



Synthesis and Spectro-Electrochemical Properties of New Metallophthalocyanines Having High Electron Transfer Capability

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ABSTRACT

It is important to synthesis and examine the redox properties of phthalocyanines and related macrocycles in order to reveal their possible applications. In this paper, new Zn²⁺, Co²⁺ and Mn²⁺ phthalocyanine complexes containing substituted 1,2,4-triazole groups on peripheral positions have been prepared and characterized by classical methods and electrochemistry in detail. The use of triethylamine and acetone combination in the synthesis of nitrile structures **3a** and **3b**, the starting compounds for phthalocyanines, both increased yield of products and shortened reaction time compared to classical synthesis of nitrile structures. The electron transfer capability of new metallophthalocyanines (ZnPcs, CoPcs and MnPcs) was investigated in detail via cyclic voltammetry (CV), square wave voltammetry (SWV) and *in situ* UV-vis spectroelectrochemistry. For ZnPcs, these experiments demonstrated that the complexes exhibited three well-defined reductions and two oxidations waves based on the Pc ring electroinactive nature of the Zn metal coordinated to the macrocycle. For CoPcs showed three reductions and one oxidation based on both the Pc ring and electroactive nature of Co center. Furthermore, MnPcs displayed three well-defined reductions and two oxidations waves based on either the Pc ring or electroactive Mn center.

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1. Introduction

The design, construction of novel phthalocyanines (Pcs) containing different preferential substructures within a same molecule and comprising proper metals, represent an important strategy in phthalocyanine/electrochemistry. Technological utilizations of Pc metal complexes in areas such as electrochemical sensors, electrochromism, electrocatalysis and other energy production frameworks are closely connected to their excellent electron transfer properties [1–3]. Also, phthalocyanine compounds are potential candidates as photosensitizer for photodynamic therapy [4,5]. Application possibility of Pcs depends on the solubility (and so aggregation properties) and electron transfer capability thus nature/type of substituents/metal. It is possible to design the Pcs that have high solubility and rich redox properties by binding bulky groups on appropriate positions and introducing suitable metal. Especially,

Pcs containing redox active metal centers (e.g. Cr, Co, Fe, Mn etc.) are important for their electrochemical properties. Among them, due to the electroactive nature of the Co and Mn central metals, these corresponding metallophthalocyanines (MPcs) have promising electrochemical properties due to the oxidation state range (from Mn⁺ to Mn⁴⁺ and from Co²⁺ to Co³⁺). Beside this, bulky substituents on peripheral or non-peripheral positions are used to overcome the aggregation and insolubility problem of Pcs [6,7].

The most important purpose of this study is to prepare new Pc complexes having proper features for their technological applications. Therefore, choosing suitable substituents is important for synthetic strategy. Triazoles that have a five-membered ring of two carbon atoms and three nitrogen atoms may be attractive for electrochemical behavior of Pcs if they are connected to Pc ring due to their electron-deficient nature and electron acceptor properties. On the other hand, 1,2,4-triazole derivatives have potential applications in areas such as antiproliferative, antibacterial, antitumor, antibiotics and antifungal properties [8–14].

To the best of our knowledge, there are only few studies about synthesizing triazole substituted Pcs and investigation of electro-

