İSTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF POLYSTYRENE – ZINC PHTHALOCYANINE COMPOSITES

M. Sc. THESIS
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Polymer Science and Technology

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

POLİSTİREN – ÇİNKO FTALOSİYANİN KOMPOZİTLERİNİN SENTEZİ VE KARAKTERİZASYONU

YÜKSEK LİSANS TEZİ
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HAZİRAN 2016

Yunus Alp SÜTCÜLER, a M.Sc student of İTU Graduate School of Science Engineering and Technology student ID 515141026 successfully defended the thesis entitled “SYNTHESIS AND CHARACTERIZATION OF POLYSTYRENE – ZINC PHTHALOCYANINE COMPOSITES”, which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my family,

FOREWORD

First, I would like to thank my supervisor, Professor Ahmet Gül, for his encouragement, guidance, and patience.

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June 2016 Yunus Alp SÜTCÜLER

Chemist

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ABBREVIATIONS

Pc : Phthalocyanine

PS : Polystyrene

PS-Br : Bromo-terminated polystyrene

PS-N_3 : Azido-polystyrene

ZnPc : Zinc phthalocyanine

PS-ZnPc : Polystyrene-unsymmetrical phthalocyanine compound

MPc : Metallophthalocyanine

H_2Pc : Metal-free phthalocyanine

Li_2Pc : Lithium phthalocyanine

FT-IR : Fourier transform infrared

^{1}H NMR : Proton nuclear magnetic resonance

PDT : Photo dynamic therapy

UV-Vis : Ultraviolet-visible

LIST OF SYMBOLS

A **:** Alpha

β **:** Beta

k **:** Rate constant

ppm **:** Parts per million

°C **:** Celsius

M_n **:** The number average molecular weight

M_w **:** The weight average molecular weight

M_w/M_n **:** The molecular weight distribution

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SYNTHESIS AND CHARACTERIZATION OF POLYSTYRENE – ZINC PHTHALOCYANINE COMPOSITES

SUMMARY

Composite is a material consisting of two or more different phases and having bulk characteristics importantly different from those of any of the constituents. Matrix phase is the primary phase having a continuous character. Matrix is usually more ductile and less hard phase. It holds the dispersed phase and shares a load with it. Dispersed (reinforcing) phase is embedded in the matrix in a discontinuous form. This secondary phase is called the dispersed phase. Dispersed phase is generally stronger than the matrix, consequently, it is sometimes called reinforcing phase. Matrix materials are generally polymers, ceramics or metals. The polymer matrices also called resins are by far the most common due to the versatility of their properties such as light weight, easy processing and corrosion resistance. Composite materials are designed and prepared for particular applications with desired properties such as light weight and high performance.

Polystyrene is made from petroleum, a non-sustainable, non-renewable, heavily polluting, and fast-disapperaing commodity. CD covers and plastic drinking cups are made out of the polymer polystyrene. This polymer is known to be a clear brittle plastic that is synthesized by a free radical polymerization. Polystyrene is not biodegredable. It takes several decades to hundreds of years for polystyrene to deteriorate in the environment or in a landfill. Polystyrene takes up more spaces in landfills than paper, and will eventually re-enter the environment when water or mechanical forces breach landfills. Polystyrene contains the toxic substances styrene and benzene, suspected carcinogens and neurotoxins that are hazardous to humans.

Phthalocyanines are planar macrocycle molecules related to porphyrins constituted by four isoindole units presenting an 18 π electron aromatic cloud delocalized over an arrangement of alternated carbon and nitrogen atoms. Phthalocyanines have high thermal and chemical stability. Phthalocyanines are conjugated polymers which are gaining much interest due to their special electronic and optical properties that stem from phthalocyanine macrocycle. Conjugation of the macrocycles with polymer chains enhances their processability, provides a means to control the molecular arrangement of the phthalocyanine rings, improves their solubility in common organic solvents. The main problems in the phthalocyanine chemistry are their insolubility in most of the solvents and aggregation tendency in solutions because of the molecular interactions between the macrocyclic rings. Elemental analysis used in the characterization of organic compounds, and FTIR and UV-Vis are also used in the characterization of phthalocyanine. In particular, the position of the Q-band in the visible range is influenced by the substituents and the central metal atom. Therefore, these techniques play an important role in the characterization of phthalocyanines. NMR is a useful technique for soluble phthalocyanine derivatives. However, due to

the orientations of phthalocyanine compounds to strong aggregation in solution and causing enlargement prevent a good spectrum from NMR.

Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) click reaction, which was initially postulated as a powerful tool for organic synthesis, has been extensively applied as a successful polymer functionalization technique. The cycloaddition first described by Rolf Huisgen involves an alkyne and an azide undergoing a cycloaddition leading to a triazole cycle. The reaction met the click chemistry concept criteria when its conditions were considerably softened by the use of copper catalysts: a reliable, easy, selective, and high-yielding reaction. In contrast to the uncatalyzed conditions, the use of copper(I) salts ensures of the exclusive formation of the 1,2,3-triazole, with the regioselective formation of the 1,4-regioisomer. The required conditions are indeed exceptionally soft; no high temperature or extreme pH conditions are necessary. The possible solvent range is very wide, even including water. The advantages of non-conventional conditions such as microwave irradiation were recently reported.

This study was undertaken to prepare polystyrene (PS) and asymmetric zinc phthalocyanine, azidation of polystyrene, performing click reaction between azidated polystyrene and asymmetric zinc phthalocyanine. Polystyrene was synthesized by using ATRP method and azidation was done in a step by using sodium nitrate. Azidated polystyrene and asymmetric zinc phthalocyanine were bonded with each other via Huisgen 1,3-dipolar cycloaddition.

Prepared polystyrene- asymmetric zinc phthalocyanine composite was characterized by ^{1}H-NMR, FTIR, and UV-Vis spectroscopy. The results were taken from FTIR spectroscopy showing that preparing of phthalocyanine and polystyrene, azidation of polystyrene and Huisgen 1,3-dipolar cycloaddition were performed successfully. Also, UV-Vis spectrum demonstrated the purity of produced phthalocyanine and polystyrene. ^{1}H-NMR spectrum shows that the forming of triazole structure and azido-terminated polystyrene- unsymmetrical zinc phthalocyanine composite.

POLİSTİREN – ÇİNKO FTALOSİYANİN KOMPOZİTLERİNİN SENTEZİ VE KARAKTERİZASYONU

ÖZET

Kompozit malzemeler iki veya daha fazla bileşenden oluşan ve bileşenlerinden farklı özelliklere sahip olan yapılardır. Matris fazı genellikle daha çok esneyebilen ve daha az sertliğe sahip olan sürekli bileşendir. Matris fazı takviye fazını tutar ve yükü onunla paylaşır. Takviye fazı matris fazına tutunur ve matris fazından daha güçlüdür. Takviye fazı kompozit özelliklerini geliştirmek için kullanıldığından bazen güçlendirici faz olarak nitelendirilir. Matris fazı genellikle polimer, seramik ve metallerden oluşur. Polimer matrisleri genellikle reçine olarak adlandırılır ve hafiflik, kolay işlenilebilirlik, iyi korozyon dayanımı gibi çeşitli özelliklere sahiptir. Kompozit malzemeler özel uygulamalar için istenen özelliklerde tasarlanır ve bu özelliklere uygun bileşenler seçilerek hazırlanır.

Polistiren petrolden üretilir. Sürdürülebilirlik ve yenilenebilirlik açısından uygun olmayan bu ürün ayrıca çevre kirliliğine neden olmaktadır. CD koruyucu kaplar ve plastik bardaklar polistirenden üretilebilmektedir. Serbest radikal polimerizasyonu ile üretilebilen bu polimer kırılgan, sert bir yapıya sahiptir ve geri dönüşümü yoktur. Polistirenin doğada parçalanması onlarca, yüzlerce yıl sürer. Atık depolama alanlarındaki polistirenden üretilen malzemelerin miktarı, atık kağıt türevlerinin miktarından fazladır ve bu malzemeler zamanla su ve mekanik kuvvetlerin etkisiyle doğaya karışır. Polistiren türevleri stiren ve benzen gibi sağlığa zararlı, tehlikeli bileşenlere sahiptir, bundan dolayı kanser ve diğer sağlık sorunlarına neden olabilmektedir.

Ftalosiyaninler düzlemsel moleküllerdir ve 18 π elektronuna sahip olup isoindol yapılarından oluşurlar. Ftalosiyaninler yüksek termal ve kimyasal kararlılığa sahip, ana yapısı karbon ve azot elementlerinden oluşan makro yapılardır. Ftalosiyaninler çok özel elektronik ve optik özelliklere sahip olan konjuge makrohalkalardır. Polimer zinciriyle halkalar arasındaki konjugasyon, ftalosiyanin bileşiğinin işlenebilirliğini ve yapısal düzenlemeye olanak sağlayarak organik çözücülerde çözünebilirliğini sağlamıştır. Ftalosiyaninler hakkındaki en büyük problemler ise çözücülerin çoğunda çözünmemeleri ve halkalar arasındaki moleküler etkileşimden dolayı agregasyon eğilimi göstermeleridir. Ftalosiyaninlerin karakterizasyonu için FTIR, UV-Vis ve NMR spektroskopi teknikleri kullanılabilir. UV-Vis spektrumunda Q bandının görünür bölgedeki yeri merkez atoma ve sübstitüentlere doğrudan bağlıdır. Bu nedenle bu teknik ftalosiyaninlerin yapısal incelemesinde önemli rol oynamaktadır. Çözünebilen ftalosiyaninler için ise NMR spektroskopisi de uygun bir analiz tekniğidir. Ancak ftalosiyaninlerdeki yoğun etkileşimler ve agregasyon göz önünde bulundurulduğunda NMR spektrumunun yapı hakkında kesin bilgi vermesi mümkün olmayabilir.

Ftalosiyanin geniş metal-iyon kimyası, hem çok ilginç hem de çok fonksiyonludur. Örneğin, spesifik ftalosiyaninler yarı iletken özellik gösterebildikleri gibi, kimyasal transformasyonların değişiminde de katalitik etki sergilerler. Bunun yanında biyokimyasal sistemlerin aydınlatılması için yapılan model çalışmalarda da irdelenmektedirler. Ftalosiyaninlerin temel kullanım alanlarından birisi de endüstriyel renklendiricilerdir.

Bakır katalizli azid- alkin siklokatılma klik reaksiyonu organik sentezlerde ve polimerlerin işlevselleştirilmesinde çok kullanılan bir yöntemdir. Triazol oluşumu gözlenen azid-alkin katılması ilk olarak Rolf Huisgen tarafından keşfedilmiştir. Bu reaksiyon "klik reaksiyonu" olarak bilinmektedir ve bakır katalizli yapıldığında reaksiyon şartları güvenilir, yüksek verimli, seçici ve kolaydır. Bakır katalizli reaksiyon katalizör kullanmadan yapılan reaksiyona göre 1,2,3-triazol yapısının oluşması bakımından çok daha verimli ve güvenilirdir. Yüksek sıcaklık sıcaklığa ya da pH ayarlama işlemine ihtiyaç duyulmaz. Kullanılabilecek solvent çeşitleri oldukça fazladır. Geleneksel olmayan yöntemin kullanımının avantajlarından biri mikrodalga ışınları yayılmasıdır.

Yaptığımız çalışmada azidlenmiş polistiren ve uç alkil bileşiği içeren asimetrik çinko ftalosiyanin klik reaksiyonu ile birbirine tutturulmuş ve triazol halkasının oluştuğu gözlenmiştir. Polistiren ATRP metodu ile sentezlenmiş ve devamında sodyum nitrat ile reaksiyona sokularak azidleme işlemi yapılmıştır. Asimetrik ftalosiyanin ise merkez atomu çinko olarak sentezlenmiş ve kolon kromatografisi ile saflaştırılmıştır. Azidlenmiş polimer ile asimetrik çinko ftalosiyanin azid-alkin siklokatılma reaksiyonu ile birbirine bağlanmış ve polistiren-ftalosiyanin kompoziti elde edilmiştir.

Çalışmada kullanılan ligandlardan biri ve sentezlenen ftalosiyanin daha önce literatürde bulunmayan, ilk kez sentezlenen bileşiklerdir. Ftalosiyanin agregasyon ve düşük çözünürlük özellikleri göz önüne alınarak sentezlenmiştir. Agregasyonu mümkün olduğunca azaltabilecek ve çözünürlüğün artmasını sağlayacak büyük gruplu ligand tercih edilmiştir. Sentez için kullanılan yöntemde çok sayıda yan ürün oluştuğu için kromatografik yöntemlerle ayırma yapılmış ve deneysel çalışmaların ileri safhalarında kullanılabilecek ürün elde edilmiştir. Ayrıca hedef bileşiğin üretilmesinde klik reaksiyonundan faydalanılacağı için bu reaksiyonda yer alacak bileşikler bu reaksiyona uygun olarak modifiye edilmek zorundadır. Sentezlenen ftalosiyanin bileşiği alkin grubu içerdiği için reaksiyona uygundur. Kullanılan bromo polistiren ise azidlenerek klik reaksiyonu için uygun hale getirilmiştir. Son olarak azidlenmiş polistiren ve asimetrik çinko ftalosiyanin bileşiği klik reaksiyonu kullanılarak birbirine tutturulmuş ve hedeflenen ürün başarıyla sentezlenmiştir. Çeşitli cihazlarla yapılan işlemler incelenmiş ve işlem basamakları kontrol edilerek deneysel çalışmalar tamamlanmıştır.

Hazırlanan polistiren-asimetrik çinko ftalosiyanin kompoziti ^{1}H-NMR, FTIR ve UV-Vis spektroskopi yöntemleri kullanılarak analiz edilmiştir. FTIR spektrumu incelendiğinde sentezlenen ligandın, asimetrik çinko ftalosiyaninin, polistirenin ve azidlenme işleminin başarıyla yapıldığı görülmüştür. Ayrıca UV-Vis spektrumu incelendiğinde asimetrik çinko ftalosiyanin yapısının başarıyla saf olarak elde edildiği anlaşılmıştır. Tüm bunlara ek olarak ^{1}H-NMR spektrumları incelendiğinde polistirene ait azidleme reaksiyonunun başarıyla tamamlandığı ve son olarak klik reaksiyonu ile elde edilen polistiren-asimetrik çinko ftalosiyanin kompozitinin hedeflendiği gibi sentezlendiği görülmüştür.

Çalışma kapsamında yapılan spektral analizler, sentezin her aşamasında belirli piklerin varlığı veya yokluğunu içermesi sebebiyle reaksiyonların mükemmel bir şekilde takip edilmesini sağlamıştır.

Hazırlanan polistiren-asimetrik çinko ftalosiyanin kompoziti, yüksek teknoloji uzmanları tarafından ileri araştırmalar yapılmayı hak etmektedir. İlerleyen zamanda sentezlenen bileşik ile ilgili farklı çalışmalar yapılması tasarlanmaktadır.

1. INTRODUCTION

Polystyrene is made from petroleum, a non-sustainable, non-renewable, heavily polluting, and fast-disappearing commodity. The environmental impacts of polystyrene production in the categories of energy consumption, greenhouse gas effect, and total environmental effect ranks second highest, behind aluminum. Polystyrene is not biodegredable. It takes several decades to hundreds of years for polystyrene to deteriorate in the environment or in a landfill.

The word phthalocyanine is derived from the Greek terms for naphtha (rock oil) and cyanine (dark blue). Professor Linstead of the Imperial College of Science and Technology first used the term "phthalocyanine" in 1933, to describe a class of organic compounds [23]. Phthalocyanines (Pcs) were discovered accidentally. In 1907, Braun and Tcherniac, at the South Metropolitan Gas Company in London, upon examining the properties of a cyanobenzamide that they made from the reaction of phthalamide and acetic anhydride, found a trace amount of a blue substance after heating o-cyanobenzamide, cooling, dissolving in alcohol, and filtration. This substance undoubtedly was phthalocyanine.

The grace and efficiency of the structures and function detected in nature, has long directed scientists’ efforts both on understanding how nature functions through observation and apery and on creating novel, synthetic biomaterials combining the optimized by evolution properties of biomolecular structures with that of synthetic components. Taking into account the multifunctional and, most of the times, chemically fragile nature of biological entities, the major challenge into this direction is a chemical one: the need to proceed through bioorthogonal reactions and under the benign reaction conditions that would preserve and respect the multifunctionality and structure of biologically derived components [41].

This study was undertaken to prepare polystyrene (PS) and asymmetric zinc phthalocyanine, azidation of polystyrene, performing click reaction between azidated polystyrene and asymmetric zinc phthalocyanine. Polystyrene was synthesized by using ATRP method and azidation was done in a step by using sodium azide. Azidated polystyrene and asymmetric zinc phthalocyanine were bonded with each other via Huisgen 1,3-dipolar cycloaddition.

Prepared polystyrene- asymmetric zinc phthalocyanine composite was characterized by ^{1}H-NMR, FTIR, and UV-Vis spectroscopy. The results were taken from FTIR spectroscopy showing that preparing of phthalocyanine and polystyrene, azidation of polystyrene, and Huisgen 1,3-dipolar cycloaddition were performed successfully. Also, UV-Vis spectrum demonstrated purity of produced phthalocyanine and polystyrene.

2. THEORETICAL PART

2.1 Composites

“Composite” word was firstly used in a broad sense in 1950, and it has been used domestically from about the 1960s. Composite material is a kind of complex multi-component multi-phase system, and it is hard to be defined definitely [2]. Composite molecules are mixtures of materials differing in composition, where the individual constituents carry on their identities. These separate components act together to give the particular mechanical strength or stiffness to the composite. Composite is a material consisted of two or more different phases and having bulk characteristics importantly different from those of any of the constituents. Matrix phase is the primary phase having a continuous character. Matrix is usually more ductile and less hard phase. It holds the dispersed phase and shares a load with it. Dispersed (reinforcing) phase is embedded in the matrix in a discontinuous form. This secondary phase is called the dispersed phase. Dispersed phase is generally stronger than the matrix, consequently, it is sometimes called reinforcing phase [1].

2.1.1 Classification of composites

On the basis of matrix phase, composite materials can be divided into metal matrix composites (MMCs), and polymer matrix composites (PMCs), ceramic matrix composites (CMCs). The separations according to types of reinforcement are particulate composites (composed of particles), laminate composites (composed of laminates), fibrous composites (composed of fibers). Fibrous composites can be further subdivided on the basis of natural or synthetic fibers. Natural surrounding composites are mentioned to as natural composites. They can be subdivided on the basis of matrix, that is, nonbiodegradable matrix and biodegradable matrix. Bio-based composites made from nature or biofiber and biodegradable polymers are mentioned to as green composites. These can be promote subdivided as hybrid composites and textile composites. Hybrid composites comprise of a union of two or more types of fibers (Figure 2.1) [1].

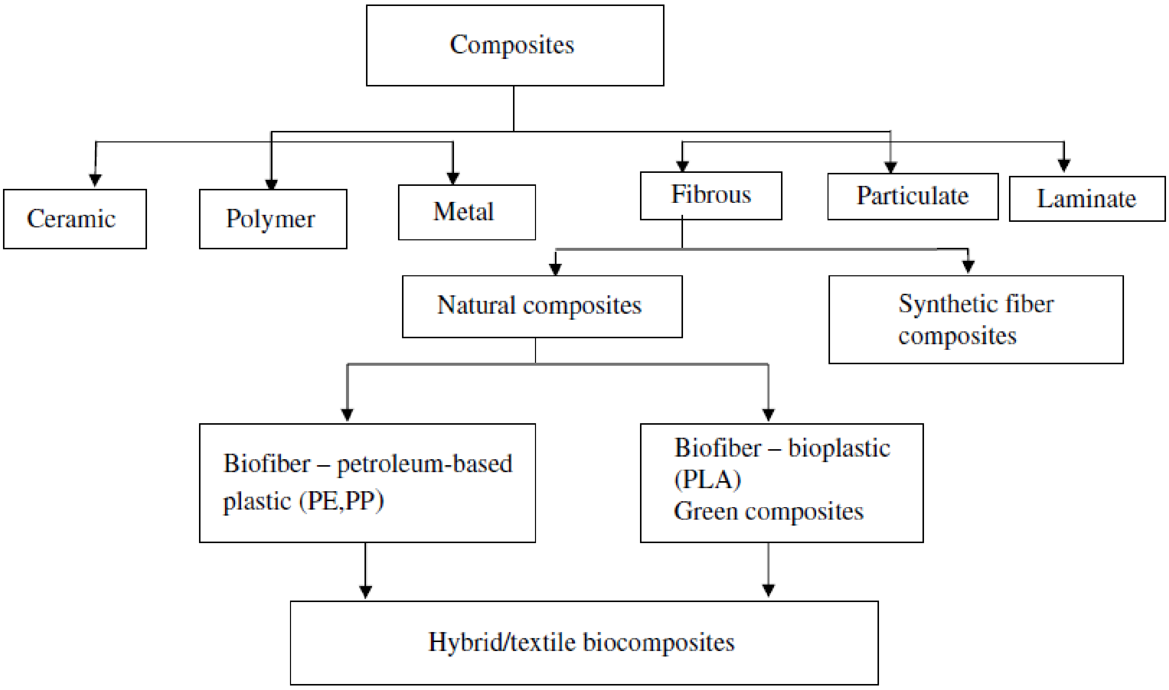


Figure 2.1: Classification of composites.

2.1.2 Features of composites

Composite materials are designed and prepared for particular applications with desired properties such as lightweight and high performance. Composite materials offer some advantages over engineering materials as discussed below.

- Composite materials provide abilities for part integration.

- Composite structures provide in-service monitoring or online process monitoring with the help of embedded sensors [5].

- Composite materials offer a high stiffness [4].

- Composites have a high strength.

- The fatigue strength is much higher for composite materials.

- Composite materials can be designed for superior corrosion resistance to particular hostile environments.

- They provide increased amount of design flexibility.

- Composite materials provide good impact properties (Figure 2.2).

- Noise and vibration properties are better for composites than metals [5].

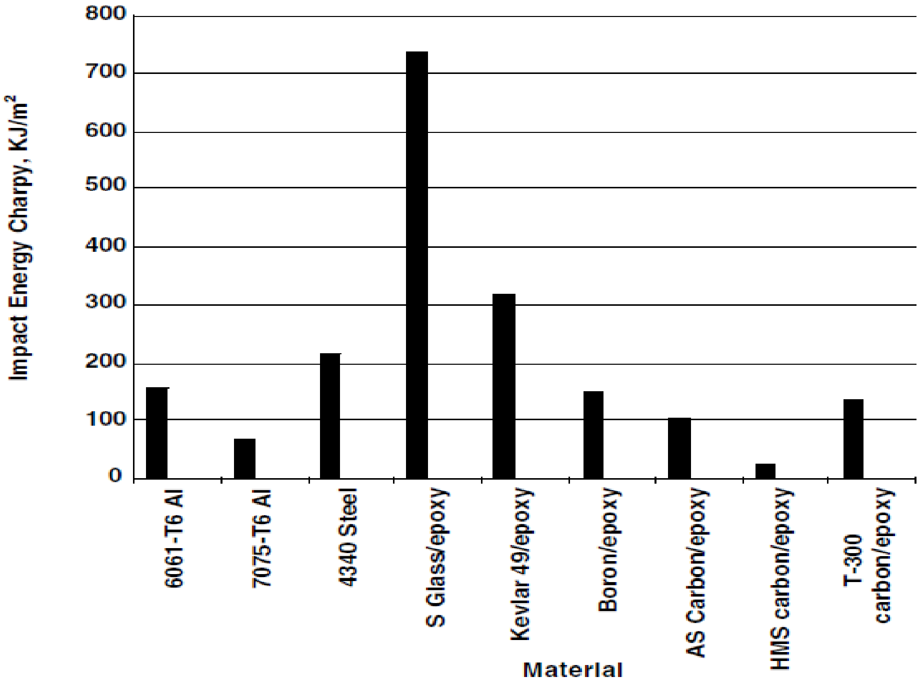


Figure 2.2: Impact properties of some kind of composites.

