

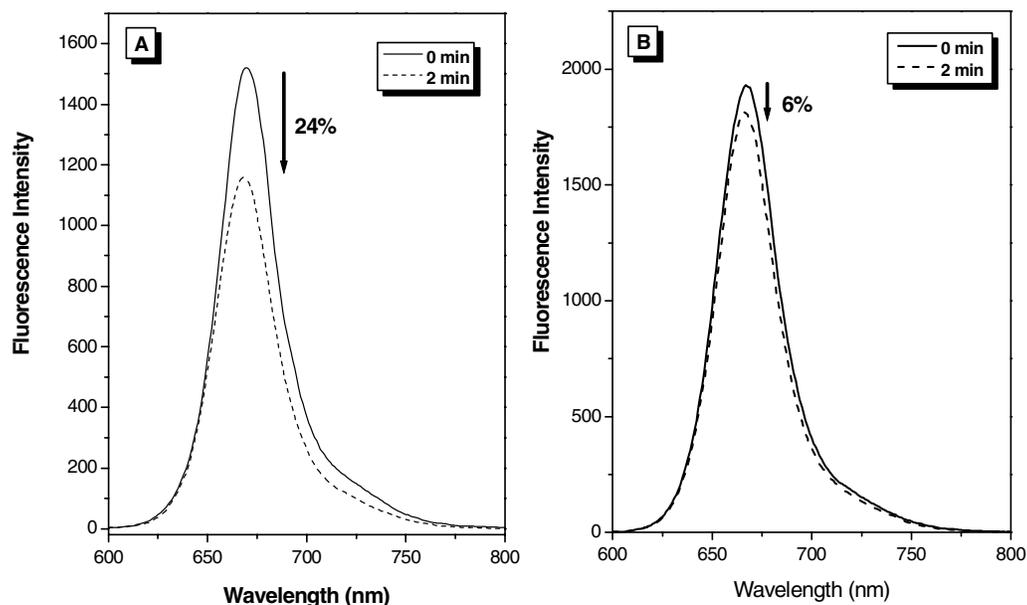
## Supporting Information

### *Sample Preparation and Irradiation*

Dye concentrations in methanol were determined spectrophotometrically using the aforementioned extinction coefficients. Samples contained 10 mM sodium phosphate buffer (pH = 7) and 20% methanol in water to give a total volume of 1 mL. Respective dyes were added from concentrated methanol solutions by titration with a 10  $\mu$ L syringe.

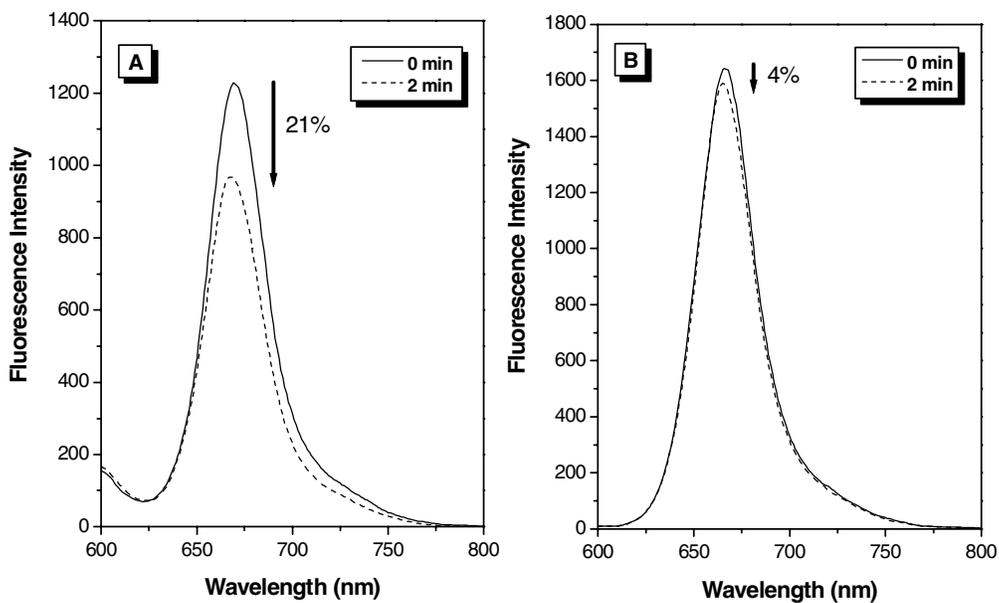
Samples were irradiated in quartz cuvettes placed in a room temperature water bath to filter infrared light. The dyes were irradiated for two minutes by a 150 watt Hg(Xe) lamp for two minutes. For direct irradiation of the dyes, a 550 nm long pass filter (Oriel, filter # 59502) was placed between the lamp and the sample. When Eosin Y was irradiated, a band pass filter (Oriel, filter # 59830,  $325 \text{ nm} < \lambda < 525 \text{ nm}$ ) was utilized. In both cases, a neutral density filter that blocked 90% of the incident light was also used. Both absorbance and fluorescence spectra were recorded before and after irradiation, and cuvettes were wrapped in aluminum foil between scans and irradiation to prevent unintentional photobleaching of the dyes.

