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RAPID COMMUNICATIONS

PHYSICAL REVIEW B **84**, 241301(R) (2011)

# Existence of continuous-wave threshold for organic semiconductor lasers

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(Received 8 October 2011; published 5 December 2011)

We develop a model that predicts two threshold pump intensities in optically pumped organic semiconductor lasers (OSLs); one for pulsed lasing, $I_{PS}$, and another for continuous-wave (CW) lasing, $I_{CW}$. The theory predicts a decrease in $I_{CW}$ from 32 kW/cm$^2$, or well above the damage threshold, to 2.2 kW/cm$^2$, for a laser employing 4-(dicyanomethylene)-2-methyl-6-julolidyl-9-enyl-4H-pyran–doped tris(8-hydroxyquinoline) aluminum if the triplets can be effectively removed from the emissive guest. Based on this analysis, we demonstrate that the lasing duration can be extended to nearly 100 $\mu$s, ultimately limited by degradation of the lasing medium when a "triplet manager" molecule, 9,10-di(naphtha-2-yl)anthracene, is blended into the gain region of an otherwise conventional distributed feedback OSL. The triplet manager facilitates radiative singlet transfer while suppressing nonradiative triplet transfer to the emitter molecule, thus reducing the triplet-induced losses. Our theory conclusively shows that these lasers have entered the CW lasing regime.

DOI: 10.1103/PhysRevB.84.241301 PACS number(s): 42.60.Rn, 71.35.−y, 81.05.Fb

Optically pumped organic semiconductor lasers (OSLs) with low thresholds and wide spectral tuning ranges have attracted interest since their demonstration 15 years ago.[1–4] However, a significant obstacle to the application of OSLs has been their limitation to only pulsed operation with a maximum duration of several tens of nanoseconds.[5–7] This limitation is imposed by the buildup of triplet ($T$) excitons in the gain region that are generated from intersystem crossing (ISC) of radiative singlets ($S$).[6,8,9] Since relaxation from the triplet to the ground state is quantum-mechanically forbidden,[10] the lifetime of triplet exciton is large (several milliseconds) compared to that of a singlet (several nanoseconds), allowing the triplet population to accumulate over time. The high triplet population, together with overlapping singlet emission and triplet absorption, results in singlet and photon losses that ultimately shut down lasing, thereby preventing continuous-wave (CW) operation.

While triplet losses in liquid dye lasers can be mitigated by using quencher molecules with triplet energies lower than that of the dye,[11,12] no CW operation has been realized without dye circulation. For OSLs, gain medium circulation is not possible; however, several efforts have been made to mitigate, although not eliminate, triplet losses to the extent that CW operation can be achieved. Bornemann *et al.*[13] have used a rapidly rotating substrate to demonstrate a CW solid state dye laser, but the output was unstable. Schols *et al.*[14] have shown that "scavengers" can be used to de-excite triplets, but no lasing improvement was demonstrated. Rabe *et al.*[15] and Lehnhardt *et al.*[16] demonstrated that a polymer OSL pumped by very low duty cycle (<0.1%) pulses extended the total duration to 400 $\mu$s, although this is not a true CW operation.

Here, we introduce a "triplet manager" into the gain region, along with the guest emitter and host molecules. The manager reduces the emitter triplet population, thus extending the lasing duration. The inset of Fig. 1 shows the triplet management concept. The manager has lower triplet energy and higher singlet energy than the emitter. When either the host or the manager molecules are excited, Förster transfer[17] of singlet states to the emitter is highly efficient. Furthermore, Dexter transfer[18] of triplets leads to their trapping on the manager since it has lower triplet energy than both the guest and the host. The manager triplet absorption is shifted from the guest emission; thus, the trapped triplets do not contribute to optical losses[9] or singlet quenching.[6]

The 200-nm-thick OSL active region consists of the manager, 9,10-di(naphtha-2-yl)anthracene (ADN), codeposited into the conventional guest–host gain medium consisting of 2 vol% of the red emitting 4-(dicyanomethylene)-2-methyl-6-julolidyl-9-enyl-4H-pyran (DCM2) in tris(8-hydroxyquinoline) Al ($Alq_3$). The singlet and triplet energies are determined from fluorescence at room temperature and phosphorescence at 14 K, respectively.[19–21] Here, ADN has a lower triplet energy (1.69 eV) and higher singlet energy (2.83 eV) than $Alq_3$ ($T$ = 1.99 eV and $S$ = 2.38 eV). Furthermore, $S$ = 2.03 eV and $T$ = 1.74 eV for DCM2. This system, therefore, is energetically consistent with Fig. 1.

