

Supporting Information

Triethylamine effect on dye-sensitized upconversion luminescence and application in nanoprobe and photostability

Xiao-Bo Zhang^{1,†}, Zuo-Qin Liang^{1,†*}, Xu Yan¹, Mao-Mao Li¹, Chang-Qing Ye¹, Xiao-
Mei Wang¹, Xu-Tang Tao²

¹ *School of Materials Science and Engineering, Suzhou University of Science and Technology,*

Suzhou, 215009, China

² *State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China*

* Corresponding author.

† These authors contributed equally to this work.

E-mail: zuoqinliang@mail.usts.edu.cn (Z.-Q. Liang)

Tel.: (+86)512-68417291

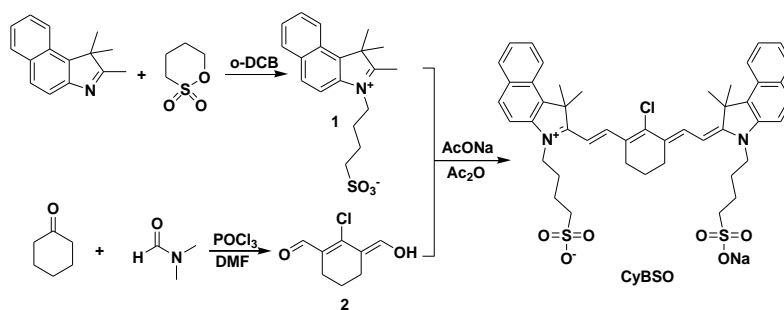
Experimental section

Chemicals

All the chemicals and reagents were used without further purification. Oleic acid (OA 85%), 1-octadecane (98%) and rare-earth chloride LnCl_3 ($\text{Ln}^{3+} = \text{Y}^{3+}$, Yb^{3+} and Er^{3+}) were obtained from Shanghai Aladdin Bio-Chem Technology Co. Ltd. 1,1,2-Trimethyl-1H-benzo[e]indole and 1,4-butane sultone were purchased from J&K Scientific Co. Ltd.

Characterization

The size and morphology of $\beta\text{-NaYF}_4:20\%\text{Yb}^{3+}, 2\%\text{Er}^{3+}$ were characterized by a FEI Talo F200s transmission electron microscopy (TEM). The powder X-ray diffraction (XRD) patterns were recorded by a Bruker D8 diffractometer in 2θ range from 10 to 80° . Zeta potential was obtained on a Malvern Zetasizer Nano instrument. The ^1H NMR and ^{13}C NMR spectra were recorded on a Qone-WNMR-I 400 MHz spectrometer at room temperature. Mass spectra were determined with a Waters Micromass Quattro Micro ESI mass spectrograph. Fourier transform infrared (FTIR) spectra were recorded by a Nicolet iS50 spectrometer from samples in KBr pellets. UV-vis absorption spectra were obtained on a Shimadzu Uv-2600 spectrophotometer. Fluorescence spectra were measured using an Edinburgh FLS920 fluorescence spectrometer. The upconversion photoluminescence spectra were performed on a Fuxiang Optic NOVA-EX spectrometer with a laser at 808 and 980 nm as the excitation source in air.



Scheme S1 Synthetic routes to CyBSO.

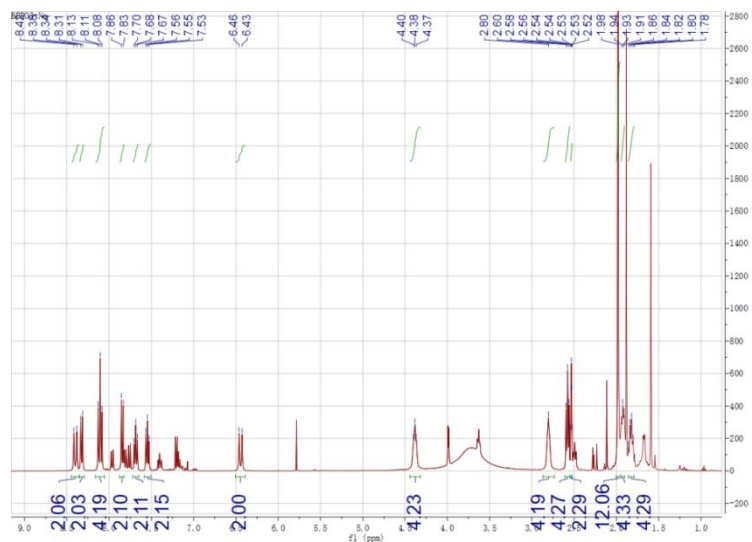


Fig. S1. ^1H NMR spectrum of CyBSO.

