Electronic Supplementary Material (ESI) for Lab on a Chip.

Supplementary Information for

"Optofluidic chlorophyll lasers"

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I. Energy level of Chla and experimental setup

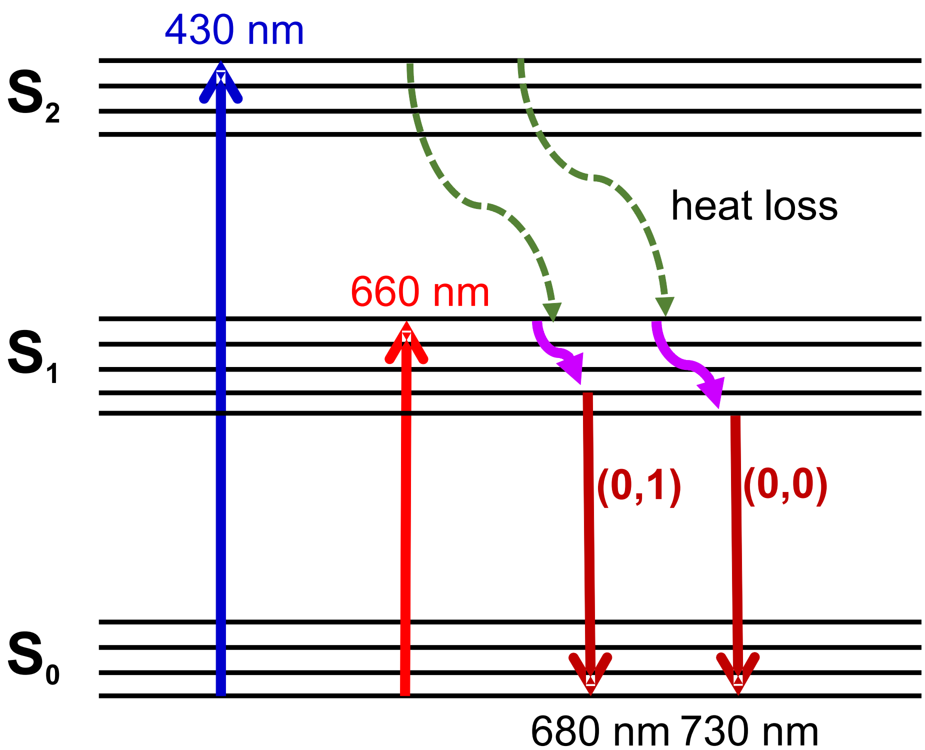


Figure S1. Energy level of Chla. S_0 stands for ground state, S_0 stands for the first excited state, and S_2 stands for higher excited states. Chla absorbs photons around 430 nm and 660 nm, whereas the emission bands at 680 nm and 730 nm in our experiment correspond to the (0,0) and (0,1) vibronic regions in the $S_1 \rightarrow S_0$ transition.

