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Temperature dependence of the amplified spontaneous emission of the poly(9,9-dioctylfluorene) β phase

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We investigated the temperature dependence of the amplified spontaneous emission (ASE) of the β phase of poly(9,9-dioctylfluorene). We show that the ASE threshold increases with temperature of about 1 order of magnitude from 17 μJ cm^{-2} at 5 K to 206 μJ cm^{-2} at 300 K due to the thermal activation of uphill energy migration to nonradiative centers that reduces the population inversion for a given excitation density. The temperature increase also changes the luminescence line-shape switching on (around 100 K) the ASE from the C-C interunit stretch vibronic replica at the expense of the phenyl-ring quadrant stretch one.

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I. INTRODUCTION

The emission properties of conjugated molecule thin films, both oligomers and polymers, have been deeply studied in the last decades both for basic physics and for applicative interests. In particular the demonstration of amplified spontaneous emission (ASE) (Ref. 1) and optically pumped lasing[2] opened the way to possible applications of conjugated molecules as active materials in laser devices. In the last years ASE has been obtained in thin films of several classes of molecules, and several prototypes of optically pumped lasers with different cavity geometries have been realized (see Ref. 3 for a recent review). A particularly important issue for the application of conjugated polymers in laser devices is the development of active systems with high gain, thus allowing low ASE and lasing thresholds. To date the best approach to minimize the ASE threshold is the realization of host-guest systems, in which lasing for excitation densities smaller than 1 μJ cm^{-2} has been demonstrated.[4] On the other hand, as well known for inorganic semiconductors, the performances of lasers active materials are often limited by nonradiative recombination processes[5] that are usually thermally activated. Thus the investigation of the temperature dependence of the light amplification in the active material is extremely important as it allows to identify, and eventually optimize, the physical processes increasing the ASE and lasing threshold.[6,7] Despite this importance to date the temperature dependence of ASE and lasing in organic thin films is limited to two poly-para-phenylene-vinylene (PPV) copolymers,[8–10] while no studies on host-guest systems have been performed.

In this Brief Report we investigated the temperature dependence from 5 to 300 K of the photoluminescence (PL) and ASE of the poly(9,9-dioctylfluorene) (PF8) β phase. This system represents a self-doped host-guest system, potentially suitable for applications to low threshold blue organic lasers.[11,12] We observe ASE at all the investigated temperatures with a threshold continuously increasing from 17 μJ cm^{-2} at 5 K to 206 μJ cm^{-2} at 300 K. We demonstrate that this effect is due to the thermal activation of exciton uphill hopping between β-phase molecules with an activation energy of 18 ± 3 meV that, increasing the probability of quenching in nonradiative defects, is also responsible for the PL quenching. We also observe that as the temperature increases, the PL line-shape changes, resulting in a switching of the vibronic replica showing ASE from the phenyl-ring quadrant stretch replica (below 100 K) to the C-C interunit stretch one. Our results are consistent with a temperature-independent-gain cross section and indicate that the ASE temperature dependence is mainly determined by the temperature dependence of the first excited singlet population.

II. EXPERIMENTAL

The samples, with a thickness of about 350 nm, were prepared by spin coating PF8 thin films from a $10^{-4}M$ chloroform solution. In order to induce the formation of the β phase, the samples were exposed to toluene vapors for about 3 h.[13,14] A β-phase content of about 3.3% has been estimated from the absorption spectra.[13] The films were pumped by a nitrogen laser (337 nm) delivering 3 ns pulses with a repetition rate of 10 Hz and a maximum pulse energy of 155 μJ focused on the sample in a 6.0 mm × 100 μm rectangular stripe by a cylindrical lens. The sample PL was collected from the sample edge dispersed by a TRIAX 320 monochromator and detected by a water cooled Si charge coupled device. The spectral resolution was about 3 Å. The PL measurements as a function of the temperature were performed from $T=5$ to 300 K in steps of 25 K in vacuum in a closed-cycle He cryostat both below and above the ASE threshold.

III. RESULTS

The PL spectra at the excitation density of 7.9 μJ cm^{-2}, well below the ASE threshold at all temperatures (see Fig. 1), clearly show the typical emission resonances of the PF8 β phase[13] with the 0-0 line at about 442 and three clear further bands at about 458, 470, and 478 nm due to 0-1 vibronic replicas for the in-plane deformation of the fluorene unit, the C-C interunit stretch ($R_{\text{C-C}}$ in the following), and the phenyl-ring quadrant stretch (R_{PhR} in the following), respectively.[13] As the temperature increases all the PL bands show a blueshift and a broadening that have been deeply discussed in Ref. 15. The PL intensity is almost constant up to about 50 K, and it progressively decreases for higher temperature.

