# Optical gain in DNA-DCM for lasing in photonic materials

**Marco Leonetti,[1,2] Riccardo Sapienza,[2] Marta Ibisate,[2] Claudio Conti,[3] and Cefe López[2,*]**

[1]*Dipartimento di Fisica, Università di Roma La Sapienza, I-00185 Roma, Italy*
[2]*Instituto de Ciencia de Materiales de Madrid (CSIC) and Unidad Asociada CSIC-UVigo, Cantoblanco, 28049 Madrid, Spain*
[3]*Research Center SOFT INFM-CNR, c/o Università di Roma Sapienza, I-00185 Roma, Italy*
*\*Corresponding author: cefe@icmm.csic.es*

We present a detailed study of the gain length in an active medium obtained by doping of DNA strands with 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran dye molecules. The superior thermal stability of the composite and its low quenching permit one to obtain an optical gain coefficient larger than 300 cm$^{-1}$. We also demonstrate that such an active material is feasible for the infiltration into photonic nanostructures, allowing one to obtain fluorescent photonic crystals and promising lasing properties.
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Nanoengineered devices and metamaterials are offering nowadays novel ways of controlling light propagation and amplification ranging from random systems [1] to photonic crystals [2]. Nanostructured lasers are typically realized on a subwavelength structured dielectric matrix, either periodically or randomly, in which an active medium is inserted to provide optical gain. Their optimization has often been focused on the increase in the matrix quality and refractive index contrast, while recently more efficient active media like fluorescent polymers [3,4] or dye doped semiconductors [5] have proven to enhance light amplification.

Within these novel materials, DNA strands intercalated with dye molecules have been proposed as efficient and stable gain media [6]. The superior thermal stability of the composite (up to 250°C) and its low quenching owing to a controlled proximity of the dye molecules attached to the DNA provide an enhancement of the emitted integrated luminescence with respect to the conventional polymer-dye composite [7]. This makes DNA-based dyes as optimal candidates to infiltrate nanostructures and to realize novel active photonic devices.

Direct-gain measurements are the best way to compare the optical amplifications and efficiencies of active media [8,9]. At variance with simple luminescence experiments, gain studies are not affected by the sample thickness uncertainty or by variations in the outcoupling owing to the edge roughness.

In this Letter we report on the characterization of the optical amplification of DNA films intercalated with a 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM) laser dye (DNA-DCM) by measuring the optical gain coefficient $g$, which reaches values as large as 300 cm$^{-1}$. We demonstrate how this material can be used to introduce an efficient gain into self-assembled photonic nanostructures.

For the sample preparation DNA-surfactant insoluble in water is dissolved in ethanol and mixed with dye ethanolic solution [10]. DNA-DCM films have been obtained by vertical deposition on a glass substrate in an oven at 45°C. Samples with different DNA to DCM weight ratios (ranging from 0.5 to 10 wt. %) and with various thicknesses (10−50 $\mu$m) have been prepared.

The optical gain coefficient has been measured with the variable stripe length (VSL) technique [9] [a sketch of the setup is given in Fig. 1(a)]. The sample is optically pumped by laser light (0.02–2 mJ/pulse, 9 ns pulse at 10 Hz repetition rate, and 532 nm wavelength) focused by a cylindrical lens to a narrow (~20 $\mu$m) stripe. The length $z$ of the illuminated area is adjusted by cutting the pump beam with a blade of
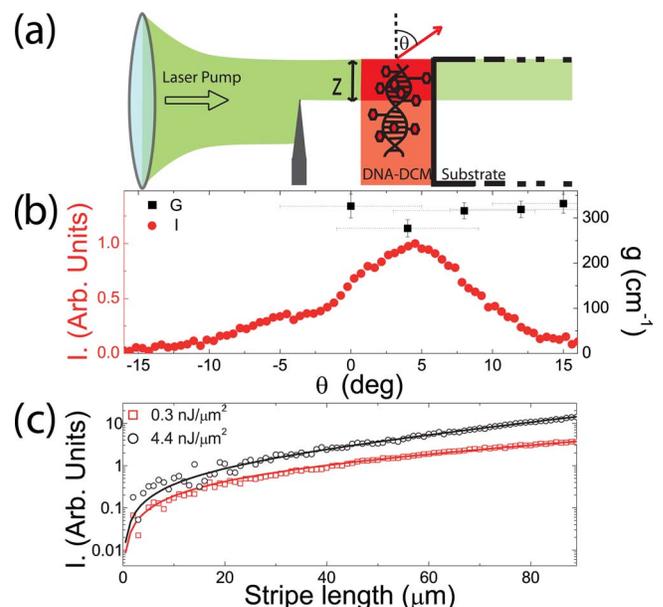


Fig. 1. (Color online) (a) VSL setup; (b) intensity from the illuminated stripe (solid circles) and optical gain coefficient $g$ (solid squares) as a function of the detection angle $\theta$, obtained by pumping below threshold (1.2 nJ/$\mu$m$^2$); (c) VSL measurement at two different pump energies. The continuous lines are fit from the model (see text).

