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Enhanced amplified spontaneous emission by assistant Förster energy transfer in DCJTB-C545T-Alq$_3$ coguest-host system

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ABSTRACT Amplified spontaneous emission (ASE) characteristics of a red fluorescent dye 4-(dicyanomethylene)-2-t-butyl-6(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB) were significantly improved by assistant Förster energy transfer. The coguest-host system was composed of an electron transport organic molecule tris(8-hydroxyquinoline) aluminum (Alq$_3$) as host 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) as assistant dopant codoped with the guest red dye DCJTB as emitter in a matrix of polystyrene (PS). It was found that the threshold and loss were greatly reduced to 0.007 mJ pulse^{-1} and 7 cm^{-1}, and the gain was significantly enhanced to 52 cm^{-1} by doping of C545T. The improvement of ASE performance in Alq$_3$:C545T:DCJTB film was attributed to the energy assistant effect of C545T, leading more exciton energy to transfer to DCJTB.

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1 Introduction

Since the discovery of the semiconductor properties in organic materials, rapid progress has been made in the synthesis and characterization of organic semiconductors and in their development as active materials for use in electronic and optoelectronic devices, such as in the field of the organic semiconductor lasers (OSLs) [1]. The demonstration of lasing action in optically pumped organic thin films [2, 3] has opened the possibility of producing electrically pumped solid-state lasers from conjugated polymers and small organic molecules. There has been growing interest in improving laser action [4, 5] by using Förster energy transfer. Many systems exhibiting efficient Förster energy transfer in organic semiconductors have been used in the studies of amplified spontaneous emission (ASE) [6, 7]. Recently, codoping of two dyes into one host are found to significantly improve electroluminescent (EL) efficiency in organic light-emitting diodes (OLEDs) by assistant energy transfer [8, 9]. However, the reports on the improvement of ASE in OSLs by this method are few.

Here, we selected 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) and 4-(dicyanomethylene)-2-t-butyl-6(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB) [10,11,12] with high fluorescence quanta efficiency as the lasing dye doped in tris(8-hydroxyquinoline) aluminum (Alq$_3$) to realize high efficiency OSLs. We reported ASE properties in a coguest-host system of two fluorescent dyes of DCJTB and C545T and electron-transporting organic material Alq$_3$ codoped into the host material of PS. It was found that the ASE performance of DCJTB was significantly enhanced by the energy assistant effect of C545T dopant.

2 Experiment

DCJTB was firstly dissolved in polystyrene (PS) by using chloroform as solvent, and then C545T and Alq$_3$ were added to make the DCJTB:C545T:Alq$_3$:PS coguest-host system. For comparison, DCJTB:PS, DCJTB:C545T:PS and DCJTB:Alq$_3$:PS systems were also fabricated by the same method. All the doping ratios in different systems were optimized before using. The optimized weight ratio of DCJTB in polymer was 4%. The ratio of DCJTB and C545T to Alq$_3$ was 1 : 1.5 : 4. The films were made by spin-coating onto quartz substrate. The film thickness is about 800 nm, controlled by the polymer viscosity and spin-coating speed. After spin-coating, samples were dried in a vacuum.

The experimental set-up to investigate the ASE properties followed [13]. The pump source was a frequency-tripled Nd:YAG laser (Spectra-Physics) delivering 10 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 en-

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ergies from the laser were measured using a calibrated laser power and energy meter (Gentec).

3 Results and discussion

Förster energy transfer is based on the strong dipole–dipole interaction between two molecules. This requires a larger overlap between the emission spectrum of the host molecule and the absorption spectrum of the guest molecule. Figure 1 shows the optical absorption and photoluminescence (PL) spectra of DCJTB, C545T, Alq$_3$ and DCJTB:C545T:Alq$_3$. The absorption spectrum at 395, 470, and 504 nm should originate from the absorption of Alq$_3$, C545T, and DCJTB, respectively. The PL spectrum at 513 C, 520 nm should originate from the emission of C545T, and Alq$_3$, respectively. It can be seen that the PL spectra of Alq$_3$ and C545T and absorption of DCJTB possess larger overlap, indicating that the effective Förster energy transfer from Alq$_3$ and C545T to DCJTB should exist. The fact that the PL emission of DCJTB:C545T:Alq$_3$ originated fully from DCJTB also further proves this point. Moreover, certain spectral overlap also exists between the PL spectrum of Alq$_3$ and absorption of C545T. This means that the energy transfer from Alq$_3$ to DCJTB by C545T molecules may also exist by the emissive processes in the case of DCJTB:C545T:Alq$_3$. It is found experimentally that this assistant energy transfer process is very important in the improvement of ASE performance. The inset of Fig. 1 shows the energy level diagram of Alq$_3$, C545T and DCJTB and the energy transfer processes between molecules.

