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The effect of the position of the trimethoxy groups as distant substituents on the spectral and acid sensing properties of phthalocyanines

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ABSTRACT

In this study, alpha and beta substituted phthalonitrile derivatives were obtained by using 3,4,5-trimethoxyphenol and 2,4,6-trimethoxyphenol, and metal-free and Co^{2+} phthalocyanine molecules were synthesized using these starting compounds. After the phthalocyanine compounds were purified and characterized by classical methods, their detailed solubility, UV–*Vis* and FT-IR spectroscopy studies were performed and it was revealed how the positions of methoxy groups changed the spectroscopic properties of phthalocyanines. In addition, during detailed UV–*Vis* studies of Pcs, it was determined that alpha-substituted Pcs gave an extra peak in 1×10^{-5} M dichloromethane solution. It was determined that this peak was caused by acid impurities in dichloromethane in trace amounts and UV–*Vis* spectra in DCM solutions with different trifluoroacetic acid(TFA) concentrations for alpha substituted Pcs (**5**–**8**) were studied and their protonation behaviour was examined. It was determined that H2Pc(**6**) was sensitive to acid even at 1.8×10^{-3} mM concentration. Thus, acid sensor device can be developed by using this Pc molecule, if desired.

1. Introduction

Phthalocyanine (Pc) complexes, closely related to natural Porphyrins which are found in chlorophyll and hemoglobin and can be containing large ring ligands, are artificial organic pigments of bright blue or green colour. They are aromatic organic macromolecules and can be easily converted into metal complexes, which are inorganic molecules, if desired. Pcs, which is the subject of interdisciplinary research, are synthesized by organic and inorganic chemists in all over the world, and physical chemists investigate their electrochemical, electrophotographic, cathode material properties of (lithium) batteries and their electrocatalytic properties, and physicists investigate their conductivity, ferromagnetic properties, switching effects, semiconductor, transistor properties, gas sensor and chemical sensor properties, and medical researchers investigate their medicinal applications, and environmental scientists investigate their purification of wastewater and poisoning of catalysts[1–6].

The investigations about the synthesis and properties of Pcs are among the most studied research topics in the world. The progress of Pc studies is during synthesis, feature detection and device fabrication. Although there are many books and articles on the synthesis and purification methods, spectroscopic, physical and chemical properties of Pcs [7–11]. There's even an extensive chemical review of Kobayashi's on chiral supramolecular Pc systems which highlights and summarizes various optically active porphyrin and Pc molecules prepared using a wide range of structural modification methods to improve the design of novel structures and their applications [12]. However, there is no specific study in the literature about changing the numbers and positions of distant substituents in Pc molecules and how this alteration changes the physical, chemical and spectroscopic properties. However, the structure of the substituents, connection points, connection bridges, their number and even the type of center metal greatly changes the properties of Pc compounds.

In this study, the effect of the position of methoxy groups on the spectral properties of metal free and CoPcs were investigated in Pc compounds that have trimethoxy groups as distant substituents. Pcs occured from the tetramerization reaction of 3 or 4-nitrophthalonitrile or their derivatives are obtained as a mixture of four regioisomers (C_{4h}, D_{2h}, C_s, C_{2v}), and even not all regioisomers can be formed in a single molar ratio[13] and that's why the positions of the substituent have been also represented by indefinite bonds in reaction diagrams (Scheme 1 and Scheme 2). Despite this, since it is very difficult to separate mixtures of regioisomers from each other, regioisomer mixtures are used for almost all Pc property measurements and Pc devices. In this

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study, it can be thought that in such cases the potential property exhibited by one of the compounds, the active compound has been blurred by the other three. In this study, the starting compounds have been also added the comparison of physical and spectral properties of Pc compounds, and positive or negative improvements in the properties of Pc compounds were found to be in full compatible with the starting compounds. All of these property changes are due to the flow efficiency of electrons direction from trimethoxyphenyl ring to the phthalonitrile ring in the starting compounds and to the the Pc ring in macromolecules. This study showed that the property changes in all compounds whose physical and spectral properties were investigated, are mostly due to alpha or beta substituted which are link positions. In our previous study, the effect of azo and oxo-linkage bridges on the physical and spectral properties of Pc compounds which contain dimethoxy groups as distant substituents was investigated [14]. It may be wondered why the methoxy group was chosen as the outer substituent in the studies. The solubility in common solvents should be high for Pcs to measure their properties, to be used in various applications and to be made into devices. It is very difficult to do the above mentioned researches using Pcs with limited solubility. Our previous studies showed that selecting methoxy groups as distant substituents and even increasing the number of methoxy groups significantly increases the solubility of Pcs in common solvents [14,15]. In addition, it may be wondered why CoPcs were chosen as metallo Pcs in the research. It is known that CoPcs are particularly sensitive to organic acids due to the redox active Co metal in their core, and there are many electrochemical studies related to this in the literature [16–19].

