

Supporting Information

Towards white-light generation through upconversion of low-power near-infrared photons

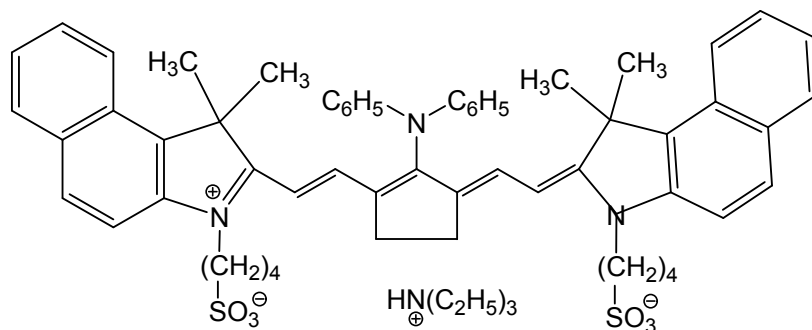
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1. Experimental

1.1. Materials

1.1.1. Dye synthesis.

The chemical structure of triethylammonium 4-(2-(2-(1,1-dimethyl-3-(4-sulfonatobutyl)-1H-benzo[e]indol-2(3H)-ylidene)ethylidene)-2-(diphenylamino) cyclopent-1-en-1yl)vinyl-1,1-dimethyl-1H-benzo[e]indol-3-ium-3-yl)butane-1-sulfonate (referred to further as dye 1859SL) is shown in Scheme 1.



Scheme S1.

The dye was synthesized as follows. A mixture of 4-(1,1,2-Trimethyl-1H-benzo[e]indole-3-ium-3-yl)butane-1-sulfonate (3.3 g, 9.6 mmol), N-((2-diphenylamino)-3-((phenylaminomethylene)cyclopent-1-en-1-yl)methylene) benzenaminiumtetrafluoroborate (2.12 g, 4.0 mmol), 15 ml acetic anhydride and 2.1 ml (15 mmol) triethylamine was refluxed for 7 min. After cooling the reaction mixture was treated by 300 ml of ethylacetate. In 3 h the precipitate was filtered off, washed by ethylacetate and dried yielding 3.2 g of crude dye. After recrystallizing from acetonitrile the yield was 1.52 g (36%). $T_{\text{decomp.}} 234-235.5^{\circ}\text{C}$; $\lambda_{\text{max}} 832 \text{ nm}$, $\epsilon=22.3 \times 10^4 \text{ l/mol}\cdot\text{cm}$ in methanol;

^1H NMR (400 MHz), δ , ppm (J, Hz): 1.29 (t, J=7.2 Hz, 9H, $\text{HN}^+(\text{CH}_2\text{CH}_3)_3$), 1.47 (s, 12H, $\text{C}(\text{CH}_3)_2$), 1.97-1.99 (m, 8H, $-\text{CH}_2-$), 2.88 (t, J=6.4 Hz, 4H, $-\text{CH}_2\text{SO}_3^-$), 2.99 (s, 4H, $-\text{CH}_2-\text{CH}_2-$, cycle), 3.19 (q, J=7.2 Hz, 6H, $\text{HN}^+(\text{CH}_2\text{CH}_3)_3$), 4.15 (t, J=5.6 Hz, 4H, N^+CH_2-), 5.9 (d, J=13.6 Hz, 2H, CH_α chain), 7.11 (t, J=7.2 Hz, 2H, ArH), 7.31-7.56 (m, 15H, ArH), 7.74 (d, J=13.6 Hz, 2H, CH_β chain), 7.86-8.06 (m, 6H, ArH); $\text{C}_{63}\text{H}_{74}\text{N}_4\text{O}_6\text{S}_2$ (1047.55); found, %: C 71.92; H 7.46; S 6.16; calcd, %: C 72.24; H 7.12; S 6.12.

NMR measurements were carried out on Varian *GEMINI 2000* spectrometer with ^1H frequencies of 400.07 MHz.

