Kingdom of Saudi Arabia
Imam Mohammad Ibn Saud Islamic University (IMSIU)
Faculty of Sciences – Department of Physics

Investigate the spectroscopy Characteristics of conjugated materials

A graduation project submitted to the Department of Physics in partial fulfillment of the requirements for the degree of Bachelor of Science in Applied Physics

by

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Abstract

This project investigated the optical properties of conjugated oligomers, specifically analysing their absorption spectra in various solvents, including hexane and chloroform, across a broad range of concentrations. The results revealed two distinct absorption peaks. Additionally, the fluorescence spectra obtained in the same solvents exhibited three different bands. The band gap of the oligomer was calculated using the intersection method applied to the normalized absorption and fluorescence spectra. Furthermore, the amplified spontaneous emission (ASE) performance of the conjugated oligomer in hexane was predictable under optical pumping from an Nd: YAG laser (355 nm), with ASE peaking at 450 nm.

الملخص:

هذا المشروع درس الخصائص البصرية للأوليغومر المترافق، مع تحليل طيف الامتصاص الخاص بها في مختلف المذيبات، بما في ذلك الهكسان والكلوروفورم، عبر نطاق واسع من التركيزات. كشفت النتائج عن وجود قمتين متميزتين في الامتصاص. بالإضافة إلى ذلك، أظهرت أطياف الفلورية التي تم الحصول عليها في نفس المذيبات ثلاثة نطاقات مختلفة. تم حساب فجوة الطاقة للأوليجومر باستخدام طريقة التقاطع التي تطبق على أطياف الامتصاص والفلورية المعادلة. علاوة على كان أداء الانبعاث التلقائي المضخم (ASE) للأوليغومر المترافق في الهكسان متوقعًا تحت الضخ البصري من ليزربطزل موجي 355 نانومتر، مع ذروة ASE عند 450 نانومتر.

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جدول المحتويات

Chapter 1 Introduction and Background.

1.1Conjugated materials

Conjugated materials are a category of organic compounds known for their distinctive electrical and optical characteristics. These materials find extensive applications across various domains, such as electronics, optoelectronics, and photonics. Their unique structure enables electrical conductivity through a process called "pi-conjugation," where electrons can move freely along the conjugated backbone, resulting in enhanced conductivity.

The history of conjugated materials dates back to the 1970s with the synthesis of the first conjugated polymer. Since then, research has flourished, uncovering a variety of conjugated materials, which can be categorized into conjugated polymers, conjugated oligomers, and small-molecule conjugated materials. Beyond their electronic properties, these materials also exhibit remarkable optical features; they can absorb and emit light across a broad spectrum with strong absorption coefficients and high quantum yields, making them valuable for numerous applications.

One of the primary applications of conjugated materials is in organic electronics. Devices constructed with these materials offer several advantages over traditional silicon-based electronics, including lower costs, flexibility, and lightweight designs. Examples of organic electronic devices include organic solar cells, organic light-emitting diodes (OLEDs), lasers, and field-effect transistors (FETs).

Conjugated Polymers
Conjugated polymers consist of long-chain polymers featuring a conjugated backbone. Often referred to as "plastics," they exhibit a range of electrical and optical properties. A prominent example is poly(3-hexylthiophene) (P3HT), widely utilized in lasers.

Small-Molecule Conjugated Materials

In contrast, small-molecule conjugated materials comprise discrete molecules with a conjugated backbone. These materials are frequently employed as active components in organic electronic devices. Examples include pentacene and fullerene.

Conjugated Oligomers

Conjugated oligomers are organic molecules characterized by a series of covalently linked conjugated monomers, forming either linear or branched structures. The conjugated backbone facilitates significant electronic delocalization, resulting in low ionization potential and high electron affinity, making them particularly appealing for organic electronics and optoelectronics.

Extensive research on conjugated oligomers has highlighted their potential in applications such as solar cells, OLEDs, organic field-effect transistors (OFETs), and amplified spontaneous emission (ASE). Their favourable properties, including high charge carrier mobility and absorption coefficients, position them as excellent candidates for these technologies. Their ability to produce amplified spontaneous emission (ASE) adds to their appeal, with research showing promising results for oligomers like HOTF and PFO, demonstrating high ASE power and photochemical stability.