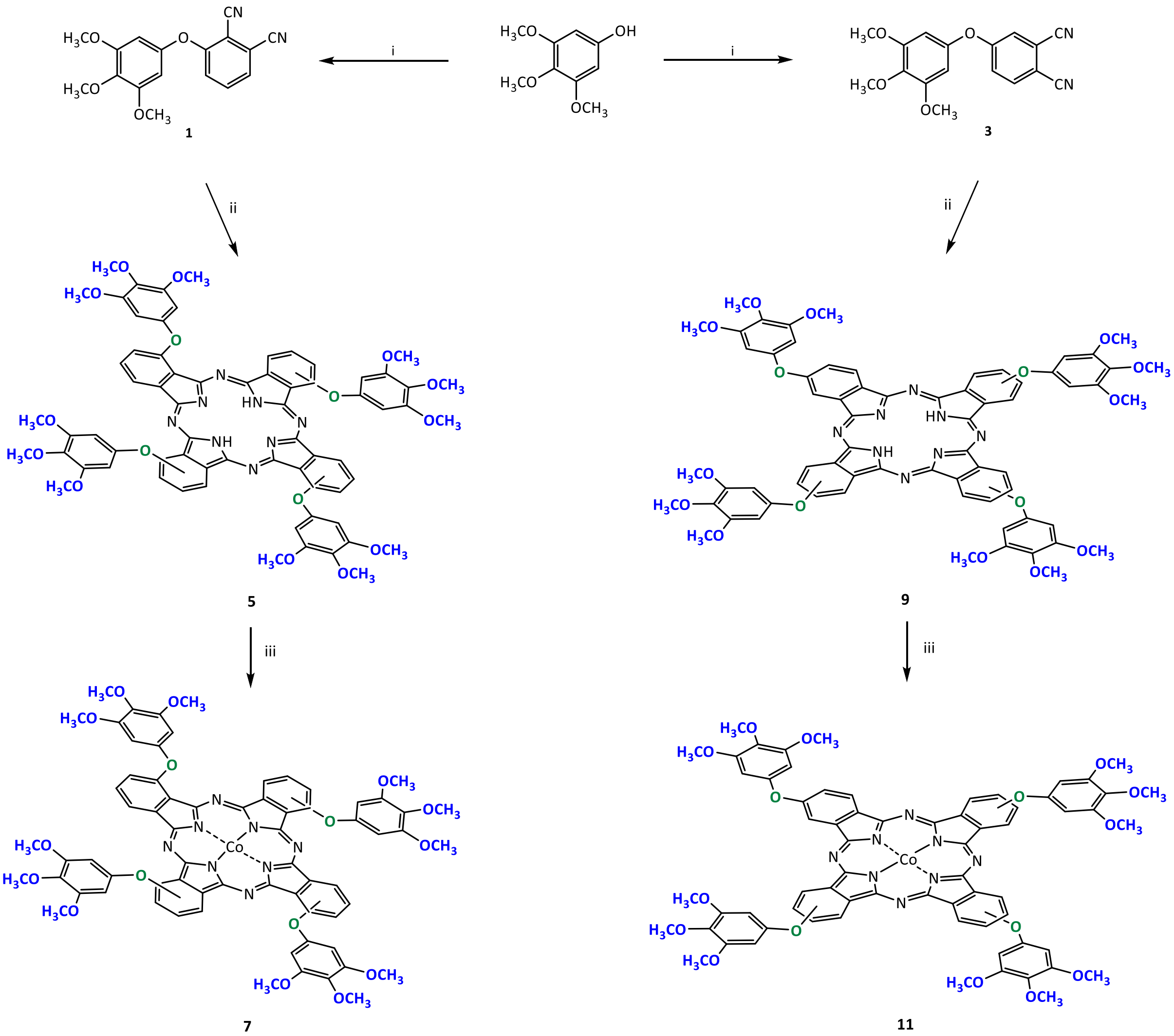
2. Experimental

In this study, isomeric trimethoxy substituted phenolic compounds were preferred to synthesize novel metal free and Co(II) Pcs. 2,4,6-trimethoxyphenoxy and 3,4,5-trimethoxyphenoxy substituted phthalonitrile compounds(**1**–**4**) have been synthesized nucleophilic aromatic substitution reaction [15,20] and metal free and Co(II) Pcs (**5**–**12**) have been achieved by using the starting compounds. The used materials, equipment and Matrix-Assisted Laser Desorption/Ionization (MALDI) sample preparation are given as supplementary information.

2.1. Synthesis

3-(3,4,5-trimethoxyphenoxy)phthalonitrile(1)

A mixture of 3-nitrophthalonitrile (0.834 g, 4.8 mmol), 3,4,5-trimethoxyphenol (0.828, 4.5 mmol), anhydrous potassium carbonate (2.663 g, 19.2 mmol), anhydrous *N*,*N*-dimethylformamide (DMF) (10 mL) was stirred for 48 h at room temperature (25 °C) in a vacuumed 50 mL flask.



Scheme 1. Synthesis route to 3,4,5-trimethoxyphenoxy substituted phthalonitriles (**1** and **3**) and their metal free phthalocyanines (**5** and **9)** and Co(II)phthalocyanines (**7** and **11)** (i) K_2CO_3, DMF, 25 °C 2 days. (ii) Li, amyl alcohol, at reflux temperature, 20 min. (ii) $NaOCH_3$, $Co(CH_3COO)_2{\cdot}4H_2O$, DMF at 160 °C for 10 min.

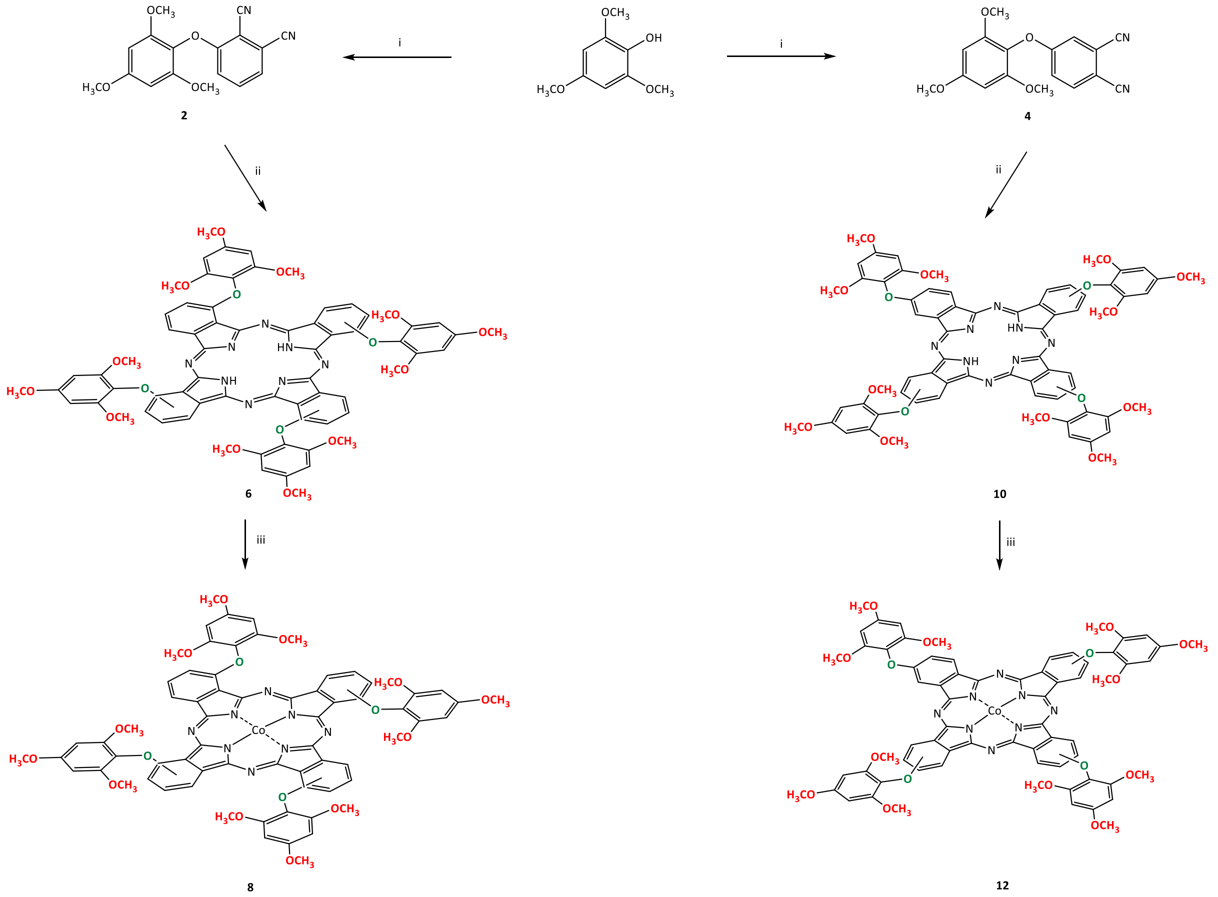
The reaction mixture was poured into ice water. The yellowish white solid precipitated was filtered, washed with 100 mL of water and dried at 80 °C for 3 h in vacuo. The purity of the product was controlled by thin layer chromotography (TLC). The structure of the purely obtained 3-(3,4,5-trimethoxyphenoxy)-phthalonitrile compound was characterized using elemental analyses, Fouirer Transform Infrared (FT-IR), Nuclear Magnetic Resonance (^{1}H NMR and ^{13}C NMR) spectroscopies. Yield: 94% (1.4 g). MP: 161–163 °C. Solubility: $CHCl_3$, CH_2CI_2 (DCM), DMF, dimethyl sulfoxide (DMSO), Toluene, CH_3OH, Acetone, *n*-Pentanol (Amyl alcohol). Elemental Analysis of $C_{17}H_{14}N_2O_4$ calculated: C, 65.80; H, 4.55; N, 9.03; found: C, 65.62; H, 4.71; N, 9.14. FT-IR (ATR) ν_{max}/cm^{-1}: 615, 807, 844, 931, 1008, 1039, 1131, 1176, 1217 (Ar-O-Ar), 1272, 1305, 1422, 1448, 1500, 1571, 1607 (Ar. C=C), 2227 (C≡N), 2823, 2845, 2950 (Alph. CH), 3093 (Ar. CH). ^{1}H NMR ($CDCl_3$) δ, ppm: 3.85(s, 6H), 3.88(s, 3H), 6.37 (s, 2H), 7.14 (dd, $J = 8.67$ Hz, $J = 0.79$ Hz, 1H), 7.48 (dd, $J = 7.72$ Hz, $J = 0.79$ Hz, 1H), 7.76 (dd, $J = 8.67$ Hz, $J = 7.72$ Hz, 1H). ^{13}C NMR ($CDCl_3$) δ, ppm: 160.30 (Ar. C), 152.50 (Ar. C), 151.60 (2xAr. C), 133.47 (Ar. C), 132.38 (Ar. C), 126.75 (Ar. C), 122.52 (Ar. C), 115.83 (Ar. C), 115.76 (CN), 113.54 (CN), 103.57 (Ar. C), 96.98 (2xAr. C), 60.82 (OCH_3), 56.16 ($2xOCH_3$). UV–*Vis* (CH_2Cl_2, 5×10^{-6} M) λ_{max} (nm), (log ε): 318(5.25), 308(5.20).

