SYNTHESIS AND CHARACTERIZATION OF TETRANITRO AND TETRAAMINO ZINC PHTHALOCYANINES AND THEIR COMBINATIONS WITH MICA-TITANIA PIGMENT

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SYNTHESIS AND CHARACTERIZATION OF TETRANITRO AND TETRAAMINO ZINC PHTHALOCYANINES AND THEIR COMBINATIONS WITH MICA-TITANIA PIGMENT

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ABSTRACT

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In the present study, tetranitro and tetraamino substituted zinc phthalocyanine were synthesized by using nitro phthalic acid precursor under microwave irradiation. The products were purified using different solvents. Molecular structures of these phthalocyanine pigments were confirmed by FT-IR and UV-visible spectroscopy analyses. Each of these pigments was settled on the surface mica-titania pigment to obtain ‘combination pigment’. Tetraamino zinc phthalocyanine was deposited on mica-titania in water and in dimethyl formamide used as solvent, while tetranitro zinc phthalocyanine was deposited in chloroform. The pH effect was investigated by using acetic acid and trifluoro acetic acid. The conditions for optimum deposition time, solvent, pH and the amount of phthalocyanine were studied. The FT-IR, XPS and elemental analysis were conducted to analyze the pigment deposited on the surface of the mica-titania substrate. Moreover, the fluorescence properties of tetranitro and tetraamino zinc phthalocyanines and their combinations by mica-titania pigment were obtained in DMF solvent. The surface morphology of synthesized pigments was analyzed by scanning electron microscopy (SEM). The paint samples of these pigments were prepared by water based styrene acrylic resin formulation. The L*a*b* color properties of the pigments were examined by color spectrophotometer.

These analyses indicated that pigments were successfully synthesized and combined with mica-titania pigment. The best result with tetranitro zinc phthalocyanine was obtained in chloroform solvent at 50°C, in 5h, and at a pH of 5; while the best result with tetraamino zinc phthalocyanine in DMF with acetic acid at 120°C, in 3h and at a pH of 4. The amount deposited increased with the amount of phthalocyanines in solution. Mica-titania substrate reduced the fluorescence of phthalocyanine pigments. But on the other side, the fluorescent property of the mica-titania were developed with combination of tetra amino and nitro phthalocyanines. It was observed that, with the increasing amount of tetranitro and tetraamino zinc phthalocyanine, the deposited amount of pigment increased on mica-titania, as well. As a result high gloss fluorescent combined pigments with different colors were successfully synthesized.

Keywords: Mica-titania, tetranitro zinc phthalocyanine, tetraamino zinc phthalocyanine, combination pigment, fluorescence.

ÖZ

TETRANİTRO VE TETRAAMİNO ÇİNKO FTALOSİYANİN PİGMENTLERİNİN SENTEZİ, ÖZELLİKLERİNİN BELİRLENMESİ VE MİKA-TİTANYUM DİOKSİT PİGMENTİ İLE BİRLEŞİK PİGMENT YAPIMI

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Bu çalışmada, nitro ftalik asit ve öncülleri kullanılarak mikrodalga ortamında tetranitro çinko ftalosiyanin ve tetraamino çinko ftalosiyanin pigmentleri sentezlendi. Elde edilen ürünler farklı çözücüler kullanılarak saflaştırıldı. Bu ftalosiyaninlerin moleküler yapıları FT-IR ve UV-visible spektroskopi analizleri ile doğrulandı. Bu pigmentler, mika-titan pigmenti üzerine çöktürülerek birleşik pigment elde edildi. Tetraamino çinko ftalosiyanin su ve dimetilformamit çözücüleri içerisinde mika-titan yüzeyine çöktürülürken, tetranitro ftalosiyanin kloroform çözücüsü içerisinde mika-titan üzerine çöktürüldü. Ortamın pH etkisi asetik asit ve trifloro asetik asit kullanılarak incelendi. En uygun koşullar çöktürme süresi, çözücü, pH ve farklı miktarda ftalosiyanin kullanımı ile araştırıldı. Mika-titan yüzeyine çöktürülmüş pigmentleri belirlemek için FT-IR, XPS ve elemental analizleri yapıldı. Bunun yanı sıra, DMF içerisinde tetranitro ve tetraamino çinko ftalosiyaninlerin ve onların mika-titan ile oluşturdukları pigmentlerin floresans özelllikleri floresans spekroskopi ile gözlendi. Sentezlenen birleştirilmiş pigmentlerin yüzey bilgileri elektron taramalı mikroskop (SEM) ile analiz edildi. Bunlara ek olarak, su esaslı stiren-akrilik reçinesindeki pigmentlerin L*a*b* renk özellikleri renk spektrofotometresi ile incelendi.

Yapılan analizler pigmentlerin başarıyla sentezlendiğini ve mika-titan üzerine çöktürüldüğünü gösterdi. En iyi sonuçlanan birleştirilmiş pigmentlerden biri, 50°C'de, 5 saatte, pH=5'te tetranitro çinko ftalosiyaninin kloroform içinde çöktürülmesi; diğeri ise 120°C'de, 3 saatte ve pH=4'te DMF ve asetik asit varlığında tetraamino çinko ftalosiyaninlerin mika-titan üzerine çöktürülmesidir. Mika-titan pigmenti üzerine çöken ftalosiyaninin floresans etkisini bir miktar azaltmaktadır. Diğer bir yandan, tetraamino ve nitro ftalosiyaninlaerin mika-titan pigmenti üzerine çöktürülmesi, mika-titanların floresans özelliklerini geliştirdiği gözlendi. Tetranitro ve tetraamino çinko ftalosiyaninlerin miktarları artmasıyla, mika-titan üzerine çöken miktarlarda artma gözlendi. Sonuç olarak, farklı renklerde, parlak görünümlü, floresans pigmentler elde edilmiştir.

Anahtar sözcükler: Mika-titan, tetranitro çinko ftalosiyanin, tetraamino çinko ftalosiyanin, bileşenli pigment, floresans.

Şevkiz ki dem-i bülbül-i şeydâdâ nihânız
Hûnuz ki dil-i gonce-i hamrâda nihânız

Biz cism-i nizâr üzre döküp dâne-i eşki
Çun rîşte-i cân gevher-i ma'nâda nihânız

Olsak n'ola bî-nâm ü nişan şöhre-i âlem
Biz dil gibi bir turfe muammada nihânız

Mahrem yine her hâlimize bâd-ı sabâdır
Dâim şiken-i zülf-i dil-ârâda nihânız

Hem gül gibi rengînî-i ma'nâ île zahir
Hem neş'e gibi hâlet-i sahbâda nihânız

Geh hâme gibi şekve-tırâz-ı gam-ı aşkız
Geh nâle gibi hâme-i şekvada nihânız

Etdik o kadar ref'-i taayyün ki Neşâtî
Âyîne-i pür-tâb-i mücellâda nihânız

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LIST OF SYMBOLS AND ABBREVIATIONS

AA	Acetic Acid
$CHCl_3$	Chloroform
DMF	Dimethyl Formamide
DMSO	Dimethyl Sulfoxide
FT-IR	Fourier Transform Infrared Spectroscopy
HCl	Hydrochloric Acid
METU	Middle East Technical University
NaOH	Sodium Hydroxide
TAZnPc	Tetraamino Zinc Phthalocyanine
TAZnPcMip	Combination pigment of Tetraamino Zinc Phthalocyanine with Mica-Titania
TFA	Trifluoro Acetic Acid
TNZnPc	Tetranitro Zinc Phthalocyanine
TNZnPcMip	Combination pigment of Tetranitro Zinc Phthalocyanine with Mica-Titania
SEM	Scanning Electron Microscopy
UV-Vis	Ultraviolet-Visible Spectroscopy
UNAM	Bilkent University National Nanotechnology Research Center
XPS	X-Ray Photoelectron Spectroscopy

CHAPTER 1

INTRODUCTION

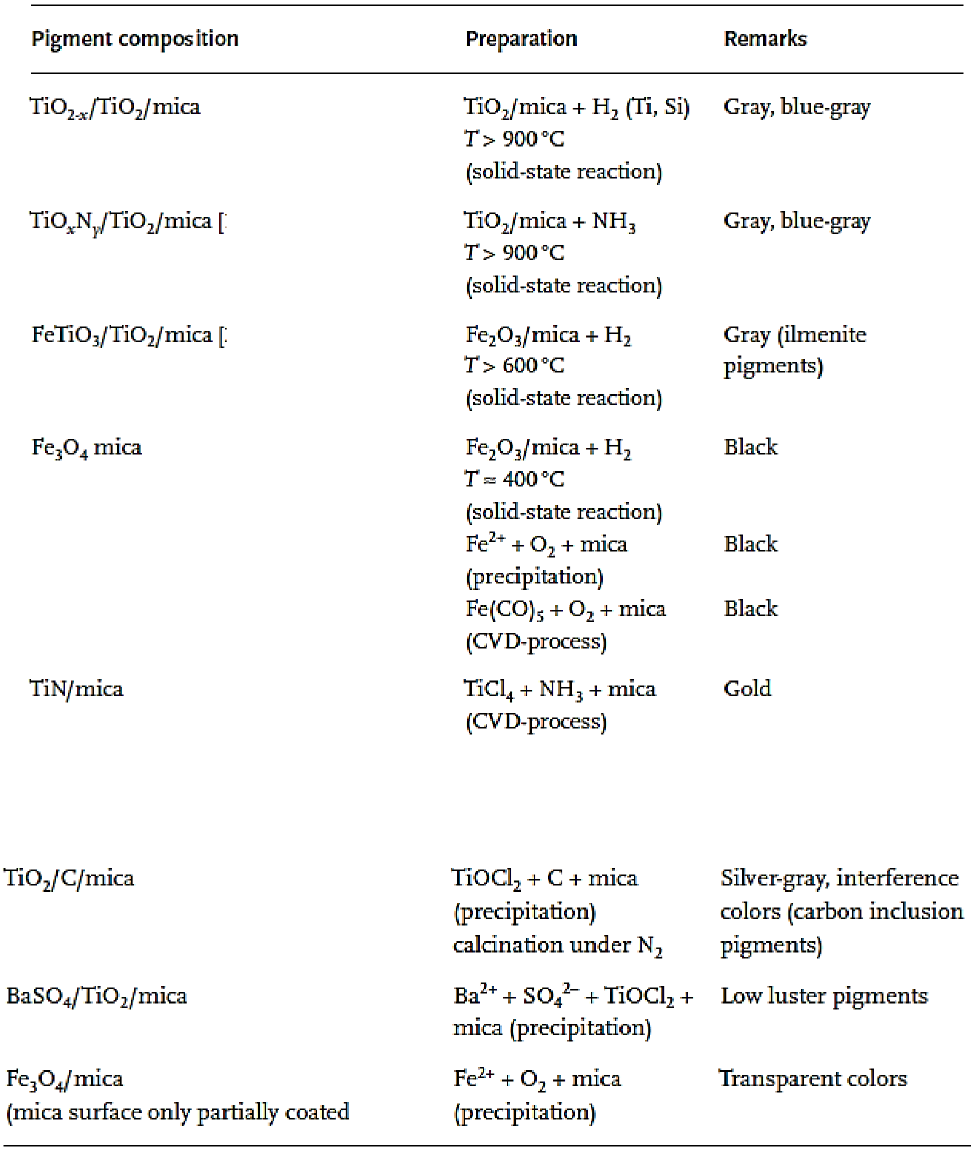
Pigments have been used as coloring agents since centuries and their properties have improved year by year. They are not only used to provide color but they also can provide magnetic, electromagnetic, and corrosion inhibiting properties. Pigments are classified with respect to their interaction with light. They are either classified according to their gloss or to their color. In the few decades, pigments with very high gloss were synthesized and commercialized under the general class name of ‘effect pigments’. Effect pigments are defined as metallic effect pigments or pearlescent pigment [1].

Color properties of materials depend on scattered light and viewing angle. Pearlescent pigments are a kind of pearl-shine appearance luster pigments because angle dependent transparent layers have different refractive indices [2]. Pearlescent pigments are very important for many applications like plastics, industrial coating, printing inks, cosmetics and automobile paint. They are used to obtain pearl, rainbow, or metallic effects. In addition, transparent color formulations are used to acquire brilliance, two tone color, luster flops [3].

The discovery of synthetic very thin micron or submicron size plates that can create an additional layer with metal oxides is a worthwhile development. Titanium dioxide coated mica flakes, or glass flakes, silica, and alumina flakes can be given as the examples. Mica has been the main constituent of the effect pigments. It can be used especially in coatings, and polymers.

Pearlescent pigments can be combined with additive pigments which improve optical properties. It is possible to obtain brilliant color and new coloristic effects by coating a colorant (absorptional pigment) with a pearlescent pigment. These new pigments are so-called ‘combination pigments’. An additional advantage of the combination pigments is that they decrease the optical dispersion problems related with conventional pigments because of their small particle size and high surface area. A way to obtain combination pigment is the coating of titanium dioxide-mica pigments with an organic or inorganic colorant. The colorants provide an additional layer on mica-titania pigments. Phthalocyanines, carbon black, dioxazines, quinacridones, perylenes iron (III) oxide are more preferable pigments for combination [3]. Table1.1 represents some pearlescent mica pigments with basic properties.

Table 1.1 Color properties of some mica-based pearlescent pigments [3].



Pigment composition	Preparation	Remarks
TiO_{2-x}/TiO_2/mica	TiO_2/mica + H_2 (Ti, Si) $T > 900\,°C$ (solid-state reaction)	Gray, blue-gray
TiO_xN_y/TiO_2/mica [	TiO_2/mica + NH_3 $T > 900\,°C$ (solid-state reaction)	Gray, blue-gray
$FeTiO_3/TiO_2$/mica [	Fe_2O_3/mica + H_2 $T > 600\,°C$ (solid-state reaction)	Gray (ilmenite pigments)
Fe_3O_4 mica	Fe_2O_3/mica + H_2 $T \approx 400\,°C$ (solid-state reaction)	Black
	$Fe^{2+} + O_2$ + mica (precipitation)	Black
	$Fe(CO)_5 + O_2$ + mica (CVD-process)	Black
TiN/mica	$TiCl_4 + NH_3$ + mica (CVD-process)	Gold
TiO_2/C/mica	$TiOCl_2$ + C + mica (precipitation) calcination under N_2	Silver-gray, interference colors (carbon inclusion pigments)
$BaSO_4/TiO_2$/mica	$Ba^{2+} + SO_4^{2-} + TiOCl_2$ + mica (precipitation)	Low luster pigments
Fe_3O_4/mica (mica surface only partially coated	$Fe^{2+} + O_2$ + mica (precipitation)	Transparent colors

Phthalocyanines can be used as additive pigments to mica-titania pigments to acquire combination pigments. Phthalocyanines are more stable aromatic macrocyclic compounds, and they are capable of combining more than 70 metallic and non-metallic ions in the aromatic rings [4]. Phthalocyanines have very attractive physical and chemical properties which show their importance in molecular functional materials. Their optical and electronic properties enable their usage in many applications such as photodynamic therapy medicines, catalysts for the photo oxidation, photoconducting agents for photocopies, deodorants, germicides, retardation films for plant growth in greenhouses. Their properties can be changed also by periphery substitutions [5]. In the last decades, there have been new areas for using phthalocyanines, such as semiconducting devices, photovoltaic solar cells, electrophotography, rectifying devices, molecular electronics, Langmuir- Blodgett films, gas sensors, liquid crystals, and electrocatalytic reagents [6, 7].

Metallophthalocyanines have highly intense absorption in the red region of visible light that can be useful for photosensitizers. To have high triplet state lifetimes and fluorescence, diamagnetic metal can be combined with phthalocyanines. Zinc, aluminum and silicon can be used as well diamagnetic metals which have efficient fluorescent property for many applications.

Functional or substituted phthalocyanines could be obtained by direct and indirect ways. Halogenated or sulfonated phthalocyanines have synthesized by substitution of the core molecule or special starting materials [8]. Substituted phthalocyanines, very little particle sizes, tend to be more soluble in many organic solvents; therefore, they are preferred in recent applications.

The main problem with phthalocyanines is their aggregation that influences their gloss negatively, because, large size aggregates absorb the light which is supposed to be reflected. In order to cope with this problem, they can be deposed on pearlescent pigments in the form of a thin layer reducing the light absorption and favoring the reflection. As a result of this combination, pigments become very brilliant in color.

The main objective of this work is the synthesis of tetranitro zinc phthalocyanine and tetraamino zinc phthalocyanine coated mica-titania combination pigments to obtain fluorescent effect pigments. Different amounts of phthalocyanines and two different solvents were used to synthesize combination pigments. Moreover, the effect of pH on the reaction was examined. Color effects and optical properties were investigated by using the pigments in a water based clear resin.

CHAPTER 2

LITERATURE REVIEW

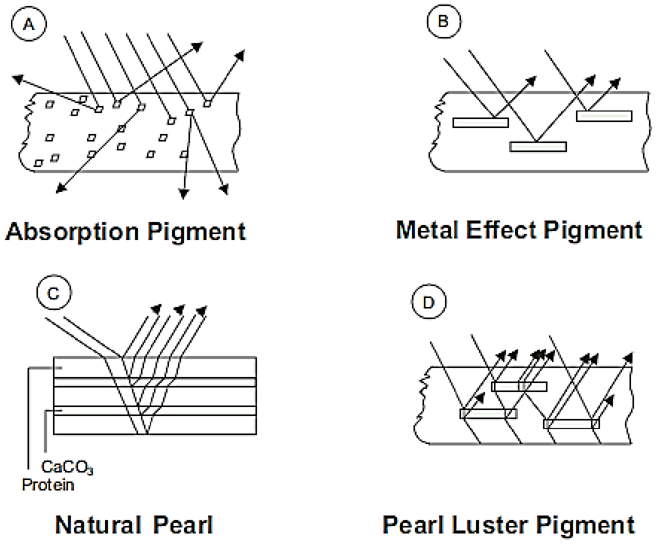
In this chapter, phthalocyanines and the methods of their production, effect pigments, and mica-titania based combination pigments and their properties were described briefly. Besides that, recent and previous studies were overviewed in this study.

2.1 Effect Pigments

Pigments are usually dispersed on the surface of the materials like in inks, plastics, paints etc. In addition, they maintain their structure after exposing to physical and chemical processes [9]. Besides generating colors, pigments are used also as filling materials, corrosion inhibitors, and they also deliver special functions due to their magnetic, electrical or electromagnetic properties [1].

Effect pigments are classified as anti-corrosive pigments, magnetic pigments, metal effect pigments, pearl luster pigments, luminescent pigments, and transparent pigments. The first two properties are not related to color; anti-corrosive pigments protect the material from environmental corrosive interactions; and magnetic pigments are used for data storage in electronics. Luminescence pigments will be addressed in the following sections. Transparent pigments are utilized to color cleaning in plastic bottles and films for packaging [10].

Figure 2.1 shows the optical features of absorption pigments, metal effect pigments, pearl and pearlescent pigments. While conventional pigments absorb and/or scatter light, effect or pearlescent pigments are composed of both pearlescent and metallic particles. Metal pigments are small metal flakes such as aluminum copper or titanium, and flaky structure generates enhanced light and color impression. Metallic effect pigments reflect nearly all the incident light, act like a mirror, and then they seem very brilliant. They are widely used in automotive topcoats. Pearlescent pigments produce the luster of natural pearls. Metallic and pearlescent pigments consist of layers that have high and low refractive index. The plates with high refractive index can settle on substrate surface in parallel alignment. The pearl luster effect is described by multiple reflections that come out of the depth and seem softly. The enhancement of the intensity of reflecting light from a flaky pigment surface due to interference with the lights coming from lower depths increase the gloss and deliver a shiny or pearlescent appearance. Pearlescent pigments can be transparent or have partially light absorptive surfaces, they resemble crystal particles [3, 9].



Absorption Pigment

Metal Effect Pigment

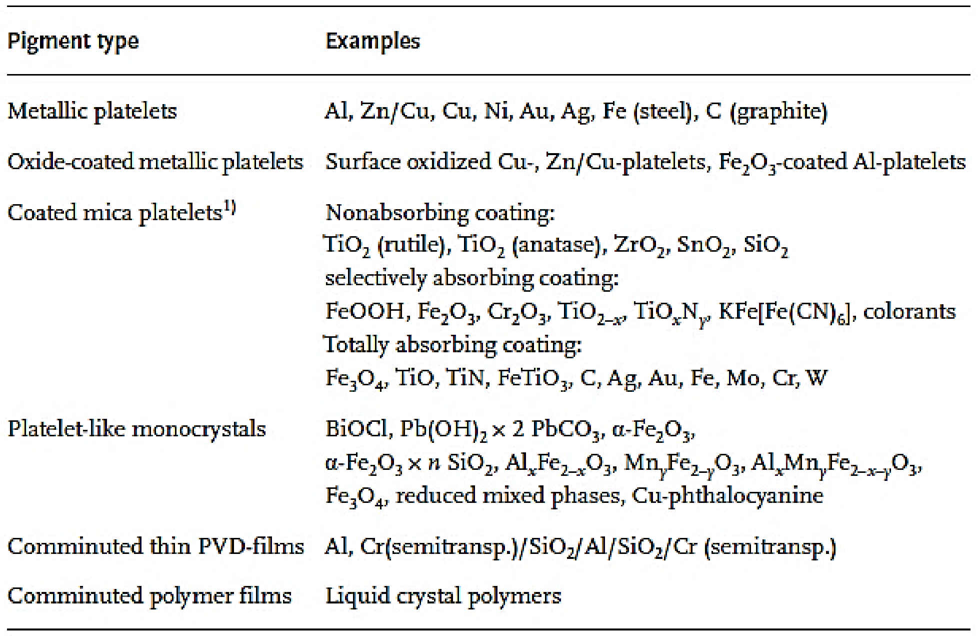
Natural Pearl

Pearl Luster Pigment

Figure 2.1 Schematic presentation of optical properties of absorption pigments, effect pigments and pearlescent pigments [3].

Table 2.1 gives some examples of the types of effect pigments. The main purposes of effect pigments can be explained as; contributing to new improvements in pigments, more intense interference colors, more capable of hiding power, stability on air conditions, and development on the dispersibility. Effect pigments can be produced by ecologically safe processes, so they can be thought of as non-toxic pigments.

Table 2.1 A brief presentation of effect pigments [3].



Pigment type	Examples
Metallic platelets	Al, Zn/Cu, Cu, Ni, Au, Ag, Fe (steel), C (graphite)
Oxide-coated metallic platelets	Surface oxidized Cu-, Zn/Cu-platelets, Fe_2O_3-coated Al-platelets
Coated mica platelets¹⁾	Nonabsorbing coating: TiO_2 (rutile), TiO_2 (anatase), ZrO_2, SnO_2, SiO_2 selectively absorbing coating: FeOOH, Fe_2O_3, Cr_2O_3, TiO_{2-x}, TiO_xN_y, $KFe[Fe(CN)_6]$, colorants Totally absorbing coating: Fe_3O_4, TiO, TiN, $FeTiO_3$, C, Ag, Au, Fe, Mo, Cr, W
Platelet-like monocrystals	BiOCl, $Pb(OH)_2 \times 2\ PbCO_3$, α-Fe_2O_3, α-$Fe_2O_3 \times n\ SiO_2$, $Al_xFe_{2-x}O_3$, $Mn_yFe_{2-y}O_3$, $Al_xMn_yFe_{2-x-y}O_3$, Fe_3O_4, reduced mixed phases, Cu-phthalocyanine
Comminuted thin PVD-films	Al, Cr(semitransp.)/SiO_2/Al/SiO_2/Cr (semitransp.)
Comminuted polymer films	Liquid crystal polymers

2.2 Mica Titania Based Pigments

The most known type of pearlescent pigments relies on natural mica plates. Coated mica pigments are produced by depositing smooth metal oxide films on very thin mica plates. Mica layers are inert and they can be used as a filler and colorant [11]. The particle size and thickness of these platelets change from 1 to 200 µm and from 200 to 500 nm, respectively. Figure 2.2 and Figure 2.3 show the structure of titanium dioxide mica pigments. The advantages of mica-titania pigments are high luster, well hiding power, the highest thermal, chemical and physical stability, non-toxicity, low price, and low density. They are used in plastics, cosmetics, printing inks, ceramic products, and lacquers [3].

