

Fluorocarbon Substituted Peripherally and Non-Peripherally Tetra Phthalocyanine Compounds: Synthesis, Characterization and Aggregation Properties

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Abstract

This work presents a series of novel peripherally and non-peripherally tetra substituted phthalocyanine derivatives containing 4-[(4,4,5,5,5-pentafluoropentyl)oxy] groups. Firstly, phthalonitrile derivatives (2 and 3) were synthesized. These phthalonitrile derivatives were used synthesis of peripherally tetra substituted (metal-free 4, manganese(III) 5, nickel(II) 6 and cobalt(II) 7) phthalocyanines and non-peripherally tetra substituted (magnesium(II) 8, zinc(II) 9, nickel(II) 10 and cobalt(II) 11) functionalized with the fluorocarbon compound "4,4,5,5,5-pentafluoro-1-pentanol". Synthesized novel compounds have been characterized by combination of the FT-IR, ¹H NMR/ ¹³C NMR, MALDI-TOF-MS and UV-Vis spectroscopy (for phthalocyanines). In the last part of the study, the effect of the solvent on the aggregation behavior of the metallophthalocyanines NiPc (6 and 10) and CoPc (7 and 11) was studied different solvents (THF, DMF, DMSO, Diethylether, Ethylacetate, CHCl₃ and ethanol). In addition, the aggregation behavior of NiPcs and CoPcs was investigated at different concentrations ranging from 2 x 10⁻⁶ to 12 x 10⁻⁶ M in CHCl₃ by UV-Vis spectroscopy.

Keywords: Fluorocarbon, Agregasyon, Non-Peripherally, Phthalocyanine, Manganese

Florokarbon Substitüte Periferel ve Non-Periferel Tetra Ftalosiyanın Bileşikleri: Sentez, Karakterizasyon ve Agregasyon Özellikleri

Öz

Bu çalışmada bir dizi yeni 4-[(4,4,5,5,5-pentafloropentil)oksi] grubu içeren periferel ve non-periferel tetra substitüte ftalosiyanın türevleri sunulmuştur. İlk olarak ftalonitril türevleri (2 ve 3) sentezlenmiştir. Bu ftalonitril türevleri florokarbon bileşiği içeren "4,4,5,5,5-pentafluoro-1-pentanol" periferel tetra substitüte (metalsiz 4, mangan(III) 5, nikel(II) 6 ve kobalt(II) 7) ve non-periferel tetra substitüte (magnezyum(II) 8, çinko(II) 9, nikel(II) 10 ve kobalt(II) 11) ftalosiyanın türevlerinin sentezinde kullanılmıştır. Sentezlenen yeni bileşikler FT-IR, ¹H NMR/ ¹³C NMR, MALDI-TOF-MS and UV-Vis (ftalosiyanınlar için) spektroskopi yöntemleri ile karakterize edilmiştir. Çalışmanın son kısmında, farklı çözücüler kullanılarak (THF, DMF, DMSO, Dietileter, Etilasetat, CHCl₃ and etanol) çözücünün Ni(II) (6 ve 10) ve Co(II) (7 ve 11) metalli ftalosiyanın kompleksleri üzerine agregasyon etkisi çalışıldı. Buna ilave olarak 2 x 10⁻⁶ ila 12 x 10⁻⁶ M arasında değişen farklı konsantrasyonlarda CHCl₃ içerisinde Ni ve Co (6, 7, 10, 11) ftalosiyanın komplekslerinin agregasyon davranışları UV-Vis spektroskopi yöntemi ile araştırıldı.

Anahtar Kelimeler: Florokarbon, Agregasyon, Non- Periferel, Ftalosiyanın, Mangan

1. Introduction

Phthalocyanine compounds (Pcs) are planer aromatic structures with 18- π electron system. Pc compounds use a lot of application area due to the their remerkable pyhsical and chemical properties. Many studies are carried out for research and development in the fields of catalysis (A. Kamiloglu et al., 2019), photodynamic therapy (PDT) (Ertem et al., 2018), new antitumor drug (Suhailah and Tamer, 2018), novel fuctional metarials (Riquelme et al., 2018), antimicrobial and antioxidant (Unluer et al., 2019), photoelectric metarials (Suziki et al., 2019) and sensors (Karaca, 2016).

An important goal of research in phthalocyanine chemistry to obtain soluble and unaggregated product because unsubstituted Pc compounds are insoluble in water and organic solvents. Aggregation of the phthalocyanines affects the solubility of Pcs because many Pcs are poorly soluble in organic solvents and water (Gureli et al., 2019). We aimed of this work, it is intended to increase solubility by attaching compounds including electron withdrawing halogen groups at peripheral or non-peripheral positions of Pcs. Because there are two main ways to overcome low solubility problem. The first contains the addition of various metal atoms, the second consists of substitution of electron-withdrawing or elecron-releasing moiethy on the peripheral or non-peripheral position of Pc ring with or without axial ligands at the metal ion (Farajzadeh et al., 2020).

Halogen substituted Pcs affect the electronic structure, reactivity and application of Pcs. Electron-withdrawing substituents decrease the electron density in the central π - system (Mack and Stillman, 2003). The electron

energy of the HOMO and LUMO levels is lowered leading to more positive potential (Weissbecker et al., 2015; Schlettwein et al., 2003). Presently research studies focus on fluorinated Pcs (Ozçeşmeci et al., 2017; Saka and Kahriman, 2019; Mori and Shibata, 2017). The presence of fluorinated groups on the peripherally or non-peripherally of the Pc ring improve their solubility in organic solvents and bring more functionality (Tian et al., 1997; Ochoa et al., 2012). Especially, the effect of fluorine atoms as substituents on the biological behavior of biologically active substances has been identified because of its high electronegativity and small size, and can be used in drug design (Goslinski and Piskorz, 2011; Shibata et al., 2009). Fluorinated Pcs show improved photosentizer activity for PDT when compaired the non-fluorinated Pcs (Erdogan et al., 2015; Lia et al., 2019). With this backround, in this work, we would like to synthesized tetra peripheral and non-peripheral substituted with four long chain fluoro groups and examined their aggregation properties.

The electronic and spectroscopic properties of Pc compounds depend on the size, nature, and position such as peripheral, non-peripheral or axial) of the substituents metal atoms in core. The aim of this study was to investigate the synthesis, spectroscopy and aggregation properties of peripheral and non-peripheral metal-free and metallo **Pc** compounds containing four long chain fluoro- groups which are used in many applications and cause high solubility.

The new phthalonitrile derivatives (**2** and **3**), the peripheral phthalocyanine compounds (H_2Pc **4**, $MnPc$ **5**, $NiPc$ **6** and $CoPc$ **7**) derived from 4-[(4,4,5,5,5-pentafluoropentyl)oxy]phthalonitrile **2** and

non peripheral metallophthalocyanine complexes (MgPc **8**, ZnPc **9**, NiPc **10** and CoPc **11**) derived from 3-(3-3-[(4,4,5,5,5-pentafluoropentyl)oxy]phthalonitrile **3** have been synthesized. The synthesized all of compounds characterized by FT-IR, ^1H NMR / ^{13}C NMR (for **2** and **3**), UV-Vis (for **4-11**) and mass spectrometry. Absorption and aggregation properties of the synthesized peripheral and non-peripheral fluorocarbon substituted Pcs are described.

2. Experimental

2.1. Materials and Equipment

All reagents and solvents were of reagent-grade quality and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego (Perrin, 1989). 4-nitrophthalonitrile, 3-nitrophthalonitrile and 4,4,5,5,5-pentafluoro-1-pentanol were obtained from commercial suppliers. All reactions were carried out under dry and oxygen free nitrogen atmosphere using schlenk system. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE III 400 MHz NMR spectrophotometer in CDCl_3 , and chemical shifts were reported (δ) relative to Me_4Si as internal standard. IR spectra were recorded on a Perkin-Elmer Spectrum one FT-IR spectrometer. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) measurements were performed on a BRUKER Microflex. Melting point was

recorded on a Gallenkamp melting point apparatus. Optical spectra in the UV-Vis region were recorded with a Perkin Elmer Lambda 25 spectrophotometer.

