Synthesis and Characterization of *p*-Type Poly(2,7-carbazole) Materials for Solar Cells

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ABSTRACT

π-Conjugated light emitting polymers are having very wide applications in many areas, especially in optoelectronic, photonic and renewable energy systems. 2,7-substituted polycarbazoles are excellent *p*-type candidates with great potential toward these applications. However, very few reports were published in literature about the applicability of poly(2,7-carbazoles) which is attributed to the difficulties in direct functionality at 2,7-positions (*meta*-).

In the present work, we report the synthesis of a 2,7-dibromo-substituted polycarbazole (poly(N-dodecylcarbazole)-2,7-diyl) material via four different consecutive steps. In first two steps, the basic 2,7-substitution was made by using commercial dibromobiphenyl and then the monomeric dodecylcarbazole was synthesized by nucleophilic substitution in the third step. Finally, the titled polymer was synthesized by Yamamoto polymerization. The structures of the intermediate products are confirmed by FTIR. The monomer and polymer were characterized by FTIR, UV-vis, emission and NMR techniques.

The polymer has shown broad absorption comparing to the parent 2,7-dibromo-substituted-carbazole and monomeric dodecylcarbazole. Similarly, PCbz has exhibited strong excimer emission in all of the most commonly used organic solvents. Nevertheless, owing to the attractive tunable optical properties poly(2,7-carbazoles) and derivatives, they could be used as smart materials for electroactive and photonic device architectures.

Keywords: Carbazole, Dodecylcarbazole, Poly(dodecylcarbazole), Excimer

ÖZ

Işık yayan π-konjuge polimerler, özellikle optoelektronik, fotonik ve yenilenebilir enerji sistemleri gibi birçok alanda çok geniş uygulama alanına sahiptirler. Bu uygulama alanları için 2,7-karbazoller büyük bir potansiyele sahip mükemmel p-tipi malzemelerdir. Ancak, karbazolün 2,7-pozisyonlarındaki modifikasyon zorluğundan dolayı literatürde poli(2,7-karbazoller)in uygulamaları ile ilgili çok az çalışma bulunmaktadır.

Bu çalışmada, bir 2,7-dibromopolikarbazol (poli(N-dodesilkarbazol)-2,7-diil) dört ardışık basamakta sentezlenmiştir. İlk iki basamakta, 2,7-pozisyonları ticari dibromobifenil maddesi kullanılarak elde edildi. Üçüncü basamakta ise dodesilkarbazol monomeri nükleofil yer değiştirme tepkimesi ile elde edilmiştir. Son olarak, polimer Yamamoto polimerizasyonu tekniği ile sentezlenmiştir. Ara ürünleri yapıları FTIR ile teyit edilmiştir. Monomer ve polimer FTIR, UV-vis, emisyon ve NMR teknikleri ile karakterize edilmiştir.

Polimer 2,7-dibromokarbazol ve dodesilkarbazol ile karşılaştırıldığında geniş bir absorpsiyon göstermiştir. Benzer şekilde, polikarbazol yaygın olarak kullanılan organik çözücülerde güçlü ekzimer emisyonu sergilemiştir. Bunula birlikte, poli(2,7-karbazoller) ilgi çekici ayarlanabilir optik özelliklerinden dolayı, elektroaktif ve fotonik cihaz mimarileri için akıllı malzemeler olarak kullanılabilirler.

Anahtar kelimeler: Karbazol, Dodesilkarbazol, Poli(dodesilkarbazol), Ekzimer

To

Jalal Hassan Khoshnaw

&

Srwa Muhammed

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"(All) praise is (due) to Allah, Lord of the worlds" [Al-Quran 1:2], who has power over everything and for his Glorious Ability and Great Power.

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LIST OF SYMBOLS/ABBREVIATIONS

$\overset{o}{\mathrm{A}}$	:	Armstrong
A	:	Absorption
A	:	Electron acceptor
AU	:	Arbitrary unit
c	:	Concentration
^{13}C NMR	:	Carbon-13 nuclear magnetic resonance spectroscopy
CC	:	Flash Column chromatography
CHL	:	Chloroform
δ	:	Chemical shift
D	:	Electron donor
DMF	:	N,N′-dimethylformamide
DMSO	:	Dimethyl sulfoxide
DSC	:	Differential scanning calorimetry
ε	:	Molar Absorption coefficient
ε_{max}	:	Maximum Extinction coefficient/Molar absorptivity
eV	:	Electron volt
E_g	:	Band gap energy
f	:	Oscillator strength
FT-IR	:	Fourier transform infrared spectroscopy
h	:	Hour
$h\nu$	:	Irradiation
^{1}H NMR	:	Proton nuclear magnetic resonance spectroscopy
HOMO	:	Highest occupied molecular orbital

IR : Infrared spectrum/spectroscopy

kcal : Kilocalorie

LED : Light emitting diode

LUMO : Lowest unoccupied molecular orbital

M : Molar concentration

max : Maximum

min : Minute

min : Minimum

mol : Mole

mp : Melting point

n : Number of electrons (in the reduction process)

NMP : *N*-methylpyrrolidinone

NMR : Nuclear magnetic resonance spectroscopy

PCbz : Polycarbazole (poly(N-dodecylcarbazole)-2,7-diyl)

ppm : Parts per million

τ_0 : Natural radiative lifetime

THF : Tetrahydrofuran

UV : Ultraviolet

UV-vis : Ultraviolet visible light absorption

$\bar{\nu}$: Wavenumber

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

$\bar{\nu}_{max}$: Maximum wavenumber/Mean frequency

V : Volt

λ : Wavelength

λ_{exc} : Excitation wavelength

λ_{em} : Emission wavelength

λ_{max} : Maximum wavelength

Chapter 1

INTRODUCTION

During the last ten years, harvesting energy from the sun light and finding environmental friendly renewable sources of energy become very interesting and important subject because of global warming, oil crisis, and dwindling of general energy sources. The focus is on generating clean power from possible sources of energy due to detrimental effect and respective environmental pollution which is as important as the efficiency of renewable energy systems. In this regard, hydroelectricity, geothermal power, wind power and solar energy conversion are emerged as efficient and green renewable energy systems. All these methods have their own advantages and disadvantages, but getting electric energy from solar energy by photovoltaics is one of the most successful ways to address growing global energy and is turn out to be very popular and attractive. The list of advantages like cheap, low-weight and flexible design make phovoltaics as a smart choice over others (Blouin N. et al. 2007, Shi F. et al. 2010).

Organic photovoltaics typically summarize the 3rd generation photovoltaics which comprises of an active light absorbing organic semiconducting material to capture the photons from sunlight. The organic molecules act as electron donating and/or electron accepting materials. Carbazoles and polycarbazoles are excellent organic donating substances with conjugated aromatic structure and are potential candidates for solar cells.

Carbazoles and Polycarbazole Materials

The preparation of several carbazole materials and their polymerization to yield polycarbazole materials are mainly attributed to the structure of carbazole unit. The carbazole unit and its structural advantages are outlined in Figure 1.1.

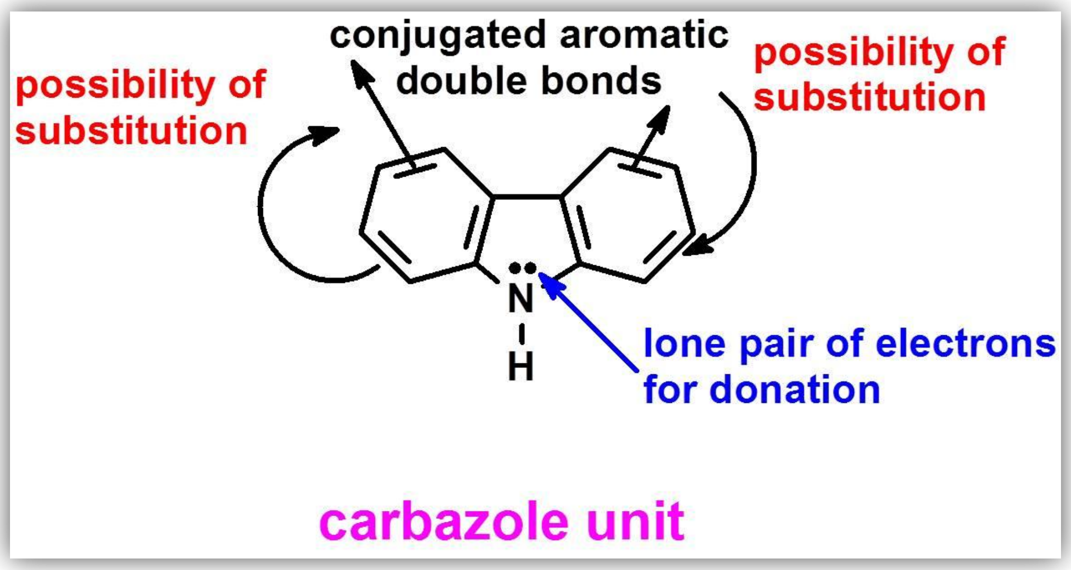


Figure 1.1: The Carbazole Sturctural Unit and its Advantages

The carbazole unit and its 2,7-position substituted 2,7-dibromocarbazole unit, and 2,7-polycarbazole unit are individually shown in Figure 1.2.

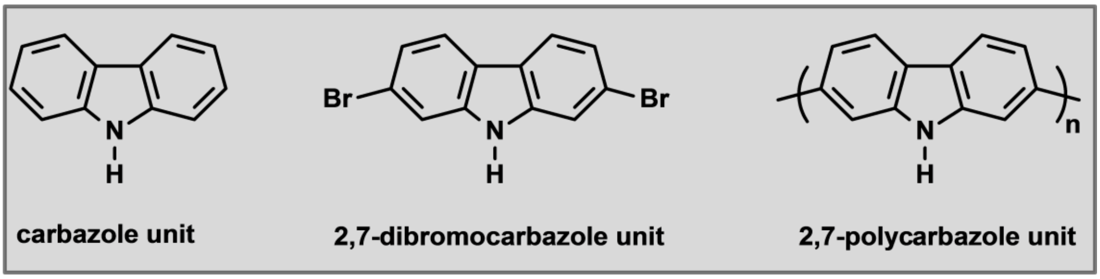
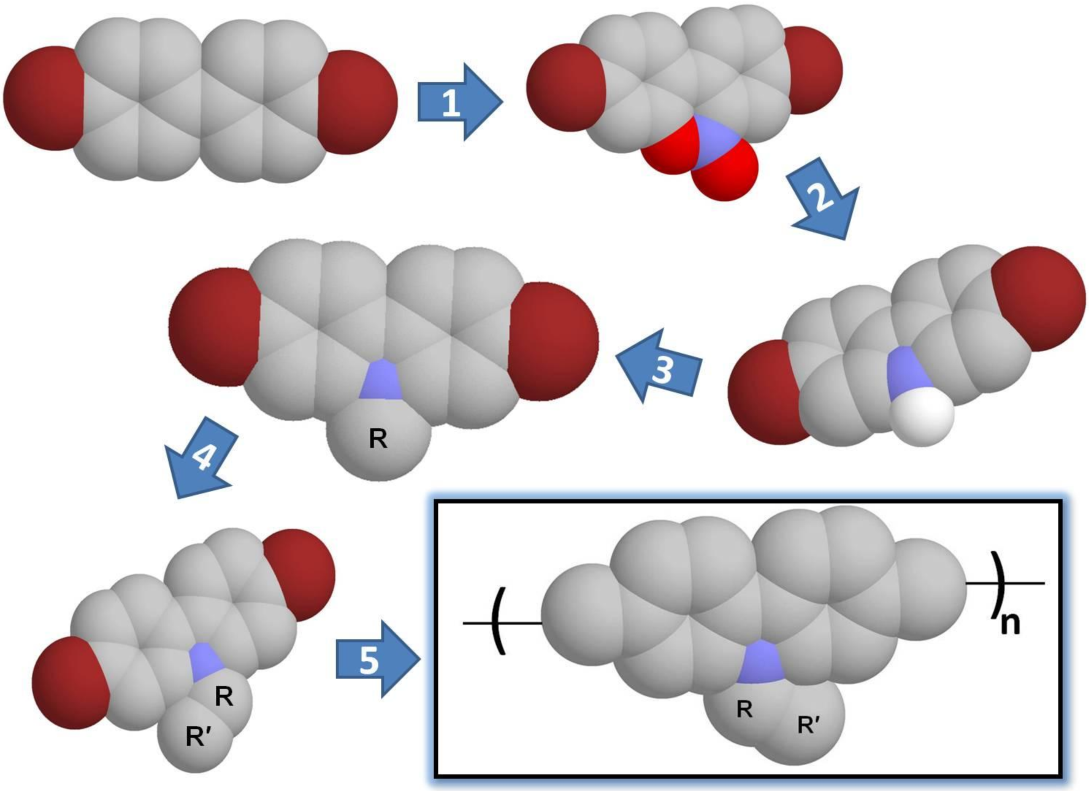


Figure 1.2: The Basic Carbazole Unit and its Structural Derivatives

Based on this economical carbazole unit and its structural advantages, various carbazole materials (for example, Figure 1.2) are readily prepared. Reactions of 9H-carbazole facilitate producton of polycarbazoles which are fully aromatic units with excellent chemical and environmental stabilities, good *p*-type charge transporting abilities, and high solubilities. Especially, the nitrogen atom present in polycarbazole units can be substituted by many types of functional groups and this feature offers versatile electrical and optical properties (Kim D. et al. 2007, Blouin N. et al. 2008). On the other hand, unsaturated bonds allow substitution at various positions. The variations in properties with respect to the substitution of functional groups on carbazole unit can be used effectively to tune the band gap energies. The ability of tuning the electrical and optical properties according to the requirement provides a wide variety of potential applications in many fields. Therefore, carbazole materials are one of the most advantageous materials investigated and poly(2,7-carbazole) derivative polymers are very superior of their kind. The family of poly(2,7-carbazole) compounds generally offer excellent optoelectronic properties and are well fit for current generation solar cells (Yuan L. et al, 2010).

The aim of this thesis is to synthesize poly(2,7-carbazole) materials with dodecyl alkyl chains at the *N*-position. In the 1st step, 2,7-substitution on carbazole was carried out, followed by N-subsitution and finally polymerization (Scheme 1.1). The proposed reaction scheme was shown below.



Scheme 1.1: General Synthesis and Design of a Poly(2,7-carbazole) Derivative

The monomeric carbazole and its polymer were characterized in detail by many techniques. Structural characterization was made via FTIR and NMR. Optical properties are studied by spectroscopic UV-vis and Fluorescence measurements.

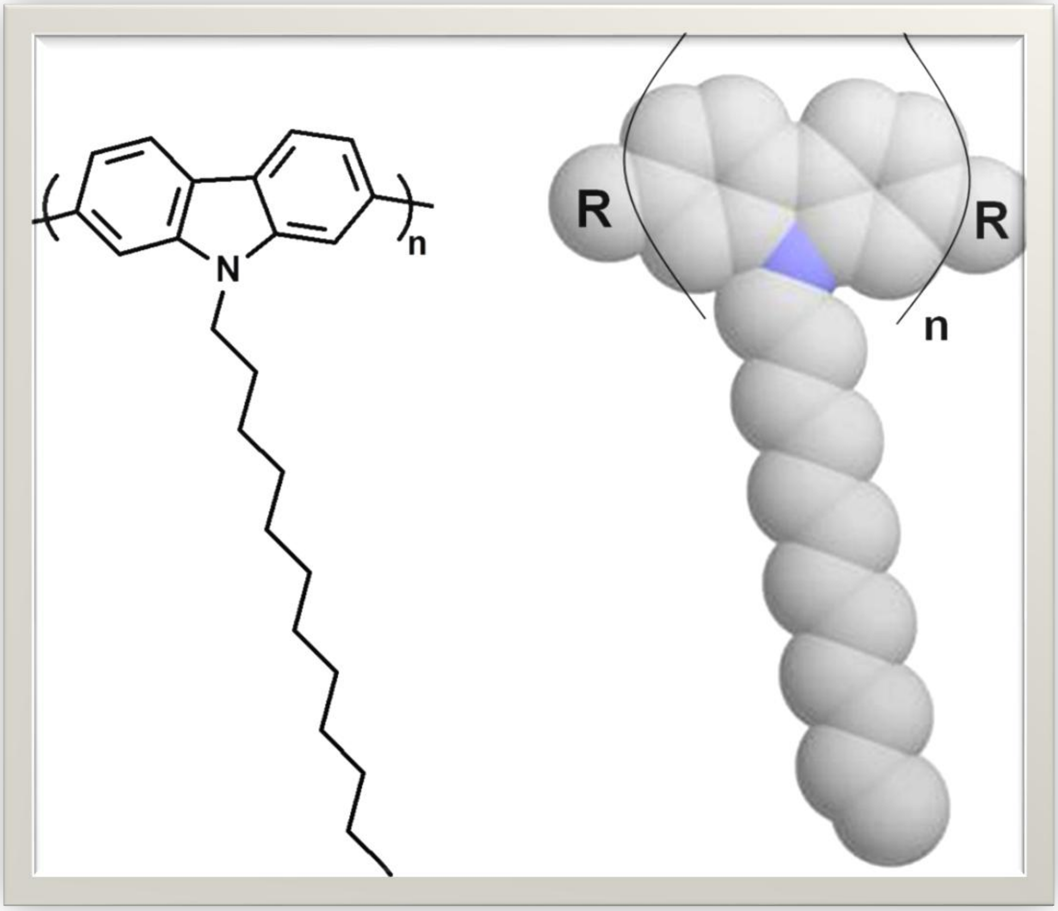


Figure 1.3: The Poly(2,7-carbazole) Synthesized (Right) and its Monomer (Left)

Chapter 2

THEORETICAL

2.1 Theoretical Aspects of Electron Donating Polycarbazoles

The key aspect of electron donation of polycarbazoles is related to their excellent π-conjugated structure. These model compounds possess bridged biphenyl units along with a fused ring providing a complete conjugation for the materials and thus resulting in low band gap energies than classical poly(*p*-phenylenes). The nitrogen atom with a lone pair of electrons contain in the polycarbazole units not only offers various functional group substitutions but also offers electron for donation. In addition, pendant carbazoyl units can be introduced to prepare polymers and copolymers with pendant carbazole groups and/or in the main polymeric chain to result in efficient conjugated polymers. It is reported that carbazole groups in the back bone of polymers (in the main chain) are capable of better charge carriers with high mobilities.

Polycarbazole derivatives are having higher potential to be used in bulkheterojunction solar cells (BHJ) instead of traditional poly(2,7-fluorenes) due to the fact that polycarbazoles are easily modulated. Charge dissociation and charge carrying ability are two very important aspects concerning BHJs and the electron rich carbazole provides optimal band gap energies. For example, poly(2,7-carbazoles) are air-stable and hence the highest occupied molecular orbital (HOMO) energies of these polymers are below the threshold of air oxidation. In the other words, poly(2,7-

carbazoles) offer lower HOMO energies and thus offering high open circuit voltages during the construction of solar cells. It is widely reported that donor acceptor interfaces are more successful designs for high efficiencies of solar cells with good charge carrying abilities comparing to the charge separation at respective electrodes (Spanggaard H. et al. 2004). Furthermore, the LUMO energies of polycarbazoles are in good accordance with the LUMOs of many kinds of electron acceptors (one example is fullerenes), i.e, LUMO of polycarbazoles are a little bit higher (at least 0.2 eV) than LUMO levels of acceptors and thus ensuring efficient charge/electron transfer from donor-D to acceptor-A material. This is the reason that a plenty of polycarbazole materials are widely used in BHJ solar cells together with nanoparticles of TiO_2 (Pokhrel B. et al. 2012) or polymers based on perylene derivatives, etc as electron acceptors.

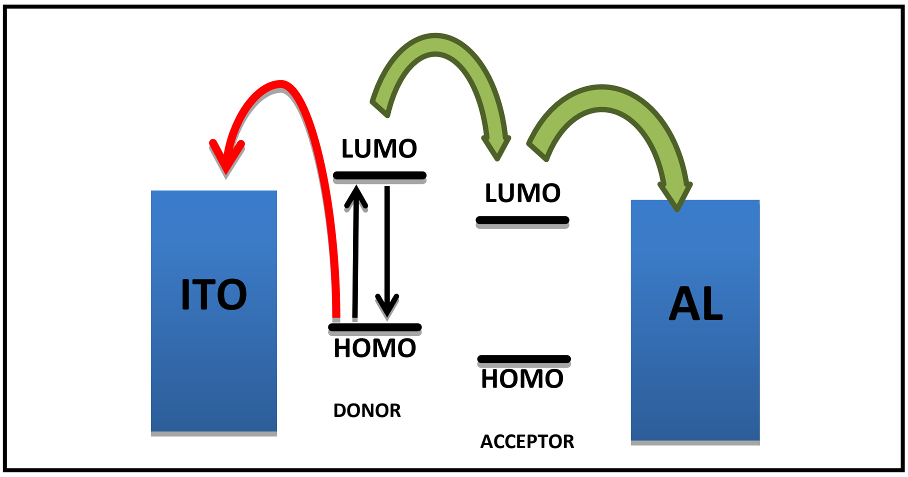


Figure 2.1: Schematic Representation of HOMO and LUMO Energy Levels of Donor-D and Acceptor-A Compounds

In summary, the mechansim of charge carriage is related to both intra- and inter-molecular hopping model between carbazole groups in the side chain. The charge mobility is greatly depend on extent of π-orbitals overlap and conformation of polymer chains.

2.2 The Structural Design and Versatility of Substitution to Carbazoles

There are many types of homopolymers and copolymers based on conjugated carbazole unit. They can be classified with respect to the position of connectivity to aromatic rings and various substituted groups that linked on the nitrogen atom. It is widely discussed that the properties of polycarbazole materials are considerably affected by the position of connectivity and substitution at nitrogen atom. The Figure 2.2 below shows numbered R-carbazole unit where the positions from 1 to 8 are available for connection of different groups and position-9 of nitrogen atom for substitution. Based on this, the very familiar types of polycarbazoles are: poly((2,7)-(1,8)-, and (3,6)-carbazole)s as homopolymers (Figure 2.3) (Dorofeev I. et al. 2011).

