Synthesis and Characterization of A New Electron Acceptor Perylene Diimide for Further Functionalization

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We certify that we have read this thesis and that in our opinion it is fully adequate in scope and quality as a thesis for the degree of Master of Science in Chemistry.

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ABSTRACT

Nowadays, novel organic substances are broadly employed in numerous sensing architectures. Clever organic compounds with profound electrochemical and photophysical properties are important for photonic applications. Importantly, electron acceptor properties of perylene derivatives are well known.

In the present project, a new perylene bisimide named as N,N′-Bis(2-(4-hydroxyphenyl)ethyl)-3,4,9,10-perylenebis(dicarboximide) (HE-PDI) has been successfully synthesized. The synthesized HE-PDI was characterized by FT-IR and its photophysical properties were studied by UV–vis absorption and emission spectroscopy techniques.

HE-PDI has high extinction coefficient and fluorescence quantum yield (Φ_f = 0.91). The synthesized HE-PDI is completely soluble in the both dipolar aprotic (DMF, DMSO, etc.) and non-polar solvents like (CHL).

Keyword: Perlyene bisimide, Electron acceptor, Fluorescence quantum yield, thermal stability.

ÖZ

Günümüzde, sentezlenen yeui organik maddeler sensor yapılar olarak uygulanmaktadırlar. Üstün elektrokimyasal ve fotofiziksel özelliklere sahip akıllı organik ürünlere ihtiyaç vardır.

Bu çalışmada N,N'-Bis (2-(4-hidroksifeniletil)-3,4,9,10-perilenebis (dikarboksimid) (HE-PDI), başarıyla sentezlenmiştir. Sentezlenen HE-PDI, FT-IR spektroskopisi ile karakterize edildi. Fotofiziksel özellikleri UV-VIS absorblama ve floresans spektroskopik teknikleriyre çalışılmıştır.

HE-PDI, çok yüksek floresans kuantum verimi ($\Phi f = 0.91$) absorblama katsayısına sahiptir. Sentezlenen yeni ürün dipolar aprotik ve apolar çözücülerde tamamiyle çözünmektedir (DMF, CHL).

Anahtar Kelimeler: perilenebisimid, electron akseptör, floresans kuantum verim, termal kararlılık.

To My Family

ACKNOWLEDGMENT

To begin with I am very pleased to extend my sincere thanks and appreciations to my respectable and virtuous supervisor Prof. Dr. Huriye İcil who allows me to work under her leadership and supervision where I learned a lot and without her I would not be able to completed my research. Words are not enough to express the extent of my thanks and gratitude to her and promising to never forget her. Thank you very much. I would like also to express my thanks to Dr. Duygu Uzun who also helped me to complete my thesis so I am realy thankful.

I would like also to express my special thanks to my loveable and precious wife who has enormous strength and support me both morally and physically during my studies in this university.

My thanks also go to my dear mother who lives immortally in my heart and to my dear brother (sherzad) for their incomparable support throughout my life and studies.

Finally, I would like to thank the Prof. Dr. Huriye İcil's Organic Chemistry group at Eastern Mediterranean University.

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LIST OF SYMBOLS/ABBREVIATION

$\overset{o}{A}$	Armstrong
A	Absorption
AU	Arbitrary Unit
Br_2	Bromine
C	Concentration
ºC	Degrees celcius
CHL	Chloroform
CO_2	Carbon dioxide
cm	Centimeter
DMF	N,N’-dimethylformamide
E_g	Energy band gap
E_s	Singlet energy
ε_{max}	Maximum extinction coefficient
f	Oscillator strength
FTIR	Fourier Transform Infrared Spectroscopy
g	Gram
h	Hour
HOMO	Highest occupied molecular orbital
H_2SO_4	Sulfuric acid
ITO	Indium tin oxide
KBr	Potassium bromide
K_f	Fluorescence Rate Constant

l	Path length
LUMO	Lowest unoccupied molecular orbital
M	Molar concentration
MeOH	Methanol
nm	Nanometer
ns	Nano second
OFET	Organic field-effect transistor
OLED	Organic light emitting diode
OLED	Organic light emitting diodes
OSC	Organic solar cell
PDA	Perylene dianhydride
PDI	Perylene diimide
Φ_f	Fluorescence quantum yield
s	Second
SC	Solar cell
τ_0	Theoretical radiative lifetime
τ_f	Fluorescence lifetime
TLC	Thin layer chromatography
UV-vis	Ultraviolet visible absorption spectroscopy
$\bar{\nu}$	Wavenumber
$\bar{\nu}_{max}$	Maximum wavenumber/Mean frequency
λ	Wavelength
λ_{max}	Absorption wavelength maximum

Chapter 1

INTRODUCTION

1.1 Perylene Chromophore

A chromophore is the structural unit which is responsible for the color. Perylene itself is the basic compound that contains this chromophore [1]. Perylene chromophore is a structural group that contains multi aromatic rings which is shown in Figure 1.1.

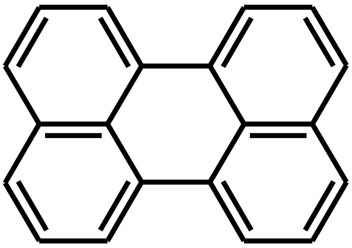


Figure 1.1: Perylene Chromophore

The perylene chromophore contains alternate double bonds with aromatic rings. The π–bond rich chromophoric structure provides brown to dark red color to the perylene compound. Moreover, the structure is very rigid in character due to the structure. In order to increase the potential applications of the π–bond rich perylene chromophoric structure, a commercial compound with anhydride groups was discovered as shown in Figure 1.2.

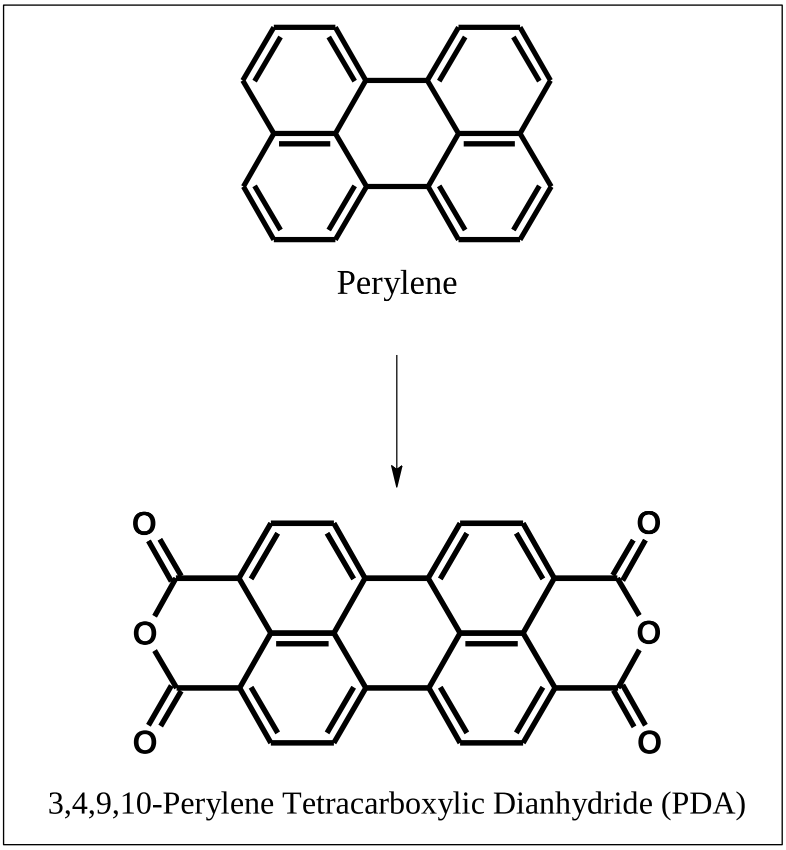


Figure 1.2: Perylene Chromophore Yielding to 3,4,9,10-Perylene Tetracarboxylic Dianhydride

3,4,9,10-Perylene tetracarboxylic dianhydride (PDA) (Figure 1.2) is responsible for the preparation of numerous perylene dyes with versatile properties [2-12].

1.2 Perylene Dyes Based on Perylene Chromophore

The rigid perylene dianhydride structure contains four carbonyl groups (interconnected as anhydride groups). The two anhydride groups offer tailoring of the whole structure to convert into imide functional groups with versatile substituents as shown in Figure 1.3 [2–4, 7–10].

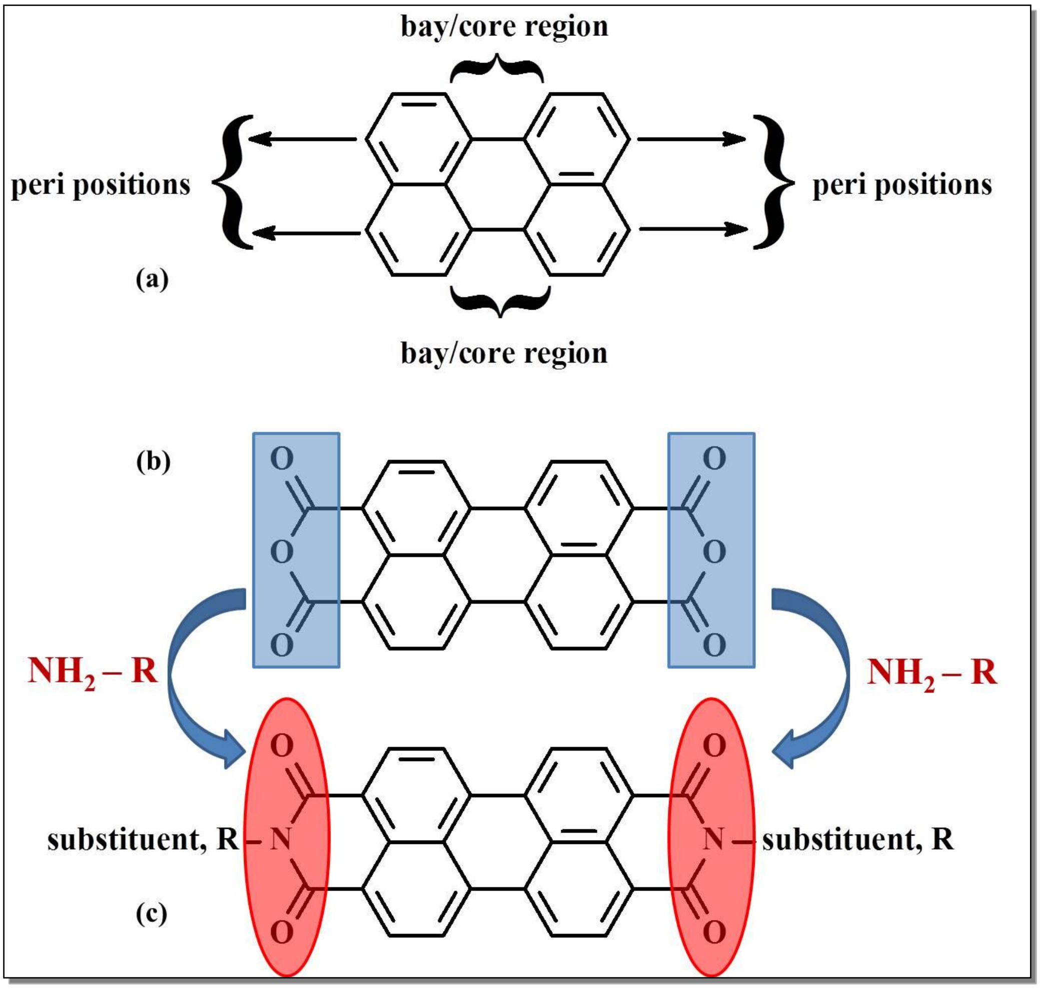


Figure 1.3: (a) Peri-positions and Bay Regions of Perylene Chromophore, (b) anhydride groups attached to the perylene core, (c) conversion of anhydride groups into imide functional groups

As shown in Figure 1.3 different derivatives of perylene dyes (namely perylene diimide, monoimide, and polyimide) were possible to synthesize by substituting various substituents at the imide regions of the perylene chromophore. Another advantageous part is the preparation of these perylene dyes are possible from the additional substitution at bay region [4, 13, 14]. The rigid structure combined with four carbonyl groups make the whole structure useful with excellent thermal, optical and electronic properties. This makes them potential candidates in various industries such as electronic and renewable energy [2–15].

The perylene diimide, monoimide and polyimide dyes that can be resulted upon substitution at various regions of perylene chromophore are having superior properties when compared to the similar π-conjugated compounds. This is attributed to the substituted structural moieties which possess the additional optical, electronic properties. The attached structural substituents generally bring harmony to result in additional strength through hydrogen bonding, stacking interactions, etc [2–15].

In the present project a new perylene bisimide named N,N′-Bis(2-(4-hydroxyphenyl)ethyl)-3,4,9,10-perylenebis(dicarboximide) (HE-PDI) has been successfully synthesized (Figure 1.4). An aliphatic substituent that has an aromatic group is introduced at imide positions to improve the solubility, photophysical and electrochemical characteristics of the perylene diimide. The synthesized HE-PDI was characterized by FT-IR and its photophysical properties were studied by UV–vis and emission spectroscopy.

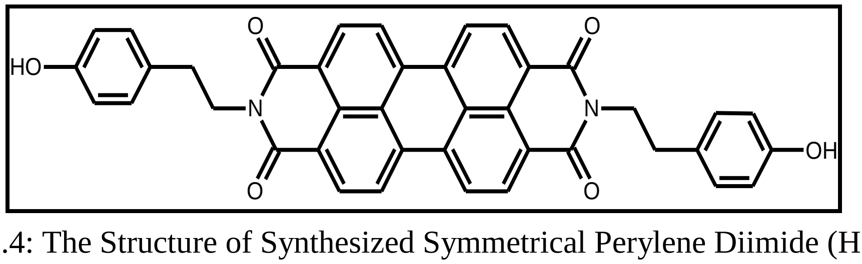


Figure 1.4: The Structure of Synthesized Symmetrical Perylene Diimide (HE-PDI)

Chapter 2

THEORETICAL

2.1 π-Conjugated Perylene Dyes

Possessing π-conjugation is usually occupying the central preference in particular design of a perylene dye due to the fact that conjugation is the core which govern and harmonize the properties [4]. The π-delocalization of the perylene core is shown in Figure 2.1.