2.2. Synthesis

2.2.1. General procedure for the synthesis of phthalonitrile derivatives **2** and **3**

The fluorocarbon-bound phthalonitrile derivatives were synthesized in dry DMF. Synthesize reaction was realized at $60\text{ }^\circ\text{C}$ by adding K_2CO_3 . 4-nitrophthalonitrile for phthalonitrile compound **2**, 3-nitrophthalonitrile for phthalonitrile compound **3** and fluorocarbon compound (4,4,5,5,5-Pentafluoro-1-pentanol) **1** were used same equivalent (1:1). The reaction medium was stirred under nitrogen atmosphere for 4 days. After four days, the reaction content was poured into ice-water and stirred to yield a crude product. The mixture was filtered and dried after 3 hour. The obtained crude product was purified using column chromatography by using chloroform solvent system. The reaction pathway is shown in Figure 1.

2.2.1.1. 4-[(4,4,5,5,5-pentafluoropentyl)oxy]phthalonitrile **2**

Yield: 66%, Color: Light pink, mp: $67\text{-}70\text{ }^\circ\text{C}$. IR (ATR), $\nu_{\text{max}}/\text{cm}^{-1}$: 3076 (Ar-H), 2232 ($\text{C}\equiv\text{N}$), 1567-1587 ($\text{C}=\text{C}$), 1483, 1418, 1308, 1278-1191 ($\text{C}-\text{O}-\text{CAr}$), 1092, 1013, 968, 905, 850, 719. ^1H NMR (400 MHz, CDCl_3), (δ :ppm): 7.76-7.74 (d, 1H, Ar-H), 7.29 (s, 1H, Ar-H), 7.23 (d, 1H, Ar-H), 4.16 (s, 2H, $\text{O}-\text{CH}_2$), 2.34-2.28 (m, 2H, $-\text{F}_2\text{C}-\text{CH}_2$),

2.20-2.19 (m, 2H, C-CH₂). ¹³C NMR (400 MHz, CDCl₃), (δ:ppm): 161.22 (C-O), 135.47, 135.32, 119.48, 119.26, 117.61 (-C≡N), 115.72 (-C≡N), 115.52, 115.12, 107.83, 67.51 (O-CH₂), 27.37 (-F₂C-CH₂), 20.41 (-C-CH₂). MALDI-TOF-MS m/z: 377.48 [M + K + MeOH]⁺.

2.2.1.2. 3-[(4,4,5,5,5-pentafluoropentyl)oxy]phthalonitrile 3

Yield: 55%, Color: Cream color mp: 101-104 °C. IR (ATR), $\nu_{\max}/\text{cm}^{-1}$: 3086 (Ar-H), 2228 (C≡N), 1581-1453 (C=C), 1348, 1293-1134 (C-O-CAr), 1015, 796, 683. ¹H NMR (400 MHz, CDCl₃), (δ:ppm): 7.69-7.67 (m, 1H, Ar-H), 7.41-7.40 (m, 1H, Ar-H), 7.27-7.25 (m, 1H, Ar-H), 4.24 (s, 2H, O-CH₂), 2.35-2.23 (m, 4H, F₂C-CH₂ and C-CH₂). ¹³C NMR (400MHz, CDCl₃), (δ:ppm): 160.75 (C-O), 134.67, 130.05, 125.56, 122.99, 117.22 (-C≡N), 116.65 (-C≡N), 115.18, 112.68, 105.22, 68.21 (O-CH₂), 27.16 (F₂C-CH₂), 20.49 (C-CH₂). MALDI-TOF-MS m/z: 341.26 [M + 2 H₂O + 1]⁺.

2.2.2. Peripheral Tetra Fluorocarbon-Substituted Phthalocyanines 4-7

Phthalonitrile derivative **2** (0.2 g, 0.65 mmol) and DBU (10 drop) in 2 ml of dry pentanol was heated and stirred at 160 °C in a sealed glass tube for 24 h under N₂. After cooling to room temperature the green crude product was precipitated with ethanol, filtered, washed with ethanol, methanol and then dried in vacuo. Finally, pure metal-free phthalocyanine (**4**) was obtained by column chromatography using silicon oxide and CHCl₃:CH₃OH as solvent system. Substituted phthalonitrile **2** (0.2 gr) and

anhydrous metal salts (MnCl₂ (41.52 mg, 0.33 mmol) for compound **5**; NiCl₂ (42.79 mg, 0.33 mmol) for compound **6**; CoCl₂ (42.87 mg, 0.33 mmol) for compound **7**) were dissolved in 3 ml of n-pentanol and 8 drops DBU. Mixture temperature was raised to 160 °C and stirred for 12 h under nitrogen atmosphere (N₂). After this time, ethanol was added to the medium and the green raw products were filtrated. Synthesized metallophthalocyanine complexes were purified on silica gel (SiO₂) column with chloroform-methanol solvent system as eluent. The reaction pathway of the phthalocyanine derivatives was shown in Figure 1.

2.2.2.1. The spectral data of peripheral phthalocyanines 4-7

H₂Pc (4): Green solid. Yield: 10 mg (5%). mp: > 300 °C. IR (ATR) $\nu_{\max}/\text{cm}^{-1}$: 3174 (N-H), 3066 (Ar-H), 2951 (Aliph. C-H), 1778, 1718, 1618, 1489, 1470, 1364, 1288, 1222, 1184, 1007, 864, 747, 624. ¹H NMR (400 MHz, CDCl₃), (δ:ppm): 7.77-7.25 (m, 10H, Ar-H), 5.59-5.04 (m, 2H, Ar-H), 4.14 (m, 8H, O-CH₂), 2.14-1.21 (m, 16H, F₂C-CH₂ and C-CH₂). UV-Vis (CHCl₃): λ_{\max} , nm (log ε): 703 (4.97), 666 (4.93), 645 (4.65), 606 (4.48), 384 (4.76), 325 (5.09), 286 (5.13). MALDI-TOF-MS, (m/z): Calculated: 1218.88; Found: 1219.91 [M + 1]⁺.

MnPc (5): Brown solid. Yield: 45 mg (21%). mp: > 300 °C. IR (ATR) $\nu_{\max}/\text{cm}^{-1}$: 3058 (Ar-H), 2918-2849 (Aliph. C-H), 1725, 1606, 1508, 1488, 1391, 1342, 1243, 1184, 1119, 1075, 1057, 907, 786, 702. UV-Vis (CHCl₃): λ_{\max} , nm (log ε): 732 (5.06), 659 (4.49), 530 (4.34), 381 (4.81), 284 (5.00).

MALDI-TOF-MS, (m/z): Calculated: 1307.26; Found: 1267.57 [M-Cl-4]⁺.

NiPc (6): Green solid. Yield: 25 mg (12%). mp: > 300°C. IR (ATR) $\nu_{\max}/\text{cm}^{-1}$: 3050 (Ar-H), 2963-2855 (Aliph. C-H), 1726, 1610, 1467, 1349, 1239, 1187, 1091, 1012, 895, 703, 679. ¹H NMR (400 MHz, CDCl₃), (δ :ppm): 7.77-7.32(m, 12H, Ar-H), 4.20 (m, 8H, O-CH₂), 3.36-2.77 (m, 16H, F₂C-CH₂ and C-CH₂). UV-Vis (CHCl₃): λ_{\max} , nm (log ϵ): 673 (5.04), 617 (4.79), 384 (4.98). MALDI-TOF-MS, (m/z): Calculated: 1275.57; Found: 1275.24 [M]⁺.

CoPc (7): Blue solid. Yield: 36 mg (17.5%). mp: > 300°C. IR (ATR) $\nu_{\max}/\text{cm}^{-1}$: 3053 (Ar-H), 2933-2860 (Aliph. C-H), 1768, 1714, 1611, 1541, 1469, 1353, 1184, 1093, 1012, 805, 793, 593. UV-Vis (CHCl₃): λ_{\max} , nm (log ϵ): 678 (5.05), 613 (4.59), 385 (4.74). MALDI-TOF-MS, (m/z): Calculated: 1275.81; Found: 1275.15 [M]⁺.