The manager concentration in (100 − $x$) vol% $Alq_3$ is $x$ vol% ADN ($x$ = 0, 10, 30, 50, 70, 100). Blended films were deposited by thermal evaporation in high vacuum ($10^{-7}$ torr) on quartz, Si, and 2-$\mu$m-thick $SiO_2$-on-Si substrates for characterizing absorption, photoluminescence (PL), and triplet absorption, respectively. The same films were deposited on gratings with a period of 430 ± 5 nm and a 50-nm depth on the $SiO_2$-on-Si to form distributed feedback (DFB) OSLs. Output from a 0.6-W laser diode at wavelength $\lambda$ = 405 nm was focused to a 150 × 250-$\mu$m spot to optically pump the thin film. $Alq_3$ and ADN pure film absorption coefficients were measured to be $4.8 \times 10^4$ and $9.1 \times 10^{-4}$ cm$^{-1}$, respectively, at $\lambda$ = 405 nm, and are assumed to contribute to the total blend film absorption proportionate to their volume. All measurements were performed in $N_2$ ambient to minimize film degradation.

Figure 2 shows the PL and lasing transients pumped at 1.6 kW/cm$^2$. From Fig. 2(a), the $Alq_3$ host undergoes a 55% reduction in PL to its steady state value within 30 $\mu$s of the onset of the pump. Previous studies have shown that this intensity roll-off is due to singlet quenching from $S$-$T$ annihilation.[6,22]

 

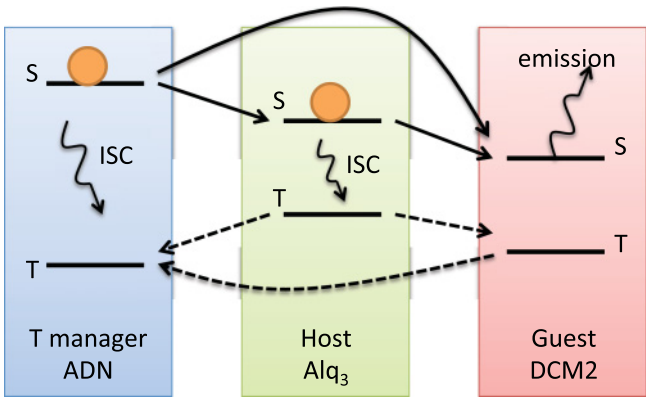


FIG. 1. (Color online) Separate channels for singlet ($S$) and triplet ($T$) formation and transfer in triplet-managed lasers. Singlets are generated (circles) on both $Alq_3$ and ADN, and Förster transferred (solid arrows) to DCM2. Triplets are generated by ISC and collected by ADN through Dexter transfer (dashed arrows).

