Improved amplified spontaneous emission by doping of green fluorescent dye C545T in red fluorescent dye DCJTB:PS polymer films

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Amplified spontaneous emission (ASE) characteristics of a red fluorescent dye, 4-(dicy-anomethylene)-2-t-butyl-6(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB), and a green fluorescent dye, (10-(2-benzothiazolyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1H,5H,11H-[1] benzopyrano [6,7,8-ij]quinolizin-11-one) (C545T) codoped polystyrene (PS) as the active medium were studied. It was found that the performance of ASE is greatly improved due to the introduction of C545T. By optimizing the concentrations of C545T and DCJTB in PS, an ASE threshold of 0.016 mJ pulse^{-1}, net gain of 52.71 cm^{-1}, and loss of 11.7 cm^{-1} were obtained. The efficient Förster energy transfer from C545T to DCJTB was used to explain the improvement of the ASE performance in the coguest system. © 2007 Optical Society of America

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1. Introduction

Since the reports of organic and polymeric materials showing high optical-gain and stimulated-emission properties, there has been growing interest in exploiting these materials in laser applications due to their wide wavelength tunability and processing flexibility in solutions,[1–3] films,[4–6] and fibers.[7,8] The unique electronic and optical properties of organic semiconductors make such laser sources a potential alternative to inorganic semiconductor lasers. For example, it has been observed that the linewidth of organic semiconductor laser emission is at least an order of magnitude narrower compared with inorganic semiconductor lasers.[9] Recently, therefore, more efforts have been devoted to synthesizing new materials, to understanding their stimulated-emission properties, and to developing device structures to improve the performance of organic lasers.

At present, amplified spontaneous emission (ASE) and lasing action have been achieved from various organic materials, including polymers,[10] organic small molecules,[11] dye-doped dendrimers,[12] and dye-doped liquid crystals.[13,14] However, efforts to make electrically pumped organic solid-state lasers have been unsuccessful because of losses, including self-absorption, scattering, and electrode absorption losses. Self-absorption problems can be well resolved by effective Förster energy transfer via the method of guest doping.[15] In organic light-emitting diodes (OLEDs), the codoping of two dyes, including fluorescence and phosphorescence dyes, has been widely used in the efficiency enhancement of OLEDs.[16] However, the ASE and lasing action in organic systems are rarely studied by this method.

In this paper, we codoped a green fluorescent dye, 10-(2-benzothiazolyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1H,5H,11H-[1] benzopyrano [6,7,8-ij]quinolizin-11-one (C545T), as assistant energy-transfer dopant and a red fluorescent dye, 4-(di-cyanomethylene)-2-t-butyl-6(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB), as the emitting dopant in polystyrene (PS) and studied the ASE of C545T:DCJTB:PS blending films. It was found that the ASE performance was greatly improved due to the doping of C545T in DCJTB:PS film with respect to C545T-undoped DCJTB:PS film. The significant improvement had been attributed to the effective Förster energy transfer from C545T to DCJTB, resulting in the realization of a low threshold, high gain, and low loss.

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2. Experimental Methods

DCJTB as the emissive dopant and C545T as the assistant dopant with different blending ratios were codoped in PS using chloroform solution. The blending films were then spin-coated onto quartz substrate. Thus the quartz-doped polymer–air structure formed an asymmetric slab optical waveguide, which supports only the fundamental transverse mode within the emission band of the doping polymer. After spin-coating, the spin-coated thin films were dried in a vacuum heater.

The experimental setup to investigate the ASE properties followed Ref. 17. The pump source was a frequency-tripled Nd-YAG laser (Spectra-Physics) delivering 5 ns pulses at $\lambda_p = 355$ nm with a 10 Hz repetition rate. The output pulse energy of the pump laser was controlled using neutral-density filters. An adjustable slit and a cylindrical lens were used before the beam splitter in order to shape the beam into a narrow stripe with a continuously varied length on the sample film. The films were pumped at normal incidence with the long axis of the pump beam perpendicular to the edge of the sample. The output signals were detected by a fiber-coupled CCD spectrometer (JY Spex CCD3000). The pumped energies from the laser were measured using a calibrated laser power and energy meter (Gentec).