In summary, conjugated oligomers represent a highly promising class of organic molecules with diverse potential applications in electronic devices, biomedical imaging, and sensing. Ongoing research in this field is expected to yield new materials and devices with enhanced performance and functionality.

1.2 Absorption

Absorption spectroscopy is a technique used to measure the amount of light absorbed by a sample as a function of wavelength. This method is based on the principle that different substances absorb light at specific wavelengths, which can be characteristic of their molecular structure. The absorption spectrum is the variation in absorption intensity as a function of wavelength. Absorption spectroscopy is used throughout the electromagnetic spectrum. Absorption spectroscopy is a powerful tool for understanding the composition and properties of materials based on their interaction with light. Transmittance is a key concept in absorption spectroscopy that quantifies how much light passes through a sample. It is defined as the ratio of the intensity of light exiting the sample (I) to the intensity of light entering the sample (I_0). The formula for transmittance (T) is given by: $T=I/I_0$. Transmittance and absorbance have a logarithmic relationship. The amount of light that the sample directly absorbs is measured by its absorbance, or absorption (A). $A=-\log10(T)$

Large values of absorbance are associated with very little light passing entirely through the sample, while small values of absorbance are associated with the majority of light passing entirely through the sample.

1.3 Fluorescence

Photoluminescence is the emission of light from a material after it has absorbed photons. This process occurs when a material, typically a semiconductor or an organic compound, absorbs light (or other electromagnetic radiation) and then re-emits it. Photoluminescence is formally divided into two categories, fluorescence and phosphorescence depending upon the electronic configuration of the excited state and the emission pathway. Fluorescence involves several key steps. When a molecule absorbs a photon, it transitions from a ground state to an excited state. This excitation can occur due to the absorption of ultraviolet or visible light. The excited state is typically short-lived, lasting only nanoseconds, after which the molecule returns to its ground state by releasing energy in the form of light. The emitted light usually has a longer wavelength than the absorbed light due to the Stokes shift, which is the difference in energy between the absorbed and emitted photons. The process of phosphorescence occurs in a manner similar to fluorescence, but with a much longer excited state lifetime. The Jablonski diagram is a graphical representation that illustrates the electronic states of a molecule and the transitions between these states during processes like fluorescence and phosphorescence, as in Figure 1.1. It provides a visual framework for understanding how light absorption and emission occur.

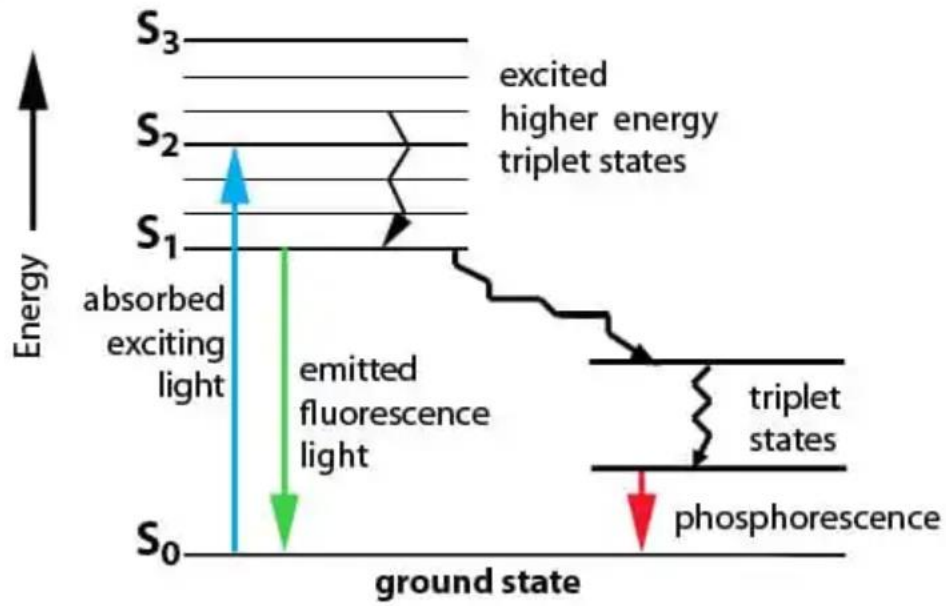

Figure1.1 Jablonski diagram illustrating the fundamental processes of fluorescence and phosphorescence.