3-(2,4,6-trimethoxyphenoxy)phthalonitrile(2)

The compound was synthesized by using 3-nitrophthalonitrile (0.500 g, 2.90 mmol), 2,4,6-trimethoxyphenol (0.543 g, 2.95 mmol), anhydrous potassium carbonate (0.8 g, 5.9 mmol), anhydrous DMF (10 mL) according procedure of the synthesis of compound **1**. Then the product was purified by column chromatography using $CHCl_3$ as mobile phase. Yield: 86% (0.775 g). MP: 191–193 °C. Solubility: $CHCl_3$, DCM, DMF, DMSO, Toluene, CH_3OH, Acetone, *n*-Pentanol(Amyl alcohol). Elemental Analysis of $C_{17}H_{14}N_2O_4$ calculated: C, 65.80; H, 4.55; N, 9.03; found: C, 65.73; H, 4.46; N, 9.12. FT-IR (ATR) ν_{max}/cm^{-1}: 723, 751, 788, 810, 916, 949, 985, 1027, 1050, 1131, 1151, 1203 (Ar-O-Ar), 1233, 1270, 1307, 1348, 1416, 1454, 1505 (Ar. C=C), 1604 (Ar. C=C), 2232 (C≡N), 2844 (Alph. CH), 2939 (Alph. CH), 3017 (Ar. CH), 3096 (Ar. CH). ^{1}H NMR ($CDCl_3$): δ, ppm 3.77 (s, 6H), 3.84 (s, 3H), 6.20 (s, 2H), 6.89 (d, $J = 8.49$, 1H), 7.37 (d, $J = 7.4$, 1H), 7.48 (t, $J = 7.95$, 1H). ^{13}C NMR ($CDCl_3$) δ, ppm: 161.71 (Ar. C), 158.75 (2xAr. C), 153.05 (Ar. C), 133.98 (Ar. C), 126.08 (Ar. C), 124.59 (Ar. C), 118.78 (Ar. C), 116.59 (Ar. C), 115.43 (CN), 113.04 (CN), 104.37 (Ar. C), 91.58(2xAr. C), 56.09 ($2xOCH_3$), 55.56 (OCH_3). UV–*Vis* (CH_2Cl_2, 5×10^{-6} M) λ_{max} (nm), (log ε): 316(5.29), 307(5.28).

4-(3,4,5-trimethoxyphenoxy)phthalonitrile(3)

The compound was synthesized by using 4-nitrophthalonitrile (0.783 g, 4.5 mmol), 3,4,5-trimethoxyphenol (0.888, 4.8 mmol), anhydrous potassium carbonate (2.663 g, 19.2 mmol), anhydrous DMF (10 mL) according to the literature[20] and characterized. MP: 178–180 °C. Solubility: $CHCl_3$, DCM, DMF, DMSO, Toluene, CH_3OH, Acetone, *n*-Pentanol(Amyl alcohol). Elemental Analysis of $C_{17}H_{14}N_2O_4$ calculated: C, 65.80; H, 4.55; N, 9.03; found: C, 65.71; H, 4.66; N, 9.05. FT-IR (ATR) ν_{max}/cm^{-1}: 626, 636, 786, 814, 843, 996, 1006, 1088, 1122, 1172, 1217 (Ar-O-Ar), 1233, 1246, 1284, 1339, 1417, 1449, 1468, 1485, 1563, 1585, 1606 (Ar. C=C), 2227 (C≡N), 2839, 2943 (Alph. CH), 2973 (Alph. CH), 3008 (Ar. CH), 3110 (Ar. CH). ^{1}H NMR ($CDCl_3$) δ, ppm: 3.85 (s, 6H), 3.89 (s, 3H), 6.33 (s, 2H), 7.27 (dd, $J = 8{,}67$, $J = 2.52$, 1H), 7.31 (d, $J = 2.52$, 1H), 7.76 (d, $J = 8.67$, 1H). ^{13}C NMR ($CDCl_3$) δ, ppm: 162.08 (Ar. C), 154.64 (Ar. C), 152.37 (2xAr. C), 135.19 (Ar. C), 134.26 (Ar. C), 122.56 (Ar. C), 121.11 (Ar. C), 115.89 (CN), 115.81 (CN), 115.52 (Ar. C), 108.92 (Ar. C), 98.23(2xAr. C), 60.97 (OCH_3), 56.09



Scheme 2. Synthesis route to 2,4,6-trimethoxyphenoxy substituted phthalonitriles (**2** and **4**) and their metal free phthalocyanines (**6** and **10)** and Co(II)phthalocyanines (**8** and **12)** (i) K_2CO_3, DMF, 25 °C 2 days. (ii) Li, amyl alcohol, at reflux temperature, 20 min. (ii) $NaOCH_3$, $Co(CH_3COO)_2{\cdot}4H_2O$, DMF at 160 °C for 10 min.

