Temporal response of optically pumped organic semiconductor lasers and its implication for reaching threshold under electrical excitation

N. C. Giebink[1,2] and S. R. Forrest[2,*]

[1]*Department of Electrical Engineering, Princeton University, Princeton, New Jersey 08544, USA*

[2]*Department of Electrical Engineering and Computer Science and Department of Physics, University of Michigan, Ann Arbor, Michigan 48109, USA*

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We study the step response of optically pumped organic semiconductor lasers and find that lasing is sustained for <150 ns following pump turn on due to annihilation quenching of guest singlet with host triplet excitons. We derive a general criterion for reaching threshold that critically depends on the pump rise time, the singlet-triplet quenching rate, and the spin statistics of exciton formation. These results imply that singlet-triplet annihilation alone fundamentally restricts lasing by electrical excitation to conditions that are not practically feasible in organic semiconductors.

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The desire for compact, inexpensive, and broadly tunable laser sources has driven intense research into the development of an organic semiconductor laser (OSL) diode.[1–3] However, only optically pumped OSLs have been demonstrated. Various exciton annihilation processes,[4,5] low charge-carrier mobility,[1] and the design of low-loss, electrically pumped cavities[3] have emerged as the primary obstacles to reaching this goal. Nevertheless, attempts to observe electrically pumped lasing in organic semiconductor cavities have been widespread, but have as yet not met with success.[3,6] In previous efforts to study the intrinsic losses of OSLs, continuous wave (CW) and quasi-CW optical pumpings above threshold were attempted, but lasing was not observed.[3] This may be due to triplet excited-state absorption, as in the case of liquid dye lasers;[7,8] however, the solid state of OSLs complicates this issue since exciton annihilation processes may be more efficient.[4,5] Examining the boundary between pulsed and CW lasing thus presents a unique opportunity for studying fundamental losses in organic semiconductors.

Here we study the onset and subsequent decay of laser emission from step-edge optical pumping of distributed feedback resonators with gain provided by the host/guest systems[1,9] of tris(8-hydroxyquinoline) aluminum (Alq_3)/4-dicyanmethylene-2-methyl-6-(*p*-dimethylaminostyryl)-4H-pyran (DCM), and 4,4′-bis(9-carbazolyl)-2,2′-biphenyl (CBP)/4, 4′-*bis*(9-ethyl-3-carbazovinylene)-1, 1′ -biphenyl (BCzVBi). We find that laser emission in both material systems is sustained for <150 ns following turn on of the pump and show that annihilation of guest singlets with host triplets created by intersystem crossing strongly quenches the laser emission. We show that this loss mechanism alone imposes a fundamental limit to reaching lasing threshold under electrical injection that requires conditions beyond what is practically attainable in organic semiconductors.

The OSLs employ second order distributed feedback (DFB) resonators and rely on efficient Förster transfer of singlet excitons from host to guest to reduce the intrinsic cavity loss.[1,10] The OSL waveguides consist of the organic gain medium of thickness d, deposited onto a sinusoidal, nanoimprinted, transparent, amorphous fluoropolymer grating supported by a glass substrate. The grating modulation depth is ~ 70 nm and the periods were $\Lambda=(407\pm4)$ nm and $\Lambda=(300\pm4)$ nm for the Alq_3/DCM and CBP/BCzVBi OSLs, respectively.

Gain media were deposited by thermal co-evaporation of host and dopant to yield films conformal to the grating that consisted of 2 wt % DCM in Alq_3 and 4 wt % BCzVBi in CBP. The Alq_3/DCM active layer thickness is $d=260$ nm, while for CBP/BCzVBi, it is thinner, with $d=140$ nm, since CBP absorbs the ultraviolet (UV) pump wavelengths more strongly[1] than Alq_3, resulting in nonuniform excitation. The OSLs were tested in a N_2 purged sample cell, with emission collected normal to the substrate.