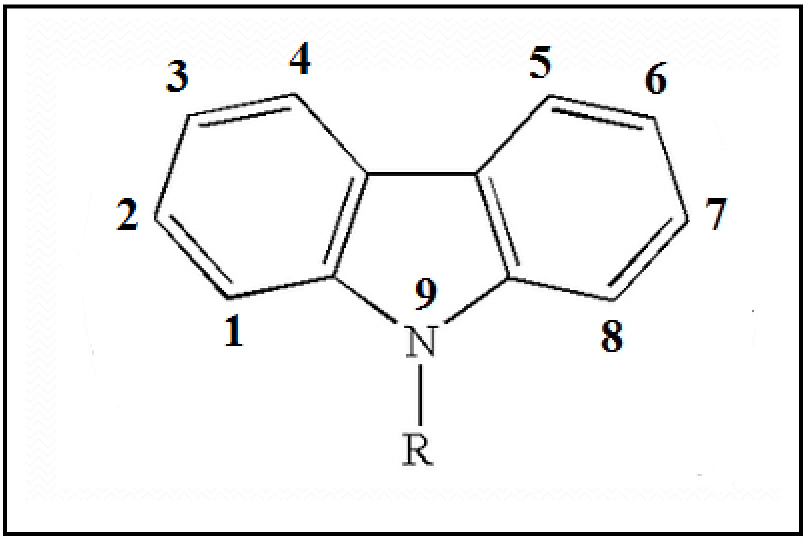
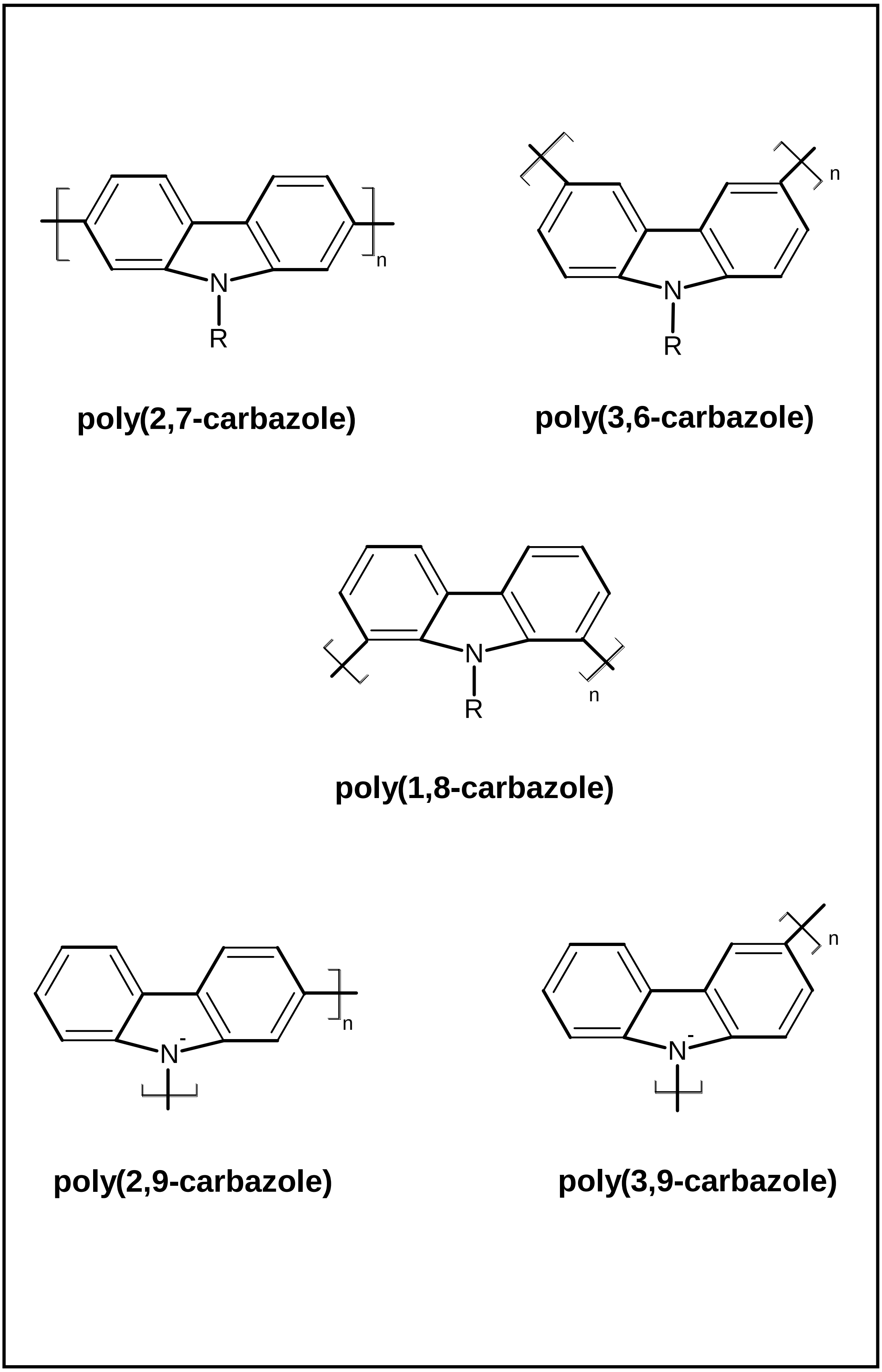


Figure 2.2: General Structure of 9-N-Substituted Carbazole



poly(2,7-carbazole)

poly(3,6-carbazole)

poly(1,8-carbazole)

poly(2,9-carbazole)

poly(3,9-carbazole)

Figure 2.3: Different Kinds of Polycarbazoles

In addition to the polymers shown in Figure 2.3, there are plenty of copolymers synthesized based on carbazole unit and the general structure is shown in Figure. 2.4 (Dijken A. et al. 2004).

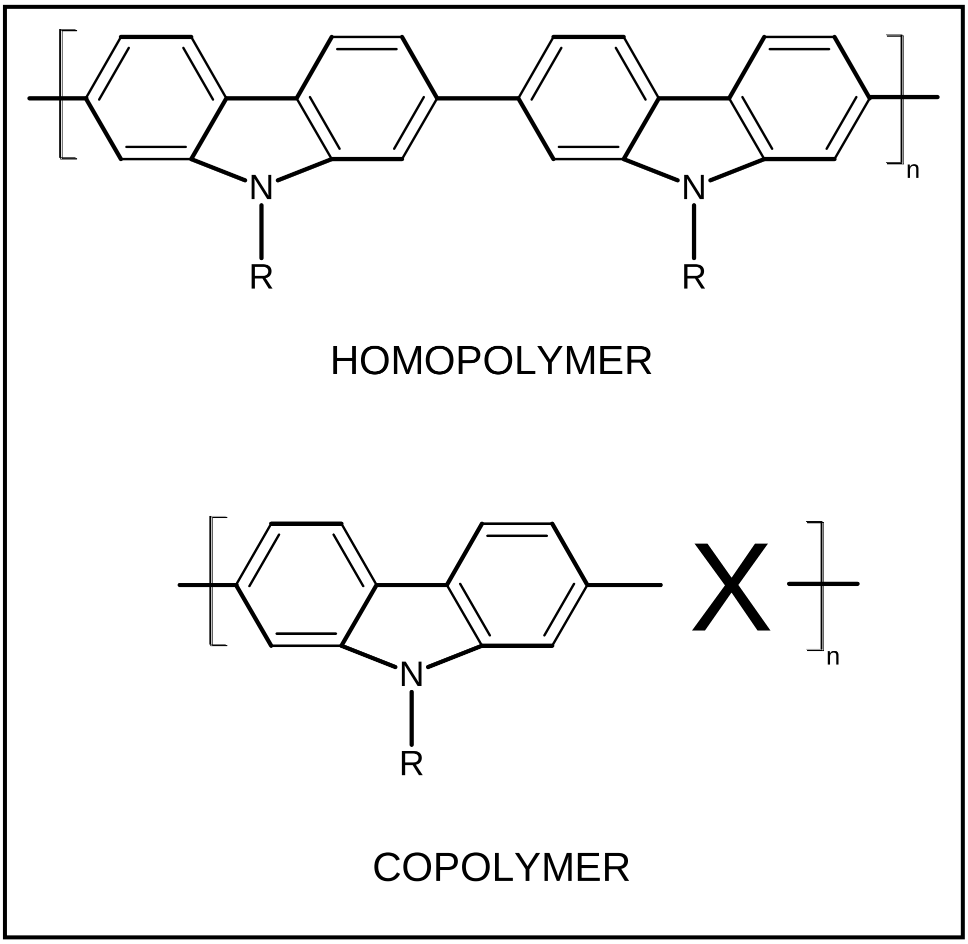


Figure 2.4: General Structures of Homo- and Co-polymers Based on Carbazole Derivatives

The main objective of preparing such a versatile and huge number of polymers based on carbazole unit is attributed to the exciting optoelectronic properties that they offer. The random polycarbazoles are generally synthesized from their corresponding monomers effectively in presence of Ni(0), whereas, the copolymers are generally prepared with Pd(0) by forming a 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-

dioxaborolane-based intermediate. Notably, copolymers have additional advantages in electronic device applications due to their better packing over random polymers.

2.2.1 2,7-Polycarbazoles and 3,6-Polycarbazoles – A Comparison

Among the polycarbazoles shown in Figure 2.3, poly(2,7-carbazole)s and poly(3,6-carbazole)s are more attractive due to their sturctural advantages and practical applicability in organic devices. In between the poly(2,7-carbazoles) and poly(3,6-carbazoles), poly(2,7-carbazoles) are having extended π-conjugation due to the substitutions at 2- and 7- positions which are *meta* to *ortho-para* and directing amino group (in other words, all phenylene units presented are linkup in *para*-position fashion). The extended π-conjugation of poly(2,7-carbazoles) offer very interesting electroactive and photoactive properties to be applied in organic devices. In addition, poly(2,7-carbazoles) offer considerably low band gaps. Although they are attractive, the synthesis of poly(2,7-carbazoles) is not striaghtforward comparing to the poly(3,6-carbazoles). However, some improvements in the synthesis were reported recently and summarizes three consecutive synthetic steps poly(2,7-carbazoles). Conclusively, among all types of polycarbazole semiconductors, both the poly(2,7-carbazoles) and poly(3,6-carbazoles) were extensively used in photo-applications because of their photoconductive properties, ability to link various substituents on the nitrogen atom and good ability to form electron-donor-acceptor complex due to electron-donating character of the carbazole unit (Tirapattur S. et al. 2003, Li C. et al. 2010).

2.3 Advantages of 2,7-Polycarbazoles

In spite of difficulty in rendering the design and synthesis of 2,7-substituted polycarbazoles, there is an opportunity to polymerize them by means of different electrochemical and chemical methodologies. Chemical oxidation is an efficient and advantageous method to produce versatile and large amounts (in multigram scales) of these compounds.

The structural advantages discussed already pointed the potential applications. In fact, the first remarkable polycarbazole compound is poly(*N*-vinylcarbazole) and is well known for its photoconductivity. This motivated the research on carbazoles and currently there are numerous polycarbazole materials that have excellent properties such as strong blue colored emission and fluorescence, high absorptivity, good hole transporting ability (charge carrier ability), absence of low energy triplet state, electron donating ability, high thermal stability, etc. Possessing these properties together is an excellent opprtunity to utilize them in unlimited applications like organic semiconductors, organic-based electronic devices such as organic light-emitting diodes, sensors, field effect transistors, and photovoltaic cells, camouflage coatings, and nonlinear optics, etc (Boudreault P. et al. 2009), (Dorofeev I. et al. 2011), (Dijken A. et al. 2004).

2.3.1 Potential Optoelectronic Applications

Nowadays technology is focused on cheap and efficient green materials and these materials are mainly based on conjugated organic materials. Therefore, the applicability of polycarbazoles in optoelectronic applications is very important. The new conjugated homopolymers and copolymers based on poly(2,7-carbazoles) have very good hole-transporting ability which is the crucial point concerning the high performance of light emitting diodes (LEDs). Many studies were focused on preparing various colourful LEDs including yellow, green, and red-light emitting polycarbazole materials. (Morin J. et al. 2005)

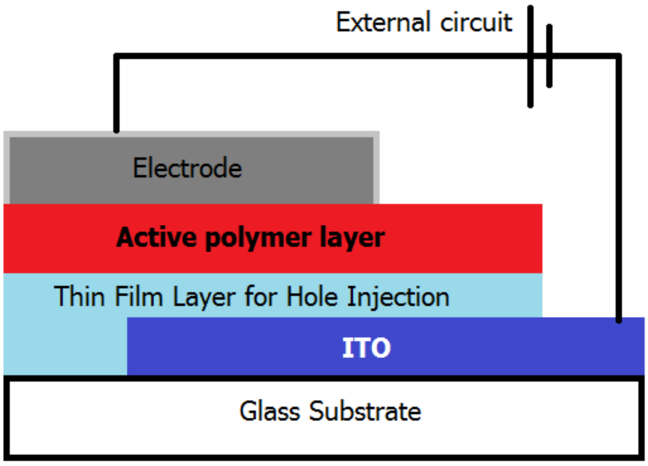


Figure 2.5: General Schematic Diagram of a Organic-Based Active Polymer Layer Containig Device Structure

On the other hand, various electron withdrawing groups were copolymerized with polycarbazoles in order to reduce the band gap energies of resulting polymeric compounds and thus to shift the light emission to higher wavelengths for more attractive properties. Light-weight illuminating materials are used in many areas like in aircrafts, LCDs, and space-shuttles.

2.3.2 Applicability in Solar Cells

In general solar cells or photovoltaic cells are the devices which convert the solar light into electrical energy without any pollutants that give negative impact on the environment. Typically organic photovoltaics are treated as third generation technological device structures that compensate the needs of energy in competition to conventional solar cells. Organic solar cells can be classified into dye sensitized, flat and bulk hetrojunction solar cells. Bulk heterojunction is simply blending or contacting of two organic semiconductor materials which differ in electrical properties. These two materials may be small organic molecules or polymers or mixed organic and inorganic materials. Polycarbazoles are widely employed in organic photovoltaics as efficient small and polymeric molecules for better charge carrying capacities. The primary aspects of solar cells are: absorption of light in the range of emission spectrum of solar light, charge dissipation and charge carriage to electrodes (Figure 2.6). Poly(2,7-carbazoles) are used in solar cells as active electron donating polymeric materials in conjunction with electron accepting molecules and thus to carry the charge effectively to respective electrodes (Figure 2.6) (Brabec C. et al. 2010).

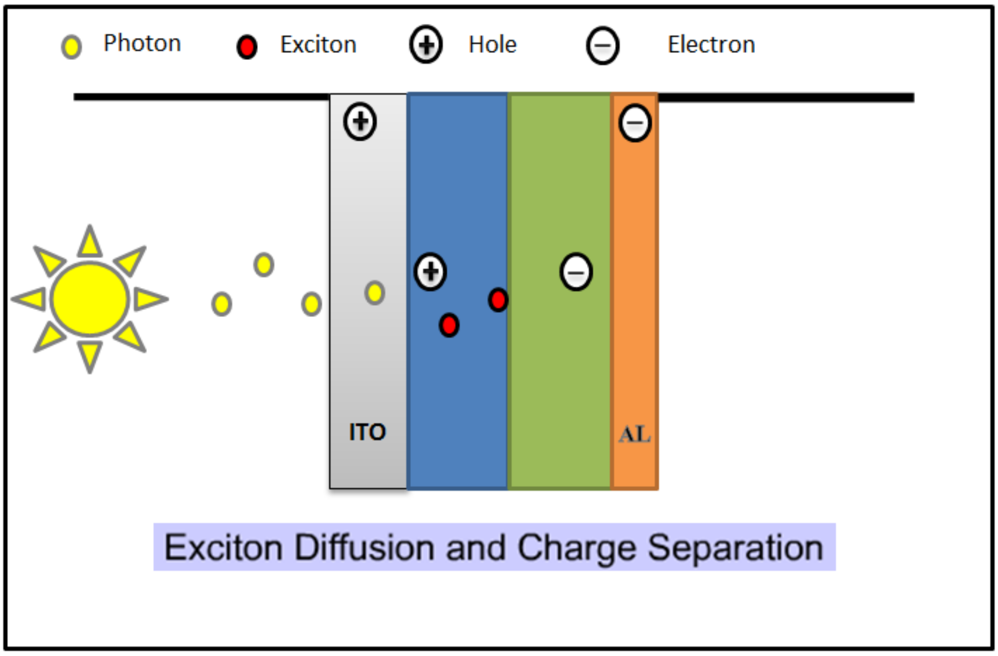


Figure 2.6: General Schematic Diagram Explaining the Exciton Diffusion and Charge Separation

When the light strikes the cells certain photons are absorbed by the surface of organic semiconductors and the excitons (electron-hole pair) is formed. Then, the donor acceptor interface causes efficient diffusion of excitons and isolates the charges. The free electrons and free holes created will be sent to the N- side and P-side, respectively. If the electrodes are arranged with an external circuit the electrical energy will be generated due to the electron circulation.

Poly(2,7-carbazoles) are widely employed in conjunction with perylene derivatives by Mullen and co-workers and obtained low efficiencies. However, the efficiencies are improved later by altering the band gap energies. It is notable that poly(2,7-carbazoles) are one of the best electron donating groups to employ them in solar cells.

Chapter 3

EXPERIMENTAL

3.1 Materials

Chemical reagents purchased from Aldrich were used without further purification, some solvents were purified before using by usual distillation processes according to the literature (Armarego and Perrin, 1990). Molecular sieves of size 4 Å (4-8 mesh) were obtained from Sigma Aldrich and were activated at 500 °C in a furnace. The activated molecular sieves were used for drying of liquid materials.

In order to investigate the photophysical properties of the synthesized compounds, spectroscopic-grade solvents were used directly after removing the dissolved oxygen by purging argon gas.

3.2 Instruments

JASCO FT-IR spectrophotometer for FTIR (spectra with KBr pellets), Varian-Cary-100 UV spectrophotometer (for solution absorption spectra), VarianCaryEclipse fluorescence spectrophotometer (for emission spectra), and Bruker DPX-400 spectrometer (for ^{1}H NMR and ^{13}C NMR spectra in $CDCl_3$ with an internal reference, TMS) were used throughout the study. Gravity column chromatography was performed for separating the samples using ethyl acetate and n-hexane (1:4) solvent mixture as an eluent with the silica gel pack.

Importantly, the concentrations of polymer solutions were prepared based on the molecular mass of monomer unit.

3.3 Methods of Syntheses

The purpose of this study is to synthesize a new electron donating poly(2,7-carbazole) containing a long alkyl chain. This section explains the step wise synthesis methodologies carried out for preparing the polycarbazole.

In part-I, 2,7-dibromocarbazole (Cbz) was synthesized in two steps.

In part-II, the monomer, 2,7-dibromo-N-dodecylcarbazole (dodecylcbz) was prepared.

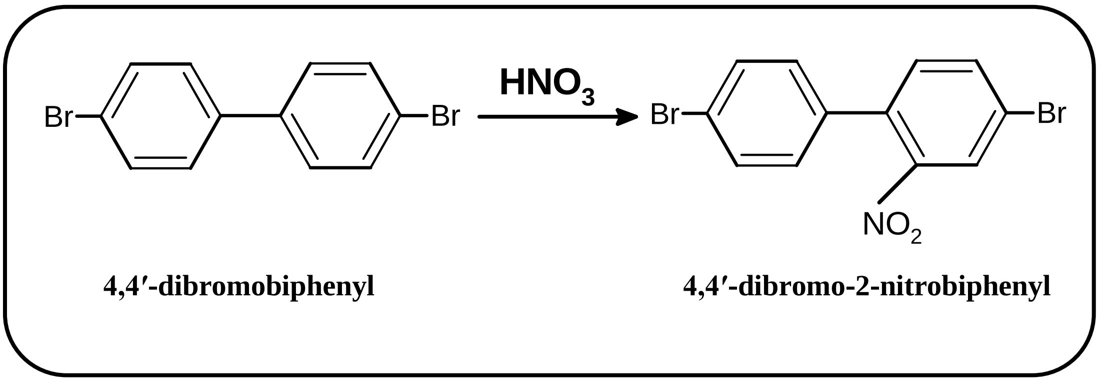
In part-III, the polymer (polycbz) was synthesized successfully using the synthesized monomer.

PART-I: Synthesis of 2,7-dibromocarbazole

The synthesis of 2,7-dibromocarbazole was carried out in two steps. It is widely discussed in literature that the substitution at 2,7-positions of the carbazole was not so easy and straightforward. The synthesis is carried out in two consecutive steps, where in the first step, nitration of 4,4′-dibromobiphenyl (DBBP) yields 4,4′-dibromo-2-nitrobiphenyl (DBNBP) which was further used in the second step to synthesize the target dibromocarbazole.

Step-1: Synthesis of 4,4′-dibromo-2-nitrobiphenyl

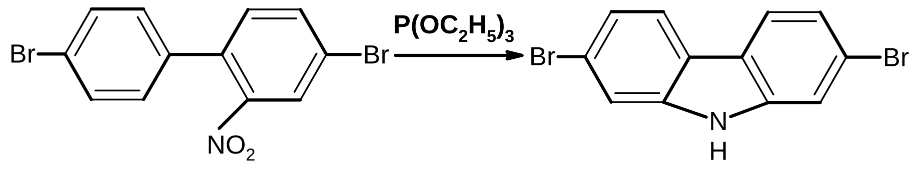
The DBNBP was synthesized from nitration of DBBP in presence of concentrated nitric acid, acetic acid, acetic anhydride and dichloromethane as shown below in Scheme 3.2. (Dierschke F. et al. 2003)



Scheme 3.2: Synthesis of 4,4′-dibromo-2-nitrobiphenyl, DBNBP

Step-2: Synthesis of 2,7-dibromocarbazole

Synthesis of 2,7-dibromocarbazole was done by using DBNBP with triethyl phosphite under argon as shown below Scheme 3.3 (Dierschke F. et al. 2003).

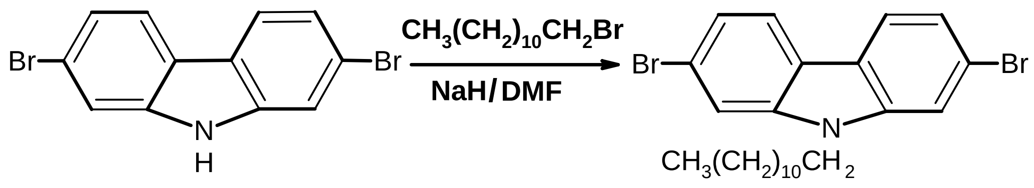


4,4′-dibromo-2-nitro biphenyl **2,7-dibromocarbazole**

Scheme 3.3: Synthesis of 2,7-dibromocarbazole

PART-II: Synthesis of the monomer, 2,7-dibromo-*N*-dodecylcarbazole

The alkylation of 2,7-dibromocarbazole was made at nitrogen of the carbazole unit by introducing an alkyl bromide (1-bromododecane) in presence of sodium hydride. The resulting compound is the 2,7-dibromo-N-dodecylcarbazole. The reaction scheme is shown below (Scheme 3.4) (Dierschke F. et al. 2003).



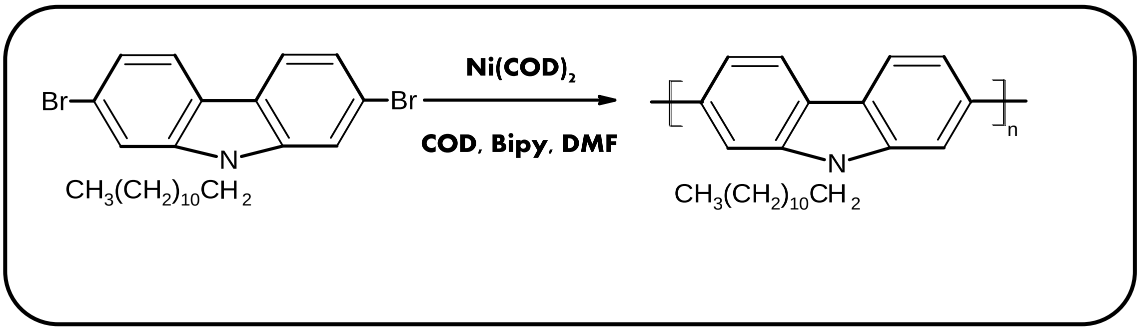
2,7-dibromocarbazole

2,7 dibromo-*N*-dodecan carbazole

Scheme 3.4: Synthesis of the Monomer, 2,7-dibromo-*N*-dodecylcarbazole

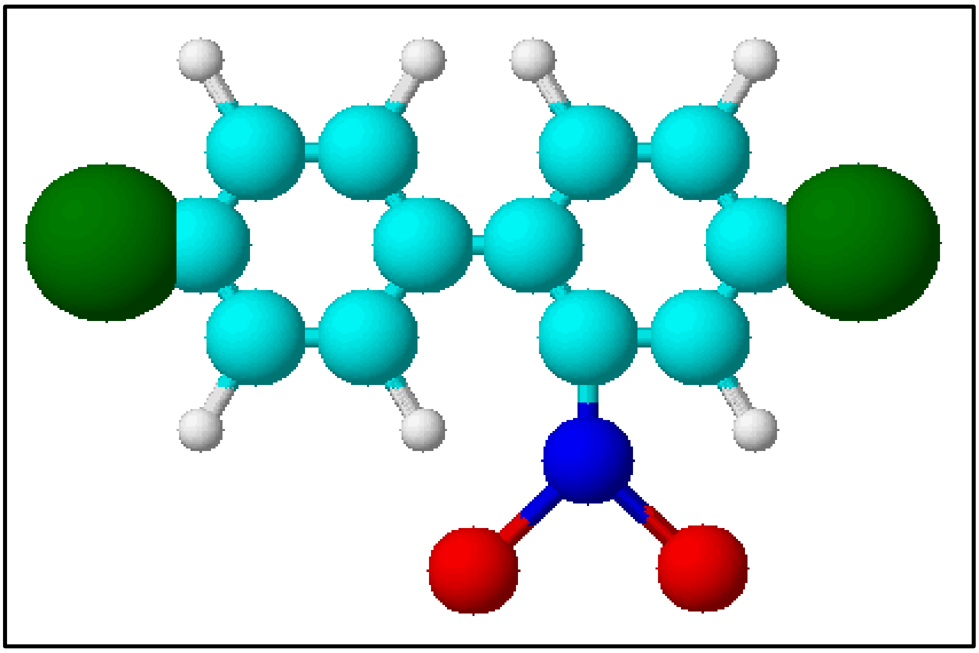
PART-III Synthesis of the polymer, poly(N-dodecylcarbazole)-2,7-diyl

Finally, the monomer synthesized in Part-II was polymerized by Yamamoto polymerization with Bis(1,5-cyclooctadiene)nickel(0) in presence of 1,5-cyclooctadiene and 2,2′-bipyridyl under argon (Li J. et al. 2006).