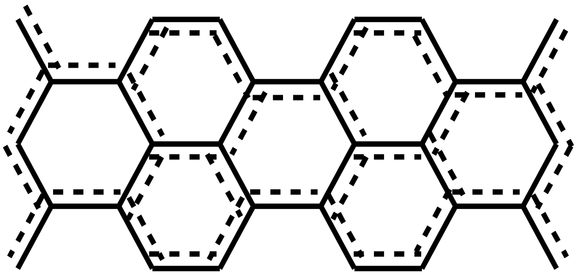


Figure 2.1: Representation of Charge Delocalization (dotted line) in a Perylene Chromophore

A versatile perylene dyes are possible to prepare depending on the necessity of application with the utility of π-conjugation [16, 17]. The most important point concerning the perylene dyes is the harmony between the central perylene core and the substituent moiety that is attached at a particular position of the perylene core. The substituents that are attached to the core should not destruct the core properties. Some π-rich perylene dyes previously reported for various applications were shown in Figure 2.2.

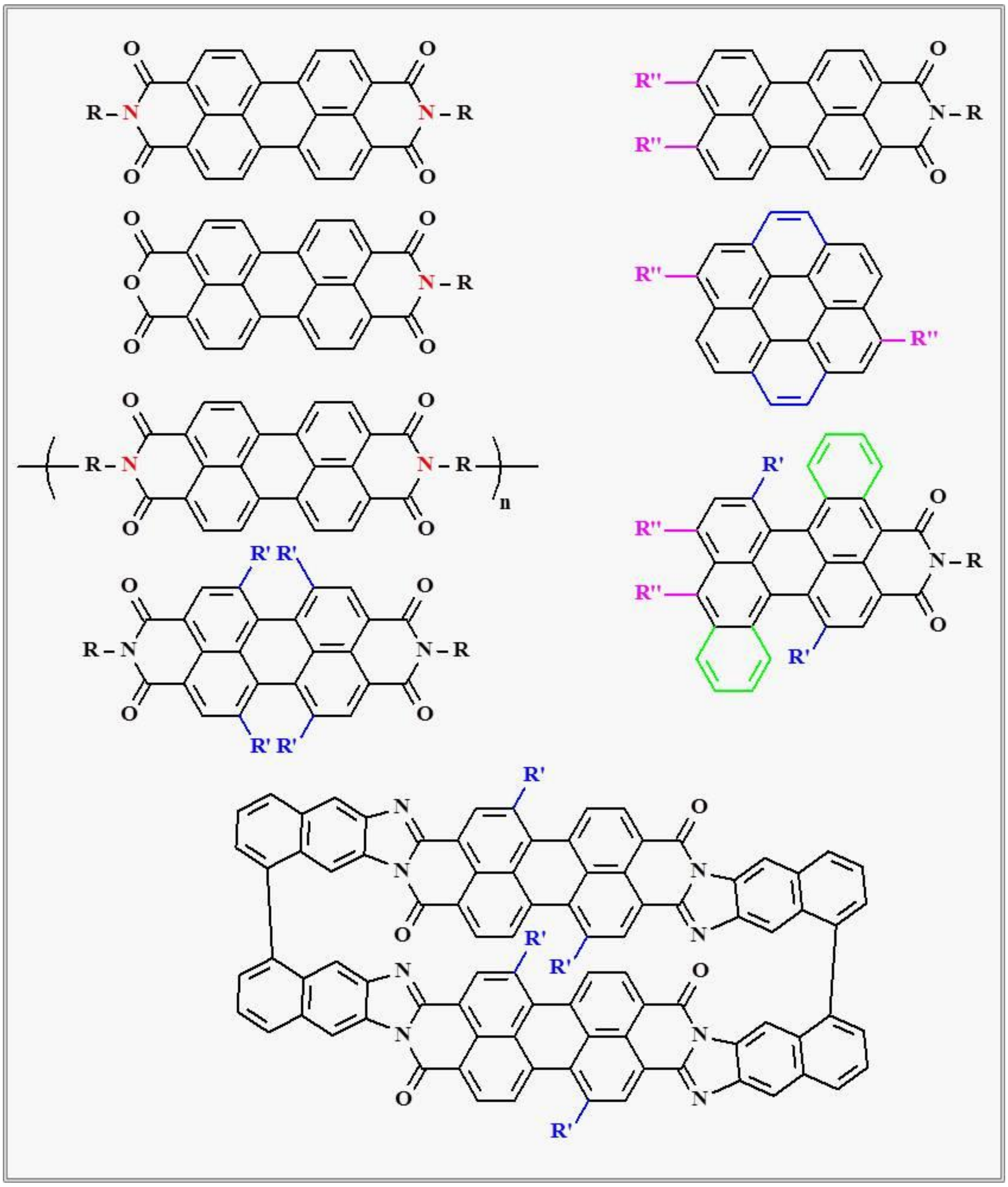


Figure 2.2: General Structures of Various π-Conjugated Perylene Dyes Reported in Literature (the substituted moieties are shown with R, R′, and R′′) [3, 18–21]

2.1.1 Structural Advantages of Perylene Chromophoric Dyes for Solar Cells

As shown in Figures 1.3 and 2.2, central perylene core offers substitution at bay region and peri-positions. The π-rich core of perylene chromophore can be attached a vast variety of substituents. Additionally, peri-positions were also readily attached by various functional moieties [22]. An efficient method of extending the conjugation is to introduce benzimidazole groups at the anhydride groups of perylene dianhydride structure (bottom compound of Figure 2.2) [23]. On the other hand, replacing the anhydride groups with imide functional units is the classical derivation of perylene dyes. The imide substitution can be carried out in different procedures to yield symmetrical and unsymmetrical perylene diimides (Figure 2.3) [2].

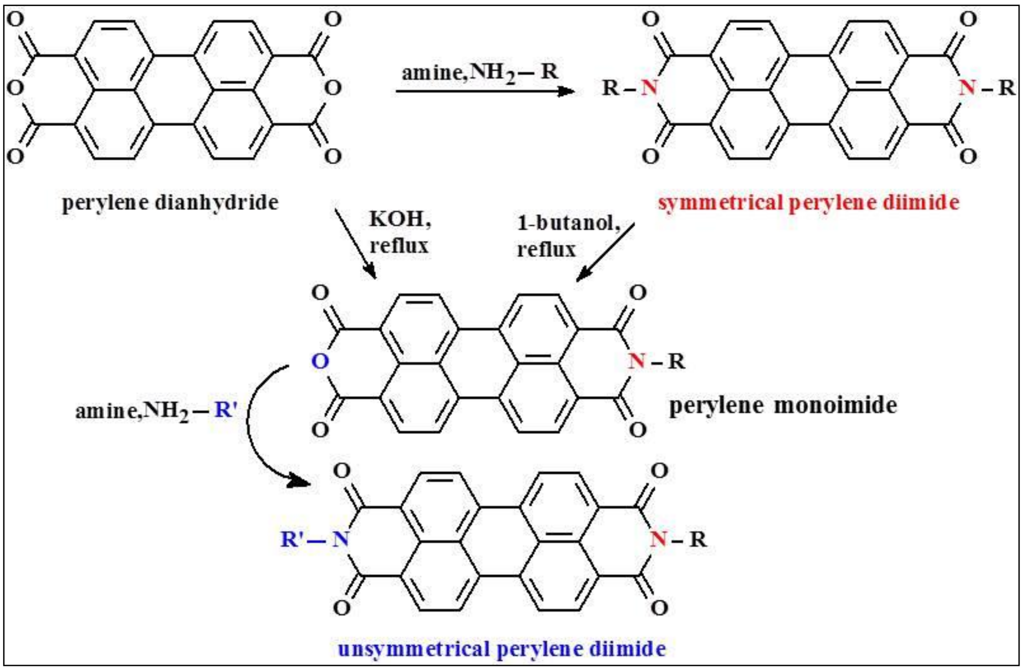


Figure 2.3: Structural Advantage of Perylene Dianhydride Chromophore to Convert it into Various Symmetrical and Unsymmetrical Perylene Dyes

The wide variety of substitution at perylene chromophore thus used to design perylene dyes according to the necessity of application.

2.1.2 Functionalization of Perylene Chromophore with Versatile Substitution

Figures 1.3 and 2.3 justify the key point of producing a vast variety of perylene dyes. The functional moieties that can be attached to perylene chromophore are also wide and offer exciting applications. The functionalization at various positions of the chromophore is discussed in Figure 2.4. The resulting functional perylene dyes that were previously reported were shown in Figure 2.5.

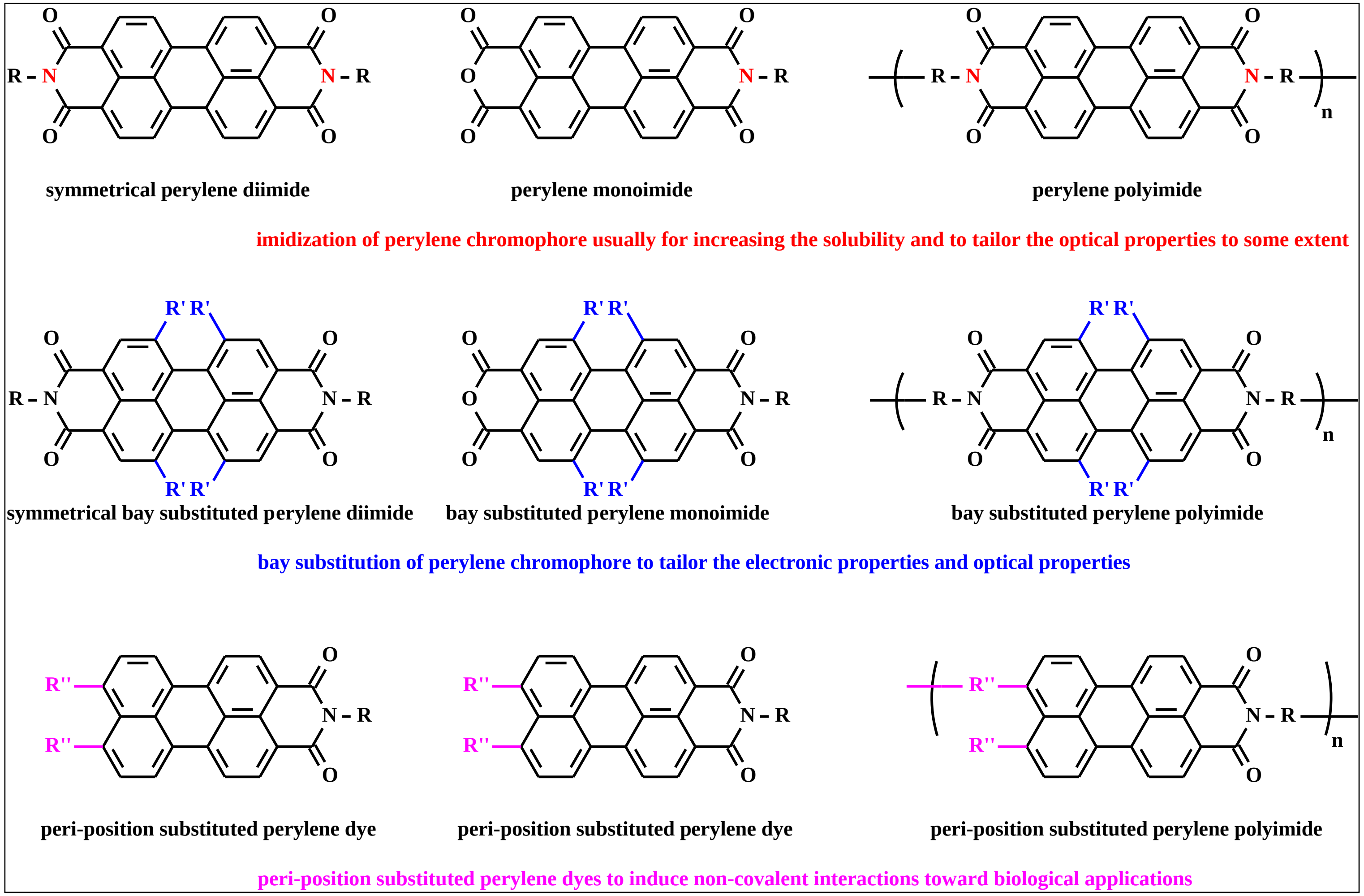


Figure 2.4: Functionalization of Perylene Chromophore to Result in Various Perylene Dyes [2–23]

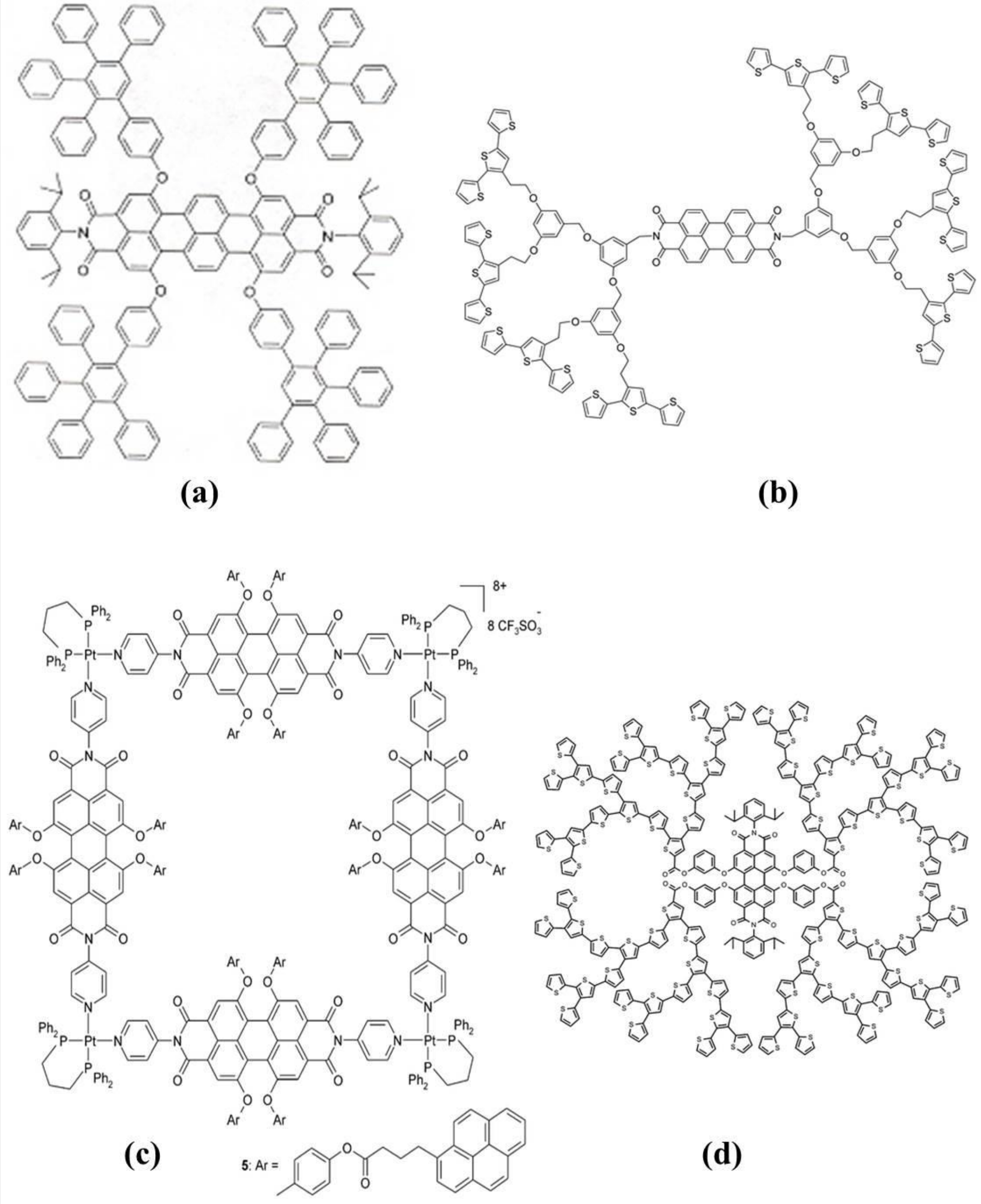


Figure 2.5: Functionalization of Perylene Dyes with Thio-, Arylene-Units to Result in Functional Perylene Archtectures, respectively [24–27]

Generally, thiophene units are widely introduced onto perylene chromophoric moieties to result in dendritic perylene architectures(structures a, b and d shown in Figure 2.5). Similarly, metal ligand introduced functionalization and aromatic unit attachment, etc are frequently followed methods (Figure 2.5 c).

