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**FLUORESCENCE EMISSION STUDIES WITH
ENERGY TRANSFER REACTIONS**

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YEMİN METNİ

Yüksek lisans tezi olarak sunduğum “Enerji Transfer Reaksiyonları ile Fluoresans Emisyon Çalışmaları” adlı çalışmanın, tarafımdan, bilimsel ahlak ve geleneklere aykırı düşecek bir yardıma başvurmaksızın yazıldığını ve yararlandığım eserlerin bibliyografyada gösterilenlerden oluştuğunu, bunlara atıf yapılarak yararlanılmış olduğunu belirtir ve bunu onurumla doğrularım.

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TUTANAK

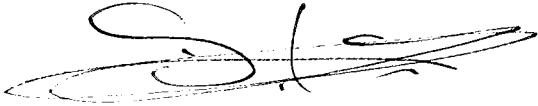
Dokuz Eylül Üniversitesi Eğitim Bilimleri Enstitüsü'nün 29/06/2001 tarih ve 08. sayılı toplantısında oluşturulan jüri, Lisansüstü Eğitim Yönetmeliği'nin 18... maddesine göre Ortaöğretim Fen Ve Matematik Alanlar Eğitimi Bölümü Kimya Eğitimi Anabilim Dalı Yüksek Lisans öğrencisi Banu KÖZ'ün "Enerji Transfer Reaksiyonları ile Floresans Emisyon Çalışmaları" konulu tezi incelenmiş ve aday 02/07/2001 tarihinde, saat 14:00'da jüri önünde tez savunmasına alınmıştır.

Adayın kişisel çalışmaya dayanan tezini savunmasından sonra 60... dakikalık süre içinde gerek tez konusu, gerekse tezin dayanağı olan anabilim dallarından jüri üyelerince sorulan sorulara verdiği cevaplar değerlendirilerek tezin başarılı..... olduğuna oy birliği..... ile karar verildi.

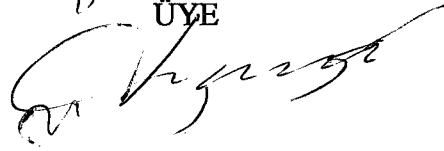
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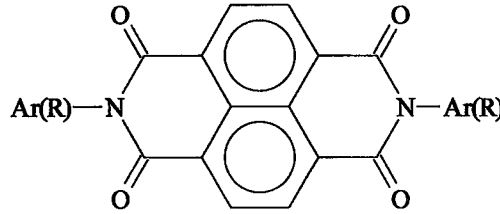


Prof. Dr. Mustafa Akbulut
ÜYE



ÖZET

Bu çalışmada 7 naftalen diimid türevinin fotofiziksel özellikleri farklı çözügenlerde araştırılmıştır.



	Ar		R
I	Fenil	V	<i>n</i> -Butil
II	<i>o</i> -Klorofenil	VI	<i>n</i> -Dodesil
III	<i>p</i> -Tolil	VII	Sikloheksil
IV	α -Naftil		

Çalışılan naftalen diimidlerin floresans kuantum verimleri $\Phi_F = 0.002-0.006$ arasında olup oldukça düşüktür. Hesaplanan floresans yarı ömürleri 5-18 ps arasındadır. Bu değerler naftalen diimidlerin, uyarılmış singlet enerji düzeyinden çok hızlı olarak sistemlerarası geçiş yaptığını göstermektedir. Aromatik donör molekülleri olan naftalen, fenantren, piren ve perilenin floresans emisyon sönümlenme çalışmaları N,N'-bis-fenil-1,4,5,8-naftalendiimid ile asetonitril çözeltisi içerisinde yapılmış ve sönümlenme hız sabitleri (k_q) difüzyon kontrol limitinin üstünde ve $2 \times 10^{10} - 8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ arasında bulunmuştur. Bu sonuçlarla, naftalen diimidlerin foto-elektron transfer proseslerinde, zayıf elektron akseptör kapasitelerine sahip oldukları kanıtlanmıştır.

Bununla birlikte aynı donör moleküllerin N,N'-bis-*n*-bütül-1,4,5,8-naphthalendiimid türevi ile de floresans emisyon sönümlenme çalışmaları gerçekleştirilmiştir. Bu türev diğer naftalen diimid türevlerine göre kloroform, asetonitril ve diklorometanda daha fazla çözünürlüğe sahiptir. Floresans sönümlenme hız sabitleri $k_q = 1 \times 10^{11} - 3 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ arasında bulunmuştur. Bu

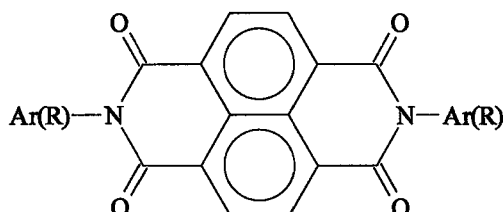
değerler de diğer sonuçlarla karşılaştırıldığında difüzyon kontrol limitinin üstündedir.

Sonuç olarak; N,N'-bis-n-bütil-1,4,5,8-naphthalendiimid türevi enerji transfer proseslerinde bir elektron akseptör molekülü olarak daha etkilidir.



ABSTRACT

In this study, the photophysical properties of seven naphthalene diimide derivatives were investigated in different solvents.



	Ar		R
I	Phenyl	V	<i>n</i> -Butyl
II	<i>o</i> -Chlorophenyl	VI	<i>n</i> -Dodecyl
III	<i>p</i> -Tolyl	VII	Cyclohexyl
IV	α -Naphthyl		

The fluorescence quantum yields of naphthalene diimides have been found rather low ($\Phi_F = 0.002-0.006$). The calculated fluorescence lifetimes were between 5-18ps. This means that the naphthalene diimides have been carried out rapid intersystem crossing processes from excited singlet state. Quenching studies of fluorescence emissions of aromatic donor molecules, i.e. naphthalene, phenanthrene, pyrene, perylene, were done by using *N,N'*-bis-phenyl-1,4,5,8-naphthalenediimide in acetonitrile solution and quenching rate constants (k_q) were found between $2 \times 10^{10} - 8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ which were above the diffusion control limit. It has been proved that the naphthalene diimides have got weak electron acceptor capacities in photo-electron transfer processes.

However, the quenching studies of fluorescence emissions of same donor molecules have also been carried out with *N,N'*-bis-*n*-butyl-1,4,5,8-naphthalenediimide. This derivate is more soluble in chloroform, acetonitrile, dichloromethane than the other naphthalene diimide derivatives. Fluorescence quenching rate constants were found between $1 \times 10^{11} - 3 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$. These values are also above diffusion control limit compared to other results.

Consequently, N,N'-bis-n-butyl-1,4,5,8-naphthalenediimide derivative is more efficient as an electron acceptor molecule in energy transfer processes.



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ABBREVIATIONS

λ :	Wavelength
ϵ :	Extinction Coefficient
T:	Transmission
A:	Absorbance
Log:	Logarithm
max:	Maximum
l:	Path Length
c:	Concentration
Φ :	Quantum Yield
Φ_F :	Fluorescence Quantum Yield
UV:	Ultra Violet
S_0 :	Ground State
S_1 :	First Excited Singlet State
S_2 :	Second Excited Singlet State
T_1 :	First Excited Triplet State
T_2 :	Second Excited Triplet State
IC:	Internal Conversion
ISC:	Intersystem Crossing
ET:	Electron Transfer

ABBREVIATIONS (CONTINUED)

EnT: Energy Transfer

CET: Coulombic Energy Transfer

nm: Nanometer

ml: Mililiter

S: Integrated Emission Spectra

U: Unknown

s: Standart

n: Refractive Index

τ_0 : Radiative Life Time

τ_F : Fluorescence Life Time

k_F : Fluorescence Rate Constant

E_s : Singlet Energy

kq: Fluorescence Quenching Rate Constant

NDI: Naphthalene Diimide

PNDI: N,N'-bis-phenyl-1,4,5,8-naphthalenediimide

1 INTRODUCTION

1.1 Theory of Fluorescence Spectroscopy

Fluorescence spectroscopy is one of the oldest analytical methods. This technique can be used in medicine, pharmaceuticals, biology and many a scientific branches other than chemistry. Just a few years ago, fluorescence spectroscopy and time-resolved fluorescence were primarily research tools in biochemistry and biophysics. This situation has changed so that fluorescence is now used in environmental monitoring, clinical chemistry, DNA sequencing, and genetic analysis by fluorescence in situ hybridisation (FISH), to name a few areas of application.

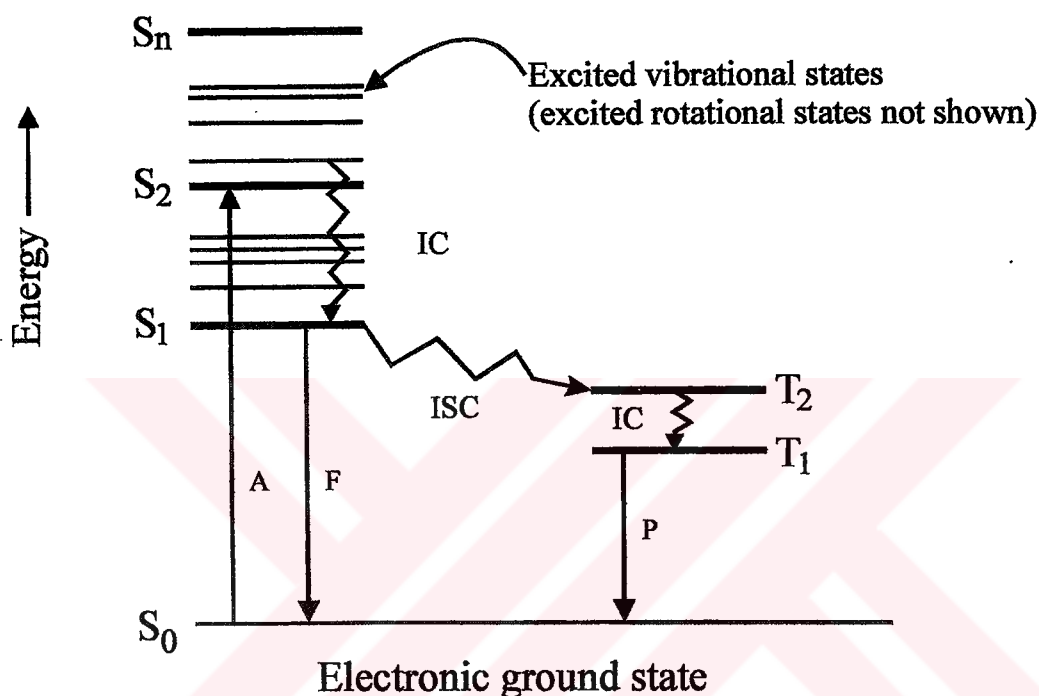
The method of determination based on the fluorescence property of substance is called fluorescence spectroscopy. With this method many substances can be determined with a precision under one millionth. Because of sensitivity fluorescence detection, and the expense and difficulties of handling radioactive substances, there is a continuing development of medical tests based on the phenomenon of fluorescence (Lakowicz, 1999).

Most compounds show the property of photoluminescence. Photoluminescence is the property of a compounds giving back a radiation absorbed in the same or longer frequency.

1.1.1 The Absorption and Emission of Light

Absorption of light by a molecule causes the excitation of an electron. The electron moves from a ground state to an excited state. Each of these electronic states may include a number of different vibrational levels. Absorption of light is from the lowest electronic vibrational state to a number of vibrational levels in the excited electronic state. After the electron has been excited, it rapidly relaxes from the highest vibrational states to the lowest vibrational state of the excited electronic state. The rate for this relaxation is on the order of picoseconds. After returning to the lowest vibrational state of the excited electronic state, the electron in the excited state can pass

the ground state by a number of different processes. The system can lose the energy by internal conversion (heat), quenching (external conversion), by emission of photon (fluorescence), or by intersystem crossing (phosphorescence). Jablonski diagram shows a few of these processes.



A= photon absorption, F= fluorescence (emission), P= phosphorescence, S= singlet state, T= triplet state, IC= internal conversion, ISC= intersystem crossing

Figure 1.1 Jablonski diagram

1. "Allowed" or singlet-singlet absorption ($S_0 + h\nu \rightarrow S_1$)
2. "Forbidden" or singlet-triplet absorption ($S_0 + h\nu \rightarrow T_1$)
3. Spin "Allowed" transition or singlet-singlet emission is referred to fluorescence ($S_1 \rightarrow S_0 + h\nu$)
4. Spin "Forbidden" transition or triplet-singlet emission is referred to phosphorescence ($T_1 \rightarrow S_0 + h\nu$)

Similarly, radiationless transitions between states of the same multiplicity and excited states of a different multiplicity are known as internal conversion (IC) and intersystem crossing (ISC).

The emission rates of fluorescence are typically 10^8s^{-1} , so that a typical fluorescence lifetime is near 10ns (10×10^{-9} s). The lifetime (τ) of a fluorophore is the average time between its excitation and its return to the ground state. It is valuable to consider a 1ns lifetime within the context of the speed of light. Light travels 30 cm or about one foot in one nanosecond. Many fluorophores display subnanosecond lifetimes.

Phosphorescence is emission of light from triplet excited states, in which the electron in the excited orbital has the same spin orientation as the ground state electron. Transitions to the ground state are forbidden and the emission rates are slow ($10^3 - 10^0\text{s}^{-1}$), so that phosphorescence lifetimes are typically milliseconds to seconds. Even longer lifetimes are possible, as is seen from “glow-in-the-dark” toys: following exposures to light, the phosphorescent substances glow for several minutes while the excited phosphors slowly return to the ground state. Phosphorescence is usually not seen in fluid solutions at room temperature. This is because there exist many deactivation processes which compete with emission, such as nonradiative decay and quenching processes.

1.1.2 Stokes' Law

In theory, the energy of the transition from the lowest energy states is the same for both absorption and emission. In practise, the average energy of the emitted photon is generally less than the corresponding absorption band. This red shift is due to a change in the local environment of the excited state during its lifetime. The reorganization of solvent dipoles will lower the energy of the excited state, causing a red shift in the emission spectra. This shift in the emission spectrum is called a Stokes shift. The magnitude of the Stokes shift depends on the polarity of the solvent. Usually, solvents of higher polarity produce larger Stokes shifts.

1.1.3 Quantum Yield

The overall efficiency of a thermal reaction is given by its “yield”, that is the fraction of reactants convertible into products; this is usually expressed in %.

In the case of a photochemical process the overall efficiency is given by the “quantum yield” which is defined as the number of molecules of photo-products formed for each photon absorbed.

$$\Phi = \frac{\text{number of molecules of product produced}}{\text{number of photons of light absorbed}}$$

In the same manner a quantum yield is the number of molecules of reactant consumed per photon of light absorbed.

The quantum yield is often separated into primary quantum yield and secondary quantum yield. The quantum yield value of a primary photo-chemical process normally fall in the range 0 to 1.0, although the quantum yield of overall (that is primary and secondary) processes can be greater than 1, depending on the secondary reactions; it can be very large in the case of chain reactions.

The quantum yield of a primary photochemical process is related to the actual rate constant for the reaction and to the rate constant (s) for all other deactivation processes of the excited state, as well as to the population of the reactive state (Suppan, 1994).

1.1.4 Fluorescence Life Time

The fluorescence life time is the most important characteristics of a fluorophore. As the lifetime determines the time available for the fluophore to interact with or diffuse in its environment, and hence the information available from its emission.

If the spontaneous emission of radition of the appropriate energy is the only pathway for a return to the initial state, the average statistical time that the molecule spends in the excited state is called the natural radiative life time.

For an individual molecule the probability of emission is time-independent and the total intensity of emission depends on the number of molecules in the excited state. In a system with a large number of particles, the rate of decay follows a first-order rate law and can be expressed as

$$I = I_0 \cdot e^{-k_0 t}$$

Where I_0 and I are the intensities of emitted radiation immediately after excitation and at a later time t , respectively; k_0 : is the rate constant and the dimension of reciprocal time. The quantity

$$\tau_0 = \frac{1}{k_0}$$

is the mean natural lifetime of the excited state (in s).

k_0 is the rate constant for spontaneous emission and the rate of spontaneous emission is given by the Einstein A coefficient. From this relation the natural radiative life time in s can be estimated as

$$\tau_0 = \frac{3,5 \times 10^8}{\nu_{\max}^2 \cdot \epsilon_{\max} \cdot \Delta \nu_{1/2}}$$

ν_{\max} : is the wavenumber in cm^{-1} of the absorption maximum

ϵ_{\max} : the molar extinction coefficient at the selected absorption wavelength

$\Delta \nu_{1/2}$: denotes the half-width of the selected absorption in wavenumber units of cm^{-1} (Turro, 1965).

Fluorescence lifetimes are estimated as $\tau_F = \tau_0 \Phi_F$ and the rates of fluorescence as $k_F = 1/\tau_0$.

Each process competing with spontaneous emission reduces the observed lifetime τ relative to the natural lifetime τ_0 . In the case where only unimolecular processes i with rate constant k_i compete with emission, one has (Klesinger et. al., 1995)

$$\tau_0 = \frac{1}{k_F + \sum_i k_i}$$

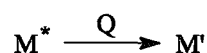
1.1.5 Fluorescence Quenching

Bimolecular deactivation mechanisms that involve the transfer of excitation energy from one molecule to another are very important in photochemistry. These deactivation processes are generally referred to as bimolecular quenching processes.

The suppression of emission by energy-transfer processes is in particular referred to as luminescence quenching. If it is not the deactivation that is of principal interest during a bimolecular process but rather the excitation of the energy acceptor molecule, the process is referred to as sensitisation.

Fluorescence quenching is a very general phenomenon that occurs through a variety of different mechanisms. All chemical reactions involving molecules in excited states can be viewed as luminescence quenching.

Photophysical quenching processes that do not lead to new chemical species can in general be represented as



Where M' is the ground state or another excited state of M . According to whether the quencher Q is a molecule M of the same kind or a different molecule self quenching or concentration quenching can be distinguished from impurity quenching by some other chemical species.

Most intermolecular deactivation processes are based on collisions between an excited molecule M^* and a quencher Q .

Except for some long-distance electron transfer and energy transfer mechanism bimolecular deactivation involves either an encounter complex ($M^* \dots Q$), or an exciplex (MQ^*) or excimer (MM^*). An exciplex or an excimer has a binding energy larger than the average kinetic energy ($3/2$) kT and represents a new chemical species with a more or less well-defined geometrical structure corresponding to a minimum in the excited state potential energy surface. This is not true for an encounter complex in which the components are separated by widely varying distances and have more random relative orientation.

Encounter complexes, exciplexes, and excimers can lose their excitation energy through either fluorescence or phosphorescence, by decay into $M + Q^*$ which corresponds to an energy transfer, by electron transfer to give $M^{\oplus} + Q^{\ominus}$ or $M^{\ominus} + Q^{\oplus}$ by internal conversion, and by intersystem crossing. All these processes lead to quenching of the excited state M^* and are therefore referred to as quenching processes (Klessinger et.al., 1995).

1.2 Instrumentation for Fluorescence Spectroscopy

Basic components of fluorescence instrumentation consists of (1) a source of light, (2) a primary filter or excitation monochromator, (3) a sample cell, (4) a secondary filter or emission monochromator, (5) a photodetector, and (6) a data readout device. In contrast to ultraviolet visible instrumentation, two optical systems are necessary.

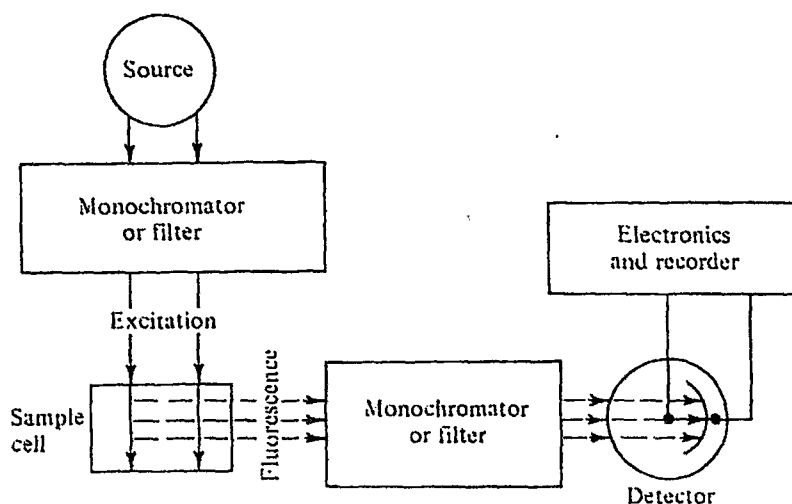


Figure 1.2 Basic components of fluorescence instrumentation.

