

Conjugate and non-conjugate controls of sensitizer to enhance dye-sensitized upconversion luminescence

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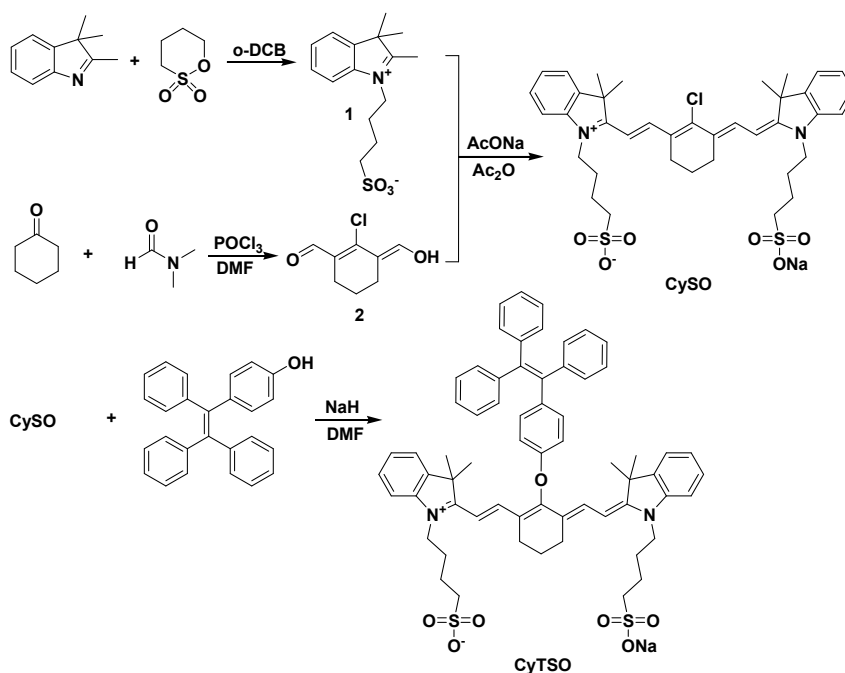
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Chemicals and instruments

All the chemicals and reagents used for synthesis are commercial available and used as received. The ¹H NMR and ¹³C NMR spectra were recorded at 25 °C using a Qone-WNMR-I 400 MHz spectrometer. Mass spectra were determined with a Waters Micromass Quattro Micro ESI mass spectrograph. The size and morphology of UCNPs were determined using a FEI Talo F200s transmission electron microscope (TEM). Powder X-ray diffraction (XRD) measurements were performed on a Bruker D8 diffractometer in the 2θ range from 10 to 80°. Fourier transform infrared (FTIR) spectra were measured in a Nicolet iS50 spectrometer from samples in KBr pellets. UV-vis absorption spectra were recorded on Shimadzu Uv-2600 spectrophotometer. Fluorescence measurements were carried out with an Edinburgh FLS920 fluorescence spectrometer. The upconversion luminescence was observed with a Fuxiang Optic NOVA-EX spectrometer.

Synthetic routes to NIR dyes CySO and CyTSO



Scheme S1 Synthetic routes to CySO and CyTSO.

Compound 1

Under N₂ atmosphere, 2,3,3-trimethylindolenine (0.80 g, 5.02 mmol) and 1,4-butylenesulfone (2.73 g, 20.0 mmol) were dissolved in *o*-DCB (20 mL) and refluxed at 120 °C for 12 h. When the temperature was cooled to 60 °C, acetone (50 mL) was added and stirring is continued for 2 min. After the mixture was cooled to room temperature, the precipitates were collected by centrifugation. Then, acetone (25 mL) was added into the filtrate to further precipitate the product and repeat for 3-5 times to afford a light pink solid (1.07 g, yield 72.3%). ¹H NMR(DMSO-d₆, 400 MHz) δ: 8.07 (t, J = 8.0 Hz, 1H), 7.86 (t, J = 8.0 Hz, 1H), 7.65-7.63 (m, 2H), 4.52 (t, J = 8.0 Hz, 2H), 2.89 (s, 3H), 2.54 (t, J = 4.0 Hz, 2H), 2.04-1.97 (m, 2H), 1.81-1.74 (m, 2H), 1.56 (s, 6H).

Compound 2

A solution of POCl₃ (14.8 mL) in DCM (14.8 mL) is added dropwise to the ice-cooled solution (5 °C) of DMF (18.4 ml) and DCM (18.4 ml). After stirring for 10 min, cyclohexanone (2.00 g, 20.4 mmol) was injected through a syringe. The reaction mixture was refluxed at 80 °C for 6 h, and then poured into ice water (100 mL). The precipitates was filtered, and washed by water (200 mL) to afford a bright yellow

solid (5.30 g, yield 75.2%).

Compound CySO

A three-necked flask was charged with compound 1 (10.3 g, 1.0 mmol), compound 2 (0.086 g, 0.50 mmol), AcONa (0.10 g, 1.22 mmol), and acetic anhydride (5 mL) under N₂ atmosphere. After stirring for 2 h at room temperature, the reaction mixture was added dropwise to ice-cooled ether. The precipitates were washed by ether and acetone, respectively. The crude product was dissolved in dichloromethane and filtered. The organic layer was evaporated to afford a green solid (0.20 g, yield 52.6%). ¹H NMR(DMSO-d₆, 400 MHz) δ: 8.28 (d, J = 6 Hz 2H), 7.65 (d, J = 4 Hz 2H), 7.51 (d, J = 4 Hz 2H), 7.45 (t, J = 8 Hz 2H), 7.30 (t, J = 8 Hz 2H), 6.40 (d, J = 8 Hz 2H), 4.25 (t, J = 8 Hz 4H), 2.76 (t, J = 8 Hz 4H), 2.56-2.53 (m, 6H), 1.88-1.80 (m, 4H), 1.80-1.75 (m, 4H), 1.70 (s, 12H). ¹³C NMR(DMSO-d₆, 100 MHz) δ: 172.56, 148.43, 143.52, 142.58, 141.54, 129.09, 126.76, 125.55, 122.90, 112.10, 102.19, 51.14, 49.42, 44.25, 27.96, 26.58, 26.34, 22.98, 20.92. MS (TOF): m/z Found: 727.4 [M+H], molecular formula C₃₈H₄₆ClN₂O₆S₂ requires 726.4.

