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Laser operation in non-doped thin films made of a small-molecule organic red-emitter

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Stimulated emission in small-molecule organic films at a high dye concentration is generally hindered by fluorescence quenching, especially in the red region of the spectrum. Here we demonstrate the achievement of high net gains (up to 50 cm⁻¹) around 640 nm in thermally evaporated non-doped films of 4-dil4‘-tert-butylbiphenyl-4-y]l]amino-4‘-dicyanovinylbenzene, which makes this material suitable for green-light pumped single-mode organic lasers with low threshold and superior stability. Lasing effect is demonstrated in a Distributed Bragg Resonator configuration, as well as under the form of random lasing at high pump intensities.

Organic optoelectronics is a very active field of research, partly driven by the rapid developments of organic light emitting diodes and photovoltaic cells. In this context, solid-state organic lasers open the way to many potential applications (in sensing, telecommunications...), due to their ability to produce coherent radiation over the whole visible spectrum, together with low-cost fabrication techniques (spin casting, thermal evaporation) on possibly large areas. While huge challenges remain to be solved in order to achieve direct electrical pumping of organic semiconductors, recent reports have shown the interest of an “indirect” electrical driving strategy, in which a small solid-state laser, a laser diode or a light-emitting diode is used as an optical pump source. Stimulated emission and lasing have been observed in numerous conjugated polymers as well as in some small molecule-based organic materials. The latter are especially attractive as they exhibit a well-defined molecular structure and can be thermally evaporated, which provides an accurate control over the layer thickness and a better film quality. However stimulated emission in small-molecule materials is generally hindered in non-doped films due to strong dipole-dipole coupling between excited-state molecules and π-π stacking interactions (overlap of the π orbitals) between neighboring conjugated segments, which can both lead to significant luminescence quenching. To limit self-quenching, the emitter is generally introduced at low concentrations in a polymeric or small-molecule organic matrix. Nonetheless, the realization of a single mode (hence laser) operation in a Distributed Bragg Reflective type cavity (DBR) is demonstrated in neat films of an organic dye (4-dil4‘-tert-butylbiphenyl-4-y]l]amino-4‘-dicyanovinylbenzene, named fvin in the following) in the deep red part of the spectrum (650 nm), pumped at 532 nm.

So far lasing in small-molecule neat films has been demonstrated in materials such as sexiphenyls, oligothiophenes or spiro derivatives. However, the reported emission wavelength lies essentially in the violet or the blue part of the spectrum, with some rare exceptions in the orange-red. Indeed, long-wavelength emission is generally achieved with extended π-conjugated planar structures, in which the probability to observe π-π stacking (and luminescence quenching) is therefore stronger. In the present work the amplified spontaneous emission (ASE) and laser operation in a Distributed Bragg Reflective type cavity (DBR) is demonstrated in neat films of an organic dye (4-dil4‘-tert-butylbiphenyl-4-y]l]amino-4‘-dicyanovinylbenzene named fvin in the following) in the deep red part of the spectrum (650 nm), pumped at 532 nm.

The molecular structure of the fvin molecule is depicted in the inset of figure 1. Femtosecond transient absorption spectroscopy studies have evidenced the formation of a quite distorted geometry in the excited state with regard to the ground state. This leads to a large Stokes shift up to 170 nm, with the consequence that red emission is achieved with a high pump intensity (up to 50 cm⁻¹).

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Fig 1: (color online) fvin emission and absorption spectrum in neat film. Inset: structure of the molecule.
The absorption and emission spectra of the \textit{fvin} molecule in a neat film configuration is presented in figure 1. The emission band is located in the deep red around 640 nm, whereas the absorption band extends from 400 to 550 nm. The 600-nm thick neat films absorbed as much as 84% of the incident light at 532 nm, in the tail of the absorption band. The \textit{fvin} neat film was realized on silica substrates through thermal evaporation under a 10⁻⁶ mbar pressure. No visible scattering was observed and the film optical quality was excellent as expected when resorting to the thin film evaporation process. The film thickness was monitored by means of a quartz microbalance in the evaporator machine to be 600 nm. Since the refractive index is 1.82 at 633 nm (determined by ellipsometry), single mode waveguiding is expected.

The variable stripe length method \textsuperscript{23} (VSL) was employed to measure the net gain coefficient of \textit{fvin} neat film. In this technique, ASE is detected from the edge of the sample for different pump excitation lengths. The silica substrate was cleaved with a diamond tip to limit scattering. The luminescence was collected via an optical fiber and sent to a spectrometer SPEX DH 720 CCD camera.