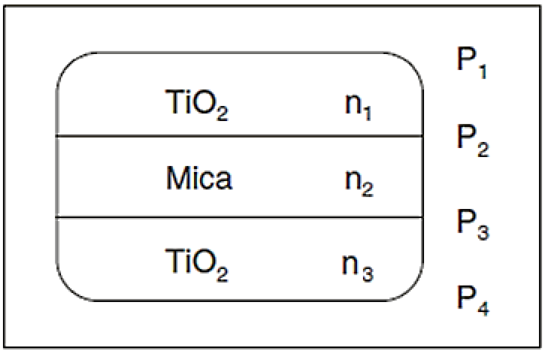


Figure 2.2 Schematic representation of structure of mica-titania pigment with the four existing interphases [3].

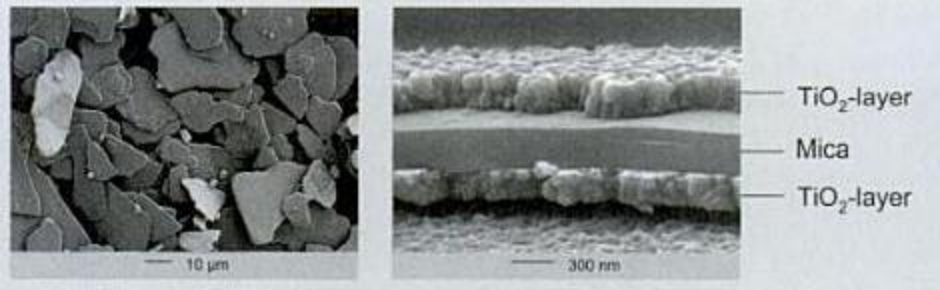


Figure 2.3 SEM image of mica pigment particle [3].

Figure 2.4 shows the manufacturing process. Firstly, mica is ground and classified according to the particle size distribution of platelets produced. After that, a wet chemical process is carried out to deposit metal oxides on platelets. Then coating, filtration, drying and calcination steps are carried out in sequence. For laboratory synthesis, according to Topuz and co-workers' study two different methods were used to synthesize titania coated mica, which are; homogeneous hydrolysis and titration methods [12].

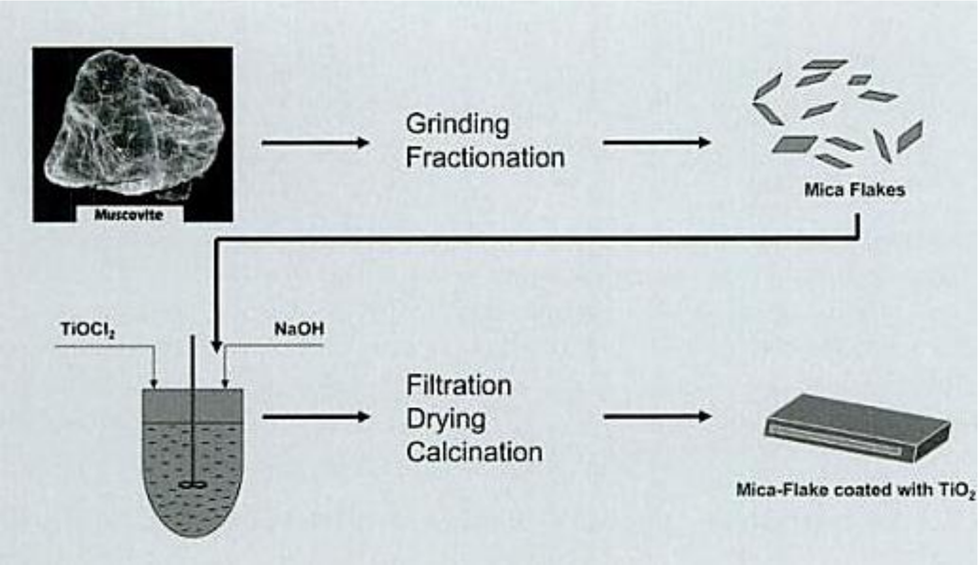
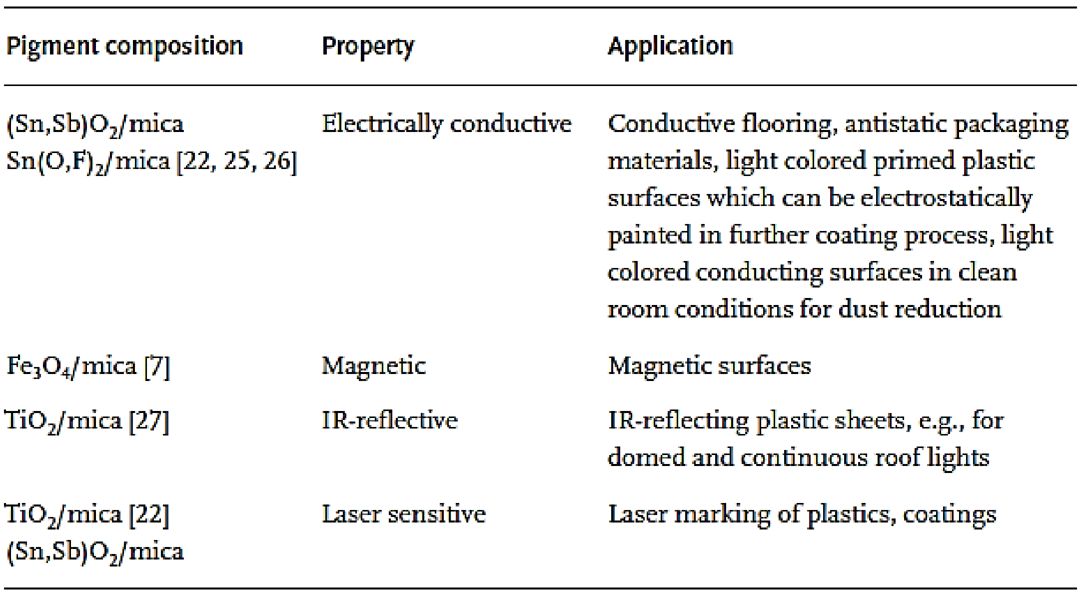


Figure 2.4 Process scheme for titania coated mica pigments [1].

The color efficiency of pearlescent pigment can be improved by introducing another pigment to the titania coated mica. By virtue of these pigments, pearlescent pigments give additional characteristics like sharper colors, more stability, and well dispersion [9]. The color is developed because of the combination of base and interference colors. Additional pigments should have small particle size and high surface area. The pigment color can be different depending on the composition and viewing angle of the additional pigment [1].

Pearlescent pigments can be used in conductive flooring, antistatic packaging materials, IR- reflecting plastic sheets, and laser marking plastics. By new additive pigments, materials gain new properties. Table 2.2 points out the functional properties of some metal oxide mica pigments.

Table 2.2 Some functional combination pigments, properties and applications [1].



Pigment composition	Property	Application
$(Sn,Sb)O_2$/mica $Sn(O,F)_2$/mica [22, 25, 26]	Electrically conductive	Conductive flooring, antistatic packaging materials, light colored primed plastic surfaces which can be electrostatically painted in further coating process, light colored conducting surfaces in clean room conditions for dust reduction
Fe_3O_4/mica [7]	Magnetic	Magnetic surfaces
TiO_2/mica [27]	IR-reflective	IR-reflecting plastic sheets, e.g., for domed and continuous roof lights
TiO_2/mica [22] $(Sn,Sb)O_2$/mica	Laser sensitive	Laser marking of plastics, coatings

2.3 Phthalocyanines

Phthalocyanines (Pc), very close to porphyrin compounds (Figure 2.5), are one of the most studied groups of functional organic pigments. Phthalocyanines and their derivatives have many important characteristics such as catalytic, optical, and electronic properties. Porphyrin structure contributes to the desirable quality of materials, as large dipole moment, polarizabilities, and hyperpolarizabilities. The nonlinear optical properties provide energy transfer with molecular control so that they have been used in data storage and electrooptical signal processing. It is important that the stability of the molecules of π-radicals makes them useful especially in photoionization processes [13]. Moreover, phthalocyanines have intense absorption in the near infrared region (750-1300 nm) that is crucial for many applications such as thermal imaging, infrared thermal imaging, and liquid crystal display devices in the security industry. This is because of the fact that near infrared region materials must have high thermal, weather and light resistance properties, and high molar extinction coefficients, as well [14-16].

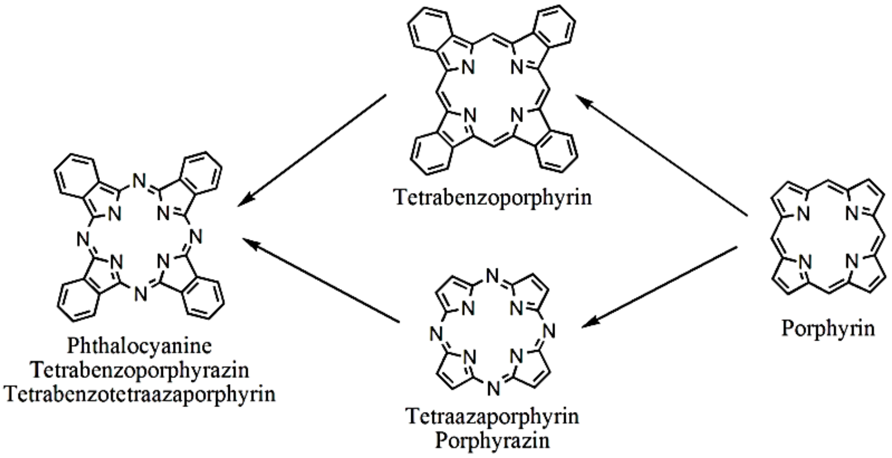


Figure 2.5 Similarity between porphyrin and phthalocyanine [17].

The interesting chemical and physical properties of phthalocyanines provide many advantages to use them in different areas. Their effective color, conductivity, chemical and thermal stability make them a good candidate for many applications. Like catalysts for the removal of sulfur from crude oil, charge- generation materials in xerograph, optical read/write discs, photodynamic reagents for cancer therapy, deodorants, antiseptic reagents, and as growth promoting and retarding agents in plants [18]. Besides these applications they have been generally used in colorants, semiconductors, electrochromism, chemical sensors, liquid crystals, Langmuir-Blodgett films, solar cells, and electrophotography [19]. Phthalocyanines can be used in these diverse areas by changing the central metal or the axial ligands or by modification of the phthalocyanine rings [20].

Phthalocyanines may or may not contain metal at the center; and copper, irons, zinc, cobalt, magnesium, and rare earth containing phthalocyanines find uses in the industry. Coordination complex of zinc, copper, iron, cobalt, and platinum demonstrates that they have high stability even in concentrated, nonoxidizing acids and bases [21]. In other words, unsubstituted phthalocyanines and their metal complexes are diagnosed by strong intermolecular cohesion which is insoluble and non-melting solids. Transition metals can be fit in these complex ligands. If unfavorable volume ratio occurs in phthalocyanine ring and metal complex, stability may decrease in these materials [22]. Figure 2.6 shows the metal and non-metal phthalocyanines.

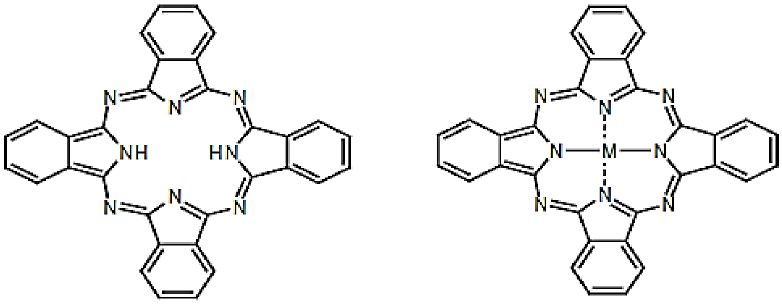


Figure 2.6 Non-metalled and metalled phthalocyanine showing the covalent and partial bonds between the central metal and the nitrogen atoms.

Phthalocyanines can be synthesized in non-substituted and metal substituted forms. Non-substituted phthalocyanines can be used as a stable color agent. Their well conductivity, thermal and chemical stability, make them a suitable choice for application in organic light emitting devices [23]. Substituted phthalocyanines are more soluble than other forms. However, aggregation is the main problem for these phthalocyanines due to their strong interactions between planar molecules in solutions. Phthalocyanine containing dendrimers and polymers overcome these difficulties. Besides that, the integration of phthalocyanines in macromolecules enhances their properties and develops new materials. Phthalocyanine containing polymers are named according to their side group, main chain or forming a polymeric cycle. Polymeric or macrocyclic phthalocyanines are not soluble in organic solvents. This makes them difficult in their usefulness and functionality [24]. The solid and solution phase of phthalocyanines can be exposed to different properties especially in nonlinear optical properties. According to the studies, dilute solutions of phthalocyanines show nonlinear optical properties, when compared with their solids. This difference can be explained by excitonic effect, related to intermolecular interactions [25].

McKeown and co-workers studied a specific phthalocyanine based network polymer. They prepared microporous material based on phthalocyanines with linking groups and phthalocyanines with solidly themselves. These materials were synthesized by the reaction of octasubstituted phthalocyanines with reactive bifunctional linking groups. These types of macromolecule polymers find place in chemoselective adsorptions, separations, and heterogeneous catalysts. Figure 2.7 demonstrates the phthalocyanine based network polymers [26].

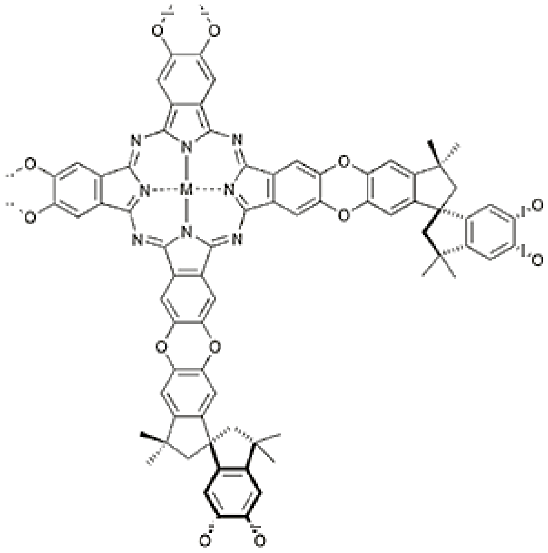


Figure 2.7 Phthalocyanine based network polymer [26].

2.3.1 Methods of Synthesis

Phthalocyanines can be synthesized in metallo or non- metallo forms. Generally, they are produced fusing phthalonitrile, metal salts or by later insertion of metals into phthalocyanines at high temperature conditions. The reaction can be carried out both in solvents or in solvent free medium. After the completion of reaction, the soluble impurities and unreactants are removed by extracting with solvents or acids and bases. Substituted phthalocyanines are more soluble in organic solvents or in acids and bases, and their purification can be carried out by chromatography, recrystallization, and extraction [27, 28]. Figure 2.8 demonstrates the basic principles of synthesis of metallophthalocyanines.

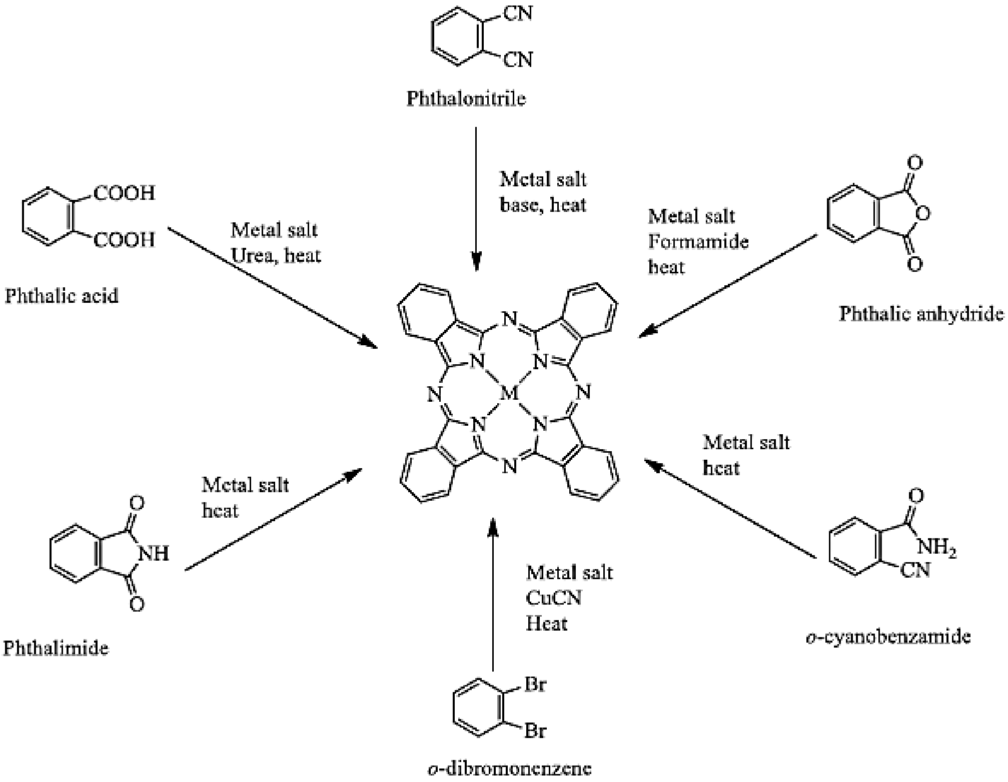


Figure 2.8 Basic principles of synthesis of metallophthalocyanines [27].

For the large scale production of phthalocyanines, phthalic anhydrate, urea, metal salts, and ammonium molybdate which is used as catalyst are heated up to 200°C [29]. On the laboratory scale, it is suggested that benzene-1,2-dicarbonitrile and metal salt must be heated in molten urea [30].

Phthalocyanines can be prepared also under microwave radiation in the presence of proper solvents in high yield. The microwave radiation supplies the high energy needed and reaction time is completed in a very short time. This is an advantage when compared with other long time and high temperature reactions. Microwave radiation heating is selective, direct, rapid, internal and controllable [31].

Safari and co-workers studied the synthesis of metal substituted octachloro-, hexadecachloro- and tetranitro phthalocyanine by microwave radiation under solvent free conditions. They prepared the tetranitro metallophthalocyanines under solvent free conditions. The 3-nitrophthalic anhydride (0.77 g), urea (4.80 g), copper (II) sulfate pentahydrate (0.12 g) and ammonium heptamolybdate (0.10 g) were ground until a homogeneous powder was obtained. Then after, the powder was placed in 25 ml beaker and irradiated in a microwave oven at high and medium power for 2 and 1 min, respectively. They also modified the purification route by using methanol and n-hexane. The solid product was filtered with water to remove excess urea. The dried phthalocyanines were treated also with degassed dimethyl sulfoxide under nitrogen atmosphere and the mixture was refluxed for 7 h at 110°C [32].

Industrially, phthalocyanines are produced using phthalic anhydrate and urea, as phthalic anhydrate is cheaper than phthalonitrile, and it gives higher yield lowering the cost. The reaction is shown in Figure 2.9.

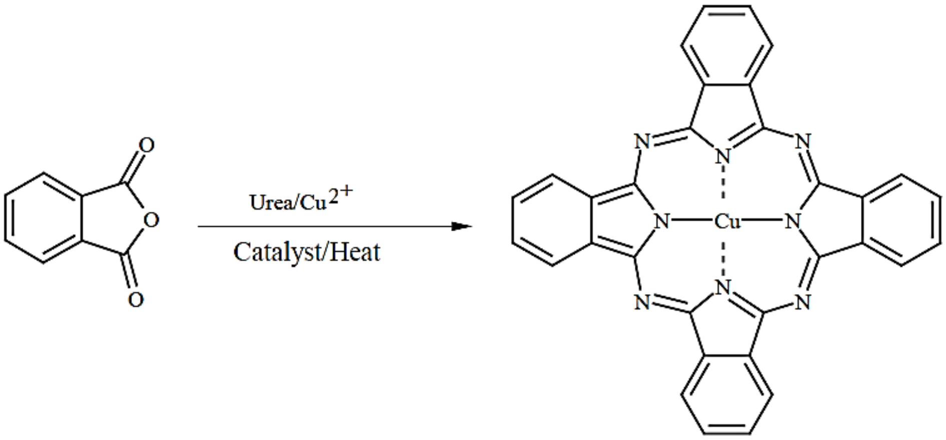


Figure 2.9 The reaction for the industrial synthesis of phthalocyanines.

Phthalocyanines absorb the visible spectrum of light. The absorption bands of molecules are related with molecule structure. Electronic transition between π-π* bonding in the 18-π-electron systems of the macrocycle leads to two absorption pikes, the Q and B bands. Figure 2.10 demonstrates the typical absorption spectrum of metallophthalocyanine (in blue color) and the unmetalled phthalocyanine (in red color) [33]. Metallophthalocyanines absorb the light in nearly 650 nm. They are very useful in some devices due to their large scattered configuration [34]. Large phthalocyanines with additional substitutions can be used in the photodynamic therapy as they have good photostabilities, high fluorescence quantum yields, and strong absorption on visible region. Unsubstituted phthalocyanines have a low solubility in water but they have ability to encapsulate in micelles, or can be used with polymeric nanoparticles [35, 36].

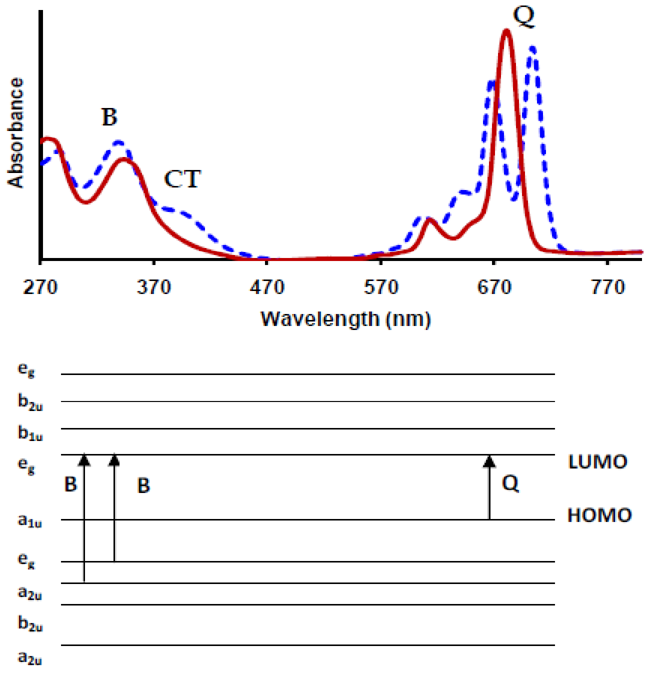


Figure 2.10 Absorption spectrum of metallophthalocyanine with Q, B electronic transition band [37].

2.3.2 Tetra- Substituted Phthalocyanines

Tetra substituted phthalocyanines are preferred when their functionality and solubility are taken into consideration. Tetra forms offer higher stability, as well. Functional phthalocyanines are more favored than other forms due to their advanced features. Some methods of synthesis of tetra substituted phthalocyanines were described briefly as substituted phthalocyanines were used in this research work.

Two double bonds occur in phthalocyanines in the perypheryl rings connecting the α and β positions (Figure 2.11). If all α and β positions are substituted the phthalocyanine is called octa-substituted. If only one is substituted it is called tetra-substituted phthalocyanines [37]. Both tetra- and octa-substituted phthalocyanines have good solubility in certain types of solvents [27].

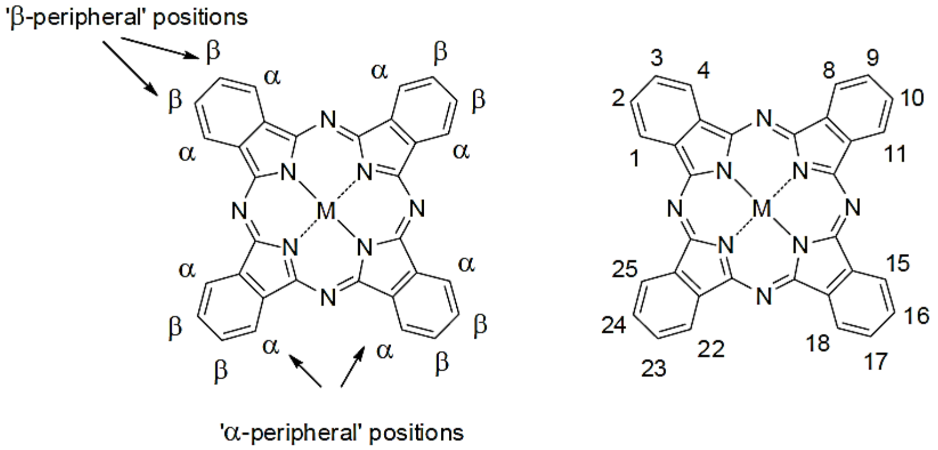


Figure 2.11 Numbering scheme for the phthalocyanine core [38].