Compound CyTSO

Under N₂ atmosphere, compound CySO (0.75 g, 1.0 mmol) was added to a mixture of 4-(1,2,2-triphenylethenyl)phenol (0.70 g, 2.0 mmol), 60% NaH (0.1 g, 2.5 mmol) and DMF (3mL). After stirring for 3 h at room temperature, the reaction was quenched by CO₂. The reaction mixture was added dropwise to ice-cooled ether. The precipitates were washed acetone for 3 times. The crude product was dissolved in dichloromethane and filtered. The organic layer was evaporated to afford a green solid (0.44 g, yield 41.0%). ¹H NMR(DMSO-d₆, 400 MHz) δ: 7.84 (d, J = 8 Hz 2H), 7.64 (d, J = 4 Hz 2H), 7.52-7.47 (m, 4H), 7.34 (t, J = 8 Hz 2H), 7.19-7.11 (m, 9H), 7.07-7.00 (m, 8H), 6.94-6.93 (m, 2H), 4.23 (s, 4H), 2.78 (s, 4H), 2.59-2.54 (m, 6H), 1.87-1.77 (m, 8H), 1.39 (s, 12H). ¹³C NMR(DMSO-d₆, 100 MHz) δ: 171.85, 162.68, 158.24, 143.69, 143.63, 142.55, 141.45, 141.11, 140.65, 140.18, 137.86, 133.21, 131.06, 130.97, 129.01, 128.29, 128.26, 128.13, 127.01, 126.99, 125.30, 122.80, 122.01, 114.35, 111.81, 100.84, 51.14, 48.98, 44.01, 27.96, 27.91, 26.49, 24.08, 22.92. MS (TOF): m/z Found: 1040.7 [M+H], molecular formula C₆₄H₆₅N₂O₇S₂ requires

1038.34.

Synthesis of NaYF₄:20%Yb³⁺,2%Er³⁺ core UCNPs

1 mmol LnCl₃ (Ln³⁺= Y³⁺, Yb³⁺, and Er³⁺) with the molar ratio of 78:20:2 in methanol (5 mL) was added into the mixture of 85% OA (7 mL) and 98% octadecene (15 mL). Under stirring, the solution was heated to 150 °C and kept for 30-40 min. When the reaction mixture was cooled down to 50 °C, 8 mL methanol solution containing NaOH (0.1 g) and NH₄F (0.16 g) were added. Keep the reaction at 50 °C for 30 min. Next, the mixture was heated to 110 °C to remove methanol and degassed at this temperature. Under N₂ atmosphere, the reaction mixture was heated to 300 °C and maintained for 1.5 h. Ethanol (20 mL) was added and the precipitate was collected by centrifugation. After centrifugal washing with ethanol and cyclohexane, the purified core nanoparticles were re-dispersed in cyclohexane (5 mL).

Synthesis of NaYF₄:20%Yb³⁺,2%Er³⁺@NaYF₄:10%Nd³⁺/10%Yb³⁺ (CS-UCNPs) core-shell UCNPs

1 mmol LnCl₃ (Ln³⁺= Y³⁺, Yb³⁺, and Nd³⁺) with the molar ratio of 80:10:10 in methanol (5 mL) 85% OA (7 mL) and 98% octadecene (15 mL) were added into a three-necked flask. After being stirred at 150 °C for 30-40 min, the reaction mixture was cooled down to 50 °C. Then cyclohexane solution (5 mL) of NaYF₄:20%Yb³⁺,20%Er³⁺ core nanoparticles along with methanol solution (8 mL) containing NaOH (0.1 g) and NH₄F (0.16 g) were added. The reaction mixture was aged at 50 °C for 30 min and degassed at 100 °C. Under N₂ atmosphere, the mixture was heated to 300 °C and maintained for 1.5 h. After cooling to room temperature, methanol (20 mL) was added to precipitate the product, which is centrifugal washing with ethanol and cyclohexane. The purified core-shell nanoparticles were re-dispersed in cyclohexane (10 mL).

Synthesis of dye-sensitized CS-UCNPs

OA-capped CS-UCNPs (15 mL) was added into ethanol (10 mL) containing HCl (0.5 mL). After ultrasonication for 30 min, the precipitate was collected by centrifugation and redispersed with DMF/ethanol (v/v= 5:1). Then the ligand free CS-UCNPs were mixed with different amount of cyanine dyes by ultrasonication for 1

min.

