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Near-infrared distributed feedback laser emission based on cascade Förster resonance energy transfer to Nile Blue aggregates

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We present the real time tunable distributed feedback lasing in the region of near-infrared light obtained in a dye doped polymeric layer via cascade energy transfer based on Förster resonance (FRET). The Rhodamine 6G and Rhodamine B laser dyes were used as a donor for FRET effect, while the Nile Blue dye served as an acceptor. The shift of the emission from visible to near-infrared region was possible due to the formation of the dyes aggregates of lower than for molecules energy levels. Therefore, through the sequence of energy transfers between molecules and aggregates, the shift between excitation and stimulated emission spectra of about 200 nm can be achieved. The use of the periodically modulated pumping beam from pulsed Nd:YAG laser allows to select and amplify particular wavelength from the gain profile according to Bragg conditions, what can be easily tuned by changing the period of the interference pattern. The reported tunability of distributed feedback emission from 725 nm to 745 nm confirmed that only Nile Blue aggregates were involved in the laser action, while donor molecules and aggregates, as well as acceptor in non-aggregated form, acted as a canal for energy transfer.

1. Introduction

The search for new luminescent dyes become nowadays increasingly focused on chemical compounds able to emit light in the region of near-infrared, due to their potential use in medicine and biomedical imaging [1–4]. On the other hand, ability for excitation of molecules in a biological tissue with the standard lasers might extend the possible strategies and design of diagnostic protocols. Highly desired feature of chromophores for such purposes is therefore as large as possible Stokes shift. Although proper molecular design may lead to enlargement of shift, it is still often too small to obtain emission in biological window of light transmission (from 650 nm to 1350 nm), while we excite using standard laser lines. One of the most common approaches is based on use of the pairs of chromophores that one of them serves as energy donator (absorber), and another one as energy acceptor (emitter). Such energy transfer might be realized by so called Förster resonance energy transfer (FRET). The efficiency of this process is determined by the overlap of donor emission band together with acceptor absorption band, thus the spectral shift between excitation and emission wavelength, anyhow larger than for single chromophore, is still limited by a molecular design of used chromophores.

In this paper we show that shift between the excitation and emission wavelength can be enlarged by cascade FRET effect, involving the assistance of chromophore aggregates. Using this strategy and common laser dyes, i.e. rhodamines (serving as FRET donor) and Nile Blue (NB) (serving as FRET acceptor), we were able to achieve the stimulated emission (STE) from aggregates of the last one (from 720 nm to 750 nm) using the second harmonic of Nd:YAG fundamental laser line (532 nm). It is worth to mention that aggregation of dye molecules could be forced by specific interactions with e.g. lipids or higher order protein structures [5,6] what can be exploited in to bio-imaging and diagnostics. The reported examples of aggregation-induced emission redshift of xanthene and phenoxazine dyes allows to conclude, that presented approach can be adopted to another classes of luminescent compounds, more biofriendly or having greater Stokes shift than those listed above.

Finally, besides medical purposes, we show that the use of slightly higher dye mixture concentration for a thin layer fabrication, enables to achieve new emission bands where J-type dimmers or higher order aggregates are being formed in the gain medium. Therefore it is feasible to engineer the polymeric dye doped

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systems in order to achieve not only the highest STE shift, but also greatest broadening of distributed feedback (DFB) lasing tuning range or lower lasing thresholds. Up to now there were just few reports concerning laser action in systems containing mixture of molecules that create pairs for energy transfer, including random lasers [7,8], “Whispering Gallery” mode lasers [9] and DFB lasers [10,11].

In our work we have utilized the periodically modulated spatial distribution of pumping light intensity to achieve the real-time tunable DFB lasing in the region of near-infrared by exciting polymeric samples containing FRET pairs. The idea of FRET between rhodamine and NB laser dyes with subsequent DFB lasing is schematically shown in Fig. 1(a).

2. Sample preparation and experimental details

In order to excite NB dye via FRET mechanism there were chosen two commercially available luminescent dyes: Rhodamine 6G (Rh6G) and Rhodamine B (RhB), differing slightly in their absorption and emission spectrum. Because NB is known to be soluble in water, we have used commercially available, water-soluble polymeric matrix, poly(vinyl alcohol) (PVA) by Sigma Aldrich (M_w: 85–124 kDa, 99+ % hydrolyzed).

The polymer and the dyes were mixed in various combinations and used to obtain series of dye doped polymeric layers, with and without coupling to provide the energy transfer. The list of fabricated samples prepared for essential studies is the following: Rh6G/PVA, RhB/PVA, Rh6G+NB/PVA, RhB+NB/PVA. The concentration of dye was selected to be high enough for aggregates formation and was equal to 1% with respect to PVA dry mass. In the case of samples containing two types of dyes the total concentration was 2%. The concentration of PVA with respect to the water was 10%, to obtain properly viscous aqueous solutions to be spincoated onto glass substrates with size $2.5 \times 2.5\ \mathrm{cm}^2$. The fabricated layers, using the procedure described above, have thickness about 2.3 μm, what was determined using Dektak 3 profilometer.

