Functional Naphthalene Diimides: Synthesis, Characterization and Optical Properties

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ABSTRACT

Unsymmetrically substituted Naphthalene Diimides have highly attractive potential in many industrial fields due to their excellent thermal and photochemical stability, high mechanical strength, and good film ability, conductivity and optical properties. Currently, a great deal of effort has been devoted to the development of novel unsymmetrically substituted Naphthalene Diimides due to their highly favorable photochemical properties, excellent thermal and photo stabilities and photo-conductive properties.

In the present study, the aim is to synthesize two unsymmetrically substituted Naphthalene Diimides. The unsymmetrical Naphthalene Diimide were prepared using two-step reaction processes starting from 1,4,5,8-naphthalenetetracarboxylic diandydride. In the first step, N-substituted-1,4,5,8-napthalenetetracarboxylic-1,8-monoanhydride-4,5-monoimide were synthesized. In the final step, the unsymmetrical Naphthalene Diimide were synthesized via condensation reaction using appropriate amine in high boiling solvent under argon atmosphere. The synthetic products were characterized by FTIR, UV-VIS Absorption, Emission.

Keywords: Unsymmetrical Naphthalene Diimide, Optical Properties, Characterization.

ÖZ

Asimetrik Naftalin Diimidler, mükemmel termal ve fotokimyasal özellikleri ile bilinmektededidiler. Ayrıca, iletkenlikleri, optik özellikleri ve iyi film yetenkleri ile fotonik uygulamalarda kullanım potansiyeline saniptirler. Yeni asimetrik Naftalin Diimidlerin sentezi muhteşem özellikleri nedeniyle büyük önem taşımaktadır.

Bu çalışmada, iki asimetrik Naftalin Diimid sentezi amaçlanmıştır. Ürünlerin karakterizasyonu spektroskopik yöntemlerte sağlanmıştır. Asımetrik Naftalin Diimıdler üç basamakta ve yüksek verimle sentezlenmiştir. İlk basamakta potasyum tuzu elde edilmiştir. İkinci basamakta naftalinmonoimid monoanhidrit maddesi sentezlenmiştir. En son, monoanhidrit ve uygun aminlerin kullanımı ile hedeflenen ürünler elde edilmiştir.

Anahtar Kelimeler: Asimetrik Naftalin Diimidleri, Optik Özellik, Karakterizasyon.

DEDICATION

To

My Family

ACKNOWLEDGEMENT

First of all, I earnestly and respectfully would like to express my profound gratitude to my research supervisor Prof. Dr. Huriye İcil, for her kindhearted and consistent support and encouragement, as well as, guiding me with her exceptional wisdom and intellect throughout my research journey.

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I would like to thank my parents, siblings and my friends back home in Kosovo that gave me a huge support through all the time that I was studying in North Cyprus. Without them I couldn’t have made this far and I am forever grateful.

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LIST OF SYMBOLS AND ABBREVIATIONS

Å	Armstrong
A	Absorption
C	Concentration
DMF	DiMethylFormamide
DMSO	Dimethyl Sulfoxide
Eqn.	Equation
Es	Singlet Energy
ε	Molar Absorption Coefficient
εmax	Maximum Extinction Coefficient
f	Oscillator Strength
FT–IR	Fourier Transform Infrared Spectroscopy
h	Hour
IR	Infrared Spectrum/Spectroscopy
kd	Rate Constant of Radiationless Deactivation
kf	Fluorescence Rate Constant
l	Path Length
M	Molar Concentration
mol	Mole
NMP	N-MethylPyrrolidinone
Φf	Fluorescence Quantum Yield
τ_0	Theoretical Radiative Lifetime
t	Time

TFAc	Trifluoroacetic Acid
UV-VIS	Ultraviolet Visible Light
Δ ν1/2	Half-Width
υ_{max}	Maximum Wavenumber
λ	Wavelength
λ_{exc}	Excitation Wavelength

Chapter 1

INTRODUCTION

1.1 Naphthalene Diimide

Last few years the application of Naphthalene Diimide (NDIs) have received more interest. They are used in areas such as: sensors, ligand-gated ion chanels,substances able to form gels, supramolecular chemistry and in medicine the NDI intercalations [1].

The structure of a Naphthalene Diimide contains a Naphthalene core that carries two imide groups which can furthermore be substituted by alkyl or aryl groups.

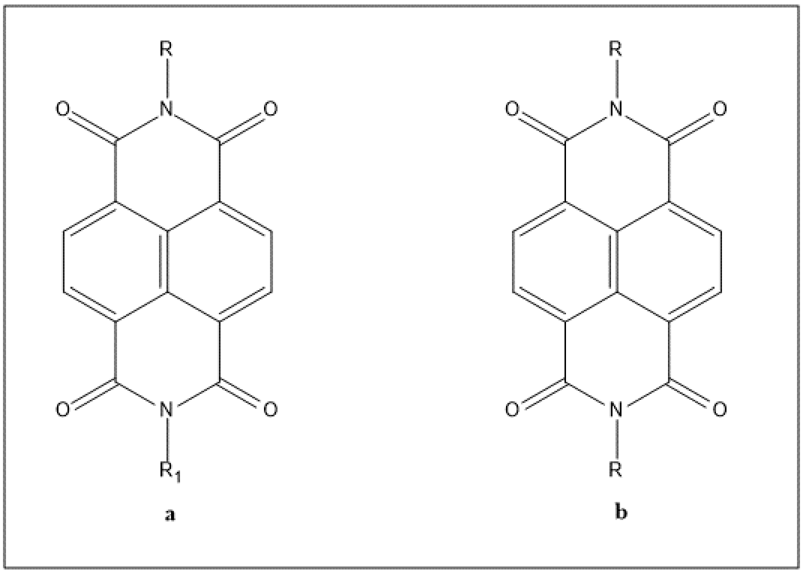


Figure 1.1: Structures of unsymmetrical (a) and symmetrical (b) NaphthaleneDiimide

Unsymmetrical substituted Naphthalene Diimides show interesting properties such as: high thermal, chemical and photochemical stability, good conductivity and excellent optical properties [2].

The synthesis of unsymmetric Naphthalene Diimide compounds with the two step procedure containing 1,4,5,8-Napthalenetetracarboxylic dianhydride. By using Ghadiri procedure at the imides were added different functional groups, hence this simple character makes it vulnerable to chemical studies of polymer [3].

1.2 1,4,5,8-Naphthalenetetracarboxylic Dianhydride

1, 4, 5, 8-Naphthalenetetracarboxylic Dianhydride is a molecule that includes a naphthalene chromophore with a conjugated system where π-electrons are delocalized [4].

1, 4, 5, 8-Naphthalenetetracarboxylic Dianhydride has received interest to scientists because the molecule is aromatic and contains carbon and hydrogen that are arranged of several aromatic rings. Several researches have demonstrated that 1, 4, 5, 8-Naphthalenetetracarboxylic Dianhydride are very stable when it comes to electron transport, stability, optical properties and large aromatic molecules [5].

The interaction of the prototypical π-conjugated compounds such as 1, 4, 5, 8-Naphthalenetetracarboxylic Dianhydride has been widely investigated due to their promising application in various molecular devices [5].

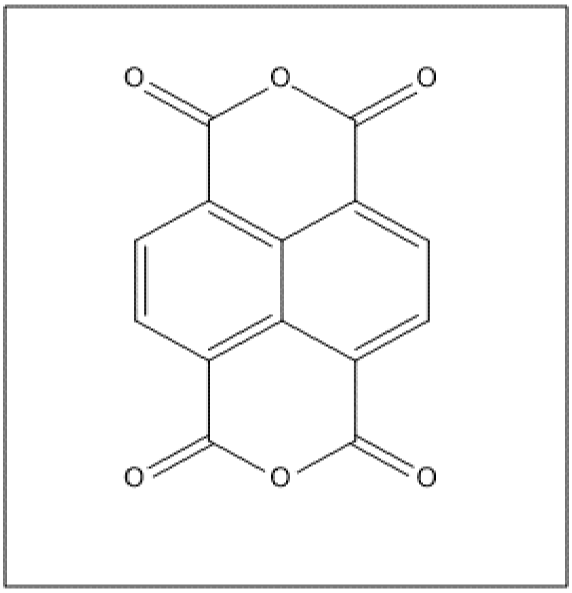


Figure 1.2: Structure of 1,4,5,8-Naphthalenetetracarboxylic dianhydride

1.3 Unsymmetrically Substituted Naphthalene Diimide

Unsymmetrical substituted Naphthalene Diimides are applied in many areas of industry as a result of their conductivity and optical properties and mechanically they are very strong [2].

Unsymmetrical NDI derivatives have great thermal stability, electron affinity, electrical conductivity, electron mobility. All these outstanding properties make unsymmetrical NDI derivatives applicable in many fields including organic solar cells with high performance.

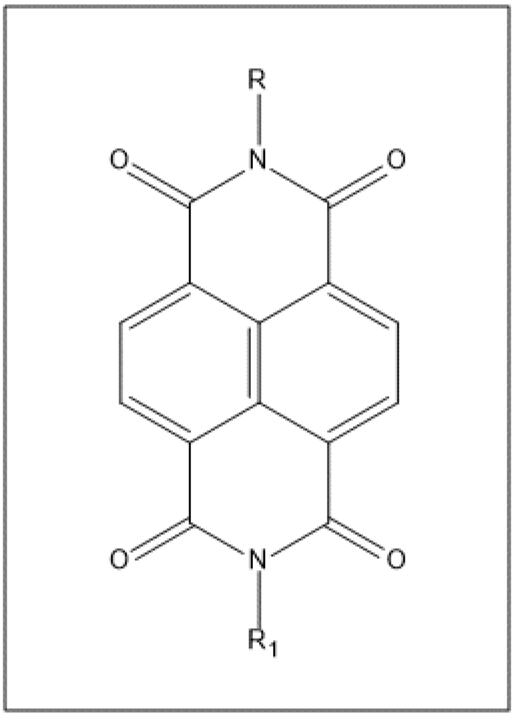


Figure 1.3: Structure of unsymmetrical chiral Naphthalene Diimide

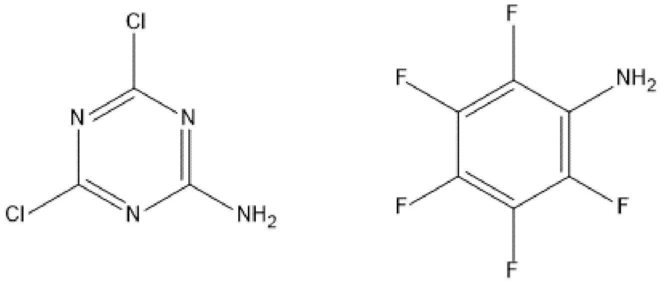
1.4 Design and Synthesis of Unsymmetrically Substituted NDI

To synthesize the unsymmetrical Naphthalene Diimide compound the Ghadiri procedure is used. By using this procedure different functional groups were added from imide position at naphthalene core [15].

Two novel unsymmetrical Naphthalene Diimide were synthesized in three steps. In the first step, 1,4,5,8-Naphthalenetetracarboxylic dianhydride was prepered using phosphoric acid (H_3PO_4).

In the second step 4-Aminophenol was substiuted to synthesise Naphthalene Monoimide called N-(4-hydroxyphenyl)-1,4,5,8-naphthalenetetracarboxylic-1,8-anhydride-4,5-imide (3). Finally, N,N'-Imidization of Naphthalene Diimide with two amines in isoquinoline at reflux yielded N-(4-hydroxyphenyl)-N'-(3,5-dichloro 2,4,6-triazinyl)-1,4,5,8-naphthalenediimide (6) and N-(4-hydroxyphenyl)-N'-(2, 3, 4,5,6-pentafluorophenyl)-1,4,5,8-naphthalenediimide (8). The structures of synthesized of 6 and 8 were shown in figure 1.4.

2-amino-4,6-dichloro-1,3,5-triazine (5) and 2,3,4,5,6-pentafluoroaniline (7) were chosen to be substituted to the monoimide because both of the amines are soluble in, methanol and acetone.



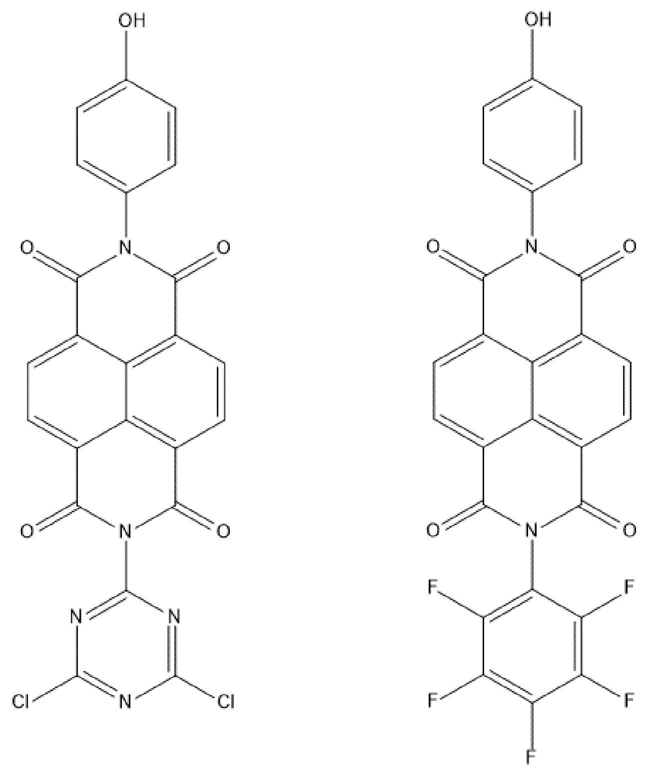
Amine I

5

Amine II

7

Figure 1.4: Structures of two different amines



(6) (8)

Figure 1.5: Structures of N-(4-Hydroxyphenyl)-N'-(3,5-Dichloro-2,4,6-Triazinyl) 1,4,5,8-Naphthalenediimide (6)
and N-(4-Hydroxyphenyl)-N'-(2, 3, 4, 5, 6-Pentafluorophenyl)-1,4,5,8-naphthalenediimide (8)

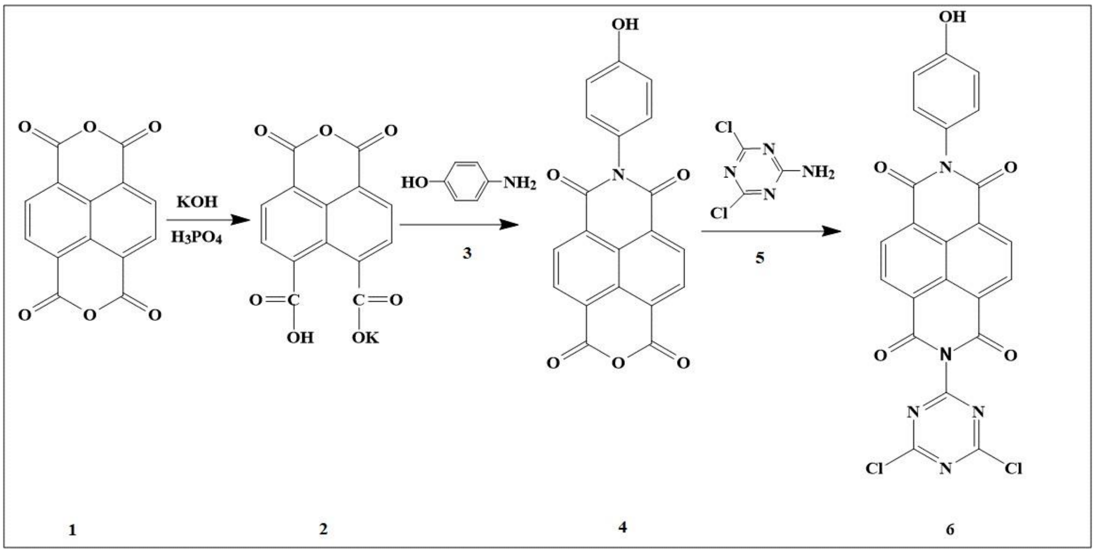


Figure 1.6: Synthesis of N-(4-Hydroxyphenyl)-N'-(3,5-Dichloro-2,4,6-Triazinyl)-1,4,5,8-Naphthalenediimide (6)

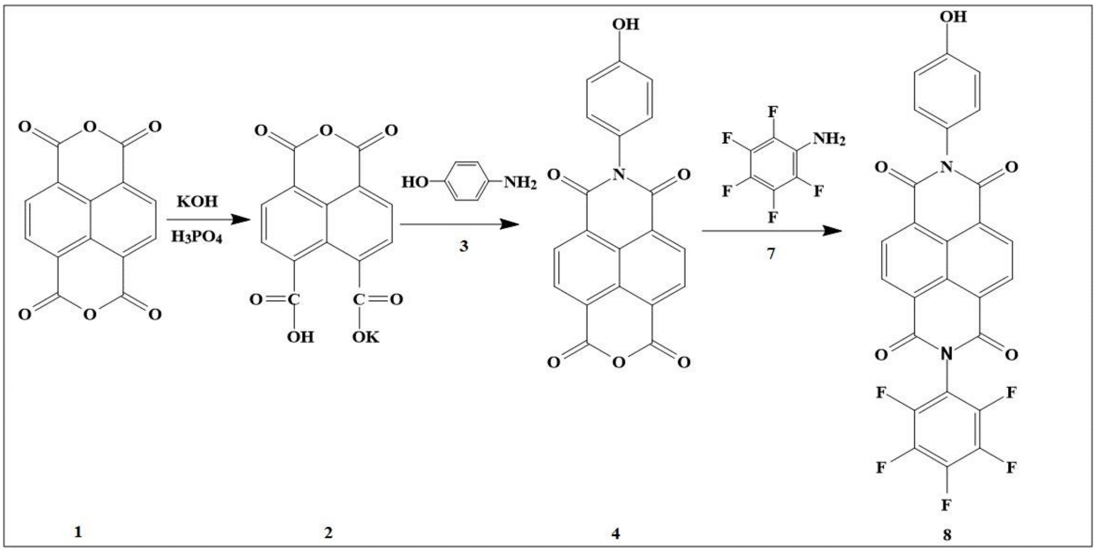


Figure 1.7: Synthesis of N-(4-Hydroxyphenyl)-N'-(2, 3, 4, 5, 6-Pentafluorophenyl)-1,4,5,8-Naphthalenediimide (8)

Chapter 2

THEORETICAL

2.1 Naphthalene Diimide Derivatives

Symmetrical Naphthalene Diimide derivatives are easily prepared from 1, 4, 5, 8-Naphthalenetetracarboxylic Dianhydride with a primary amine in high boiling point solvent such as isoquinoline and dimethylformamide (DMF).

Naphthalene Diimide derivatives have a planar aromatic core structure as a result of two imide groups which can be easy reduced. For a while Naphthalene Diimides have been overshadowed by Perylene Diimides which have same functional group and similar chemical properties. However due to Naphthalene Diimide being easy modified and having great electronic properties, Naphthalene diimide have gained a big interest from scientists. Naphthalene Diimides are the smallest from Rylene Diimides homologue. Perylene Diimides show excellent absorption properties and are pigmented, on the contrary Naphthalene Diimides have smaller aromatic core, are colorless solids due to absence of functional groups at 2, 3, 6 and 7 core positions [18].