2.1.3 Naming of composites

Composite materials can be called by reinforcement and the matrix material. According to the type of matrix materials, there are metal matrix composite material, aluminum matrix composites, polymer matrix composite material, and epoxy resin matrix composite material. Polymer matrix composites are generally named by the type of their reinforced fiber, such as glass fiber composite material (commonly known as glass fiber reinforced plastics), carbon fiber composites, and hybrid fiber composites. More particularly, the name of the reinforcement is put the front of the name of the matrix material, along with “composite material” on the back. For example, composite material with E-GF and epoxy resin can be named “E-glass fiber epoxy composite material”. For convenient writing, it can also be written as abbreviation of the reinforcement and matrix materials, with a “/” separating them, along with “composite material” on the back, and so the former “E-glass fiber epoxy composite material” is briefly called “E-GF/epoxy composite material” (traditionally called epoxy GFRP). Composite material of carbon fiber and metal matrix is called “metal matrix composites”, and can also be written as “carbon/metal composite material”. Carbon fiber reinforced carbon matrix composite material is called “carbon/carbon composite” or “C/C composite material”. The above-mentioned nomenclature can also be addressed using commodities trademark directly, for example, T300/648,M40/5208, S-GF/5245C, Kevlar49/QY8911, HT3/5405 and so on [2].

2.1.4 Polymer composites

Materials have been combined with each other for producing new materials with desired properties. A composite material is created by combining two or more materials to provide discernible improvement of properties. In a composite, substantial volume fraction of high strength, high stiffness reinforcing elements are embedded in a matrix phase.

Matrix materials are generally polymers, ceramics or metals. The polymer matrices also called resins are by far the most common due to the versatility of their properties such as light weight, easy processing and corrosion resistance [13].

2.2 General Properties and Applications of Polystyrene

Polystyrenes have been produced commercially by polymerization in an extruder [14]. Polystyrene is made from petroleum, a non-sustainable, non-renewable, heavily polluting and fast-disapperaing commodity. The environmental impacts of polystyrene production in the categories of energy consumption, greenhouse gas effect and total environmental effect ranks second highest, behind aluminum.

Polystyrene is not biodegredable. It takes several decades to hundreds of years for polystyrene to deteriorate in the environment or in a landfill. Polystyrene takes up more spaces in landfills than paper, and will eventually re-enter the environment when water or mechanical forces breach landills. Polystyrene contains the toxic subtances styrene and benzene, suspected carcinogens and neurotoxins that are hazardous to humans. Polystyrene foam, commonly known by the name "Styrofoam" is formed by adding a blowing agent to polystyrene, a petroleum-based plastic material. Polystyrene foam is light-weight (about 95% air), with good insulation properties, and is used in all types of products from cups that keep beverages hot or cold to materials that protect items during shipping. There are two widely used types of expanded polystyrene: EPS (expanded polystyrene) and XPS (extruded polystyrene). They are made from the same plastic (polystyrene), but the manufacturing processes are different. EPS begins as small plastic “beads” that are expanded and fused together, forming products such as protective packaging for electrical appliances. XPS begins as a continuous mass of molten material, which is then shaped into products such as take-out lunch boxes and trays for fresh cuts of meat at the supermarket. XPS has little recycling ability since it is often contaminated by food, and grease that render it non-recyclable [15].

Styrene, a component of polystyrene, is a known hazardous substance that medical evidence and the US Food and Drug Administration suggests leaches from polystyrene containers into food and drink. Polystyrene food containers leach Styrene when they come into contact with warm food or drink, alcohol, oils and acidic foods causing human contamination and posing a direct health risk to people. It is for this reason that it is not recommended that plastic take-out containers ever be heated in a microwave. Styrene is a suspected carcinogen and neurotoxin which potentially threatens human health. It has been detected in the fat tissue of every man, woman and child tested by the EPA in a 1986 study. Styrene has been found in human tissue samples and human nursing milk samples tested [15].

CD covers and plastic drinking cups are made out of the polymer polystyrene. This polymer is known to be a clear brittle plastic that is synthesized by a free radical polymerization. An initiator, such as benzoyl peroxide, is used to initiate the free radical polymerization of styrene. Once the radical initiator initiates the polymerization of styrene, propagation occurs which “builds up” the polymer chain. Once the polymer chain has “grown” and at a desirable length or molecular weight, the polymerization is terminated. The polymer is then isolated, possibly purified, characterized, and used for material use [16].

2.3 Polymerization Types

Synthetic polymers can be obtained via different kinds of polymerization such as condensation polymerization and addition polymerization.

The main polymerization types have also various techniques. In this section, polymerization techniques were explained.

2.3.1 Condensation polymerization

There is a very wide variety of condensation reactions that, in principle, can be used to make high polymers. However, high polymers can be obtained only in high-yield reactions, and this limitation severely restricts the number of condensation reactions having any practical importance. Some condensation polymerization examples can be seen in Figure 2.3, Figure 2.4 and Figure 2.5.

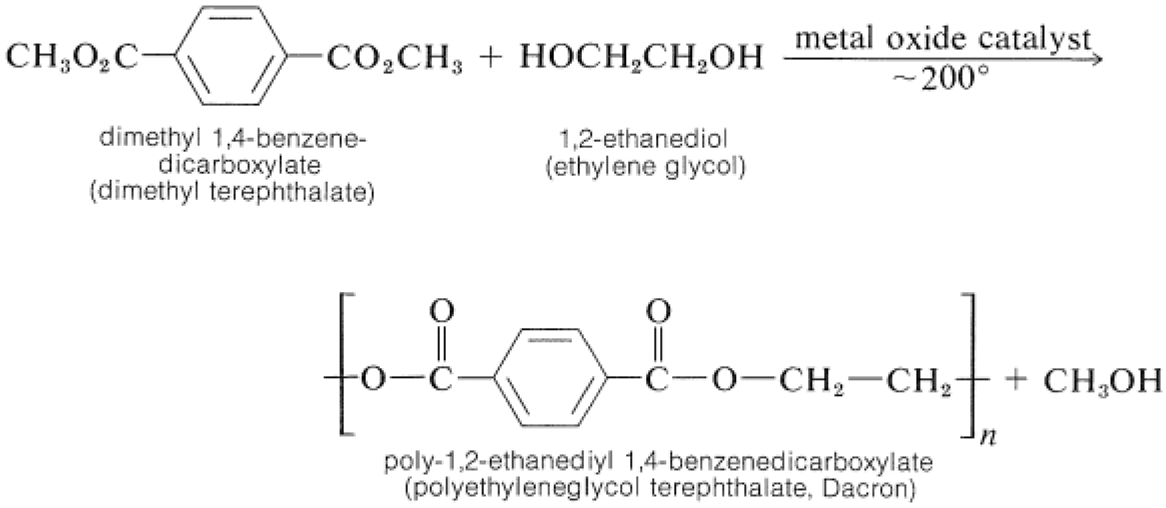
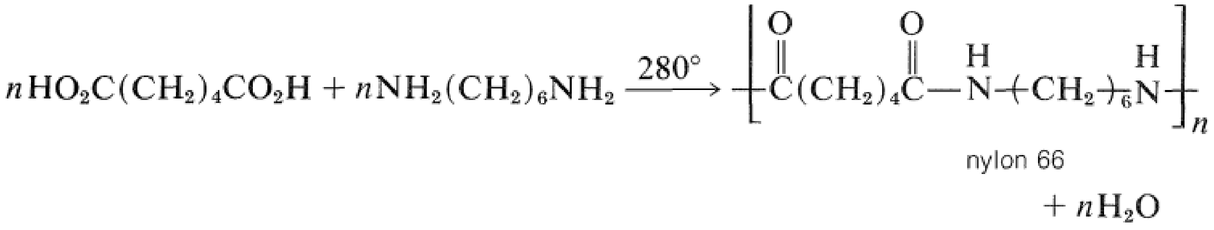


Figure 2.3: Polyester formation via condensation polymerization.



$$n\mathrm{HO_2C(CH_2)_4CO_2H} + n\mathrm{NH_2(CH_2)_6NH_2} \xrightarrow{280^\circ} \left[\overset{\overset{\large O}{\|}}{\mathrm{C}}\mathrm{(CH_2)_4}\overset{\overset{\large O}{\|}}{\mathrm{C}} - \overset{\mathrm{H}}{\mathrm{N}} -\!\left(\mathrm{CH_2}\right)_6\!- \overset{\mathrm{H}}{\mathrm{N}} \right]_n + n\mathrm{H_2O}$$

Figure 2.4: Nylon 66 formation via condensation polymerization.

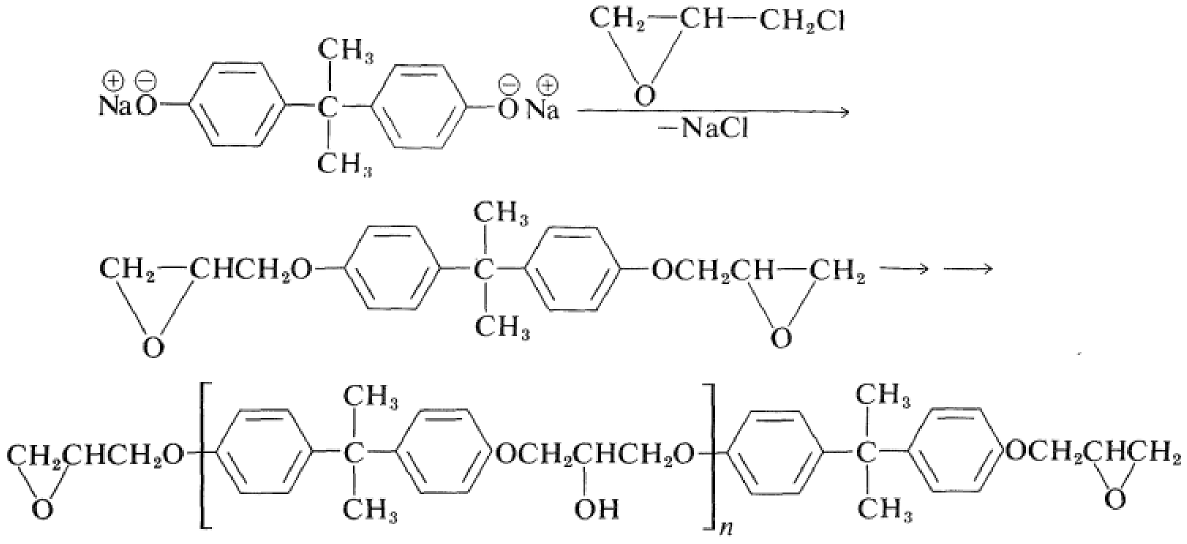


Figure 2.5: Epoxy resin synthesis via condensation polymerization.

2.3.2 Addition polymerization

Addition polymerization have two main parts which are called as radical polymerization and ionic polymerization. Also, ionic polymerization is divided to cationic polymerization and anionic polymerization.

2.3.2.1 Anionic and cationic polymerization

Polystyrene can be synthesized by also anionic and cationic polymerization, but radical polymerization was used for producing polystyrene in this work.

Stages of anionic polymerization can be seen in Figure 2.6.

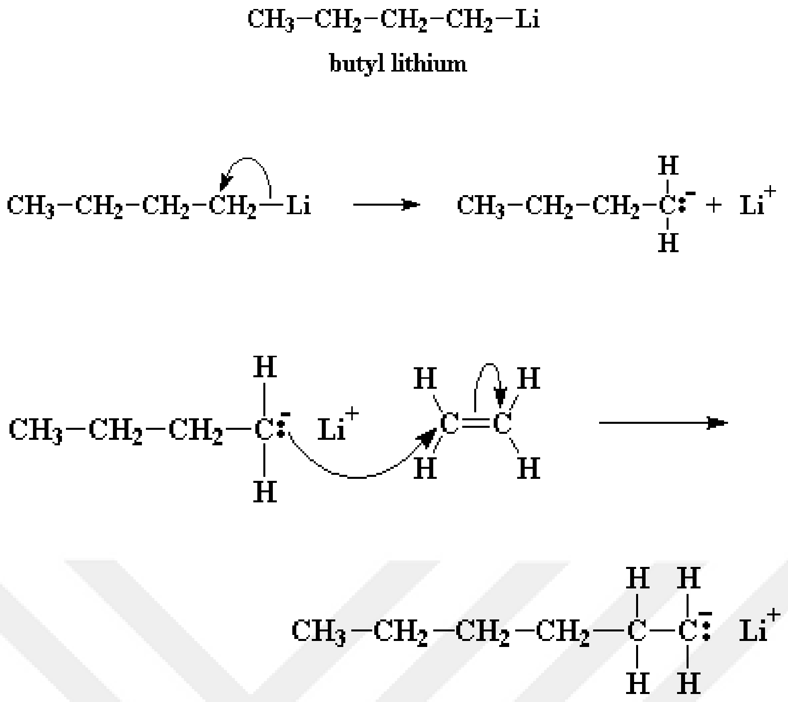


Figure 2.6: Stages of anionic polymerization.

If moisture and oxygen are rigorously excluded, the anionic groups are stable indefinitely, and if more monomer is added, polymerization will continue. Hence the name "living polymer," in contrast to a radical-induced polymerization, which only can be restarted with fresh monomer and fresh initiator, and even then not by growth on the ends of the existing chains [70].

Stages of cationic polymerization can be showed in the following figure (Figure 2.7).

Termination generally occurs via unimolecular rearrangement with the counterion. In this process, an anionic fragment of the counterion combines with the propagating chain end. This not only inactivates the growing chain, but it also terminates the kinetic chain by reducing the concentration of the initiator-coinitiator complex [20].

Initiation and propagation:

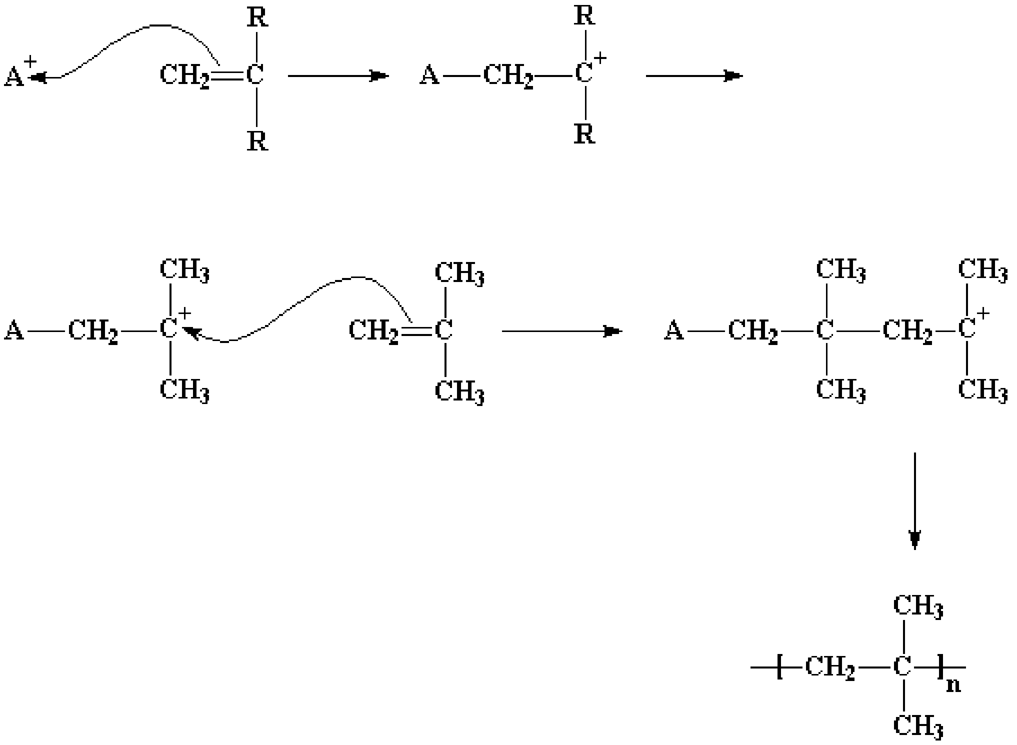


Figure 2.7: Stages of cationic polymerization.

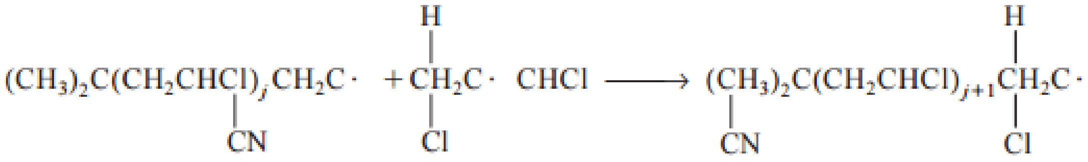
2.3.2.2 Radicalic polymerization

Radicalic polymerization needs an initiator and proceeds by adding one repeating unit at a time [18].

Initiation: Radical polymerizations are different because an initiation step is required to start the polymer chain growth [19]. Initiation can be carried out by adding a small amount of a chemical that decomposes smoothly to form free radicals. Initiators can be monofunctional and make the same free radical. In contrast, initiators can be multifunctional and make different radicals. Multifunctional initiators incorporate more than one labile group.

Propagation: The propagation progression occurs between a monomer and a radical.

An example for a propagation reaction can be shown in Figure 2.8,



$$(CH_3)_2\underset{\displaystyle CN}{C}(CH_2CHCl)_jCH_2C\cdot \;+\; CH_2\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}\cdot \;\; CHCl \longrightarrow (CH_3)_2\underset{\displaystyle CN}{C}(CH_2CHCl)_{j+1}CH_2\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}\cdot$$

Figure 2.8: Example of a propagation reaction.

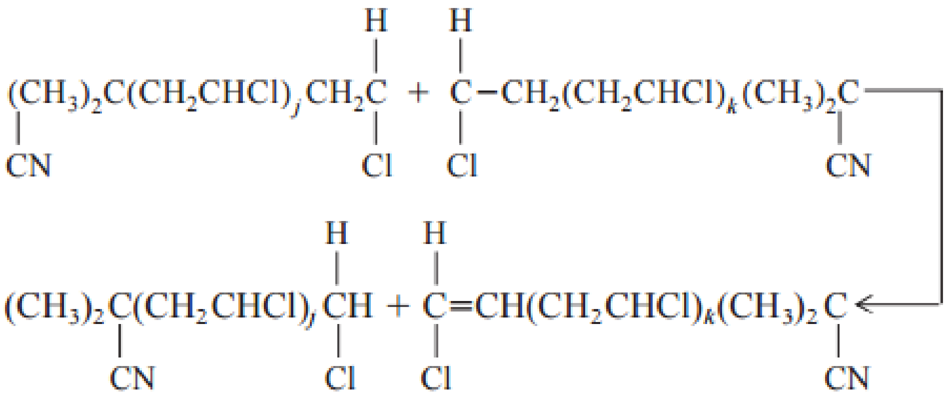
The particular reaction rates (k_p) are assumed to be indistinguishable for the addition of each monomer to the growing chain. This is generally a superb assumption once two or more monomers have been added to R_1 and for low conversions of monomer. The particular reaction rate k_i is frequently taken to be equal to k_p.

Termination: For termination, dead polymers can be obtained by two mechanisms.

1. Addition (coupling) of two growing polymers,

2. Termination by disproportionation.

An example can be seen in Figure 2.9.



$$(CH_3)_2\underset{\displaystyle CN}{C}(CH_2CHCl)_jCH_2\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}} \;+\; \overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}-CH_2(CH_2CHCl)_k(CH_3)_2\underset{\displaystyle CN}{C}$$

$$(CH_3)_2\underset{\displaystyle CN}{C}(CH_2CHCl)_j\overset{\displaystyle H}{\underset{\displaystyle Cl}{CH}} \;+\; \overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}=CH(CH_2CHCl)_k(CH_3)_2\underset{\displaystyle CN}{C}$$

Figure 2.9: An example termination scheme.

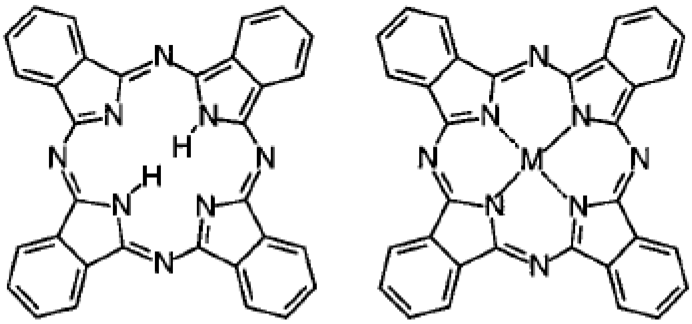
2.4 Phthalocyanines

2.4.1 General information

Phthalocyanines (Pcs) were discovered accidentally. In 1907, Braun and Tcherniac, at the South Metropolitan Gas Company in London, upon examining the properties of a cyanobenzamide that they made from the reaction of phthalamide and acetic anhydride, found a trace amount of a blue substance after heating o-cyanobenzamide, cooling, dissolving in alcohol, and filtration. This substance undoubtedly was phthalocyanine. The word phthalocyanine is derived from the Greek terms for naphtha (rock oil) and cyanine (dark blue). Professor Linstead of the Imperial College of Science and Technology first used the term "phthalocyanine" in 1933, to describe a class of organic compounds [23].

The main problems in the phthalocyanine chemistry are their insolubility in most of the solvents and aggregation tendency in solutions because of the molecular interactions between the macrocyclic rings. These problems limit their usage or causes diminishing of the properties in application steps. While the substitutions of some bulky apolar substituents such as long alkyl, alkyloxy or alkylsulfonyl groups improve their solvation in organic solvents, polar substituents such as sulfo, carboxylic acid or quaternized ammonium groups provide their solubility in aqueous media [28]. Phthalocyanines are devided to two main categories which are metal-free phthalocyanine and metallophthalocyanine. An example about structure of typical phthalocyanine compounds can be seen in Figure 2.10.

Thus, phthalocyanines are thermally and chemically stable: they can be heated up to 500 °C under high vacuum without decomposition and remain unaltered when exposed to the action of non-oxidative acids or bases. Phthalocyanines are planar macrocycles related to porphyrins constituted by four isoindole units presenting an 18 π-electron aromatic cloud delocalized over an arrangement of alternated carbon and nitrogen atoms. A great number of unique properties arise from this electronic delocalization, which makes these compounds applicable in different fields of materials science [22].



(a) (b)

Figure 2.10: (a) Metal-free phthalocyanine, (b) metallophthalocyanine.

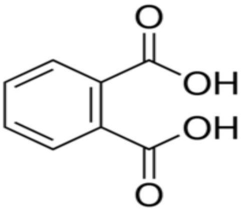
Phthalocyanines have been used in a wide range of different applications: chemical sensors [29], photodynamic therapy [30], electrochromic materials [31], liquid crystal displays [32], organic light emitting diodes (OLEDs) [33], nonlinear optical properties [34], organic solar cells [35], chemical catalysts [36], photodynamic activity [37], electronic and optoelectronic properties [38], and adsorption behavior [39].

2.4.2 Synthetic methods of phthalocyanines

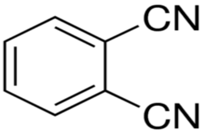
In the synthesis of phthalocyanines, as starting materials, phthalic acid (1), phthalonitrile (2), phthalic anhydride (3), phthalimide (4), diiminoisoindoline (5), o-cyanobenzamide (6) are used.

2.4.2.1 Metal-free phthalocyanines (H_2Pc)

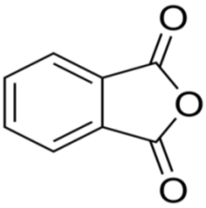
It is possible to synthesize non-metallophthalocyanines (H_2Pc) by the technique of cyclotetramerization of lots of phthalonitriles. Some precursors can be seen in Figure 2.11. Synthesis of metal-free phthalocyanines can be seen in Figure 2.12.



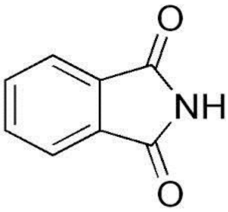
Phthalic acid (1)



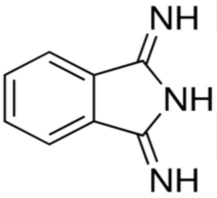
Phthalonitrile (2)



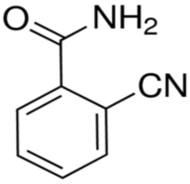
Phthalic anhydride (3)



Phthalimide (4)



Diiminoisoindoline (5)



o-cyanobenzamide (6)

Figure 2.11: Precursors that lead to phthalocyanine formation.

