Frequency up-converted lasing in polymeric composites with two-photon absorbing antenna

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Abstract: Energy-transfer-coupled polymeric composites with donors of two-absorbing dyes and acceptors of polymer gain medium are introduced for up-converted laser applications. The two-photon pumped hybrid polymer lasers show significant performance improvement with nearly 10 times reduction of lasing threshold and over 100 times extension of lifespan.

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1. Introduction

Multi-photon pumped lasing has significant advantages over the conventional method of sumfrequency generation for laser frequency up-conversion when the phase-matching cannot be fulfilled [1–14]. The up-converted lasers, realized with near infrared (NIR) wavelength pumping, are promising for applications in advanced laser technologies, microfabrications, and biophotonics. However, these potentials are hindered by high pump thresholds and short operation lifetime in currently available devices [1,15]. Recently, high quality photonic microcavities [7,9,13] and photo-stable nanocrystals [11,12,16,17] have been introduced to overcome these drawbacks. These efforts have improved the laser performance to some extent; however, the ultimate solution still relies on developing new stable materials with efficient multi-photon pumped gain at low pumping power.

Ideal gain medium for up-converted lasing should hold the ease of establishing population inversion with efficient multi-photon absorption, which makes most of the conventional laser materials unfavorable for this application. For instance, semiconducting polymers have been recognized as an excellent family for single-photon pumped lasers [18–25], but only very limited number of studies have shown the viability of such material systems for two-photon (TP) pumping [7–9]. Indirect pumping through non-radiative energy transfer (ET) can be an alternative strategy to seek new up-converted gain candidates with efficient TP absorbing donors and high gain acceptors. The donors act as TP-absorbing "antennas" that harvest the excitation energy, sensitize the acceptor via ET, and generate the population inversion necessary for laser operation [26,27]. In this study, we introduce a type of ET coupled dyepolymer composites for low threshold up-converted laser application. By optimally doping the TP absorbing dye antennas, we achieved nearly ten times reduction of the amplified spontaneous emission (ASE) threshold in poly (2-mehoxy-5-(2'- ethylhrxyloxy)-1, 4, phrnylene vinylene)) (MEH-PPV) films under NIR TP pumping. Using the dye-polymer composites, we constructed an up-converted polymer laser with the distributed feedback (DFB) structure, and improved the operation lifespan by about two orders of magnitude. The ET-based TP pumping mechanisms of the novel dye-polymer hybrid composites were investigated by time-resolved photoluminescence (TRPL) spectroscopy.

2. Experimental methods

The polymer of MEH-PPV was purchased from American Dye Source, Inc (Product ID: ADS100RE), and the naphthalimide dye used in this study was purchased from the company of BASF (Product ID: Lumogen Violet 570), respectively. We co-dissolved the polymer (1 mg/mL) and dye in chlorobenzene with a range of blend ratio. The blend samples were kept stirring in a dark environment overnight. The solvent was evaporated to increase the concentration of polymer to 10 mg/mL in blend solution before coating onto the substrates. The plastic additive naphthalimide dye is well compatible to the polymer, and 80-100 nm thick blend films with good quality can be formed on glass substrate with spinning rate of 1000 rpm. The silica DFB structures were prepared with interference lithography and reactive ion etching. The gratings have periods of ~400 nm and depths of ~120 nm. Blend films were spin-cast on the grating with proper thickness controlled by the spinning rate for second-order mode coupling.

For optical study, NIR femtosecond pulses with pulse duration of 90 fs from an optical parametric amplifier (Opera Sola, Coherent) pumped by a regenerative amplifier (Libra, Coherent) were used. The laser worked at the frequency of 1 kHz with tunable wavelength. For time integrated PL study, we used a cylindrical lens to focus the excitation beam with a strip width about 200 μ m and length of 500 μ m. The pumping beams were normally excited at the sample and emission spectra were measured with a fiber spectrometer (1 nm spectral resolution, USB 2000 + , Ocean-Optics). Laser pulses with different pulse energy were focused to a spot with diamter of 200 μ m for nonlinear transmission measurement. The technique of optical Kerr gating was utilized to do TRPL studies with excitation at 800 nm. Kerr medium of 5 mm thick carbon sulfide cell with temporal resolution about 2 ps were used as transient gates. The PMT (5784-20, Hamamatsu) was used to record the TRPL traces with band pass optical filters at 650 (10) nm. The emission spectra at different decay time were recorded with a 0.5 m spectragraph (sp2500i, Princeton Instruments) equipped a liquid nitrogen cooled CCD.