1.1.2. Sample preparation

Erbium(III) chloride hexahydrate and anhydrous calcium chloride were obtained from Sigma-Aldrich. Aqueous solutions of 1859SL of the required concentration were prepared in distilled water. Mixtures of 1859SL and $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ or 1859SL and CaCl_2 have been prepared by addition of a certain amount of the inorganic salt powder to the solution followed by treatment of the solution mixture in an ultrasound bath. Films were prepared on microscopy glass substrates via drop-casting.

1.2. Methods

Absorption spectra were recorded using an AvaSpec-2048 single beam and an OLIS Cary 14 double beam spectrophotometers. Solutions were measured using a 10 mm quartz cuvette; pure solvent was used as a reference. Photoluminescence (PL) spectra were recorded using an AvaSpec-2048 and a SPEX Fluorolog 1680 spectrometers. In case of AvaSpec-2048, a halogen lamp (500 W) was used as an excitation source, combined with specific filters (SZS-26 + IKS-1) that cut off the required excitation spectral bands. In case of SPEX Fluorolog 1680, light from a Xenon lamp was used as an excitation source which was directed through a double monochromator to select the excitation wavelength. The light was directed at the sample and the fluorescence of the sample was collected at a right-angle to the excitation light (dilute solutions) or in a front-face geometry (solid state samples). The fluorescence signal was directed through a double monochromator and detected using a PMT. The transmission wavelength of the second monochromator was scanned while the response of the PMT is measured giving a fluorescence spectrum. In order to confirm the absence of artefacts, the spectra were re-measured at a specific excitation wavelength using different excitation sources (Xe-lamp and Ti-sapphire laser with the incident laser power controlled by two polarizers crossed at an adjusted angle and placed in front of the sample).

Emission lifetimes were measured by a single photon counting regime using a Life Spec-II spectrometer (Edinburgh Instruments Ltd.) with ≈ 100 ps time resolution. A picosecond pulsed diode laser with a specific wavelength of 670 nm was used as an excitation source. The pulse repetition rate was up to 20 MHz and pulse width was 50 ps. Before and after each fluorescence lifetime measurement, the instrument response function (IRF) was measured using a scattered laser light from a diluted suspension of microparticles. The width of the resulting IRF was determined to be ~ 200 ps (FWHM). The measured sample emission was detected with a delayed gate pulse, and then the signal was dispersed in a monochromator and focused onto a single photon avalanche photodiode (iD Quantique). Measurements were done at room temperature in ambient conditions.

Charge distribution over the molecule has been simulated using a Gaussian 0.3 software package. For simplicity, the substituents with sulfo-groups in 1859SL have been replaced by methyl-groups.

2. Additional experimental data

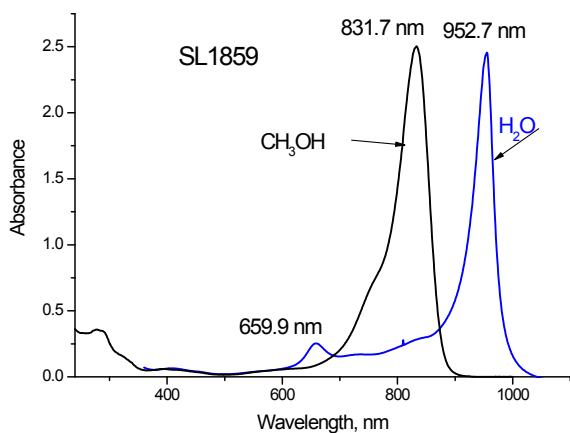


Figure S1. Comparison of the electronic absorption spectra of 1859 SL in methanol and water (10^{-5} M), reduced to the same maximum.

