Solid-state laser devices based on an optically-confined oligothiophene-S,S-dioxide

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We investigated the gain properties of spin coated films of a soluble substituted quinque-thiophene under ns pulsed optical excitation. The oligomer exhibits a clear line narrowing, due to amplified spontaneous emission assisted by waveguiding film slab, for excitation fluences larger than 0.8 mJ cm^{-2} . The oligothiophene was employed as the active medium of different organic resonators. In particular, we report about directly printed organic distributed-feedback resonators, exploiting the one-dimensional periodic modulation of the organic surface. The devices exhibit single-mode emission between 630 and 640 nm, with a full width half maximum of about 1 nm and a pump threshold as low as $140 \mu\text{J/cm}^2$ at room temperature. These results make the substituted oligothiophenes excellent candidates as active media of optically-confined nanostructures.

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1 Introduction Over the last few years conjugated molecular systems, both polymers and oligomers, have attracted increasing interest by virtue of their technological application to optoelectronic devices such as light emitting diodes [1], field-effect transistors [2], solid-state lasers [3] and photovoltaic elements [4]. The advantages in using organics, with respect to inorganic materials, stand in the easy synthesis, processability, and tuning of their electronic properties. All these characteristics make them excellent candidates for low cost, large area devices eventually employing flexible substrates [5]. Moreover, the observation of amplified emission from a wide range of organic compounds has driven the interest in organic semiconductor lasers, and in the photophysics of the excited state of molecules. A number of conjugated compounds have been demonstrated to show optical gain, and optically pumped lasing has been achieved by different cavity geometries [6].

In this scenario, functionalized thiophene-based oligomers have been found to be suitable candidates for photonic applications, because of their wide color tunability, good chemical stability, general high solubility in all common organic solvents and very good film-forming capability. Due to their typical low photoluminescence (PL) efficiency [7] unsubstituted and alkyl-substituted oligothiophenes have not been fully exploited as active layers in optoelectronic devices, whereas recently a novel class of thiophene-based oligomers, characterised by the functionalization of the thienyl Sulphur atom with two Oxygens, was found to exhibit high PL efficiency, thus overcoming this drawback [8]. Whereas in conventional oligothiophenes the typical solid-state Herring-bone structure can lead to a quenching of photoluminescence [9], in oligothiophene-S,S-dioxides the presence of a strongly dipolar sulphonyl group introduces

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novel electrostatic intermolecular interactions, counteracting the tendency of the molecules to self-organize in parallel layers. Furthermore, prototype thiophene-S,S-dioxide molecules were found to be characterised by reduced Inter-System Crossing rate and non radiative de-excitation processes [10]. This allowed us to reach PL efficiency in the solid phase, η_{PL} , as high as 70% [11]. Moreover, optical gain with a cross section of $6 \times 10^{-16} \text{ cm}^2$ and lasing with a threshold of $10 \mu\text{Jcm}^{-2}$ have been recently demonstrated [6].

One of the main advantages of soluble conjugated molecules for the realization of solid-state laser devices stands in low-cost deposition and processing techniques, such as spin coating or direct printing. Moreover the usually broad density of states and the strong electron–phonon coupling give rise to broad gain spectra, which can be used to obtain spectral tuning of the laser emission [12]. We exploit here the gain properties of a quinquethiophene-S,S-dioxide (T5oCx) to realize distributed feedback (DFB) resonators, which present single-mode emission between 630 and 640 nm, with a full width half maximum of about 1 nm and a pump threshold as low as $140 \mu\text{J}/\text{cm}^2$ at room temperature.

2 Experiment T5oCx (molecular structure in the inset of Fig. 1) films were spin-cast onto Corning glass substrates, from chloroform solutions. The films were then patterned by room-temperature nano-imprinting with a master grating (period $\Lambda = 600 \text{ nm}$) fabricated by electron-beam lithography (Fig. 1). The oligomer grating presented 300 nm features, with a height of more than 110 nm. The printed DFB device was then excited by the third harmonic ($\lambda = 355 \text{ nm}$) of a 3 ns *Q*-switched Nd:YAG laser (Spectra-Physics, repetition rate of 10 Hz). The excitation beam was focused on the sample by a cylindrical lens, providing a rectangular excitation stripe of width $\cong 500 \mu\text{m}$. The DFB emission at room temperature was dispersed by a monochromator and detected by a Si charge coupled device, providing a spectral resolution of about 0.1 nm. Untextured film deposition were also characterised by line-narrowing experiments to probe the optical gain properties of the active compound.