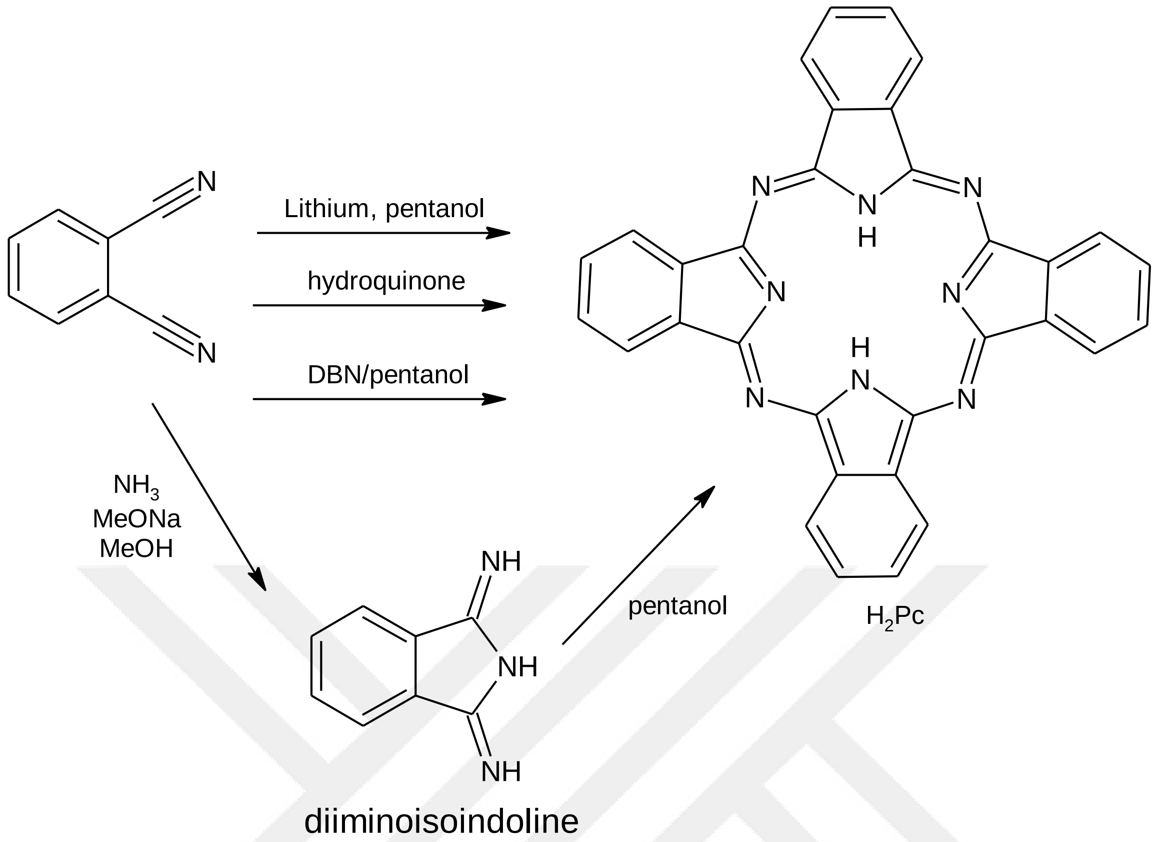


Figure 2.12: Scheme for the synthesis of non-metallophthalocyanines and starting materials.

- Reacting lithium in boiling pentanol under reflux and hydrolysis,
- Melting with hydroquinone,
- DBU, boiling in pentanol,
- Under reflux, boiling with ammonia, methanol, sodium methoxide,
- Under reflux, boiling with an alcohol having high boiling point,

2.4.2.2 Metallophthalocyanines (MPc)

In the synthesis of metallophthalocyanines, like non-metallophthalocyanines, there are lots of possible synthetic methods. The common point of all kinds of synthetic methods is that these methods include many steps and these occur at high temperatures (Figure 2.13).

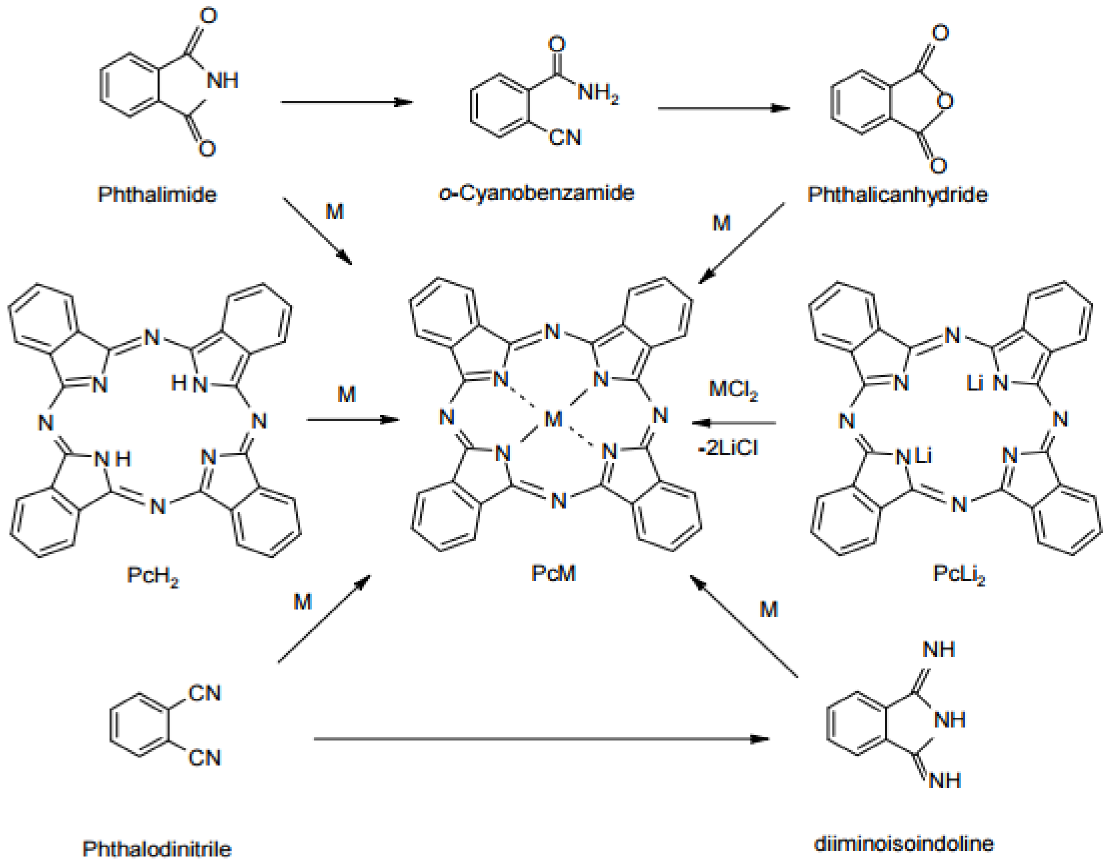


Figure 2.13: Scheme for the synthesis of metallophthalocyanines and starting materials.

Boiling phthalimide or phthalic anhydride structures in solvents having high boiling points and urea and metal salts with the catalysis of molybdate.

- Boiling of diiminoisoindoline or phthalonitrile in DMF, pentanol, hexanol with metal salts
- Boiling Li_2Pc in ethanol
- Adding metal to non-metallophthalocyanines

2.4.2.3 Synthesis of substituted phthalocyanines

Substituted phthalocyanines can be obtained with phthalonitrile derivative. Substituted phthalocyanines are prepared by substitution of the phthalocyanine ring. Consequently, tetra or octa substituents can be obtained.

2.4.2.4 Tetrasubstituted phthalocyanines

Phthalocyanines that have most researches on them are tetra-substituted complexes. The reason of this case is their high solubilities in many organic solvents because of their tetrasubstituent contents. These complexes are used in physical, chemical, biological and electrochemical areas.

Tetra-substituted phthalocyanines are divided into peripheral and non-peripheral, according to the position of the substituents of the macrocyclic structures.

In the synthesis of tetra-substituted phthalocyanine in the peripheral location, most used method is the following three steps synthesis of 4-nitrophthalonitrile compound that was prepared from phthalimide and that the base-catalyzed nucleophilic substitution reaction of the compound is modified [61]. Synthesis of 4-nitrophthalonitrile can be seen in Figure 2.14. 4-nitrophthalonitrile can react with various nucleophiles in a strong polar solvent such as DMSO or DMF. Acidic protons in nucleophiles are cut off with a base such as Na_2CO_3 or K_2CO_3. Nucleophiles attack to the ring and nitro group is removed in the form of sodium nitrite [62,63].

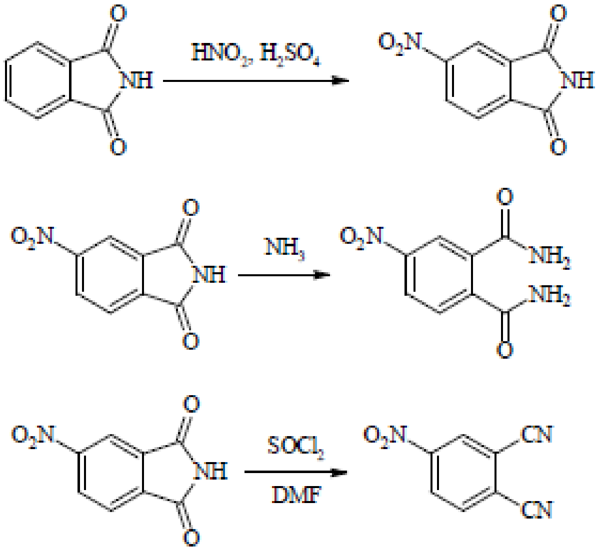


Figure 2.14: 4-Nitrophthalonitrile synthesis.

In the synthesis tetra-substituted phthalocyanines, as a result cyclotetramerization of a monosubstituted starting material, four isomers mixtures in symmetry of D_{2h},

$C_{4h}C_{2v}$ and C_s are obtained statistically in ratio of 4: 2: 1: 1 conformational isomers (Figure 2.15).

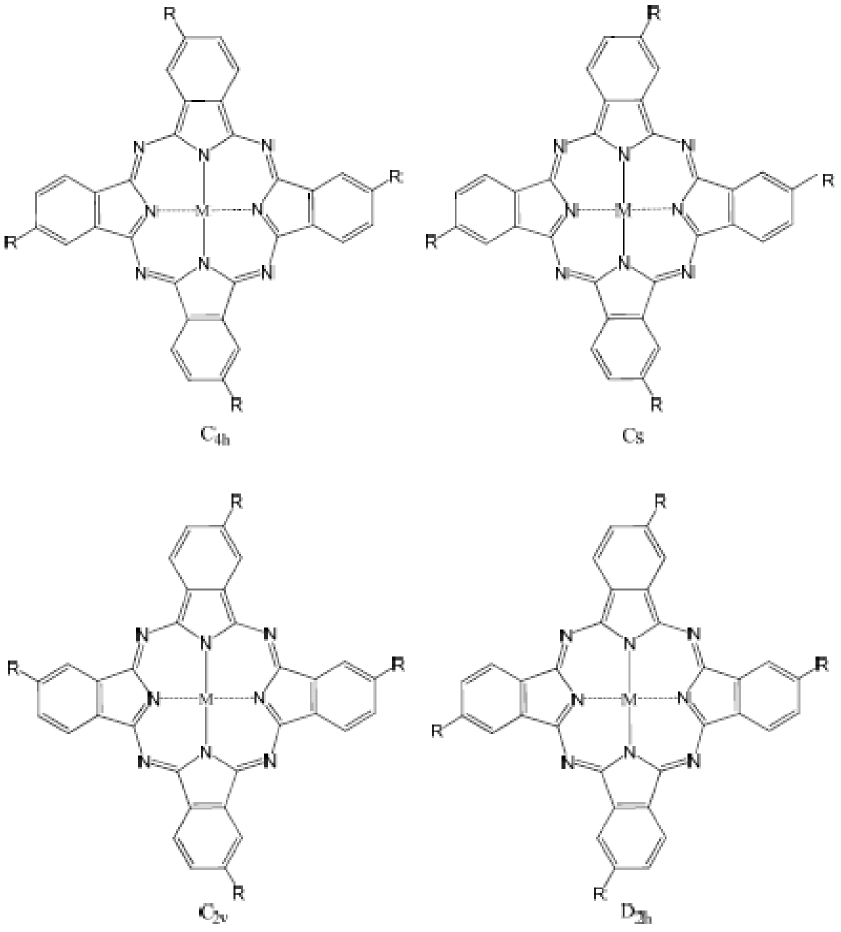
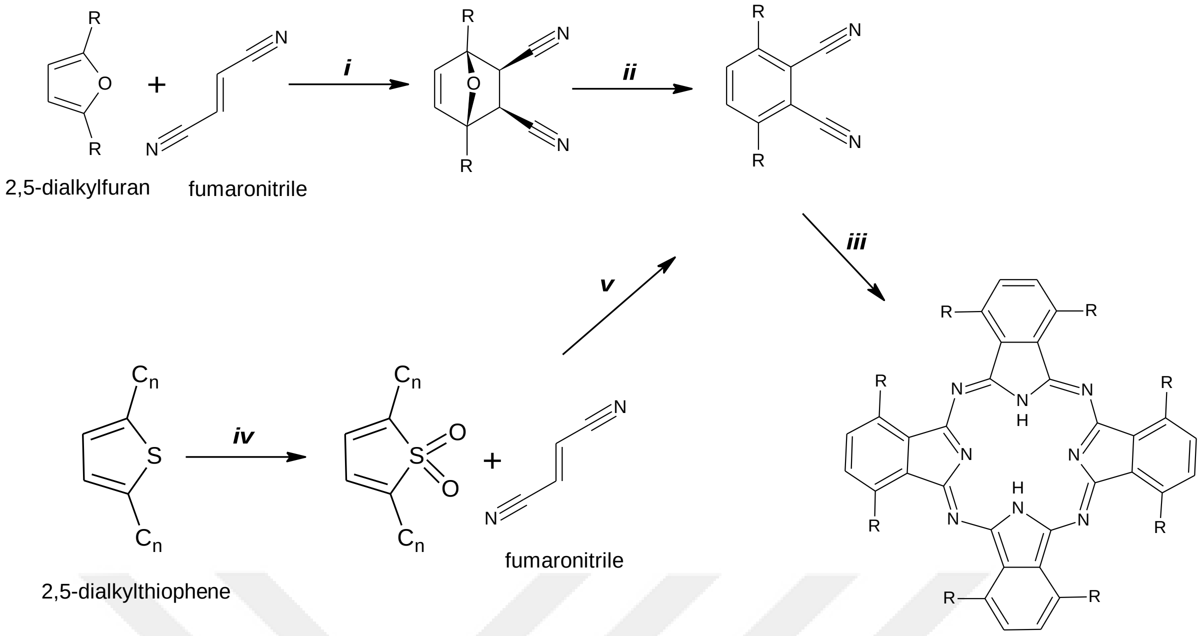


Figure 2.15: Structural isomers of tetra-substituted phthalocyanines.

2.4.2.5 Octasubstituted phthalocyanines

By using 4,5-disubstituted phthalonitrile, mostly more larger than pentyl ($-C_5H_{11}$), peripheral octa substituted phthalocyanines with one isomer can be synthesized. The resulting structures are structures that show liquid crystal property and, soluble in organic solvents. Phthalocyanines containing eight substituents in peripheral positions are obtained with two methods. In the first method, the o-xylene compound is brominated to yield 4,5-dibromo-o-xylene are obtained, with the result that of bromination with N-bromosuccinimide is synthesized 1,2-bromomethyl-4,5-dibromobenzene. Primary alkyl groups are substituted reacting with suitable nucleophiles, and then bromo groups bonded to benzene rings are converted to nitro groups by Rosenmund-Von Braun synthesis [64].



$R = C_nH_{2n+1}$;H_2Pc-onp-C_n; $R = CH_2OC_nH_{2n+1}$; H_2Pc-onp-C_1OC_n

Figure 2.16: Non-peripherally Octasubstituted Phthalocyanines' Synthesis (H_2Pc-onp-C_n).

For the synthesis of non-peripheral octa-alkyl-substituted phthalocyanines that have liquid crystallinity (MPc-onp-C_n), Cook and his group developed two new methods. 3,6-dialkyl phthalonitrile required for the synthesis are synthesized from the appropriate 2,5-dialkyl furan or thiophene. Approproate dinitrile derivatives are synthesized as the result of Diels Alder ring addition reaction between fumaronitrile and five heteroring (Figure 2.16).

2.4.2.6 New methods for synthesis of phthalocyanines

Studies in order to improve the synthesis of phthalocyanine compounds are increasing recently. By using these improved methods, it is intended to create more economical, quicker, easier, and more efficient reactions. At the first of these methods is the synthesis of phthalocyanine using microwave energy.

2.4.3 Purification of phthalocyanines

Phthalocyanines (Pcs) have been synthesized with nearly all metals of the periodic table. The metal-free phthalocyanines (H_2Pc) are normally formed as a one-pot multiple-step reaction from derivatives of phthalic acid, phthalic anhydride, phthalimide, or phthalonitrile usually by fusion or in a high boiling solvent such α-chloronaphthalene [53]. When the reaction is carried out in presence of metal salt, the metal phthalocyanines PcM are formed. Insoluble (unsubstituted) phthalocyanines can be mainly purified by sublimation at high temperature at 450°C under vacuum, by dissolution in concentrated acids followed by precipitation in water, or by extensive extraction with organic solvents. However, soluble (substituted) phthalocyanines can be purified by recrystallization from organic solvents or by chromatography on alumina or silica gel. Wagner and co-workers reported the technical details of a simple train sublimation (carrier gas) system for purification of MPcs and studied the effect of sublimation on the physical properties of MPcs [54].

The other techniques for purification of phthalocyanines are;

- GPC (Gel Permeation Chromatography)
- HPLC (High Performance Liquid Chromatography)
- Column Chromatography using aluminium oxide and silica gel
- Sublimation
- For phthalocyanines with low solubility, purification by washing in various solvents; for phthalocyanines with high solubility, purification by washing in different organic solvents are applied.

2.4.4 Characterization of phthalocyanines

Elemental analysis used in the characterization of organic compounds, and FTIR and UV-Vis are also used in the characterization of phthalocyanine. In particular, the position of the Q-band in the visible range is influenced by the substituents and the central metal atom. Therefore, these techniques play an important role in the characterization of phthalocyanines.

NMR is a useful technique for soluble phthalocyanine derivatives. However, due to the orientations of phthalocyanine compounds to strong aggregation in solution and causing enlargement prevent a good spectrum from NMR.

Recent developments related to the mass spectrometer facilitate the characterization of phthalocyanines. In particular, fast atom bombardment (FAB) and matrix-assisted laser desorption ionization (MALDI) have begun to constitute an important part in the characterization of high molecular mass phthalocyanines.

2.4.4.1 FTIR spectra of phthalocyanines

The main difference between metal-free phthalocyanines with metallophthalocyanines is that the N-H stretching vibrational band is seen near 3298 cm^{-1}.

In both metal-free phthalocyanines and metallophthalocyanines, the characteristic band due to C-H stretching of the aromatic ring is around 3000-3050 cm^{-1}, C-C stretching vibration band is around 1450-1600 cm^{-1}and outside the plane of C-H bending band is observed between 750-800 cm^{-1}.

2.4.4.2 ^{1}H-NMR spectra of phthalocyanines

In unsubstituted phthalocyanine, protons at the peripheral and non-peripheral positions give a signal of equal intensity. Octasubstituted phthalocyanines are formed from a single isomer, tetrasubstituted phthalocyanines are located as a mixture of isomers. Therefore, tetra-substituted phthalocyanines' spectrum signals stand out wider than the octa-substituted phthalocyanines. Because of substituents added to the ring and ligands in the axial position, ^{1}H-NMR spectrum of metallophthalocyanines becomes more complicated. Magnetic field signals can shift to low field or high field according to the nature and position of substituents. Generally, the electron donating groups when sliding signals to lower field, electron withdrawing groups shift to strong field. Also, phthalocyanines having electron donating non- peripheral substituents generally shift to lower fields comparing with their derivatives peripherally substituted comprising the same groups [57].

The metal-free phthalocyanine in the ^{1}H-NMR spectrum, as a proof of the aromatic structure of the phthalocyanine ring, because of diamagnetic anisotropy, the chemical shift of the NH proton in the ring stands out as the wide and broad peak in strong fields [58].

2.4.4.3 UV-Vis spectra of phthalocyanines

Chemical and electronic properties of phthalocyanine are coming from the 18 π-electron system. Generally, UV-Vis spectrum of phthalocyanines signal at 650-720 nm Q band; B, less intensity between 300-400 nm (SORET) called as the characteristic band peaks [59]. Severe Q band ground state (HOMO) and the excited state (LUMO) is due to the π-π * transitions between energy levels. B (SORET), the band between the orbital a_2 or b_2 and orbital e_g, is caused by the transitions. In metal-free phthalocyanine spectra, there is a splitting in the Q band.

2.4.5 Recent developments on phthalocyanines

In chemical synthesis, the term “selectivity” refers to the discrimination displayed by a reagent, when it reacts with two different reactants or functional groups. Highly selective reactions proceed with minimal reliance on protecting groups and contribute to both atom and step economy. Biological and synthetic systems operate somewhat differently when it comes to impose selectivity in chemical transformations. In nature, the biological catalysts, more particularly porphyrins such as cytochromes, are responsible for catalyzing oxidation-reduction processes and electron transfer reactions on which all forms of life are dependent. These enzymes are tailored towards a specific substrate and work with high levels of stereo-, regio-, and chemo-selectivity. However, high price, stability, and bulk availability issues limit their practical utility [55].

Phthalocyanines (Pcs) have structural similarity with porphyrins and are very stable π-conjugated macrocyclic compounds that can form complexes with almost all metals and offer a high architectural flexibility in structure. Due to their greater stability than porphyrins, metal phthalocyanines (MPcs) attract great attention for their applications as catalysts for selective organic transformations including oxidation-reduction processes and electron transfer reactions [56].

Although several catalyzed synthetic methodologies are being developed, controlling reaction selectivity still stands as one of the major challenges in organic synthesis. In this regard, these recent advances clearly evidenced the promising future of MPcs in catalyzing the challenging organic transformations in which high selectivity is required. Currently, visible light absorbing photocatalysts are emerging as powerful tools in synthetic organic chemistry in which their electron/energy transfer potential is being utilized for sensitization of organic molecules. In this regard, MPc photosensitizers, which strongly absorb in the visible region and have long triplet lifetime, have great potential to be developed for efficient photocatalytic reactions [60].

2.5 Click Chemistry

The grace and efficiency of the structures and function detected in nature, has long directed scientists' efforts both on understanding how nature functions through observation and apery and on creating novel, synthetic biomaterials combining the optimized by evolution properties of biomolecular structures with that of synthetic components. Taking into account the multifunctional and, most of the times, chemically fragile nature of biological entities, the major challenge into this direction is a chemical one: the need to proceed through bioorthogonal reactions and under the benign reaction conditions that would preserve and respect the multifunctionality and structure of biologically derived components [41].

Different click reactions applied in different field of science and yielded extremely reliable process for the synthesis of building block and compound libraries. The various reactions is classified below [44]. Some examples about click reactions can bee seen in Figure 2.17.

1. Cycloaddition reaction [45] and Diels Alder reaction [46].
2. Nucleophilic substitution reaction particularly rings opening reaction of strained heterocyclic electrophiles [47].
3. Carbonyl chemistry of the non-aldol type.
4. Addition to carbon-carbon multiple bonds specifically oxidation reaction, epoxidation [48]; hydroxylation; dihydroxylation [49]; aziridination [50].
5. Thiol-ene click reactions [51].
6. Azide-Phosphine reaction [52].

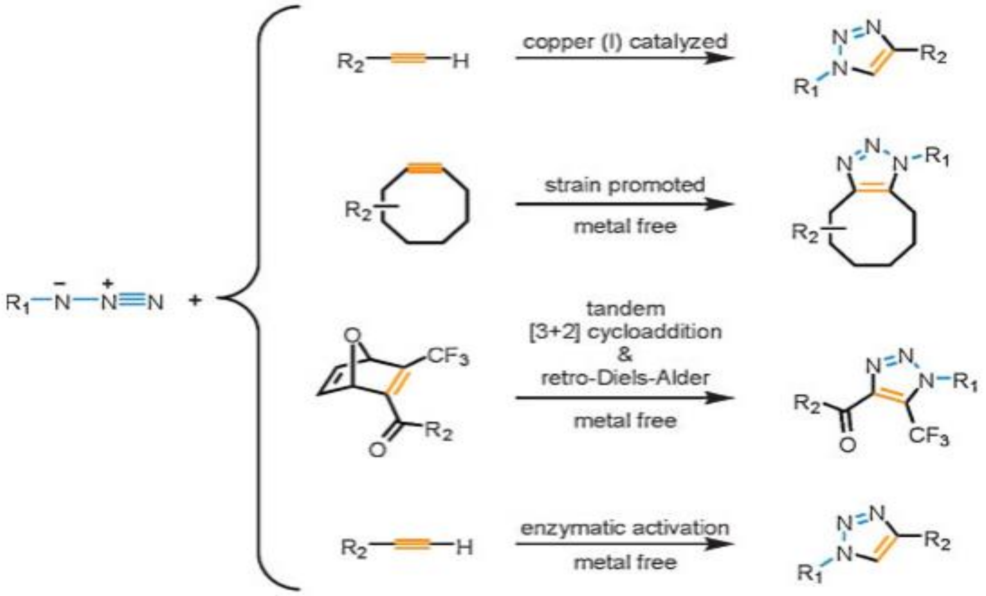


Figure 2.17: General scheme some kind of ‘‘click’’ chemistry cycloaddition reactions.