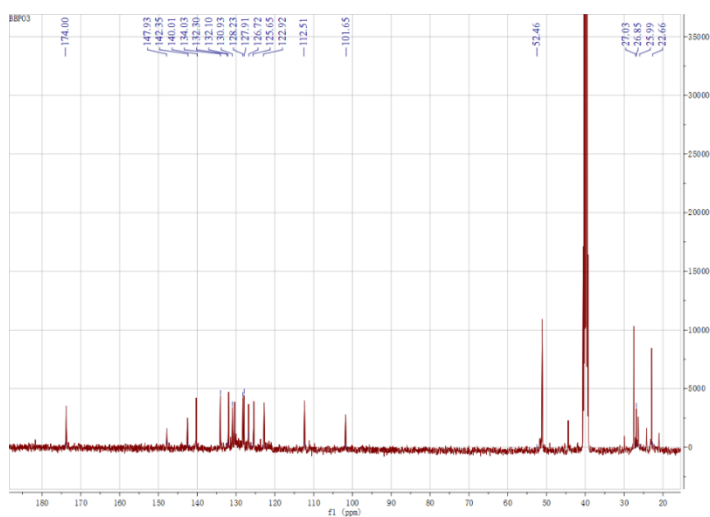


Fig. S2. ^{13}C NMR spectrum of CyBSO.

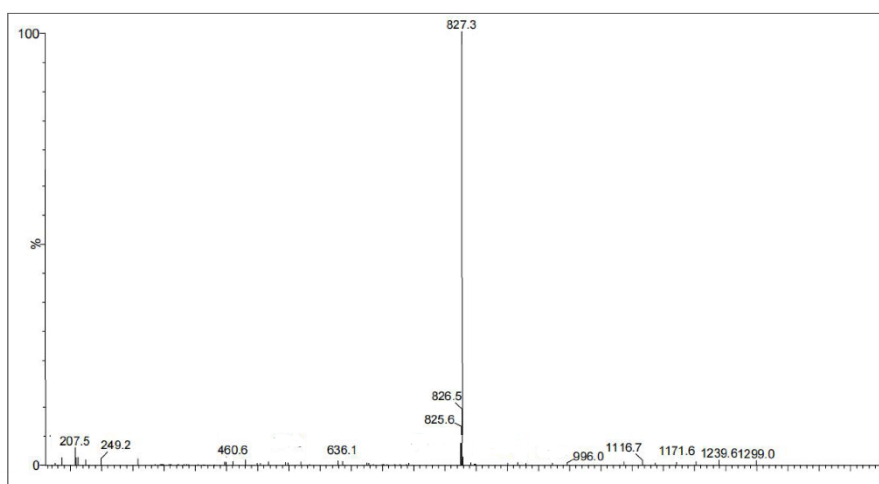


Fig. S3. Ms spectrum of CyBSO.

Synthesis

Synthesis of compound 1

A round-bottom was charged with 1,1,2-trimethyl-1H-benzo[e]indole (1.05 g, 5 mmol), 1,4-butane sultone (2.73 g, 20 mmol) and o-DCB (20 mL). Under N₂ atmosphere, the mixture was refluxed at 120 °C for 12 h. When the temperature was cooled to 60 °C, acetone (50 mL) was added and kept stirring for 2 min. The reaction mixture was cool to room temperature to afford a light blue precipitation (1.23 g, yield 71.2%). ¹H NMR (DMSO-d₆, 400 MHz) δ: 8.39 (d, J = 4 Hz, 1H), 8.31 (d, J = 4 Hz, 1H), 8.24 (d, J = 4 Hz, 2H), 7.81 (t, J = 8 Hz, 1H), 7.75 (d, J = 8 Hz, 1H), 4.64 (t, J = 8 Hz, 2H), 2.98 (s, 3H), 2.56 (t, J = 4.0 Hz, 2H), 2.10-2.03 (m, 2H), 1.85-1.82 (m, 2H), 1.78 (s, 6H).

