Diffusion-Driven Continuous-Wave-Pumped Organic Dye Lasers - Supplementary Information

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1. Rate equation model of excited state dynamics

The hemispherical cavity is formed from a concave spherical mirror with radius of curvature $R_1 = R$ and a planar mirror ($R_2 = \infty$) separated by a physical distance L_c. The intra-cavity medium has a refractive index n_c. The mirrors are distributed Bragg reflectors (DBRs) that consist of alternating layers of high refractive index (n_H) and low refractive index (n_L) dielectric materials that result in a high reflectivity stopband. A series of Hermite-Gaussian longitudinal modes (TEM_{00}) and associated transverse modes (TEM_{ij}) are supported, with wavelengths given by

$$\lambda_q = 2L_{opt} \times \left[q + \frac{1}{\pi}(i+j+1)\cos^{-1}\left(\sqrt{1-\frac{L}{R}}\right)\right]^{-1} \quad (1)$$

where q is the longitudinal mode number, $L = L_c + L_{DBR}$ and $L_{opt} = n_c L_c + n_{av} L_{DBR}$, with L_{DBR} being the penetration depth of the optical mode into the mirrors, given by $L_{DBR} = L_{DBR,1} + L_{DBR,2}$. The penetration depth into a particular mirror depends upon whether it is terminated with a high index (DBR, n_H) or low index (DBR, n_L) material [1].

$$L_{DBR,nH} = \frac{\lambda_{DBR} n_c}{4 n_{av} \Delta n} \quad (2)$$

$$L_{DBR,nL} = \left(\frac{\lambda_{DBR} n_{av}}{4 n_c \Delta n}\right) + \left(\frac{\lambda_{DBR} \Delta n}{2\pi^2 n_c n_{av}}\right) \quad (3)$$

where $n_{av}^{-1} = 2(n_H^{-1} + n_L^{-1})$ and $\Delta n = n_H - n_L$. The DBR stopband center wavelength is λ_{DBR}. In our system, both mirrors are high-index terminated, hence $L_{DBR,1}$ and $L_{DBR,2}$ are described by $L_{DBR,nH}$.

The photonic mode volume, V_γ, of the longitudinal modes is given by

$$V_\gamma = \frac{\pi \omega_0^2 L}{4} \quad (4)$$

$$\omega_0^2 = \frac{\lambda_q L_{opt}}{\pi}\sqrt{\frac{R}{L} - 1} \quad (5)$$

where ω_0 is the mode waist (radius) on the flat mirror.

We use a series of coupled rate equations to model the exciton population dynamics and emission characteristics of the dye-laser system. The energy levels and available exciton relaxation pathways are shown in Supplementary Figure 1.

The model considers a population of initially unbleached dye molecules ($N'_{Bl,i}$) present in the mode volume of the optical cavity. Since V_γ extends into the mirrors, the dye does not occupy the full photonic mode volume, but instead a volume V approximated by

$$V = V_\gamma \frac{L_c}{L} \quad (6)$$

The population of molecules in the mode volume is then $N'_{Bl,i} = V \times N_{den}$ where N_{den} is the molecular density. At room temperature we assume that all of the dye molecules are in the ground state, $|0\rangle$, prior to optical pumping.

We consider CW excitation with a monochromatic laser source of power P_{in} and wavelength λ_{src} focused to a spot of full-width half-maximum of ω_{src}^{FWHM} on the planar mirror. The focused laser spot photon distribution has a radial Gaussian profile given by

$$f(r) = \frac{P_{src}^{peak}}{\sqrt{2\pi}\omega_{src}} \exp\left(-\frac{r^2}{2\omega_{src}^2}\right) \quad (7)$$

where P_{src}^{peak} is the peak photon source intensity, $\omega_{src} = \omega_{src}^{FWHM}/2\sqrt{\ln 4}$, and r is distance from the spot center. The source function is normalized such that

$$2\pi \int_0^\infty r f(r)\, dr = P_{src} \quad (8)$$

where $P_{src} = P_{in}\lambda_{src}/hc$ is the number of source photons per unit time. The number of photons that enter the cavity mode and excite molecules is then

$$P = 2\pi \int_0^{\omega_0} r f(r)\, dr \times (1 - R_{src}) \times \exp\left(-\alpha_{src} N_{den} \frac{L_c}{1 - R_{src}}\right) \quad (9)$$

