PURCELL EFFECT IN POLYMER FILMS

by

İbrahim Sarpkaya

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ABSTRACT

PURCELL EFFECT IN POLYMER FILMS

In this thesis, the Purcell effect in polymer thin films is studied. According to the Purcell effect, fluorescence of an atom or molecule can be enhanced or inhibited when it is confined to microcavity. As an application of the Purcell effect, fluorescence lifetime measurements of perylene dye molecules, which are embedded in PEG film, is studied using time-correlated single photon-counting techniques. The emission rate of perylene dye molecules are enhanced due to the photonic cavity effect. An inhibition in the lifetime value of the perylene dye molecules is observed to change from 3.67 ns to 1.55 ns.

ÖZET

POLİMER FİLMLERDE PURCELL ETKİSİ

Bu tezde polimer ince filmlerde Purcell etkisi incelenmiştir. Purcell etkisine göre, mikro-oyuk içerisine hapsedilen atom veya molekülün ışıması yükseltilir veya engellenebilir. Purcell etkisinin uygulaması olarak, zaman korelasyonlu tek foton sayma tekniği kullanılarak polyethylene glycol (PEG) film içerisine yerleştirilmiş perylene boya moleküllerinin ışıma ömürleri çalışıldı. Perylene boya moleküllerinin ışıma oranı, fotonik oyuk etkisinden dolayı arttırıldı. Perylene boya moleküllerinin ışıma ömürlerinin 3.67 ns'den 1.55 ns'ye kısaldığı gözlemlendi.

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LIST OF SYMBOLS/ABBREVIATIONS

k_{isc}	Rate constant for intersystem crossing
k_r^S	Rate constant for radiative daactivation $S_1 \rightarrow S_0$ with emission of fluorescence
k_{ic}^S	Rate constant for internal conversion $S_1 \rightarrow S_0$
k_r^T	Rate constant for radiative deactivation $T_1 \rightarrow S_0$ with emission of phosphorescence
k_{nr}^T	Rate constant for non-radiative deactivation(intersystem crossing) $T_1 \rightarrow S_0$
I	Fluorescence intensity
Q	Cavity quality factor
V	Volume of the cavity
λ	Emission wavelength
τ	Lifetime
ADC	Anolog-to-digital converter
CFD	Constant function discriminator
PGA	Programmable gain amplifier
PEG	Polyethylene glycol
$P-Si$	Porous slicon
PMT	Photomultiplier tube
TAC	Time-to-amplitude converter
$TCSPC$	Time-correlated single photon counting
WD	Window discriminator

1. INTRODUCTION

There has been a considerable growth in the use of fluorescence in the biological sciences during the past two decades. Besides environmental monitoring, clinical chemistry , DNA sequencing, and genetic analysis by fluorescence *in situ* hybridization, fluorescence is used for cell identification and sorting in flow cytometry, and to reveal the localization and movement of intracellular substances in cellular imaging by means of fluorescence microscopy [1]. In fluorescence microscopy, the fluorescence lifetime and the fluorescence intensity both have been used for characterization of cells [2]. Measurements of lifetime of a fluorescent chromophore can improve the potential of fluorescence microscopy. Fluorescence lifetime is an intrinsic property of a chromophore and is independent of chromophore concentration, photobleaching, excitation intensity, but dependent on pH, ion concentrations, and local environment that affects the non-radiative rate of a chromophore [3].

Fluorescence from an atom or molecule may be alternatively enhanced or inhibited when it is confined in a microcavity. Also, fluorescence lifetime of a fluorophore changes because of the changing of the fluorescence emission rate. This effect was first discussed by Purcell [11] and is explained in detail in the Chapter 2.

The main objective of this thesis is to experimentally demonstrate the Purcell effect for perylene dye molecules in a polymer thin film. In order to realize this, a polyethylene glycol-porous silicon structure as a microcavity is used.

The chapters in the thesis are ordered as follows: In Chapter 2, the fluorescence process and fluorescence lifetime is given. Also, time-correlated single photon-counting (TCSPC) technique, which is the basis of time-domain measurements, is presented. As a last part of Chapter 2, the Purcell effect is explained. In Chapter 3, sample preparation and optical setup for fluorescence spectroscopy and lifetime measurements are given. Results of lifetime measurements and emission spectra of perylene dye molecules are discussed in this chapter.

2. REVIEW

2.1. Fluorescence Process

Fluorescence and phosphorescence are particular cases of luminescence which is an emission of ultraviolet, visible or infrared photons from an electronically excited species. In fluorescence and phosphorescence phenomenon the mode of excitation is absorbtion of a photon, which brings the absorbing species into an electronic excited state. The emission of photons accompanying deexcitation is then called photoluminescence (fluorescence, phosphorescence or delayed fluorescence), which is one of the possible physical effects resulting from interaction of light with matter. This can be illustrated via Figure2.1 [4].

Because of the its non-invasive property, fluorescence is generally used to obtain the information about the location of molecules in cells and can be determined with high sensitivity and signal specificity by using suitable techniques. Apart from the information which is about the locations of labelled macromolecules on the micron scale, information about the immediate molecular environment in the nanometer range can be obtained by using the fluorescence process [20]. There are some physical and chemical parameters that characterize the microenvironment and can thus affect the fluorescence characteristics of a molecule. These are polarity, hydrogen bonds, pH, pressure, viscosity, temperature, quenchers, electric potential, ions [4].

2.1.1. Fluorescent Probes

Fluorescence probes represent the most important area of fluorescence spectroscopy. The wavelength and time resolution required of the instruments is determined by the spectral properties of the fluorophers. Furthermore, the information available from the experiments is determined by the properties of the probes [5]. As a consequence of the strong influence of the surrounding medium on fluorescence emission, fluorescent molecules are currently used as probes for the investigaton of physicochem-