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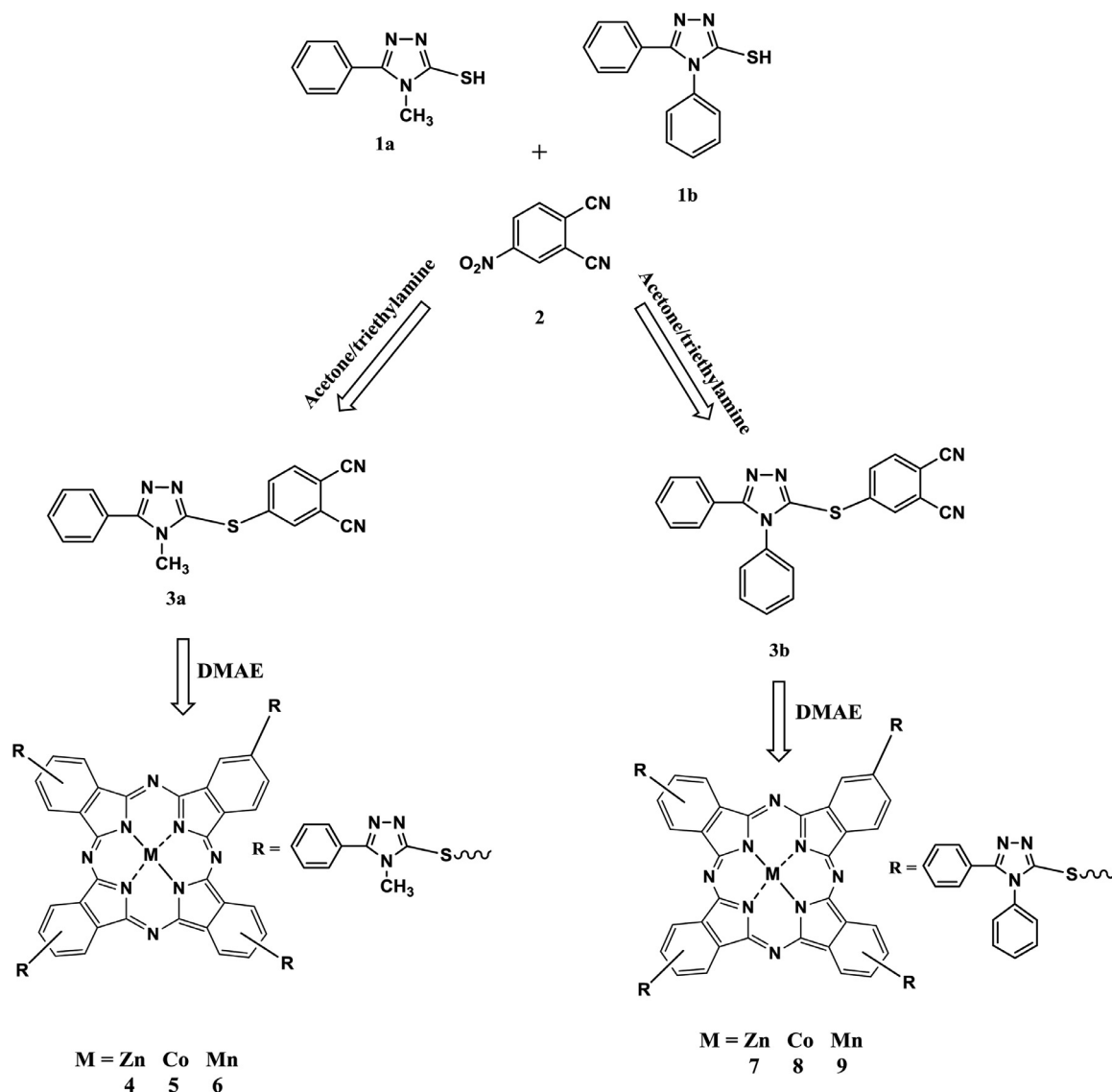


Fig. 1. The schematic representation of the synthetic procedure of the prepared compounds.

chemical properties but the interest of scientists is increasing [15–17]. Tanyeli et al. attracted attention the promising results of the triazole substituted Pcs for photochromic applications [18]. Furthermore, Kantekin et al. and Avcıata and co-workers pointed out the utilization of triazole substituted Pcs in electrocatalytic, electrochromic, non-linear optical, electrochromic data storage and display technologies [15–17,19].

Based on the above viewpoints, this study is mainly concentrated on the preparation of MPcs (Zn, Co and Mn) containing a group of novel triazole groups on peripheral positions. The electrochemical characteristics of two different substituted groups namely methyl and phenyl peripheral MPc derivatives were investigated. The paper comprises largely synthesis of Pc complexes that possibly have rich electron transfer capability, details of synthesis steps, structural confirmation and studies on electrochemical behavior via cyclic voltammetry (CV), square wave voltammetry (SWV) and *in situ* UV-vis spectroelectrochemistry on glassy carbon/platinum working electrode in the solution of dimethylformide (DMF)/tetrabutylammonium perchlorate (TBAP).

2. Experimental

2.1. Materials and reagents

All reagents were analytical grade and used without further purification. Reactions were carried out under dry and oxygen-free nitrogen atmosphere using standard Schlenk techniques. Initially, compounds **1a** and **1b** were synthesized following the procedures, respectively [20,21]. The compounds **3a** and **3b** were re-synthesized by partially changing the reaction conditions [22,23]. ZnPcs **4** and **7** were re-synthesized by partially changing the reaction conditions [22]. All solvents were dried and purified as described by Perrin and Armarego before use [24]. All the chemicals were obtained from Fluka Chemie AG (Buchs, Switzerland) and Sigma-Aldrich (St. Louis, MO, USA).

2.2. Equipments

¹H NMR, ¹³C NMR spectra were recorded on a Varian XL-400 NMR spectrometer and chemical shifts were reported (δ) relative