2.2 Important Properties of Perylene Dyes

The most important properties of perylene dyes are generally classified into three types: (i) photophysical, (ii) electorchemical and (iii) thermal properties [2–15].

Perylene derivatives are generally exhibit high thermal stabilities (above 350 ^{o}C) due to the rigid conjugated aromatic structure. There is a possibility in increment and reduction of thermal stability with respect to imidization or bay substitution. However, most of the perylene dyes exhibit an increase in thermal stability when aromatic functional moieties are attached [2–15].

2.2.1 Photophysical Characterization

The optical properties of perylene derivatives are explored through photophysical characterization. One of the most exciting properties of perylene dyes are optical properties due to their strong light absorption and emission characteristics. The absorption spectra, fluorescence spectra and excitation spectra could be measured in solution and solid-state by respective spectrophotometers. The data obtained through the spectra can be analysed and the optical parameters can be evaluated [2–15]. The optical parameters give a clear optical profile of the compound to explore its ability in utilizing various applications. Usually, the measured absorption and fluorescence/emission spectra can give the following optical data.

(i) Absorption strength (measured in terms of molar absorptivity and oscillator strength)

(ii) The singlet energy data (the energy required to pass to excited state)

(iii) The fluorescence ability

(iv) The radiative lifetime data, etc.

The perylene derivatives usually possess very strong absorption capacities with high molar absorption coefficients. The π-conjugated structure causes the compound to absorb in the visible region of the electromagnetic spectrum. The high absorption coefficients of perylene dyes make them to utilize in organic solar cells. Icil and co-workers reported a very huge absorption capacity of naphthalene dyes [28] which are belonging to the family of rylene derivatives like perylene dyes [28]. However, they have also reported high maximum absorption coefficients of various perylene dyes [2, 3, 5–15]. High absorption is one of the primary requirements of dyes concerning organic material based solar cells. Therefore, perylene dyes are considered as potential candidates for solar cell applications. The singlet energy data that can be obtained from its corresponding absorption spectrum gives an idea of electronic transition from ground state to excited state. Generally, perylene dyes excite to first, second and third vibrational levels of first excited singlet state from ground state [2, 3, 5–15].

One of the most attracting properties of perylene dyes is their fluorescence capacity. They are capable of emitting all the light that is absorbed. Therefore, their fluorescence spectra are like mirror images of their corresponding absorption spectra. Fluorescence quantum yield is the measure of fluorescence capacity and perylene dyes usually exhibit unity (=1) fluorescence quantum yields in solutions [9]. The fluorescence of perylene derivatives is usually in the visible region of the electromagnetic spectrum and therefore emits intense green, orange, yellow and red colors. They also exhibit good fluorescence rate constants. Absorption and emission in solution and solid-states are the most key points to consider them in relevant potential applications industrially [12].

The photophysical properties are usually affected to some extent upon attaching various functional moieties at the imide positions of the perylene chromophore. The substitution at bay region with relevant moieties greatly alters the photophysical properties [17]. However, the substitution at imide positions could bring good solubilities to increase the processability of perylene derivatives (Figures 2.3 and 2.4) [3].

The substituents attached at various positions of perylene chromophore could usually cause hydrogen bonding, π–π stacking, aggregation, photoinduced electron transfer (charge transfer) and energy transfer, self-assembly, and folding, etc. These listed phenomena are non-covalent interactions which could greatly alter the photophysical characteristics of the system [2–28].

2.2.2 Electrochemical Characterization

The π-conjugated perylene chromophoric system is electrically active as it can undergo redox changes. The four carbonyl groups (interconnected with anhydride groups) accept at least two electrons to form a monoanion and dianion, respectively. This makes the perylene dyes excellent electron acceptors [2, 3, 10, 12]. However, the substituent moieties that attached especially at bay region could bring oxidising capacity by donating an electron. Usually, this is carried out by attaching thiophene moieties both at the imide and the bay regions of perylene chromophore (Figures 2.4 and 2.5) [17]. The redox behaviour of perylene dyes is usually examined through cyclic and squarewave voltammetry techniques. The data is analyzed to estimate the molecular orbital energies (HOMO, highest occupied molecular orbital and LUMO, lowest unoccupied molecular orbital) and resulting band gap (E_g) energies. These energy values decide the potential of being utilized in organic solar cells as efficient *n*-type/*p*-type semiconductors [2, 3, 10, 12].

2.3 Concept of Solar Cells

The conventional silicon solar cells were proved to be the major renewable energy resources which can directly convert solar light into electricity. The efficiencies of these silicon solar cells depend on the quality of silicon. However, they have limitations of high cost, complex processing steps, and environmental pollution [1]. The organic solar cells based on synthesized organic materials are emerging as competent devices to replace the conventional solar cells [1].

Organic solar cells employ π-conjugated organic materials that are capable of producing free charges. Usually this is carried out by employing an electron acceptor and an electron donor as a blend. Later, the blend is enclosed with a suitable positive and a negative electrode. When the sunlight strikes the blend material, the electron donor material delivers a free electron leaving a hole behind. The free electrons will be accepted by the electron accepting material and it passes the free electron to respective electrode. On the other hand, the holes will be migrated to respective electrode. When the electrodes are connected to an internal circuit, the charges freely circulate and produce electric current (Figure 2.6) [22].

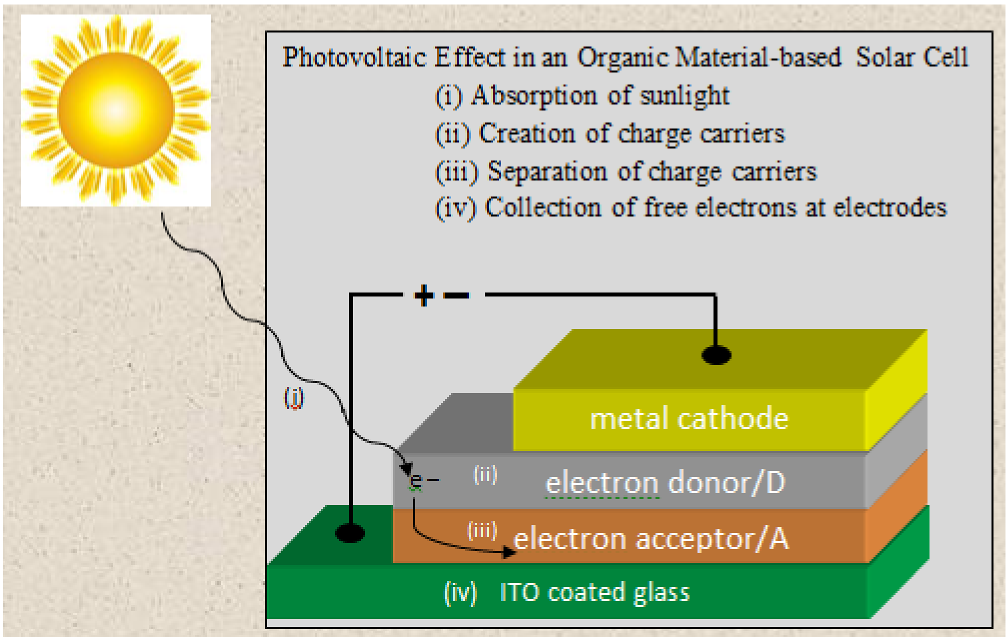


Figure 2.6: The Organic Solar Cell Construction with the Blend of Electron Donating and Accepting Materials

2.4 Applications of π-Conjugated Perylene Dyes

Perylene derivatives have profound application profile in many areas. When attached positively charged substituent which can also able to induce hydrogen bonding, there is a great possibility to bind to DNA. As perylene dyes are emissive, they can also be used in fluorescent and biological labelling. When bound to DNA, G-quadruplex structures can be formed which can prevent telomerase. On the other hand, the optical and electrochemical properties of perylene dyes are more attractive toward electronic applications [29].

2.4.1 Perylene Dyes as Renewable Energy Materials

Perylene dyes are excellent electron acceptors and are electroactive due to the four carbonyl groups present in their structure. The π-conjugation helps in stabilizing the charge and therefore the compounds acts as good *n*-type semiconductors. Therefore, perylene dyes are used in organic solar cells. Figure 2.6 explains the detailed mechanism involved in organic solar cells [17, 22, 27, 30–32].

2.4.2 Perylene Dyes in Molecular Electronics

Perylene dyes possess interesting optical properties and can be tailored by attaching suitable functional moieties. The strong absorption and emission properties are thus possible depending on the substituent attached. The light emitting capacities in conjunction with the *n*-type semiconducting property, perylene dyes are employed in organic light emitting diodes (OLEDs) and organic field effect transistors (OFETs). Several fluorescent sensors are reported based on perylene dyes which is attributed to the high emissive capacities of perylene dyes [16,17,27,30–32].

Chapter 3

EXPERIMENTAL

3.1 Materails

Perylene-3,4,9,10-tetracarboxylic acid dianhydride obtained from FLUKA. Isoquinoline, Tyramine, Zinc acetate and m-cresol were obtained from SIGMA ALDRICH.

Some required solvent like aceton, ethanol were obtained from SIGMA ALDRICH and purified by simple distillation.

3.2 Instruments

Infrared Spectra

Infrared Spectra (FT-IR) were recorded in the solid states by using potassium bromide (KBr) pellets with a JASCO FT-IR spectrophotometer.

Ultraviolet (Uv-vis) Absorption Spectra

Ultraviolet (Uv-vis) Spectra at different solvents were measured with Varian Cary 100 spectrophotometer.

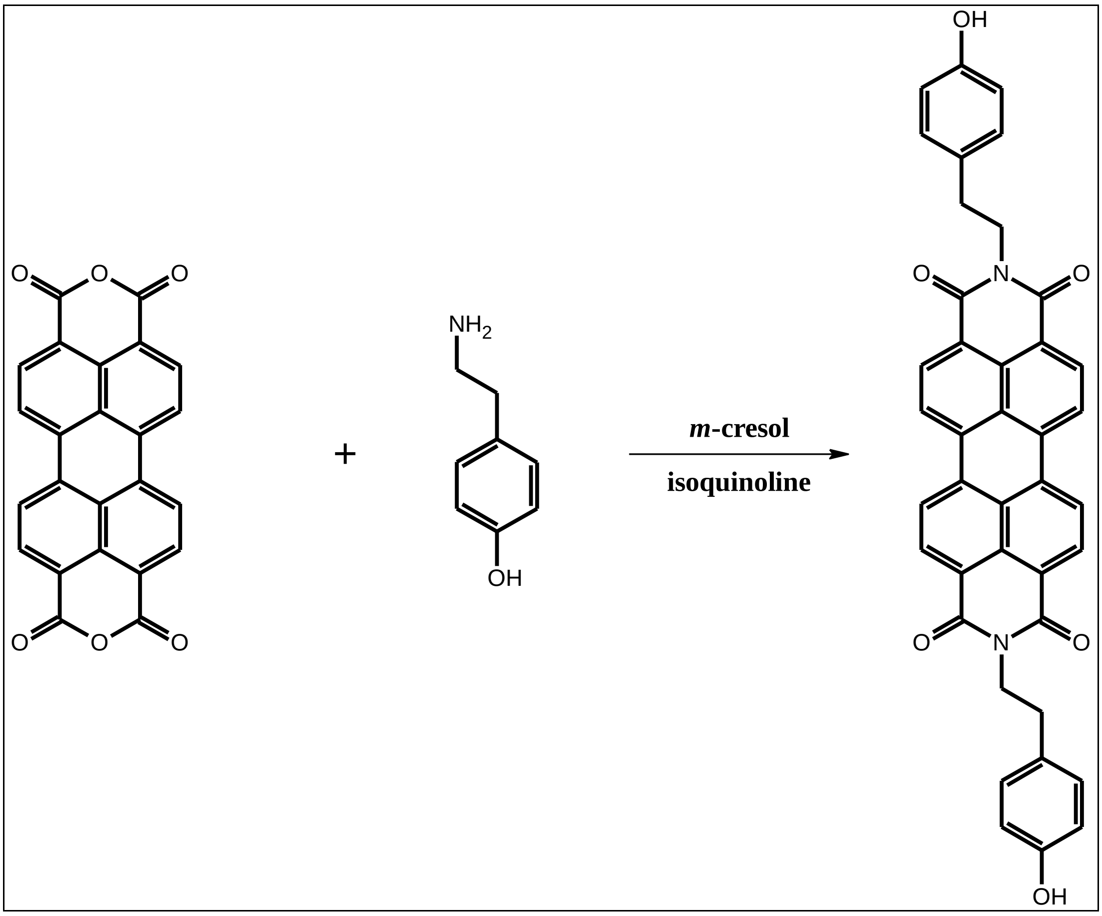
Emission/Fluorescence spectra

Emission/Fluorescence spectra were measured by using Varian/Cary Eclipse spectrophotometer.