The β-substituted phthalocyanines are more soluble due to out of plane bending of their substance, as seen in Figure 2.12 [9]. The α-crystal has low stability, and the pigment can return to more stable β forms with the increase in temperature above 218°C [39].

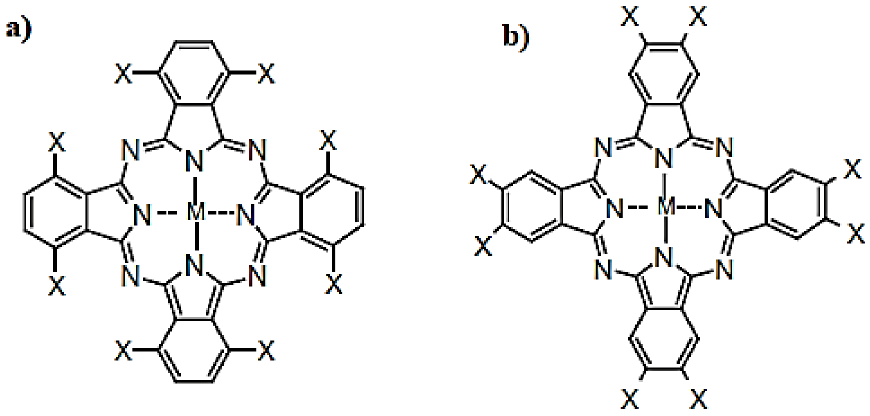


Figure 2.12 Structure of a) α and b) β octasubstituted phthalocyanines [37].

Kobayashi et al. investigated 35 phthalocyanines according to the effect of peripheral substitution on the electronic absorption and fluorescence spectra. They mostly used alkyl thio groups as an electron releasing group, while nitro and phenylsulfonyl groups are used as an electron withdrawing group. In their work, α and β position groups joined the phthalocyanine molecule, so that the B and Q bands shift to longer wavelength. α and β position groups shows totally different effects. What they found is that, non-metallophthalocyanines have lower splitting of the Q band with increasing wavelength, and electron releasing groups are more effective than α-position phthalocyanines. In addition, 16-electron substituted phthalocyanines have larger Q band absorption coefficients, than tetra and octa-substituted phthalocyanines [5].

Substituents and the peripheral phenyl groups of phthalocyanine structure affect the nature of electronic conductivity of complexes. In 1991, Singerski et al. investigated the electrical conductivity of nickel (II) tetra-amino phthalocyanine. According to that research, amine groups on the peripheral benzene ring have great effect on the increase of electrical conductivity [40].

Alzeer and co-workers studied the synthesis of tetra substituted zinc phthalocyanines as well as non-metallic forms. Tetranitro zinc phthalocyanines were produced using 4-nitrophthalic anhydride (2.0 g), urea (3.0 g), zinc chloride (383 mg), and ammonium molybdate (13 mg) all dissolved in nitrobenzene (15 ml). The mixture was stirred under nitrogen atmosphere at 185^{o}C for 4 hours (Figure 2.13). The reaction mixture was cooled and diluted with toluene (80 ml). The resulting precipitate was washed with toluene, water, methanol/ether (1:9), and ethyl acetate/hexane (2:1). The dried product was a dark green solid. The IR spectrum showed peaks at 1513, 1321, 1080, 754, 726 cm^{-1}. The molecular formula of tetranitro zinc phthalocyanine is $C_{32}H_{13}N_{12}O_8Zn$, and its molecular weight is 757 g/mol [41].

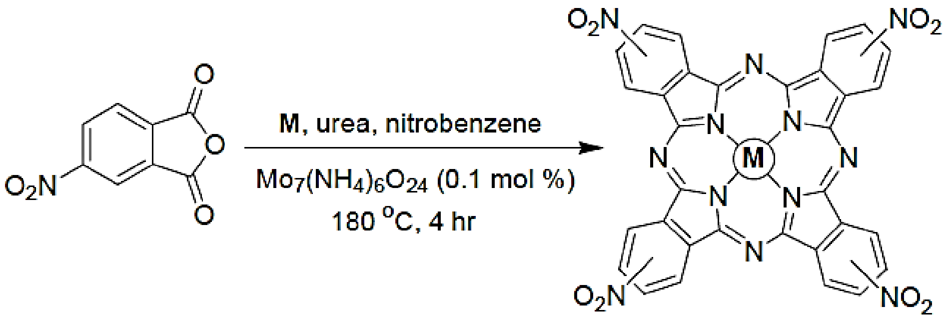
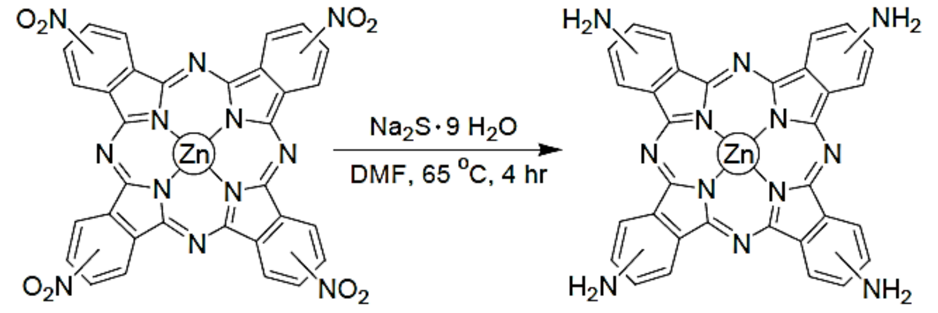


Figure 2.13 Synthesis of tetranitro zinc phthalocyanine [41].



tetranitro-zinc-phthalocyanine (**1**):

tetramino-zinc-phthalocyanine (**2**):

Figure 2.14 Synthesis of tetraamino zinc phthalocyanine [41].

They also synthesized tetraamino zinc phthalocyanine using sodium sulfide nonahydrate (7.4 g) and tetranitro zinc phthalocyanine (1.95 g) in 50 ml DMF. The reaction was carried out under nitrogen atmosphere at 65°C. After 4 hours, the mixture was cooled down to room temperature and diluted with ice water. The resulting matter is filtered by methanol/ether (1:9), and ethyl acetate. The product was dried and a dark green solid was obtained. The IR spectrum had peaks at 1603,

1490, 344, 1092, 1044, 822, 743 cm^{-1}. The molecular formula of tetraamino zinc phthalocyanine is $C_{32}H_{21}N_{12}Zn$, and its molecular weight is 637 g/mol.
Achar and Lokesh studied the tetraamino phthalocyanines having cobalt, nickel, and copper at the center. The synthesis reaction was carried out by the reduction of nitro groups with sodium sulphide. They also investigated electrical conductivities of tetraamino phthalocyanines. They reported that the complexes increased the conductivity 10^5-10^6 times, when compared with unsubstituent phthalocyanines [40].

Yenilmez and co-workers studied the synthesis of tetra substituted cobalt, zinc, and copper phthalocyanines. Microwave radiation was used to synthesize Co and Zn phthalocyanines from phthalonitrile, metal salts ($CoCl_2$ and Zn $(CH_3COO)_2$), and 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) in hexanol. Cu-phthalocyanine compound was produced by reaction of phthalonitrile, copper (II) chloride at 160 °C with the presence of DBU. Phthalocyanines were purified by using column chromatography. Furthermore, they reported the aggregation properties and fluorescence behavior of these phthalocyanines [31].

2.3.3 Zinc Phthalocyanines

Metallophthalocyanines have been investigated prevalently due to their increasing usage in many areas [34, 42, 43]. The presence of central metal ion affects and improves the photophysical behavior of metallophthalocyanines very strongly. It is proven that, diamagnetic ions such as Zn^{2+}, Al^{3+}, and Si^{4+} increase both triplet quantum yields and triplet lifetimes with a closed shell [44, 45].

Zinc (II) phthalocyanine (ZnPc) complexes have been studied intensively by virtue of their photosensitizing properties [46-49]. They have high fluorescent properties, leading to their widely usage in photodynamic therapy. Moreover, the special chemical group at the periphery of zinc phthalocyanine compounds may be

selectively preferred by some tumor cells, and the phthalocyanines with these structures are called third generation photosensitizers [50].
Metallophthalocyanines, as mentioned before, tend to aggregate in solution, which results in a decrease in the photosensitizing property. The addition of functional groups to peripheral position also affect the chemical properties of metallophthalocyanine complex [51]. It can be clearly said that, functional groups make dissolution in organic solvent easier via increasing the distance between macrocycle rings carrying the π-electrons. Solvents also influence the photochemical and photophysical behaviors of metallophthalocyanine complexes [52, 53].

Nombona et al. investigated fluorescence behavior of zinc phthalocyanines having naphthol and carboxyl groups. The synthesis was achieved by using the mixed phthalonitrile cyclotetramerization of 3-(1-naphthoxy) phthalonitrile with a carboxylic acid phthalonitrile [54].

2.3.4 The pH and Solvent Sensitiveness of Phthalocyanines

Phthalocyanines contain high number of conjugated π-electrons that make electron transfer possible. Electron transfer reactions can be controlled by taking and giving proton which leads to the modification of the structure [55]. Generally, phthalocyanines and their metal derivatives have been used as electron donors rather than electron acceptors, unless high electron taking group is stationed on the macrocycle [56].

The main purpose of the phthalocyanine protonation is their significant advantage on the photophysical and structural properties. Protonation of the nitrogen atoms on the external section of the ring decreases the symmetry. It leads to a shift in the absorption of the Q band which is desired especially in photodynamic applications. However, there are limited investigations in protonation of the phthalocyanine on the redox quality. Strong acid is required to protonate the phthalocyanines that have low basicity [13, 57]. Protonation of phthalocyanines has been generally applied to insoluble ones. They are protonated in two different ways: the isoindole nitrogen and meso-nitrogen (Figure 2.15). Phthalocyanine protonation ordinarily occurs at the meso-nitrogen atom because of the hardness of structural deformation at the isoindole-nitrogen atom [58]. Nitrogen and hydrogen bound covalently with each other.

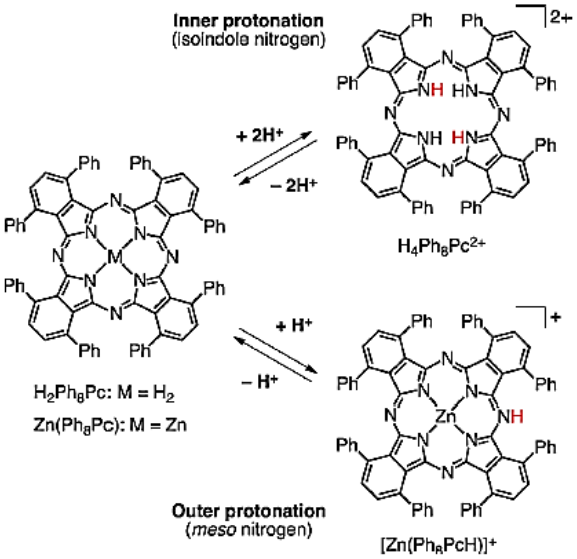


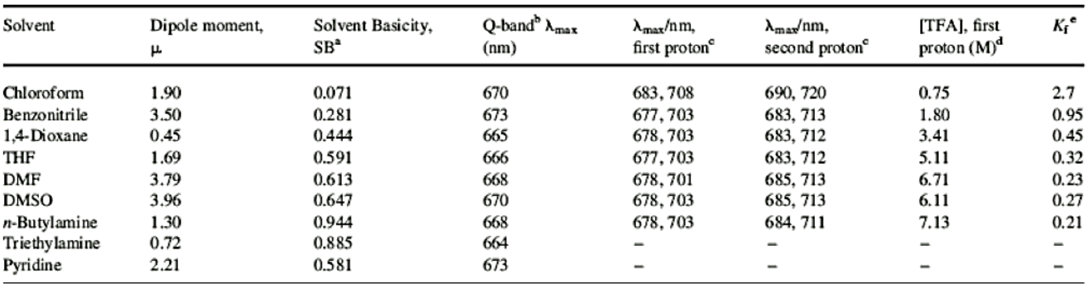
Figure 2.15 Isoindole –nitrogen and meso- nitrogen protonation of phthalocyanine [59].

Fukuzumi et al. studied on structures and photoinduced electron transfer of protonated porphyrins and metallophthalocyanines. Metaled azoporphyrins contribute to acid-base interaction with four nitrogen atoms. According to their results, protonated porphyriniods increase the chance of producing supramolecules as well as make the control of redox potentials easier [59].

Tetra-substituted phthalocyanines have red shift in the Q band that is a desirable point in photosensitizers in photodynamic therapy. A red shift was carried out upon protonation. However, fluorescence decreased when the protonation is applied to tetra-substituted phthalocyanines. This attributed to decrease in energy triple state [60].

Ogunsipe and Nyokong worked on protonated and unprotonated zinc phthalocyanine and its derivatives to observe the ring substituents, axial ligands, and the effect of solvents on fluorescence. Protonation was achieved by TFA. Concentrated sulfuric acid was used to get tri- and tetra- protonation of the substance. Their results were summarized like that: Ring substituted zinc phthalocyanines were not protonated due to aggregation in the solution, additional acids increased the aggregation, axial ligands in the solvent vanished when protonation in the solvent, occurred and the probability of protonation was decreased with the strong basicity. Besides that, for in all circumstances, fluorescence decreased with protonation (Table 2.3) [61].

Table 2.3 Effect of solvent on the Q band maxima of protonation of zinc phthalocyanine [61].



Solvent	Dipole moment, μ	Solvent Basicity, SB[a]	Q-band[b] λ_{max} (nm)	λ_{max}/nm, first proton[c]	λ_{max}/nm, second proton[c]	[TFA], first proton (M)[d]	K_f[e]
Chloroform	1.90	0.071	670	683, 708	690, 720	0.75	2.7
Benzonitrile	3.50	0.281	673	677, 703	683, 713	1.80	0.95
1,4-Dioxane	0.45	0.444	665	678, 703	683, 712	3.41	0.45
THF	1.69	0.591	666	677, 703	683, 712	5.11	0.32
DMF	3.79	0.613	668	678, 701	685, 713	6.71	0.23
DMSO	3.96	0.647	670	678, 703	685, 713	6.11	0.27
n-Butylamine	1.30	0.944	668	678, 703	684, 711	7.13	0.21
Triethylamine	0.72	0.885	664	–	–	–	–
Pyridine	2.21	0.581	673	–	–	–	–

Maree et al. reseached the effects of solvents on the photochemical and photophysical behavior of zinc phthalocyanines. They used zinc phthalocyanines, zinc octaphenoxyphthalocyanine and zinc octaesronephthalocyanine besides tetrahydrofuran, dimethylsulphoxide, N,N'- dimethlyformamide etc. as aromatic solvents. They investigated influence of the solvents on the ground state spectra because the photosensitized reactions and their capability of generate singlet oxygen are very important. According to the experimental results, zinc phthalocyanine and its derivatives give high fluorescence quantum yields in tetrahyrdrofuran [50].

Topal and co-workers examined the α, and β substitued zinc phthalocyanines' pH sensitivities in diverse solutions, upon protonation. Phthalocyanine efficiency is strongly depend on protonation. They used PVC and ethyl cellulose as basic matrix materials for immobilization of phthalocyanines, and THF for a solvent. They seen the decreasing in the fluorecence emission on the Q band due to the protonation. According to them, tetra-substituted zinc phthalocyanines are manageble "high resolution pH sensitive molecular probes" for the pH range of 2.0-8.0 [62].

2.4 Fluorescence

Luminescence is the emission of light from excited molecules of any substance. It is considered in two different categories, which are fluorescence and phosphorescence. Fluorescence is a phenomenon that occurs when a material absorbs the radiation at a certain wavelength, and then reemitted at different wavelengths. In luminescence the initially absorbed excitation energy is always higher than the released energy of luminescent system. The efficiency of luminescence efficiency; is called quantum yield and it denotes. The ratio of the energy emitted to energy absorbed [9]. In order to understand clearly, the energy levels of the molecule must be examined. In the ground single state, the initial state of the molecule absorbs all radiation. In the singlet state all electrons of the molecule are paired in an electronic state. In the triplet state the spin of electrons align in the same direction. Figure 2.16 is a schematic representation of the distinction between ground state, single state, and triple state.

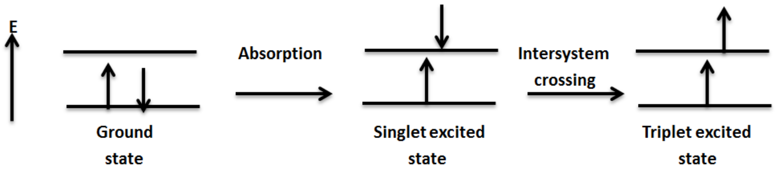


Figure 2.16 Distinction between ground, singlet and triple states.

In fluorescence, the excited electrons in single state lose energy through a mechanism called ‘internal conversion’, and they go down to lower energy states and go back to ground state. The time spent in the excited state is generally 10^{-8} s; consequently a general fluorescence lifetime is near 10^{-9} m [63]. It is quite a long time compared to 10^{-12} s for deexcitation of electrons from the higher levels of excited state.

The other category, phosphorescence, is the triple excited state light emission. The term is typically used to define long lived luminescence. The electrons in the singlet state undergo transformation by a mechanism called ‘interval conversion’ and the spins are aligned in the same direction. This state is called triplet state and it has lower energy than the singlet state. Therefore the lifetime of electrons is much longer, and is around 10^{-3} to 10^{0}s. The reason of illumination of phosphorescent materials in the dark is the long periods of spin inversion. Returning to the discussion on the difference between fluorescence and phosphorescence; fluorescence is an emission from an excited state that can be achieved by direct photoexcitation, whereas phosphorescence is emitted from triplet state [64].

The basic principles of light absorption by molecules, consists of the part of the molecule from a lower electronic state which is usually the lowest energy (ground state), to a higher energy state (excited state). In UV, near infrared, visible spectrum region, electronic transition is formed as shown in Figure 2.17 [65].

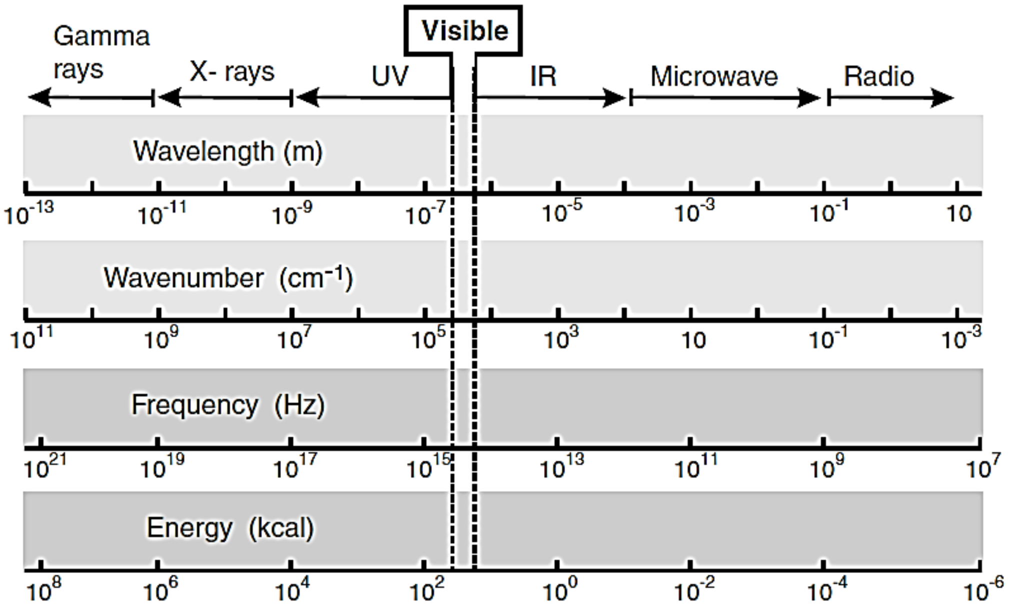
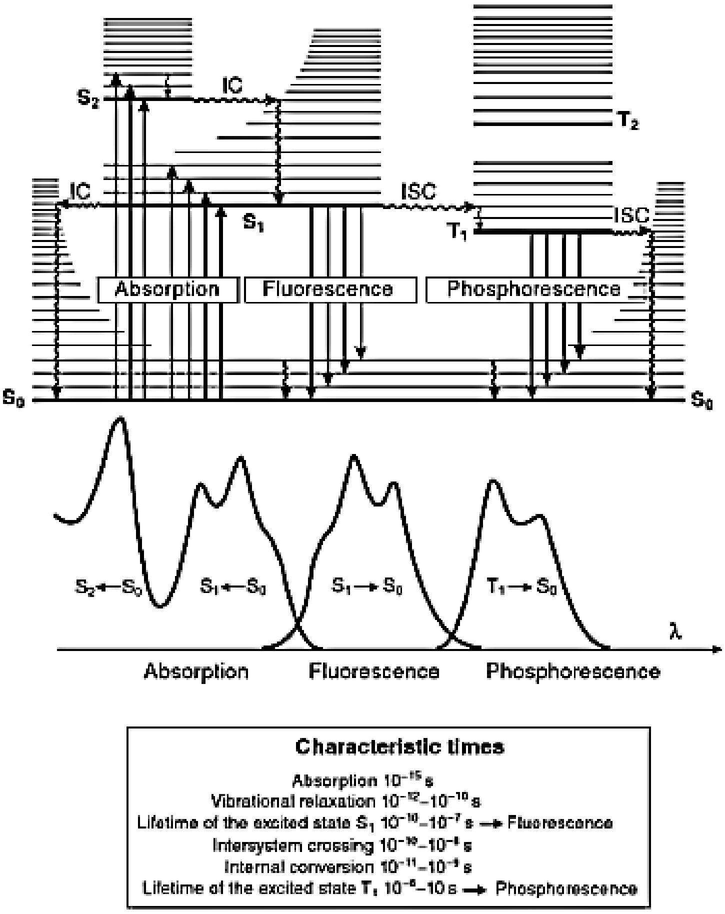


Figure 2.17 Electromagnetic spectrum [65].

During the absorption and emission processes, many changes may happen in electronic and vibrational states. The Perrin- Jablonski diagram (Figure 2.18) is suitable for understanding photon absorption, fluorescence, phosphorescence, and electron transition processes. S_0 is the ground state, S_1 and S_2 are singlet excitation states, and T_1, and T_2 are the triplet states. It is important to note that absorption is very fast process, nearly 10^{-15} s, with respect to other processes. Fluorescence typically comes about at lower energies of longer wavelengths. Vibrational relaxation is about 10^{-12} s and generally happens via collision and rotation of electrons generally before returning to the ground state (S_0). Internal conversion (IC) is also another route of energy returning from the lower levels. In absorption and emission processes, $S_1 \rightarrow S_0$ transitions are the most likely than $S_1 \rightarrow S_n$ transitions. The transition may occur from ground state to various excited states (S_1, S_n). Fluorescence happens from S_1 to S_0, but phosphorescence occurs from T_1 to S_0 [64, 65].



Characteristic times

Absorption 10^{-15} s
Vibrational relaxation 10^{-12}–10^{-10} s
Lifetime of the excited state S_1 10^{-10}–10^{-7} s → Fluorescence
Intersystem crossing 10^{-10}–10^{-8} s
Internal conversion 10^{-11}–10^{-9} s
Lifetime of the excited state T_1 10^{-6}–10 s → Phosphorescence

Figure 2.18 Perrin-Jablonski diagram and illustration of the relative positions of absorption, fluorescence, and phosphorescence spectra [64].

2.4.1 Fluorescent Pigments

Luminescent pigments absorb the incoming radiation, and then convert it into low energy radiation with longer wavelength. If the absorbed radiation is in near-UV region but not in visible region the emitted light falls into visible region, and thus the intensity of visible region becomes augmented. This is actually what fluorescent radiation is, and the light becomes brilliant. The pigments are commonly activated by the near-UV and visible violet wavelengths [66]. Fluorescent pigments are inorganic and usually crystalline materials that emit light when activated by UV radiation. The well-known commercial inorganic fluorescents are zinc sulfide, and combined zinc and cadmium sulfides known as a daylight fluorescent pigments [67].

Figure 2.19 demonstrates an example for non-fluorescent and fluorescent pigment. It is clearly seen that the intensity of conventional non- fluorescent orange pigment is less than the fluorescent one. Non–fluorescent pigment absorbs white light and reflect 600nm wavelength (orange band) of the visible spectrum. However, a fluorescent orange pigment absorbs white light and transform to lower wavelength colors such yellow, green, blue, violet [9].