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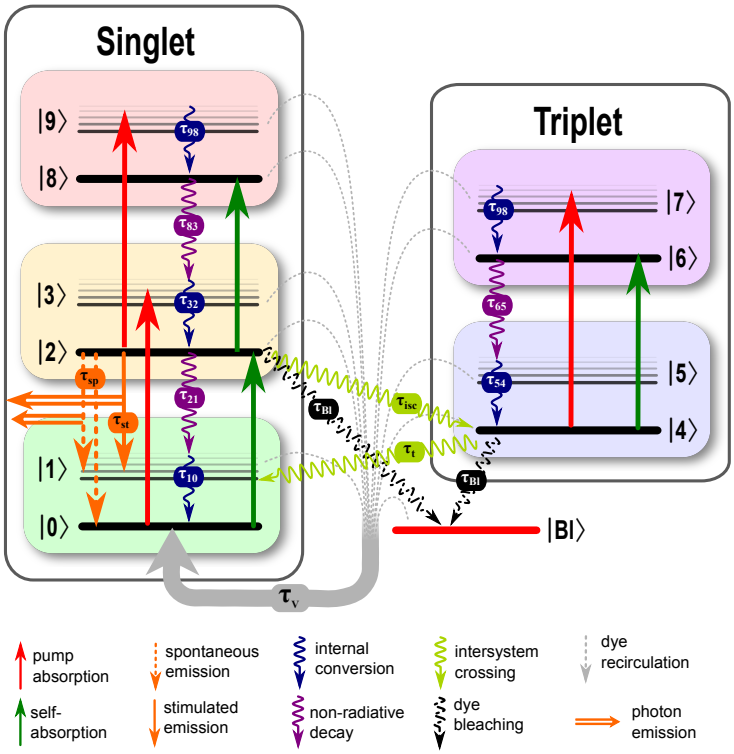

Figure 1 Energy levels and transitions included in the rate equation.

Supplementary Equation 9 includes three factors that take into account the photons incident on the mode volume cross section, the photons that can pass into the cavity mode due to reflectivity of the planar mirror at the pump wavelength (R_{src}), and the absorption of the admitted photons given the dye absorption cross section at λ_{src} (α_{src}) and the effective cavity length due to the weak cavity effect at λ_{src}.

Optical pumping results in a population transfer from $|0\rangle$ to the vibrationally excited first electronically excited singlet state $|3\rangle$ which non-radiatively relax on the picosecond timescale (τ_{32}) to the vibrational ground state of the excited singlet $|2\rangle$. From here, excitons can relax back to the vibrational manifold of the electronic ground state $|1\rangle$ either non-radiatively or radiatively with lifetimes τ_{21} and τ_{sp}, respectively, before relaxing back to $|0\rangle$ with $\tau_{10} \approx \tau_{32}$. Non-radiative intersystem crossing from $|2\rangle$ to the triplet state $|4\rangle$ may also occur, however this is a spin-forbidden transition, and hence has a long associated lifetime of τ_{isc}. The relationship between the $|1\rangle$ decay rates and the dye quantum yield $\mathrm{QY}_{\mathrm{dye}}$ is given by

$$\tau_{21} = \frac{\mathrm{QY}_{\mathrm{dye}}\,\tau_{\mathrm{isc}}\,\tau_{\mathrm{sp}}}{\tau_{\mathrm{isc}}(1-\mathrm{QY}_{\mathrm{dye}}) - \mathrm{QY}_{\mathrm{dye}}\,\tau_{\mathrm{sp}}} \tag{10}$$

Spontaneous radiative $|2\rangle \rightarrow |0\rangle$ or $|2\rangle \rightarrow |1\rangle$ emission can also result in the stimulated emission of a further photon at a rate proportional to the cavity photon density, the spontaneous emission coupling factor ($\beta = F_p(F_p+1)^{-1}$) and the cavity confinement factor ($\Gamma_s = VV_\gamma^{-1}$).

Excited state absorptions of pump photons can also be included in the form of first excited singlet to second excited singlet ($|2\rangle \rightarrow |9\rangle$) and first excited triplet to second excited triplet ($|4\rangle \rightarrow |7\rangle$) transitions, defined by the relative pump absorption coefficients $\eta^{S_1S_2}$ and $\eta^{T_1T_2}$. However, since the absorption cross-section of these transitions is an order of magnitude smaller than the ground state pump absorption [2], and the ground state population is always at least an magnitude larger than the population of $|4\rangle$ and three orders of magnitude larger than the population of $|2\rangle$, we set these coefficients to zero in the data presented here, such that only the ground state absorbs pump photons i.e. $\eta^{S_0S_1} = 1$, $\eta^{S_1S_2} = \eta^{T_1T_2} = 0$.