Following nature’s lead, we strive to produce substances by joining small units together with heteroatom links. The aim is to develop an expanding set of powerful, selective, and modular block that work dependably in both small and large scale applications. We have called the foundation of this approach click chemistry, and have determined a set of rigorous criteria that a process must meet to be useful in this context. The reaction must be modular, wide in scope, give very high yields, produce only harmless byproducts that can be removed by nonchromatographic methods, and be stereospecific. The needed process properties include simple reaction conditions (ideally, the process should be insensitive to oxygen and water), readily available starting materials and reagents, the use of no solvent or a solvent that is benign (such as water) or easily removed, and simple product isolation. Purification required must be by nonchromatographic methods, such as crystallization or distillation, and the product must be stable under physiological conditions [42].

Of the reactions that have been identified as fulfilling the rigorous needs of “click” chemistry, the Huisgen 1,3-dipolar cycloaddition of alkynes (1) and azides (2) to create triazoles (3) was, from the beginning, considered to be the ideal “click” reaction (Figure 2.18). Azide and alkyne functionalities are readily introduced, and have a high forbearance for the presence of other functional groups as well as high kinetic stability. The cycloaddition in its original form as defined by Huisgen generally needs raised temperatures and generates a mixture of the 1,4 and 1,5-disubstituted regioisomers (3) and (4) [43].

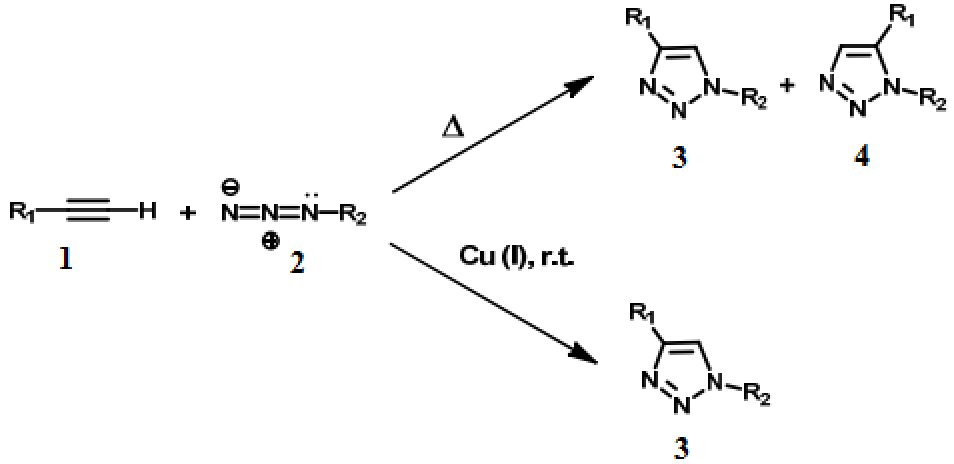


Figure 2.18: Huisgen 1,3-dipolar cycloaddition.

2.6 Previous Studies of Phthalocyanine-Polymer Composites

Ohkita and co-workers (2013) investigated the light-harvesting efficiency of P3HT:PCBM solar cells can be improved by incorporating near-IR dye molecules such as silicon phthalocyanine derivatives with bulky axial groups (SiPc). In order to study the size effect of the axial groups on the dye sensitization in P3HT:PCBM solar cells, they synthesized five SiPc derivatives with different axial groups: $SiPc[OSi(C_nH_{2n+1})_3]_2$ ($SiPc_n$, n = 2, 3, 4, 6) and $SiPc[OSi(iBu)_2C_{18}H_{37}]_2$ ($SiPcB_{18}$). The power conversion efficiency (PCE) increased in the order of n = 2–4, reached the maximum at around n = 4 and 6, and then decreased for $SiPcB_{18}$ with the longest axial groups [65]. As a result, the PCE was improved to 4.2%, which is larger by 10% than that of P3HT:PCBM control cells without dye molecules. They therefore conclude that the butyl or hexyl chain in the axial ligand is the most appropriate for the dye sensitization in P3HT:PCBM solar cells (Figure 2.19).

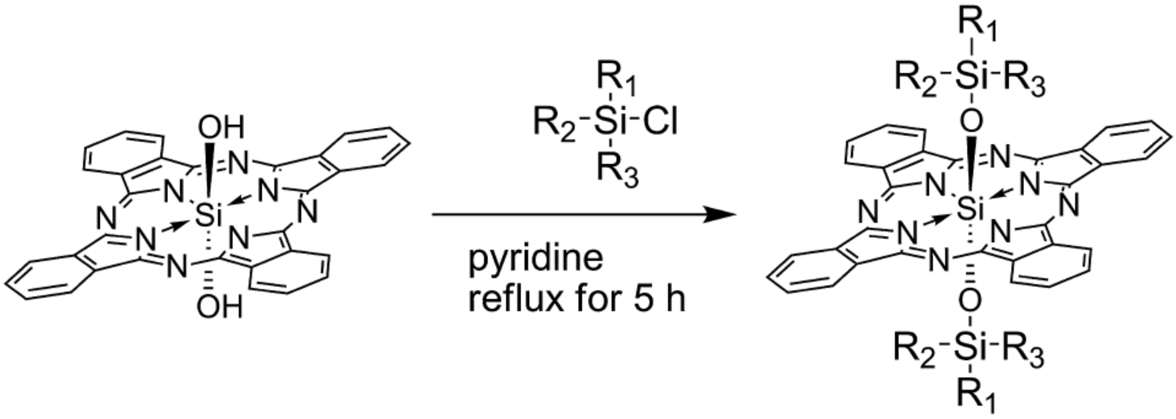


Figure 2.19: Synthetic scheme of SiPc[OSi(C_nH_{2n+1})$_3$]$_2$ (SiPc$_n$, n = 2, 3, 4, 6) and SiPc[OSi(iBu)$_2C_{18}H_{37}$]$_2$ (SiPcB$_{18}$).

Mert and co-workers (2014) synthesized unsymmetrically terminal alkynyl substituted zinc (II) phthalocyanine (ZnPc) through an efficient statistical condensation reaction with the unprotected phthalonitrile (2) is reported for the first time [66]. Isolated ZnPc bearing one terminal alkynyl group is a good precursor for Cu(I)-catalyzed azidealkyne 1,3-dipolar cycloaddition (CuAAC) reaction which is classified under the term “click chemistry”. This was approved by the successful click reaction between ZnPc and azide end-functional well-defined polymers obtained by atom transfer radical polymerization (ATRP), and consecutive azidation of corresponding bromo end-functional polymers. The click-reaction efficiencies for the formation of Pc-end functional poly(tert-butyl acrylate) (PtBA), and polystyrene (PS) have been found to be 75, 93% respectively (Figure 2.20). Functionalization of ZnPc with PS increased the chemical stability of the complex but decreased the electrochemical reversibility during redox reactions. *In situ* electrocolorimetric measurements of the complexes allowed the quantification of color coordinates of the each electrogenerated anionic and cationic redox species.

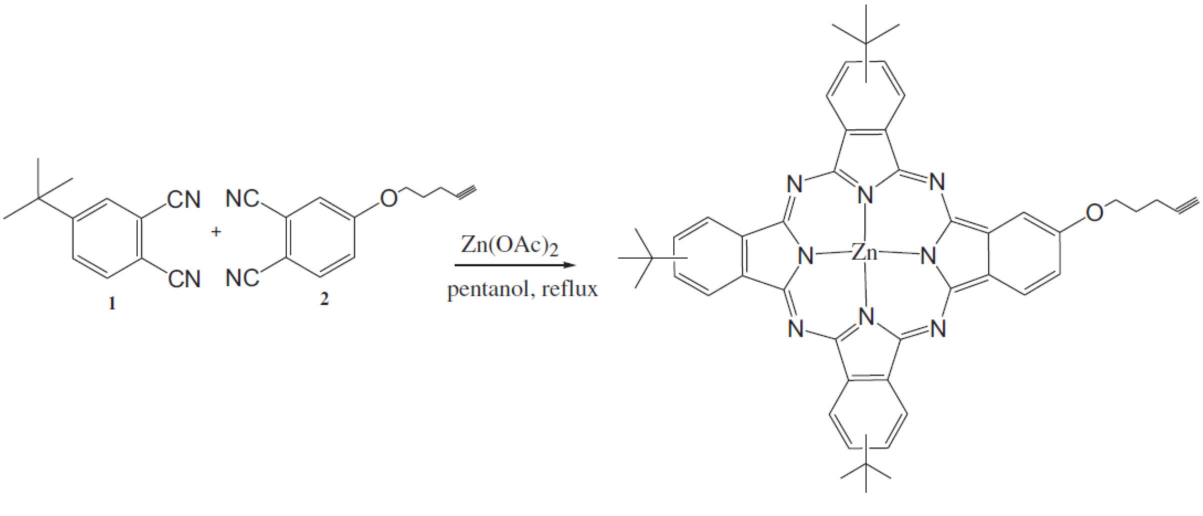
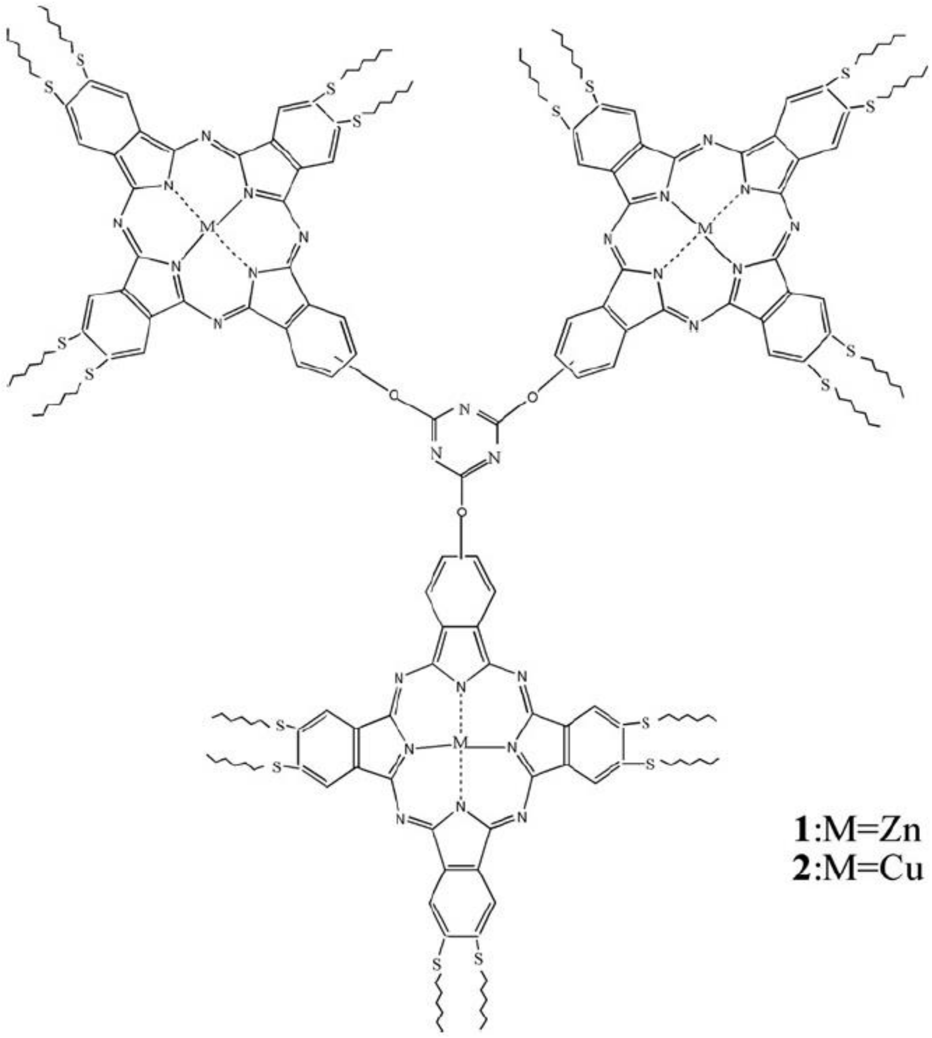


Figure 2.20: The synthesis of unsymmetrical zinc (II) phthalocyanine.

Bekaroğlu and his collaborators (2011) investigated the non-linear absorption and optical limiting properties of two trimeric metallo-phthalocyanines, namely 2,4,6-tris[2-oxa-9,10,16,17,23,24-hexa(hexylthio) phthalocyaninato M(II)]-s-triazine (M=Zn for ZnPc and Cu for CuPc) doped polyvinyl chloride (PVC) thin film in the nanosecond regime by using the open-aperture Z-scan technique [67]. The measurements were performed using 4 ns pulses generated from a frequency-doubled Nd:YAG laser at 532 nm wavelength. OL parameters of the ratio of the excited state to ground state absorption cross-sections κ, the effective nonlinear absorption coefficient β_{eff}, the linear absorption coefficient α_0 and the saturation density or energy density F_{sat} values were determined. The results show that MPc/PVC composite displays much larger nonlinear absorption coefficient and lower saturable fluence for optical limiting when compared to the same Pc molecules in solution. The results indicated that both compounds exhibited good OL performances. ZnPc shows slightly better OL parameters than that of CuPc (Figure 2.21).



1:M=Zn
2:M=Cu

Figure 2.21: Chemical structure of investigated compounds (M=Zn, Cu).

Nyokong and her co-workers (2013) worked on the antimicrobial photo-activities of a series of low symmetrically substituted phthalocyanine complexes in solution and in a fiber matrix [68]. Phthalocyanine complexes were successfully electrospun into a polystyrene polymer. The fiber diameter ranged from 240 nm to 390 nm in average. The modified polymer fiber showed successful singlet oxygen production with the Ge monocarboxy phthalocyanine modified fiber giving the highest singlet oxygen quantum yield value of 0.46 due to lack of aggregation when in the polymer. All the unsymmetrically substituted complexes showed antimicrobial activity towards *S. aureus* under illumination with visible light. The symmetrical ZnPc and ZnTPCPc showed no activity under illumination with light in the fiber matrix due to low singlet oxygen production (Figure 2.22).

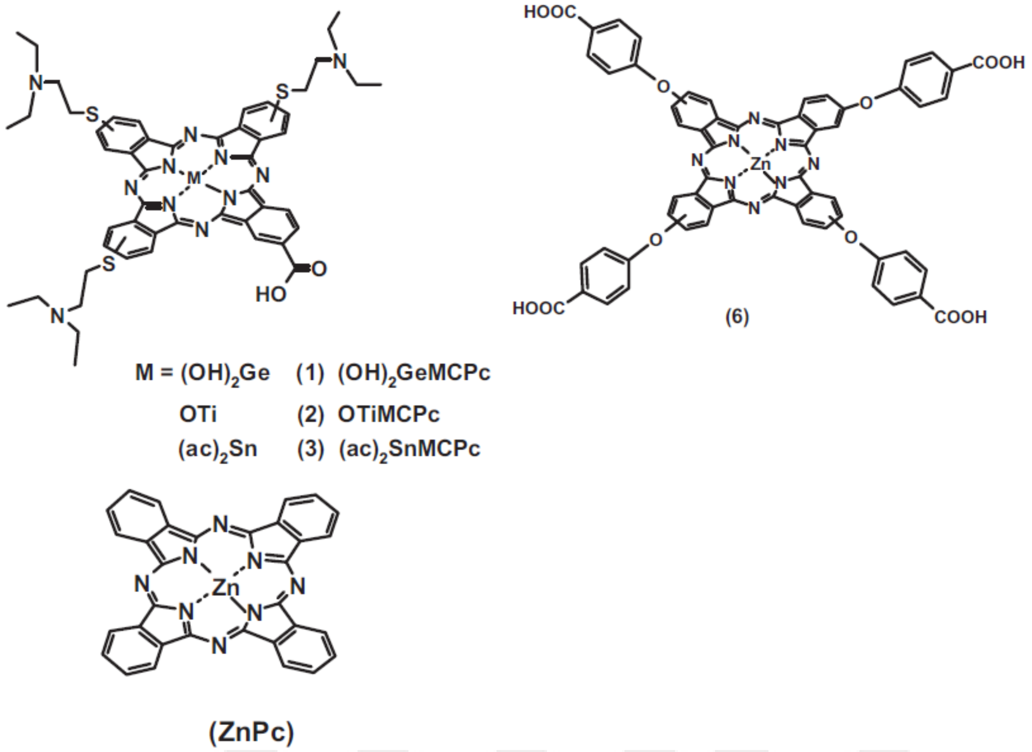


Figure 2.22: Molecular structures of the low symmetrically substituted complexes. MCPc = monocarboxy phthalocyanine (complexes 1-3), TPCPc = tetraphenylcarboxyphthalocyanine (6) and ZnPc.

Pochtennyi and co-workers (2014) investigated the electrical conductivity and adsorption–resistive response to nitrogen dioxide of composite films containing copper phthalocyanine nanoparticles dispersed into the polystyrene matrix [69]. The results are analyzed using the two level model of hopping conductivity. The contributions to the conductivity from intrinsic and impurity localization centers are singled out, and the concentrations of the localization centers in copper phthalocyanines free of impurities as well as the electron localization radii in impurity and intrinsic states are determined.

3. EXPERIMENTAL WORK

3.1 Instruments and Chemicals

- Instruments:

Perkin-Elmer Spectrum One FT-IR Spectrometer, Scinco UV-Vis
Spectrophotometer, Bruker-Spectrospin Inova 500 Mhz ^{1}H-NMR Spectroscopy.

- Chemicals:

Copper(I)bromide (Cu(I)Br), chloroform ($CHCl_3$), styrene (C_8H_8), methanol (CH_3OH), tetrahydrofuran (C_4H_8O), N,N-dimethylformamide (C_3H_7NO), sodium azide (NaN_3), sodium sulfate (Na_2SO_4), dichloromethane (CH_2Cl_2), potassium carbonate (K_2CO_3), ethanol (C_2H_6O), n-pentanol ($C_5H_{12}O$), n-hexane (C_6H_{14}), calcium chloride ($CaCl_2$), zinc acetate ($Zn(CH_3COO)_2$), nitric acid (HNO_3), 1,8-diazabicyclo[5.4.0]undec-7-ene ($C_9H_{16}N_2$), 1-phenylethyl bromide (C_8H_9Br), 4-ethynylbenzyl alcohol (C_9H_8O), dimethylaminoethanol (DMAE) ($C_4H_{11}NO$), N,N,N′,N″,N″pentamethyldiethylenetriamine ($C_9H_{23}N_3$).

3.2 Preparation of Polymers

3.2.1 Synthesis of PS-Br (1)

Cu(I)Br (0.125 g, 0.87 mmol), and PMDETA (0.4 mL, 3 mmol) were added to a 25 mL round bottom flask. The contents of the flask were degassed by flowing nitrogen through the flask for 15 min. Previously distilled styrene (5 mL, 0.04 mol) and 1-phenylethyl bromide (0.16 g, 0.87 mmol) were degassed separately and added to the flask. The solution was stirred at 110 °C for 1.5 h under N_2. The mixture was dissolved in chloroform and run through a neutral alumina column to remove the copper complex and then concentrated by rotary evaporation. The polymer was precipitated into excess methanol (3x) and filtered. The polymer was dried at 40 °C under vacuum [66]. M_n= 10000, ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 6.41 -7.25 (m, Ar-H, 5H), 3.65 (br, 1H, CH(Ph)-Br end group of PS), 1.30-2.10 (m,-CH_2-CH(Ph)- 2H).

3.2.2 Synthesis of PS-N_3 (2)

PS-Br (2 g, 0.80 mmol) was dissolved in DMF (15 mL) and NaN_3 (0.52 g, 8.0 mmol) was added to the flask. After stirring overnight at room temperature, it was filtered and evaporated to remove the DMF. CH_2Cl_2 (100 mL) was added, and the reaction mixture was washed three times with distilled water. The organic layer was dried with anhydrous Na_2SO_4, and the solvent was removed in vacuum. The polymerization mixture was diluted with THF and precipitated in methanol (Figure 3.1). The recovered polymer PS-N_3 was dried in vacuum oven at 40 °C for 24 h [66]. Yield: 92 %. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 6.41 -7.25 (m, Ar-H, 5H), 3.41 (br, 1H, CH(Ph)-N_3 end group of PS), 1.25-1.80 (m,-CH_2-CH(Ph)- 2H). FTIR ν (cm^{-1}): 3060-3025 (Ar-H), 2918-2849 (CH, aliphatic), 2011 (-N_3), 1601,1492,1451 (C=C), 1067,1028,906,840,754,695.

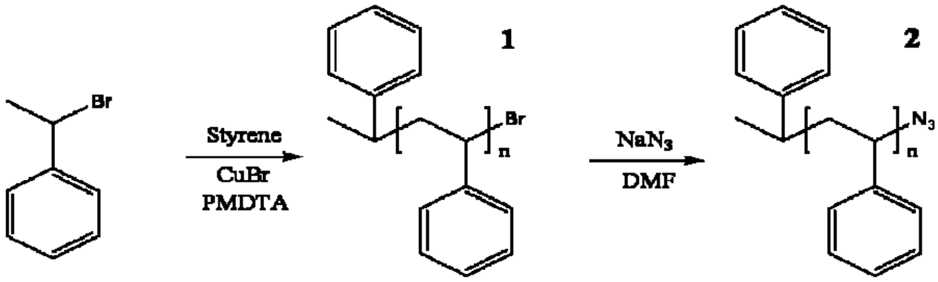


Figure 3.1: Polymerization and azidation process of styrene.

3.3 Synthetic Steps of Non-symmetrical Phthalocyanine Compound

3.3.1 Synthesis of 4-nitrophthalimide

40 g of phthalimide is added in to the mixture of 200 mL of sulfuric acid and 50 mL of nitric acid cooled in an ice-bath, as portions and stirred within 1-1,5 hours also it is provided to keep internal temperature at 10-15°C. After stirring for 30 min. in the ice-bath, the internal temperature is risen to 35°C. By the way, yellow particles are dissolved. Through an hour, the mixture is stirred at this temperature and cooled to 0°C, then poured into nearly 1 kg of ice water. 4-nitro phthalimide (5-nitro-1H-isoindole-1,3(2H)-dione) with yellow color is precipitated and filtered. Until removing acidity of the solution, it is washed with distilled water and crystallized

from 900 mL ethanol (Figure 3.2). Bright yellow crystals are filtered, washed with cold ethanol, then dried in the vacuum oven at 80-90°C [72]. Yield: 31 g (77 %), M.P. 195°C.

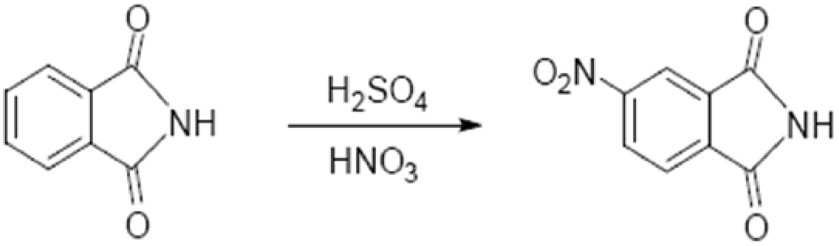


Figure 3.2: Synthesis of 4-Nitrophthalimide.

3.3.2 Synthesis of 4-nitro phthalamide

30 g of 4-nitro phthalimide is stirred in 168 mL of 32% ammonia solution at room temperature. After this, the solution is filtered, washed with cold diluted water and THF. During the reaction the color of 4-nitro phthalimide is yellow, it converts to white with the formation of 4-nitrobenzene-1,2-dicarboximide. This color change shows that the reaction occurred [72]. Yield: 24 g (73 %), M.P. 197°C, $C_8H_7N_3O_4$ (Figure 3.3).

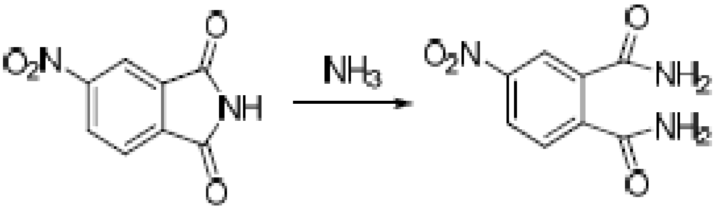


Figure 3.3: Synthesis of 4-nitro phthalamide.