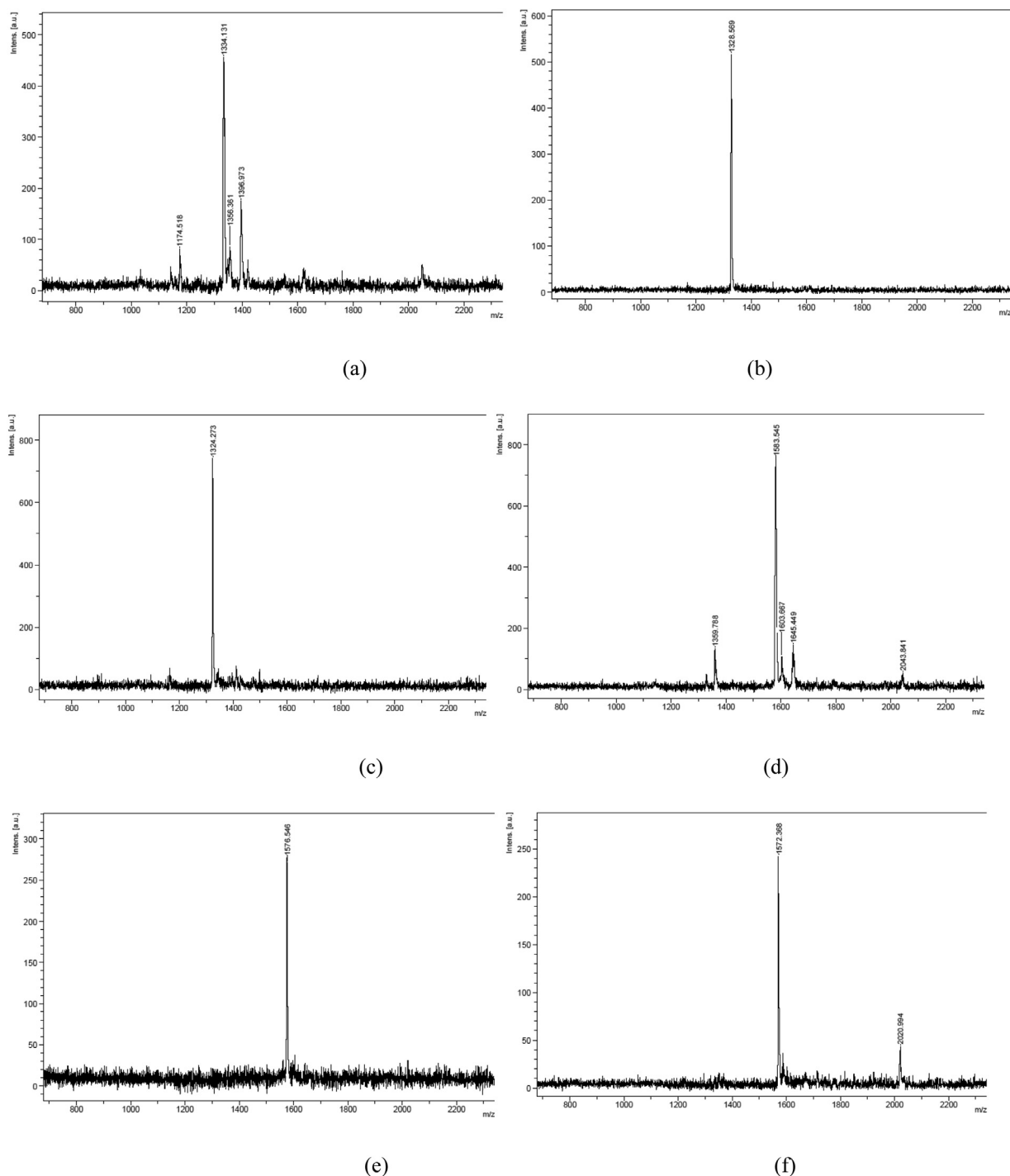


Fig. 2. MALDI-TOF spectra of MPcs (4-9); (a) defines ZnPc (4); (b) defines CoPc (5); (c) defines MnPc (6); (d) defines ZnPc (7); (e) defines CoPc (8); (f) defines MnPc (9)

to Me₄Si (tetramethylsilane) as internal standard. IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer with ATR technique. The mass spectra were measured with a Bruker Daltonics Microflex mass and MALDI-TOF spectrometer. Methanol and chloroform were used as solvents in mass analysis and all mass analysis were conducted in positive ion mode. UV-Vis spectra were recorded with a Perkin Elmer Lambda 25 spectrophotometer. Cyclic (CV) Voltammetry and Square Wave Voltammetry were carried out by a Princeton Applied Research model 2263 potentiostat controlled by an external PC. A three-electrode system [BAS model

(Bioanalytical System Inc.) solid cells tand] was used for CV and SWV measurements in DMF, and it consisted of glassy carbon (3.0 mm diameter) disc electrodes as the working electrode, a platinum wire counter electrode, and an Ag/AgNO₃ reference electrode.

The reference electrolyte content (Ag / 0.001 M AgNO₃ (dry solvent: CH₃CN) was prepared fresh each time. *In situ* UV-vis, spectroelectrochemical experiments were performed with a home-built thin-layer cell that utilized a light transparent platinum gauze working electrode. Potentials were applied and monitored with a Princeton Applied Research model 2263 potentiostat.

Time-resolved UV-vis spectra were recorded on an Agilent model 8453 diode array spectrophotometer.