Under pulsed N_2 laser excitation ($\lambda_{pump}=337$ nm, 0.8 ns pulse width), we clearly observe lasing as distinguished by existence of a threshold, spectral linewidth collapse, emergence of a well-defined beam, and characteristic laser "speckle."[11] This occurs for the Alq_3/DCM and CBP/BCzVBi OSLs at threshold pump energy densities of $E_{th}=(1.5\pm0.5)$ $\mu J/cm^2$ and $E_{th}=(1.3\pm0.5)$ $\mu J/cm^2$, respectively.[12] Using the host absorption coefficients[3,9] at λ_{pump}, we calculate the corresponding average threshold singlet exciton densities to be $N_{th}=5.2\times10^{16}$ cm^{-3} and $N_{th}=1.5\times10^{17}$ cm^{-3} for Alq_3/DCM and CBP/BCzVBi, respectively. Lasing occurs for Alq_3/DCM at $\lambda_L=633.7$ nm, near the peak of the DCM gain spectrum, while CBP/BCzVBi lases at $\lambda_L=473.8$ nm, near the (0,1) BCzVBi emission vibronic. In both cases the linewidth is <0.1 nm and lasing evolves from the long-wavelength side of the transverse electric (TE) stop band, since this mode is more tightly confined and the lasers are index coupled.[13]

The OSL responses to pumping with an acousto-optically modulated multiline-ultraviolet Ar^+ laser ($\lambda_{pump}=334$, 351, 364 nm) are recorded with a monochromator and streak camera. The spectrally resolved step response of the CBP/BCzVBi OSL to a 200 ns pulse with a 45 ns rise time is shown for increasing pump intensity in Figs. 1(a)–1(c). In Fig. 1(a), only BCzVBi spontaneous emission is observed at a pulse intensity $I_0=1.5$ kW/cm^2, closely following the pump temporal profile. At $I_0=1.7$ kW/cm^2, a sharp increase of emission intensity and spectral narrowing marks the ini-