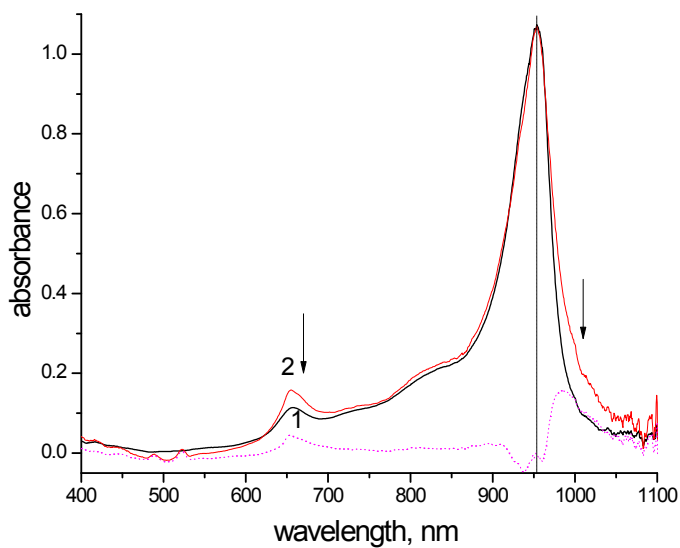


Figure S2. Comparison of the electronic absorption spectra normalized to the same maximum of aqueous solutions of (1) neat dye 1859SL (10^{-5} M) and (2) the mixture of dye (10^{-5} M) and ErCl₃ (10^{-1} M); the dotted curve is the difference of the spectra (2) and (1) and arrows indicate the effect induced by ErCl₃.

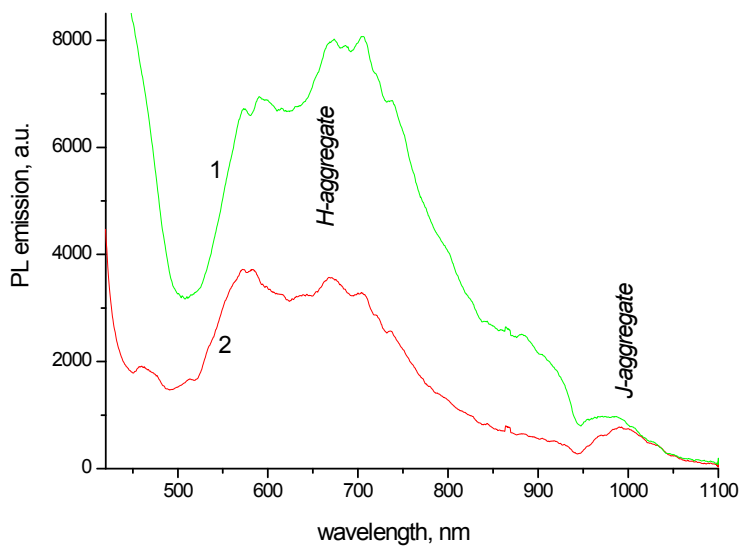


Figure S3. Emission spectra of (1) neat dye film, (2) film of dye-ErCl₃ (1:1 molar ratio) mixture, $\lambda_{\text{exc}} = 398$ nm. The excitation was provided from the Ha lamp (500 W) through an interference filter 398 nm with the IR region blocked by a SZS-26 filter.

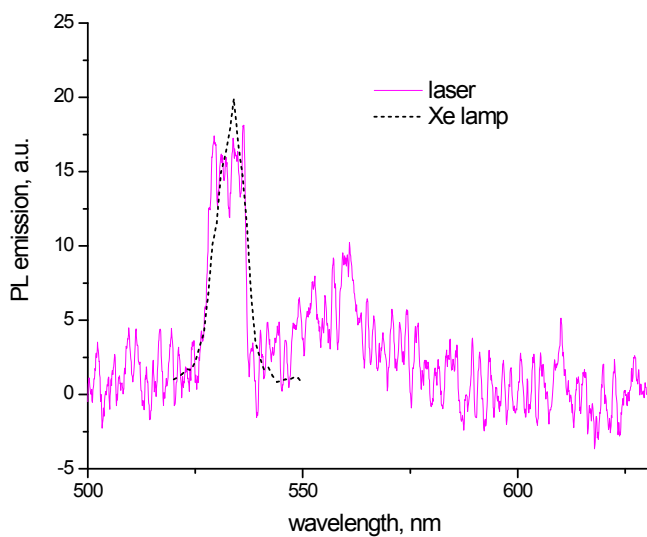


Figure S4. Comparison of normalized upconversion emission of the dye-CaCl₂ film upon excitation by Xe-lamp (~ 100 mW/cm²) and Ti-sapphire laser (750 mW/cm²) at $\lambda_{\text{exc}} = 800$ nm. It should be noted that the films are unstable to burning under high excitation intensities (> 1 W/cm²).