The fluorescence process involves three key events, each occurring over timescales that differ by several orders of magnitude (see Table 1). The excitation of a susceptible molecule by an incoming photon takes place in femtoseconds (10^{-15} seconds). In contrast, the vibrational relaxation of excited-state electrons to the lowest energy level is significantly slower, measured in picoseconds (10^{-12} seconds). The final event-emission of a longer wavelength photon and the return of the molecule to its ground state-occurs over a relatively long timescale of nanoseconds (10^{-9} seconds). A typical Jablonski diagram depicts the singlet ground state (S(0)) alongside the first (S(1)) and second (S(2)) excited singlet states as a series of horizontal lines. In Figure 1, transitions between these states are represented by straight or wavy arrows, depending on whether the transition involves the absorption or emission of a photon (straight arrow) or results from molecular internal conversion or non-radiative relaxation processes (wavy arrows). Vertical upward arrows indicate the instantaneous nature of excitation processes, while wavy arrows denote events that occur over a much longer timescale.

1.4 Amplified Spontaneous Emission

Amplified Spontaneous Emission (ASE) refers to the enhancement of spontaneously emitted photons as they traverse an active medium, a process driven by stimulated emission that occurs under pumping, typically from a laser source. This amplified emission along the axis of a cylindrical channel with intense excitation produces a narrow cone of intense light that exits in the z-direction. ASE is a critical factor in assessing the suitability of gain materials for stimulated emission and is considered a mirror-less laser, exhibiting many of the characteristics of traditional lasers. Additionally, ASE is a vital area of investigation in optical research, with a wide range of applications, including fluorescence studies, lifetime measurements, pumping sources, and sensing technologies... ASE has many applications, such as fluorescence studies, and lifetime measurement. Moreover, utilized and sensing measurement.

CHAPTER 2 Materials and Experimental Setup

2.1 Solvent and Material

This project aims to study the spectral properties, determine the energy gap, and investigate the ASE spectra of conjugated oligomer. To accomplish this, the spectrum features of absorption and fluorescence, as well as all mirrorless laser properties, were investigated.

The material used in this study is a conjugated oligomer with a molecular weight of 1500 g/mole. It was bought from a Canadian company named American Dye Source, Inc. Quebec, and used without any purification. The conjugated oligomer was dissolved in different solvents at many concentrations, starting from 0.5 mg/ml, and diluted many times. Figure 2.1 shows the image of the CO samples dissolved in hexane.

Fig.2.1 Image of the CO sample dissolved in Hexane.

2.2 Optical measurements

The absorption spectra of the conjugated material in various solvents were measured over a wide range of 250-800 nm using the SHIMADZU-1900I UV-Vis-NIR Spectrophotometer, as shown in Figure 2.2. This instrument is equipped with exceptional tools, advanced software, and high performance, making it ideal for research laboratories. The SHIMADZU-1900I Spectrophotometer is recognized as a crucial device for research projects.

Fig.2.2 image of the SHIMADZU-1900I UV-vis NIR Spectrophotometer.

Fluorescence spectra of the material were obtained using a FLS 1000 spectrofluorometer at a temperature over a wide wavelength range of 200-800 nm, as shown in Figure 2.3 (a and b). This instrument is distinguished by its unique features, enabling it to measure samples with high accuracy and deliver uncompromised results. Consequently, it is in high demand in research projects for its exceptional performance...