3.3 Synthetic Method for N,N′-Bis(2-(4-hydroxyphenyl)ethyl)-3,4,9,10-perylenebis(dicarboximide)(HE-PDI).

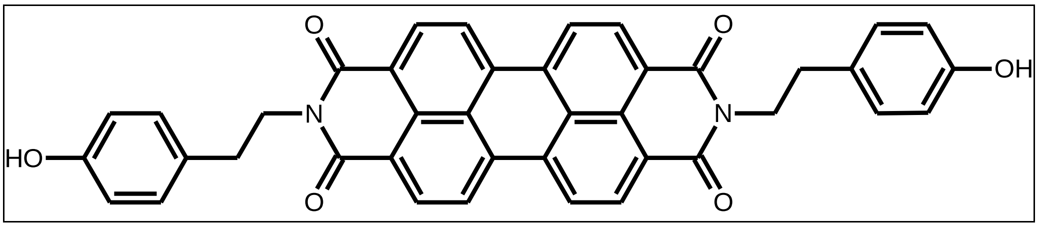
The purpose of this project is to design and synthesize a new electron acceptor perylene bisimide derivative for solar cell applications. (N,N′-Bis(2-(4-hydroxyphenyl)ethyl)-3,4,9,10-perylenebis(dicarboximide)(HE-PDI) for this purpose was synthesized by a condensation reaction in one step.

The general reaction for the synthesis of N,N′-Bis(2-(4-hydroxyphenyl)ethyl)-3,4,9,10-perylenebis(dicarboximide), (HE-PDI) is shown in Scheme 3.1



Schem 3.1: Synthesis of N,N′-Bis(2-(4-hydroxyphenyl)ethyl)-3,4,9,10-perylenebis(dicarboximide)(HE-PDI).

3.3.1 Synthesis of N,N′-Bis (2-(4-hydroxyphenyl)ethyl*)*-3,4,9,10-Perylenebis (dicarboximide) (HE-PDI)



A mixture of perylene-3,4,9,10-tetracarboxylic acid dianhydride (1.044 g, 2.66 mmol), Tyramine (0.879 g, 6.41 mmol), Zinc acetate (0.561g, 2.556 mmol), m-cresol (40 mL) and isoquinoline (4 ml) were stirred under Ar atmosphere. The reaction mixture heated at 80° C for 1 hour, at 120° C for 1 hour, at 150° C for 2 hours, at 180° C for 3 hours and finally was heated at 200° C for 3 hours. Then the warm solution poured into 250 ml of ethanol. After precipitation the precipitate filtered off via suction filtration and purified by ethanol soxhlet for 20 hours. The pure product dried at 100° C in vaccum oven for 24 hours.

Yield: 95.77%**,** (1.607) **Color :** Brown Solid**.**

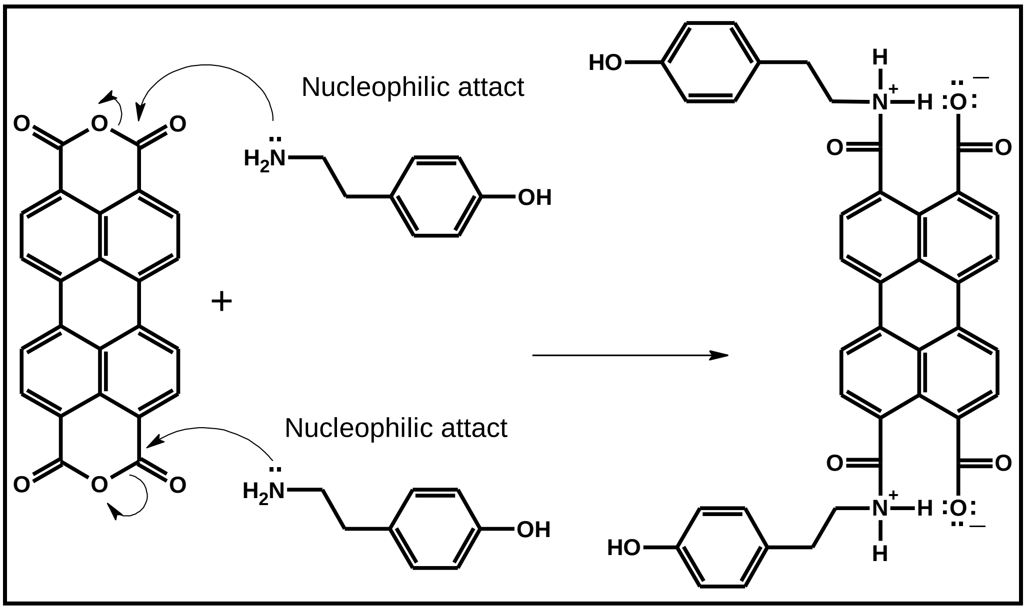
FT-IR (KBr, cm^{-1}) : ν =3387, 3010, 2926, 1691, 1648, 1593, 1339, 1577, 1260, 809 746.

UV-Vis ($CHCl_3$) λ_{max}/nm; (ε_{max}/L.mol^{-1}.cm^{-1}) : 459 (7240), 488 (10500), 525 (13700).

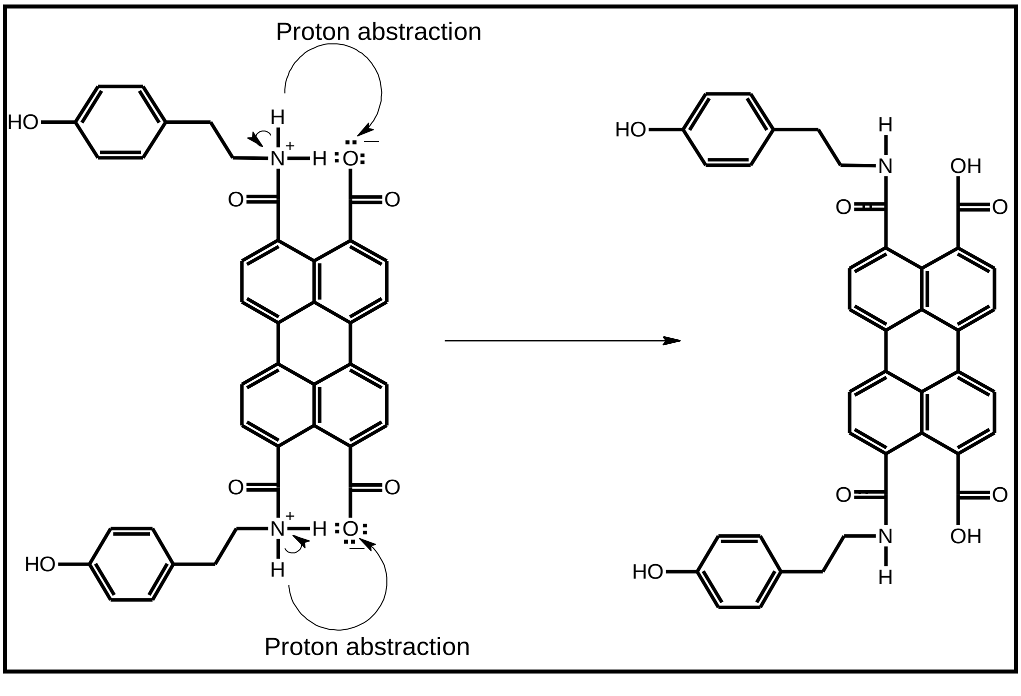
Emission ($CHCl_3$) (λ_{max}/nm) : 533, 574, 622; Φ_f = 0.91

3.4 Reaction Mechanisms

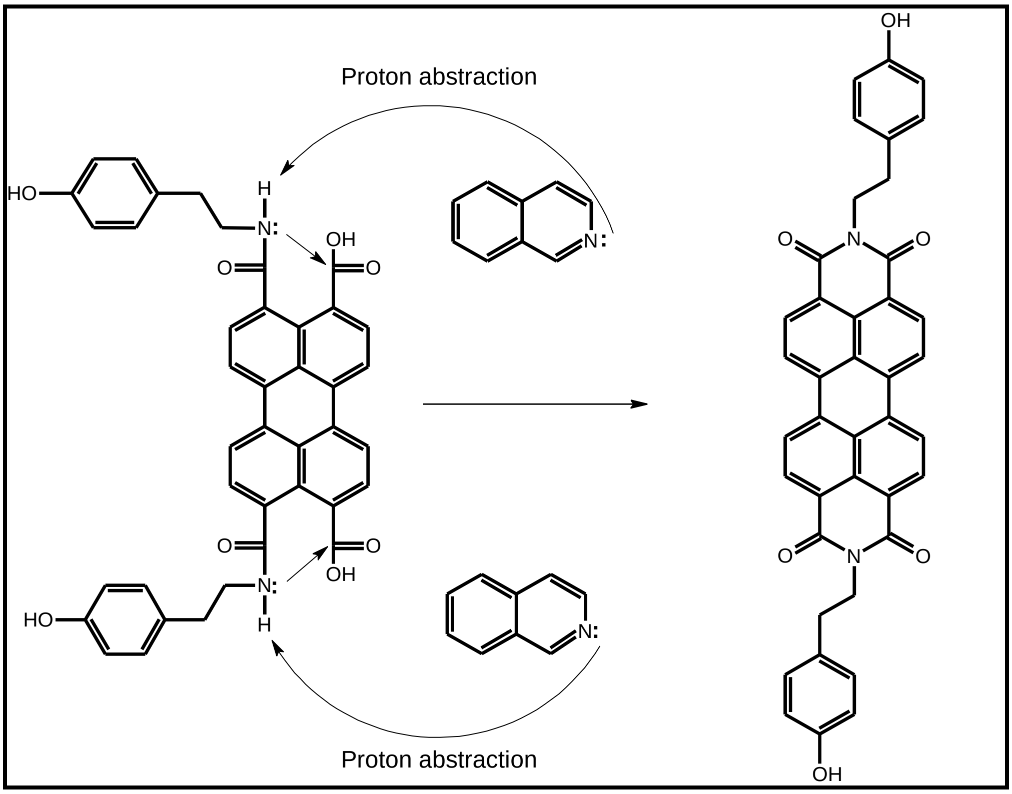
STEP 1



STEP 2



STEP 3


Proton abstraction
HO
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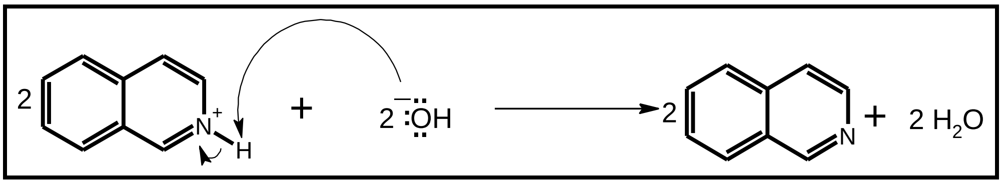
Proton abstraction

STEP 4


2
N+
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N
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Chapter 4

DATA AND CALCULATIONS

4.1 Calculations of Fluorescence Quantum Yield (Φ_f)

The fluorescence quantum yield is the ratio of absorbed photons to emitted photons through fluorescence and formulated as:

$$\Phi_f = \frac{\textbf{number of photons emitted}}{\textbf{number of photon absorbed}}$$

Fluorescence quantum yield is an important parameter to indicate the properties of a molecule if it emits all the absorbed light or if it deactivate the absorbed light by heat. Williams et al. method is one of the well known and used comparative method in order to calculate Φ_f of a compound by using well standard samples that is characterized and its Φ_f is known. It is considerd that, at the same excitation wavelength, both the test and standard compounds solutions have absorbed equal number of photons. The ratio of integrated fluorescence intensities of the two solutions compounds give the quantum yield value. The unknown compound's Φ_f value is calculated by using the given below and a standard compound that its Φ_f is known [33].

Calculation of Fluorescence Quantum Yield (Φ_f)

$$\boldsymbol{\Phi_f(U) = \frac{A_{std}}{A_u} \times \frac{S_u}{S_{std}} \times \left[\frac{n_u}{n_{std}}\right]^2 \times \Phi_{std}}$$

Φ_f (U) : Fluorescence quantum yield of unknown

A_{std} : Absorbance of the reference at the excitation wavelength

A_u : Absorbance of the unknown at the excitation wavelength

S_{std} : The integrated emission area across the band of reference

S_u : The integrated emission area across the band of unknown

n_{std} : Refractive index of reference solvent

n_u : Refractive index of unknown solvent

Φ_{std} : Fluorescence quantum yield of reference

Φ_f calculation of HE-PDI in DMF

N,N′-bis(dodecyl)-3,4,9,10-perylenebis(biscarboximide) was used as reference. Its Φ_f = 1 in chloroform [9]. Both the reference and synthesized HE-PDI were excited at the excitation wavelength, $\lambda_{exc} = 485$ nm.

A_{std} = 0.1055

A_u = 0.12

S_u = 4401.87

S_{std} = 4129.22

n_{std} = 1.446

n_u = 1.428

$$\Phi_f = \frac{0.1055}{0.12} \times \frac{4401.87}{4129.22} \times \left[\frac{1.428}{1.446}\right]^2 \times 1$$

Φ_f = 0.91

4.2 Calculation of Molar Absorptivity (ε_{max}) of N,N′-Bis(2-(4-hydroxyphenyl) ethyl)-3,4,9,10-perylenebis(dicarboximide)

According to Beer-Lambert Law, the maximum molar absorptivity was calculated for HE-PDI, by using formula given below:

$$\varepsilon_{max} = \frac{A}{cl}$$

ε_{max} : Maximum molar absorptivity in ($L \cdot mol^{-1} \cdot cm^{-1}$) at λ_{max}

A : Absorbance

c : Concentration ($mol \cdot L^{-1}$)

l : Cell length (cm)

The ε_{max} Calculation of HE-PDI

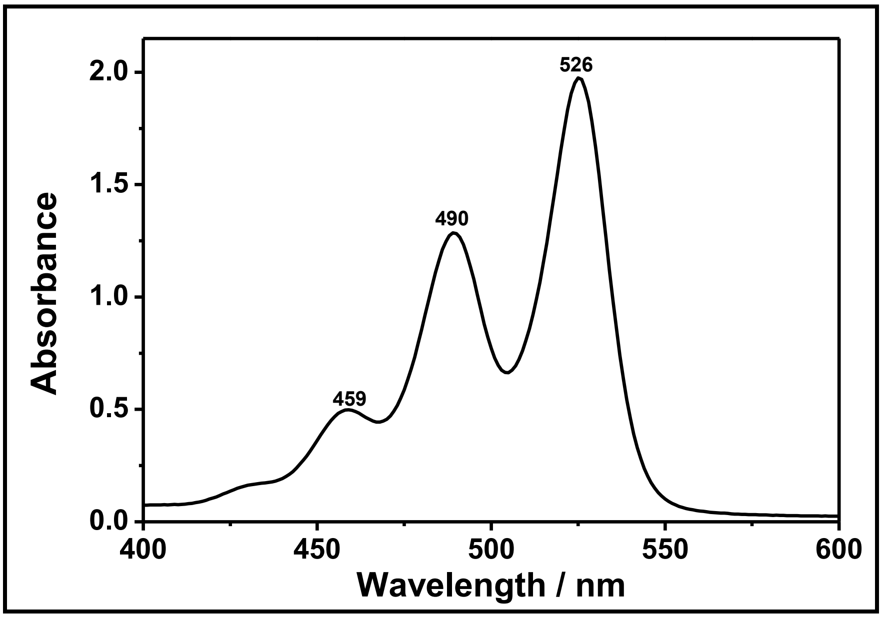

Figure 4.1: Absorption Spectrum of HE-PDI in DMF at 1×10^{-5} M

From the Figure 4.1

C = 1×10^{-5} M

A = 1.02 at $\lambda_{max} = 526$nm. l = 1 cm

$\Rightarrow \varepsilon_{max} = \frac{1.02}{1\times10^{-5}\text{M}\times 1\text{cm}}$ = 102000 L • mol^{-1} • cm^{-1}

$\Rightarrow \varepsilon_{max}$ of HE − PDI = 102000 L • mol^{-1} • cm^{-1}

Similarly, the molar absorptivity of HE-PDI in different solvents were calculated and the results are listed in the Table 4.2.