In order to fully demonstrate the advantage of the Alq$_3$:C545T:DCJTB system over C545T:DCJTB, Alq$_3$:DCJTB and DCJTB films in the improvement of ASE characteristics, we studied the threshold, gain and loss of the Alq$_3$:C545T:DCJTB film and compared them with those of C545T:DCJTB, Alq$_3$:DCJTB, DCJTB films. The optically pumping emission spectra of four samples are showed in Fig. 2, in which all the pumping energy is above their ASE thresholds. Only one emissive peak in the red region was observed for all samples, which obviously originated from the emission of DCJTB molecules. No emissive peak from Alq$_3$ and C545T was observed. This indicates that the energy transfer from Alq$_3$ and C545T to DCJTB is very effective. It also should be noted that the emissive peak of DCJTB in Alq$_3$:C545T:DCJTB is shifted to a longer value of 650 nm compared with the case of DCJTB, C545T:DCJTB and Alq$_3$:DCJTB. The red shift should be attributed to the dilution role of Alq$_3$ and C545T in DCJTB emission in Alq$_3$:C545T:DCJTB because the higher net gain always takes place at the peak furthest from the absorption edge and therefore less self-absorption [1].

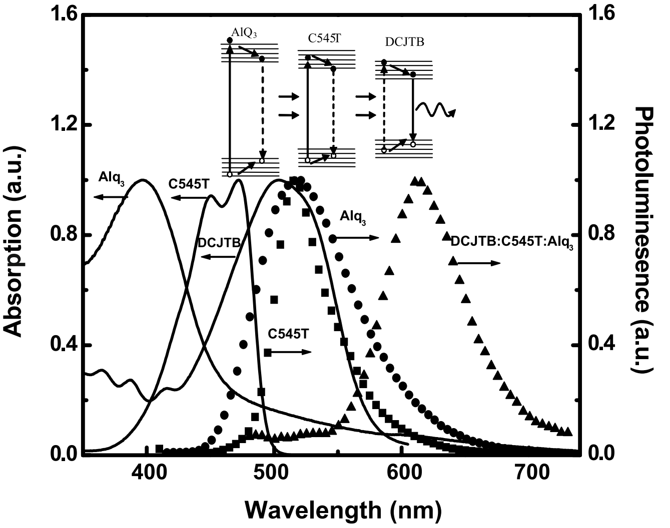

FIGURE 1 Absorption spectra of thin films of Alq$_3$, DCJTB and C545T and photoluminescence spectra of Alq$_3$, C545T and Alq$_3$:C545T:DCJTB films. Inset shows the principal photophysical processes that occur in the Alq$_3$:C545T:DCJTB system

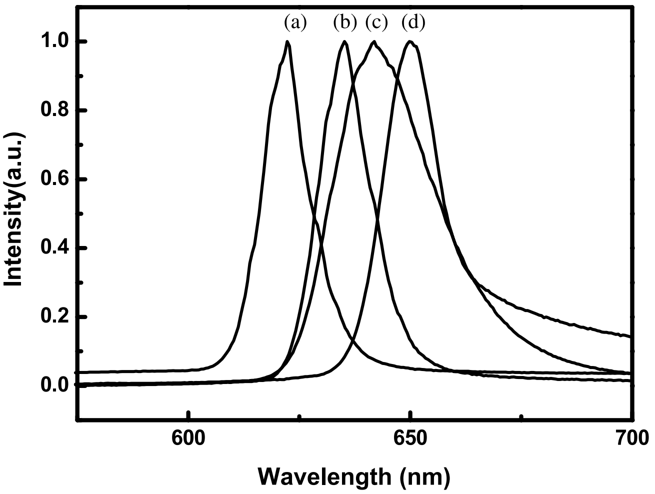

FIGURE 2 Emission spectra of DCJTB (**a**), C545T:DCJTB (**b**), Alq$_3$:DCJTB (**c**) and Alq$_3$:C545T:DCJTB (**d**) pumped by an optically pulsed laser at above lasing threshold

The threshold, gain and loss properties of Alq$_3$:C545T:DCJTB are indeed improved with respect to these cases of DCJTB, C545T:DCJTB and Alq$_3$:DCJTB. The output emis-