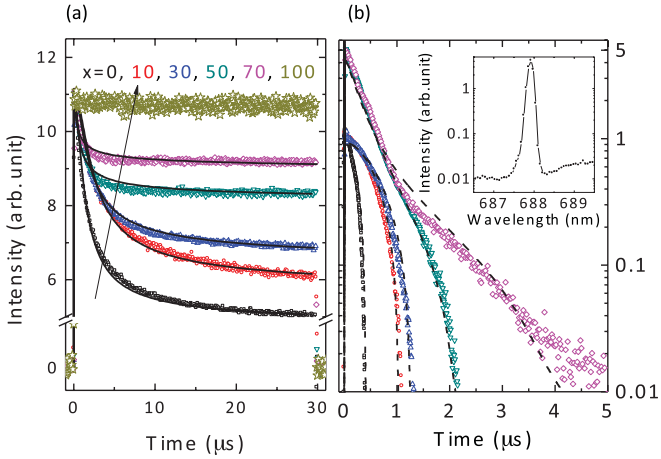


FIG. 2. (Color online) (a) PL and (b) lasing transients measured at 1.6 kW/cm$^2$ pump intensity for different host blends. PL transients are normalized by the peak intensities, and lasing transients are normalized to 1 for $x = 0$, 10, and 30 ADN blends and to 5 for $x = 50$ and 70 ADN blends. The fits are obtained by the model described in the text, with the parameters summarized in Table I. The inset shows the lasing spectrum of an $x = 70$ OSL.

That is, following the onset of the optical pump, the singlet density rapidly reaches a peak and subsequently decays due to annihilation by the slowly increasing triplet population.[22] The existence of the long-term steady state PL intensity below its peak suggests saturation of the guest triplet population. By including the ADN manager into the host blend with $x = 10$–70, the PL transient quenching is reduced to 17%. Further increasing to $x > 70$ can eliminate quenching entirely. We infer, therefore, that triplets are transferred from $Alq_3$ to DCM2, while the transfer from ADN to DCM2 is forbidden, consistent with the triplet energy relation $T(Alq_3) > T(DCM2) > T(ADN)$. However, morphology degradation under high pump intensity occurs for $x > 50$, consistent with the previous observation of morphological instability of ADN.[23]

In Fig. 2(b), more than a 10-fold increase in lasing time (from ~400 ns to 4.5 $\mu$s) is observed when $x$ increases from 0 to 70. Lasing is not observed for $x = 100$ due to degradation. The inset shows a typical lasing spectrum of a 70% ADN OSL centered at $\lambda = 687.9$ nm, with a full width half maximum of 0.15 nm limited by the spectrometer resolution. The threshold pulsed pump intensity, $I_{PS}$ (characterized by an abrupt spectral narrowing from >30 to <0.5 nm and a significant increase in the slope efficiency) was obtained using a 30-ns pump pulse (Table I).

To understand the transient PL and lasing dynamics, we extend previous work[6,9,22,24] to include triplet Dexter transfer from host blend to guest, and guest triplet saturation. Hence, the coupled laser rate equations are

$$\frac{dS}{dt} = \frac{\eta I}{e_p d} - k_S S - k_{ISC} S - k_{ST} S T_G - \gamma \frac{c}{n_{\text{eff}}} p, \quad (1)$$

$$\frac{dT_H}{dt} = k_{ISC} S - k_{HG} \exp\left(-\frac{2}{L}\sqrt[3]{\frac{1}{N_0 - T_G}}\right) T_H, \quad (2)$$

$$\frac{dT_G}{dt} = k_{HG} \exp\left(-\frac{2}{L}\sqrt[3]{\frac{1}{N_0 - T_G}}\right) T_H, \text{ and} \quad (3)$$

$$\frac{dP}{dt} = (\Gamma\gamma - \alpha_{CAV} - \Gamma\sigma_{TT} T_G)\frac{c}{n_{\text{eff}}} P + \Gamma\beta k_S S, \quad (4)$$

where $S$, $T_H$, $T_G$, and $P$ are guest singlet, host blend triplet (including both ADN and $Alq_3$), guest triplet, and lasing mode photon densities, respectively; $t$ is time; $\eta$ is the fraction of the pump emission absorbed by the organic film; $I$ is the pump intensity; $e_p = 3.06$ eV is the pump photon energy; $d =$ 200 nm is the OSL gain medium thickness; $k_S = (6.7 \pm 0.5) \times 10^8$ s$^{-1}$ is the guest singlet natural decay rate (measured from a 2% DCM2:$Alq_3$ film excited by 1.5-ns-wide $N_2$ laser pulses); $k_{ISC}$ is the host ISC rate; $k_{ST}$ is the guest $S$-$T$ annihilation