Table 4.1: Molar Absorptivity (ε_{max}) Data of HE-PDI in Different Solvents

Solvent	**Concentration (M)**	**Absorbance**	**λ_{max} (nm)**	**ε_{max} ($\text{M}^{-1}\text{cm}^{-1}$)**
DMF	1×10^{-5}	1.02	526	102000
CHL	1×10^{-5}	0.81	525	81000

4.3 Data of Full Width Half Maximum (FWHM, $\Delta\bar{\nu}_{1/2}$)

The full width at half maximum absorptions is called a half-width that can be calculated by the following equation.

$$\Delta\bar{\nu}_{1/2} = \bar{\nu}_{I} - \bar{\nu}_{II}$$

Where:

$\bar{\nu}_{I}, \bar{\nu}_{II}$: The frequencies from the absorption spectrum (cm^{-1})

$\Delta\bar{\nu}_{1/2}$: Half-width of the selected maximum absorption (cm^{-1})

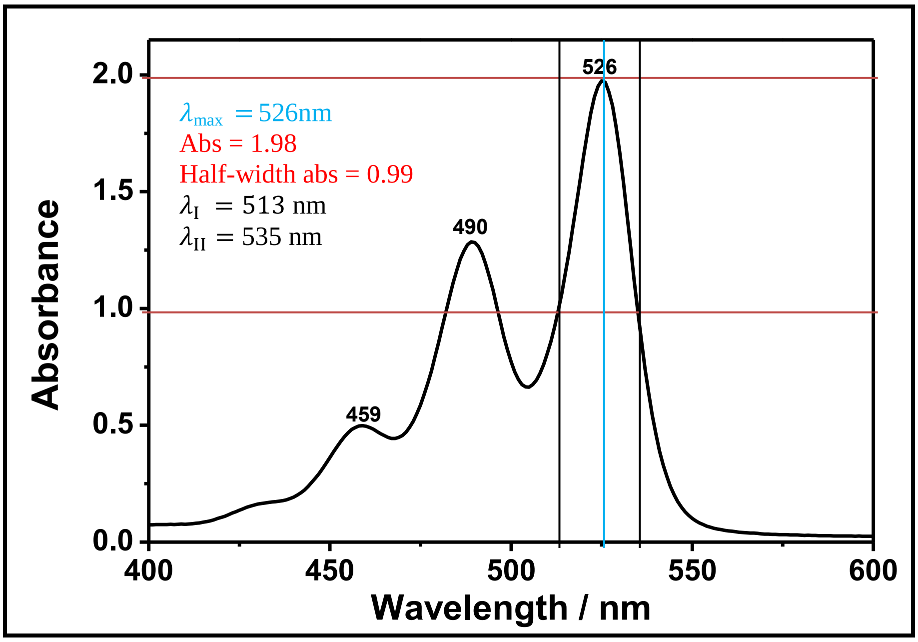

Figure 4.2: FWHM Representation and Absorption Spectrum of HE-PDI in DMF at 1×10^{-5} M

According to Figure 4.2

λ_{max} = 526nm

Abs = 1.98

Half-width abs = 0.99

λ_{I} = 513 nm

λ_{II} = 535 nm

$$\Rightarrow \lambda_{I} = 513\ \text{nm} \times \frac{10^{-9}\text{m}}{1\ \text{nm}} \times \frac{1\text{cm}}{10^{-2}\text{m}} = 5.13 \times 10^{-5}\text{cm}$$

$$\Rightarrow \bar{\nu}_{\text{I}} = \frac{1}{5.13\times 10^{-5}\text{cm}} = 19493.18 \ \text{cm}^{-1}$$

$\lambda_{\text{II}} = 535$ nm

$$\Rightarrow \lambda_{\text{II}} = 535 \text{ nm} \times \frac{10^{-9}\text{m}}{1 \text{ nm}} \times \frac{1\text{cm}}{10^{-2}\text{m}} = 5.35 \times 10^{-5}\text{cm}$$

$$\Rightarrow \bar{\nu}_{\text{II}} = \frac{1}{5.35\times 10^{-5}\text{cm}} = 18691.56 \text{ cm}^{-1}$$

$$\Delta\bar{\nu}_{1/2} = \bar{\nu}_{\text{I}} - \bar{\nu}_{\text{II}} = 19493.18 \text{ cm}^{-1} - 18691.56\text{cm}^{-1} = 801.62 \text{ cm}^{-1}$$

$$\Rightarrow \Delta\bar{\nu}_{1/2} = 801.62 \text{ cm}^{-1}$$

The half-width of the chosen absorptions of HE-PDI in different solvents were calculated in similar way and the data are listed in Table 4.2.

Table 4.2: (FWHM, $\Delta\bar{\nu}_{1/2}$) Data of the Selected Absorptions of HE-PDI in Different Solvents

Solvent	**Concentration (M)**	**λ_{max} (nm)**	**λ_{I} (nm)**	**λ_{II} (nm)**	**$\Delta\bar{\nu}_{1/2}$ (cm^{-1})**
DMF	1×10^{-5}	526	513	535	801.62
CHL	1×10^{-5}	525	503.5	536.6	1225.11

4.4 Theoretical Radiative Lifetime calculations ($\boldsymbol{\tau}_0$)

The radiative lifetime of an excited molecule can be calculated according to this equation [34]:

$$\boldsymbol{\tau_0} = \frac{\mathbf{3.5 \times 10^8}}{\bar{\boldsymbol{\nu}}^{\mathbf{2}}_{\boldsymbol{max}} \times \varepsilon_{\boldsymbol{max}} \times \boldsymbol{\Delta\bar{\nu}_{1/2}}}$$

Where,

$\boldsymbol{\tau}_0$: Theoretical radiative lifetime (ns)

$\bar{\nu}_{max}$: Frequency of the maximum absorption band (cm^{-1})

ε_{max} : Maximum molar absorptivity ($L \bullet mol^{-1} \bullet cm^{-1}$) at λ_{max}

$\Delta\bar{\nu}_{1/2}$: Full width half maximum of the selected absorption (cm^{-1})

Theoretical Radiative Lifetime $\boldsymbol{\tau_0}$ of HE-PDI:

With the help of calculated ($\varepsilon_{\boldsymbol{max}}$ and $\Delta\bar{\nu}_{1/2}$) of nominated absorptions of HE-PDI, From the Figures 4.1 and 4.2, at $\lambda_{max} = 526$

$$\lambda_{\max} = 526 \text{ nm} \times \frac{10^{-9}\text{m}}{1 \text{ nm}} \times \frac{1\text{cm}}{10^{-2} \text{ m}} = 5.26 \times 10^{-5}\text{cm}$$

$$\Rightarrow \bar{\nu}_{\max} = \frac{1}{5.26 \times 10^{-5}\text{cm}} = 19011.40 \text{ cm}^{-1}$$

$$\Rightarrow \bar{\nu}^2_{\max} = (19011.40 \text{ cm}^{-1})^2 = 3.614 \times 10^8 \text{cm}^{-2}$$

The theoretical radiative lifetime of HE-PDI can be calculate from the above equation.

$$\boldsymbol{\tau}_0 = \frac{3.5 \times 10^8}{\bar{\nu}^2_{max} \times \varepsilon_{max} \times \Delta\bar{\nu}_{1/2}} = \frac{3.5 \times 10^8}{(19011.40)^2 \times 102000 \times 801.62}$$

$$\Rightarrow \quad = 11.8 \times 10^{-9}\text{s}$$

$$\Rightarrow \boldsymbol{\tau}_0 = 11.8 \text{ ns}$$

Similarly, the theoretical radiative lifetimes of HE-PDI in different solvents were calculated and the data were listed in Table 4.3.

Table 4.3: Theoretical Radiative Lifetime (τ_0) of HE-PDI in Different Solvents

Solvent	**λ_{max} (nm)**	**ε_{max} ($M^{-1}cm^{-1}$)**	**$\Delta\bar{\nu}_{1/2}$ (cm^{-1})**	**$\bar{\nu}^2_{max}$ (cm^{-2})**	**τ_0 (ns)**
DMF	526	102000	801.62	3.614×10^8	11.8
CHL	525	81000	1225.11	3.628×10^8	9.72

4.5 Theoretical Fluorescence Lifetime Calculations (τ_f)

Theoretical fluorescence lifetimes can be calculated according to the following equation shown below. It indicates the theoretical average time of the molecule stays in the excited state before fluorescence [34].

$$\boldsymbol{\tau}_{\mathbf{f}} = \boldsymbol{\tau}_{\mathbf{0}} \, . \, \boldsymbol{\Phi}_{\mathbf{f}}$$

Where,

$\boldsymbol{\tau}_{\mathbf{f}}$: Fluorescence lifetime (ns)

$\boldsymbol{\tau}_{\mathbf{0}}$: Theoretical radiative lifetime (ns)

$\boldsymbol{\Phi}_{\mathbf{f}}$: Fluorescence quantum yield

The theoretical fluorescence lifetime $\boldsymbol{\tau}_{\mathbf{f}}$ of HE-PDI was calculated in DMF:

$$\boldsymbol{\tau}_{\mathbf{f}} = \boldsymbol{\tau}_{\mathbf{0}} \, . \, \boldsymbol{\Phi}_{\mathbf{f}}$$

$$= 11.8 \times 0.91$$

$$\boldsymbol{\tau}_{\mathbf{f}} = 10.74 \text{ ns}$$

4.6 Calculations of Fluorescence Rate Constant (K_f)

The theoretical fluorecence rate constants for the synthesized perylene compounds can be calculated by the equation given below.

$$\boldsymbol{k_\mathrm{f} = \frac{1}{\tau_0}}$$

Where,

K_f : Theoretical fluorecence rate constant (s^{-1})

τ_0 : Theoretical radiative lifetime (s)

The Fluorescence Rate Constant of HE-PDI in DMF

$$k_\mathrm{f} = \frac{1}{11.8\times 10^{-9}} = 8.47 \times 10^{7}$$

Similarly, the fluorecence rate constant of HE-PDI in different solvents were calculated and the data were listed in Table 6.3.

Table 4.4: Fluorecence Rate Constant (K_f) of HE-PDI in Different Solvents

Solvent	**Concentration**	**τ_0 (ns)**	**K_f**
DMF	1×10^{-5}	11.8	8.47×10^{7}
CHL	1×10^{-5}	9.72	10.3×10^{7}

4.7 Oscillator Strength Calculations (f)

The electronic transition strength of an electron that deduced by dimensionless quantity is called oscillator strength. It can be calculated according to the given below equation.

$$\boldsymbol{f} = 4.32 \times 10^{-9} \times \Delta\bar{\nu}_{1/2} \times \varepsilon_{\max}$$

Where,

f : Oscillator Strength

$\Delta\bar{\nu}_{1/2}$: Half-width of the Selected Absorption (cm^{-1})

ε_{max} : Maximum molar absorptivity in ($L \bullet mol^{-1} \bullet cm^{-1}$) at maximum wave length (λ_{max})

Oscillator Strength of HE-PDI in DMF

⇨ $f = 4.32 \times 10^{-9} \times \Delta\bar{\nu}_{1/2} \times \varepsilon_{max}$

⇨ $f = 4.32 \times 10^{-9} \times 801.62 \times 102000$

⇨ $f = 3.53 \times 10^{-1}$

Oscillator strength of radiationless deactivation for HE-PDI in different solvents are shown in Table 4.7.

Table 4.5: Oscillator Strength (f) Data of HE-PDI in Different Solvents

Solvent	**Concentration**	$\Delta\bar{\nu}_{1/2}$ **(cm^{-1})**	ε_{max} **($M^{-1}cm^{-1}$)**	f
DMF	1×10^{-5}	801.62	102000	0.353
CHL	1×10^{-5}	1225.11	81000	0.429

4.8 Singlet Energy Calculations (E_s)

Singlet energy is the necessary amount of energy required to encourage the electron transfer from the ground state to an excited state.

$$E_{\mathrm{s}} = \frac{2.86 \times 10^{5}}{\lambda_{\max}}$$

Where:

E_{s} : The singlet energy (kcal . mol^{-1})

$\lambda_{\max}$: The maximum absorption wavelength in ($\mathring{\mathrm{A}}$)

Singlet Energy of HE-PDI in DMF:

$$\lambda_{\max} = 526 \text{ nm} \times \frac{10\,\mathring{\mathrm{A}}}{nm} = 5260\ \mathring{\mathrm{A}}$$

$$E_{\mathrm{s}} = \frac{2.86 \times 10^{5}}{\lambda_{\max}} = \frac{2.86 \times 10^{5}}{5260} = 94.39 \text{ kcal . mol}^{-1}$$

$$E_{\mathrm{s}} = 54.37 \text{ kcal . mol}^{-1}$$

The singlet energies of HE-PDI in different solvents were calculated similarly as shown above and were presented in Table 4.8.

Table 4.6: Singlet Energy (E_{s}) Data of HE-PDI in Different Solvents

Solvent	**$\lambda_{\max}$ ($\mathring{\mathrm{A}}$)**	**E_{s} (kcal mol^{-1})**
DMF	5260	54.37
CHL	5250	54.47

4.9 Calculation of Optical Band Gap Energies (E_g)

The measurement of the optical band gap energies of materials can be calculated from the following equation:

$$\boldsymbol{E_{\mathrm{g}} = \frac{1240\ \mathrm{eV\ nm}}{\lambda}}$$

Where,

E_g : Energy band gap in units of eV

λ : Cut-off wavelength of the absorption band in units of nm

The band gap energy of HE-PDI in DMF:

From the maximum absorption band, the cut-off wavelength of the absorption band (0→0 absorption band) can be estimated by induction it to zero.

