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Electrochemical properties of non-peripherally and peripherally tetra-[(1-benzylpiperidin-4-yl)oxy] substituted phthalocyanines

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Abstract

In this study, 1-benzylpiperidin-4-oxy substituted non-peripheral and peripheral metal free (**3, 7**), chloro manganese (III) (**4, 8**), oxotitanium (IV) (**5, 9**) and Cu(II) (**6, 10**) phthalocyanine complexes are synthesized and electrochemical properties were examined. Novel phthalocyanines compounds have been characterized by Fourier transform infrared, electronic spectroscopy, and mass spectra. Electrochemistry of non-peripherally and peripherally tetra-[(1-benzylpiperidine-4-yl)oxy] substituted metal-free and metallophthalocyanines were investigated by cyclic voltammetry (CV). Owing to the redox inactivity of the metal-free and Cu^{2+} ion of metal free (**3, 7**) and Cu(II) (**6, 10**) phthalocyanines, Phthalocyanine based reductions and oxidation processes are recorded. Unlike, electrochemical analyses showed that chloro manganese (III) (**4, 8**) and oxotitanium (IV) (**5, 9**) phthalocyanines illustrated metal based redox processes in addition to the Pc ring based reactions. The manganese (III) (**4, 8**) and the oxotitanium (IV) (**5, 9**) phthalocyanines extra metal based redox processes were observed with those of Pc rings.

Keywords: Titanium, manganese, electrochemistry, redox-active, piperidine

1. Introduction

Phthalocyanines (Pcs), which have been the subject of many studies for many years, are very important compounds for technological systems and are considered to be key compounds in solving many problems in the future. Phthalocyanine (Pc) compounds are widely used in the production of high-tech materials thanks to their optical, electrical and thermal properties and have attracted great attention in many fields such as; photovoltaic cells, thin film, liquid crystal, gas sensor, chemical sensor, corrosion inhibitor, optical data storage, semiconductors in recent years [1–8]. Pcs are used in many areas of technology due to their interesting electrochemical properties [9], and for this reason, electrochemical investigations play an important role in their industrial applications. Since phthalocyanines are compounds with electron exchange capacity and interesting electrochemical properties, a great deal of work has been done on their usability in various electrochemical applications [10]. The phthalocyanine ring is a redox active ring that can be oxidized by donating electrons at the HOMO (a1u) or reduced by taking electrons at the LUMO (eg). The ring-centered redox process of phthalocyanines results from the fact that reduction and oxidation reactions occur through the ring. In the alternating voltammograms of metal-free and metalated phthalocyanines, the characteristic reductions and oxidations of the ring-centered redox process are observed as redox peaks or pairs at certain potentials. By using working electrodes in electrochemical methods, it is possible to investigate the electrode reaction of many molecules and to elucidate their electrochemical behavior.

The electron transfer property of the phthalocyanine ring depends on both the type, position [11] and number of substituents and the interaction of the substituents with the phthalocyanine ring and the central metal ion [12–14]. For example, when metals or substituents are different, the HOMO-LUMO transition energies of Pc compounds can change significantly [15]. Electron donating ligands (such as amine, ether, thioether, methoxy groups) attached to the phthalocyanine ring increase the electron density of the center metal, facilitating oxidation and making reduction more difficult, while shifting the redox process to negative

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potentials. It has been reported in the literature that metallophthalocyanines containing especially redox active metals in the ring center such as Co(II), Mn(III) and, Ti(IV)O etc. at the ring center exhibit excellent electrocatalytic properties [16,17].

For compounds containing the piperidine ring system in their chemical structure, many pharmacological activities such as antibacterial, antifungal, anticancer, antioxidant, antiulcer, and renin inhibitor have been reported [18–24]. In addition, the electrochemical properties of many groups of compounds containing piperidine rings have been examined and it has been reported that they show very different electrochemical properties [25–27].

In this work, the synthesis of the metal-free, Mn(III), oxotitanium (IV) and, Cu(II) Pc complexes containing non-peripheral and peripheral position piperidine moiety were carried out. The electrochemical properties of the new compounds were comparatively examined according to the bonding the position of the substituent to the Pc ring and changing central metal atom.

2. Experimantal

2.1. Materials and methods

The materials and equipment used in this study were set out in the supplementary information to the article.

2.2. Synthesis

2.2.1. *1(4), 8(11), 15(18), 22 (23) – Tekrakis - [1-benzylpiperidin -4-yl) oxy] phthalocyanine (**3**)*

3-[(1-benzylpiperidin-4-yl)oxy]phthalonitrile (**1**) (0.20 g, 0.63 mmol) was dissolved in 2 mL dry n-pentanol and three drops of 1,8-diazabicyclo[5.4.0]undec-7-ene was added to the reaction medium. The reaction mixture was stirred at 160 °C for 24 hours. After the mixture cooled to room temperature, n-hexane was added (20 mL) and the precipitate was filtered. The obtained green product was purified by column chromatography using chloroform-methanol (10:2) solvent system.

Yield: 22 mg (11 %), M.p.: >300 °C (decomposition). FT-IR ν_{max}/cm^{-1}: 3028 (Ar-H), 2922-2809 (Aliph. C-H), 1724, 1584, 1491, 1454, 1267, 1104, 1040, 1028, 975, 797, 743, 697. MALDI-TOF, *m/z*: Calc.: 1271,55 for $C_{80}H_{78}N_{12}O_4$, Found: 1271,05 [M]$^+$. UV/vis (Chloroform, 1x10^{-5} M): λ, nm (log ε): 316 (4.85), 352 (4.72), 629 (4.48), 662 (4.61), 697 (5.05), 727 (5.10).

2.2.2. *1(4), 8(11), 15(18), 22 (23) – Tekrakis - [1-benzylpiperidin -4-yl) oxy] phthalocyaninato chloro manganese (III) (**4**)*

3-[(1-benzylpiperidin-4-yl)oxy]phthalonitrile (**1**) (0.20 g, 0.63 mmol) was dissolved in 2 mL dry n-pentanol, than anhydrous $MnCl_2$ (0.1 g, 0.32 mmol) and three drops of 1,8-diazabicyclo[5.4.0]undec-7-ene were added to the reaction medium. The reaction mixture was stirred at 160 °C for 24 hours. After the mixture cooled to room temperature, n-hexane was added (20 mL) and the precipitate was filtered. The obtained green product was purified by column chromatography using chloroform-methanol (10:3) solvent system.

Yield: 36 mg (17%), M.p.: >300 °C (decomposition). FT-IR ν_{max}/cm^{-1}: 3023 (Ar-H), 2924-2803 (Aliph. C-H),1586, 1486, 1323, 1228, 1118, 1040, 797, 739, 696. MALDI-TOF, *m/z*: Calc.: 1359,95 for $C_{80}H_{76}N_{12}O_4MnCl$, Found: 1324,09 [M-Cl]$^+$. UV/vis (Chloroform, 1x10^{-5} M): λ, nm (log ε): 331(4.72), 358 (4.85), 543 (4.38), 687 (4.46), 765 (5.13).

2.2.3. *1(4), 8(11), 15(18), 22 (23) – Tekrakis - [1-benzylpiperidin -4-yl) oxy] phthalocyaninato oxotitanium (IV) (**5**)*

3-[(1-benzylpiperidin-4-yl)oxy]phthalonitrile (**1**) (0.20 g, 0.63 mmol) was dissolved in 2 mL dry n-pentanol, than anhydrous $Ti(OBu)_4$ (0.22 mL, 0.63 mmol) and three drops of 1,8-diazabicyclo[5.4.0]undec-7-ene were added to the reaction medium. The reaction mixture was stirred at 160 °C for 24 hours. After the mixture cooled to room temperature, petroleum ether was added (20 mL) and the precipitate was filtered. The obtained green product was purified by column chromatography using chloroform-methanol (10:1) solvent system.