2.3. 4-(4-methyl-5-phenyl-4H-1,2,4-triazole-3-yl-tio)phthalonitrile (3a)

After mixing compound **1a** (1 g, 5.24 mmol) and triethylamine (1.11 mL, 7.86 mmol) in 30 mL of dry acetone at room temperature for 15 min., compound **2** (0.91 g, 5.24 mmol) in 10 mL of dry acetone was added dropwise to the mixture. Then, the mixture was stirred for another 9 h at room temperature. The reaction was monitored by thin-layer chromatography (TLC) and the optimal time of each reaction was determined. At the end of this period, the solvent was evaporated to dryness and residue extracted by chloroform/water system for 3 times. Then the pure product was obtained by column chromatography using silica gel as stationary phase (chloroform:methanol, 100:1.7). Yield: 1.31 g (%79). FT-IR (ATR), ν/cm^{-1} : 3102-3027 (Ar-CH), 2956 (Aliphatic-CH), 2235 ($\text{C}\equiv\text{N}$), 1585-1552 ($\text{C}=\text{C}/\text{C}=\text{N}$), 1472-1379 ($\text{C}-\text{N}/\text{C}-\text{S}$). $^1\text{H-NMR}$ (CDCl_3), (δ :ppm): 7.78-7.72 (m, 5H/Ar-H), 7.59 (s, 3H/Ar-H), 3.75 (s, 3H/ CH_3). $^{13}\text{C-NMR}$ (CDCl_3), (δ :ppm): 157.62, 145.25, 140.96, 134.03, 131.92, 130.93, 129.19, 128.73, 126.26, 117.04, 114.86 ($\text{C}\equiv\text{N}$), 114.51 ($\text{C}\equiv\text{N}$), 114.07, 32.45 ($-\text{CH}_3$). MS (ESI), (m/z): Calculated: 317.13; found: 318.30 [$\text{M} + \text{H}$] $^+$.

2.4. 4-(4,5-diphenyl-4H-1,2,4-triazole-3-yl-tio)phthalonitrile (3b)

After mixing compound **1b** (0.43 g, 1.72 mmol) and triethylamine (0.36 mL, 2.58 mmol) in 30 mL of dry acetone at room temperature for 15 min., compound **2** (0.29 g, 1.72 mmol) in 10 mL of dry acetone was added dropwise to the mixture. Then, the mixture was stirred for another 9 h at room temperature. The reaction was monitored by thin-layer chromatography (TLC) and the optimal time of each reaction was determined. At the end of this period, the solvent was evaporated to dryness and residue extracted by chloroform/water system for 3 times. Then the pure product was obtained by column chromatography using silica gel as stationary phase (chloroform:methanol, 100:1.7). Yield: 0.46 g (%70).

FT-IR (ATR), ν/cm^{-1} : 3062-3021 (Ar-CH), 2233 ($\text{C}\equiv\text{N}$), 1584-1550 ($\text{C}=\text{C}/\text{C}=\text{N}$), 1496-1386 ($\text{C}-\text{N}/\text{C}-\text{S}$). $^1\text{H-NMR}$ (CDCl_3), (δ :ppm): 7.69 (s, 3H/Ar-H), 7.58-7.55 (t, 1H/Ar-H), 7.51-7.46 (m, 4H/Ar-H), 7.43-7.40 (t, 1H/Ar-H), 7.35-7.31 (m, 2H/Ar-H), 7.13-7.11 (d, 2H/Ar-H). $^{13}\text{C-NMR}$ (CDCl_3), (δ :ppm): 156.51, 146.62, 140.26, 133.77, 133.28, 133.24, 130.56, 130.51, 130.14, 128.75, 128.36, 127.33, 125.77, 116.69, 114.85 ($\text{C}\equiv\text{N}$), 114.45 ($\text{C}\equiv\text{N}$), 114.26. MS (ESI), (m/z): Calculated: 379.13; found: 380.24 [$\text{M} + \text{H}$] $^+$.

2.5. General synthetic procedure for MPcs (4-9)

As shown in Fig. 1, for the synthesis of MPcs **4-6** compound **3a**, and for MPcs **7-9** compound **3b** were used as starting materials. The mixtures of equivalent amounts of the starting materials (compounds **3a** (for MPc **4-6**; 0.55 mmol) and **3b** (for MPcs **7-9**; 0.55 mmol)) and corresponding metal salts ($\text{Zn}(\text{CH}_3\text{CO}_2)_2$ for ZnPcs (**4** and **7**; 0.55 mmol), CoCl_2 for CoPcs (**5** and **8**; 0.55 mmol) and MnCl_2 for MnPcs (**6** and **9**; 0.55 mmol)) in *N,N*-dimethylaminoethanol (DMAE) medium under N_2 atmosphere were prepared and the temperatures were gently raised to 170 $^\circ\text{C}$. The reaction was monitored by thin-layer chromatography (TLC) and the optimal time of each reaction was determined. These reaction mixtures were stirred for 15 hours at these temperatures and after cooling, methanol:water (3:1) was added and precipitated crude products were filtered. These dark green crude products were washed by hot ethanol, acetone and ethyl acetate, respectively.