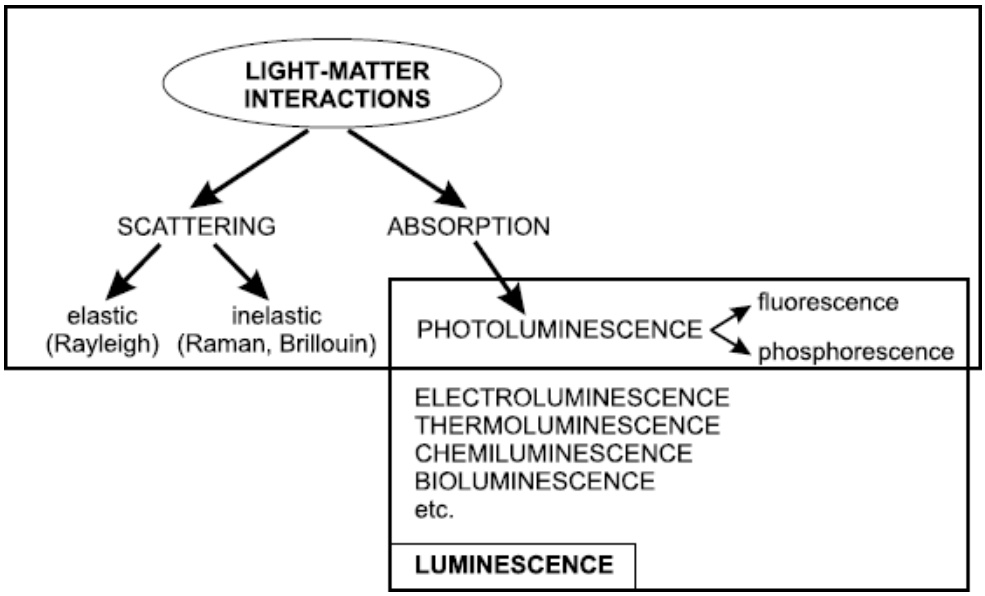

Figure 2.1. Position of fluorescence and phosphorescence in the frame of light-matter interactions

ical, biochemical and biological systems. A lot of information in various fields such as polymers, solid surfaces, living cells, proteins, vesicles, surfactant solutions, biological membranes, nucleic acids, fluoroimmunochemistry can be obtained by using the fluorescence probes. Fluorophores can be broadly divided into two main classes as intrinsic and extrinsic. Intrinsic fluorophores are those that occur naturally. These include the aromatic amino acids, NADH, flavins, derivatives of pyridoxyl, and chlorophyll [4]. In some cases in which fluorescence doesnot exist, fluorescence is obtained adding the extrinsic fluorophores to the sample. Furthermore, they can be added to the samples to change the spectral properties of the sample. Extrinsic fluorophores include dansyl, fluorescein, rhodamine, and numerous other substances [5].

2.1.2. Characteristics of Fluorescence Emission

The processes that occur between the absorption and emission of light are usually illustrated by the Jablonski diagram which is shown in Figure 2.2. Jablonski diagrams are used when we are discussing light absorbtion and emission. In figure 2.2 we can describe singlet ground, first and second electronic states as S_0, S_1, S_2 respectively.

The fluorophores can be found in a number of vibrational energy levels at each

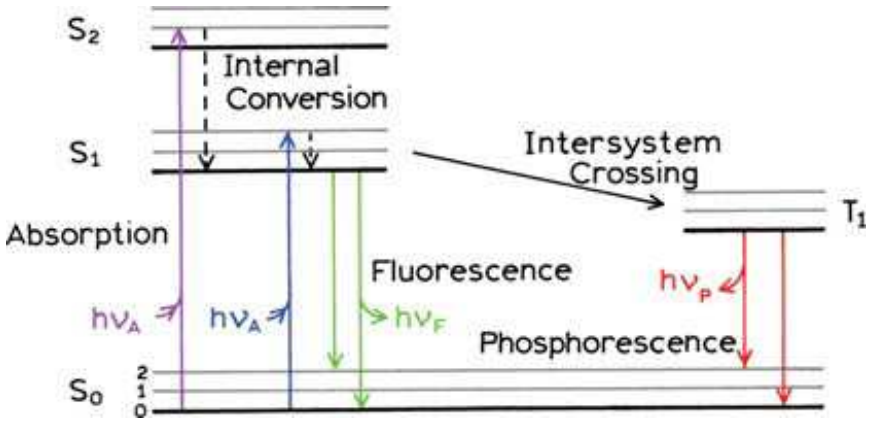

Figure 2.2. One form of Jablonski diagram [5].

energy states. The horizontal lines and numbers are used in order to show that these energy levels. Also, the transitions between states are depicted as vertical lines to illustrate the instantaneous nature of light absorption. Following the light absorbtion, several processes usually occur. When a fluorophore is illuminated with a light, it is usually excited to some higher vibrational level of either S_1 or S_2. In condensed phases molecules rapidly return to the lowest vibrational level of S_1. This process is called internal conversion and generally occurs within 10^{-12} s or less. Since fluorescence lifetimes are typically near 10^{-8} s, internal conversion is generally complete prior to emission. Hence, fluorescence emission generally results from a thermally equilibrated excited state, that is, the lowest energy vibrational state of S_1 [5].

Furthermore, molecules in the S_1 state can also undergo a spin conversion to the first triplet state T_1. Phosphorescence can be explained as emission from T_1 and conversion of S_1 to T_1 is called intersystem crossing. Transition from T_1 to the singlet ground state is forbidden, and as a result the rate constants for triplet emission are several orders of magnitude smaller than those for fluorescence.

2.2. Fluorescence Lifetimes And Quantum Yields

The fluorescence lifetime and quantum yields are the most important characteristics of a fluorophore. The lifetime is important, because it determines the time available for the fluorophore to interact with or diffuse in its environment, and hence

the information available from its emission[5]. Quantum yield is the ratio of the number of emitted photons to the number of absorbed photons [4]. We can explain the meanings of lifetime and quantum yields via the Jablonski diagram via Figure 2.3 [5].

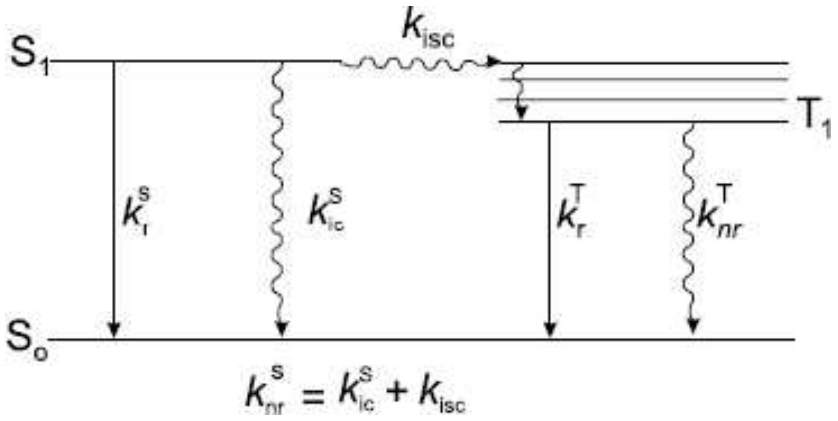

Figure 2.3. A simplified Jablonski diagram to illustrate the meaning of quantum yields and lifetimes