Photon losses due to self-absorption by the electronic singlet and triplet states of the stimulated emission is also included, with the contribution defined by the dye self-absorption cross sections $\sigma_{\mathrm{abs}}^{S_0S_1}$, $\sigma_{\mathrm{abs}}^{S_1S_2}$ and $\sigma_{\mathrm{abs}}^{T_1T_2}$.

Photobleaching results in a population transfer from the first excited singlet and (more importantly) the first excited triplet state into a bleached state, which effectively reduces the number of photoactive molecules in the system. This results in the rapid loss of lasing in most dye laser systems. In the current system, bleached dye molecules can quickly diffuse out of the cavity mode volume to be replaced with unbleached molecules. The lifetime associated with this recirculation process is given by Equation 1 in the main text.

Molecules in all other excited states can also diffuse out of the cavity mode, and so the model includes available

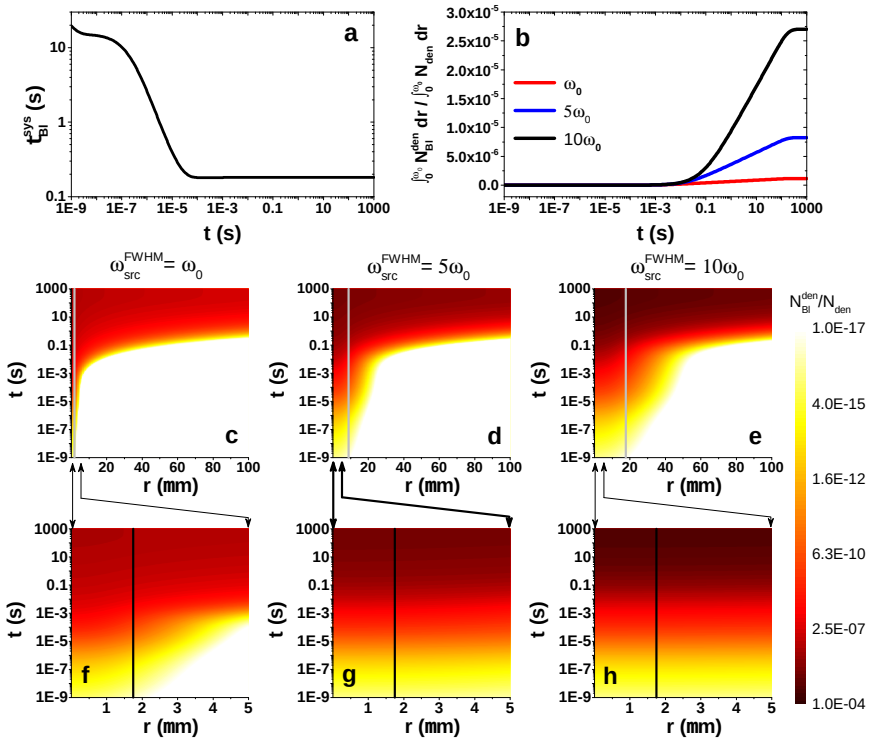

Figure 2 (a) Characteristic system bleaching time τ_{Bl}^{sys} as a function of time. (b) Fraction of photobleached molecules in the region ω_0 for a series of excitation spot sizes (ω_{src}^{FWHM}) as a function of time. Photobleached population density (as a fraction of total molecular population density) as a function of radius r and time t for ω_{src}^{FWHM} equal to (c) ω_0, (d) $5\omega_0$ and (e) $10\omega_0$. The solid grey line shows the position of ω_{src}^{FWHM}. (f)-(h) show the same as (c)-(e) over a smaller range of r. The solid black line shows the extent of ω_0. The pump power P_{in} for all data presented in this figure is 20 mW, well above the observed lasing threshold.

pathways from all considered exciton states to the ground state governed by the time constant τ_V. This assumes that all molecules diffusing into the cavity are in the ground state. In practice, this would require that the pump only excites molecules in the mode volume, a simplification in this case since in reality the pump spot is larger that ω_0. We explore this effect in the following section.