Synthesis of compound 2

To a stirred 5 °C solution of DMF (18.4 ml) and DCM (18.4 ml) was added dropwise POCl₃ (14.8 mL) dissolved in DCM (14.8 mL). After stirring for 10 min, cyclohexanone (2.00 g, 20.4 mmol) was injected via syringe. The reaction mixture was heated to 80 °C for 8 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%).

Synthesis of CyBSO

Under N₂ atmosphere, compound 1 (0.35 g, 1 mmol), compound 2 (0.086 g, 0.5 mmol) and AcONa (0.10 g, 1.22 mmol) were added to a stirred solution of acetic anhydride (5 mL). After stirring for 2 h at room temperature, the reaction mixture was added dropwise to ice-cooled ether (40 mL). The precipitates were filtered, and then washed by ether and acetone for 2 times. The crude product was dissolved in dichloromethane and filtered. The filtrate was concentrated to give a green solid (0.38 g, yield 44.8%). ¹H NMR(DMSO-d₆, 400 MHz) δ: 8.40 (d, J = 8 Hz, 2H), 8.32 (d, J = 6 Hz, 2H), 8.11 (t, J = 8 Hz, 4H), 7.74 (d, J = 6 Hz, 2H), 7.68 (t, J = 8 Hz, 2H), 7.55 (t, J = 8 Hz, 2H), 6.65 (d, J = 6 Hz, 2H), 4.40-4.37 (m, 4H), 2.80 (s, 4H), 2.58 (t, J = 8 Hz, 4H), 2.54-2.52 (m, 2H), 1.98 (s, 12H), 1.94-1.91 (m, 4H), 1.86-1.78 (m, 4H). ¹³C NMR (DMSO-d₆, 400 MHz) δ: 174.00, 147.93, 142.35, 140.01, 134.03, 132.30, 132.10, 130.93, 128.23, 127.91, 126.72, 125.65, 122.92, 112.51, 101.65, 52.46, 27.03, 26.85,

25.99, 22.66. MS (TOF): m/z Found: 827.4 [M-Na+H]⁺; molecular formula C₄₆H₅₀ClN₂O₆S₂ requires 826.4 [M-Na]⁺.

Synthesis of oleic acid coated β -NaYF₄:20%Yb³⁺,2%Er³⁺ (UNs)

To a mixture solution of 85% OA (7 mL) and 98% 1-octadecene (15 mL) was added 1 mmol LnCl₃ (Ln³⁺= Y³⁺, Yb³⁺, and Er³⁺) with the molar ratio of 78:20:2. The suspension was heated to 150 °C and kept for 30-40 min. When the reaction mixture was naturally cooled to 50 °C, NaOH (0.1 g) and NH₄F (0.16 g) dissolved in methanol (4 mL) were added and keep the reaction at 50 °C for 30 min. After being stirred at 110 °C for 30 min to remove methanol, the solution heated to 320 °C and maintained for 1.5 h under Ar. Ethanol (20 mL) was added and the precipitate was collected by centrifugation. After centrifugal washing with ethanol and cyclohexane for 3 times, the collected nanoparticles were redispersed in cyclohexane.

Synthesis of CyBSO-sensitized UNs

OA-capped UNs (15 mL) was added into the solution containing ethanol (10 mL) and HCl (0.5 mL). After ultrasonication for 30 min, the ligand free UNs was collected by centrifugation and redispersed in DMF/ethanol (v/v= 5:1). Dye-sensitized UNs hybrids were obtained by mixing ligand free UNs with different concentration of cyanine dyes by ultrasound for 1 min.