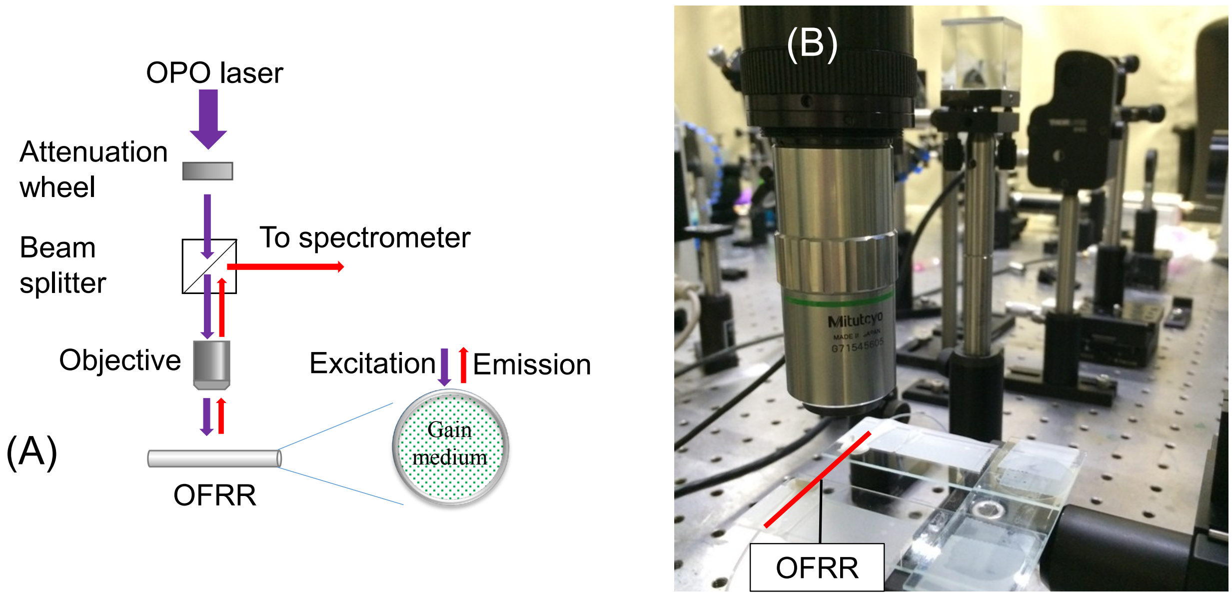


Figure S2. (A) Illustration of the experimental setup. (B) Picture of the experimental setup. The red line indicates the position of the OFRR, as the actual OFRR is too thin to be visible.

II. Laser emission of Chla at a high concentration

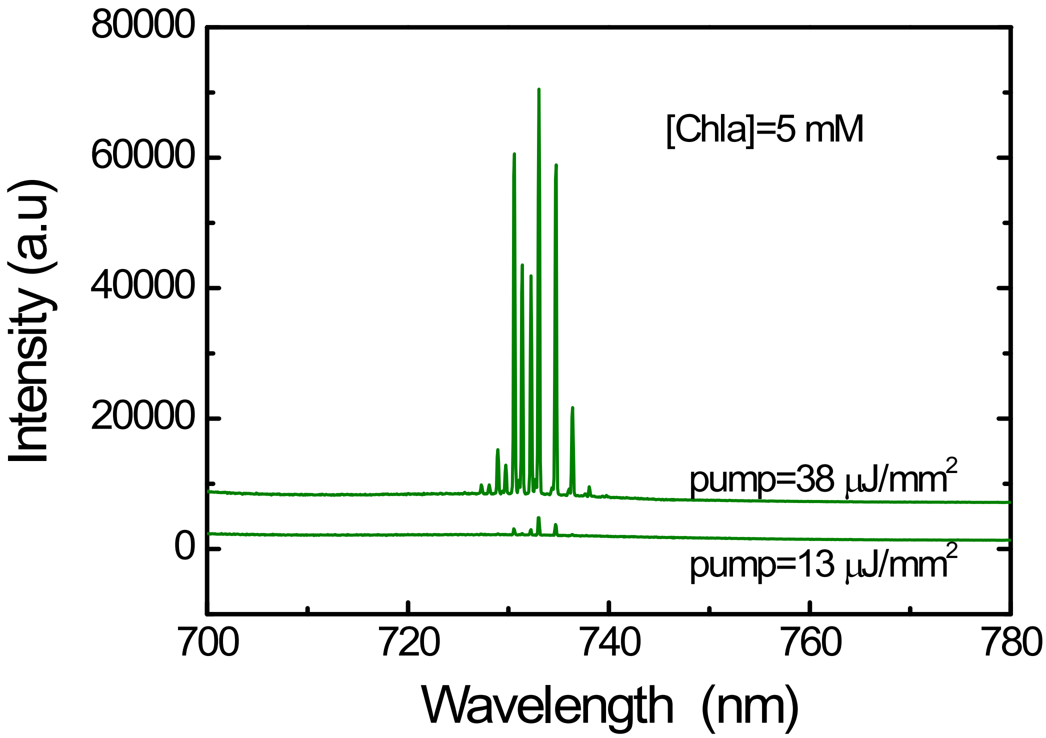


Figure S3. Lasing at the 730 nm band can be achieved even with the Chla concentration as high as 5 mM in ethanol. Curves are vertically shifted for clarity.

III. Measurement of absorption and emission cross section of Chla

The absorption cross section (σ_a) of chlorophyll *a* (ethanol as solvent) was calculated by using

$$\sigma_a(\lambda) = 3.8\times10^{-21}\varepsilon(\lambda),$$

where ε is the extinction coefficient and is derived from the absorbance (A) measured in our lab using a NanoDrop 2000c spectrophotometer (Thermal Scientific). Here A=[Chla]εL, where [Chla] is the concentration of Chla ([Chla]= 0.01 μM) and L is the optical path (L=1mm). The absorption cross section of Chla is shown in Fig. S4 and the normalized absorption cross section is shown in Fig. 1b.

