Synthesis and electrochemical and spectroelectrochemical characterization of chloromanganese(III) phthalocyanines

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Abstract: The synthesis of novel, symmetrical, tetrasubstituted manganese phthalocyanine complexes bearing 4 hexylthio, 2',3',4',5',6'-pentafluorobenzyloxy, 2',3',5',6'-tetrafluoro-4'-hexylthio-benzyloxy, and 2',3',5',6'-tetrafluoro-4'-pentoxy-benzyloxy units is reported. The new compounds have been characterized by using elemental analyses and UV-Vis, FT-IR, and mass spectroscopic data. The electrochemical properties of the manganese phthalocyanine complexes were investigated by cyclic and square wave voltammetry and the nature of the observed redox processes was studied by spectroelectrochemistry.

Key words: Phthalocyanines, manganese, cyclic voltammetry, spectroelectrochemistry

1. Introduction

Phthalocyanines (Pcs) are one of the porphyrin analogs that possess a number of unusual properties. Following the first synthesis in 1907, metallophthalocyanines (MPcs) were used mainly as green and blue dyestuffs in industry. In recent years, the applications of MPcs have expanded to areas such as molecular electronics, chemical sensors, electrochromic devices, nonlinear optics, liquid crystals, photosensitizers for photodynamic therapy, and electrocatalytic reagents.[1−7]

Pcs are known to have low solubility in common organic solvents due to the increasing steric interactions. The solubility of Pcs is a very important factor for the investigation of their chemical, physical, and electrochemical properties and applications. The solubility of Pcs can be improved by introducing various functional groups on the periphery.[8−13] Moreover, specificity in the applications of Pcs can be introduced by changing the central metal ions. For example, if redox active metal ions such as Co^{2+}, Fe^{3+}, and Mn^{3+} are used, the Pc complex can be used as an electrocatalyst and electrochemical sensor under homogeneous and heterogeneous conditions.[14,15] Manganese phthalocyanine (MnPc) complexes show electrochemically active behavior with oxidation states of the central manganese ion ranging from Mn^{I} to Mn^{IV}.[16−20] It is necessary to examine the electron transfer behavior of newly synthesized MnPc complexes in solution in order to study further applications.

In our previous studies, pentafluorophenyl substituted phthalonitriles and their highly soluble MPc (M: Zn, Co, Ni) complexes at the peripheral positions were synthesized[10,11,21,22] and photophysical and electrochemical properties of these MPcs were studied.[7,10,22,23] In the present paper, we describe the synthesis and the spectroscopic and electrochemical characterization of a series of new MnPc complexes that are easily soluble in organic solvents, namely [2, 9/10, 16/17, 23/24-tetrakis(hexylthio)phthalocyaninato]manganese(III) chloride,

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[2, 9/10, 16/17, 23/24-tetrakis(2',3',4',5',6'-pentafluorobenzyloxy)phthalocyaninato]manganese(III) chloride, [2, 9/10, 16/17, 23/24-tetrakis (2',3',5',6'-tetrafluoro-4'-hexylthio-benzyloxy) phthalocyaninato]manganese(III) chloride, and [2, 9/10, 16/17, 23/24-tetrakis(2',3',5',6'-tetrafluoro-4'-pentoxy-benzyloxy)phthalocyaninato]manganese(III) chloride.

2. Results and discussion

2.1. Synthesis and characterization

Manganese(III) phthalocyanine complexes **1** and **3** were prepared by the template reaction of corresponding phthalonitrile precursors with anhydrous $MnCl_2$ using high-boiling point solvents (pentanol and DMF). Complex **2** was synthesized by reaction of metal-free phthalocyanine (2, 9/10, 16/17, 23/24-tetrakis[2',3',4',5',6'-pentafluoro benzyloxy]phthalocyanine) with metal salt ($MnCl_2$) in DMF at 145 °C under N_2 atmosphere. 4-(2',3',4',5',6'-Pentafluorobenzyloxy)phthalonitrile was converted into complex **4** bearing 4 (2',3',5',6'-tetrafluoro-4'-pentoxy)benzyloxy groups on the periphery by the 'Li method' in pentanol. The direct conversion of Li_2Pc to complex **4** was achieved without isolating the unmetallated Pc complex. Substitution of the *para*-fluorine atom in the pentafluorobenzyloxy group with an alkoxy group from the solvent also occurred during the synthesis. We have mentioned earlier that various functionalized fluorinated phthalocyanines were prepared by regioselective substitution reaction of the *para*-fluorine atoms of 4-(2',3',4',5',6'-pentafluorobenzyloxy) phthalonitrile by several nucleophiles.[21,24,25]