3.3.3 Synthesis of 4-Nitrophthalonitrile

70 mL of dry dimethyl formamide was cooled to 0 °C in an ice bath by bubbling nitrogen gas through a three-necked flask and 7 mL of thionyl chloride was added slowly without exceeding the internal temperature of 5 °C, stopped adding of nitrogen gas and calcium chloride tube was attached to the top of the flask. At the same time the color turned to yellow (Figure 3.4). Then 10 g (48 mmol) of 4-nitro phthalimide was added in portions at 0-5 °C. Stirring in ice bath was continued for 1 hour. The mixture was stirred at room temperature for 2 hours and poured into 500 g of ice-water. White product was filtered, it was washed with water, then with 250 ml

of 5 % sodium bicarbonate solution, again with water and dried in a vacuum oven in 110-120 °C [72]. $C_8H_3N_3O_2$ yield 7.4 g (90 %) M.P. 141°C.

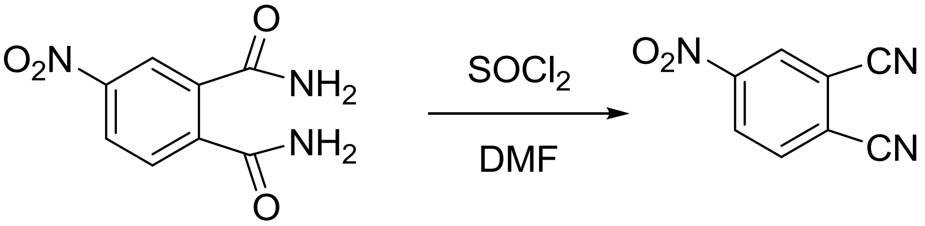
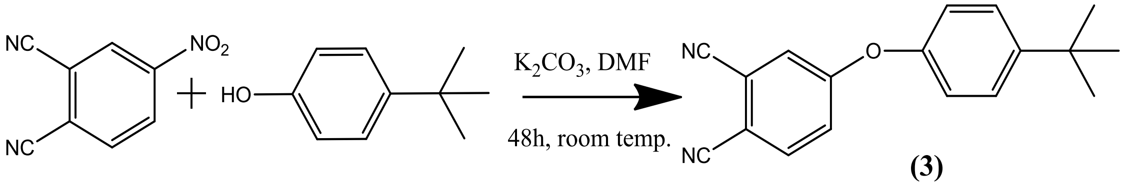


Figure 3.4: Synthesis of 4-Nitrophthalonitrile.

3.3.4 Synthesis of 4-(4-tert-butylphenoxy)phthalonitrile (3)

In an argon atmosphere, 1.59 g (11.48 mmol) of anhydrous K_2CO_3 was added in 0.53 g portions at 1-h intervals to a solution of 1.72 g (11.48 mmol) of 4-tert-butylphenol and 1 g (5.74 mmol) of 4-nitrophthalonitrile in 10 mL of dry N,N-dimethylformamide (DMF). The mixture was stirred for 48 h at room temperature under argon. After 48 h the undissolved salt was filtered, 200 mL of cold water was added, and then the mixture was stirred rapidly. The resulting precipitate was filtered by vacuum and washed with water (Figure 3.5). The crude product was recrystallized from ethanol. White crystals was obtained [73]. Yield: 47%; mp: 114-116 °C. FTIR ν, cm^{-1}: 3226, 3084, 2962, 2903, 2868, 2231, 1668, 1584, 1504, 1480, 1410, 1394, 1279, 1241, 1109, 1179, 1109, 1088, 1019, 953, and 872; ^{1}H-NMR ($CDCl_3$): δ 6.97-7.71 (Ar-H, 7H), 1.35 (s, 9H), and $C_{18}H_{16}N_2$ O; MW: 276.34 g/mol.

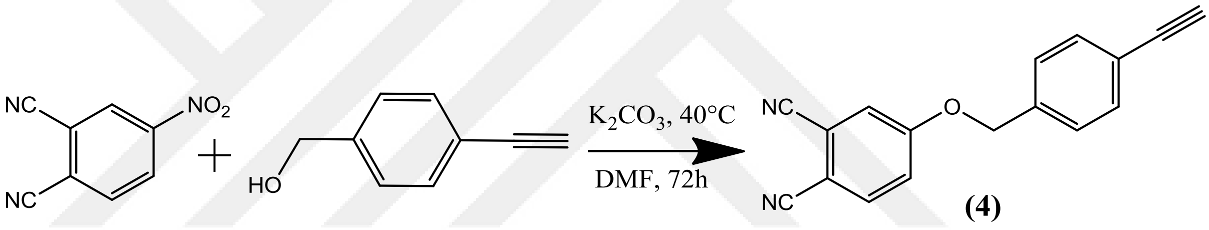


(3)

Figure 3.5: Synthesis of 4-(4-tert-butylphenoxy)phthalonitrile.

3.3.5 Synthesis of 4-((4-ethynylbenzyl)oxy)phthalonitrile (4)

0.297 g (2.25 mmol) of 4-ethynylbenzyl alcohol and 4-nitrophthalonitrile 0.389 g (2.25 mmol) were added successively with stirring to dry N,N-dimethylformamide (5 mL). After they were dissolved, anhydrous K_2CO_3 0.56 g (4.05 mmol) was added portion wise for 2h and the mixture was stirred vigorously at 40 °C for 72 h under nitrogen. Then the solution was poured into ice water (200 mL). The solution was acidified with conc. HCl until precipitation occured (pH = 1–2). The yellow brownish product was collected by centrifugation and rinsed with ethanol. Finally, the solid was dissolved in a minimum amount of chloroform and then added to n-hexane dropwise (Figure 3.6). The brownish crystals were filtered and dried. Cream colored crystals. Yield: 55%; mp: 132 °C. FTIR ν, cm^{-1}: 3269 (–C≡C–H), 3081 (Ar–H), 2930 (alkyl CH), 2233 (C≡N), 2105 (C≡C), 1260 (C–O–C); ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 7.73 (1H, d, Ar-H), 7.55 (2H, d, Ar-H), 7.37 (2H, d, Ar-H), 7.34 (1H, d, Ar-H), 7.25 (1H, d, Ar-H), 5.17 (2H,s, -O-CH2), 3.13 (1H, s, -C≡C–H); ^{13}C NMR (500 MHz;$CDCl_3$), (δ: ppm): 70.47 (O-CH_2), 82.91 (-C≡), 78.23 (≡C–H), 107.86 (aromatic C), 115.09 (C≡N), 115.54 (C≡N), 117.58 (aromatic C), 119.69 (aromatic C), 119.92 (aromatic C), 122.78 (aromatic C), 127.30 (aromatic C), 132.66 (aromatic C), 133.92 (aromatic C), 134.13 (aromatic C), 135.09 (aromatic C), 135.29 (aromatic C), 161.45 (-O-(Aromatic -C=)) and $C_{17}H_{10}N_2O$; MW: 258.27g/mol.



(4)

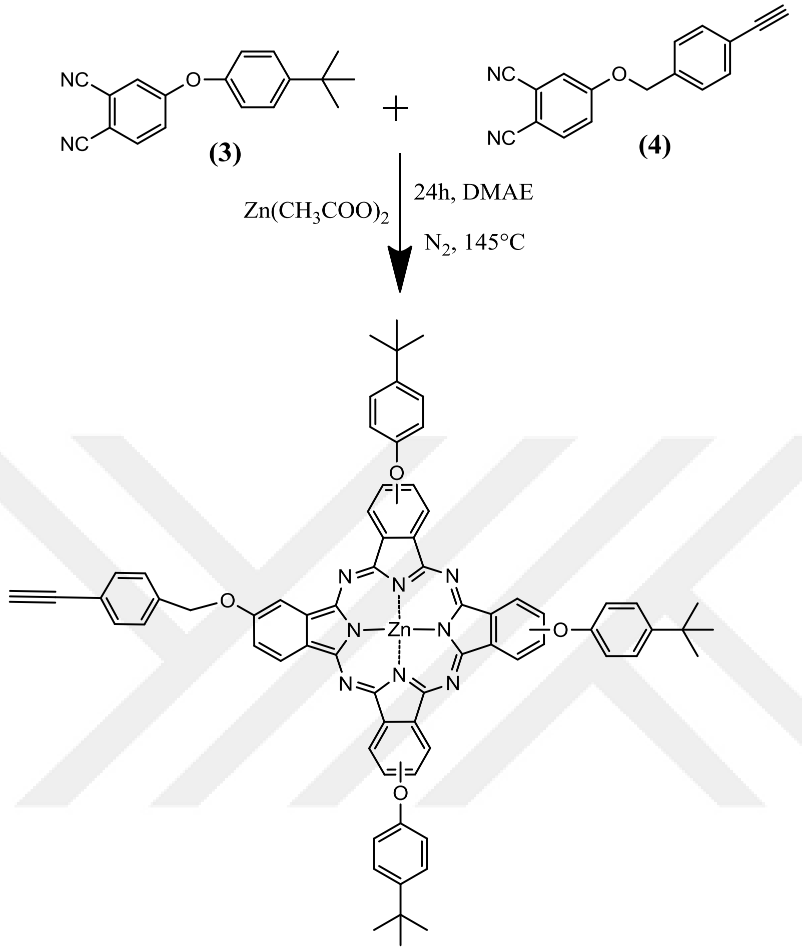
4-((4-ethynylbenzyl)oxy)phthalonitrile

Figure 3.6: Synthesis of 4-((4-ethynylbenzyl)oxy)phthalonitrile.

3.3.6 Synthesis of 9(10),16(17),23(24)-Tris-(t-butylphenoxy)-{4-ethynylbenzyloxy} phthalocyaninatozinc(II) (5)

4 (52 mg, 0.2 mmol), **3** (165 mg, 0.6 mmol), and zinc acetate were added into a solution of DBU (0.5 mL) and pentanol (3 mL). The mixture was stirred under N_2 at 145°C. After 24 hours, the mixture was cooled and the resulting precipitate was collected by centrifugation. The solid was washed with mixture of MeOH and water (1:3) and dried to afford a dark green solid the purification was carried out by column chromatography on silica gel using hexane/ THF (2:1) as the eluent to afford **5** as a green solid (Figure 3.7). Yield: 11%. FTIR ν, cm^{-1} 3285 (–C≡C–H), 3073 (Ar–H), 2956–2866 (alkyl CH), 2105 (C≡C), 1226 (C–O–C). ^{1}H NMR (500 MHz; CDCl3; Me4Si: dH, ppm) 7.10–7.91 (28H,b, Ar–H), 5.17 (2H, s, O–CH_2), 3.12

(1H,s, –C≡C–H), 1.40–1.13 (27H, m, -C(CH$_3$)$_3$). UV-vis (in THF): l, nm (log e) 352 (4.71), 675 (5.10)



(5)

Figure 3.7: Synthesis of novel zinc(II)phthalocyanine **5**.

3.4 Synthesis of PS- Zinc Phthalocyanine Composites via Click Chemistry

Zinc phthalocyanine (0.177 g, 0.0885 mmol), DMF (3 mL) were added to a 25 mL of Schlenk tube and stirred until a homogenous mixture is obtained and then added PMDETA (27.7 mL, 0.1326 mmol), CuBr (0.0190 g, 0.1326 mmol), polystyrene (0.02 g, 0.0221 mmol). The reaction mixture was stirred under nitrogen at 45 °C for 48 h. After the specified time, the polymer was isolated by diluting polymer mixture with tetrahydrofuran (THF) and passing through an alumina column to remove the metal salt. The excess of THF was evaporated under reduced pressure. The resulting polymer was dissolved in THF, precipitated in 10-fold excess of diethyl ether. The dissolution-precipitation procedure was repeated two times (Figure 3.8). The recovered green product was dried in a vacuum oven at 40°C for 24 h [71]. Yield: 86 %. FTIR ν, cm^{-1}: 3026 (Ar–H), 2930 (alkyl CH), 1260 (C–O–C); ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 8.1 (s, 1H, -N-CH=), 7.7-6.4 (br, Ar-H), 5.2 (s, -O-CH_2), 5.17 (br, 1H, CH(Ph)-triazol-PS), 2.0-0.7 (m, aliphatic protons of Pc and PS).

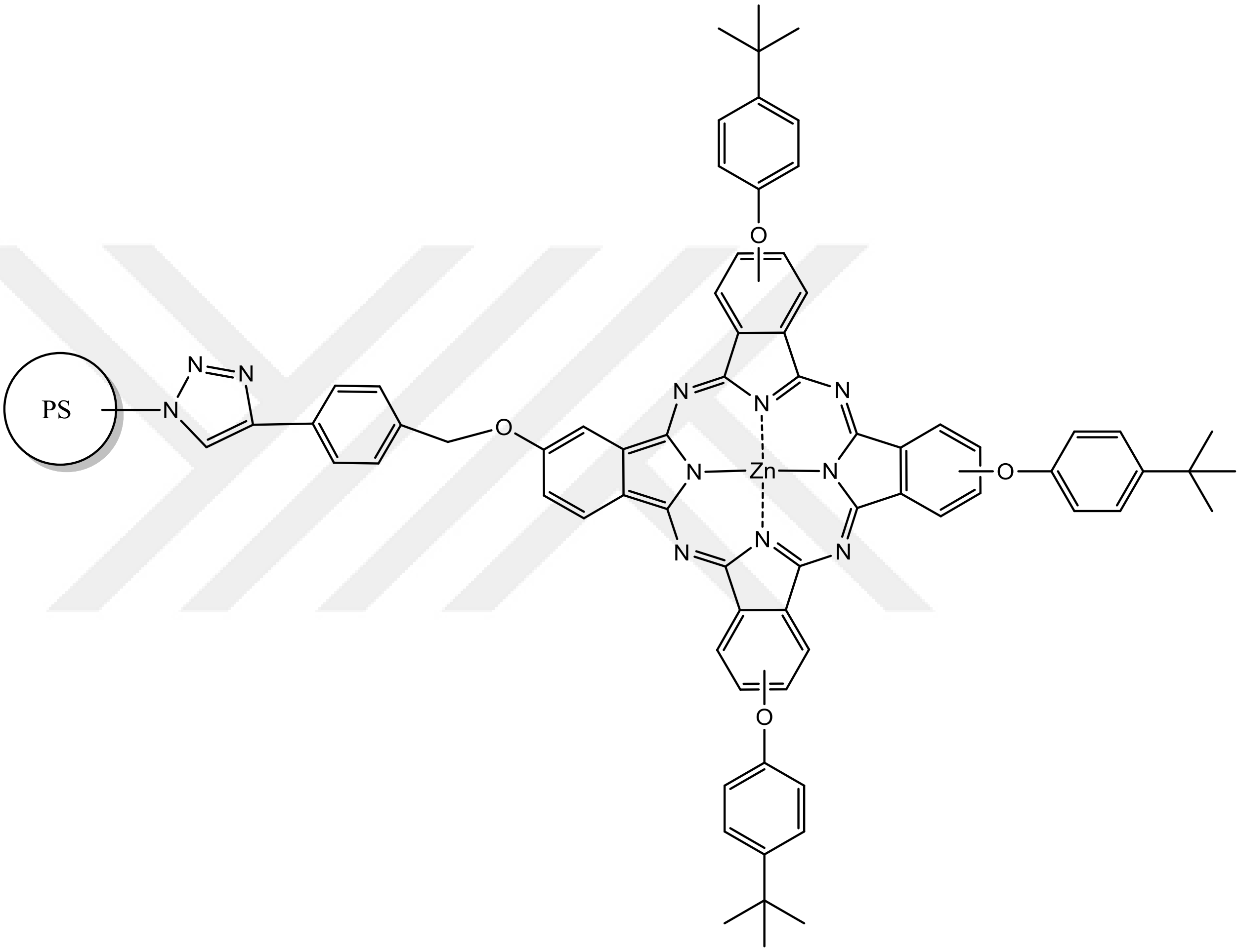


Figure 3.8: PS- Zinc Phthalocyanine Composites.

4. RESULTS AND DISCUSSION

4.1 Synthesis

In chemical synthesis, the term “selectivity” refers to the discrimination displayed by a reagent, when it reacts with two different reactants or functional groups. Highly selective reactions proceed with minimal reliance on protecting groups and contribute to both atom and step economy. Due to their greater stability than porphyrins, metal phthalocyanines (MPcs) attract great attention for their applications as catalysts for selective organic transformations including oxidation-reduction processes and electron transfer reactions [56].

We first synthesized **5** via a method which is mentioned in experimental part and characterized the new product. The direct statistical reaction of **3** and **4** in a ratio of approximately 3:1 gave six products, the desired AAAB could be easily separated by column chromatography as a second fraction. The column chromatography performed by using the solvent mixture of THF:toluene in a ratio of approximately 1:3. The seperated fraction of phthalocyanine was washed with excess of cold methanol and dried at room temperature under vacuum. Taking into account that utilization of Pcs in click chemistry requires terminal alkyne functionality and good solubility. Prepared unsymmetrical phthalocyanine have a terminal -C≡C-H group. This is important for the future of our process.

On the other hand bromo-end functional polystyrene was synthesized by ATRP method. Prepared polystyrene was azidated by the reaction with sodium azide and DMF. After this reaction PS-N_3 was obtained by precipitation with THF and methanol in a ratio of 1:10. The product was dried under vacuum at 40 °C.

The last step of our work was click reaction between alkynl-end unsymmetrical phthalocyanine and azidated polystyrene. PS-N_3 chains were reacted with the ZnPc in DMF with CuBr/PMDETA as catalyst to produce zinc phthalocyanine-terminated polymers. After the synthesis process, characterization of ZnPc, bromo-end functional polystyrene and Pc-PS composite were done.

4.2 Characterization

4.2.1 Characterization of novel phthalonitrile precursor (4)

The characterization of the new compound synthesized in this study was performed with FTIR, ^{1}H-NMR, ^{13}C-NMR, and similar methods. The relevant FTIR and NMR spectra were given in Appendixes Figure A.5 and Figure A.11. When the FTIR spectrum of the compound is investigated, the CH stretching vibration of characteristic ethynyl group (-C≡CH) was observed at 3269 cm^{-1} and C≡C stretching vibration peak was seen at 2105 cm^{-1}. Again, the aromatic and alkyl C-H stretching vibrations were observed at 3081 and 2930 cm^{-1}, respectively. As a last remark, since we have observed the C≡N stretching vibration peak at 2233 cm^{-1} and etheric oxygen bridge in C-O-C moiety in the phthalonitrile compound at 1260 cm^{-1}, this compound was successfully synthesized by means of FTIR data.

Again, the ^{1}H and ^{13}C NMR spectral data are in perfect harmony with the expected values for the phthalonitrile **4**, so the compound was successfully synthesized. When the ^{1}H-NMR spectrum of the compound is examined, the group of seven aromatic protons of the structure were observed between δ 7.74 – 5.24 ppm; two protons of the O-CH$_2$ group appeared at δ 5.17 and, the C≡C-H proton was found at δ 3.13 ppm. The ^{13}C NMR of the compound revealed that all protons of the 17 C group were at their expected positions. The most characteristic peaks of the compound were the C≡N peak at δ 115.09 – 115.54 ppm, the O-CH$_2$ peak at δ 70.47 ppm, the -C≡ peak at δ 82.91 ppm, the ≡C-H peak at δ 78.23 ppm and -C≡ carbon at δ 82.91 ppm. Lastly, the remaining aromatic carbon peaks were observed between δ 135-29 – 107.86 ppm range.

4.2.2 Characterization of the unsymmetrical ZnPc (5)

The unsymmetrical ZnPc was characterized by using ^{1}H-NMR, FTIR and UV-Vis spectroscopy. Infra-red spectrum further showed the presence of terminal alkynyl group bands around 3285 cm^{-1}, 2105 cm^{-1} and tert-butyl groups bands around 1393 cm^{-1}, 1361 cm^{-1} and 1336 cm^{-1}. The ^{1}H-NMR spectrum of ZnPc showed characteristic signals for the aromatic Pc ring protons between δ 7.10 and δ 7.91 ppm corresponding to the required number of Pc protons. Moreover the ^{1}H-NMR spectrum showed the signals at δ 5.17 ppm specific to CH_2-O protons, δ 3.12 for C≡C-H proton and δ 1.13-1.40 for C-$(CH_3)_3$ protons. The UV-Vis spectra of the studied zinc phthalocyanine **5** in THF was given in Appendixes Figure A.9. The π–π* transitions for the B and Q-band absorption were observed at 352 and 675 nm, respectively.

4.2.3 Characterization of azido-polystyrene (2)

The FT-IR spectra of azidoterminated polystyrene (PS-N_3) exhibits the expected characteristic signal at 2011 cm^{-1} due to the N_3 stretching vibration, hence confirming the presence of azido groups. In the ^{1}H-NMR spectra, for PS-N_3, a signal at 3.65 ppm, assigned to CH-Br, disappeared, and a new peak appeared at 3.41 ppm, indicating CH linked to the azide end group.

4.2.4 Characterization of phthalocyanine-terminated polystyrene

At the final step of the study, we prepared the targeted PS-ZnPc composites by the standard copper-catalyzed click reaction by using the azido-terminated polystyrene and terminal alkynyl substituted zinc phthalocyanine we obtained earlier. Every phase of this process was monitored with spectroscopic techniques in a detailed manner. In this context, firstly we understood that the targeted composite was formed by examining the FTIR spectra. The following spectra show the FTIR of each step.

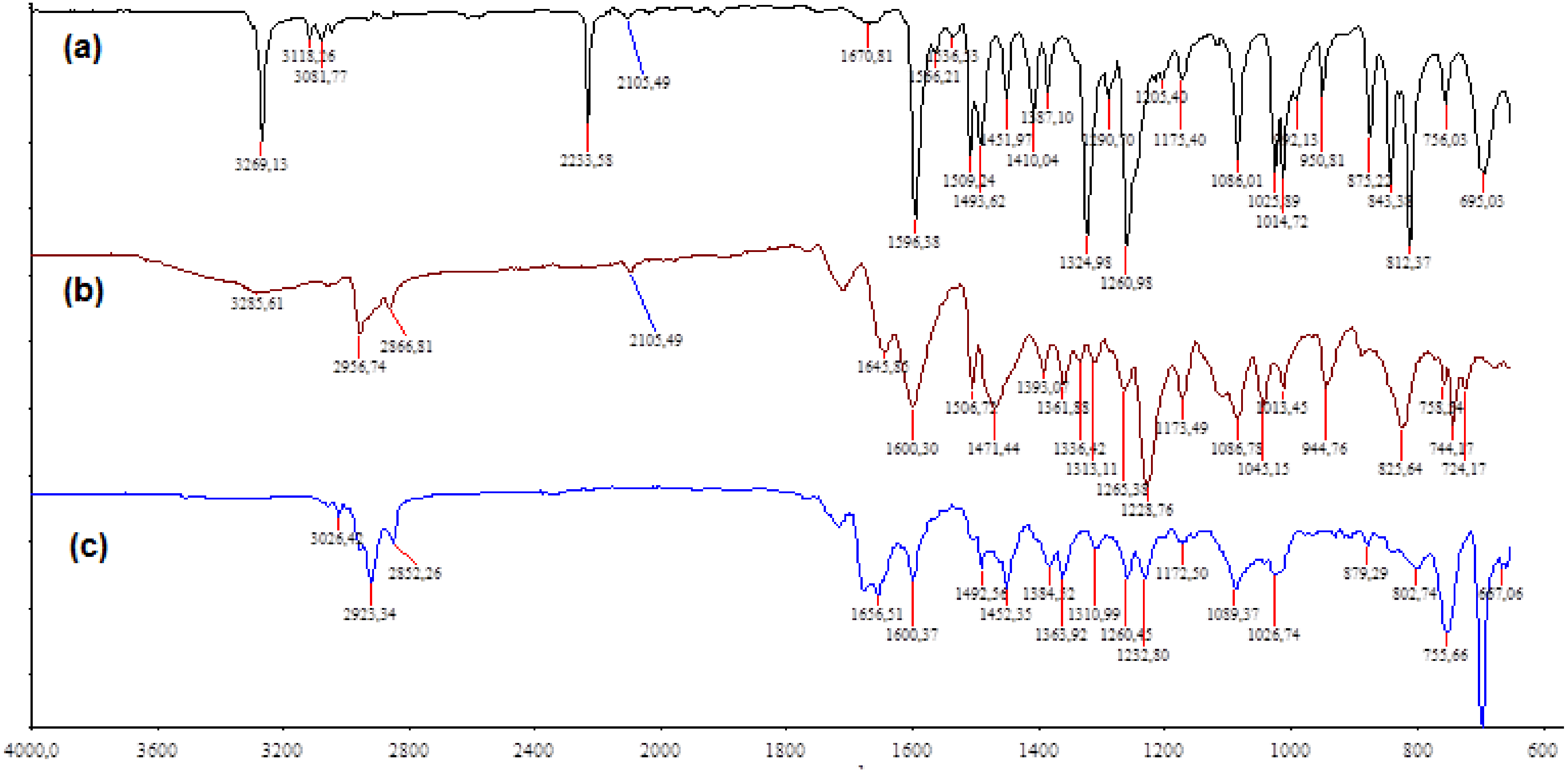


Figure 4.1: FTIR spectrum of (a) 4, (b) ZnPc, (c) PS-ZnPc

In Figure 4.1, it was apparently shown that the click reaction occurred over the ZnPc substrate. Since we monitored the C≡C-H peak, which is characteristic for monosubstituted **4** compound as we took it as a model for click reaction, the reaction was seen to proceed successfully. C≡C and C-H stretching vibrations of the FTIR spectrum of ZnPc compound were seen at 3269 and 2105 cm^{-1}, respectively, and this obviously proves that the Pc obtained has an ethynyl moiety. After click reaction, the FTIR can be seen in Figure 4.1 (c) and it proves the formation of triazol ring by opening of the triple bond after 1,3-dipolar cycloaddition, as evident in the absence of the peaks 3269 and 2105 cm^{-1}.