3. Results and discussion

The pumping scheme is schematically described in Fig. 1(a). The polymeric gain composites consist of plastic additive naphthalimide dye as the TP absorbing donor and the polymer MEH-PPV as the acceptor. If highly efficient ET is achieved, the energy absorbed by the dye will transfer to the polymer with minimal loss and generate optical gain by building up

population inversion in polymer. To test this idea, we compared the emission properties of the dye-polymer composites with NIR femtosecond pulse excitation at 750 nm. The power-dependent photoluminescence (PL) emission spectra recorded from neat and blend polymer films (with dye mass ratio of 70%) are shown in Figs. 1(b) and 1(c), respectively. Emission from both films was observed with power-dependent spectral profiles. From Fig. 1(b), the line-width of spontaneous emission (SPE) from neat polymer films is about 50 nm at low level excitation and becomes narrower (~17 nm) under excitation above thresholds (370-450 μ J/cm²) — a signature of transition from SPE to ASE (also known as gain-induced line-width narrowing). In contrast, emission peaks from the blend films red-shift slightly [Fig. 1(c)], and the threshold for ASE transition in blend films is ~40 μ J/cm², which is nearly one order below that in neat films. With detuning the excitation wavelength (700-800 nm), the sharp emission peak with almost no wavelength change can be observed with a slight variation of the threshold.



Fig. 1. Frequency up-converted emission properties of ET-coupled dye-polymer blend films. (a) Diagram of the mechanism of ET based TP pumped lasing. (b) and (c) are typical emission spectra from a neat polymer film and a blend film with different excitation flux at 750 nm. Inset of (c) shows normalized spontaneous emission (SPE) and amplified spontaneous emission (ASE) spectra from the blend film recorded with excitation flux of 13 μ J/cm2 and 150 μ J/cm2. (d) Emission intensity from the neat and blend films is plotted as functions of excitation flux. Threshold behaviors can be found with the slope change. (e) ASE thresholds for the blend films versus dye doping level.

We plotted the power-dependent emission intensity from the neat and blend films in Fig. 1(d). TP-pumped emission is much stronger in the blend film. TP-pumped SPE intensity is quadratically dependent on the excitation flux. Above the threshold, higher order power-dependence of emission intensity emerges due to gain amplification. The effective TPA coefficients of blend films estimated by the power-dependent nonlinear transmission measurement [Fig. 2] are about seven times larger than that of neat films. Since dye doping doesn't directly enhance the TPA of polymer, the increased emission must come from the contribution of ET caused by the TP absorbing dye antenna. As a result, the threshold required for ASE transition is significantly reduced due to the improvement of pumping efficiency.



Fig. 2. Nonlinear transmission is plotted as functions of the excitation flux in neat and blend films with excitation of femtosecond pulses at 750 nm.

With the framework of ET-coupled pumping mechanism, we can control the thresholds of blend films by varying the acceptor-donor ratio. The thresholds for different dye mass ratios are shown in Fig. 1(e). Clearly, there exists a critical point of dye mass ratio to achieve the lowest threshold. When the dye mass ratio increases before reaching the point, the excitation threshold required for population inversion in polymer reduces since multiple donors may transfer energy to an acceptor prior to saturation. This explains the monotonic decrease of thresholds with the increase of dye doping in the blend films (donor mass ratio $<\sim70\%$). However, further increase of dye mass ratio results in low density of luminescent chromophores, leading to the increase of threshold (donor mass $> \sim70\%$).

ET rate between individual phosphor units is dependent on the spectral overlap and donoracceptor (D-A) separation distance. Dye emission band from 420 nm to 550 nm locates mostly in the absorption band of polymer [Fig. 3(a)]. In the blend films, the polymer-based PL emission dominates as a characteristic of the efficient ET [Fig. 3(b)]. However, since the inter-molecular interaction in a concentrated dye film may also quench the emission, we tried to evaluate the ET rate in blend solutions. We fixed the dye concentration and tested dye emission lifetime in the solutions with a variety of blend ratios [the inset in Fig. 3(b)]. Measurement results [Fig. 3(b), inset] showed that the emission lifetime decreases with the increase of acceptor-to-donor ratio. ET from dye to polymer is the main reason for the variation of the decay rate since the average interaction between dye molecules remains the same in all solutions.