Pcs have low solubility in most organic solvents; however, introduction of substituents on the Pc core increases the solubility. All studied Pcs **1**–**4** (Scheme) were soluble in most organic solvents, such as THF, DMF, $CHCl_3$, acetone, and DMSO (except for **3**). Column chromatography with silica gel using $CHCl_3$ and a $CHCl_3$:ethyl acetate (1:4) mixture as the mobile phase was used to purify complexes. The complexes were obtained in moderate yields (35%, 73%, 42%, and 38% for **1**–**4**, respectively). Due to the presence of single substituents on each phthalonitrile precursor, the Pcs were isolated as a mixture of isomers as expected for tetra-substituted Pcs.[26,27] No attempt was made to separate the isomers of the complexes.
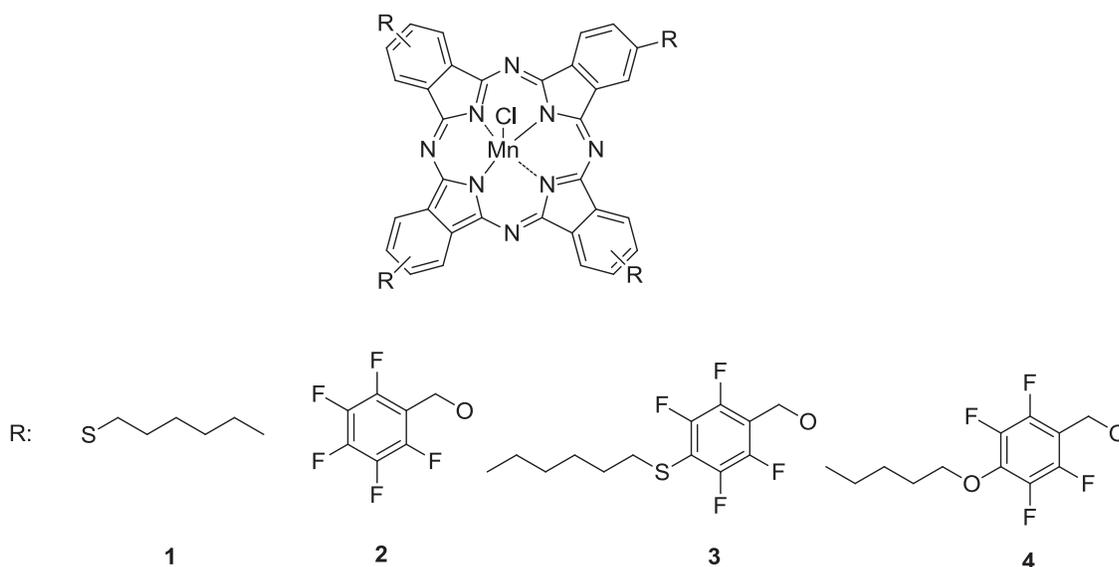
Scheme. Molecular structure of tetra-substituted manganese(III) phthalocyanine complexes (**1**–**4**).

Characterization of the new complexes involved a combination of elemental analysis and spectroscopic data (FT-IR, UV-Vis, and mass). Spectral investigations for all these complexes were consistent with the assigned structures.

In the FT-IR spectra of **1**, **3**, and **4**, the formation of the corresponding manganese(III) phthalocyanine complexes (**1**, **3**, and **4**) was confirmed by the disappearance of the characteristic C≡N stretch at 2234, 2232, and 2233 cm^{-1} of 4-(hexylthio)phthalonitrile, 4-[2',3',5',6'-tetrafluoro-4'-hexylthio)benzyloxy]phthalonitrile, and 4-(2',3',4',5',6'-pentafluorobenzyloxy)phthalonitrile, respectively. Disappearance of the NH stretching band at 3290 cm^{-1} in the inner core was confirmed by the formation of complex **2**. Pcs **1** and **3** also have similar aliphatic CH stretching bands for the corresponding peripheral substituents. In the case of **4**, the FT-IR spectral data clearly indicated the formation of complex **4** with the presence of alkoxy groups by the intense stretching bands at 2952–2862 cm^{-1}.