Scheme 3.5: Synthesis of poly[*N*-dodecylcarbazole]-2,7-diyl

3.4 Synthesis of 4,4′-dibromo-2-nitrobiphenyl

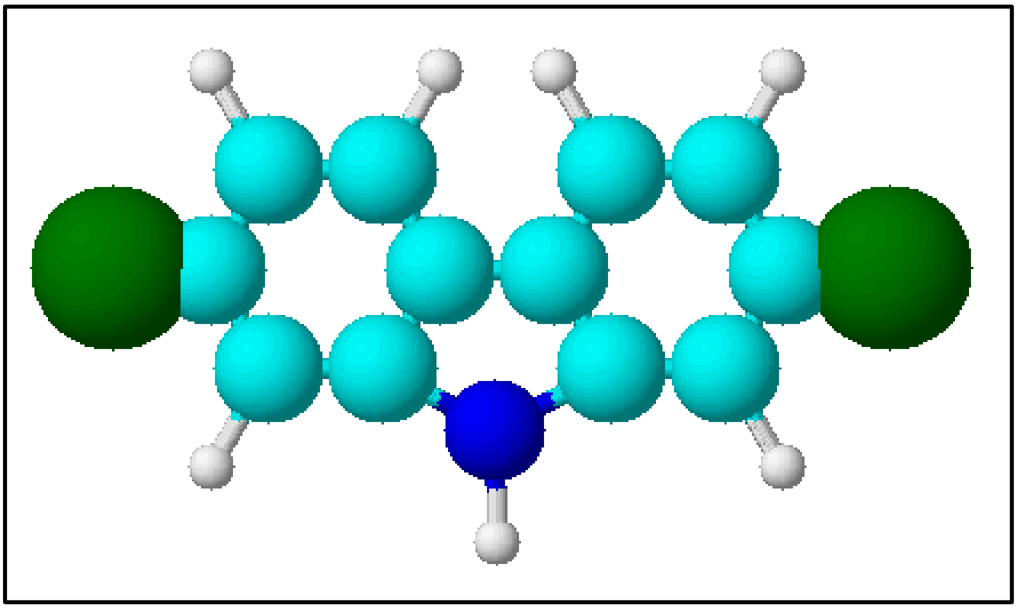


To a mixture of concentrated nitric acid (15 mL) and acetic acid (15 mL) was added drop wise a solution of DBBP (2.00 g, 6.41 mmol) in dichloromethane (15 mL) and acetic anhydride (40 mL). The reaction was carried out at room temperature for an hour and then slightly heated to 40 ^{o}C and stirred for 3 h. After obtaining the deep orange colored solution, reaction completion was confirmed by TLC and added 10% NaOH (100 mL) to partially neutralize the acid and extracted with dichloromethane (4×75 mL). The collected organic layer was vacuum dried to yield a yellow colored tacky precipitate. The crude product was recrystallized using methanol to give a pure 4,4′-dibromo-2-nitrobiphenyl product.

Yield: 88% (2 g), Yellow colored solid.

mp: 126 ^{o}C (Lit: 124 ^{o}C).

3.5 Synthesis of 2,7-dibromocarbazole

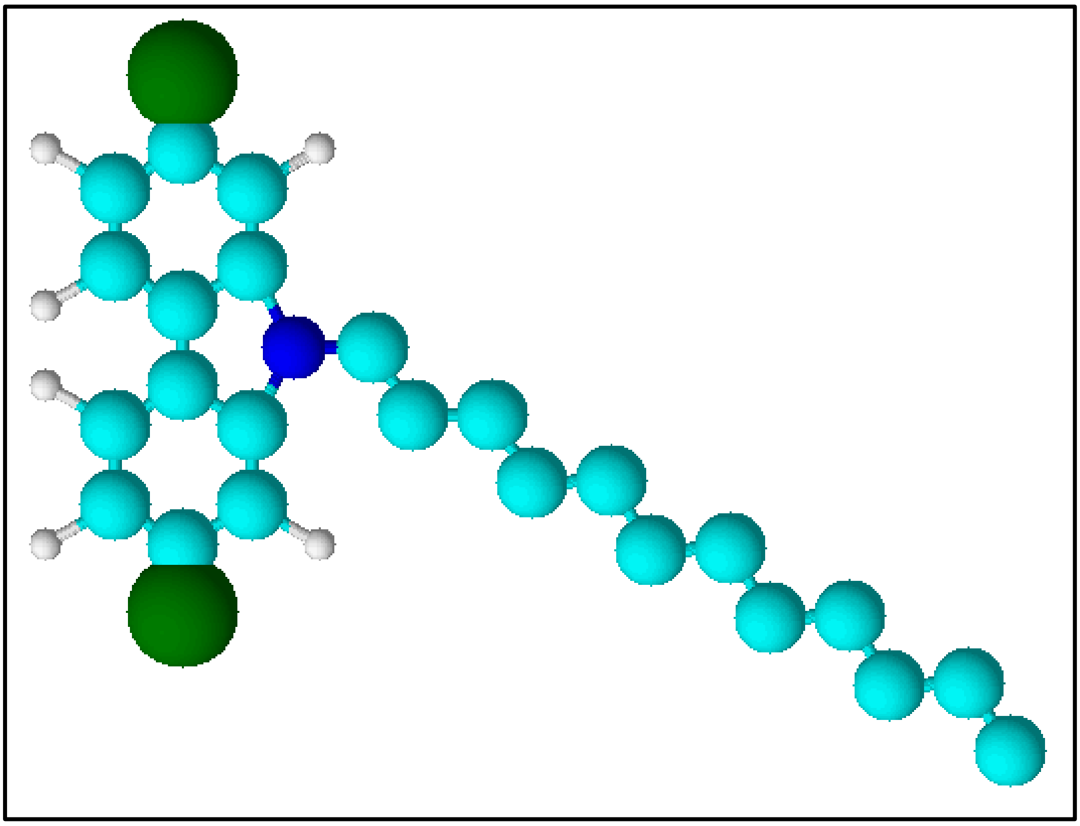


A three-necked balloon under argon was added nitrobiphenyl (2 g, 5.6 mmol) and triethylphosphite (30 mL) and refluxed for 18 h as reported in literature (Dierschke F. et al. 2003).The reaction was quenched with water and extracted with dichloromethane. The combined organic dichloromethane layers were evaporated to yield white solid as the title product.

Yield: 50% (0.9 g), White solid.

mp: 236 ^{o}C (Lit: 234 ^{o}C).

3.6 Synthesis of 2,7-dibromo-N-dodecylcarbazole

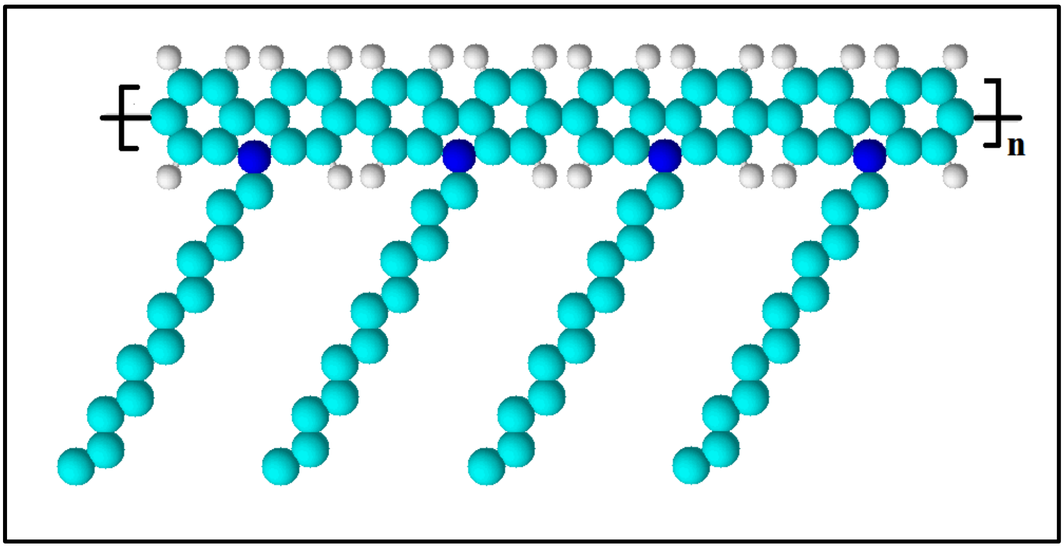


A three-necked balloon was equipped with an argon tap, condenser, magnetic stirring bar and thermometer and purged argon gas for 10 min. Anhydrous N,N-dimethylformamide (30 mL) was added and purged argon gas for another 15 min. Sodium hydride (NaH) (0.09 g, 3.75 mmol) was slowly added and stirred at room temperature for an hour. To the mixture, 2,7-dibromocarbazole (0.5 g, 1.53 mmol) was added followed by 1-bromododecane (0.5 ml, 20.8 mmol) and heated the reaction mixture for 20 h at 70 ºC by gradually increasing the temperature.

Afterwards, distilled water (40 mL) was added to quench the reaction and extracted with (3 × 100 mL) of dichloromethane (CH_2Cl_2). The organic layer was dried using sodium sulfate and the solvent was removed under vacuum to yield white colored 2,7-dibromocarbazole.

Yield: 83%, Color: White solid.

3.7 Synthesis of poly(*N*-dodecane-2,7-carbazole)



A three-necked balloon was equipped with an argon tap, condenser, magnetic stirring bar and thermometer and purged argon gas for 10 min. Anhydrous N,N-dimethylformamide (15 mL) and toluene (15 mL) were added and purged argon gas for another 15 min. Bis-(1,5-cyclooctadiene)nickel(0) and bipyridyl in 1,5-cyclooctadiene and toluene (5 mL) were added followed by bromobenzene and stirred at room temperature for an hour. To the mixture, 2,7-dibromo-N-dodecylcarbazole (0.5 g, 1.53 mmol) was added and heated the reaction mixture for 3 d at 80 °C by gradually increasing the temperature.

Afterwards, the reaction mixture was poured in a mixture of methanol and HCl (1:1) and added extracted with chloroform (3 × 100 mL). The combined organic layer was again extracted with saturated EDTA solution (100 mL) and the final organic layer was dried in vacuuo to yield brown colored liquid polymer.

Yield: 85%, Color: brown colored liquid.

FT-IR (KBr, cm^{-1}): ν = 3010, 2920, 2850, 1631, 1464, 1095.

UV-Vis ($CHCl_3$) (λ_{max},nm; (ε_{max},L mol^{-1} cm^{-1})/monomer): 244, 271, 307 (74), 335, 348.

Fluorescence, λ_{max} ($CHCl_3$, nm): 365 nm.

Chapter 4

DATA AND CALCULATIONS

4.1 Calculation of Maximum Absorption Coefficient (ε_{max})

Beer-Lamberts low gives the following equation (4.1) which is used to calculate extinction coefficient of the compounds.

$$\varepsilon_{max} = A / cl \qquad (4.1)$$

Where,

(ε_{max}): Maximum absorption coefficient in $L.mol^{-1}.cm^{-1}$ at λ_{max}

(A): Absorbance

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

(l): Path length in cm

ε_{max} **Caculation of Poly(*N*-dodecyl-2,7-carbazole)**:

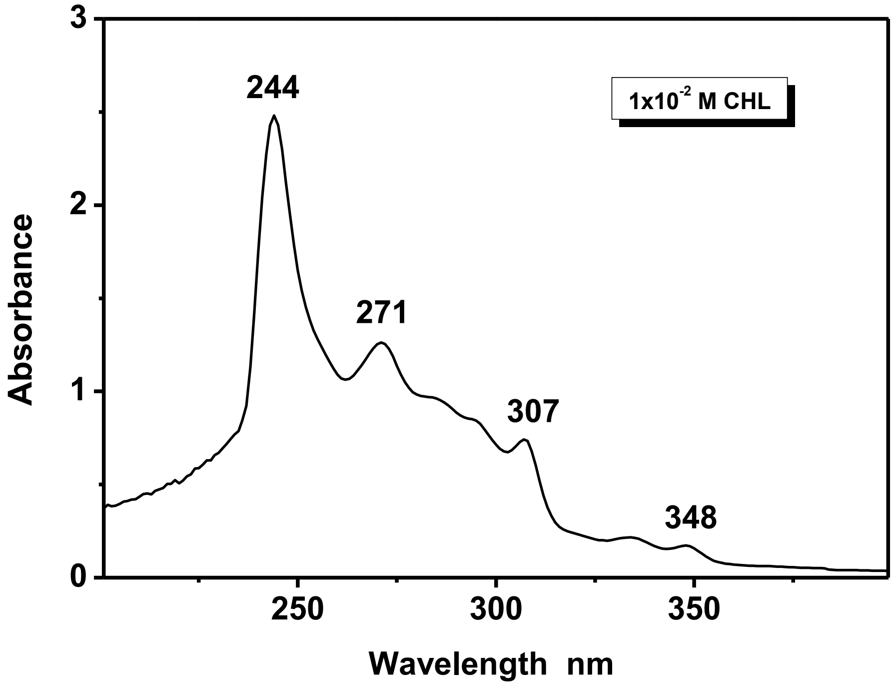


Figure 4.1: Absorption Spectrum of PCbz in Chloroform at ($1x10^{-2}$ M)

According to the data of absorption spectra of PCbz in (Figure 4.1) at wavelength, λ_{max} =307 nm the absorbance is 0.74415 for concentration of $1x10^{-2}$ M.

$$\varepsilon_{max} = \frac{0.74415}{1*10^{-2}\text{M}*1\text{ cm}} = 74.415 \text{ L.mol}^{-1}.\text{cm}^{-1}/\text{per monomer unit}$$

ε_{max} of Poly(*N*-dodecyl-2,7-carbazole) = 74.415 $\text{L.mol}^{-1}.\text{cm}^{-1}$

4.2 Calculation of Full Width Half Maximum (FWHM) of Selected Absorption ($\Delta\bar{\upsilon}_{1/2}$)

By the following equation, the FWHM of Selected Absorption ($\Delta\bar{\upsilon}_{1/2}$) can be calculated.

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

Where,

$\Delta\bar{\upsilon}_{1/2}$: FWHM of Selected maximum Absorption in cm $^{-1}$

$\bar{\upsilon}_{I} - \bar{\upsilon}_{II}$: The frequencies from the absorption spectrum in cm $^{-1}$

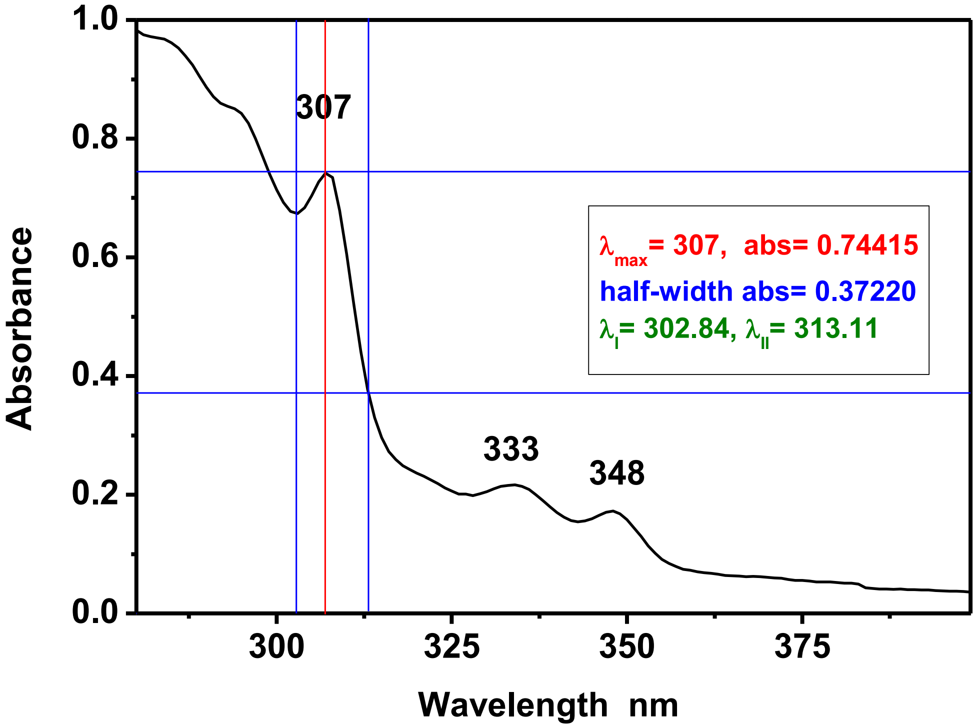


Figure 4.2: Absorption Spectrum of PCbz in Chloroform at (1x10 $^{-2}$ M) and FWHM Representation

From Figure 4.2,

$\lambda_I = \quad 302.84 \text{ nm}$

$\rightarrow \lambda_I = 302.84 * \frac{10^{-9}\,m}{1\,nm} * \frac{1\,cm}{10^{-2}m} = 302.84 * 10^{-7}$

$\rightarrow \bar{\upsilon}_I = \frac{1}{302.84 * 10^{-7}} = 3.302 * 10^{4} \text{ cm}^{-1}$

$\lambda_{II} = \quad 313.11 \text{ nm}$

$\rightarrow \lambda_{II} = 313.11 * \frac{10^{-9}\,m}{1\,nm} * \frac{1\,cm}{10^{-2}m} = 313.11 * 10^{-7}\text{cm}$

$\rightarrow \bar{\upsilon}_{II} = \frac{1}{313.11 * 10^{-7}} = 3.193 * 10^{4} \text{ cm}^{-1}$

$\Delta\bar{\upsilon}_{1/2} = \bar{\upsilon}_I - \bar{\upsilon}_{II} = 3.302 * 10^{4} \text{ cm}^{-1} - 3.193 * 10^{4} \text{ cm}^{-1} = 10.9 * 10^{2} \text{ cm}^{-1}$

$\rightarrow \Delta\bar{\upsilon}_{1/2} = 1090 \text{ cm}^{-1}$

4.3 Calculation of Natural Radiative Lifetime (τ_0)

The equation which shown below is used for calculation of theoretical radiative lifetime (τ_0) (Turro. Et al, 1965)

$$\tau_0 = \frac{3.5 * 10^8}{\varepsilon_{max} * \bar{\upsilon}^2_{\text{max}} * \Delta\bar{\upsilon}_{1/2}}$$

Where,

τ_0 : Natural radiative lifetime in ns

$\bar{\upsilon}_{max}$: Mean frequency for the maximum absorption band in cm $^{-1}$

$\Delta\bar{\upsilon}_{1/2}$: The half-width of selected absorption band in units of cm $^{-1}$

$\boldsymbol{\varepsilon_{max}}$**:** The maximum molar extinction coefficient at the selected absorption wavelength in L. mol $^{-1}$ .cm $^{-1}$

Theoretical radiative lifetime of Poly(*N*-dodecyl-2,7-carbazole):

λ_{max}= 307 nm, which obtained from Figure 4.1 and Figure 4.2

ε_{max} = 74.415 L.mol $^{-1}$.cm $^{-1}$

$\Delta\bar{\upsilon}_{1/2}$ = 1090 cm $^{-1}$

$\lambda_{max} = 307 \text{ nm} * \frac{10^{-9} m}{1\, nm} * \frac{1\, cm}{10^{-2}\, m} = 307 * 10^{-7}$ cm

$\rightarrow \bar{\upsilon}_{max} = \frac{1}{307 * 10^{-7}\, cm} = 3.25732 * 10^{4}$ cm $^{-1}$ = 32573.2 cm $^{-1}$

$\rightarrow \bar{\upsilon}^2_{max} = (40983.6 \text{ cm}^{-1})^{2} = 1.06101 * 10^{9}$ cm $^{-1}$

Now, after collecting the all data the theoretical radiative lifetime can be calculated.

$$\rightarrow \tau_0 = \frac{3.5*10^8}{\varepsilon_{max} *\bar{\upsilon}^2_{\mathrm{max}} * \Delta\bar{\upsilon}_{1/2}} = \frac{3.5*10^8}{74.415 * 1.06101 * 10^{9} * 1090}$$

$\rightarrow \tau_0 = 40.6688 * 10^{-7}$ s

$\rightarrow \tau_0 = 40.6688 * 10^{-7} * 10^9 = 4066.88$ ns/per mass of one monomer unit

Table 4.1: Theoretical Radiative Lifetime Data of PCbz in DMF and MeOH

Solvent	**λ_{max}(nm)**	**ε_{max}($M^{-1}.cm^{-1}$)**	**$\bar{\nu}^2_{max}$(cm^{-2})**	**$\Delta\bar{\nu}_{1/2}$(cm^{-1})**	**τ_0 (ns)**
$CHCl_3$	307	74.42	$1.061 * 10^{9}$	1090	4066.8
DMF	305.55	70.22	$1.071 * 10^{9}$	1360	3421.9
MeOH	304.63	75.68	$1.077 * 10^{9}$	1446	2969.6

4.4 Calculation of Fluorescence Rate Constants (k_f)

Fluorescence Rate constants (k_f) can be calculated theoretically by next equation.