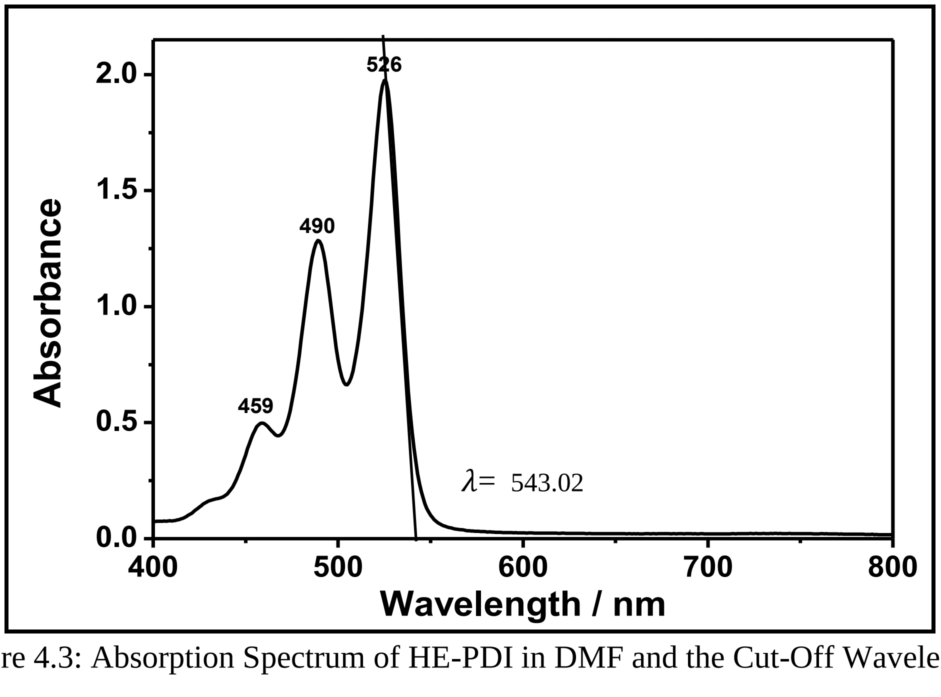

Figure 4.3: Absorption Spectrum of HE-PDI in DMF and the Cut-Off Wavelength

$$E_{\mathrm{g}} = \frac{1240\ \mathrm{eV\ nm}}{\lambda}$$

$$E_g = \frac{1240\ eV\ nm}{\lambda} = \frac{1240\ \text{eV nm}}{543.02} = 2.283\ eV$$

The band gap energies of HE-PDI in different solvents were calculated in the same way that is used above and the data listed in the Table 4.9.

Table 4.7: Band Gap Energies (E_g) Data of HE-PDI in Different Solvents

Solvent	**Concentration (M)**	$\boldsymbol{\lambda}_{\mathbf{max}}$ $(\overset{0}{\text{A}})$	**Cut-off (nm)**	$\boldsymbol{E}_{\mathbf{g}}$ **(eV)**
DMF	1×10^{-5}	526	543.02	2.283
CHL	1×10^{-5}	525	541.87	2.288