The primary filter or excitation monochromator selects specific bands or wavelengths of radiation from the light source and directs them through the sample in the sample cell. The resultant luminescence is isolated by secondary filter or emission monochromator and directed to the photodetector which measures the intensity of the emitted reaction.

The excitation monochromator is located between the light source and the sample and the emission monochromator between the sample and the photomultiplier tube. For quantitative analysis, one selects the desired excitation and emission wavelengths and compares the relative fluorescence intensities of standard and unknown samples (Willard et. al., 1981).

For an ideal instrument, the directly recorded emission spectra would represent the photon emission rate or power emitted at each wavelength, over a wavelength interval determined by the slit widths and dispersion of the emission monochromator. Similarly, the excitation spectrum would represent the relative emission of the fluorophore at each excitation wavelength. Hence, the excitation spectrum of a fluorophore is typically superimposable on its absorption spectrum. However, this is rarely observed because the wavelength responses of almost all spectrofluorometers are dependent on wavelength.

Figure 1.3 shows a schematic diagram of a general-purpose spectrofluorometer.

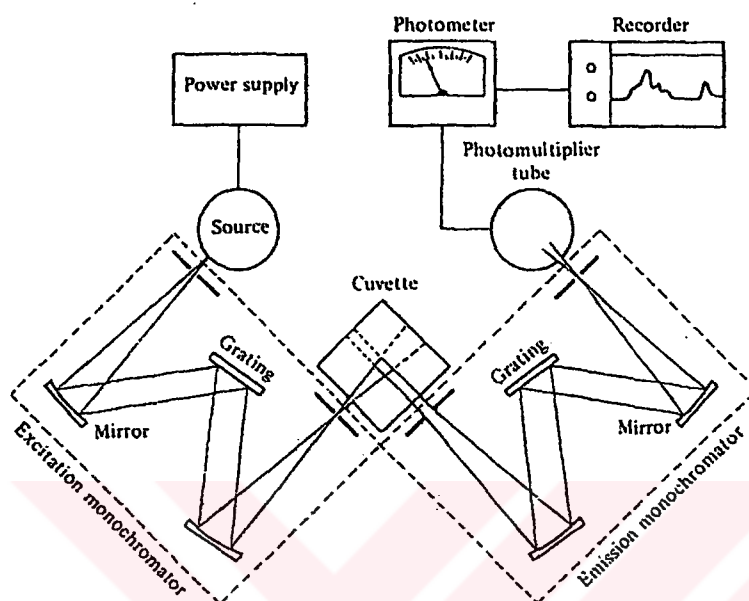
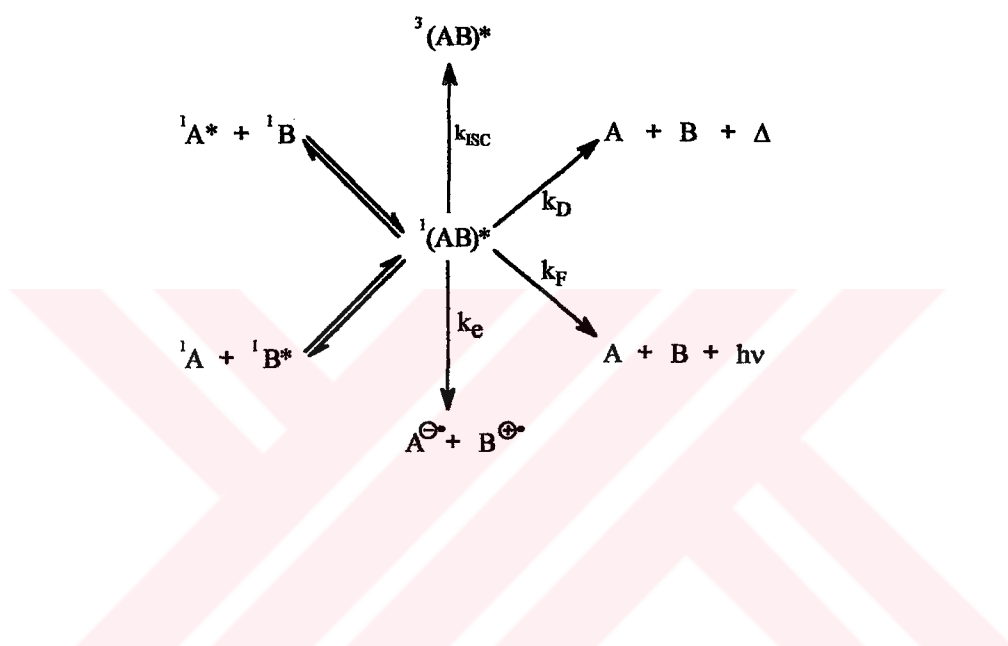


Figure 1.3 Schematic diagram of a spectrofluorometer

1.3 Photoinduced Energy And Electron Transfer Processes:

Usage of solar radiation as photochemically is carried out by the transfer of energy one molecule, which can absorb light, to another molecule. Molecules that can absorb solar radiation and transfer it to other molecules are called photosensors. The required chemical reactions can be occurred by using photosensors with their energy and electron transfer processes. For example, photosynthesis in nature start chemical reactions by photo-energy or electron transfer processes. Electron or energy transfer processes occur by solar radiation or photo-induction.

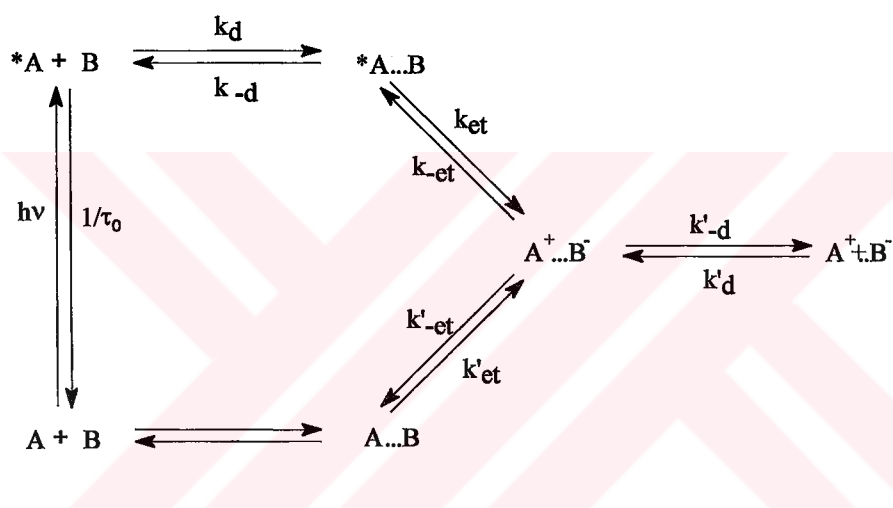
According to the following scheme, electron transfer, intersystem crossing and energy transfer can all compete with fluorescence in deactivating an exciplex $^1(AB)^*$ formed from molecules acceptor (B) and donor (A).



In polar solvents, polar exciplexes (contact ion pairs) dissociate into nonfluorescent radical ions (loose ion pairs or free ions) due to the stabilization of the separated ions by solvation (Klessinger et. al., 1995).

1.3.1 Kinetics of Electron Transfer Quenching

Quenching process by electron transfer occurs as follows: First, Molecule A is excited. Then in this state, excited molecule A goes into diffusional interaction with molecule B. Thus, they have become suitable for electron transfer. At this point, they have gained dipole character. From this dipole, either ion pair occurs or molecule goes back to the ground state by back electron transfer. These processes are shown as schematically in Figure 1.4 and fluorescence quenching rate constant equation is given below.

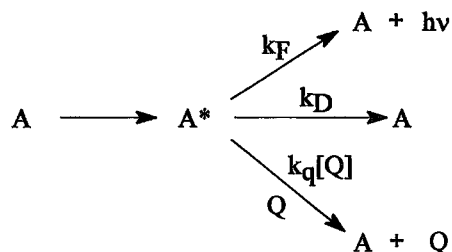


$$k_q = \frac{k_d}{1 + \frac{k_{-d}}{k_{et}} + \frac{k_{-d}}{k_s} \frac{k_{-et}}{k_{et}}} \quad k_s = k'_{-d} + k'_{-et}$$

Figure 1.4 Kinetics of Electron Transfer Quenching

1.3.2 Kinetics of Bimolecular Photophysical Processes:

In the absence of photochemical reactions, in excited state, molecule A^* can be deactivated by emission, by radiationless decay, or by quenching:



The quantum yield of fluorescence is then

$$\Phi_F^Q = \frac{k_F}{k_F + k_D + k_q[Q]}$$

While in the absence of quencher,

$$\Phi_F = \frac{k_F}{k_F + k_D}$$

The ratio $\frac{\Phi_F}{\Phi_F^Q}$ of the quantum yield of fluorescence without quencher to that with quencher is given by

$$\frac{\Phi_F}{\Phi_F^Q} = \frac{k_F + k_D + k_q[Q]}{k_F + k_D} = 1 + \frac{k_q[Q]}{k_F + k_D} = 1 + \tau_F \cdot k_q[Q]$$

τ_F is the excited state lifetime in the absence of quencher. $\frac{\Phi_F}{\Phi_F^Q}$ equation is known as the Stern-Volmer equation if $\frac{\Phi_F}{\Phi_F^Q}$ is plotted against the quencher concentration $[Q]$ a straight line of slope $k_q \cdot \tau_F$ will result (Klessinger et. al., 1995).

It is also useful to transform the Stern-Volmer relation into the form

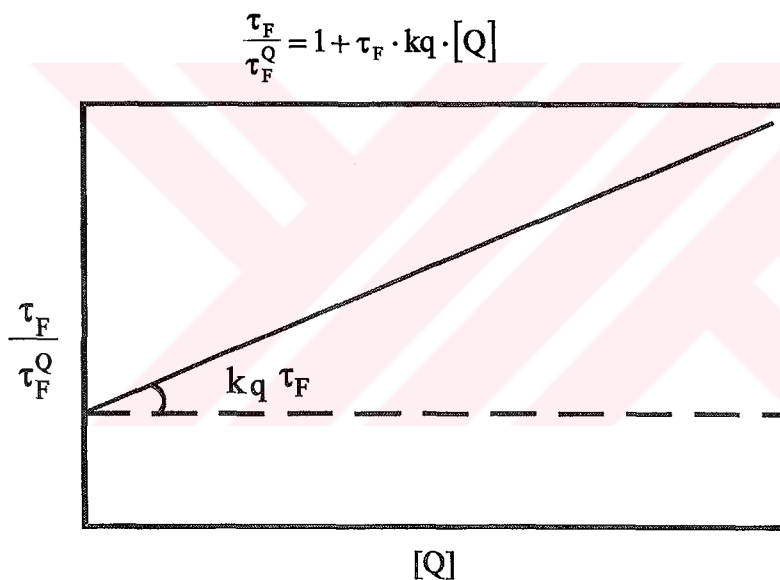


Figure 1.5 Stern-Volmer Equation

1.3.3 Thermodynamics of Energy Transfer

Another process in bimolecular interaction is energy transfer. Electronic energy transfer is the turning back of an excited donor molecule A to its ground state, at the same time transferring its electronic energy to an acceptor molecule B.

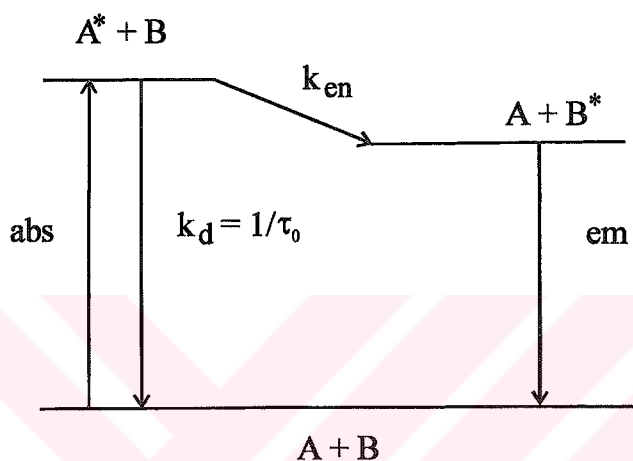
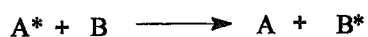


Figure 1.6 Thermodynamics of Energy Transfer

Energy transfers can either occur radiatively by absorption of the emitted radiation or by a nonradiative way.

1.3.3.1 Radiative Energy Transfer

Radiative energy transfer is a two-step processes in which there is no direct interaction of donor (A) and acceptor (B).



The efficiency of radiative energy transfer, frequently described as “trivial” because of its conceptual simplicity (Förster 1969), depends on a high quantum efficiency of emission by the donor and high light absorbing power of the acceptor in the same region of the spectrum (Klessinger et. al., 1995).

1.3.3.2 Radiationless Energy Transfer

The radiationless energy transfer can also occur via two different mechanisms. The Coulombic or the Electron Exchange mechanism.

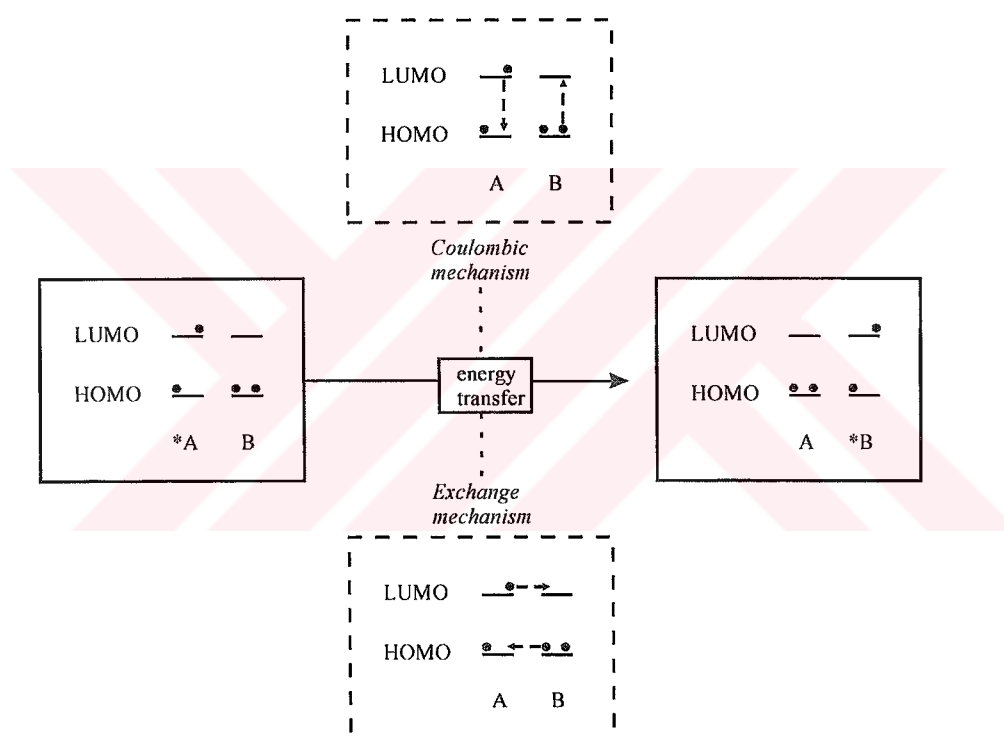


Figure 1.7 Orbital comparison of the coulombic an exchange mechanisms of electronic energy transfer

Energy transfer according to the Coulombic mechanism, which is also referred to as the Förster Mechanism, is based on classical dipole-dipole interactions. This is in fact the interaction of the transition moments of the excitation $B \rightarrow B^*$ and the deactivation $A^* \rightarrow A$. As the excited electron of A^* falls to the lower orbital of A there is a change in dipole moment which produces an electric field; this field is proportional to the transition moment \vec{M} and to the inverse cube of the distance. An electron in the

molecule B there fore experiences a force proportional to \vec{M}/r^3 , and as it moves towards a higher orbital it produces its own electric field which, results in a force being applied on the electron in molecule A* .

Dipole-dipole interaction is a rather shallow distance (<100 Å) compared to orbital overlap interaction of electron exchange.

Coloumbic Energy Transfer is used during photosynthesis (green plant) and in energy migration in rigid systems (macromolecules, polymers...).

The energy transfer related to Electron exchange mechanism is a process which occurs between an excited molecule A* and a ground state molecule B. The first requirement is of course that the excitation energies should be in the order $E(A - A^*) \geq E(B - B^*)$; the second requirement is that the orbitals should allow exergonic electron transfer from ϕ_A^* to ϕ_B^* and from ϕ_B to ϕ_A . The two electron transfers are simultaneous. This double electron transfer requires the spatial overlap of the orbitals so that the molecules A* and B must be in close contact (van der Walls or hard sphere contact) (Suppan P., 1994).

Exchange Energy Transfer is used in population of spin-forbidden states with high efficiency, in useful reactions (energy transfer photosensitization), in mechanistic studies (identification of reactive excited states), in selective excited-state quenching and in quenching of undesired photoreactions.

1.4 Literatures related with Perylene-bis-diimides and Naphthalene-bis-diimides.

Perylene diimides are known to be excellent thermal and photo-stable sensitizers (Langhals, 1995). Absorption in the visible region (450-530 nm) enables them for use in solar applications. Further more they are potentially suitable as photosensitizers, photon counters and laser dyes. The high stabilities of these compounds to heat and light prove them to be useful for plastics and textile materials (Rademacher, et. al., 1982; Lukac, et. al., 1983; Langhals, 1985; Ford et. al., 1987). Photostability, emission characteristics, and laser dye capacities have been studied by Sandrai et. al. (1984), by Ford et. al. (1987) and by Ebeid et. al. (1988). Electron transfer reactions of perylene diimides have been observed by El-Daly et. al. (1992) and by Wasielewski (1992). Energy and electron transfer processes proceed through singlet states. Fluorescence quantum yields of unity and high energy difference between singlet and triplet states (54-27 kcal/mol⁻¹, respectively), are taken as evidences to singlet state photo processes (Içli et. al, 1995; Içli et. al, 1996).

Some of bis-N,N'-aryl and alkyl diimides of perylene have been discovered as brilliant, red, technical pigments by Kardos in 1913 (Langhals, 1995). Due to their low solubility however their high fluorescent potential could not be discovered until 1959. Nearly all perylene dyes are thermally and photochemically stable (Içli et. al, 1997). The photostability and solubility depend strongly on the substituents. To obtain readily soluble perylene dyes are very important in respect to use their strong fluorescence capacity. Generally bulky aliphatic substituents enhance the solubility (Langhals, 1991).

The fluorescence quantum yield is about unity for the most derivatives (Içli et. al., 1997). The soluble perylene diimides can be used as light emitting species in oxalate chemiluminescent devices (Dugliss, 1987) due to their chemical stability. The UV/VIS spectra of these dyes depend weakly to the substituents. Recently perylene diimides are used as sensitizing dye in semiconductor systems (Ferrere et. al., in press).

Naphthalenic imides are compounds of current interest in biological and medical areas as well as in supramolecular chemistry and material science. Biological applications rely mainly on their pharmacological activity as local anesthetics (Mattocks

et. al., 1948; Dasettimo et. al., 1989), tumoridicals (Brana et. al., 1981; Kirshenbaum et. al., 1994), and antivirals (Rideout et. al., 1993; Chanh et. al., 1993; Hayes et. al., 1996). In recent years, the use of naphthalenic imides in photochemotherapy has also been developed, particularly with the hydroperoxy substituted derivatives (known as photo-Fenton reagents) (Saito et. al., 1990; Matsugo et. al., 1991; Saito, 1992).

