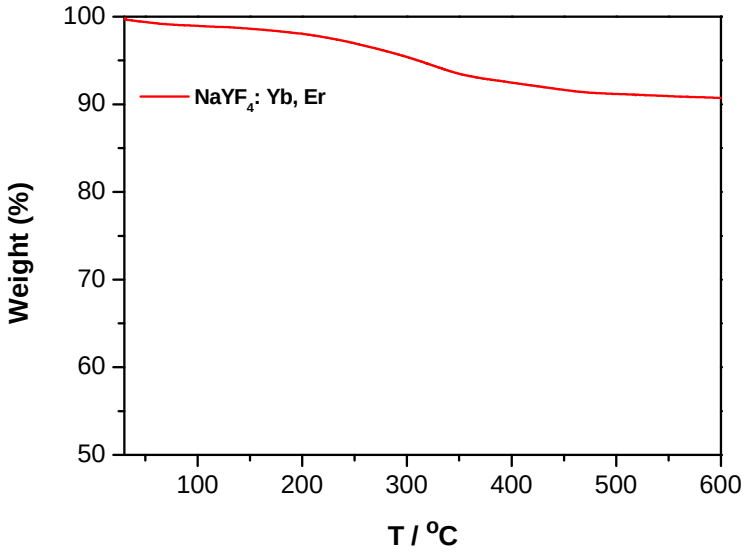



**Figure S3** TGA curves of the as prepared UCNPs-red. To evaluate the ligand content in as-prepared UCNPs sample, thermogravimetric analysis (TGA) was performed. TGA curves show two weight loss stages in the range of 30 to 600 °C. The first weight loss stage in the temperature range of 30-200 °C is due to the loss (1-1.2 wt %) of absorbed water from the sample. The second stage from 200 to 600 °C is attributed to the combustion of the organic groups in the samples, and the weight loss in this stage reflects the ligand content. It is clear that the content of oleic acid ligands in as-prepared UCNPs-red is about 9.08 wt %.

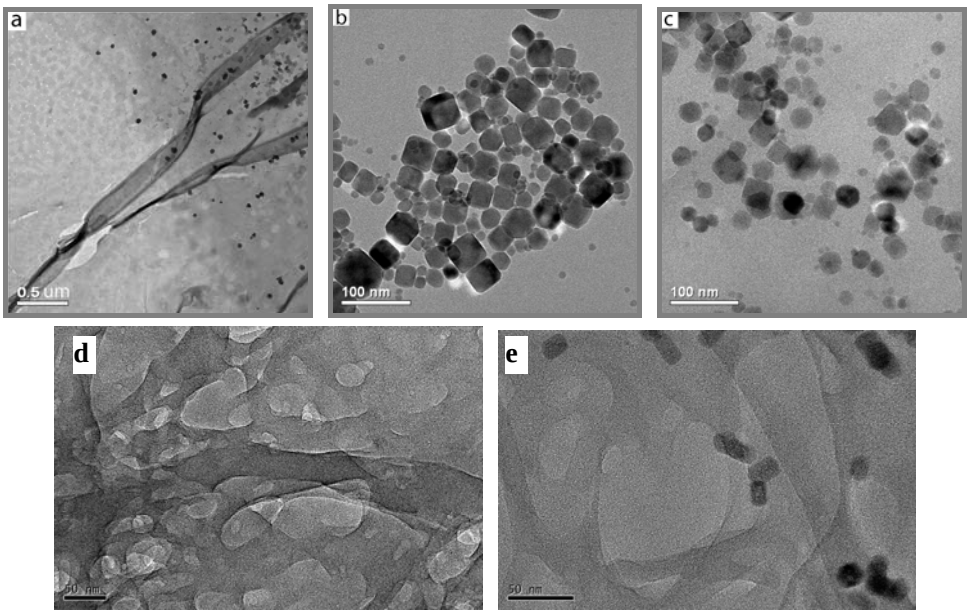



**Figure S4.** TEM images of a) **B** xerogel (C = 2.3 × $10^{-2}$ M, stained with 2.0 wt% aqueous phosphotungstic acid); b) UCNPs-Red; c) **B**-UCNPs-Red (C = 2.3 × $10^{-2}$ M, 1.5 wt% of UCNPs); d) **B** xerogel without stain; e) **B**-UCNPs-Red (C = 2.3 × $10^{-2}$ M, 1.0 wt% of UCNPs). All samples are drop casted from n-hexanol on carbon-coated TEM grids. Samples a-c were measured by JEM-2011; while d, e were measured by JEM-2100F (scale bar, 50 nm).

**Table S1.** Gelation ability of **A** and **B** at the room temperature

| **Solvent** | **A** -CGC (mg ml $^{-1}$) | **B** -CGC (mg ml $^{-1}$) |
|---|---|---|
| i-Propanol | S | PG |
| n-Propanol | P | S |
| n-Pentanol | S | CG (20) |
| n-Hexanol | S | CG (15) |
| n-Octanol | S | CG (25) |
| Dichloromenthane | P | PG |
| Chloform | S | S |
| Acetone | I | I |
| Cyclohexane | I | I |
| Acetonitrile | I | I |
| Ethyl acetate | I | I |
| p-Xylene | I | I |
| Tetrahydrofuran | OG (28) | CG (18) |
| 1-Methyl-2-pyrrolidone | S | S |

P = Precipitation; S = Solution; PG = Partial gel; CG = Clear gel; I = Insoluble.

