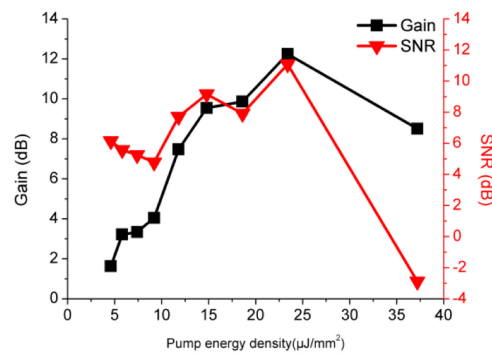
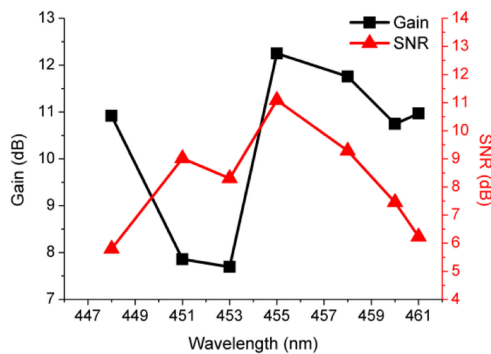
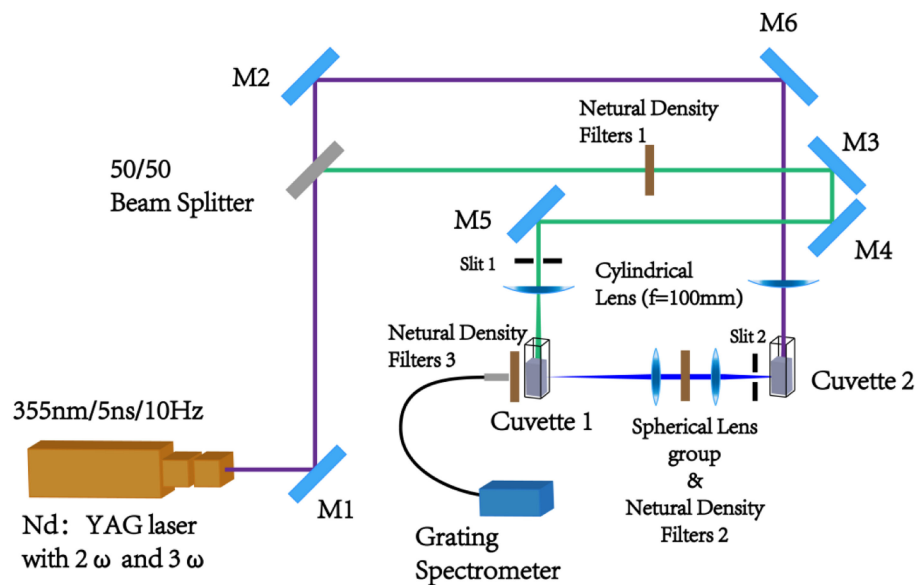


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**Abstract:** We studied the optical signal amplification properties of coumarin 460 (C460) in solution. An optical signal amplification experiment was performed using a side-pumping setup. Amplification of more than 7 dB was achieved over a 13-nm spectral width in the signal wavelength range of 448–461 nm with gains above 10 dB at 448 nm and in the 455–461-nm range. The signal-to-noise ratio (SNR) of the entire band was 5.8–11.1 dB. When the solution concentration and pump energy were 0.001 M (mol/L) and 117  $\mu$ J, respectively, the optical gain reached a maximum of 12.25 dB. Thus, the gain and SNR were measured by adjusting the pump energy and solution concentration to determine the optimal concentration of coumarin 460 in methanol solution in the amplifier. Additionally, amplification of the spontaneous emission was found to seriously reduce the SNR, adversely affecting the optical gain.