2.2.1. Excited-state lifetimes

If we consider a dilute solution of a fluorescent species A whose concentration is [A] (in mol L^{-1}), a certain number of molecules A at time 0 is brought to the S_1 excited state when it exposes a very short pulse of light. These excited molecules then return to S_0, either radiatively or non-radiatively, or undergo intersystem crossing. As in classical chemical kinetics, the differential equation which gives us the rate of disappearance of excited molecules can be written as follows.

$$-\frac{d[^1A^*]}{dt} = (k_r^S + k_{nr}^S)[^1A^*] \tag{2.1}$$

Integration of this equation yields the time evolution of the concentration of excited molecules $[^1A^*]$. Let $[^1A^*]_0$ be the concentration of excited molecules at time 0 resulting from pulse light excitation. Integration leads to $[^1A^*] = [^1A^*]_0 e^{-\frac{t}{\tau_S}}$ where τ_S, the lifetime of excited state S_1, is given by

$$\tau_S = \frac{1}{k_r^S + k_{nr}^S} \tag{2.2}$$

The fluorescence intensity can be defined as the amount of photons emitted per unit time (s) and per unit volume of solution (liter:L) according to

$$A^* \overset{k_r^S}{\rightarrow} A + photon \tag{2.3}$$

The fluorescence intensity i_F at time t after excitation by a very short pulse of light at time 0 is proportional, at any time, to the instantaneous concentration of molecules still excited $[^1A^*]$; the proportionality factor is the rate constant for radiative de-excitation k_r^S:

$$i_F(t) = k_r^S[^1A^*] = k_r^S[^1A^*]_0 e^{-\frac{t}{\tau_S}} \tag{2.4}$$

$i_F(t)$, the gama pulse response of the system, decreases according to a single exponential. It should be emphasized that, in any practical measurement of fluorescence intensity, the measured quantity is proportional to i_F, the proportionality factor depending on instrumental conditions. The measured fluorescence intensity is denoted as I_F and given by $I_F(t) = I_0 e^{-\frac{t}{\tau_S}}$.

If the only way of de-excitation from S_1 to S_0 was fluorescence emission, the lifetime would be $\frac{1}{k_r^S}$. This is called the radiative lifetime and denoted by τ_r.

After the γ- pulse excitation, triplet state can be occupied a fraction of excited molecules, from which they return to the ground state either radiatively or nonradiatively. The concentration of molecules in the triplet state decays exponentially with a time constant τ_T which represents the lifetime of the triplet state

$$\tau_T = \frac{1}{k_r^T + k_{nr}^T} \tag{2.5}$$

For organic molecules, the lifetime of the singlet state ranges from tens of picoseconds to hundreds of nanoseconds, whereas the triplet lifetime is much longer(microseconds to seconds).

2.2.2. Quantum yields

The fluorescence quantum yield Φ_F can be explained as the fraction of excited molecules that return to the ground state S_0 with emission of fluorescence photons:

$$\Phi_F = \frac{k_r^S}{k_r^S + k_{nr}^S} = k_r^S \tau_S \tag{2.6}$$

In other words,the quantum yield is the ratio of the number of emitted photons to the number of absorbed photons [4]. The quantum yield can be close to unity if the radiationless decay rate is much smaller than the rate of radiative decay. Also, the energy yield of fluorescence is always less than unity because of Stokes losses [5].

2.3. Fluorescence Lifetime Measurements

Fluorescence measurements can be performed using either steady state or time resolved measurements. As a most common type, steady-state measurements are carried out with constant illumination and observation. In this type of measurement, the sample is exposed to a continuous beam of light, and the intensity or emission spectrum is recorded. The second type of measurement is time-resolved, which is generally used for measuring intensity decays or anisotropy decays. In the time-resolved measurements, sample is illuminated with a pulse of light, where the pulse width is typically shorter than the decay time of the sample [5]. This causes fluorescence emission whose intensity decreases exponentially with time. The fluorescence lifetime for a sample which consists of a single fluorescent species can be defined by the time over which the fluorescence intensity drops to about 37% of its initial value. This can be illustrated via Figure 2.4 [21]. This intensity decay is recorded with a high-speed detection system that permits the intensity or anisotropy to be measured on the ns timescale.

Time resolved measurements are generally used in fluorescence spectroscopy, particularly for studies of biological macromolecules and for cellular imaging. Time-resolved measurements can be performed by using two distinct methods which are

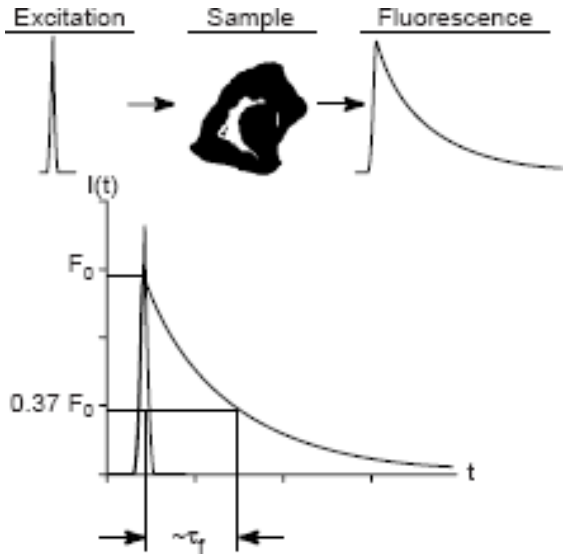

Figure 2.4. Principles of time domain method for the determination of fluorescence lifetimes

time-domain, and frequency domain[5]. In our experiment, we have used time domain method for lifetime measurements. For this reason, we can explain time tomain method in more detail.

2.3.1. Time-Domain Lifetime Measurements

Time-domain techniques use the fact that is based on the excitation of the sample with a pulse radiation source, the dedection of single fluorescence photons, and the build up of histogram of the photon dedection times [6]. The time dependent intensity is measured following the excitation pulse, and the decay time τ is calculated from the slope of a plot of log I(t) versus t, or from the time at which the intensity decreases to $\frac{1}{e}$ of the intensity at $t = 0$ [5]. Today, most of the time domain measurements are carried out using time-correlated single-photon counting.