2.2.3. Non-Peripheral Tetra Fluorocarbon Substituted Phthalocyanines 8, 9, 10 and 11

Synthesis and purification of tetra non-peripheral substituted phthalocyanine compounds **8-11** were similar to peripheral tetra substitue phthalocyanine compounds. The mixture of phthalonitrile compound **3** (0.2 g), 1,8-diazabicyclo [4.5.0] undec-7-ene (DBU) (10 drops), n-pentanol (3.0 ml) and metal salts (31 mg MgCl₂ for **8**; 60 mg Zn(ac)₂ for **9**; 42.79 mg NiCl₂ for **10** and 42.87 mg CoCl₂ for **11**) were heated to 160 °C and stirred for 12 h at this temperature. After cooling at room temperature, the reaction mixture was precipitated by the addition of ethanol and filtered off. Synthesized metallophthalocyanine

complexes were purified with coloumn chromatography by using silica gel and chloroform-methanol solvent system. The reaction pathway of the phthalocyanine derivatives was shown in Figure 1.

2.2.3.1. The spectral data of non-peripheral phthalocyanines 8, 9, 10 and 11

MgPc (8): Green fluid (oily). Yield: 65 mg (33%). en: > 300°C. IR (ATR) $\nu_{\max}/\text{cm}^{-1}$: 3090 (Ar-H), 2928-2857 (Aliph. C-H), 1630, 1574, 1487, 1354, 1322, 1192, 1060, 827, 588. ¹H NMR (400 MHz, CDCl₃), (δ :ppm): 7.62-6.90 (m, 12H, Ar-H), 4.23 (m, 8H, O-CH₂), 3.44-2.77 (m, 8H, F₂C-CH₂), 2.51 (m, 8H, C-CH₂). UV-Vis (CHCl₃): λ_{\max} , nm (log ϵ): 698 (4.99), 629 (4.29), 321 (4.78). MALDI-TOF-MS, (m/z): Calculated: 1241.19; Found: 1241.75 [M]⁺.

ZnPc (9): Blue fluid (oily). Yield: 70 mg (33%). en: > 300°C. IR (ATR) $\nu_{\max}/\text{cm}^{-1}$: 3060 (Ar-H), 2930-2858 (Aliph. C-H), 1614, 1571, 1488, 1353, 1321, 1198, 1060, 923, 655. ¹H NMR (400 MHz, CDCl₃), (δ :ppm): 7.80-7.21 (m, 12H, Ar-H), 4.24 (m, 8H, O-CH₂), 3.39 (m, 8H, F₂C-CH₂), 2.79 (m, 8H, C-CH₂). UV-Vis (CHCl₃): λ_{\max} , nm (log ϵ): 700 (4.98), 630 (4.27), 385 (4.34), 327 (4.49). MALDI-TOF-MS, (m/z): Calculated: 1282.26; Found: 1283.30 [M + 1]⁺.

NiPc (10): Green fluid (oily). Yield: 90 mg (45%). mp: > 300°C. IR (ATR) $\nu_{\max}/\text{cm}^{-1}$: 3077 (Ar-H), 2931-2858 (Aliph. C-H), 1726, 1633, 1579, 1488, 1354, 1323, 1190, 1079, 905, 679. ¹H NMR (400 MHz, CDCl₃), (δ :ppm): 7.57-7.12 (m, 12H, Ar-H), 4.26 (m, 8H, O-CH₂), 3.46 (m, 8H, F₂C-CH₂), 2.51 (m, 8H, C-CH₂). UV-Vis (CHCl₃): λ_{\max} , nm

(log ϵ): 694 (5.05), 625 (4.14), 384 (4.43), 322 (5.02). MALDI-TOF-MS, (m/z): Calculated: 1275.57; Found: 1276.91 [M + 1]⁺.

CoPc (11): Blue fluid (oily). Yield: 75 mg (37%). mp: > 300°C. IR (ATR) $\nu_{\max}/\text{cm}^{-1}$: 3060 (Ar-H), 2929-2858 (Aliph. C-H), 1614, 1488, 1444, 1322, 1197, 1140, 1083, 923, 710, 679. UV-Vis (CHCl₃): λ_{\max} , nm (log ϵ): 696 (5.04), 625 (4.41), 385 (4.59). MALDI-TOF-MS, (m/z): Calculated: 1275.81; Found: 1276.42 [M + 1]⁺.

Peripherally and non-peripherally tetra substituted phthalocyanines **4-11** were prepared by cyclotetramerization of 4-[(4,4,5,5,5-pentafluoropentyl)oxy]phthalonitrile **2** or 3-[(4,4,5,5,5-pentafluoropentyl)oxy]phthalonitrile **3** in the

presence of n-pentanol at 160 °C under a N₂ atmosphere in the presence of 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) as a strong base (Figure 1). All synthesized novel compounds **2-11** were characterized using spectroscopic methods such as FT-IR, ¹H NMR, ¹³C NMR and UV-Vis spectroscopic methods, as well by MALDI-TOF-MS. All methods gived satisfactory results.

3. Results and Discussion

3.1. Synthesis and Spectral Characterization

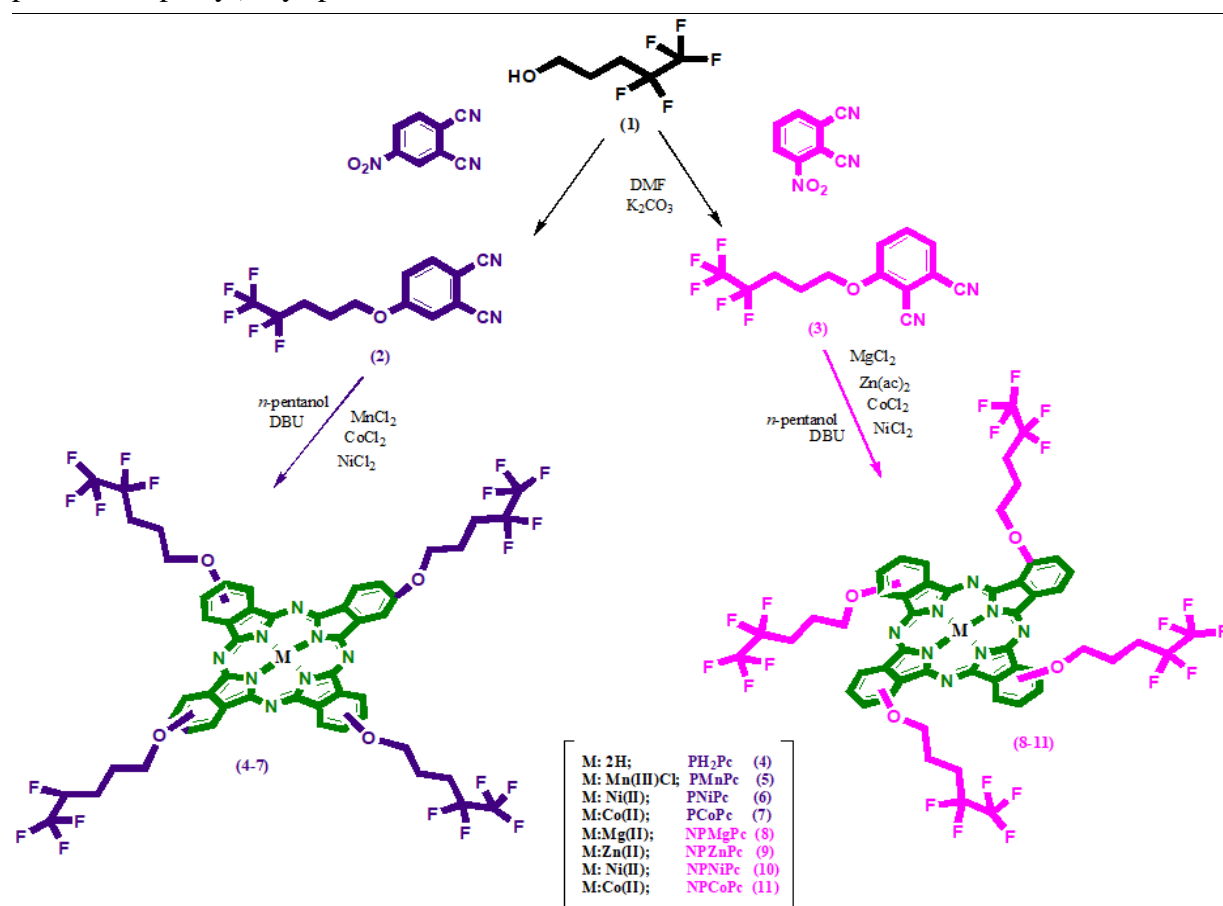


Figure 1. The synthesis route of compounds

The peripheral fluoro atoms confer increased solubility of the phthalocyanine compounds in both more polar solvent such as N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), tetrahydrofuran (THF) and halogenated solvents such as chloroform (CHCl₃) and dichloromethane (CH₂Cl₂).