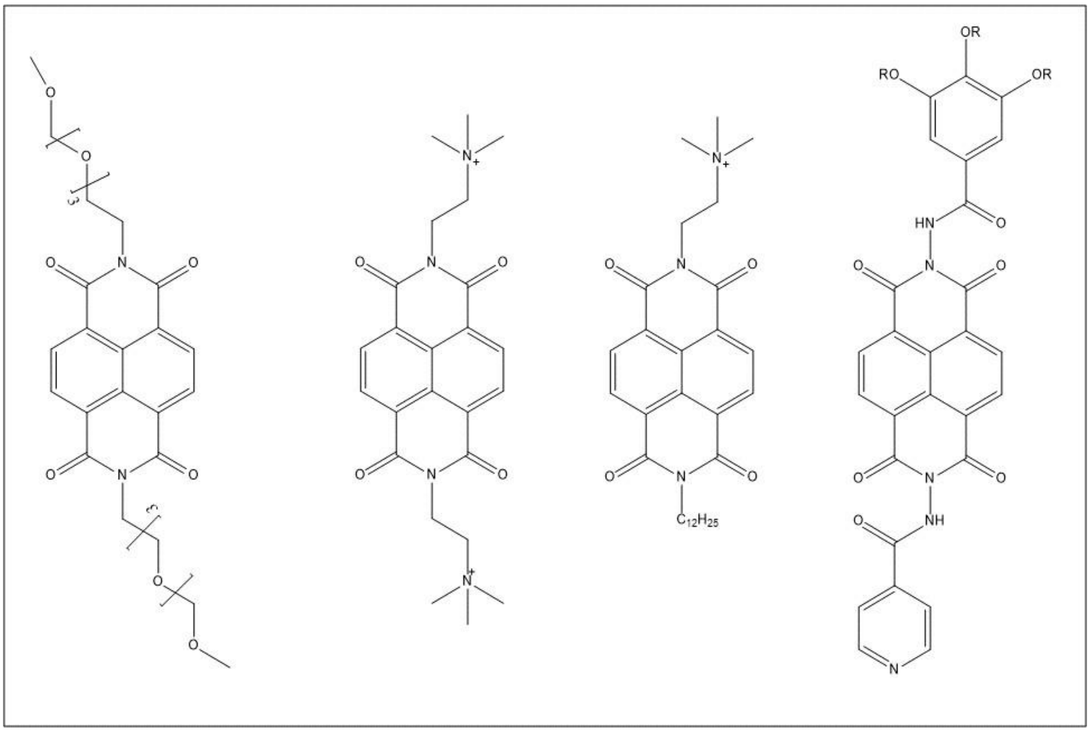


Figure 2.1: Structures of some symmetric and asymmetric Naphthalene Diimidederivatives [1].

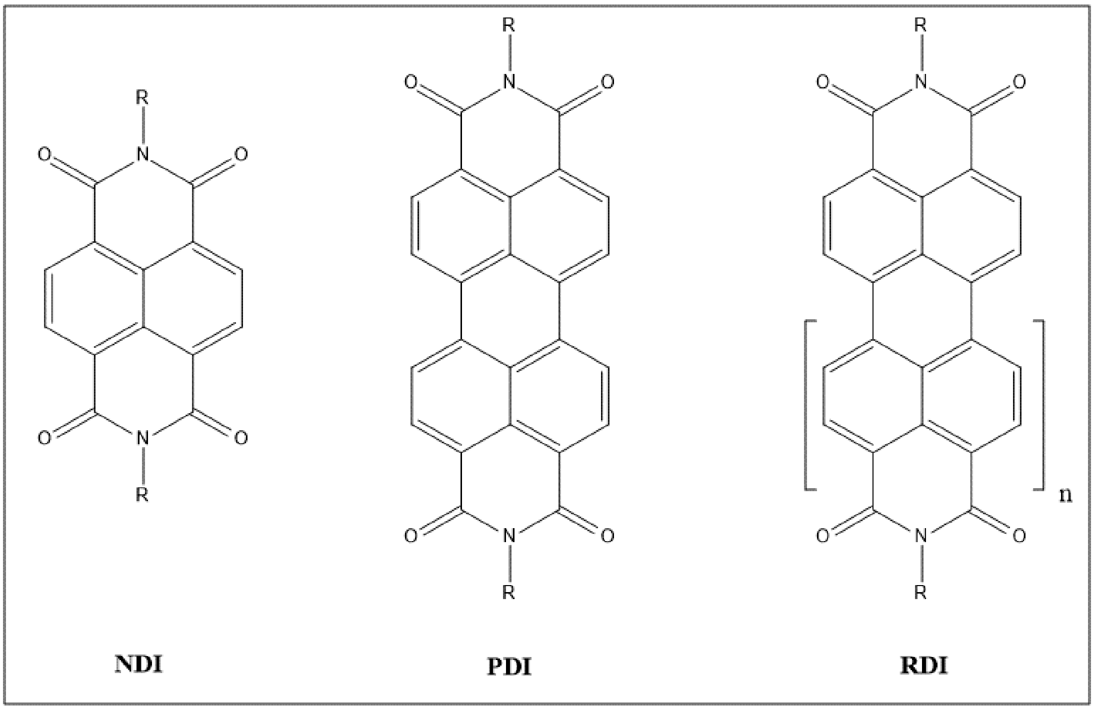


Figure 2.2: General steuctures of Naphthalene Diimide (NDI), Perylene Diimide(PDI) and Rylene Diimide (RDI) [18].

2.2 Properties of Naphthalene Diimide Derivatives

The solubility of Naphtahlene Diimide derivatives in various organic solvents can be improved by introducing bulcky aromatic substituents on imide positipns to prevent aggregation which decreases solubility. The solubility of N-aryl derivatives increases in the following order: Xylene < Toluene < Ethylacetate < DMF < Acetonitrile < THF < $CHCl_3$ < CH_2Cl_2 [17].

To increase the luminescence a common strategy is to incorporate the electron-donating moieties into Naphthalene Diimides core through covalent bond [9].

The procedure to adjust the luminescence characteristics are invalved because the separation of by-product tends to be monotone and often can be chemically unstable [8].

During the last few years, Naphthalene Diimides have been developed as strong air-stable n-type semiconductors due to their great packing behavior and electron poor character [10].

2.2.1 Optical Characteristics of Naphthalene Diimides Derivatives

Optical characteristics of Naphthalene Diimide derivatives can be described by long aromatic π- system. Core-unsubstituted Naphthalene Diimides derivatives with larger π-system such as Perylene Diimide show maximum absorbance at about 530 nm and fluorescence emission varying from 500 to 560nm, while Terrylene Diimides show absorption maxima at 650nm and they show fluorescence at 670nm. Meanwhile the Quaterrylene Diimides show absorption at 760nm and fluorescence maxima 780nm near infrared region [11].

Naphthalene Diimide derivatives with alkylamino and arylamino functional groups show some changes in absorption and emission as various substituted groups at the imide. H-NMR spectra of both these substituents show a peak for the amino proton at 9-11 ppm even when the polarity of the solvents is high. The optical properties of Naphthalene Diimide derivatives show that the substituted groups at the naphthalene center have a huge impact on the electronic characteristics [11].

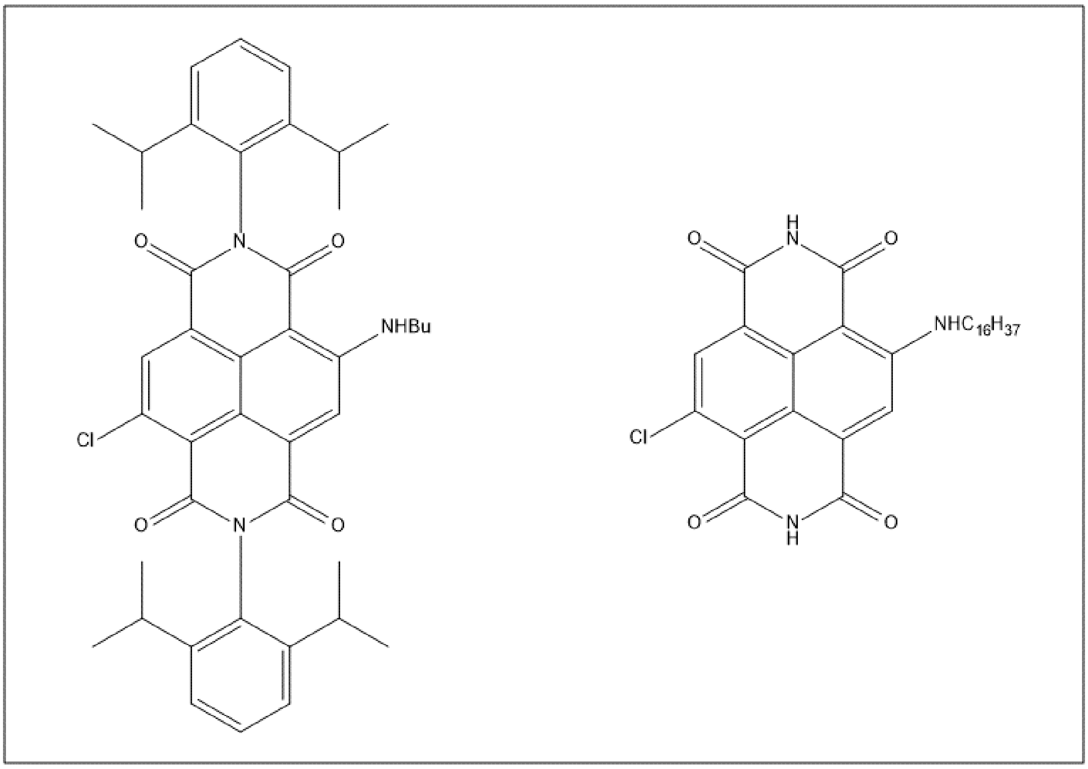


Figure 2.3: Structure of some NDIs derivatives by amino substituent [11].

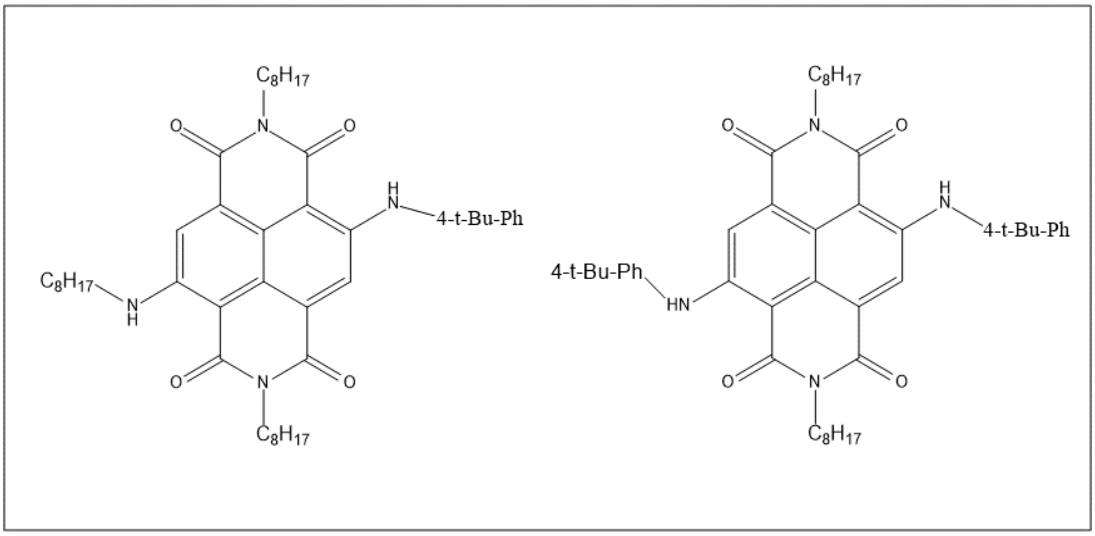


Figure 2.4: Structure of some NDIs derivatives by arylamino substituent [11].

2.2.2 Electron Transfer

Naphthalene Diimides perform very fast electron transfer via singlet or triplet excited state which has been proven from the photooxidation studies [12].

Electron transfer occurs when electrons relocate from a donor molecule to an acceptor molecule, releasing energy that it can be used for chemical work. Electron transfer reactions are being focused on by many scientists. This is because electron transfer reactions can be used as a model to study solvent effects, also it can be used in some processes such as: molecular signaling, conversion of solar energy, photosensitizers catalysis [16].

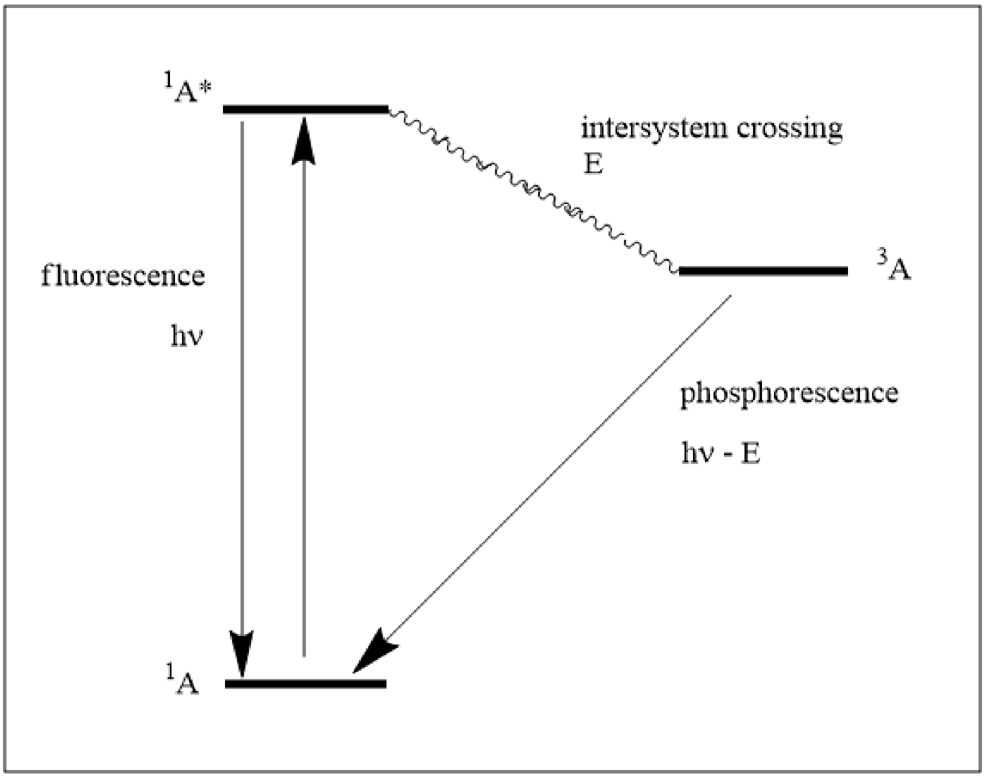


Figure 2.5: Molecule excitation to its singlet excited state and to triplet state succeeded by intersystem crossing.

2.3 Application of Naphthalene Diimide

Naphthalene Diimides have attracted a lot of interest of their ability application in catalysis, photoluminescence, photovoltaic, photo and electrochromism and anion transport due to their expanded π-electron-deficient plane [8].

Naphthalene Diimide derivatives are convertible in coordination as a result of their big interconnected planar structure and great ability of electron transfer [6].

In order to discover new anticancer agents some asymmetric Naphthalene Diimide derivatives modified by short amino chain have been synthesized. The substituent group of these derivatives have the main role at the effect of anticancer agents [7].

The tendency of Naphthalene Diimides (NDI) to form n-type over p-type semiconductors made them great candidates in the design of conducting materials. Also they are being included into larger multicomponent assemblies through intercalation due to their compactability, electron deficiency and their ability of self-organization [3].

Structure of NDIs contains a hydrophobic naphthyl center and four hydrophilic carbonyl groups and that’s what make them soluble in low polarity solvents such as: C_7H_8, Dichloromethane (DCM), $CHCl_3$ and polar aprotic solvents as: C_2H_3N, Dimethylformamide (DMF) and Dimethylsulfoxide (DMSO) [3].

2.3.1 Naphthalene Diimide Derivatives in Organic Solar Cell, Photovoltic Technology

Finding an advance material that are used as an electron acceptor in organic photovoltaics is becoming a priority. These materials should react good into donor/acceptor reactions, even though it is a difficult system because some properties should be improved at the same time such as: energy levels of molecular orbitals, light accumulation [13].

Naphthalene Diimide derivatives have been used as an electron acceptor in photovoltaic cells (PV) because their structure is not bulky and are not difficult to be substituted [14].

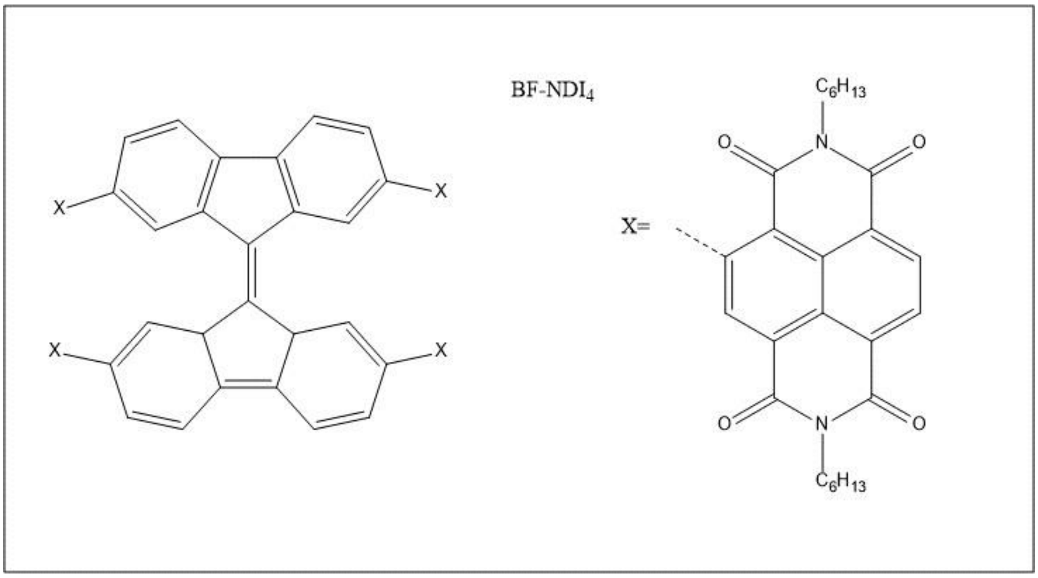


Figure 2.6: Structure of BF-NDI4 where Naphthalene Diimide is acting like an electron donor and Bifluorenylidene (BF) is used as a core [14].

Chapter 3

EXPERIMENTAL

3.1 Materials

All the chemical materials that were used in the synthesis of Naphthalene Diimide derivatives were commercial grade. Following the literature, molar concentrations of some solvents were changed from adding distilled water [15].

1,4,5,8-Naphthalenetetracarboxylic anhydride, 4-Aminophenol, isoquinoline, were obtained from Sigma Aldrich and were not purified.

As substituents two different amines were used: 2-amino-4,6-dichloro-1,3,5-triazine and 2,3,4,5,6-pentafluoroaniline.

Thin Layer Chromatography (TLC aluminum sheets 5×10 cm silica gel 60 F254) which visualize by UV light was used to control the progress of the reactions and to control the purity of the products.

3.2 Instrumentations

To record IR spectrum (JASCO FR-6200) FT-IR spectrophotometer was used through KBr pellets.

Drying oven was used: Nabertherm, 30-3000°C.

Cary-100 UV-VIS Spectrophotometer was used to measure Ultraviolet Absorption spectra.

Varian Cary Eclipse Fluorescence Spectrophotometer was used to measure Emission spectra and Fluorescence Quantum yield.