The mass spectra of **1**–**4** confirmed the proposed structures. In the MALDI-TOF mass spectrum of **1**, in addition to the [M+1]$^+$ peak at m/z = 1066.73, a fragment ion peak corresponding to the loss of [[M+1]-Cl]$^+$ at 1031.68 was easily identified. In the case of **3** and **4**, molecular ion peaks were found at m/z = 1778.41 [M+1]$^+$ and 1659.56 [M]$^+$. A fragment ion peak corresponding to the loss of [[M+1]-Cl]$^+$ for compounds **2** and **4** was found at m/z = 1351.42 and 1625.31, respectively. The elemental analyses were satisfactory.

2.2. Ground-state electronic absorption spectra

The best indications for Pc systems are given by their UV-Vis spectra in solution. They have 2 distinct bands, the Q band in the visible region (600–700 nm) and the B (Soret) band in the UV region (300–350 nm). These bands are transitions that arise from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc^{-2} ring. The Q and B bands depend largely on the type of group present at the peripheral position of the Pc compound and the nature of the metallic substitution.

The UV-Vis spectra of MnPcs **1**–**4** were recorded in THF. The UV-Vis spectra of **1**–**4** are typical of manganese(III) phthalocyanine complexes with a red-shifted Q band at 723, 718, 721, and 719, respectively. The red shift is a result of the lowering of the HOMO–LUMO gap, by either the destabilizing of the HOMO or stabilizing of the LUMO by the central metal.[28] Furthermore, these complexes (**1**–**4**) have an absorption band near 500 nm, interpreted as a charge transfer absorption (phthalocyanine→metal, LMCT).[28,29] Comparison of the UV-Vis spectra of PcMn(Cl) **2**–**4** and the corresponding complexes of pentafluorophenyl substituted metallophthalocyanines (ZnPc, CoPc, and NiPc) shows that the central metal (M) leads to the bathochromic shift of the Q band (718–723 nm) and to the bathochromic shift of the B-band (373–389 nm). Furthermore, the Q band of **1** was red-shifted by 36 nm when compared to the corresponding NiPc. This is good agreement with the theoretical results.[11,21,30] Similar bathochromic shift of the Q band was observed in order of **1** > **3** > **4** > **2** substituted complexes of Mn(III)Cl. Compared to the Q bands of **1** and **3**, the Q bands of **2** and **4** were red-shifted by 3–5 nm. The effect of electron-donating thiol substitution on the peripheral positions of all Pcs causes a shift in the Q bands to longer wavelengths.[21,31]

2.3. Electrochemical measurements

Electrochemical studies were carried out with the aim of finding the redox potentials of manganese phthalocyanine complexes **1**–**4**. Cyclic voltammetry (CV) and square wave voltammetry (SWV) measurements were performed in deaerated DMF using tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte

system on a glassy carbon working electrode. The half-wave potentials ($E_{1/2}$) and difference between the first oxidation and reduction processes ($\Delta E_{1/2}$) for the complexes are presented in the Table. All complexes displayed 3 reduction processes and 1 oxidation process versus SCE. Figures 1 and 2 show the CV and SWV results of complexes **1** and **4**, respectively.

Table. The electrochemical potentials of manganese phthalocyanine complexes.

Compound	Ox	Mn^{III}/Mn^{II}	Mn^{II}/Mn^{I}	RR	$\Delta E_{1/2}$
1	1.12^a	–0.12	–0.85	–1.41	1.24
2	1.08^a	–0.14	–0.76	–1.42	1.22
3	1.13^a	–0.13	–0.84	–1.42	1.26
4	1.10^a	–0.14	–0.78	–1.43	1.24