2.5.1. {2,9,16,24-tetrakis[(4-methyl-5-phenyl-4H-1,2,4-triazol-3-yl)sulfanyl]-29H,31H-phthalocyaninato(2-)- $\kappa^4\text{N}^{29},\text{N}^{30},\text{N}^{31},\text{N}^{32}$ } ZnPc (**4**)

Yield: 0.24 g (% 34). FT-IR (ATR), ν/cm^{-1} : 3059 (Ar-CH), 2954 (CH_3), 1647-1600 ($\text{C}=\text{C}/\text{C}=\text{N}$), 1470-1383 ($\text{C}-\text{N}/\text{C}-\text{S}$). $^1\text{H-NMR}$ ($\text{DMSO}-d_6$), (δ :ppm): 8.92-8.68 (m, 5H/Ar-H), 7.90-7.60 (m, 27H/Ar-H), 4.05 (s, 6H/ CH_3), 3.69 (s, 6H/ CH_3). UV-Vis (DMF) $\lambda_{\text{max/nm}}$: 691 (4.95), 622 (4.31), 363 (4.68). MS (ESI), (m/z): Calculated: 1334.88; found: 1334.13 [M] $^+$.

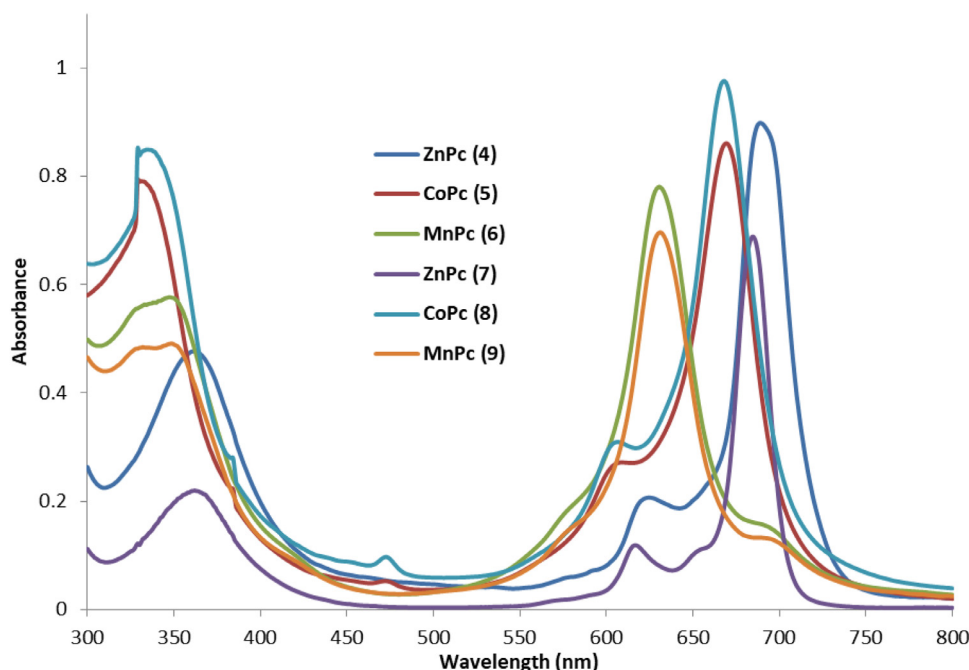


Fig. 3. UV-Vis spectra of MPcs (4-9) in DMF at 1×10^{-5} M concentration.

Table 1

Electrochemical half-wave potentials of ZnPcs (4 and 7) and some selected phthalocyanines from literature

ZnPcs	Pc ⁻⁴ /Pc ⁻⁵	Pc ⁻³ /Pc ⁻⁴	Reductions Pc ⁻² /Pc ⁻³	Oxidations Pc ⁻² /Pc ⁻¹	Pc ⁻¹ /Pc ⁰	^b ΔE	^c ΔE	^d ΔE	References
		^a E _{1/2} (V)	^a E _{1/2} (V)	^a E _{1/2} (V)	^a E _{1/2} (V)	(V)	(V)	(V)	
4	-2.27*	-1.53	-1.15	0.23	0.45	0.22	1.38	0.38	tw
7	-	-1.54	-1.14	0.19	0.44	0.25	1.33	0.40	tw
P-CfZnPc	-1.94*	-1.31	-0.98	0.49	-	-	1.47	0.33	[25]
ZnPc(SC ₂ H ₄ OH) ₈	-1.76	-1.11	-0.74	0.64	-	-	1.38	0.37	[26]
Zn(htpc)	-	-1.10	-0.79	0.70	0.90	0.20	1.49	0.31	[27]