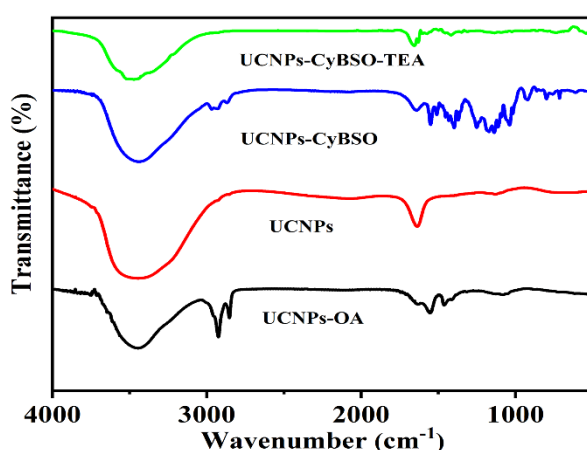


Fig. S4. FTIR of OA-capped UNs, ligand-free UNs, CyBSO-sensitized UNs, and CyBSO-sensitized UNs in large amount of TEA.

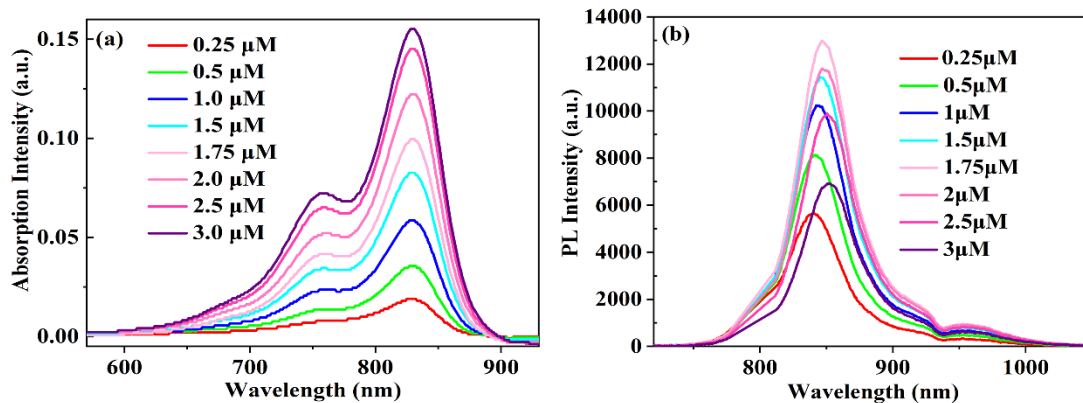


Fig. S5. Absorption (a) and PL (b) spectra of CyBSO with different concentrations in the presence of UNs (1 mg/mL).

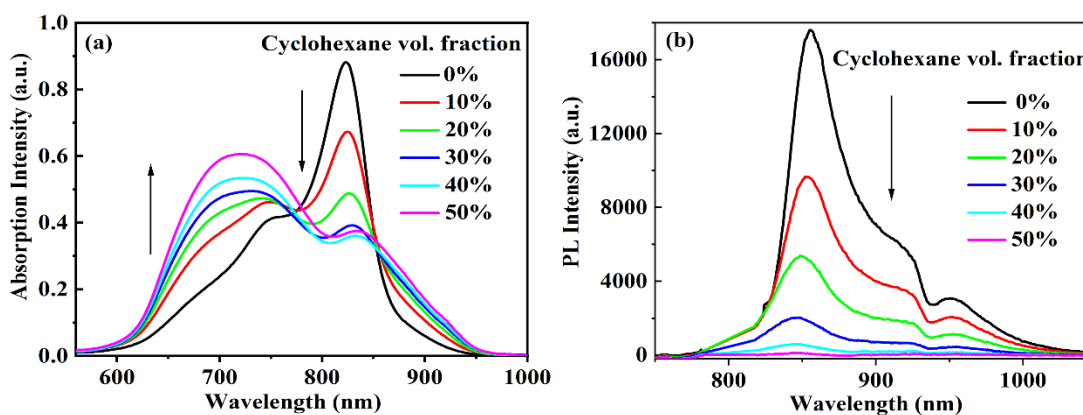


Fig. S6. Absorption (a) and PL (b) spectra of CyBSO (10 μM) in acetone/cyclohexane mixtures with different volume fractions of cyclohexane.