The process of click reaction was also monitored over the polymer structure.

The successful azidation was observed with a N_3-based stretching peak at 2011 cm^{-1}, visible in the spectrum of PS-N_3 but not PS-Br. Additionally, the characteristic peak of the azide group can be monitored to see the click reaction coming true. The absence of 2011 cm^{-1} FTIR peak in PS-N_3 in the spectrum of click product is another proof for successful transformation (Figure 4.2).

UV-Vis spectra are useful to differentiate between azide-containing polystyrene and the click product. When the UV-Vis spectrum of the click product was examined, the Q and B bands of the phthalocyanine macrocycle were observed at 675 and 352 nm, respectively. In addition to the previous observation, the peak at 362 nm is the proof of successful azidation of the PS-Br structure, with the special band of azidation. The composite’s UV-Vis spectrum shows that this peak at 362 nm disappears completely after cyclization. These UV-Vis data can be used as proof for obtaining the desired final structure as expected (Figure 4.3).

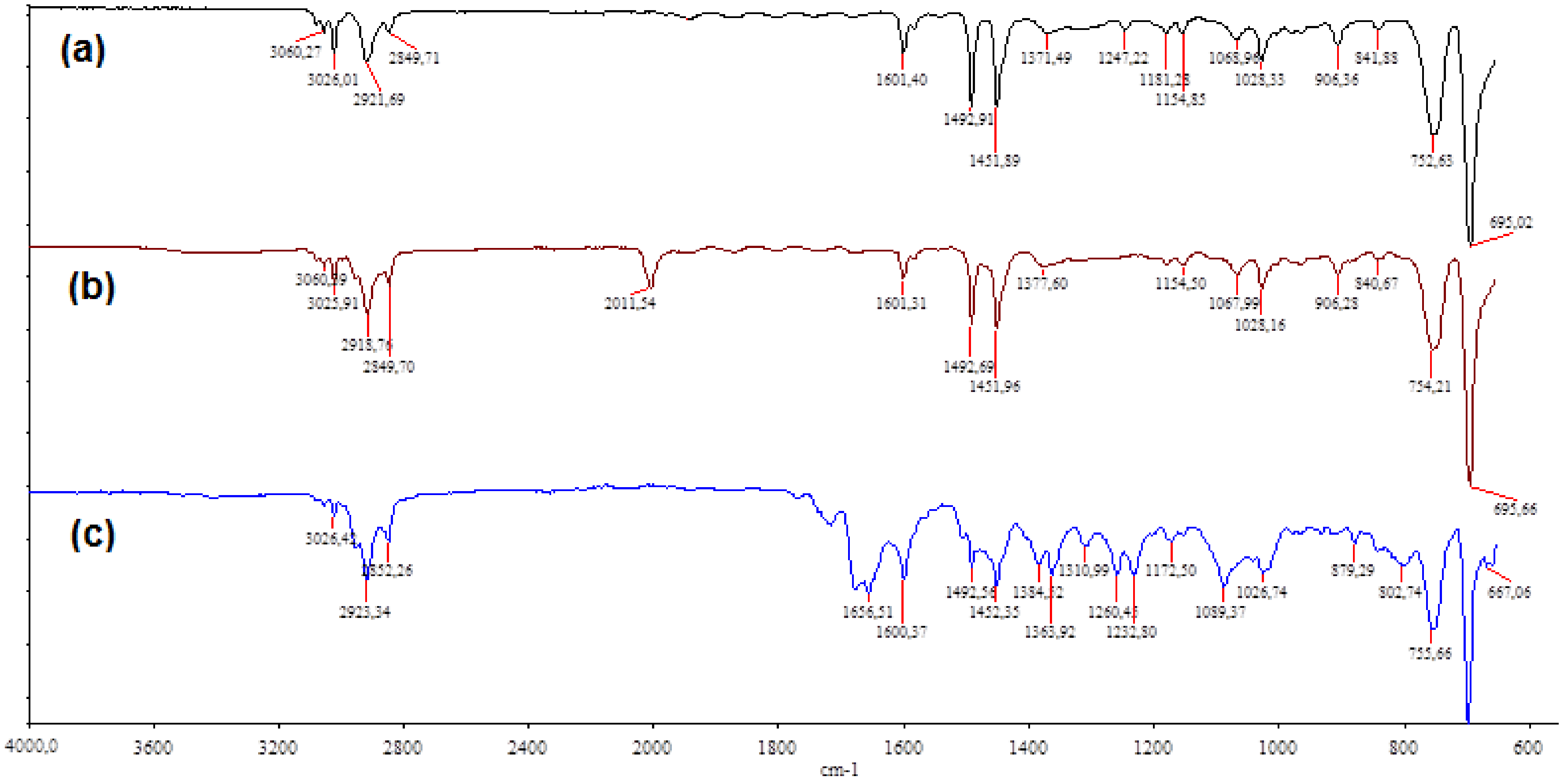


Figure 4.2: FTIR spectrum of (a) PS-Br, (b) PS-N_3, (c) PS-ZnPc.

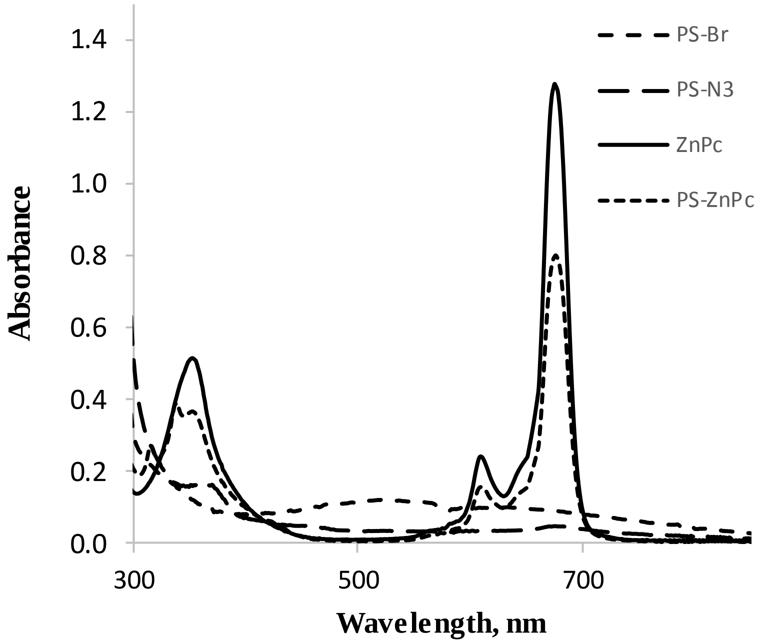


Figure 4.3: UV-Vis spectrum of (a) PS-Br, (b) PS-N_3, (c) PS-ZnPc.

In addition to these analyses, ^{1}H-NMR spectrum was examined to see the steps of click procedure and the results. PS-Br and PS-N_3 spectra were examined and the CH-Br peak at δ 3.65 ppm shifted to δ 3.41 after azidation. Lastly, the ^{1}H-NMR spectrum of the final compound had the above-mentioned peak at δ 5.17 ppm. The peak at δ 5.20 ppm is due to the -O-CH_2 group of the zinc phthalocyanine. The ^{1}H-NMR spectrum of the click product showed a triazole peak at δ 8.1 ppm. The peaks between δ 6.5 – 7.8 ppm are both due to the aromatic benzene ring protons of the phthalocyanine and polymeric backbone.

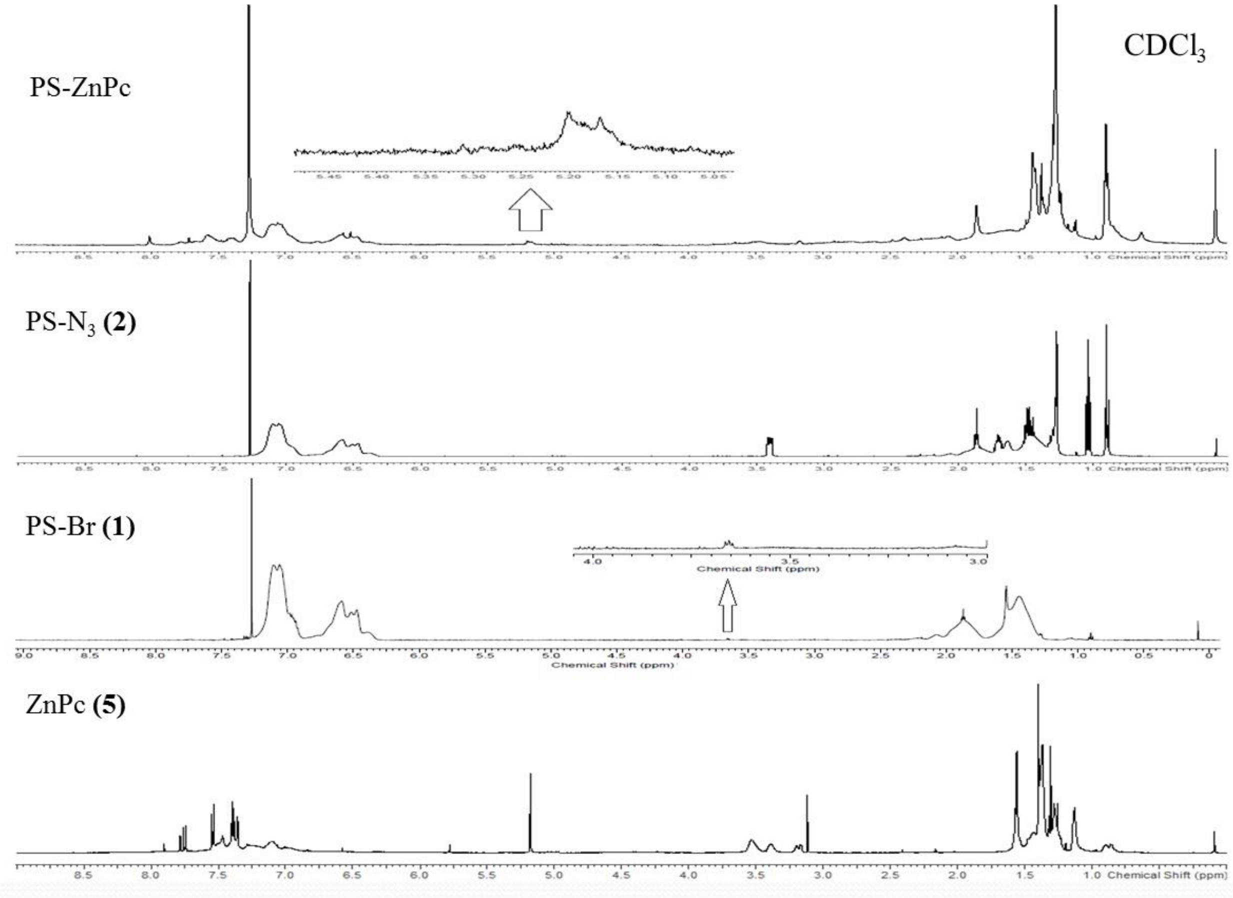


Figure 4.4: ^{1}H-NMR spectrum of ZnPc, PS-Br, PS-N_3, PS-ZnPc.

A consideration of the above data shows that the –CH-Br peak at δ 3.65 for PS-Br converts to δ 3.41 ppm for the –CH-N_3 moiety. Moreover, the shifting of δ 3.41 ppm signal to δ 5.17 ppm after click reaction is indicative of a change of the chemical environment of the PS proton, which is caused by the triazole ring after click reaction (Figure 4.4). The newly formed peak at δ 8.1 ppm around the aromatic region is due to the triazole ring. All of these ^{1}H-NMR data show us that every phase of the synthesis provided us with the expected molecules.

5. CONCLUSION

Phthalocyanines are important materials finding applications in many fields from photocatalytic events to photodynamic therapy. A frequently encountered problem in phthalocyanine based materials is aggregation of planar molecules which prohibit number of photochemical events. In the present work by combining phthalocyanine with a polystyrene backbone a solution to above cited problems have been proposed. Therefore, we can say that various applications of synthesized polystyrene-unsymmetrical zinc phthalocyanine composites deserve to be investigated by high-tech experts.

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APPENDIXES

APPENDIX A: Spectral data of the compounds.

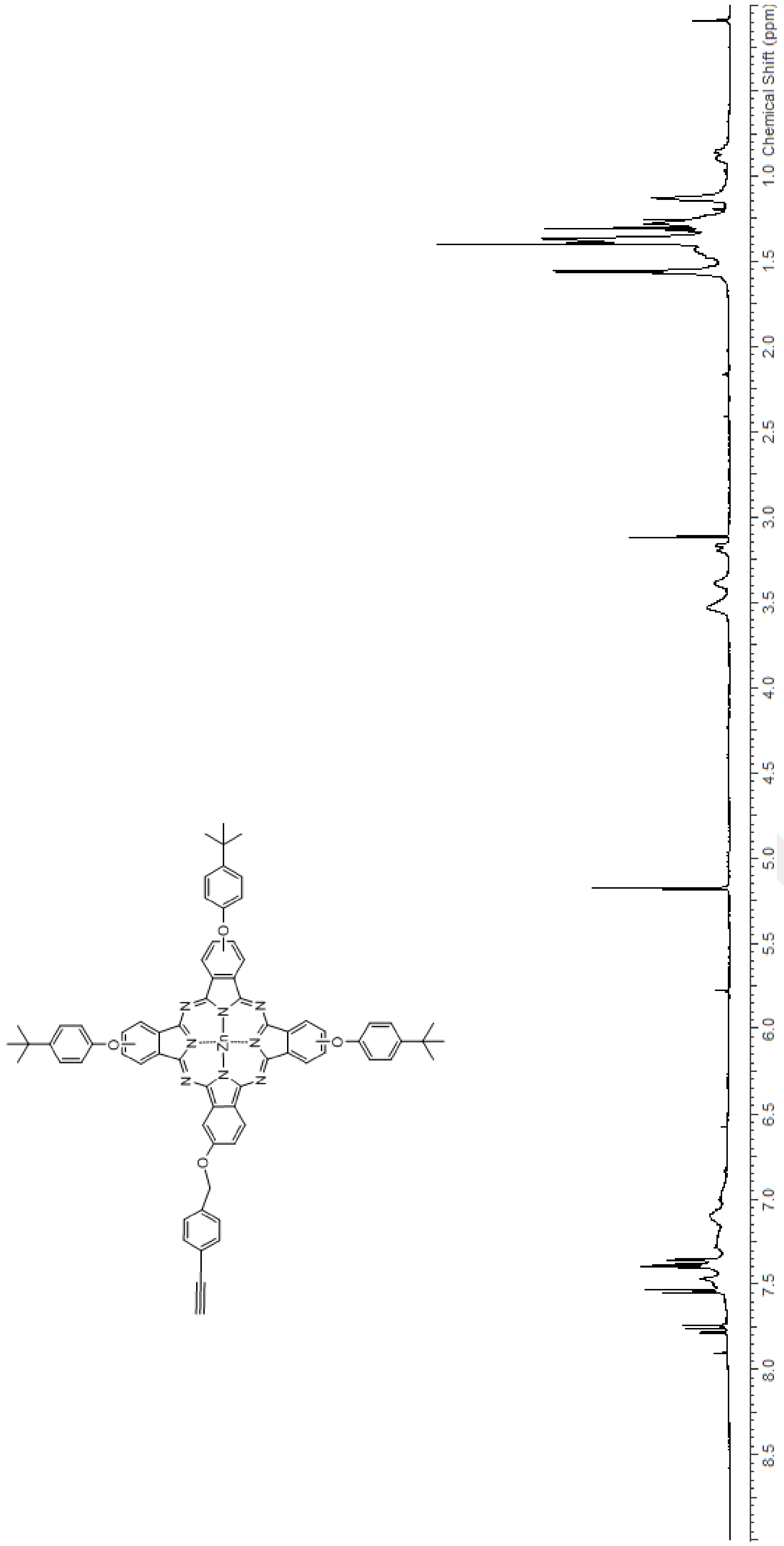

Figure A. 1: ^{1}H-NMR spectrum of unsymmetrical ZnPc.

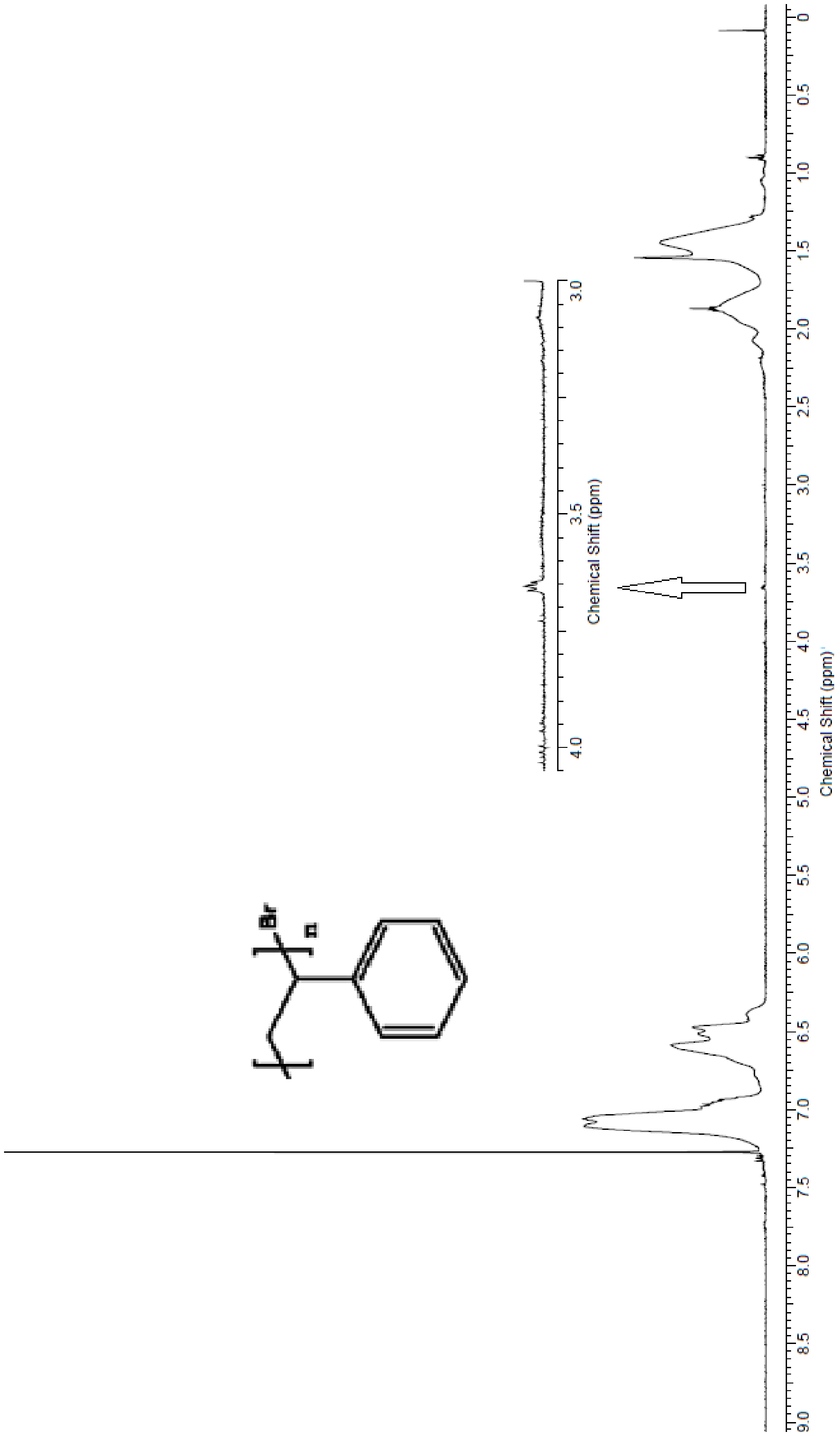

Figure A. 2: ^{1}H-NMR spectrum of PS-Br.

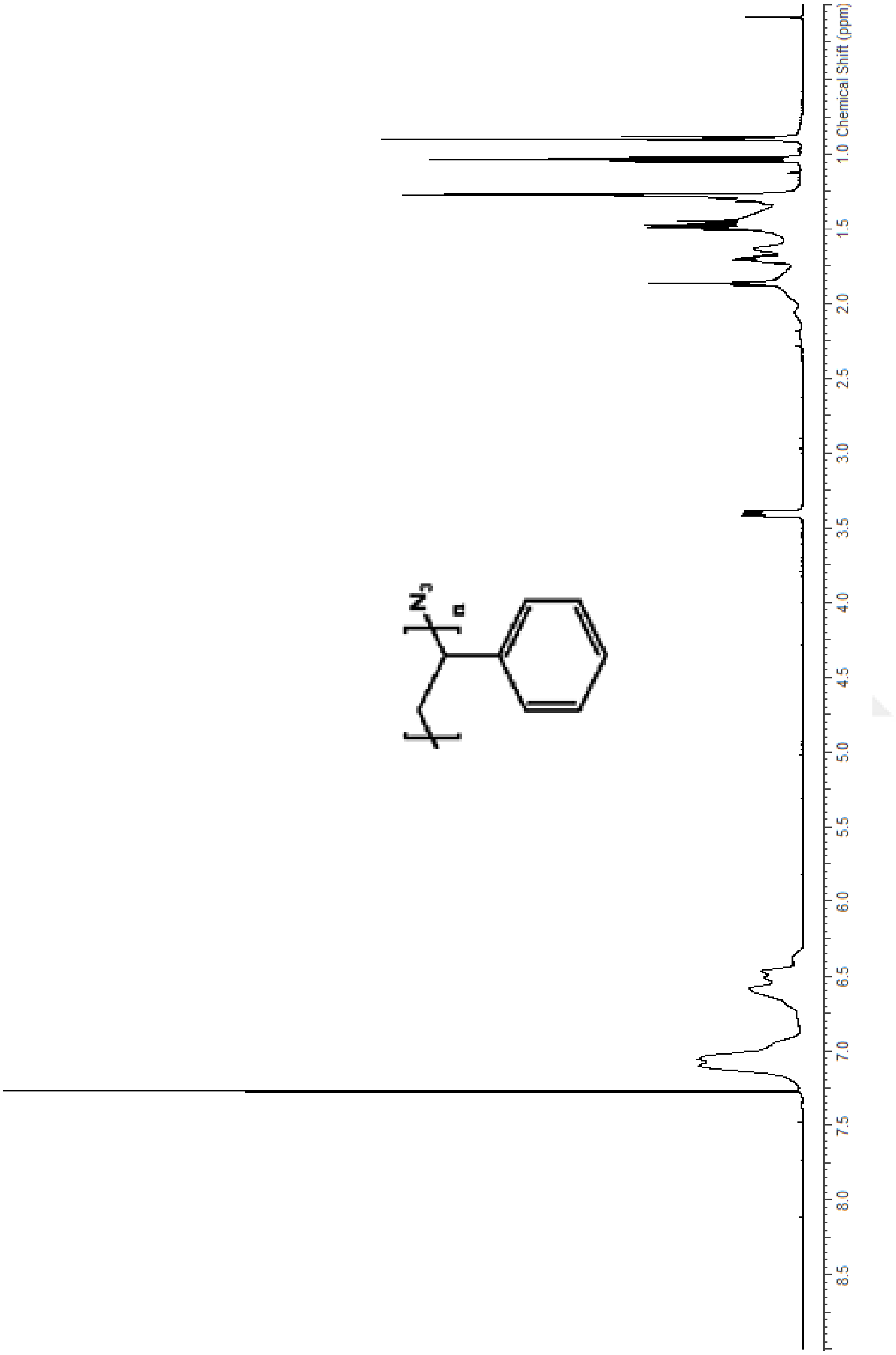

Figure A. 3: ^{1}H-NMR spectrum of PS-N_3.