TABLE I. Parameters for PL and lasing transients fits and the corresponding measured pulsed ($I_{PS}$) and calculated CW ($I_{CW}$) lasing threshold intensities.

| Device (%ADN) | $I_{TH}$† (kW/cm$^2$) | $k_{HG}$* ($10^{10}$ s$^{-1}$) | $k_{ISC}$* ($10^7$ s$^{-1}$) | $N_0$* ($10^{18}$ cm$^{-3}$) | $\sigma_T T$† ($10^{-17}$ cm$^2$) | $\sigma_{\text{stim}}$* ($10^{-16}$ cm$^2$) | $I_{CW}$ (kW/cm$^2$) |
|---|---|---|---|---|---|---|---|
| 0 | 0.93 | 4.0 | 3.3 | $5.0 \pm 0.4$ | $4.0 \pm 0.3$ | 1.9 | 32 |
| 10 | 0.75 | 3.5 | 2.6 | $3.9 \pm 0.3$ | $3.8 \pm 0.3$ | 2.0 | 19 |
| 30 | 0.72 | 13 | 2.3 | $2.8 \pm 0.3$ | $3.6 \pm 0.4$ | 2.4 | 8.8 |
| 50 | 0.45 | $3.0 \times 10^3$ | 1.7 | $1.5 \pm 0.2$ | $4.3 \pm 0.6$ | 2.1 | 3.7 |
| 70 | 0.43 | $5.0 \times 10^5$ | 1.3 | $0.92 \pm 0.08$ | $4.1 \pm 0.4$ | 2.3 | 2.2 |

†Parameters from measurement.
*Parameters from fits to data.

rate; $\gamma = \sigma_{\rm stim} S$ is the gain; $\sigma_{\rm stim}$ is the stimulated emission cross section; $c$ is the speed of light; and $n_{\rm eff} = 1.6$ and $\Gamma = 0.69$ are the effective refractive index and optical confinement factor for the $SiO_2$ ($n = 1.48$)/organic ($n = 1.82$)/air ($n = 1$) waveguide.[25] Also, $k_{HG}$ is the host–guest Dexter transfer coefficient, $L$ is the guest–host van der Waals radius (~1 nm), $N_0$ is the guest triplet saturation population, $\alpha_{CAV}$ is the cavity loss without contributions from triplet absorption, $\alpha_{TT}$, $\sigma_{TT}$ is the guest triplet absorption cross section, and $\beta \approx 10^{-4}$ is the spontaneous emission factor.[26] For PL, we have $P = 0$, and the intensity is proportional to $S$. We assume that the host triplet population does not interact with $S$ or $P$; this is tested by fits to the data, as well as via direct triplet absorption measurements. Now, $N_0$ is determined from the saturation of PL quenching due to the balance of triplet transfer from $Alq_3$ to DCM2, and is determined from triplet trapping on ADN. Introducing $N_0$ avoids the complication of treating individual triplet transfer in the ternary blend.

Free parameters $k_{ST}$, $k_{ISC}$, $k_{HG}$, and $N_0$ are used in fitting the PL transients. To test for model consistency, transients at four pump intensities (1.6, 1.3, 0.93, and 0.56 kW/cm$^2$) yield a single set of parameter values summarized in Table I. For all films, $k_{ST} = 2.0 \times 10^{10}$ cm$^3$/s, as expected for guest $S$-$T$ annihilation due to resonant energy transfer that is only dependent on DCM2 singlet emission and triplet absorption. As $x$ increases, fewer triplets are transferred from $Alq_3$ to DCM2 and more are trapped on ADN; thus, $N_0$ decreases from $5.0 \times 10^{18}$ to $9.2 \times 10^{17}$ cm$^{-3}$ when $x = 70$, leading to decreased PL transient roll-off. The ~$10^5$ increase in $k_{HG}$ seems surprising; however, the Dexter transfer rate is determined by $k_{\rm Dex} = k_{HG} \exp[-\frac{2}{L}\sqrt[3]{\frac{1}{N_0 - T_G}}]$. Thus, for $T_G = 0.7 N_0$, $k_{\rm Dex}$ only increases from $7.6 \times 10^4$ s$^{-1}$ ($x = 0$) to $4.4 \times 10^5$ s$^{-1}$ ($x = 70$), consistent with the shorter PL quenching time at higher $x$.