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

Where,

K_f : Fluorescence rate constant in s^{-1}

τ_0 : Theoretical radiative lifetime in s

Fluorescence Rate constants (k_f) of Poly(*N*-dodecyl-2,7-carbazole):

→ $k_f = \frac{1}{\tau_0}$

→ $k_f = \frac{1}{40.6688 * 10^{-7}\ s} = 24.5888 * 10^4\ s^{-1}$

→ $K_f = 24.58 * 10^4\ s^{-1}$ / per mass of one monomer unit

Table 4.2: Fluorescence Rate Constants Data of PCbz in DMF and MeOH

Solvent	**K_f s^{-1}**
$CHCl_3$	$24.58 * 10^4$
DMF	$29.22 * 10^4$
MeOH	$33.67 * 10^4$

4.5 Calculation of Oscillator Strengths (f)

The Calculation of Oscillator Strengths (f) can be defined as a dimensionless quantity to deduce the strength of an electronic transition, and it can be calculated by next equation.

$$f = 4.32 * 10^{-9}\, \Delta\bar{\upsilon}_{1/2}\, \varepsilon_{max}$$

Where,

f : The Oscillator Strengths

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

ε_{max} : The maximum molar extinction coefficient at the selected absorption wavelength in (L. mol $^{-1}$ .cm $^{-1}$)

The Oscillator Strengths (f) Poly(*N*-dodecyl-2,7-carbazole:

→ $f = 4.32 * 10^{-9}\, \Delta\bar{\upsilon}_{1/2}\, \varepsilon_{max}$

→ $f = 4.32 * 10^{-9} * 1090 * 74.415$ = 0.003504

→ f = 0.003504/per mass of one monomer unit

Table 4.3: The Oscillator Strengths Data of PCbz in DMF and MeOH

Solvent	f
$CHCl_3$	0.00350
DMF	0.00412
MeOH	0.00472

4.6 Calculation of Singlet Energies (E_s)

The amount of energy which requires for transition of electron from ground state to excited state called singlet energy, and it can be calculated by next equation.

$$E_s = \frac{2.86 * 10^5}{\lambda_{max}}$$

Where,

E_s: The singlet energy in (Kcal.mol $^{-1}$)

λ_{max}: The maximum absorption wavelength in (Å)

The Singlet Energies (E_s) Poly(*N*-dodecyl-2,7-carbazole:

→ $E_s = \frac{2.86*10^5}{\lambda_{max}} = \frac{2.86*10^5}{3070} = 93.15$ Kcal.mol $^{-1}$