(2xOCH$_3$). UV–*Vis* (CH$_2$Cl$_2$, 5×10^{-6} M) λ_{max} (nm), (log ε): 304(5.30), 295(5.30).

4-(2,4,6-trimethoxyphenoxy)phthalonitrile(4)

The compound was synthesized by using 4-nitrophthalonitrile (0.730 g, 4.23 mmol), 2,4,6-trimethoxyphenol (0.793, 4.30 mmol), anhydrous potassium carbonate (1.167 g, 8.46 mmol), anhydrous DMF (10 mL) according procedure of the synthesis of compound **3**. The light brown product was purified by column chromatography using CHCl$_3$ as mobile phase. Yield: 89% (1.17 g). MP: 153–155 °C. Solubility: CHCl$_3$, DCM, DMF, DMSO, Toluene, CH$_3$OH, Acetone, *n*-Pentanol. Elemental Analysis of $C_{17}H_{14}N_2O_4$ calculated: C, 65.80; H, 4.55; N, 9.03; found: C, 65.87; H, 4.66; N, 8.92. FT-IR (ATR) ν_{max}/cm^{-1}: 686, 719, 750, 820, 843, 880, 912, 949, 1027, 1054, 1086, 1122, 1155, 1203(Ar-O-Ar), 1279, 1307, 1353, 1426, 1459, 1482, 1508 (Ar. C═C), 1592 (Ar. C═C), 2232 (C═N), 2843 (Alph. CH), 2939 (Alph. CH), 2976 (Alph. CH), 3017 (Ar. CH), 3086 (Ar. CH). ^{1}H NMR (CDCl$_3$) δ, ppm: 3.77 (s, 6H), 3.86 (s, 3H), 6.23 (s, 2H), 7.15 (d, *J* = 2.41, 1H), 7.21 (dd, *J* = 8.7, *J* = 2.41, 1H), 7.68 (d, *J* = 8.7, 1H). ^{13}C NMR (CDCl$_3$) δ, ppm: 162.10 (Ar. C), 158.72 (Ar. C), 153.04 (2xAr. C), 135.06 (Ar. C), 123.96 (Ar. C), 120.35 (Ar. C), 119.75 (Ar. C), 117.24 (Ar. C), 115.78 (CN), 115.28 (CN), 108.04 (Ar. C), 91.51 (2xAr. C), 56.11 (2xOCH$_3$), 55.63 (OCH$_3$). UV–*Vis* (CH$_2$Cl$_2$, 5×10^{-6} M) λ_{max} (nm), (log ε): 302(5.35), 293(5.35).

General procedure for the synthesis of Metal-Free Phthalocyanines

3,4,5-trimethoxyphenoxy substituted and 2,4,6-trimethoxyphenoxy substituted metal-free Pcs were also synthesized by heating of the mixture 0.20 g (0.644 mmol) the phthalonitrile derivatives (**1**, **2**, **3**, or **4**) and lithium metal (10 eq) in 2 mL amyl alcohol at reflux temperature for about 20 min. After the reactions were complete, the mixture was cooled to room temperature and precipitated by pouring into acetic acid. The green raw product was filtered. The H2Pcs were cleaned by washing up with acetic acid–water (70% by mass) mixture, water, methanol, and acetonitrile in a Soxhlet apparatus, respectively. The molecular structure of the pure compound **5**, **6**, **9** and **10** were characterized using Ultraviolet/Visible (UV–*Vis*), FT-IR, Matrix-Assisted Laser Desorption/Ionization time-of- flight (MALDI-TOF) mass spectroscopies.

1(4),8(11),15(18),22(25)-Tetrakis(3,4,5-trimethoxyphenoxy) phthalocyanine(5)

Solubility: CHCl$_3$, DCM, tetrahydrofuran (THF), Toluene, DMF, DMSO. Yield: 32.2 mg (16.00%). MP > 350 °C. Elemental analysis of $C_{68}H_{58}N_8O_{16}$ calculated: C, 65.69; H, 4.70; N, 9.01, found C, 65.51; H, 4.76; N, 9.15. FT-IR (ATR) ν_{max}/cm^{-1}: 746, 772, 797, 864, 933, 1009, 1124, 1219(Ar-O-Ar), 1332, 1463, 1586(Ar. C═C), 2851(Alph. CH), 2920(Alph. CH), 3063(Ar. CH), 3281 (NH). UV–*Vis* (CH$_2$Cl$_2$, 1×10^{-5} M) λ_{max} (nm), (log ε): 779(4.28), 721(4.99), 692(4.98), 660(4.63), 625 (4.46), 323(4.70). MALDI-TOF-MS; calculated molecular weight: 1243.25, found molecular weight: 1244.13 (M + H)$^+$.

1(4),8(11),15(18),22(25)-Tetrakis(2,4,6-trimethoxyphenoxy) phthalocyanine(6)

Solubility: CHCl$_3$, DCM, THF, Toluene, DMF, DMSO. Yield: 56 mg (28.00%). MP > 350 °C. Elemental analysis of $C_{68}H_{58}N_8O_{16}$ calculated: C, 65.69; H, 4.70; N, 9.01, found C, 65.53; H, 4.81; N, 8.82. FT-IR (ATR) ν_{max}/cm^{-1}: 693, 748, 805, 862, 945, 1023, 1050, 1129, 1200(Ar-O-Ar), 1229, 1325, 1422, 1459, 1495(Ar. C═C), 1592 (Ar. C═C), 2840(Alph. C—H), 2938(Alph. C—H), 3009(Ar. C—H), 3292(N—H). UV–*Vis* (CH$_2$Cl$_2$, 1×10^{-5} M) λ_{max} (nm), (log ε): 725(5.06), 695(5.03), 661 (4.54), 629(4.43), 353(4.59), 315(4.65). MALDI-TOF-MS; calculated molecular weight: 1243.25, found molecular weight: 1243.28 (M)$^+$.

2(3),9(10),16(17),23(24)-Tetrakis(3,4,5-trimethoxyphenoxy) phthalocyanine(9)

Solubility: CHCl$_3$, DCM, THF, Toluene, DMF, DMSO. Yield: 72.4 mg (36.00%). MP > 350 °C. Elemental analysis of $C_{68}H_{58}N_8O_{16}$ calculated: C, 65.69; H, 4.70; N, 9.01, found C, 65.78; H, 4.58; N, 9.12. FT-IR (ATR) ν_{max}/cm^{-1}: 716, 744, 777, 816, 920, 987, 1047, 1089, 1119, 1207(Ar-O-Ar), 1252, 1319, 1336, 1414, 1446, 1495, 1592(Ar. C═C), 2832(Alph. CH), 2934(Alph. CH), 3067(Ar. CH), 3289(NH). UV–*Vis* (CH$_2$Cl$_2$, 1×10^{-5} M) λ_{max} (nm), (log ε): 701(4.99), 667(4.99), 637(4.68), 606(4.51), 341(4.84), 289(4.66). MALDI-TOF-MS; calculated molecular weight: 1243.25, found molecular weight: 1244.26 (M + H)$^+$.