**Index Terms:** Laser dye, coumarin 460, tunable optical amplifier.

## 1. Introduction

After the third industrial revolution, the rapid development of the fields of computer science and information technology has become the main driving force for social and economic development. Optical fiber communication technologies are rapidly emerging and playing an important role in these fields. In the current optical fiber communication systems monopolized by inorganic materials, almost all types of optical fiber communication devices are built using inorganic materials. In the beginning of the 21<sup>st</sup> century, plastic optical fiber (POF) communication systems achieved considerable progress in the field of short-range communication [1], [2]. Organic polymer fiber, as a kind of POF, has been widely used in short-distance communication and laser display in recent years. To realize organic communication systems with the same efficiency as the traditional inorganic communication systems, optical devices made of organic materials are required. Compared with the traditional single-wavelength amplifier, the tunable amplifier is not only aimed at a specific wavelength but can amplify a spectral band. When this technology is applied to laser display, it can provide true wavelength signals with more wavelengths, and greatly simplify the optical path. In addition, organic optical amplifiers are also used in temperature sensors [3], lidars [4], and even

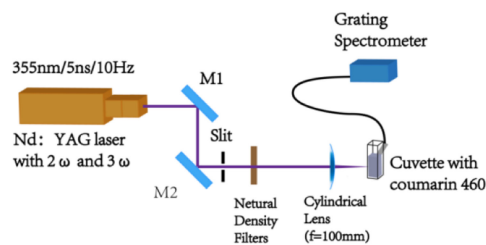


Fig. 1. Experimental setup to determine the gain and loss coefficients.

cancer treatments [5]. In this experiment, coumarin 460 was used as the working medium of the amplifier. As a stable, low-cost, high-gain luminescent material, coumarin 460 has applications in many fields. Coumarin 460 can be used as a laser dye [6], a luminescent phosphor in LEDs [7], [8], a luminescent probe and sensor in biological applications [9], and a fluorescer in rewritable optical drives [10]. Many authors have performed experiments using other dyes as the gain media both in solution and in polymer. Lam and Damzen [11] studied pyrromethene 650 as a material with potential applications in optical amplification. In a 7-mm-long polymethylmethacrylate (PMMA) sample, they achieved gains of 26 dB using a dye concentration of 120 ppm in PMMA and M. C. Ramon *et al.* [12] achieved a gain of 41 dB in solution using rhodamine 640. Additionally, the internal optical gain values measured at 625 and 650 nm were found to be 26 and 8 dB with dye and PMMA dispersions, respectively. But in the blue light band, especially for the low loss band (450 nm) of the organic polymer fiber blue light research is scarce. In this study, we focused on the amplifying properties of a coumarin 460 as a laser dye in methanol as a test material for such applications.

## 2. Experimental Details

Before performing the light amplification experiment using coumarin 460, we characterized the coumarin 460 solution in a quartz cuvette having a 1-cm path length. Absorption measurements were performed using a UNIC UV-2800A UV-Vis spectrophotometer, and photoluminescence was measured using a Shimadzu fluorescence spectrophotometer (shown in Fig. 3(b)). Next, we used the optical path shown in Fig. 1 to obtain the gain and loss coefficients of coumarin 460.

The cuvette shown in Fig. 1 was optically pumped at 355 nm using a Q-switch, a neodymium-doped yttrium aluminum garnet [ $\text{Nd}^{3+}:\text{YAG}$ ] that was laser pumped using a triple frequency module, providing a 5-ns pulse with a 10-Hz repetition rate. The pump wavelength was chosen to match the absorption band of coumarin 460 having high absorption efficiency, as determined by the absorption spectral measurements described above. Pump energy adjustment was achieved using a calibrated neutral density filter in the optical path. The pump beam was focused using a cylindrical lens with a focal length of 10 cm and spatially filtered through an adjustable slit to create a narrow excitation stripe of  $5 \text{ mm} \times 550 \mu\text{m}$  on the sample. When the excitation intensity was sufficiently high, i.e., above the amplified spontaneous emission (ASE) threshold, the spontaneously emitted photons in the fringe region of the waveguide were amplified by stimulated emission, which caused most of the light to be emitted in the direction of the fringes. To efficiently collect this ASE output, the stripe was aligned such that its end abutted the edge of the sample and the fiber bundle was aligned along the stripe axis and placed close to the sample edge from which the ASE emanated. To investigate the net gain of the solution, we used the variable stripe length method [13], [14]. This technique involves pumping a sample using a variable-length stripe (5 mm) and monitoring the edge emission as a function of stripe length. Then, the gain  $\sigma_{\text{gain}}(\lambda)$  is determined by fitting the output intensity versus the stripe length variation to the expected small-signal regime dependence [11].