3.3 Synthesis of N (4 hydroxyphenyl) 1,4,5,8–naphthalenetetracarboxylic–1,8–anhydride–4,5 – imide, Naphthalene Monoimide (4)

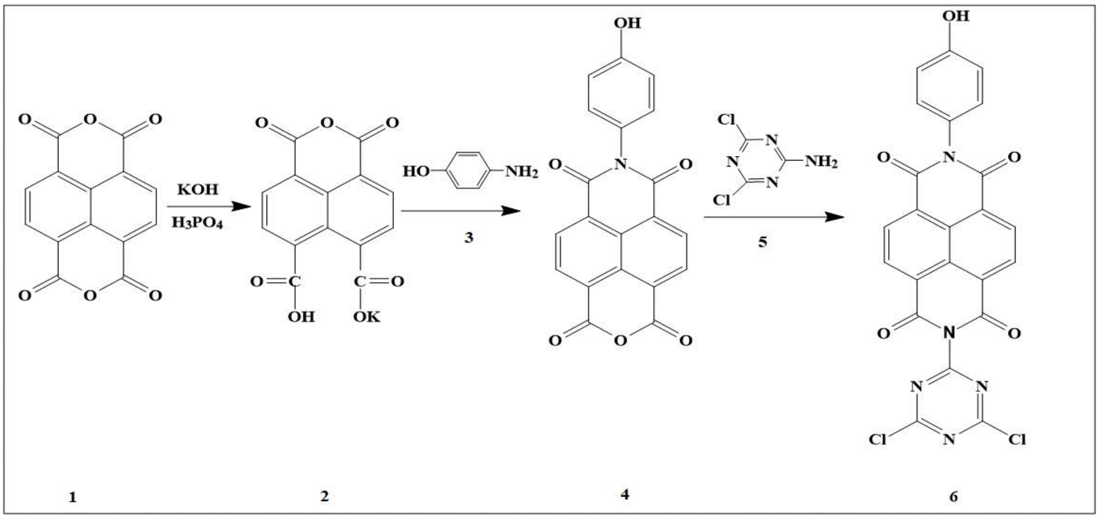
2.0g (7.5 mmol) of 1,4,5,8-Naphthalenetetracarboxylic dianhydride, 350 mL water, 65 mL (1.0 M) potassium hydroxide were added and stirred with a magnetic stirrer for 2 hours with no heat in a closed system. The solution was acidified with phosphoric acid until the P^H reaches the value of 6.4 from the starting value of 14. In the solution was added 0.8g (7.5 mmol) 4-Aminophenol and was stirred at 110 °C for 29 hours. The mixture was filtered by using vacuum filtration; then the filtrate was acidified with acetic acid (10%). Another vacuum filtration was done where the precipitate is collected (Naphthalene Monoimide). To wash the precipitate from impurities the Soxhlet procedure was done. Water was chosen as a solution. The product was dried by vacuum oven for 3 hours.

3.4 Synthesis of N‑(4‑hydroxyphenyl)‑N'‑(3,5‑dichloro‑2,4,6 triazinyl)‑1,4,5,8‑naphthalenediimide (6)

In 0.45g Naphthalene Monoimide were added 40 mL isoquinoline and 1.072g 2-Amino-4,6-dichloro-1,3,5-triazine. The solution was stirred under argon in a closed system at 80°C (3h), 120°C (6h), 160°C (8h) and at 190°C (5h). The warm solution was poured in 300mL methanol. The solution was filtrated by vacuum filtration. The precipitate was washed by Soxhlet procedure where methanol is used as a solvent. Finally, the pure product was dried by vacuum oven.

Yield: 85% (0,54 g)

Color: brown



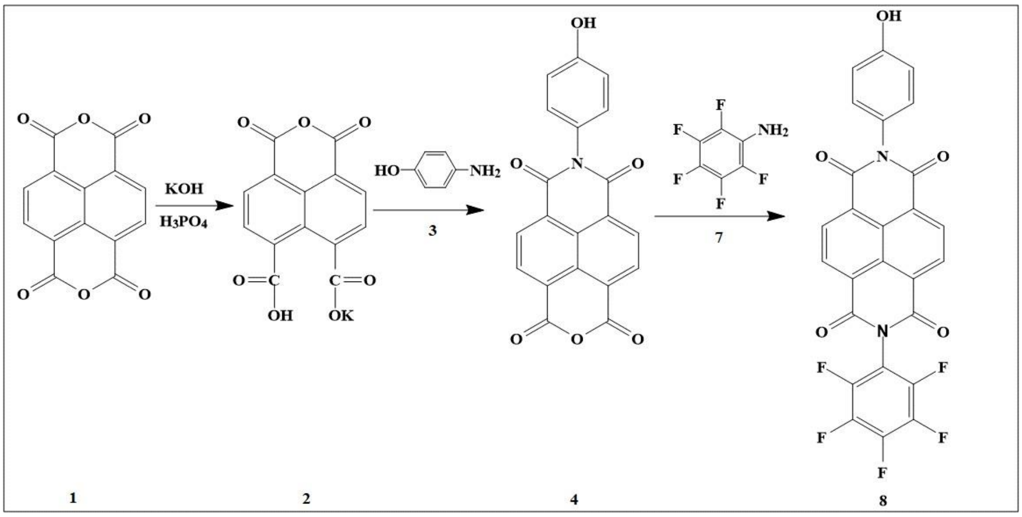
Scheme 3.1: Synthesis of N‑(4‑Hydroxyphenyl)‑N'‑(3,5‑Dichloro‑2,4,6‑Triazinyl)‑1,4,5,8‑Naphthalenediimide (6)

3.5 Synthesis of N‑ (4‑hydroxyphenyl)‑ N'‑ (2,3, 4, 5, 6 pentafluorophenyl)‑1,4,5,8‑naphthalenediimide (8)

In 0.45g Naphthalene Monoimide were added 40 mL isoquinoline and 1.19g 2,3,4,5,6-pentafluoroaniline. The solution was stirred under argon in a closed system at 80°C (3h), 120°C (6h), 160°C (8h) and at 190°C (5h). The warm solution was poured in 300mL methanol. The solution was filtrated by vacuum filtration. The precipitate was washed by Soxhlet procedure where methanol is used as a solvent. Finally, the pure product was dried by vacuum oven.

Yield: 85 % (0.78 g)

Color: dark brown



Scheme 3.2: Synthesis of N‑(4‑Hydroxyphenyl)‑N'‑(2, 3, 4, 5, 6‑Pentafluorophenyl)‑1,4,5,8‑Naphthalenediimide (8)

Chapter 4

DATA AND CALCULATIONS

4.1 Calculations of Maximum Molar Absorptivity (ε_{max})

The maximum molar absorbitivity (ε_{max}) can be calculated in accordance to Beer-Lambert law

$$\varepsilon_{max} = A/cl \qquad (1)$$

A: absorption

c: concentration of the solution

l: path length of the cell holder

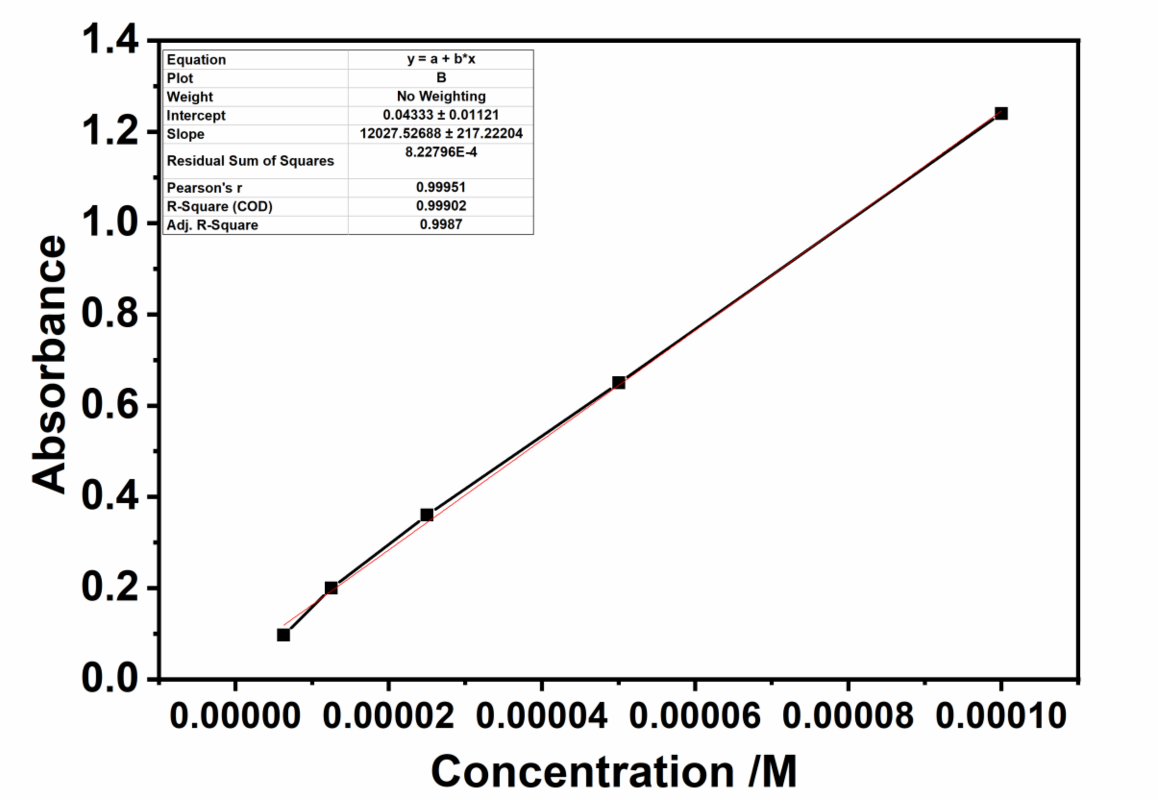
Following the similar method. The maximum molar absorptivity (ε_{max}) of the synthesized compounds 6 and 8 were listed below.

Table 4.1: The maximum extinction coefficient of 6 and 8 in DMF

Compound	Concentration (M)	Absorbance	λ_{max}(nm)	ε_{max}(L M^{-1} cm^{-1})
6	1×10^{-4}	1.24	378	12030
8	1×10^{-4}	1.16	378	11500

Table 4.2: The maximum extinction coefficient of 6 and 8 in NMP

Compound	Concentration (M)	Absorbance	λ_{max}(nm)	ε_{max}(L M^{-1} cm^{-1})
6	5×10^{-5}	1.37	377	26000
8	5×10^{-5}	1.06	378	19000



Equation	y = a + b*x
Plot	B
Weight	No Weighting
Intercept	0.04333 ± 0.01121
Slope	12027.52688 ± 217.22204
Residual Sum of Squares	8.22796E-4
Pearson's r	0.99951
R-Square (COD)	0.99902
Adj. R-Square	0.9987

Figure 4.1: Absorbance versus Concentration Plot of 6 in DMF

Slope = ε_{max} = 12030 M^{-1}cm^{-1}

4.2 Calculation of Fluoroscence Quantum Yield (ɸf)

$ɸ_{f(U)}=\frac{Astd}{A_u} \times \frac{St}{Sstd} \times \left[\frac{nu}{n_{std}}\right]^2 \times ɸ(std)$ (2)

Fluorescence quantum yield of 6 in NMP

$ɸ_f$ (std) = 0.27

A_{std} = 0.1055

A_u = 0.1002

S_u = 196.24

S_{std} = 7824.32

n_{std} = 1.3616

n_u = 1.465

$ɸ_{f\ (U)} = \frac{Astd}{A_u} \times \frac{St}{Sstd} \times \left[\frac{nu}{n_{std}}\right]^2 \times ɸ\ (std)$

$ɸ_f$ (std): fluorescence quantum yield of reference

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

A_u: absorbance of the unknown at the excitation wavelength

S_u: the intergrated emission area across the band of the unknown

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

n_{std}: refractive index of reference solvent

n_u: refractive index of unknown solvent

$ɸ_{f\ (U)} = \frac{0.1055}{0.1002} \times \frac{196.24}{7824.32} \times \left[\frac{1.465}{1.3616}\right]^2 \times 0.27 = 8.25 \times 10^{-3}$

Table 4.3 : Fluorescence quantum yields of 6 and 8 in DMF and NMP

Solvents	ϕ_f 6	ϕ_f 8
DMF	0.01	0.01
NMP	0.01	0.01

4.3 Calculations of Maximum Absorption Half-width ($\Delta\nu_{1/2}$)

The maximum absorption half-width can be calculated by the formula:

$$\Delta_{V_{1/2}} = V_1 - V_2 \qquad (3)$$

$\Delta\nu_{1/2}$: maximum absorption half-width

ν_I, ν_{II}: frequencies from absorption spectrum

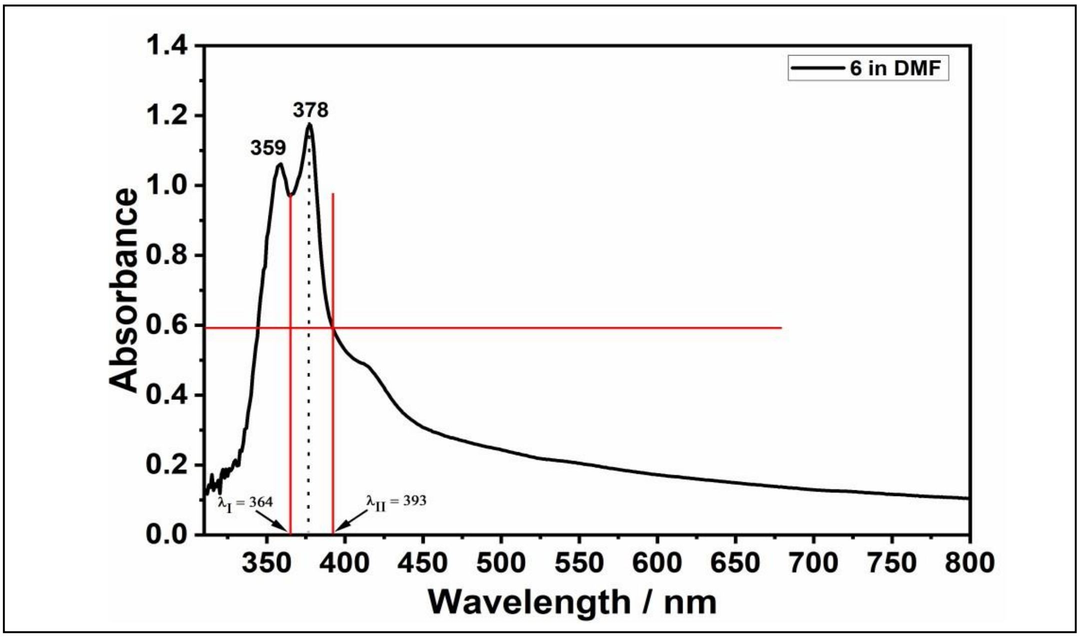


Figure 4.2: Absorption Spectrum of 6 in DMF

λ_I = 364 nm

$$\lambda_I = 364 \text{ nm} \times \frac{10^{-9} m}{1\ nm} \times \frac{1\ cm}{10^{-2}} = 3.64 \times 10^{-5} \text{ cm}$$

$$\nu_I = \frac{1}{\lambda I} = \frac{1}{3.64 \times 10^{-5}\ cm} = 27472.53 \text{ cm}^{-1}$$

λ_{II} = 393 nm

λ_I= 393 nm $\times \frac{10^{-9} m}{1\, nm} \times \frac{1\, cm}{10^{-2}} = 3.93 \times 10^{-5}$ cm

$\nu_I = \frac{1}{\lambda I} = \frac{1}{3.93 \times 10^{-5}\, cm}$ = 25445.3 cm^{-1}

$\Delta\nu_{1/2} = \nu_I - \nu_{II}$ = 27472.53 cm^{-1} – 25445.3 cm^{-1} = 2027.23 cm^{-1}

Determining the half-width of the compounds is necessary to calculate the theoretical radiative lifetimes. The half-width values were calculated as shown below in Table 4.4 and 4.5.

Table 4.4: Absorption half-width of 6 in DMF and NMP

Solvent	λ_I (nm)	λ_{II} (nm)	$\Delta\nu_{1/2}$ (cm^{-1})
DMF	364	393	2030
NMP	366	391	1750

Table 4.5: Absorption half-width of 8 in DMF and NMP

solvent	λ_I (nm)	λ_{II} (nm)	$\Delta\nu_{1/2}$ (cm^{-1})
DMF	371	429	3645
NMP	375	430	3400

4.4 Calculations of Theoretical Radiative Lifetimes (τ_0)

The theoretical radiative lifetimes can be calculated by the formula:

$$\tau_0 = \frac{3.5 \times 10^8}{v_{max}{}^2 \times \varepsilon_{max} \times \Delta_{v_{1/2}}} \quad (4)$$

τ_0: theoretical radiative lifetime

ν_{max}: mean frequency of the maximum absorption

ε_{max}: maximum molar absorptivity

$\Delta\nu_{1/2}$: maximum absorption half-width

Theoretical radiative lifetime of 6 in DMF

The theoretical radiative lifetime of 6 can be calculated from all the data obtained from Figure 4.1 and 4.2:

λ_{max}= 378 nm

λ_{max}= 378 nm $\times \frac{10^{-9} m}{1\,nm} \times \frac{1\,cm}{10^{-2}} = 3.78 \times 10^{-5}$ cm

$\nu_{max} = \frac{1}{\lambda max} = \frac{1}{3.78\times10^{-5}\,cm}$ = 26445.03 cm^{-1}

ν^2_{max}= $(26455.03\ cm^{-1})^2 = 6.99 \times 10^8\ cm^{-2}$

$$\tau_0 = \frac{3.5 \times 10^8}{v_{max}{}^2 \times \varepsilon_{max} \times \Delta_{v_{1/2}}}$$

$\tau_0 = \frac{3.5 \times 10^8}{6.99\times10^8 \times 12027.53 \times 2027.23} = 2.05\times10^{-8}$ cm

τ_0= 20.5 ns

The theoretical radiative lifetimes of 6 and 8 in different solvents were calculated with similar method and the results are presented below:

Table 4.6: Theoretical radiative lifetimes of 6 in DMF and NMP

Solvents	λ_{max} (nm)	ε_{max} (L.M^{-1}.cm^{-1})	ν^2_{max} (cm^{-1})^2	$\Delta\nu_{1/2}$ (cm^{-1})	$\tau_\circ$ (ns)
DMF	378	12027.53	6.99×10^8	2027.23	20
NMP	377	25780.65	7.03×10^8	1746.95	11

Table 4.7: Theoretical radiative lifetimes of 8 in DMF and NMP.