3. Results and Discussions

In DCJTB:PS thin films, we found that 4% concentration of DCJTB in PS showed the best ASE performance.[17] Therefore we studied the effect of the doped fluorescent dye C545T on the ASE performance by fixing DCJTB concentration at 4% and changing C545T concentrations in our experiment. It can be seen that the introduction of C545T in DCJTB:PS improves the ASE performance, i.e., reducing ASE threshold and loss and enhancing ASE gain.

Figure 1 shows the emission spectra of C545T:DCJTB-PS film with 4% of DCJTB and 24% of C545T pumped at below and above threshold. It can be seen that at low pump energy (<0.016 mJ pulse^{-1}), the emission spectrum exhibits a broad peak of spontaneous emission, similar to the normal photoluminescence (PL) spectra of the C545T:DCJTB:PS film. As the pumping energy is increased above the threshold, a substantial reduction in full width at half-maximum (FWHM) of the emissive spectrum is observed. The FWHM is generally ~10 nm or more. This collapse of the FWHM in emissive spectrum is one of the signatures of the presence of ASE.

To particularly demonstrate the effect of C545T doping in DCJTB:PS on ASE, we compare the threshold, gain, and loss of C545T:DCJTB:PS films with those of DCJTB:PS films. The output emission intensity integrated over all wavelengths as a function of the pumped intensity in C545T(24%):DCJTB(4%):PS and DCJTB(4%):PS is shown in Fig. 2. For pumped intensity below the threshold value, the emission intensity increases in proportion to the pump intensity slowly. Above the threshold, the emission intensity increases sharply with pump intensity. Therefore the threshold pumped energy for ASE can be easily discerned at ~0.016 and 0.07 mJ pulse^{-1} for C545T:DCJTB:PS and DCJTB:PS, respectively. Obviously, the threshold of C545T:DCJTB:PS is 4.4 times lower than that of DCJTB-PS.

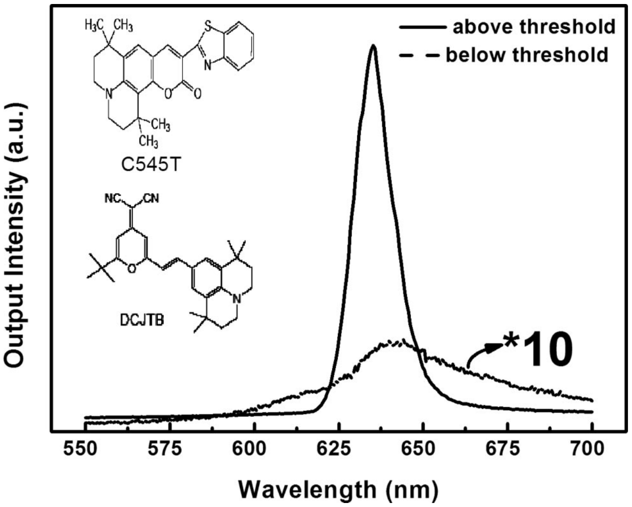

Fig. 1. Emission spectra of C545T:DCJTB-PS system pumped by optically pulsed laser at below (dashed curve) and above (solid curve) lasing threshold. The below threshold spectrum was multiplied by a factor of 10. The inset shows the chemical structure formulas of C545T and DCJTB.

