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# **FRET-Tuned Resonant Random Lasing**

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**ABSTRACT:** We report the fabrication and characterization of a novel type of optical gain material. A biopolymeric matrix (DNA–lipid complex) doped with two families of organic dyes is combined with a strongly scattering medium. While the optical gain of the biopolymer complex is controlled via the FRET efficiency between the incorporated dyes, multiple scattering provides the necessary feedback to achieve lasing. This introduces two mechanisms to control the lasing wavelength: optical gain (via resonant energy transfer) and resonant scattering. In this way, an organic laser with a spectral tunability range over 40 nm is demonstrated.



# INTRODUCTION

Organic materials with large optical gain are essential for the fabrication of efficient organic solid state lasers (OSL). Despite inorganic lasers superiority in established areas, OSLs are an exciting alternative in applications where color tunability, mechanical flexibility, large-area low processing, or reduced costs are needed.<sup>1</sup> The potential of these devices can be further boosted by using a combination of two emitters forming a Förster resonance energy transfer (FRET) pair.<sup>2</sup> In doing so, optical excitation from a donor molecule (D) is resonantly transferred via long-range dipole-dipole interaction to a neighboring acceptor (A), which then emits a photon. This approach extends the potential of an OSL by increasing the spectral tunability of the device by properly choosing the D/A pair, lowers the threshold of the device by separating excitation and emission bands, and helps engineer the pumping by pushing the actual absorption deeper toward the blue rendering more dyes viable with the same pumping source. After a pioneering demonstration in organic dye-doped polymeric matrices deposited on one-dimensional (1D) gratings,<sup>3</sup> the feasibility of this approach has been also shown in the other main OSL systems such as liquid crystals.<sup>4</sup>

Among the requirements for an organic matrix to be used as OSL, beyond optical gain one wishes to have a large transparency window, ease of fabrication, and physical stability. In recent years there has been a growing interest in biopolymers as functional materials for photonics. Among the explored biological organic matrixes, DNA has certainly concentrated most of the attention.<sup>5</sup> This is due to its optical and physical properties such as its transparency, nonlinear optical properties, etc.<sup>6</sup> Further, modifying it with lipid chains, such as in the DNA–cetyltrimethylammonium (CTMA) complex, makes it soluble in organic solvents and hence easier to process. From the point of view of an organic optical gain material, the DNA–CTMA supramolecular structure allows site-specific incorporation of molecules providing improved

quantum yield of certain dyes,<sup>7</sup> good photobleaching stability, and enhanced load capabilities before concentration quenching.<sup>8</sup> Further, efficient lasing from dye-doped DNA–CTMA complexes deposited on 1D gratings has been demonstrated,<sup>9</sup> paving the way for a new material to be used as OSL.

These two paths (FRET and DNA) were brought to a convergence over the past few years when DNA–CTMA complexes were explored as organic hosts where FRET between different families of organic dyes can take place.<sup>10</sup> Just recently FRET-controlled amplified spontaneous emission in thin films of dye-doped DNA–CTMA was demonstrated,<sup>11</sup> which pointed to the possibility of reaching FRET-based lasing once optical feedback was provided. So far such feedback can be achieved at great cost by the use of gratings, employing high Q optical microcavities<sup>12,13</sup> that provide a high degree of control or through multiple scattering in disordered media,<sup>14–17</sup> which provides none.

Here we show a method to easily fix the spectral position of the lasing mode in a random system by simply adjusting the FRET efficiency through the relative donor to acceptor concentration. We have introduced DNA–CTMA loaded with two families of dyes in a photonic glass<sup>18</sup> consisting of a perfectly disordered array of monodisperse micrometer-sized dielectric spheres, which provides optical feedback via multiple scattering. In doing so, random lasing<sup>19</sup> is achieved. While in recent reports of FRET-based random lasing the wavelength was fixed,<sup>14–17</sup> we demonstrate the possibility of deterministically controlling the spectral position of the lasing emission via the FRET efficiency of the biopolymeric gain medium. Additionally, we introduce a further degree of spectral control of the lasing system by using the resonances associated with the scatterers, a characteristic of photonic glasses.<sup>20</sup> By changing

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the sphere size for a given D/A ratio for which random lasing takes place in the A emission spectral range, the lasing mode is shifted by ca. 40 nm. These results show how controlling the FRET-based gain medium as well as the photonic environment providing optical feedback allows to tune the spectral position of the random lasing mode over a 40 nm spectral range without resorting to complex fabrication procedures and simply using colloidal self-assembly techniques.