The experimental setup is depicted in figure 2. The 532-nm pump beam was produced by a Nd:YVO₄ Q-switched laser (PowerChip, Teem Photonics®) with frequency doubling through a Spiricon camera. After selecting only the central part of this line to form a thin stripe (320-µm full width at 1/e², measured by a DH 720 CCD camera) and focused with a cylindrical L₂ lens, we obtained a uniform excitation intensity onto the sample, an adjustable sharp edge blade, positioned on a translation stage, enabled to vary the length of the stripe. The films were pumped at normal incidence with a pump beam polarization parallel to the sample collection edge. In order to avoid the complex intensity modulation due to Fresnel diffraction effects after the blade edge\textsuperscript{19}, and as it is not easy in practice to put the blade and the sample very close to each other, the latter were instead optically conjugated through a 1:1 imaging system. We thus managed to produce an intensity profile of the imaged pump stripe with abrupt edges (as shown in the inset of figure 2), provided that the imaging lens had a large enough numerical aperture to collect the high spatial-frequency information contents of the far-field optical losses at the domain boundaries\textsuperscript{19}.

Fig 2 : (color online) experimental setup.Inset : Stripe intensity profile on the sample when the razor blade is set at 10 mm of the sample without imaging lens (A) and with imaging lens (razor blade and sample are conjugates) (B). C is a photograph of the pumped sample with the collection fiber on the left.

Fig 3 : (color online) net gain (gain minus losses) measurement with the VSL method. Inset : net gain versus pump fluence.
The \( f_{\text{vin}} \) capabilities in a laser cavity were first tested upon appending a DBR resonator to the waveguide. To obtain a periodic modulation of the film thickness, we used a very simple all-optical method based on direct laser ablation through a phase mask. The experimental setup is described in detail in ref. 26. We used an ArF excimer laser (\( \lambda = 193 \text{ nm} \), energy per pulse = 300 \( \mu \text{J} \), repetition rate of 10 Hz) to illuminate a phase mask: the diffracted orders interfere in the vicinity of the mask, creating an interference pattern with a pitch that can be shown to be, under the conditions of this work, the same as the period of the mask.\(^7\) Local ablation of the organic material is obtained for illumination times on the order of a minute (several hundreds of pulses).

The optimal pitch \( \Lambda \) for a Bragg grating is given by the Bragg formula \( 2n_{\text{eff}}\Lambda = m\lambda \), where \( n_{\text{eff}} \) is the effective index of the waveguide and \( m \) is the Bragg order. Here, we used a mask with a 1090 nm period, leading to laser emission at the \( m=6 \) order. The periodicity of the grating extends over several millimeters with a modulation depth of 200 nm. The grating structure appears under an AFM microscope to be smooth, free of redeposition debris and groove defects.

For the sake of demonstrating the existence of a laser effect, this unoptimized phase mask was chosen because it was readily available. However, the laser threshold could be lowered by using a lower-order resonator made by a lower-pitch phase mask.

We used a DBR configuration in which two Bragg gratings (with the same 1090 nm pitch) facing each other were engraved in a PMMA layer before the evaporation of a 695 nm thick \( f_{\text{vin}} \) layer (see inset in figure 4). The pump stripe (active region) was located between the two mirrors. Several samples with various distances between the two Bragg mirrors were realized. We observed laser operation as demonstrated in figure 4. The laser spectrum peaks at 647 nm as expected from the Bragg formula with \( n_{\text{eff}} = 1.82 \). The polarization of the laser beam was parallel to the layer (TE). A typical curve showing the variation of the laser intensity with pump power is shown on figure 4 (inset). The lasing threshold is relatively high (60 \( \mu \text{J/cm}^2 \)) because of the high order Bragg configuration.

Interestingly, we also observed that under high pump fluences, lasing can occur without any resonator, under the form of \textit{random lasing}, a phenomenon that has been already observed in some films of conjugated polymer and small molecules.\(^8\) Indeed, we observed that the ASE spectrum, for fluences higher than typically 0.3 \( \text{mJ/cm}^2 \), was highly structured, exhibiting multiple narrow peaks with a spectral width limited here by the spectrometer resolution (1 nm). The physical origin of the feedback still remains unclear in this system and is under study.

In summary, we have demonstrated single mode laser action in a thermally evaporated neat film of a red-emitting dye at 647 nm, with a very simple DBR patterning technique. The optical gain was measured for different pump powers with the variable stripe length method and a maximum value of 50 cm\(^{-1}\) was obtained. In order to obtain more accurate fits, a simple way to avoid the complex intensity modulation provided by Fresnel diffraction on the edges of the slab was presented. The fact that \( f_{\text{vin}} \) molecule exhibits optical gain and ASE with a threshold as low as 22 \( \mu \text{J/cm}^2 \) in a neat film configuration shows that quenching effects are tremendously reduced compared to classical dyes such as DCM or rhodamine, in which emission is totally suppressed in neat films. Consequently, in a single mode waveguide configuration, a higher gain can be obtained for the same pump power in a neat film of \( f_{\text{vin}} \) than in a doped film of DCM. Laser operation in the red (at 647 nm) was demonstrated with a DBR resonator fabricated with a very simple technique. At last, random lasing with coherent feedback was observed for pump fluences exceeding \( \sim 0.3 \text{mJ/cm}^2 \).

The present results give very favourable implication for the use of \( f_{\text{vin}} \) material as red-emitting organic laser material with a pumping wavelength in blue or green region.

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Fig 4 : (color online) fluorescence, ASE and laser spectrum in the DBR configuration. Inset : Laser chip design (here the pump stripe length is 2 nm).