To model the lasing transients in Fig. 2(b), three additional parameters—$\sigma_{TT}$, $\sigma_{\rm stim}$, and $\alpha_{CAV}$—are required. Here, $\alpha_{TT}(\lambda)$ was measured following Lehnhardt *et al.*,[9,21] and $\sigma_{TT} = \alpha_{TT}/N_0$ is shown in Table I at $\lambda = 680$ nm. The nearly constant $\alpha_{TT}(\lambda)$ spectra and $\sigma_{TT}$ for all $x$ are consistent with the assumption that only guest triplets absorb the laser emission (i.e. host and manager absorptions are negligible). Furthermore, $\alpha_{CAV} = \Gamma \sigma_{\rm stim} S_{PS}$, where $S_{PS} = \eta I_{PS}/(e_p d k_S)$ is the pulse threshold singlet population. Here, triplet buildup under short excitation pulses is negligible. With these measurements and assumptions, the lasing transients are fit using only a single free parameter, $\sigma_{\rm stim}$ (Table I). The effect of ADN as a triplet manager lies in its ability to decrease $N_0$, while $k_{ST}$ and $\sigma_{TT}$ remain unchanged since they are intrinsic to DCM2.

The net gain $g(t) = \Gamma \sigma_{\rm stim} S(t) - \alpha_{CAV} - \Gamma \sigma_{TT} T_G(t) = 0$ determines the threshold singlet population dynamics, $S_{TH}(t)$, which are plotted in Fig. 3 for the $Alq_3$ host (squares) and the optimized ($x = 70$) blend host (stars), using the parameters in Table I. Surprisingly, two distinct threshold singlet populations emerge from the fits, with a CW threshold population ($S_{CW}$) occurring at a density larger than that needed for pulsed lasing ($S_{PS}$). As $t \to 0$, triplet loss $\Gamma \sigma_{TT} T_G \ll \alpha_{CAV}$, giving $S_{PS} = \alpha_{CAV}/(\Gamma \sigma_{\rm stim})$. With time, $T_G$ increases, concomitantly increasing the associated loss until $\Gamma \sigma_{TT} T_G > \alpha_{CAV}$. Finally,

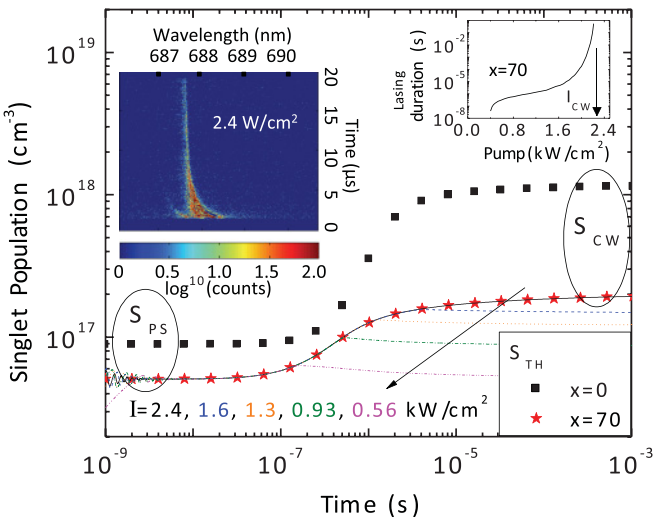


FIG. 3. (Color) Simulated threshold singlet population, $S_{TH}(t)$ with ($x = 70$, stars) and without (squares) a triplet manager, and $S(t)$ (lines) for the $x = 70$ OSL. Lasing occurs when $S \geqslant S_{TH}$. The dashed lines correspond to lasers that have exceeded their pulsed threshold singlet population ($S_{PS}$) but not their CW threshold ($S_{CW}$). In the left inset is a streak camera image of laser emission for a triplet-managed OSL ($x = 70$) measured at a 2.4 kW/cm$^2$ pump intensity and a 18-$\mu$s pulse width. In the right inset is a simulated lasing duration evolution with increasing pump power for a $x = 70$ triplet-managed OSL.