Solvents	λ_{max} (nm)	ε_{max} (L.M^{-1}.cm^{-1})	ν^2_{max} (cm^{-1})^2	$\Delta\nu_{1/2}$ (cm^{-1})	$\tau_\circ$ (ns)
DMF	378	11463.87	6.99×10^8	3644.15	12
NMP	378	18304.95	6.99×10^8	3410.85	8

4.5 Calculation of Theoretical Fluorescence Lifetime (τ_f)

Theoretical fluorescence lifetime can be calculated by the formula

$$\tau_f = \tau_0 \times \phi_f \tag{5}$$

Theoretical Fluorescence Lifetime of 6 in DMF

τ_f = 20.5 ns × 0.01 = 0.205 ns

Table 4.8: Theoretical fluorescence lifetimes of 6 in DMF and NMP

Solvent	τ_0 (ns)	ϕ_f	τ_f (ns)
DMF	20.50	0.01	0.21
NMP	11.04	0.01	0.11

Table 4.9: Theoretical fluorescence lifetimes of 8 in DMF and NMP

Solvent	τ_0 (ns)	ϕ_f	τ_f (ns)
DMF	11.90	0.01	0.12
NMP	8.00	0.01	0.08

4.6 Calucations of Fluorescence Rate Constant (k_f)

Fluorescence rate constant can be calculated from the formula

$$k_f = \frac{1}{\tau_0} \tag{6}$$

K_f: fluorescence rate constant

τ_o: theoretical radiative lifetime

Fluorescence rate constant of 6 in DMF

$$k_f = \frac{1}{\tau_0} = \frac{1}{2.05\times10^{-8}} = 4.87 \times 10^7 \text{ s}^{-1}$$

Table 4.10: Fluorescence rate constant of 6 in DMF and NMP

Solvent	τ_o (s)	k_f (s^{-1})
DMF	2.05×10^{-8}	4.87×10^7
NMP	1.1×10^{-8}	9.05×10^7

Table 4.11: Fluorescence rate constant of 8 in DMF and NMP

Solvent	τ_o (s)	k_f (s^{-1})
DMF	1.19×10^{-8}	8.3×10^7
NMP	8×10^{-8}	1.25×10^8

4.7 Calculations of Rate Constant of Radiotionless Deactivation (k_d)

Rate constant of radiotionless deactivation can be calculated by the formula shown below:

$$k_d = \left(\frac{kf}{\phi f}\right) - k_f \tag{7}$$

k_f: fluorescence rate constant

ϕ_{f}: fluorescence quantum yield of reference

Rate constant of radiotionless deactivation of 6 in DMF

$$k_d = \left(\frac{\mathbf{kf}}{\boldsymbol{\phi}\mathbf{f}}\right) - kf \quad = \left(\frac{\mathbf{4.87x10^7}}{\mathbf{0.01}}\right) - 4.87\times10^7 = 4.82\times10^9 \ s^{-1}$$

Table 4. 12: Rate constant of radiotionless deactivation of 6 in DMF and NMP

Solvent	.k_f (s^{-1})	ϕ_f	K_d (s^{-1})
DMF	4.87×10^7	0.01	4.82×10^9
NMP	9.05×10^7	0.01	8.96×10^9

Table 4. 13: Rate constant of radiotionless deactivation of 8 in DMF and NMP

Solvent	.k_f (s^{-1})	ϕ_f	K_d (s^{-1})
DMF	8.35×10^7	0.01	8.27×10^9
NMP	1.25×10^8	0.01	1.23×10^{10}

4.8 Calculations of Oscillator Strength (*f*)

The oscillator strength is the quantity with no dimension that corresponds the strength of electronic transitions. The oscillator strength can be calculated by the formula

$$f = 4.32\times 10^{-9}\times \Delta\nu_{1/2} \times \varepsilon_{max} \qquad (8)$$

f: oscillator strength

ε_{max}: maximum molar absorptivity

$\Delta\nu_{1/2}$: maximum absorption half-width

Oscilator strength of 6 in DMF

$f = 4.32\times 10^{-9} \times \Delta\nu_{1/2} \times\varepsilon_{max} = 4.32\times 10^{-9} \times 2027.23 \times 12027.53 = 0.105$

The oscillator strengths of 6 and 8 in different solvents are presented below:

Table 4.14: Oscillator strengths of 6 in DMF and NMP

Solvent	$\Delta\nu_{1/2}$ (cm-1)	ε_{max} (M-1 cm-1)	f
DMF	2027.23	12027.53	0.105
NMP	1746.95	25780.65	0.194

Table 4.15: Oscillator strengths of 8 in DMF and NMP

Solvent	$\Delta\nu_{1/2}$ (cm^{-1})	ε_{max} (M^{-1} cm^{-1})	f
DMF	3644.15	11463.87	0.18
NMP	3410.85	18304.95	0.27

4.9 Calculations of Singlet Energy (E_s)

The singlet energy can be calculated by the formula

$$E_s=\frac{2.86\times10^5}{\lambda\text{max}} \qquad (9)$$

E_s: singlet energy

λ_{max}: the wavelength at maximum absorption

Singlet energy of 6 in DMF

λ_{max} = 378 nm

E_s = 378 nm × 10 Å/ 1nm= 3780 Å

$$E_s=\frac{2.86\times10^5}{3780} = 75.66 \text{ kcal mol}^{-1}$$

Table 4.16: Singlet energies of 6 in DMF and NMP

Solvent	λ_{max} (Å)	E_s (kcal mol^{-1})
DMF	3780	75.66
NMP	3770	75.86

Table 4.17: Singlet energies of 8 in DMF and NMP

Solvent	λmax (Å)	Es (kcal mol^{-1})
DMF	3780	75.66
NMP	3780	75.66

4.10Calculations of Optical Band Gap Energies (E_g)