$$I_{\text{out}} = \exp[\sigma_{\text{gain}}(\lambda)l + a]. \quad (1)$$

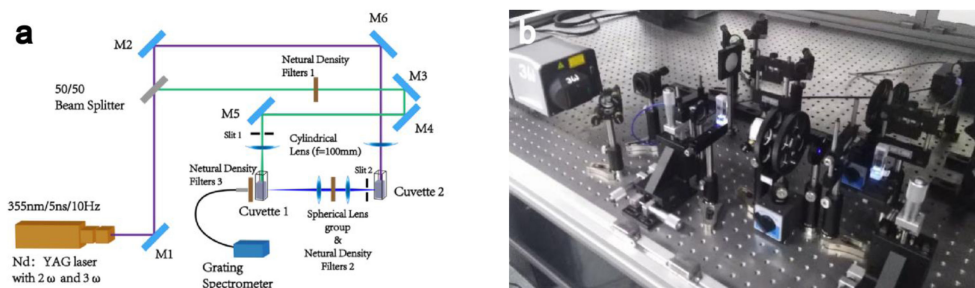


Fig. 2. (a) Experimental setup to examine the optical amplification of the coumarin 460 solution. (b) Experimental device built on optical platform

Here,  $I_{out}$  is the ASE intensity,  $l$  is the length of the stripe, and  $a$  is a constant. Further, we measured the corresponding waveguide losses by the stripe displacement method, wherein the length of the stripe was kept constant (5 mm) but the stripe was gradually moved away from the edge of the sample so that the ASE signal had to travel across an increasingly large unpumped region. Then, the output ASE signal should depend on the distance from stripe to the end of the sample edge as follows:

$$I_{out} = \exp[\sigma_{loss}(\lambda)x + b] \quad (2)$$

where  $x$  is the length of the unpumped region between the edge of the sample and the end of the stripe,  $\sigma_{loss}(\lambda)$  is the waveguide loss coefficient (modeled as effective absorption).

Next, we tested the amplification performance of coumarin 460 in methanol solution and used signal beam of different wavelengths for the amplification test to measure the gain and signal-to-noise ratio (SNR). Fig. 2 shows the experimental setup of the amplifier using the 355-nm laser with the Q-switch, neodymium-doped yttrium aluminum garnet [ $\text{Nd}^{3+}:\text{YAG}$ ] laser pump, and triple frequency module to provide a 5-ns pulse with a 10-Hz repetition rate. The beam was passed through a 50/50 beam splitter; half of the laser energy was used as the amplifier pump beam, and the other half was used to pump the cuvette 2 that contained coumarin 460 in methanol as the signal output medium. Both beams were focused on the solution using a cylindrical mirror with a 10-cm focal length. Cuvette 2 acted as a magnified spontaneous emission module, producing a weak beam with  $<5$ -nm spectral width. After passing through a pair of convex lenses ( $f = 5$  cm), the weak signal beam entered the amplifier, which was a cuvette filled with coumarin 460 in methanol solution. The signal beam was spatially filtered using pinholes between the two convex lenses and intersected the pump light at the end of the amplifier. To synchronize the pump and signal, the pump light needed to pass the delay path. When the signal beam entered one end of the cuvette, the spot area was approximately  $1/4\pi$  mm<sup>2</sup>. The signal energies were controlled independently by inserting calibrated neutral density filters into the beam path. To collect the emitted light from Cuvette 1, we used a fiber bundle coupled with a grating spectrograph. Additionally, the emission was monitored during all the measurements to ensure that photo bleaching did not affect any of the results.

### 3. Results and Discussion

By measuring a series of concentrations of the coumarin 460 solution using the optical path shown in Fig. 1, we obtained the corresponding gain and loss coefficients for each solution by fitting Equations 1 and 2. The gain and loss coefficients for different concentrations of the solution are shown in Fig. 3(a). From the figure, we can see that the loss coefficient was approximately 0 for the solutions of each concentration except the  $2.1 \times 10^{-2}$  and  $4.3 \times 10^{-2}$  M solutions, which showed a slight increase in the loss coefficient due to the increase in concentration. The  $1 \times 10^{-3}$  M solution had the largest gain coefficient at 455 nm. The gain decreased rapidly with increasing concentration.