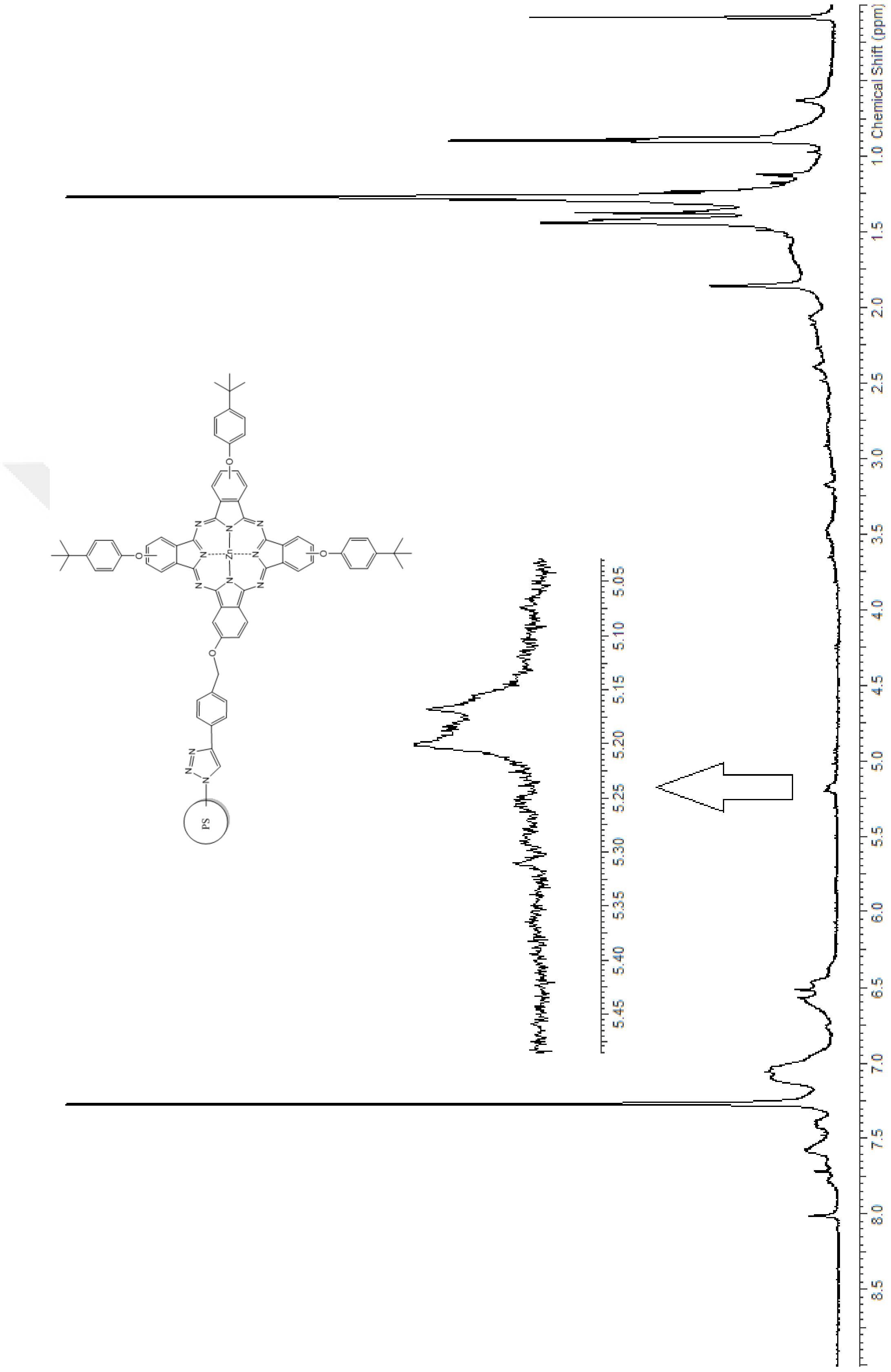

Figure A. 4: ^{1}H-NMR spectrum of PS-ZnPc.

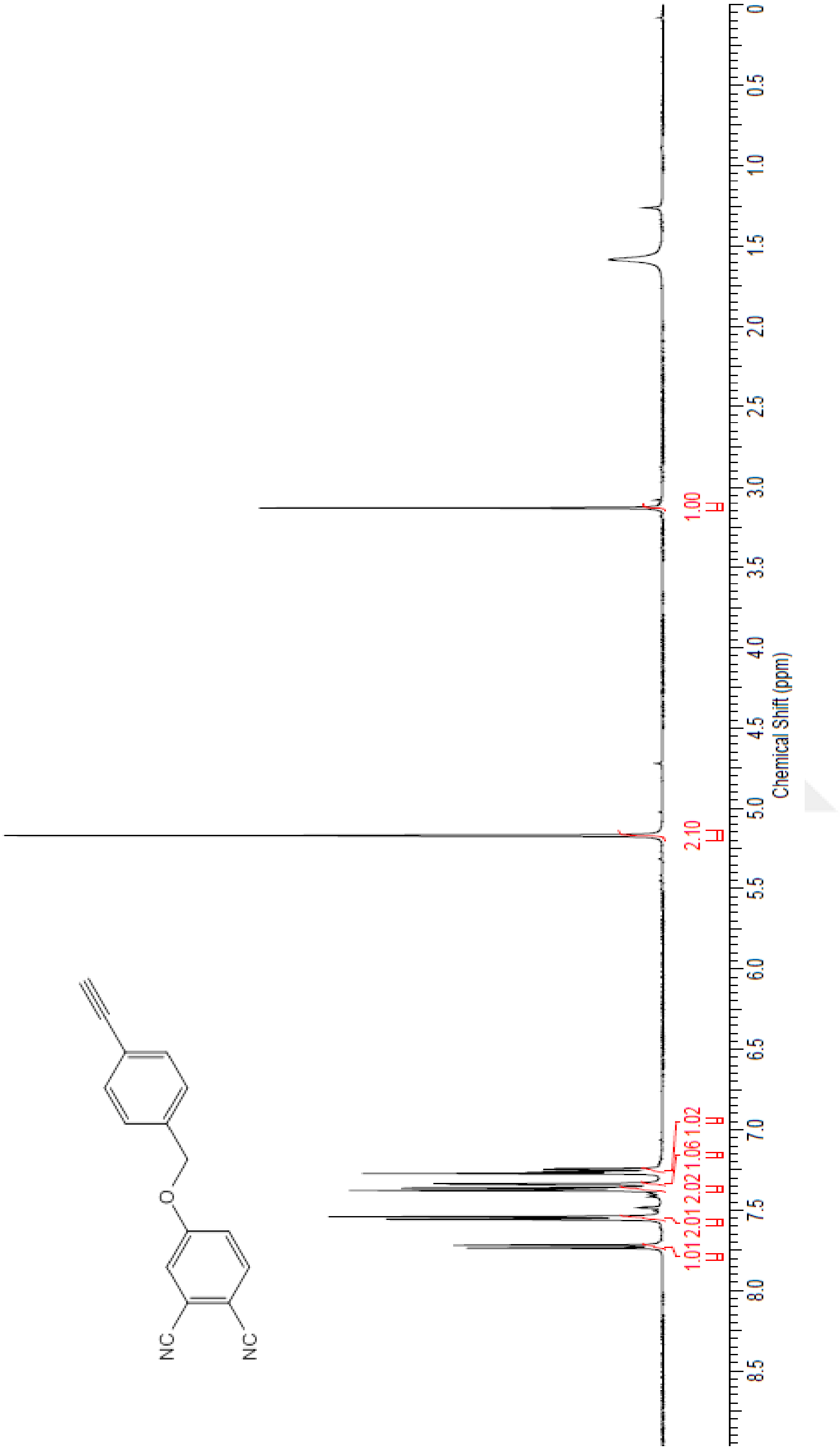

Figure A. 5: ^{1}H-NMR spectrum of 4-((4-ethynylbenzyl)oxy)phthalonitrile.

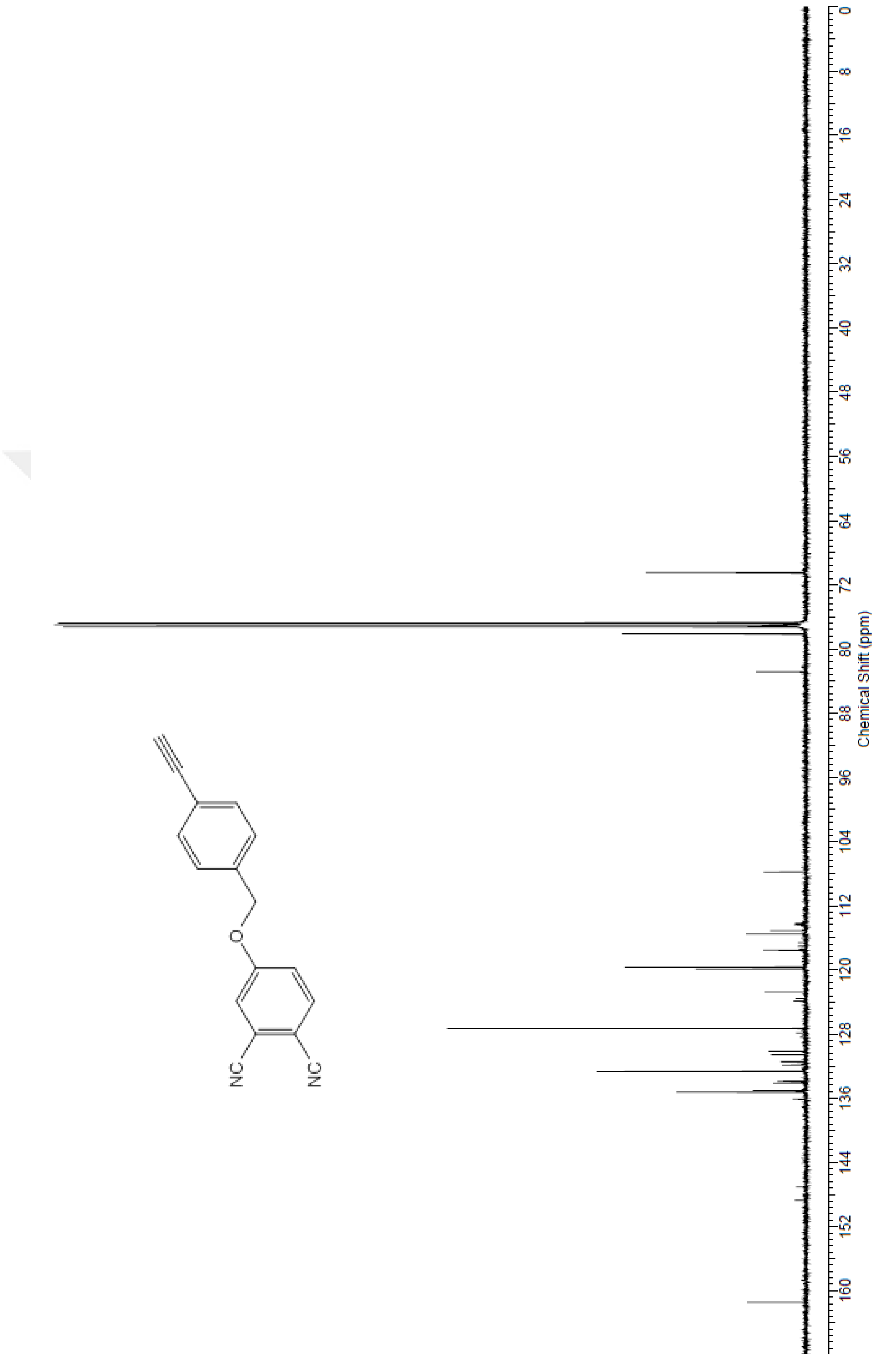

Figure A. 6: ^{13}C-NMR spectrum of 4-((4-ethynylbenzyl)oxy)phthalonitrile.

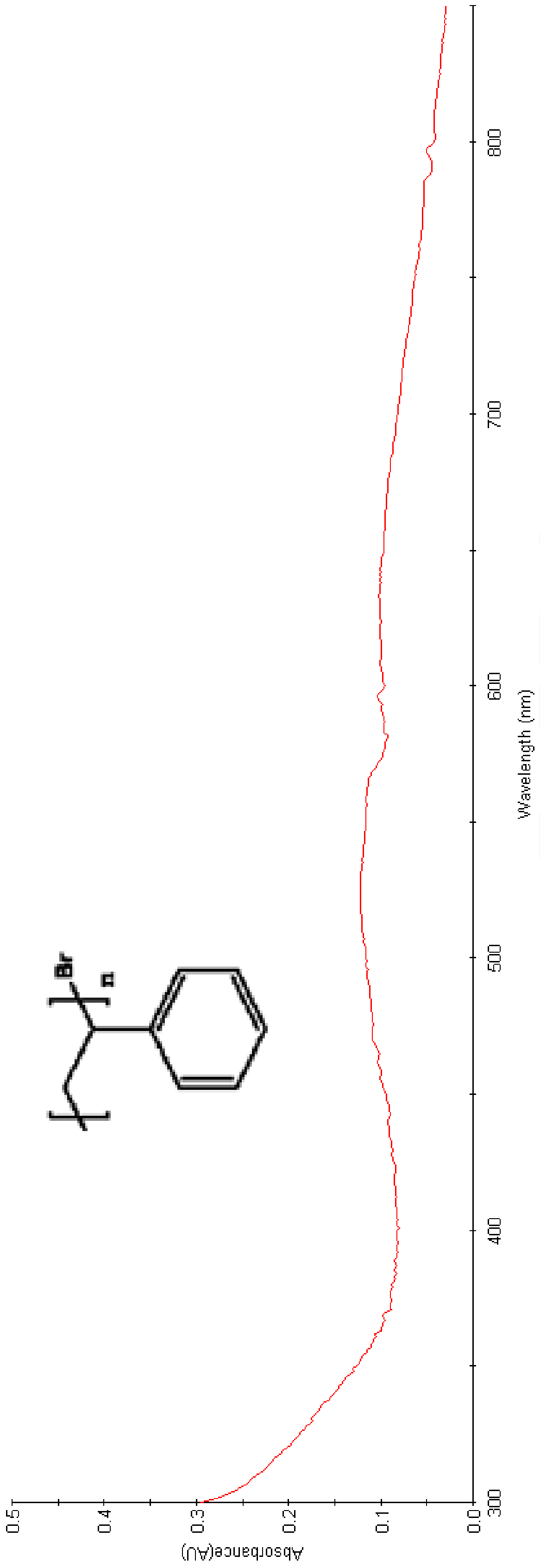

Figure A. 7: UV-Vis spectrum of PS-Br.

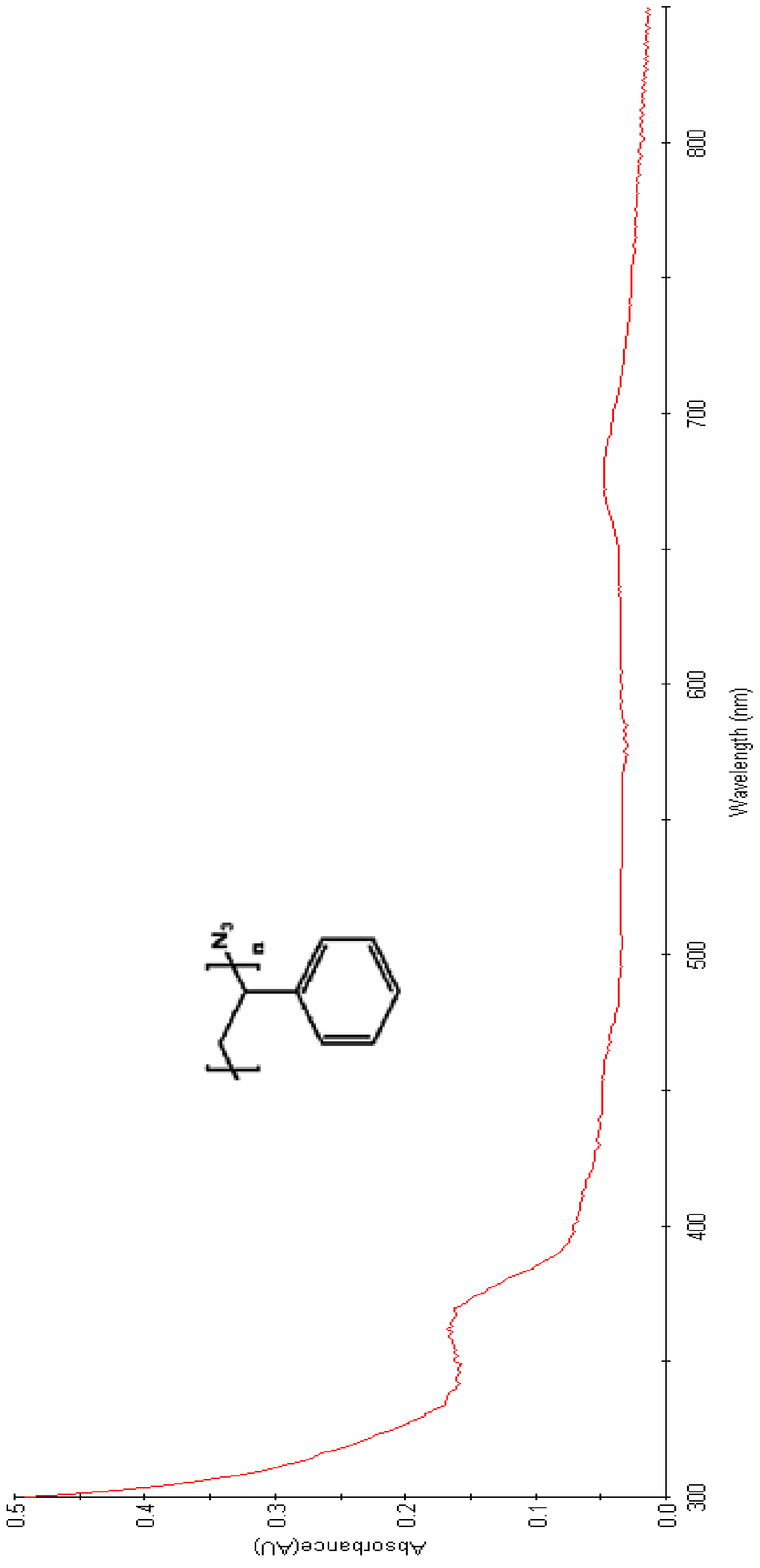

Figure A. 8: UV-Vis spectrum of PS-N_3.

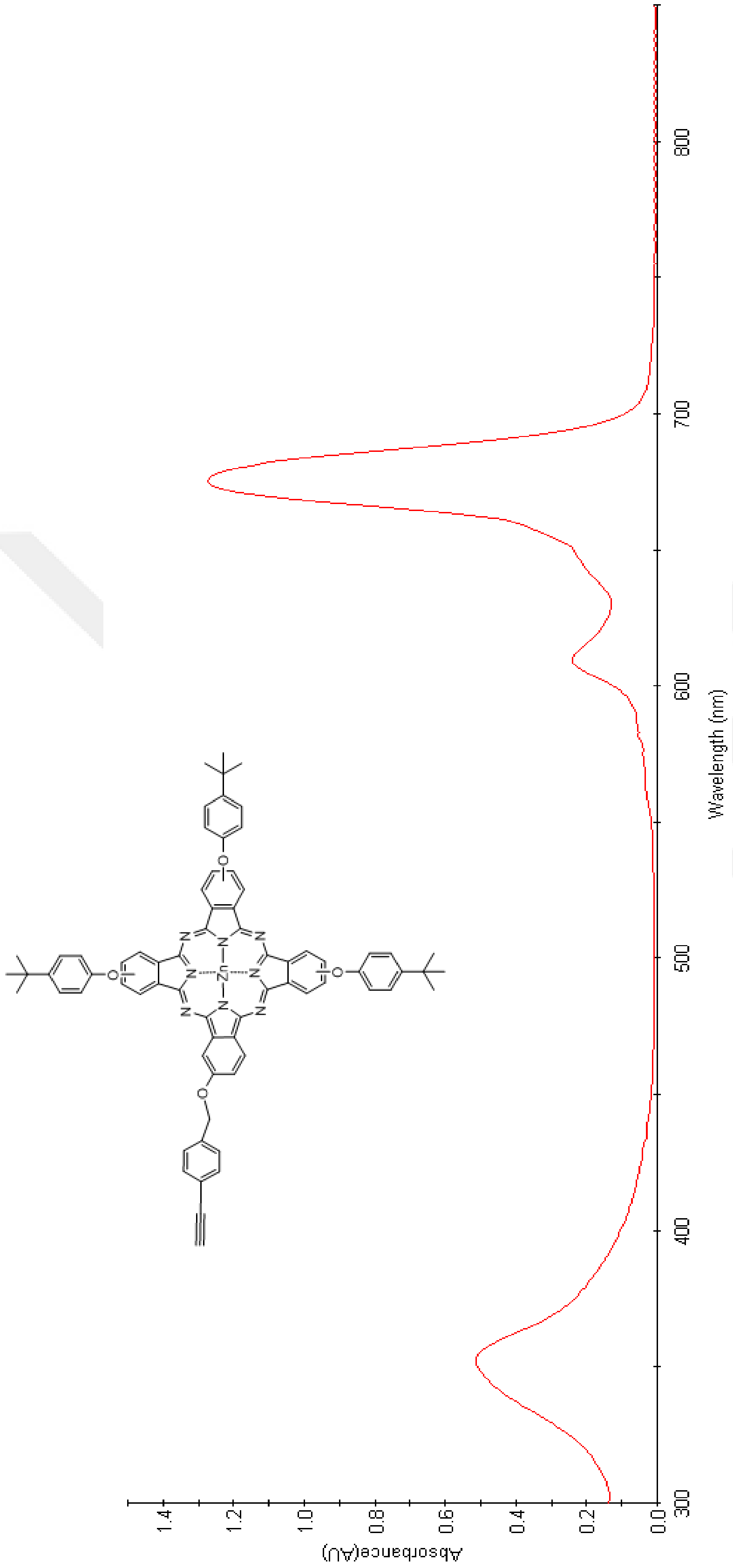

Figure A. 9: UV-Vis spectrum of ZnPc.

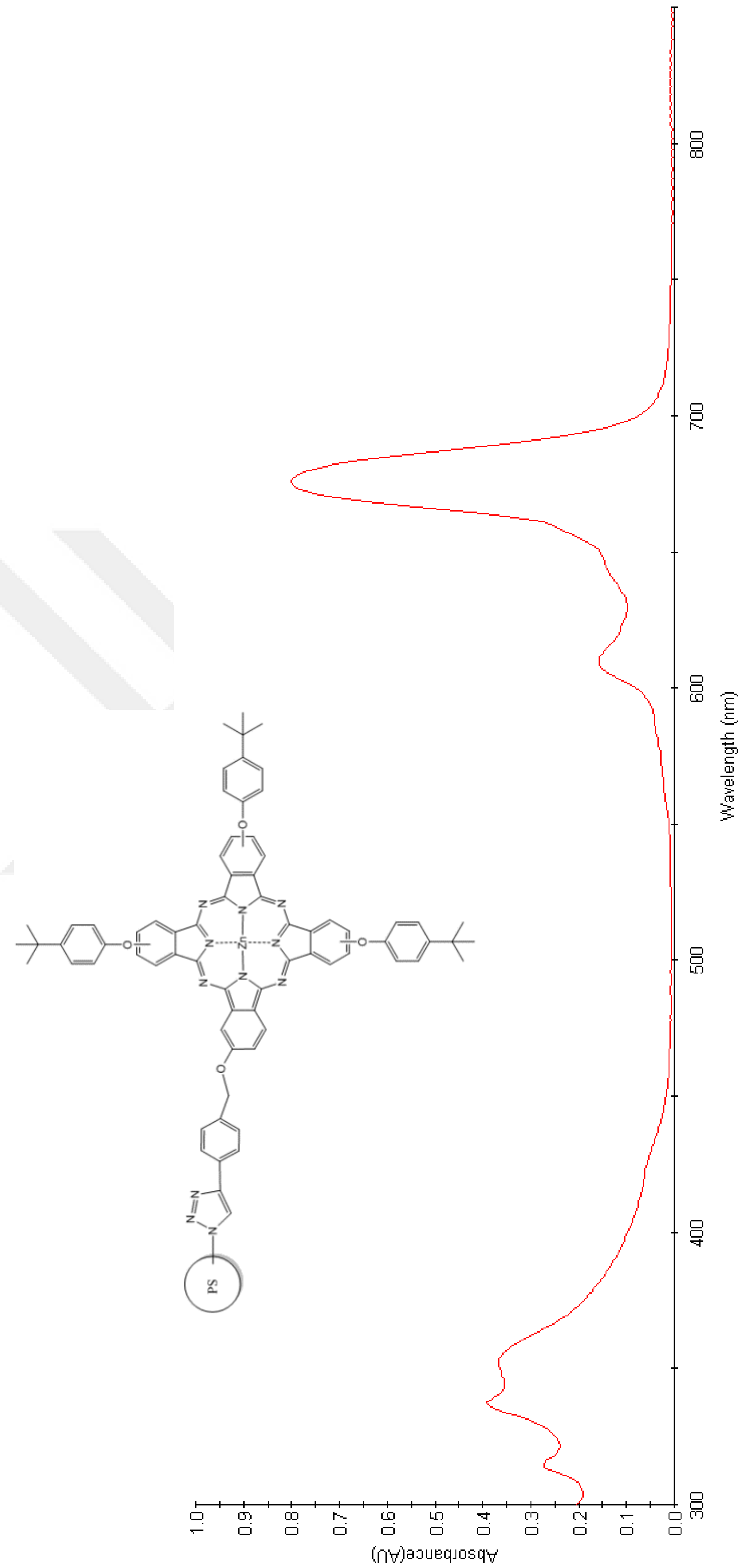

Figure A. 10: UV-Vis spectrum of PS-ZnPc.