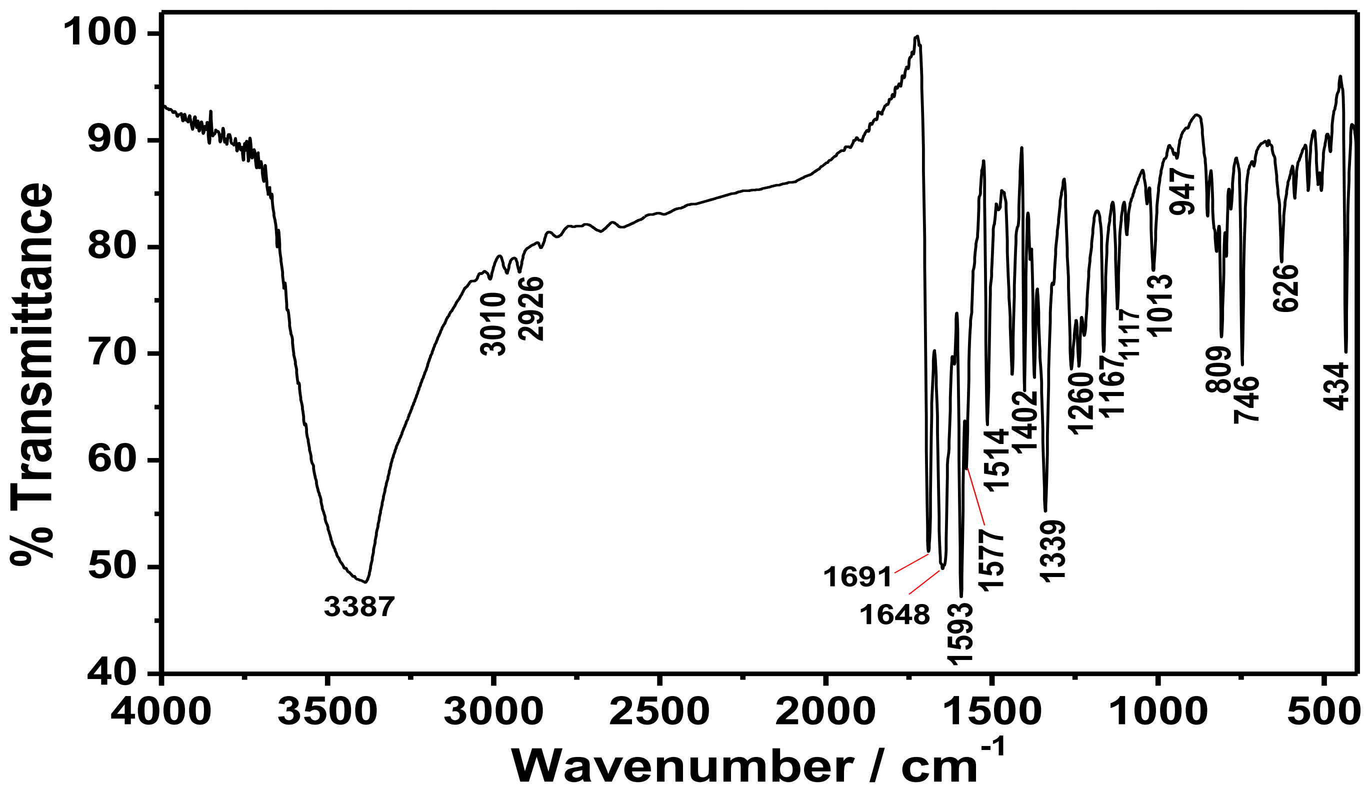

Figure 4.4: FTIR spectrum of HE-PDI

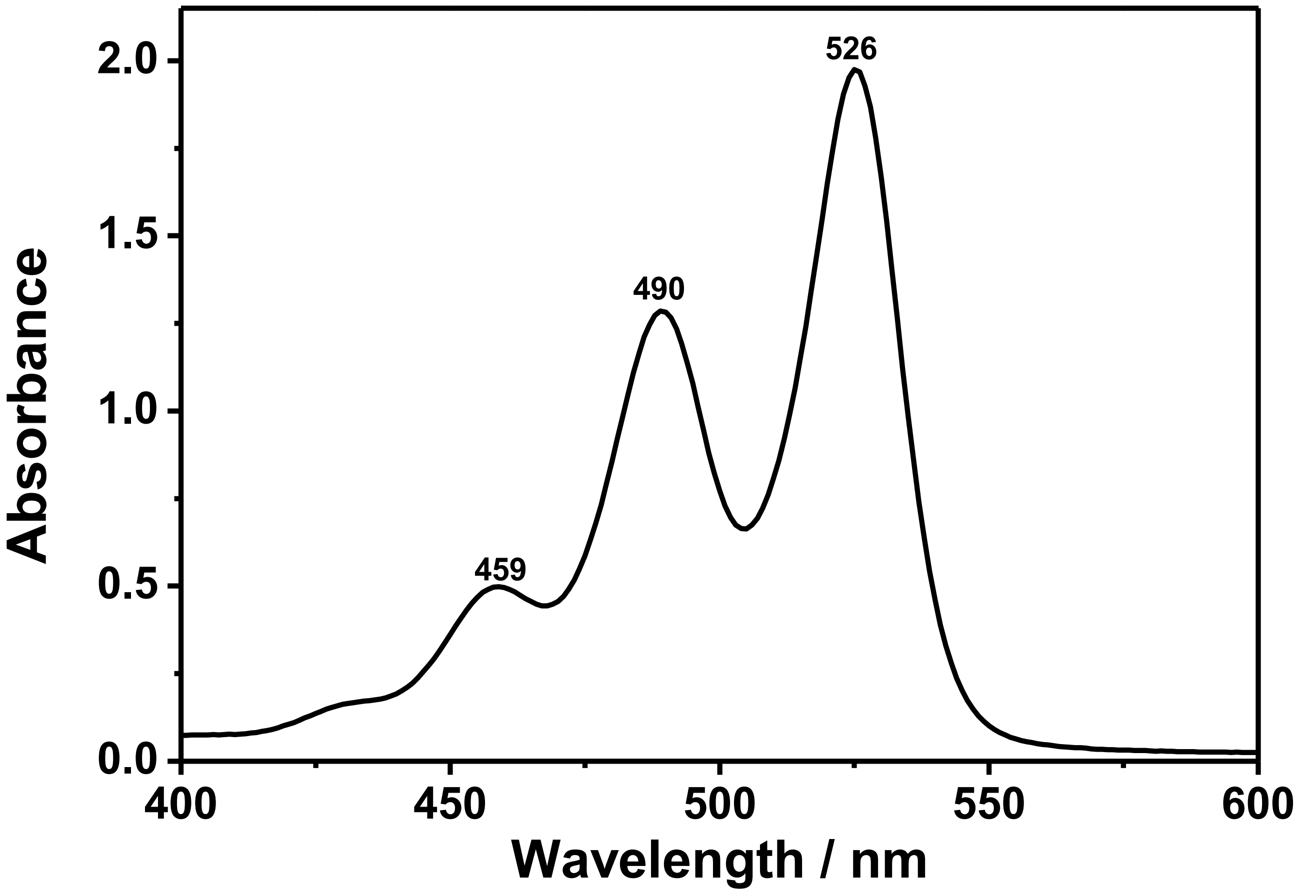

Figure 4.5: Absorption spectrum of HE-PDI in DMF

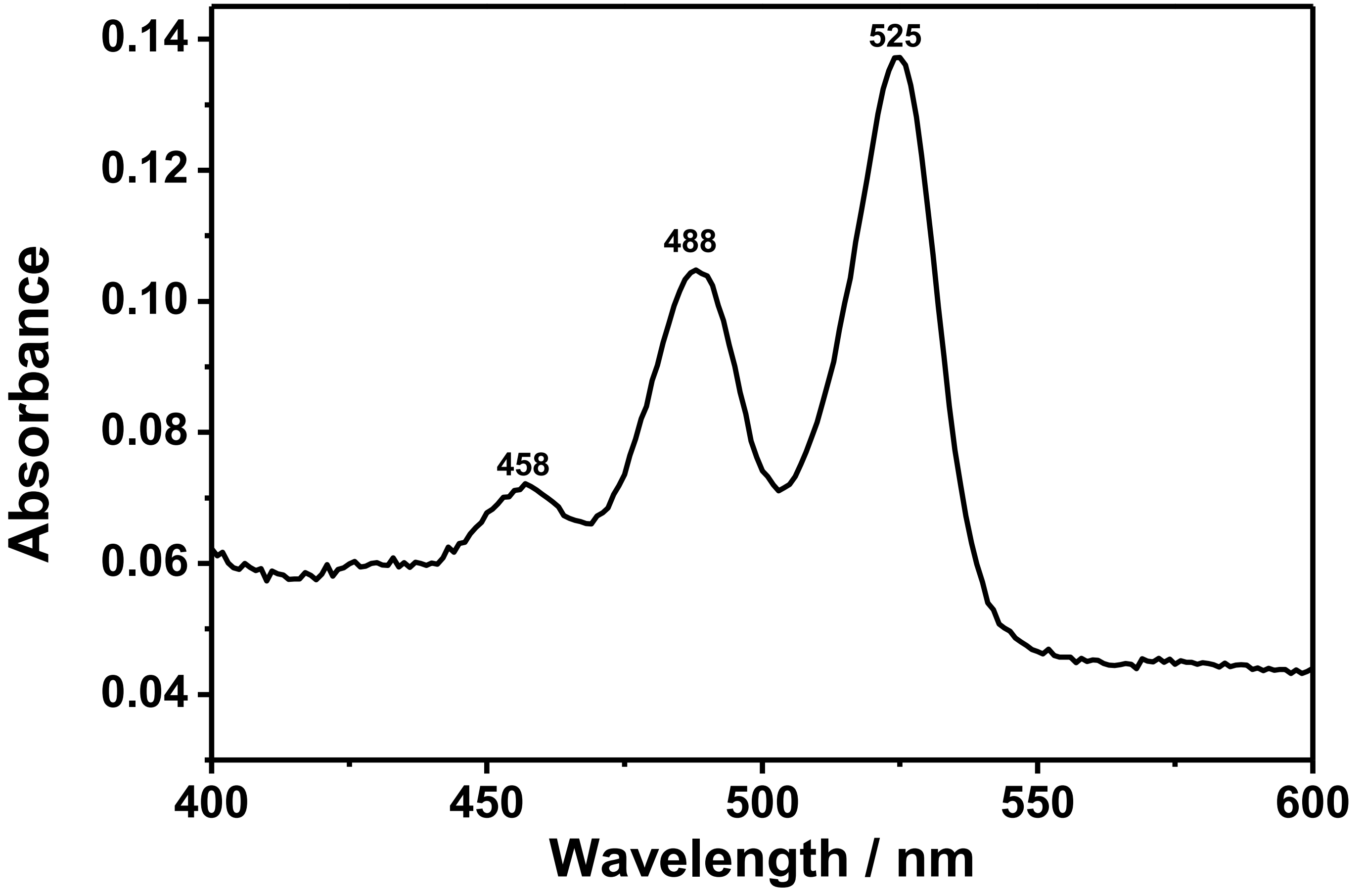

Figure 4.6: Absorption spectrum of HE-PDI in CHL

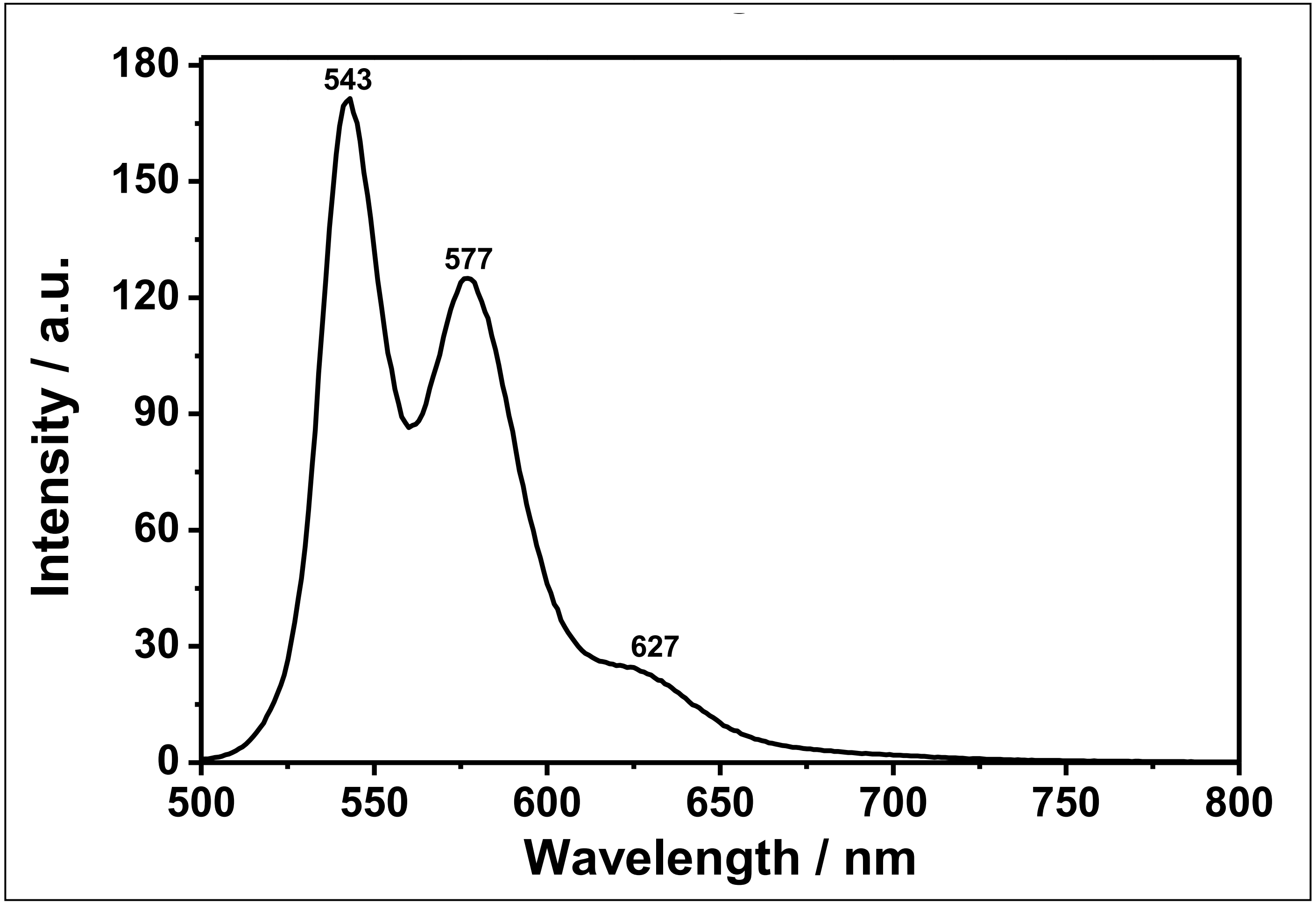

Figure 4.7: Emission spectrum (λexc = 485 nm) of HE-PDI in DMF

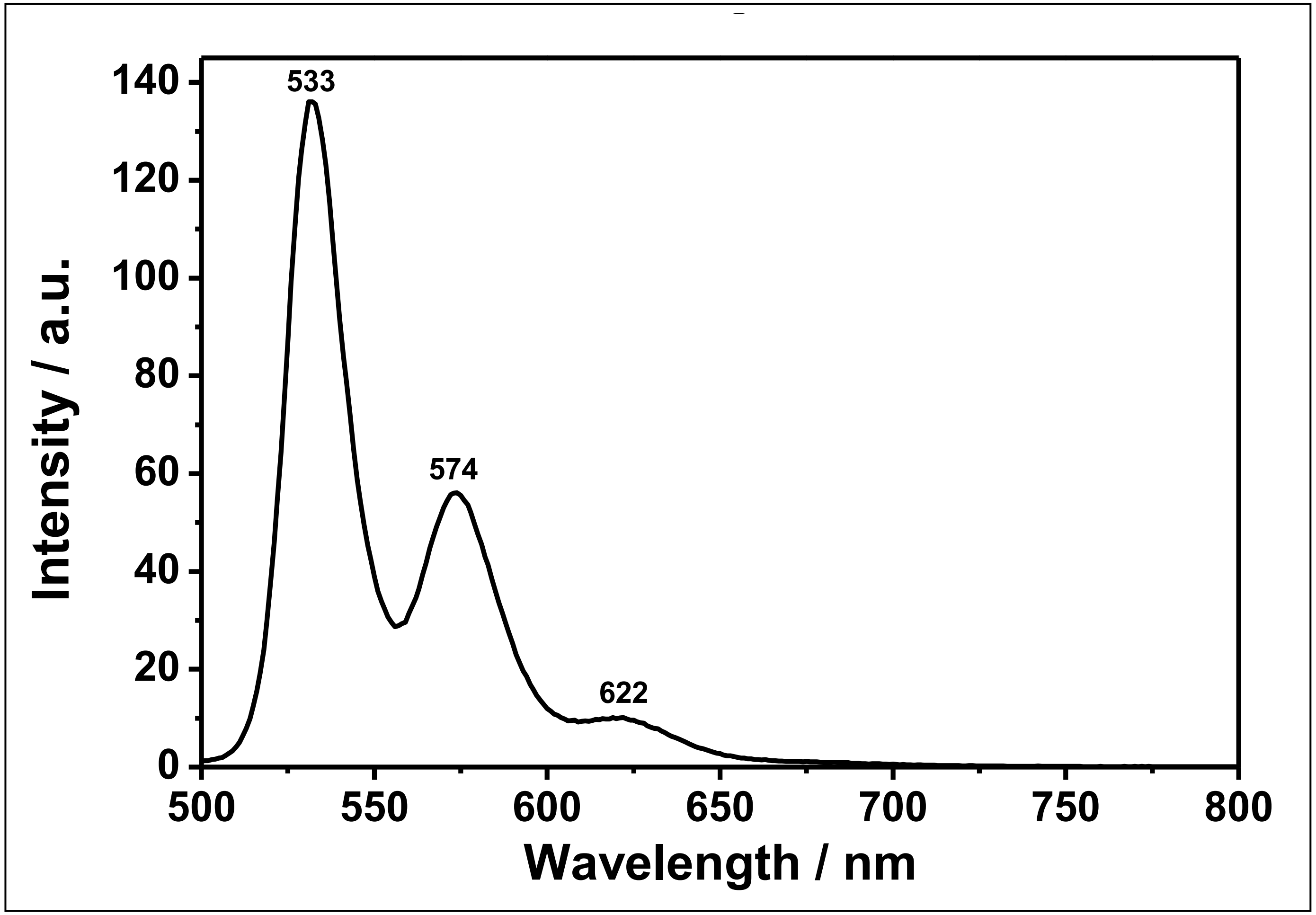

Figure 4.8: Emission spectrum (λexc = 485 nm) of HE-PDI in CHL

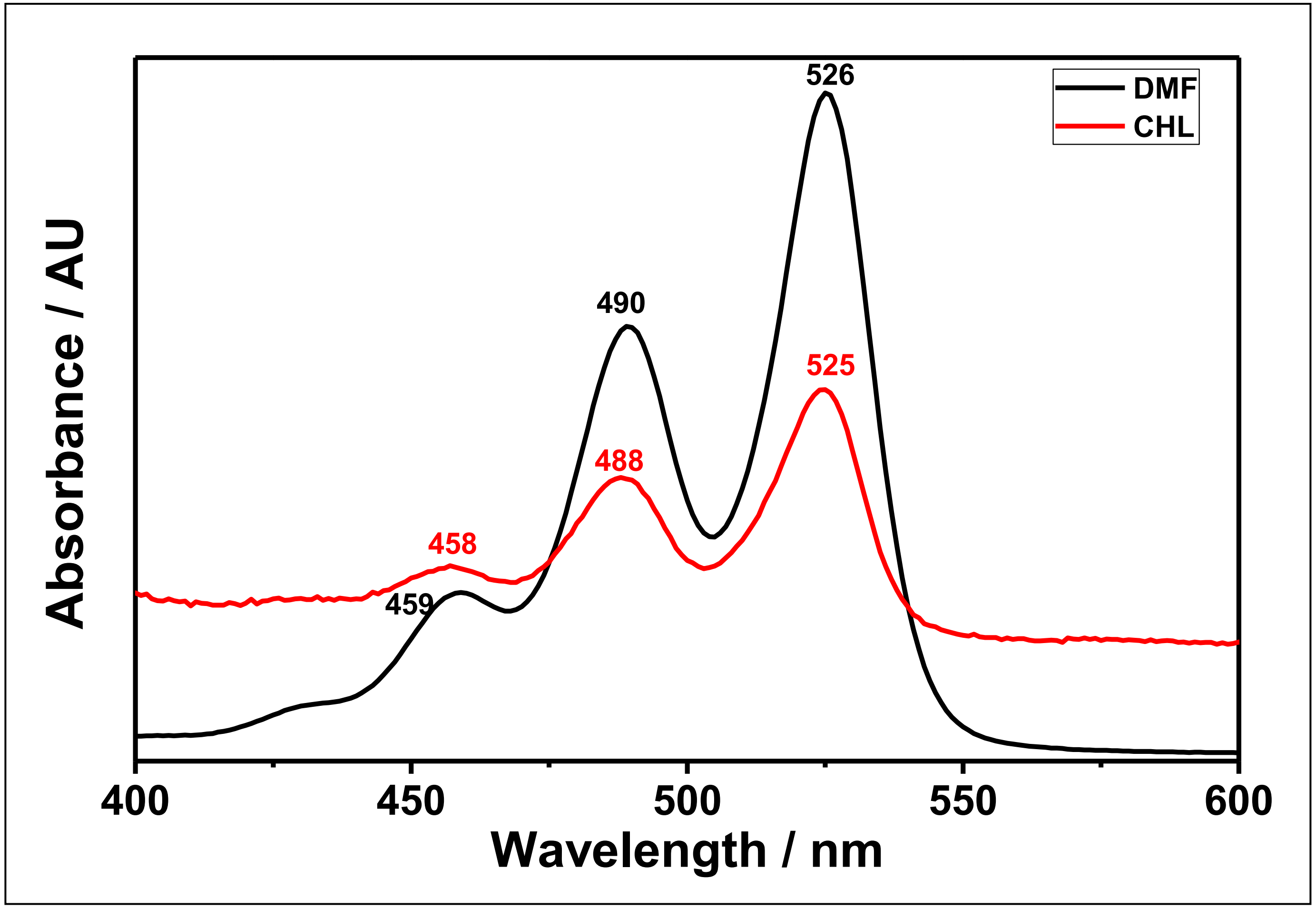

Figure 4.9: Absorption spectrum of HE-PDI in DMF and CHL

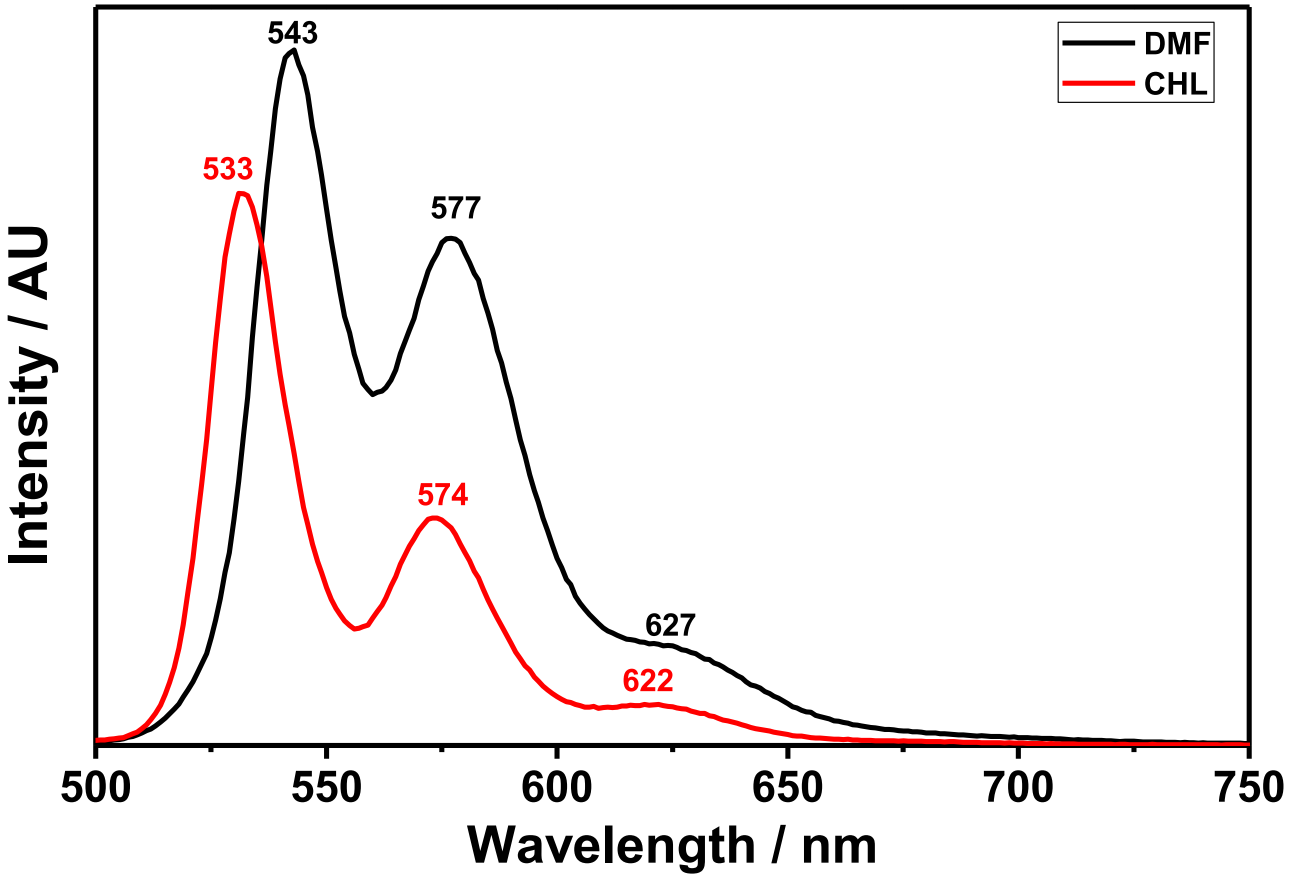

Figure 4.10: Emission spectra (λexc = 485 nm) of HE-PDI in DMF and CHL

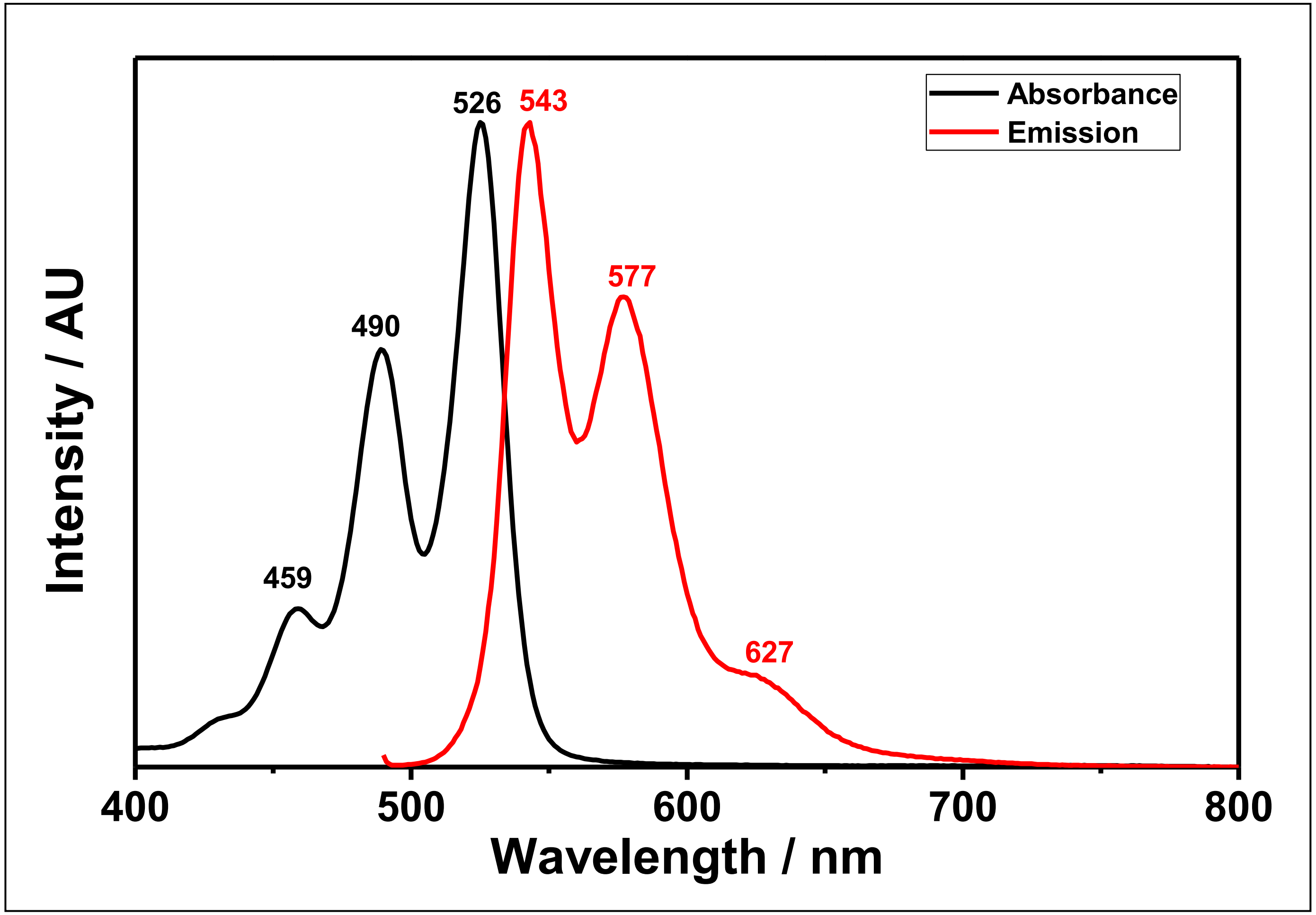

Figure 4.11: Comparison of Absorbance and Emission of HE-PDI in DMF

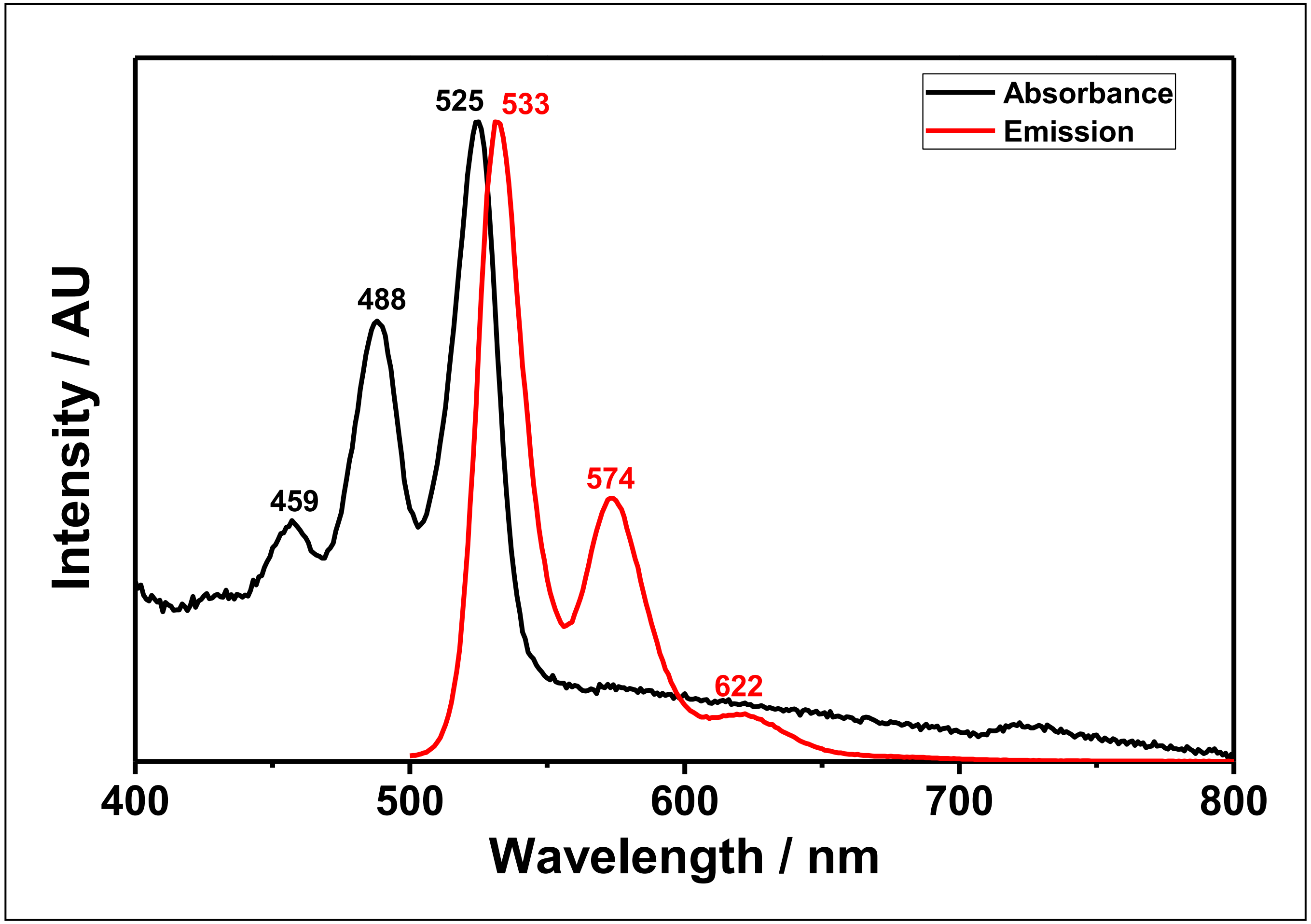

Figure 4.12: Comparison of Absorbance and Emission of HE-PDI in CHL

Chapter 5

RESULTS AND DISCUSSION

5.1 Synthesis of N,N′-bis(2-(4-hydroxyphenyl)ethyl)-3,4,9,10-perylenebis(dicarboximide) (HE-PDI).

The novel perylene diimide, N,N′-Bis(2-(4-hydroxyphenyl)ethyl)-3,4,9,10-perylenebis(dicarboximide) (HE-PDI) was successfully synthesized. Naturally occurring monoamine compound, Tyramine, that has aromatic and aliphatic groups together introduced at imide positions of perylene core by the condensation reaction with perylene dianhydride (PDA).

The synthesized perylene compound HE-PDI was purified and characterized by FT-IR spectroscopy. The photophysical and optical characteristics were studied by UV-vis and emission spectroscopy.

5.2 Structural Analysis of Synthesized Perylene Dye

The structure of N,N′-Bis(2-(4-hydroxyphenyl)ethyl*)*-3,4,9,10-perylenebis(dicarboximide) was fundamentally characterized by FT-IR spectrum to confirm the functional groups present in the structure. The main functional groups in the structure of the HE-PDI are completely present in the FT-IR spectrum.

Figure 4.4, the IR spectrum of HE-PDI, shows O–H stretching at 3387 cm^{-1}, aromatic C–H stretching at 3010 cm^{-1}, aliphatic C–H stretching at 2926 cm^{-1}, imide C=O stretching at 1691 and 1648 cm^{-1}, aromatic C=C stretching at 1593 and 1577 cm^{-1}. C–N stretching at 1339 cm^{-1}, C–O at 1260 cm^{-1} and aromatic C–H bending at 809 and 746 cm^{-1} that confirms HE-PDI structure.

5.3 Solubility of Synthesized Perylene Dyes

The N,N′-Bis(2-(4-hydroxyphenyl)ethyl)-3,4,9,10-perylenebis(dicarboximide) completely soluble in both dipolar aprotic solvents DMF and non-polar solvents CHL at room temperature. On the other hand, it is not soluble in polar protic solvents like MeOH.

Table 5.1: Solubility the HE-PDI in Different Solvents

Solvent	**HE-PDI)**	**color**
DMF	(+ +)	Light purple
CHL	(+ +)	Light purple

(+ +) : soluble at room temperature.

The thin layer chromatography (TLC) analysis for HE-PDI did not run thus the product is a polar compound.

5.4 Analyses of UV-vis Absorption Spectra

Figure 4.5, the UV-vis absorption of N,N′-Bis(2-(4-hydroxyphenyl)ethyl)-3,4,9,10-perylenebis(dicarboximide) in dipolar aprotic solvent (DMF) shows three characteristic absorption peaks at 459, 490 and 526 nm respectively. These are characteristic π→π* electronic transitions absorption peaks of perylene chromophore representing 0→2, 0→1, and 0→0 transitions, respectively. The 0→0 electronic transition peak at 526 nm is higher in absorption intensity. On the other hand, HE-PDI shows the lowest intensity at 0→2 electronic transition. Commonly, the characteristic perylene dye absorption peaks show regular increase in the absorption from 0→2 to 0→0 electronic transition and thus the highest intensity belongs to 0→0 transition.