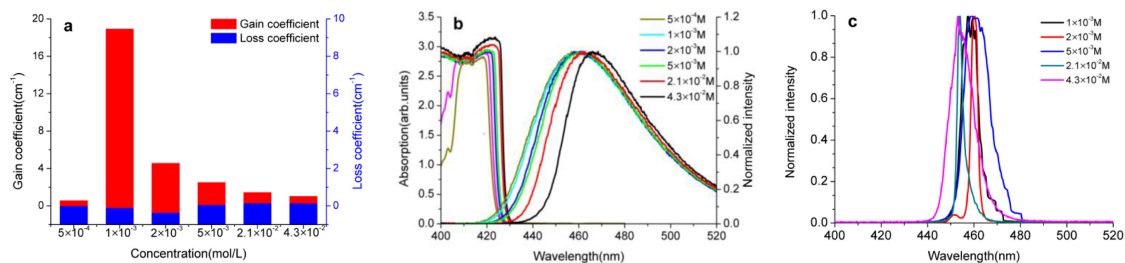


Fig. 3. (a) Gain and loss coefficients for different concentrations of coumarin 460 in methanol. (b) Absorption and photoluminescence for different concentrations of coumarin 460 in methanol. (c) ASE spectra of coumarin 460 solutions at various concentrations.

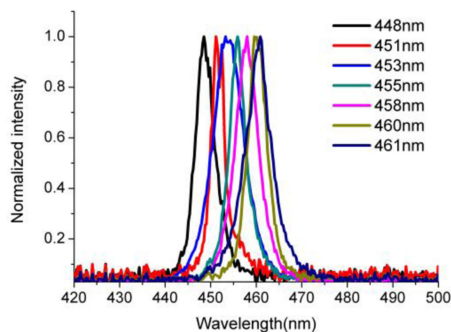


Fig. 4. Different wavelengths of signal beams.

When the concentration of the solution was  $5 \times 10^{-4}$  M, the gain coefficient of the solution was lower than that of the higher-concentration solutions because the concentration was too low. ASE intensity of the solution was not as high as for other concentrations because the concentration was too low. This can be explained by the fact that there is no sufficient concentration of working substance to generate ASE under pumping. The absorption and steady-state photoluminescence (PL) spectra of coumarin 460 in solution are shown in Fig. 3(b). In this figure, the absorption and photoluminescence spectral positions for this series of  $1 \times 10^{-3}$ – $4.3 \times 10^{-2}$  M coumarin 460 solutions did not change considerably. The PL and ASE spectra were excited at 355 nm. The absorption and emission peaks measured in solution were Stokes shifted by 35 nm, which allowed the spectra of the emitted and excitation light to be completely separated without interfering with each other. The centers of several ASE peaks shown in Fig. 3(c) are between 450 and 460 nm, which is 30 nm apart from the absorption peak. Thus, no obvious absorption occurred in the region where the ASE was located. Additionally, we can see from the figures that the 355-nm wavelength for pumping had a high excitation efficiency corresponding to the absorption peak and the ASE phenomenon occurred when the self-absorption of the solution is negligible.

Because the ASE spectrum of the coumarin 460 solution depends on the polarity of the solvent, the coumarin 460 powder was dissolved in a mixed solution of methanol and toluene in volume ratios of 2:8, 6:4, 8:2, and 10:0 to prepare a solution with 0.002 M concentration. Furthermore, by finely adjusting the distance between the cylindrical mirror and Cuvette 2 to approximately 10.5 cm, an ASE output with a 448–461-nm wavelength was obtained (Fig. 4). This phenomenon allows us to test the spectral range of the amplifier using an ASE beam emitted from a solution containing solvents with different polarities than the signal. For the optical amplification test, we maintained average signal and pump light energies of 0.145 and 235  $\mu$ J, respectively. The pump light could control the pump energy using a neutral filter placed in the optical path. When performing optical

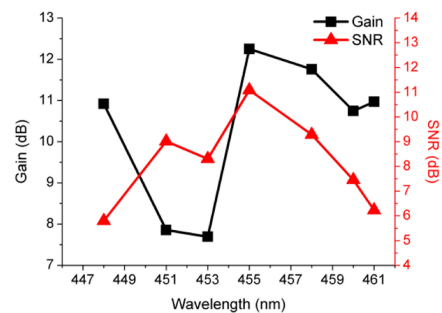


Fig. 5. Gain and SNR for different wavelengths of signal for a coumarin 460 solution at 0.001 M.