### *Direct Photobleaching of Cyanine Dyes: Fluorescence Spectra*



**Figure S1.** Fluorescence spectra recorded before and after 2 minutes irradiation with visible light ( $\lambda > 550 \text{ nm}$ ) for 5.0  $\mu$ M **S5** (A) and **F8-S5** (B) in aqueous sodium phosphate buffer (10 mM, pH = 7.0), 20% methanol,  $\lambda_{\text{ex}} = 545 \text{ nm}$ . Percent photobleaching calculated as the average loss in fluorescence at 670 nm for three separate trials.

*Sensitized Photobleaching of Cyanine Dyes by Eosin Y: Fluorescence Spectra*



**Figure S2.** Eosin Y-sensitized reduction in fluorescence of cyanine dyes. Fluorescence spectra recorded before and after 2 minutes irradiation with visible light ( $\lambda < 550$  nm, UV cutoff) for 5.0  $\mu\text{M}$  **S5** (A) and **F8-S5** (B) in aqueous sodium phosphate buffer (10 mM, pH = 7.0), 20% methanol, [Eosin Y] = 5.0  $\mu\text{M}$ . Percent photobleaching calculated as the average loss in fluorescence at 670 nm for three separate trials.

## *Dye Synthesis*

### **3,3'-diethyl-4,4',5,5',6,6',7,7'-octafluorothiadicarbocyanine ethyl sulfate (F8-S5)**

To a 10 mL round-bottomed flask containing 2-methyl-4,5,6,7-tetrafluorobenzothiazole (1.0 g, 4.5 mmol), was added diethyl sulfate (1.7 mL, 13.5 mmol) and the reaction mixture was stirred at 140 °C for 26 h, under nitrogen atmosphere. After cooling to 60 °C, 1 mL of pyridine was added and stirred for 10 min. Then the mixture was cooled to room temperature, 1.0 mL of 1,3,3'-trimethoxypropene was added and the mixture further stirred for 30 minutes. After completion of the reaction, ether was added and the precipitated product was filtered, washed several times with ether and dried to give crude 3,3'-diethyl-4,4',5,5',6,6',7,7'-octafluorothiadicarbocyanine ethyl sulfate (**F8-S5**) (534 mg, 36%). Pure dye was obtained by recrystallization twice from ethanol, as a purple colored powder. <sup>1</sup>H NMR (500 MHz, d<sub>6</sub>-DMSO) δ 7.89 (2H, t, *J* = 12.65 Hz), 6.79 (2H, d, *J* = 12.8 Hz), 6.61 (1H, t, *J* = 12.10 Hz), 4.43 (4H, q, *J* = 7.08 Hz), 3.72 (2H, q, *J* = 7.08 Hz), 1.40 (6H, t, *J* = 7.15 Hz), 1.10 (3H, t, *J* = 7.15 Hz); MS *m/z* = 535.10 (M<sup>+</sup>).

### **3,3'-diethyl-2,2'-thiadicarbocyanine ethyl sulfate (S5)**

To a 10 mL round-bottomed flask containing 2-methylbenzothiazole (**1**) (0.5 mL, 4 mmol), was added diethyl sulfate (1.5 mL, 12 mmol) and the reaction mixture was stirred at 120 °C for 18 h, under nitrogen atmosphere. After completion of the reaction, the reaction mixture was cooled and the precipitate was washed with dry ethyl ether to give the alkylated product (**2**). To a suspension of alkyl derivative (**2**) and malonaldehyde bis(phenylimine) monohydrochloride (100 mg, 0.39 mmol) in 5 mL methanol, was added 0.5 mL triethylamine followed by 1.5 mL acetic anhydride. The mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure, then the crude product was washed with ether and purified by silica gel chromatography (10% methanol in ethyl acetate). Further recrystallization from ethanol/ethyl ether mixture afforded 3,3'-diethyl-2,2'-thiadicarbocyanine ethyl sulfate (**S5**) as dark blue crystals (44 mg, 22%). <sup>1</sup>H NMR (500 MHz, d<sub>6</sub>-DMSO) δ 7.99 (2H, d, *J* = 7.45 Hz), 7.77 (2H, t, *J* = 12.6 Hz), 7.72 (2H, d, *J* = 8.3 Hz), 7.55 (2H, t, *J* = 7.7 Hz), 7.40 (2H, t, *J* = 7.7 Hz), 6.55 (2H, d, *J* = 13.05 Hz), 6.47 (1H, t, *J* = 12.35 Hz), 4.40 (4H, q, *J* = 7.13 Hz), 3.73 (2H, q, *J* = 7.15 Hz), 1.32 (6H, t, *J* = 7.1 Hz), 1.09 (3H, t, *J* = 7.1 Hz).