Figure 3 shows the pump-length dependence of ASE in C545T(24%):DCJTB(4%):PS and DCJTB(4%):PS films. The pump-length dependence of ASE is fitted by the expression based on a one-dimensional approximation[18,19] describing the rate of change of fluorescence intensity with length of the pumped region,

$$\frac{\mathrm{d}I}{\mathrm{d}x} = AP_0 + gI_x, \tag{1}$$

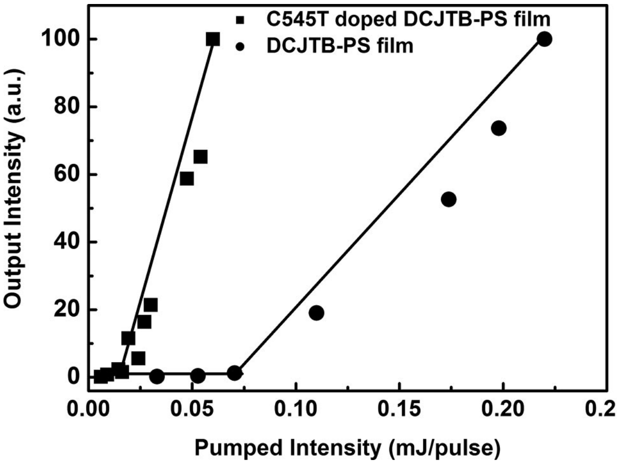

Fig. 2. Output emission intensity integrated over all wavelengths as a function of pump intensity for DCJTB-PS film (circles) and C545T:DCJTB-PS film (squares), separately.

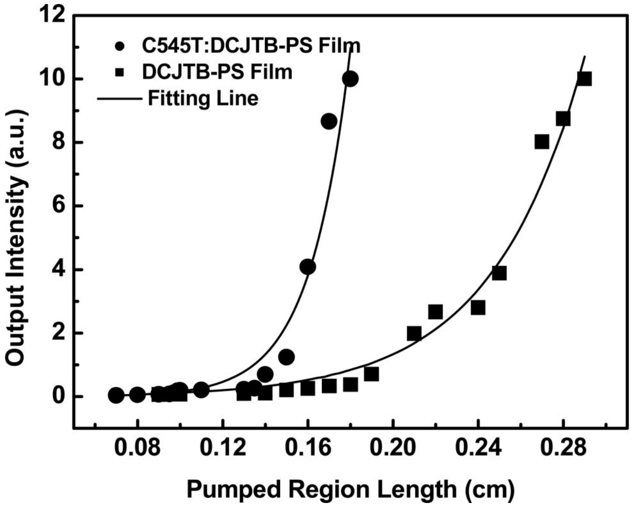

Fig. 3. Dependence of the emission intensity at peak wavelength on the excitation length at indicated pump intensities for DCJTB-PS film and C545T:DCJTB-PS film, separately. Pumped intensity is 0.08 mJ pulse^{-1}.

$$I = \frac{A_{(\lambda)} I_p}{g_{(\lambda)}} (e^{g_{(\lambda)} L} - 1), \tag{2}$$

where $g_{(\lambda)}$ is the net optical gain per length at wavelength L, P_0 and I_p are the pump intensity of the laser, A is a parameter proportional to fluorescence quantum yield, and I is the ASE intensity propagating along the x axis. The solid curves in Fig. 3 are the fit of Eq. (2) to experimental data. By fitting, the net modal gain of 52.71 cm^{-1} and 23.03 cm^{-1} at pump energies of 0.08 mJ pulse^{-1}, respectively, for C545T:DCJTB:PS and DCJTB:PS are obtained. The C545T:DCJTB:PS film shows much higher net gain than the DCJTB:PS film.

For the measurement of the loss coefficient in the waveguide, we kept the pumped length constant ($l = 0.3$ cm) and moved the pumped region away from the edge of the sample. Since the emission from the end of the pump stripe remains constant, the detected signal from the edge of the sample should decrease as

$$I = I_0 e^{(-\alpha x)}, \tag{3}$$

where α is the waveguide loss coefficient, and x is the length of the unpumped region from the end of the pump region to the edge of the sample; thus the loss coefficient can be estimated. Figure 4 shows the emission intensity as a function of distance from the film edge for C545T(24%):DCJTB(4%):PS and DCJTB(4%):PS films. The solid curves are the fit of Eq. (3) to experimental data. A loss coefficient of 11.7 cm^{-1} is obtained for C545T:DCJTB:PS film, which is much lower than a loss coefficient of 26.95 cm^{-1} for DCJTB:PS film. The low loss coefficient should be related to a nonrandom distribution of the DCJTB dye molecules in PS due to the effects of the space and effective energy transfer of C545T molecules and thus high PL efficiency and low self-absorption.