2.3.2. Time-Correlated Single-Photon Counting (TCSPC)

The TCSPC technique makes use of the fact that for low-level, high-repetition-rate signals, the light intensity is so low that the probability of detecting one photon in one signal period is far less than one. For this reason, it is unnecessary to provide

for the possibility of detecting several photons in one signal period. It is adequate to record the photons, measure their time in the signal period, and build up a histogram of the photon times.[4] The principle of TCSPC can be depicted by figure 2.5 [5]. The

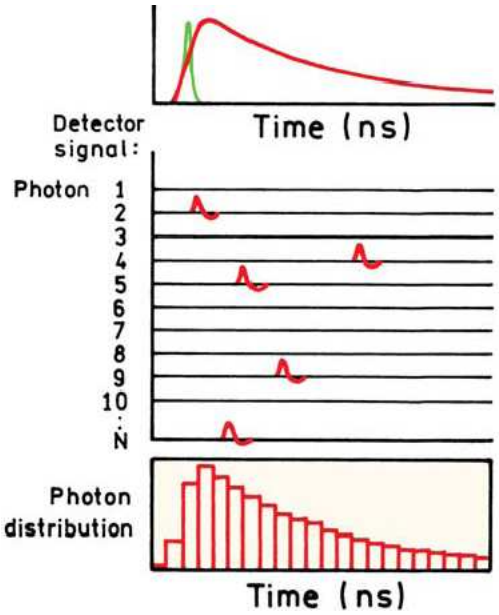

Figure 2.5. Principle of TCSPC

electronics which are used in order to measure the time delay between excitation and emission can be easily understood from the figure 2.6. The experiment starts with the

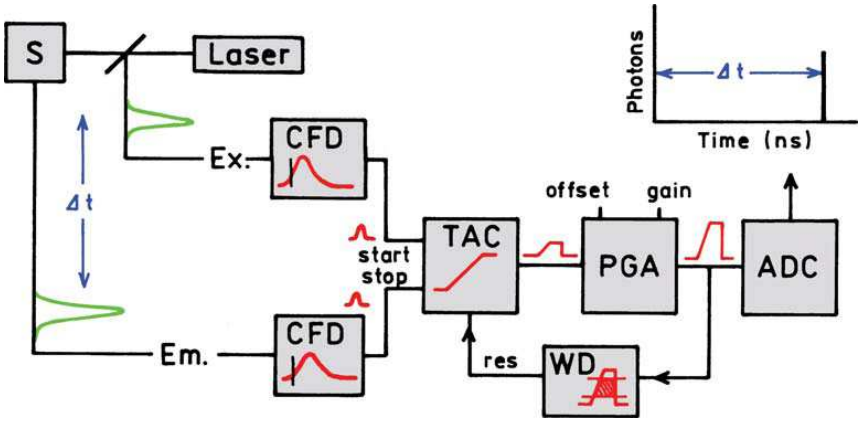

Figure 2.6. Electronic schematic for TCSPC

excitation pulse that the sample expose and sends a signal to the electronics. After that, this signal is passed through a constant function discriminator(CFD) for measuring the arrival time of the pulse exactly. This signal is passed to a time-to-amplitude

converter(TAC), which generates a voltage ramp that is a voltage that increases linearly with time on the nanosecond timescale. Also, a pulse from the single detected photon is caught by the second channel. Again a CFD is used for measuring the arrival time of the signal exactly and it sends a signal to cease the voltage ramp which, is provided by TAC. The voltage that TAC has is proportional to the time delay ($\Delta(t)$) between the excitation and emission signals. In order to amplify the voltage, a programmable gain amplifier(PGA) is used. After the this process, voltage is converted to a numerical value by the anolog-to-digital converter(ADC). False readings can be minimized limiting the signal to a given range of voltages. In case of the signal is not within this range the event is blocked by a window discriminator(WD). The voltage is converted to a digital value that is stored as a single event with the measured time delay. A histogram of the decay is obtained repeating this process numerous times with a pulsed-light source [5].

2.4. Purcell Effect

Spontaneous emission by which matter may lose energy resulting in the creation of a photon [8] is the most visible evident of the dynamical interaction between matter and vacuum. The fundamental function of vacuum fields is to drive the every excited atom to its ground state and this can be regarded as a basic fact of nature [9].

Because of the problem of the interaction of atoms or molecules with the radiation field in its quantum ground state and in the presence of electromagnetic boundaries many researcher who are from both experimental and theoretical domain have studied this topic [10].

After the prediction of the controllable spontaneous emission by Purcell [11] it is understood that, according to the Fermi's " golden rule ", properties of the spontaneous emission of a fluorescent probe depend not only on the quantum mechanical parameters of emitter but also on the density of propagating photon modes in the emitter's optical environment [12].

The spontaneous emission rate, which is called the Einstein's A_{21} coefficient is

the probability of photon emission per unit time, and is given by the Fermi's "golden rule".

$$A = [|< f \mid H \mid i >|^2 / \hbar^2]\rho(\nu) \tag{2.7}$$

Here $\mid i >$ is the excited state of the atom in the absence of any photons, $\mid f >$ is the final state of the atom with a single photon, H is the Hamiltonian for the atom-field interaction, $\rho(\nu)$ is the density of photon states, and the matrix element is volume normalized [9]. Einstein's coefficient A_{21} and decay time of emission are written as k_r^S and $\tau = \frac{1}{k_r^S}$ respectively in the fluorescence process. The spontaneous emission rate from an atom or molecule can be alternatively enhanced or inhibited by confining it inside a photonic microcavity, depending on whether or not the emission spectrally coincide with the cavity resonance. This effect was first observed by Purcell [11], who observed that the spontaneous emission rate A_{21} for a two-state system is increased if the atom is confined into a cavity which is tuned to the transition frequency, ν [10]. In this case, the partial spontaneous emission rate associated with the transition is multiplied by $\eta_{cav} = 3Q\lambda^3/4\pi^2V$ where Q is the cavity quality factor, V its volume, and λ the transition wavelength. Physically, the cavity enhances the strength of the vacuum fluctuations at ν, increasing the transition rate. Also, decay rate can be decreased when the cavity is mistuned. Spontaneous emission can be inhibited when the ν has value below the fundamental frequency of the cavity [9].

The spontaneous emission lifetimes can be modified by using the confocal resonators. This concept extended to short planar cavities at optical wavelengths, where experiments using flowing dye, dye-containing films and semiconductors as the active media have demonstrated significant lifetime changes [13]. However, some requirements must be satisfied to detect such cavity-induced spontaneous emission lifetime changes in one-dimensional cavities. First, the optically active media must have very high internal quantum efficiencies. Second, the cavity quality factor Q has to be high enough for observing the spontaneous emission lifetime changes but low enough for photon reabsorption to be negligible [14]. There are some reasons responsible for lifetime changes such as nonradiative energy loss process, pump-dependent spectra, and

the effects of self absorption of emitted light by the active media [13]. Much of the previous experimental work on cavity enhancement at visible wavelengths was performed using Fabry-Perot cavities.