Yield: 29 mg (14 %), M.p.: >300 °C (decomposition). FT-IR ν_{max}/cm^{-1}: 3066-3028 (Ar-H), 2953-2852 (Aliph. C-H), 1724, 1584, 1488, 1455, 1267, 1081, 1040, 852, 745, 697. MALDI-TOF, *m/z*: Calc.: 1333.44 for $C_{80}H_{76}N_{12}O_5Ti$, Found: 1273,93 [M-TiO+2]$^+$. UV/vis (Chloroform, 1x10^{-5} M): λ, nm (log ε): 321 (4.95), 355 (4.87), 661 (4.71), 694 (5.03), 728 (5.21).

2.2.4. *1(4), 8(11), 15(18), 22 (23) – Tekrakis - [1-benzylpiperidin -4-yl) oxy] phthalocyaninato copper (II) (**6**)*

3-[(1-benzylpiperidin-4-yl)oxy]phthalonitrile (**1**) (0.20 g, 0.63 mmol) was dissolved in 2 mL dry n-pentanol, than anhydrous $CuCl_2$ (0.04 g, 0.32 mmol) and three drops of 1,8-diazabicyclo[5.4.0]undec-7-ene were added to the reaction medium. The reaction mixture was stirred at 160 °C for 24 hours. After the mixture cooled to room temperature, ethyl alcohol was added (20 mL) and the precipitate was filtered. The obtained blue-green product was purified by column chromatography using chloroform-methanol (10:2) solvent system.

Yield: 44 mg (21 %), M.p.: >300 °C (decomposition). FT-IR ν_{max}/cm^{-1}: 3063-3028 (Ar-H), 2954-2851 (Aliph. C-H), 1727, 1589, 1455, 1458, 1236, 1191, 1080, 853, 747, 696. MALDI-TOF, *m/z*: Calc.: 1333,10 for $C_{80}H_{76}N_{12}O_4Cu$, Found: 1333,90 [M]$^+$. UV/vis (Chloroform, 1x10^{-5} M): λ, nm (log ε): 313 (4.75), 344 (4.74), 634 (4.60), 706 (5.23).

2.2.5. *2(3), 9(10), 16(17), 23(24)- Tetrakis- [1-benzylpiperidin-4-yl) oxy] phthalocyanine (**7**)*

To synthesize compound **7**, the synthetic procedure of compound **3** was followed except that **2** was used instead of **1**. The amounts of the reagents were: 4-[(1-benzylpiperidin-4-yl)oxy]phthalonitrile (**2**) (0.20 g, 0.63 mmol). Solvent system for column chromatography; chloroform/methanol (10:2).

Yield: 23 mg (23%), M.p.: >300 °C (decomposition). FT-IR ν_{max}/cm^{-1}: 3065-3028 (Ar-H), 2927-280 (Aliph. C-H), 1607, 1470, 1338, 1232, 1093, 1042, 1007, 733, 696. MALDI-TOF, *m/z*: Calc.: 1271,55 for $C_{80}H_{78}N_{12}O_4$, Found: 1271,18 $[M]^+$. UV/vis (Chloroform, 1x10^{-5} M): λ, nm (log ε): 342 (4.80), 393 (4.50), 609 (4.39), 642 (4.55); 669 (4.91), 706 (4.97).

2.2.6. *2(3), 9(10), 16(17), 23(24)- Tetrakis- [1-benzylpiperidin-4-yl) oxy] phthalocyaninato chloro manganese (III) (**8**)*

To synthesize compound **8**, the synthetic procedure of compound **4** was followed except that **2** was used instead of **1**. The amounts of the reagents were: 4-[(1-benzylpiperidin-4-yl)oxy]phthalonitrile (**2**) (0.20 g, 0.63 mmol), anhydrous $MnCl_2$ (0.1 g, 0.32 mmol). Solvent system for column chromatography; chloroform/methanol (10:3).

Yield: 72 mg (34 %), M.p.: >300 °C (decomposition). FT-IR ν_{max}/cm^{-1}: 3065-3023 (Ar-H), 2926-2806 (Aliph. C-H), 1603, 1463, 1404, 1333, 1230, 1052, 1036, 743, 697. MALDI-TOF, *m/z*: Calc.: 1359,95 for $C_{80}H_{76}N_{12}O_4MnCl$, Found: 1324,02 $[M\text{-}Cl]^+$. UV/vis (Chloroform, 1x10^{-5} M): λ, nm (log ε): 388 (4.75), 530 (4.33), 661 (4.43), 736 (5.04).

2.2.7. *2(3), 9(10), 16(17), 23(24)- Tetrakis- [1-benzylpiperidin-4-yl) oxy] phthalocyaninato oxotitanium (IV) (**9**)*

To synthesize compound **9**, the synthetic procedure of compound **5** was followed except that **2** was used instead of **1**. The amounts of the reagents were: 4-[(1-benzylpiperidin-4-yl)oxy]phthalonitrile (**2**) (0.20 g, 0.63 mmol), $Ti(OBu)_4$ (0.22 mL, 0.63 mmol). Solvent system for column chromatography; chloroform/methanol (10:1).

Yield: 40 mg (19 %), M.p.: >300 °C (decomposition). FT-IR ν_{max}/cm^{-1}: 3066-3028 (Ar-H), 2953-2852 (Aliph. C-H), 1724, 1584, 1488, 1455, 1267, 1081, 1040, 852, 745, 697. MALDI-TOF, *m/z*: Calc.: 1333.44 for $C_{80}H_{76}N_{12}O_5Ti$, Found: 1333,90 $[M]^+$, 1273,63 $[M\text{-}TiO+2]^+$. UV/vis (Chloroform, 1x10^{-5} M): λ, nm (log ε): 346 (4.96), 397 (4.68), 637 (4.70), 669 (4.95), 705 (5.27).

2.2.8. *2(3), 9(10), 16(17), 23(24)- Tetrakis- [1-benzylpiperidin-4-yl) oxy] phthalocyaninato copper (II) (**10**)*

To synthesize compound **10**, the synthetic procedure of compound **6** was followed except that **2** was used instead of **1**. The amounts of the reagents were: 4-[(1-benzylpiperidin-4-yl)oxy]phthalonitrile (**2**) (0.20 g, 0.63 mmol), anhydrous $CuCl_2$ (0.04 g, 0.32 mmol). Solvent system for column chromatography; chloroform/methanol (10:2).

Yield: 71 mg (34%), M.p.: >300 °C (decomposition). FT-IR ν_{max}/cm^{-1}: 3061-3030 (Ar-H), 2921-2851 (Aliph. C-H C-H), 1607, 1467, 1399, 1341, 1230, 1116, 1093, 1043, 852, 744, 697. MALDI-TOF, *m/z*: Calc.: 1333,10 for $C_{80}H_{76}N_{12}O_4Cu$, Found: 1333,78 $[M]^+$. UV/vis (Chloroform, 1x10^{-5} M): λ, nm (log ε): 338 (4.97), 383 (4.41), 615 (4.72), 682 (5.24).