3 Results and discussion For low absorbed excitation powers (less than about 1 mJ cm^{-2}) T5oCx films exhibit a broad (full width half maximum $> 120 \text{ nm}$) and featureless PL spectrum, whereas, for higher pump energies, a narrow peak, ascribed to amplified spontaneous emission (ASE) assisted by a waveguiding effect due to the different refractive index of substrate, gain medium and air, appears at 625 nm (Fig. 2). The ASE integrated intensity increases approximately exponentially for excitation densities up to about 1.9 mJ cm^{-2} . The occurrence of optical gain under long-pulse (ns) pump conditions and the strong chemical stability suggest T5oCx as active medium for organic lasers operating under steady-state excitation and under high injection-densities. In this context, DFB resonators [13], namely one-dimensional photonic crystals [14], can offer a much more effective control on the optical mode density, i.e. the emitted spectrum of devices, with respect to external cavities [6], as the coupling between electronic excitations and photons directly depends on the optical mode density through the Fermi's golden rule. The lasing wavelength, λ_m , of a DFB resonator [13], can be estimated by the cavity geometry via the relation:

Fig. 1 Silicon template grating for the T5oCx-based DFB, imaged by Scanning Electron Microscopy. The master was obtained by electron-beam writing and subsequent reactive ion etching by a CF_4/Ar mixture. Inset: molecular structure of T5oCx.

Fig. 2 Normalized emission spectra from T5oCx films, under different absorbed excitation fluences. PL spectrum of the unpatterned film under low excitation density (0.6 mJ cm^{-2} , full dots), and under high excitation density (1.6 mJ cm^{-2}), where ASE-induced line-narrowing is evident. The laser emissions from the DFB devices are peaked at 630 nm (device “A”, continuous line), and at 638 nm (device “B”, dotted line) (excitation densities about 1 mJ cm^{-2}).

$$m\lambda_m = 2n_{\text{eff}}\Lambda, \quad (1)$$

where m is an integer and n_{eff} indicates the effective refractive index of the propagating mode. The DFB lasers can exhibit a very high wavelength selectivity, however their spectral characteristics can be strongly affected by the occurrence of distortions induced by the fabrication technique on the organic materials, which may cause broad or multi-mode laser emission. We found for our patterned films single-mode DFB emission, with a narrow ($\text{FWHM} < 1 \text{ nm}$) peak at 630 nm (device “A”) and at 638 nm (device “B”), depending on the imprinted sample. This may be attributed to writing defects during the electron-beam exposure, or most likely, to alignment differences during the nanoimprinting, which can cause slight differences in the duty-cycle of the periodic grating and consequently in n_{eff} . Both the low-energy and the high-energy emitting DFB present a linear input-output characteristic (with similar slope efficiencies), as expected for laser action, and a pump threshold of 140 and $650 \text{ } \mu\text{J/cm}^2$, respectively (Fig. 3). The lower threshold with respect to the ASE in the untextured films is due to the optical feedback induced by the patterned structure. In both devices, one can see a residual luminescence band (DFB spectra in Fig. 2), which is often observed in organic distributed cavities, and attributed to a non-sufficient feedback action by the DFB resonator [15].

The optical confinement in the DFB device is in fact provided by the surface periodicity at the interface T5oCx/air, which determines a spatial modulation of both the refractive index, n , and the gain of the medium. In particular, the DFB emission, namely the coupling of the guided optical modes with the free radiation, is closely related to the underlying band-structure of the one-dimensional photonic crystal, occurring mostly at the band-edge corresponding at the lower cavity losses [14, 16]. From the measured thresholds, taking into account that the net gain due to ASE within the oligomer waveguide slab is higher at 630 nm than at 638 nm, we infer that device “A” experiences a weaker optical feedback with respect to device “B”.

Fig. 3 DFB peak emission intensity vs. fluence of the absorbed excitation beam, for the 630 nm-device, “A”, (full circles), and for the 638 nm-device, “B” (open squares). The solid lines are linear fits to the experimental data. For the low-energy emitting DFB, the emission for absorbed excitation fluences larger than 1.55 mJ cm^{-2} could not be measured, probably because of the strong degradation of the printed grating.

4 Conclusion The excellent processability and film-forming capability, together with the excellent luminescence and gaining performances, indicate thienyl-S,S-dioxide oligomers as appealing competitors of conjugated polymers for the realization of organic-based, solid-state semiconductor lasers. We recall that these compounds also present very good electroluminescence properties, exhibiting luminances up to 10500 cd/m² and external quantum efficiencies up to 0.45% for several hours of operation in air atmosphere [17]. For these reasons, the optical confinement of these compounds, directly patterned by novel nanofabrication techniques, can be a strategic route for the realization of electrically-injected lasers. We reported here about red-emitting DFB devices, with pump thresholds as low as 140 $\mu\text{J}/\text{cm}^2$ at room temperature. The investigation of the possible dependence of the device performances on the periodicity (order) of the surface grating, aiming at better controlling the stimulated emission by more effective optically-confined structures, is currently underway in our laboratory.

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