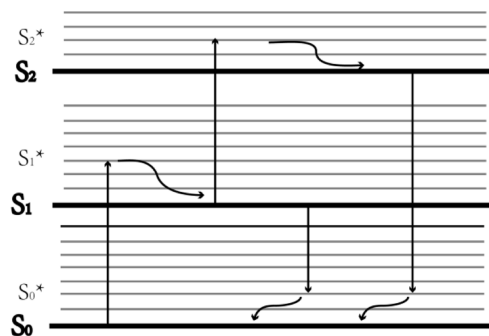


Fig. 6. Energy-level diagram of a typical dye molecule.

amplification experiments using the optical path shown in Fig. 2, a response-calibrated neutral density filter was used when necessary to prevent saturation of the grating spectrometer. In high-gain systems and when the amplifier is a cuvette containing the coumarin 460 in methanol solution, the ASE must be considered to accurately calculate the signal amplification. In solution, ASE could be observed clearly without the presence of a signal beam. Even without feedback, its emitted radiation exhibited a low divergence angle and a strong spectral narrowing characteristic, i.e., the characteristics of ASE.

According to the gain coefficient results, the gain coefficient was the largest when the concentration of the methanol solution containing coumarin 460 was 0.001 M. Therefore, a solution with this concentration was first used as the working medium of the amplifier. Cuvette 2 was filled with coumarin 460 solution containing solvents with different polarities as described above, and the wavelength of the signal beam was changed to test the amplification performance of the amplifier at different wavelengths. The gain of the signal beam wavelength from 448 to 461 nm is shown in Fig. 5. At 455 nm, a maximum band gain of 12.25 dB was achieved. The minimum gain was 7.85 dB at 453 nm. In the figure, the gain in the wavelength range of 448–461 nm is appears greater than 7 dB, and the gain is greater than 10 dB at approximately 448 and 455–461 nm. The maximum SNR for each wavelength is shown by the solid blue line in Fig. 5. Clearly, the SNR increased with increasing wavelength and decreased only slightly at 453 nm until a maximum value of 11.1 dB at 455 nm was reached. Then, the SNR decreased with increasing wavelength. The gain curve has two peaks because of the intra-molecular-charge-transfer and twisted intra-molecular-charge-transfer (TICT) excited states and the common features of the laser-active optical material [15]. These states are extremely stable in a polar environment, allowing fluorescence to be emitted. Fig. 6 shows an energy-level diagram of an amplifier operating at different signal beam wavelengths. The dye molecules were excited by the pump light from  $S_0$  (the primary energy level) to  $S_1$  (the high energy level). When the signal beam passed through the excited dye molecules, the

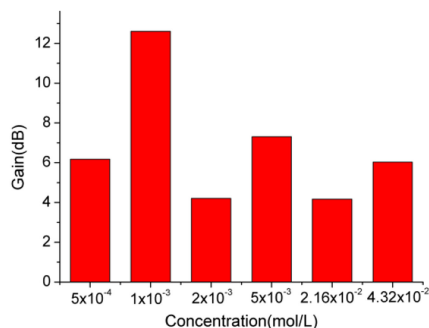


Fig. 7. Gain for different coumarin 460 solution concentrations.

latter transitioned from  $S_1$  to  $S_0$  to yield a broad spectrum dominated by photons with the same wavelength and phase as the signal beam. This is because these energy levels contain a large number of dense sub-levels. In addition, some dye molecules were excited to  $S_2$ , which is the TICT state. During the optical amplification process, the dye molecules transitioned from this state to  $S_0$  and released many photons with the same wavelength as the signal beam; further, the wavelengths of these photons were lower than the wavelength of ordinary light emission (455 nm). Because the time pulse of the pump laser is 5 ns, no crossover occurred between the systems in the working medium; as such, the accumulation of the triplet group could be ignored. When the wavelength of the signal beam was 455 nm, the gain was 12.25 dB. The wavelength of the light should be maintained at 455 nm, and the concentration of the solution in the amplifier can be fine-tuned to obtain the most functional amplifier.

By fine-tuning the solubility of coumarin 460 in methanol for the amplifier, the intensity of a certain signal beam can be maintained and gain under pumping at different energy intensities can be recorded. Furthermore, for the same test beam path, we characterized the gain characteristics of coumarin 460 as a function of the changes in the dye solution concentration. We prepared solutions with the following concentrations:  $5 \times 10^{-4}$ ,  $1 \times 10^{-3}$ ,  $2 \times 10^{-3}$ ,  $5 \times 10^{-3}$ ,  $2.1 \times 10^{-2}$ , and  $4.3 \times 10^{-2}$  M. Fig. 7 shows the gain of the amplifier at different coumarin 460 solution concentrations. The maximum gain was 12.25 dB when the solution concentration was  $1 \times 10^{-3}$  M. Although a  $5 \times 10^{-4}$  M solution could not exhibit ASE at the same pumping energy as  $235 \mu\text{J}$ , the weak signal could still be amplified. When the concentration was increased to  $4.3 \times 10^{-3}$  M, the signal could still be amplified to some extent; however, because of the absorption by the higher-concentration solution, the ability of this solution to amplify small signals was limited.