3. Results and discussion

3.1. Synthesis and characterization

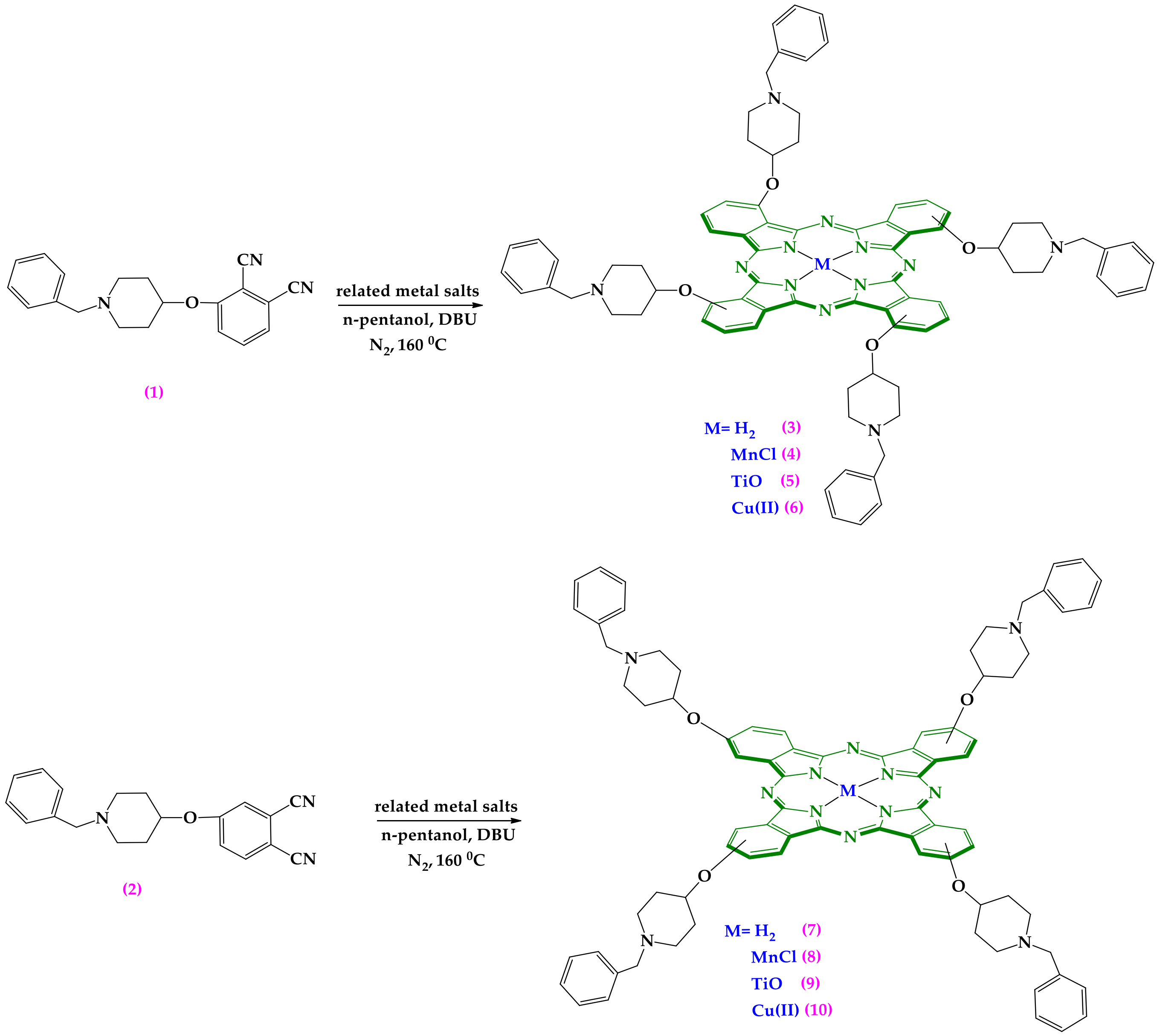
The phthalonitrile **1** [28] and **2** [29] were synthesized according to the procedures in a previously published paper. The synthesis method of Pc compounds is shown in detail in Scheme 1.

Structural characterization of the novel synthesized compounds was performed using FT-IR, UV-Vis, MALDI-TOF mass spectroscopic techniques.

Non-peripheral and peripheral metal-free (**3, 7**), MnPc (**4**, **8**), TiPc (**5**, **9**) and CuPc (**6**, **10**) Pc compounds were accomplished by treatment of phthalonitrile **1** and **2** in the presence of the corresponding anhydrous metal salts; without metal, anhydrous $MnCl_2$, $Ti(OBu)_4$ and $CuCl_2$. The reaction yields obtained for these compounds at 160 °C in dried *n*-pentanol are 11% for **3**, 17% for **4**, 29% for **5**, 21% for **6**, 23% for **7**, 34% for **8**, 19% for **9** and 21% for **10**, respectively. All synthesized Pc compounds were purified using column chromatography.

In the FT-IR spectra of non-peripheral (**3–6**) and peripheral (**7–10**) Pc compounds**,** the disappearance of -C≡N peak showed at 2233 cm^{-1} and 2230 of compounds **1** and **2** is an indication that cyclotetramerisation of phthalonitriles have occurred. The NMR spectra of **4**, **6**, **8** and **10** could not be determined because of the presence of paramagnetic manganese and copper atoms [30]. The spectra of the other's synthesized Pcs were not determined because of probable aggregation at the concentration for NMR measurements.

Mass spectra of Pc compounds (**3–10**) supported their proposed structures the appearance of molecular ion peaks at at 1271,05 as $[M]^+$ for **3** (**Fig. S1**), 1324,09 as $[M\text{-}Cl]^+$ for **4** (**Fig. S2**), as 1273,93 $[M\text{-}TiO+2]^+$ for **5** (**Fig. S3**), 1333,90 as $[M]^+$ for **6** (**Fig. 1**), 1271,18 as $[M]^+$ for **7** (**Fig. 2**), 1324,09 as $[M\text{-}Cl]^+$ for **8** (**Fig. S4**), 1333,90 as $[M]^+$, 1273,63 $[M\text{-}TiO+2]^+$ for **9** (**Fig. 3**) and 1333,78 as $[M]^+$ for **10** (**Fig. S5**).



Scheme 1. Synthesis of new phthalocyanines **3–10** (related metal salts; anhydrous $MnCl_2$, $Ti(OBu)_4$, $CuCl_2$)

3.2. UV-vis absorption spectra

UV-Vis spectroscopy is known to be one of the best methods to characterize Pc complexes. Two characteristic peaks called Q and B bands are observed in the UV spectra of Pc s [29]. In the UV region, the Q band generally appears at around 600–750 nm while the B band arises at about 300–450 nm. Absorption of the Q-band of the Pc compounds in the UV-vis spectrum is affected to a different degree by the central metal, ligand-bound in the axial position, solvent, binding position of the substituent and, aggregation [31].

The UV-vis spectra of the metal-free Pc complexes **3** and **7** showed intense double Q band absorption at λ_{max}: 727, 697 nm for **3** and 706, 669 nm for **7**, as expected (**Fig. 4**). The B band signals of these compounds are at λ_{max}: 352, 316 nm for **3** and 393, 342 nm for **7.** Metallophthalocyanine complexes **4–6** and **8–10** exhibited intense Q band caused by π-π* transitions at λ_{max}: 765 (with single shoulders 687) nm for **4** (**Fig. 5**), 728 (with double shoulders 661 and 622) nm for **5** (**Fig. 6**), 706 (with single shoulders 634) nm for **6** (**Fig. 7**), 736 (with single shoulders 661) nm for **8** (**Fig. 5**), 705 (with double shoulders 669 and 606) nm for **9** (**Fig. 6**) and 682 (with single shoulders 661) nm for **10** (**Fig. 7**).

The B bands of these Pc were observed in the UV region at λ_{max}: 352, 316 nm for **3**; 358 and 331 nm for **4**; 355, 321 nm for **5**; 344, 313 nm for **6;** 393, 342 nm for **7**, 388 nm for **8**; 397, 346 nm for **9** and 383, 338 nm for **10.**

When a comparison is made between these data obtained, the Q bands of the non-peripheral Pcs **3–6** are red shifted 11, 21, 23 and, 24 nm according to the corresponding peripheral substituted Pcs **7–10** respectively in chloroform. It is a well-known fact that the substitution of the Pcs at non-peripheral positions causes a significant degree red shifted of the Q band [32, 33].