The emission cross section of a laser transition, $\sigma_e(\lambda_L)$ can be derived from the fluorescence spectrum and the quantum yield [1]:

$$\sigma_e(\lambda) = \frac{\lambda^4 E(\lambda)}{8\pi c n^2 \tau_F},$$

where $E(\lambda)$ is the fluorescence quantum distribution of Chla. It is proportional the fluorescence intensity, but normalized to the quantum yield, q, *i.e.*, $\int E(\lambda)\cdot d\lambda = q$ (q=0.32 for Chla in ethanol [2]). τ_F is the fluorescence lifetime (τ_F~5 ns [3]). c is the speed of light in vacuum and n is the surrounding medium refractive index (n=1.36 for ethanol),. The emission cross section of Chla is shown in Fig. S4 and the normalized emission cross section is shown in Fig. 1b.

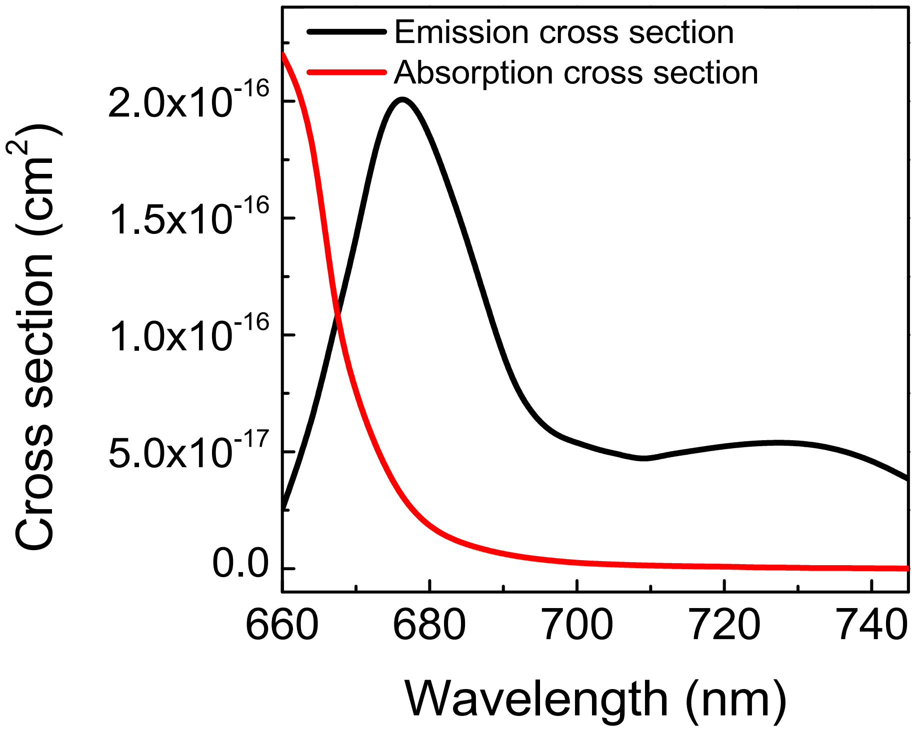


Figure S4. Absorption cross sections (black curve) and emission cross sections (red curve) of Chla in ethanol from 660 nm to 745 nm.