$T_G$ reaches its saturation density $N_0$, at which point the triplet loss can no longer increase, giving $S_{CW} = (\alpha_{CAV} + \Gamma \sigma_{TT} N_0)/(\Gamma \sigma_{\rm stim})$. Figure 3 also shows $S(t)$ for several pump intensities, $I$, for the host–manager blend, with the lasing duration vs $I$ plotted in the inset. Due to the saturation of $T_G$ and thus $S_{TH}$, at $I$ greater than the CW pump intensity threshold, $I_{CW} = 2.2$ kW/cm$^2$, the lasing duration is no longer affected by triplet loss and approaches infinity. Table I also gives $I_{CW}$ for all $x$ in blended hosts. With larger $N_0$, and thus increased triplet loss, the $Alq_3$-host OSL has $I_{CW} = 32$ kW/cm$^2$. Due to organic film damage at such high intensities, the CW lasing threshold in the absence of a manager has not been previously reported.

Neglecting the change in singlet population due to stimulated emission (c.f. Eq. (1)), the CW threshold is approximately

$$I_{CW}(N_0) = e_p d (k_S + k_{ISC} + k_{ST} N_0) \frac{\alpha_{CAV} + \sigma_{TT} N_0}{\eta \Gamma \sigma_{\rm stim}} \qquad (5)$$

compared to the pulse threshold $I_{PS} = I_{CW}(N_0 \approx 0)$. From Eq. (5), $I_{CW}$ is a *quadratic* function of guest triplet saturation population: $k_{ST} N_0$ is from $S$-$T$ quenching that reduces the gain, and $\Gamma \sigma_{TT} N_0$ is due to triplet absorption, increasing loss.

To test the existence of this CW regime, we excited an $Alq_3$/ADN ($x = 70$)/DCM2 laser at 2.4 kW/cm$^2$, or just above the calculated value of $I_{CW}$ using the parameters in Table I. Figure 3, left inset, shows a streak camera image of this emission over a 20-$\mu$s duration. Lasing becomes weaker (leading to the apparent spectral narrowing) but does not turn off at the end of the long pulse, consistent with theory. Indeed, we observed a nearly 100-$\mu$s lasing duration[21] when pumped by a single pulse, although film degradation due to high optical pump intensities ultimately limits the lasing duration. Hence,

while this OSL has clearly exceeded its CW threshold, the laser operates quasi-CW due to material degradation.

Interestingly, the lasing wavelength blue shifts from $\lambda = 688.1$ nm to $\lambda = 687.7$ nm during the lasing period, as shown in Fig. 3, left inset. Wavelength shifts have been observed in liquid dye lasers,[12] where they have been attributed to the competition of triplet absorption with the gain spectrum. In thin film single-mode DFB OSLs, where the triplet absorption is largely constant,[21] the shift is more likely due to changes in the effective refractive index with increasing triplet density.

$I_{CW}$ can be further reduced and the lasing time can be extended by using a more stable, lower triplet energy manager and a better match between the manager emission and the guest absorption than is achieved with ADN. Then, the smaller saturation guest triplet population contributes negligible loss, in which case $I_{CW} \rightarrow I_{PS}$. The design concept can be applied to the eventual development of electrically pumped OSLs, where 75% of the injected electrons result in triplets[27] compared to only a few percent in optical pumping.

In conclusion, we show the existence of a CW threshold at a higher pump intensity than the pulsed threshold observed in all previous OSL studies. Based on our analysis, we demonstrate a lasing duration of up to 100 $\mu$s by introducing a triplet manager into the OSL gain medium. The reduced triplet-induced loss of the triplet-managed OSL decreases $I_{CW}$ from 32 kW/cm$^2$ to a more practical value of 2.2 kW/cm$^2$ observed here.