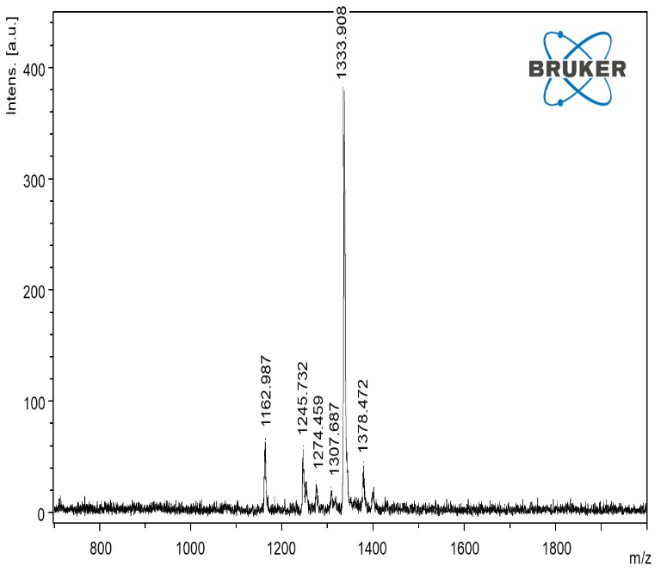


Figure 1. Mass spectrum of compound **6**

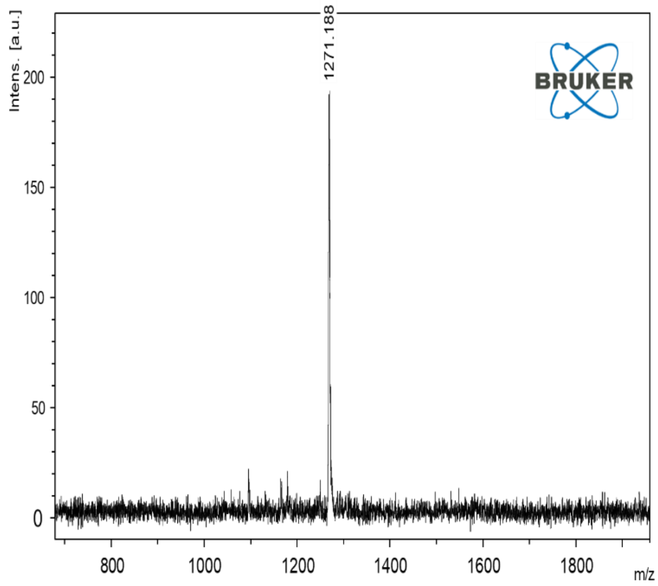


Figure 2. Mass spectrum of compound **7**

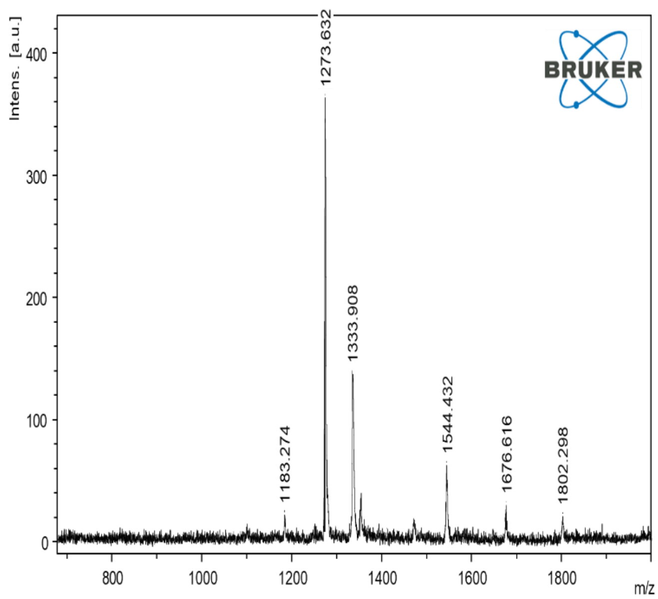


Figure 3. Mass spectrum of compound **9**

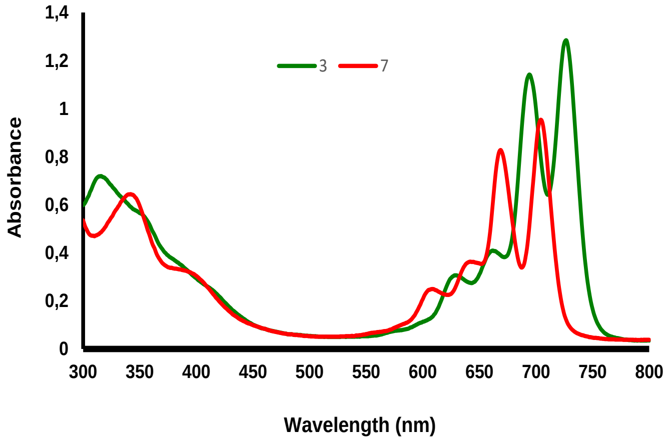


Figure 4. Absorption spectra of compounds **3** and **7** in chloroform at 1.10-5M

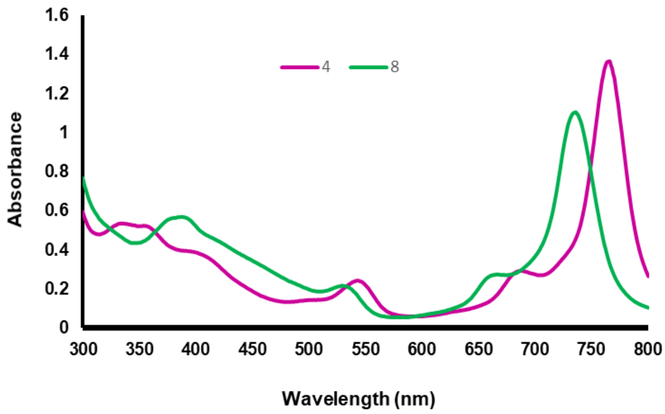


Figure 5. Absorption spectra of compounds **4** and **8** in chloroform at 1.10-5M

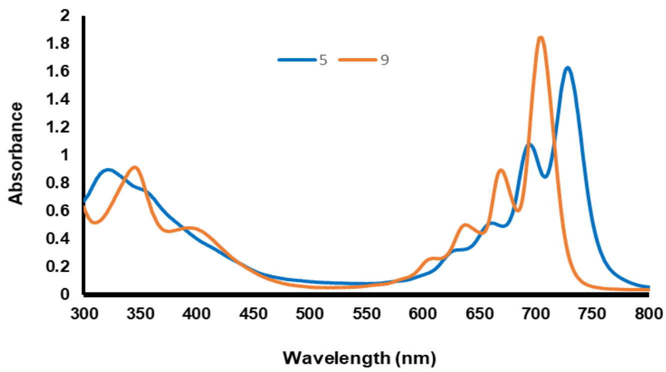


Figure 6. Absorption spectra of compounds **5** and **9** in chloroform at 1.10-5M

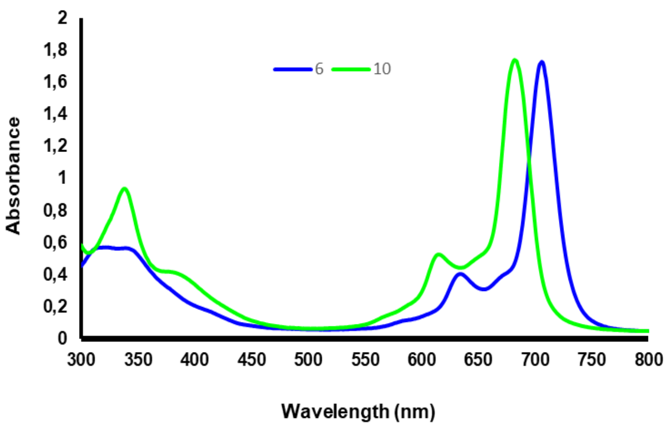


Figure 7. Absorption spectra of compounds **6** and **10** in chloroform at 1.10-5M

The manganese Pc complexes, unlike other Pc complexes, exhibit remarkable absorption properties in the UV-Vis spectrum. Although it is known in the literature that the main absorption Q bands of MnPc shift to red in the range of 710–890 nm [34]. We could see this shift of Q band in the UV spectrum of the **4** and **8** (at λ_{max}: 765 and 736 nm, respectively) synthesized compounds (**Fig. 5**).

Additionally, the characteristic broad peak of the manganese Pcs between 470 nm and 570 nm appears in the region by the charge-transfer (CT) exciton owing to the existence of unsaturated manganese ions as a metal atom [35–37]. CT bands of the compounds 4 and 8 were observed as a broad peak at λ_{max}: 543 and 530 nm, respectively.