→ $E_s = 93.15$ Kcal.mol $^{-1}$

Table 4.4: The Singlet Energies Data of PCbz in DMF and MeOH

Solvent	**E_s**
$CHCl_3$	93.15
DMF	93.61
MeOH	93.89

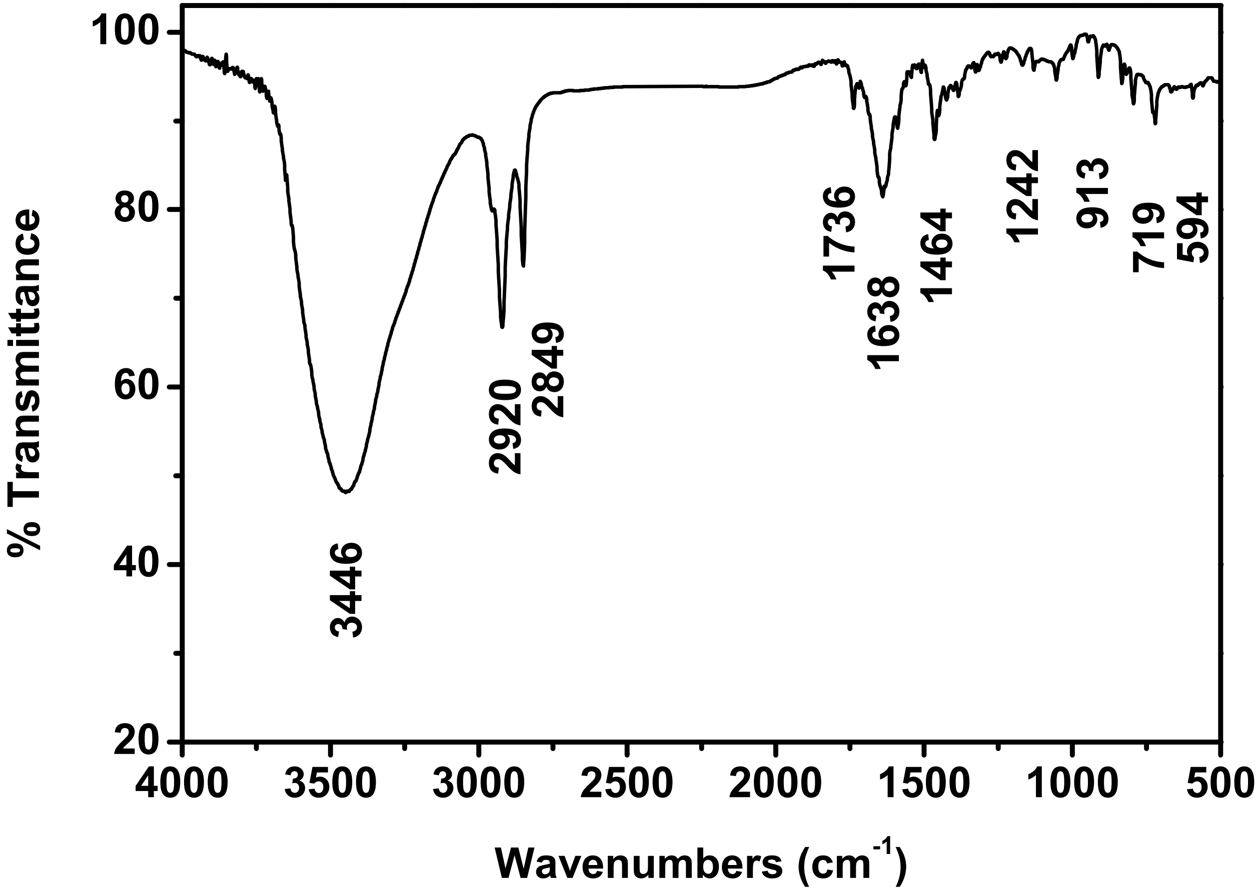


Figure 4.3: FTIR Spectrum of Monomer, Dodecylcarbazole

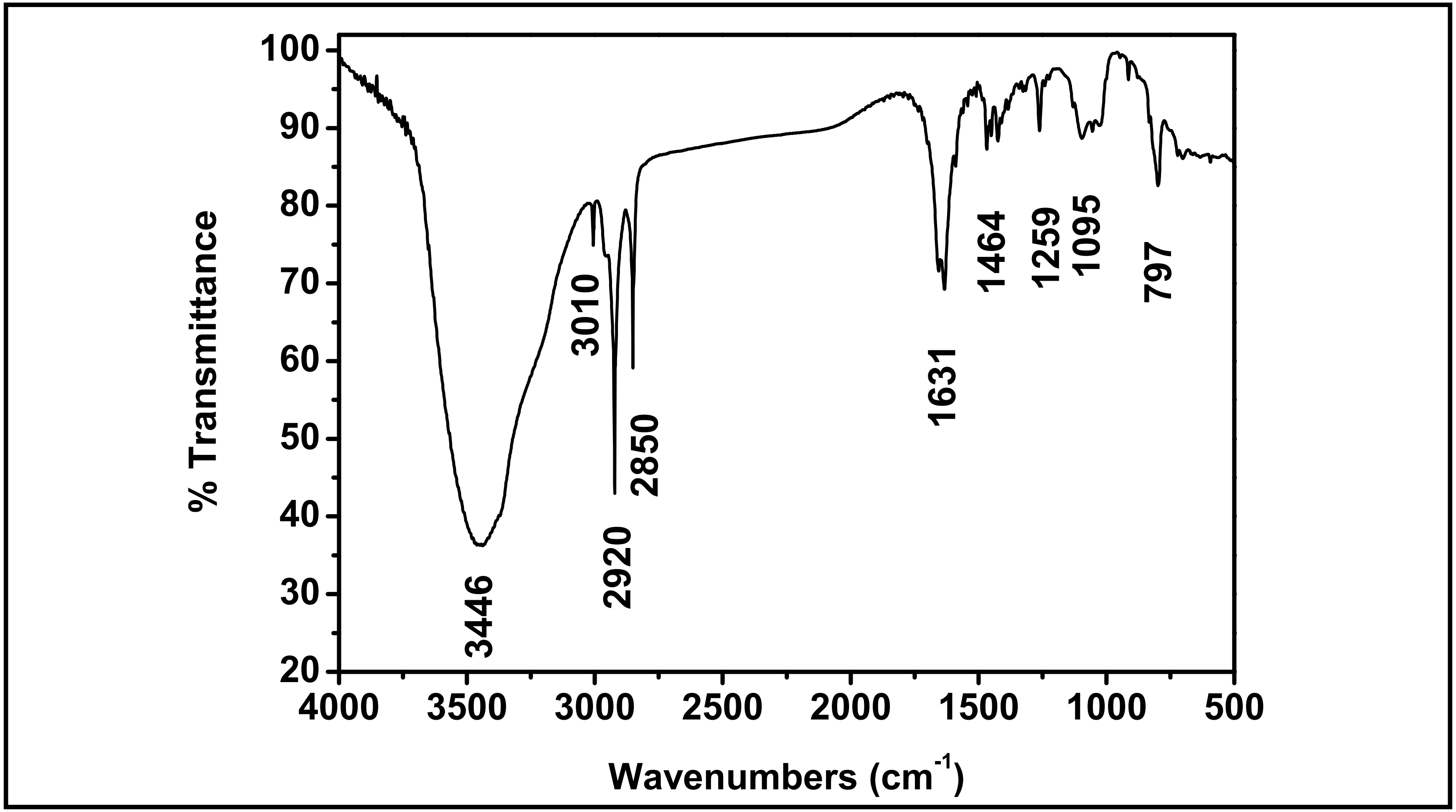


Figure 4.4: FTIR Spectrum of Polycarbazole

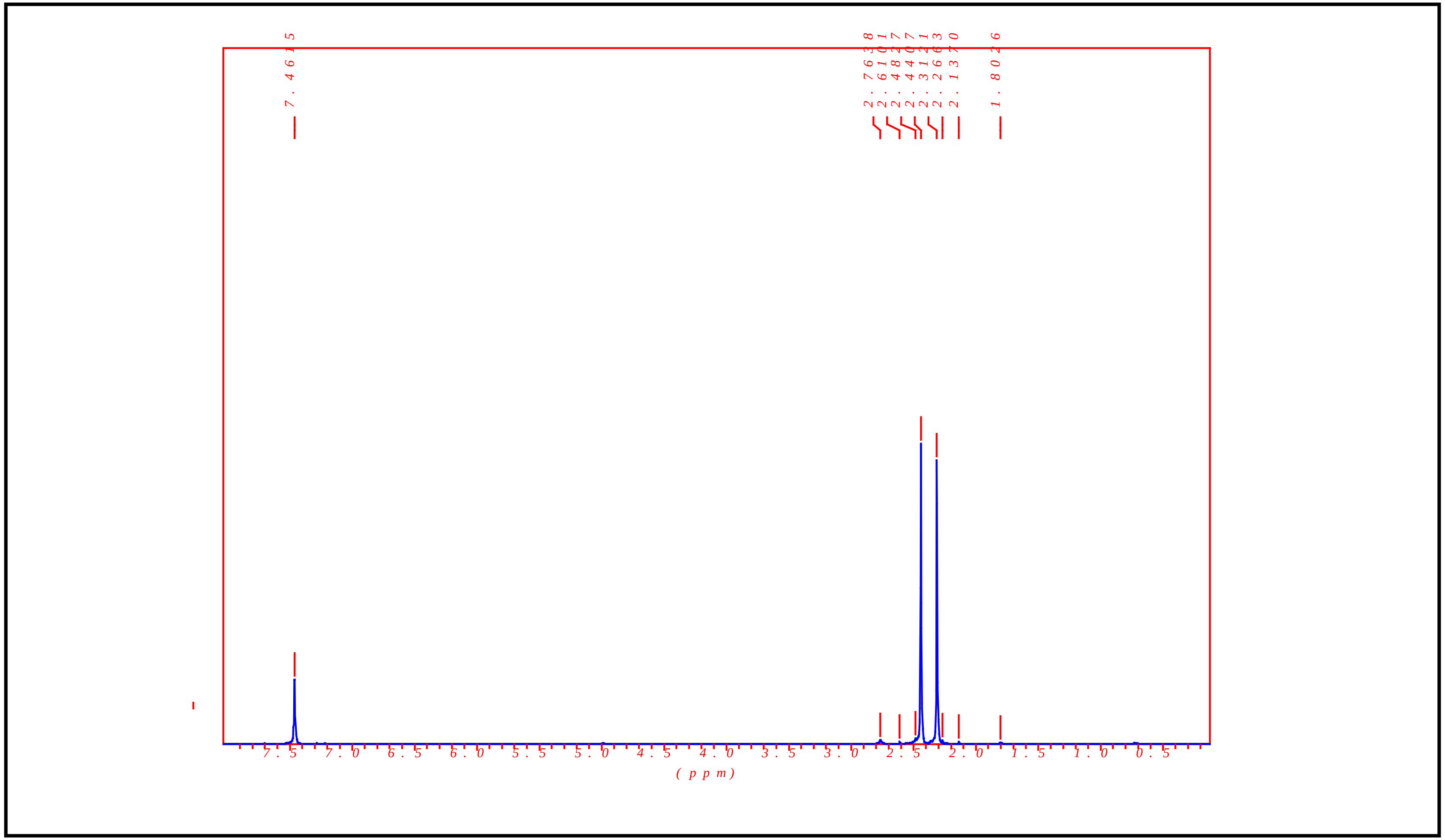


Figure 4.5: ^{1}H NMR Spectrum of Polycbz in $CDCl_3$

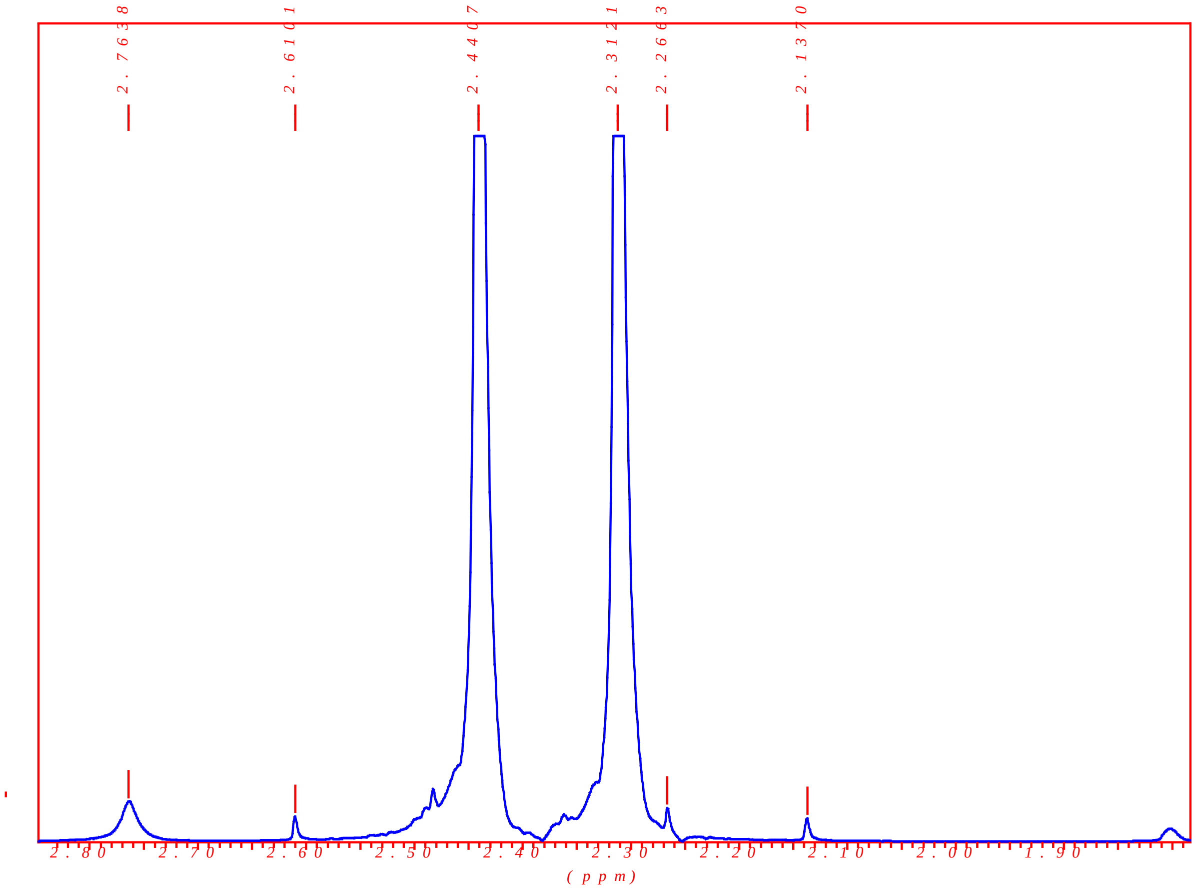


Figure 4.6: Expanded ^{1}H NMR Spectrum of Polycbz in $CDCl_3$

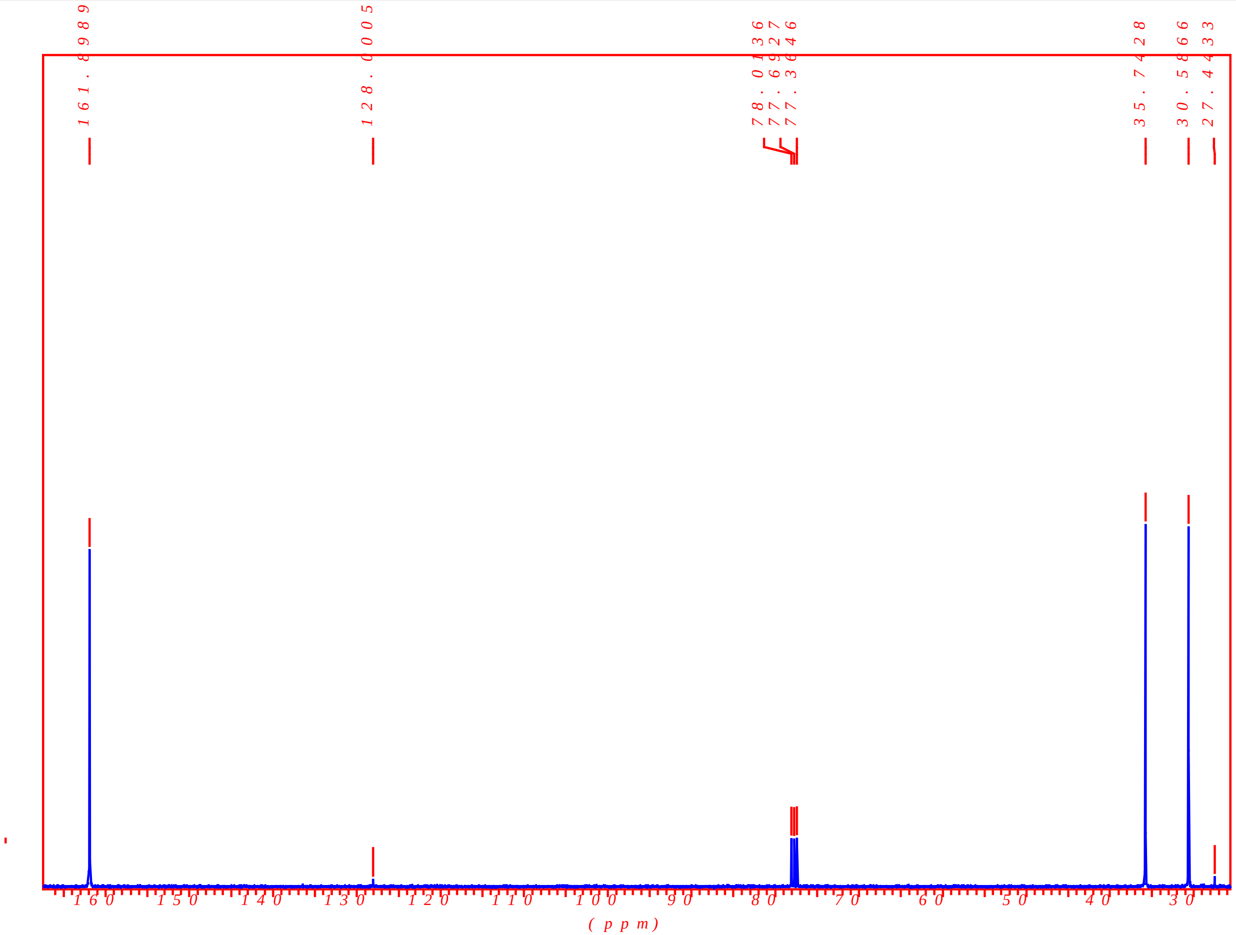


Figure 4.7: ^{13}C NMR Spectrum of Polycbz in $CDCl_3$

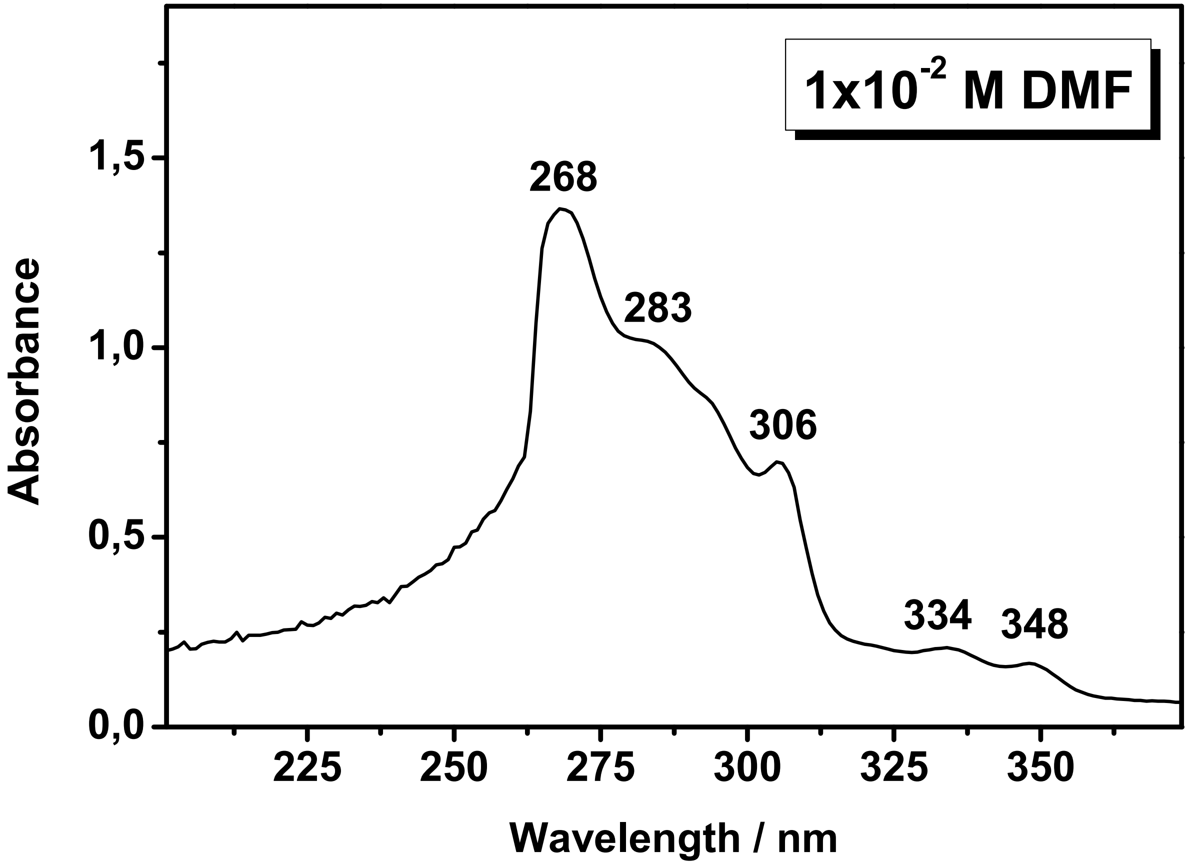


Figure 4.8: Absorption Spectrum of PCbz in Dimethylformamide at $1x10^{-2}$ M

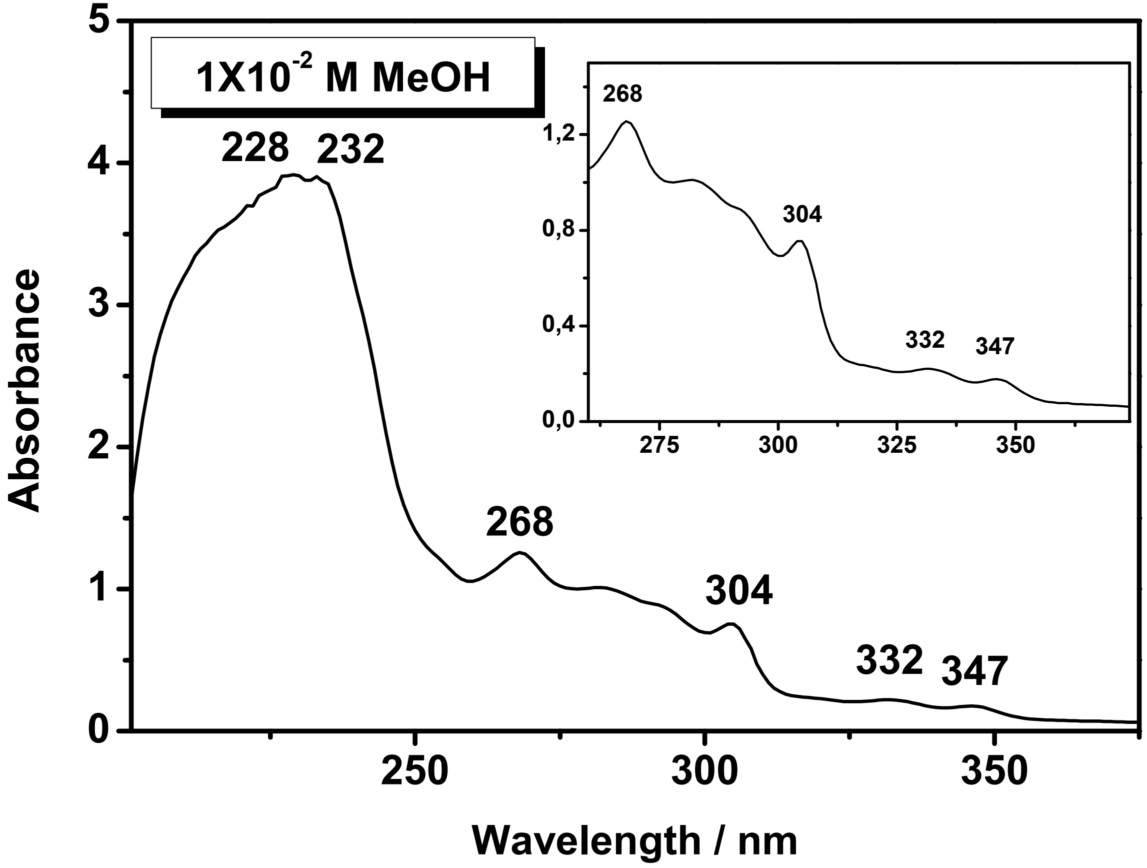


Figure 4.9: Absorption Spectrum of PCbz in Methanol at $1x10^{-2}$ M

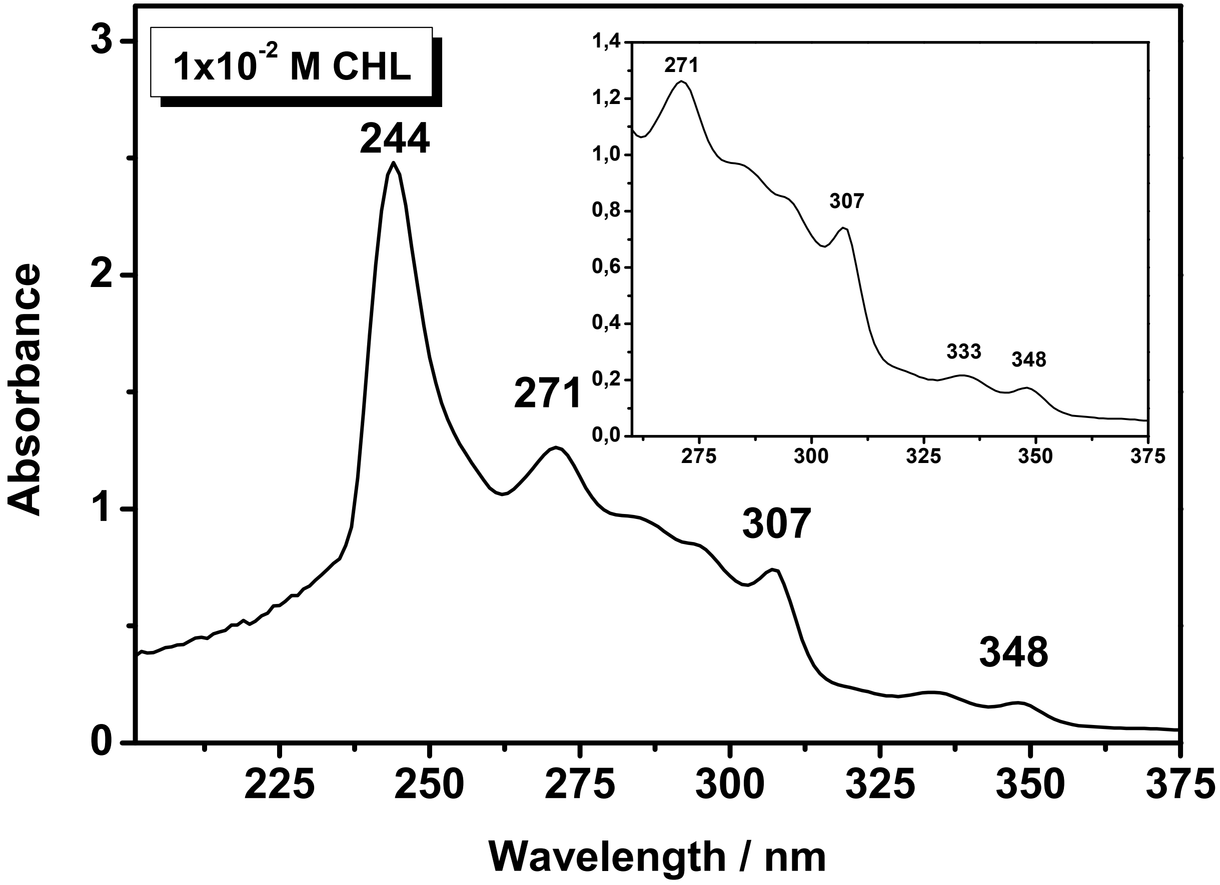


Figure 4.10: Absorption Spectrum of PCbz in Chloroform at 1x10^{-2} M

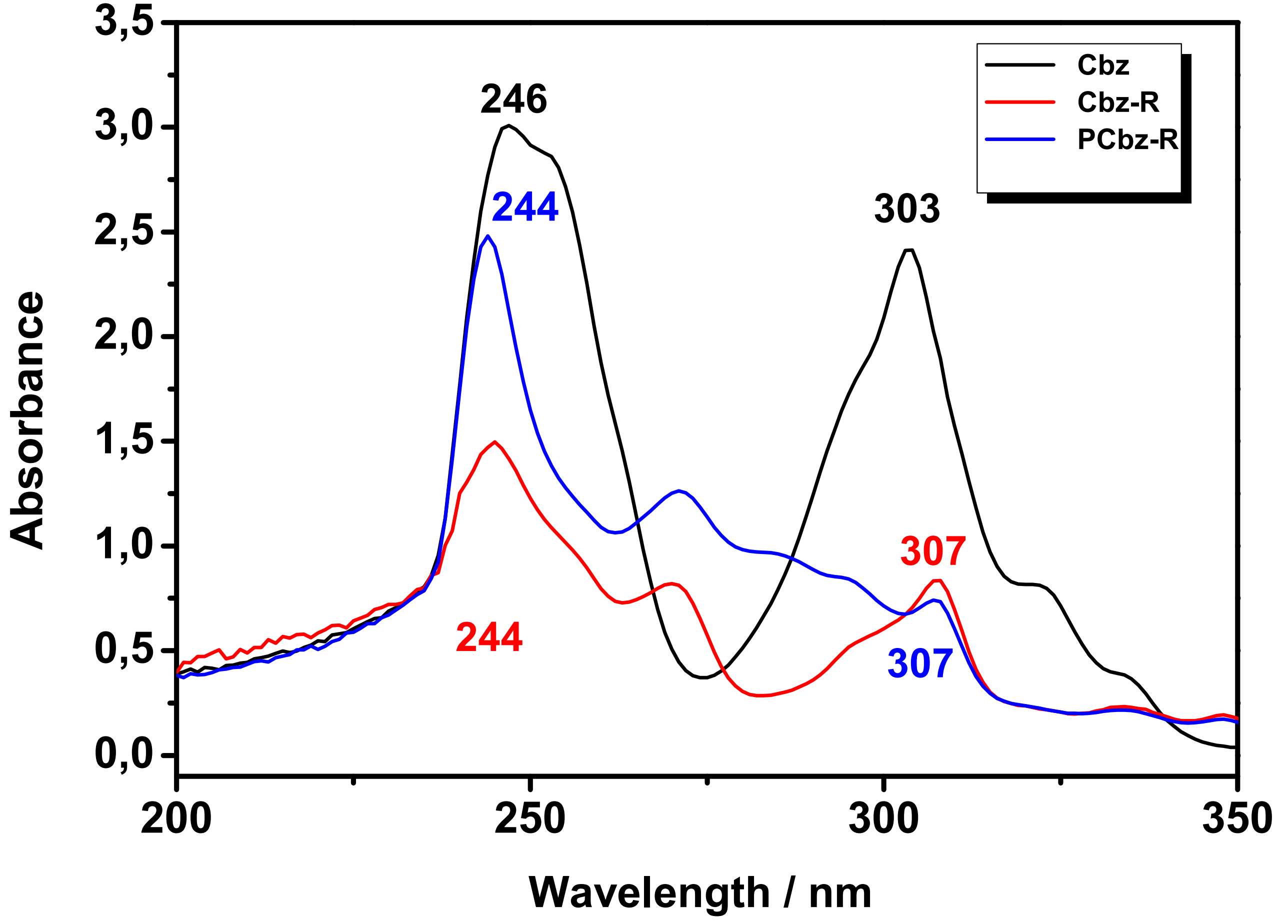


Figure 4.11: Absorption Spectrum of 1 × 10^{-2} M PCbz and 1 × 10^{-4} M Cbz-R, Cbz in Chloroform

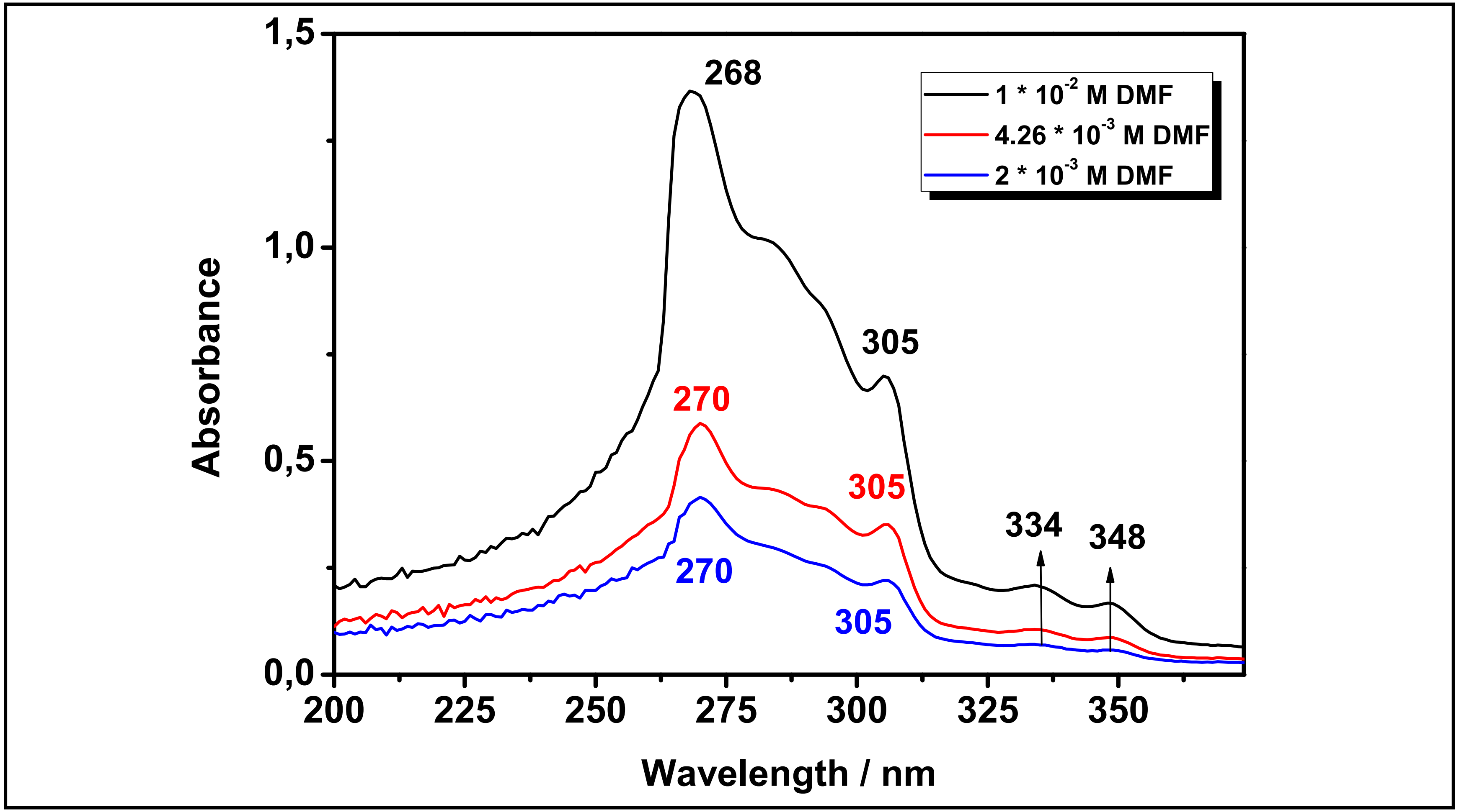


Figure 4.12: Variable-concentration Absorption Spectra of PCbz in Dimethylformamide

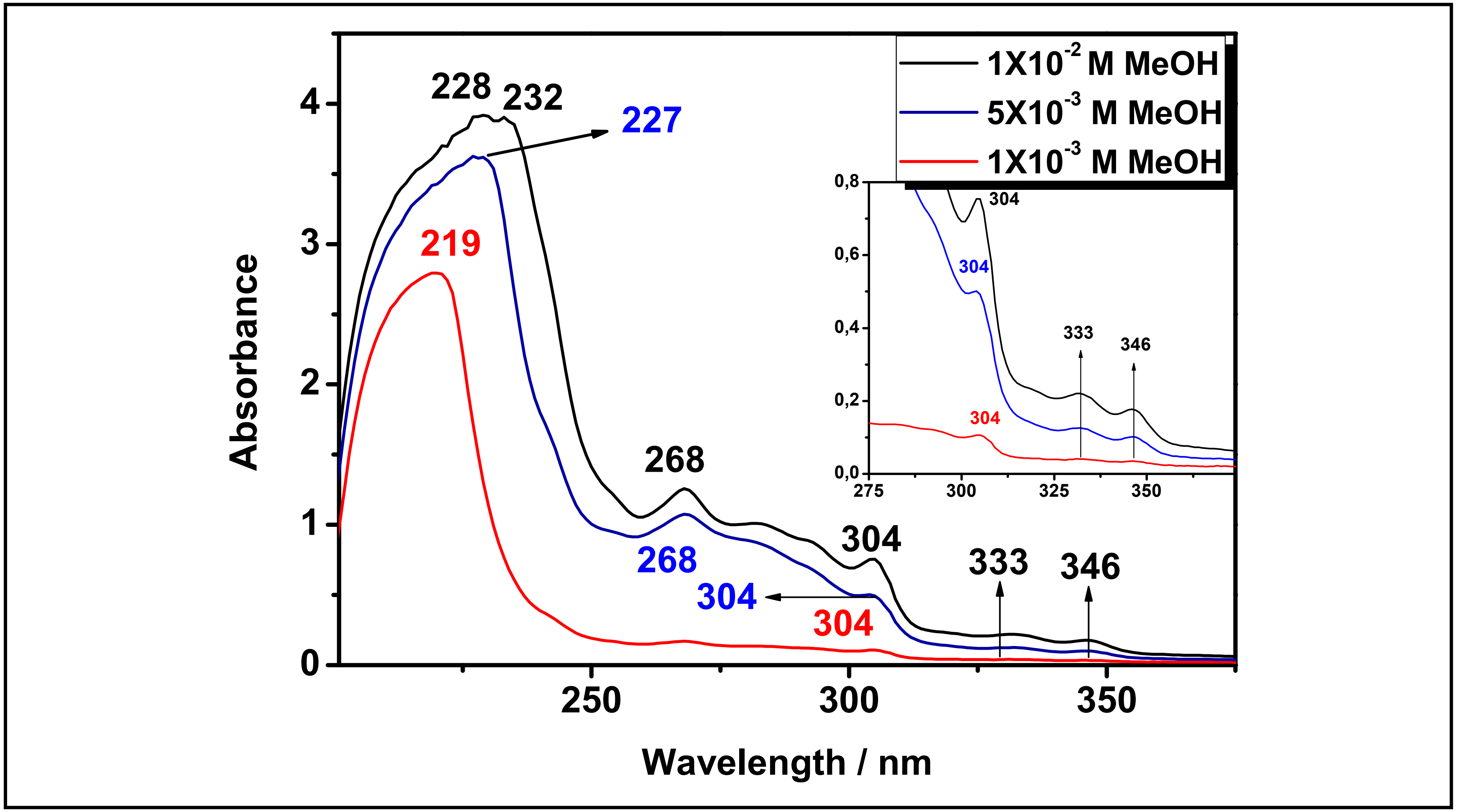


Figure 4.13: Variable-concentration Absorption Spectra of PCbz in Methanol

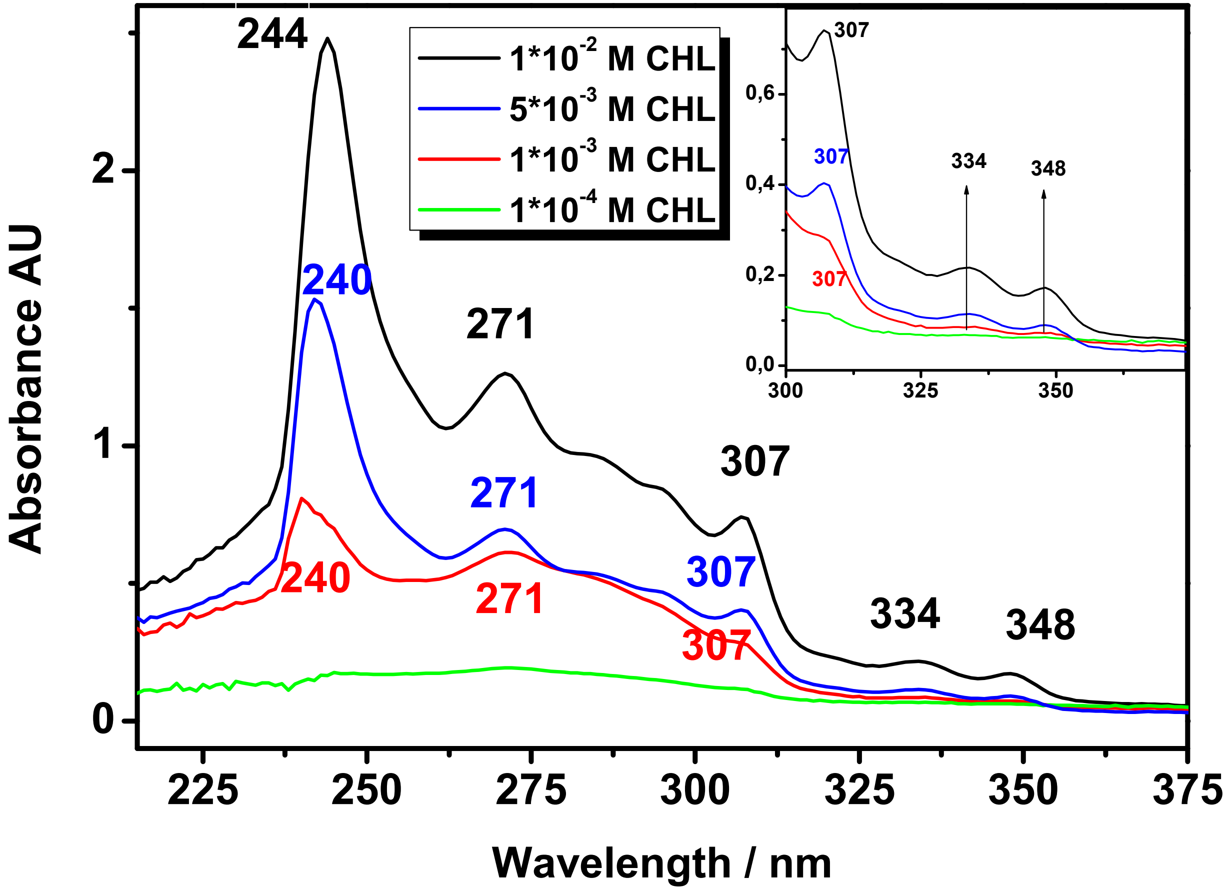


Figure 4.14: Variable-concentration Absorption Spectra of PCbz in Chloroform

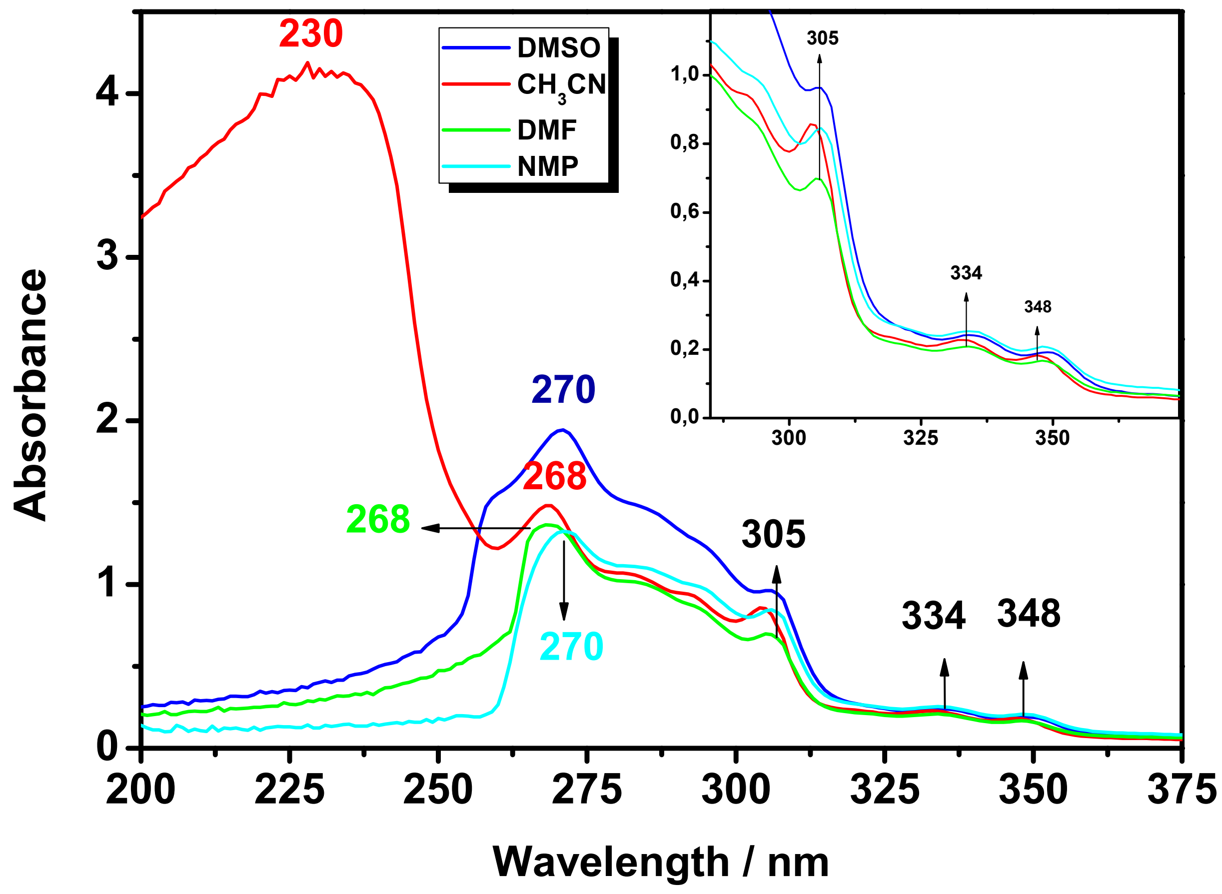


Figure 4.15: Absorption Spectra of PCbz in Various Dipolar Aprotic Solvents at 1×10^{-2} M

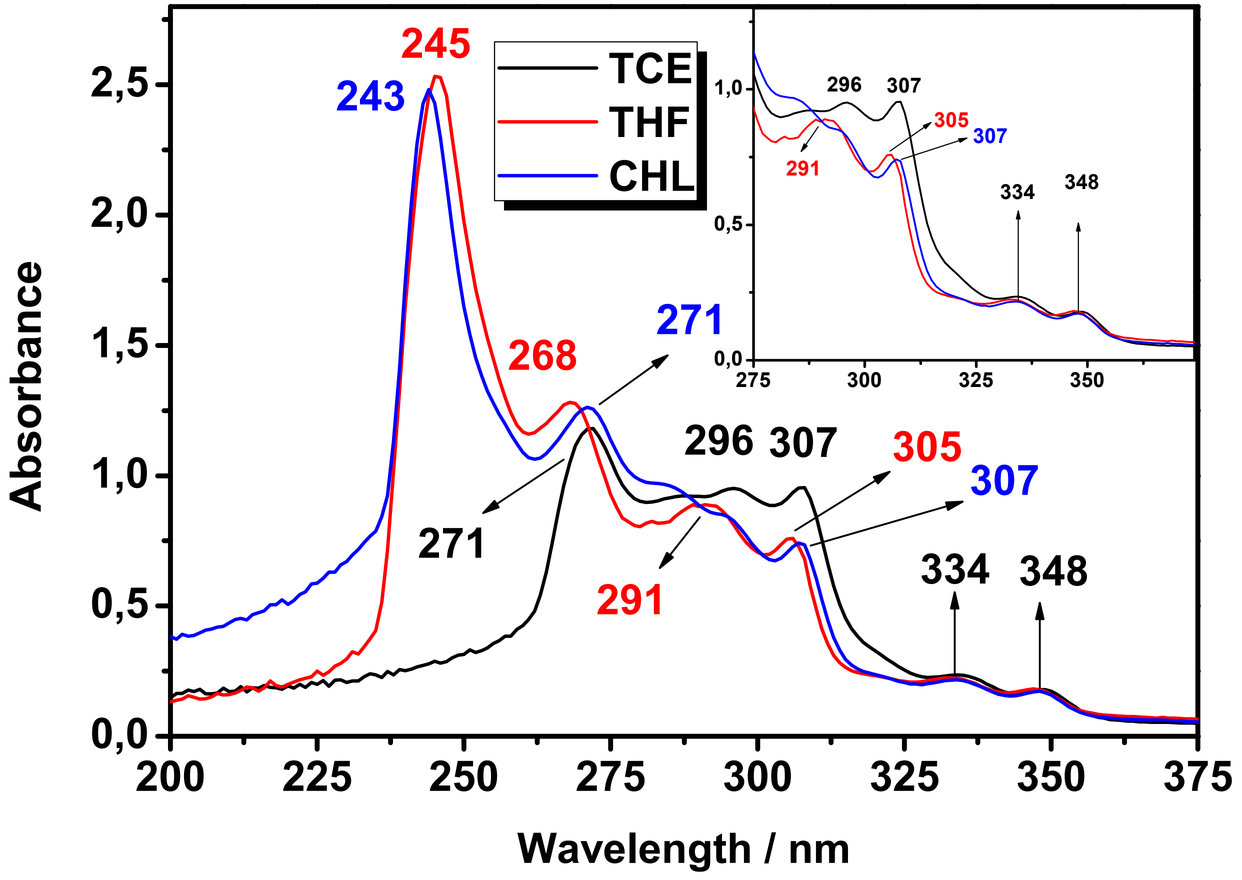


Figure 4.16: Absorption Spectra of PCbz in Different Kinds of Solvents with Varying Polarity at 1x10^{-2} M