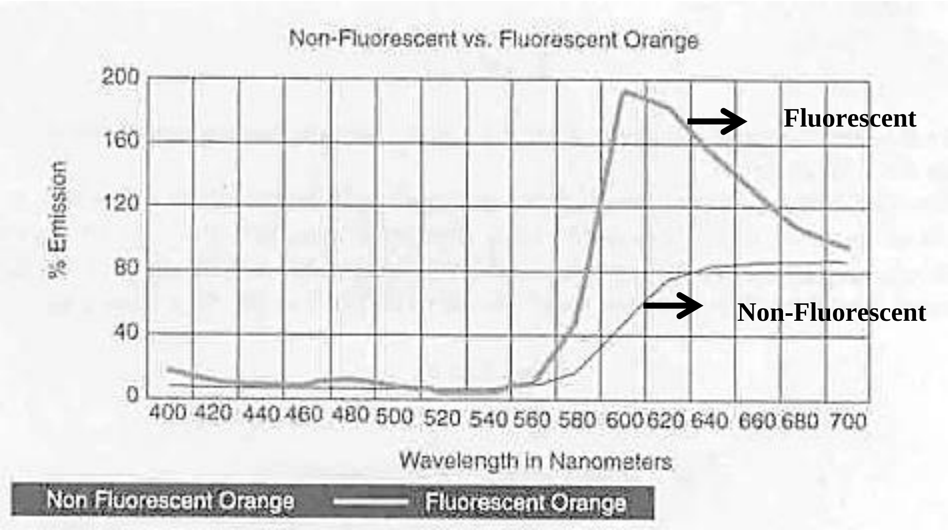


Figure 2.19 Non-fluorescent vs. fluorescent orange [9].

Most of daylight fluorescent pigments are comprised of fluorescent dyes. They can be dissolved or dispersed in a polymer matrix and used in paints, plastics or printing inks [6].

Metallophthalocyanines have photosensitizing tendencies, which gives absorption intense in the red visible region. In order to obtain efficient sensitization, high triplet state quantum yields and long lifetime are required. This criterion may be achieved by using diamagnetic metals with phthalocyanines such as zinc, aluminum, or silicon. Durmus et al. studied zinc phthalocyanines because of theirs long triplet lifetimes. Photochemical and photophysical properties of peripheral and non-peripheral tetra-substituted zinc phthalocyanines were investigated by them. In addition, they reported the solvent effect on photochemical and photophysical parameters of zinc phthalocyanines [68].

Camur et al. synthesized new peripherally and non-peripherally tetra-substituted metal free and zinc phthalocyanines with functionalities of phenyloxyacetic acid. They investigated photophysical and photochemical change with respect to metal-non-metal samples, the position of the -COOH groups and peripheral or non-peripherally molecules. According to their study peripherally and non- peripherally substituted zinc phthalocyanines gave effective singlet oxygen quantum yields [69].

Kobayashi and co-workers investigated the effect of substituent groups on electronic absorption and fluorescence spectra of metal free and zinc phthalocyanines in 35 phthalocyanine compounds. The position and bandwidths of phthalocyanines were detected with change of the type, number, and positions of peripheral substituents and central metal atom. They tackled 35 phthalocyanines with electron releasing alkoxyl or alkylthio groups and electron recovering nitro or sulfonyl groups. Consequently, they reported metal free and zinc phthalocyanines' electronic absorption and fluorescence emission spectra [5].

2.4.2 Measurement of Fluorescence

Fluorescence spectroscopy has similar instrumentations like to UV absorption spectroscopy. One of the most essential differences between absorption and fluorescence instruments depends on the source. In absorption unit, it is measures that transmittance or absorbance of sample. Fluorescence unit is designed to measure of intensity, spectrum, lifetime and polarization.

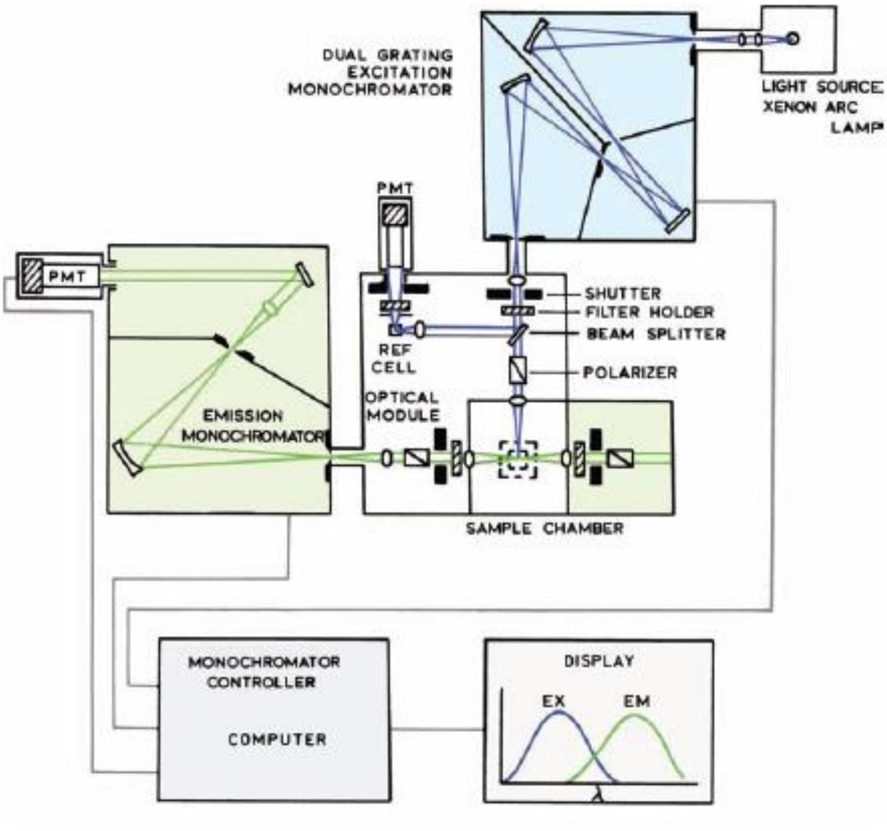


Figure 2.20 Schematic diagram of fluorescence spectroscopy [70].

Figure 2.20 demonstrates typically fluorescent spectroscopy. It has a xenon lamp that is a source of exciting light. The instrument includes monochromators to picking out excitation and emission wavelengths. Photomultipler tube (PMT) detects the fluorescence and it is processes by a computer to quantify. Graphical representation is obtained as an output [63].

Fluorescence spectrophotometers are recorded as both emission and excitation spectra but the data is generally presented as emission spectra. Typical fluorescence emission spectrum and absorption spectrum are shown in Figure 2.20 which is plotted intensity versus wavelength (nm) or wavenumber (cm^{-1}).

An emission spectrum is related to the distribution of wavelength, while excitation spectrum is related to the emission intensity. Both of them are measured at single excitation wavelength. An excitation spectrum is a broad curve and it is dependent on the chemical structure of the molecules where solvent effect is excluded. Emission spectrum can be recorded differently on different instruments due to their sensitivities of wavelength [71] .

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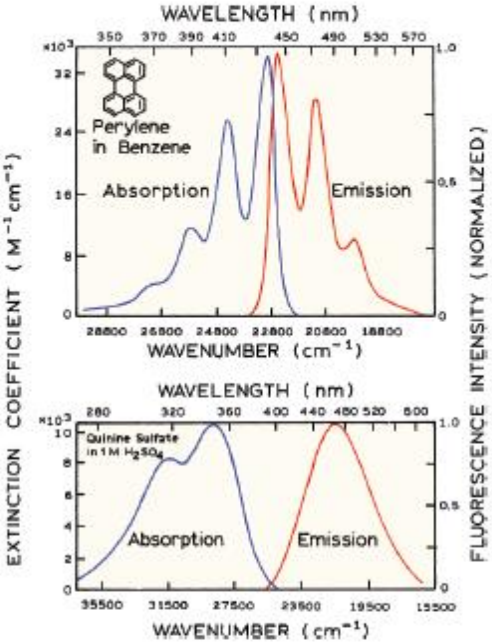


Figure 2.21 Absorption and emission spectrum of perylene and quinine [63].

As seen in Figure 2.21 the absorption energy is higher than the emission energy, because of the wavelength distribution. Actually, the molecule absorbs the total energy and then it is released in the medium, such as photon emission. The absorption spectrum forms in ground state while the fluorescence and phosphorescence spectrum occur in excited state. The fluorescence spectrum displays a maximum emission corresponding to the transition of emission. Emission is a very fast process that lifetime is within the picosecond to nanosecond range. For this reason, the fluorophore should be excited steadily to observe fluorescence emission [63].

CHAPTER 3

EXPERIMENTAL

In this part, the materials and their properties used in the experiments were explained. Besides that, the synthesis and characterization method of zinc phthalocyanines and its derivatives as well as their deposition on mica-titania were described in detail.

3.1 Materials

- 3- Nitrophthalic acid
- Urea
- Zinc chloride
- Ammonium heptamolybdate
- Sodium sulfide
- Dimethyl formamide (DMF)
- Chloroform
- Ethyl acetate
- Diethyl ether
- Acetic acid
- Trifluroacetic acid (TFA)

Detailed properties of the materials were given in Appendix-D.

3.2 Procedure

In this study, the experiments were carried out in four main steps: (i) synthesis of tetranitro zinc phthalocyanine, (ii) synthesis of tetraamino zinc phthalocyanine, (iii) deposition of these pigments onto mica-titania pigment, (iv) film application, there synthesized pigments were mixed with water based styrene-acrylic resin. Detailed descriptions of these experiments were given below. Figure 3.1 shows the steps of the experiments. In every step, different characterization methods were applied separately.

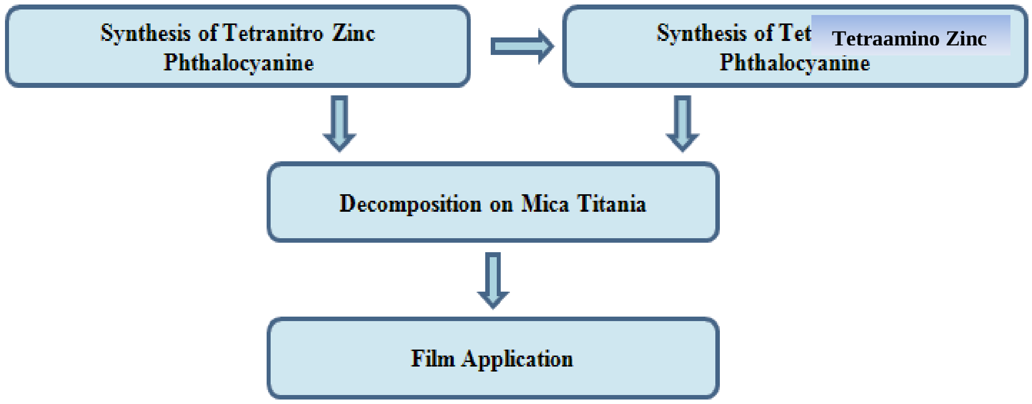


Figure 3.1 General routes of the experiments.

3.2.1 Synthesis of Tetranitro Zinc Phthalocyanine

3-nitrophthalic acid, urea, and ammonium molybdate were ground in an agate mortar for nearly 10 minutes. Then zinc chloride was added on them and suppressed again with mixture. The mixture was taken in a flask with 7 ml distilled water and the reaction was carried out by microwave oven (600W). The reaction time was nearly 3 minutes. The following step was purification to get rid of unreacted materials and impurities. Ethyl acetate, diethyl ether, methanol and water were used in the purification process. The rest of the filtrated pigment was dried in oven at 120°C. Figure 3.2 shows the reaction for the synthesis of tetranitro zinc phthalocyanine.

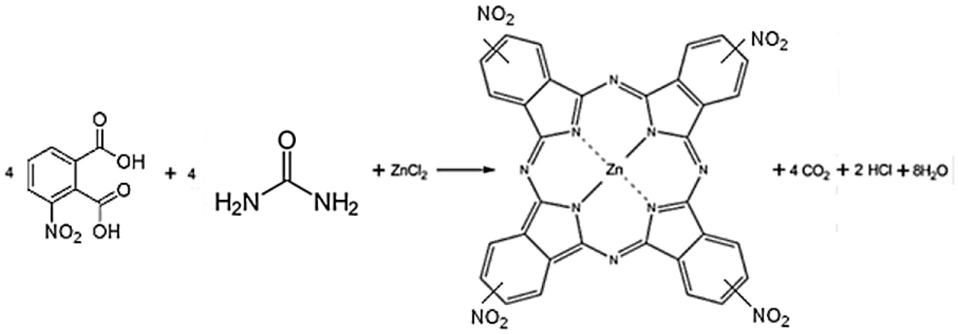


Figure 3.2 Synthesis reaction of tetranitro zinc phthalocyanine.

3.2.2 Synthesis of Tetraamino Zinc Phthalocyanine

Tetranitro zinc phthalocyanine was mixed with 100 ml water, and then sodium sulfide was added into this solution. The reaction was carried out at 65°C for 4 hours. The next step was the removal of unreacted materials and impurities from the product. HCl, NaOH and water were used in the purification step. The rest of the filtrated pigment was dried in an oven at 120°C. Figure 3.3 shows the reaction for the synthesis of tetraamino zinc phthalocyanine.

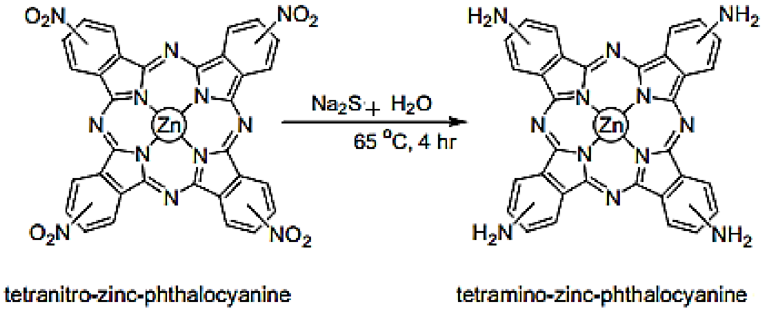


Figure 3.3 Synthesis reaction of tetraamino zinc phthalocyanine.

3.2.3 Preparation of Combination Pigments of Tetranitro and Tetraamino Zinc Phthalocyanine with Mica-Titania

At the beginning of this step, the specific amount of tetranitro and tetraamino zinc phthalocyanines was dissolved in the solvent. After then mica-titania was introduced into the reactor. Three different solvents, DMF, water, and chloroform, were used to observe their effects on the deposition of phthalocyanine pigments onto mica-titania. The boiling temperatures of solvents were taken as the maximum reaction temperature. The amount of pigment, the pH and the reaction time were taken as the experimental parameters. Acetic acid and trifluroacetic acid were used to change the pH of the medium. Experiment parameters and procedure were given briefly in Table 3.1, and Figure 3.4, respectively. Other tables show the parameters in detail.

Table 3.1 Parameters used in combination pigments experiments[a].

Experiment Groups	Pigment – Solvent Combination	Parameters		
		T (°C)	**pH**	**t (h)**
G-1	TAZnPc – DMF	120	8	1-3-6
G-2	TAZnPc – DMF – AA	120	4-5	3
G-3	TAZnPc – DMF – TFA	120	3-4-5	3
G-4	TAZnPc – Water	90	7	1-3-6
G-5	TNZnPc – DMF	120	8	3
G-6	TNZnPc – $CHCl_3$	60	5	5
G-7	TNZnPc – $CHCl_3$ – AA	60	3-4	5
G-8	TNZnPc – $CHCl_3$ – TFA	60	1-2-3	5

[a] Amount of pigment in each experiment (g): 0.005 – 0.01 – 0.015 – 0.02 – 0.04 – 0.06

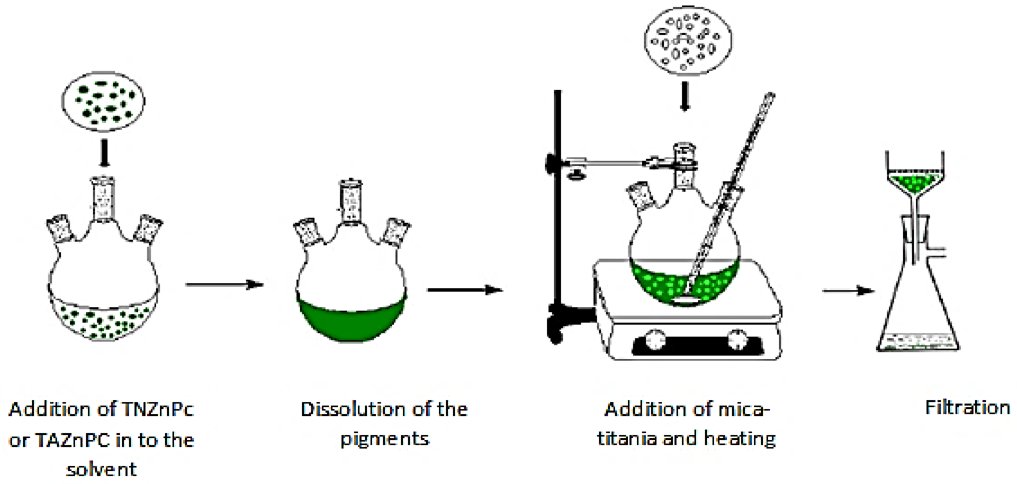


Figure 3.4 Experimental procedures for combination of TNZnPc and TAZnPc with mica-titania.

Table 3.2 Parameters of combination of mica-titania with DMF – TAZnPc experiment.

G-1 (DMF – TAZnPc)	amount of organic pigment, g	w% of g pigment/g mica-titania	pH
G-1_s1	0.005	0.03	8
G-1_s2	0.01	0.07	8
G-1_s3	0.015	0.10	8
G-1_s4	0.02	0.13	8
G-1_s5	0.04	0.27	8
G-1_s6	0.06	0.40	8

Table 3.3 Parameters of combination of mica-titania with DMF - AA– TAZnPc experiment.

G-2 (DMF–TAZnPc–AA)	amount of organic pigment, g	w% of g pigment/g mica titania	pH
G-2_s1	0.005	0.03	4–5
G-2_s2	0.01	0.07	4–5
G-2_s3	0.015	0.10	4–5
G-2_s4	0.02	0.13	4–5
G-2_s5	0.04	0.27	4–5
G-2_s6	0.06	0.40	4–5

Table 3.4 Parameters of combination of mica-titania with DMF – TFA – TAZnPc experiment.

G-3 (DMF–TAZnPc–TFA)	amount of organic pigment, g	w% of g pigment/g mica titania	pH
G-3_s1	0.005	0.03	3–4–5
G-3_s2	0.01	0.07	3–4–5
G-3_s3	0.015	0.10	3–4–5
G-3_s4	0.02	0.13	3–4–5
G-3_s5	0.04	0.27	3–4–5
G-3_s6	0.06	0.40	3–4–5

Table 3.5 Parameters of combination of mica-titania with Water – TAZnPc experiment.

G-4 (Water – TAZnPc)	amount of organic pigment, g	w% of g pigment/g mica titania	pH
G-4_s1	0.005	0.03	7
G-4_s2	0.01	0.07	7
G-4_s3	0.015	0.10	7
G-4_s4	0.02	0.13	7
G-4_s5	0.04	0.27	7
G-4_s6	0.06	0.40	7

Table 3.6 Parameters of combination of mica-titania with DMF – TNZnPc experiment.

G-5 (DMF– TNZnPc)	amount of organic pigment, g	w% of g pigment/g mica titania	pH
G-5_s1	0.005	0.03	8
G-5_s2	0.01	0.07	8
G-5_s3	0.015	0.10	8
G-5_s4	0.02	0.13	8

Table 3.7 Parameters of combination of mica-titania with $CHCl_3$ – TNZnPc experiment.

G-6 ($CHCl_3$ – TNZnPc)	amount of organic pigment, g	w% of g pigment/g mica titania	pH
G-6_s1	0.005	0.03	5
G-6_s2	0.01	0.07	5
G-6_s3	0.015	0.10	5
G-6_s4	0.02	0.13	5
G-6_s5	0.04	0.27	5
G-6_s6	0.06	0.40	5

Table 3.8 Parameters of combination of mica-titania with $CHCl_3$ – AA – TNZnPc experiment.

G-7 ($CHCl_3$ –TNZnPc – AA)	amount of organic pigment, g	w% of g pigment/g mica titania	pH
G-7_s1	0.005	0.03	3–4
G-7_s2	0.01	0.07	3–4
G-7_s3	0.015	0.10	3–4
G-7_s4	0.02	0.13	3–4
G-7_s5	0.04	0.27	3–4
G-7_s6	0.06	0.40	3–4

Table 3.9 Parameters of combination of mica-titania with $CHCl_3$ – TFA – TNZnPc experiment.

G-8 **($CHCl_3$–TNZnPc– TFA)**	**amount of organic pigment, g**	**w% of g pigment/g mica titania**	**pH**
G-8_s1	0.005	0.03	1–2–3
G-8_s2	0.01	0.07	1–2–3
G-8_s3	0.015	0.10	1–2–3
G-8_s4	0.02	0.13	1–2–3
G-8_s5	0.04	0.27	1–2–3
G-8_s6	0.06	0.40	1–2–3

3.2.4 Paint Preparation

The produced mica phthalocyanine pigments were mixed with water based styrene-acrylic resin to investigate the fluorescence property of paint. In this procedure, white sprit which is a solvent was first mixed with pigments to aid the separation of pigment particles from each other. Then, the mixture was introduced into styrene-acrylic resin (Betapol SA-5017B) supplied by BETEK Boya San. A.Ş. After well mixing, films were applied on glass plates by a paint applicator. Films were dried at room temperature and then measurements were carried out. In Table 3.10 the simple formulation of the paint was given.

Table 3.10 Water based paint formulation [72].

Formulation	**% (w/w)**
Water Based Styrene-Acrylic Resin (50 %w/w)	**88.00**
White Sprit	**10.00**
Mica-titania-Phthalocyanine Pigments	**2.00**

3.3 Characterization Methods

In this study, various characterization methods were used which are FTIR spectroscopy, SEM, EDX, XPS, elemental analysis, UV-Vis, fluorescence spectrophotometer, color spectroscopy. Details of these methods and instruments are described below.

3.3.1 Fourier Transform Infrared (FTIR) Spectroscopy

Molecular structures and functional groups of the tetranitro and tetraamino zinc phthalocyanines and their combinations with mica-titania were analyzed. (Instrument: Thermo Scientific Nicolet 6700.)

3.3.2 Scanning Electron Microscopy (SEM)

Morphology of the pigments was characterized by using SEM which is located in Metallurgical and Materials Engineering (METE) department in METU. It is JSM-6400 Electron Microscope (JEOL), equipped with NORAN System 6 X-ray Microanalysis System &Semafore Digitizer.

3.3.3 Energy Dispersive X-Ray Spectroscopy (EDS)

Chemical characterization of the pigments was done with using EDX which is an analytical technique. The device is equipped with SEM spectroscopy system.

3.3.4 UV-Visible Spectrophotometer

To observe the UV absorbance properties of tetranitro and tetraamino zinc phthalocyanines, UV-Visible spectroscopy was utilized. It is Cary 5000 model device located in Chemical Engineering department in METU.

3.3.5 Fluorescence Spectrophotometer

Fluorescence properties of tetranitro and tetraamino zinc phthalocyanines, and their combinations with mica-titania pigments were measured by using a fluorescent spectrophotometer (Model: Cary Eclipse Varian) located in UNAM (Ulusal Nanoteknoloji Araştırma Merkezi).

3.3.6 CHNS/O Elemental Analysis

Elemental analysis was investigated to determine nitrogen content of the combination pigments. This equipment is located in UNAM, and it is Thermo scientific Flash 2000.

3.3.7 X-Ray Photoelectron Spectroscopy (XPS)

XPS is a quantitative spectroscopic technique used to identify elemental composition. The equipment is located in UNAM, and it is Thermo K-Alpha - Monochromated high-performance XPS spectrometer.