In addition to the biological interest, naphthalenic imides have been used for technological purposes, such as in optical brighteners (Dollars et. al., 1975) and laser dyes (Pardo et. al., 1989). More recently, there has been 1,4,5,8-naphthalenediimide derivatives, mainly due to their electron acceptor properties (Viehbeck, A., et. al., 1990; Zhong, C. J., et. al., 1992), which make them suitable for a series of applications, including the formation of Langmuir-Blodgett films (Cammarata et. al., 1990; Cammarata et. al., 1992; Kwan et. al., 1992), the preparation of electrically conducting materials (Heywang et. al., 1989; Miller et. al., 1993), nanotube-like structures (Kimizuka et. al., 1995) and as models for the photosynthetic reaction center (Hasharoni et. al., 1995; Hasharoni et. al., 1996).

1.5 Photochemical Aspects of N,N'-bis-aryl (alkyl) 1,4,5,8-naphthalene diimides in Literature

Several photochemical reactions are known for naphthalenimides; in particular, excited states of phthalimides and 1,2- and 2,3-naphthalenimides are attacked by olefins, leading to ring-expanded products. Rather different reactions are observed for 1,8-naphthalenimides. N-Substituted-1,8-naphthalenimides are remarkably stable in the absence of electron-donating groups. Irradiation of 1,8-naphthalenimides does not lead to ring expansion: Instead, the 1,8-derivatives react with both amines and olefins primarily through electron transfer processes. (Demeter et. al., 1993; Kubo et. al., 1985; Somich et. al., 1987) Quenching of the triplet state of N-phenyl-1,8-naphthalenimide by aliphatic amines produces ketyl radicals by a hydrogen atom abstraction mechanism, but H atom abstraction from alkyl groups by imides of this type has not been reported (Fox et. al., 1995).

Fox and Green have demonstrated an effective intramolecular photoinduced electron transfer from nitroxyl radical to 1,4,5,8-naphthalene diimide moiety. The

production of an anion proves that ET is a major quenching route, but other mechanisms may also contribute. These pathways include energy transfer (EnT), as well as electron exchange- (EX-) enhanced internal conversion ($S_1 \rightarrow S_0$, Figure 1.8) or intersystem crossing ($S_1 \rightarrow T_n$ or $T_1 \rightarrow S_0$, Figure 1.9). Schemetically, electron exchange with a radical can be represented as simultaneous (or very rapidly coupled) forward and reverse electron transfers (Figure 1.8).

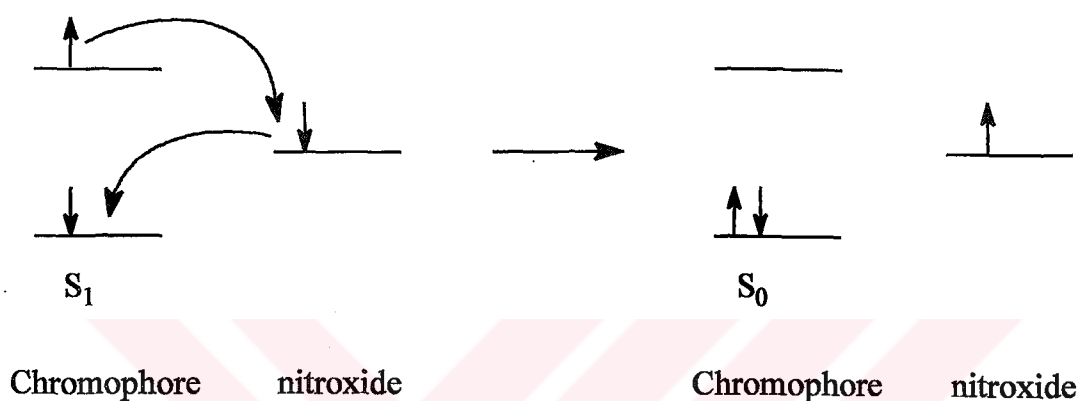


Figure 1.8 Fluorescence Quenching by Electron Exchange

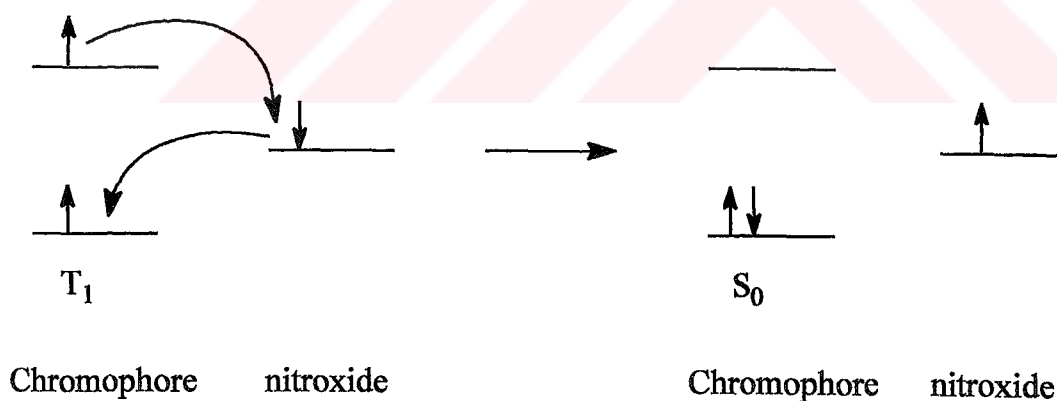


Figure 1.9 Triplet Quenching by Electron Exchange

There are two arguments for the existence of reactive $n-\pi^*$ states in the diimides investigated. First, the singlet to triplet intersystem crossing is most rapid for $\pi,\pi^* \leftrightarrow n,\pi^*$ states. The very rapid observed conversion to the triplet manifold indicates that the transition is not forbidden. The large absorption cross section for the diimides indicates that excitation is to a π,π^* state, and this must correspond to S_1 because of the small Stokes shift. The triplet formed must then be n,π^* . Second, the high reported efficiency for photoinduced electron transfer to N-phenyl-1,8-naphthalenimide (Demeter et. al., 1993) indicates involvement of an n,π^* state because π,π^* states are considerably less reactive to electron abstraction reactions (Turro et. al., 1978).

In literature for the simple phthalimides the lowest singlet excited state has typical $n-\pi^*$ character, which accounts for the low absorption coefficient and very weak fluorescence observed (Berci et. al, 1988; Almeida et. al., 1991). However, for naphthalimides, the lowest excited state is predominantly π,π^* in character, although significant differences have been found in the behaviour of the three types of naphthalimide (Barros et. al., 1997). Whereas 1,2 and 2,3 naphthalimides fluoresce with high to moderate quantum yields (Φ_F) in acetonitrile solution ($\Phi_F \sim 0,8$ and $0,2$ respectively), the fluorescence of 1,8-naphthalimides is quite weak ($\Phi_F \sim 0,06$) (Barros et. al., 1993; Wintgens et. al., 1994). These trends have been explained by the fast intersystem crossing from the excited π,π^* singlet state to a close-lying n,π^* triplet state, which is particularly efficient in the case of the 1,8 naphthalimides (Barros et. al., 1997).

Barros, T.C. et al have also investigated the effect of addition of a second imide group to the structure of 1,8-naphthalimides, as in 1,4,5,8 naphthalenediimides. $S_0 \rightarrow S_1$ (π,π^*) transition energy obtained from the intersection of the absorption and emission spectra is 75 kcal/mol^{-1} for N,N'-dibutyl-1,4,5,8-naphthalenediimide. This value is lower than that for the analogous compound N-butyl-1,8-naphthalimide (Barros et. al., 1993), where the transition energy for the first transition (π,π^*) is 81 kcal/mol . The decrease in transition energy shows that the addition of second imide group helps to stabilize the π,π^* state, suggesting a strong π conjugation between the carbonyl groups and the naphthalene ring in N,N'-dibutyl-1,4,5,8-naphthalenediimide.

Barros, T.C. et al. (1997) can conclude that the fluorescence quantum yields for naphthalenic imides decrease in the order 1,2-naphthalimides > 2,3-naphthalimides > 1,8-naphthalimides > 1,4,5,8-naphthalenediimides. The most probable explanation for the low quantum yield of diimide N,N'-dibutyl-1,4,5,8-naphthalenediimide is the fast intersystem crossing to a triplet level, as proposed by Wintgens et al. (1994) for 1,8-naphthalimides and by Green and Fox et. al. (1995) for N,N'-didodecyl-1,4,5,8-naphthalenediimide, an analogue of N,N'-dibutyl-1,4,5,8-naphthalenediimide.

Katz and co workers developed the organic semiconductor F15. This research is an important step in plastic electronics.

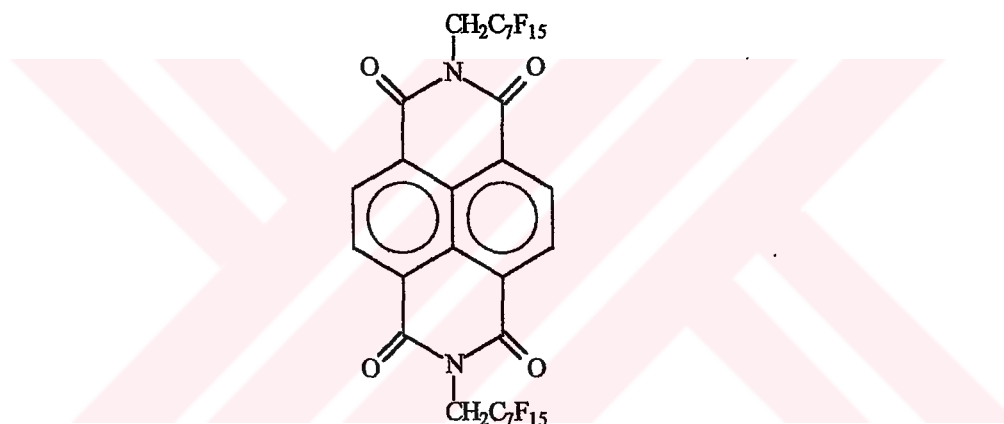


Figure 1.10 F15 as an Organic Semiconductor

By attaching fluorinated alkyl chains to an electron acceptor have synthesized in a long-sought molecule as an organic semiconductor with a reasonably high electron mobility that is also soluble and air-stable. Such devices, based on organic semiconductors, are expected to be simpler and less expensive to make than conventional inorganic devices. To perform well at high speeds and low power levels, the logic elements of such applications will need be fabricated from n-type and p-type organic semiconductors, in which the charge carriers are electrons and holes, respectively. Stable

p-type organic semiconductors have been developed, but practical n-type organic semiconductors have been elusive until now.



2 MATERIALS AND METHODS

2.1 Materials

1,4,5,8-Naphthalene tetracarboxylic acid dianhydride, aniline, *o*-chloroaniline, *p*-toluidine, α -naphthylamine, *n*-butylamine, *n*-dodecylamine, cyclohexylamine, phenanthrene, naphthalene, anthracene, pyrene and perylene were obtained from Fluka and Merck, and were used as supplied. All the organic solvents that were used (acetonitrile, chloroform, methanol), were of spectrophotometric grade.

Synthesized compounds were analysed at Shimadzu IR 4570 spectrophotometer for IR spectroscopy, at JASCO V-530 UV-VIS spectrophotometer for UV-VIS spectroscopy, at JEOL JNM-GX 400FT 400MHz NMR for NMR spectroscopy analysis. Fluorescence emission spectra were recorded at a PTI QM1 fluorescence spectrophotometer.

Fluorescence quantum yields of naphthalene diimides were measured with reference to absorption and fluorescence emission of anthracene.

2.2 Experiments

2.2.1 General Preparation Methods of N,N'-bis-aryl(alkyl)-1,4,5,8-naphthalenediimides

N,N'-bis-aryl(alkyl)-1,4,5,8-naphthalenediimides were prepared by the method that were employed for the synthesis of N-substituted perylene diimides (Içli et. al., 1997).

1,4,5,8-Naphthalene tetracarboxylic acid dianhydride was reacted with appropriate amine derivative in m-cresol/isoquinoline at elevated temperatures ($>200^{\circ}\text{C}$) for 4-6h in order to yield the naphthalenediimide. Molecular structures were analysed by IR and proton NMR spectra.

2.2.2 Quenching of Aromatic Hydrocarbon's Fluorescence with N,N'-bis-phenyl-1,4,5,8-naphthalenediimide in Acetonitrile

2.2.2.1 Initial Preparations:

- ❖ All of the solution concentrations of the luminescent compound were prepared to be less than 10^{-5} M and the UV absorbance value on the excitation wavelength were generally used no more than 2 and no less than 0,1. The volumes of prepared solutions were between 5-10 ml.
- ❖ Concentrations of the solutions of quencher should be up to 10^{-3} M. Quenching studies were carried out each time by adding one drop of quencher into 7ml of luminophore solution. The final concentration of solution was between 10^{-7} - 10^{-6} M.
- ❖ Quantitative absorption spectrum (expressed in the molar absorbency units) of quencher has been taken previously, because all the concentrations of quencher have been evaluated with its use.

- ❖ Fluorescence lifetime of luminescent compound has been calculated previously. To calculate fluorescence lifetime, the fluorescence band on which we were going to quench was used.

2.2.2.2 Experimental Procedure:

- ❖ To begin with, the absorption and the emission of solvent have been measured blank. These spectra have been subtracted from the naphthalene diimide solutions to correct the absorption and emission spectra.
- ❖ The absorption and fluorescence intensities of the initial solutions were measured.
- ❖ The solution of quencher were added dropwise to the solution of luminescent compound. After taking the spectrum, the solution poured back into the flask from the cell. Each spectrum was taken sequentially by addition of another portion of quencher. It was necessary to avoid fluctuations of concentration in all mixtures. By adding of each drop of quencher was observed the change in absorption and emission spectra. Optical density in the region of absorption or emission of luminescent compound must not be higher than 1,2-1,4, because the formula for correction of luminescence spectra on reabsorption and inner-filter effects do not work properly at high absorbances. Finally, we have taken the absorption and the emission spectra from 10 to 20 times at different concentrations of quencher. These spectra was evaluated by using Stern-Volmer equation as theoretically in order to obtain the results of energy transfer.

2.2.3 Quenching of Aromatic Hydrocarbon's Fluorescence with N,N'-bis-n-butyl-1,4,5,8-naphthalenediimide in Acetonitrile, Chloroform and Dichloromethane

2.2.3.1 Initial Preparations

- ❖ All of the solution concentrations of the luminescent compound were prepared to be less than 10^{-5} M.

- ❖ Quenching emission experiments were also carried out by addition of N,N'-bis-n-butyl-1,4,5,8-naphthalenediimide between 1,0-1,6 mg into 100 ml. luminophore solution.
- ❖ Quantitative absorption spectrum of quencher has been taken previously, because all the concentrations of quencher have been evaluated with its use.

2.2.3.2 Experimental Procedure

- ❖ To begin with, the absorption and the emission of solvent have been measured. These spectra have been subtracted from the naphthalene diimide solutions to correct the absorption and emission spectra.
- ❖ The absorption and fluorescence intensities of the initial solutions were measured.
- ❖ All of the quencher were added solidly to the solution of luminescent compound. After taking spectrum the solution poured back into the flask from the cell. Each spectrum was taken sequentially by addition of another portion of quencher. It was necessary to avoid fluctuations of concentration in all mixtures.
- ❖ By adding of each time solidly of quencher was observed changes in absorption and emission spectra. Finally; we have taken the absorption and the emission spectra from 10 to 20 times at different portions of quencher. These spectra was evaluated by using Stern-Volmer equation as theoretically in order to obtain the results of energy transfer.

3 RESULTS AND DISCUSSION:

3.1 UV-VIS spectroscopy studies

UV absorption spectra of naphthalene diimides have shown three characteristic bands at 377,357 and 340nm in acetonitrile solutions. In according with the reported data of Barros et.al. (1993) (Fig. 3.1 and Table 3.1). N-aryl (alkyl) substitution did not alter absorption wavelengths λ , and molar extinction coefficient ϵ . Solubility differences in acetonitrile were observed among the seven derivatives. Most soluble naphthalene diimides were found to be the alkyl derivatives of V, VI and VII. The n-butyl derivative V was observed to be the most soluble in acetonitrile, chloroform and dichloromethane solvents. The least soluble naphthalene derivative was o-chlorophenyl derivative II. In general low solubilities of naphthalene diimides have caused the difficulties on measurements of absorption spectra. All the acetonitrile solutions were colorless.

Table 3.1 UV –VIS spectroscopic data (λ (nm) and ϵ ($1 \text{ mol}^{-1} \text{ cm}^{-1}$)) of synthesized N,N'-bis-aryl (alkyl) 1,4,5,8-naphthalenediimides in acetonitrile

	Ar (R)	λ_1	ϵ_1	λ_2	E_2	λ_3	ϵ_3
I	Phenyl	377	32500	357	27800	340	17160
II	<i>o</i> -Chlorophenyl	376	42900	356	35100	339	20300
III	<i>p</i> -Tolyl	376	32800	356	9500	339	18800
IV	α -Naphthyl	377	33000	357	29000	340	17500
V	<i>n</i> -Butyl	377	43500	356	35100	339	21100
VI	<i>n</i> -Dodecyl	377	33900	357	28700	340	19100
VII	Cyclohexyl	378	30600	358	25800	342	15500

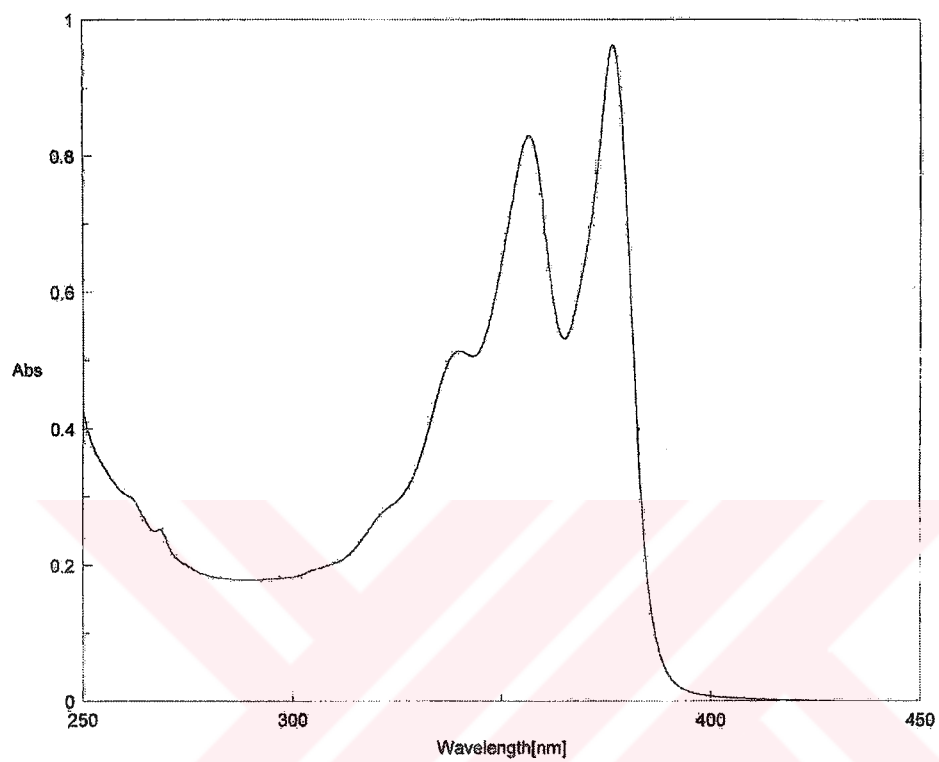


Figure 3.1 UV absorption spectrum of N,N'-bis-phenyl-1,4,5,8-naphthalenediimide (I; PNDI) in acetonitrile