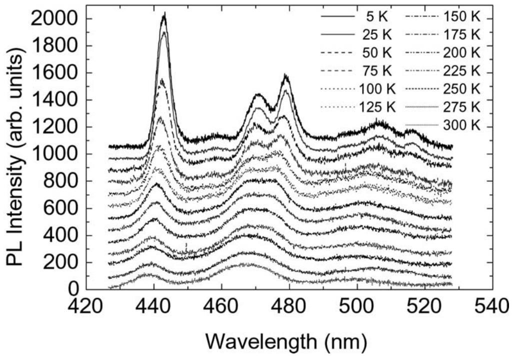

FIG. 1. PL spectra at an excitation density of 7.9 μJ cm^{-2} as a function of the temperature (the spectra are vertically offset for clarity).

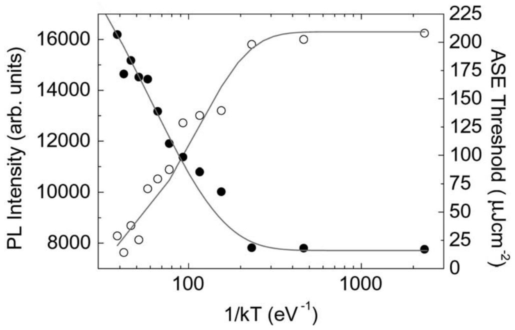

FIG. 3. Temperature dependence of the total PL intensity (empty dots) and ASE threshold (full dots). The continuous lines are the best-fit curves with the equations described in the Brief Report.

Moreover the peak intensity of the two main 0-1 phonon replica[16] $R_{\text{C-C}}$ and R_{PhR} show a different temperature dependence indicating an individually different temperature dependence of the corresponding Huang-Rhys factor that leads to a temperature dependence of their relative intensity (see inset of Fig. 4).

As the excitation density increases ASE is observed at all the investigated temperatures for high enough excitation density. In order to determine the ASE threshold the PL spectra were measured while continuously varying the excitation density with a variable neutral filter, in order to determine the minimum excitation density necessary to observe the PL line-shape variation due to the ASE band appearance (see Fig. 2). The minimum excitation density necessary to see ASE in the spectrum (see Fig. 3), which will be considered as the ASE threshold,[17] is almost constant for temperatures up to 50 K (17 μJ cm^{-2}), and it progressively increases up to 206 μJ cm^{-2} at $T=300$ K. The low-temperature values of the threshold is comparable, considering the different pump pulse time length, with the values reported by Rothe *et al.*,[12] while lower values, between 10 and 100 times, have been reported at room temperature by Heliotis *et al.*[19] and by Ryu *et al.*,[20] under almost resonant nanosecond excitation. While we recently demonstrated that the β-phase content and film losses variation can lead to ASE threshold variation up to 1 order of magnitude,[11] this difference suggest that resonant pumping prevents the polaron generation from higher-lying singlet states,[21] thus reducing the photoinduced absorptions competing with ASE and thus lowering the threshold. The close similarity between the temperature dependence of the PL intensity and of the ASE threshold strongly suggests that the same processes are responsible for both the observed effects.

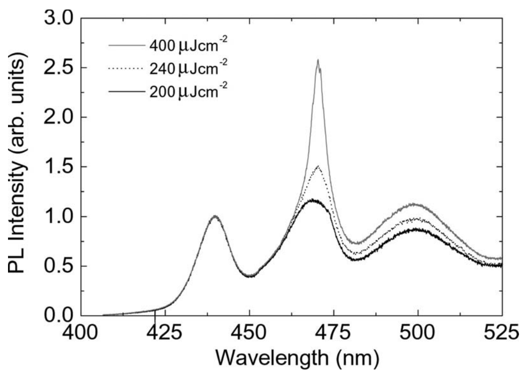

FIG. 2. PL spectra at $T=300$ K as a function of the excitation density below, just above, and above the ASE threshold (the 0-0 line intensity has been normalized to 1 for clarity)

Finally, in order to investigate the temperature effects on the ASE spectra, we performed the measurements also at an excitation density of 2.2 *m*J cm^{-2}, which is well above the ASE threshold for all the investigated temperatures. At $T=5$ K ASE is observed at about 477 nm, thus from the 0-1 phenyl-ring quadrant stretch vibronic replica band R_{PhR}. As the temperature increases the ASE band shows a blueshift and an intensity reduction similar to the PL R_{PhR} one up to 100 K. For temperatures higher than 100 K a second ASE band becomes visible around 470 nm, coinciding with the spectral region of the $R_{\text{C-C}}$ vibronic replica. The interplay between the two ASE bands leads to a total intensity increase and to a blueshift stronger than the PL one. The intensity of this second band progressively increases with temperature, at the expense of the 477 nm one, and dominates the emission spectra for $T \geq 225$ K. For $T \geq 225$ K the blueshift and the intensity reduction are again similar to the PL ones.