3.3.8 Color Spectrophotometer

Paint properties and colors of the pigments were investigated by using X-Rite 65 color spectrophotometer.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Preliminary Studies

In the first experiment tetranitro zinc phthalocyanine was synthesized using 3-nitro phthalic acid, urea, and zinc chloride. The reaction yield is nearly 89.1 %. The FT-IR spectrum of tetranitro zinc phthalocyanine (TNZnPc) given in Figure 4.1 has two peaks at 3200 and 3090 cm^{-1} because of the aromatic C-H stretching of the zinc phthalocyanine. The peak at 1740 cm^{-1} corresponds to anhydride, C=O bonds, whereas the one at 1640 cm^{-1} shows C=C macrocycle ring deformation. The peak at 1600 cm^{-1}, is due to bending of the N-H groups, and the characteristic peaks of nitro groups are seen at 1540 and 1360 cm^{-1}. The peaks at 1300 cm^{-1} is because of C-C stretching in isoindole, at 1160, 1120, 1050 cm^{-1} those correspond to the C-H bending in plane deformation, C-N stretching in isoindole, and C-N in plane bending, respectively. The peaks at 930, 830, 720, 575 cm^{-1} are formed by virtue of C-H bending out of plane deformation.

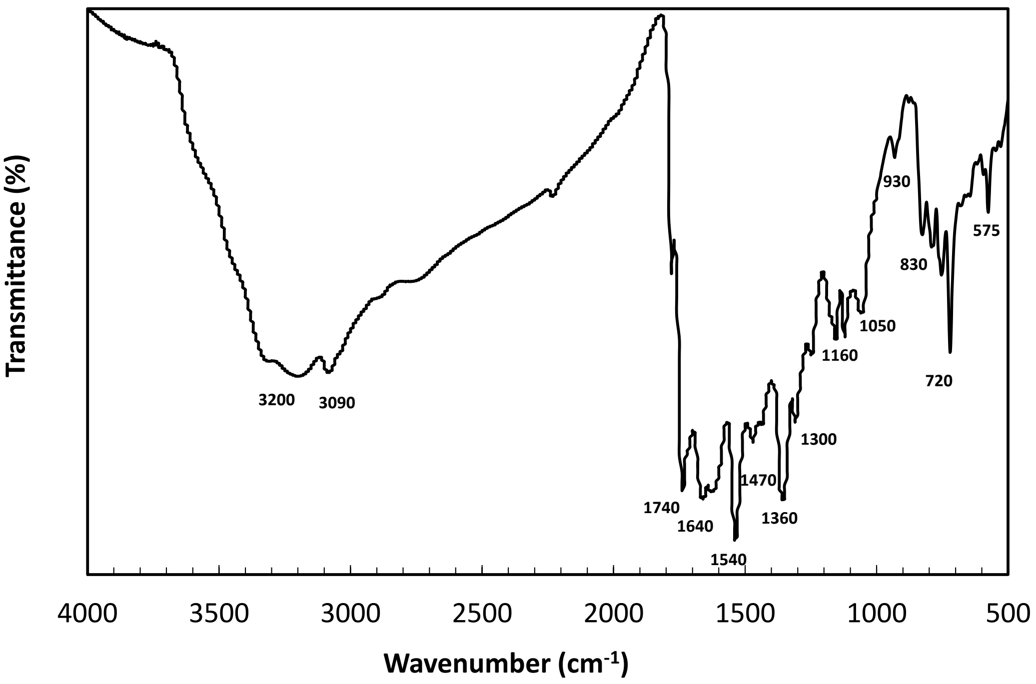


Figure 4.1 FT-IR spectrum of TNZnPc.

The FT-IR spectrum of TAZnPc is given in the Figure 4.2. The peak that belongs to the N-H, stretching is seen at 3300 cm^{-1}. The characteristic nitro peaks in TNZnPc complexes disappear after the reduction which is converted to amino groups in TAZnPc. The peaks at 1620, 1340 cm^{-1} correspond to the stretching vibrations of C-C and C-N of the TAZnPc plane, respectively. The stretch vibrations of C=N and N-H of amino groups are found at 1620 cm^{-1} and 3300 cm^{-1}, respectively. As a result of repeated experiments, the reproducible findings are obtained.

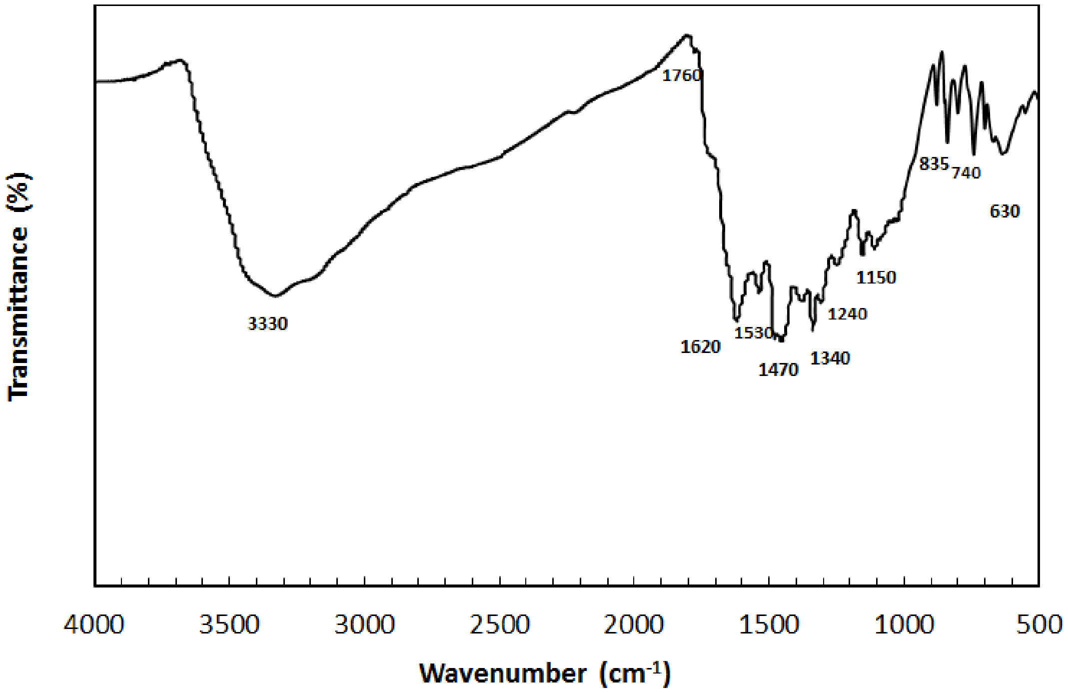


Figure 4.2 FT-IR spectrum of TAZnPc.

The UV-visible spectrum of TNZnPc and TAZnPc pigments are given in Figure 4.3 and Figure 4.4, respectively. Both of the pigments show absorption at three different points. The characteristic absorption of the phthalocyanine molecules in the B band region (UV region) is seen at around 300-400 nm and the Q band region (visible) appears at around 600-800 nm. TNZnPc complexes are deep green color than TAZnPc complexes and their absorption in the B band region occurred at 340 nm and at 349 nm, respectively. Furthermore, TNZnPc and TAZnPc show absorption in the Q band region at 670 nm and, 765 nm, respectively.

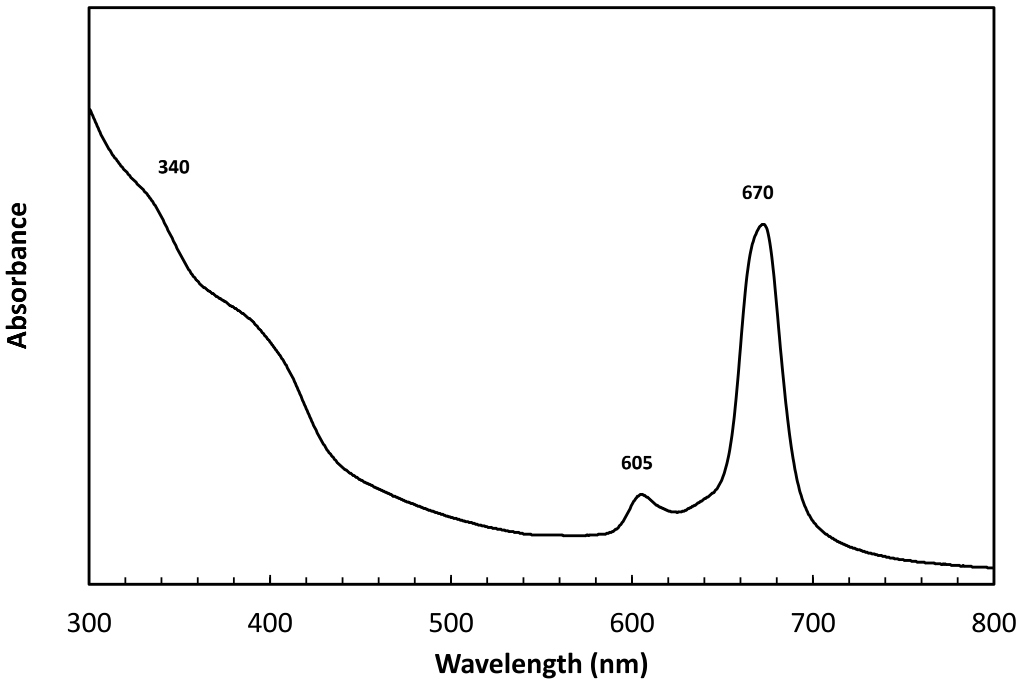


Figure 4.3 UV-Vis spectrum of TNZnPc.

The appearance of the second band in the high energy region of the Q band is due to the aggregation in DMF solution. Besides that the small band formed at 605 nm for TNZnPc and at 680 nm for TAZnPc pigments. Aggregation in phthalocyanine molecules occurs via intermolecular π-π interactions. On the other hand, amino groups interact with DMF to form hydrogen bonding, which provides the high energy in the Q band region.

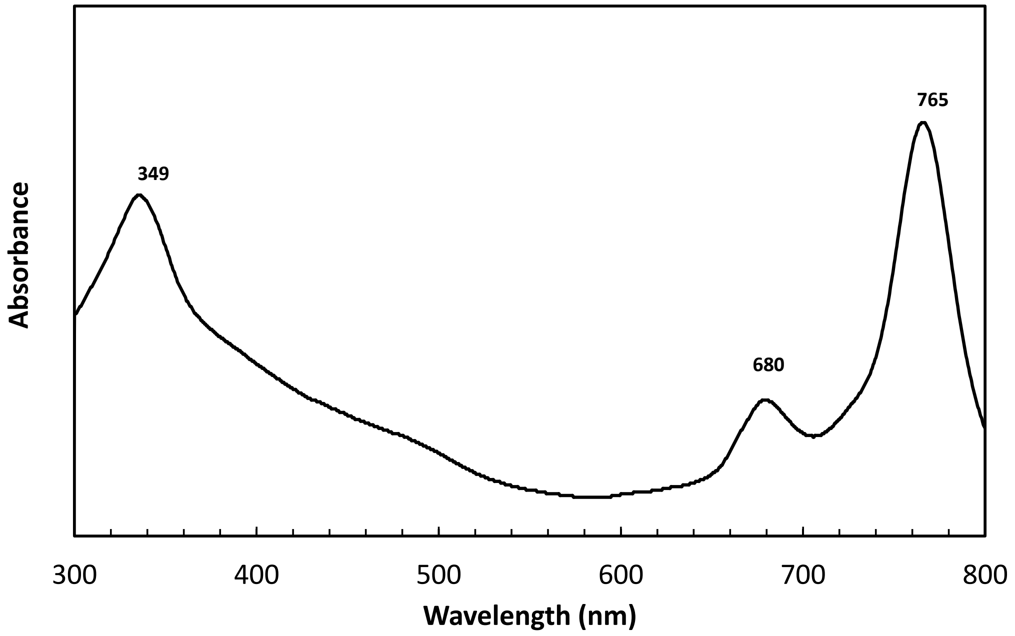


Figure 4.4 UV-Vis spectrum of TAZnPc.

Figure 4.5 and Figure 4.6 show the fluorescence spectrum of the TNZnPc pigment and TAZnPc pigment, respectively. Pigments dispersed in DMF have no fluorescence property according to Kahya’s study at different concentrations. TNZnPc pigment is excited at 385 nm and its emission peak is at 475 nm and 685 nm. High energy region has higher intensity than small energy region. TAZnPc pigment was excited at 375 nm and its emission peak is at 465 nm and it has small peak at 800 nm.

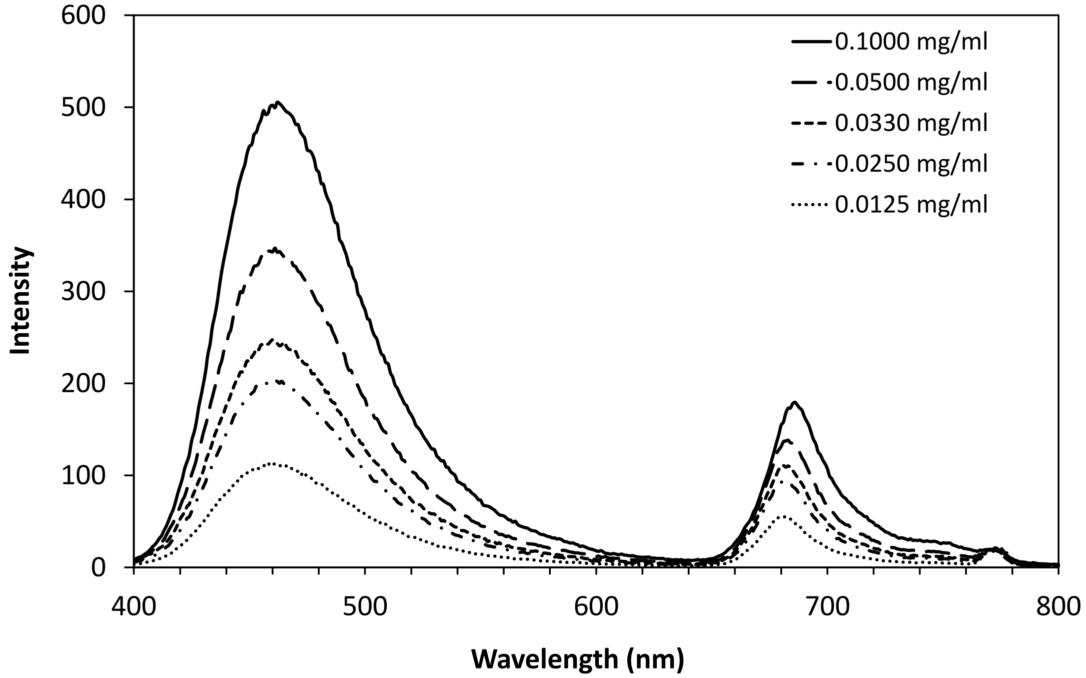


Figure 4.5 Fluorescence spectra of TNZnPc.

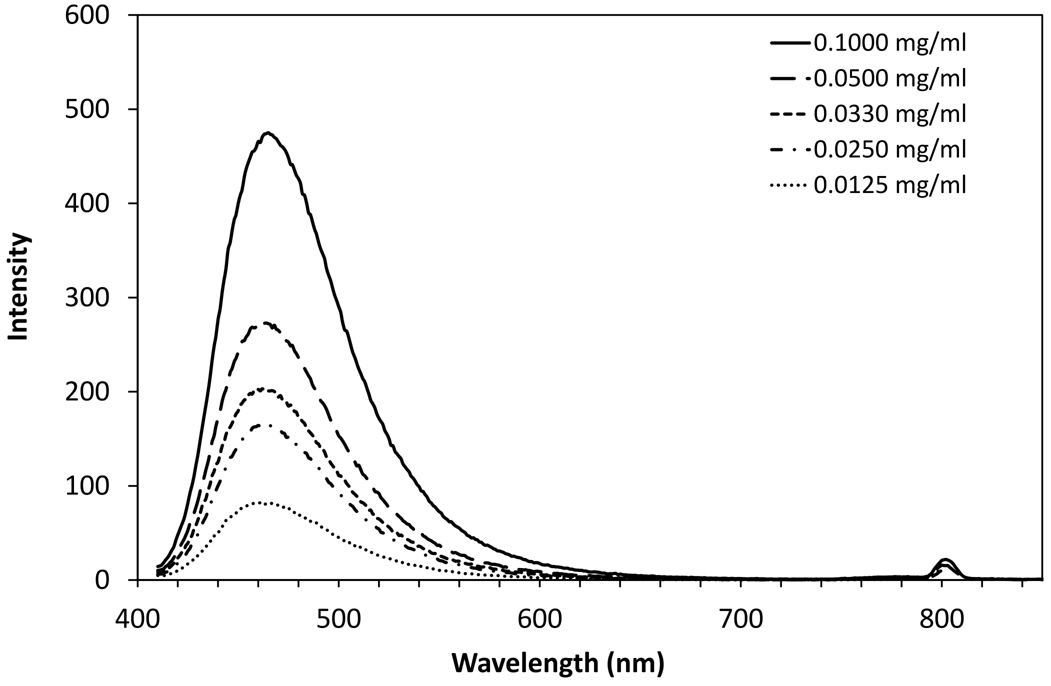


Figure 4.6 Fluorescence spectra of TAZnPc.

According to Figure 4.7 the fluorescent intensities of TNZnPc and TAZnPc show similar tendency. Although, their emission peaks are different from each other.

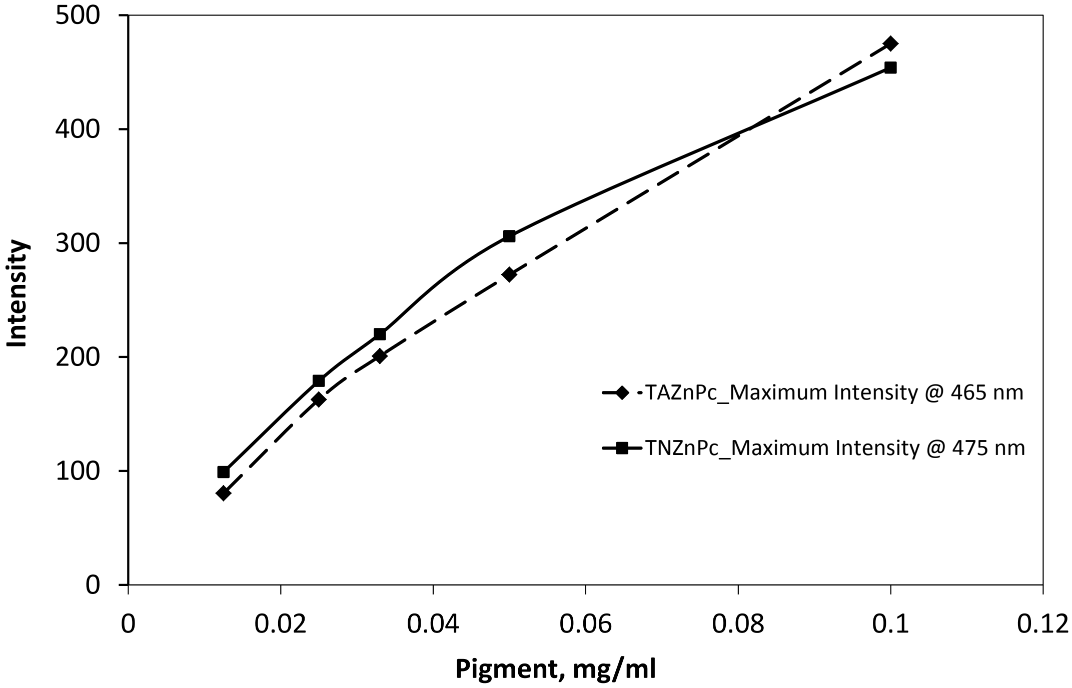


Figure 4.7 Fluorescence emissions comparing of TAZnPc and TNZnPc.

4.2 Combination pigments

Combination pigments were obtained by using TNZnPc and TAZnPc pigments. Nitro combination pigments have green color and amino combination pigments have gray color. Both of them show same behavior on increasing the amount of depositions, and they get darker in color. Their colors became lighter when the solvent acidity was increased. This may be related to the protonation of the pigments. Figure 4.8 gives the photo TNZnPcMip and TAZnPcMip pigment samples.

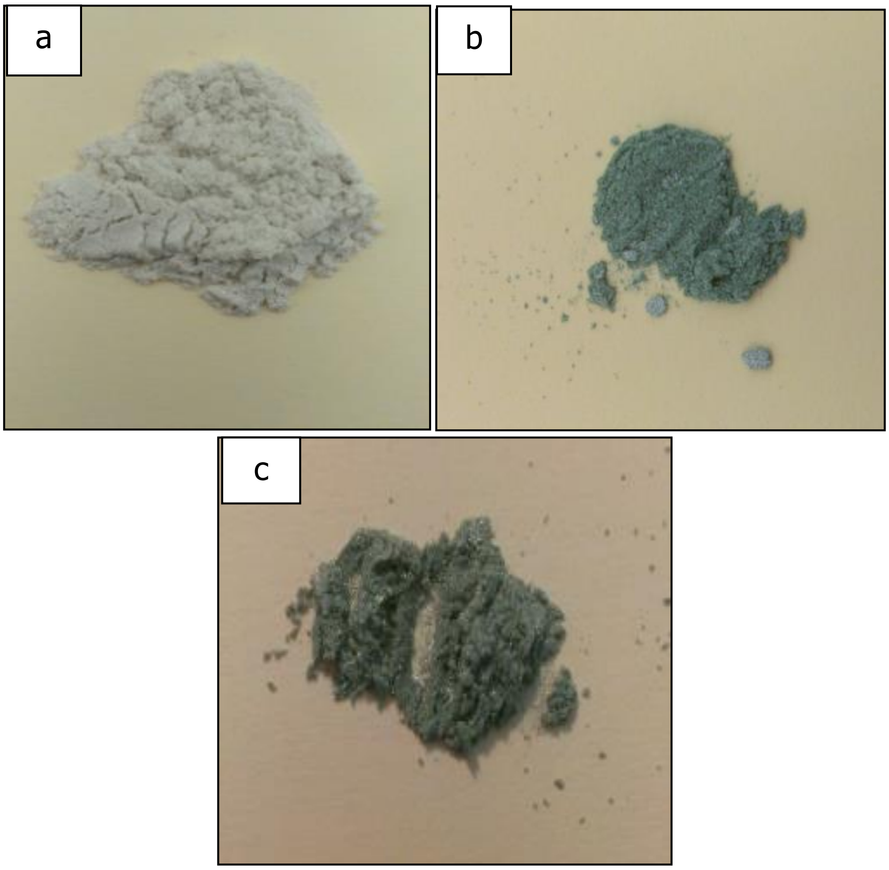


Figure 4.8 Pictures of combination pigments, (a) mica-titania, (b) TAZnPcMip, and (c) TNZnPcMip.

In the initial experiment, different temperatures and reaction times were studied for each solvent. As a result, optimum conditions were decided for the next study. After determining the optimum temperature and reaction time, the effect of the amount of phthalocyanine pigments were investigated. In addition, the pH values of the samples were changed in solvents by using trifluoro acetic acid, and acetic acid.

Firstly, the combination pigment experiments were conducted by using DMF with TAZnPc, TNZnPc and water with TAZnPc pigments in the range between 0.01g and 0.08g. However these experiments were not successful as deduced from the FT-IR results. Then after, $CHCl_3$ was used which is more acidic solvent. The protonation of the pigments started to decompose TAZnPc in DMF. For the protonated pigments, acetic acid and trifluoro acetic acid were used. Experiments of the protonation were made in DMF and $CHCl_3$.

Time and temperature studies were conducted in the experiments. The temperature and time were set as 120° C and 3 hours for DMF solvents; 50° C and 5 hours for $CHCl_3$, and 90° C and 3 hours for water, respectively.

4.2.1 FT-IR Results of Combination Pigments

The FT-IR results of some combination pigments produced were analyzed in this part. Figure 4.9 shows the FT-IR spectra of TNZnPcMip pigment (at 50°C, pH=5 and 0.001 TNZnPc), TNZnPc pigment and mica-titania pigment. According to the graph, the characteristic peaks for TNZnPc were seen in the range 1500-1300 cm^{-1} (red circle).