Spectroscopic techniques were used to assign the structures of phthalonitrile compounds **2** and **3**. In the FT-IR spectra, the disappearance of the OH groups and the presence of characteristic bands for nitrile (C≡N) groups at 2232 cm⁻¹, 2228 cm⁻¹ respectively, and ether (C–O–CAr) groups at 1278-1191 cm⁻¹ (for **2**), 1293-1134 cm⁻¹ (for **3**) were indicative of successful coupling.

¹H NMR spectra of phthalonitrile **2** and **3**, the methylene protons (O–CH₂/ F₂C–CH₂/ C–CH₂) appeared at δ = 4.16 / 2.34 / 2.20 ppm for **2** and δ = 4.24 / 2.35 / 2.20 for **3**, respectively. The aromatic protons of compounds **2** and **3** appeared around at δ = 7.79-7.23 ppm for **2** and δ = 7.69-7.23 ppm for **3** (Figure 2). The ¹³C NMR spectra of **2** and **3** showed the presence of nitrile carbon atoms (C≡N) at δ = 117.61 and 115.72 ppm for **2** and 117.22 and 116.65 ppm for **3**, methylene carbon atoms (O–CH₂) at 67.51 ppm for **2** and 68.21 ppm for **3**, (-F₂C–CH₂) at 27.37 ppm for **2** and 27.16 ppm for **3** and (C–CH₂) at 20.41 ppm for **2** and 20.49 ppm for **3**, respectively. Their mass spectra were confirmed the proposed structure (Figure 3).

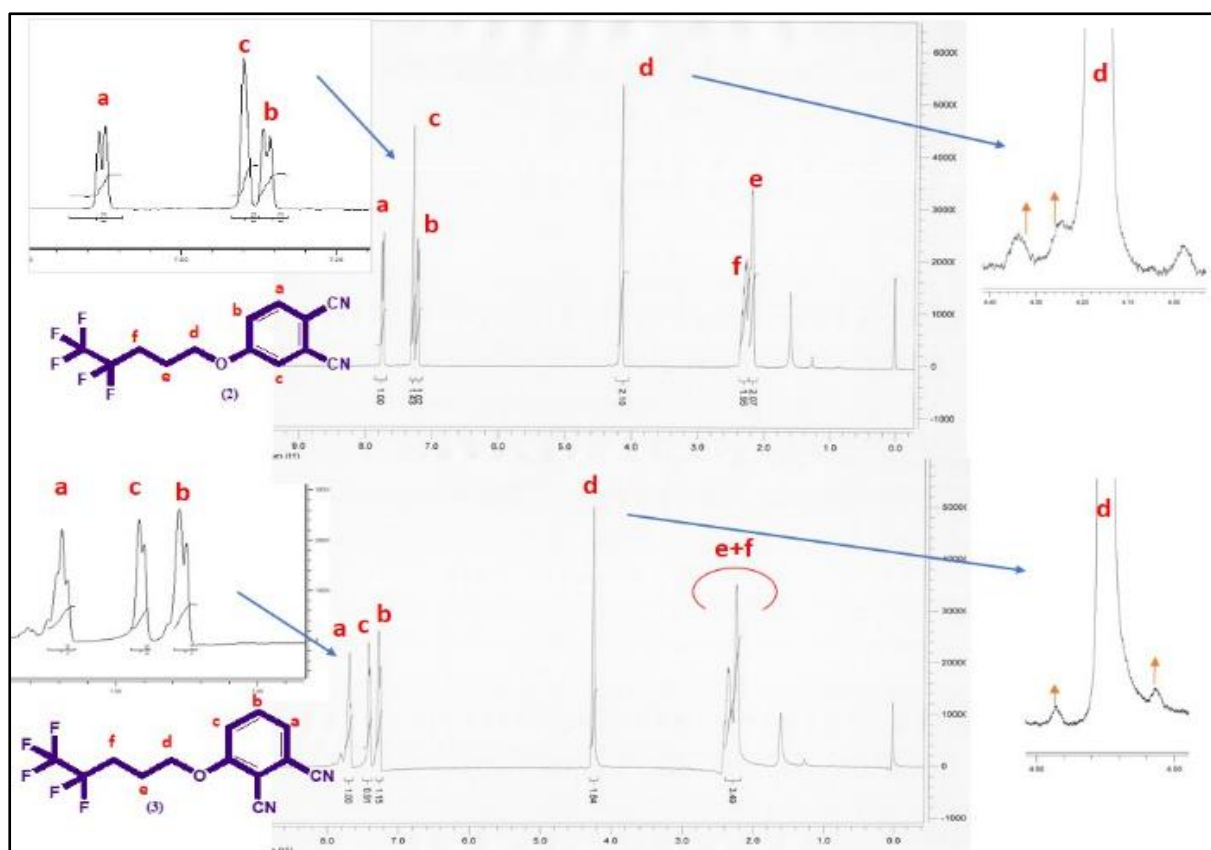


Figure 2. ¹H NMR spectra of phthalonitrile compounds **2** and **3**

While compound **2** was used to synthesize peripheral tetra substituted metalfree (H_2Pc) **4** and metallophthalocyanines (MPc) **5-7**, compound **3** was used non-peripheral tetra substituted metallophthalocyanines **8-11**.