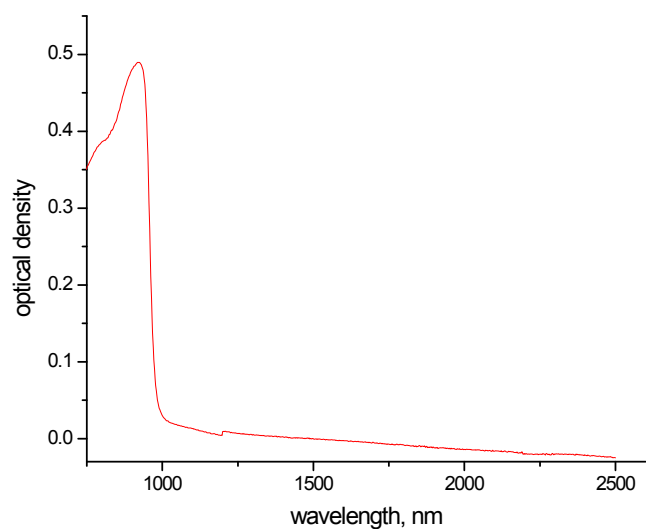


Figure S5. Electronic absorption spectrum of the film of 1859 SL in the near-IR region.

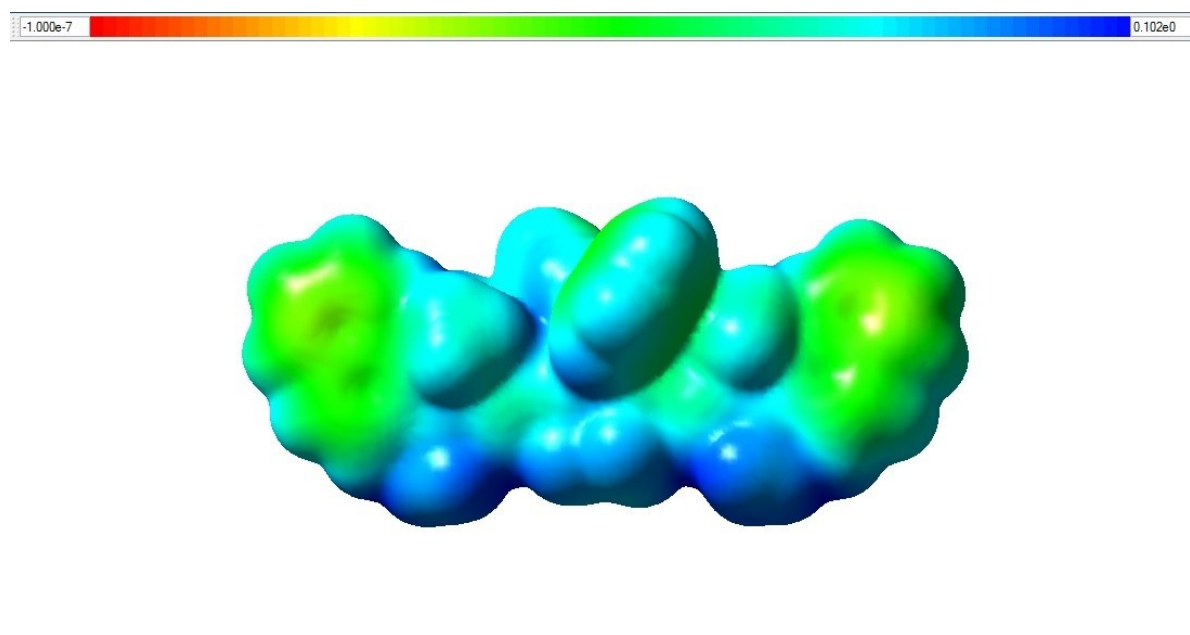


Figure S6. Charge distribution over a model molecule, where the substituents with sulfo-groups have been replaced by methyl-groups in 1859SL. The charge is changing from positive (blue) to negative (red). It is seen that the molecule has a certain CT state, since molecular core is charged positively, while it is

gradually relaxed towards peripheral molecular groups, so that the molecule also corresponds to the A- π -D- π -A structure.