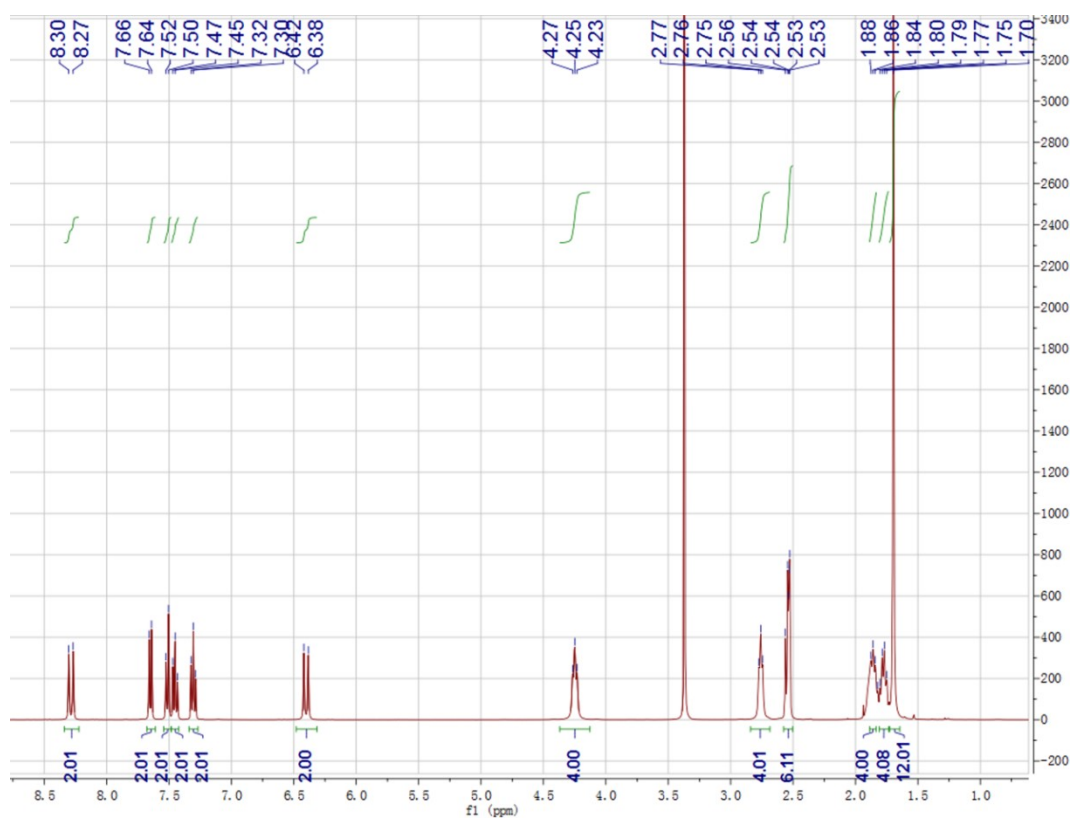


Fig. S1 ¹H NMR spectrum of CySO in DMSO-d₆.

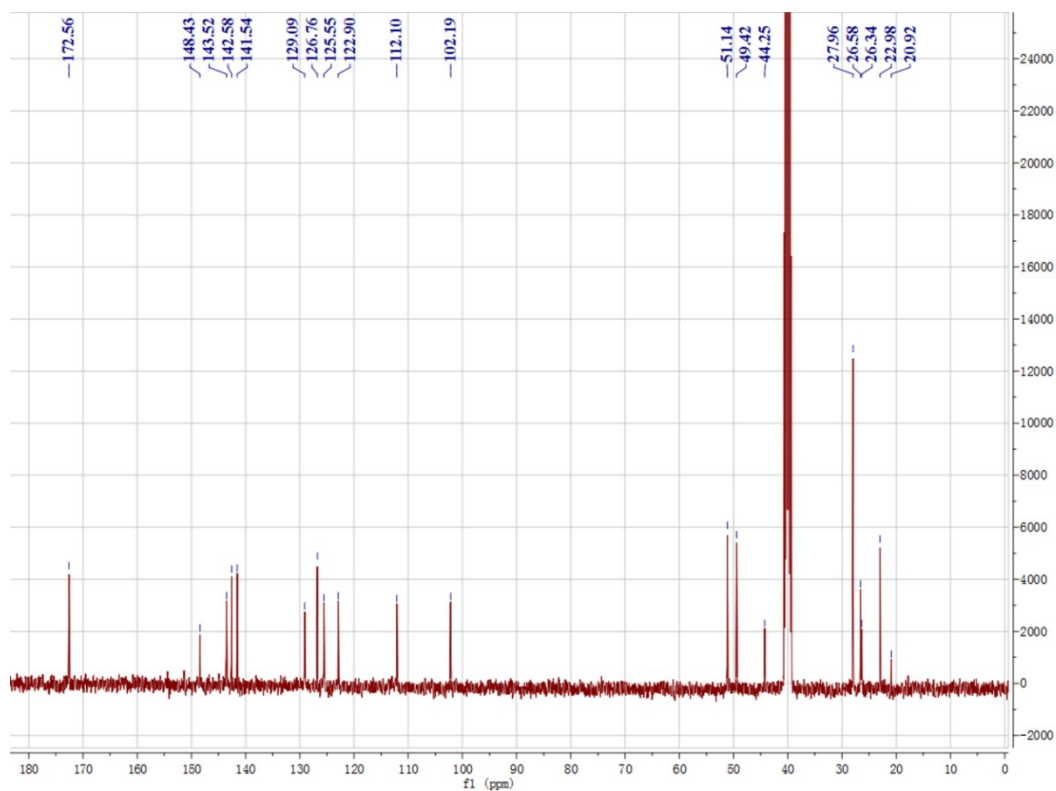


Fig. S2 ¹³C NMR spectrum of CySO in DMSO-d₆.

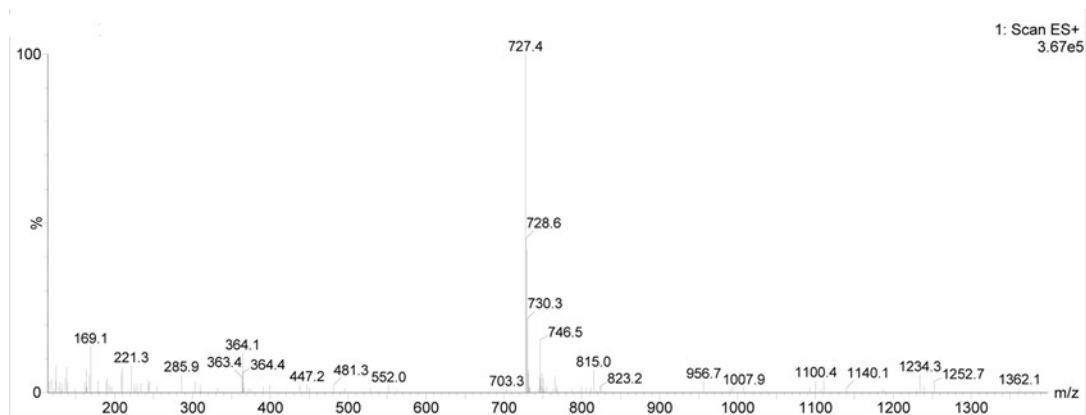


Fig. S3 Mass spectrometry spectrum of CySO.