# EXPERIMENTAL DETAILS

**Sample Preparation.** All chemicals were used as received without further purification. Salmon DNA sodium salt and cetyltrimethylammonium (CTMA) chloride were purchased from Sigma-Aldrich. 4-(Dicyanomethylene)-2-methyl-6-(4-di-methylaminostyryl)-4*H*-pyran (DCM) and 1,1',3,3,3',3'-hexamethylindodicarbocyanine Iodide (Cy5) were provided by Exciton, and the polystyrene (PS) spheres (3% polydispersity) were commercially acquired from Thermo Scientific and Microparticles.

In a typical procedure, 1 g of salmon DNA sodium salt dissolved in 200 mL of water (7.5 mM) was added drop by drop to 200 mL of the CTMA chloride aqueous solution (15.8 mM) under magnetic stirring. After 5 h the precipitated DNA–CTMA complex was collected by centrifugation, washed 3 times with water, and dried at 70  $^\circ$ C for 12 h.

Dye-doped DNA–CTMA complexes were prepared by the addition of 1.37 mL of a DCM solution (0.5 g/L) in a mixture of ethanol:chloroform (1:1 v/v) to 0.1 g of DNA–CTMA dissolved in 5 mL of ethanol. For the Cy5 addition an ethanolic solution was prepared (1 g/L). The corresponding volume of Cy5 solution for each ratio was added to the DCM–DNA–CTMA solutions. The solvents were evaporated and the dye-doped DNA–CTMA complexes were dissolved in 5 mL of ethanol.

The photonic glasses were prepared by the addition of 0.2 mL of the dye-doped DNA–CTMA complex ethanolic solutions (20 g/L) on 1.5 mL of aqueous PS spheres suspension (66.7 g/L). The mixtures were deposited in confined areas made by fixing methacrylate cylinders of 1 cm height and 1 cm diameter with impermeable gum to clean, hydrophilic glass substrates. The samples were left inside an oven at 55 °C for a time long enough as to allow the total evaporation of the liquid.

**Optical Measurements.** The photoluminescence (PL) measurements were performed pumping at  $\lambda = 485$  nm with a pulsed laser source (OPerA-Solo from Coherent) delivering 150 fs pulses with a 1 kHz repetition rate. PL spectra were collected with a fiber-coupled spectrophotometer (USB4000 from Ocean Optics). Time-resolved measurements were performed with a time-correlated single photon counting system (Becker & Hickl). PL decay curves were fitted to a log-normal distribution of decay rates as described in ref 11.

Lasing experiments were performed using a nanosecondpulsed tunable laser (EKSPLA NT342A-SH) delivering 5 ns long pulses at 485 nm. The laser beam was focused to a 200  $\mu$ m spot on the photonic glass surface. A single-pulse configuration was used. The laser power incident on the sample was controlled by using combinations of calibrated neutral density filters.

# RESULTS AND DISCUSSION

DNA–CTMA loaded photonic glasses were fabricated according to previously described methods (see above) using 1300 nm diameter spheres.<sup>11,21</sup> Two different dyes were incorporated into the biopolymeric matrix: DCM and Cy5 as donor and acceptor, respectively. The FRET pair was chosen so that D excitation falls in the visible, thus far from absorption by the polystyrene spheres comprising the photonic glass, and does not overlap with the A excitation. Both requirements are satisfied with this pair given optical excitation of the D is carried out with  $\lambda = 485$  nm (see Figure 1). Using this pump wavelength the PL of the D was 2 orders of magnitude larger than that of the A for two control glasses infiltrated with either D only or A only doped DNA–CTMA.



**Figure 1.** Normalized absorption (dashed) and emission (solid line) of donor (red) and acceptor (black lines) species. Vertical dotted line at 485 nm corresponds to the wavelength of optical pumping. Top: chemical structure for donor (DCM) and acceptor (Cy5).

The donor concentration in the DNA–CTMA was fixed for all samples and corresponded to 1 DCM molecule per 37 DNA base pairs (bp). The A/D ratio  $Q_{AD}$  was changed for different samples in order to control the FRET efficiency. Different values of  $Q_{AD}$  were considered: 0.01, 0.02, 0.04, 0.1, and 0.2. We next studied the optical response of the biopolymer-loaded photonic glasses by means of PL and time-resolved measurements. Figure 2a–c shows PL measurements of samples containing DCM-Cy5 with different  $Q_{AD}$  values. By increasing the amount of A molecules, we can see how part of the D excitation is transferred to them, as no direct excitation of the acceptor is taking place (see above).