The model includes modification of the spontaneous emission rate through the Purcell factor F_p of the cavity. We use the definition

$$F_p = \frac{3}{4\pi^2}\left(\frac{\lambda_l}{n_c}\right)^3 \frac{Q_{eff}}{V_\gamma} \tag{11}$$

where Q_{eff} is the effective Q-factor of the system, given by $Q_{eff}^{-1} = \left(Q_T^{-1} + Q_E^{-1}\right)$. Here, Q_T is the Q-factor of the cavity system containing the dye molecules (i.e. incorporating photon losses to the scattering/absorption due to the dye molecules), and is equal to the cavity finesse ($\mathscr{F}$) multiplied by the longitudinal mode number. Cavity mode photons therefore leave the cavity with a time constant of $\tau_{loss} = Q_T \frac{\lambda_l}{2\pi c}$, where λ_l is the laser emission wavelength.. We use a lower-bound value of 1078 for the finesse, concomitant with the measured cavity emission linewidth of 0.03 nm. Q_E is the Q-factor of the emitter (i.e. the dye). The modified spontaneous emission lifetime due to the cavity is then $(F_P + 1)\tau_{sp}$.

Within the description provided above, the rate equations that describe the exciton populations N0, N1, … of the molecular states $|0\rangle, |1\rangle, \ldots$ are

$$\frac{dN0}{dt} = \underbrace{-P\eta^{S_0S_1}\frac{(N0-N3)}{N'_{Bl}}}_{\text{laser pumping to N3}} \underbrace{-v_g\sigma_{abs}^{S_0S_1}\Gamma_s\phi_l\frac{N0-N2}{V}}_{\text{self-absorption of emitted laser photons to N2}} + \underbrace{\frac{N1}{\tau_{10}}}_{\text{non-radiative transfer from N1}} + \overbrace{(F_p+1)\frac{(1-\beta\Gamma_s)}{\tau_{sp}}N2}^{\text{spontaneous emission from N2}} + \underbrace{\frac{1}{\tau_V}\sum_{i=1}^{9}N_i + \frac{N_{Bl}}{\tau_V}}_{\text{population recycling due to diffusion}} \tag{12}$$

$$\frac{dN1}{dt} = \underbrace{+(F_p+1)\frac{\beta\Gamma_s}{\tau_{sp}}\phi_l(N2-N1)}_{\text{stimulated emission from N2}} + \underbrace{(F_p+1)\frac{\beta\Gamma_s}{\tau_{sp}}N2}_{\text{spontaneous emission from N2}} \tag{13}$$

$$+\overbrace{\frac{\mathrm{N2}}{\tau_{21}}}^{\substack{\text{non-radiative}\\ \text{transfer}\\ \text{from N2}}}+\underbrace{\frac{\mathrm{N4}}{\tau_{\mathrm{t}}}}_{\substack{\text{non-radiative}\\ \text{transfer}\\ \text{from N4}}}-\overbrace{\frac{\mathrm{N1}}{\tau_{10}}}^{\substack{\text{non-radiative}\\ \text{transfer}\\ \text{to N0}}}-\underbrace{\frac{\mathrm{N1}}{\tau_{\mathrm{V}}}}_{\substack{\text{diffusive}\\ \text{population}\\ \text{recycling to N0}}}$$

$$\frac{d\mathrm{N2}}{dt}=-\underbrace{(F_p+1)\frac{\beta\Gamma_s}{\tau_{\mathrm{sp}}}\phi_{\mathrm{l}}(\mathrm{N2}-\mathrm{N1})}_{\text{stimulated emission to N1}}-\underbrace{(F_p+1)\frac{\mathrm{N2}}{\tau_{\mathrm{sp}}}}_{\substack{\text{spontaneous}\\ \text{emission to}\\ \text{N1 and N0}}} \tag{14}$$

$$-\underbrace{\nu_g\sigma_{\mathrm{abs}}^{S_1S_2}\Gamma_s\phi_{\mathrm{l}}\frac{(\mathrm{N2}-\mathrm{N8})}{V}}_{\substack{\text{self-absorption of emitted}\\ \text{laser photons to N8}}}-\overbrace{\frac{\mathrm{N2}}{\tau_{21}}}^{\substack{\text{non-radiative}\\ \text{transfer}\\ \text{to N1}}}-\underbrace{\frac{\mathrm{N2}}{\tau_{\mathrm{isc}}}}_{\substack{\text{non-radiative}\\ \text{transfer}\\ \text{to N4}}}+\overbrace{\frac{\mathrm{N3}}{\tau_{32}}}^{\substack{\text{non-radiative}\\ \text{transfer}\\ \text{from N3}}}$$