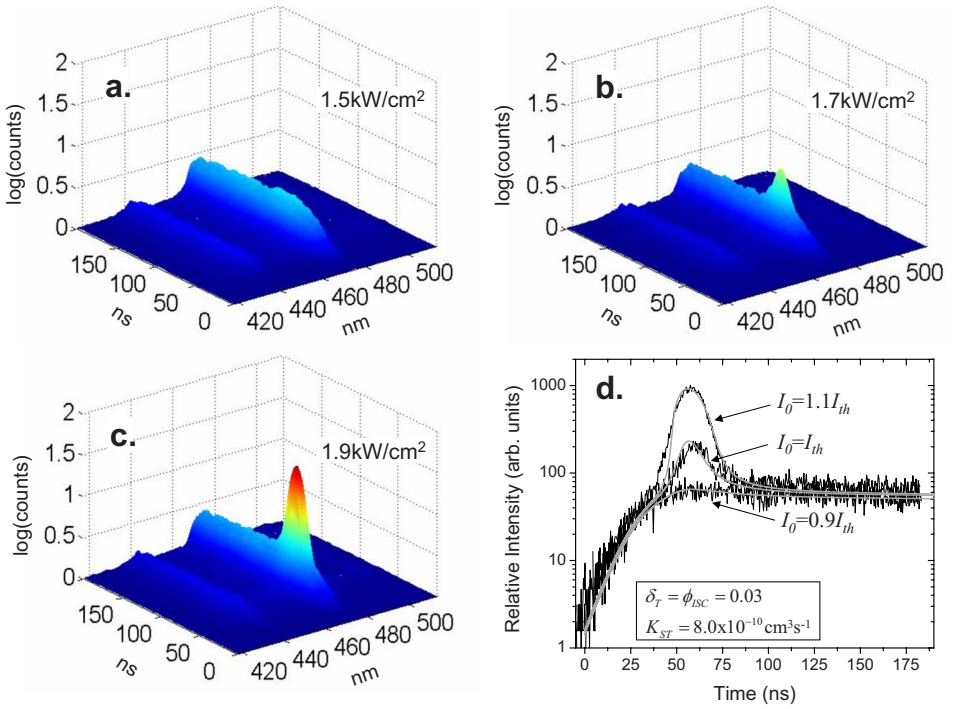

FIG. 1. (Color online) Spectrally resolved CBP/BCzVBi OSL step responses for a 200 ns Ar^+ laser pump pulse with intensity below, at, and above threshold. Only CBP/BCzVBi spontaneous emission is evident below threshold in (a). At threshold, in (b), spectral narrowing and an increase in intensity at the laser line $\lambda_L = 474$ nm are observed. Lasing is established above threshold in (c), although it is quenched at $t > 80$ ns. (d) Fits (gray lines) to the intensity transient data of (a)–(c) at the lasing wavelength (black lines) using the model presented in the text.

tiation of lasing at $t=45$ ns [see Fig. 1(b)]. Above threshold [see Fig. 1(c)], lasing persists for $45<t<80$ ns, with a well-defined beam and laser speckle visible to the eyes. This behavior is qualitatively similar for Alq_3/DCM, but in that case, lasing persists for $30<t<130$ ns and the threshold is only $I_0=0.70$ kW/cm^2 (Ref. 12). Further increase in pump intensity generally increases the lasing duration for both OSLs; however, it never exceeded 150 ns even for pump intensity twice that of threshold.

Since neither host/guest system energetically forms a donor/acceptor pair,[14] free charge densities are expected to be insignificant in these experiments. Consequently, quenching of laser emission is due to the accumulation of long-lived triplet excitons. To determine whether host or guest triplets are most active in quenching, we examine the lasing recovery kinetics[3] of the Alq_3/DCM and CBP/BCzVBi devices, as well as a third OSL with a 200 nm thick layer of 2 wt % DCM doped into CBP as the gain medium. This third device lased at $\lambda_L=626.3$ nm under N_2 laser excitation, with a threshold approximately ten times higher than that of the other OSLs.

Lasing recovery was probed using an initial 200 ns Ar^+ laser pump pulse ($I_0=2.0$ kW/cm^2) followed with time delay τ by a N_2 laser pulse of energy density approximately 1.5 times that of threshold. Figure 2 shows the recovery of laser intensity during the second pulse as a function of τ, normalized to the intensity in the absence of the initial pulse, where the data were obtained by randomly varying τ to eliminate potential degradation effects over the course of the measurement. Laser emission from the trailing pulse is reduced for small τ due to quenching from triplets generated during the initial pulse and it slowly recovers for increasing τ. Aside from an early ($\tau<10$ μs), rapid change common for all three OSLs, Alq_3/DCM recovers with a mono-exponential time constant $\tau_{rec}=(40\pm3)$ μs. This contrasts strongly with the recovery of the two CBP-based OSLs, which both show $\tau_{rec}\geq 700$ μs. This clearly indicates that *host* triplets are responsible for quenching and rules out the possibility of device heating since the thermal time constants of all devices are equivalent.