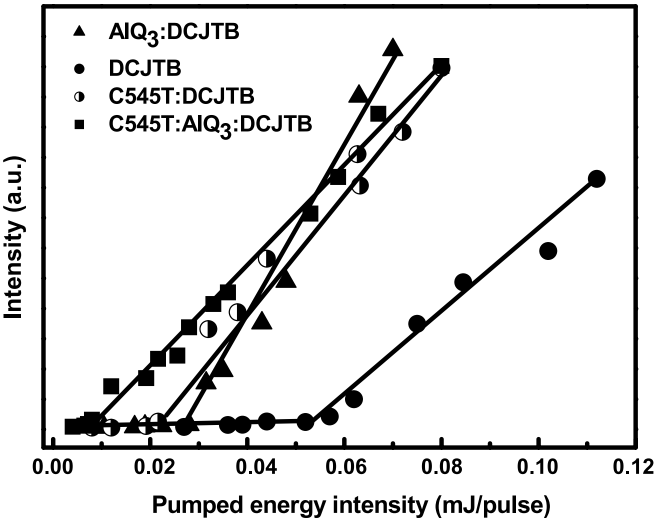

FIGURE 3 Output emission intensity integrated over all wavelengths as a function of pump intensity for DCJTB, Alq$_3$:DCJTB, C545T:DCJTB and Alq$_3$:C545T:DCJTB films

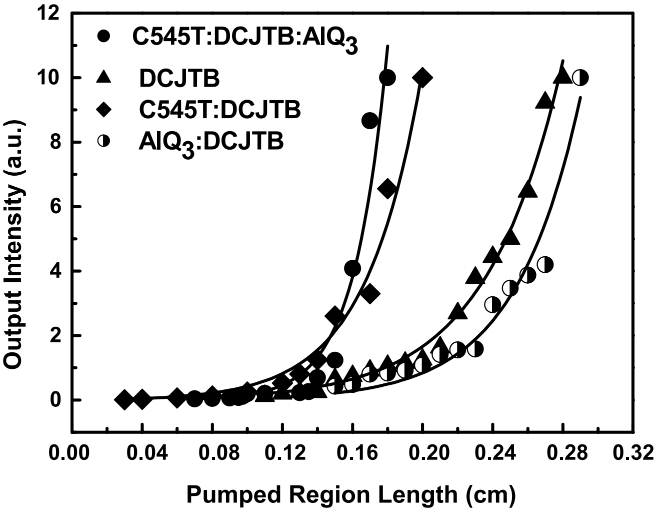

FIGURE 4 Dependence of the emission intensity at the peak wavelength on the excitation length at indicated pump intensities for DCJTB, Alq_3:DCJTB, C545T:DCJTB and Alq_3:C545T:DCJTB films (pumped intensity is 0.07 mJ pulse^{-1})

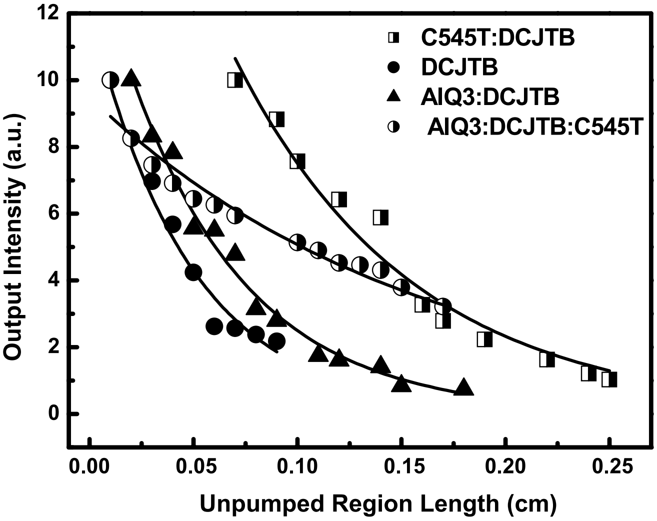

FIGURE 5 The intensity of light emitted from the edge of a waveguide as a function of the distance between the pump stripe and the edge of DCJTB, Alq_3:DCJTB, C545T:DCJTB and Alq_3:C545T:DCJTB films

sion intensities of the four samples integrated over all wavelengths as a function of the pumped intensity are plotted in Fig. 3. For pumped intensities below the threshold values, all the emission intensities increase in proportion to the pump intensity slowly. Above the threshold, all the emission intensities increase sharply. Therefore, the threshold pumped energy for ASE can be easily discerned at ~ 0.007 mJ pulse^{-1} for Alq_3:C545T:DCJTB film, corresponding to a real energy density of 0.175 mJ pulse^{-1} cm^{-2} (a 0.8 mm wide and 5 mm long narrow strip), which is much lower than these thresholds of 1.425 mJ pulse^{-1} cm^{-2} (0.045 mJ pulse^{-1}) of DCJTB, 0.55 mJ pulse^{-1} cm^{-2} (0.021 mJ pulse^{-1}) of C545T:DCJTB and 0.7 mJ pulse^{-1} cm^{-2} (0.028 mJ pulse^{-1}) of Alq_3:DCJTB films.