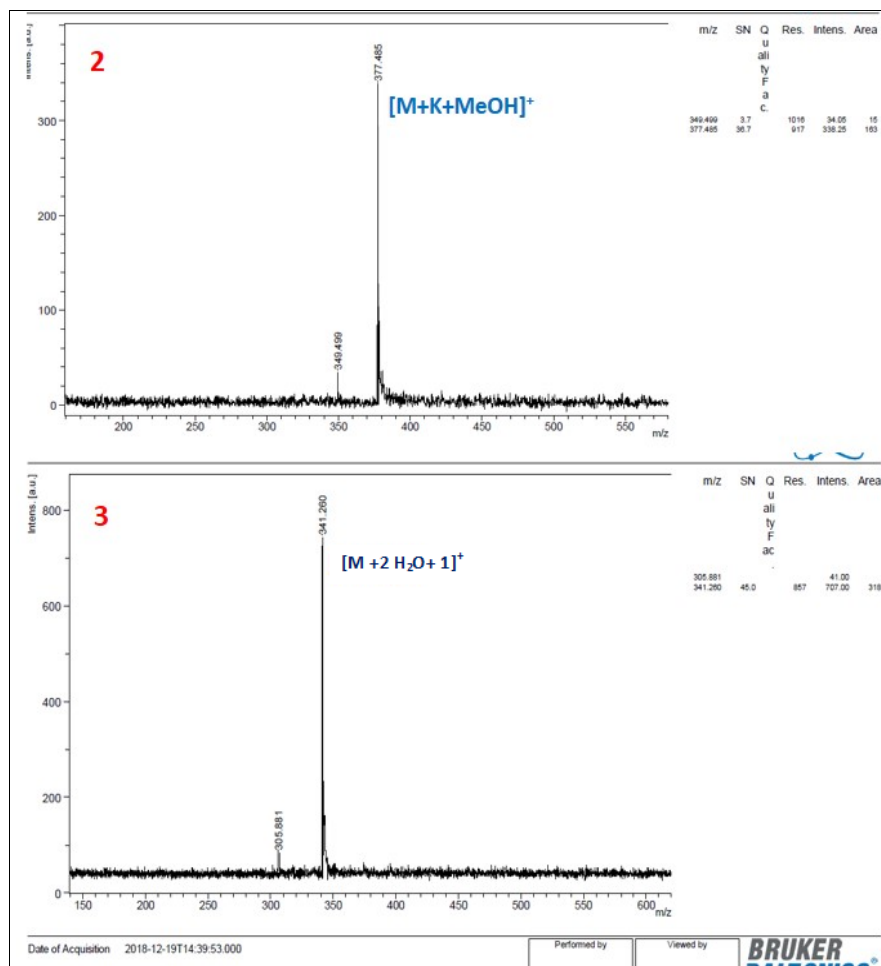


Figure 3. MALDI-TOF MS spectra of phthalonitrile compounds **2** and **3**

In the IR spectrum of H_2Pc **4** showed the presence of $-NH$ vibration band at 3174 cm^{-1} and disappearance of the $C\equiv N$ band 2232 cm^{-1} , as an important proof of the formation of H_2Pc **4**. Also, the disappearance of the $C\equiv N$ vibration bands at is considered as evidence of the formation of Mn(III) phthalocyanine **5**, nickel(II) phthalocyanines **6** and **10**, magnesium(II) phthalocyanine **8**, zinc(II) phthalocyanine **9** and cobalt(II) phthalocyanines **7** and **11** (Supplementary

Information Figure 1 is an example for IR spectra).

In the MALDI-TOF-MS spectra of the metal-free **4** and metallophthalocyanines **5-11**, the presence of molecular ion peaks at $m/z = 1219.91 [M + 1]^+$ for **4**; $1267.57 [M-Cl- 4]^+$ for **5** (Figure 5); $1275.24 [M]^+$ for **6**; $1275.15 [M]^+$ for **7**; $1241.75 [M]^+$ for **8**, $1283.30 [M + 1]^+$ for **9**, $1276.91 [M + 1]^+$ for **10** and $1276.42 [M + 1]^+$ for **11** (Figure 4)

respectively, confirmed the proposed structure.

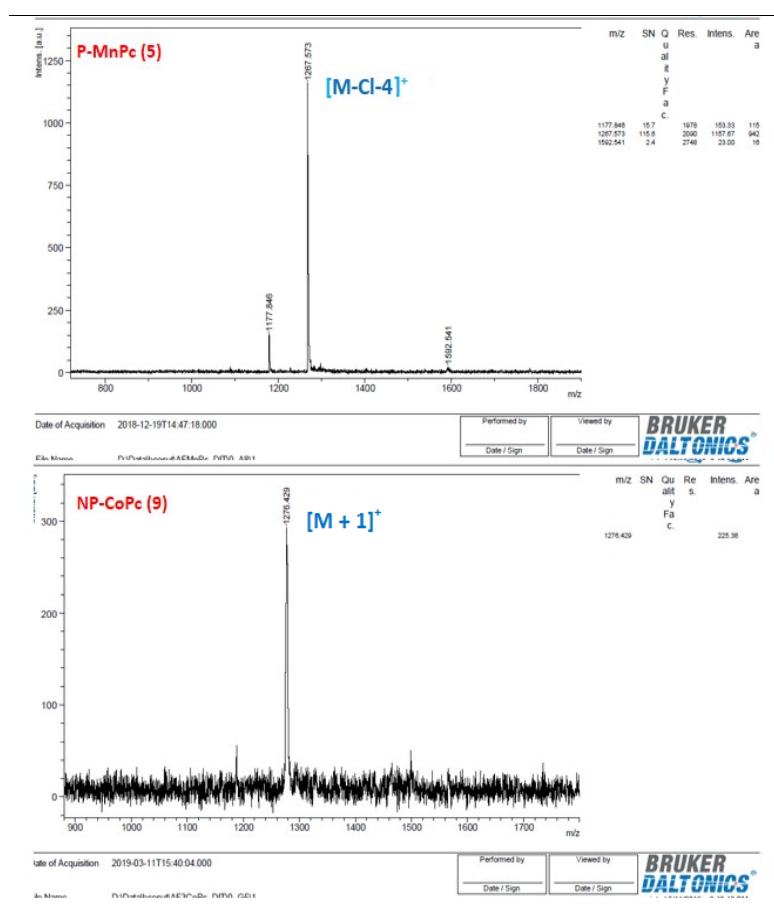


Figure 4. MALDI-TOF MS spectra of peripheral MnPc **5** and non-peripheral CoPc **11**.

3.2. UV-Visible absorption spectra

The UV-Vis absorption spectra of metal-free and metallo-phthalocyanines **4-11** in CHCl_3 are given in Figures 5 and 6. One of the best proofs for the formation of Pcs are supplied via their ground state electronic absorption spectra in studied solution. Phthalocyanine compounds in the UV-visible (UV-Vis) spectrum demonstrate typical two absorption bands. The first one is in the UV region at 300-500 nm called as the B band. The second one is in the visible region at 600-800 nm known as the Q band (Leznoff and Lever, 1989-1996). The novel synthesized phthalocyanine compounds **4-11** showed characteristic Q-

and B band in electronic spectra. The UV-Vis spectrum of peripheral metal-free phthalocyanine **4** was studied at room temperature in CHCl_3 (chloroform). As shown in Figure 5, a split Q band which is characteristic of metal-free phthalocyanine, with two shoulders was observed, as expected (Leznoff and Lever, 1989-1996). These bands were observed at 703 nm ($\log \epsilon = 4.97$) and 666 nm ($\log \epsilon = 4.93$) with two shoulders at 645 nm ($\log \epsilon = 4.65$) and 606 nm ($\log \epsilon = 4.48$) for metal-free Pc **4**. The B band absorptions were observed at 384 nm ($\log \epsilon = 4.76$), 325 nm ($\log \epsilon = 5.09$) and 286 nm ($\log \epsilon = 5.13$).

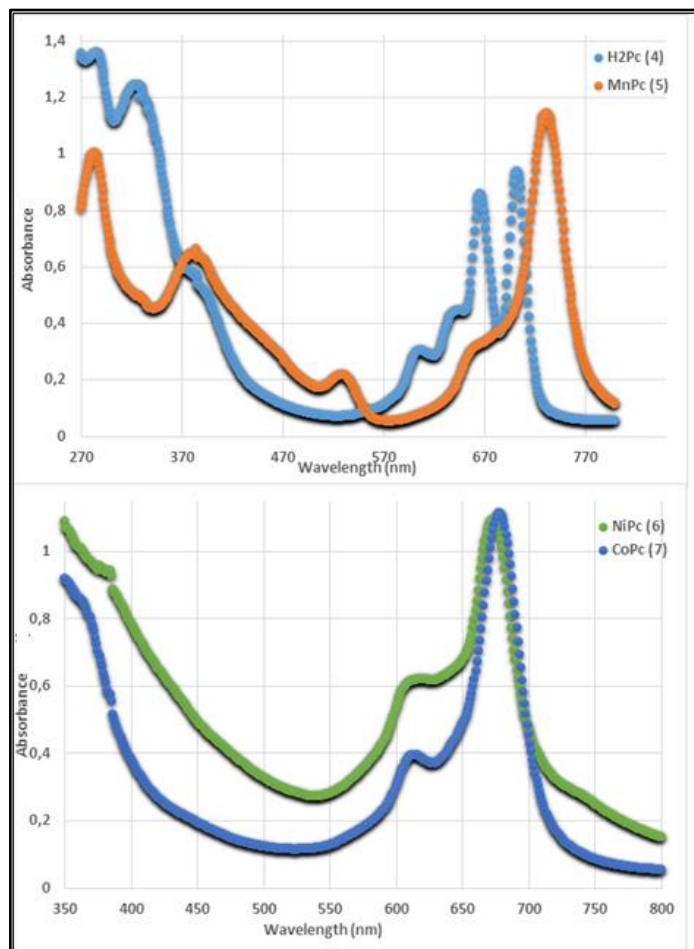


Figure 5. UV-Vis spectra of peripheral phthalocyanine compounds **4**, **5**, **6** and **7** in CHCl_3 at 5×10^{-5} M.