**Table S2.** Gelation ability of **A** and **B** in presence of UCNPs

| **Solvent** | **UCNPs-A** | **UCNPs-B** |
|---|---|---|
| i-Propanol | S | PG |
| n-Propanol | S | S |
| n-Pentanol | CG | CG |
| n-Hexanol | CG | CG |
| n-Octanol | CG | CG |
| Dichloromenthane | P | PG |
| Chloform | S | S |
| Acetone | I | I |
| Cyclohexane | I | I |
| Acetonitrile | I | I |
| Ethyl acetate | I | I |
| p-Xylene | I | I |
| Tetrahydrofuran | CG | CG |
| 1-Methyl-2-pyrrolidone | S | S |

P = Precipitation; S = Solution; PG = Partial gel; CG = Clear gel; I = Insoluble. UCNPs-**A:** $C_{\mathbf{A}} = 3.2 \times 10^{-2}$ M, UCNPs/**A**/solvent = 4 mg/10 mg/0.4 ml; UCNPs-**B**: $C_{\mathbf{B}} = 2.3 \times 10^{-2}$ M, UCNPs/**B**/solvent = 4 mg/10 mg / 0.5 ml. All the samples were treated with ultrasound for 120 s (0.31 W cm$^{-2}$, 40 KHz) before gelation.

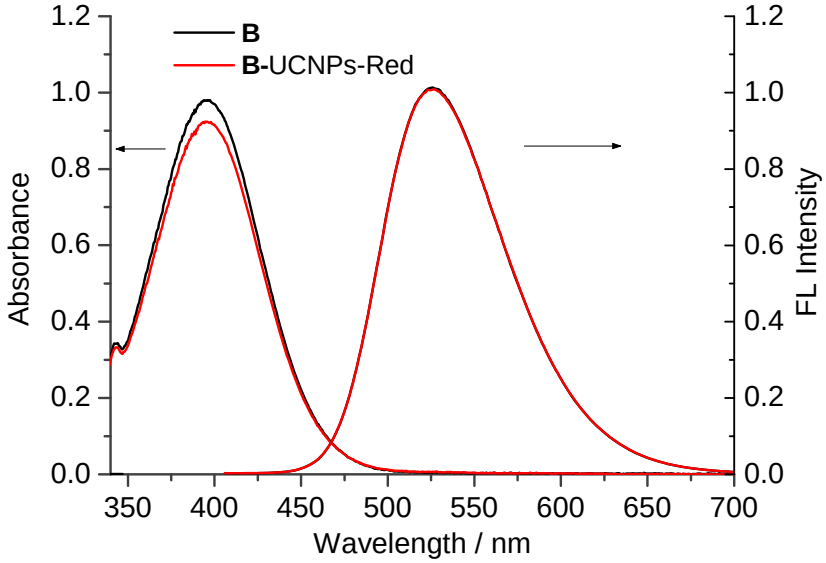



**Figure S5** Normalized absorption and fluorescence spectra of **B** (C = $1.0 \times 10^{-4}$ M, 25 ºC, 1 cm cell) and **B**-UCNPs-Red (λex = 390 nm, C = $1.0 \times 10^{-4}$ M, 1.5 wt % of UCNPs-Red, 25 ºC, 1 cm cell) in n-hexanol.

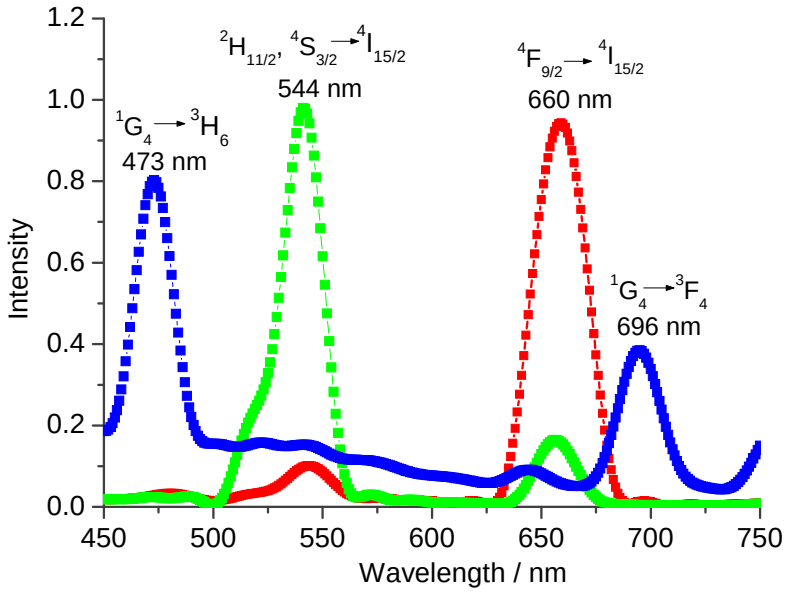



**Figure S6** Fluorescence spectra of UCNPs-Red (red line), UCNPs-Green (green line), UCNPs-Blue (blue line) (25 ºC, 1 cm cell, $\lambda_{ex}$ = 980 nm, power density = 50 W $cm^{-2}$) in n-hexanol.

## References

[1] J. C. Wu, T. Yi, T. M. Shu, M. X. Yu, Z. G. Zhou, M. Xu, Y. Zhang, J. T. Han, F.Y. Li, C. H. Huang, *Angew. Chem.* **2008**, *120*, 1079-1083.
[2] Wang, L. H.; Li, Y. D. *Chem. Mater.* **2007**, *19*, 727-734.
[3] F. Wang, X. Liu, *J. Am. Chem. Soc.* **2008**, *130*, 5642-5643.