In order to ensure that such process is taking place by means of resonant energy transfer we also performed time-resolved measurements. In this experiment PL was collected at  $\lambda = 620$  nm so that only signal from the donor was considered. Figure 2d-f shows PL decay curves for the same samples as in Figure 2a-c. Here we can see how as the excitation is transferred from D to A, decay curves become faster and multiexponential, pointing to a distribution of FRET processes. As previously described<sup>11</sup> PL decay curves can be successfully fitted to a log-



Figure 2. (a–c) PL spectra for photonic glasses ( $d_{sph}$  = 1300 nm) with A/D ratio 0.01, 0.1, and 0.2. (d–f) Decay curves for identical samples (gray curves) together with theoretical fits to a log-normal distribution of decay rates (black curves).

normal distribution of decay rates  $\Gamma$ . From the fit we can extract a most frequent value of the distribution  $\Gamma_{\rm mf}$  from which an effective FRET efficiency  $\eta_{\rm eff}$  is defined:  $\eta_{\rm eff} = \Gamma_{\rm FRET} / (\Gamma_{\rm FRET} + \Gamma_{\rm D})$ , where  $\Gamma_{\rm D}$  is the decay rate of the donor in the absence of acceptor and  $\Gamma_{\rm FRET}$  can be extracted from the  $\Gamma_{\rm mf}$ .

The evolution of  $\eta_{eff}$  with the A/D concentration ratio  $Q_{AD}$  is plotted in Figure 3 and, after an initial increase, shows a



**Figure 3.** Evolution of the effective FRET efficiency as a function of the A/D ratio in the DNA–CTMA matrix for photonic glasses with  $d_{\rm sph} = 1300$  nm.

saturation at ca. 50%. This behavior corresponds to a saturation in  $\Gamma_{\text{FRET}}$ , contrary to the linear relationship obtained for other FRET pairs.<sup>11</sup> This fact is likely related with the poorer spectral overlap of the present FRET pair as compared with the one studied in a similar system in the past (Coumarin 480-DMASPI) where FRET efficiencies close to 90% were observed. Assuming a similar random distribution of molecules in the polymeric matrix, a poorer spectral overlap entails a smaller Förster radius R<sub>0</sub> defined as the distance between D and A for which D can lose its excitation via radiative or FRET paths with equal probability. Thus, in order to achieve a 100% FRET efficiency, the D/A separation in the present case will be shorter than with the previous chromophore combination. This can be an issue in a polymeric backbone like ours, where the supramolecular structure of the DNA-CTMA complex imposes a lower limit to the separation between D/A. A similar saturation behavior has been observed in 2D FRET systems consisting of a surface monolayer of biotin to which D or A labeled streptavidin was added. In that case, the D/A

distance of closest approach is given by the separation between biotins in the surface.<sup>22</sup> In order to determine such distance of closest approach in our system, a detailed knowledge of the D and A distribution in the DNA–CTMA matrix is needed, which is out of the scope of the present work.

In the presence of a medium with optical gain, a disordered structure can provide the necessary feedback to achieve random lasing via multiple scattering provided the scattering strength is proportionate to the gain.<sup>20</sup> Thus, we optically pumped the above-described photonic glasses doped with different QAD ratios and all having a sphere diameter  $d_{\rm sph} = 1300$  nm. Since we keep the sphere size fixed the photonic environment does not change, and the response will be solely determined by the balance between the emission and transfer rates, in other words, by the FRET efficiency  $\eta_{\text{eff}}$ . Figure 4 shows emission spectra for low (gray) and high (black) pump powers. Depending on the  $Q_{\rm AD}$  ratio and hence the FRET efficiency, three scenarios are observed: for  $Q_{\rm AD} \leq 0.04~(\eta_{\rm eff} \leq {\rm ca.~30\%})$  random lasing is observed for frequencies close to the PL maximum of the donor (see Figure 4a). In this situation FRET is marginal and can be seen as a loss mechanism for the D, which, not overcoming the optical gain, does not prevent lasing at the D frequency. The influence of FRET is nevertheless revealed by the raised lasing threshold, which increases from 1.2  $\mu$ W for the glass containing DNA-CTMA loaded with the D only, a value similar to that measured in DCM doped DNA-CTMA films deposited on a 1D grating.9 As the FRET efficiency is increased up to 30%, so do losses (through FRET) and the lasing threshold rises to 4.8 μW.