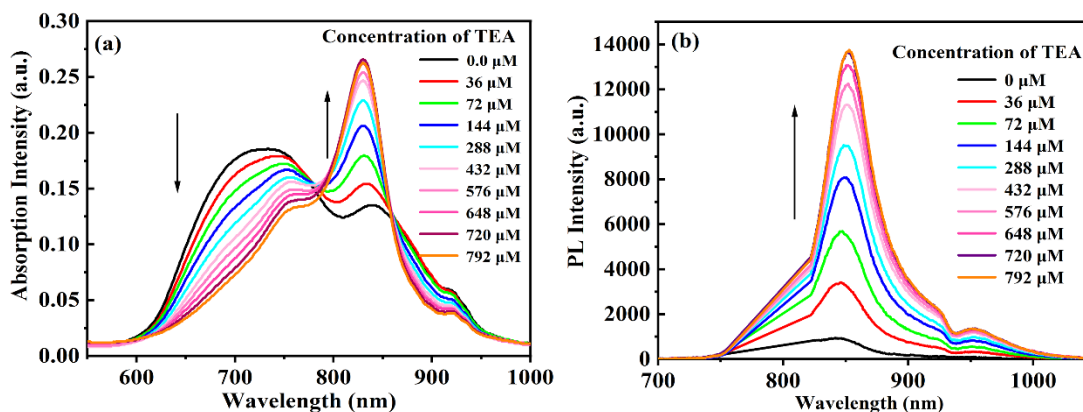


Fig. S7. Influences of TEA on the absorption (a) and PL (b) spectra of CyBSO in a 50% cyclohexane/acetone mixture (10 μM).

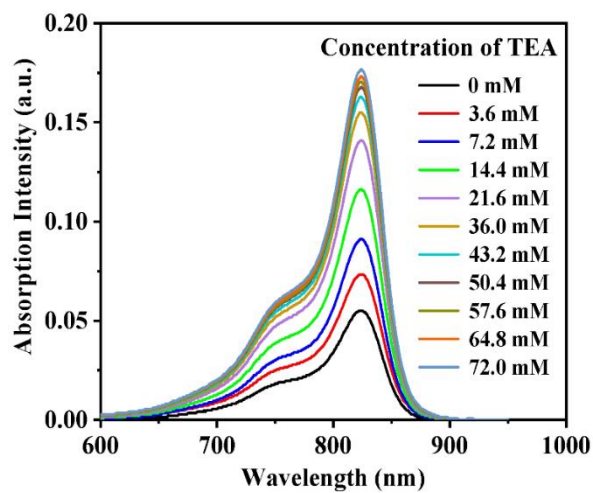


Fig. S8. Absorption spectra of the supernatant phase consisting of free CyBSO in ethanol with different concentration of TEA.

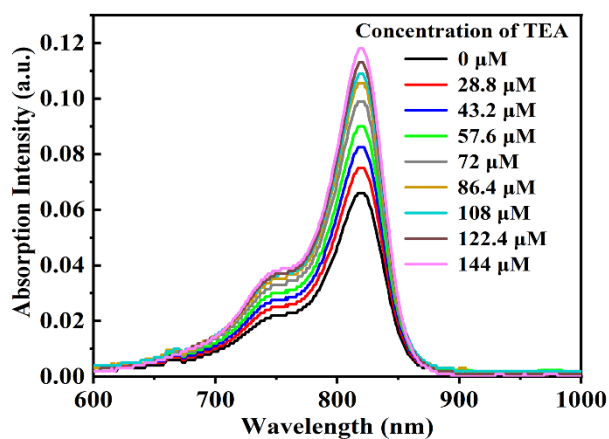


Fig. S9. Absorption spectra of the supernatant phase consisting of free CyBSO in methanol with different concentration of TEA.

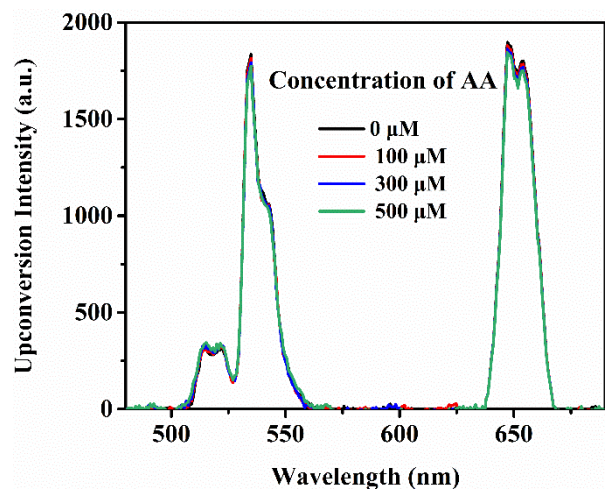


Fig. S10. Upconversion luminescence of the CyBSO (3.5 μM)-sensitized UNs (1 mg/mL) in heptanol without TEA after addition varying concentrations of AA.