Metal-free phthalocyanines give two equal bands in the 600-700 nm range, while metallo phthalocyanines give a single band. The intensity of $\pi \rightarrow \pi^*$ transitions varies with the metal ion (Aktas Kamiloglu et al., 2018). The electronic absorption spectra of the synthesized MnPc **5**, NiPcs **6** and **10**, MgPc **8**, ZnPc **9** and CoPcs **7** and **11** complexes were measured in CHCl_3 . The electronic spectrum of the fluorocarbon-substituted peripheral manganese phthalocyanine **5** showed the single Q band at 732 nm. This result confirmed that the manganese phthalocyanine **5** showed a highly red-shifted Q band. The Pcs with the axial ligand show a shift of the Q band to the

red region which is needed for some application. The manganese derivatives showed red-shifted Q band relative to the other analogs due to the Mn(III) metal center of the complex (Nyokong, 2010). Q band absorption of the MnPc **5** was observed at 732 nm ($\log \epsilon = 5.06$) and 659 nm ($\log \epsilon = 4.49$). B band absorption for compound **5** was observed at 381 nm ($\log \epsilon = 4.81$) and 284 nm ($\log \epsilon = 5.00$) (Figure 5).

The UV-Vis spectra of the peripheral NiPc **6** and CoPc **7** and their non-peripheral derivatives **9** and **10** were shown in Figures 5 and 6 (Table 1). The nickel(II) phthalocyanine complexes **6** and **10** showed

characteristic absorption in Q band region at 673 nm ($\log \epsilon = 5.04$) and 694 nm ($\log \epsilon = 5.05$) nm without splitting, with weaker absorption at 617 nm ($\log \epsilon = 4.79$) and 625 nm ($\log \epsilon = 4.14$), respectively.

These complexes showed absorption in the B band region at 384 nm ($\log \epsilon = 4.98$) for compound **6** and 384 nm ($\log \epsilon = 4.43$) and 322 nm ($\log \epsilon = 5.02$) for compound **10**. According to these results, the nickel(II) phthalocyanines **6** and **10** have the same metal ion in core but they have different substituent position. It is known that nonperipheral phthalocyanines give absorbance value at higher wavelength (Yanik et al., 2009). The Q band intense of them were similar but the non peripheral

NiPc **10** showed red-shifted (near 21 nm) Q band comparing to the peripheral NiPc **6**. In the UV-Vis absorption spectra of cobalt(II) phthalocyanines **7** and **11**, Q band absorptions were observed at 678 nm ($\log \epsilon = 5.05$) and 613 nm ($\log \epsilon = 4.59$) for compound **7** and 696 nm ($\log \epsilon = 5.04$) and 625 nm ($\log \epsilon = 4.25$) for compound **11**.

According these results, non peripheral CoPc **11** showed red-shifted (near 18 nm) Q band comparing to the peripheral CoPc **7** (Figures 5 and 6). As shown in Figure 6, The UV-Vis spectrum of the non-peripherally MgPc **8** and ZnPc **9** complexes showed characteristic absorption singlet peak in Q band region at 698 nm ($\log \epsilon = 4.99$) for MgPc **8** and 700 nm ($\log \epsilon = 4.98$) for ZnPc **9**.

Table 1. Absorption spectral data of novel NiPc and CoPc compounds (**6** and **10**; **7** and **11**) in CHCl_3 at 5×10^{-5} M.

Compound	Q band		B band
	λ_{max} (nm) ($\log \epsilon$)		λ_{max} (nm) ($\log \epsilon$)
*PNiPc 6	673 (5.04)	617 (4.79)	384 (4.98)
**NPNiPc 10	694 (5.05)	625 (4.43)	384 (4.43); 322 (5.02)
PCoPc 7	678 (5.05)	613 (4.59)	385 (4.74)
NPCoPc 11	696 (5.04)	625 (4.41)	385 (4.59)

*P: Peripheral NiPc

**NP: Non-Peripheral NiPc

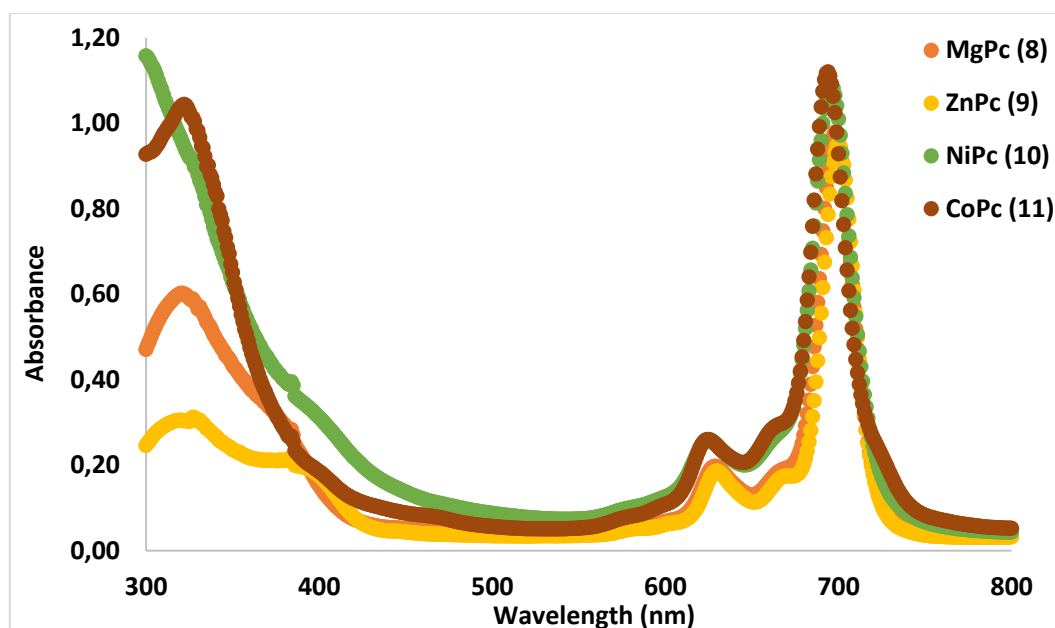


Figure 6. UV-Vis spectra of non-peripheral phthalocyanine compounds **8**, **9**, **10** and **11** in CHCl_3 at 5×10^{-5} M.

When synthesized peripherally metallo phthalocyanines (**5-7**) compared, they have same peripherally but they have different metal ions in core. Therefore, the long wavelength absorbance in Q band was observed $\text{MnPc (5)} > \text{CoPc (7)} > \text{NiPc (6)}$. The high absorbance value in Q band was observed $\text{MnPc (5)} > \text{CoPc (7)} > \text{NiPc (6)}$. When we compare non- peripherally tetra substituted metallo phthalocyanines (**8-11**), the long wavelength absorbance in Q band was observed $\text{ZnPc (9)} > \text{MgPc (8)} > \text{CoPc (11)}$ substituent, metal ions and structure of the substituents (Gök et al., 2014; Gök et al., 2018). Aggregasyon is major problem of the phthalocyanine compounds. In our present study, aggregation behavior of the nickel phthalocyanines (Peripheral NiPc **6** and Non

11) $>$ NiPc (**10**) and the high absorbance value in Q band was observed NiPc (**10**) $>$ CoPc (**11**) $>$ MgPc (**8**) $>$ ZnPc (**9**). These data clarify the usability of these complexes in different application areas of phthalocyanine.