2(3),9(10),16(17),23(24)-Tetrakis(2,4,6-trimethoxyphenoxy) phthalocyanine(10)

Solubility: CHCl$_3$, DCM, THF, Toluene, DMF, DMSO. Yield: 92 mg (46.00%). MP > 350 °C. Elemental analysis of $C_{68}H_{58}N_8O_{16}$ calculated: C, 65.69; H, 4.70; N, 9.01, found C, 65.78; H, 4.64; N, 8.92. FT-IR (ATR) ν_{max}/cm^{-1}: 699, 741, 807, 923, 1003, 1054, 1091, 1124, 1152, 1203 (Ar-O-Ar), 1339, 1390, 1418, 1455, 1497(Ar. C═C), 1596 (Ar. C═C), 2836(Alph. C—H), 2930(Alph. C—H), 3003(Ar. C—H), 3284(N—H). UV–*Vis* (CH$_2$Cl$_2$, 1×10^{-5} M) λ_{max} (nm), (log ε): 704(4.99), 667(4.82), 640(4.59), 606(4.39), 343(4.77), 288(4.55). MALDI-TOF-MS; calculated molecular weight: 1243.25, found molecular weight: 1243.09 (M)$^+$.

General procedure for the synthesis of cobalt(II) Phthalocyanines

3,4,5- trimethoxyphenoxy substituted and 2,4,6- trimethoxyphenoxy substituted Co(II)Pcs were also synthesized by heating of the mixture 0.050 g (0,04 mmol) H2Pcs (**5**, **6**, **9** or **10**), 0.010 g NaOCH$_3$, Co (CH$_3$COO)$_2$·4H$_2$O salt and 2 mL DMF at 160 °C for about 10 min. The Co (II)Pcs **7**, **8**, **11** and **12** were purified like metal-free Pcs and the molecular structure of them were characterized using UV–*Vis*, FT-IR, MALDI-TOF-MS spectroscopies.

1(4),8(11),15(18),22(25)-Tetrakis(3,4,5-trimethoxyphenoxy) phthalocyaninato cobalt(II)(7)

Solubility: CHCl$_3$, DCM, THF, Toluene, DMF, DMSO. Yield: 37.8 mg (18.00%). MP > 350 °C. Elemental analysis of $C_{68}H_{56}N_8O_{16}Co$ calculated: C, 62.82; H, 4.34, N, 8.62; found: C, 62.97; H, 4.48; N, 8.48. FT-IR (ATR) ν_{max}/cm^{-1}:745, 782, 800, 954, 1003, 1038, 1119, 1175, 1227(Ar-O-Ar), 1328, 1463, 1583(Ar. C═C), 2825(Alph. C—H), 2935(Alph. C—H), 3063(Ar. C—H). UV–*Vis* (CH$_2$Cl$_2$, 1×10^{-5} M) λ_{max} (nm), (log ε): 688(4.99), 621 (4.37), 320 (4.64). MALDI-TOF-MS; calculated molecular weight: 1300.17, found molecular weight: 1301.09 (M + H)$^+$.

1(4),8(11),15(18),22(25)-Tetrakis(2,4,6-trimethoxyphenoxy) phthalocyaninato cobalt(II)(8)

Solubility: CHCl$_3$, DCM, THF, Toluene, DMF, DMSO. Yield: 47 mg (90.00%). MP > 350 °C. Elemental analysis of $C_{68}H_{56}N_8O_{16}Co$ calculated: C, 62.82; H, 4.34; N, 8.62; found: C, 62.73; H, 4.42; N, 8.70. FT-IR (ATR) ν_{max}/cm^{-1}: 734, 798, 899, 940, 977, 1050, 1092, 1133, 1201(Ar-O-Ar), 1239, 1325, 1417, 1459, 1490(Ar. C═C), 1592(Ar. C═C), 2839 (Alph. C—H), 2934(Alph. C—H), 3003(Ar. C—H). UV–*Vis* (CH$_2$Cl$_2$, 1×10^{-5} M) λ_{max} (nm), (log ε): 695 (5.04), 659 (4.37), 623 (4.33), 314 (4.50). MALDI-TOF-MS; calculated molecular weight: 1300.17, found molecular weight: 1300.13 (M)$^+$.

2(3),9(10),16(17),23(24)-Tetrakis(3,4,5-trimethoxyphenoxy) phthalocyaninato cobalt(II)(11)

Solubility: CHCl$_3$, DCM, THF, Toluene, DMF, DMSO. Yield: 102 mg (49.00%). MP > 350 °C. Elemental analysis of $C_{68}H_{56}N_8O_{16}Co$ calculated: C, 62.82; H, 4.34, N, 8.62; found: C, 62.68; H, 4.43, N, 8.71. FT-IR (ATR) ν_{max}/cm^{-1}: 751, 821, 858, 951, 991, 1056, 1091, 1121, 1177, 1217(Ar-O-Ar), 1269(Ar-O-Ar), 1328, 1344, 1411, 1463, 1498, 1596 (Ar. C═C), 2828(Alph. C—H), 2935(Alph. C—H), 3003(Ar. C—H), 3063 (Ar. C—H). UV–*Vis* (CH$_2$Cl$_2$, 1×10^{-5} M) λ_{max} (nm), (log ε): 674(5.00), 607 (4.37), 325(4.74). MALDI-TOF-MS; calculated molecular weight: 1300.17, found molecular weight: 1301.92 (M + H)$^+$.

2(3),9(10),16(17),23(24)-Tetrakis(2,4,6-trimethoxyphenoxy) phthalocyaninato cobalt(II)(12)

Solubility: CHCl$_3$, DCM, THF, Toluene, DMF, DMSO. Yield: 45 mg (86.00%). MP > 350 °C. Elemental analysis of $C_{68}H_{56}N_8O_{16}Co$ calculated: C, 62.82; H, 4.34, N, 8.62; found: C, 62.99; H, 4.28; N, 8.51. FT-IR (ATR) ν_{max}/cm^{-1}: 713, 755, 816, 947, 1026, 1050, 1096, 1100, 1130, 1200, 1221(Ar-O-Ar), 1344, 1404, 1465(Ar. C═C), 1596(Ar. C═C), 2837(Alph. C—H), 2939(Alph. C—H), 3005(Ar. C—H). UV–*Vis* (CH$_2$Cl$_2$, 1×10^{-5} M) λ_{max} (nm), (log ε): 678 (4.99), 608 (4.43), 328 (4.74), 291 (4.74). MALDI-TOF-MS; calculated molecular weight: 1300.17, found molecular weight: 1300.58 $(M)^+$.