IV. DISCUSSION

In order to determine the physical origin of the observed effects we start from the analysis of the PL intensity temperature dependence. The presence of a PL quenching only above a critical temperature is the typical signature of the thermal activation of a nonradiative decay channel.[22] Starting from the rate equation for the first excited singlet population density n_1 it is easy to show that in the steady state,[23] $n_1 = \rho_{\gamma\text{abs}}\tau$, where $\rho_{\gamma\text{abs}} = D/(d\Delta t E_\gamma)$ is the density of photons absorbed per unit of time (D is the excitation density in J cm^{-2}, E_γ is the pump laser photon energy, Δt is the pulse width, and d is the film thickness) and τ is the total excited-state lifetime. Moreover, assuming the presence of a thermally activated nonradiative decay with activation energy ΔE, thus with rate $\tau_{\text{nr}}^{-1} = \tau_{\text{act}}^{-1}\exp(-\Delta E/kT)$, in parallel with a temperature-independent decay with rate $1/\tau_0$, we obtain

$$I_{\mathrm{PL}}(T)=\frac{I_0}{1+\dfrac{\tau_0}{\tau_{\mathrm{act}}}e^{-\Delta E/kT}}, \qquad (1)$$

where I_0 is the PL intensity at $T=0$ K and k is the Boltzmann constant.

The best-fit curve (see Fig. 3) well reproduces the experimental data for $\tau_0/\tau_{\mathrm{act}}=2.0\pm 0.5$ and $\Delta E=(18\pm 3)$ meV. We observe that the obtained value of ΔE is very close to the PL linewidth at $T=5$ K of the 0-0 PL line[13] (about 25 meV). As this value can be considered as a lower limit for the energy disorder at low temperature for the β-phase excitons the close similarity between these two energies strongly suggest that observed nonradiative process is related to the thermal activation of exciton uphill hopping[25] between β-phase molecules. This hopping, increasing the volume of space that an exciton can sample before recombination, increases the probability of the interaction with nonradiative traps or defects,[26,27] thus leading to the observed PL quenching.

Concerning the temperature dependence of the ASE threshold we observe that in order to have light amplification, the gain of the active material has to be larger than the losses α, thus (within the four-level approximation) $g=\sigma n_1>\alpha$, where σ is the gain cross section. The threshold condition can be thus expressed as $\sigma n_1^{\mathrm{thr}}=\alpha$ which gives, by using the relationship between n_1 and D,

$$D^{\mathrm{thr}}=d\Delta t E_\gamma \frac{\alpha}{\sigma}\frac{1}{\tau}. \qquad (2)$$

The best-fit curve of the experimental data to Eq. (2), with ΔE fixed to 18 meV, nicely reproduces the data (see Fig. 3), assuming that both the gain cross section σ and the losses α are temperature independent. This result allows us to conclude that the observed temperature dependence of the ASE threshold is mainly due to the progressive decrease in the population inversion n_1 with temperature that leads to a progressive increase in the excitation density necessary to reach the threshold.

Concerning the temperature dependence of the ASE spectra we observe that when only one ASE band is visible in the spectra, thus for $T\leq 100$ K and $T\geq 225$ K, both the blueshift and the intensity of the ASE are very close to the PL one, indicating that the temperature effects on the ASE are determined by the same processes (increased energy migration and exciton temperature)[15] determining the PL temperature dependence. In the intermediate temperature interval $125\leq T\leq 200$ K the observed progressive transition from ASE of the 0-1 R_{PhR} vibronic replica to ASE of the $R_{\mathrm{C\text{-}C}}$ one is instead attributed to the relative intensity increase in $R_{\mathrm{C\text{-}C}}$ with respect to R_{PhR} (see inset of Fig. 4) that progressively makes the ASE from $R_{\mathrm{C\text{-}C}}$ stronger than the one from R_{PhR}.

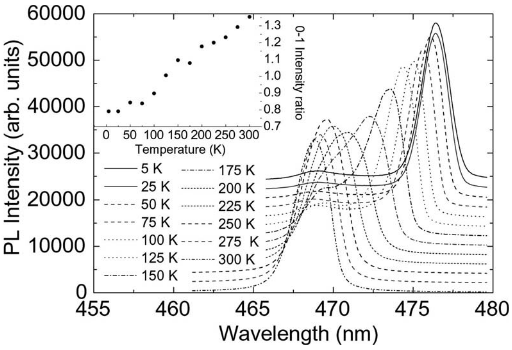

FIG. 4. ASE spectra at an excitation density of 2.2 mJ cm^{-2} as a function of the temperature (the spectra are vertically offset for clarity). Inset: peak intensity of the $R_{\mathrm{C\text{-}C}}$ 0-1 replica relative to the R_{PhR} one as a function of the temperature.

V. CONCLUSIONS

In conclusion we investigated the temperature dependence of the PL and of the ASE in the poly(9,9-dioctylfluorene) PF8 β phase. Our results indicate that the PL is progressively quenched as the temperature increases due to the thermal activation of exciton uphill hopping between different β-phase molecules that increases the probability of the exciton interaction with nonradiative traps or defects. We demonstrated that this process alone can explain the observed increase in the ASE threshold with temperature, indicating that the gain cross section is not significantly dependent on the temperature. These results suggest that the development of active materials for organic lasers with high thermal stability requires the engineering of the nonradiative decay processes affecting the PL intensity.

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