3.3. Aggregation properties of peripheral (NiPc **6** and CoPc **7**) and non-peripheral (NiPc **10** and CoPc **11**)

Aggregation depends on the solvent, concentration, temperature, position of peripheral NiPc **10**) and cobalt phthalocyanines (Peripheral CoPc **7** and Non peripheral CoPc **11**) were investigated in different solvents and increased concentration by UV-Vis spectroscopy (Figures7-10)

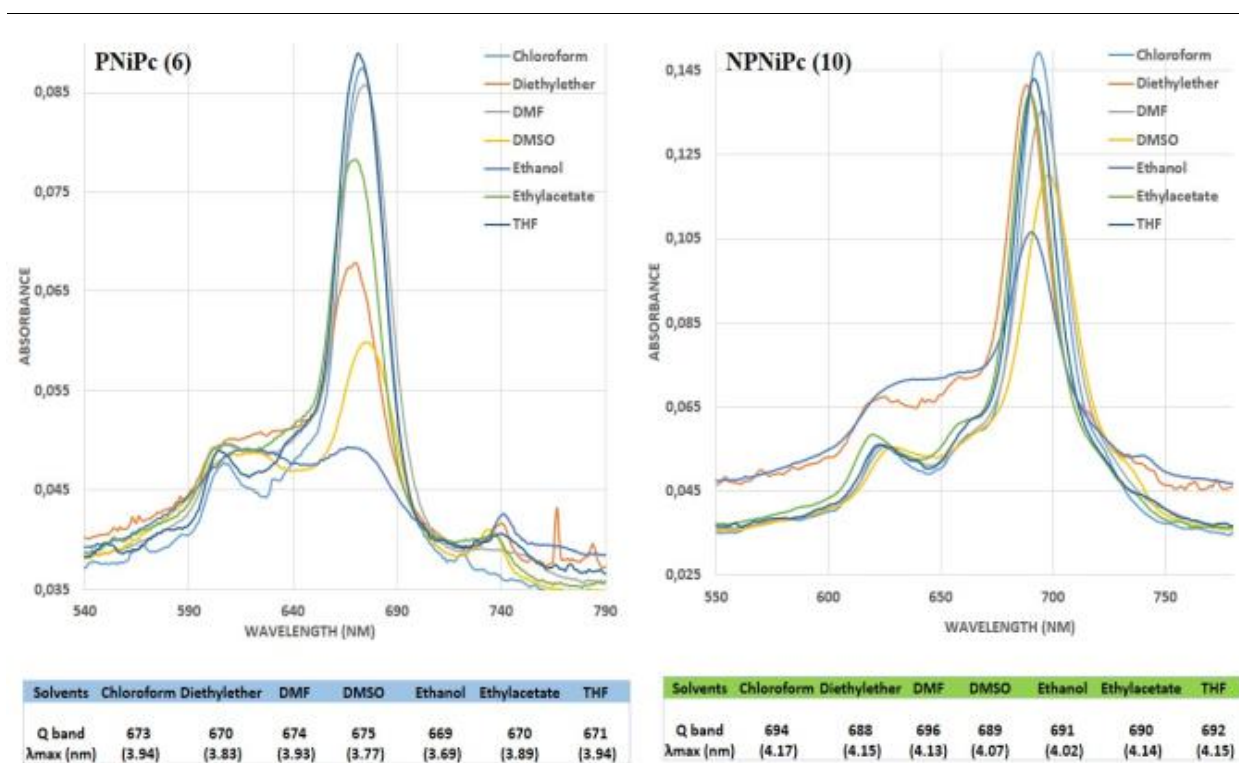


Figure 7. Absorption spectra of peripheral and non-peripheral NiPc phthalocyanine compounds **6** and **10** in different solvents at 1×10^{-5} M.

Different solvent effect

It is known that absorption intensities of Q bands and wavelength are markedly changed by the solvent. The aggregation properties of NiPc **6** and **10** and CoPc **7** and **11** were investigated in different solvents such as diethylether, CHCl_3 , DMF, DMSO, ethanol, ethylacetate and THF (Figure 7 for NiPc complexes, Figure 8 for CoPc complexes).

As shown in Figure 7, the Q band in the spectrum of peripheral NiPc **6** was broadened in ethanol, DMSO, ethylacetate, diethylether due to the raising the dielectric constant of the medium. According to these results, NiPc **6** was not aggregated only in THF and chloroform when compared with other solvents.

In the UV-Vis spectrum, the Q band of the non-peripheral NiPc **10** was most broadened in ethanol. NiPc **10** showed the highest absorbance value in CHCl₃ and lowest absorbance value in ethanol in the UV-Vis spectrum. As a shown Figure 7, in the UV spectra, the Q band of the NiPc **6** shifted to the lowest wavelength (*H-aggregation*) in chloroform and THF solvents, while the Q band of the NiPc **10** shifted to the lowest wavelength only in diethylether solvent. As a

shown Figure 8, the UV-Vis absorption spectra of the CoPc **7** and **11** showed the highest absorbance value in diethylether and the lowest absorbance value in DMSO and THF, respectively. The CoPc **7** and **11** in the ethylacetate, diethylether, ethanol and THF solvents showed shift to the lower wavelength (*H-aggregation*) in comparison with the other solvents in the UV-Vis absorption spectrum.

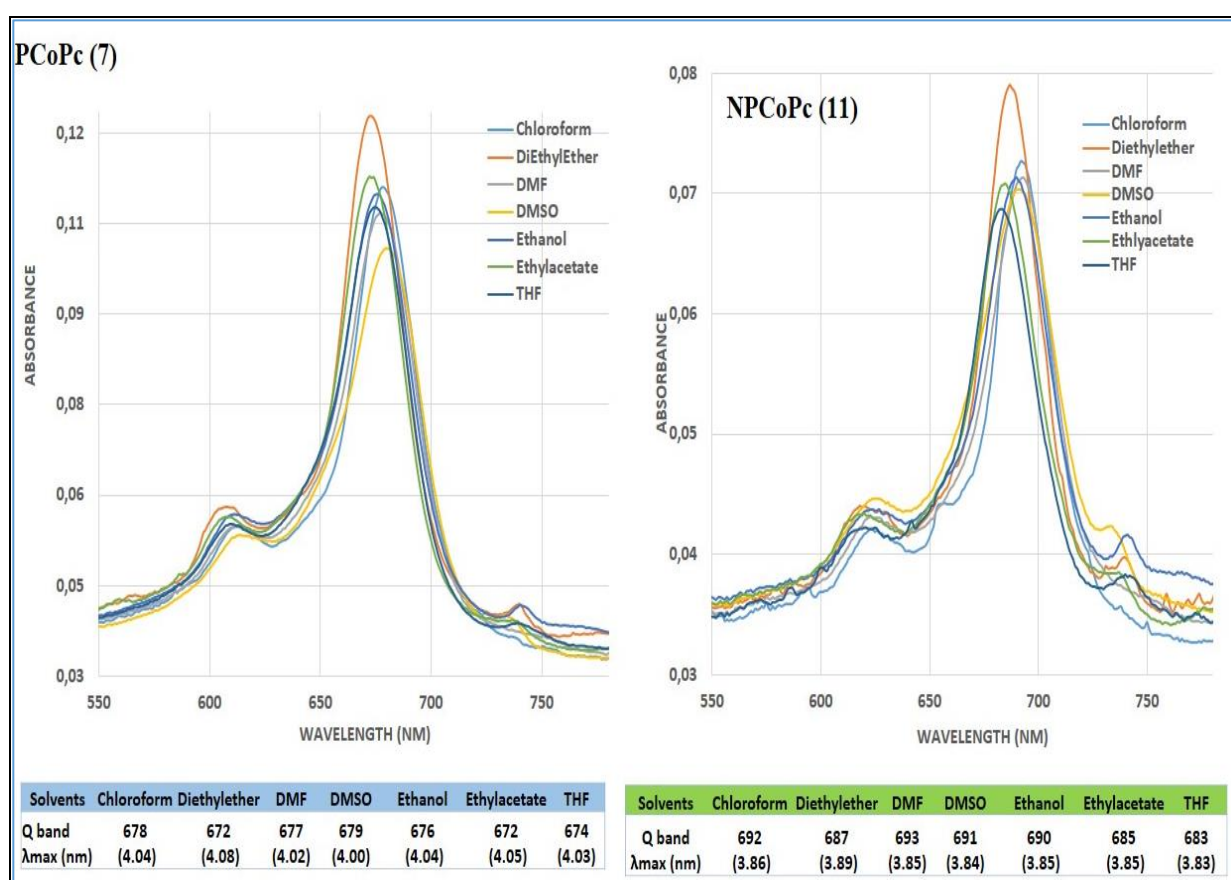


Figure 8. Absorption spectra of peripheral and non-peripheral CoPc phthalocyanine compounds **7** and **11** in different solvents at 1×10^{-5} M.