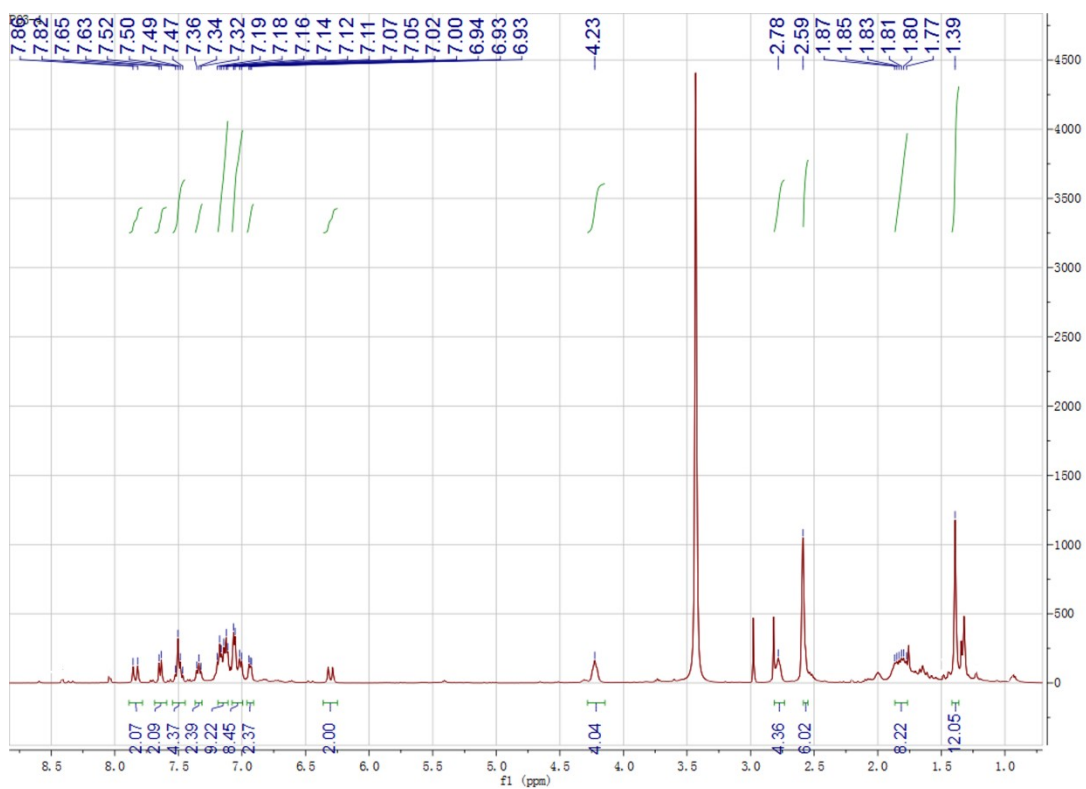


Fig. S4 ^1H NMR spectrum of CyTSO in DMSO-d_6 .

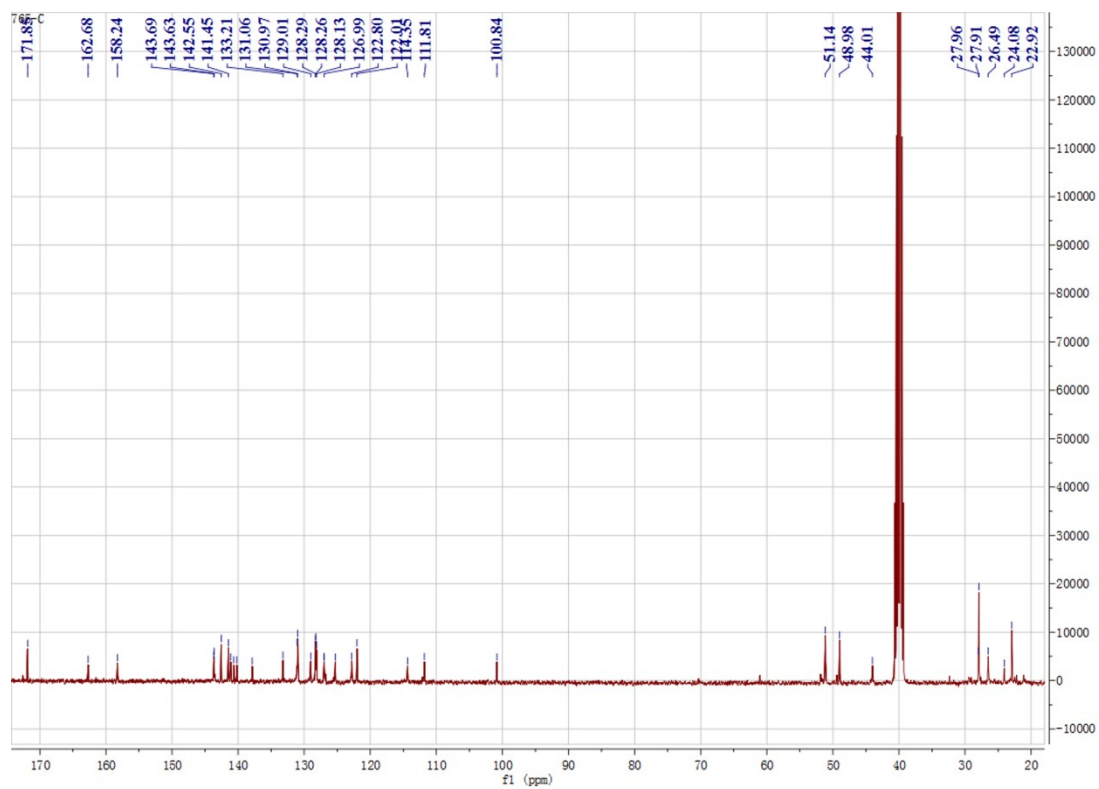


Fig. S5 ^{13}C NMR spectrum of CyTSO in DMSO-d_6 .