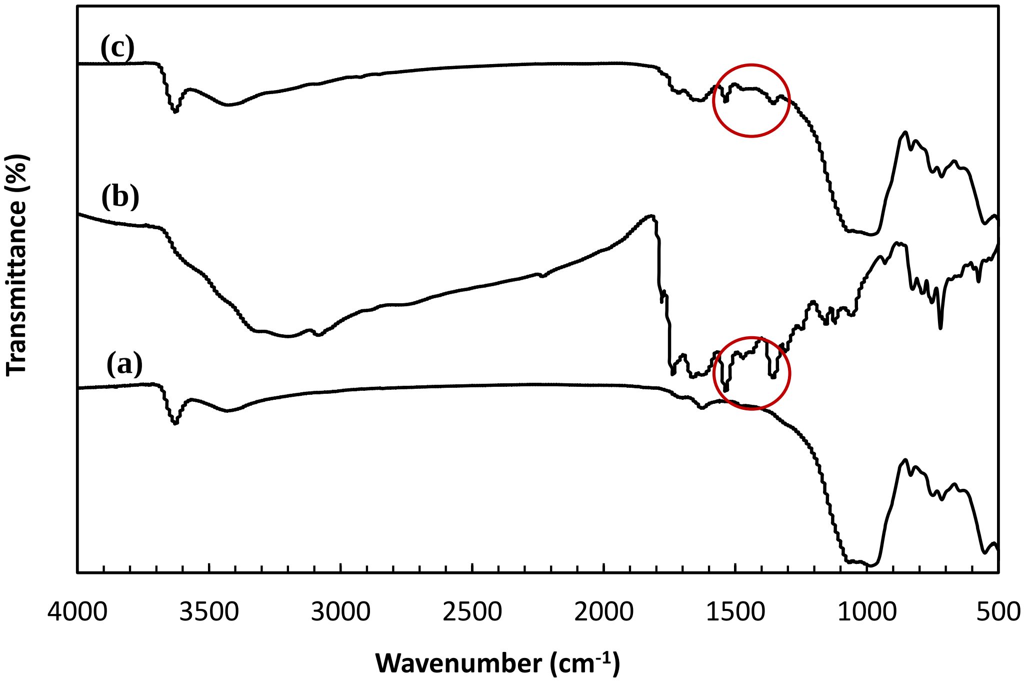


Figure 4.9 FT-IR spectra of TNZnPcMip 0.01 g TNZnPc in $CHCl_3$, pH=5; (a) mica-titania, (b) TNZnPc, and (c) TNZnPcMip.

In order to see these peaks clearly, the FT-IR spectrum in the range 500 cm^{-1} and 1700 cm^{-1} was replotted in Figure 4.10.

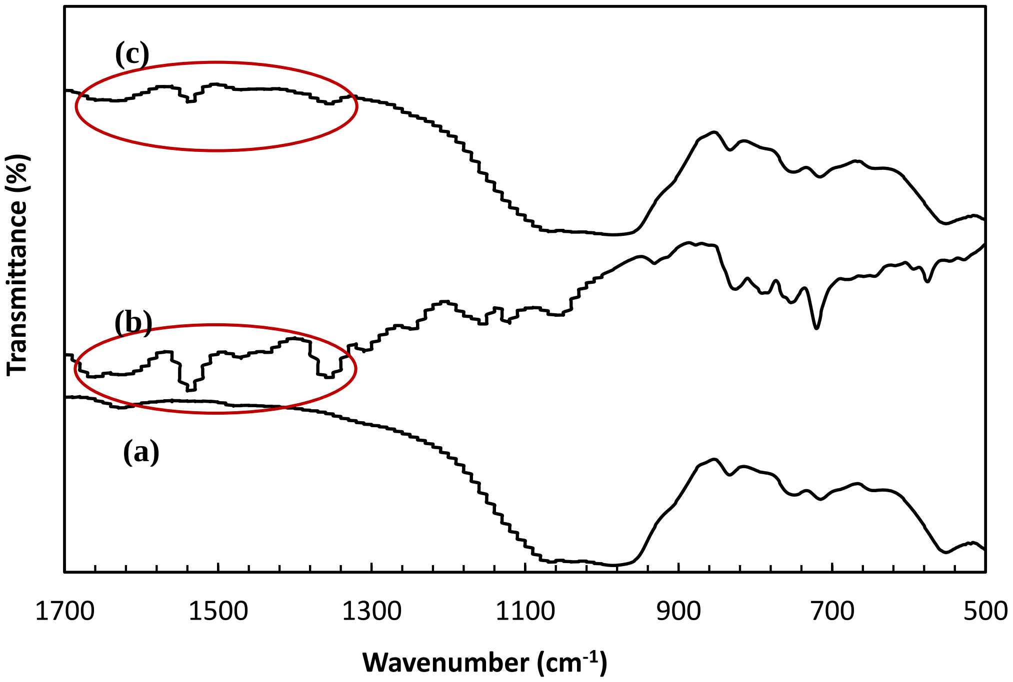


Figure 4.10 FT-IR spectra of TNZnPcMip 0.01 g TNZnPc in $CHCl_3$, pH=5 at 1700-500 cm^{-1}; (a) mica-titania, (b) TNZnPc, and (c) TNZnPcMip.

The protonation of TNZnPc couldn't be achieved when acetic acid was used but it was accomplished with trifluoro acetic acid. However, the color of TFA protonated TNZnPc pigment was lighter than unprotonated TNZnPc in $CHCl_3$. Figure 4.11 presents the FT-IR spectrum of pigments treated with DMF - TFA mixture. It can be seen easily that the intensity of FT-IR peak decreased. The reason for decrease in the intensity may be that trifluoro acetic acid is very strong acid and the pH of the reaction is very low.

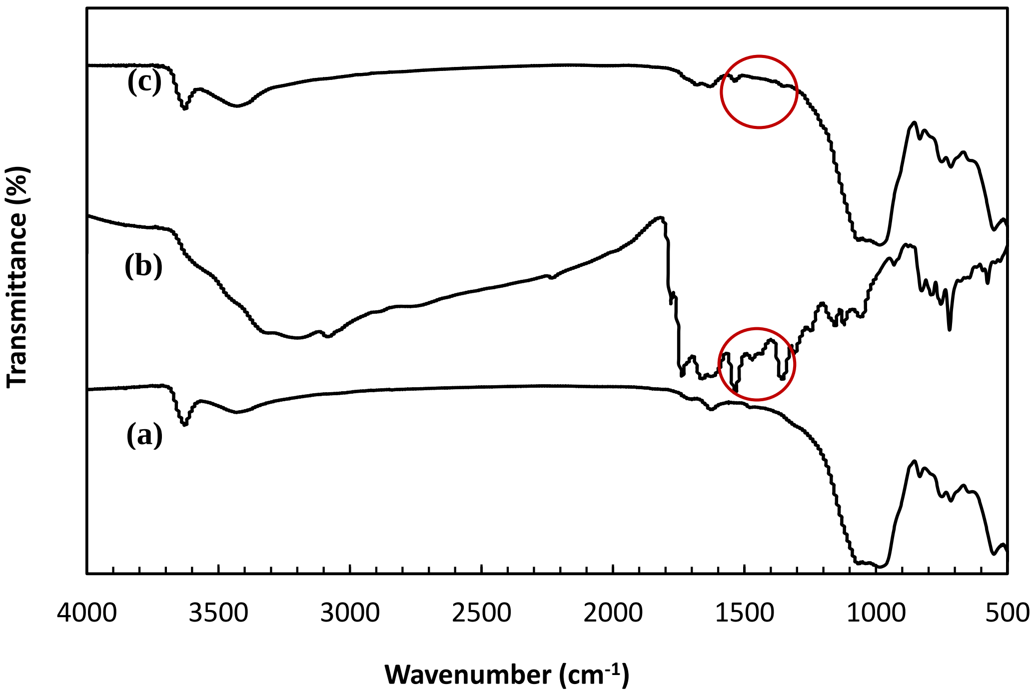


Figure 4.11 FT-IR spectra of TNZnPcMip 0.01 g TNZnPc in $CHCl_3$+ TFA, pH=2; (a) mica-titania, (b) TNZnPc, and (c) TNZnPcMip.

Figure 4.12 shows that the FT-IR spectra of TAZnPc in DMF with acetic acid. TAZnPc characteristic peaks can be seen around at 1600-1400 cm^{-1}.

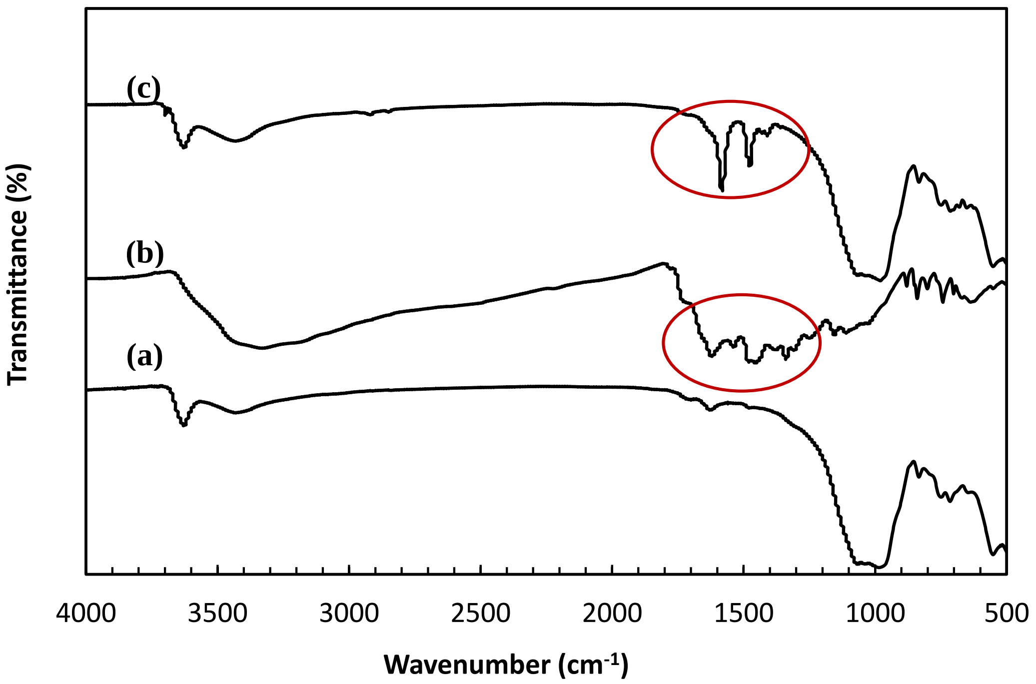


Figure 4.12 FT-IR spectra of TAZnPcMip 0.01 g TAZnPc in DMF+AA, pH=4; (a) mica-titania, (b) TAZnPc, and (c) TAZnPcMip.

In order to see these peaks clearly, the FT-IR spectrum in the range between 500 cm^{-1} and 1700 cm^{-1} was replotted in Figure 4.13.

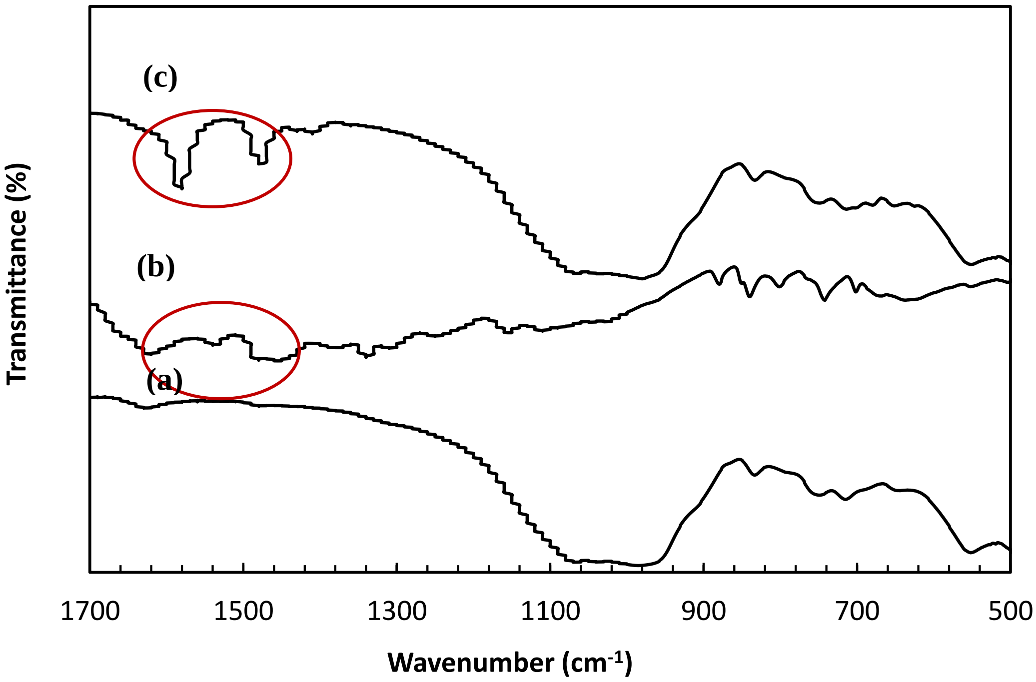


Figure 4.13 FT-IR spectra of TAZnPcMip 0.01 g TAZnPc in DMF+AA, pH=4 at 1700-500 cm^{-1}; (a) mica-titania, (b) TAZnPc and (c) TAZnPcMip.

It can be said from the visual observation of the pigments that mica-titania substrate was successfully coated with phthalocyanine based pigments. The FTIR spectrum also supports it. However, the identifying peaks came out to be very small as small amounts of phthalocyanine based pigments were deposited on the substrate. The elemental analysis based on nitrogen identification can prove the deposition of phthalocyanine based pigments on the substrate.

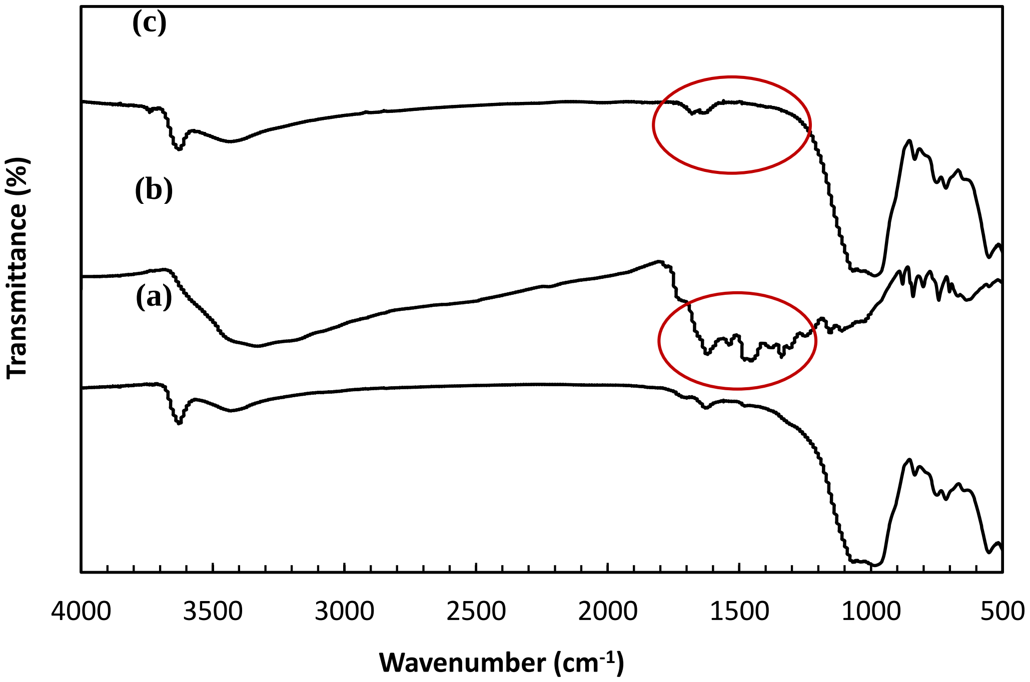


Figure 4.14 FT-IR spectra of TAZnPcMip 0.01 g TAZnPc in DMF+TFA, pH=3; (a) mica-titania, (b) TAZnPc, and (c) TAZnPcMip.

4.2.2 SEM and EDS

In order to display pigments on mica-titania pigment, SEM micrographs were investigated. Figure 4.15 shows the mica-titania pigment samples at different magnifications. Mica has plate structure and TiO_2 crystals could be seen on the surface.

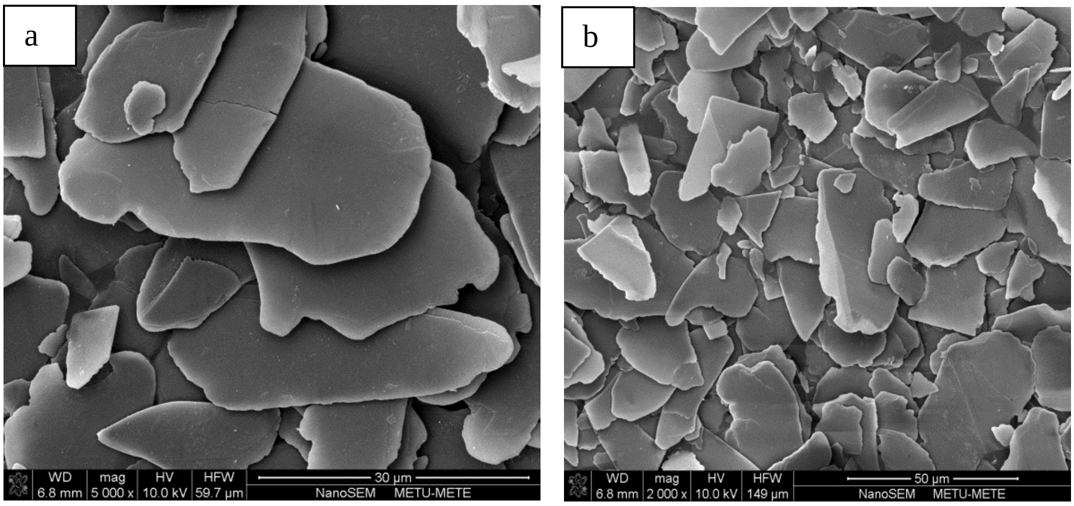


Figure 4.15 SEM micrographs of mica-titania pigment; (a) high magnification (×5000), (b) low magnification (×2000).

Figure 4.16 and Figure 4.17 shows SEM micrographs of the TAZnPcMip pigments and TNZnPcMip pigments, respectively.

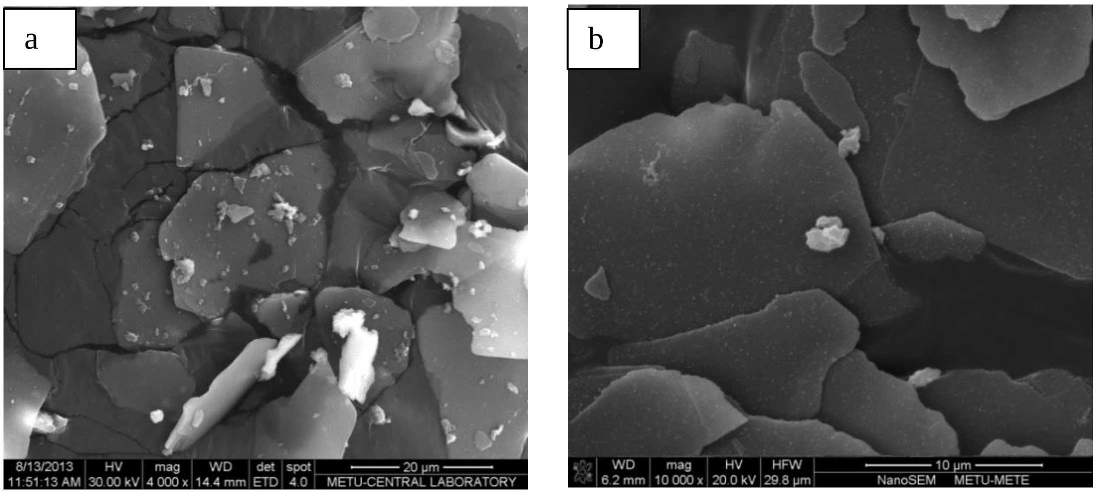


Figure 4.16 SEM micrographs of TAZnPcMip synthesized at 120°C in DMF+AA; (a) low magnification (×4000), (b) high magnification (×10000).

It is seen from these SEM micrographs that TNZnPc and TAZnPc pigments randomly deposited on mica-titania. Fine agglomerates of phthalocyanine pigments are seen in small quantities on the surface of substrate.

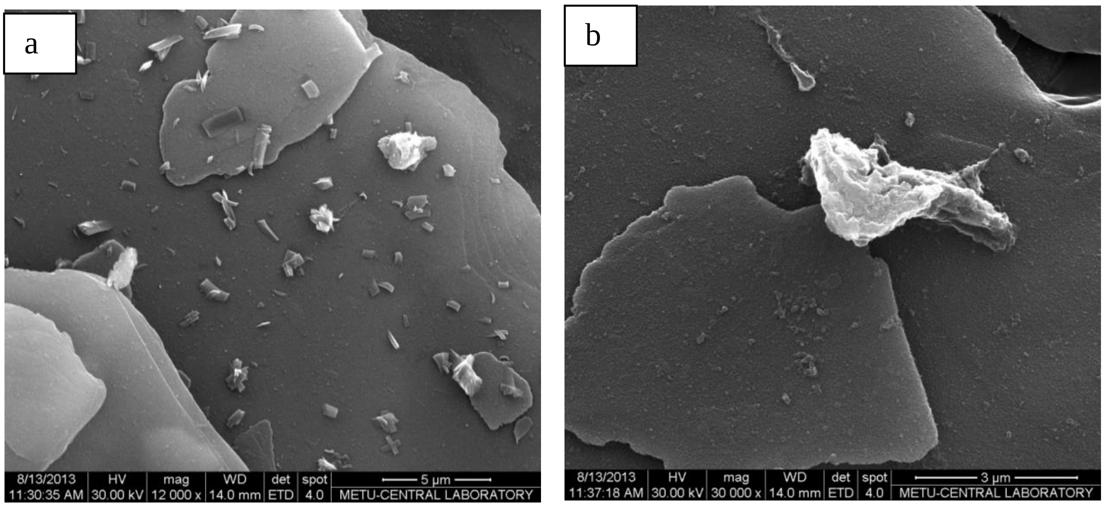
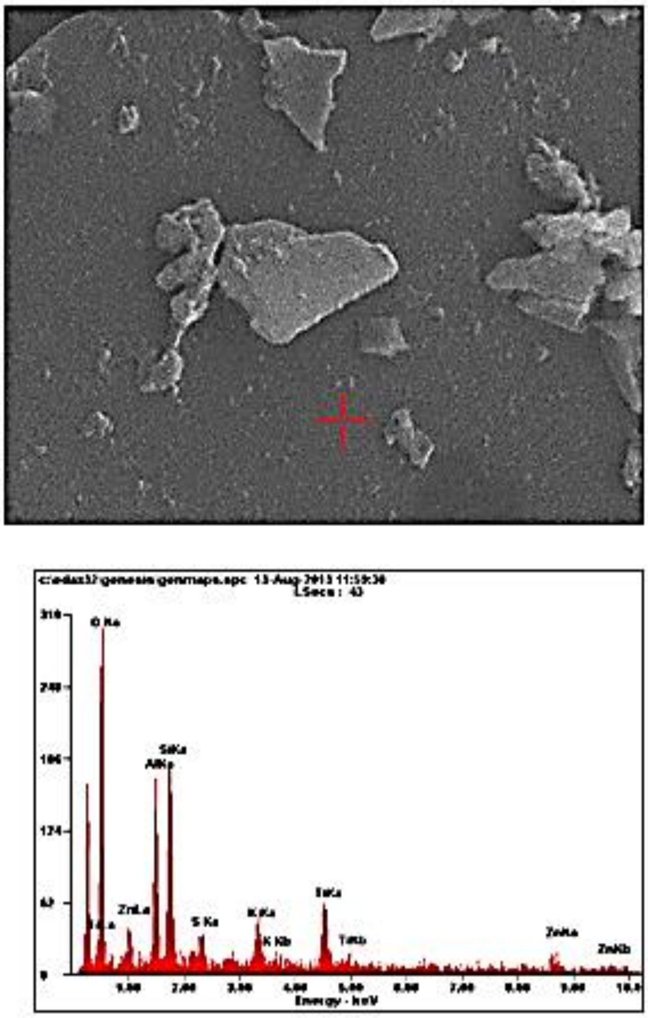
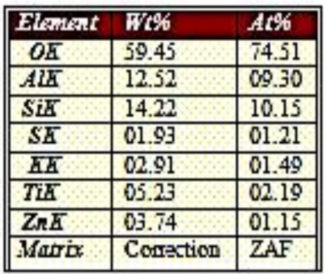


Figure 4.17 SEM micrographs of TNZnPcMip synthesized at 50°C in $CHCl_3$; (a) low magnification (×12000), (b) high magnification (×30000).