Optical band gap energies can be calculated by the formula

$$E_g = \frac{1240\ eV\ nm}{\lambda\ nm} \tag{10}$$

λ: cut-off wavelength of the absorption band

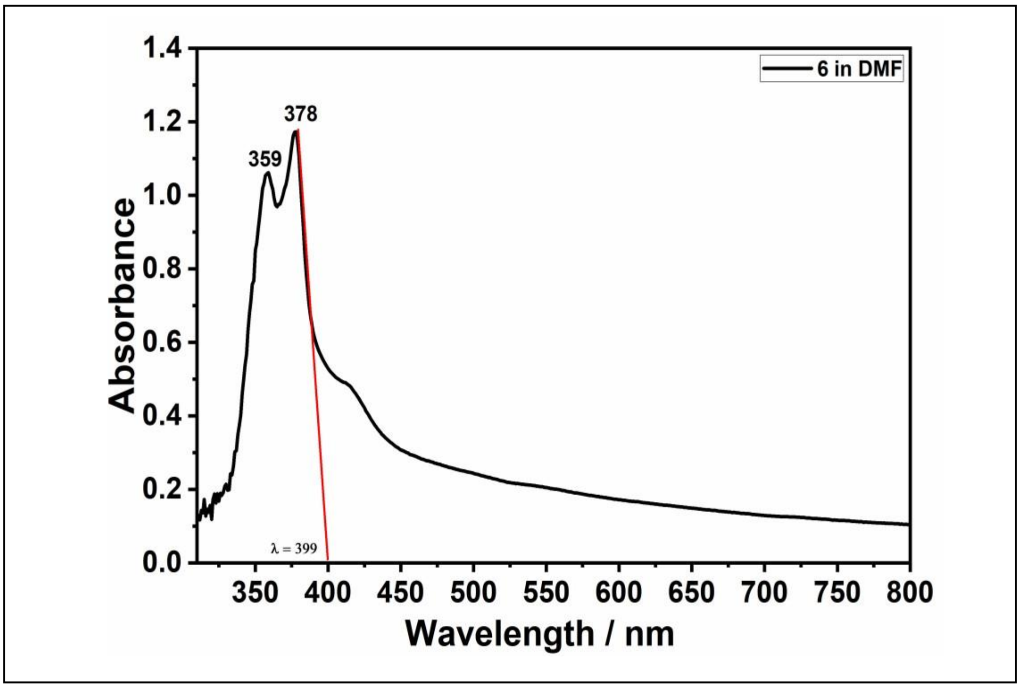


Figure 4.3: Absorption Spectrum of 6 in DMF showing the cut-off wavelength

Band gap energy of 6 in DMF

$$E_g = \frac{1240\ eV\ nm}{399\ nm} = 3.1\ eV$$

Table 4.18: Band gap energies of 6 in DMF and NMP

Solvent	λ (nm)	Eg (eV)
DMF	399	3.1
NMP	405.14	3.06

Table 4.19: Band gap energies of 8 in DMF and NMP

Solvent	λ (nm)	E_g (eV)
DMF	454	2.73
NMP	445.56	2.78

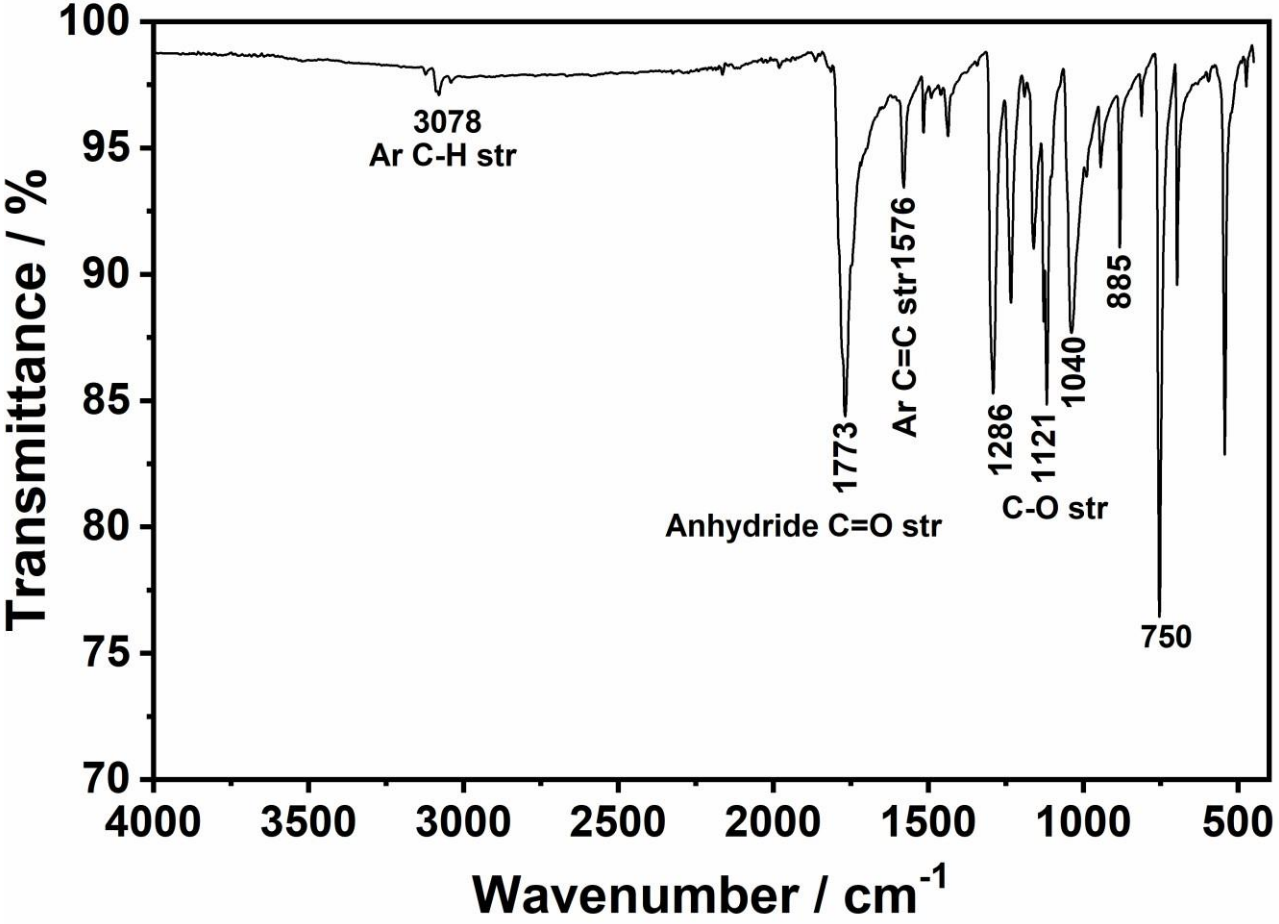


Figure 4.4: FTIR spectrum of 1,4,5,8-Naphthalenetetracarboxylic dianhydride

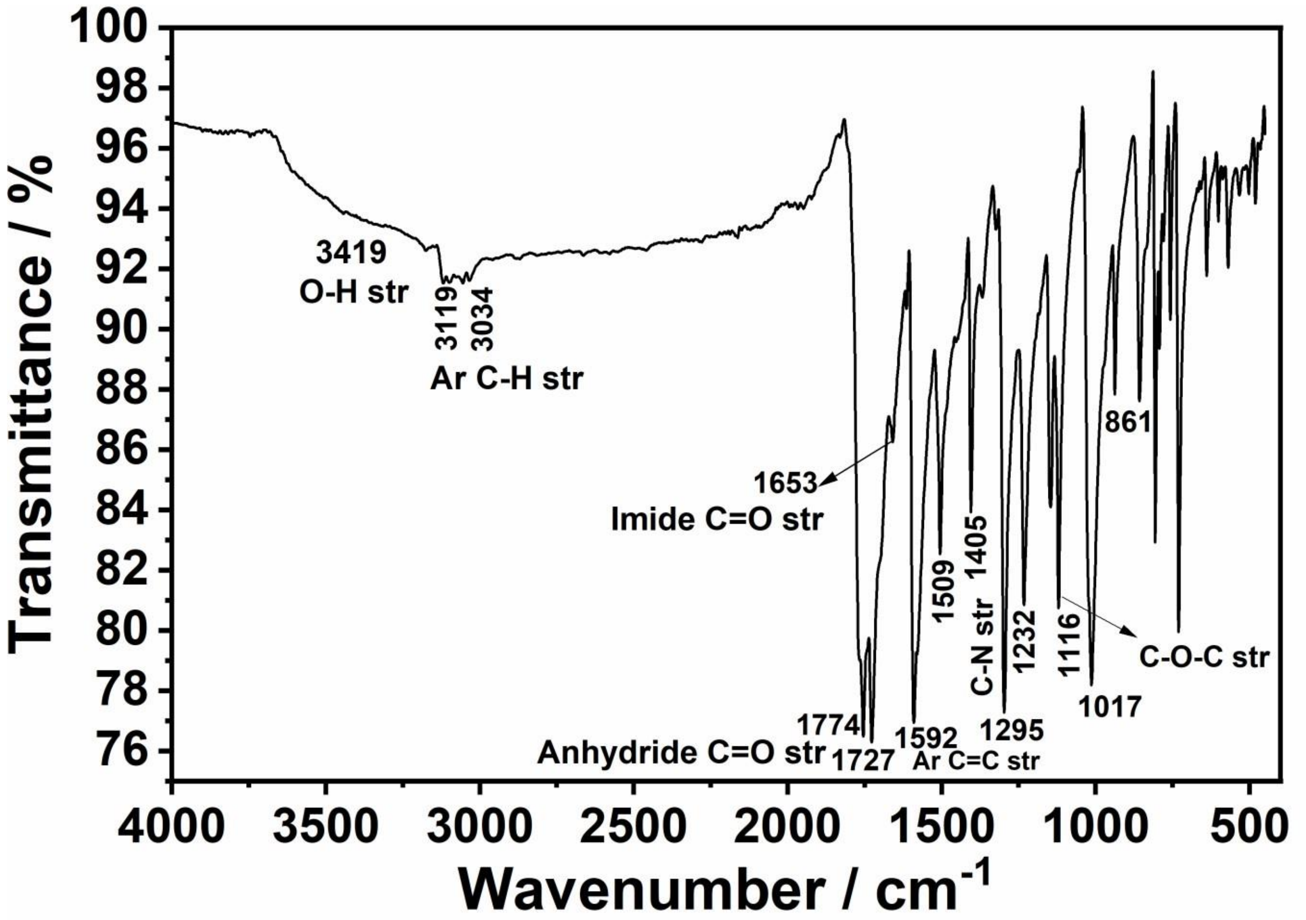


Figure 4.5: FTIR spectrum of Naphthalene Monoimide

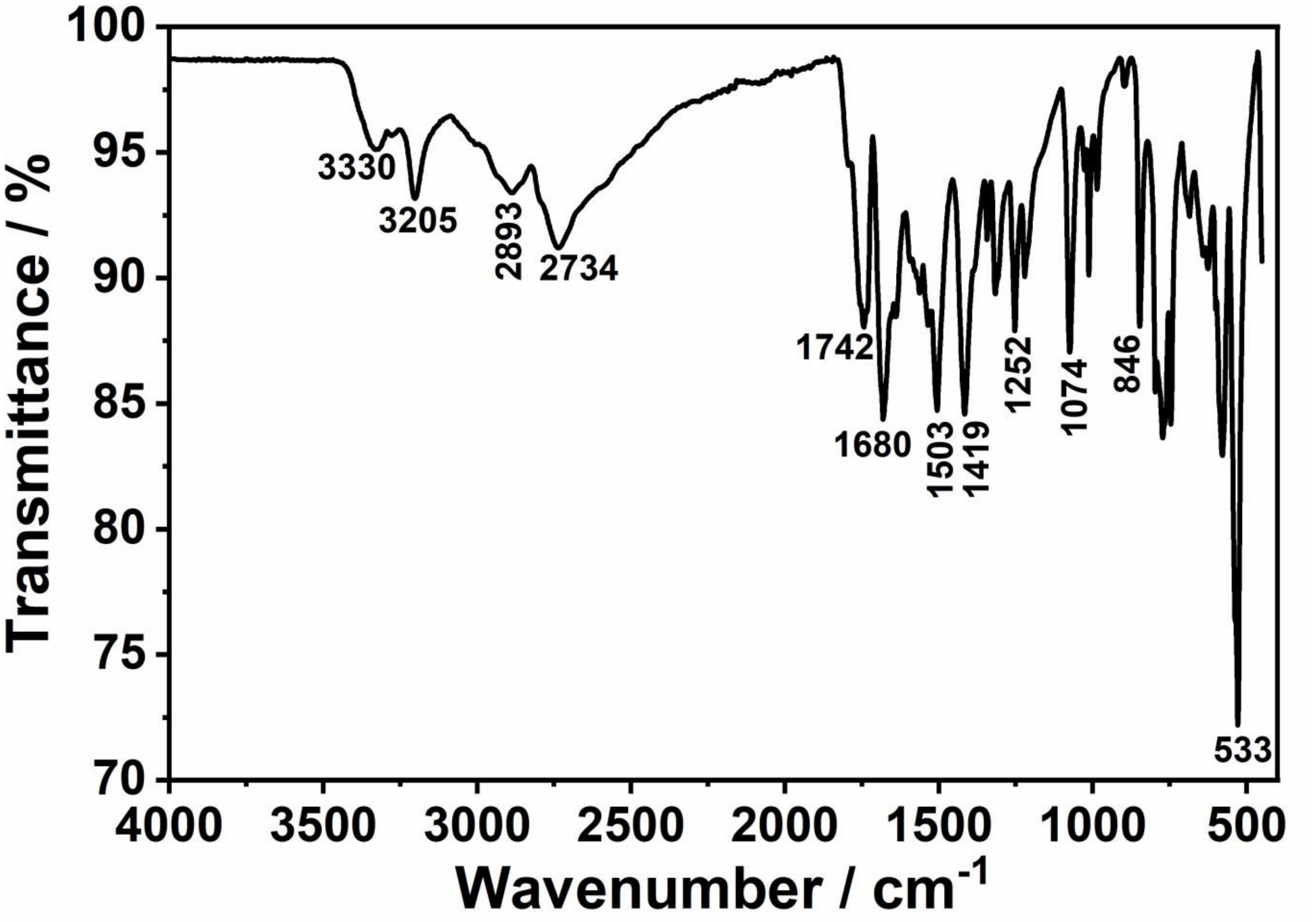


Figure 4.6: FTIR spectrum of 2-amino-4,6dichloro-1,3,5-triazine

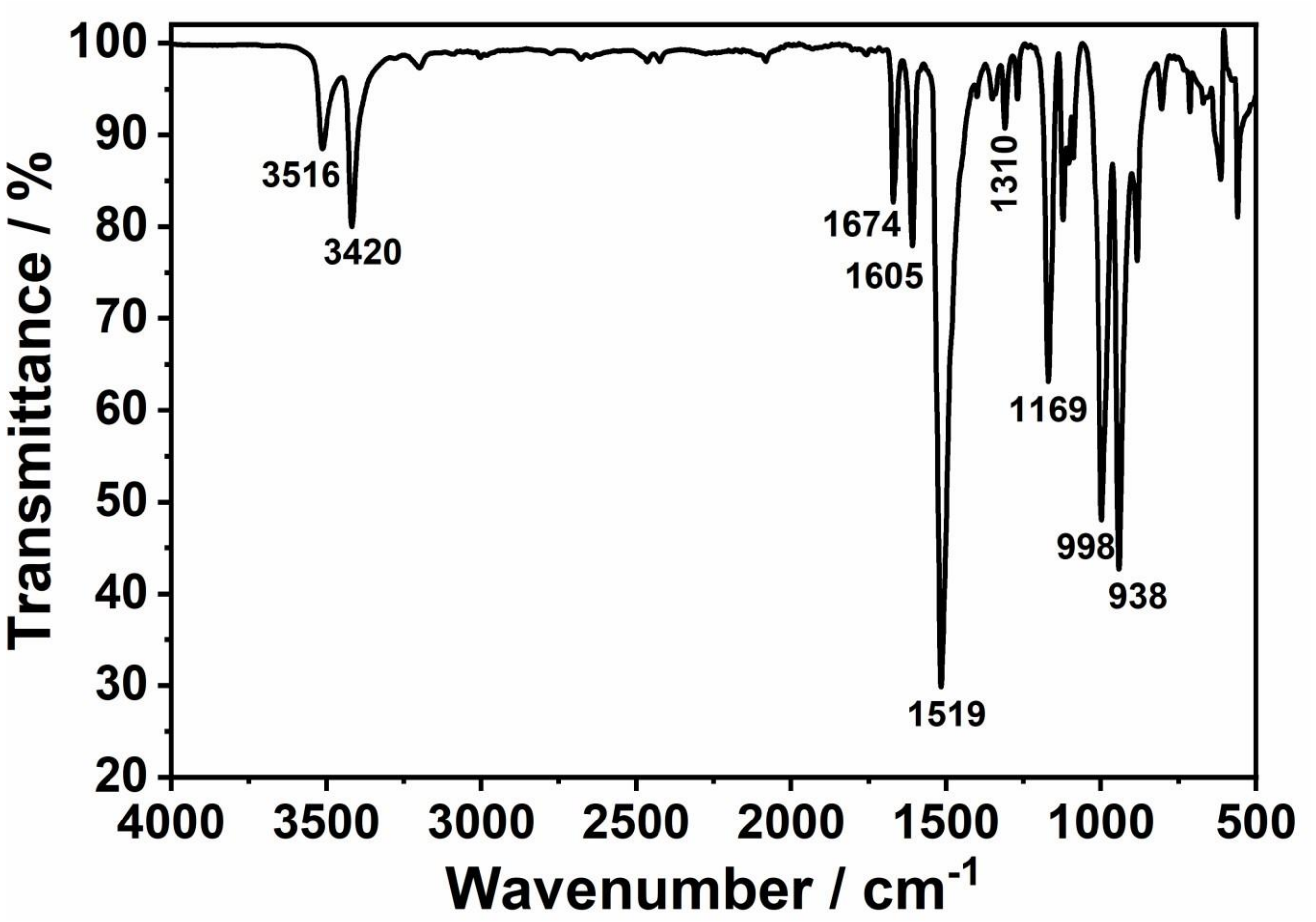


Figure 4.7: FTIR spectrum of 2,3,4,5,6-pentafluorine aniline

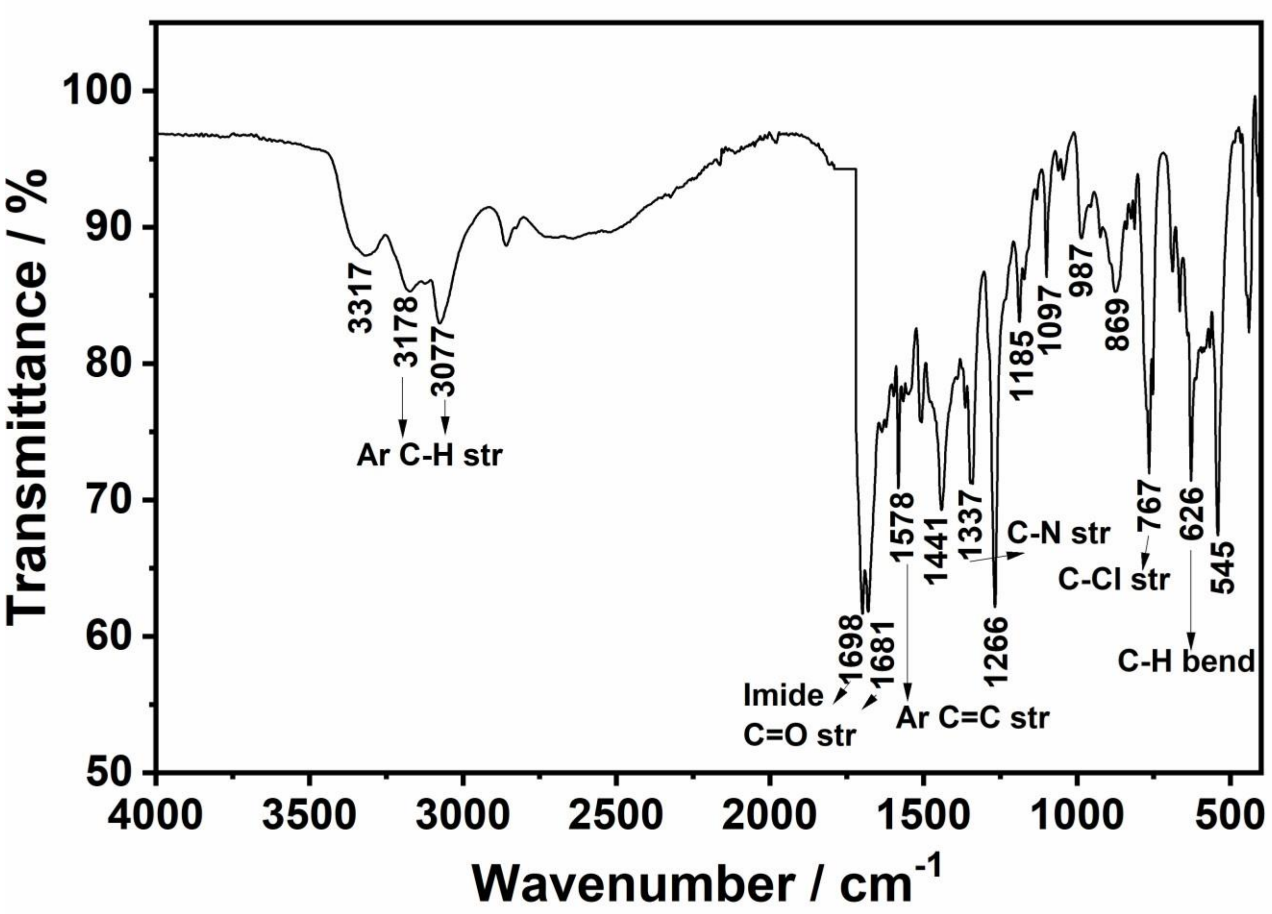


Figure 4.8: FTIR spectrum of 6

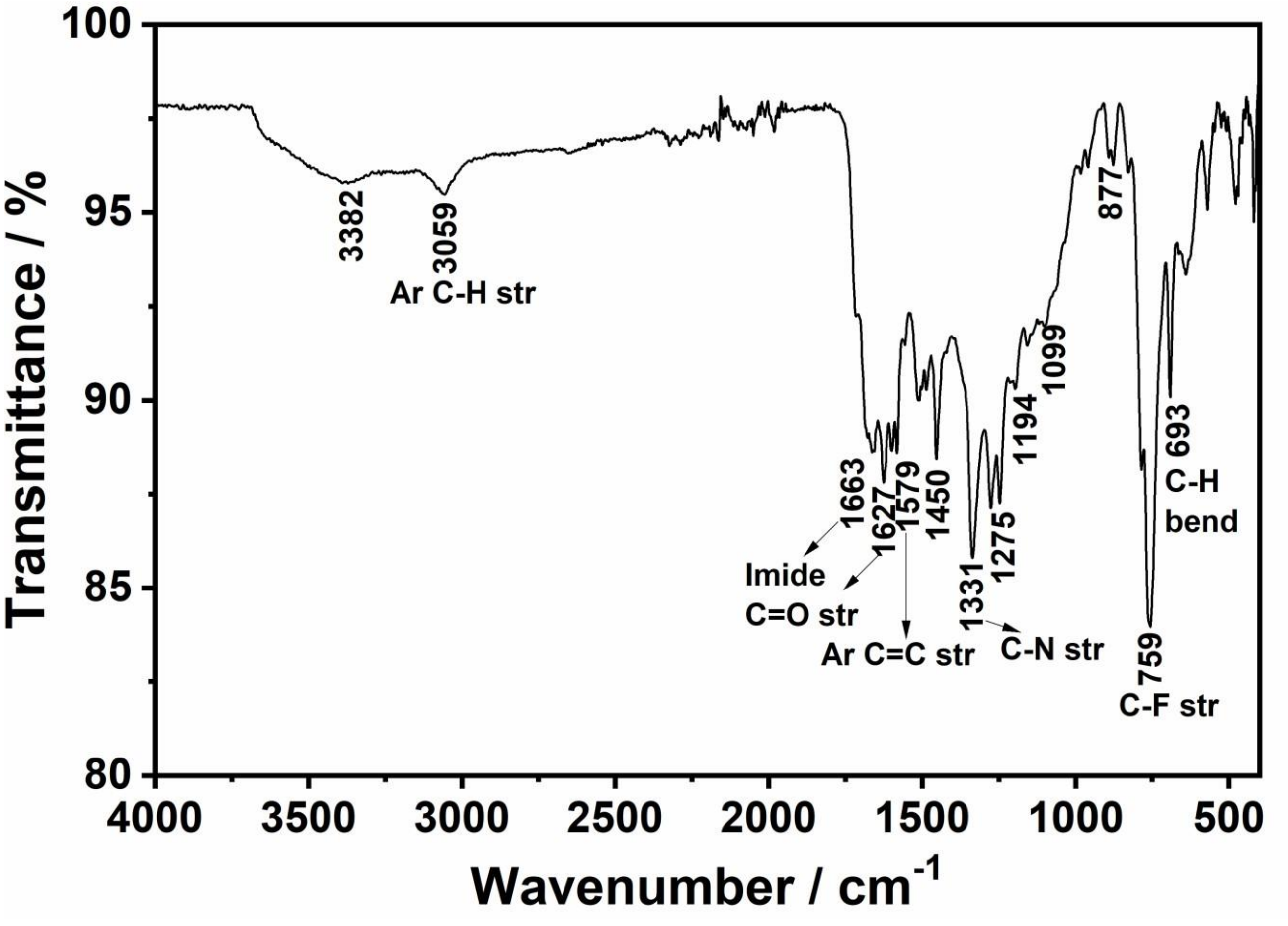


Figure 4.9: FTIR spectrum of 8

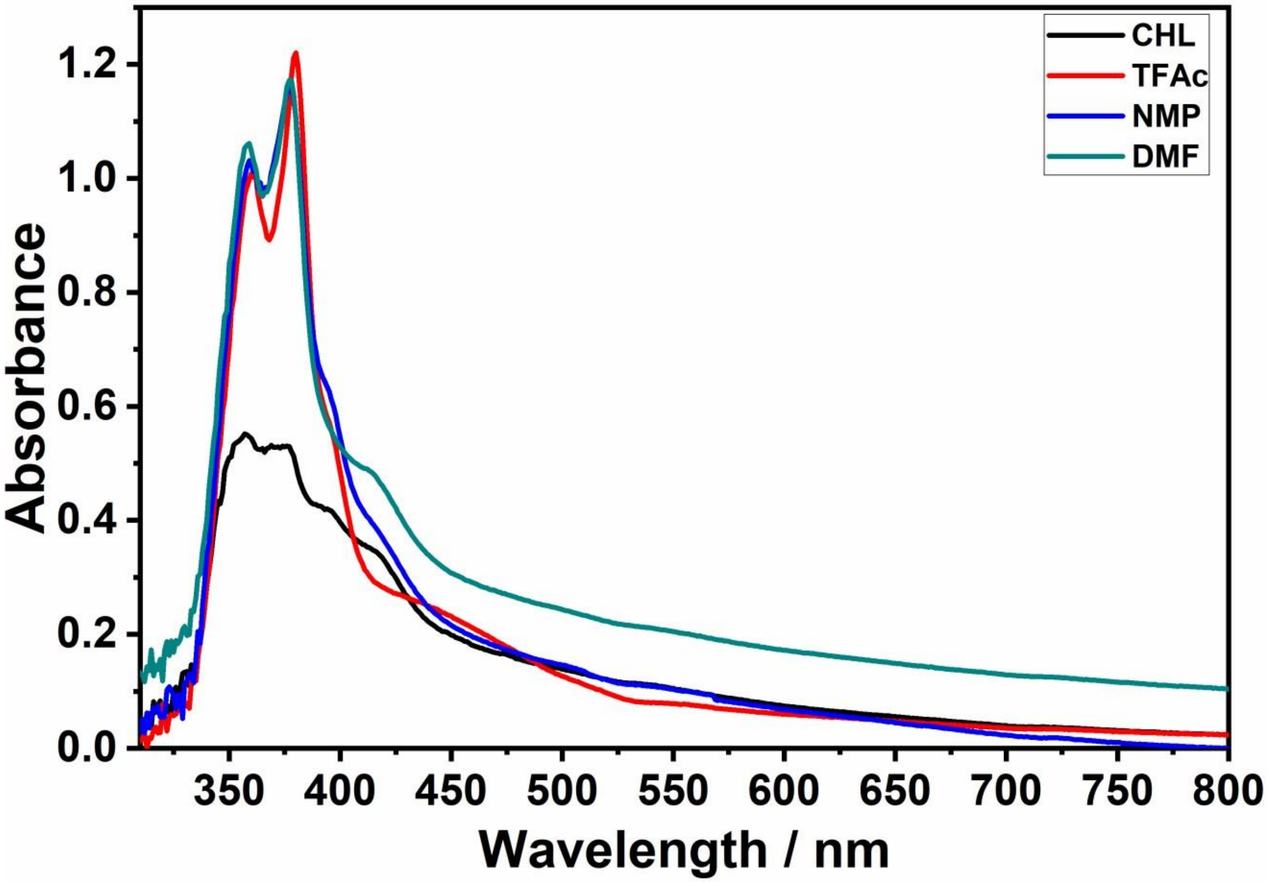


Figure 4.10: Absorption spectrum of 6 in different

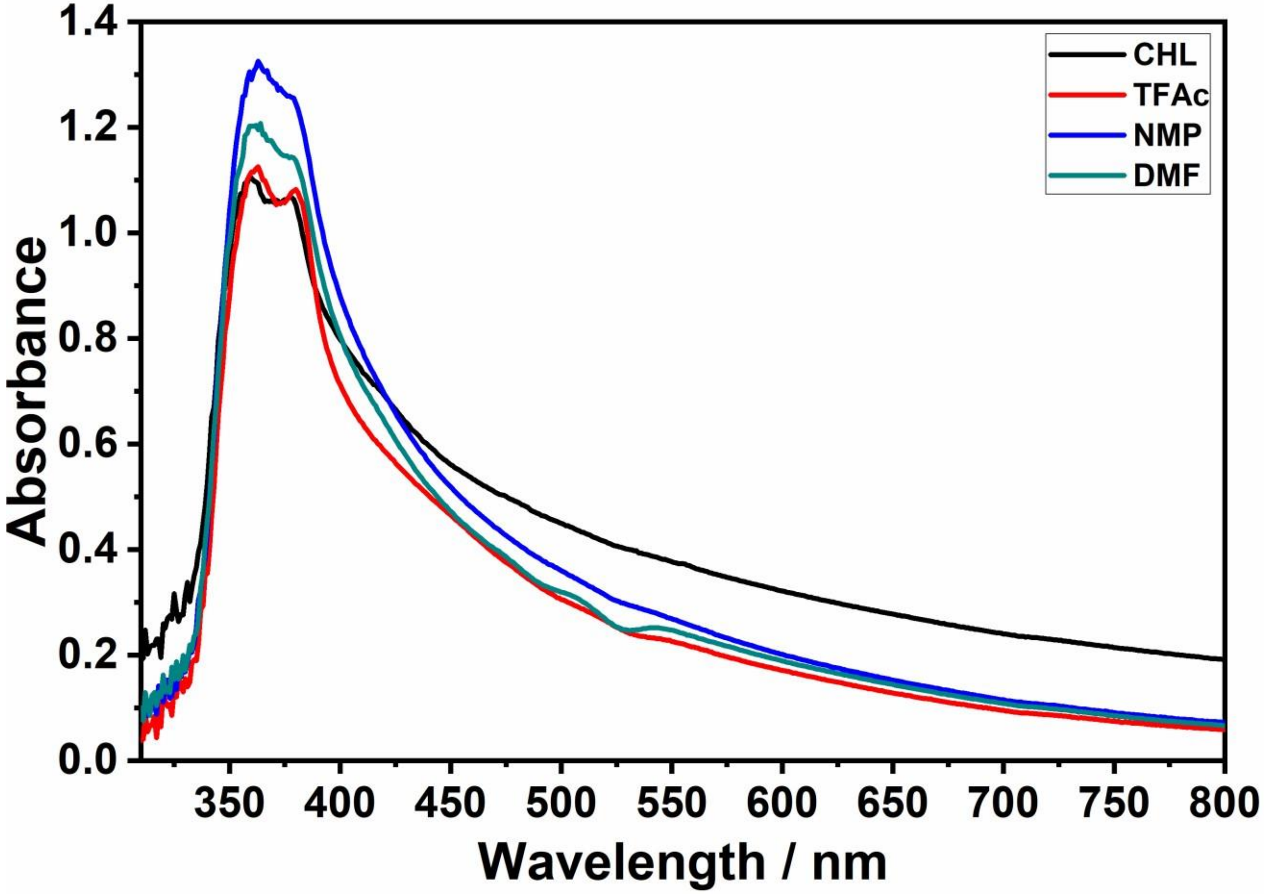


Figure 4.11: Absorption spectrum of 8 in different solvents

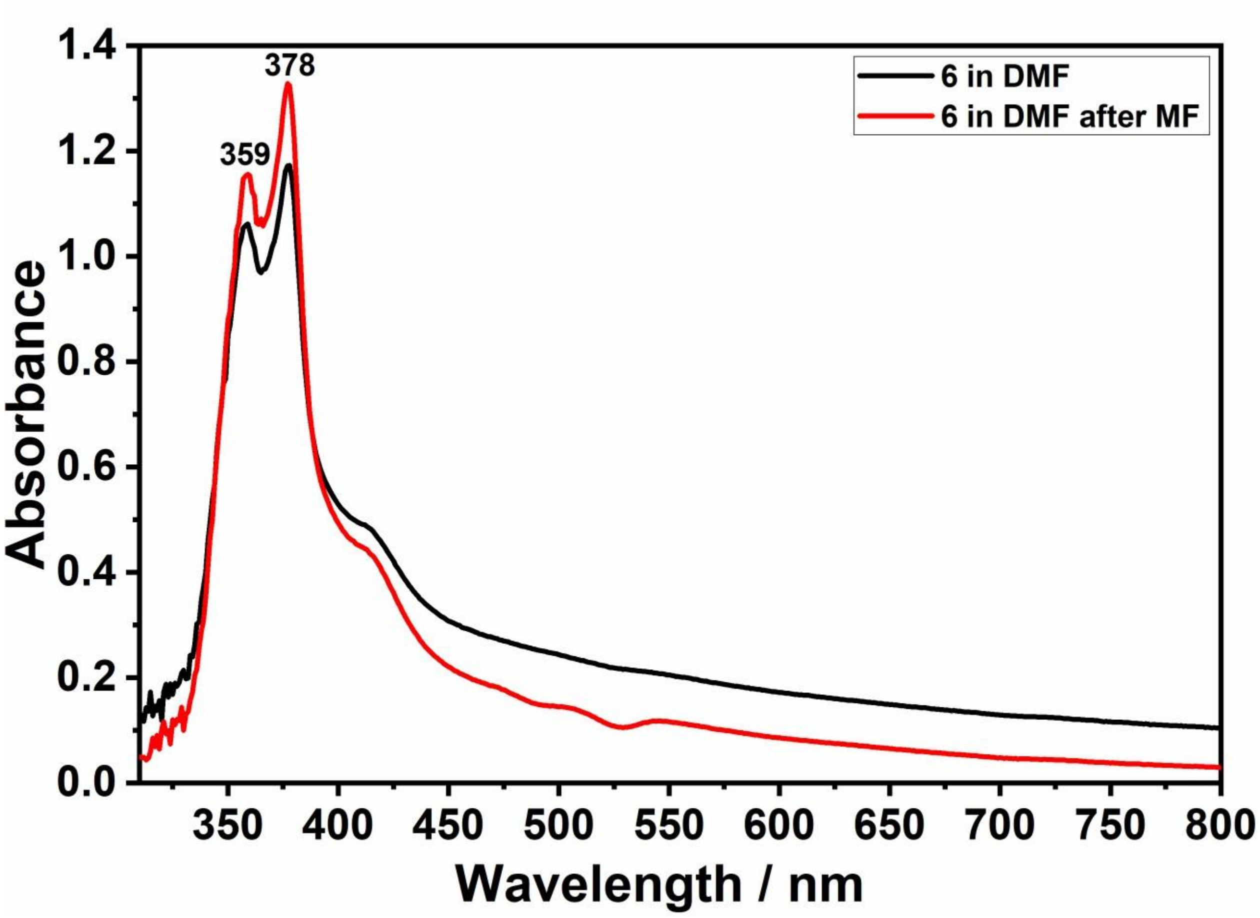


Figure 4.12: Absorption spectrum of 6 before and after microfiltration in DMF

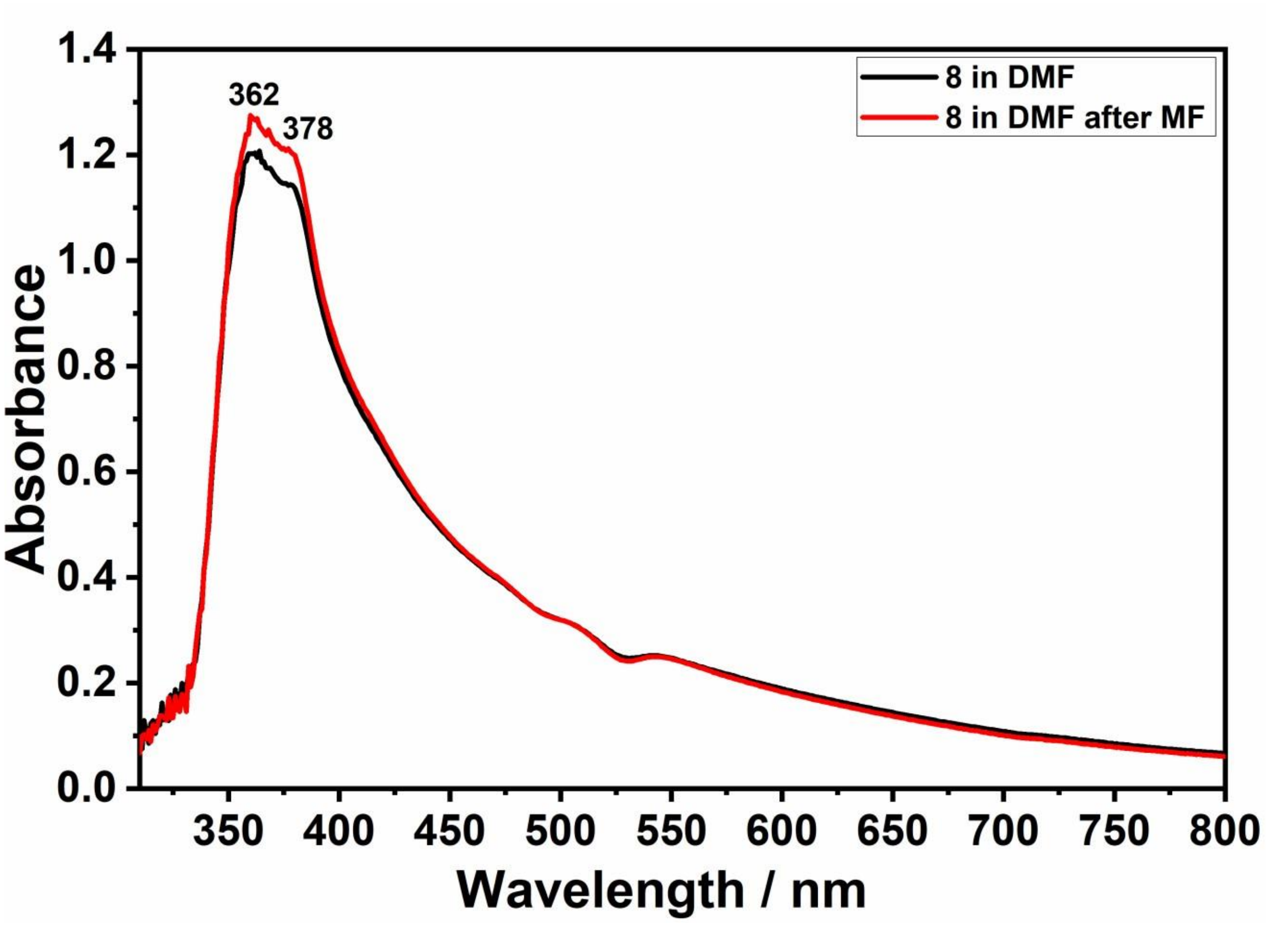


Figure 4.13: Absorption spectrum of 8 before and after microfiltration in DMF

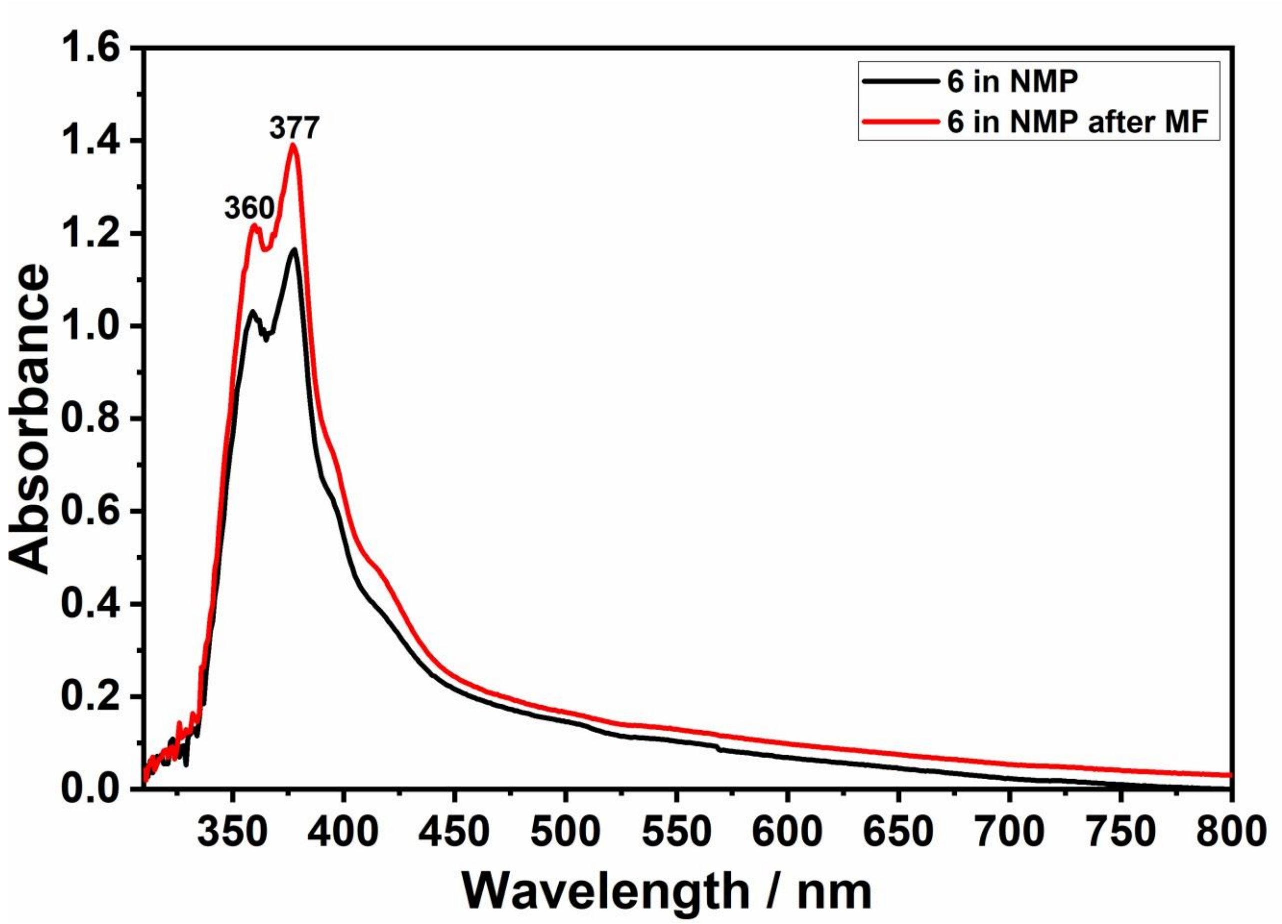


Figure 4.14: Absorption spectrum of 6 before and after microfiltration in NMP

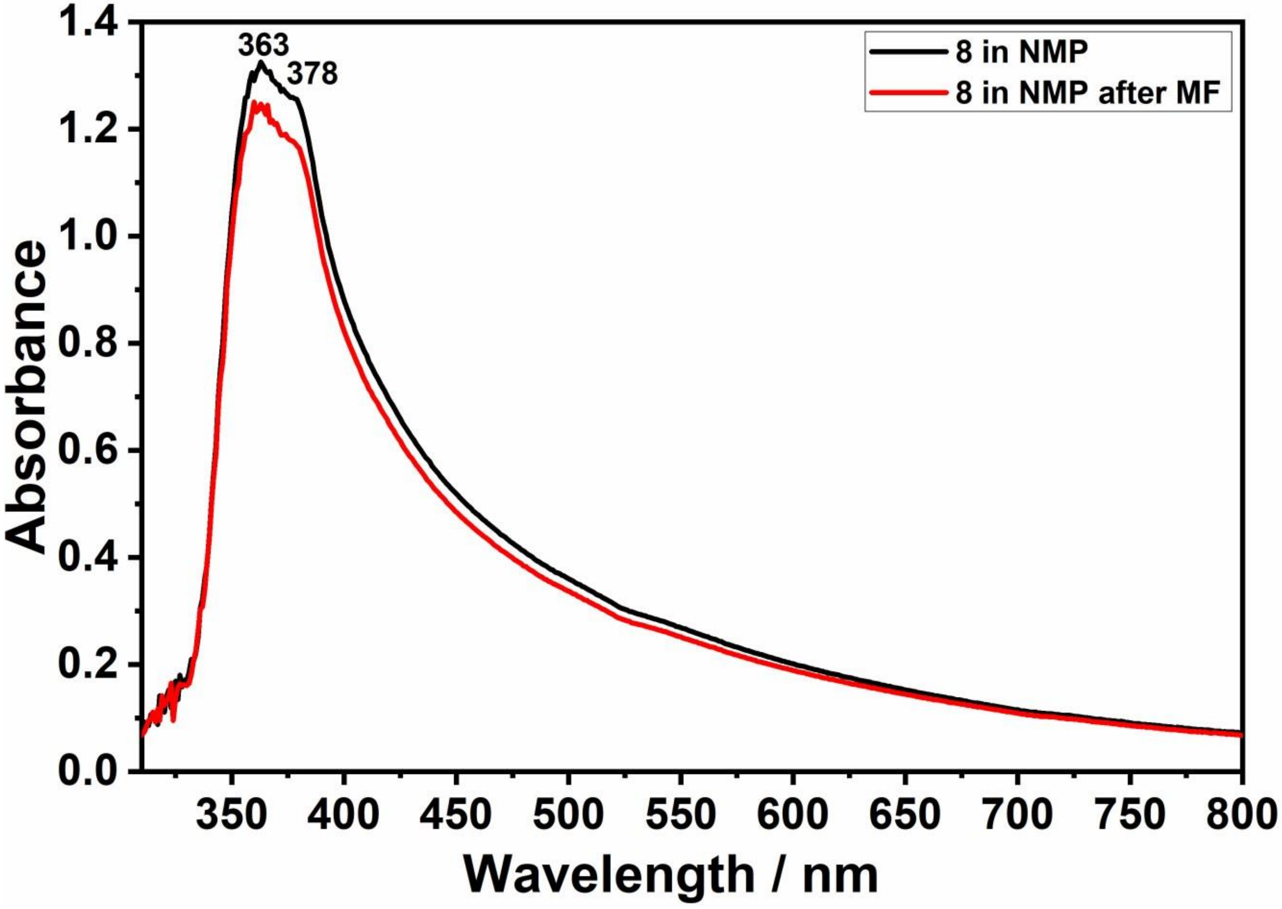


Figure 4.15: Absorption spectrum of 8 before and after microfiltration in NMP

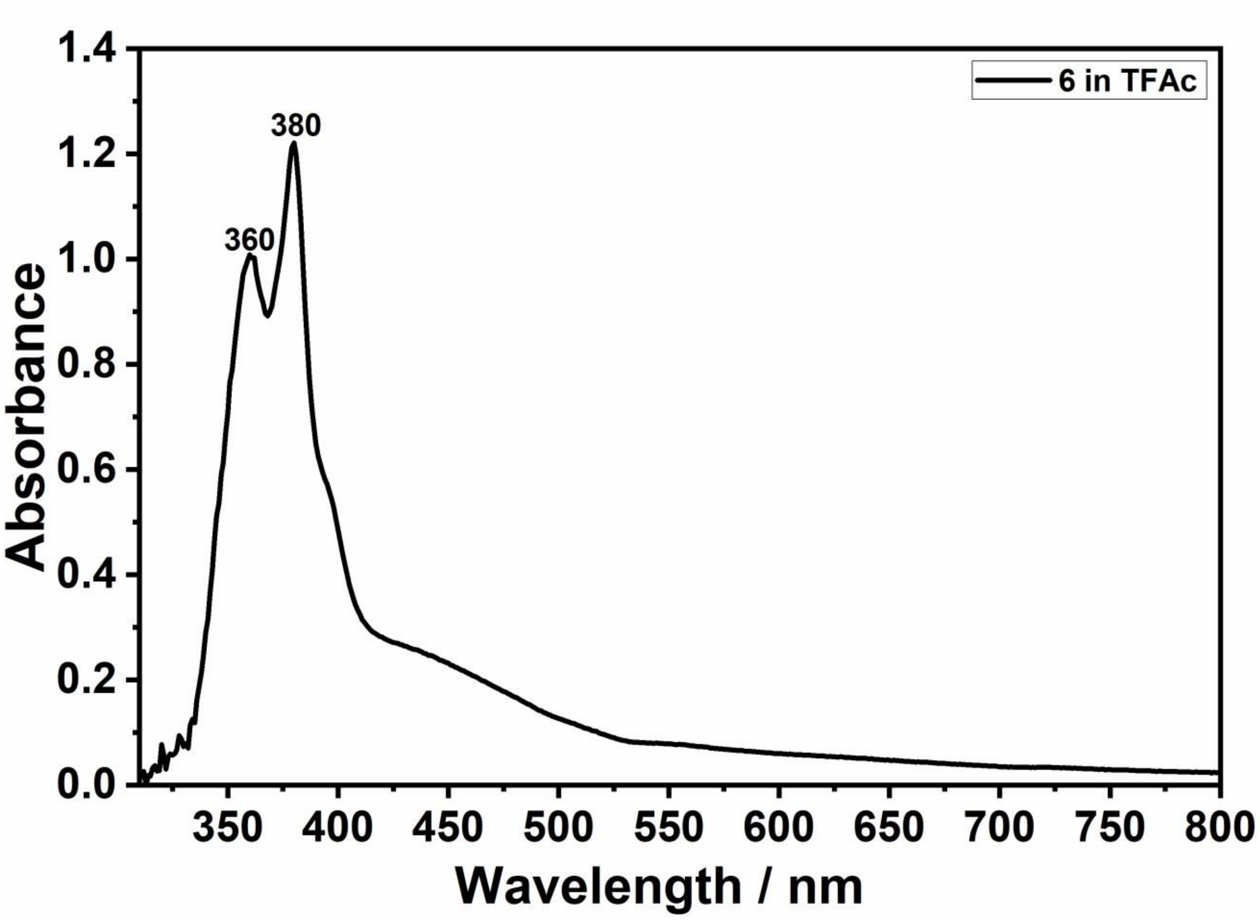


Figure 4.16: Absorption spectrum of 6 in TFAc

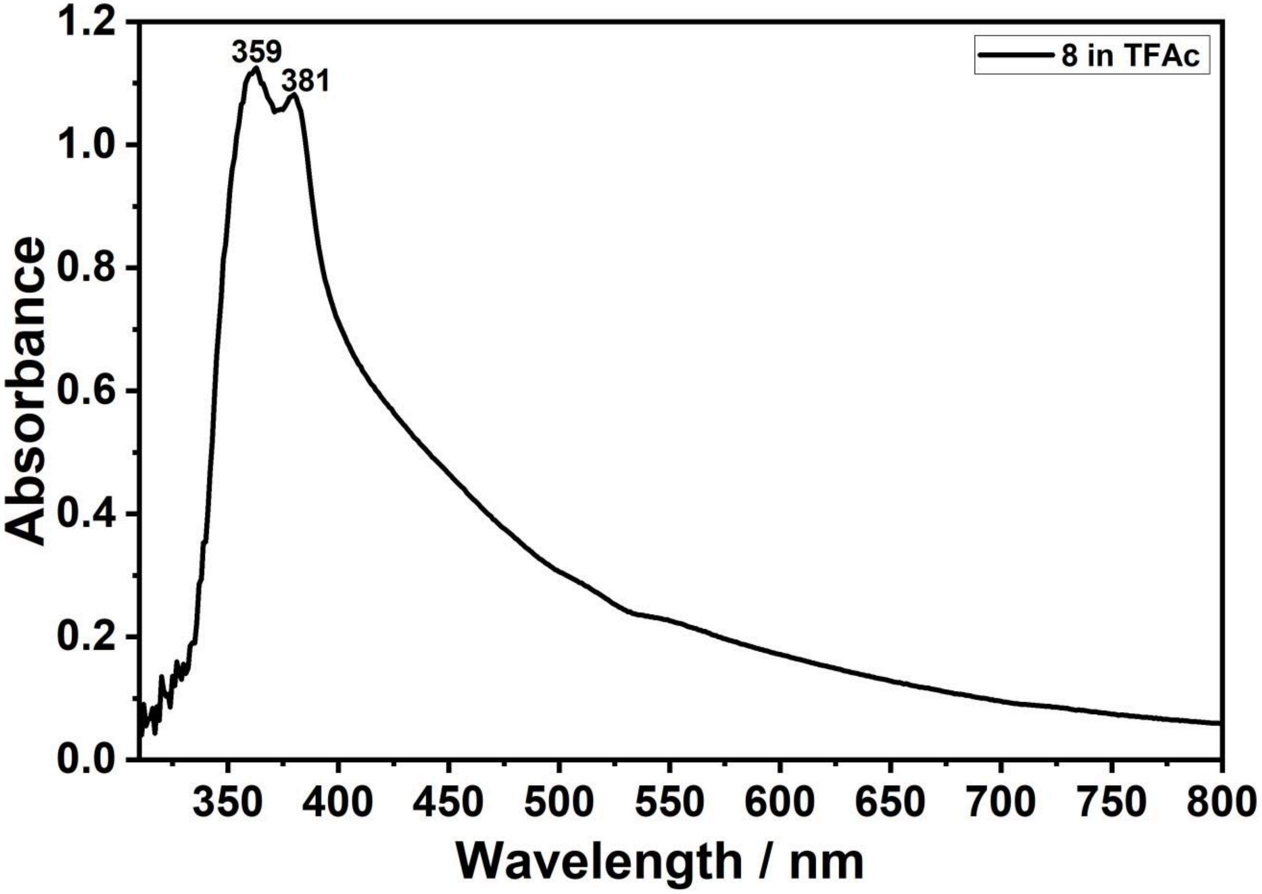


Figure 4.17: Absorption spectrum of 8 in TFAc

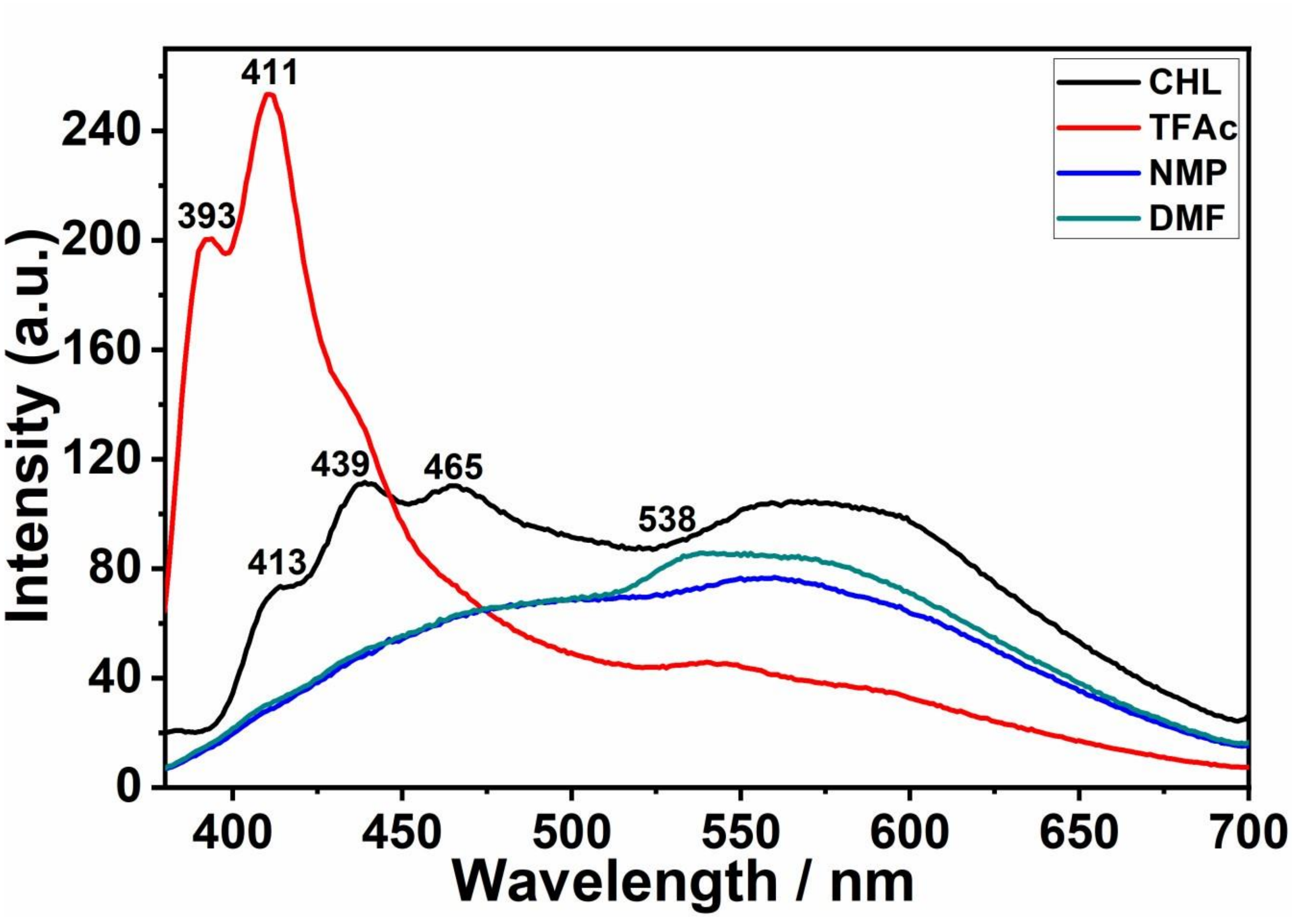


Figure 4.18: Emission spectrum of 6 in different solvents

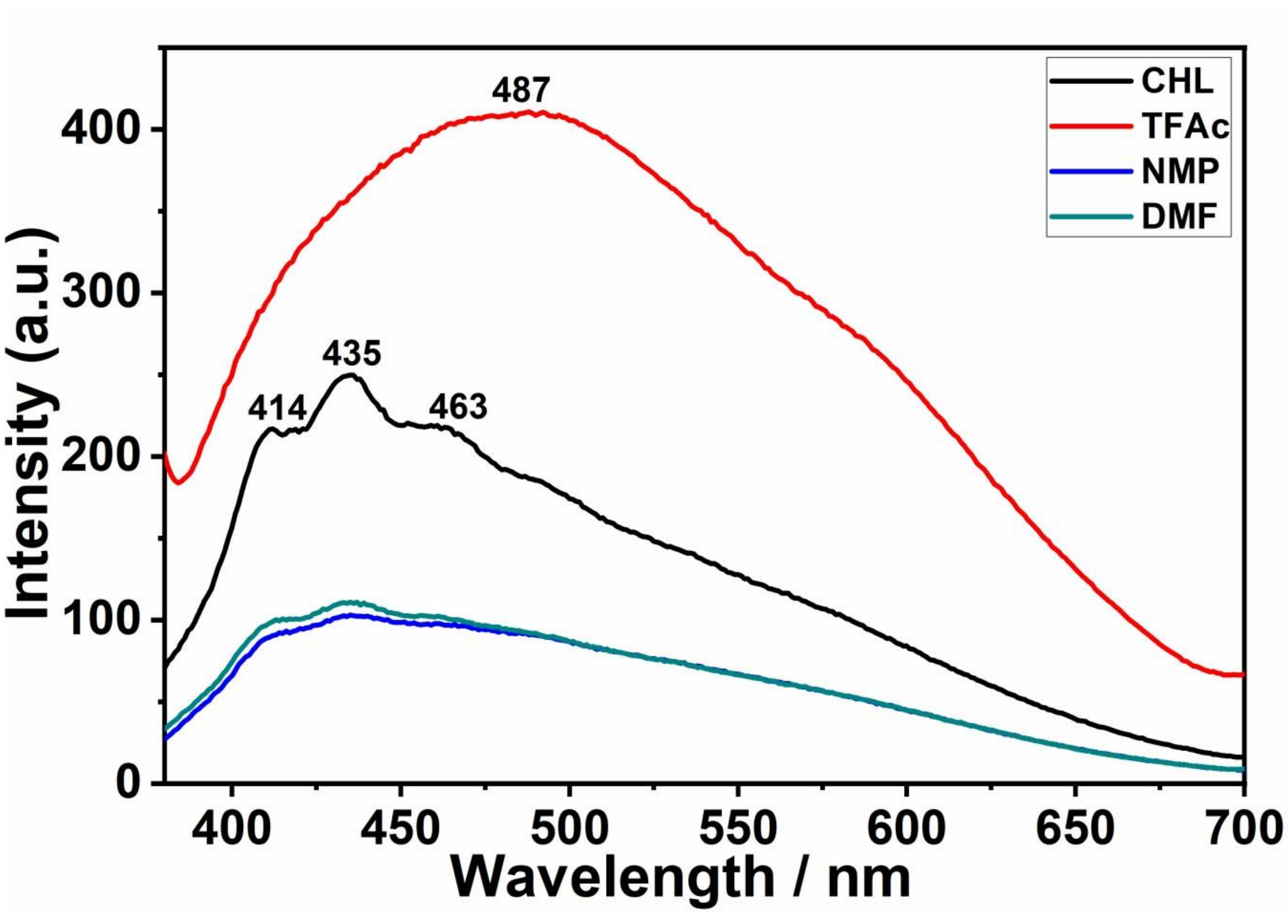


Figure 4.19: Emission spectrum of 8 in different solvents