Upon further increase of the efficiency up to 40%, energy is more efficiently transferred (nonradiatively) to the acceptor, which prevents lasing from the D, and a spectral narrowing of the emission of both D and A takes place (see Figure 4b). For this efficiency, losses are already too large for the D and optical gain too small for the A, so lasing does not take place for either species. Finally, for an efficiency of ca. 50% ( $Q_{AD} = 0.2$ ), energy transfer to the A is large enough so as to provide the necessary optical gain to observe lasing close to its PL maximum (Figure 4c). In this case a lasing threshold of 5  $\mu$ W was measured (see Figure 4d). Three similar scenarios were observed in the system consisting of DNA–CTMA thin films without photonic glass, where the absence of feedback prevented the observation of lasing and only amplified spontaneous emission was observed.<sup>11</sup>



**Figure 4.** (a–c) Emission intensity below (gray) and above (black line) threshold for samples containing DNA–CTMA with  $Q_{AD}$  ratios of 0.01, 0.1, and 0.2, respectively. (d) Emitted intensity (black) and full width at half-maximum (fwhm) (open circles) as a function of pump power for the  $Q_{AD}$  = 0.2 case (threshold power = 3.5  $\mu$ W).

As mentioned above, photonic glasses provide random lasers with spectral tunability via the presence of Mie-like resonances associated with their constituting scatterers. Combining this property with the variable optical gain provided by FRET can greatly extend the tunability of the system. In order to demonstrate this hypothesis we fabricated samples having different sphere diameters and containing dyes in DNA–CTMA with the largest A/D ratio ( $Q_{AD} = 0.2$ ). Figure 5a shows the lasing spectra above threshold (color lines) for different glasses (which was  $3.5-8 \ \mu W$  for all samples) together with the PL spectra (gray line). Here we can see how by changing the sphere diameter we were able to spectrally tune the lasing mode by 42 nm.

In order to interpret the shift in the lasing mode we measured the total transmission of identical samples containing no organic dyes so that absorption does not affect the experimental spectra. In a photonic glass the resonant behavior of the scatterers forming the random medium modulates its transport properties introducing resonance maxima and minima in the transport mean free path  $l_t$ . Such oscillating behavior is directly measured by the total transmission T spectrum since in the diffusive regime T  $\propto l_t/L$  where L is the sample thickness.<sup>23</sup> At frequencies for which a Mie resonance appears, a minimum in  $l_t$  takes place, and light matter interaction is maximized by lengthening the path inside the system. In this situation the random lasing mode shifts from the maximum in optical gain



**Figure 5.** (a) PL from a photonic glass containing a  $Q_{AD} = 0.2$  ratio (gray curve) and random lasing spectra for samples having different sphere diameter: 438 (black), 930 (magenta), 1000 (blue), and 1280 nm (red curve). Total transmission (gray) and emission above the lasing threshold (black curve) for samples having 438 (b) and 1000 nm diameter spheres (c).

toward the resonant frequency, in a compromise between optical gain and scattering strength.

As a reference we considered a sample with 438 nm diameter spheres, which in the spectral range of interest presents no noticeable resonances in its total transmission (see Figure 5b). Here random lasing is present at  $\lambda = 699$  nm, close to the maximum in the A PL. By using spheres with a diameter of 1000 nm we see how the lasing takes place at  $\lambda = 726$  nm, close to the minimum in total transmission representing a minimum in  $l_t$  (see Figure 5c). A total spectral shift of 42 nm was observed using the above-mentioned sphere diameters. This tunability approach has been also demonstrated for samples containing the donor molecule only, and similar (38 nm) spectral shifts were achieved.<sup>23</sup>

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In summary, we have combined organic dye-loaded DNA-lipid complexes with strongly scattering photonic media in order to achieve a novel optical material with tunable lasing properties. These results demonstrate that the variable optical gain achievable deterministically with D/A-loaded DNA-CTMA permits to control which of the species involved in a FRET phenomenon is lased. Additionally the resonant behavior of the scatterers when a photonic glass is used lends itself as a second degree of freedom, which boosts tunability up to over 100 nm for appropriate choice of D and A molecules and sphere diameters. While this is a mere proof of principle, further improvement of the tuning can be achieved by coupling the D absorption through one photonic glass resonance at the same time that the emission of the A is coupled to another resonance of the same glass or one from an alloyed glass. Hence, a careful design of the gain medium as well as of the system providing

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# **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

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