$$^a E_{1/2}(V) = (E_{pa} + E_{pc})/2$$

$$^b \Delta E = E_{1/2}(\text{oxd}_2) - E_{1/2}(\text{oxd}_1)$$

$$^c \Delta E = E_{1/2}(\text{oxd}_1) - E_{1/2}(\text{red}_1)$$

$$^d \Delta E = E_{1/2}(\text{red}_1) - E_{1/2}(\text{red}_2);$$

* Irreversible peak; tw: this work

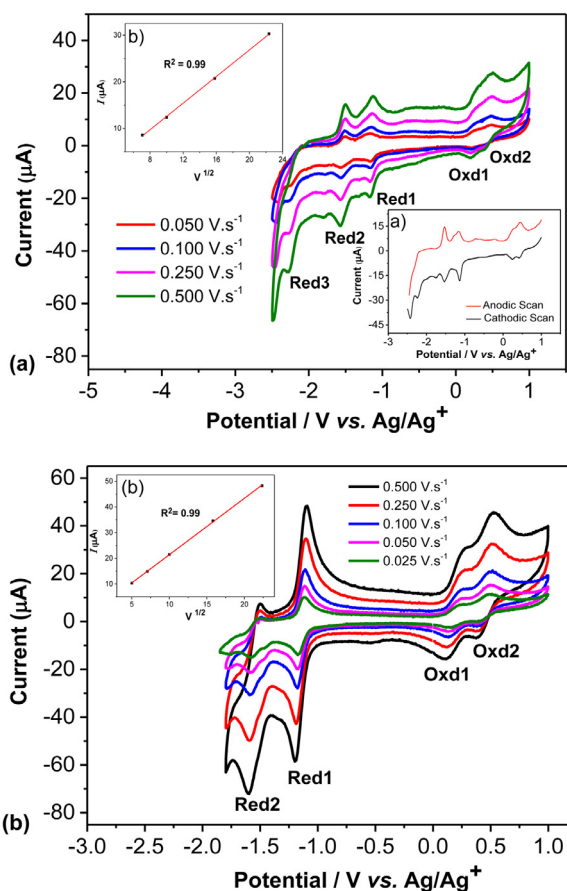


Fig. 4. CVs of 4 (a) and 7 (b) in DMF solution containing 0.2 M TBAP at scan rates between 0.025 and 0.500 V s⁻¹. Inset a: SWV of 4, inset b: the plots of *I*_c vs. scan rate *v* for the first reduction process. Conditions for SWV: pulse PH/PW 0.025 V for 0.01 s; step height 2.00 mV; scan rate: 0.100 V s⁻¹.

2.5.2. {2,9,16,24-tetrakis[(4-methyl-5-phenyl-4H-1,2,4-triazol-3-yl)sulfanyl]-29H,31H-phthalocyaninato(2-)-κ⁴N²⁹,N³⁰,N³¹,N³²}CoPc (5)

Yield: 0.28 g (% 40). FT-IR (ATR), *ν*/cm⁻¹: 3050 (Ar-CH), 2955 (CH₃), 1604-1522 (C=C/C=N), 1470-1396 (C-N/C-S). UV-vis (DMF) λ_{max}/nm: 671 (4.93), 598 (4.38), 335 (4.89). MS (ESI), (*m/z*): Calculated: 1328.40; found: 1328.57 [M]⁺.

2.5.3. {2,9,16,24-tetrakis[(4-methyl-5-phenyl-4H-1,2,4-triazol-3-yl)sulfanyl]-29H,31H-phthalocyaninato(2-)-κ⁴N²⁹,N³⁰,N³¹,N³²}MnPc (6)

Yield: 0.27 g (% 39). FT-IR (ATR), *ν*/cm⁻¹: 3063 (Ar-CH), 2956 (CH₃), 1603-1501 (C=C/C=N), 1471-1389 (C-N/C-S). UV-vis (DMF) λ_{max}/nm: 634 (4.88), 579 (4.27), 351 (4.76). MS (ESI), (*m/z*): Calculated: 1324.41; found: 1324.27 [M]⁺.