variable position. The light produced by spontaneous decay, amplified by stimulated processes, and emitted in the direction $z$ of the stripe is focused by a spherical doublet lens (NA = 0.16) to a fiber-coupled spectrograph. The optical gain coefficient $g$ is obtained by fitting the measured emitted intensity $I(z)$ integrated in a wavelength range of 8 nm around the emission maximum at 620 nm [Fig. 1(c)] with

$$I(z) = \frac{A_0}{g}[\exp(gz) - 1].\qquad(1)$$

In Eq. (1), $g$ is the modal gain defined as in [9] and $A_0$ is a scaling factor accounting for the number of excited molecules and the collection efficiency.

Figure 1(b) (solid circles) shows the emission intensity as a function of the detection angle $\theta$. The asymmetric emission is due to the weak waveguiding effect in the stripe (of refractive index $n \sim 1.53$) [8]. Solid squares in Fig. 1(b) show that the gain does not depend on $\theta$. We performed all measurements by integrating the signal between $\theta = 0°$ and $10°$.

Figure 2(a) shows the optical gain coefficient $g$ as a function of the DNA-DCM weight percentage. The optimal amplification efficiency is obtained for a dye density between 2 and 3 wt. %, while at higher concentrations quenching phenomena decrease the effective optical amplification. This value slightly differs from [7], where the maximal light emission is obtained at 1 wt. %. It is important to notice that these gain measurements are not affected by the uncertainty in the sample thickness or outcoupling at the sample edge, which are all included in the prefactor $A_0$. Figure 2(b) shows the optical gain coefficient as a function of the pump power for an optimal DNA-DCM ratio of 3 wt. %. For energies higher than $4 \; \text{nJ}/\mu\text{m}^2$, the gain coefficient saturates, while above $9 \; \text{nJ}/\mu\text{m}^2$ the gain reduction is due to optical damage. It is remarkable that the maximum measured value for $g$ ($\sim 300 \; \text{cm}^{-1}$) is 1 order of magnitude greater than that reported for doped plastic materials [8]. As a comparison, dyes in liquid solution present a value of $g$ in the range of $100–10,000 \; \text{cm}^{-1}$ [11].
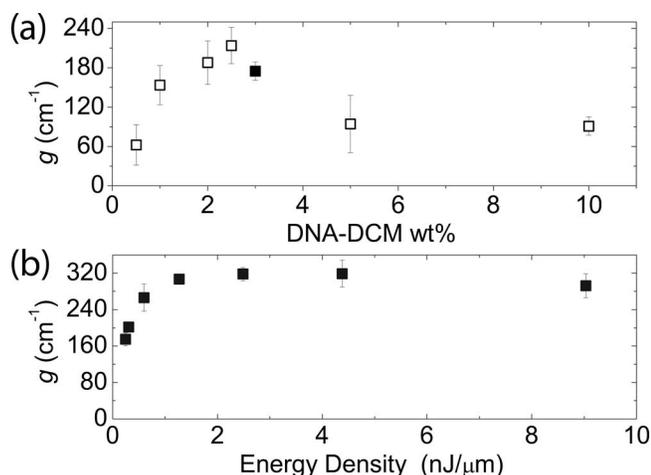
The synthesized DNA-DCM is in the form of a solution that can be dried into a film but also easily infiltrated in nanostructured dielectric materials or added at their assembly stage. We followed both strategies. Because of the high polarity of the compound, it destabilizes colloidal solutions of polymeric beads like polystyrene or polymethyl methacrylate. This prevents the formation of a stable colloidal crystal but helps the deposition of active polymeric photonic glasses [12] made by micrometer-sized polystyrene beads arranged in a disordered fashion. Conversely, it does not affect colloidal silica solutions from which active photonic crystals [13] can be efficiently grown. Post-assembly infiltration is feasible but less efficient owing to the high viscosity of the DNA-DCM composite. We have grown photonic crystals and photonic glasses with the DNA-DCM (dye content of 3 wt. %).

Two different structures have been realized by vertical deposition from a water solution containing 450 nm silica beads with and without 0.2 wt. % of the DNA-DCM. Figure 3(a) compares the reflectivities in the $\langle 111 \rangle$ direction for the two samples: the Bragg peak is shifted by $\sim 30$ nm by the presence of a homogeneous layer of the DNA-DCM polymer coating the spheres (confirmed by scanning electron microscopy inspection) that modifies the medium average refractive index. The infiltration process changes the filling fraction but not the quality of the opal, lowering the peak reflectivity to $\sim 0.4$ owing to contrast decrease, but essentially preserving its linear optical properties.