The variable stripe length method [14] was employed to measure the net modal gain of the doped polymer films. This method involves the detection of ASE emitted from the film edge as a function of excitation length. Figure 4 shows the pump-length dependence of ASE in C545T:DCJTB, Alq_3:DCJTB, DCJTB and Alq_3:C545T:DCJTB films, separately. The emission clearly follows a super-linear increase in intensity with excitation length in each case, as expected for amplified spontaneous emission. The output intensity is described by

$$I = \frac{A_{(\lambda)} I_P}{G_{(\lambda)}} (e^{G_{(\lambda)} L} - 1) , \tag{1}$$

where $A_{(\lambda)}$ is a constant related to the cross-section for spontaneous emission, I_P is the pumped energy intensity, $G_{(\lambda)}$ is the net gain coefficient and L is the pumped stripe length. The solid lines in Fig. 4 are the fit of the experimental data to (1), giving net modal gains of 23, 28.5, 31.3 and 52 cm^{-1} at pump energies of 0.07 mJ pulse^{-1} for DCJTB, Alq_3:DCJTB, C545T:DCJTB and Alq_3:C545T:DCJTB films, respectively. It can be seen that Alq_3:C545T:DCJTB sample shows a much higher net gain. This indicates that the Alq_3:C545T:DCJTB system is a great promising organic gain medium material for the fabrication of low cost solid-state lasers.

The loss coefficient of the waveguide was measured by using the method, where 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

$$I = I_0 e^{(-\alpha x)} , \tag{2}$$

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 5 shows the emission intensity as a function of distance from film edge for DCJTB, Alq_3:DCJTB, C545T:DCJTB and Alq_3:C545T:DCJTB films, respectively. The solid lines are the fit to (2), giving a loss coefficient of 7 cm^{-1} for the Alq_3:C545T:DCJTB film. This value is much smaller than the 11.76, 17.58 and 20.6 cm^{-1} loss coefficient of C545T:DCJTB, Alq_3:DCJTB and DCJTB films under the same experiment conditions. The low loss coefficient in Alq_3:C545T:DCJTB film should be attributed to further low self-absorption and energy loss due to effective Förster energy transfer from Alq_3 to DCJTB by the assistant effect of C545T. This effect is based on Förster energy transfer between molecules. Cascade energy transfer between two dopants allows a high efficiency [15].

The Förster energy transfer rate via induced dipole–dipole interactions between organic molecules [16] is given by

$$K = \frac{1}{\tau_H} \frac{1}{R^6} \left(\frac{3}{4\pi} \int \frac{c^4}{\omega^4 n^4} F_H(\omega) \sigma_D(\omega) \, d\omega \right) , \tag{3}$$

where $F_H(\omega)$ is the normalized fluorescence spectrum of the host material, $\sigma_D(\omega)$ is the normalized optical absorption cross section of the dopant, τ_H is the natural radiative lifetime of the host, and R is the mean distance between host and dopant molecules. For efficient energy transfer (i.e., for K large), the overlap between $F_H(\omega)$ and $\sigma_D(\omega)$ must be large, which is the case between Alq_3 and DCJTB, and between

	DCJTB	DCJTB:Alq_3	C545T:DCJTB	C545T:DCJTB:Alq_3
Gain (cm^{-1})	23	28.5	31.3	52
Threshold (mJ/pulse)	0.057	0.028	0.022	0.007
Loss (cm^{-1})	20.6	17.58	11.76	7

TABLE 1 The threshold, gain and loss of DCJTB, Alq_3:DCJTB, C545T:DCJTB and Alq_3:C545T:DCJTB films (the pump energy for gain and loss test is 0.07 mJ $pulse^{-1}$)

C545T and DCJTB, as shown in Fig. 2. Thus the pump energy is first absorbed by Alq_3 host molecules, and then subsequently transferred to DCJTB guest molecules by C545T molecules, and finally radiatively recombines on DCJTB molecules, leading the DCJTB emission.

Table 1 summarizes the threshold, gain and loss of DCJTB, Alq_3:DCJTB, C545T:DCJTB and Alq_3:C545T:DCJTB films. It can be seen that the ASE performance in Alq_3:C545T:DCJTB film is greatly improved due to effective energy transfer from Alq_3 to DCJTB by the assistant effect of C545T molecules. Our results indicate that the coguest-host system, with at least two guests doped into one host with effective Förster energy transfer, should be a promising method to achieve high performance organic lasers.

4 Conclusions

We have presented a detailed study of ASE in the C545T:DCJTB:Alq_3 coguest-host system. A lower ASE threshold, larger net gain, and lower loss are achieved due to effective Förster energy transfer in C545T:DCJTB:Alq_3. To the best of our knowledge, this is the first study on ASE in coguest-host systems and the very low threshold value renders the coguest-host systems a very promising material for further electrically pumped organic semiconductor lasers.

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