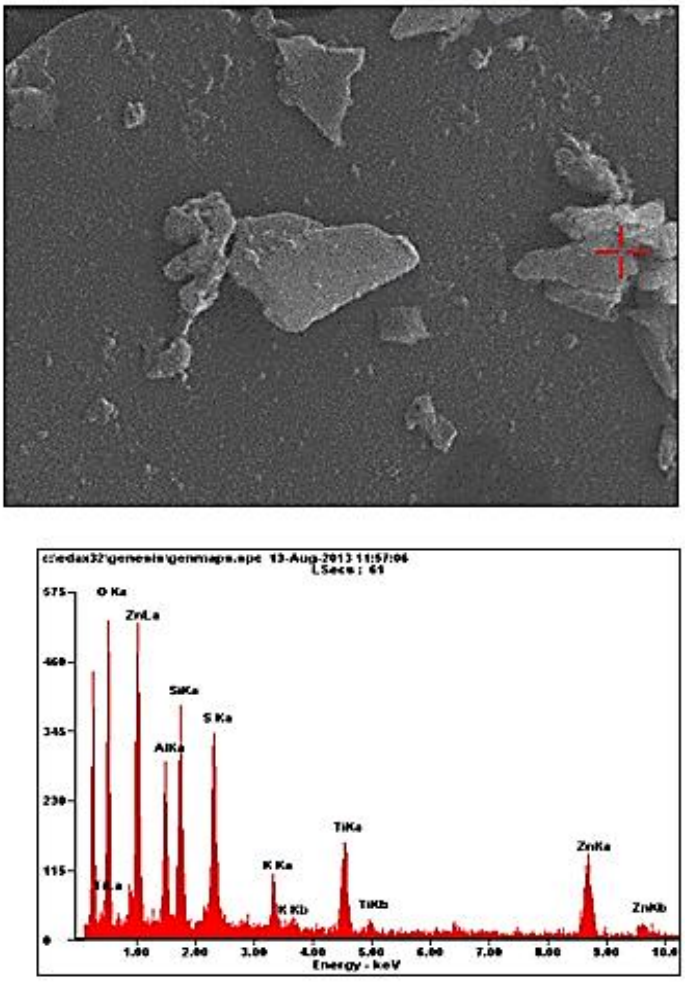
The distribution of elemental content can be analyzed from EDX data. When the signal was sent onto mica-titania plate where seems to be no deposition, little amount of Zn elements was detected. However, when the signal was directed to the bright and large particles, the amount of Zn showed a sharp increase. (See Figure 4.18 and 4.19)

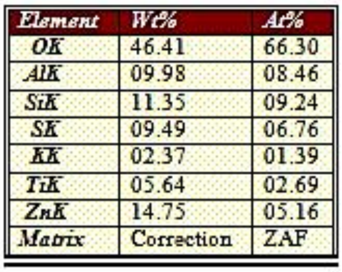




Element	Wt%	At%
OK	59.45	74.51
AlK	12.52	09.30
SiK	14.22	10.15
SK	01.93	01.21
KK	02.91	01.49
TiK	05.23	02.19
ZnK	03.74	01.15
Matrix	Correction	ZAF

Figure 4.18 EDX results of on mica-titania TNZnPcMip sample synthesized at 50°C in $CHCl_3$.





Element	Wt%	At%
OK	46.41	66.30
AlK	09.98	08.46
SiK	11.35	09.24
SK	09.49	06.76
KK	02.37	01.39
TiK	05.64	02.69
ZnK	14.75	05.16
Matrix	Correction	ZAF

Figure 4.19 EDX results of on zinc pigment TNZnPcMip sample synthesized at 50°C in $CHCl_3$.

According to these results, TNZnPc and TAZnPc pigments deposited on mica-titania pigment with randomly and thin film form.

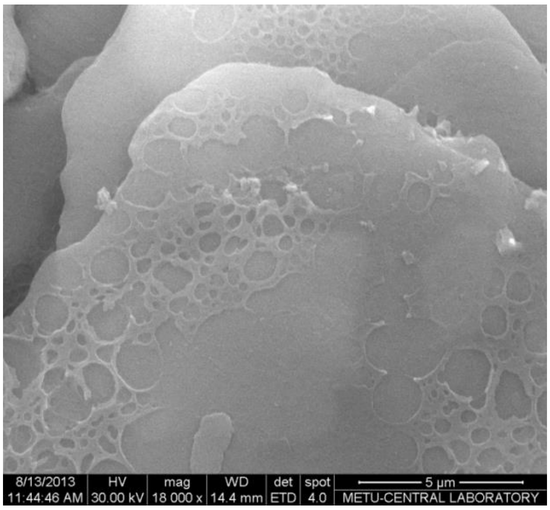


Figure 4.20 SEM micrographs of TNZnPcMip synthesized at 50°C in $CHCl_3$ +TFA (Magnification: ×18 000).

Under very high magnification (Figure 4.20) the surface seemed to be eroded, and it may be due to use of trifluoro acetic acid.

4.2.3 Elemental Analysis

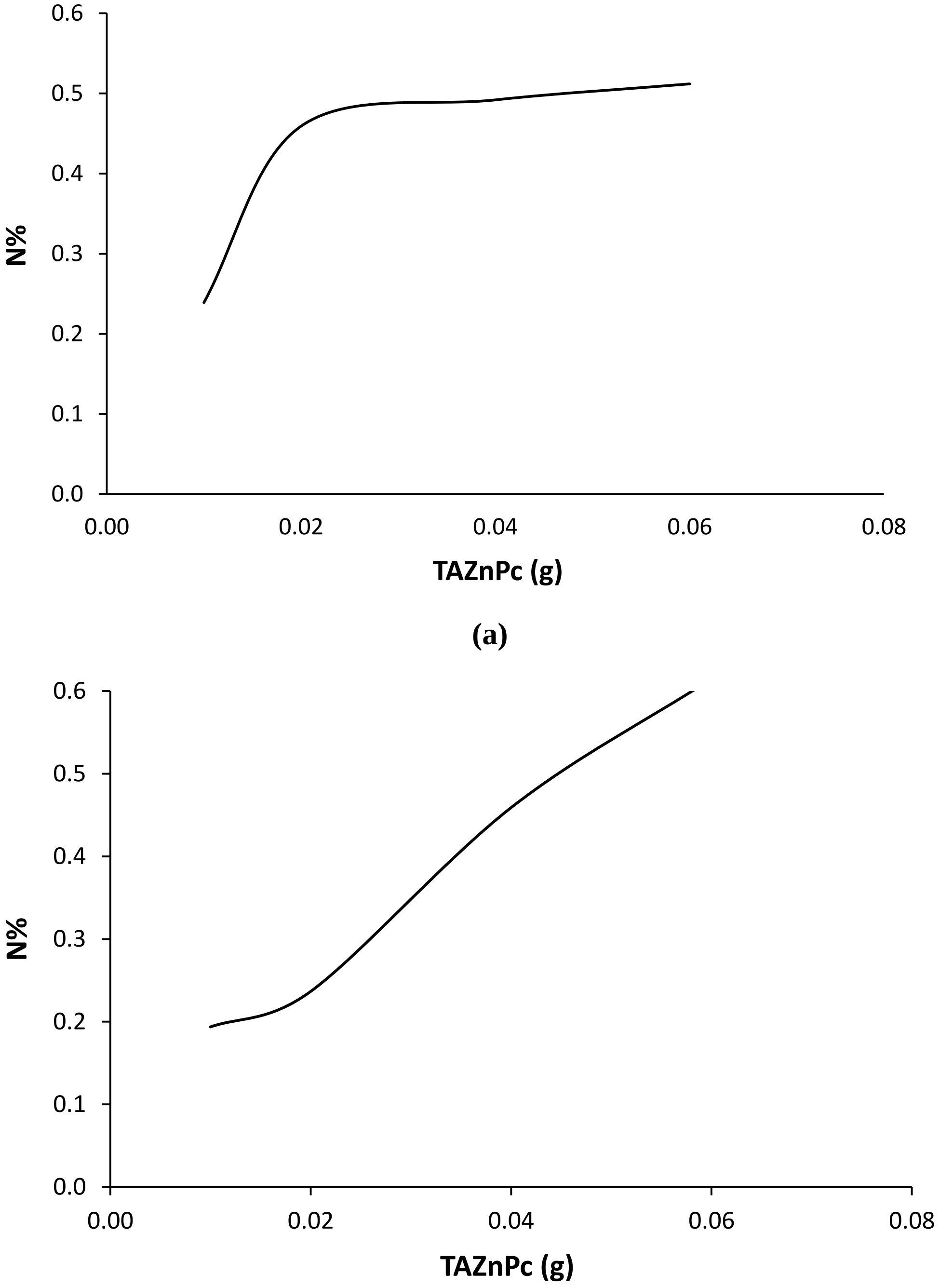
Elemental analysis was carried out to verify that TNZnPc and TAZnPc pigments have deposited on mica-titania surface. The effect of the amount of phthalocyanine pigments on the combination pigments under different solvents was investigated by elemental analysis based on nitrogen, because, nitrogen is not expected to exist in any other chemical except phthalocyanine pigments. The amount of deposited phthalocyanine pigments on mica-titania surfaces were calculated by using mass percent of nitrogen. Table 4.1 shows the results of deposition of TAZnPc pigments on the substrate using, (i) DMF plus acetic acid, and (ii) DMF plus trifluoro acetic acid. An example calculation of the weight percent of TAZnPc was given in Appendix-B.

Table 4.1 Mass percent of N and TAZnPc on mica-titania.

Sample	**Solvent**	**Amount of TAZnPc (g)**	**N % (wt.)**	**TAZnPc% (wt.)**
Mica-titania	-	0	0	0
TAZnPcMip 1 (G-2_s2)*	DMF+AA	0.01	0.24	0.91
TAZnPcMip 2 (G-3_s2)	DMF+TFA	0.01	0.19	0.72
TAZnPcMip 3 (G-2_s4)	DMF+AA	0.02	0.46	1.74
TAZnPcMip 4 (G-3_s4)	DMF+TFA	0.02	0.23	0.87
TAZnPcMip 5 (G-2_s5)	DMF+AA	0.04	0.49	1.86
TAZnPcMip 6 (G-3_s5)	DMF+TFA	0.04	0.46	1.74
TAZnPcMip 7 (G-2_s6)	DMF+AA	0.06	0.51	1.93
TAZnPcMip 8 (G-3_s6)	DMF+TFA	0.06	0.61	2.31

*** See Table – 3.1, 3.3, 3.4.**
DMF: Dimethyl formamide, AA: Acetic acid, TFA: Trifluoro acetic acid.

According to the results, the deposition increases when the amount of TAZnPc pigment increases in the medium. ‘DMF plus TFA’ solvent mixture is less efficient than ‘DMF plus acetic acid’ mixture. The latter is better only at the last data point. However, both of them have close results. Figure 4.21 shows the proportional change of the experiments.



(a)

(b)

Figure 4.21 Relation between mass percent of N and TAZnPc for; (a) DMF+AA samples, (b) DMF+TFA samples.

Table 4.2 indicates the results of deposition of TNZnPc pigments in the presence of '$CHCl_3$ plus acetic acid' and '$CHCl_3$ plus trifluoro acetic acid'. An example calculation of the weight percent of TNZnPc was given in Appendix-B.

Table 4.2 Mass percent of N and TNZnPc on mica-titania.

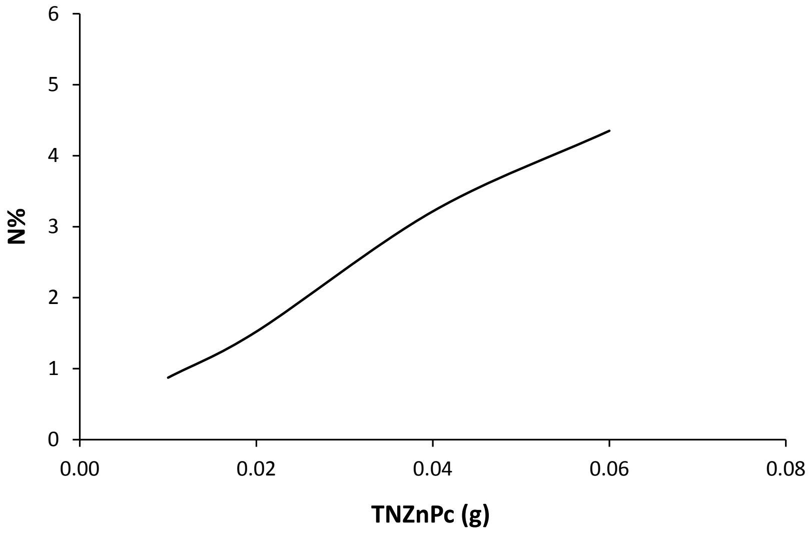
Sample	Solvent	Amount of TNZnPc (g)	N % (wt.)	TNZnPc% (wt.)
Mica-titania	-	0.00	0.00	0.00
TNZnPcMip 1 (G-6_s2)*	$CHCl_3$	0.01	0.88	3.98
TNZnPcMip 2 (G-7_s2)	$CHCl_3$+AA	0.01	0.62	2.83
TNZnPcMip 3 (G-8_s2)	$CHCl_3$+TFA	0.01	0.46	2.10
TNZnPcMip 4 (G-6_s4)	$CHCl_3$	0.02	1.52	6.95
TNZnPcMip 5 (G-7_s4)	$CHCl_3$+AA	0.02	0.57	2.60
TNZnPcMip 6 (G-8_s4)	$CHCl_3$+TFA	0.02	0.41	1.87
TNZnPcMip 7 (G-6_s5)	$CHCl_3$	0.04	3.26	14.71
TNZnPcMip 8 (G-7_s5)	$CHCl_3$+AA	0.04	1.21	5.44
TNZnPcMip 9 (G-8_s5)	$CHCl_3$+TFA	0.04	1.41	6.35
TNZnPcMip 10 (G-6_s6)	$CHCl_3$	0.06	4.41	19.88
TNZnPcMip 11 (G-7_s6)	$CHCl_3$+AA	0.06	1.16	5.25
TNZnPcMip 12 (G-8_s6)	$CHCl_3$+TFA	0.06	2.58	11.65

*** See Table – 3.7, 3.8, 3.9.**

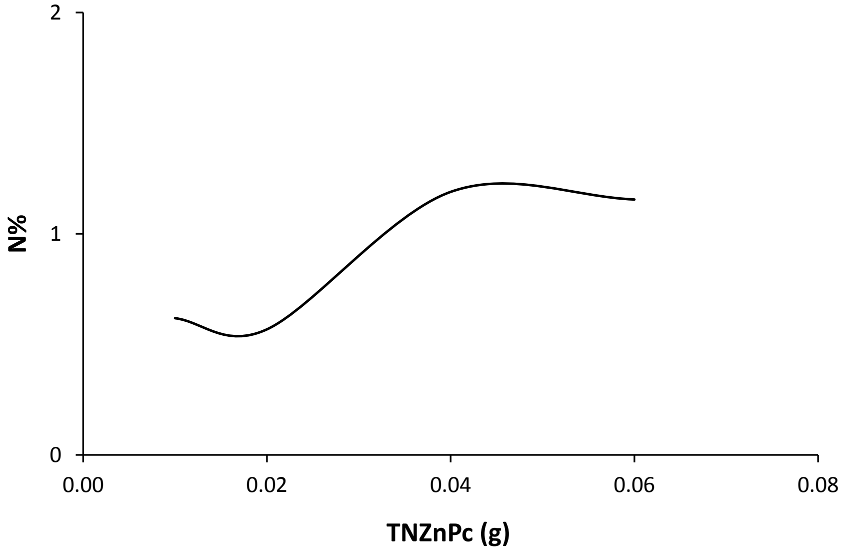
$CHCl_3$: Chloroform, AA: Acetic acid, TFA: Trifluoro acetic acid.

As expected, when the amount of phthalocyanine increases in the reaction, deposition on mica-titania surfaces also increases. The best result is obtained in

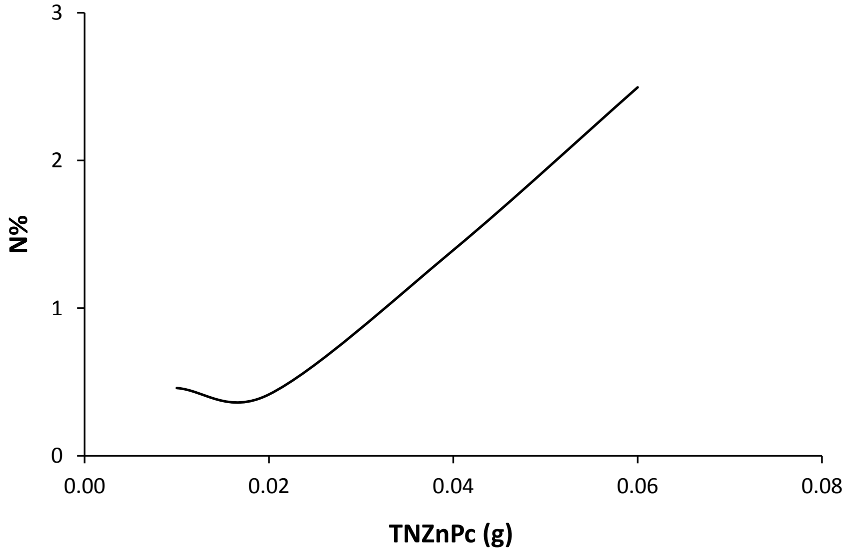
$CHCl_3$ experiments with unprotonated pigments. It is understood that, lower pH value are not suitable for this experiment.



(a)



(b)



(c)

Figure 4.22 Relation between mass percent of N and TNZnPc for; (a) $CHCl_3$, (b) $CHCl_3$+AA, (c) $CHCl_3$+ TFA.

4.2.4 XPS

XPS measures elemental composition of the samples. Table 4.3 and Table 4.4 show weight percent of nitrogen and zinc, respectively.

Table 4.3 Mass percent of Zn for DMF+AA, DMF+TFA, $CHCl_3$ experiments.

Amount of Phthalocyanine Pigment (g)	Zn % of DMF+AA Experiment	Zn % of DMF+TFA Experiment	Zn % of $CHCl_3$ Experiment
0.01	0.83	6.97	2.76
0.02	1.16	5.86	2.58
0.04	2.95	4.25	2.57
0.06	4.94	4.6	1.99

Table 4.4 Mass percent of N for DMF+AA, DMF+TFA, $CHCl_3$ experiments.

Amount of Phthalocyanine Pigment (g)	N % of DMF+AA Experiment	N % of DMF+TFA Experiment	N % of $CHCl_3$ Experiment
0.01	7.02	6.05	2.67
0.02	14.84	5.03	6.51
0.04	5.63	6.73	7.08
0.06	7.1	6.75	8.43

Mass percent of zinc and nitrogen are not related to each other. It is very difficult to measure accurately the nano-sized powder particles. Especially for XPS, the surface of the samples should be smooth and thin film in order to obtain reliable results. The change of nitrogen content with the initial amount of TAZnPc is given in Figure 4.23 for better view although the data is available in Table 4.4.

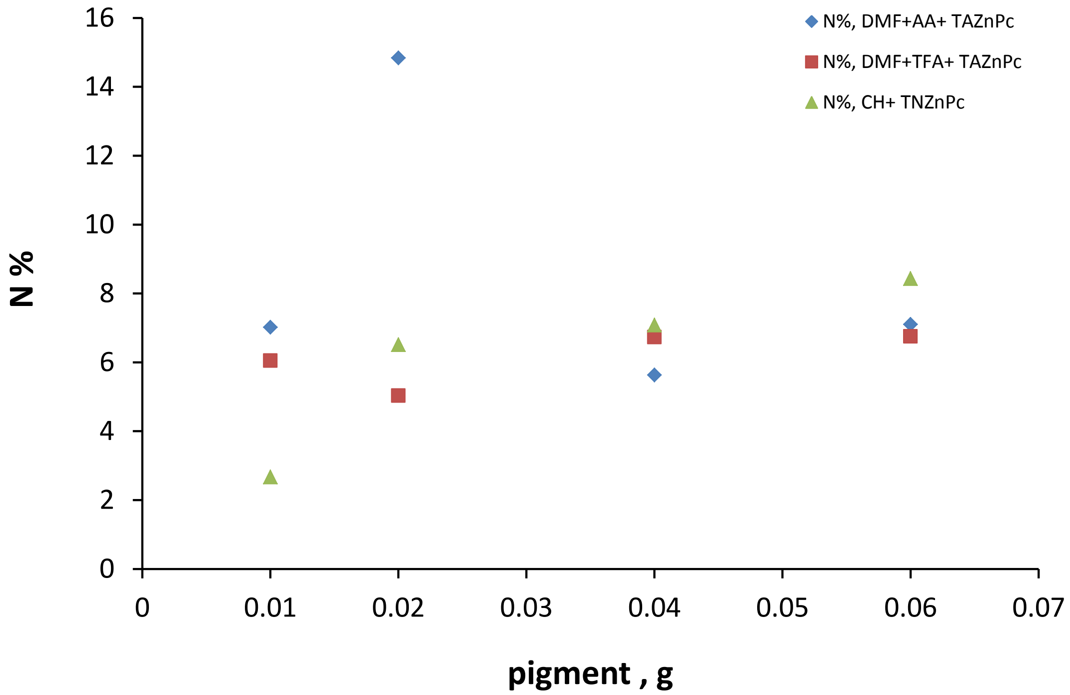


Figure 4.23 Relation between mass percent of N in DMF+AA, DMF+TFA, and $CHCl_3$ experiments.

4.2.5 Fluorescence

As mentioned in Section 4.1, TNZnPc and TAZnPc pigments have fluorescent property which can be affected by different solvents or substituents. In these experiments, TNZnPc and TNZnPc pigments have combined with mica-titania pigments to observe mica-titania's fluorescence property. Both positive and negative contributions were observed.

In the first, fluorescence of mica-titania was measured in DMF. Mica-titania is insoluble in this solution, so emission was measured after mixing for one minute. The samples were prepared in the concentrations of 0.1, 0.05, 0.033, 0.025, 0.0125 mg/ml (mica-titania in mg/ DMF in ml). After that, the solution of combination pigments was prepared. The amount of deposited pigments on the mica-titania was calculated depending on the elemental analysis results. According to the elemental analysis, the best result of deposition was obtained with TNZnPcMip in chloroform.

Thus, the fluorescent analysis of the combination pigment was done only for TNZnPc in chloroform. Figure 4.24 shows the fluorescence spectrum of TNZnPcMip in chloroform. The samples were excited at 385 nm. As expected, TNZnPcMip samples have two emissions which are at 475 nm and 688 nm. After mixing for one minute, the samples were measured before they precipitate.

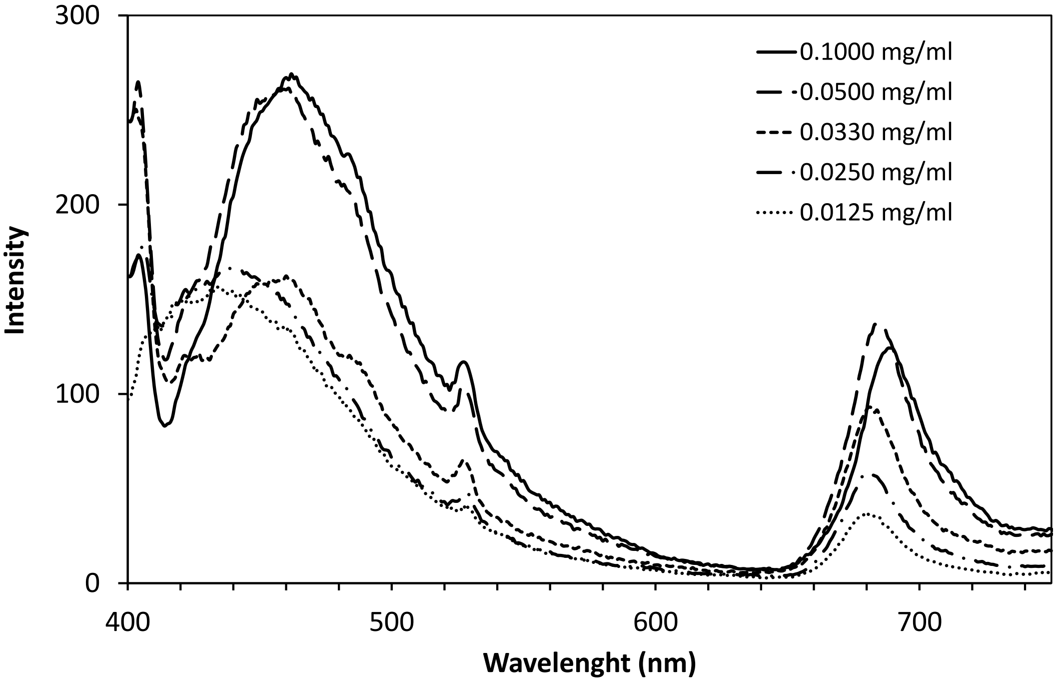


Figure 4.24 Fluorescence spectra of TNZnPcMip in chloroform samples at different ratios.