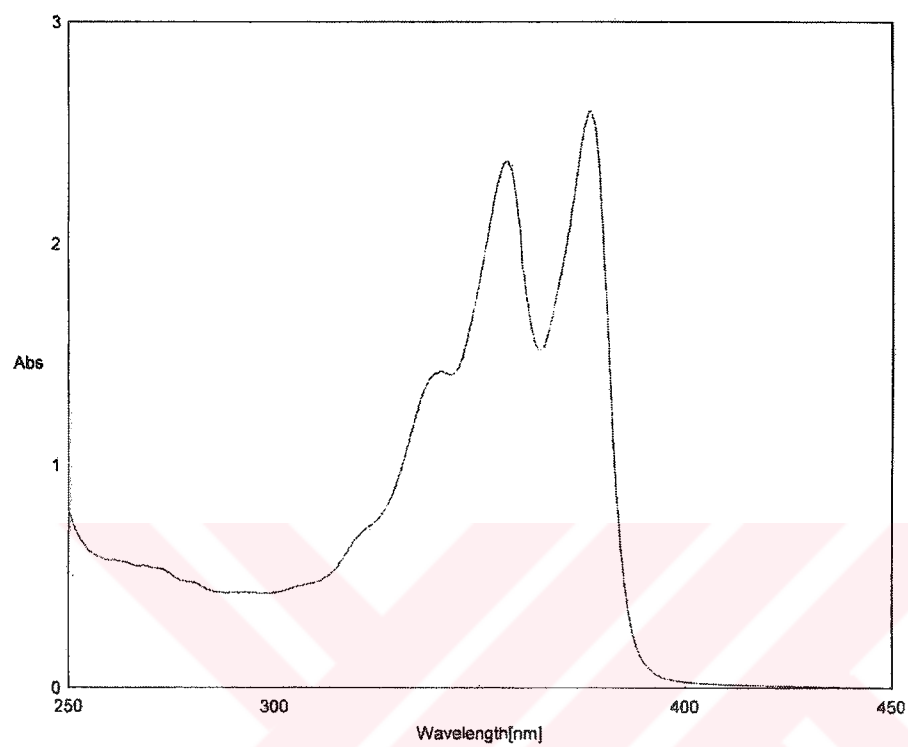


Figure 3.2 UV absorption spectrum of N,N'-bis-*o*-Chlorophenyl-1,4,5,8-naphthalenediimide in acetonitrile

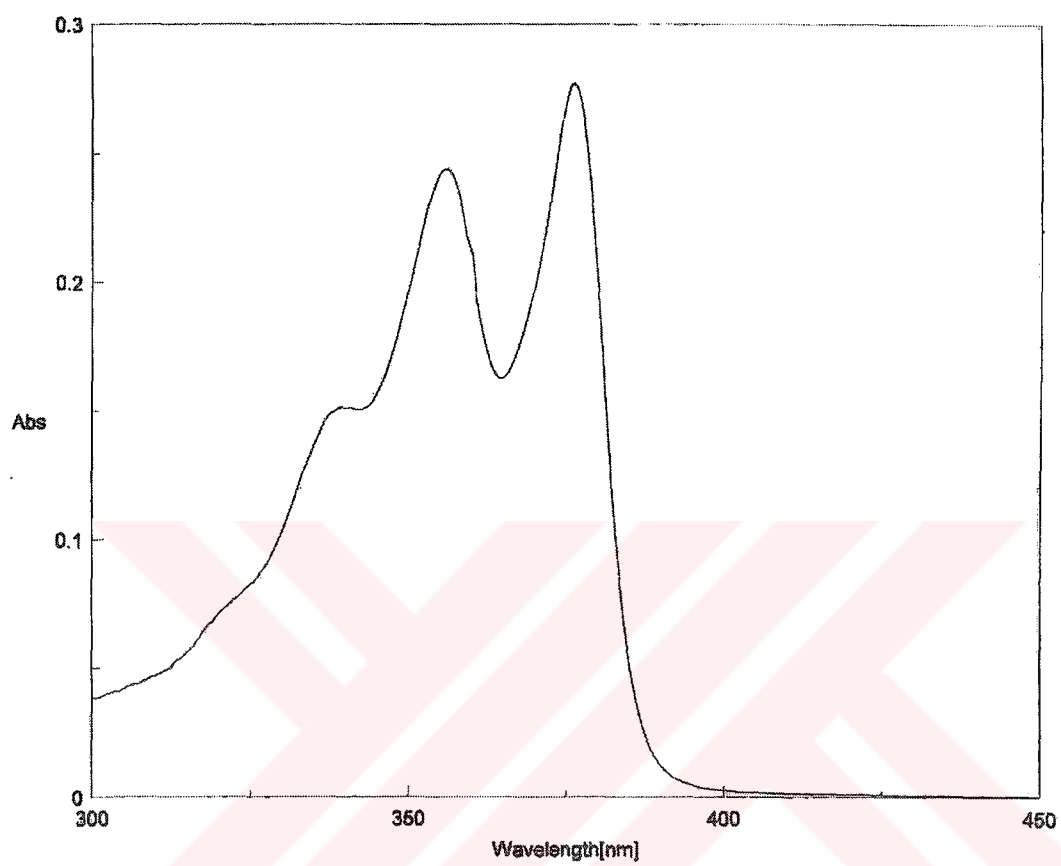


Figure 3.3 UV absorption spectrum of N,N'-bis-*p*-Tolyl-1,4,5,8-naphthalenediimide in acetonitrile.

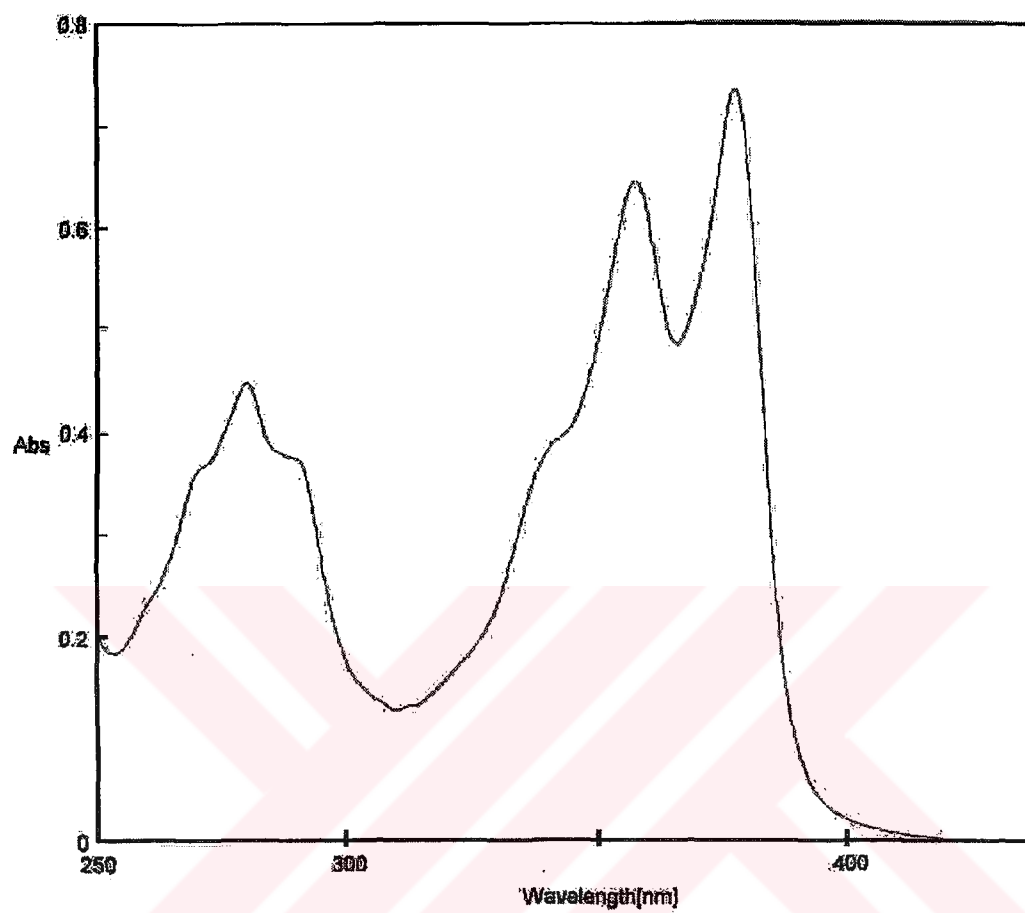


Figure 3.4 UV absorption spectrum of N,N'-bis- α -naphthyl-1,4,5,8 naphthalenediimide in acetonitrile.

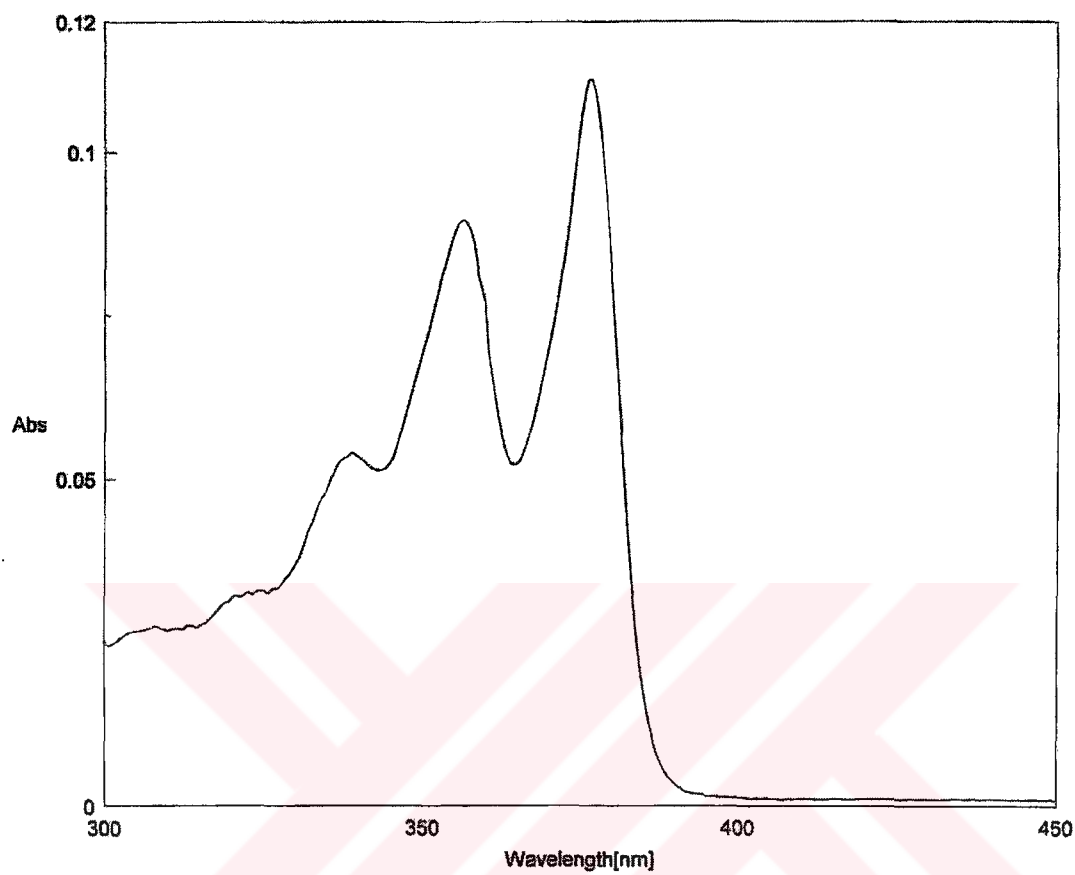


Figure 3.5 UV absorption spectrum of N,N'-bis-n-butyl-1,4,5,8-naphthalenediimide in acetonitrile.

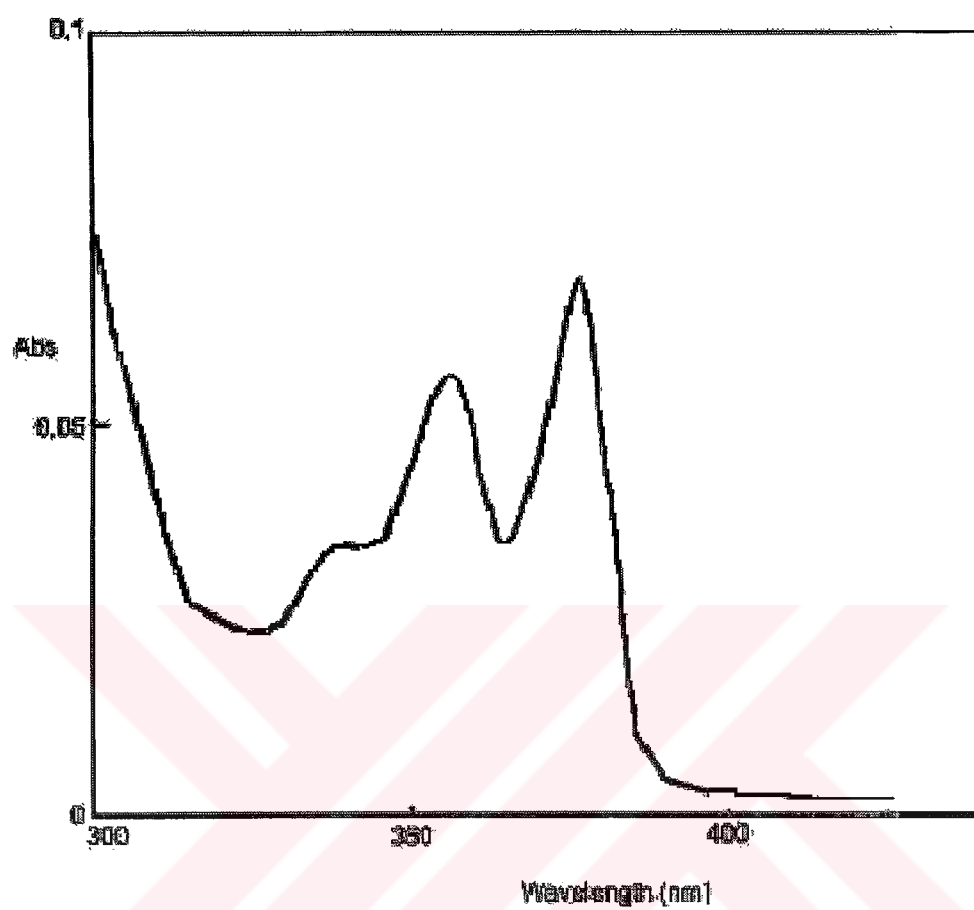


Figure 3.6 UV absorption spectrum of N,N'-bis-n-dodecyl-1,4,5,8-naphthalenediimide in acetonitrile.

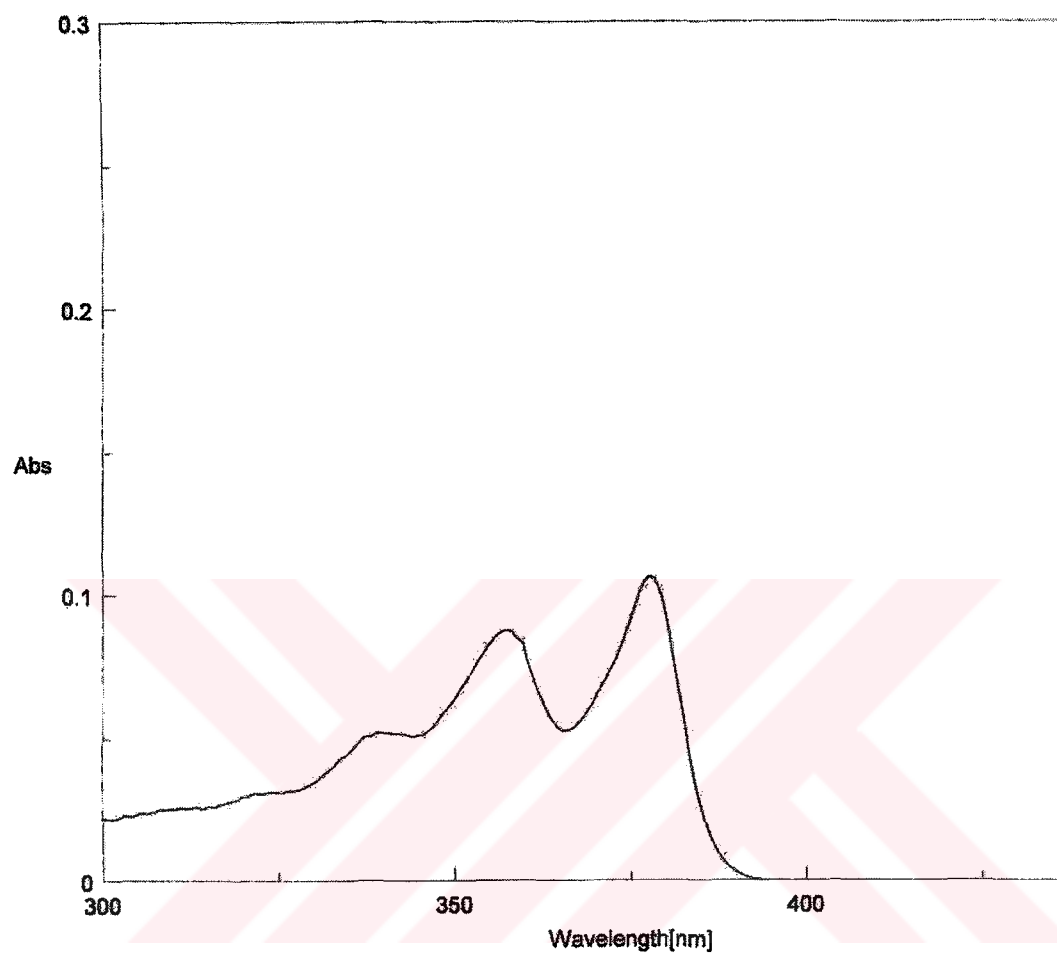


Figure 3.7 UV absorption spectrum of N,N'-bis-cyclohexyl-1,4,5,8-naphthalenediimide in acetonitrile.

3.2 Emission Spectroscopy Studies

Fig. 3.8 shows the absorption and emission spectra of *N,N'*-bis-*n*-butyl-1,4,5,8-naphthalenediimide (V). Mirror image appearance of the absorption and emission spectra is evident. In general, the solvent variation does not alter the absorption and emission spectra, arising from limited vibrational motions of the atoms of the carbon skeleton and evidence to the very rigid structure of the naphthalene diimide molecule.

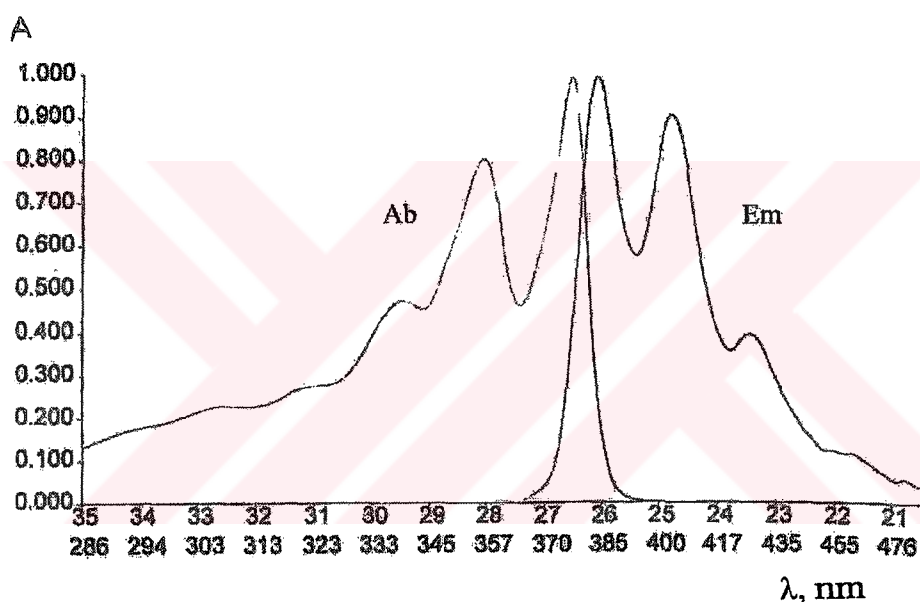


Figure 3.8 Absorption (Ab) and Emission (Em, $\lambda_{exc} = 356$ nm) spectra of *N,N'*-bis-*n*-butyl-1,4,5,8-naphthalenediimide (V) in acetonitrile.