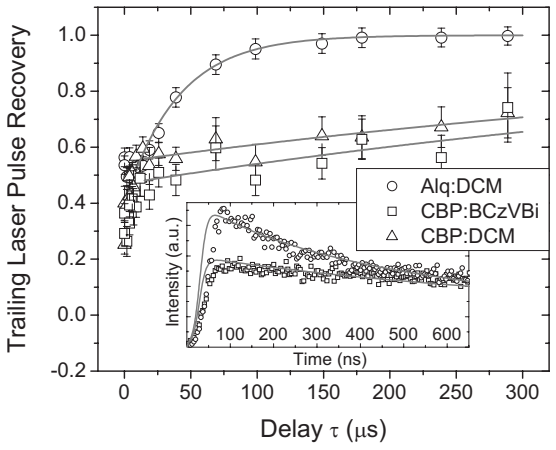

FIG. 2. Double pulse lasing recovery of Alq_3/DCM (circles), CBP/BCzVBi (squares), and CBP/DCM (triangles) OSLs. The lasing intensity due to the trailing N_2 laser pulse is shown vs delay, τ, from the initial 200 ns Ar^+ laser pulse. Gray lines show monoexponential fits, where the Alq_3/DCM OSL recovers with time constant $\tau_{rec}=(40\pm3)$ μs. The OSLs with a common CBP host recover with $\tau_{rec}\geq 700$ μs. Inset: Photoluminescence step response of Alq_3/DCM and CBP/BCzVBi films to an 800 ns Ar^+ laser pump pulse. Quenching in each transient is due to single-triplet annihilation (STA), as inferred from fits to the model in the text (gray lines). A strongly varying intensity profile through the CBP/BCzVBi film thickness due to its high absorption coefficient results in reduced apparent quenching of the initial transient and is accounted for in the fit.

Host triplet quenching of laser emission proceeds either via increased cavity loss from triplet-triplet absorption, as in liquid dye lasers,[8] or by guest singlet-host triplet annihilation (STA). In this case, singlet donors transfer their energy to triplet acceptors through dipole-dipole coupling.[15] Both processes are related through the triplet-triplet (TT) absorption cross section, σ_{TT}, of the host. The inset of Fig. 2 suggests that STA is the dominant loss mechanism here. Shown are bare PL transients (sample region with no grating) of the Alq_3/DCM and CBP/BCzVBi films obtained using an 800 ns Ar^+ laser pulse at their corresponding threshold intensities. Both transients show quenching, which could not result from increased TT absorption of the photoluminescence, since the optical density calculated assuming reasonable triplet densities and cross sections is $N_T\sigma_{TT}d \ll 0.1$. Triplet data available in the literature are in agreement with this conclusion, i.e., the triplet lifetimes reported[9,16] for Alq_3 and CBP coincide with the values of τ_{rec} determined above. Additionally, Alq_3 triplet-triplet absorption[16] overlaps DCM emission, spanning from $\lambda=450-700$ nm and peaking at $\sigma_{TT}\sim 5\times 10^{-18}$ cm^2.

The laser rate equations[8,17] that describe these results are

$$\frac{dN_S}{dt} = R(t)[1-\delta_T] - \left(\frac{1}{\tau_S} + K_{ST}N_T\right)N_S - \gamma\frac{c}{n_{\text{eff}}}S, \quad (1)$$

$$\frac{dS}{dt} = [\Gamma\gamma - \alpha_{\text{cav}}]\frac{c}{n_{\text{eff}}}S + \Gamma\beta_{\text{sp}}\frac{N_S}{\tau_S}, \quad (2)$$

$$\frac{dN_T}{dt} = R(t)\delta_T - \frac{N_T}{\tau_T}. \quad (3)$$

Here, N_S and N_T are the guest singlet and host triplet exciton densities, S is the photon density in the lasing mode, and α_{cav} is the total cavity loss. The triplet lifetime is τ_T, which is much longer than the singlet lifetime, τ_S, and hence is taken as infinite. The effective index, n_{eff}, and transverse modal confinement factor, Γ, are both evaluated at λ_L, while $\beta_{\text{sp}}\approx 10^{-4}$ is the spontaneous emission factor.[17] The average excitation rate, $R(t)=I_0(t)[1-\exp(-\alpha d)](dh\nu)^{-1}$, depends on the host absorption coefficient at the pump wavelength, α, the pump photon energy, $h\nu$, and its intensity, $I_0(t)$. The gain, γ, is[7,18] $\gamma=N_S\sigma_{\text{stim}}$, where $\sigma_{\text{stim}}=\lambda_L^4 f(\lambda_L)\phi_{\text{fl}}(8\pi c n_{\text{eff}}^2\tau_S)^{-1}$ is the guest stimulated emission cross section and $f(\lambda)$ is its photoluminescence spectrum normalized to the fluorescence quantum yield, ϕ_{fl}. Finally, we use $\alpha_{\text{cav}}=\Gamma\gamma_{\text{th}}$ to estimate α_{cav} from the pulsed threshold densities, N_{th}, since triplet buildup (and thus STA) is negligible under such short pulses.