$$-\underbrace{P\eta^{S_1S_2}\frac{(\mathrm{N2}-\mathrm{N9})}{\mathrm{N}'_{\mathrm{Bl}}}}_{\text{laser pumping to N9}}+\underbrace{\nu_g\sigma_{\mathrm{abs}}^{S_0S_1}\Gamma_s\phi_{\mathrm{l}}\frac{\mathrm{N0}-\mathrm{N2}}{V}}_{\substack{\text{self-absorption of emitted}\\ \text{laser photons from N0}}}-\underbrace{\frac{\mathrm{N2}}{\tau_{\mathrm{Bl}}}}_{\substack{\text{dye}\\ \text{bleaching}}}-\overbrace{\frac{\mathrm{N2}}{\tau_{\mathrm{V}}}}^{\substack{\text{diffusive}\\ \text{population}\\ \text{recycling to N0}}}$$

$$\frac{d\mathrm{N3}}{dt}=+\underbrace{P\eta^{S_0S_1}\frac{(\mathrm{N0}-\mathrm{N3})}{\mathrm{N}'_{\mathrm{Bl}}}}_{\text{laser pumping from N0}}+\overbrace{\frac{\mathrm{N8}}{\tau_{83}}}^{\substack{\text{non-radiative}\\ \text{transfer}\\ \text{from N8}}}-\underbrace{\frac{\mathrm{N3}}{\tau_{32}}}_{\substack{\text{non-radiative}\\ \text{transfer}\\ \text{to N2}}}-\overbrace{\frac{\mathrm{N3}}{\tau_{\mathrm{V}}}}^{\substack{\text{diffusive}\\ \text{population}\\ \text{recycling to N0}}} \tag{15}$$

$$\frac{d\mathrm{N4}}{dt}=-\underbrace{P\eta^{T_1T_2}\frac{(\mathrm{N4}-\mathrm{N7})}{\mathrm{N}'_{\mathrm{Bl}}}}_{\text{laser pumping to N7}}-\underbrace{\nu_g\sigma_{\mathrm{abs}}^{T_1T_2}\Gamma_s\phi_{\mathrm{l}}\frac{(\mathrm{N4}-\mathrm{N6})}{V}}_{\substack{\text{self-absorption of emitted}\\ \text{laser photons to N6}}} \tag{16}$$

$$+\overbrace{\frac{\mathrm{N2}}{\tau_{\mathrm{isc}}}}^{\substack{\text{non-radiative}\\ \text{transfer}\\ \text{from N2}}}+\underbrace{\frac{\mathrm{N5}}{\tau_{54}}}_{\substack{\text{non-radiative}\\ \text{transfer}\\ \text{from N5}}}-\overbrace{\frac{\mathrm{N4}}{\tau_{\mathrm{t}}}}^{\substack{\text{non-radiative}\\ \text{transfer}\\ \text{to N1}}}-\underbrace{\frac{\mathrm{N4}}{\tau_{\mathrm{Bl}}}}_{\substack{\text{dye}\\ \text{bleaching}}}-\overbrace{\frac{\mathrm{N4}}{\tau_{\mathrm{V}}}}^{\substack{\text{diffusive}\\ \text{population}\\ \text{recycling to N0}}}$$

$$\frac{d\mathrm{N5}}{dt}=+\underbrace{\frac{\mathrm{N6}}{\tau_{65}}}_{\substack{\text{non-radiative}\\ \text{transfer}\\ \text{from N6}}}-\overbrace{\frac{\mathrm{N5}}{\tau_{54}}}^{\substack{\text{non-radiative}\\ \text{transfer}\\ \text{to N4}}}-\underbrace{\frac{\mathrm{N5}}{\tau_{\mathrm{V}}}}_{\substack{\text{diffusive}\\ \text{population}\\ \text{recycling to N0}}} \tag{17}$$

$$\frac{d\mathrm{N6}}{dt}=+\underbrace{\nu_g\sigma_{\mathrm{abs}}^{T_1T_2}\Gamma_s\phi_{\mathrm{l}}\frac{(\mathrm{N4}-\mathrm{N6})}{V}}_{\substack{\text{self-absorption of emitted}\\ \text{laser photons from N4}}}+\overbrace{\frac{\mathrm{N7}}{\tau_{76}}}^{\substack{\text{non-radiative}\\ \text{transfer}\\ \text{from N7}}}-\underbrace{\frac{\mathrm{N6}}{\tau_{65}}}_{\substack{\text{non-radiative}\\ \text{transfer}\\ \text{to N5}}}-\overbrace{\frac{\mathrm{N6}}{\tau_{\mathrm{V}}}}^{\substack{\text{diffusive}\\ \text{population}\\ \text{recycling to N0}}} \tag{18}$$