3.3. Electrochemical studies

Electrochemical responses of non-peripherally and peripherally tetra-[(1-benzylpiperidine-4-yl)oxy] substituted metallophthalocyanines **3–10** were investigated using cyclic voltammetry (CV) in DCM/TBAP electrolyte at room temperature. The peak potential separation (ΔE_p), half-wave potential ($E_{1/2}$) and the potential difference between the first half-peak processes ($\Delta E_{1/2}$), are listed in **Table 1**.

Table 1. Voltammetric analysis results of the phthalocyanines.

Phthalocyanines	Label	$^{a}E_{1/2}$	$^{b}\Delta E_p$ (mV)	$^{c}\Delta E_{1/2}$
Metal-free 3	R_1	-0.85	154	1.73
	R_2	-1.24	162	
	O_1	0.88	158	
Metal-free 7	R_1	-0.82	83	1.75
	R_2	-1.13	85	
	O_1	0.93	166	
MnPc 4	R_1	-0.18	142	1.04
	R_2	-1.05	154	
	R_3	-1.59	166	
	O_1	0.86	150	
MnPc 8	R_1	-0.22	80	1.14
	R_2	-1.00	147	
	R_3	-1.54	160	
	O_1	0.92	171	
TiOPc 5	R_1	-0.59	140	1.40
	R_2	-0.80	145	
	R_3	-1.00	154	
	R_4	-1.20	148	
	O_1	0.81	161	
TiOPc 9	R_1	-0.77	160	1.62
	R_2	-1.07	161	
	R_3	-1.41	167	
	O_1	0.85	150	
CuPc 6	R_1	-0.96	159	1.83
	R_2	-1.43	172	
	O_1	0.87	161	
CuPc 10	R_1	-0.93	87	1.94
	R_2	-1.26	82	
	O_1	1.01	164	

a: $E_{1/2}$ values ((E_{pa}+E_{pc})/2) were given versus SCE at 0.100 Vs^{-1} scan rate. b: ΔE_p= E_{pa}-E_{pc}. c: $\Delta E_{1/2}$ = $E_{1/2}$ (first oxidation)-$E_{1/2}$ (first reduction)

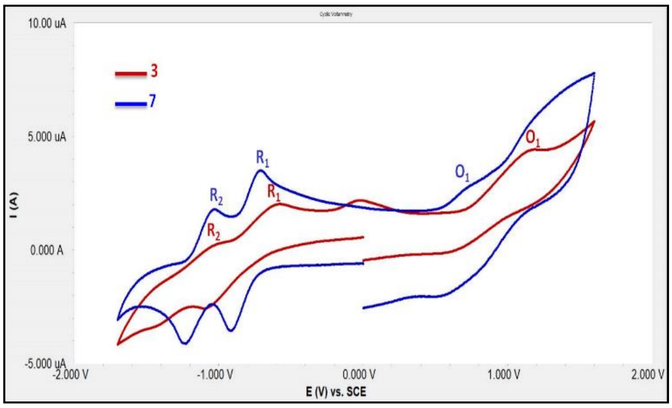


Figure 8. Cyclic voltamogram of metal-free phthalocyanines **3** and **7**

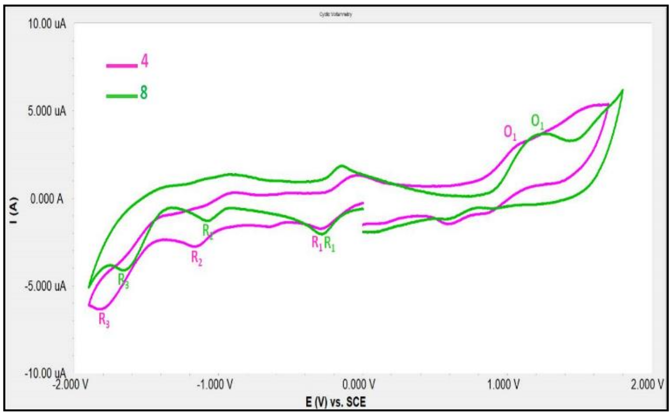


Figure 9. Cyclic voltamogram of manganese(III) phthalocyanines **4** and **8**

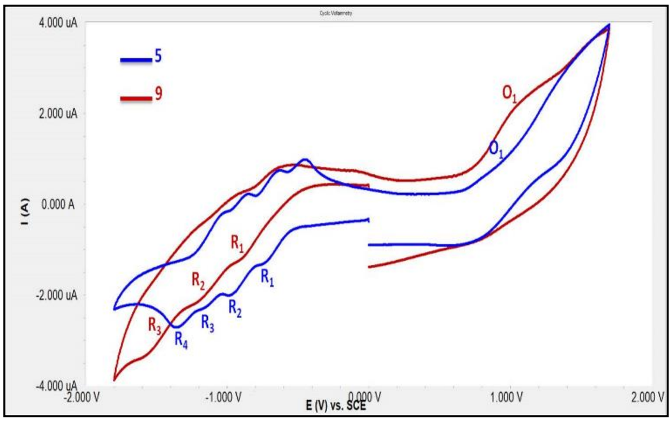


Figure 10. Cyclic voltamogram of titanium(IV) phthalocyanines **5** and **9**

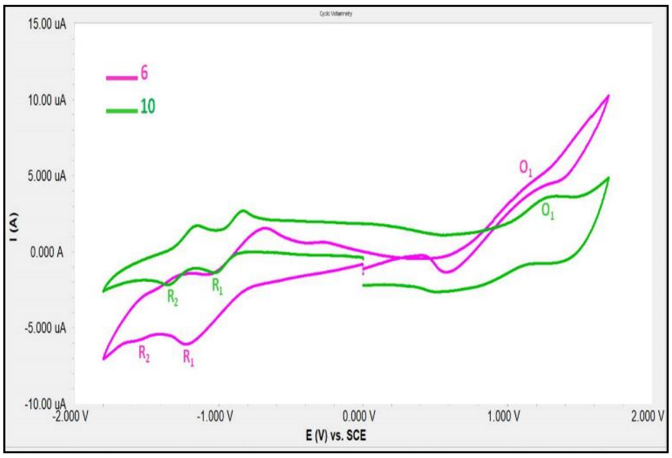


Figure 11. Cyclic voltamogram of copper(II) phthalocyanines **6** and **10**

Fig. 8 shows CV of non-peripherally and peripherally tetra-[(1-benzylpiperidine-4-yl)oxy] substituted metal-free Pcs compounds **3** and **7** in DCM/TBAP electrolyte on a Pt working electrode. When Fig. 8 was examined, it was determined that metal-free Pcs (**3, 7**) gave two Pc ring-based reduction peaks in the cathodic region. The half-wave peak potentials of the reduction peaks, expressed as R_1 and R_2, are $E_{1/2}$: -0.85 V (R_1), -1.24 V (R_2) for the compound **3** and $E_{1/2}$: -0.82 V (R_1), -1.13 v (R_2) for the compound **7.** Based on the calculated ΔE_P values, it was determined that all of the reduction peaks denoted as R1 and R_2 for metal-free Pcs (**3, 7**) were quasi-reversible character. During the potential scanning in the anodic region, the half-wave peak potentials of the oxidation peaks symbolized by O_1 for metal-free Pcs (**3, 7**) were calculated as $E_{1/2}$ = 0.88 V for **3** and $E_{1/2}$ = 0.93 V for **7**. Based on the ΔE_P values of the oxidation peaks symbolized by O_1, it has been revealed that both of them have quasi-reversible character.