Different concentration effect

The aggregation behaviors of NiPc **6** and **10** and CoPc **7** and **11** compounds were also investigated at in CHCl₃ from concentration between 12 x 10⁻⁶ and 2 x 10⁻⁶ M. In the UV-Vis spectrum, intensity of absorption of the Q band increases as the concentration increases and no new band is formed (Lia et al., 2019). The effect of changing concentration on the aggregation properties of NiPc **6** and **10** and CoPc **7** and **11** can be seen in Figures 9 and 10. All of the NiPc and CoPc did not aggregate in CHCl₃ at the concentrations between 2 x 10⁻⁶ and 12 x

10⁻⁶ M. The intensity of the Q-band absorption was reduced while concentration decreased, and no expansion of the Q band or new band formation did not observe which indicate that these phthalocyanines do not aggregate in this solvent at the studied concentration range. The Lambert-Beer law ($A = \epsilon.l.c$) was applied to all novel phthalocyanine compounds synthesized in this study (**6**, **7**, **10** and **11**) at six different concentrations (from 2 × 10⁻⁶ M to 12 × 10⁻⁶ M) (Özdemir et al., 2020).

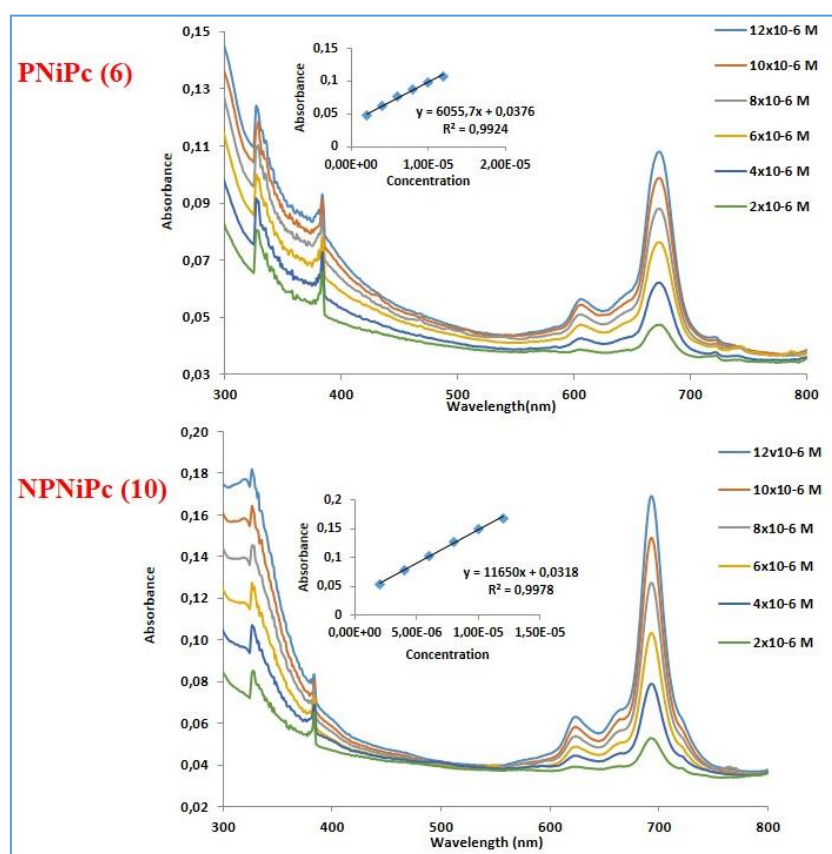


Figure 9. Absorption spectra of the peripheral NiPc **6** and non-peripheral NiPc **10** in CHCl₃ at different concentrations: 2 x 10⁻⁶; 4 x 10⁻⁶; 6 x 10⁻⁶; 8 x 10⁻⁶; 10 x 10⁻⁶; 12 x 10⁻⁶ M.

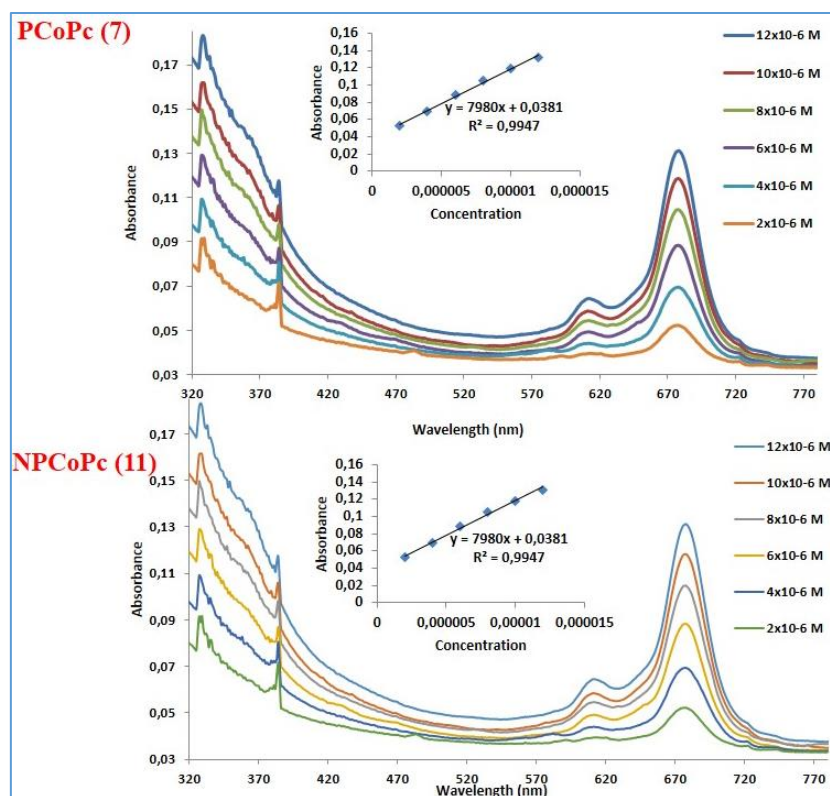


Figure 10. Absorption spectra of the peripheral CoPc **7** and non-peripheral CoPc **11** in CHCl_3 at different concentrations: 2×10^{-6} ; 4×10^{-6} ; 6×10^{-6} ; 8×10^{-6} ; 10×10^{-6} ; 12×10^{-6} M.

4. Conclusion

As a result, we have synthesized and characterized novel peripheral tetra (H_2Pc , MnPc , NiPc and CoPc) and non-peripheral (MgPc , ZnPc , NiPc and CoPc) which are substituted with fluorocarbon compound. The structures of the synthesized all compounds have been fully characterized by a combination of FT-IR, ^1H NMR, ^{13}C NMR, MALDI-TOF-MS and UV-Vis. Also, we studied aggregation behaviour of the fluoro-group substituted peripheral and non-peripheral NiPc (**6** and **10**) and CoPc (**7** and

11) in the concentration of ranging from 2×10^{-6} to 12×10^{-6} M are compatible with the Lambert Beer law. While the concentration was increase, the intensity of absorption of the Q band increase. The electronic absorption spectra showed all MPCs were non-aggregable and also well soluble in common organic solvents. The non-peripheral tetra substituted phthalocyanines were showed red-shifted Q bands when compared to the peripheral tetra phthalocyanine.

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