$$\frac{d\mathrm{N7}}{dt}=+\underbrace{P\eta^{T_1T_2}\frac{(\mathrm{N4}-\mathrm{N7})}{\mathrm{N}'_{\mathrm{Bl}}}}_{\text{laser pumping from N4}}-\overbrace{\frac{\mathrm{N7}}{\tau_{76}}}^{\substack{\text{non-radiative}\\ \text{transfer}\\ \text{to N6}}}-\underbrace{\frac{\mathrm{N7}}{\tau_{\mathrm{V}}}}_{\substack{\text{diffusive}\\ \text{population}\\ \text{recycling to N0}}} \tag{19}$$

$$\frac{d\mathrm{N8}}{dt}=+\underbrace{\nu_g\sigma_{\mathrm{abs}}^{S_1S_2}\Gamma_s\phi_{\mathrm{l}}\frac{(\mathrm{N2}-\mathrm{N8})}{V}}_{\substack{\text{self-absorption of emitted}\\ \text{laser photons from N2}}}+\overbrace{\frac{\mathrm{N9}}{\tau_{98}}}^{\substack{\text{non-radiative}\\ \text{transfer}\\ \text{from N9}}}-\underbrace{\frac{\mathrm{N8}}{\tau_{83}}}_{\substack{\text{non-radiative}\\ \text{transfer}\\ \text{to N3}}}-\overbrace{\frac{\mathrm{N8}}{\tau_{\mathrm{V}}}}^{\substack{\text{diffusive}\\ \text{population}\\ \text{recycling to N0}}} \tag{20}$$

$$\frac{d\mathrm{N9}}{dt}=+\underbrace{P\eta^{S_1S_2}\frac{(\mathrm{N2}-\mathrm{N9})}{\mathrm{N}'_{\mathrm{Bl}}}}_{\text{laser pumping from N2}}-\overbrace{\frac{\mathrm{N9}}{\tau_{98}}}^{\substack{\text{non-radiative}\\ \text{transfer}\\ \text{to N8}}}-\underbrace{\frac{\mathrm{N9}}{\tau_{\mathrm{V}}}}_{\substack{\text{diffusive}\\ \text{population}\\ \text{recycling to N0}}} \tag{21}$$

$$\frac{d\phi_{\mathrm{l}}}{dt}=-\frac{\nu_g\Gamma_s\phi_{\mathrm{l}}}{V}\Big[\underbrace{\sigma_{\mathrm{abs}}^{S_0S_1}(\mathrm{N0}-\mathrm{N2})}_{\substack{\text{self-absorption}\\ \text{losses due to}\\ \text{ground state}\\ \text{absorption}}}+\underbrace{\sigma_{\mathrm{abs}}^{S_1S_2}(\mathrm{N2}-\mathrm{N8})}_{\substack{\text{self-absorption}\\ \text{losses due to}\\ \text{excited state}\\ \text{absorption}}} \tag{22}$$

$$+\underbrace{\sigma_{\mathrm{abs}}^{T_1T_2}(\mathrm{N4}-\mathrm{N6})}_{\substack{\text{self-absorption}\\ \text{losses due to}\\ \text{triplet}\\ \text{absorption}}}\Big]+\underbrace{(F_p+1)\frac{\beta\Gamma_s}{\tau_{\mathrm{sp}}}\phi_{\mathrm{l}}(\mathrm{N2}-\mathrm{N1})}_{\text{stimulated emission N2}\rightarrow\text{N1}}$$

$$+\underbrace{(F_p+1)\frac{\beta\Gamma_s}{\tau_{\mathrm{sp}}}\mathrm{N2}}_{\substack{\text{spontaneous emission}\\ \text{N2}\rightarrow\text{N1}}}-\overbrace{\frac{\phi_{\mathrm{l}}}{\tau_{\mathrm{loss}}}}^{\text{cavity losses}}$$

$$\frac{d\mathrm{N}'_{\mathrm{Bl}}}{dt}=-\underbrace{\frac{\mathrm{N4}}{\tau_{\mathrm{Bl}}}}_{\substack{\text{dye bleaching}\\ \text{from N4}}}-\overbrace{\frac{\mathrm{N2}}{\tau_{\mathrm{Bl}}}}^{\substack{\text{dye bleaching}\\ \text{from N2}}}+\underbrace{\frac{\mathrm{N_{Bl}}}{\tau_{\mathrm{V}}}}_{\substack{\text{bleached}\\ \text{population}\\ \text{recycling due}\\ \text{to diffusion}}} \tag{23}$$