3. Result and discussion

3-(3,4,5-trimethoxyphenoxy)phthalonitrile **(1)**, 3-(2,4,6-trimethoxyphenoxy)phthalonitrile **(2)**, 4-(3,4,5-trimethoxyphenoxy)phthalonitrile **(3)**, 4-(2,4,6-trimethoxyphenoxy)phthalonitrile **(4)** starting compounds were obtained nucleophilic aromatic substitution reaction between 3- or 4-nitrophthalonitrile and correspond trimethoxyphenol compounds [15,20]. These compounds were purified and characterized by elemental analyses, FT-IR, UV–*Vis*, ^{1}H and ^{13}C NMR spectra.

In FT-IR spectrum CN bands appeared at 2227 cm^{-1} for compounds **1** and **3**, and 2232 cm^{-1} for compounds **2** and **4**, Ar-O-Ar bands differed as 1217 cm^{-1} and 1203 cm^{-1} in alpha substituted and beta substituted starting compounds, respectively. The Ar-O-CH_3 stretching bands appeared at 1131 cm^{-1} for compounds **1** and **3**, and 1122 cm^{-1} for compounds **2** and **4**. While the FT-IR bands of the Ar-O-Ar bonds were affected by the positions of the nitrile groups, it was observed that the Ar-O-CH_3 stretching bands differed according to the positions of the methoxy groups in distant substituents (Fig. S1).

In the ^{1}H NMR spectrum, it has been observed that the chemical shift values are in the higher area for 2,4,6-trimethoxy substitute phthalonitrile (6.20 ppm for alpha substituted compound/6.22 ppm for beta substituted compound) than 3,4,5-trimethoxy substitute phthalonitrile (6.37 ppm for alpha substitue/6.32 ppm for beta substitute). Besides this clear change, all other peaks resonated in the higher field for 2,4,6-trimethoxy substitute phthalonitrile compounds. The methoxy groups at the 2, 4 and 6 positions increase the electron density on both the 3 position C atoms and the 1 position O atom. Increasing the electron density on the oxygen atom increases the electron density in the aromatic ring where the nitrile groups are located, by the resonance effect. Since this result causes shielding of protons, it shifts the chemical shift of protons in the molecule to the higher area (Figs. S2-S5).

The melting points of the starting compounds ligands (Compound **1**–**4**) were measured under atmospheric pressure (1 atm) and determined as 162, 192, 178 and 154 °C, respectively. OCH_3 groups at the 2, 4 and 6 positions maximize the electron flow between the rings. These electrons will be more withdrawn by the CN groups in both the ortho and para positions. But when they pull from the para position, the electrons have delocalized in the whole molecule more. Thus, the electrons are distributed homogeneously throughout the molecule, no charge accumulation occurs in any part of the molecule, and an apolar molecule is formed. This situation causes the melting point of the molecule to decrease. Therefore, it is expected to have the lowest melting point of compound **4** and the highest melting point of compound **2**. This theoretical knowledge has precisely matched with practical measurements.

The metal-free Pcs(**5**, **6**, **9** and **10**) have been achieved by heating the correspond phthalonitrile compound and metallic lithium, in *n*-pentanol at reflux temperature for about 20 min and Co(II)Pcs(**7**, **8**, **11** and **12**) were obtained by stirring the mixture of pure correspond metal-free Pcs, $NaOCH_3$ and $Co(CH_3COO)_2{\cdot}4H_2O$ in 2 mL DMF at 160 °C for 5 min. In this method, the strongly basic $NaOCH_3$ salt was used to rip off the relatively acidic central NH protons of metal-free Pcs.

The novel Pc compounds were characterized by standard methods (elemental analysis, FT-IR, UV–*Vis,* MALDI-TOF-MS spectroscopy).

In the FT-IR spectra of the Pc compounds, the stretching bands of the aromatic C=C bonds were observed at approximately 1600 cm^{-1}, and the stretching bands of the C—O—C bonds around 1200 cm^{-1}, as in the starting compounds. The stretching bands of N—H bonds in the Pc centre were also observed around 3300 cm^{-1} (3281, 3292, 3289 and 3284 cm^{-1} for compound **5**, **6**, **9** and **10**, respectively) in the spectrum of metal-free Pcs. The CN stretching band around 2200 cm^{-1} found in the starting materials was not found in the FT-IR spectra of any type of Pcs. This result shows that the Pc reactions and purification processes were successful (Figs. S7 and S8).

UV–*Vis* spectra of 1×10^{-5}M DCM, chloroform, toluene and DMSO of solutions of all Pc compounds were measured and the results are shown in (Fig. 1, Fig. 2 and Table 1). The CoPcs (**7**, **8**, **11** and **12**) showed single Q bands (except Pc **7** and Pc **11** in DCM) region between 610 and 740 nm, while the metal free Pcs (**5**, **6**, **9** and **10**) showed split Q bands region between 640 and 745 nm in all solvents. When the Q bands values of 2,4,6-trimethoxyphenoxy derivative Pc compounds (**6**, **8**, **10** and **12**) have been compared with that of 3,4,5-trimethoxyphenoxy derivatives (**5**, **7**, **9** and **11**), it has been observed 3 or 6 nm red-shifts in the UV–*Vis* spectra of Pc compounds (Figs. S9-S12 and Table 1). In 2,4,6-trimethoxyphenoxy substituted Pc which their positions are more suitable for electron transfer, outer substituents increase the electron density in the Pc ring. Therefore, the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) decreases and electronic transitions occur with lower energy. Thus, wavelength of electronic transitions more increases and Q bands of the Pcs have been observed in red region.

While UV–*Vis* measurements of Pc compounds were made with different solvents, the effects of concentration changes of Pcs on UV absorption bands were investigated. As a result, when the concentrations of the Pc solutions decreased, the absorbance values of the UV bands of the Pcs decreased proportionally in accordance with the Lambert Beer Law Equation.