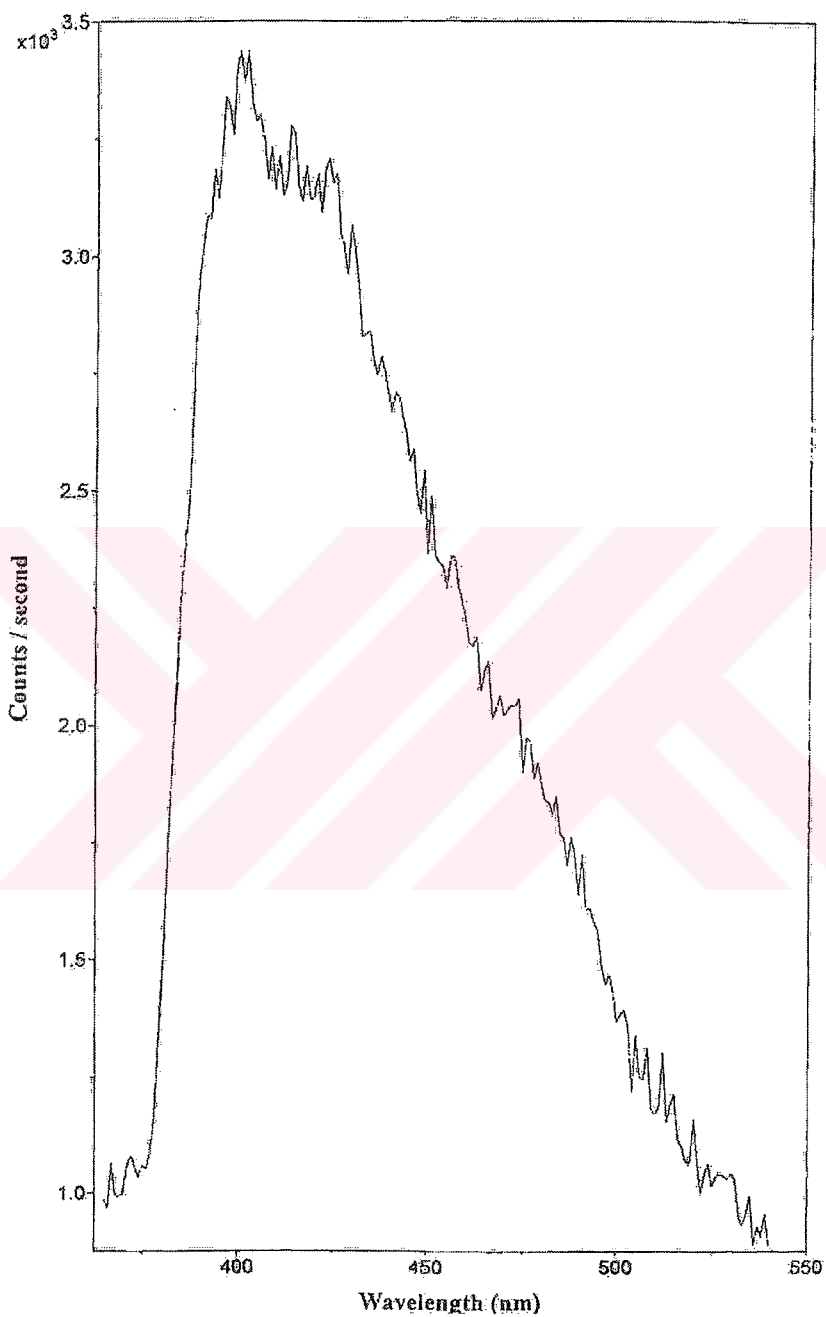


Figure 3.9 Emission spectrum of N,N'-bis-phenyl-1,4,5,8-naphthalenediimide in acetonitrile

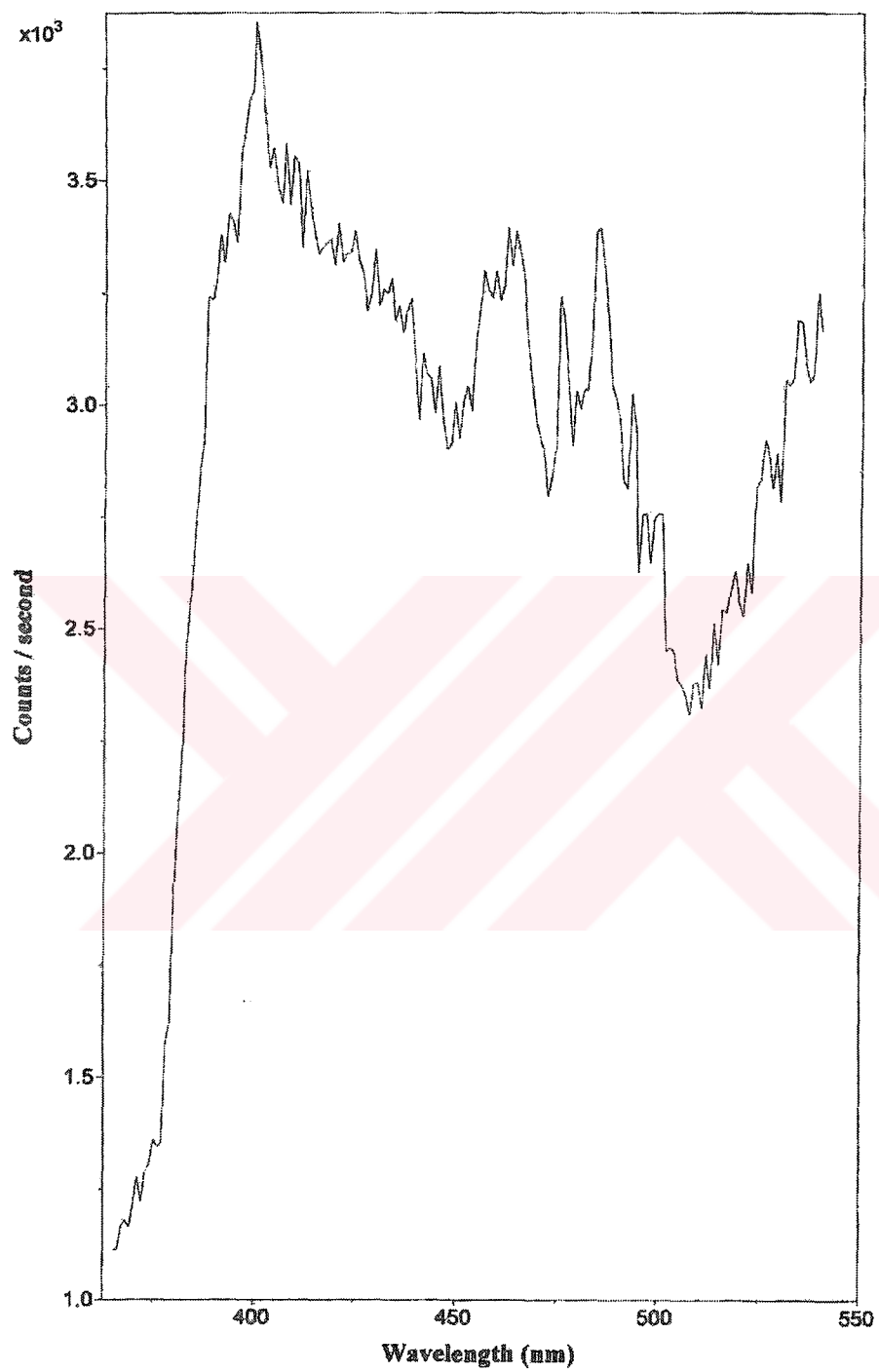


Figure 3.10 Emission spectrum of N,N'-bis-*o*-chlorophenyl-1,4,5,8-naphthalenediimide in acetonitrile

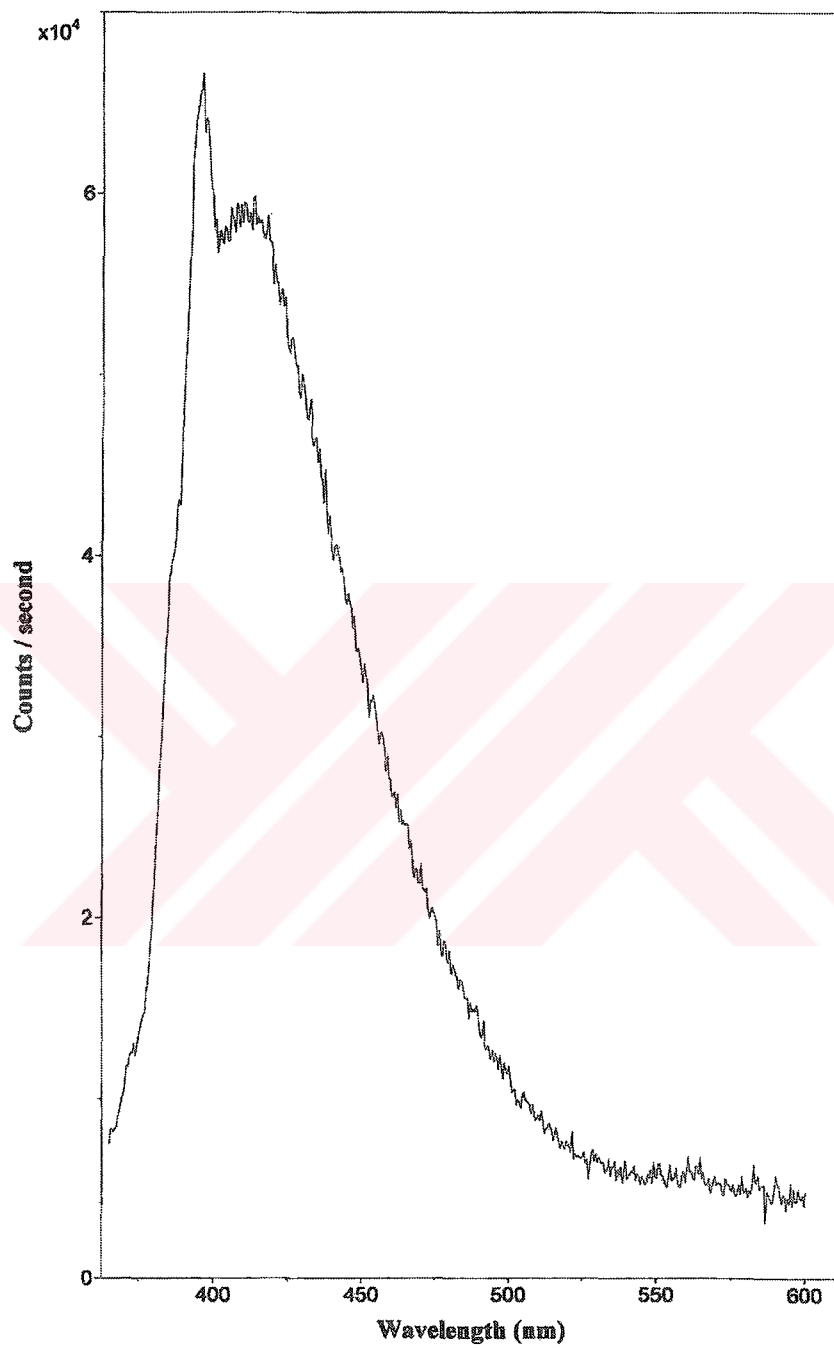


Figure 3.11 Emission spectrum of N,N'-bis-*p*-tolyl-1,4,5,8-naphthalenediimide in acetonitrile

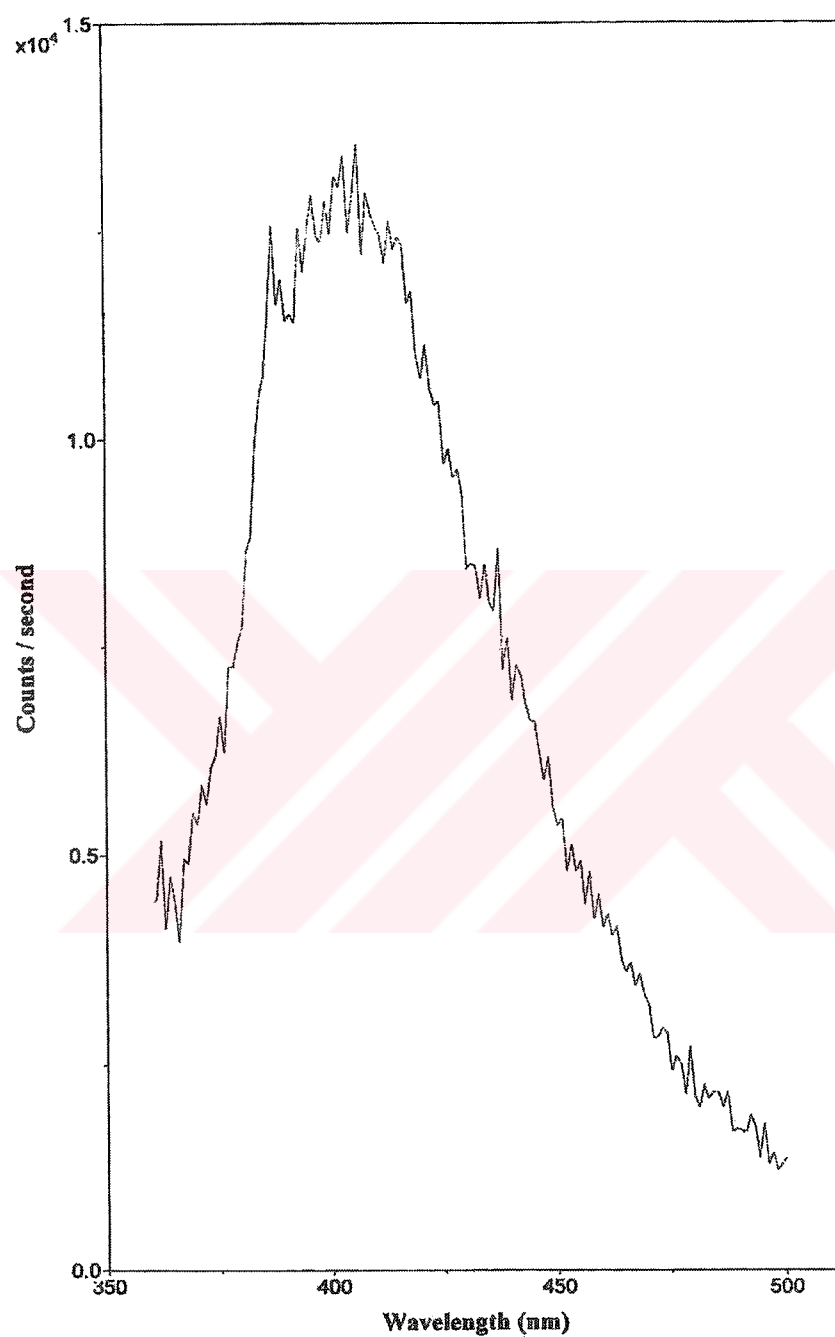


Figure 3.12 Emission spectrum of N,N'-bis- α -naphthyl-1,4,5,8-naphthalenediimide in acetonitrile

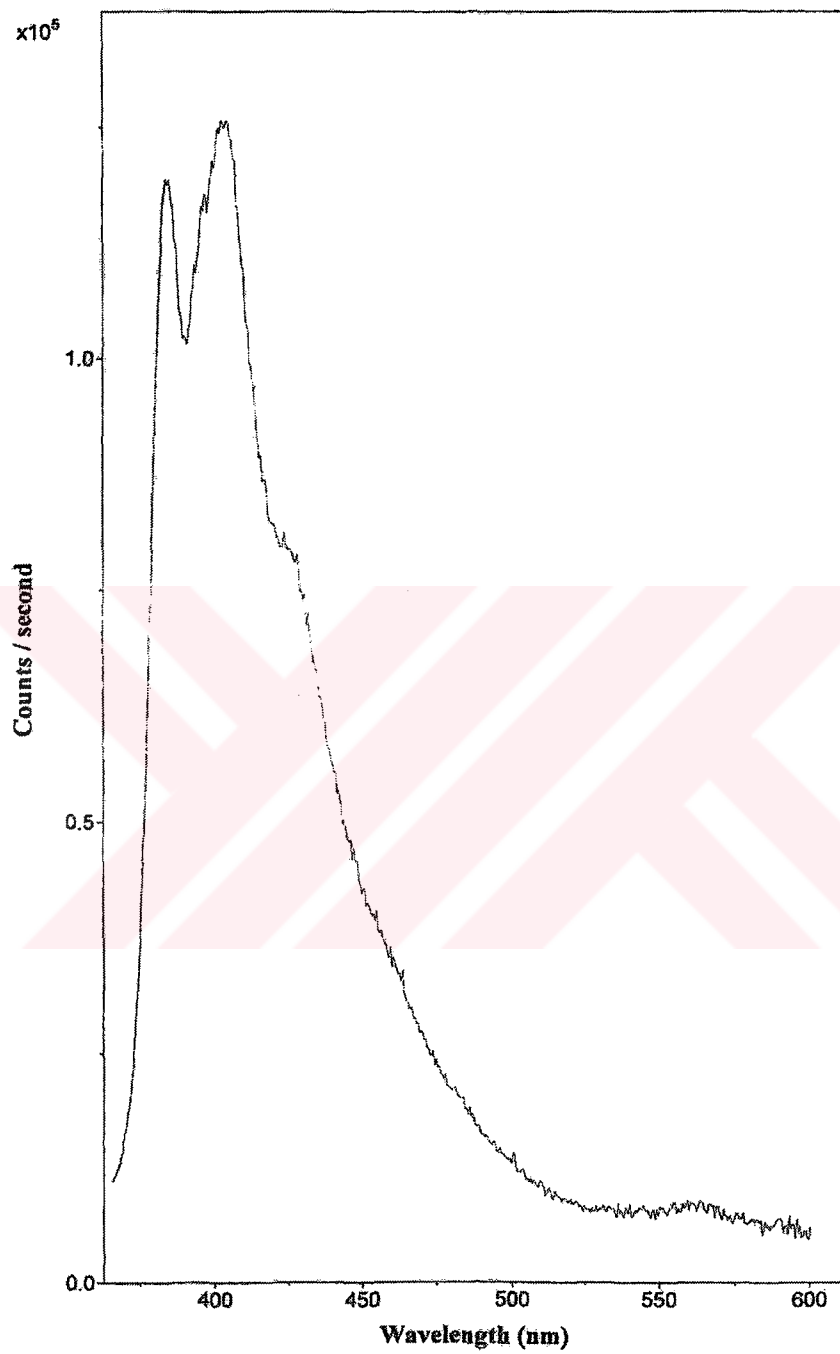


Figure 3.13 Emission spectrum of N,N'-bis- n-butyl-1,4,5,8-naphthalenediimide in acetonitrile