Fig. 3. (a) Normalized absorption and emission spectra of the donor dye and acceptor polymer in chlorobenzene solution. (b) TPP emission spectra from solution with different dye polymer ratio (0.05 mg/mL Dye, 0.05 mg/mL Dye and 0.005 mg/mL polymer, 0.05 mg/mL Dye and 0.01 mg/mL polymer, 0.01 mg/L polymer) and blend films (Dye:Polymer = 10:1). The excitation source is femtosecond pulses at 750 nm.

We can use the primary model of Förster type ET [28] to interpret the observed phenomena. The ET rate from donors can be expressed as

$$\Gamma_{ET} = k(N_A / N_D) d_{DA}^{-6}, \tag{1}$$

where Γ_{ET} is the ET rate, k is spectral-overlap-dependent parameter (as a constant for specific phosphors), d_{DA} is the average donor-acceptor separation distance, and N_A / N_D is the acceptor to donor ratio [29]. Total ET rate is linearly dependent on the acceptor to donor mass ratio ($\Gamma_{ET} \propto (m_A / m_D)$) if not saturated. The donor emission lifetime with donor-acceptor ratio dependence can be expressed as $t^{-1} = (\frac{m_A}{L_B} \Gamma_c + t_0^{-1}) (\Gamma_c = k \frac{M_D}{L_B} d_{DA}^{-6}$ is a

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$$t^{-1} = (\frac{m_A}{m_D}\Gamma_c + t_0^{-1}) (\Gamma_c = k \frac{M_D}{M_A} d_{DA}^{-6}$$
 is a

constant, where M_A and M_D are the molecular weights of acceptor and donor, respectively, and t_0 is the PL lifetime of the pure dye solution). From the fitting curve, the ET rate estimated with dye:polymer ratio of 20:1 is about 0.2 ns⁻¹ in solution with 0.05 mg/mL dye. With these parameters, we can estimate the ET rate in a blend film with donor-acceptor mass ratio 1:1 to be in the scale of ~10¹¹ s⁻¹. This rate is fast enough to compete over the spontaneous relaxation and build up the population inversion in polymer.



Fig. 4. Time-resolved study on the emission properties of dye-polymer composites. (a) Logarithm plot of time-resolved photoluminescence traces with excitation near threshold [Fitting parameters are listed in Table 1]. Inset shows the growth traces. (b) and (c) are counter plots of the SPE and ASE as functions of decay time and emission wavelength from the blend film.

For better understanding the mechanism, we performed TRPL experiments on blend films with the method of optical Kerr gating. Figure 4(a) shows the TRPL traces at 650 nm recorded from the blend films at excitation near the ASE threshold. Both growth and decay processes in TRPL traces are power dependent. The growth increases slightly with pumping power, and the fast decay component is distinct at high level pumping. For quantitative analysis, we fit the traces with a function including exponential growth and bi-exponential decay components. The best fitting ($R^2 > 99.8\%$) parameters are listed in Table 1.

Table 1. Time evolution details of TP pumped emission properties in blend films under excitation at near the ASE threshold. Table listed the best fitting parameters [R²>99.8%] for the growth and decay processes.

	Growth	Decay			
Excitation		Fast component		Slow component	
(I_{th})	Time (ps)	Time(ps)/Rate(10^{10} s ⁻¹)	Amplitude(%)	Time(ps)	Amplitude(%)
0.72	20.2	56.2/1.78	50.1	146.4	49.9
0.80	19.1	59.7/1.68	50.0	140.1	50.0
0.90	17.9	57.0/1.75	50.5	130.2	49.5
1.00	16.2	55.1/1.82	66.7	163.5	33.3
1.10	15.9	42.2/2.37	65.1	149.1	34.9
1.13	14.6	31.2/3.20	69.1	136.7	30.9
1.35	13.6	27.8/3.60	78.6	147.2	21.4