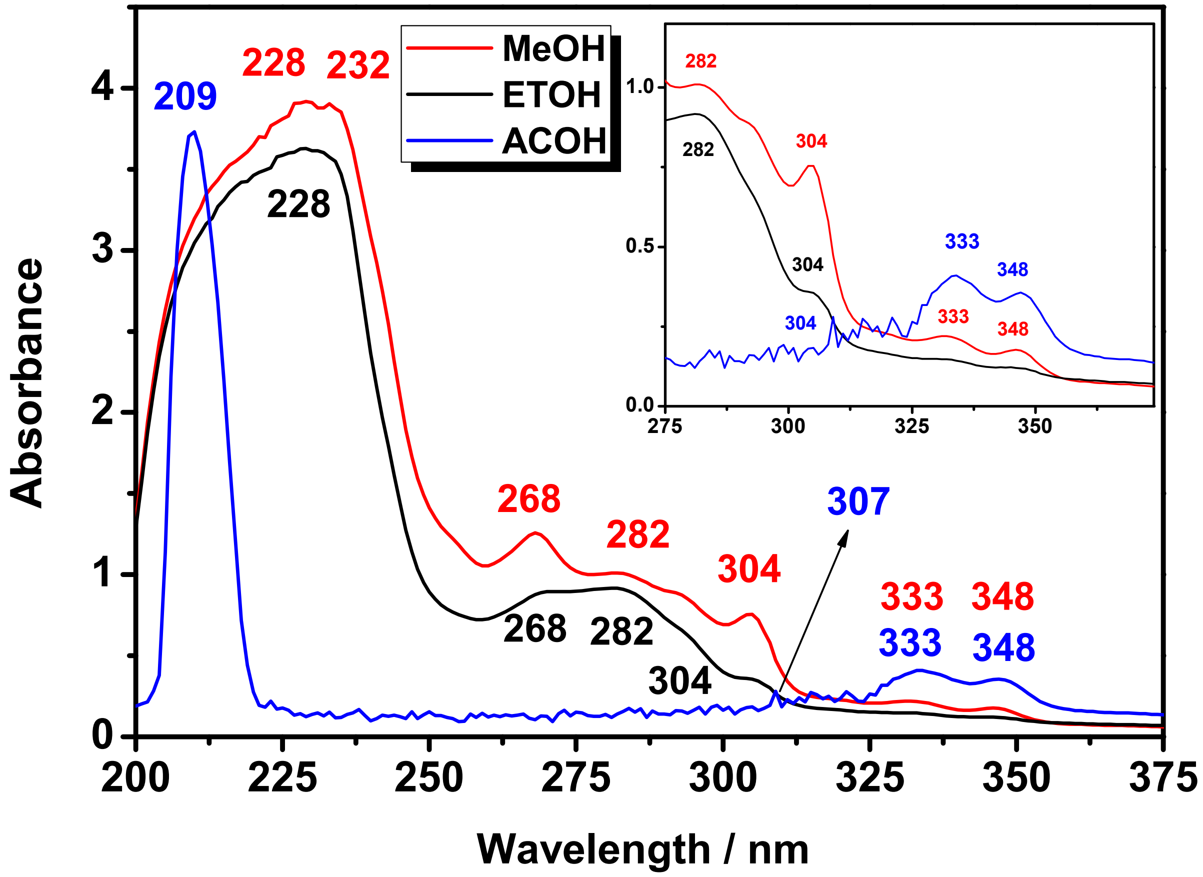


Figure 4.17: Absorption Spectra of PCbz in Polar Protic Solvents at 1×10^{-2} M

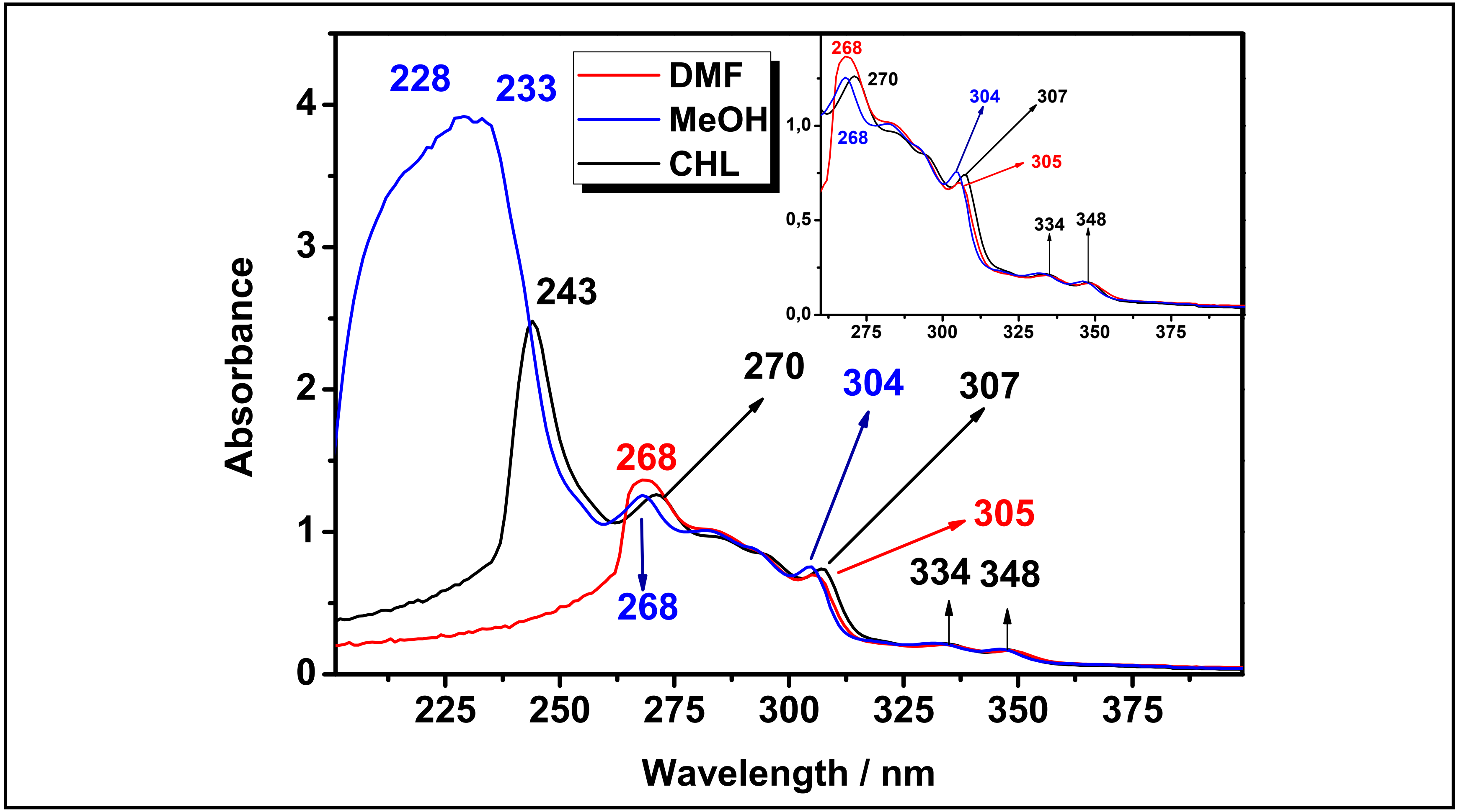


Figure 4.18: Absorption Spectra of PCbz in Different Kinds of Solvents with Varying Polarity at $1x10^{-2}$ M

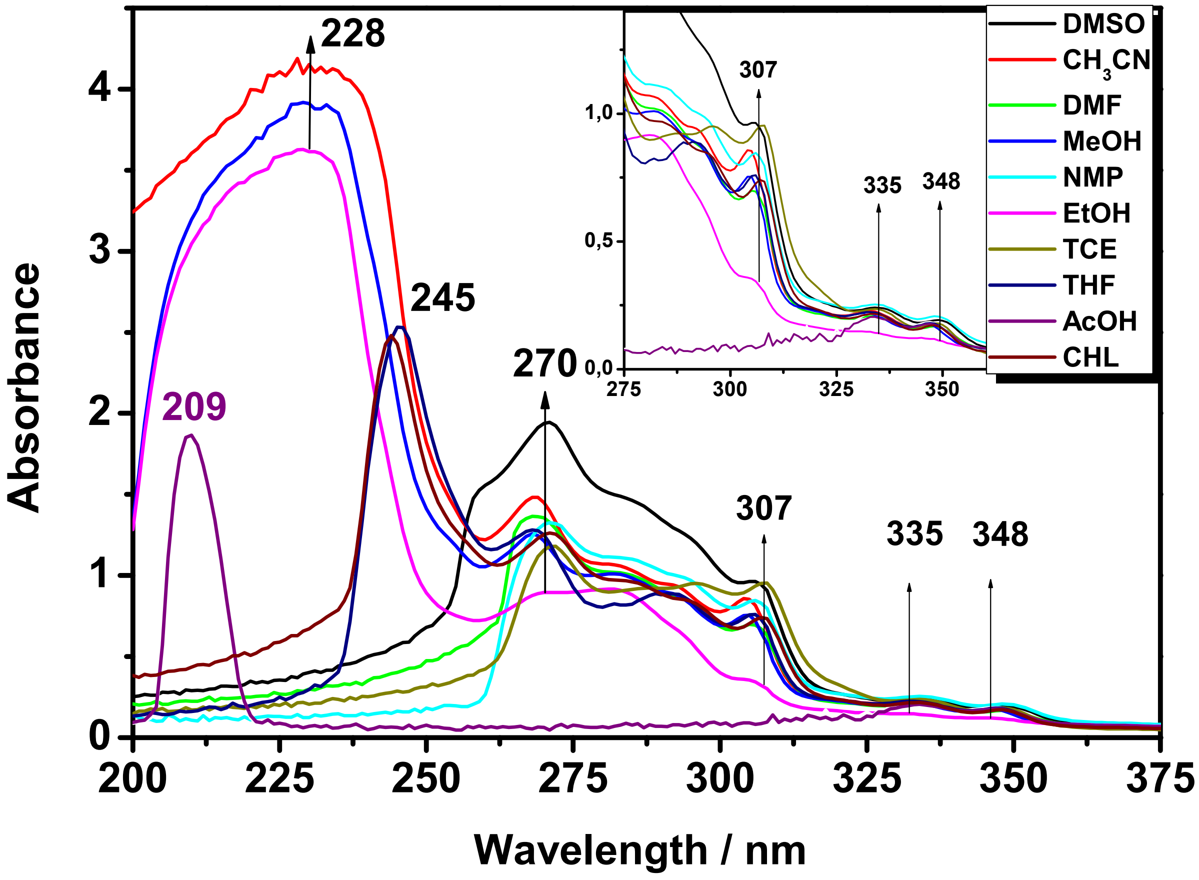


Figure 4.19: Absorption Spectra of PCbz in Different Solvents at 1x10^{-2} M

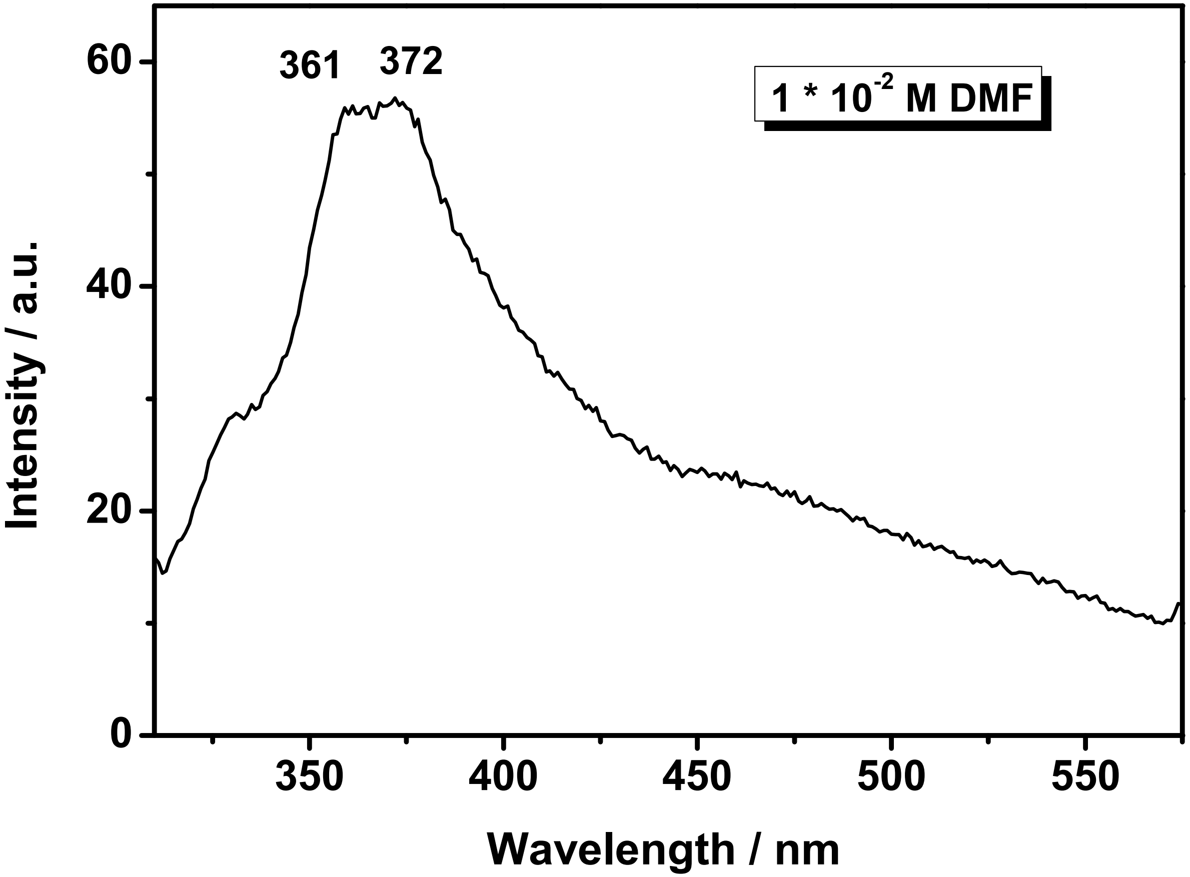


Figure 4.20: Emission (λ_{exc} = 295.5) Spectrum of PCbz in Dimethylformamide

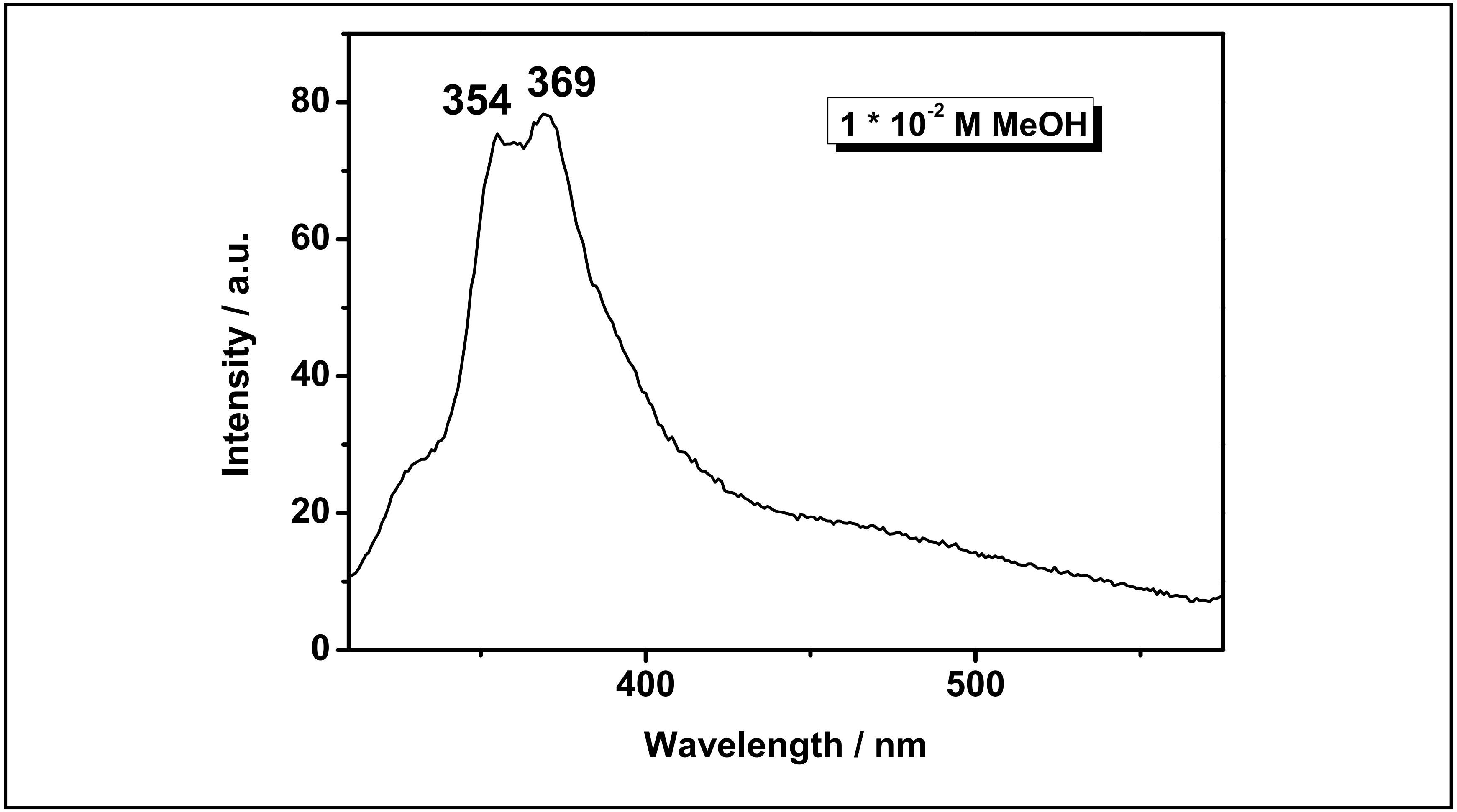


Figure 4.21: Emission ($\lambda_{exc\ =}$ 295.5) Spectrum of PCbz in Methanol

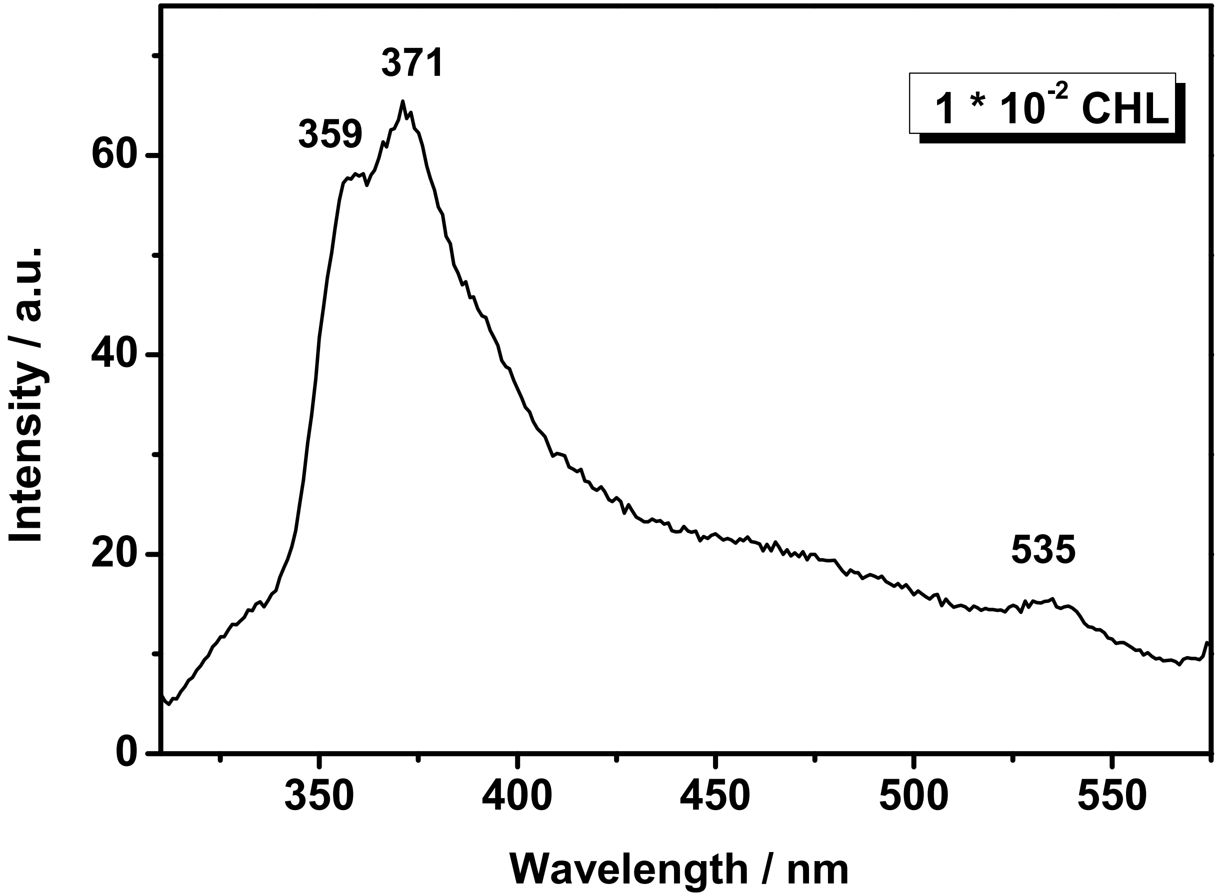


Figure 4.22: Emission ($\lambda_{exc\,=}$ 295.5) Spectrum of PCbz in Chloroform

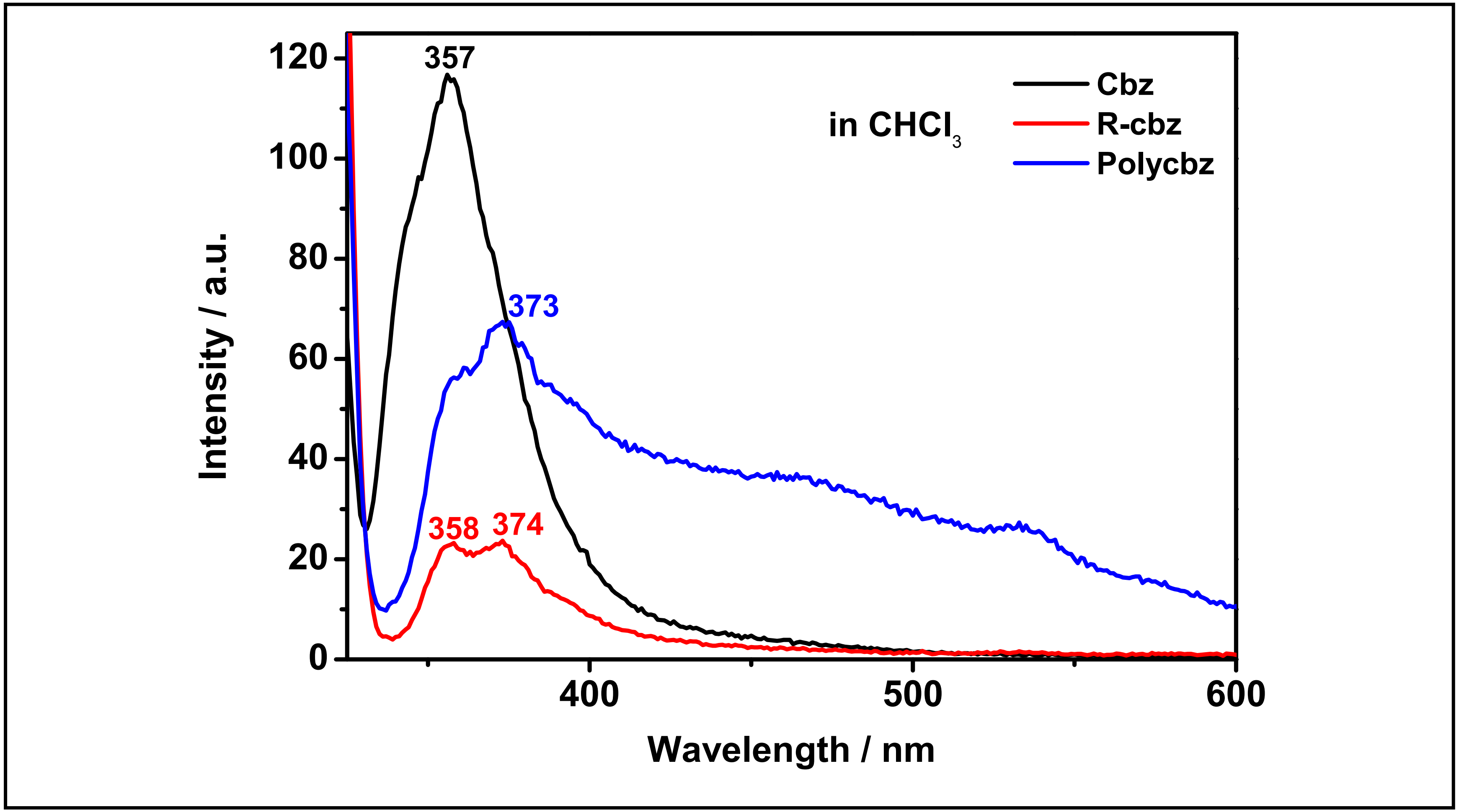


Figure 4.23: Comparison of Emission (λ_{exc} = 295.5) Spectra of Carbazole, Dodecylcarbazole and Polycarbazole in Chloroform