Fig. 9 shows CV of non-peripherally and peripherally tetra-[(1-benzylpiperidine-4-yl)oxy] substituted manganese(III) Pcs (**4** and **8**) in DCM/TBAP electrolyte on a Pt working electrode. Since manganese(III) and titanium(IV) Pcs have redox active metal ions, they show both ring and metal-based reduction processes [38–40]. During cathodic potential screening of MnPcs (**4, 8**), it was determined that they gave two metal-centered reduction processes, R_1= -0.18 V, R_2= -1.05 V for **4** and R_1= -0.22 V, R_2= -1.00 V for **8**, respectively. Again, during the cathodic potential scan, it was determined that they gave Pc ring-centered reduction processes, with R_3= -1.59 V for **4** and R_3= -1.54 V for **8**, respectively. In addition, it has been observed that the reduction peaks indicated by R_1, R_2 and R_3 for manganese(III) Pcs **4** and **8** have quasi-reversible character according to the calculated ΔE_P values. During the potential scan in the anodic region, the half-wave peak potentials of the oxidation peaks symbolized by O_1 for MnPcs (**4, 8**) were calculated as $E_{1/2}$= 0.86 V for **4** and $E_{1/2}$= 0.92 V for **8**. Based on the ΔE_P values of the oxidation peaks, it was determined that both of them were quasi-reversible.

Fig. 10 shows CV of non-peripherally and peripherally tetra-[(1-benzylpiperidine-4-yl)oxy] substituted titanium(IV) Pcs (**5** and **9**) in DCM/TBAP electrolyte on a Pt working electrode. As shown in **Fig. 10**, non-peripheral substituted oxotitanium(IV) Pc compound **5** has 4 reduction peaks in the cathodic region (R_1= -0.59 V, R_2= -0.80 V, R_3= -1.00 V, R_4= -1.20 V) and 1 oxidation peak in the anodic region (O_1= 0.81 V). Also, peripheral substituted oxotitanium(IV) Pc compound **9** has 3 reduction peaks (R_1= -0.77 V, R_2= -1.07 V, R_3= -1.41 V) in the cathodic region and 1 oxidation peak (O_1= 0.85 V) in the anodic region. During the cathodic potential screening of compound **5**, two metal-centered reduction processes (R_1= -0.59 V and R_3= -1.00 V), two Pc ring-based reduction processes (R_2= -0.80 V and R_4= -1.20 V) were observed. During the cathodic potential scanning of compound **9** showed one metal-centered reduction process (R_2 = -1.07 V) and two Pc ring-based reduction processes (R_1 = -0.77 V and R_3= -1.41 V).

Fig. 11 shows CV of non-peripherally and peripherally tetra-[(1-benzylpiperidine-4-yl)oxy] substituted copper (II) Pcs **6** and **10** in DCM. As shown in Fig. 11, **CuPcs** (**6** and **10**) gave 2 Pc ring-based reduction peaks in the cathodic region. The reduction peaks symbolized as R_1 and R_2, respectively, are $E_{1/2}$: -0.96 V (R_1), -1.43 V (R_2) for compound **6** and $E_{1/2}$: -0.93 V (R_1), - 1.26 V (R_2) for compound **10**. Based on the calculated ΔE_P values of the reduction peaks expressed as R_1 and R_2 for **CuPcs** (**6, 10**), it was determined that they were semi-reversible for non-peripheral substituted copper (II) Pc **6** and reversible for peripheral substituted copper (II) Pc **10**. During the potential scanning in the anodic region, the half-wave peak potentials of the oxidation peaks symbolized by O_1 for **CuPcs** (**6, 10**) were calculated as $E_{1/2}$= 0.87 V for **6** and $E_{1/2}$ = 1.01 V for **10**. Based on the ΔE_P values of the oxidation peaks symbolized by O_1, it was determined that both of them were semi-reversible.

Additionally, $\Delta E_{1/2}$ values, which determine the HOMO-LUMO energy levels, were calculated for the synthesized metal free Pcs (**3, 7**), manganese (III) Pcs (**4, 8**), oxotitanium(IV) Pcs (**5, 9**) and copper (II) Pcs (**6, 10**). The HOMO-LUMO energy level was calculated as $\Delta E_{1/2}$ = 1.73 V, $\Delta E_{1/2}$= 1.75 V for metal free Pcs (**3, 7**); $\Delta E_{1/2}$ = 1.04 V, $\Delta E_{1/2}$= 1.14 V for MnPcs (**4, 8**); $\Delta E_{1/2}$ = 1.40 V, $\Delta E_{1/2}$ = 1.62 V for TiPcs (**5, 9**); and $\Delta E_{1/2}$ = 1.83 V, $\Delta E_{1/2}$ = 1.94 V for CuPcs (**6, 10**).

4. Conclusion

In this paper, non-peripherally and peripherally tetra-[(1-benzylpiperidine-4-yl)oxy] substituted metal-free **(3, 7),** manganese (III) **(4, 8),** oxotitanium (IV) **(5, 9)** and copper (II) **(6, 10)** phthalocyanine compounds were presented. Characterization of these newly synthesized compounds was carried out using spectroscopic methods such as FT-IR, mass spectroscopy, UV/vis and, MALDI-TOF. Among the new compounds, especially the manganese (III) Pc compounds **(4 and 8)** showed a significant, red-shifted absorption of the Q-band in the UV region that this desired for the application of Pc compounds.

Electrochemical studies of non-peripherally and peripherally tetra-[(1-benzylpiperidine-4-yl)oxy] substituted metal-free (**3, 7**), manganese (III) (**4, 8**), oxotitanium (IV) (**5, 9**) and copper (II) (**6, 10**) Pc compounds were defined with voltammetric analysis.

According to the results, metal-free Pcs (**3**, **7**), and copper (II) Pcs (**6**, **10**) showed common Pc assigned electron transfer reactions. On the other hand, owing to the redox activity of Mn^{III} and Ti^{IV} metal centers of manganese (**4**, **8**), oxotitanium Pcs (**5**, **9**) compounds extra metal based redox processes were observed with those of Pc rings. Additionally, manganese (III) (**4**, **8**), oxotitanium (IV) Pcs **(5, 9)** compounds with rich redox activity are important for electrochemical applications.

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Supplementary Informations

1. Experimental

1.1. Materials and Methods

All reagents and solvents used were dried and purified as described in Perrin and Armarego. [1]. 1-benyzlpiperidin-4-ol were purchased from commercial supplier. 3-nitrophthalonitrile [2], 4-nitro phthalonitrile [3], compound **1** [4] and compound **2** [5] were synthesized according to the procedures.

All electrochemical measurements were carried out with Gamry Interface 1000 potentiostat/galvanostat utilizing a three-electrode configuration at 25 °C. The working electrode was a Pt disc with a surface area of 0.071 cm^2. A Pt wire was served as the counter electrode and saturated calomel electrode (SCE) was employed as the reference electrode and separated from the bulk of the solution by a double bridge. Electrochemical grade tetrabuthylammonium perchlorate (TBAP) in extra pure dichloromethane (DCM) was employed as the supporting electrolyte at a concentration of 0.10 mol/dm.