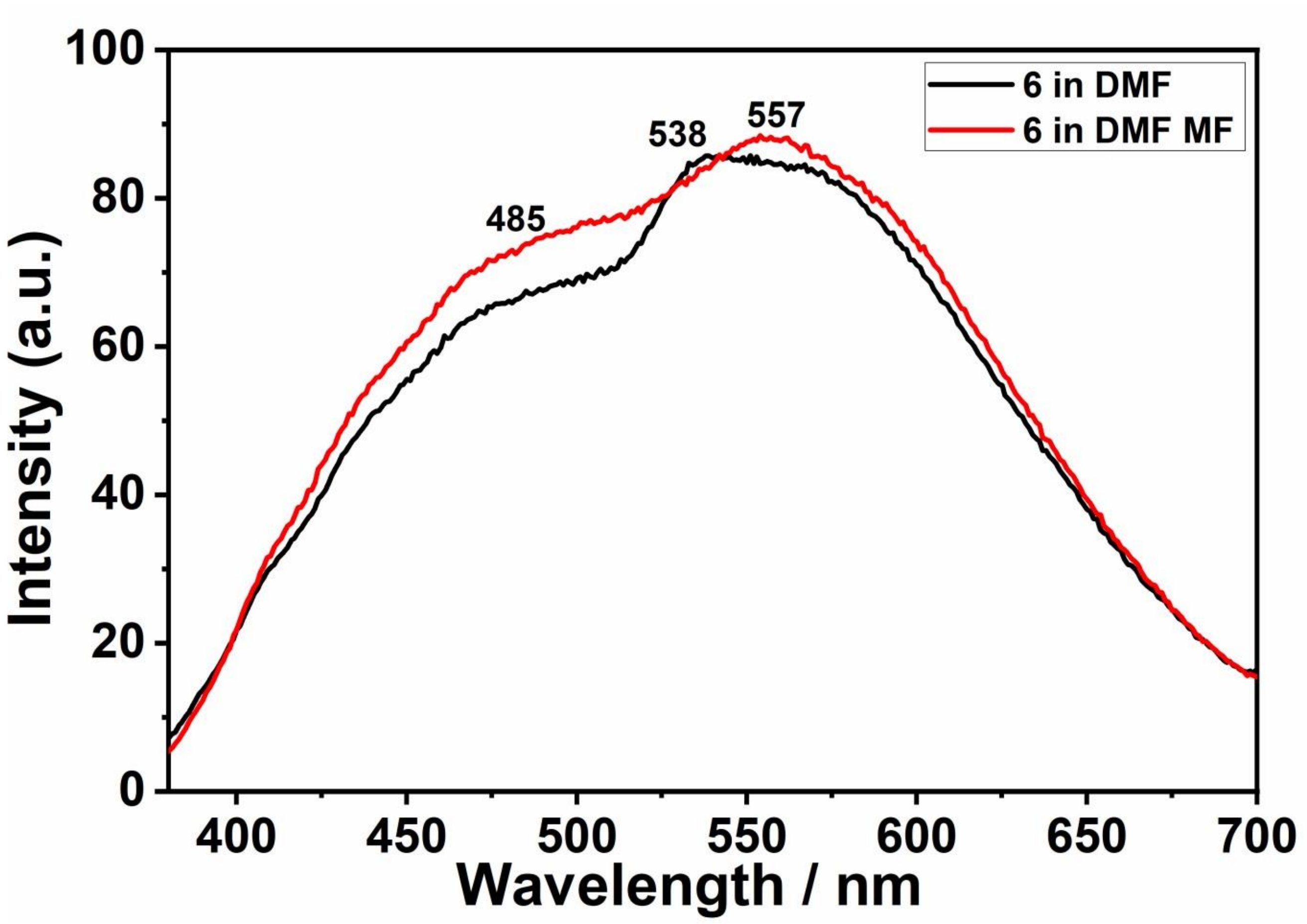


Figure 4.20: Emission spectrum of 6 before and after microfiltration in DMF

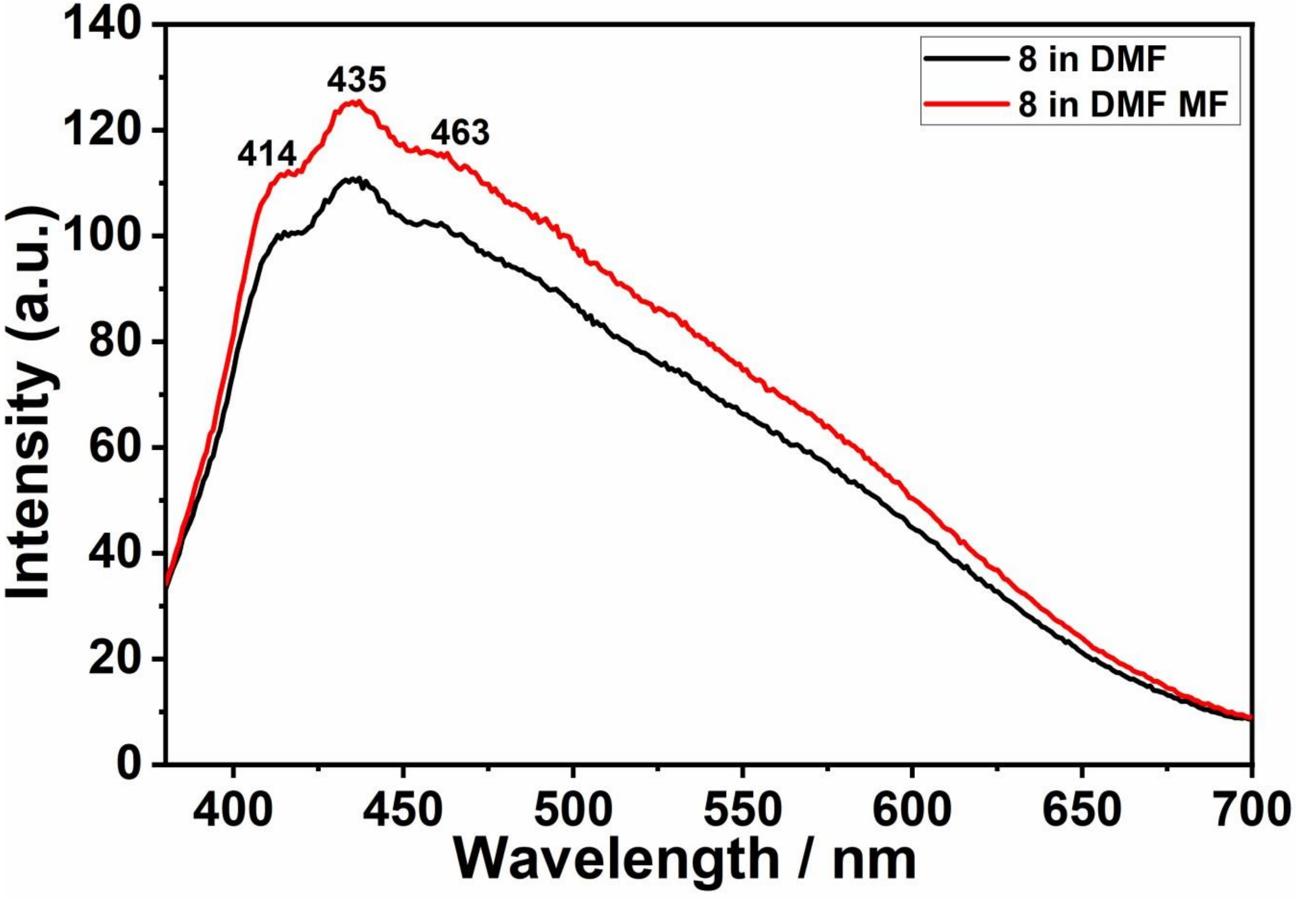


Figure 4.21: Emission spectrum of 8 before and after microfiltration in DMF

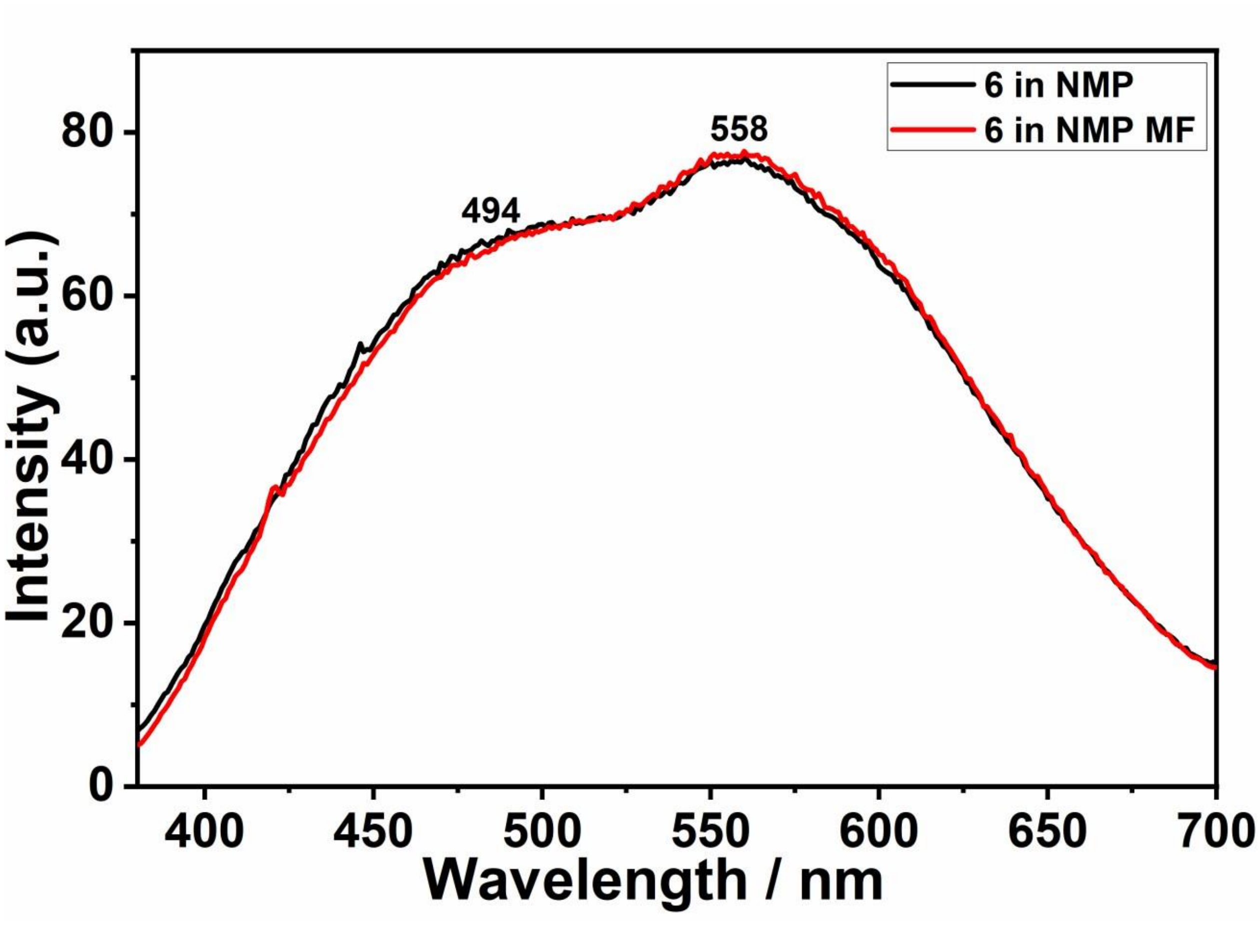


Figure 4.22: Emission spectrum of 6 before and after microfiltration in NMP

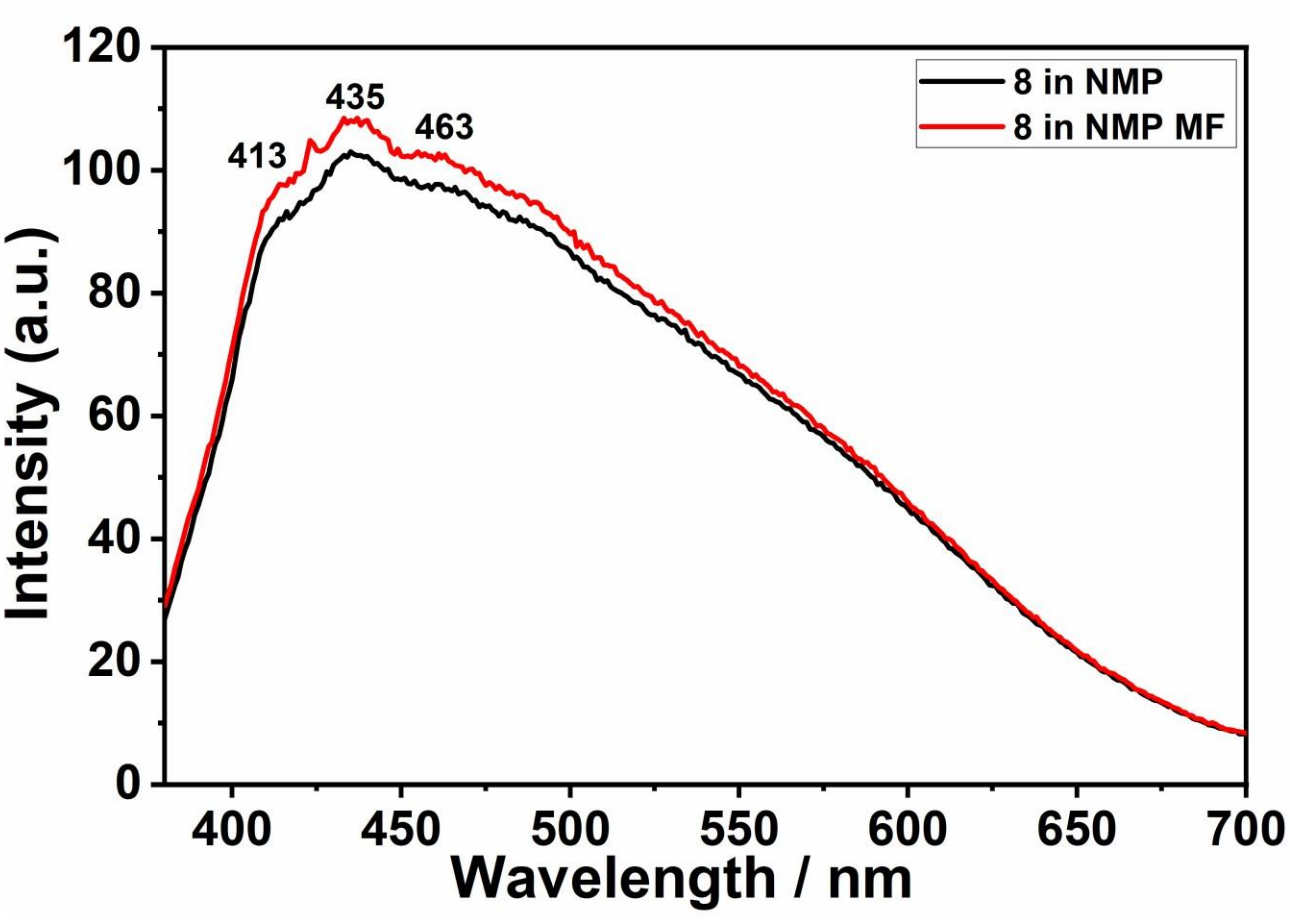


Figure 4.23: Emission spectrum of 8 before and after microfiltration in NMP

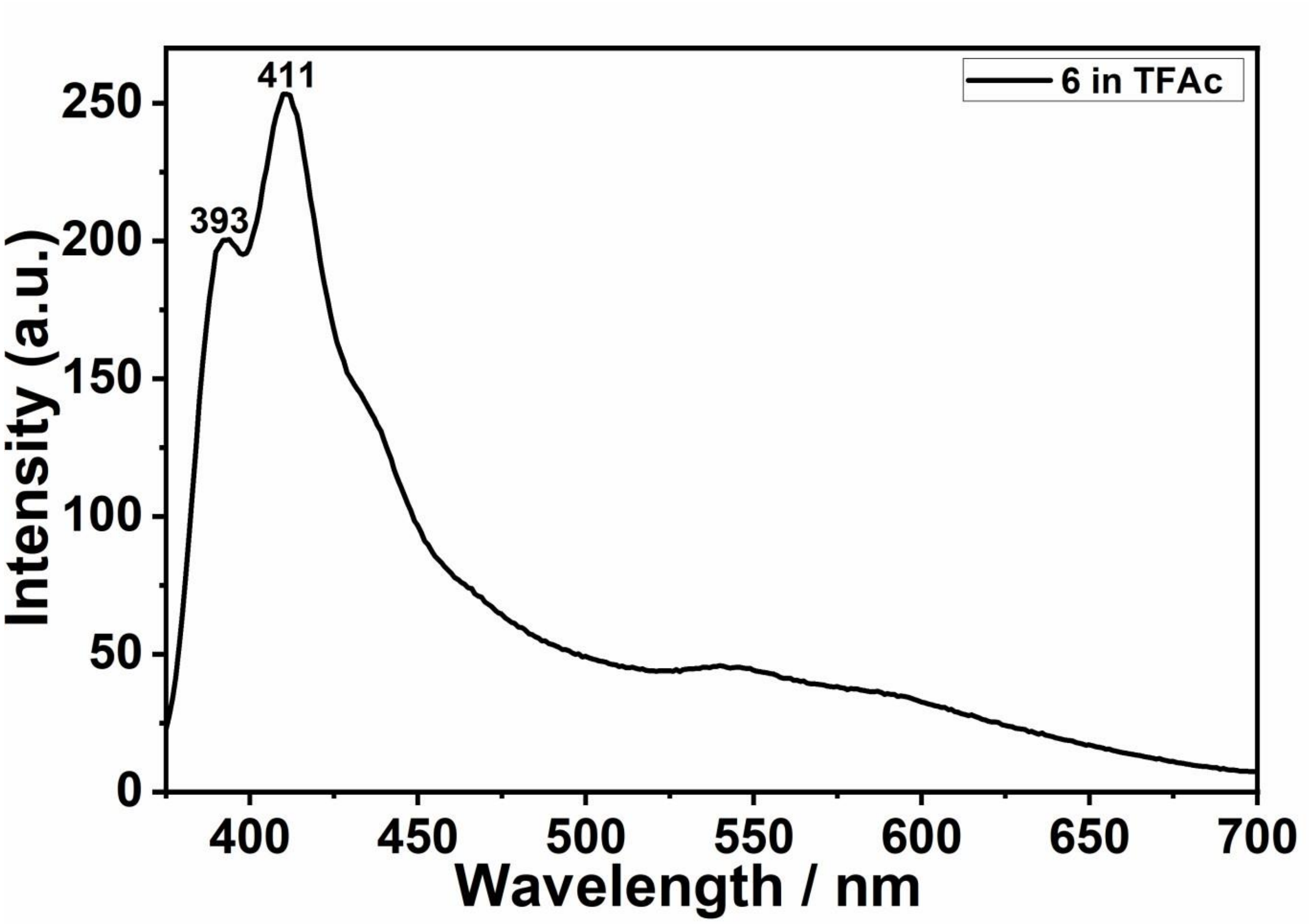


Figure 4.24: Emission spectrum of 6 in TFAc

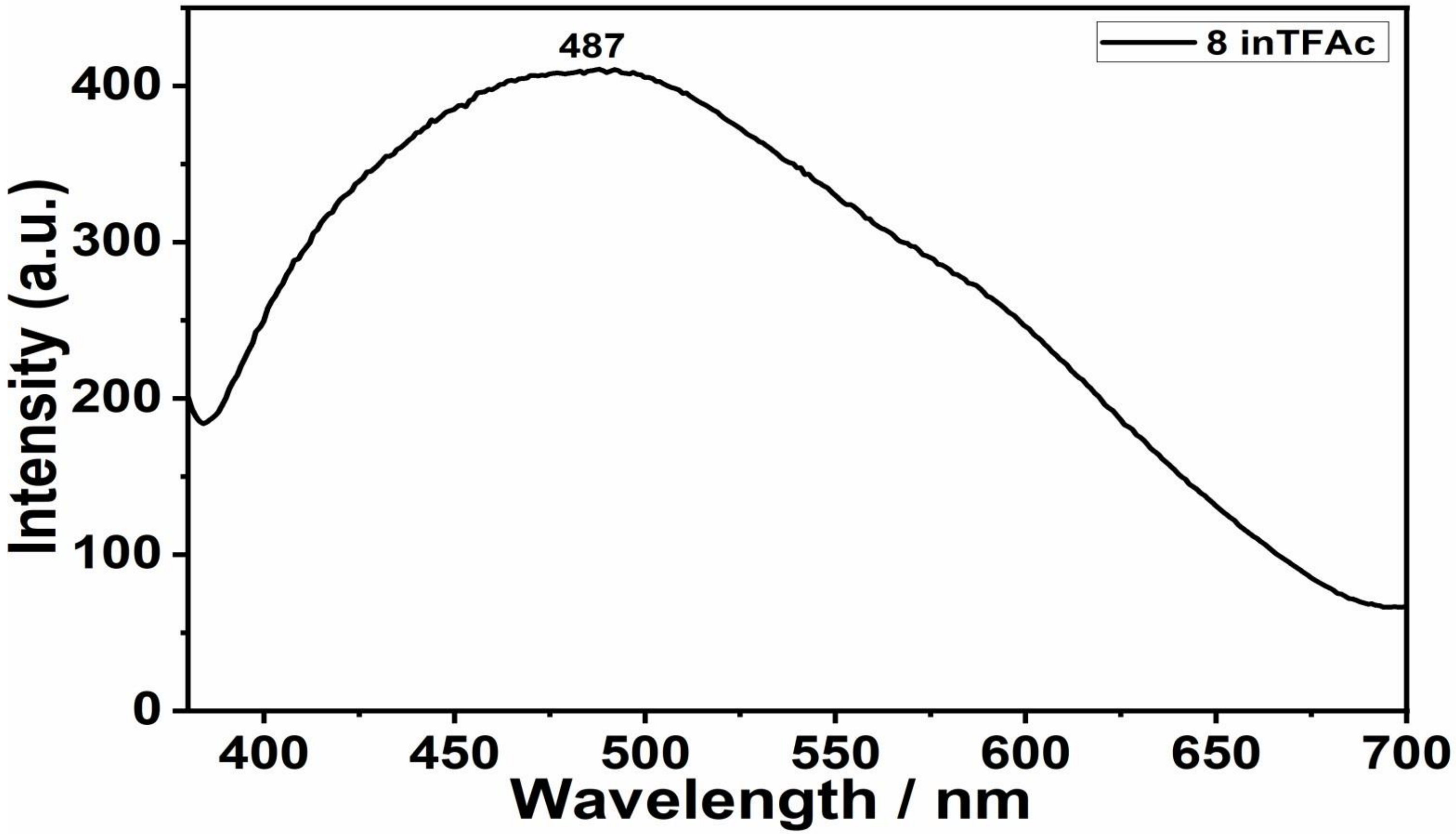


Figure 4.25: Emission spectrum of 8 in TFAc

Chapter 5

RESULTS AND DISCUSSION

5.1 Synthesis of Compound 6 and 8

The synthetic route of 6 and 8 is shown in Scheme 3.2. The unsymmetrical Naphthalene Diimides were synthesized via condensation reaction using appropriate amine in high boiling solvent under argon atmosphere. The preparation of 6 was successfully achieved by condensation of 1,4,5,8-naphthalenetetracarboxylic dianhydride with 4-aminophenol and 2-amino-4,6dichloro-1,3,5-triazine and similar 8 was synthesized successfully by condensation of 1,4,5,8-naphthalenetetracarboxylic dianhydride with 4-aminophenol and 2,3,4,5,6-pentafluoroaniline.

The synthetic products were characterized by FTIR, UV-VIS, Emission. The optical and photochemical properties were explored.

5.2 Solubility of the synthesized 6 and 8

The solubility of 6 and 8 were studied in detail. 6 and 8 are soluble in mostly polar aprotic solvents such as: DMF, NMP, DMSO and DMAc and in polar protic solvent (TFAc) (Table 5.1). Both of the products were insoluble in polar aprotic solvent such as acetonitrile. 6 was insoluble in DCM, a polar aprotic solvent.

Table 5.1: Solubility test

Solvent	6	8
CHL	+ - light brown	+ - light brown
TFA_C	+ + light brown	+ + brown
NMP	+ + brown	+ + brown
DMF	+ + light brown	+ + brown
DMA_C	+ + light brown	+ + light brown
DMSO	+ + light brown	+ + brown
Acetonitrile	- -	- -
DCM	- -	- -
H_2O	- -	- -

(+ +) is soluble at room temperature, (+ -) is partially soluble at room temperature, (--)insoluble, (- +) is soluble on heating at 60 °C.

5.3 Analysis of FTIR Spectra