RR: Ring reduction. Ox: Oxidation. $E_{1/2} = (E_{pa} + E_{pc})/2$ at 0.100 Vs^{-1} vs. SCE. $\Delta E_{1/2} = E_{1/2}$ (first oxidation) – $E_{1/2}$ (first reduction). ^{a}: Determined by SWV.
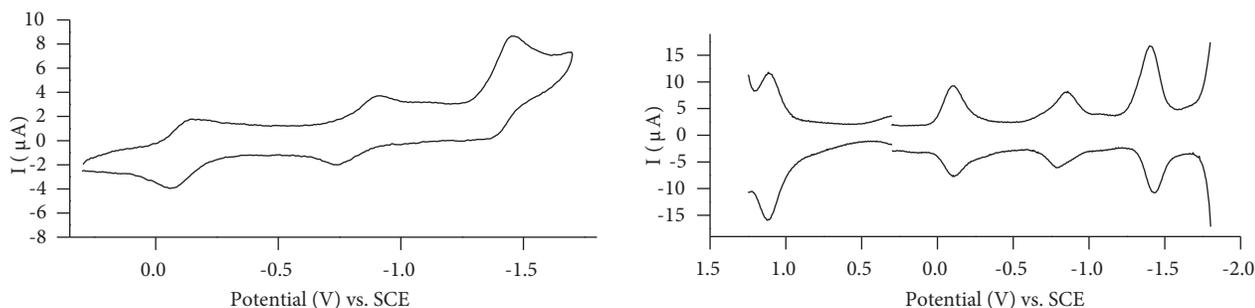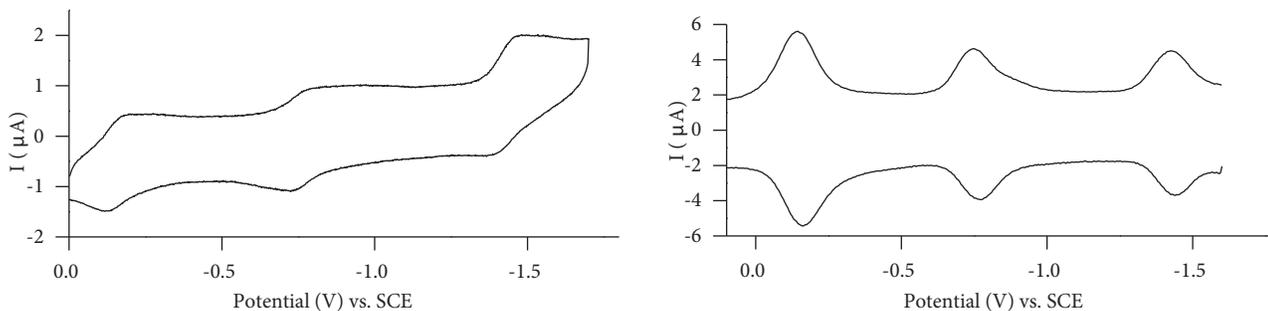

Figure 1. CV and SWV of **1** in DMF/TBAP.

Figure 2. CV and SWV of **4** in DMF/TBAP.

2.4. Spectroelectrochemical measurements

Spectroelectrochemical experiments were employed to examine the origin of the redox processes. In comparison with the results of detailed spectroelectrochemical studies reported in the literature, the first reduction couple is ascribed to the formation of manganese(II) species and the second reduction couple is ascribed to the formation of manganese(I) or Pc^{-3} species.[16−20,28,32−39] Figure 3a shows the in situ UV-Vis spectral changes during controlled potential reduction of **1** at –0.30 V. Shift of the Q band from 719 to 679 nm and the B band from 382 to 345 nm with increase in intensity and a decrease in intensity of the charge transfer band at 497 nm appeared during the first reduction. A blue shift of the Q band and disappearance of the charge transfer band