After focusing, the spot size of the pump light was  $5 \times 1 \text{ mm}^2$ . The spot could not be focused accurately on the amplifier because too high of an optical density will cause more ASE, which would take up many particles in the low energy level and seriously affect the performance of the optical amplifier. In Fig. 8(a), the black solid line (filled squares) shows that when the pump energy is low, the generated amplified signal can be almost ignored (gain of less than 2 dB). According to the spectral observation, most of the luminescence was the photoluminescence of the working substance itself. Additionally, the gain increased linearly with the pump optical density until the  $25\text{-}\mu\text{J}/\text{mm}^2$  optical amplifier produced a strong ASE that caused the gain to drop sharply. Similarly, the SNR also gradually increased from 5 to  $25 \mu\text{J}/\text{mm}^2$ . Subsequently, the optical density continued to increase, the amplifier had a strong ASE, and the SNR dropped sharply. As shown by the black solid line (filled squares) in Fig. 8(b), at a pumping energy of approximately  $46 \mu\text{J}$  per pulse, the intensity of the luminescence changed drastically: the output intensity increased sharply. The spectrum showed a central line at 455 nm, and the full width at half maximum was maintained at approximately 5 nm. The output rose sharply to approximately  $117 \mu\text{J}$  per pulse. When the pumping energy was increased further, the output intensity no longer showed a sharp increase in the high slope but changed to a slowly increasing state similar to an abrupt change. Because the triplet absorption of the excited state is negligible and the quantum efficiency is close to 1,

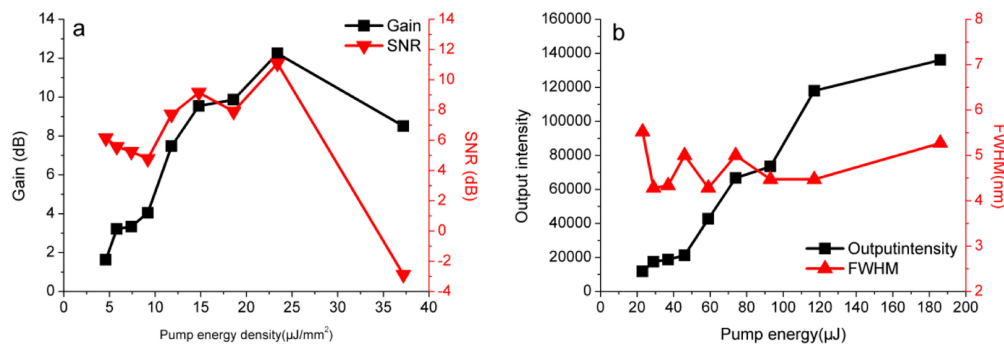


Fig. 8. (a) Relationship between the pump-energy density at 355 nm, and the gain and SNR of the coumarin 460 solution at 0.001 M. (b) Output intensity (filled squares) and FWHM (filled triangles) vs. pump energy for the coumarin 460 solution at 0.001 M.

almost all the absorbed photons were likely re-emitted. Under low pump energy conditions, most of the photons were emitted in the form of fluorescence. As the pump energy increased, more of the absorbed photons were re-emitted after the pump energy reached the ASE threshold and the spectrum narrowed. This is because the ASE emission caused the unfavorable consumption of the S0 particle group, which seriously affected the performance of the amplifier.

#### 4. Conclusion

We studied the gain properties of coumarin 460 in solution in detail. The gains of the signal beam wavelengths from 448 to 461 nm obtained via optical amplification experiments were greater than 7 dB. The optical gain was greater than 10 dB when the signal beam wavelengths were 448 and 455–461 nm. Moreover, we measured the SNR of the amplifier under the same conditions, which were between 5.8 and 11.1 dB. The maximum gain and SNR, which could be obtained when the signal beam wavelength was 455 nm, were 12.25 and 11.1 dB, respectively. By adjusting the pump energy and concentration of the coumarin 460 solution in the amplifier, we found that the most suitable concentration was 0.001 M; this result was consistent with the gain coefficient results, where the maximum optical gain and SNR were 12.25 and 11.1 dB. During the experiment, the pump amplification energy and appearance of ASE had serious adverse effects on the optical amplification performance. These results show that coumarin 460 has a good potential for use in amplifiers. It can be mixed in a polymer to fabricate a polymer fiber amplifier, allowing the development of a more compact device for applications that require high gain over the gain range.