One of the experiments which have demonstrated the effects of cavity on the lifetime values of dye molecules was produced by A.M.Vredenberg *et al* [13]. They have used Er^{3+} ions which were embedded at low concentration into a thin SiO_2 film, surrounded by high reflectivity Si/SiO_2 planar distributed Bragg reflectors. This system is ideal for measuring cavity-induced lifetime changes because of the small self-absorption of the Er^{3+} ion and the narrow atomic emission spectrum. They have obtained longer and shorter lifetime than in the no-cavity structure because of the cavity resonance wavelength which is shorter than the average emission wavelength in the case of longer lifetime and vice versa [13].

Another experiment which is performed by P.Goy *et al* [15] have demonstrated the enhanced atomic spontaneous emission in a resonat cavity. They have performed their experiment with Rydberg atoms of Na excited in a niobium superconducting cavity resonant at 340 GHz. In this experiment, the cavity which is made of two spherical niobium mirrors close to the configuration at a distance L from each other was used. The cavity is tuned to resonance with the transition by varying of L. As a result, they have shown that partial spontaneous emission probability in Na is increased in a high Q cavity from its free-space value from $\Gamma_0 = 150s^{-1}$ up to $\Gamma_{cavity} = 8 \times 10^4 s^{-1}$.

An alternative method, in which the emission wavelength, instead of the changing resonant wavelength, is tuned by the quantum-confined Stark effect under a fixed cavity resonant characteristic, to demonstrate the cavity-induced spontaneous emission lifetime changes in semiconductor microcavities, is performed by K.Tanaka *et al* [14].

Investigations of spontaneous emission from microcavities, dielectric slabs, interfaces, water-in-oil micelles, phospho lipid bilayers, and biological membranes are the examples of studies which are based on the Purcell Effect [16]. Also, effects of a cavity on the spontaneous emission rates are of interest in connection with bright light

emitting diodes and low threshold lasers or implementations of quantum computing or quantum cryptography. In the case of quantum cryptography, a detailed control of spontaneous emission is necessary for single photon devices [17].

In the following chapter, the Purcell effect is observed for perylene dye molecules which are embedded in PEG thin film.

3. EXPERIMENTAL WORK AND RESULTS

3.1. Sample Preparation

3.1.1. Perylene as a fluorescent probe

In fluorescence experiments, aromatic molecules are generally used as a fluorescent probe. Polynuclear aromatic hydrocarbons, such as anthracane and perylene, are also fluorescent, and the emission from such species is used for environmental monitoring of oil pollution [5]. We have used perylene as a fluorescent molecule in our experiments. Perylene,$C_{20}H_{12}$ is the member of a type of polynuclear aromatic hydrocarbon which is different from naphthalene, anthhrocene, pyrene, dibenzanthracene, benzperylene, coronene, and ovalene [18]. The chemical structure of perylene is shown in Figure 3.1 [4]. Perylene dye molecules are obtained from Fluka Co. For the first part of

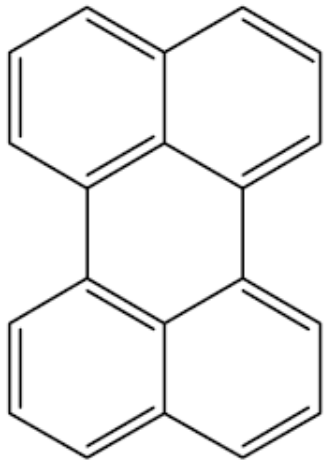

Figure 3.1. Chemical Structure of Perylene

experiment, they are dissolved in pure toluene with a distinct molar concentrations to obtain the monomer and excimer spectra. In the second part of the experiment, as an aplication of the Purcell effect, perylene+PEG+P-Si structure is used.

3.1.2. Preparation of PEG+Perylene+P-Si Structure

There are two distinct methods for preparing the P-Si nanostructures. These are stain etching and electrochemical anodization. We have used second method in our experiment. P-Si samples are prepared by electrochemical anodization of p-type silicon wafers at low current densities in HF : C_2H_5OH (1:1) solutions under illumination of white light. The porosity of the samples are examined by scanning electron microscopy (SEM). Figure 3.2 shows the SEM picture of porous slicon structure. P-Si is saturated by perylene. Perylene is dissolved in toluene and the solution is deposed on the surface of a sample by a syringe [19]. After this process, the surface of the sample is coated with PEG, which is dissolved in double distilled water. This structure can be easily depicted via Figure3.3

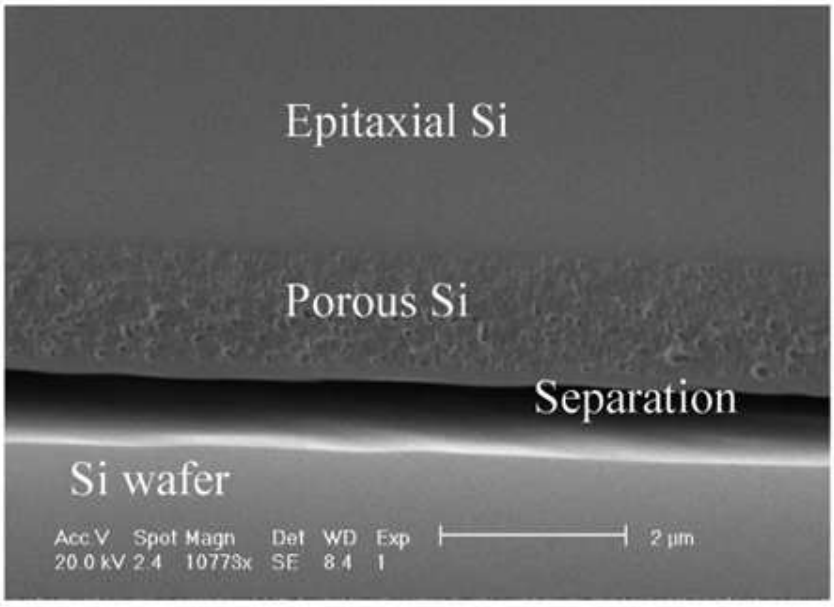

Figure 3.2. Porous silicon structure [20].