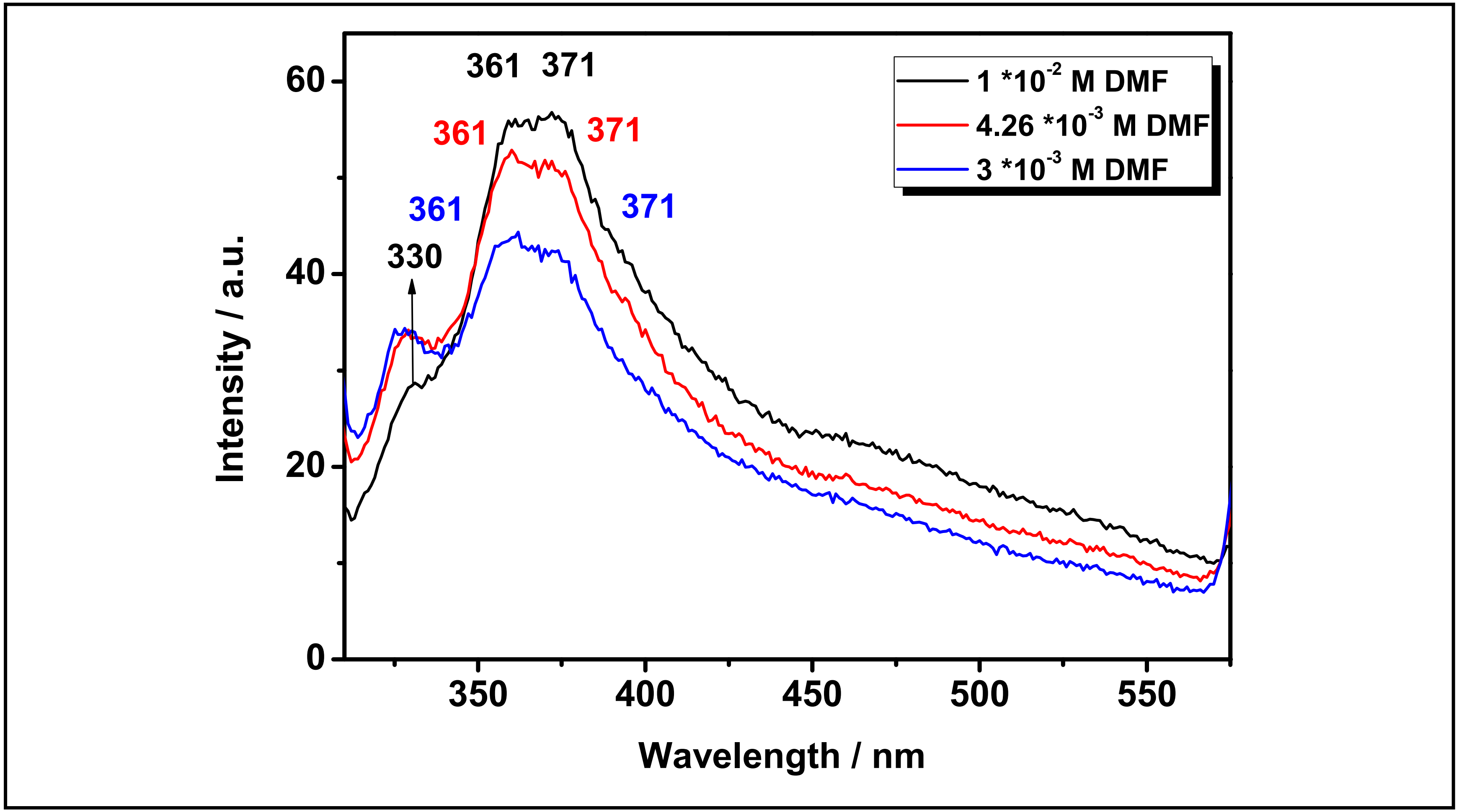


Figure 4.24: Variable-concentration Emission ($\lambda_{exc\,=}$ 295.5) Spectra of PCbz in DMF

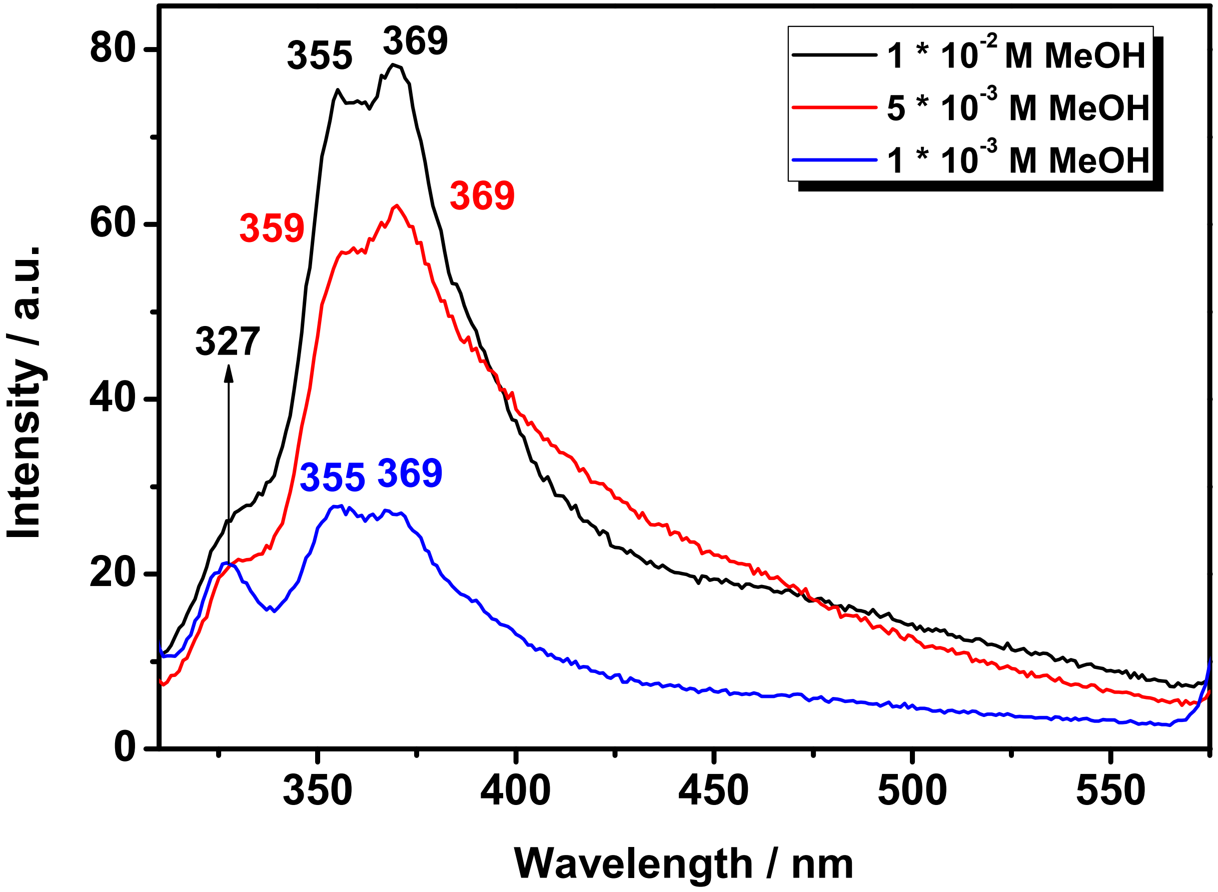


Figure 4.25: Variable-concentration Emission ($\lambda_{exc\,=}$ 295.5) Spectra of PCbz in Methanol

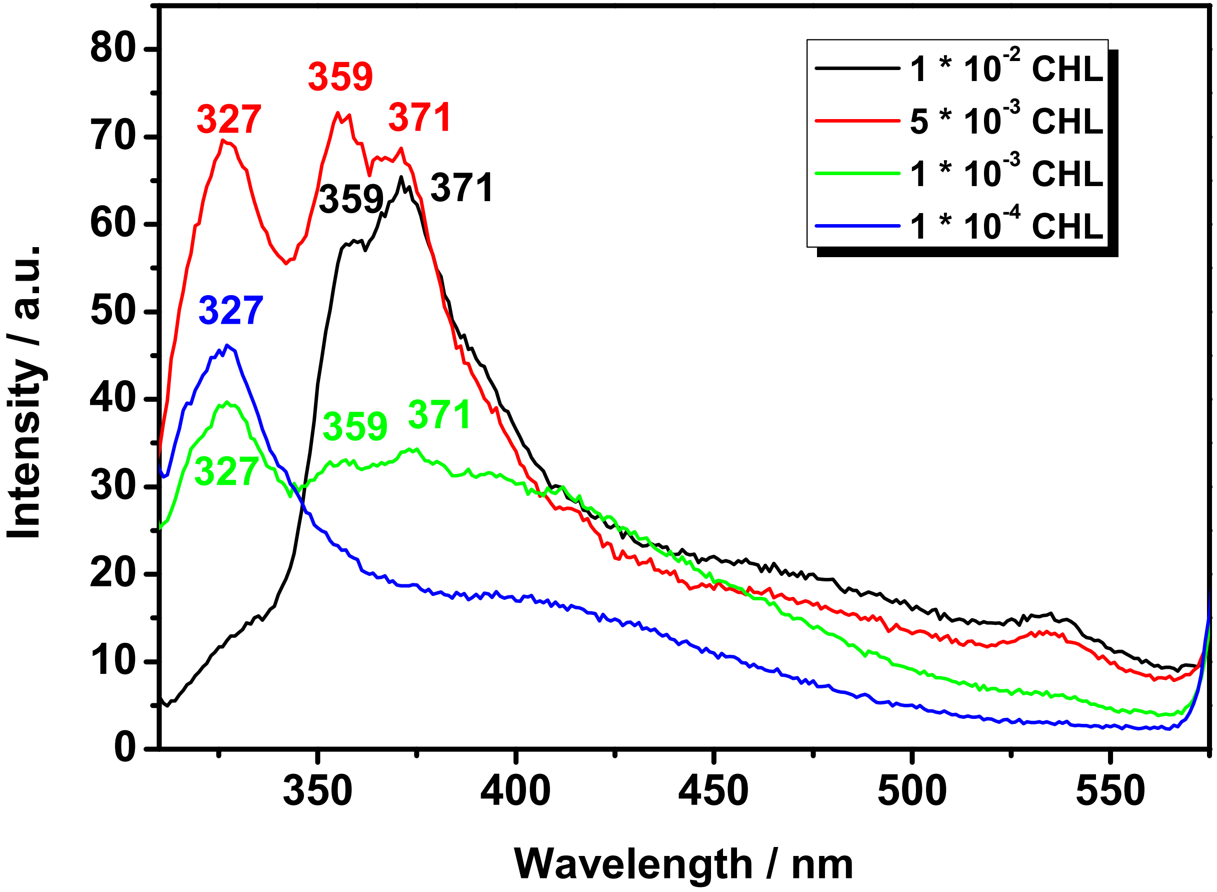


Figure 4.26: Variable-concentration Emission ($\lambda_{exc\,=}$ 295.5) Spectra of PCbz in Chloroform

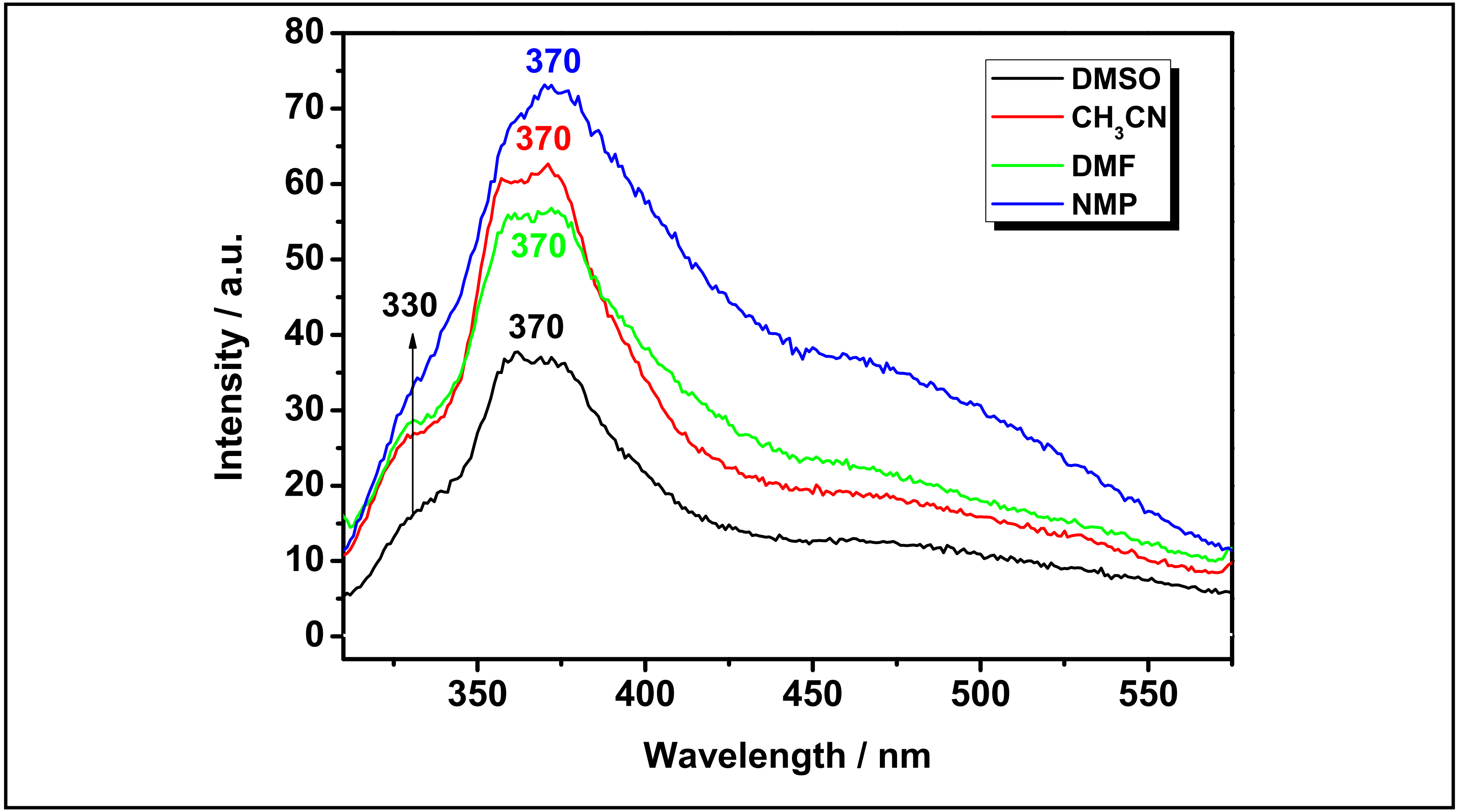


Figure 4.27: Emission ($\lambda_{exc\,=}$ 295.5) Spectrum of PCbz in Dipolar Aprotic Solvents at $1x10^{-2}$ M

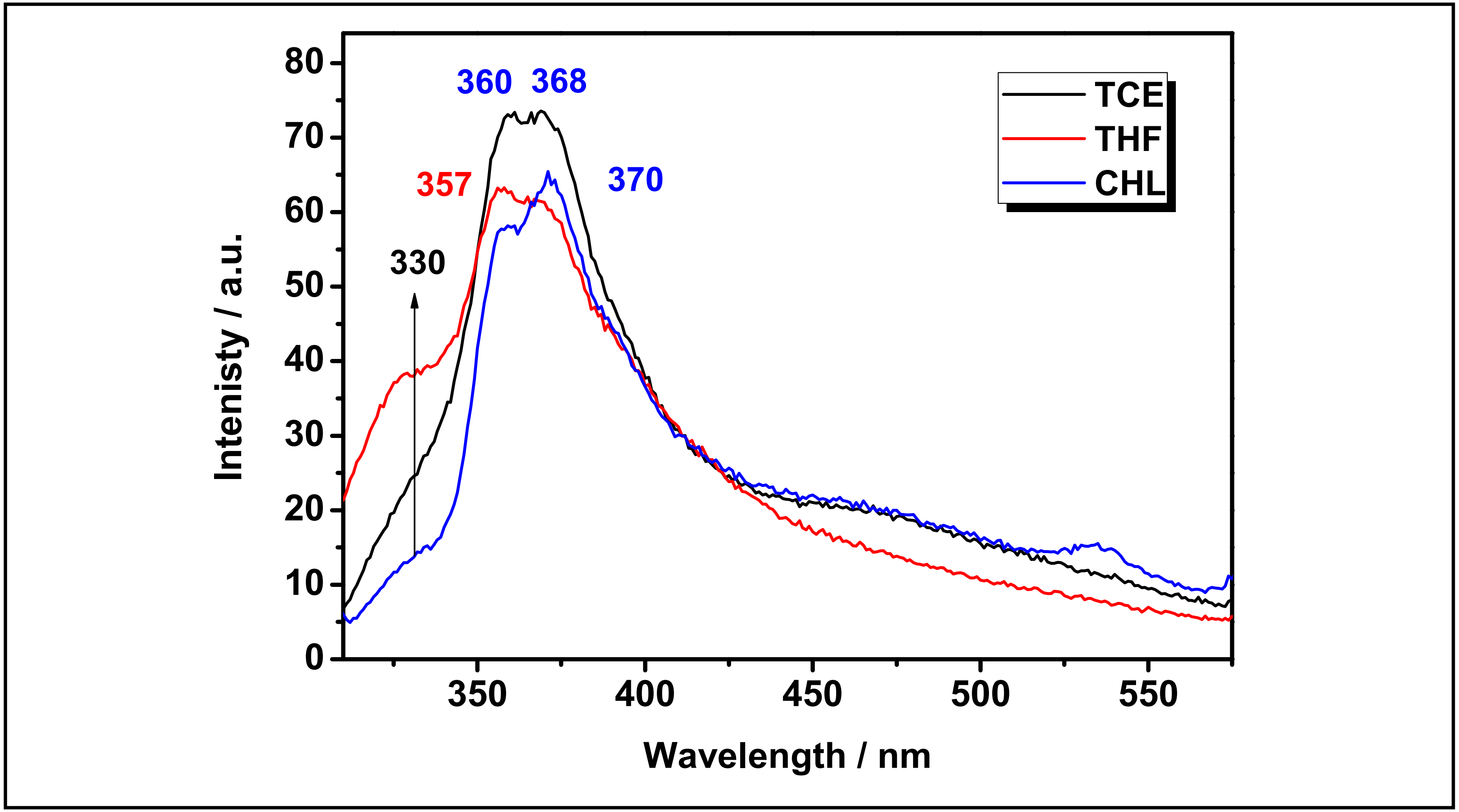


Figure 4.28: Emission ($\lambda_{exc} = 295.5$) Spectra of PCbz in Different Kinds of Solvents with Varying Polarity at $1x10^{-2}$ M

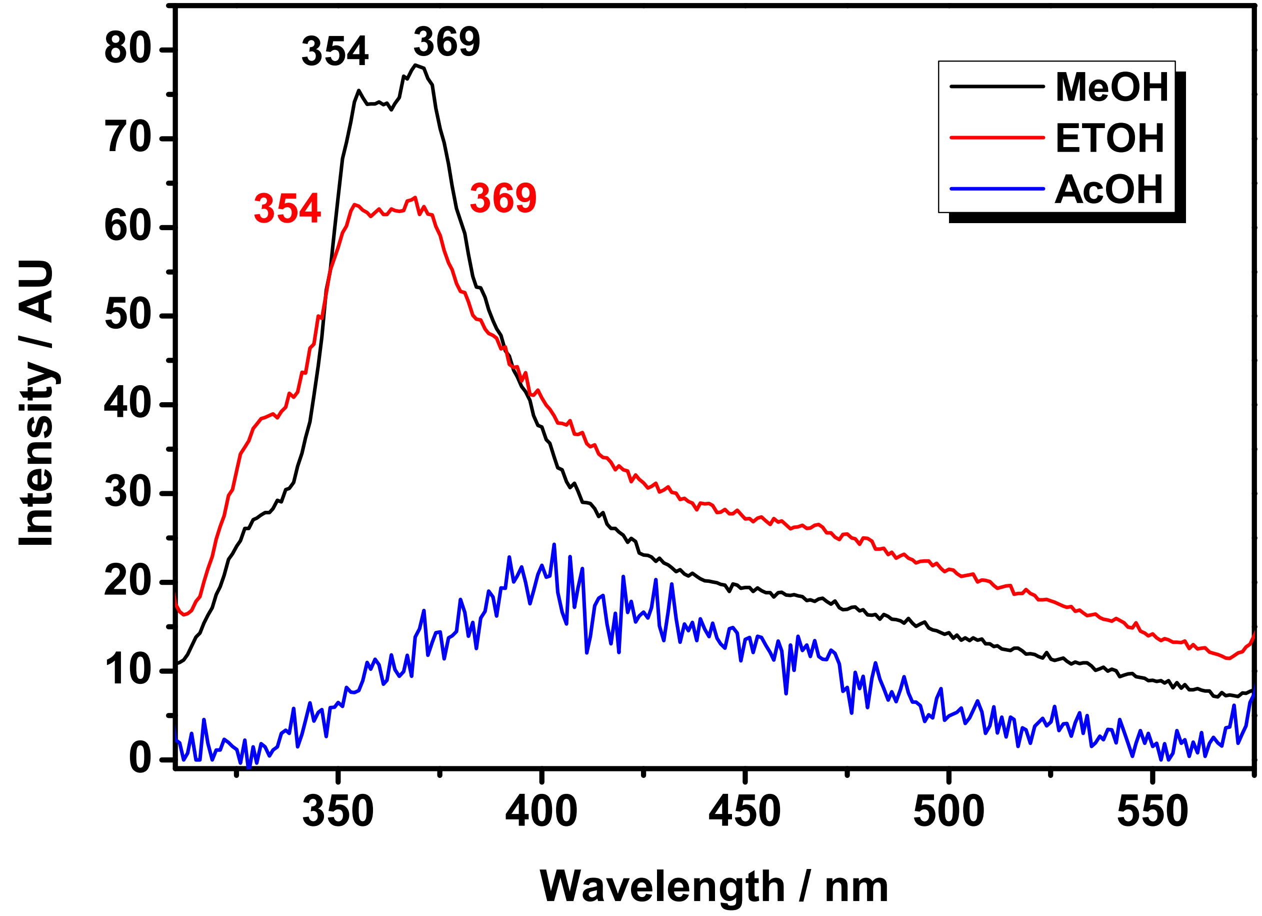


Figure 4.29: Emission ($\lambda_{exc} = 295.5$) Spectra of PCbz in Polar Protic Solvents at $1x10^{-2}$ M