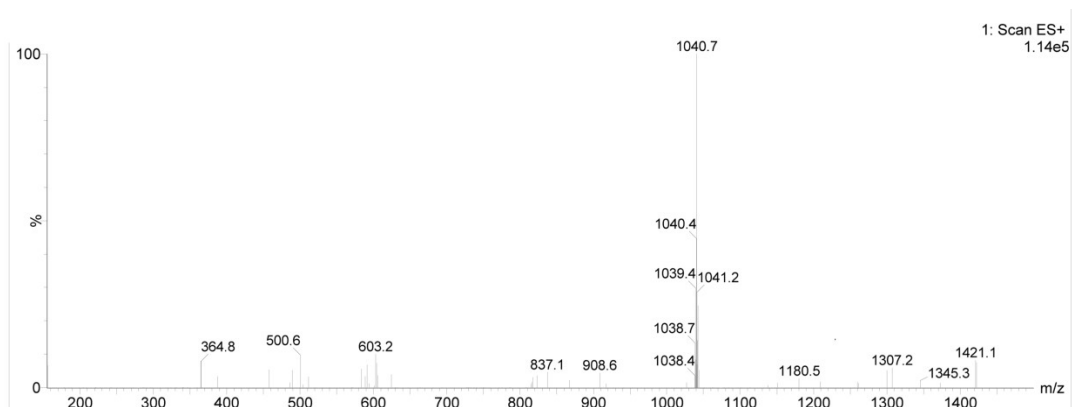


Fig. S6 Mass spectrometry spectrum of CyTSO.

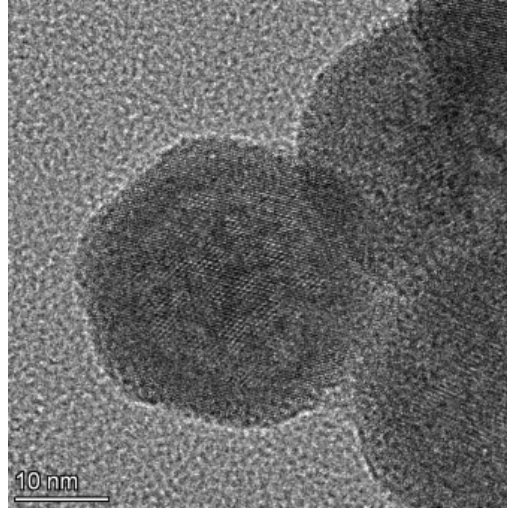


Fig. S7 TEM images of CS-UCNPs.

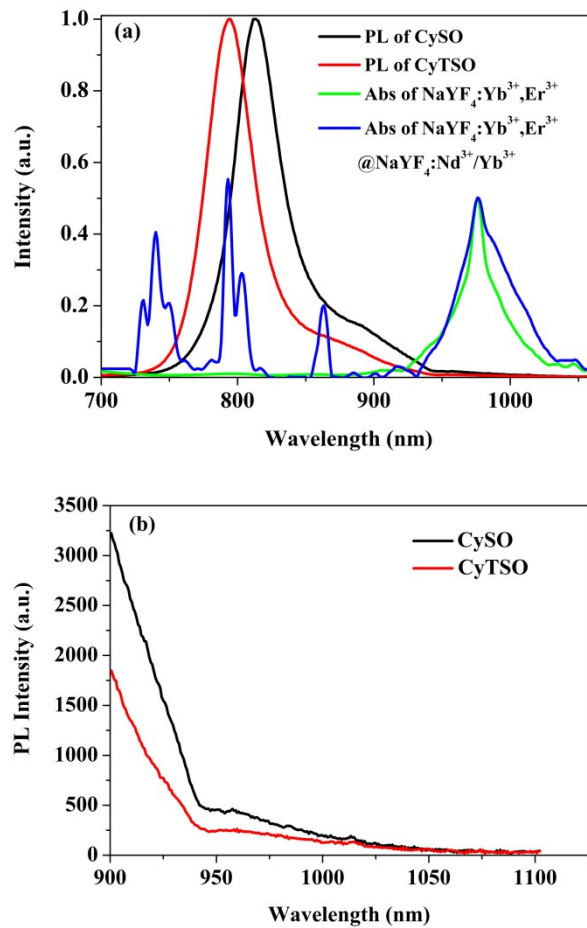


Fig. S8 (a) Absorption spectra of $\text{NaYF}_4:20\%\text{Yb}^{3+},2\%\text{Er}^{3+}$ and $\text{NaYF}_4:20\%\text{Yb}^{3+},2\%\text{Er}^{3+}@NaYF_4:10\%\text{Nd}^{3+}/10\%\text{Yb}^{3+}$ and PL spectra of CySO and CyTSO. (b) Locally amplified absorption spectra of CySO and CyTSO.

The overlap integral J is defined as (Eq.S1) [1]:

$$J = \frac{\int f_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda}{\int f_D(\lambda)d\lambda} \quad (S1)$$

where ε_A represent the molar absorptivity of the acceptor (CS-UCNPs) in unit of $M^{-1}cm^{-1}$, f_D is the emission spectrum of donor (cyanine dye), and λ is the wavelength in nm.