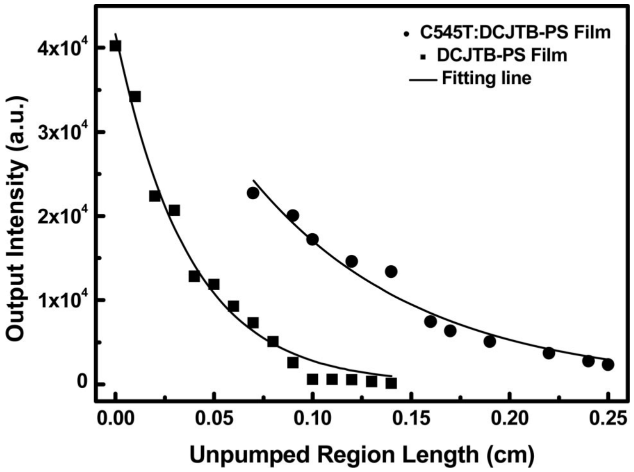

Fig. 4. Intensity of light emitted at $\lambda_{\text{peak}} = 640$ nm from the edge of a waveguide as a function of the distance between the pump stripe and the edge of the DCJTB-PS film and the C545T:DCJTB-PS film, separately.

Table 1 summarized the ASE threshold, gain, and loss values of DCJTB(4%):PS and C545T:DCJTB(4%):PS with different concentrations of C545T. It is clearly seen that the introduction of C545T fluorescent dye indeed reduces the threshold and loss and enhances the net gain, and the doping concentration of C545T also has an effect on the ASE performance. As given in Table 1, 24% of C545T in a C545T:DCJTB:PS blending film shows the lowest threshold of 0.016 mJ pulse^{-1}, the highest gain of 52.7 cm^{-1}, and the smallest loss of 11.7 cm^{-1}. To the best of our knowledge, these are the best ASE performances reported so far in organic doping polymer films.

As the PL spectrum of C545T and the absorption spectrum of DCJTB show in Fig. 5, the great improvement of the ASE performance in C545T:DCJTB:PS films should be attributed to the effective Förster energy transfer from the C545T molecule to the DCJTB molecule due to the large spectral overlap.

The Förster energy-transfer rate via induced dipole–dipole interactions between organic molecules is generally given by[20]

$$K = \frac{1}{\tau_H}\left(\frac{R_0}{R}\right)^6, \tag{4}$$

Table 1. Dependence of Threshold, Gain, and Loss on Doped Concentrations

DCJTB:C545T	1:0	1:3	1:4	1:6	1:8
Gain (cm^{-1})	23.03	31.32	47.84	52.71	42.7
Loss (cm^{-1})	26.95	17.58	14.56	11.7	14.6
Threshold (mJ/pulse)	0.07	0.029	0.021	0.016	0.023
Peak wavelength (nm)	633	639	640	642	641

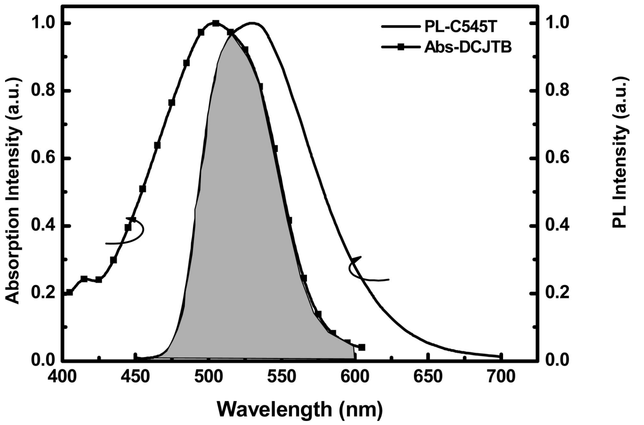

Fig. 5. Photoluminescence spectrum of C545T and absorption spectra of DCJTB.