Additionally, in order to prove the formation of the dye aggregates in the materials, six samples of each luminescent compound in PVA, with concentration ranging from 0.1% to 2.0%, were created. Similarly, water solutions of dye/polymer mixture were prepared, but this time with 2% PVA/H_2O concentration. These supplementary samples were deposited by casting 0.35 ml of each solution onto heated glass plates (65 °C) with the same size, i.e. $2.5 \times 2.5\ \mathrm{cm}^2$, and left to dry out.

The studies of luminescent properties of rhodamines and NB FRET pairs in polymeric layers were conducted using three experimental routes. The first one were the regular measurements of basic optical properties, i.e. excitation and linear emission spectra, measured with the use of FL-4500 (Hitachi) spectrofluorometer. Excitation spectra were measured for emission at 720 nm wavelength whereas emission spectra were measured while excitation at 480 nm and 500 nm for Rh6G and RhB respectively.

The second type of measurements was devoted to the studies of emission decay times. These experiments were conducted in time-correlated single photon counting mode using a Horiba/Jobin-Yvon Fluorolog-3 apparatus. A 490 nm Nano-LED (pulse duration < 250 ps) was used to excite the donor molecule. The decay of the luminescence was monitored at the wavelength of 570 nm where emission from donor dyes occurs. In the presence of quencher the energy is transferred from donor to acceptor causing the shortening of donor luminescence decay time. Therefore the efficiency of energy transfer can be calculated approximately from the equation [12]:

$$\Phi = \left(1 - \frac{\tau_{DA}}{\tau_D}\right) \cdot 100\% \qquad (1)$$

where: τ_{DA} is donor decay time constant in presence of an acceptor and τ_D is donor alone decay time constant. The rest of energy is dissipating radiatively from donor molecules. Instrument response was measured using scattering by a non-absorbing water suspension of LUDOX polymer.

The last type of measurements was carried out in the experimental set-up schematically presented in Fig. 1(b) in order to check whether measured samples are able to generate light in the process of STE. As a source of excitation, the light of a nanosecond pulsed Nd:YAG laser (Surelite II by Continuum) was used. As it is shown in Fig. 1(b1) the third harmonic of the laser can be utilized to pump the optical parametric oscillator (OPO, Horizon I by Continuum) that is able to generate tunable light of the wavelengths from 200 nm to 2700 nm. Using this system it is possible to address exact maximum of absorption band of each measured dye, and perform measurements of amplified spontaneous emission (ASE). Additionally it gives the opportunity to excite only the NB molecules, in FRET pair containing samples, without necessity of pumping rhodamine dyes, and observe ASE which determines the gain profile for the final DFB laser emission. The experimental set-up allows driving the laser beam to the beam separator, where only second harmonic is extracted (Fig. 1(b2)). This beam is then

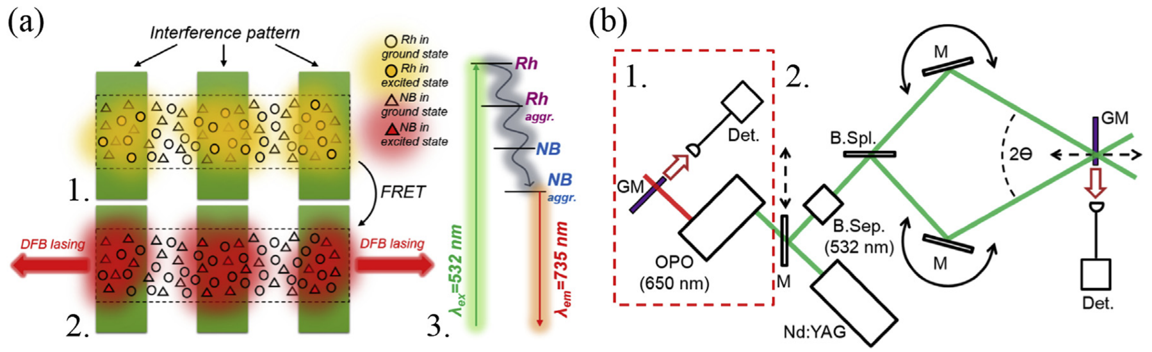

Fig. 1. The scheme of the DFB lasing in infrared region via energy transfer. The use of two interfering beams results in formation of temporal population diffraction grating in a gain medium. Rhodamine molecules undergo excitation by 532 nm wavelength laser beam (a1) followed by non-radiative energy transfer to NB which subsequently emit in infrared region. If period of the grating matches Bragg conditions for emitted wavelength, DFB lasing occurs (a2). Around 200 nm shift between excitation and emission wavelengths can be achieved due to sequence of FRET transfers involving molecular and aggregated forms of dyes (a3). Part (b) describes experimental set-up use for STE or DFB lasing measurements. Nd:YAG – nanosecond pulsed laser working at 1064 nm wavelength, able to generate second and third harmonics, 532 nm and 355 nm respectively; OPO – optical parametric oscillator pumped with third harmonic; Det. – detector, B.Sep. – beam separator; B.Spl. – beam splitter; M – mirror; GM – gain medium; 2θ – angle of beams intersection.