Fluorescence spectral data are generally presented as emission spectra. Emission spectra vary videly and are dependent upon the chemical structure of the fluorophore and the solvent in which it is dissolved [5]. In our experiments, we have obtained the emission spectrum of perylene, which is dissolved in toluene. Also, some fluorophores can display two distinct emission spectra depending on its concentration in the com-

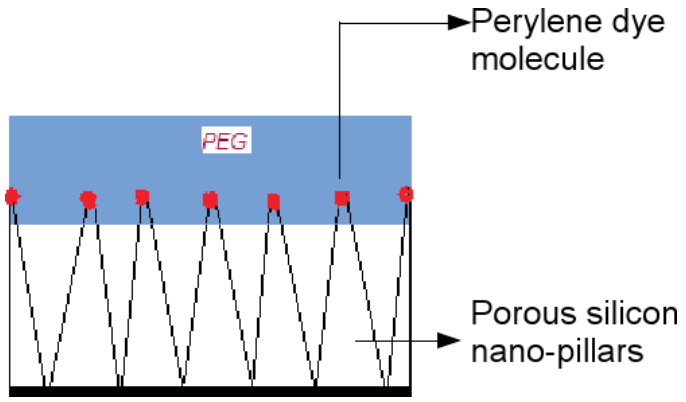

Figure 3.3. PEG+perylene+porous silicon structure

plexes such as pyrene and perylene.

3.2. Optical Setup

3.2.1. Optical Setup for Fluorescense Spectroscopy

The fluorescence spectroscopy setup which, is used to obtain the emission spectrum of perylene, is shown in Figure3.2. In this setup, the picosecond diode laser (PDL

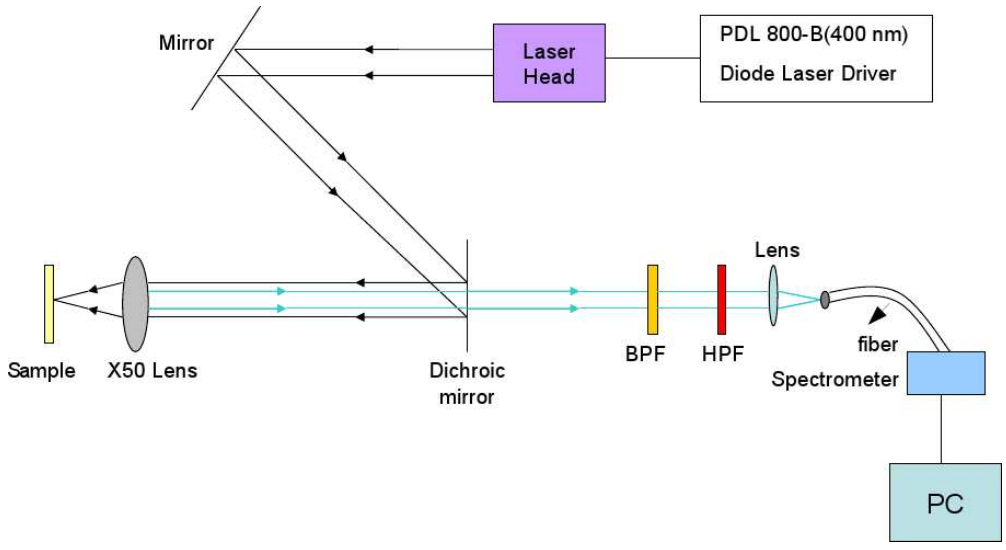

Figure 3.4. Optical setup for fluorescence spectroscopy

800-B), which is triggered by its internal oscillator (settable at 2.5, 5, 10, 20 and 40 MHz), is used as the excitation source. The driver unit is physically separate from the

actual laser head, which is attached via a flexible cable. This permits to place the small laser head conveniently anywhere in the optical setup. Another instrument which is used to focus the excitation beam onto the sample is a microscope objective (Nikon 50X). After excitation, the fluorescent sample emits light at a longer wavelength than that of the excitation light. To filter out the fluorescence emission from the scattered excitation suitable dichroic mirrors, and cutoff filters are utilized. Finally, fluorescence photons are collected via a fiber optic spectrometer (Ocean Optics).

3.2.2. Optical Setup for Fluorescence Lifetime Measurements

The experimental setup for fluorescence lifetime measurements with TCSPC is very similar to that of spectroscopy setup is shown in Figure 3.3. The main difference between these two setups is that in this setup,as a photon dedector PMT is used with the TimeHarp 200 which is a compact user friendly TCSPC system on a single PCI board. After the excitation of sample with same picosecond diode laser(PDL 800-B), emission from the sample is collected by means of the microscope objective(Nikon50X). The other essential equipment in this setup is the dichroic mirror, which is mounted at a $^o45$ angle with respect to the excitation light to filter out the fluorescence emission from the scattered excitation light. Finally, the fluorescence light is directed to the photon dedector(PMT) via some appropriate collection optics(microscope objective or a lens).

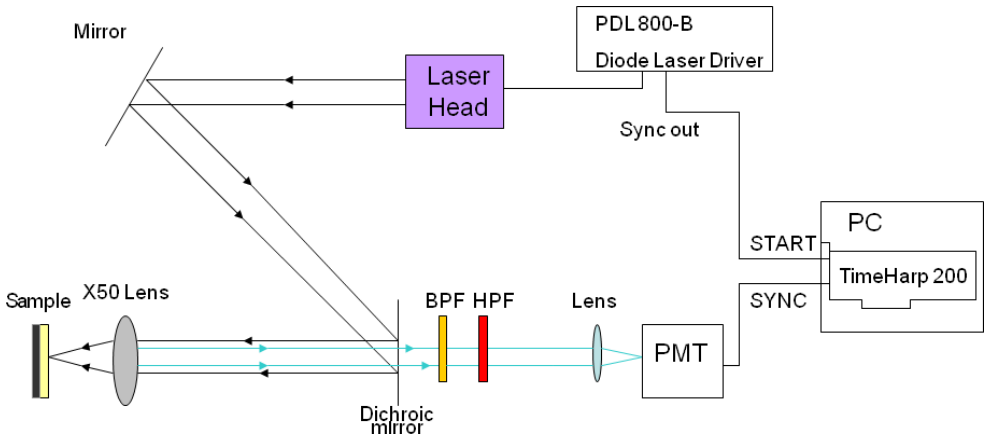

Figure 3.5. Optical setup for fluorescence lifetime measurements

3.3. Results

3.3.1. Perylene Spectrum

Fluorescence spectral data are generally presented as emission spectra. Emission spectra vary widely and are dependent upon the chemical structure of the fluorophore and the solvent in which it is dissolved [5]. Typical emission spectrum of perylene is shown in Figure 3.6. In our experiment, we have obtained the emission spectrum of