From Eqs. (1)–(3), we find the bimolecular STA quenching rate, K_{ST}, and the triplet formation yield, δ_T, defined as the fraction of excitations that result in a host triplet. Under optical excitation, $\delta_T\rightarrow\phi_{\text{ISC}}$, the host intersystem crossing yield,[15] and for electrical excitation, $\delta_T\rightarrow\chi_T$, the triplet spin formation fraction.[19]

In Fig. 1(d), $S(t)$ is calculated from Eqs. (1)–(3) and fit to the CBP/BCzVBi lasing transients from Figs. 1(a)–1(c); analogous fits are obtained for Alq_3/DCM. These fits also include the data from the inset of Fig. 2, where the calculated intensity is directly proportional to the singlet density, since net gain is absent in the bare films. Agreement is obtained for all fits, yielding the following parameters: $\phi_{\text{ISC}}=0.03$, $K_{ST}=8.0\times 10^{-10}$ cm^3 s^{-1} and $\phi_{\text{ISC}}=0.15$, $K_{ST}=1.9\times 10^{-10}$ cm^3 s^{-1} for CBP/BCzVBi and Alq_3/DCM, respectively, which are typical of literature reported values.[4,16] We note, however, that δ_T and K_{ST} are correlated, hence the values determined are not independent.

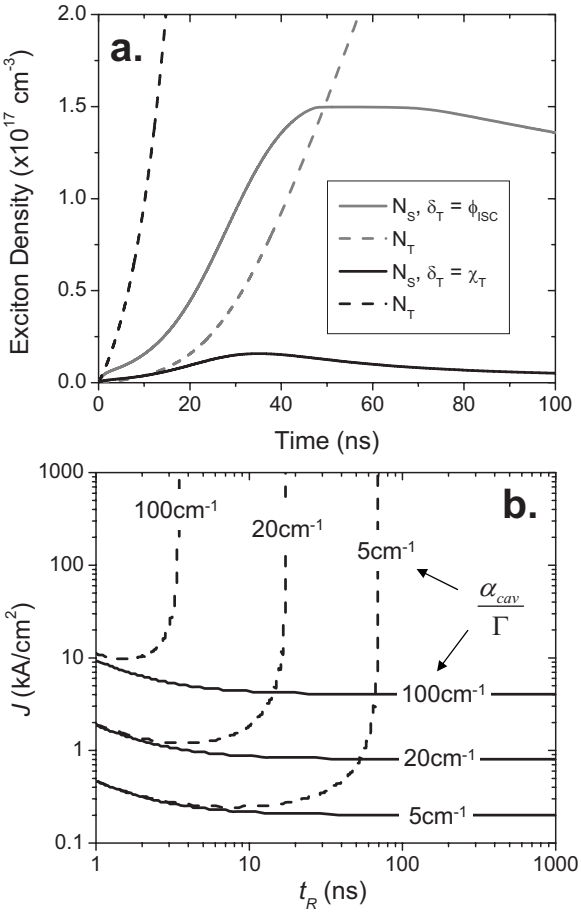

FIG. 3. (a) Singlet (N_S) and triplet (N_T) densities extracted from the CBP/BCzVBi model for the cases of optical and electrical pumping. When the triplet formation fraction $\delta_T=\phi_{\text{ISC}}=0.03$, the rate of triplet generation is low and the singlet density exceeds that of triplets for $t<50$ ns, allowing threshold to be reached (gray lines). When $\delta_T=\chi_T=0.75$, triplets always outnumber singlets and singlet-triplet annihilation (STA) prevents lasing (black lines). (b) Laser threshold criteria calculated from Eq. (4) in the text. The contours indicate the maximum cavity loss, $\alpha_{\text{cav}}/\Gamma$, capable of lasing for different combinations of rise time, t_R, and current density, J. In the presence of STA, with $K_{\text{ST}}=1.9\times 10^{-10}$ (dashed lines), the curves asymptote vertically, making lasing impossible for any J in devices with rise times that exceed t_R. Eliminating STA relaxes the rise-time requirement (solid lines) and leads to lower threshold current densities.