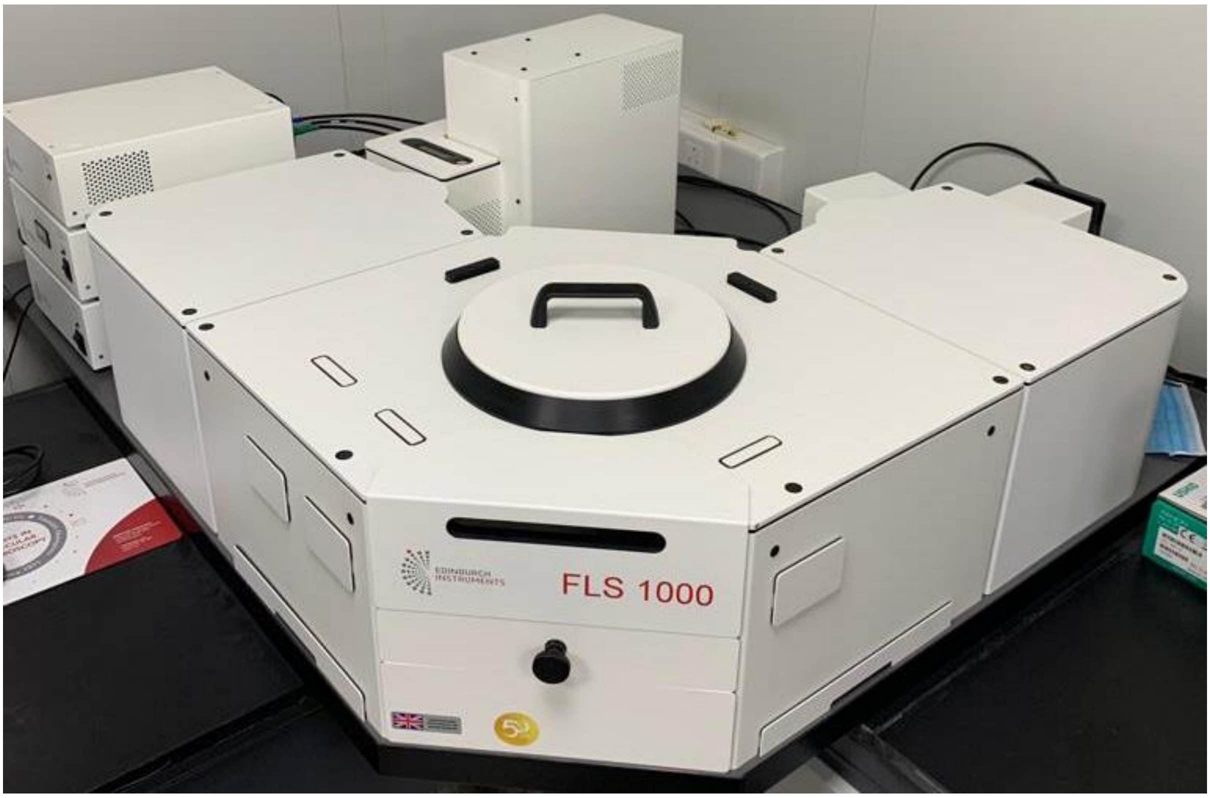

Fig.2.3(a) FLS 1000 spectrofluorometer was used to obtain fluorescence spectra.

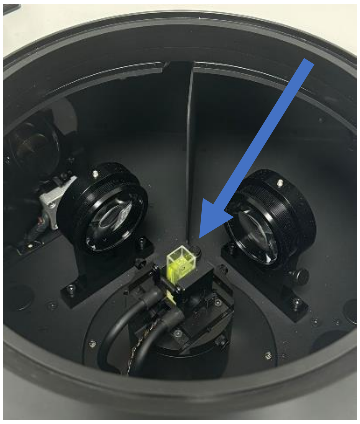

Fig.2.3. (b) Sample of conjugated oligomer in Hexane inside the FLS 1000 spectrofluorometer.

2.3 Optical pumping laser system.

A laser is a device that generates monochromatic electromagnetic radiation through the optical amplification of photons via a stimulated emission process. There are various types of lasers available, each with numerous applications in everyday life. This study utilized a solid-state Nd: YAG pulsed laser, specifically the 355 nm third harmonic Nd: YAG pulsed laser sourced from Les Ulis, France. In the framework of transverse pumping, a quartz cylindrical lens with a focal length of 5 cm was employed to collimate the pulse from the 355 nm Nd: YAG laser into a linear profile. The material solutions, contained in a polished quartz cuvette measuring 1 cm x 1 cm x 4 cm, were excited by the focused pulse. Under optimal pumping conditions, the solution exhibited Laser-Induced Fluorescence (LIF) and Amplified Spontaneous Emission (ASE). The detection system utilized was the Ocean Optics USB4000 spectrometer, provided by Ocean Optics.