$$R_0 = \left[\frac{3}{4\pi} \int \frac{c^4}{\varpi^4 n^4} F_H(\varpi) \sigma_D(\varpi) \mathrm{d}\varpi \right]^{1/6}, \qquad (5)$$

where $F_H(\varpi)$ is the normalized fluorescence spectrum of the host material, $\sigma_D(\varpi)$ is the normalized optical absorption cross section of the dopant, τ_H is the natural radiative lifetime of the host, R is the mean distance between molecules, and R_0 is the effective Förster radius. To realize an effective Förster energy transfer between two molecules (i.e., for large K), two conditions have to be satisfied: the larger overlap between $F_H(\varpi)$ and $\sigma_D(\varpi)$, and the distance R between two molecules less than Förster radius R_0. As shown in Fig. 5, there is a larger overlap between the PL spectrum of C545T and the absorption spectrum of DCJTB, and the distance R between C545T and DCJTB is changed by optimizing the C545T concentration in C545T:DCJTB:PS, leading to the most effective Förster energy transfer from C545T to DCJTB. Actually, the effective Förster energy transfer from C545T to DCJTB can be further confirmed from the fact that the PL emission of C545T: DCJTB:PS blending film is fully originated from the emission of DCJTB molecules, as shown in Fig. 6, where the absorption and PL spectra of C545T: DCJTB:PS film are given. Here the PL is measured by using 400 nm of excitation wavelength, which is mainly absorbed by C545T molecules. Besides the effective energy transfer, the doping is also used in blocking the aggregation of DCJTB emissive molecules due to the spacing role of C545T molecules, thereby reducing the concentration quenching.

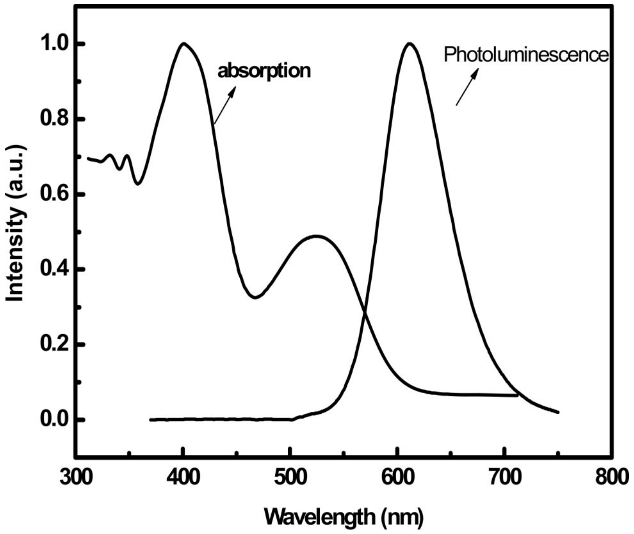

Fig. 6. Absorption and PL spectra of C545T:DCJTB-PS film.

4. Conclusions

We have realized an ASE with lower threshold and higher gain in C545T:DCJTB:PS films due to the dopant of a green fluorescent dye, C545T. By optimizing the doping concentration of C545T, a threshold of 0.016 mJ pulse^{-1} and a net gain of 52.71 cm^{-1} were achieved, showing potential application as a gain medium in organic lasers. The significant ASE improvement has been attributed to the effective Förster energy transfer from C545T molecules to DCJTB molecules.