To demonstrate the effect of exciton spin statistics on OSL performance, the singlet and triplet exciton densities calculated for the fit above threshold in Fig. 1(d) are shown in Fig. 3(a). When $\delta_T=\phi_{\text{ISC}}=0.03$, the generation rate of triplets is small, resulting in an early time period ($t<50$ ns) during which $N_S>N_T$, leading to high gain and minimal quenching. This allows threshold to be reached, at which

point N_S clamps to its threshold value of 1.5×10^{17} cm^{-3}. Since the triplet lifetime is long ($\tau_T \gg$ pump pulse width), $N_T(t)$ is proportional to the integral of the pump over time, t. Thus, when $t>70$ ns, N_T has accumulated to a level at which STA is efficient, reducing N_S below threshold and terminating laser emission. The situation changes drastically when the same model is applied assuming electrical spin statistics ($\delta_T=\chi_T=0.75$). In this case, triplets always outnumber singlets since their generation rate is higher. Consequently STA becomes efficient early on and prevents N_S from reaching its threshold value.

Following this analysis, Eqs. (1) and (3) can be used to derive a general criterion for reaching the lasing threshold

$$R_0(1-\delta_T)t_R N_{\text{th}}^{-1}\int_0^1 u\,\exp[t_R/\tau_S(u-1) + 1/6K_{\text{ST}}R_0\delta_T t_R^2(u^3-1)]du \geq 1, \quad (4)$$

where a linear increase in excitation rate to R_0 over time t_R is assumed under the condition $\tau_T \gg t_R$. For electrical excitation, $R_0 \sim J(qx_{\text{EML}})^{-1}$, where q is the electronic charge and x_{EML} is the width of the exciton recombination zone.

In Fig. 3(b), this criterion is applied to an electrically pumped Alq_3/DCM OSL, assuming $\delta_T=\chi=0.75$ and a 50 nm thick recombination zone. Several contours of the critical cavity loss, $\alpha_{\text{cav}}/\Gamma$ ($=N_{\text{th}}\sigma_{\text{stim}}$), which meet the threshold criterion, are shown as a function of drive current, J, and rise time, t_R, for the cases of K_{ST} determined for Alq_3/DCM (dashed lines) and $K_{\text{ST}}=0$ (solid lines). When STA is active, it is not possible to reach threshold at *any current density* if the cavity loss dictates a maximum rise time smaller than is achievable for the electrically pumped device. For example, a previously fabricated Alq_3/DCM laser diode structure[3] was estimated to have $\alpha_{\text{cav}}/\Gamma \cong 150$ cm^{-1}. To reach threshold, this would require $J>20$ kA/cm^2 and $t_R<3$ ns, a combination that is unreachable with current materials and light emitting device architectures. Clearly, either K_{ST} must be eliminated or host triplets must be rapidly quenched. From Fig. 3(b), when $K_{\text{ST}}\rightarrow 0$, the rise-time constraint disappears and threshold is achievable at a significantly lower current density. This can be accomplished using a host/guest system with no spectral overlap between the guest emission and σ_{TT} of the host,[15] although this is generally difficult, since in most materials, absorption by the triplet tends to be spectrally broad and redshifted from that of the ground state.[7]

In addition to the significant quenching effects of STA, quenching due to singlet-polaron annihilation must also be considered since it has been predicted to be comparable or greater in magnitude to the STA observed here.[4] However, since even the *minimal* requirements imposed by STA are not attainable in organic semiconductors, an electrically injected OSL is unlikely to be realized without a significant breakthrough in materials design and device architecture that *simultaneously* eliminates both STA and polaron annihilation losses. As a result, indirect electrical pumping schemes[20,21] not subject to such losses may instead provide the most practical route to an electrically pumped OSL, in which case the threshold criterion developed here is directly applicable.

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*stevefor@umich.edu

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