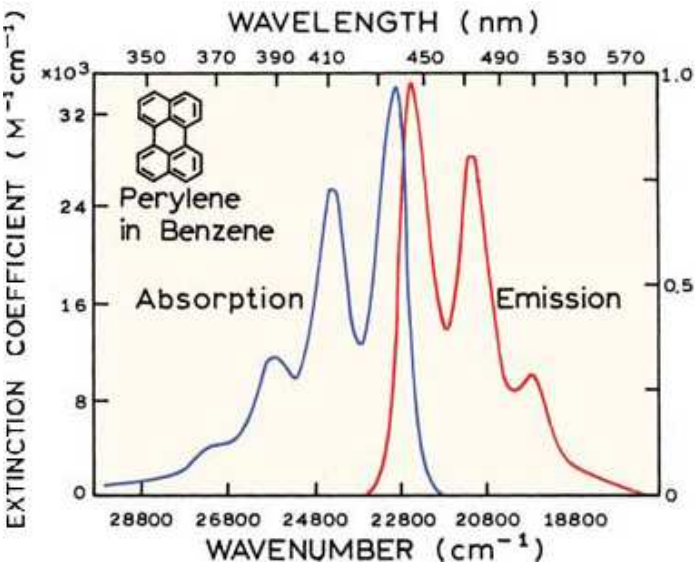

Figure 3.6. Absorption and fluorescence emission spectra of perylene in benzene

perylene which is dissolved in toluene. Also, some fluorophores can display two distinct emission spectra depending on its concentration in the complexes such as pyrene and perylene.

3.3.2. Monomer Spectrum of Perylene

This spectrum is obtained using the perylene dye molecules which are dissolved in pure toluene with a 2×10^{-4} molar concentration. In this spectrum, three emission peaks, which are located at 450, 480 and 510 nm, are observed when excitation wavelength is 400 nm.

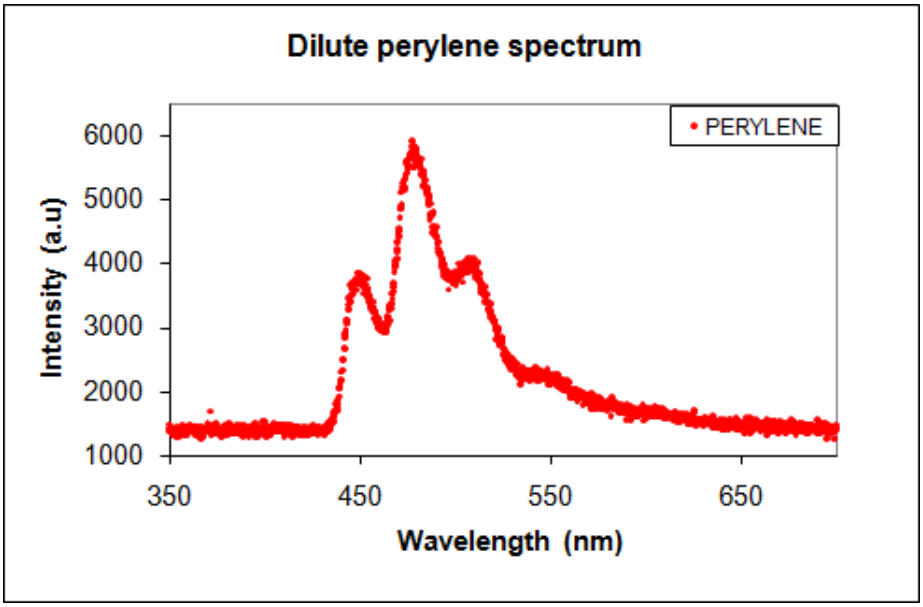

Figure 3.7. Dilute emission spectrum of perylene

3.3.3. Excimer Spectrum of Perylene

This spectrum is obtained by using the perylene dye molecules which are dissolved in pure toluene with 10^{-3} molar concentration. There is only one emission peak which is located at 580 nm in the excimer emission spectrum of perylene.

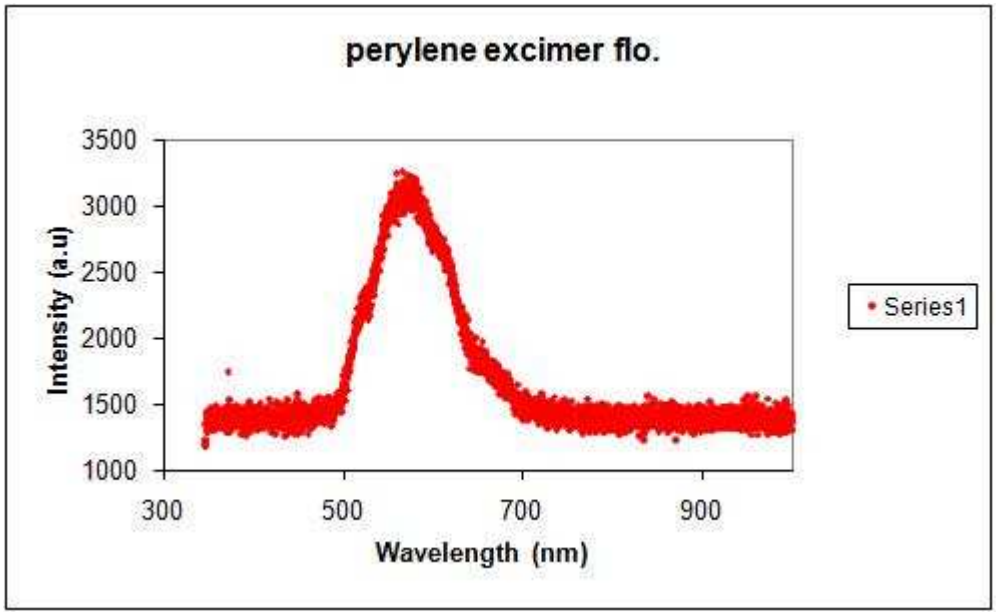

Figure 3.8. Excimer emission spectrum of perylene

3.3.4. Perylene Lifetime Measurements

The fluorescence lifetime of perylene dye molecules are measured using the optical setup shown in Figure 3.5. The fluorescence lifetime is determined using the TimeHarp 200, which is a compact easy-to-use TCSPC system on a single PCI board. After the lifetime histogram is obtained, FluoFit decay fit software package (from PicoQuant)is used to obtain the lifetime value of perylene. The double exponential fit, instead of a single is done by the FluoFit software to obtain the exact values of the lifetimes. In