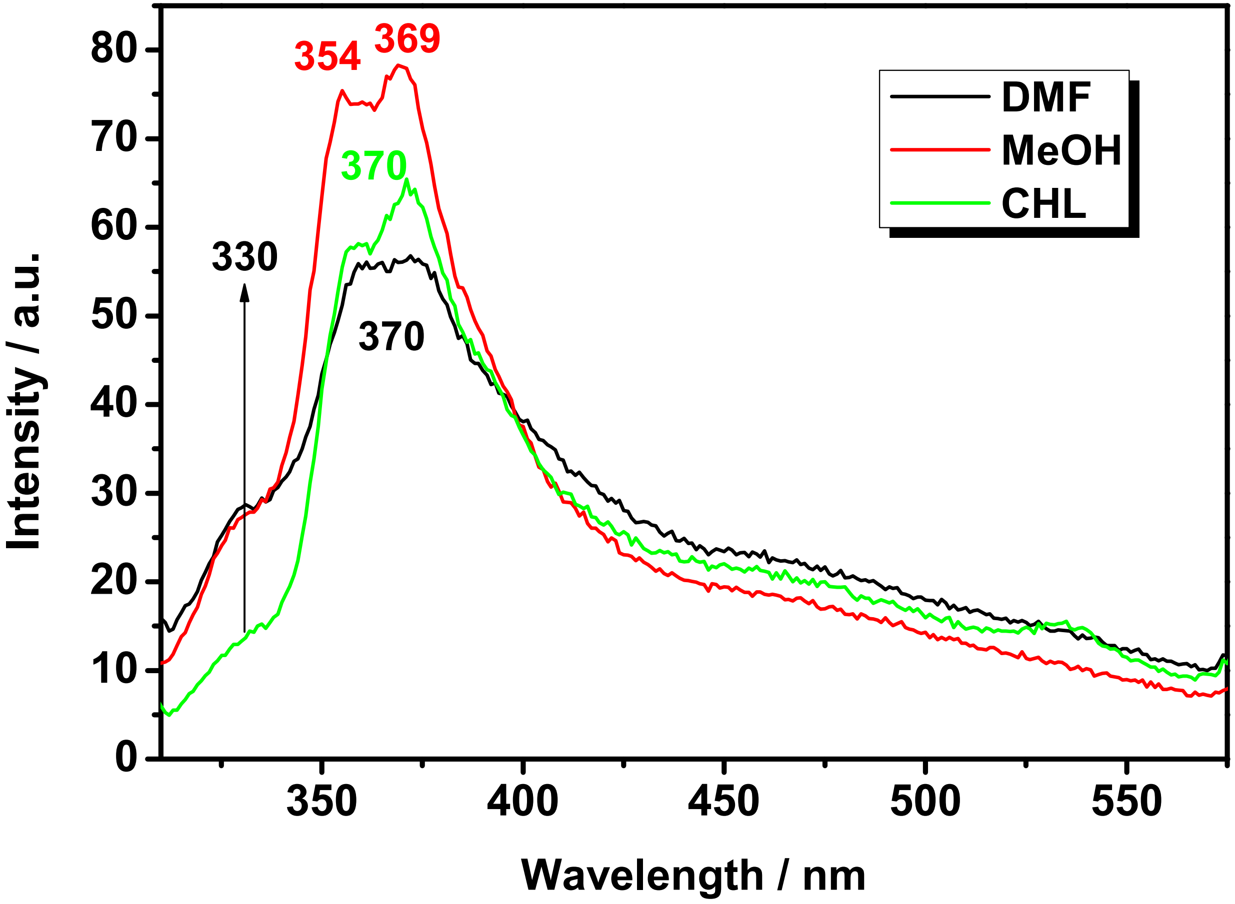


Figure 4.30: Emission ($\lambda_{exc} = 295.5$) Spectra of PCbz in Different Types of Solvents with Varying Polarity at $1x10^{-2}$ M

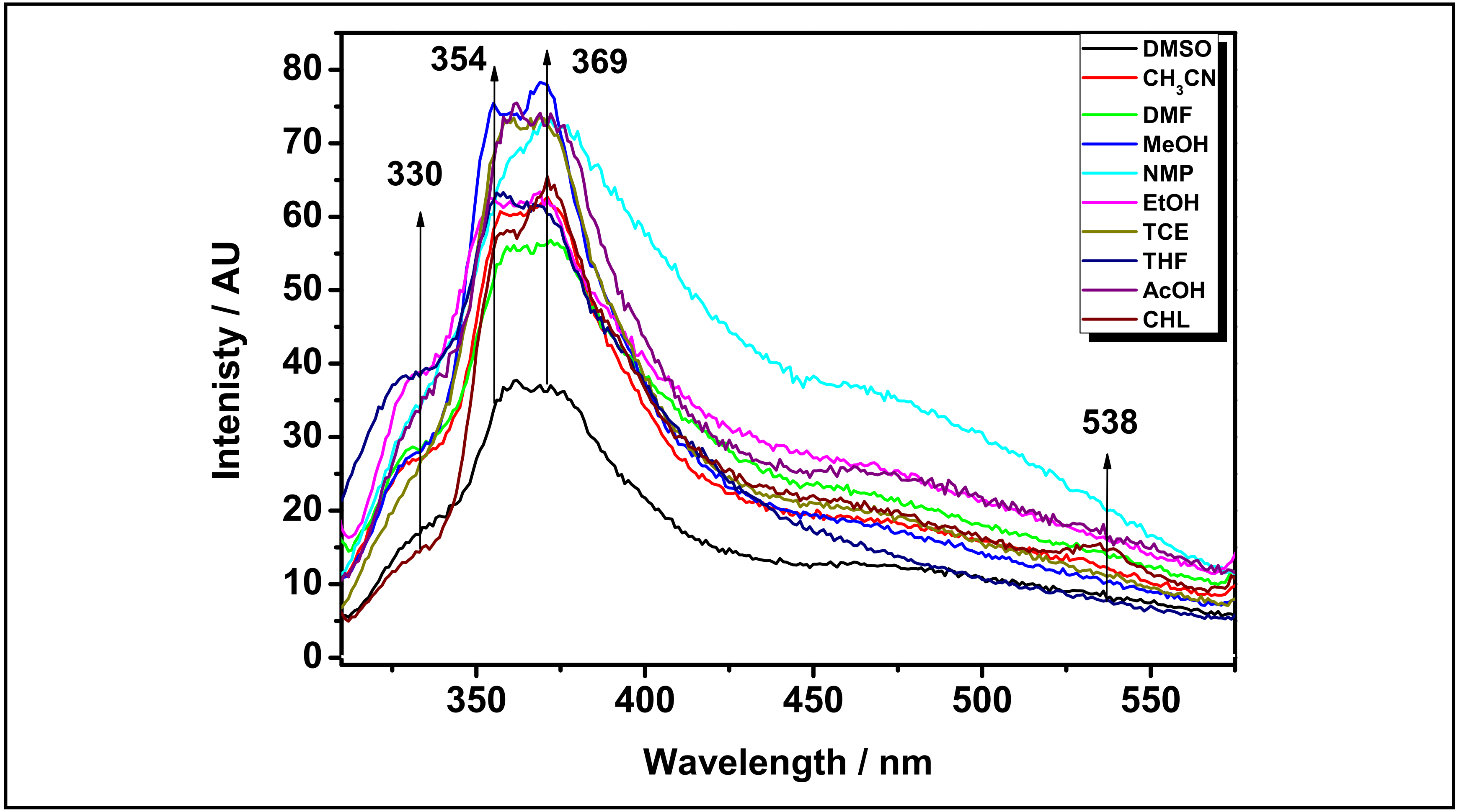


Figure 4.31: Emission ($\lambda_{exc\,=}$ 295.5) Spectra of PCbz in Different Solvents at 1x10^{-2} M

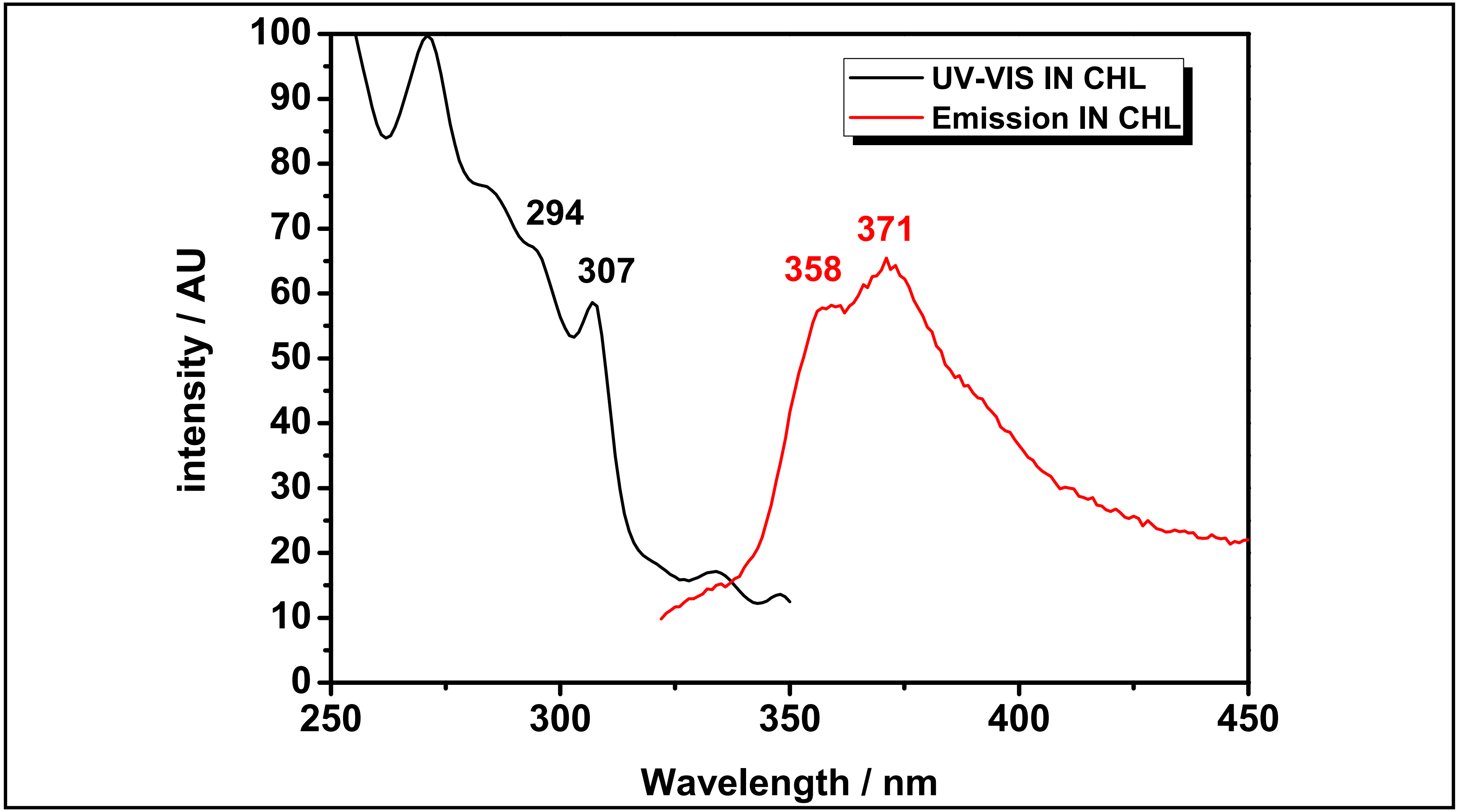


Figure 4.32: Mirror Image Representation of Absorption and Emission ($\lambda_{exc} = 295.5$) Spectra of Polymer in Chloroform at $1x10^{-2}$ M

Chapter 5

RESULTS AND DISCUSSION

5.1 Synthesis of Polycarbazole and Structural Characterization

The poly(*N*-dodecylcarbazole)-2,7-diyl was suceessfully synthesized in four steps. The first two steps include the synthesis of 2,7-dibromo substitution and ring closing mechanism to yield 2,7-dibromo-substituted carbazole. As 2,7-position substitution mechanism is not straight, this was carried out in two steps by using the starting material, dibromobiphenyl. Cadogan ring closing mechanism is one of the useful steps to prepare such materials although the yield is low.

In the third step, the monomer was synthesized with the help of strong base and consequent nucleophilic substitution to the alkyl bromide chain yielded N-alkyl-2,7-dibromo carbazole material.

In the final step, the monomer was polymerized in presence of Nickel(0) by Yamamoto polymerization mechanism. The resultant poly(*N*-dodecylcarbazole)-2,7-diyl is characterized first by thin layer chromatography (TLC) and FTIR techniques and confirmed the formation.

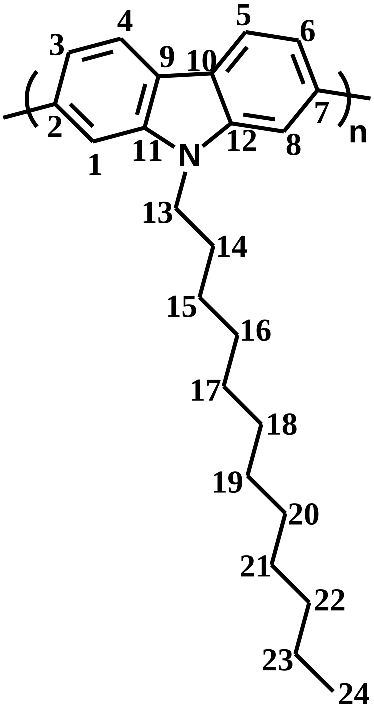
The TLC has shown only two spots under 365 nm where the high polar one is the probable dimer/trimer/oligomer of the monomer (confirmed by FTIR) and the detailed characterization of this compound was subjected to further research.

The polymer spot was isolated and characterized in detail.

Figures 4.3 and 4.4 show the FTIR spectra of monomer and polymer, respectively. The monomer has shown aliphatic C–H stretch at 2926 and 2853 cm^{-1} and strong aromatic C=C stretch at 1600 cm^{-1} which are completely proving the structure of N-alkyl 2,7-dibromo carbazole. The IR spectrum of the polymer is similar to that of monomer’s IR spectrum but broad and stronger stretches were noticed.

The polymer was oily compound and has shown complete solubility in most of the traditional organic solvents at room temperature. The high solubility of the polymer is an added advantage for processing of the material in commercial applications.

5.2 NMR Spectra Analysis



^{1}H NMR (400 MHz, CDCl$_3$, ppm): 7.46 (s, 6Ar-H (C – 1,3-6,8)), 2.76 (s, CH$_2$, H-C(13), 2.44 – 2.31 (br d, 10CH$_2$, H-C(14-23), 1.80 (s, CH$_3$, H-C(24)) (Figures 4.5 and 4.6).

^{13}C NMR (100 MHz, CDCl$_3$, ppm): 161.89, 128 (C–2,7,(9–12)), 35.74, 30.59 (C–(13–23)), 27.44 (C – 24) (Figure 4.7).

5.3 Optical Properties

a) Absorption Spectra

The absorption spectra of polycarbazole in three different kinds of solvents are shown in Figures 4.8 – 4.10 (at 1×10^{-2} M per monomer unit). All the three absorption spectra show a broad absorption with small shoulders included in the spectrum at around 268, 283, 306, 344, and 348 nm, respectively. The peak maxima are similar to that of carbazole and monomeric carbazole (2,7-dibromo-N-dodecyl carbazole) (Figure 4.11). Figure 4.11 shows the higher intense and high energy peak (responsible for forbidden transitions, $S_0 \rightarrow S_2$ transitions) dominating the $\pi\rightarrow\pi^*$ electronic transitions absorption at around 303 nm for all the three types of carbazole derivatives. There are two major differences noticed in the comparison of absorption spectra – (i) the absorption peak maximum at 307 nm is very low in absorption intensity comparing to the intensities of same $\pi\rightarrow\pi^*$ electronic transition absorptions of carbazole and monomer, dodecylcarbazole; (ii) the absorption is broader for polymer when compared to the absorptions of the other two carbazole derivatives (especially, at 283 nm and 273 nm, the absorption of dodecylcarazole and carbazole were zero, respectively).

The interesting broader absorption of polymer is attributed to the increase in conjugation of rich aromatic units present in the polymer chains and therefore leading to stronger $\pi\rightarrow\pi^*$ electronic absorptions.

Figures 4.12 – 4.14 show variable-concentration absorption spectra of the polymer in three kinds of solvents. Obviously, in dipolar aprotic, protic and nonpolar solvents, the absorption is increased corresponding to the increase in concentration of the polymer solution (the concentrations are measured per monomer unit).

Figure 4.15 shows the comparison of absorption spectra of polymer in various dipolar aprotic solvents. When the polarity of the solvent increased gradually, the absorption of forbidden transitions gradually increased. The absorption in acetonitrile is quite different from other absorption spectra with strong absorption at around 230 nm. This is due to the structure of CH_3CN which contains cyanide functional group and the consequent intermolecular interactions.

Figure 4.16 shows comparison of absorption spectra of polymer in various nonpolar solvents. In TCE (with dielectric constant: 8.42), the absorption spectrum is different from the other absorption spectra in THF and $CHCl_3$ (with dielectric constants: 7.58 and 4.81, respectively), where the high energy peak responsible for $S_0 \rightarrow S_2$ transition at around 243 nm is completely vanished. This can be due to the high polar ground state in TCE solution of the polymer. It can be noted that the peak at 307 nm is also increased in intensity. The other two absorption spectra in chloroform and THF show two high intensity forbidden absorption transitions at 243, 268 nm and two broad $\pi \rightarrow \pi^*$ electronic absorption shoulder bands at 296 and 307 nm, respectively.

Similar results were noticed in different absorption spectra recorded in various protic solvents of varying polarities. In methanol and ethanol the polymer shows very broad high intense forbidden transitions at about 228 nm with a weak 268 nm peak followed by $\pi \rightarrow \pi^*$ absorption bands at about 282 and 304 nm. The absorption in acetic acid is very weak comparing to the absorption spectra of other polar solvents (Figure 4.17).

Figures 4.18 and 4.19 show comparison of polymer absorption spectra in different kinds of solvents with varying polarity. Clearly, polar protic solvent methanol induces more intense high energy bands and in nonpolar solvent chloroform, the same trend was noticed. In DMF, the polymer absorption is more intense at 268 nm but the effect of forbidden transitions is greately reduced comparing other two absorption spectra. These details are also evident in the comparison of all absorption spectra presented in Figure 4.19.

Table 4.1 lists the maximum absorption wavelengths, molar absorptivities, FWHMs, and natural radiative lifetimes data of polycarbazole per mass of one monomer unit in three different kinds of solvents of varying polarity. Comparatively, in three solvents, the molar absorptivities are closer to each other. Due to the FWHMs data, pcbz in chloroform has highest natural radiative lifetime.

Tables 4.2 – 4.4 list the natural/theoretical fluorescence rate constants (Table 4.2), oscillator strengths (Table 4.3), and singlet energies (Table 4.4) data in three different kinds of solvents of varying polarity.

b) Emission Spectra

The emission spectra of polymer in three different kinds of solvents are shown in Figures 4.20 – 4.22 (at 1×10^{-2} M per monomer unit at λ_{exc} = 295.5 nm). All the three emission spectra show a broad excimer emission at 365 nm around with weak shoulders included in the spectrum at around 485 nm, respectively. The excimer peak is similar to that of dodecylcarbazole with much broader excimer emission (Figure 4.23). Figure 4.23 shows that the excimer emissions of both monomer and polymer are red shifted comparing to parent carbazole unit with a small separation in the excimer peak maxima. The polymer’s excimer emission is much broader and is attributed to the strong π–π interactions of conjugated aromatic units.

The interesting broader excimer emission of polymer is attributed to the increase in conjugation of rich aromatic units present in the polymer chains and therefore leading to stronger π–π interactions.

Figures 4.24 – 4.26 show variable-concentration emission spectra of the polymer in three kinds of solvents. Obviously, in dipolar aprotic, protic and nonpolar solvents, the excimer emission at about 365 nm is decreased upon decreasing the concentration, contrarily; the monomer emission at around 330 nm is increased gradually. This is more evident for the concentration of 10^{-3} M in methanol and chloroform and the concentrations below this.

Figure 4.27 shows the comparison of emission spectra of polymer in various dipolar aprotic solvents. When the polarity of the solvent increased gradually, the excimer emission is gradually decreased. This is due to the polar nature of the solvent and its interactions with the polymer molecules.

Figures 4.28 and 4.29 show the comparison of emission spectra of polymer in various nonpolar and protic solvents. Contrary to the trend observed in dipolar aprotic solvents, when the polarity of the solvent is increased gradually, the excimer emission is gradually increased in nonpolar and protic solvents.

Figure 4.30 shows comparison of absorption spectra in three different kinds of solvents with varying polarity. In nonpolar, dipolar aprotic and polar protic solvents the excimer emission is observed and is similar in three solvents. Similarly, the excimer emissions in all of the common organic solvents for the polymer solutions are presented in Figure 4.31.

Although the absorption and emission spectra comparison of polymer in chloroform solution does not represent mirror image spectra, they show the clear differences in molecular interactions of excited and ground states (Figure 4.32). The absorption is weak at around 307 nm but the polycarbazole moiety emits strong excimer light emission.

Chapter 6

CONCLUSION

The poly(N-dodecylcarbazole)-2,7-diyl is synthesized successfully in four steps. In the first and second steps, commercial dibromobiphenyl was converted to 2,7-dibromo-substituted-carbazole via nitration and Cadogan ring closing mechanisms, respectively. In the third step, the monomer was synthesized by reacting with 1-bromododecane via nucleophilic substitution reaction. Finally, the polymer is synthesized in the fourth step via Yamamoto polymerization.

The structure of the polymer was confirmed by FTIR and NMR spectra. The FTIR of polycbz clearly evidenced the differences in absorptions corresponding to monomer. Interestingly, the thin layer chromatography shows that there was a high polar dimer/trimer/oligomeric molecule produced along with the polymer and was separated successfully.

The optical properties of the polymer are quite interesting as the polymer shows broader absorption in all of the most common organic solvents used when compared to the absorptions of carbazole and dodecyl carbazole derivatives.

The emission spectra reveal the strong excimer light emission capability of the polymer in all of the most commonly used organic solvents.

Interestingly, in dipolar aprotic solvents, the excimer emission is decreased upon increasing the polarity of the solvent; contrarily, the excimer emission is increased with the gradual increase in polarity of nonpolar and protic solvents.

The concentration dependence on excimer emission was also investigated and the results in nonpolar, dipolar aprotic and protic solvents revealed that the excimer emission is gradually decreased upon decreasing the concentration of polymer solution. In contrary, the monomer emission is increased.

The concentration dependent and solvent dependent excimer emission is applicable where the tuning of light emission is crucial. Conclusively, the polymer has delivered substantial excimer light emission which is very useful concerning the commercial optoelectronic devices based on organic materials.

Combining the tunable optical properties with electron donating ability, poly(2,7-carbzoles) make excellent materials for photovoltaics and organic material devices.

REFERENCES

Brabec C. and et al. (2010). Polymer–Fullerene Bulk-Heterojunction Solar Cells. Adv. Mater. 22, 3839–3856.

Boudreault P. and et al. (2009). Polycarbazoles for plastic electronics. Polym. Chem. 1, 127–136.

Dierschke F. and et al. (2003). Efficient Synthesis of 2,7-Dibromocarbazoles as Components for Electroactive Materials. Synthesis. 16, 2470–2472.

Dorofeev I. and et al. (2011). New Approach to Poly(2,7-carbazoles). Russian Journal of General Cemistry. 12, 18

Dijken A. and et al. (2004). Carbazole Compounds as Host Materials for Triplet Emitters in Organic Light-Emitting Diodes: Polymer Hosts for High-Efficiency Light-Emitting Diodes. J. Am. Chem. Soc. 126, 7718-7727.

Li J. and et al. (2006). Polyphenylene-Based Materials for Organic Photovoltaics. Chem. Rev. 110, 6817–6855.

Li J. and et al. (2006). Poly(2,7-carbazole(and perylene tetracarboxydiimide: a promising donor/acceptor pai for polymer solar cells. J. Mater. Chem., 16,96-100.

Morin J. and et al. (2005). Polycarbazoles: 25 Years of Progress. Macromol. Rapid Commun. 26, 761–778.

Pokhrel B. and et al. (2012). Study of Optical and Photovoltaic Properties of N-Alkyl Substituted Polycarbazole Derivative and Its Copolymer with Thiophene. Materials and Manufacturing Processes, 27: 43–48.

Spanggaard H. and et al. (2004). A brief history of the development of organic and polymeric photovoltaics. Solar Energy Materials & Solar Cells. 83, 125–146.

Tirapattur S. and et al. (2003). Steady-state and time-resolved studies of 2,7-carbazole-based conjugated polymers in solution and as thin films: determination of their solid state fluorescence quantum efficiencies. Chemical Physics Letters. 370, 799–804.