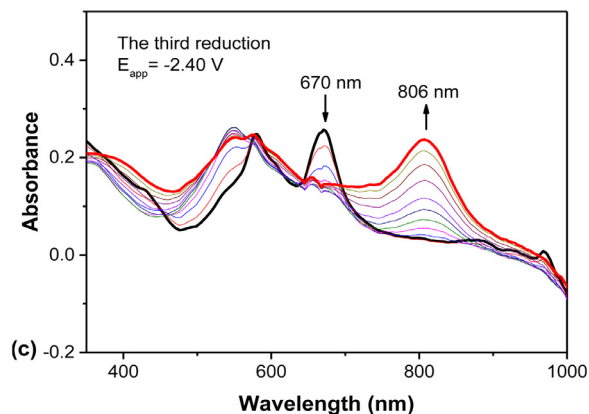
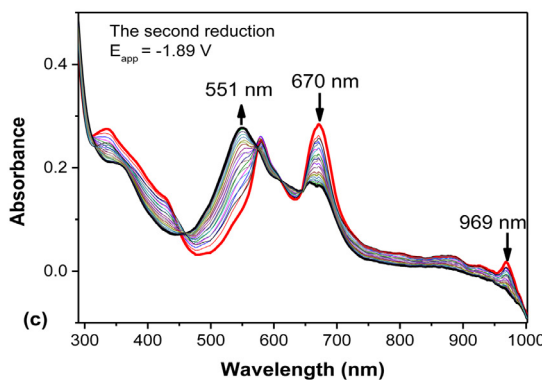
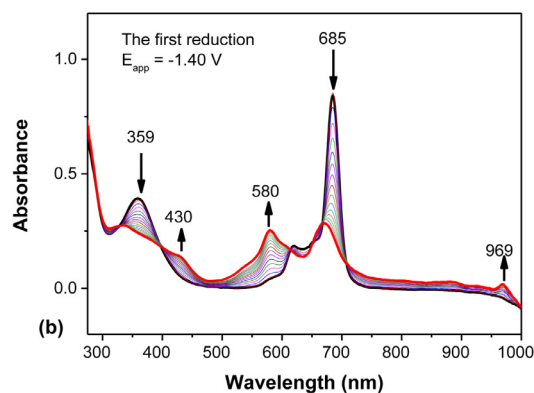


Fig. 5. Time-resolved UV-vis spectral changes of 4 during the first reduction (*E*_{app} = -1.40 V) (a), the second reduction (*E*_{app} = -1.89 V) (b), and the third reduction (*E*_{app} = -2.40 V) (c) in DMF solution containing 0.2 M TBAP in a thin-layer cell at a scan rate of 0.100 V s⁻¹.

2.5.4. {2,9,16,24-tetrakis[(4,5-diphenyl-4H-1,2,4-triazol-3-yl)sulfanyl]-29H,31H-phthalocyaninato(2-)- $\kappa^4 N^{29}, N^{30}, N^{31}, N^{32}$ }ZnPc (**7**)

Yield: 0.27 g (% 31). FT-IR (ATR), ν/cm^{-1} : 3061 (Ar-CH), 1647-1597 (C=C/C=N), 1495-1383 (C-N/C-S). $^1\text{H-NMR}$ (DMSO- d_6), (δ :ppm): 8.58 (bs, 6H/Ar-H), 7.88 (bs, 4H/Ar-H), 7.57-7.49 (m, 26H/Ar-H), 7.42-7.37 (m, 16H/Ar-H). UV-vis (DMF) $\lambda_{\text{max/nm}}$: 686 (4.30), 620 (4.05), 370 (4.30). MS (ESI), (m/z): Calculated: 1583.16; found: 1583.55 [M] $^{+}$.

2.5.5. {2,9,16,24-tetrakis[(4,5-diphenyl-4H-1,2,4-triazol-3-yl)sulfanyl]-29H,31H-phthalocyaninato(2-)- $\kappa^4 N^{29}, N^{30}, N^{31}, N^{32}$ }CoPc (**8**)

Yield: 0.22 g (% 25). FT-IR (ATR), ν/cm^{-1} : 3061 (Ar-CH), 1660-1597 (C=C/C=N), 1495-1394 (C-N/C-S). UV-vis (DMF) $\lambda_{\text{max/nm}}$: 670 (4.98), 608 (4.49), 340 (4.92). MS (ESI), (m/z): Calculated: 1576.68; found: 1576.55 [M] $^{+}$.

2.5.6. {2,9,16,24-tetrakis[(4,5-diphenyl-4H-1,2,4-triazol-3-yl)sulfanyl]-29H,31H-phthalocyaninato(2-)- $\kappa^4 N^{29}, N^{30}, N^{31}, N^{32}$ }MnPc (**9**)

Yield: 0.17 g (% 20). FT-IR (ATR), ν/cm^{-1} : 3061 (Ar-CH), 1598 (C=C/C=N), 1497-1387 (C-N/C-S). UV-Vis (DMF) $\lambda_{\text{max/nm}}$: 634 (4.83), 583 (4.20), 353 (4.68). MS (ESI), (m/z): Calculated: 1572.69; found: 1572.37 [M] $^{+}$.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic pathway used during the preparation of the starting materials (**3a** and **3b**) and MPcs (**4** and **9**) was already given in Fig. 1. The characterizations of the structures of new compounds have been achieved by ^1H and $^{13}\text{C-NMR}$, FT-IR, UV-Vis spectroscopy and mass spectral data.