Figures (4.7 and 4.8) show FTIR spectra of 6 and 8. Figure 4.7, the IR spectrum of 6 provides information of characteristic absorption bands at 3178 and 3077 (aromatic C-H stretch), 1698 (Imide C=O stretch), 1578 (aromatic C=C stretch), 1337 (C-N stretch), 767 (C-Cl stretch) and 626 (C-H bend). Figure 4.8, the IR spectrum of 8 provides information of characteristic absorption bands at 3059 (aromatic C-H stretch), 1663 (Imide C=O stretch), 1579 (aromatic C=C stretch), 1331 (C-N stretch), 759 (C-F stretch) and 693 (C-H bend).

5.4 Optical Properties

The optical properties of the synthesized compounds 6 and 8 were investigated using UV-Vis and emission spectroscopy.

Figure 4.9 shows the UV-Vis spectra of 6 in various organic solvents with different polarities. Figures 4.11 and 4.13 show that the absorption bands of 6 before and after microfiltration are similar, all concentrations before microfiltration were 1×10^{-4} M, the pore size of the micro filter was 0.2 μm SPR.

Figure 4.10 shows the UV-Vis spectra of 8 in various organic solvents with different polarity.

Figure 4.12 and 4.14 show that the shape of the absorption bands of 8 in DMF and NMP before and after microfiltration (λ_{max} = 362, 378 nm) are similar.

Figure 4.17 and 4.18 show the emission spectra of 6 and 8 in various organic solvents with different polarities with λexc. =260 nm. All the optical parameters for compounds 6 and 8 were listed in tables 5.2 and 5.3.

.

Table 5.2: Optical and Photochemical Constant of 6

Solvents	λ_{max} (nm)	ε_{max} (M^{-1} L)	ϕ_f	$\Delta\nu_{1/2}$ (cm^{-1})	$\tau_{\circ}$ (ns)	τ_f (ns)	k_f (s^{-1})	k_d (s^{-1})	f	E_s (Kcal.mol)	E_g (eV)
DMF	378	12027.53	0.01	2027.23	20.5	0.205	4.8×10^7	4.8×10^9	0.105	75.66	3.1
NMP	377	25780.65	0.01	1746.95	11	0.11	9×10^7	8.9×10^9	0.194	75.86	3.06

Table 5.3: Optical and Photochemical Constant of 8

Solvents	λ_{max} (nm)	ε_{max} (M^{-1} L)	ϕ_f	$\Delta\nu_{1/2}$ (cm^{-1})	$\tau_{\circ}$ (ns)	τ_f (ns)	k_f (s^{-1})	k_d (s^{-1})	f	E_s (Kcal.mol)	E_g (eV)
DMF	378	11463.87	0.01	3644.15	11.9	0.11	8.3×10^7	8.2×10^9	0.18	75.66	2.73
NMP	378	18304.95	0.01	3410.85	8	0.08	1.2×10^8	1.23×10^9	0.27	75.66	2.78

Chapter 6

CONCLUSION