$$\frac{d\mathrm{N_{Bl}}}{dt}=+\underbrace{\frac{\mathrm{N4}}{\tau_{\mathrm{Bl}}}}_{\substack{\text{dye bleaching}\\ \text{from N4}}}+\overbrace{\frac{\mathrm{N2}}{\tau_{\mathrm{Bl}}}}^{\substack{\text{dye bleaching}\\ \text{from N2}}}-\underbrace{\frac{\mathrm{N_{Bl}}}{\tau_{\mathrm{V}}}}_{\substack{\text{bleached}\\ \text{population}\\ \text{recycling due}\\ \text{to diffusion}}}=-\frac{d\mathrm{N}'_{\mathrm{Bl}}}{dt} \tag{24}$$

where $\mathrm{N_{Bl}}$ is the number of *bleached* molecules and $\mathrm{N}'_{\mathrm{Bl}}$ is the number of *unbleached* molecules. ν_g is the group velocity of the lasing mode and ϕ_{l} is the number of photons in the cavity at the lasing wavelength. This can be related to the output power by $\mathrm{P_{out}}=\frac{hc}{\lambda_{\mathrm{l}}}\frac{\phi_{\mathrm{l}}}{\tau_{\mathrm{rad}}^{\mathrm{cav}}}$ where $\tau_{\mathrm{rad}}^{\mathrm{cav}}$ is the photon decay ctime constant of the unperturbed cavity given by

$Q_{\mathrm{rad}}^{\mathrm{cav}} \frac{\lambda_l}{2\pi c}$. In line with previous estimates [2], we assume the presence of the dye reduces the cavity Q by a factor of 2, giving a total cavity photon loss time constant of $\tau_{\mathrm{loss}} = \frac{1}{2}\tau_{\mathrm{rad}}^{\mathrm{cav}}$. All parameter values used in the model are listed in Supplementary Table 1.

We note that the vibrationally excited energy levels N3, N5, N7 and N9 can be neglected in the CW regime due to their fast relaxation times, and only the vibrational ground states considered. However, we leave them here for completeness and to allow the model to be applied to ultrafast pumping schemes.

2. Diffusion modelling of photobleaching dynamics

We use the diffusion equation to model the effect of changing the laser spot size on the photobleaching dynamics of the system.

$$\frac{\partial \mathrm{N}_{\mathrm{Bl}}^{\mathrm{den}}(r,t)}{\partial t} - D_i^* \triangle \mathrm{N}_{\mathrm{Bl}}^{\mathrm{den}}(r,t) = \frac{1}{\tau_{\mathrm{Bl}}^{\mathrm{sys}}(t)} \frac{\left[\mathrm{N}_{\mathrm{den}} - \mathrm{N}_{\mathrm{Bl}}^{\mathrm{den}}(r,t)\right]}{\mathrm{N}_{\mathrm{den}}} f(r) \qquad (25)$$

where $\mathrm{N}_{\mathrm{Bl}}^{\mathrm{den}}(r,t)$ is the density of bleached molecules and $\triangle$ is the Laplacian operator in polar co-ordinates. The source term $f(r)$ is described in the main text.

From Supplementary Equation 23 (neglecting the volume recycling term) we can assign the time constant related to the photobleaching of the system as $\tau_{\mathrm{Bl}}^{\mathrm{sys}}(t) = \tau_{\mathrm{Bl}} \frac{\mathrm{N}'_{\mathrm{Bl}}(t)}{\mathrm{N4}(t)+\mathrm{N2}(t)}$. We use values for $\mathrm{N}'_{\mathrm{Bl}}(t)$, $\mathrm{N2}(t)$ and $\mathrm{N4}(t)$ as found from equations 13-24 when the system is pumped at 20 mW with a spot size of 10 μm. The time dependence of $\tau_{\mathrm{Bl}}^{\mathrm{sys}}$ is shown in Supplementary Figure 2(a). At short times after pumping begins, this value is large (i.e. slow bleaching), since most photobleaching occurs from the triplet (N4) states which take time to populate due to the relatively low intersystem crossing rate. As these states populate over longer timescales, the photobleaching rate increases and $\tau_{\mathrm{Bl}}^{\mathrm{sys}}$ reduces by two orders of magnitude until the system enters the quasi-steady state regime and the bleaching time stabilizes.