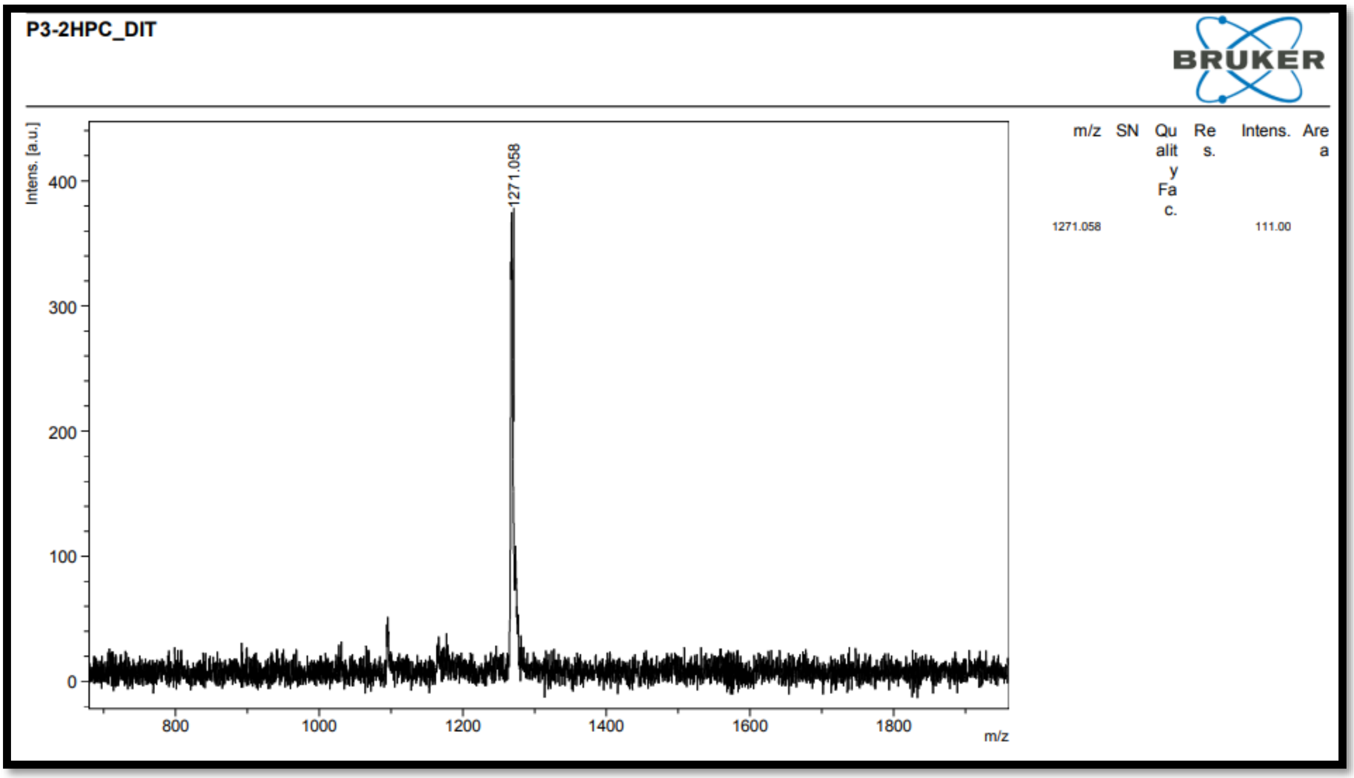

Figure S1. Mass spectrum of compound **3**

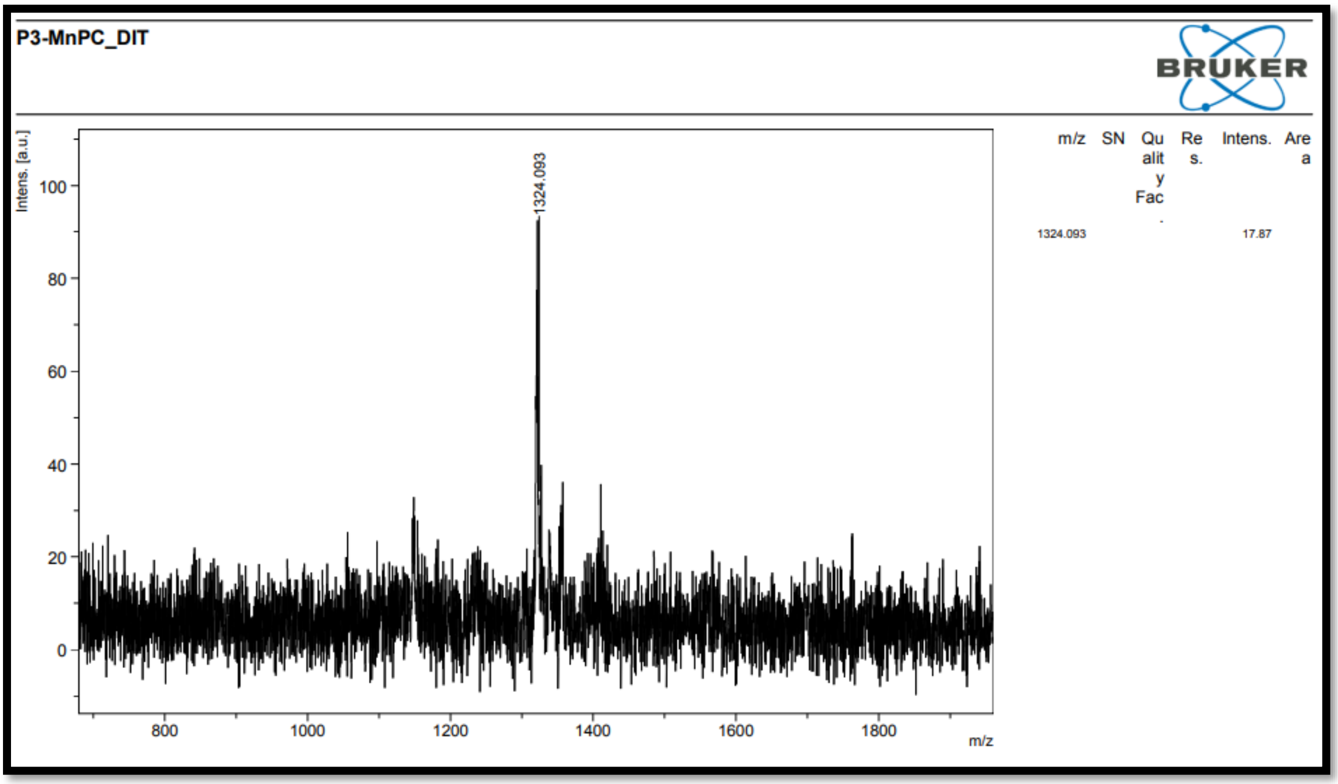

Figure S2. Mass spectrum of compound **4**

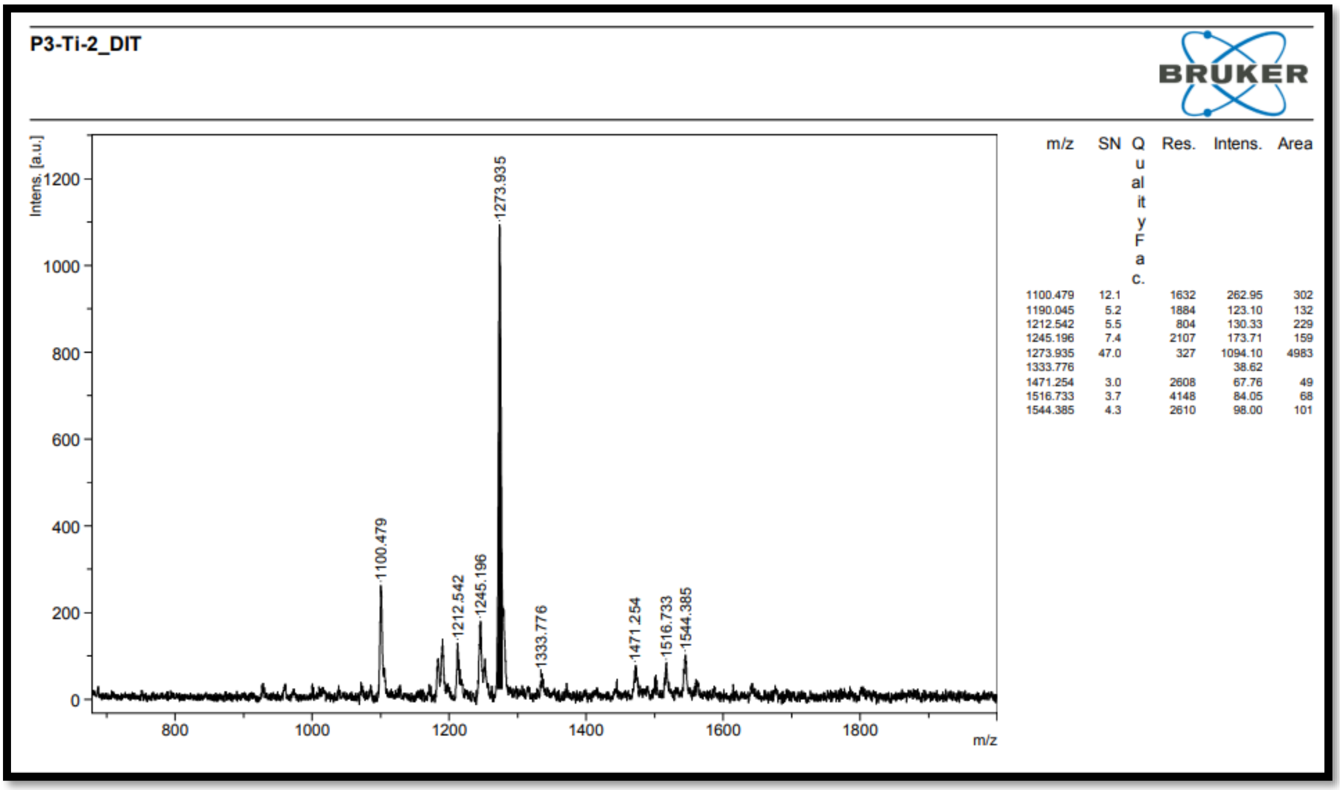

Figure S3. Mass spectrum of compound **5**