We thank the Air Force Office of Scientific Research (C. Lee) and Universal Display Corp. for financial support of this work. In addition, we thank N. C. Giebink and M. Slootsky for helpful discussions.

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[1] V. G. Kozlov, V. Bulovic, P. E. Burrows, and S. R. Forrest, Nature **389**, 362 (1997).
[2] F. Hide, M. A. Díaz-García, B. J. Schwartz, M. R. Andersson, Q. Pei, and A. J. Heeger, Science **273**, 1833 (1996).
[3] N. Tessler, G. J. Denton, and R. H. Friend, Nature **382**, 695 (1996).
[4] V. Bulovic, V. G. Kozlov, V. B. Khalfin, and S. R. Forrest, Science **279**, 553 (1998).
[5] V. G. Kozlov, G. Parthasarathy, P. E. Burrows, V. B. Khalfin, J. Wang, S. Y. Chou, and S. R. Forrest, IEEE J. Quantum Electron. **36**, 18 (2000).
[6] N. C. Giebink and S. R. Forrest, Phys. Rev. B **79**, 073302 (2009).
[7] I. D. W. Samuel and G. A. Turnbull, Chem. Rev. **107**, 1272 (2007).
[8] M. A. Baldo, R. J. Holmes, and S. R. Forrest, Phys. Rev. B **66**, 035321 (2002).
[9] M. Lehnhardt, T. Riedl, T. Weimann, and W. Kowalsky, Phys. Rev. B **81**, 165206 (2010).
[10] N. J. Turro, *Modern Molecular Photochemistry* (University Science Books, 1991), pp. 38–51.
[11] F. P. Schäfer, *Dye Lasers* (Springer, 1990), pp. 52–59.
[12] B. B. Snavely, in *Proceedings of the IEEE* (1969), Vol. 57, pp. 1374.
[13] R. Bornemann, U. Lemmer, and E. Thiel, Opt. Lett. **31**, 1669 (2006).
[14] S. Schols, A. Kadashchuk, P. Heremans, A. Helfer, and U. Scherf, Chem. Phys. Chem. **10**, 1071 (2009).
[15] T. Rabe, K. Gerlach, T. Riedl, H.-H. Johannes, W. Kowalsky, J. Niederhofer, W. Gries, J. Wang, T. Weimann, P. Hinze, F. Galbrecht, and U. Scherf, Appl. Phys. Lett. **89**, 081115 (2006).
[16] M. Lehnhardt, T. Riedl, U. Scherf, T. Rabe, and W. Kowalsky, Org. Electron. **12**, 1346 (2011).
[17] V. G. Kozlov, V. Bulovic, P. E. Burrows, M. Baldo, V. B. Khalfin, G. Parthasarathy, S. R. Forrest, Y. You, and M. E. Thompson, J. Appl. Phys. **84**, 4096 (1998).
[18] M. A. Baldo, M. E. Thompson, and S. R. Forrest, Nature **403**, 750 (2000).
[19] M. A. Baldo and S. R. Forrest, Phys. Rev. B **62**, 10958 (2000).
[20] I. Tanaka, Y. Tabata, and S. Tokito, Phys. Rev. B **71**, 205207 (2005).
[21] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.84.241301.
[22] Y. Zhang, M. Whited, M. E. Thompson, and S. R. Forrest, Chem. Phys. Lett. **495**, 161 (2010).
[23] S.-W. Wen, M.-T. Lee, and C. H. Chen, J. Display Technol. **1**, 90 (2005).
[24] C. Gartner, C. Karnutsch, U. Lemmer, and C. Pflumm, J. Appl. Phys. **101**, 023107 (2007).
[25] S. L. Chuang, *Physics of Photonic Devices*, 2nd ed. (Wiley, 2009), pp. 257–290.
[26] L. A. Coldren and S. W. Corzine, *Diode Lasers and Photonic Integrated Circuits* (Willey, New York, 1995).
[27] M. A. Baldo, D. F. O'Brien, M. E. Thompson, and S. R. Forrest, Phys. Rev. B **60**, 14422 (1999).