When $\omega_{\mathrm{src}}^{\mathrm{FWHM}}$ is changed, we renormalize the source function $f(r)$ such the number of photons absorbed in the cavity mode remains constant i.e. as the laser is more tightly focused, the power is reduced, hence the excited state dynamics as given by the rate equation model are unchanged. In all cases the number of absorbed photons correspond to a 20 mW pump with a spot size of 10 μm. We note that this is clearly an approximation since it assumes the population dynamics inside and outside of the cavity mode are the same. This is not the case, as no lasing is observed above threshold outside of the cavity. However, this approach does allow us to examine the effect of pump focusing on the photobleaching dynamics of the system.

Supplementary Figure 2(b) shows the ratio of bleached to unbleached molecules within the cavity mode volume, as calculated from Supplementary Equation 25, as a function of time for a series of excitation spot sizes. It can be seen that, independent of spot size, bleaching becomes apparent after approximately 0.1 s, and reaches a maximum after 100 s. The plateauing of the bleached population on long timescales is due to the self-diffusion of dye molecules out of the cavity mode volume. The full bleached molecule density distributions as a function of radius r and time t are shown in Supplementary Figure 2(c)-(e) for $\omega_{\mathrm{src}}^{\mathrm{FWHM}} = \omega_0$, $5\omega_0$ and $10\omega_0$ respectively. The pump FWHM is shown as a solid grey line. It can be seen that for increasing $\omega_{\mathrm{src}}^{\mathrm{FWHM}}$, the region bleached by the pump increases in size, as is expected. The data from Supplementary Figure 2(c)-(e) are reproduced in parts (f)-(h) for the region around ω_0. The cavity mode radius is shown as a solid black line. The extent of the bleaching around ω_0 for the larger spot sizes becomes apparent. To limit molecular bleaching and to achieve true continuous lasing operation it is therefore important to tightly focus the excitation spot and ideally match the FWHM to the size of the cavity mode. While this is not possible with our current flow cell design, it is an engineering issue that is easily surmountable.

References

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[2] S. L. Chua, B. Zhen, J. Lee, J. Bravo-Abad, O. Shapira, and M. Soljacic, J. Mater. Chem. C **2**, 1463 (2014).

Cavity finesse, $\mathscr{F}$	1078
Cavity Q-factor, $Q_{\mathrm{rad}}^{\mathrm{cav}}$	$2Q_{\mathrm{T}}$
Dye quantum yield, $\mathrm{QY}_{\mathrm{dye}}$	0.9
Dye Q-factor, Q_{E}	23
Dye concentration, $\mathrm{N}_{\mathrm{den}}$	8.5 mM
Dye self-diffusion coefficient, D_i^*	4×10^{-6} $\mathrm{cm^2 s^{-1}}$
Dye absorption coefficient at λ_{src}, α_{src}	46400 $\mathrm{cm^{-1}M^{-1}}$
Pump wavelength, λ_{src}	532 nm
Lasing mode wavelength, λ_{l}	643 nm
DBR high refractive index, n_{H}	2
DBR low refractive index, n_{L}	1.5
Intracavity refractive index, n_c	1.36
DBR central wavelength, λ_{DBR}	640 nm
DBR reflectivity at λ_{src}, R_{src}	0.2
Spontaneous emission lifetime, τ_{sp}	5 ns
Intersystem crossing lifetime, τ_{isc}	100 ns
Triplet quenching lifetime, τ_{t}	10 μs
Dye bleaching lifetime, τ_{Bl}	8 ms
Internal conversion lifetime, τ_{10}, τ_{32}, τ_{98}, τ_{76}, τ_{94}	1 ps
Absorption cross section at λ_{src}, α_{src}	46,400 $\mathrm{cm^{-1}}$ $\mathrm{M^{-1}}$
Ground state self-absorption cross section, $\sigma_{\mathrm{abs}}^{S_0S_1}$	1×10^{-19} $\mathrm{cm^2}$
Singlet self-absorption cross section, $\sigma_{\mathrm{abs}}^{S_1S_2}$	1×10^{-17} $\mathrm{cm^2}$
Triplet self-absorption cross section, $\sigma_{\mathrm{abs}}^{T_1T_2}$	1×10^{-17} $\mathrm{cm^2}$
Fraction of pump absorbed by ground state $\eta^{S_0S_1}$	1
Fraction of pump absorbed by singlet $\eta^{S_1S_2}$	0
Fraction of pump absorbed by triplet $\eta^{T_1T_2}$	0

Table 1 Parameters used in the rate equation model. All other parameters appearing in the rate equations can be derived from the above using the relations given in the text.