The Förster distance or Förster radius (R_0) is defined as (Eq.S2) [1]:

$$R_0^6 = \frac{9\ln 10}{128\pi^5 N_A} \cdot \frac{\kappa^2 \gamma_D}{n^4} \cdot J \quad (S2)$$

Where κ is an orientation factor between the acceptor (CS-UCNPs) and donor (cyanine dye) ($\kappa^2 = 2/3$), n is the refractive index, γ_D is quantum of the donor (cyanine dye), N_A is Avogadro's number, and J is the overlap integral.

The calculation procedures are as follows:

$$\rho_{NaYF_4} = 4.21 g/cm^3 = 4.21 \times 10^{-21} g/nm^3 \text{ (use as the density of CS-UCNPs)}$$

The average diameter of CS-UCNPs is 30 nm. $V_{NaYF_4} = 14130 nm^3$ (in a spherical approximation)

The average weight of CS-UCNPs is $5.949 \times 10^{-17} g$, So the calculated molecular weight is $6 \times 10^{23} \times 5.949 \times 10^{-17} = 3.57 \times 10^7 g/mol$.

The mass concentration of CS-UCNPs for absorption spectrum is 10 mg/mL (Fig. S8a), So the corresponding molar concentration is $2.8 \times 10^{-7} mol/L$.

The path length through the sample for absorption spectrum (i.e., the thickness of the cuvette) is 0.2 cm.

According to the Eq.S1, the calculated J values are $4.97 \times 10^{16} M^{-1} cm^{-1} \cdot nm^4$ for CySO/CS-UCNPs and $4.71 \times 10^{16} M^{-1} \cdot cm^{-1} \cdot nm^4$ for CyTSO/CS-UCNPs. According to the Eq.S2, the obtained Förster distances are 2.13 nm for CySO/CS-UCNPs and 2.25 nm for CyTSO/CS-UCNPs.

Table S1 The results of J and R_0 .

	CySO	CyTSO
$\int fD(\lambda) d\lambda$	0.16142	0.3047
$\int fD(\lambda)\varepsilon_A(\lambda) \lambda^4 d\lambda$	8.0212×10^{-13}	1.4351×10^{-12}
J ($M^{-1} \cdot cm^{-1} \cdot nm^4$)	4.96915×10^{16}	4.70994×10^{16}
γ_D	11.1%	16.3%
R_0 (nm)	2.13	2.25

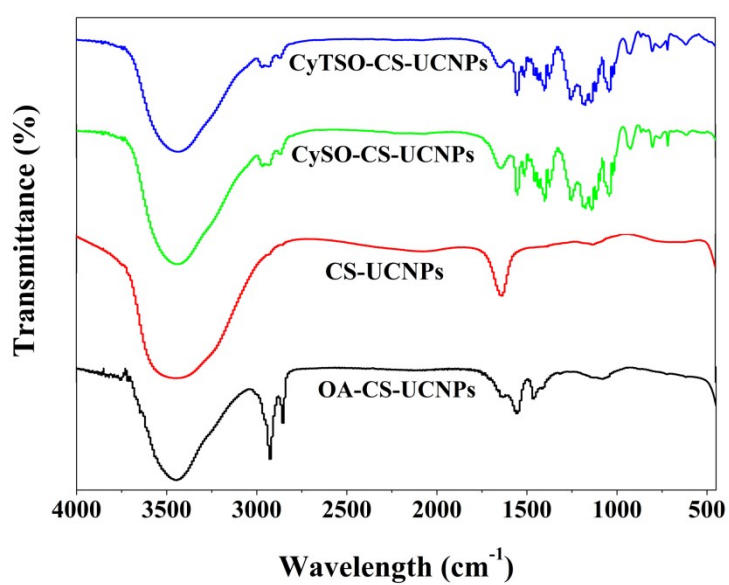


Fig. S9 FTIR of OA-capped CS-UCNPs, ligand free CS-UCNPs, and CySO and CyTSO sensitized CS-UCNPs.

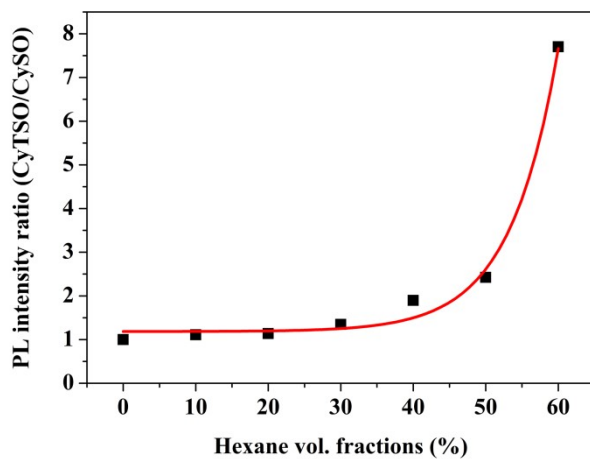


Fig. S10 PL intensity ratio of CyTSO and CySO (2×10^{-5} M) in acetone/hexane mixtures with different volume fractions of hexane.