characterize the Mn(III) reduction process, so these spectral changes suggest that the first reduction couple observed at –0.12 V was the reduction of Mn(III) to Mn(II). Clear isosbestic points at 387, 513, and 702 nm reveal that this is a clean reduction. Figure 3b shows spectral changes observed during the second reduction process. There is debate about the reduction of the $Mn(II)Pc^{-2}$ species; some studies offer metal reduction to the $Mn(I)Pc^{-2}$ species and others ring reduction to the $Mn(II)Pc^{-3}$, forming a monoanion radical.[28,32−37] Decrease in the Q band intensity and formation of 2 new bands at 519 and 851 nm with well-defined isosbestic points at 649 and 751 nm can characterize a metal-based reduction. Decrease in the Q band intensity at 678 nm and formation of a new band at 551 nm suggests that the third reduction is ring-based. During the oxidation process of **1** the absorption of the Q band decreases in intensity with a shift to 725 nm and the band at 497 nm is shifted to 503 nm. These spectral changes can characterize a ring-based oxidation process in manganese phthalocyanines.
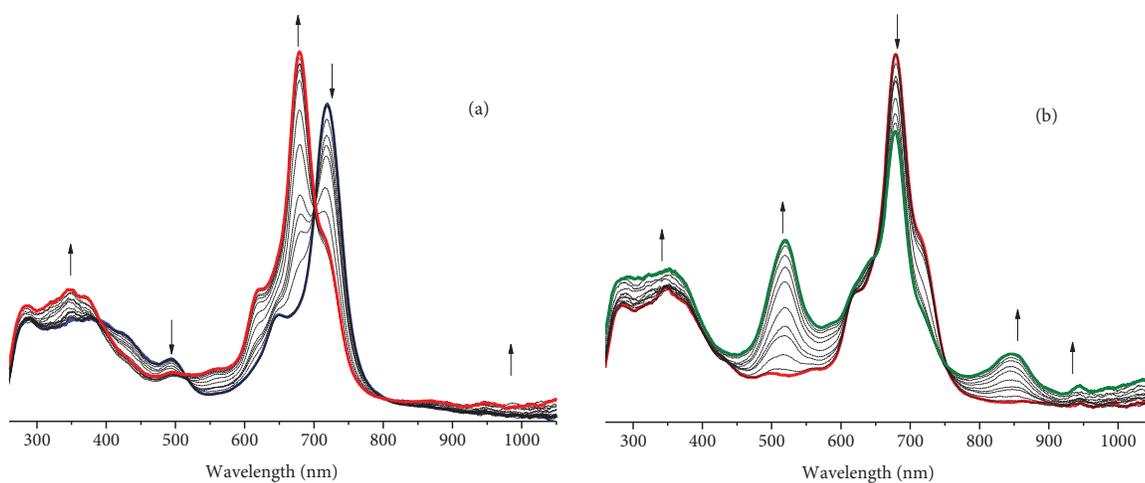

Figure 3. Electronic absorption spectra of **1** under reduction at –0.3 V (a) and –1.0 V (b).

Shift of the Q band from 717 to 678 nm with increasing B band from 380 to 375 nm and a decrease in intensity of the charge transfer band at 497 nm appeared during the first reduction with clear isosbestic points at 518 and 701 nm, suggesting that the first reduction is manganese-based. First the increase and then the decrease in the Q band intensity and formation of 2 new bands at 516 and 846 nm also show that the second reduction is manganese-based. Decrease in the Q band intensity at 678 nm with the band at 518 nm and formation of a new band at 565 nm with isosbestic points at 496, 540, 604, and 749 nm suggest that the third reduction is ring-based. During the oxidation process of **2** the absorption of the Q band and the band at 497 nm decreases in intensity, suggesting that these spectral changes are ring-based oxidation process.

Complexes **3** and **4** showed similar changes during the reduction and oxidation processes and the changes are compatible with the other manganese phthalocyanines. Figures 4a and 4b show the in situ UV-Vis spectral changes during controlled potential reduction of **3**. The Q band of the complex **3** shifted from 721 to 679 nm, the B band shifted from 379 to 348 nm with increase in intensity, and the charge transfer band at 497 nm disappeared during the first reduction with clear isosbestic points at 385, 520, and 702 nm. The Q band of complex **4** shifted from 718 to 680 nm, the B band shifted to 354 nm with an increase in intensity, and the charge transfer band at 498 nm disappeared during the first reduction with clear isosbestic points at 392, 515, and 701 nm. The decrease in the Q band intensities and formation of 2 new bands at 521 and 846 nm for complex **3** and at 514 and 845 nm for complex **4** show the manganese-based second reduction. Decrease in