IV. Required population inversion at the lasing threshold for various Chla concentrations

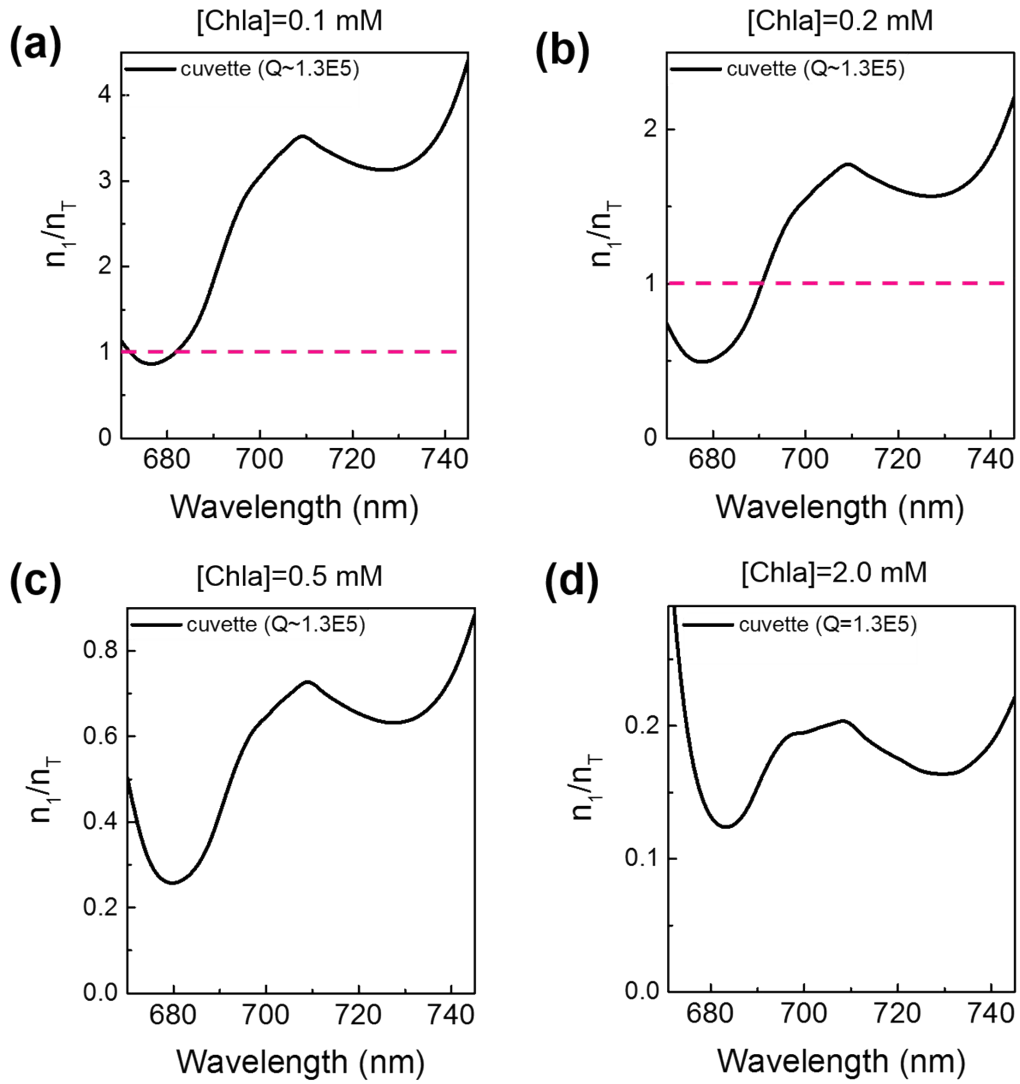
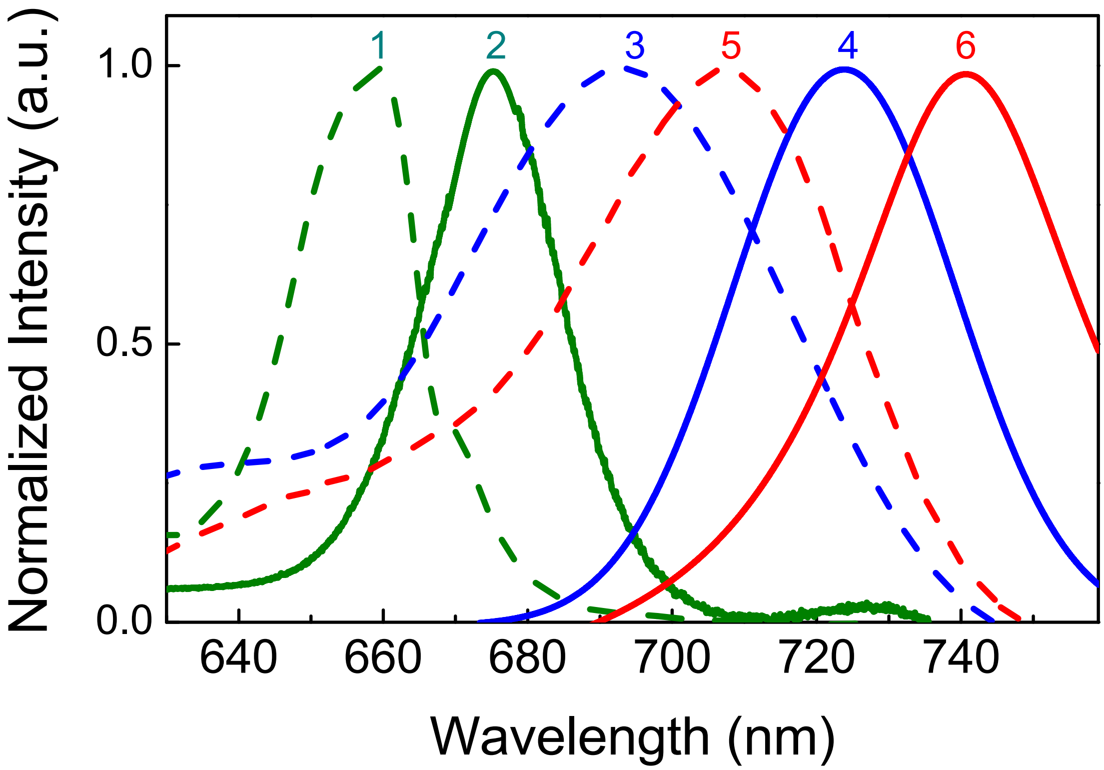