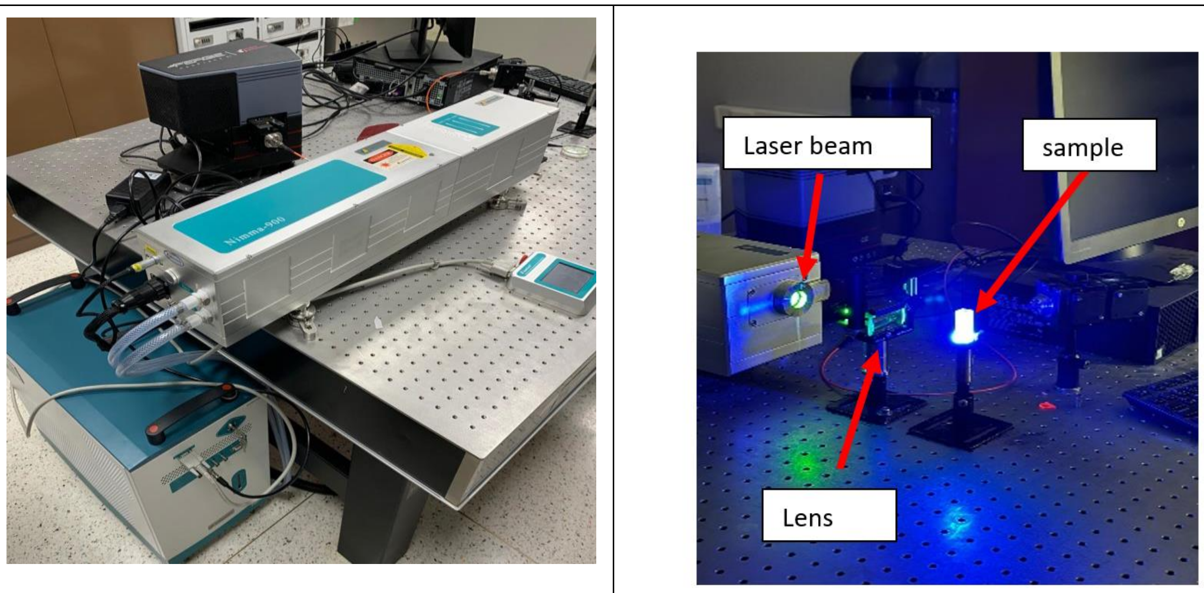

Figure 2.4(a and b) Nd: YAG laser.

Fig. 2.4 Schematic of Experimental setup of ASE generation in solutions using transverse pumping.

Chapter3. Result and Discussion.

3.1 Optical properties of conjugated oligomer.

The absorption spectra of oligomer in different concentrations under different solvents environments such as Hexane and Chloroform were measured as presented in Fig 3.1. The solvents showed two bands at approximately 342 nm and 367 nm due to electronic bands $S_{00}$and S_{01}, respectively. The absorption band profile remained the same, and optical density increased with increasing the concentration.