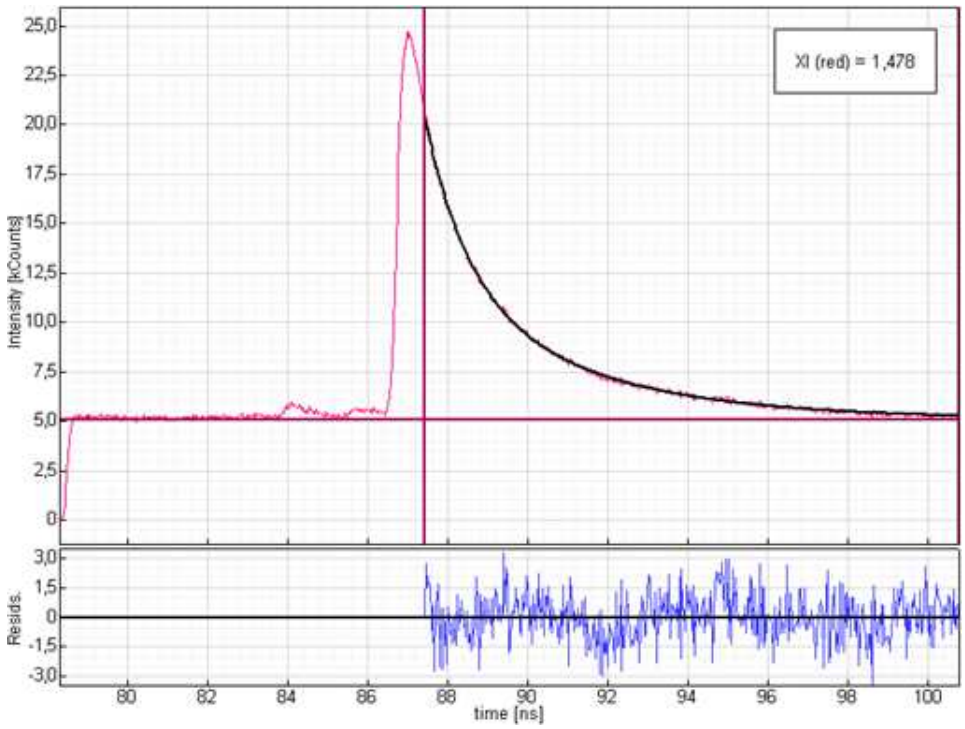

Figure 3.9. Decay lifetime of perylene dye molecules

this software program, lifetime calculations are done according to the following formula

$$I(t) = \sum_{i=1}^{n} A_i e^{-\frac{t}{\tau_i}} \tag{3.1}$$

The lifetime histogram is obtained for perylene dye molecules which is shown in Figure 3.9 in free space and found fluorescence lifetime as $\tau = 3,67ns$. As an application of the Purcell effect, we have used perylene dye molecules with PEG and

P-Si structure, which is described in Figure 3.3. The lifetime histogram, which is shown in Figure 3.10, is obtained for perylene dye molecules which are embedded in PEG+P-Si structure and found fluorescence lifetime as $\tau = 1,55ns$.

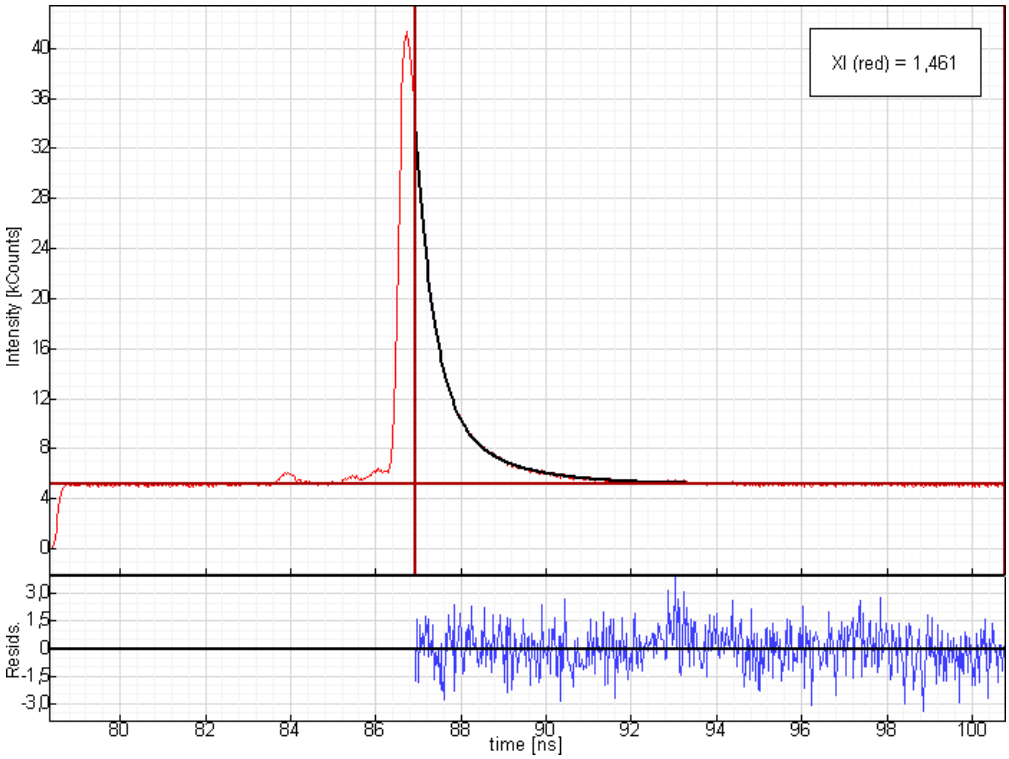

Figure 3.10. Lifetime of perylene dye molecules embedded in PEG

From these results, it can be concluded that the electronic transition energy coincides with the photonic cavity mode energy for perylene dye molecules. In this case, the spontaneous emission rate for perylene dye molecules which, are embedded in PEG film cavity, is enhanced and this causes an inhibition in the lifetime value of perylene dye molecules. Also, because the thickness of the PEG film is comparable with the emission wavelength of the perylene dye molecules, an enhancement is observed in the spontaneous emission rate.

4. CONCLUSIONS

In this thesis, Purcell Effect in polymer films is studied. The fluorescence lifetime of perylene dye molecules are obtained using time correlated single photon counting techniques. Also, the spontaneous emission spectra for perylene dye molecules are obtained. Two distinct emission spectra for perylene dye molecules are found due to its concentration in the complexes. The fluorescence lifetime of the perylene dye molecule is measured to be $\tau = 3.67$ ns.

As an application of the Purcell Effect, PEG(polyethylene glycol) film with porous silicon structure is used to change the fluorescence lifetime of perylene dye molecules. As a result of the interaction between perylene molecules and PEG film cavity, an inhibition is observed in the lifetime of perylene dye molecules. The lifetime of perylene dye molecules, which were embbeded in PEG film, is found as $\tau = 1,55$ ns.

As a future work, different polymers and dye molecules can be used to observe the enhancement or inhibition for the spontaneous emission rates and fluorescence lifetimes. Also, we can obtain the map of the fluorescence lifetimes by scanning the one area of the sample with approptiate optical instruments.

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