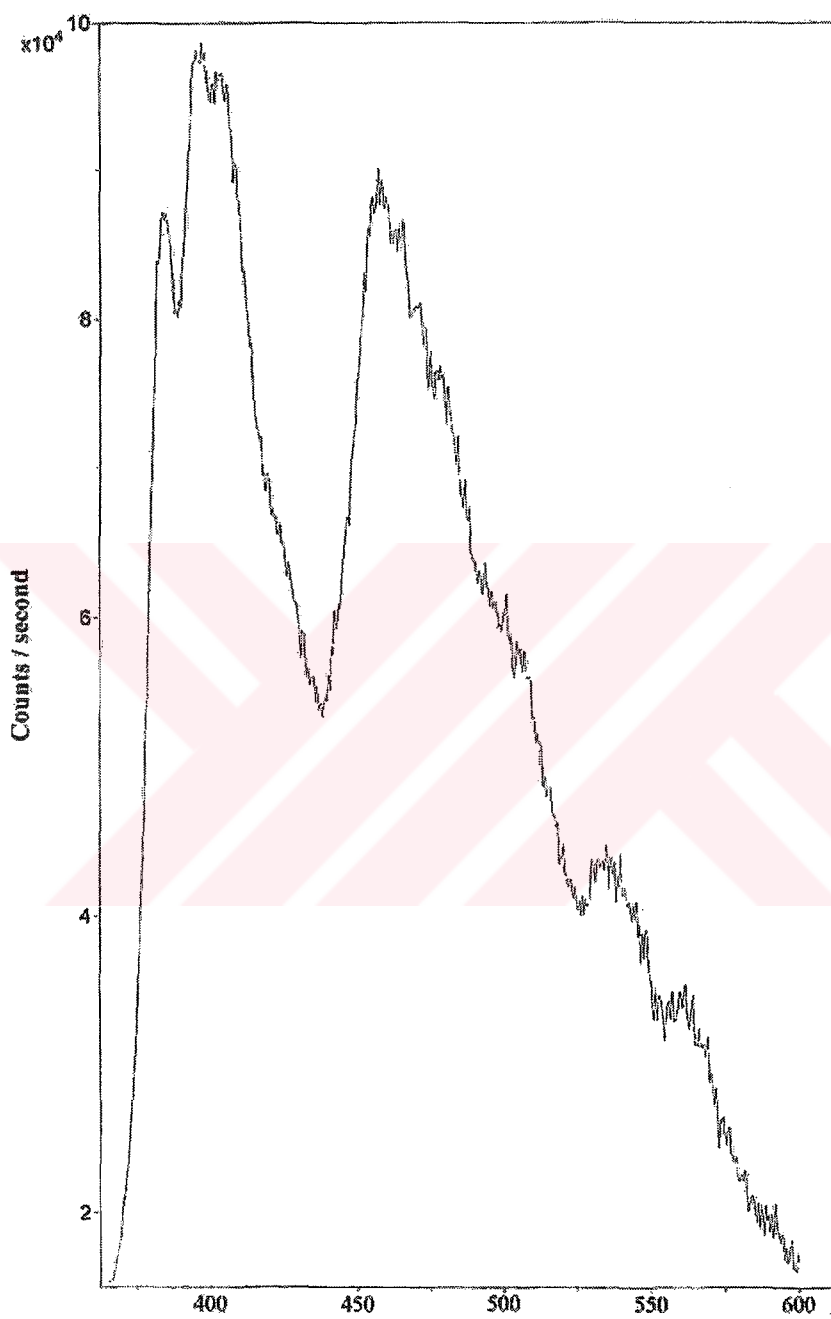


Figure 3.14 Emission spectrum of N,N'-bis-n-dodecyl-1,4,5,8-naphthalenediimide in acetonitrile

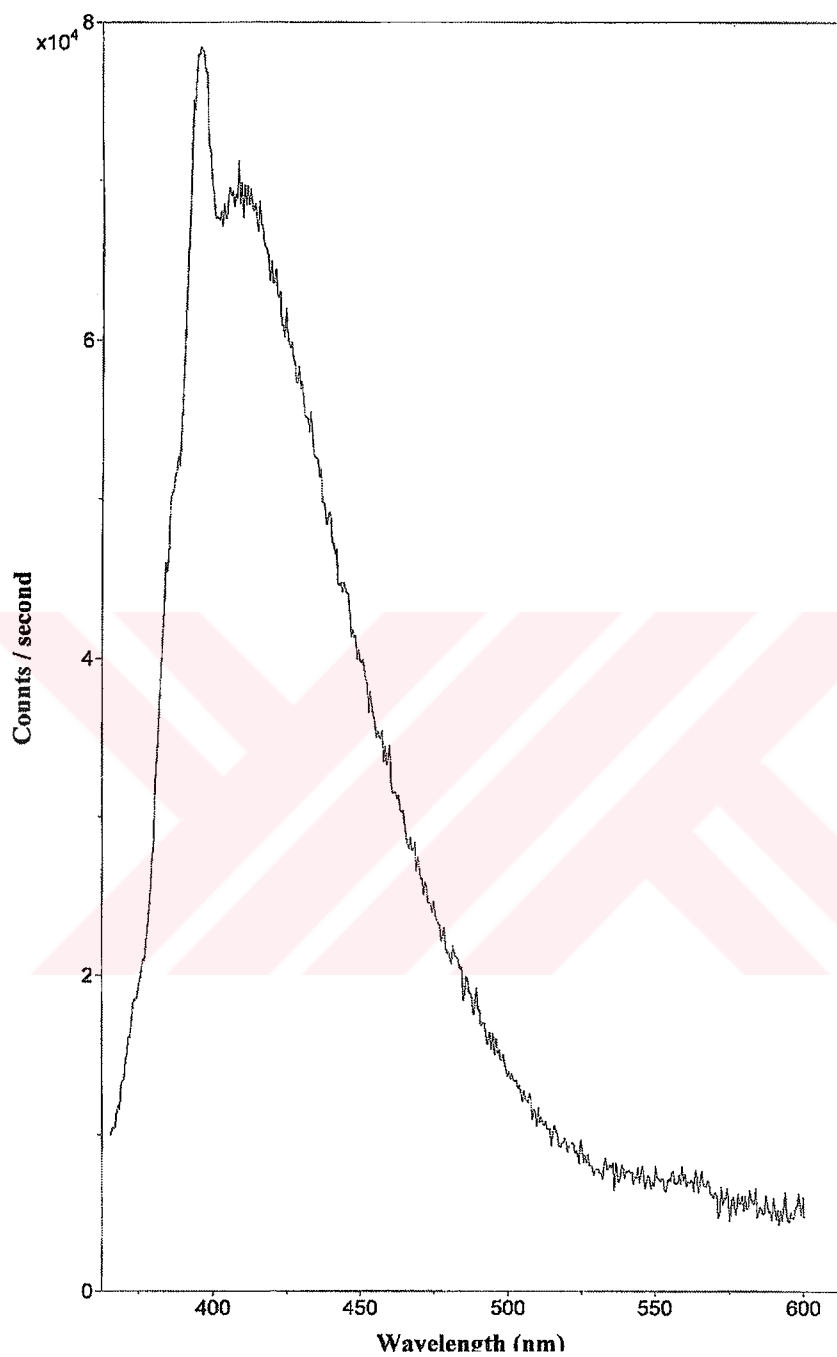


Figure 3.15 Emission spectrum of N,N'-bis-cyclohexyl-1,4,5,8-naphthalenediimide in acetonitrile

3.3 Calculation of Maximum Extinction Coefficients of N,N'-bis-aryl(alkyl)-1,4,5,8-naphthalenediimides at Different Wavelengths

The formula below is used to calculate the maximum coefficients (ϵ_{\max}) at different wavelengths.

$$A = \log \frac{1}{T}$$

$$\epsilon_{\max} = \frac{A}{c \cdot l}$$

A: absorbance

T: transmission

ϵ_{\max} : maximum extinction coefficient

c: concentration

l: path length of the cell.

3.4 Calculations of ϵ_{\max} at Different Wavelengths (λ):

ϵ_{\max} of N-N'-bis (phenyl)-1,4,5,8-naphthalenediimide in acetonitrile:

$$c = 2,96 \times 10^{-5} \text{ M} \quad l = 1 \text{ cm}$$

$$\epsilon_{\max} = \frac{A}{c \cdot l}$$

$$\lambda_1 = 377 \text{ nm} \rightarrow A = 0,9635$$

$$\epsilon_1 = \frac{0,9635}{2,96 \times 10^{-5} \times 1} = 32500 \text{ l.mol}^{-1}.\text{cm}^{-1}$$

$$\lambda_2 = 357 \text{ nm} \rightarrow A = 0,8303$$

$$\epsilon_2 = \frac{0,8303}{2,96 \times 10^{-5} \times 1} = 27800 \text{ l.mol}^{-1}.\text{cm}^{-1}$$

$$\lambda_3 = 340 \text{ nm} \rightarrow A = 0,5138$$

$$\epsilon_3 = \frac{0,5138}{2,96 \times 10^{-5} \times 1} = 17160 \text{ l.mol}^{-1}.\text{cm}^{-1}$$

3.5 Fluorescence Quantum Yield

3.5.1 Method of Measurement of Fluorescence Quantum Yields

The quantum yield can measure several ways. A common practice is to measure quantum yields relative to that of a standard compound, excited under identical conditions.

The fluorescence quantum yield were measured by the formula:

$$\Phi_U = \frac{A_s}{A_u} \times \frac{S_u}{S_s} \times \left[\frac{n_u}{n_s} \right]^2 \times \Phi_s$$

Φ_u : Quantum yield of unknown

Φ_s : Quantum yield of standard

A_s : Absorbance of the standard

A_u : Absorbance of the unknown

S_u : Integrated emission area across the unknown band

S_s : Integrated emission area across the standard band

n_u : Refractive index of the unknown (Lide, 1997-1998)

n_s : Refractive index of the standard (Lide, 1997-1998)

Suitable reference probes for fluorescence quantum yield calculations are given in Table3.2

Table 3.2 Recommended fluorescence quantum yield references in various emission ranges (Eaton, 1988)

Region (nm)	Compound	Solvent	Φ_F
270-300	Benzene	Cyclohexane	$0,05 \pm 0,02$
300-380	Tryptophan	H ₂ O (PH 7,2)	$0,14 \pm 0,02$
300-400	Naphthalene	Cyclohexane	$0,23 \pm 0,02$
315-480	2-Aminopyridine	0,1 N H ₂ SO ₄	$0,60 \pm 0,05$
360-480	Anthracene	Ethanol	$0,27 \pm 0,03$
400-500	9,10-Diphenylanthracene	Cyclohexane	$0,90 \pm 0,02$
400-600	Quinine bisulfate	1 N H ₂ SO ₄	0,546
600-650	Rhodamine 101	Ethanol	$1,0 \pm 0,02$
600-650	Cresyl Violet	Methanol	$0,54 \pm 0,03$
550-900	Tris(4,4'-bipyridyl) ruthenium (II) dichloride	Deoxygenated water	$0,042 \pm 0,002$

3.6 Fluorescence Quantum Yields Calculations for Naphthalene diimide

The calculations are done for 356 nm excitation wavelength according to the method explained. N,N'-bis-phenyl-1,4,5,8-naphthalenediimide is taken as standard for the calculation of fluorescence quantum yield Φ_F . The integrated emission area is given from the emission spectra at 356 nm excitation wavelength Φ_F calculations are done according to the formula given:

$$\Phi_U = \frac{A_s}{A_u} \times \frac{S_u}{S_s} \times \left[\frac{n_u}{n_s} \right]^2 \times \Phi_s$$



3.7 Fluorescence Quantum Yield of N,N'-bis-phenyl-1,4,5,8-naphthalenediimide

Φ_F of N,N'-bis-phenyl-1,4,5,8-naphthalenediimide in acetonitrile phase.

$$\lambda_{\text{exc}} = 356 \text{ nm}$$

$$l = 1,0 \text{ cm}$$

$$A_{\text{NDI}} = 0,5704$$

$$S_{\text{NDI}} = 1,2 \times 10^6 \text{ (counts/cm.sec)}$$

Anthracene is taken as standard

$$\lambda_{\text{exc}} = 339 \text{ nm}$$

$$l = 1,0 \text{ cm}$$

$$A_{\text{Ant}} = 0,0993$$

$$S_{\text{Ant}} = 2,8157 \times 10^7 \text{ (counts/cm.sec)}$$

$$\Phi_{\text{NDI}} = \frac{A_{\text{Ant}}}{A_{\text{NDI}}} \times \frac{S_{\text{NDI}}}{S_{\text{Ant}}} \times \left[\frac{n_u}{n_s} \right]^2 \times \Phi_{\text{Ant}}$$

$$\Phi_{\text{NDI}} = \frac{0,0993}{0,5704} \times \frac{1,2 \times 10^6}{2,8157 \times 10^7} \times 1 \times 0,27 = 0,002$$

For acetonitrile refractive index $n_s = n_u = 1,33723$

3.8 Fluorescence Quenching Studies with N,N'-bis-phenyl-1,4,5,8-naphthalenediimide

Naphthalene diimides are known to be electron acceptors (Fox et. al., 1995). N,N'-bis-phenyl-1,4,5,8-naphthalenediimide is found to quench effectively the fluorescence emissions of aromatic donor molecules of naphthalene, phenanthrene, pyrene and perylene, in spite of its very low fluorescence quantum yield. Figure 3.16-3.23 shows the quenching of fluorescence emissions of Naphthalene, Phenanthrene, Pyrene, Perylene by addition of N,N'-bis-phenyl-1,4,5,8 naphthalenediimide (I, PNNDI) and the Stern-Volmer plot. All the spectra were corrected for inner and absorption effects before calculations. Fluorescence quenching rate constants of aromatic hydrocarbons of naphthalene diimides, exceeding the diffusion control limit ($k_q > 10^{10} \text{ M}^{-1} \text{ s}^{-1}$).

Calculated quenching rates are above the diffusion control limit for all the aromatic hydrocarbons. Calculated quenching rate constants are shown in Table 3.3 The differences of k_q values are seen to be about three-fold from naphthalene to phenanthrene (from $2,6 \times 10^{10}$ to $7,2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) and four-fold from pyrene to perylene (from $1,9 \times 10^{10}$ to $7,6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). These enhancements may be attributed to an increase on aromaticity of the condensed ring systems. A similar study with perylene diimides has resulted in enhancement of quenching rates in parallel to an increase in aromaticity of condensed rings. But the rates of quenching were reported to have increased five-fold from naphthalene to phenanthrene (from $4,4 \times 10^{11}$ to $2,8 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$) and hundred -fold from phenanthrene to dihydrocarbazolo-carbazole (from $2,8 \times 10^{12}$ to $2,5 \times 10^{14} \text{ M}^{-1} \text{ s}^{-1}$) in presence of perylene diimides. Energy transfer is seen to be more effective between aromatic donors and perylene diimides, compared to that between aromatic donors and naphthalene diimides. In general, fluorescence quenching of aromatic donors by naphthalene diimides and perylene diimides may be assumed to be at a comparative scale.

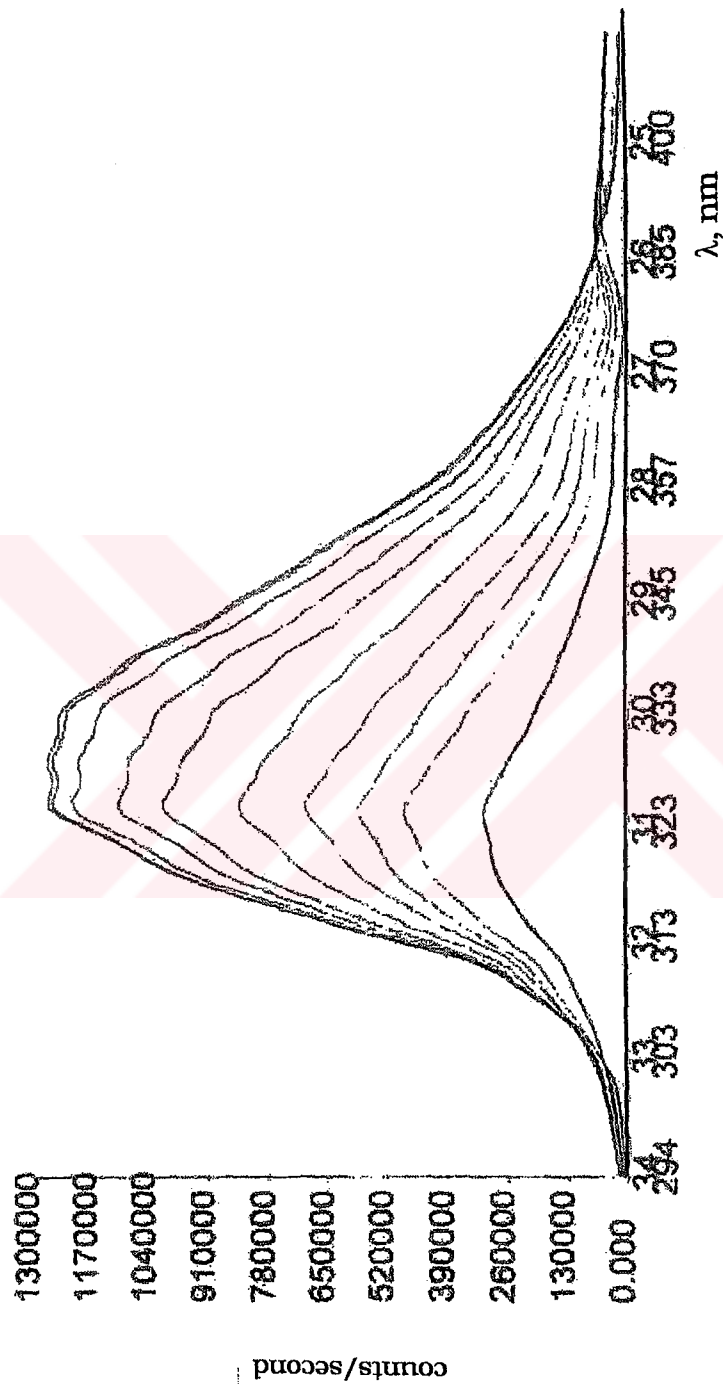


Figure 3.16 Fluorescence quenching of naphthalene by N,N'-bis-phenyl-1,4,5,8-naphthalenediimide (1:PNDI) in acetonitrile at quencher concentrations of 9×10^{-7} - 9×10^{-5} M

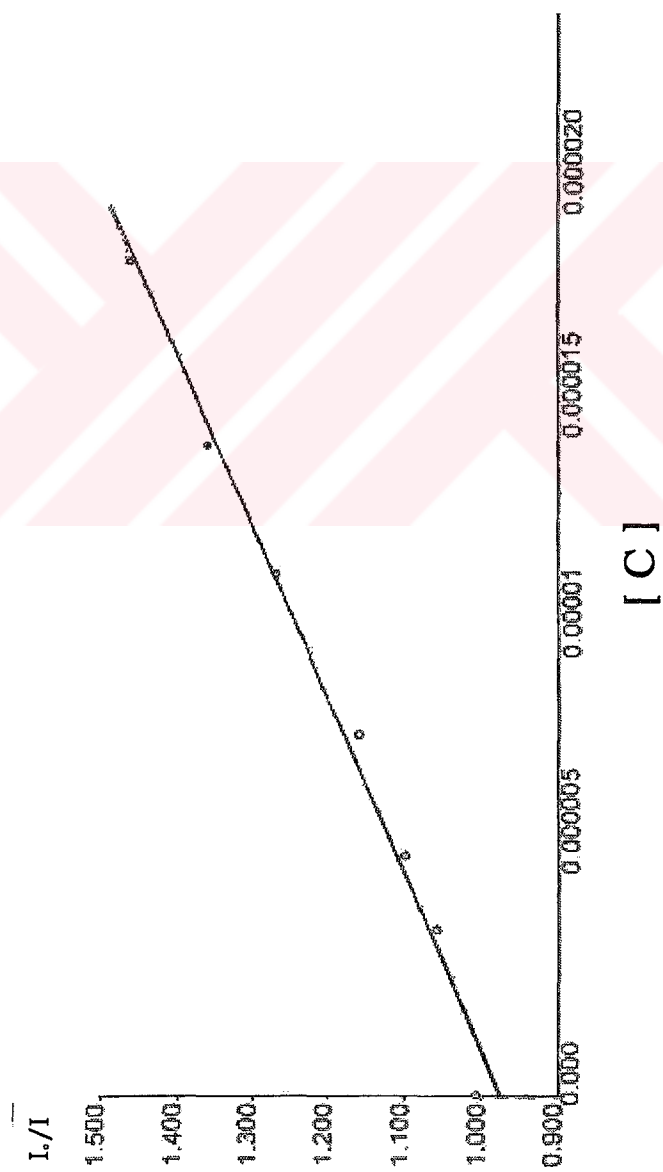


Figure 3.17 Stern-Volmer plot for fluorescence quenching of naphthalene, in presence of increasing quencher concentrations, in acetonitrile