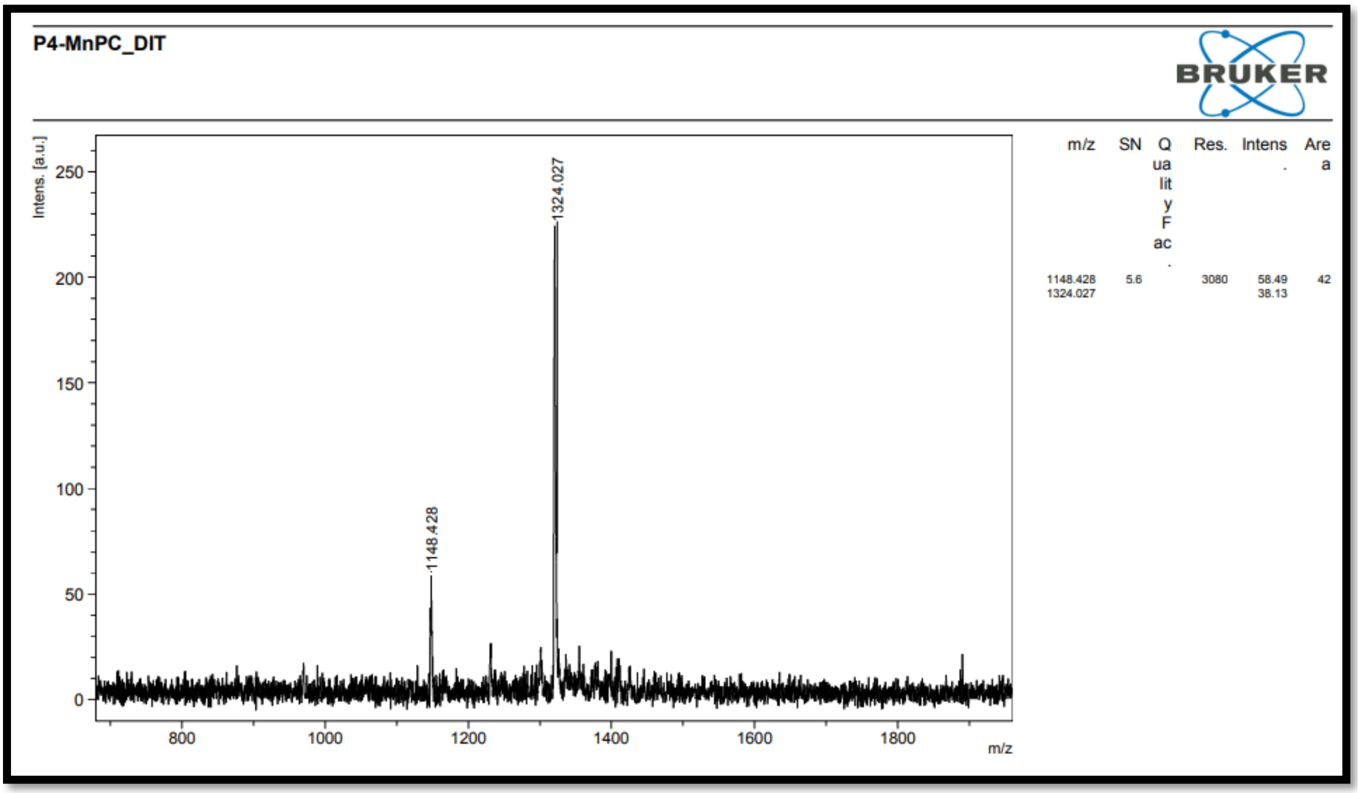

Figure S4. Mass spectrum of compound **8**

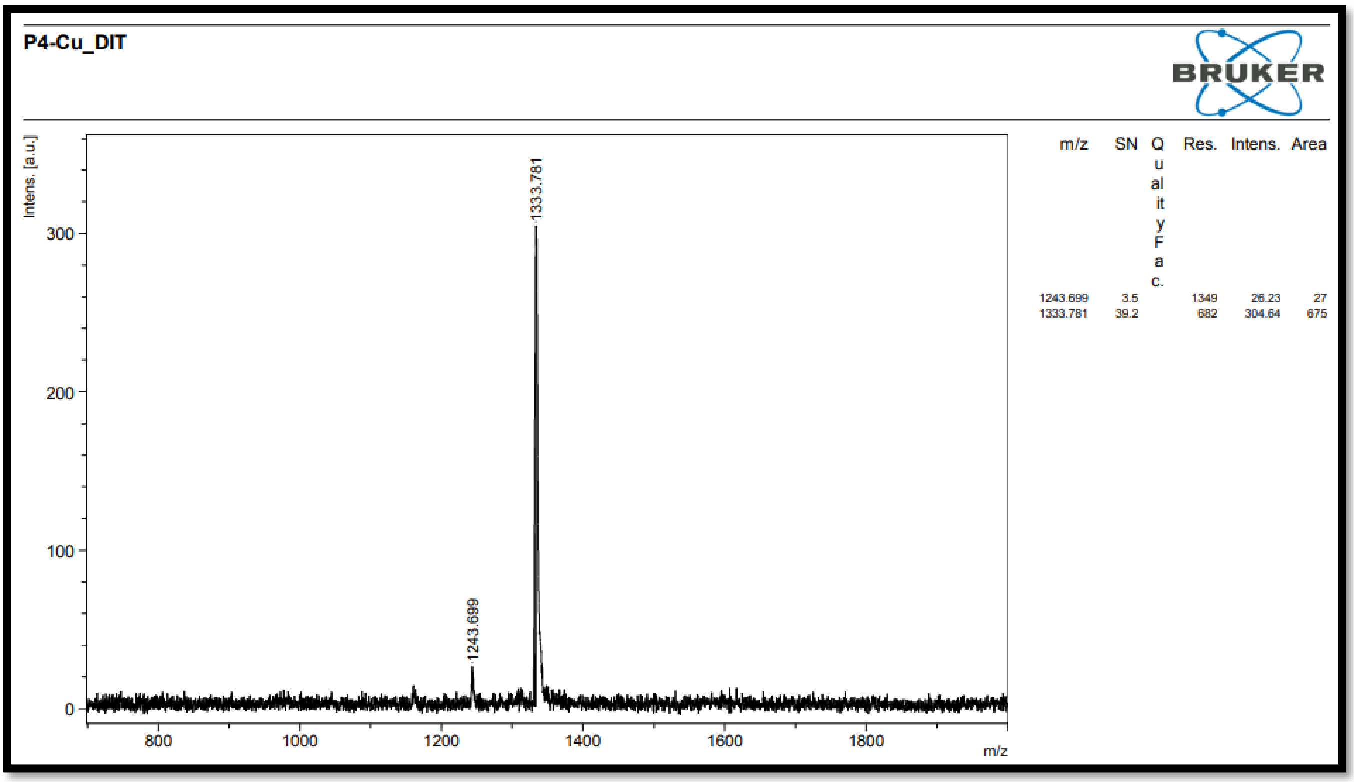

Figure S5. Mass spectrum of compound **10**

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