The aim of this thesis was to synthesize two novel unsymmetrically substituted Naphthalene Diimides for wide range applications such as photovoltaics. The preparation of N‑(4‑Hydroxyphenyl)‑N'‑(3,5‑Dichloro‑2,4,6‑Triazinyl)‑1,4,5,8Naphthalenediimide (6) was successfully achieved through condensation reaction of 1,4,5,8-naphthalenetetracarboxylic dianhydride with 4-aminophenol and 2-amino-4,6-dichloro-1,3,5-triazine and similar N‑(4‑Hydroxyphenyl)‑N'‑(2, 3, 4, 5, 6 Pentafluorophenyl)‑1,4,5,8‑Naphthalenediimide (8) was synthesized successfully by condensation of 1,4,5,8-naphthalenetetracarboxylic dianhydride with 4-aminophenol and 2,3,4,5,6-pentafluoroaniline. The synthesized compounds 6 and 8 have been characterized by spectroscopy methods and their photophysical properties were determined using UV-vis and emission spectrophotometer.

The solubility of 6 and 8 were studied in detail. 6 and 8 are soluble in mostly polar aprotic solvents such as: DMF, NMP, DMSO and DMAc and in polar protic solvent (TFAc) (Table 5.1). Both of the products were insoluble in polar aprotic solvent such as acetonitrile. 6 was insoluble in DCM, a polar aprotic solvent.

Excimer-like emissions were obtained in polar protic and polar aprotic solvents for Naphthalene Diimides.

Complete characterization of the Naphthalene Diimides and its photophysical, photochemical and electrochemical properties will be explored in future studies.

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APPENDIX

Curriculum Vitae

Personal Information

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Phone	+377 44 959 892
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Date of birth	18/03/1995
Citizenship(s)	Kosovar, Bosnian
Marital Status	Single

Education

2001-2010	“Zenun Çoçaj”, Gjonaj, Prizren, Kosovo
2010-2013	“Loyola Gymnasium”, Prizren, Kosovo
2014-2018	University of Prishtina “Hasan Prishtina”
	Engineering Chemistry (BS)
2018-present	Eastern Mediterranean University
	Faculty of Arts & Sciences
	Department of Chemistry (MS)

Work Experience

2019-2019	I worked as a chemistry teacher for middle school and high school students at Eastern Mediterranean Doğa College, Famagusta, North Cyprus.

Skills

Language	Albanian, English, Bosnian
Computer	Microsoft Applications, ChemDraw