The UV-vis absorption spectrum of HE-PDI is shown in Figure 4.6. The spectrum shows three major characteristic absorption peaks in nonpolar solvent chloroform at 458, 488 and 525 nm respectively. There is no aggregation noticed. The 0→0 electronic transition is highest in intensity at 525 nm while the 0→2 electronic transition is lowest in intensity at 458 nm which means a gradual increase in the absorption intensities. These three characteristic absorption peaks are due to characteristic π→π* electronic transitions of perylene structure.

The Figure 4.9 shows the absorption spectrum of HE-PDI in DMF and CHL for comparison. HE-PDI has similar electronic properties in dipolar aprotic and nonpolar solvents.

5.5 Analyses of Emission Spectra

The emission spectrum of N,N′-Bis(2-(4-hydroxyphenyl)ethyl)-3,4,9,10-perylenebis (dicarboximide) in dipolar aprotic solvent (DMF) is shown in Figure 4.7. It shows three characteristic perylene chromophoric emission peaks at 543, 577 and 627 nm respectively. The three emission peaks represents 0→0, 1→0, and 2→0 electronic transitions of perylene chromophore and the highest intensity at 543 nm while the lowest intensity is at 627 nm. The absorption and emission spectra are mirror images of each other.

The emission spectrum of N,N′-Bis(2-(4-hydroxyphenyl)ethyl)-3,4,9,10-perylene bis(dicarboximide) in nonpolar solvent, CHL is shown in Figure 4.8. It shows three characteristic perylene chromophoric emission peaks at 533, 574 and 622 nm respectively. The three emission peaks represent the 0→0, 1→0, and 2→0 electronic transitions of perylene chromophore and the highest intensity at 533 nm while the lowest intensity is at 622 nm. The absorption and emission spectra are mirror images of each other.

The Figure 4.10 shows the emission spectrum of HE-PDI in both DMF and CHL for comparison. HE-PDI has similar electronic properties in dipolar aprotic and nonpolar solvents. 10 nm bathochromic shift observed in DMF at 0→0 electronic transition.

The absorption and emission spectra overlap of HE-PDI are shown in Figure 4.11 and 4.12 respectively. In dipolar aprotic solvent DMF and nonpolar solvent CHL, HE-PDI’s absorption and emission spectra are mirror images of each other and 17 nm and 8 nm Stokes shifts observed respectively. The strong absorptions display well-defined vibronic structure. The high fluorescence quantum yield ($Q_f = 0.91$) also shows that almost all the absorbed light is emmited.

Chapter 6

CONCLUSION

A novel perylene diimide N,N′-Bis(2-(4-hydroxyphenyl)ethyl)-3,4,9,10-perylenebis (dicarboximide) (HE-PDI) was successfully synthesized. An aliphatic substituent that has an aromatic group is introduced at imide positions to improve its solubility, photophysical and optical properties.

After the purification of HE-PDI, it is characterized via FT-IR spectra in order to confirm all the functional groups in its structure.

The photophysical and optical properties of HE-PDI were studied by using UV-vis and emission spectroscopies. The absorption spectra recorded for HE-PDI shows the three characteristic absorption peaks of perylene chromophore. Also, the emission spectra of HE-PDI shows three characteristic emission peaks of perylene chromophore.

HE-PDI has high extinction coefficient (102000, 81000) in both DMF and CHL respectively and high fluorescence quantum yield ($\Phi_f = 0.91$). It's absorption and emission spectra are mirror images.

The synthesized HE-PDI is completely soluble in the both dipolar aprotic solvents DMF and non-polar solvents CHL.

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