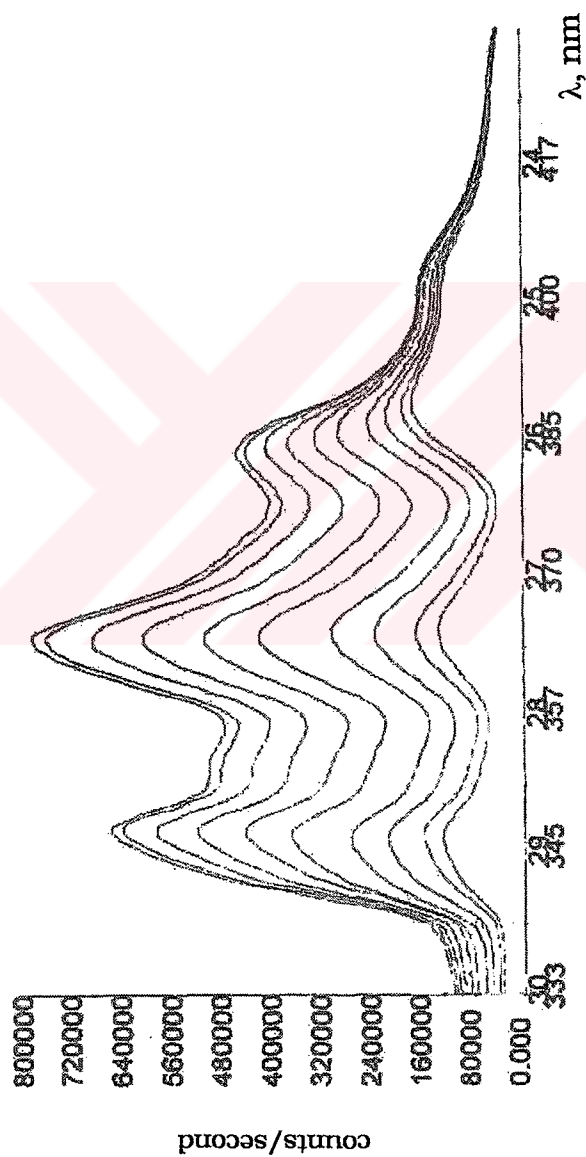


Figure 3.18 Fluorescence quenching of phenanthrene by N,N'-bis-phenyl-1,4,5,8-naphthalenediimide (I:PNDI) in acetonitrile at quencher concentrations of 1×10^{-6} - 8×10^{-5} M

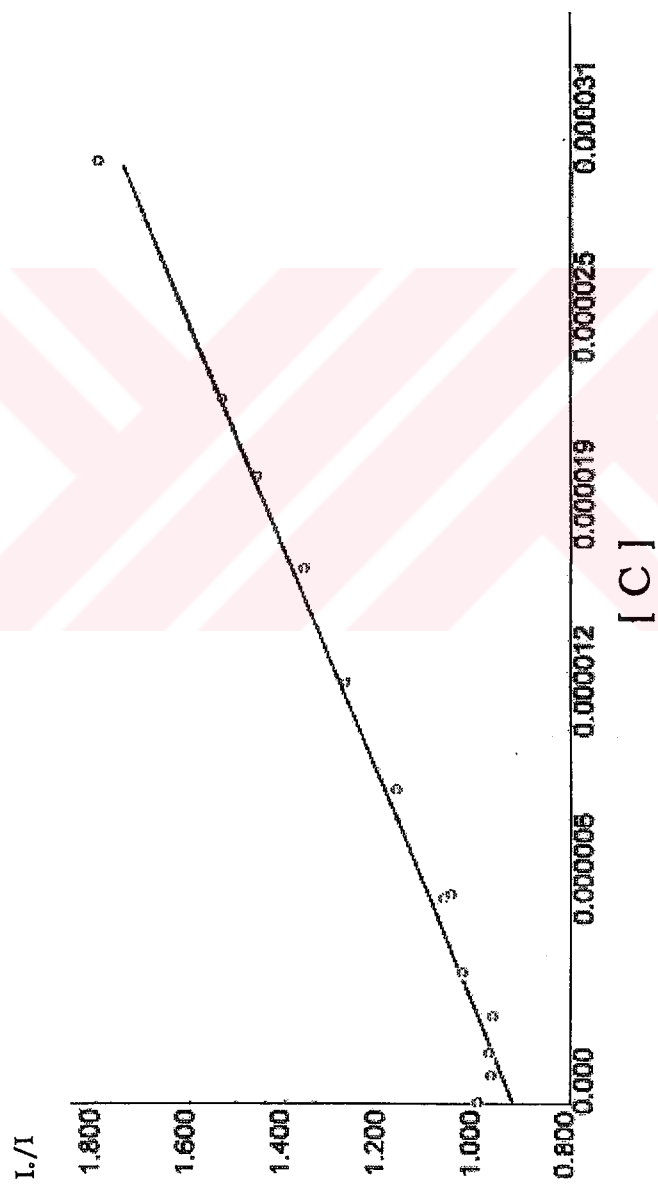


Figure 3.19 Stern-Volmer plot for fluorescence quenching of phenanthrene, in presence of increasing quencher concentrations, in acetonitrile

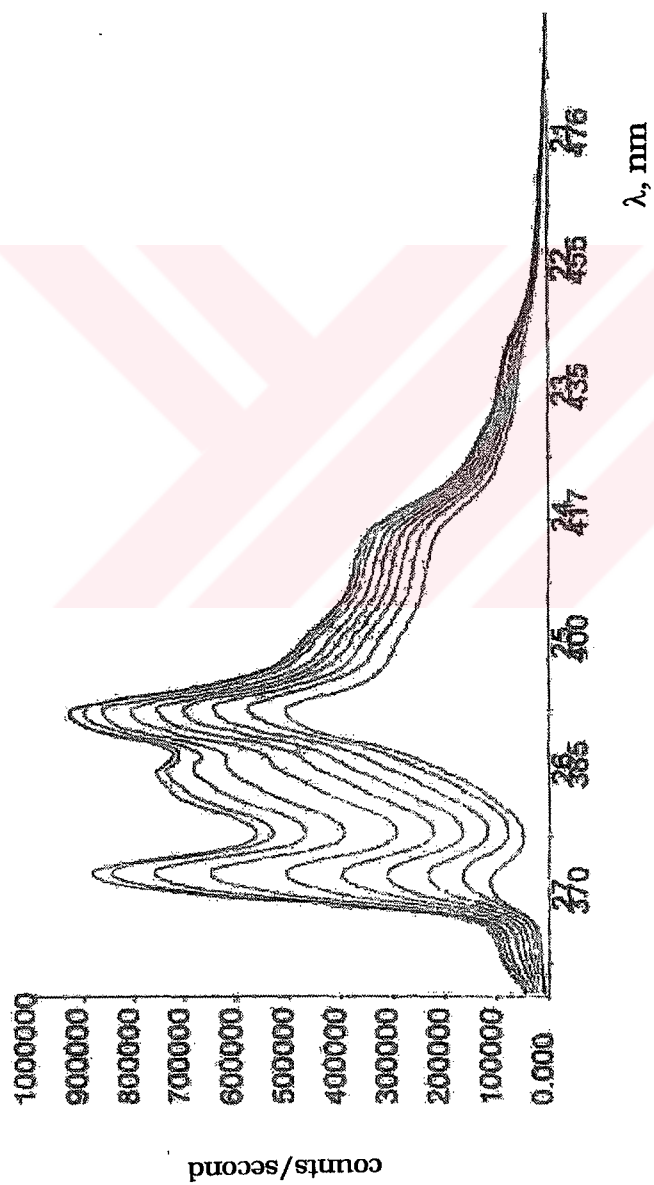


Figure 3.20 Fluorescence quenching of pyrene by N,N'-bis-phenyl-1,4,5,8-naphthalenediimide (1:PNDI) in acetonitrile at quencher concentrations of 1×10^{-6} - 10^{-5} M

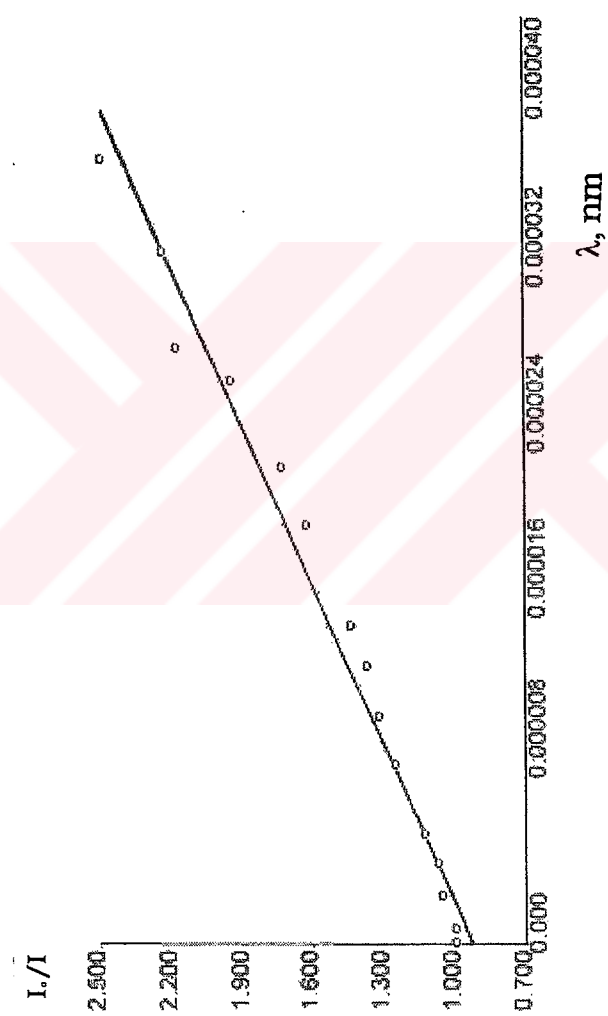


Figure 3.21 Stern-Volmer plot for fluorescence quenching of pyrene, in presence of increasing quencher concentrations, in acetonitrile

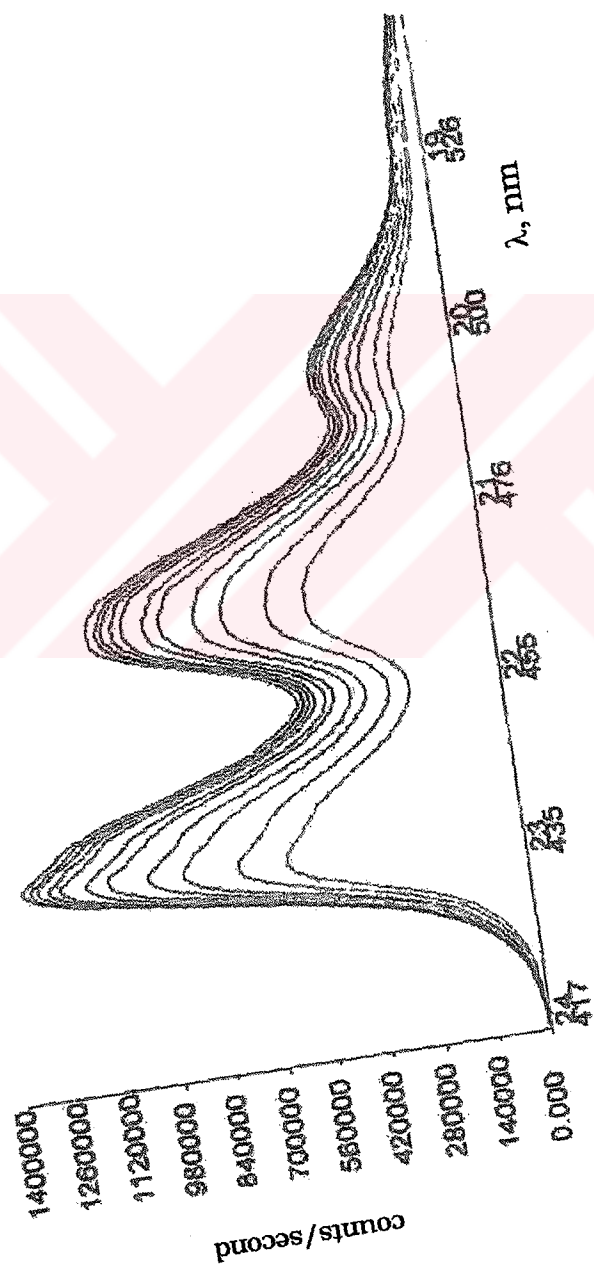


Figure 3.22 Fluorescence quenching of perylene by N,N'-bis-phenyl-1,4,5,8-naphthalenediimide (PNDI) in acetonitrile at quencher concentrations of 1×10^{-5} - 3×10^{-4} M

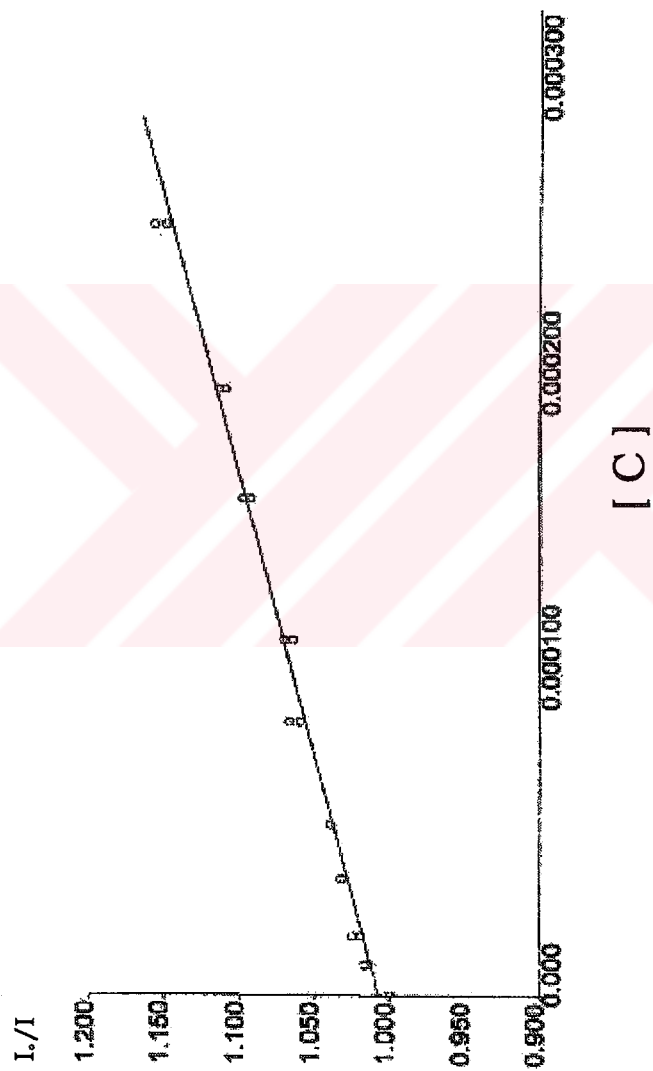


Figure 3.23 Stern-Volmer plot for fluorescence quenching of perylene, in presence of increasing quencher concentrations, in acetonitrile

Table 3.3 Fluorescence quenching rate constants of condensed aromatic π -electron donor molecules by the addition of *N,N'*-bis-*N*-phenyl-1,4,5,8-naphthalenediimide (I: PNDI) in acetonitrile

Compound	k_q ($M^{-1}s^{-1}$)
Naphtalene	$(2,63 \pm 0,55) \times 10^{10}$
Phenanthrene	$(7,18 \pm 1,36) \times 10^{10}$
Pyrene	$(1,91 \pm 0,24) \times 10^{10}$
Perylene	$(7,62 \pm 0,65) \times 10^{10}$

3.9 Fluorescence Quenching Studies with N,N'-bis-n-butyl-1,4,5,8-naphthalene diimide

N,N'-bis-n-butyl-1,4,5,8-naphthalenediimide is the most soluble derivative among the other naphthalenediimide derivatives in acetonitrile, chloroform and dichloromethane solvents. For this reason, fluorescence quenching studies were done by using N,N'-bis-n-butyl-1,4,5,8-naphthalenediimide. It was found that N,N'-bis-n-butyl-1,4,5,8-naphthalenediimide quenched fluorescence emissions of naphthalene and anthracene molecules. Calculated quenching rate constants are shown in Table 3.4.

Table 3.4 Fluorescence quenching rate constants of condensed aromatic π -electron donor molecules by the addition of N,N'-bis-n-butyl-1,4,5,8-naphthalene diimide.

Compound	Solvent	k_q ($M^{-1}s^{-1}$)
Naphthalene	Dichloromethane	$1,25 \times 10^{11}$
Anthracene	Acetonitrile	$1,82 \times 10^{11}$
Anthracene	Chloroform	$3,21 \times 10^{11}$

It is seen that quenching rate constants are above the diffusion control limit for naphthalene and anthracene in different solvents. However fluorescence quenching rates increased by the increase of π -electrons of donor molecules. Anthracene emissions is quenched by using N,N'-bis-n-butyl-1,4,5,8-naphthalenediimide derivative in acetonitrile 1,5 times faster respect to naphthalene and also anthracene is quenched by using N,N'-bis-n-butyl-1,4,5,8-naphthalenediimide derivative in chloroform 2,5 times faster respect to naphthalene. (Table 3.4)

3.10 Radiative Lifetime and Fluorescence Quenching Rate Constant Calculation of Anthracene

Figure 3.24 shows the UV absorption of anthracene in acetonitrile. The radiative lifetime τ_0 calculated from the formula:

$$\tau_0 = \frac{3,5 \times 10^8}{\nu_{\max}^2 \cdot \epsilon_{\max} \cdot \Delta\nu_{1/2}}$$

$$\nu = \frac{1}{\lambda} \text{ nm}$$

$$\epsilon = \frac{A}{l \cdot c} \text{ (l.mol}^{-1} \cdot \text{cm}^{-1}\text{)}$$

$$\nu_{\max} = \frac{1}{0,356} \times 10^4 \text{ cm}^{-1} = 2,81 \times 10^4 \text{ cm}^{-1}$$

$$\epsilon_{\max} = 5763$$

$$\Delta\nu = \left(\frac{1}{0,346} \times 10^4 - \frac{1}{0,359} \times 10^4 \right) = 0,1 \times 10^4 \text{ cm}^{-1}$$

$$\tau_0 = \frac{3,5 \times 10^8}{(2,81 \times 10^4)^2 \times 5763 \times 0,1 \times 10^4} = 76 \times 10^{-9} \text{ s}^{-1}$$

Figure 3.26 shows the Stern-Volmer plot drawn from emission intensities anthracene versus to quencher N,N'-bis-n-butyl-1,4,5,8-naphthalenediimide concentrations. Bimolecular quenching rate constant (k_q) calculated from the slopes of plots.