the Q band intensity at 678 nm with the band at 520 nm with isosbestic points at 498, 534, 606, and 707 nm for complex **3** and decrease in the Q band intensity with an increase together with the band at 514 nm with isosbestic points at 601 and 741 nm for complex **4** suggest phthalocyanine ring-based reduction. During the oxidation process the absorption of the Q band and the charge transfer band decreasing in intensity suggest that these spectral changes are ring-based.
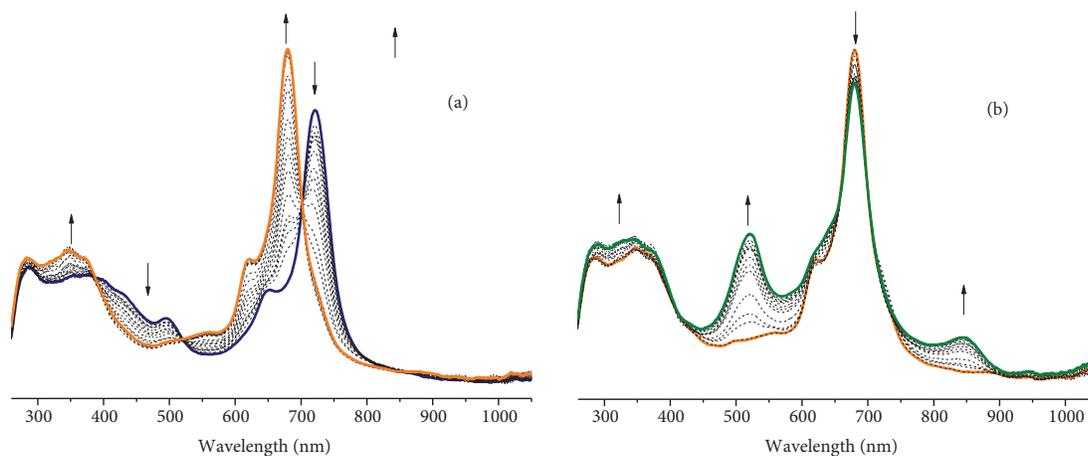

Figure 4. Electronic absorption spectra of **3** under reduction at –0.3 V (a) and –1.0 V (b).

Figures 5a and 5b show the in situ UV-Vis spectral changes of complex **4** without purging with nitrogen gas. Complex **4** gives a new band at 622 nm in the first reduction process, which belongs to the formation of the MnPc μ-oxo complex.[28] In the second reduction process the band at 622 nm decreases in intensity and the Q band at 676 nm increases in intensity.
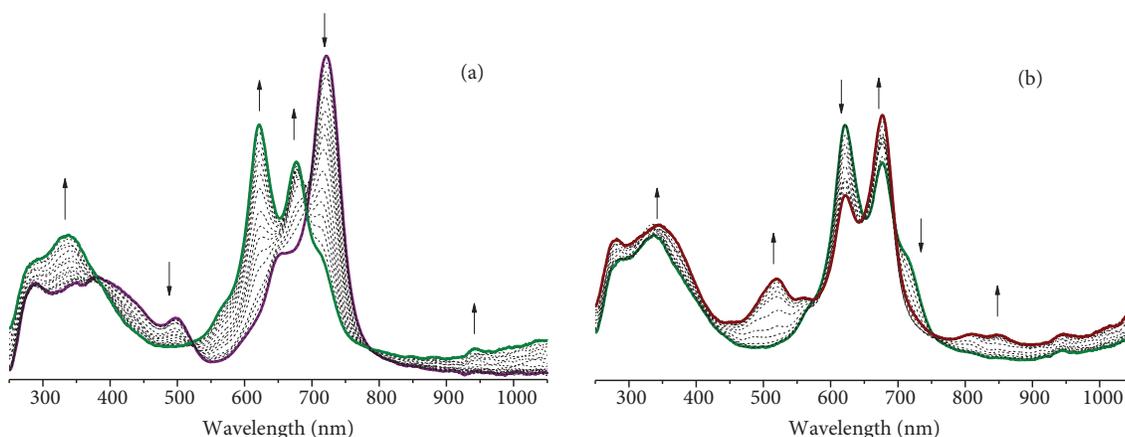

Figure 5. Electronic absorption spectra of **4** under reduction at –0.3 V (a) and –1.0 V (b).