UV–*Vis* graphs of the DCM solutions of Pcs at different concentrations are given as an example (Figs. S13-S14). It is known that chloroform and DCM solvents form HCl in their storage bottle over time. It is known that especially alpha-substituted ZnPc's and MgPc's sense this trace amount of acid and they give extra protonation band in solutions prepared with these solutions under the influence of acid [21–23]. In the UV–*Vis* spectrum of alpha-substituted Pcs (**5**–**8**) solutions prepared using DCM, an extra peak was observed on the right side of the splitting (or non-splitting for CoPcs) Q band and the absorbance value of this peak have increased as the concentration of DCM solution decreased (Fig. S15). This peak was thought to be caused by the trace amount of acid in DCM and it was observed that this peak disappeared when 1 drop (0.05 mL) of pyridine was added to the solution (Fig. S16). This situation, which was previously encountered only in alpha-substituted ZnPc and MgPc in the literature [23], was also seen for the first time in alpha-trimethoxyphenoxy substituted H2Pcs (**5** and **6**) and CoPcs (**7** and **8**) incidentally. For these Pc compounds, UV–*Vis* spectra in DCM solutions with different trifluoroacetic acid(TFA) concentrations were studied and their protonation behaviour was examined, and as an example, UV–*Vis* graphs of H2Pc(**6**) and CoPc(**8**) were showed in Figs. 3 and 4. The protonation study of alpha substituted Pc compounds showed that at 65 mM acid concentration, metal-free Pcs are protonated at most once, while CoPc are protonated twice. TFA concentrations of the Pc solutions have been studied as 65, 8, 1, 1.2×10^{-1}, 1.5×10^{-2}, 1.8×10^{-3} mM for H2Pcs and 65.0, 32.0, 16.0, 8.0, 2.0, 5×10^{-1}, 1.2×10^{-1}, 3.0×10^{-2}, 7.5×10^{-3} mM for CoPcs. The acid sensing susceptibility have been determined as 1.5×10^{-2}, 1.8×10^{-3}, 3.0×10^{-2} and 7.5×10^{-3} for H2Pc(**5**), H2Pc(**6**), CoPc(**7**) and CoPc(**8**), respectively. Thus, acid sensor device can be developed by using H2Pc(**6**), if desired (Figs. 3 and 4). In UV–*Vis* studies with DCM, it was observed that the absorbance of protonation peak was more intense in 2,4,6-trimethoxyphenoxy substituted Pcs than in 3,4,5-derivatives. As mentioned above, since the Pc rings are more electron-dense in the 2,4,6-trimethoxyphenoxy substituted derivatives Pcs, the protonation capabilities of the central nitrogen atoms of these species have increased.

While the molecular ion peaks $[M]^+$ for H2Pc (**6**), H2Pc (**10**), Co(II)Pc (**8**) and Co(II)Pc (**12**) were observed at 1243.28, 1243.09, 1300.13 and 1300.58 Da, protonated molecular ion peaks $[M+H]^+$ for H2Pc (**5**), H2Pc (**9**), Co(II)Pc (**7**) and Co(II)Pc (**11**) were observed at 1244.13, 1244.26, 1301.09 and 1301.92 Da, respectively, in the MALDI-TOF mass spectra of Pcs as measured by 2,5-dihydroxybenzoic acid matrix. These mass values matched with the theoretically calculated mass values for the molecular ions of all complexes (Figs. S17-S24).

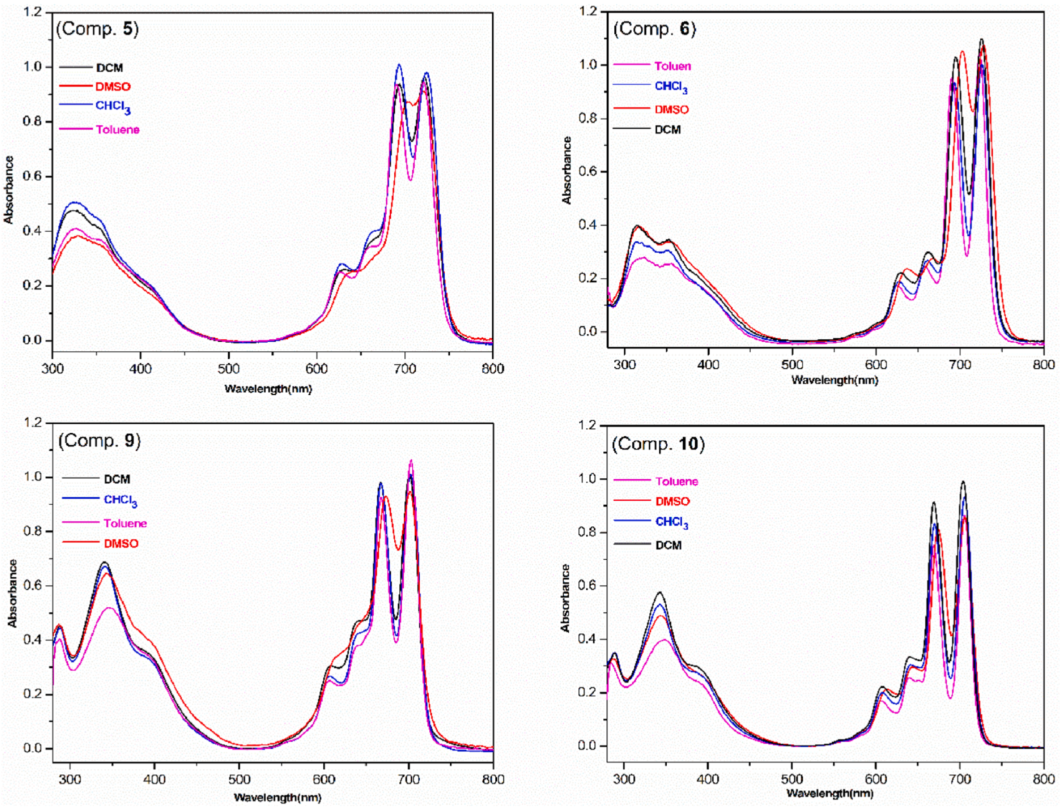


Fig. 1. UV–*Vis* spectra of 1 × 10^{-5}M solution of metal free Pcs (**5**, **6**, **9** and **10**) in DCM, chloroform, toluene and DMSO.