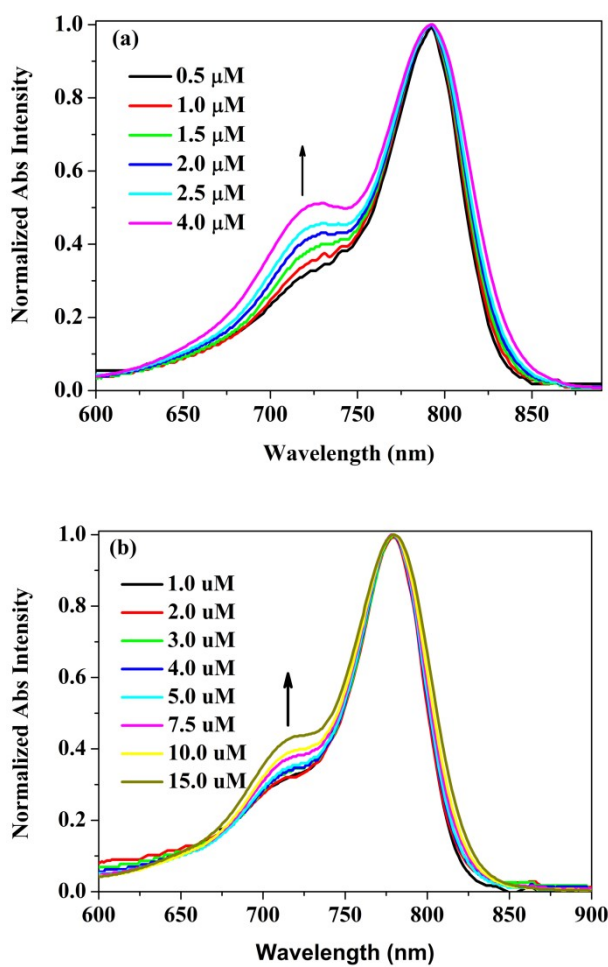
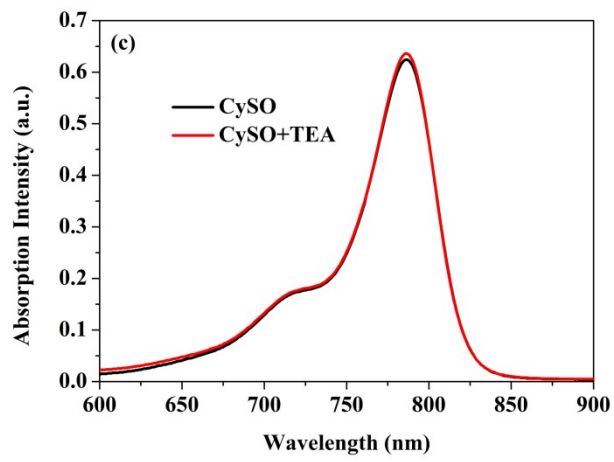
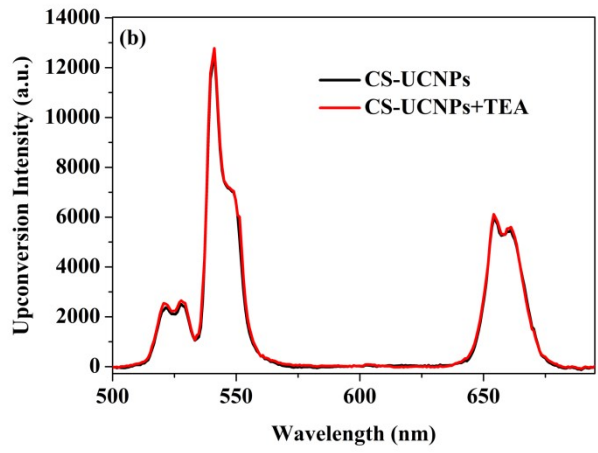
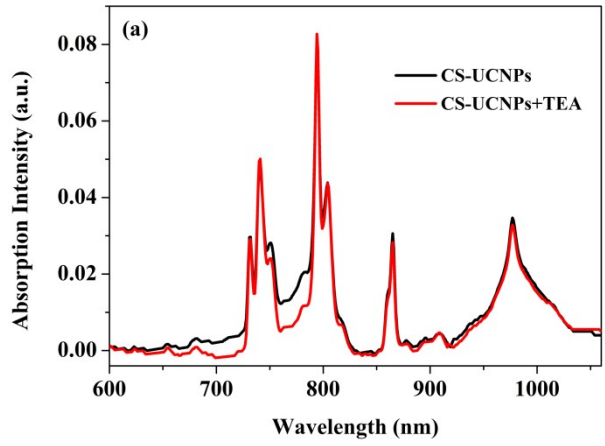


Fig. S11 Normalized absorption spectra of CySO and CyTSO attached on CS-UCNPs (1 mg/mL).