Calculations:

Quenching rate constant (k_q);

$[C]_{n\text{-butyl}}$	I_0/I
0	1,0
$0,32 \times 10^{-4}$	1,1
$0,65 \times 10^{-4}$	1,5
$0,94 \times 10^{-4}$	1,9
$1,26 \times 10^{-4}$	2,0
$1,61 \times 10^{-4}$	3,0

Slope = $1,3855 \times 10^{-4}$

$$\text{Slope} = k_q \cdot \tau_0 \quad k_q = (\text{slope} / \tau_0)$$

$$k_q = (1,3855 \times 10^{-4}) / (76 \times 10^{-9}) = 1,82 \times 10^{11} \text{ M}^{-1} \cdot \text{s}^{-1}$$

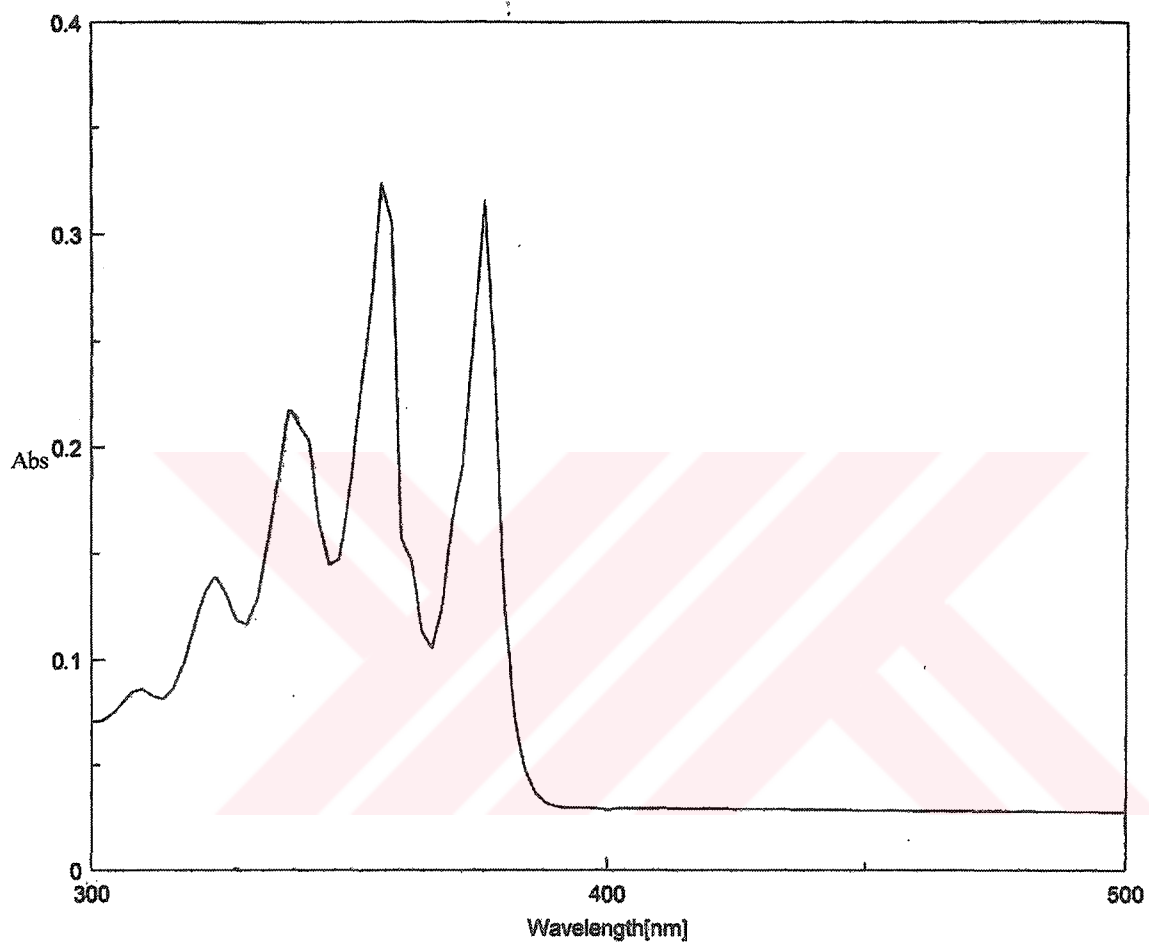


Figure 3.24 UV absorption spectrum of anthracene in acetonitrile

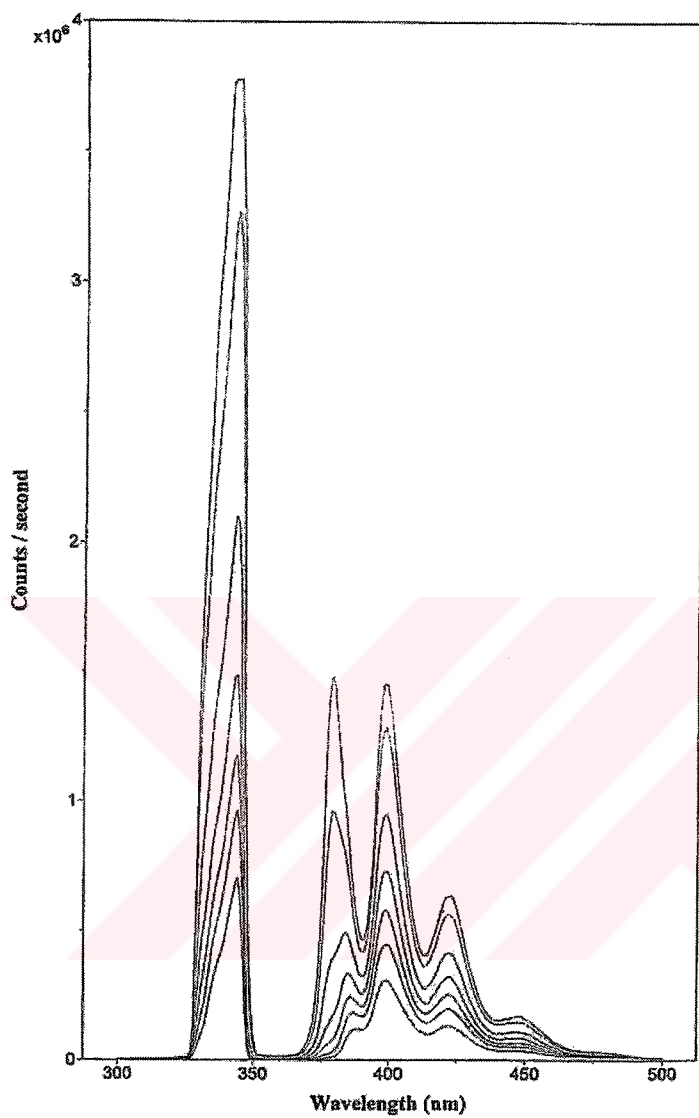


Figure 3.25 Fluorescence quenching of anthracene by N,N' -bis-*n*-butyl-1,4,5,8-naphthalenediimide in acetonitrile at quencher concentrations of 3×10^{-5} - 2×10^{-4}

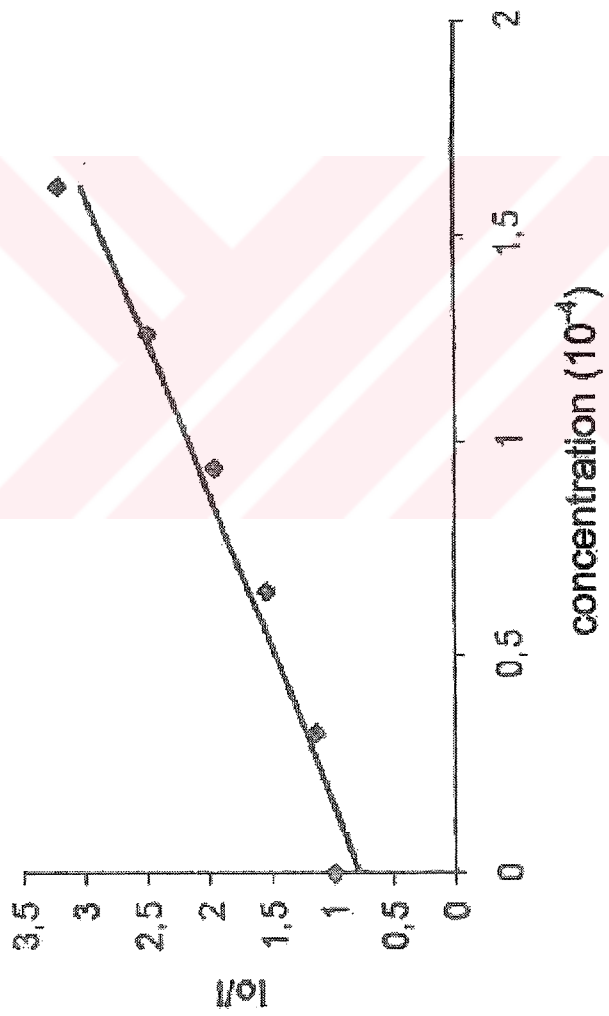


Figure 3.26 Stern-Volmer plot for fluorescence quenching of anthracene in presence of increasing quencher concentrations, in acetonitrile.

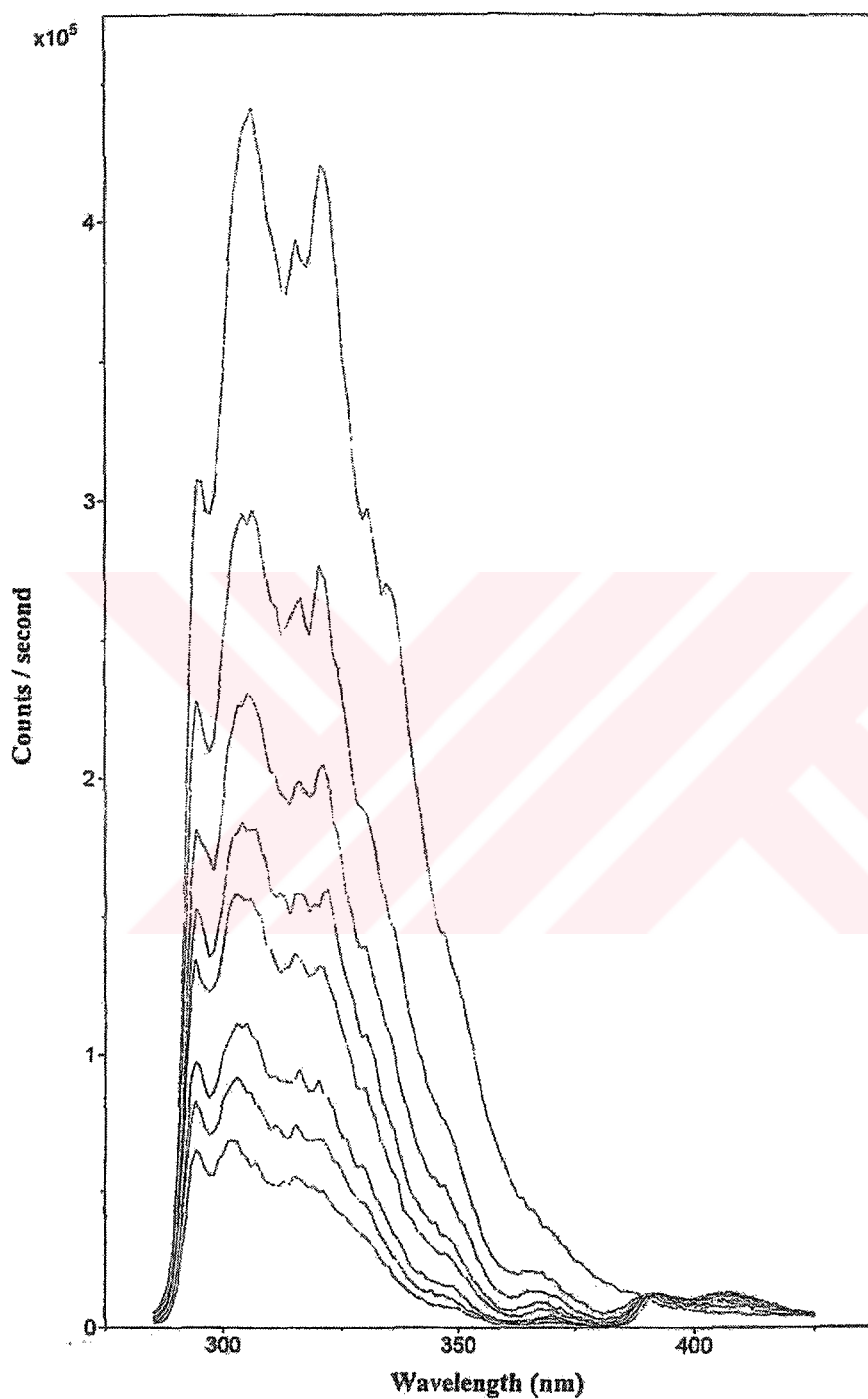


Figure 3.27 Fluorescence quenching of naphthalene by N,N'-bis-n-butyl-1,4,5,8-naphthalenediimide in dichloromethane at quencher concentrations of 3×10^{-5} - 2×10^{-4}

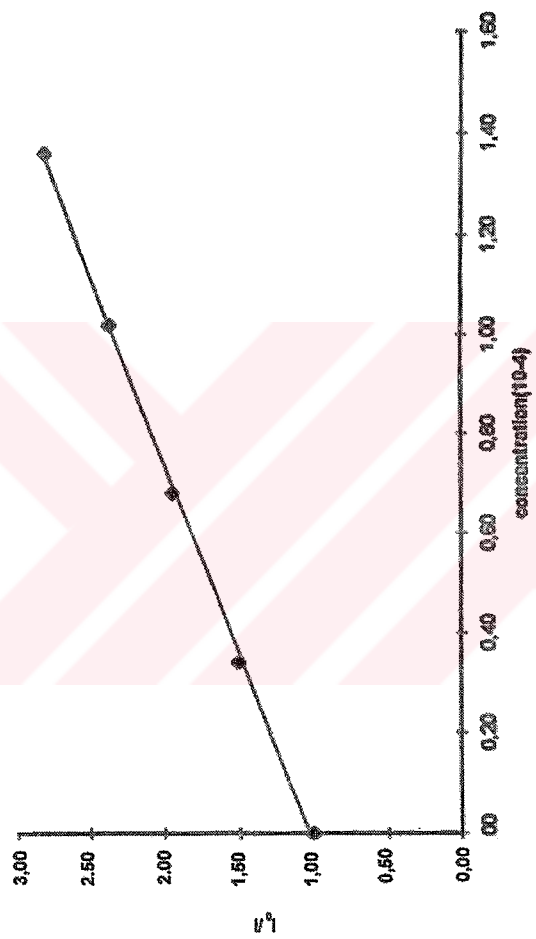


Figure 3.28 Stern-Volmer plot for fluorescence quenching of naphthalene in presence of increasing quencher concentrations in chloroform.

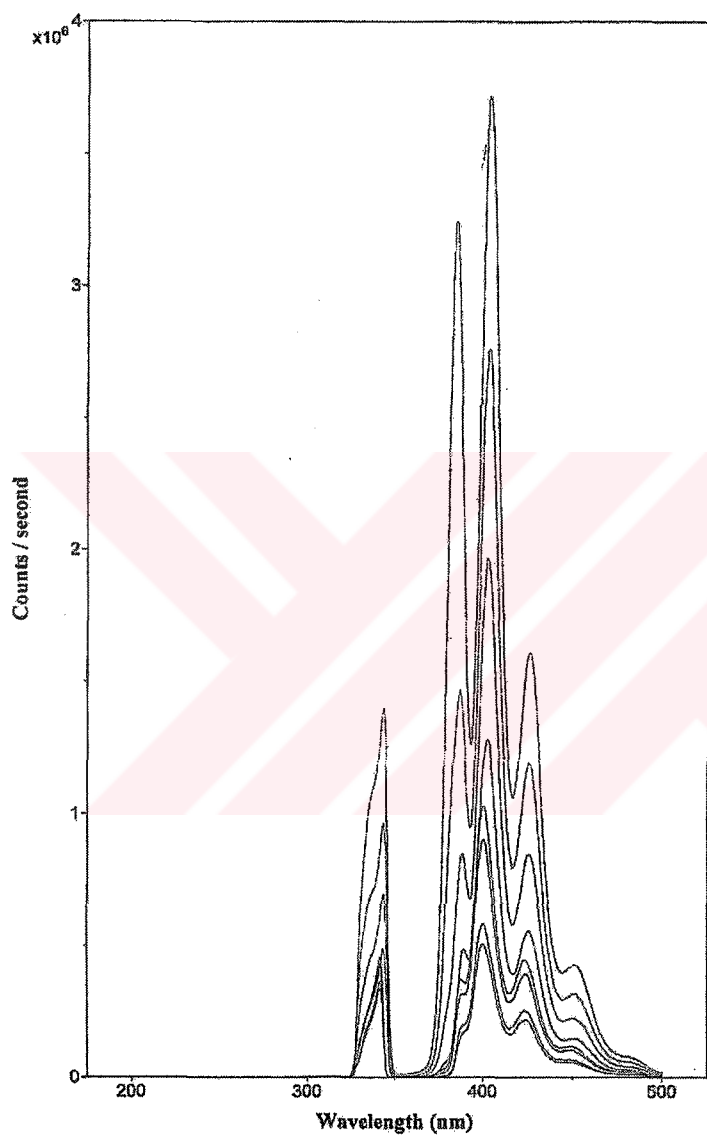


Figure 3.29 Fluorescence quenching of anthracene by N,N' -bis-*n*-butyl-1,4,5,8-naphthalenediimide in chloroform quencher concentrations of 3×10^{-5} - 2×10^{-4}

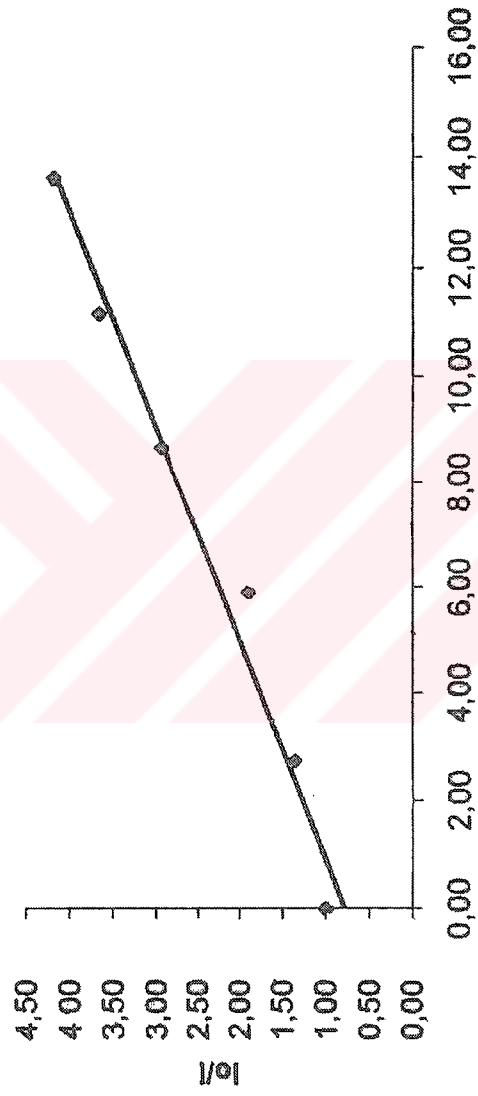


Figure 3.30 Stern-Volmer plot for quenching of anthracene in presence of increasing quencher concentrations, in chloroform.

The properties of seven different naphthalene diimide compounds were examined. The N-substituents of 1,4,5,8-naphthalenediimide have little effect on absorption and emission bands. However they have large effect on solubility and fluorescence quantum yields. All of the photophysical parameters obtained from UV-VIS absorption and emission spectra of naphthalene diimide derivatives are listed in Table 3.5

Table 3.5 Fluorescence quantum yields Φ_F , radiative lifetimes τ_0 (ns), fluorescence lifetimes τ_F (ps), fluorescence rate constants, k_F , (10^8 s^{-1}), and singlet energies, E_s (kcal mol^{-1}) data of naphthalene diimides in acetonitrile.

	Ar (R)	λ_{max}	ϵ_{max}	Φ_F	τ_0	τ_F	k_F	E_s
I	Phenyl	377	32500	0,002	3,1	6,2	3,2	75,9
II	<i>o</i> -Chlorophenyl	376	42900	0,002	2,3	4,6	4,3	76,1
III	<i>p</i> -Tolyl	376	32800	0,004	3,1	12,4	3,2	76,1
IV	α -Naphthyl	377	33000	0,005	3,1	15,5	3,2	75,9
V	n-Butyl	377	43500	0,006	2,3	13,8	4,3	75,9
VI	n-Dodecyl	377	33900	0,006	3,0	18,0	3,3	75,9
VII	Cyclohexyl	378	30600	0,004	3,1	12,4	3,2	75,7

These results show that the emission characteristics of naphthalene N,N' -disubstituted imides are strongly depend on steric and electronic effects of the bulky substituents bonded the imide nitrogen. Low fluorescence were found especially for aryl derivatives. Butyl and dodecyl derivatives have higher fluorescence than the other derivatives. Thus, even slight distortions of bulky substituents in the geometry of imide cycle would result in dissappearing of fluorescence. The lowest excited energy levels of naphthalene diimides are the characteristic of $n-\pi^*$. That's why, fluorescence quantum yields were observed in the range of 0,002-0,006 in acetonitrile. The calculated fluorescence lifetimes were between 5-18 ps. This means that, rapid intersystem crossing processes of naphthalene diimides have carried out from excited singlet state

Quenching experiments of fluorescence emissions of aromatic donor molecules such as naphthalene, phenanthrene, pyren, perylene were done by using N,N' -bis-phenyl-1,4,5,8-naphthalenediimide in acetonitrile solution and quenching rate constants were found between $k_q=2 \times 10^{10}$ - $8 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ which were above the diffusion control limit. Quenching experiments were repeated by using N,N' -bis-n-butyl-1,4,5,8-naphthalenediimide and quenching rate constants were found between $k_q=1 \times 10^{11}$ - $3 \times 10^{11} \text{ M}^{-1}\text{s}^{-1}$. These values are also above diffusion control limit compared to other results.

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