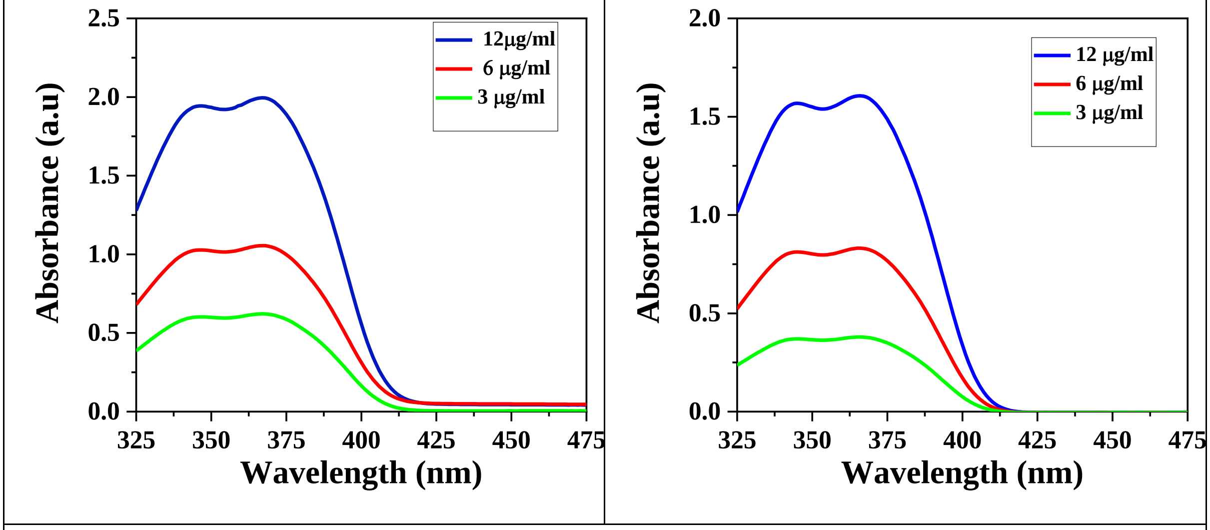

Fig. 3.1 Absorption spectra of oligomer in hexane and chloroform.

The fluorescence spectra of conjugated oligomer for different concentrations ranging from 1 mg/ml to 6 μg/ml and solvent environments like hexane and chloroform are presented in Fig. 3 .1. Generally, in all solvent environments and for low concentration, there are three fluorescence bands. For example, in hexane, the bands are around 425 nm, 440nm, and 475 nm. The different solvent environment induces the characteristics wavelength (spectral) shift. The bands at 425 nm and 440nm are due to vibrational bands S_{00} and S_{01}. This new band is a singlet and could be attributed to S_{0-3}. The band 475 nm is due to aggregation formation).

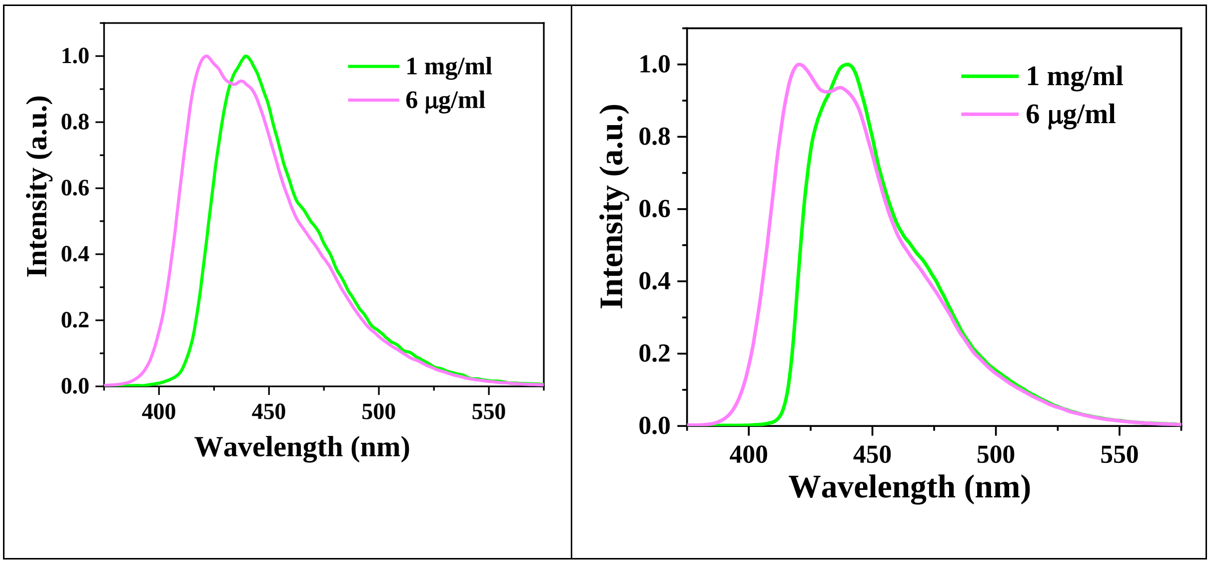

Fig. 3.2. The fluorescence spectra of the oligomer of different concentrations and solvents.