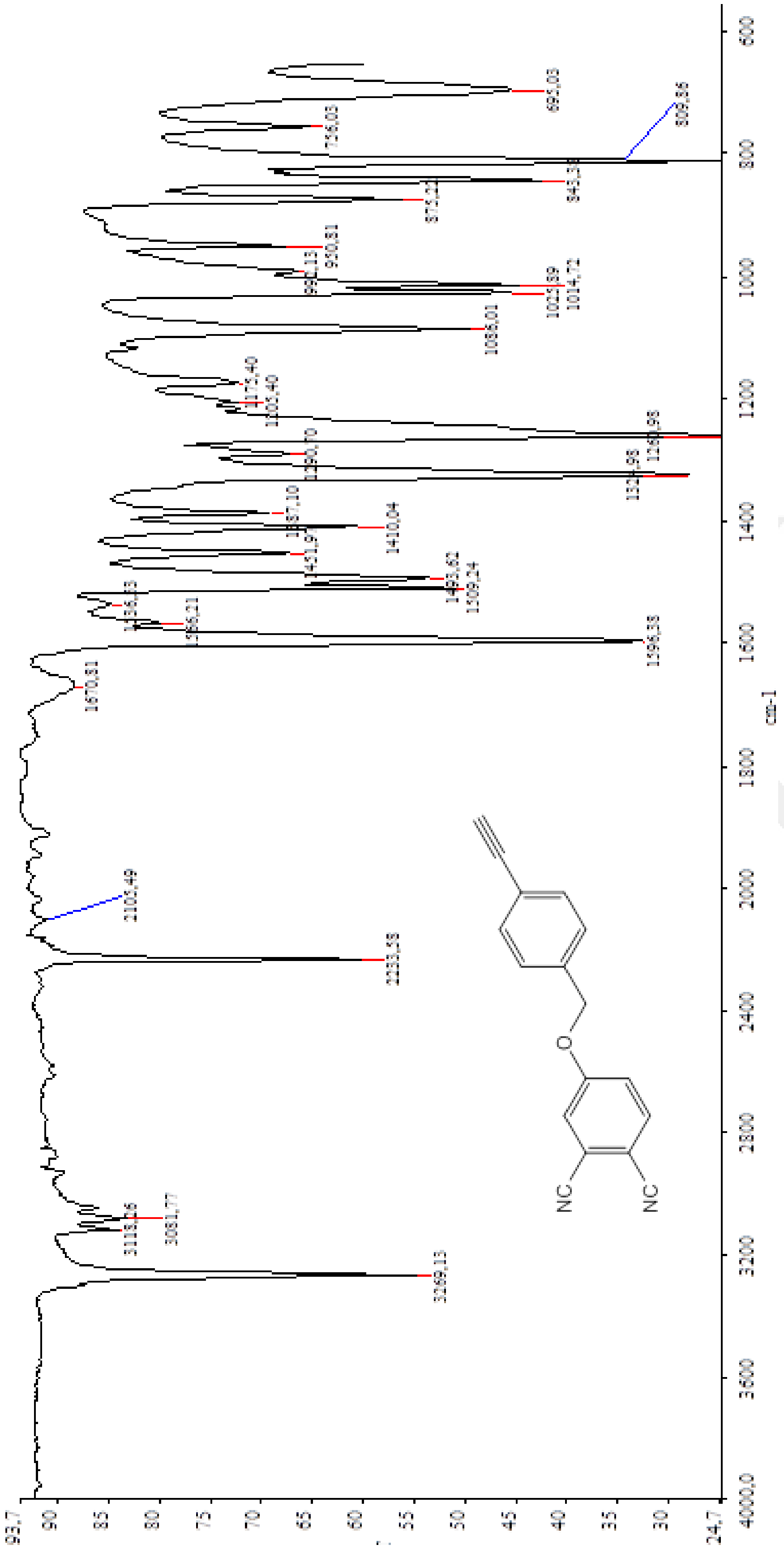

Figure A. 11: FT-IR spectrum of **(4)**.

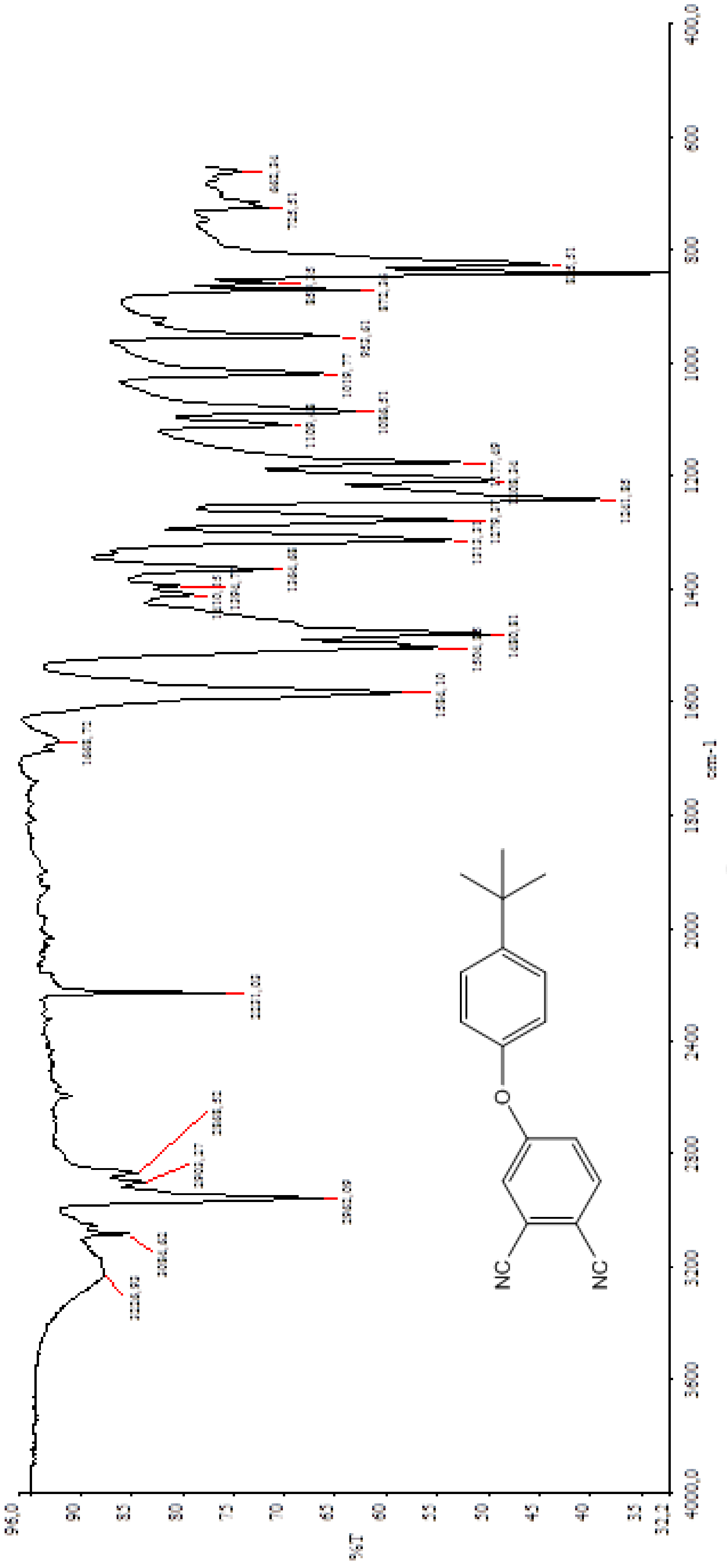

Figure A. 12: FT-IR spectrum of **(3)**.

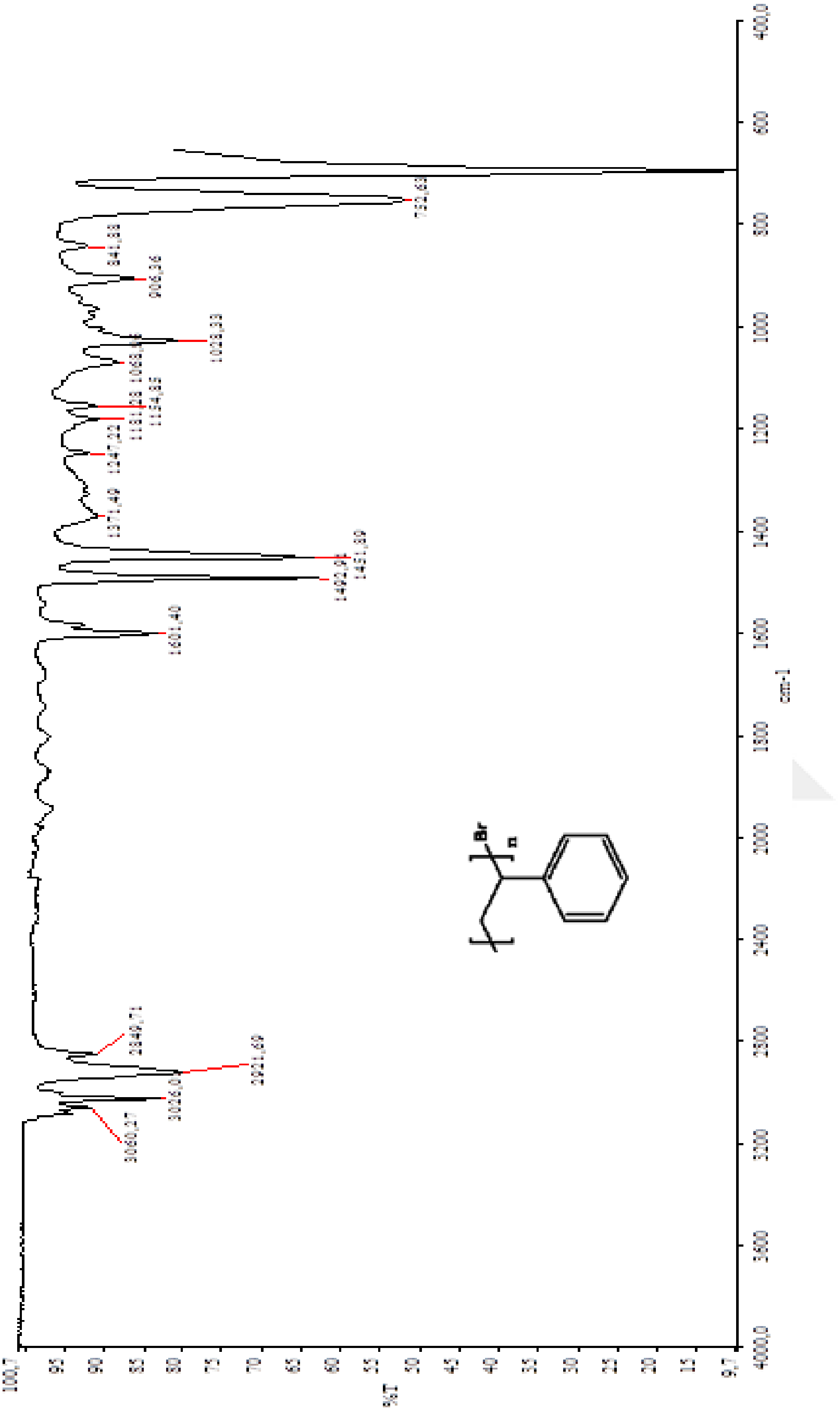

Figure A. 13: FT-IR spectrum of PS-Br.

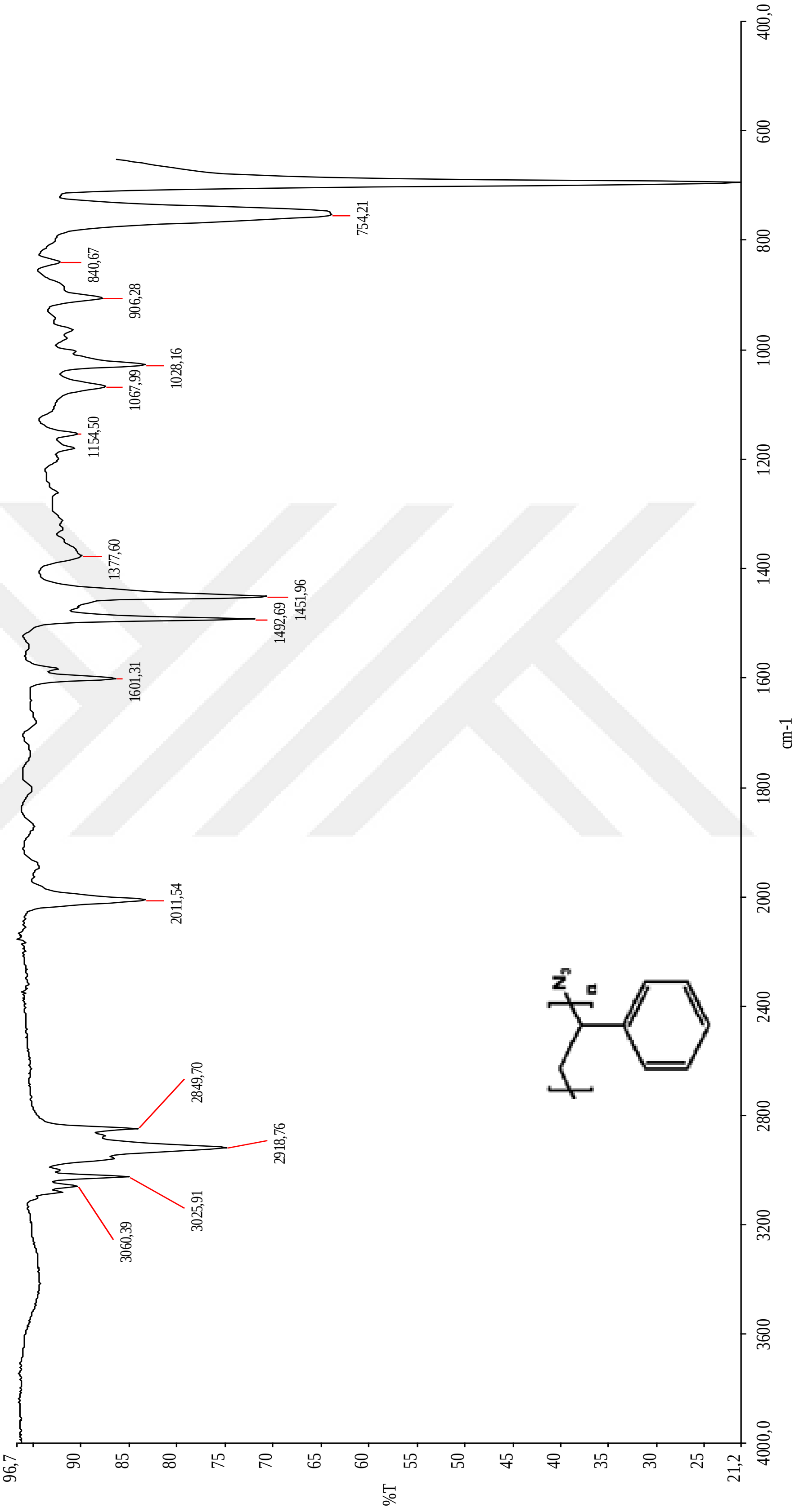

Figure A. 14: FT-IR spectrum of PS-N_3.

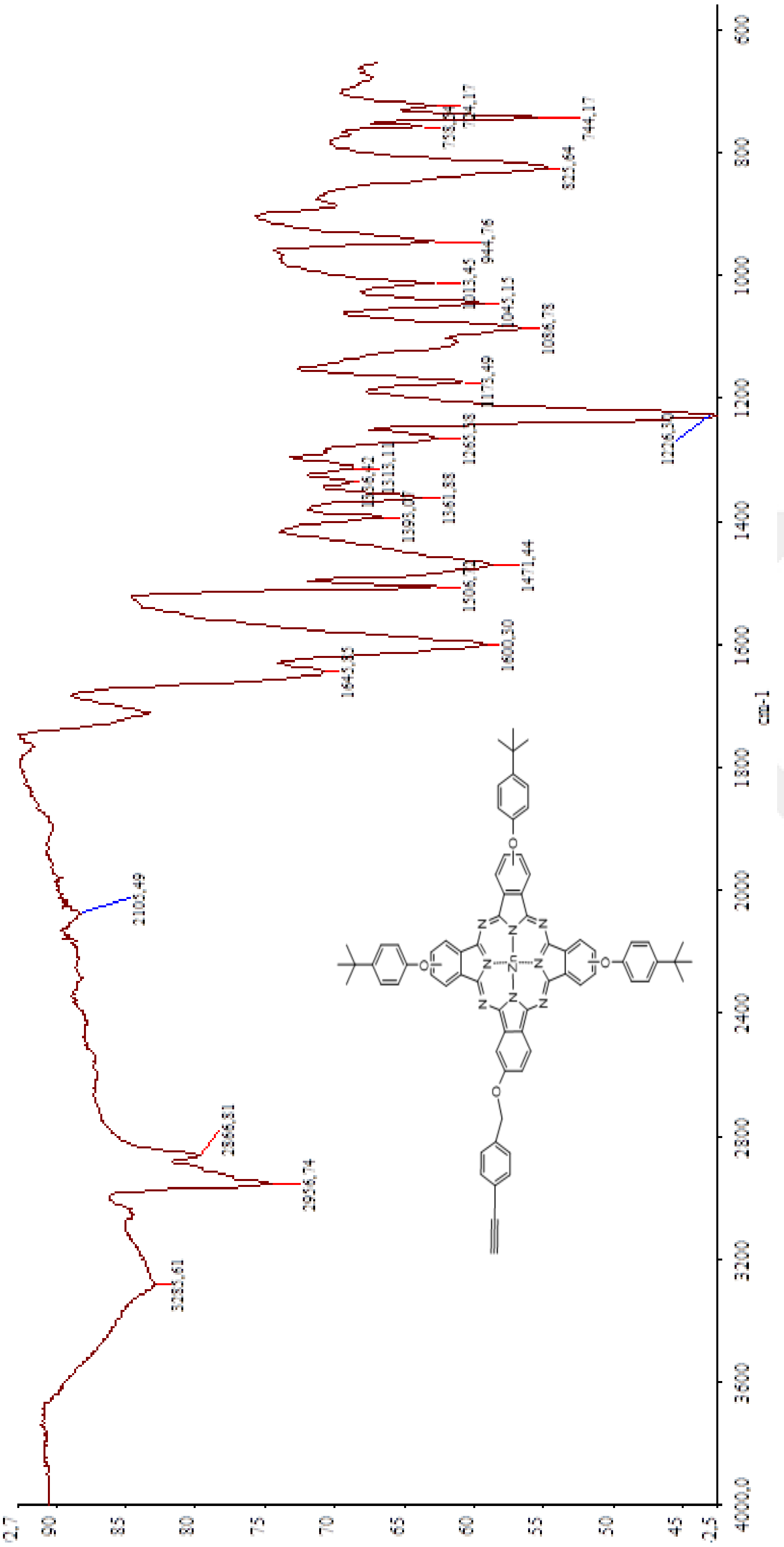

Figure A. 15: FT-IR spectrum of ZnPc.

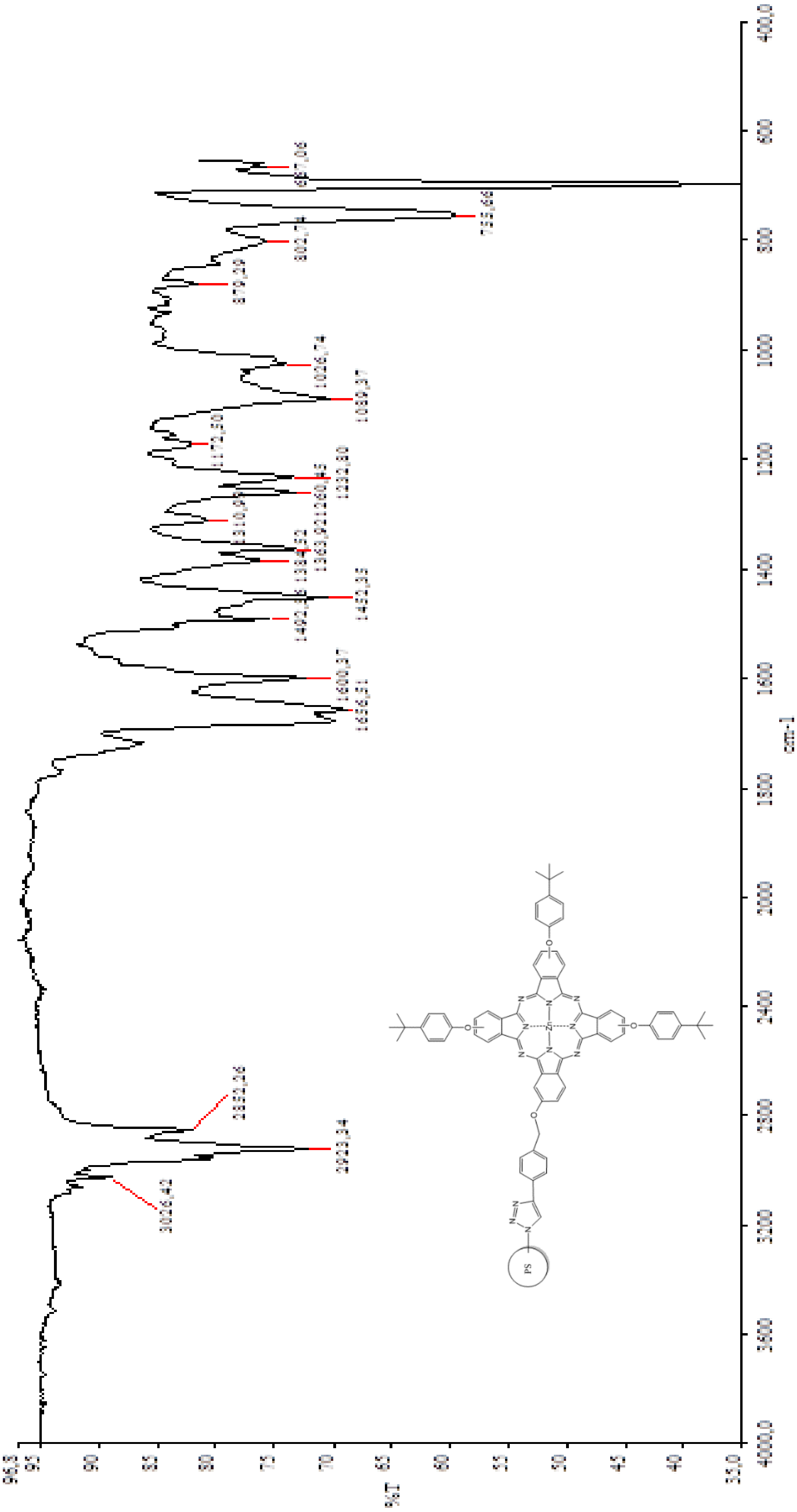

Figure A. 16: FT-IR spectrum of PS-ZnPc.

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