Figure S5. Fraction of Chla molecules in the excited states needed at the threshold for (a) 0.1 mM, (b) 0.2 mM, (c) 0.5 mM, and (d) 2.0 mM of Chla based on Eq. (2) in the main text with η=1.0 and Q_0=1.3x10^5, which corresponds to the situation where a low Q-factor 1-cm long cuvette is used as the laser cavity. In all concentrations, the minimum occurs around 680 nm, suggesting that the lasing band at 680 nm is dominant. Lasing at the 730 nm band either is non-physical (*i.e.*, $n_1/n_T>1$) or requires much higher excitation.



V. Normalized absorption and emission spectrum of Chla, AF680, and AF700

Figure S6. (a) Normalized absorption (dashed line) and emission (solid line) spectrum of Chla (Curves 1 and 2), AF680 (Curves 3 and 4), and AF700 (Curves 5 and 6) in ethanol.

VI. Lasing profile for Alexa Fluor 680

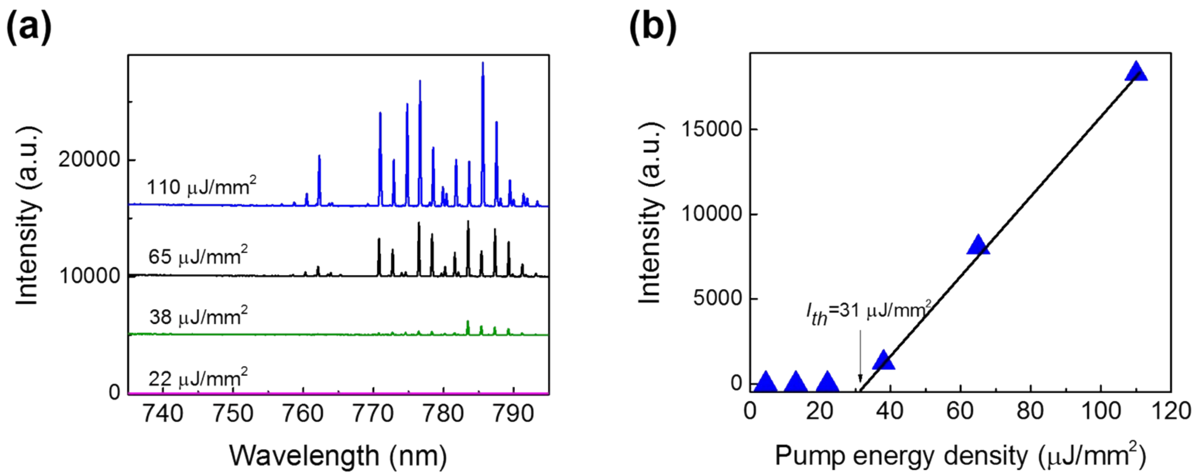


Figure S7. (a) Lasing spectra of AF680 (5 mM) alone in ethanol under various pump energy densities. Excitation wavelength=430 nm. Curves are vertically shifted for clarity. (b) Spectrally integrated (745 nm – 790 nm) laser output as a function of pump energy density extracted from (a). Solid line is the linear fit above the threshold, showing a lasing threshold of approximately 31 μJ/mm^2.