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References

1. S. Qian, J. B. Snow, H. Tzeng, and R. K. Chang, "Lasing droplets: highlighting the liquid–air interface by laser emission," Science **231,** 486–488 (1986).
2. N. M. Lawandy, R. M. Balachandran, A. S. L. Gomes, and E. Sauvain, "Laser action in strongly scattering media," Nature **368,** 436–438 (1994).
3. S. V. Frolov, Z. V. Vardeny, and K. Yoshino, "Cooperative and stimulated emission in poly(*p*-phenylene-vinylene) thin films and solutions," Phys. Rev. B **57,** 9141–9147 (1988).
4. F. Hide, M. A. Diaz-Garcia, B. J. Schwartz, M. R. Andersson, Q. Pei, and A. J. Heeger, "Semiconducting polymers: a new class of solid-state laser materials," Science **273,** 1833–1836 (1996).
5. V. G. K. Fozlov, V. Bulovic, P. E. Burrows, and S. R. Forrest, "Laser action in organic semiconductor waveguide and double-heterostructure devices," Nature **389,** 362–364 (1997).
6. N. Tessler, G. J. Denton, and H. Friend, "Lasing from conjugated-polymer microcavities," Nature **382,** 695–697 (1996).
7. S. V. Frolov, A. Fujii, D. Chinn, Z. V. Vardeny, K. Yoshino, and R. V. Gregory, "Cylindrical microlasers and light emitting devices from conducting polymers," Appl. Phys. Lett. **72,** 2811–2813 (1998).
8. F. Marlow, M. D. McGehee, D. Zhao, B. F. Chmlka, and G. D. Stucky, "Doped mesoporous silica fibers: a new laser material," Adv. Mater. **11,** 632–636 (1999).
9. V. G. Kozlov, G. Parthasarath, P. E. Burrows, and S. R. Forrest, "Optically pumped blue organic semiconductor lasers," Appl. Phys. Lett. **72,** 144–146 (1998).
10. N. Tessler, "Lasers based on semiconducting organic materials," Adv. Mater. **11,** 363–370 (1999).
11. V. G. Kozlov, V. Bulovic, P. E. Burrows, M. Baldo, V. B.

Khalfin, G. Parthasarathy, and S. R. Forrest, "Study of lasing action based on Förster energy transfer in optically pumped organic semiconductor thin films," J. Appl. Phys. **84,** 4096–4108 (1998).

12. S. Yokoyama, A. Otomo, and S. Mashiko, "Laser emission from high-gain media of dye-doped dendrimer," Appl. Phys. Lett. **80,** 7–9 (2002).
13. M. Ozaki, M. Kasano, D. Ganzke, W. Haase, and K. Yoshino, "Mirrorless lasing in a dye-doped ferroelectric liquid crystal," Adv. Mater. **14,** 306–309 (2002).
14. F. Araoka, K.-C. Shin, Y. Takanishi, K. Ishikawa, H. Takezoc, Z. G. Zhu, and T. M. Swager, "How doping a cholesteric liquid crystal with polymeric dye improves an order parameter and makes possible low threshold lasing," J. Appl. Phys. **94,** 279–283 (2003).
15. F. P. Schafer, *Dye Lasers* (Springer, 1977).
16. M. A. Baldo, M. E. Thompson, and S. R. Forrest, "High-efficiency fluorescent organic light-emitting devices using a phosphorescent sensitizer," Nature **403,** 750–753 (2000).
17. W. Lu, B. Zhong, and D. G. Ma, "Amplified spontaneous emission and gain from optically pumped films of dye-doped polymers," Appl. Opt. **43,** 5074–5078 (2004).
18. K. L. Shaklee and R. F. Leheny, "Direct determination of optical gain in semiconductor crystals," Appl. Phys. Lett. **18,** 475–477 (1971).
19. Y. Sorek, R. Reisfeld, I. Finkelstein, and S. Ruchin, "Light amplification in a dye-doped glass planar waveguide," Appl. Phys. Lett. **66,** 1169–1171 (1995).
20. T. Förster, *Modern Quantum Chemistry. Part 2. Action of Light and Organic Molecules* (Academic, 1965).