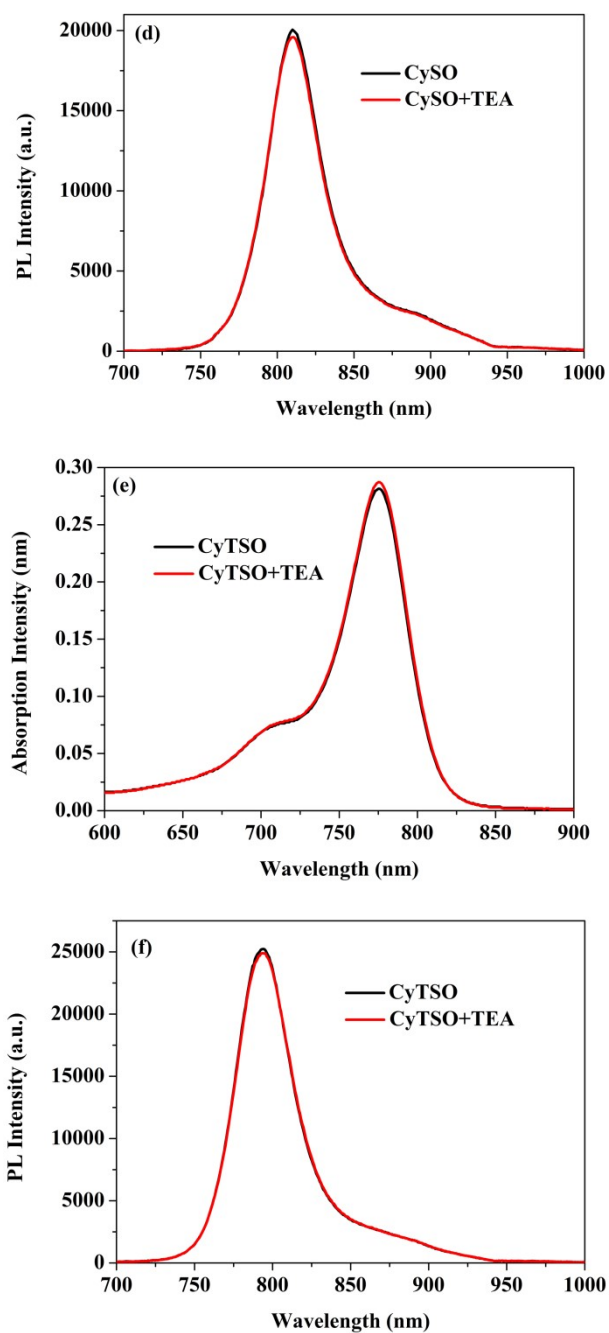


Fig. S12 Influences of TEA (0.36 M) on the absorption and PL spectra of ligand-free CS-UCNPs (10 mg/mL) (a, b), CySO (5.0 μ M) (c, d) and CyTSO (5.0 μ M) (e, f).

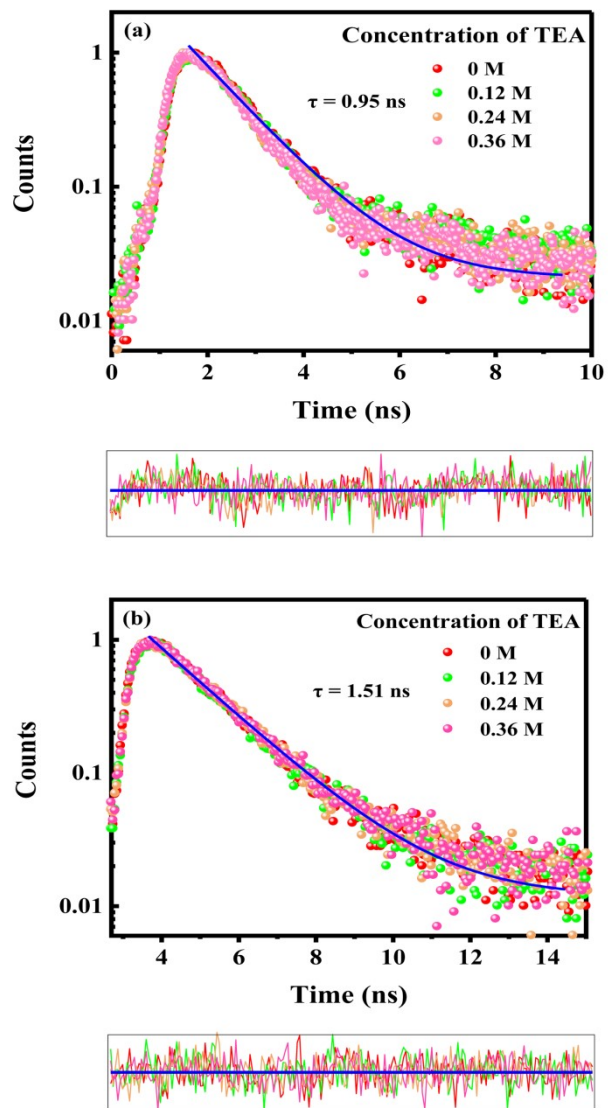
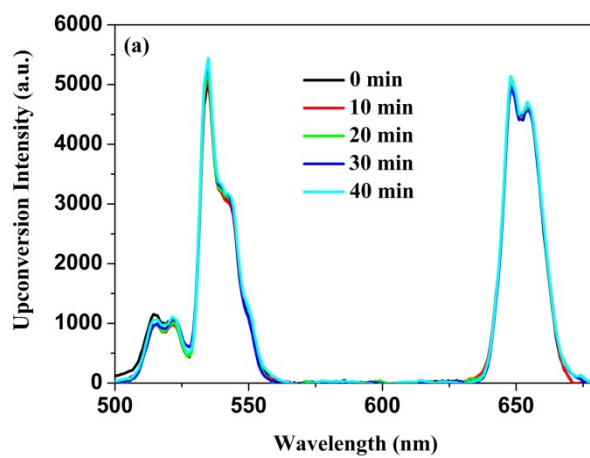


Fig. S13 Fluorescence decay curves of CySO (a) and CyTSO (b) with TEA as a function of concentration.



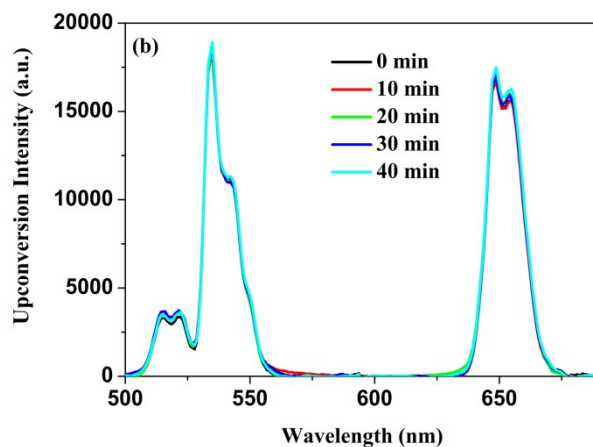


Fig.S14 Upconversion luminescence of CySO-sensitized CS-UCNPs (a) and CyTSO-sensitized CS-UCNPs (b) degassed for 0, 10, 20, 30 and 40 min with Ar.

References

- [1] X. D. Wang, R. R. Valiev, T. Y. Ohulchanskyy, H. Agren, C. H. Yang and G. Y. Chen, *Chem. Soc. Rev.*, 2017, **46**, 4150-4167.