VII. Laser threshold for cascade FRET and Alexa Fluor 700

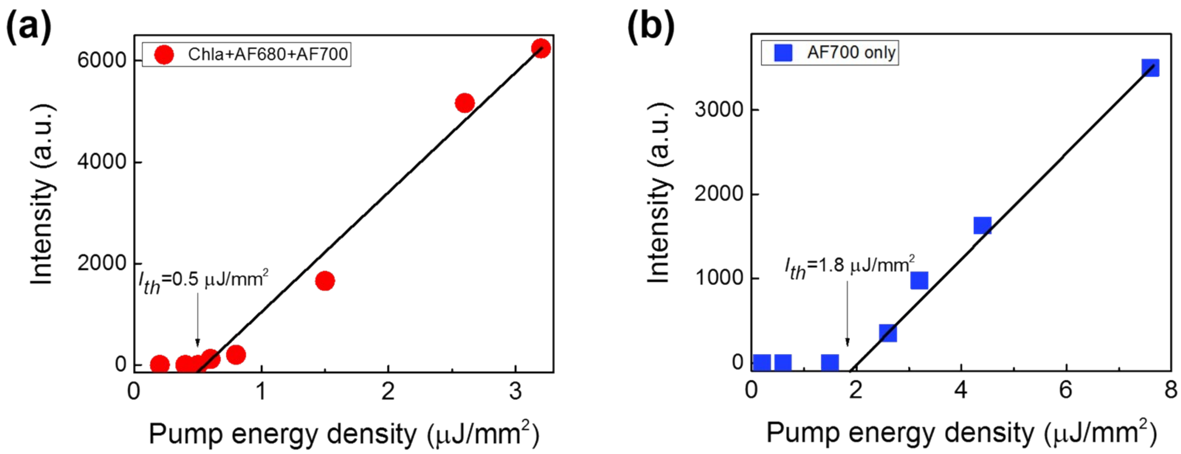


Figure S8. Spectrally integrated (800 nm – 825 nm) laser output as a function of pump energy density of (a) cascade FRET laser emissions (CHla+AF680+AF700) and (b) AF700 laser emissions. Solid line is the linear fit above the threshold, showing a lasing threshold of approximately 0.5 μJ/mm^2 and 1.8 μJ/mm^2, respectively. [Chla]=5 mM, [AF680]=5 mM, and [AF700]=5 mM for all experiments. Excitation wavelength=430 nm.

VIII. Another example of cascade FRET laser using Chla as the donor

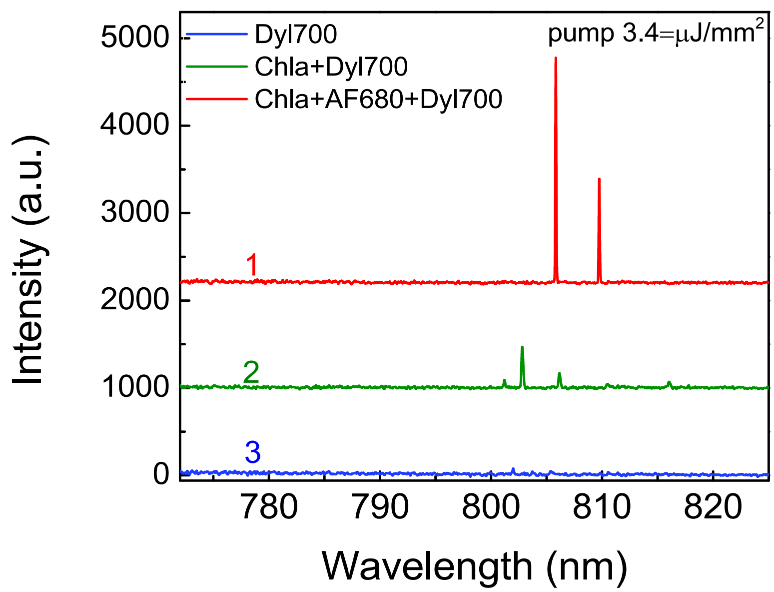


Figure S9. Emission spectra of mixture of Chla-AF680-Dyl700 in ethanol (Curve 1), mixture of Chla-Dyl700 in ethanol (Curve 2), and Dyl700 alone in ethanol (Curve 3) under the same pump energy density of 3.4 μJ/mm^2. [Dyl700]=5 mM, [AF680]=5 mM, and [Chla]=5 mM for all curves. Excitation wavelength=430 nm. Dyl700: DyLight 700-B1.

References:

1. Deshpande A-V, Beidoun A, Penzkofer A, Wagenblast G (1990) Absorption and emission spectroscopic investigation of cyanovinyl diethylaniline dye vapors. *Chem. Phys*. 142: 123−131.
2. Losev, A-P, Sagun E-I, Kochubeev G-A, Nichiporovich I-N (1986) Fluorescence quantum yields, lifetimes, and critical distances for energy transfer for chlorophyll a and its pheophytin in solutions. *J. Appl. Spec.* 45: 798-803.
3. Čermák, K, Kaplanová M (1980) Fluorescence lifetimes of chlorophyll a. *Czech. J. Phys*. 30: 713-716.