The CO optical energy gap can be calculated by intersecting the normalized absorption and fluorescence spectra. The E_g of an oligomer dissolved in hexane and chloroform, obtained by the intersection of absorption and fluorescence spectra method, were presented in Figures 3.3. Where the E_gs of CO in hexane and chloroform were eV and 3.077 and 3.081eV respectively.

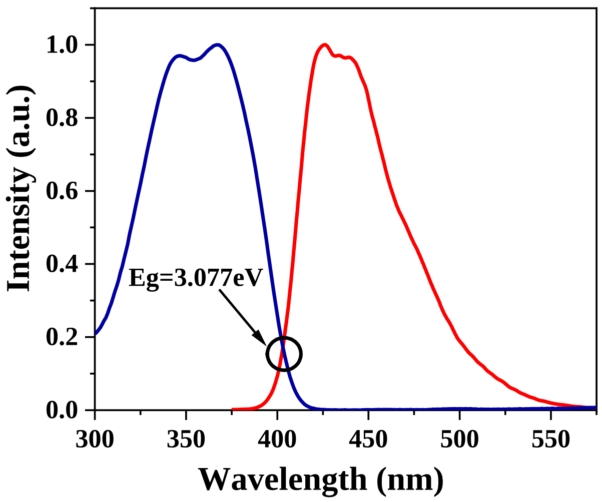

Fig. 3.3 Band gap energy of oligomer hexane.

3.2 Amplified spontaneous emission of oligomer.

Amplified spontaneous emission arises as a result of stimulated emission and amplification of spontaneously emitted photons in an active medium with a single pass gain. Because it includes the majority of laser features, ASE without feedback might be considered a mirrorless laser. Many conjugated polymers and oligomers can create an optically pumped ASE.

A conjugated oligomer of concentration 1mg/ml in hexane was kept in a cuvette and pumped by a pulsed Nd: YAG 3rd harmonic (355 nm) described in the experimental set-up. When the energy pump of the laser was 1 mJ, the oligomer produced ASE at 443 nm, with a narrower FWHM of 7 nm, as shown in Fig. 3.4

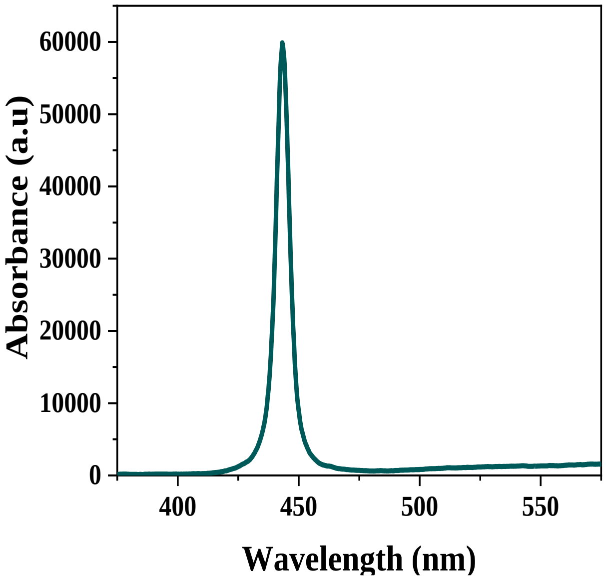

Fig. 3.4 The ASE spectrum of the oligomer dissolved in hexane

Chapter 4. Conclusion.

In summary, we studied the optical properties of the conjugated oligomer in hexane and chloroform. The conjugated oligomer was completely dissolved in these solvents. The results reveal that the absorption spectra have two different peaks, and the fluorescence spectra have three different features corresponding to concentration. The band gap energies were determined using the intersection and derivatives method. Under a suitable pump energy excitation, amplified spontaneous emission has been reported in hexane. ASE bands in are centred at around 443 nm.

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