3. Experimental

All reagents and solvents were of reagent-grade quality, obtained from commercial suppliers. The solvents were stored over molecular sieves (4 Å). The homogeneity of the products was tested in each step by TLC (SiO$_2$). All reactions were carried out under nitrogen atmosphere in dried solvents. 4-(Hexylthio)phthalonitrile;[30]

2, 9/10, 16/17, 23/24-tetrakis(2',3',4',5',6'-pentafluorobenzyloxy)phthalocyanine;[11] 4-(2',3',5',6'-tetrafluoro-4'-hexylthio-benzyloxy)phthalonitrile;[21] and 4-(2',3',4',5',6'-pentafluoro-benzyloxy)phthalonitrile[11] were synthesized according to published methods. IR spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer with ATR capability; electronic spectra were recorded on a Scinco SD 1000 single-beam UV-Vis spectrophotometer using 1-cm path length cuvettes at room temperature. Mass spectra were recorded on a Bruker Microflex MALDI-TOF/MS spectrometer. Melting points were determined on a Büchi Melting Point B-540 apparatus. Elemental analyses were performed on a Thermo Flash EA 1112.

Electrochemical measurements were carried out on a Gamry Reference 600 potentiostat/galvanostat utilizing a 3-electrode cell configuration in DMF containing 0.1 mol dm^{-3} TBAP. The cell consists of glassy carbon working electrode (surface area of 0.071 cm^2), a platinum wire counter electrode, and a saturated calomel reference electrode. In situ UV-Vis absorption spectra were measured with an Ocean Optics HR2000+ diode array spectrophotometer. For in situ spectroelectrochemical measurements, an optically transparent thin-layer quartz cell of path length 1 mm was employed, in which a Pt gauze electrode, a Pt wire, and a SCE were used for the working, counter, and reference electrodes, respectively.

3.1. [2, 9/10, 16/17, 23/24-Tetrakis(hexylthio)phthalocyaninato]manganese(III) chloride (1)

A mixture of 4-(hexylthio)phthalonitrile (0.245 g, 1 mmol), anhydrous MnCl$_2$ (0.031 g, 0.250 mmol), and 2 drops of 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU) was dissolved in n-pentanol (2 mL). The reaction mixture was heated with stirring at 145 °C under nitrogen atmosphere for 24 h. After cooling the mixture to room temperature, it was treated with ethanol (20 mL) and the mixture was filtered off. The residue was washed several times with ethanol, water, and methanol and then dried in vacuo. Finally, pure product was obtained by chromatography on a silica gel column using CHCl$_3$ as an eluent. Yield: 0.093 g (35%); mp > 200 °C; anal. calcd. for C$_{56}$H$_{64}$ClMnN$_8$S$_4$: C, 62.99; H, 6.04; N, 10.49%. Found: C, 63.11; H, 6.03; N, 10.52%. IR: ν_{max}, cm^{-1} 2950–2870 (alkyl C-H). UV-Vis (THF): λ_{max}, nm (log ε) 354 (4.81), 495 (4.30), 723 (4.93). MS (MALDI-TOF): m/z 1031.68 [[M+1]-Cl]$^+$, 1066.73 [M+1]$^+$.

3.2. [2, 9/10, 16/17, 23/24-Tetrakis(2', 3', 4', 5', 6'-pentafluorobenzyloxy) phthalocyaninato]manganese(III) chloride (2)

A solution of 2, 9/10, 16/17, 23/24-tetrakis(2',3',4',5',6'-pentafluorobenzyloxy) phthalocyanine (0.100 g, 0.077 mmol) and anhydrous MnCl$_2$ (0.012 g, 0.092 mmol) was refluxed in DMF (1.5 mL) with stirring for 4 h under N$_2$ atmosphere. The resulting suspension was cooled to room temperature and then poured into water (20 mL). The precipitate was filtered off and washed with water, hot ethanol, and hot hexane. Pure product was obtained by chromatography on a silica gel column using CHCl$_3$ as an eluent. Yield: 0.078 g (73%); mp > 200 °C; anal. calcd. for C$_{60}$H$_{20}$ClF$_{20}$MnN$_8$O$_4$: C, 51.95; H, 1.45; N, 8.08%. Found: C, 51.73; H, 1.49; N, 8.11%. IR: ν_{max}, cm^{-1} 3083 (aryl C-H), 2950–2890 (alkyl C-H), 1338 (C-F), 1049 (C-O), 1217 (C-O-C). UV-Vis (THF): λ_{max}, nm (log ε) 373 (4.77), 496 (4.29), 718 (4.93). MS (MALDI-TOF): m/z 1351.42 [[M+1]-Cl]$^+$.