As seen in the Figure 4.24, emission peaks have shifted to the right as the amount of TNZnPcMip is increased. In other words there is frequency shift (i.e. so called red-shift) to lower frequencies. The increase of TNZnPcMip on the substrate decreases the photon energies more effectively.

Figure 4.25 represents to fluorescence effect of TNZnPcMip, TNZnPc, and mica-titania pigments. Fluorescence property of mica-titania is very low and fluorescence of combination pigment is between that of TNZnPc and mica-titania pigment.

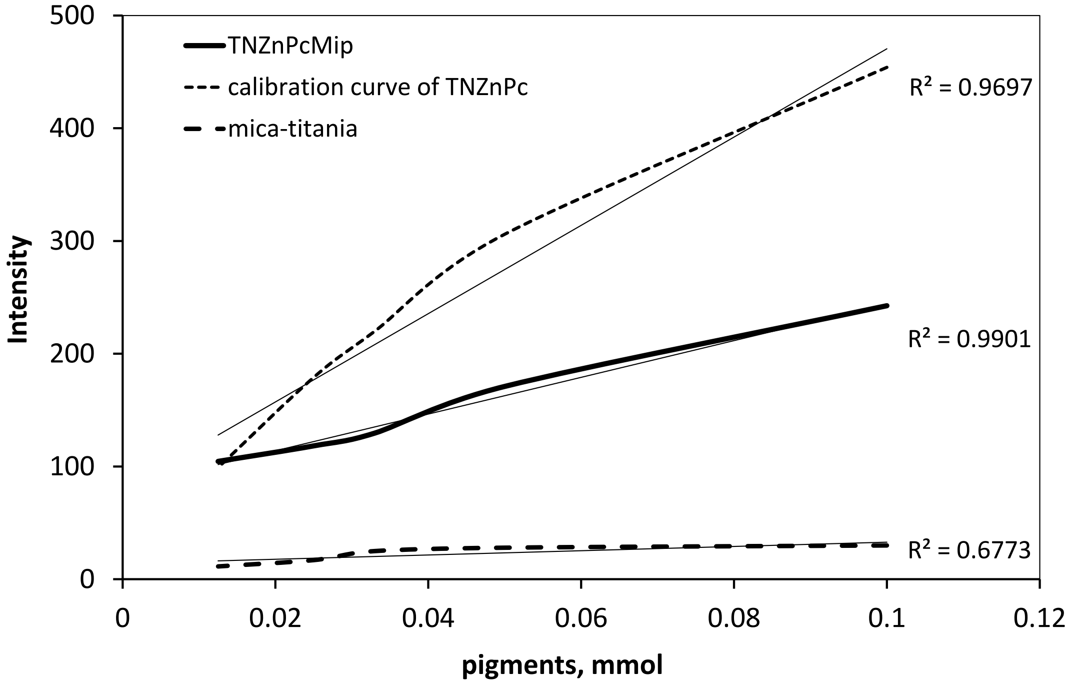


Figure 4.25 Comparison of fluorescence effect of TNZnPcMip, TNZnPc, and mica-titania.

In order to better interpret the consequences, experimental results were compared with the expected fluorescence according to Rule of Mixtures (ROM) results. Expected fluorescence according to Rule of Mixtures results were calculated as shown below:

Expected Fluorescence expected fluorescence according to ROM =
[(Fluorescence of TNZnPc) × (mass % of TNZnPc)] + [(Fluorescence of mica-titania) × (mass % of mica-titania)]

Detailed calculations and results were given in Appendix-C. According to these calculations, the experimental fluorescence of deposition pigments has increased synergistically when compared with the expected fluorescence according to Rule of Mixtures. This situation indicates that the experiments have positive results, as expected.

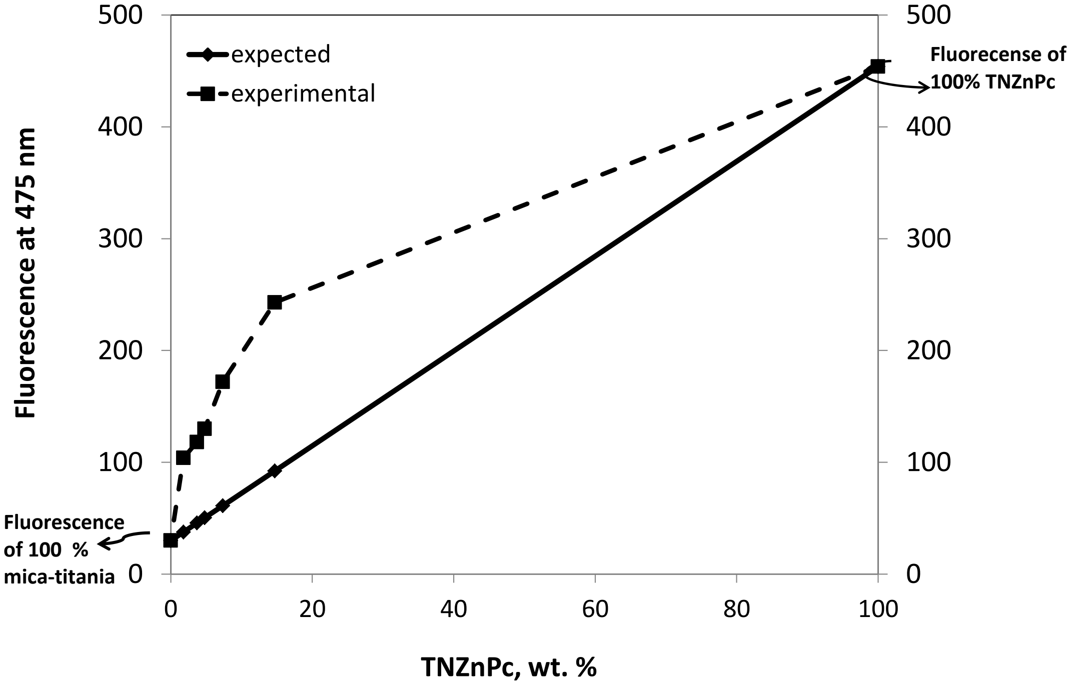


Figure 4.26 Comparison of experimental and expected fluorescence according to Rule of Mixtures (ROM) value with respect to mass percent of TNZnPc pigment.

Fluorescence increment was calculated as shown below:

$$\%\,Increment = \frac{(Last\ value - First\ value) \times 100}{First\ value}$$

Detailed calculations were given in Appendix-C. Accordingly, the fluorescence of combination pigment increase about 50 % on the average compared to mica-titania pigment.

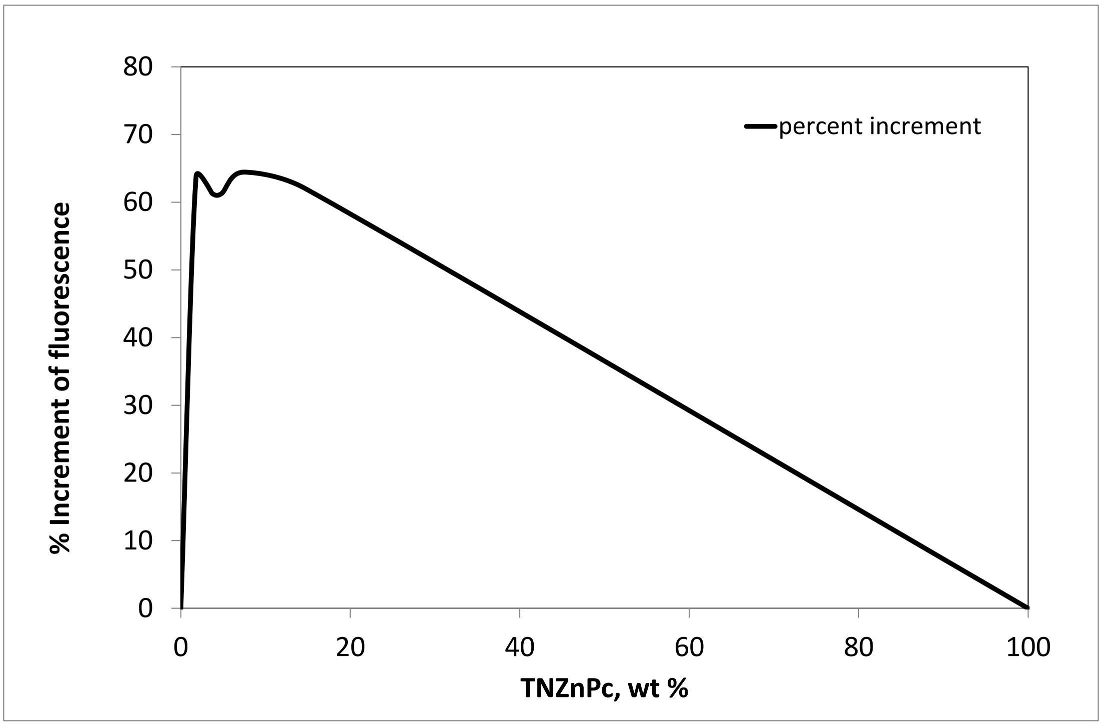


Figure 4.27 Percent increment of fluorescence.

4.2.6 Optical Properties of Paints Manufactured with Combination Pigments

Optical properties of combination pigments were investigated via styrene-acrylic based paint formulations. Initially, standard paint was prepared and measured, containing only mica-titania pigment. Then, other combination pigment samples were measured and compared with the reference.

Color properties of the paints were characterized according to L*a*b values of the samples. The L* term refers to the lightness of the paint while a* is for redness and b* is for the yellowness. Positive a* values refer that the sample is less red than the paint. Negative a* values indicate the greenish samples. As for positive b* values means refer that the sample is less yellow than the paint and negative b* values indicates the bluish samples. dL*, da*, and db* specify that the difference between the sample and the standard. dE* so-called Euclidian distance represents the difference in the total color. It is given by the following formula.

$$\Delta E^* = \left[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \right]^{1/2}$$

Table 4.5 and Table 4.6 list the values of the paints of the combination pigments.

Table 4.5 The L*a*b* values of the paints of TNZnPcMip.

Name of sample	**dL***	**da***	**db***	**dE***
Mica-titania (standard)	0.00	0.00	0.00	0.00
G-6_s2 (0.01g TNZnPc in CH_3Cl)	-0.57	0.01	0.35	0.07
G-6_s4 (0.02g TNZnPc in CH_3Cl)	-1.36	-0.11	-0.18	0.61
G-6_s5 (0.04g TNZnPc in CH_3Cl)	-0.6	-0.04	0.1	0.57
G-7_s4 (0.02g TNZnPc in CH_3Cl+TFA)	0.04	-0.18	0.32	0.89
G-7_s5 (0.04g TNZnPc in CH_3Cl+TFA)	0.58	-0.22	0.68	0.02

Table 4.6 The L*a*b* values of the paints of TAZnPcMip.

Name of sample	dL*	da*	db*	dE*
Mica-titania (standard)	0.00	0.00	0.00	0.00
G-2_s2 (0.01g TAZnPc in DMF+AA)	-0.58	-0.19	0.22	0.44
G-2_s4 (0.02g TAZnPc in DMF+AA)	0.51	-0.04	0.46	0.58
G-2_s5 (0.04g TAZnPc in DMF+AA)	0.97	0.1	0.63	0.84
G-3_s2 (0.01g TAZnPc in DMF+TFA)	1.03	-0.12	0.42	0.9
G-3_s4 (0.02g TAZnPc in DMF+TFA)	-0.33	0.05	0.34	0.42
G-3_s5 (0.04g TAZnPc in DMF+TFA)	0.58	0.19	0.63	0.83

Figure 4.28 shows the comparative color properties of the combination pigments based on different TAZnPcMip and TNZnPcMip samples.

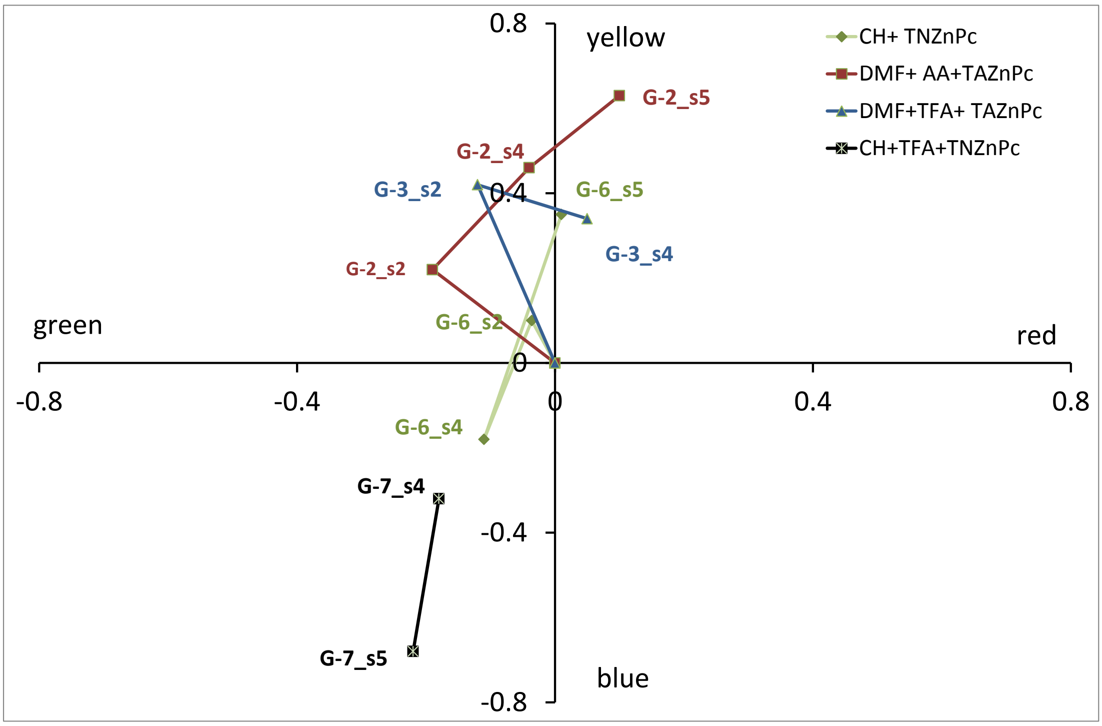


Figure 4.28 The comparative color properties of combination pigments based on different phthalocyanine deposition.

According to Figure 4.28, samples have mostly been in green and yellow area. The blue line samples represent G-3 pigments which shifts to yellow area while the red line samples represent G-2 pigments which also shifts to green-yellow area. The green line samples represent G-6 pigments which are in blue , green , and yellow region , while the black line samples represents G-7 pigments which are in blue region.

CHAPTER 5

CONCLUSIONS

1. Tetranitro zinc phthalocyanines were synthesized by using nitrophthalic acid precursors under microwave radiation. Tetraamino zinc phthalocyanines were produced by reducing tetranitro groups of the phthalocyanines using sodium sulfide in water.

2. While tetranitro zinc phthalocyanines were deposited onto mica-titania pigment in chloroform solvent, tetraamino zinc phthalocyanines were deposed onto mica-titania pigment in DMF.

3. Combination of tetranitro group pigment with mica-titania was achieved by using trifluoro acetic acid by decreasing the pH. The best condition for the experiment is the state of pH 5.

4. Combination of tetraamino group pigment with mica-titania was obtained by using acetic acid and trifluoro acetic acid which decrease the pH. The optimum value for the pH is 4.

5. Different amounts of the pigments were deposited onto mica-titania pigment at different durations of reaction. With increasing initial amount of pigment, the amount deposited also increases.

6. Tetranitro and tetraamino zinc phthalocyanine pigments were found to be in amorphous form on the mica-titania substrate.

7. Tetra substituted zinc phthalocyanine pigments have fluorescent property, and render pearlescent appearance when combined with mica-titania.

8. The fluorescent properties of mica-titania are improved by combining with tetranitro zinc phthalocyanine pigment.

CHAPTER 6

RECOMMENDATIONS

1. Fluorescent measurements may have done in diverse ways such as changing the morphology of the samples.

2. Different solvents could be used in deposition experiments, and their effects on pH need can be examined.

3. TAZnPc pigments are soluble in water and a small color change was observed. These experiments can be tried at different conditions such as pressure, pH, and temperature.

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APPENDIX A

FT-IR RESULTS OF THE OTHER EXPERIMENTS

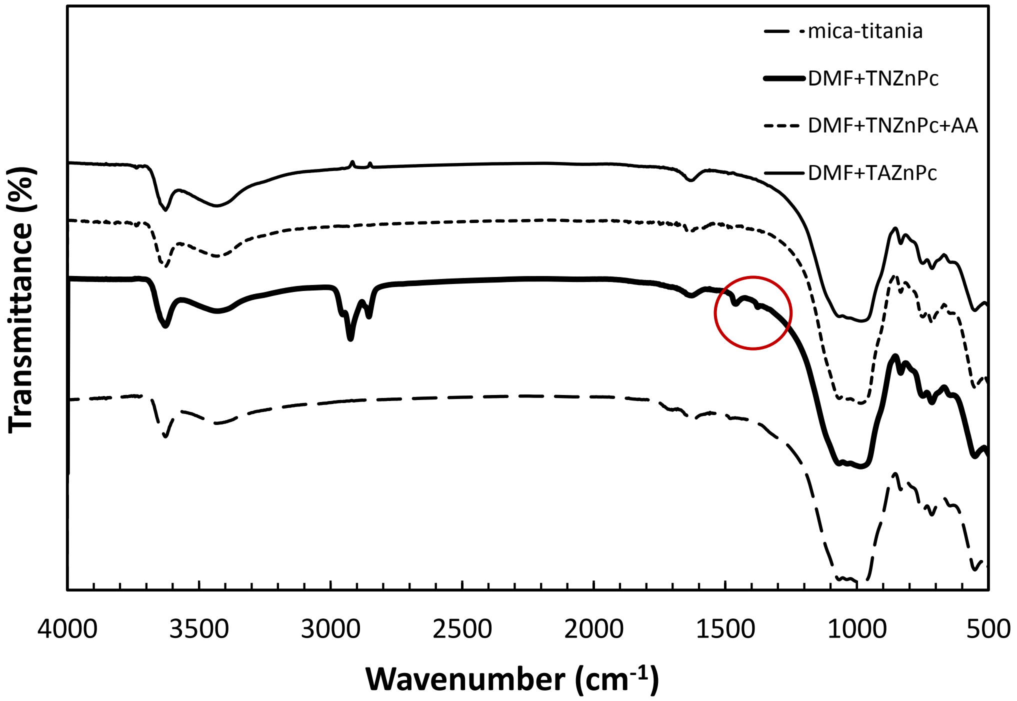

Figure A.1 FT-IR spectra of DMF with TNZnPc, DMF+AA with TNZnPc, and DMF with TAZnPc.

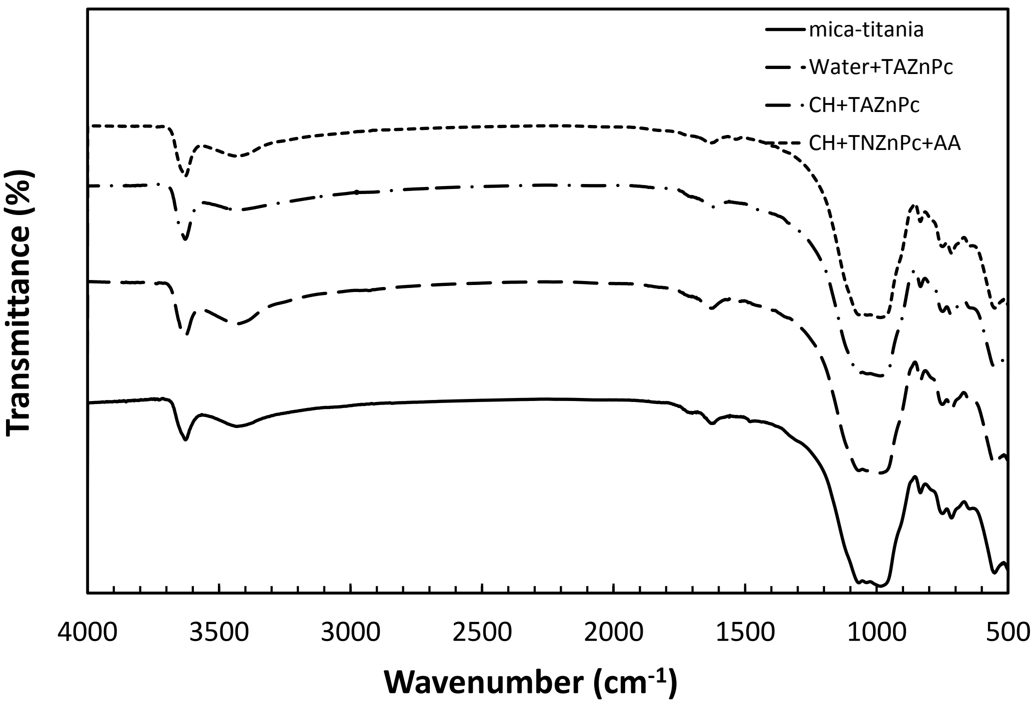

Figure A.2 FT-IR spectra of $CHCl_3$ with TAZnPc, $CHCl_3$ +AA with TNZnPc, and water with TAZnPc.

APPENDIX B

ELEMENTAL ANALYSIS RESULTS OF COMBINATION PIGMENTS

To calculate the amount of zinc phthalocyanes on mica-titania sufraces, elemental analysis results of the amount of nitrogen was used. 1 mol TNZnPc is 757 g, 1mol TAZnPc is 637 g, and they contains same amount of nitrogen which is 112g. Example calculations were given in below.

$$Mass\ \%\ TNZnPc = \frac{(\%\ N\ in\ the\ sample) \times (molecular\ weight\ of\ TNZnPc)}{(Amount\ of\ N\ in\ TNZnPc)}$$

$$wt\ \%\ TNZnPc = \frac{(0.88) \times (757)}{(168)} = 3.98$$

$$Mass\ \%\ TAZnPc = \frac{(\%\ N\ in\ the\ sample) \times (molecular\ weight\ of\ TAZnPc)}{(Amount\ of\ N\ in\ TAZnPc)}$$

$$wt\ \%\ TAZnPc = \frac{(0.24) \times (637)}{(168)} = 0.91$$

APPENDIX C

EXPECTED FLUORESCENCE OF THE PIGMENTS CALCULATIONS

To calculate of expected fluorescence of the combination pigments, this equation was used:

$$\textit{Expected Fluorescence} = [(\textit{Fluorescence of TNZnPc}) \times (\textit{mass \% of TNZnPc})] + [(\textit{Fluorescence of mica-titania}) \times (\textit{mass \% of mica-titania})]$$

An example calculation was given in below.

Expected fluorescence of 0.05 mg/mg TNZnPcMip = [(243) x (14.7/100)] + [(30) x (100-14.7)/100] = 92.33

The rest of calculations' results were given in Table-C.

Table-C The expected fluorescence results of TNZnPcMip samples.

TNZnPc wt %	TNZnPcMip fluorescence (experimental)	TNZnPcMip Fluorescence %	Mica-Titania wt %	Mica-T. Fluorescence %	Total Fluorescence (expected)
100.00	454	454.00	0.00	0.00	454.00
14.70	243	66.74	85.30	25.59	92.33
7.35	172	33.37	92.65	27.80	61.16
4.80	130	21.79	95.20	28.56	50.35
3.70	118	16.80	96.30	28.89	45.69
1.80	104	8.17	98.20	29.46	37.63
0.00	30	0.00	100.00	30.00	30.00

APPENDIX D

SYNTHESIS MATERIALS FOR PHTHALOCYANINES

Table-D Properties of materials used in this study.

Chemical	Chemical formula	Molecular weight (g/mol)	Density (g/cm^3) (25 °C)
3-nitrophthalic acid	$O_2NC_6H_3$-1,2-$(CO_2H)_2$	211.13	1.671
Urea	$(NH_2)_2CO$	60.16	1.32
Zinc chloride	$ZnCl_2$	136.3	2.91
Ammonium heptamolybdate	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	1235.9	2.5
Sodium sulfide	Na_2S	78.04	1.86
Dimethyl formamide (DMF)	$(CH_3)_2NCHO$	73.1	0.94
Chloroform	$CHCl_3$	119.4	1.48
Ethyl acetate	$CH_3COOCH_2CH_3$	88.11	0.897
Diethyl ether	$(C_2H_5)_2O$	74.12	0.71
Acetic acid	CH_3COOH	60.01	1.049
Trifluoro acetic acid	CF_3COOH	114.02	1.489