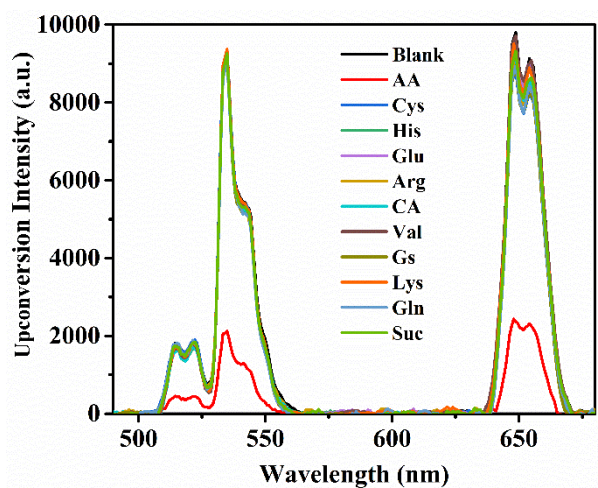


Fig. S11. Upconversion spectra of AA over interfering substances, including blank, AA, Cys, His, Glu, Arg, CA, Val, Gs, Lys, Gln and Suc (500 μM).

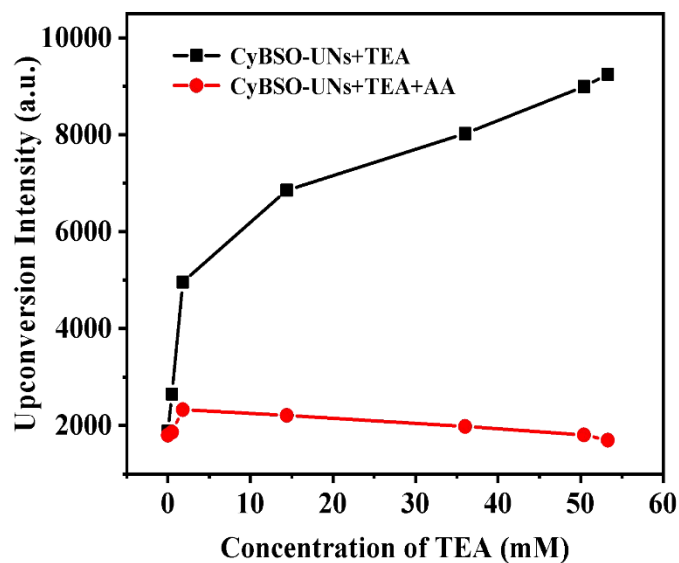


Fig. S12. Influence of AA (500 μM) on the upconversion luminescence of CyBSO (3.5 μM)-sensitized UNs at 541 nm in heptanol containing varied concentrations of TEA.

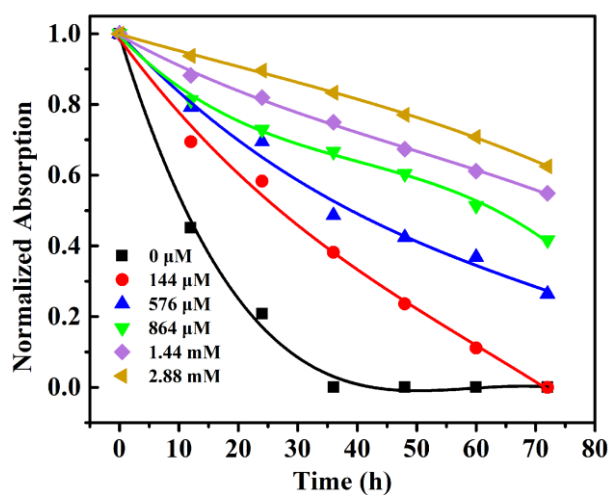


Fig.S13. Photostability of CyBSO (1.75 μM) in ethanol with varied concentrations of TEA under the irradiation of an incandescent lamp and without air protection.