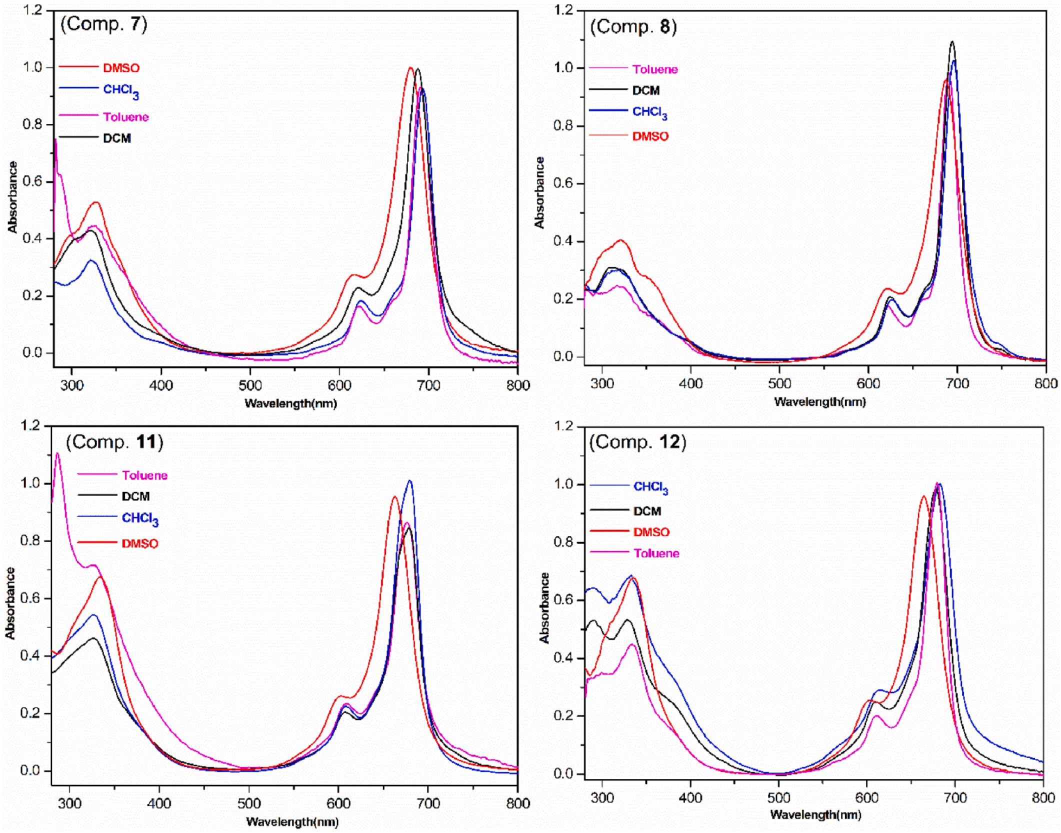


Fig. 2. UV–*Vis* spectra of 1 × 10^{-5}M solution of Co(II)Pcs (**7**, **8**, **11** and **12**) in DCM, chloroform, toluene and DMSO.

Table 1
Absorption spectral data for the Pc compounds in DCM (1 × 10^{-5} M).

Compound	Q band, λ_{max} (nm)	Log ε	B band, λ_{max} (nm)	Log ε
3,4,5-Alpha Substituted H2Pc(5)	721, 692	4.99, 4.98	323	4.73
2,4,6-Alpha Substituted H2Pc(6)	725, 695	5.06, 5.03	353	4.59
3,4,5-Beta Substituted H2Pc(9)	701, 667	4.99, 4.99	341	4.84
2,4,6-Beta Substituted H2Pc(10)	704, 667	4.99, 4.82	343	4.77
3,4,5-Alpha Substituted CoPc(7)	688	4.99	320	4.64
2,4,6-Alpha Substituted CoPc(8)	695	5.04	314	4.50
3,4,5-Beta Substituted CoPc(11)	674	5.00	325	4.74
2,4,6-Beta Substituted CoPc(12)	678	4.99	328	4.74

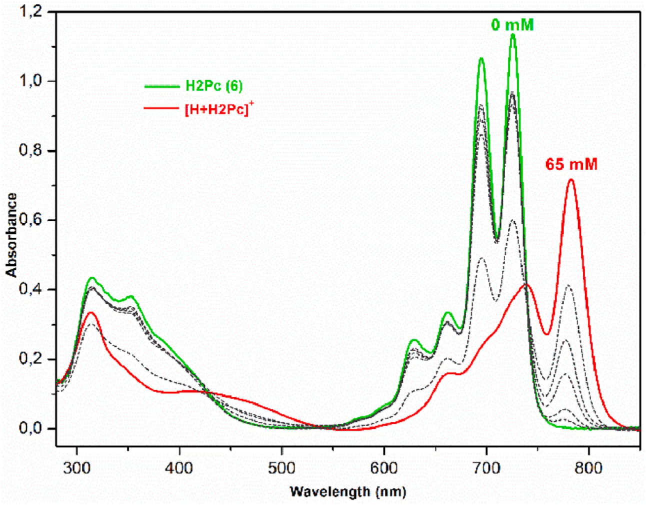


Fig. 3. UV–*Vis* Spectrums for 1(4),8(11),15(18),22(25)-tetrakis(2,4,6-trimethoxyphenoxy)phthalocyanine (**6**) in DCM with different TFA concentrations.

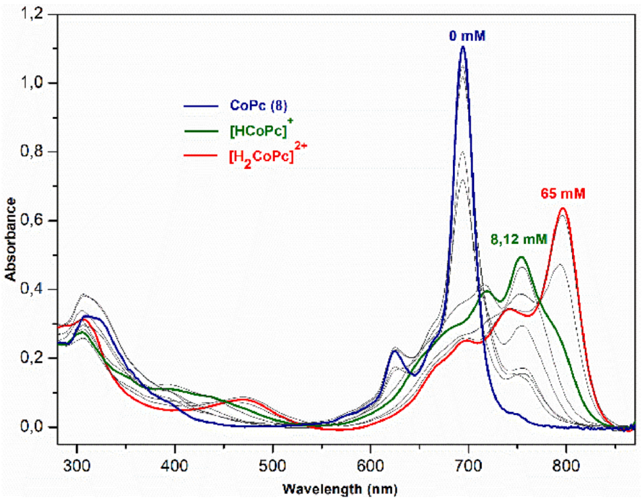


Fig. 4. UV–*Vis* Spectrums for 1(4),8(11),15(18),22(25)-tetrakis(2,4,6-trimethoxyphenoxy)phthalocyaninato cobalt(II) (**8**) in DCM with different TFA concentrations.

4. Conclusion

The novel isomeric trimethoxyphenoxy substituted H2Pcs and CoPcs were synthesized, purified and their spectral features were compared. The melting points of the starting compounds (**1**, **2**, **3** and **4**), which are used in the synthesis of phthalocyanines and are the isomers, the differences between the chemical shift values in the ^{1}H NMR spectrum and the wave numbers in the FT-IR spectrum were determined. The practical results were proof of theoretical knowledge. In particular, the UV–*Vis* spectra of the Pcs have been extensively studied to see how much effective the positions of the methoxy groups on the outer substituents of the Pc compounds with their value of the Q bands. It is described in all organic literature that the OCH_3 groups increase the electron density in the ortho and para positions of the benzene rings with the resonance effect and this electronic delocalization continues when the oxygen atom is attached to the sp^2 carbon atoms. This important knowledge has been practically proven in this study and this situation is important for choosing the peripheral and non-peripheral substituents and its position for Pc compounds applications.

In addition to, during detailed UV–*Vis* studies of Pcs, it was determined that alpha-substituted Pcs gave an extra peak by sensing trace amounts of acid in 1 × 10^{-5} M dichloromethane, in this study. The UV–*Vis* absorption of this peak was found to be inversely proportional to the concentration of the solution. Because, the amount of acid corresponding to each Pc molecule increases, protonation increases and the number of protonated species in the solution also increases when the solution has been diluted with acidic solvents. UV–*Vis* spectra in DCM solutions with different trifluoroacetic acid(TFA) concentrations for alpha substituted Pcs (**5**–**8**) were studied and their protonation behaviour was examined. It was determined that H2Pc(**6**) was sensitive to acid even at 1.8 × 10^{-3} mM concentration. Thus, acid sensor device can be developed by using this Pc molecule, if desired.

CRediT authorship contribution statement

Rüveyda Ağcaabat: Investigation, Validation, Resources. **Cansu Bilen Şentürk:** Investigation, Validation, Resources. **Zafer Odabaş:** Supervision, Visualization, Writing – original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2022.115929.

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