#### References

- [1] W. Li *et al.*, "2.5 Gbit/s transmission over 200 m PPMA graded index polymer optical fiber using a 645 nm narrow spectrum laser and a silicon APD," *Microw. Opt. Technol. Lett.*, vol. 20, pp. 163–166, 1999.
- [2] Plastic Optical Fiber Trade Organization, "Present state-of-the-art of plastic optical fiber (POF) components and systems," *Internet Commun.*, 2004. [Online]. Available: <http://pofco.com/downloads/WP-TIA-POFTO.pdf>
- [3] V. R. Anand, S. Mathew, C. L. Linslal, J. Peter, P. Radhakrishnan, and M. Kailasnath, "Tunable amplified spontaneous emission from dye doped hollow polymer optical fiber," *J. Lumin.*, vol. 201, pp. 1–4, 2018.
- [4] Y. Yang *et al.*, "Solid-state 589 nm seed laser based on Raman fiber amplifier for sodium wind/temperature lidar in Tibet, China," *Opt. Exp.*, vol. 26, pp. 16226–16235, 2018.
- [5] S. Marengo, "Imaging of small objects embedded in diffusing media using a time-gated femtosecond pumped dye amplifier," *Opto-Canada: SPIE Regional Meeting Optoelectronics, Photon. Imag.*, vol. 1031339, 2017. [Online]. Available: <https://doi.org/10.1117/12.2283913>
- [6] K. Kato, "3547-Å pumped high-power dye laser in the blue and violet," *IEEE J. Quantum Electron.*, vol. 11, no. 7, pp. 373–374, Jul. 1975.
- [7] T. Song, G. Zhang, Y. Cui, Y. Yang, and G. Qian, "Encapsulation of coumarin dye within lanthanide MOFs as highly efficient white-light-emitting phosphors for white LEDs," *J. Photochemistry Photobiology B. Biol.*, vol. 183, pp. 302–308, 2018.



- [8] H. Jung, H. Lee, S. Kang, D. Shin, K. Kay, and J. Park, "New anthracene derivatives containing coumarin moiety for organic light-emitting diodes," in *Proc. KJF Int. Conf. Organic Mater. Electron. Photon. 2016*, vol. 654, pp. 90–95, 2017.
- [9] K. Benson, A. Ghimire, A. Pattammattel, and C. V. Kuma, "Protein biophosphors: Biodegradable, multifunctional, protein-based hydrogel for white emission, sensing, and ph detection," *Adv. Functional Mater.*, vol. 27, 2017, Art. no. 1702955.
- [10] S. Song, H. Takezoeb, and S. Jeong, "Rewritable, light-driven recordings in a full-colour fluorescent polydimethylsiloxane elastomer," *J. Mater. Chemistry C*, vol. 6, pp. 10704–10713, 2018.
- [11] S. Y. Lam and M. J. Damzen, "Characterisation of solid-state dyes and their use as tunable laser amplifiers," *Appl. Phys. B*, vol. 77, pp. 577–584, 2003.
- [12] M. C. Ramon *et al.*, "A characterization of rhodamine 640 for optical amplification: Collinear pump and signal gain properties in solutions, thin-film polymer dispersions, and waveguides," *J. Appl. Phys.*, vol. 97, 2005, Art. no. 073517.
- [13] K. L. Shaklee and R. F. Leheny, "Direct determination of optical gain in semiconductor crystals," *Appl. Phys. Lett.*, vol. 18, pp. 475–477, 1971.
- [14] M. D. McGehee, R. Gupta, S. Veenstra, E. K. Miller, M. A. Díaz-García, and A. J. Heeger, "Amplified spontaneous emission from photopumped films of a conjugated polymer," *Physical Rev. B*, vol. 58, pp. 7035–7039, 1998.
- [15] V. K. Sharma, P. D. Sahare, A. Pandey, and D. Mohan, "Optical gain characteristics of C 460 and C 450," *Spectrochimica Acta Part A, Mol. Biomolecular Spectrosc.*, vol. 59, pp. 1035–1043, 2003.