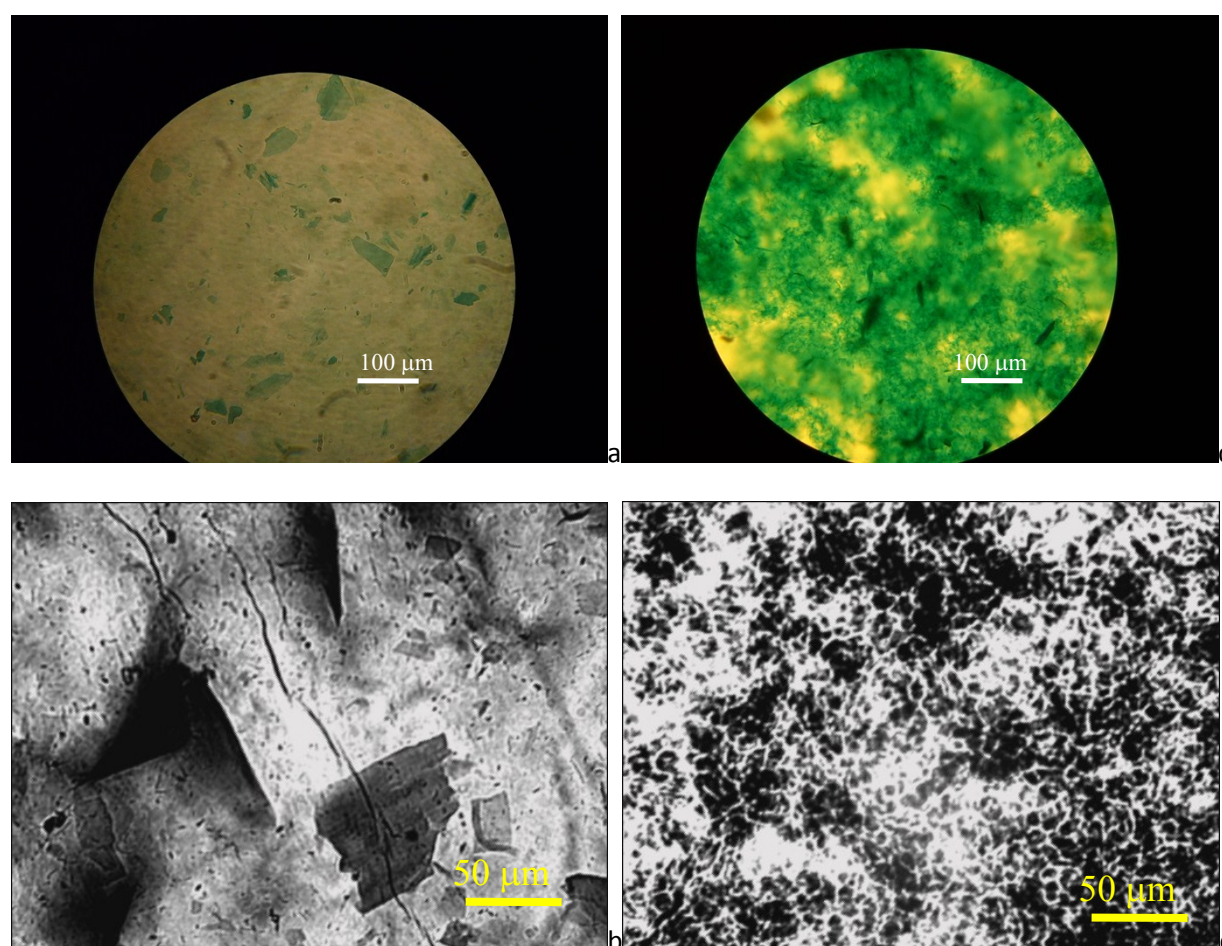


Figure S7. Morphology of (a,b) neat dye and (c,d) dye:ErCl₃ (1:10 molar ratio) films as observed through optical microscope. In (a) the flat dye crystals while in (b) more disordered morphology can be observed.