The slow decay component with power-independent lifetime in the range of 130-150 ps can be assigned to the spontaneous relaxation process. The fast lifetime component in the range of 55-60 ps has a weak dependence on the excitation flux below the threshold. With a slight increase of the excitation flux from the threshold, the decay rate increases to two times and the amplitude ratio increases from 50% to ~80%. The equation proposed by Martini & et al. [30] can be modified as

$$dN(t) / dt = -N(t) / \tau - \beta N^{2}(t) / \sqrt{t} - f[g(N(t))],$$
(2)

where τ is the intra-chain exciton fluorescence lifetime, β is the exciton-exciton annihilation coefficient, and f[g(N(t))] is relaxation rate related to net gain (which is very sensitive to the excitation close to the threshold). We can assign the observed slow component (130-160 ps) as the fluorescence from intra-chain exciton and fast component (55-60 ps) as the contribution from spontaneous emission associated to multiple excitons at low pumping level. The power-dependent fast component should be attributed to the net gain amplification. To clarify the difference between the SPE and ASE dynamics in the blend films, the emission spectra are plotted at different delay times with excitation blow (half of) and above (twice of) the threshold in Figs. 4 (b) and 4(c), respectively. The emission intensity normalized to the maximum value was plotted in the same two-order logarithm scales for comparison. Different from a broad distribution in spectral and temporal domains of SPE, ASE distributes in a narrower emission band and in a short time scale of ~ 10 ps, confirming the dominant contribution of the gain-related relaxation for the fast decay component. In the time-resolved studies on single-photon pumped stimulated emission in polymer, a time lag of several picoseconds in the build-up time between SPE and ASE processes was frequently observed owing to the formation of a large population of excitons [31]. The absence of time lag in this study [(Fig. 4(a), inset)] is probably caused by the ET pumped scheme. The build-up time constants (10-20 ps, Table 1) of the emission in the blend film are much slower than that measured on single photon pumped emission in the neat polymer films previously [30,31]. This time constant should be the character of ET since the direct optical absorption should be much faster. With excitation at higher pump level, more ET channels from donors to acceptors will be activated, resulting in the power dependence of build-up time constants. The ET time in the regime is sufficient to compete with the spontaneous relaxation and to generate the population inversion in the polymer acceptors [32].



Fig. 5. Typical lasing emission spectrum from DFB composite laser is shown in comparison with ASE spectra from a blend film. Inset shows the excitation threshold at different excitation wavelength.

We then demonstrate the frequency up-converted lasers by covering the dye-polymer composites on top of silica DFB gratings. Under the excitation at 750 nm, sharp lasing peak with a line-width of ~2 nm was recorded with excitation above the threshold of 30 μ J/cm². The emission peak is narrower than ASE emission, indicating the successful coupling of TP-pumped gain into the DFB structures [Fig. 5]. This up-converted laser can be pumped with broad NIR excitation wavelengths, and the lasing threshold varies when excitation wavelength detunes from 700 nm to 800 nm [Inset, Fig. 5]. This wavelength dependence of threshold is caused by the dispersion of TP absorption of dye in the wavelength range. A more

important advantage for the practical applications is the lifespan extension of such composites. In an ambient test with an excitation power at two times above the thresholds, the lifespan of neat films is only in the order of 10^4 shots while that of the blend films can reach 10^6 shots, comparable to the single-photon pumped polymer lasers [33].

4. Conclusions

In conclusion, we have introduced ET-coupled dye-polymer composite materials as a promising candidate for TP-pumped laser applications. Time-integrated and time-resolved spectroscopic studies have been carried out to investigate the emission properties of the hybrid composites and the underlying mechanisms. Compared with neat polymer films, frequency up-converted gain-induced ASE has been observed in blend films with significantly-reduced thresholds. The ASE decay lifetime, dependent on the excitation power, is found to be in the order of 10 ps. We have also demonstrated a low threshold TP-pumped DFB laser, with over 100 times of lifespan extension. The excitation threshold is orders of magnitude lower as compared with previously characterized semiconductor nanocrystals [11,12,17], nanodisks [13], and nanowires [10], and the current system is among the lowest in TP-pumped polymer lasers to the best of our knowledge [7–9]. Such composite gain materials can be used as an alternative method to circumvent the two major drawbacks in traditional TP-pumped systems, i.e. high threshold and short lifespan, with potential to push forward the practical applications of frequency up-converted lasers. Similar to other polymeric gain medium, the composites can be incorporated to various resonators to form different types of micro/nano-lasers [34,35]. The required pumping wavelength and threshold power are readily available in today's commercial lasers for multi-photon microscopy, so the composites introduced here can be implanted as laser sources for light-activated therapeutics studies. The ET pumping idea is generally valid, and one can choose the functionalized donors or acceptors to develop up-converted laser sensors [36,37]. These implications can be done in vivo since the NIR pumping sources can penetrate deeply inside the tissue. Still, more interesting applications of such up-converted lasers can be envisioned as new polymeric composite materials are further developed for using as efficient TP-pumped gain materials.

Acknowledgments

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