3.3. [2, 9/10, 16/17, 23/24-Tetrakis(2',3',5',6'-tetrafluoro-4'-hexylthio-benzyloxy) phthalocyaninato]manganese(III) chloride (3)

A mixture of 4-[2',3',5',6'-tetrafluoro-4'-hexylthio-benzyloxy]phthalonitrile (0.200 g, 0.473 mmol) and anhydrous MnCl$_2$ (0.015 g, 0.119 mmol) in 2 mL of dry DMF was heated and stirred at 140 °C in a glass sealed tube for

20 h under nitrogen atmosphere. After cooling to room temperature, water was added to the reaction mixture. The solid product was precipitated, collected by filtration, and washed with water and ethanol. Finally, the solid product was chromatographed on column chromatography with silica gel using $CHCl_3$:ethyl acetate (1:4) as the eluent. Yield: 0.088 g (42%); mp > 200 °C; anal. calcd. for $C_{84}H_{72}ClF_{16}MnN_8O_4S_4$: C, 56.68; H, 4.08; N, 6.29%. Found: C, 56.57; H, 4.09; N, 6.30%. IR: ν_{max}, cm^{-1} 2956–2855 (alkyl C-H), 1310 (C-F), 1097 (C-O), 1271 (C-O-C). UV-Vis (THF): λ_{max}, nm (log ε) 389 (4.75), 494 (4.27), 721 (4.95). MS (MALDI-TOF): m/z 1778.41 [M+1]$^+$.

3.4. [2, 9/10, 16/17, 23/24-Tetrakis(2',3',5',6'-tetrafluoro-4'-pentoxy-benzyloxy) phthalocyaninato]manganese(III)chloride (4)

Freshly cut lithium (0.123 g, 17.739 mmol) was dissolved in 15 mL of pentanol by heating at 80 °C, and then 4-(2',3',4',5',6'-pentafluorobenzyloxy)phthalonitrile (0.200 g, 0.617 mmol) was added to the solution while stirring and the solution was left to reflux under nitrogen atmosphere for 1 h. The solution turned dark green as soon as lithium metal was added (possibly forming Li_2Pc). Anhydrous $MnCl_2$ (0.019 g, 0.155 mmol) was then added to the solution and the solution was stirred at reflux temperature for 3 h. The reaction mixture was cooled to room temperature; the solid product was precipitated by adding water and was washed with hot water. The product was isolated by silica gel column chromatography first with $CHCl_3$ and then with $CHCl_3$:ethyl acetate (1:4) as the eluent. Yield: 0.097 g (38%); mp > 200 °C; anal. calcd. for $C_{80}H_{64}ClF_{16}MnN_8O_8$: C, 57.89; H, 3.89; N, 6.75%. Found: C, 57.99; H, 3.90; N, 6.76%. IR: ν_{max}, cm^{-1} 2952–2862 (alkyl C-H), 1341 (C-F), 1077 (C-O), 1277 (C-O-C). UV-Vis (THF): λ_{max}, nm (log ε) 357 (4.63), 496 (4.05), 719 (4.94). (MALDI-TOF): m/z 1659.56 [M]$^+$, 1625.31 [[M+1]-Cl]$^+$.

4. Conclusion

Four new tetrasubstituted manganese phthalocyanine complexes with different moieties at peripheral positions were reported. All complexes were characterized by elemental analysis, FT-IR, mass spectroscopy, and electronic spectroscopy. Compounds **1**–**4** have good solubility in various organic solvents and are nonaggregated (in THF) within a wide concentration range. Well-defined redox processes were observed and confirmed using spectroelectrochemical studies. Electrochemical and spectroelectrochemical properties of the complexes are in harmony with similar manganese phthalocyanines with small potential shifts.

Acknowledgment

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