The DNA-DCM can also be efficiently infiltrated in a disordered nanostructured system like photonic [12] glasses made of 920 nm polystyrene beads, as the presence of the DNA contributes to the disordered flocculation of the beads. The total transmittivities of the samples with pure DNA (1 wt. %) and



Fig. 2. Optical gain coefficient $g$ plotted as a function (a) of DNA-DCM weight percentage and (b) of pump pulse energy density for a DNA to DCM ratio of 3 wt. % [solid square in (a)].
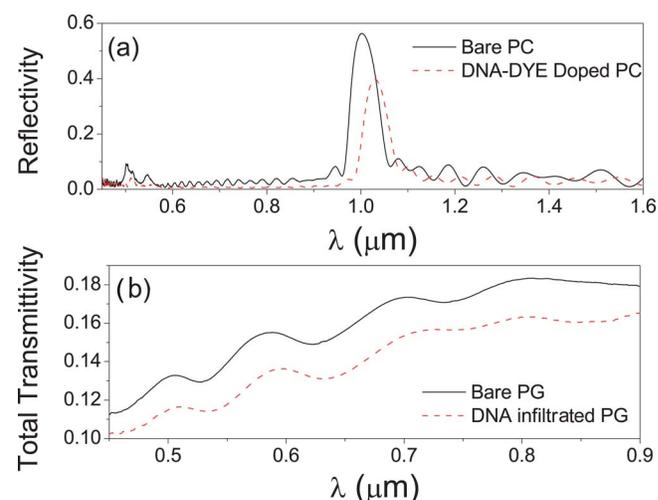


Fig. 3. (Color online) (a) Reflectivity as a function of wavelength measured for infiltrated (dashed curve) and bare (continuous curve) photonic crystals in the $\langle 111 \rangle$ direction. The Bragg peak is evident around 1 $\mu$m; (b) total transmissivity as a function of wavelength in bare (continuous curve) and DNA-filled (dashed curve) photonic glasses.

with only HCl as the flocculation agent are compared in Fig. 3(b). This test is performed without the DCM to avoid the effect of the large dye absorption. The characteristic Mie resonances in the total transmission [14] are unperturbed by the presence of a small quantity of the DNA coating the spheres. Having proven the feasibility of a non-destructive DNA-DCM infiltration, we have performed a lasing experiment on samples, with and without DNA, obtaining random lasing (RL) in photonic glasses but not photonic crystal lasing, owing to the low refractive index contrast.

RL is the process of the emission of stimulated light from a disordered active dielectric medium, which may be produced upon sufficiently intense laser pumping [15,16] resulting in an isotropic and spectrally narrow ($\sim 1-20$ nm) emission [1]. The RL threshold is determined by the scattering mean-free path ($\ell_s$) and the gain length ($\ell_g = 1/g$); its minimization is achieved by reducing the critical length necessary for the net amplification, which is defined in the diffusive approximation as $L_c = \pi \sqrt{\ell_g \ell_s/3}$ [17]. For the photonic glass infiltrated by the DNA-DCM (1 wt. %), $\ell_g$ is $\sim 40$ $\mu$m, while $\ell_s$ ranges between 1 and 3 $\mu$m; thus $L_c$ results to be $\sim 10-20$ $\mu$m. This value for $L_c$, smaller than the thickness of our sample ($\sim 50$ $\mu$m), allows for the RL emission when pumping the DNA-DCM infiltrated photonic glass with the pump laser focused to a 300 $\mu$m spot. In Fig. 4(a) the normalized emission intensity is plotted versus the wavelength for different pump pulse energies. The spectral FWHM narrows from 85 to 15 nm by increasing the pump energy. Figure 4(b) shows the peak intensity

(open squares) and FWHM (open triangles) as a function of the pump energy. We have obtained a clear efficiency advantage as the lasing threshold occurs at 0.5 nJ/$\mu$m$^2$. This is at least 1 order of magnitude lower than that obtained in previous similar experiments with dry photonic glasses infiltrated with $\sim 10$ times more DCM dye [18]. An identical sample infiltrated with the same amount of the DCM (without DNA) does not show significant amplification [Fig. 4(b), filled circles] or line narrowing.

In conclusion, we reported on the DNA-DCM infiltrated in nanostructured photonic materials. We measured optical gain coefficients with values as high as $\sim 300$ cm$^{-1}$, with low quenching, and with a large thermal stability. Careful characterization of the gain length in the active material allows one to predict the lasing threshold and to efficiently design novel light-emitting disordered or ordered nanostructures.

Fig. 4. (Color online) RL from DNA-DCM infiltrated photonic glass. (a) Emission spectra from DNA-DCM infiltrated photonic glass at different pump powers, below and above the RL threshold ($\sim 0.5$ nJ/$\mu$m$^2$). (b) Peak emission (open squares) and FWHM (open triangles) as a function of pump energy for DNA-DCM infiltrated photonic glass. Continuous line results from a linear fit to the points above threshold (0.5 nJ/$\mu$m). As a reference, the filled circles plot the peak intensity of a photonic glass infiltrated only with DCM.

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