The compounds **3a** and **3b** were prepared by the reaction between 4-nitrophthalonitrile and corresponding triazole containing starting material (**1a** and **1b**) in polar aprotic solvent acetone at room temperature in 9 h and silica gel column chromatography were used for purification. Unlike the work of Akçay et al. [22], in the reaction medium, triethylamine / acetone mixture was used instead of K_2CO_3 / DMF. As a result of the study, the yield of both products **3a** and **3b** increased. In addition, improvements were also made to the reaction temperature and time. In the study of Akçay et al., while the temperature and duration of the environment was 50 °C and 5 days, the duration and temperature in this study were realized at room temperature and 9 hours. Thus, an eco-friendly method has been developed that can be realized more efficiently and in a short time [23].

The disappearances of the SH stretching vibrations of **1a** and **1b** and the appearance of new vibrations at 2235 and 2233 cm^{-1} that belong to $\text{C}\equiv\text{N}$ groups prove the formation of **3a** and **3b** in terms of the IR spectral data. Furthermore, mass, ^1H and $^{13}\text{C-NMR}$ spectral data also demonstrate the structural confirmations of the mentioned compounds [25].

Since DMAE can be used as both solvent and base, DBU was not used in metal phthalocyanine synthesis. Unlike the work of Akçay

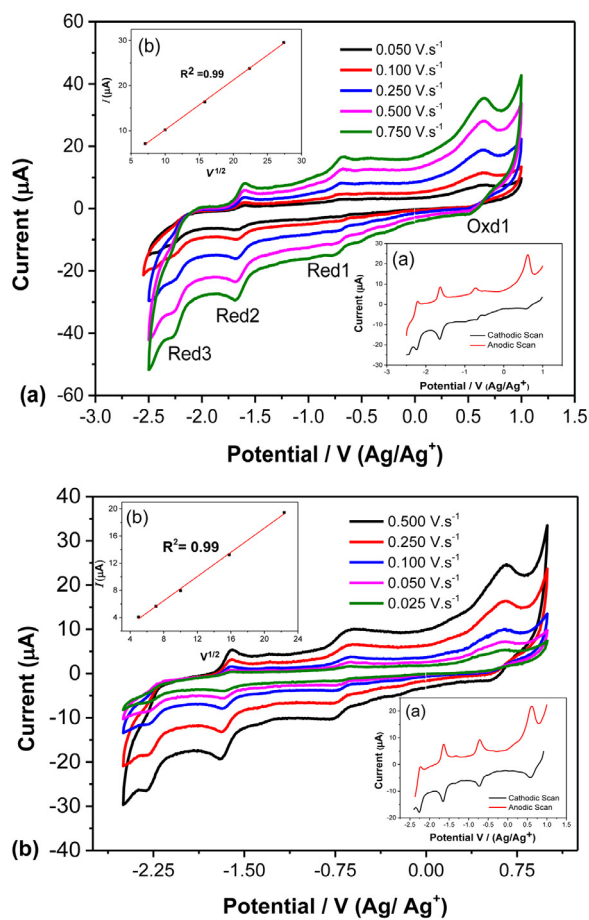


Fig. 6. CVs of **5** (a) and **8** (b) in DMF solution containing 0.2 M TBAP at scan rates between 0.025 and 0.500 V.s^{-1} . Inset a: SWVs of **5** and **8**. Inset b: the plots of I_p vs. scan rate v for the first reduction process. Conditions for SWV: pulse PH/PW 0.025 V for 0.01 s; step height 2.00 mV; scan rate 0.100 V.s^{-1} .

et al [22], It was tried for 15 hours instead of 24 hours. At the end of this period, almost the same, partially better yields were obtained.

The preparations of the new MPc derivatives (**4-9**) were performed by cyclotetramerization of the corresponding substituted phthalonitrile compounds (**3a** and **3b**) by corresponding metal salts in DMAE. The green colored products of the cyclotetramerization reactions were in four possible isomers that are C_{4h} , C_{2v} , C_s and D_{2h} as expected and no effort made to separate these mixtures due to unnecessary. The solubilities of all Pc complexes were soluble in common organic solvents such as THF, dichloromethane, chloroform, DMF, DMSO. The disappearances of $\text{C}\equiv\text{N}$ vibrations of compounds **3a** and **3b** are important proofs for the formation of the MPc derivatives (**4-9**) according to their IR spectral data. The $^1\text{H-NMR}$ spectra of ZnPcs (**4** and **6**) were very similar to those of

Table 2
Electrochemical half-wave potentials of CoPcs (**5** and **8**) and some selected phthalocyanines from literature

CoPcs	$\text{Pc}^{-3}/\text{Pc}^{-4}$	Reductions $\text{Pc}^{-2}/\text{Pc}^{-3}$	Oxidations $\text{Co}^{+2}/\text{Co}^{+}$	$\text{Co}^{+2}/\text{Co}^{+3}$	$\text{Pc}^{-2}/\text{Pc}^{-1}$	ΔE	References
	$^a E_{1/2}(\text{V})$	$^a E_{1/2}(\text{V})$	$^a E_{1/2}(\text{V})$	$^a E_{1/2}(\text{V})$	$^a E_{1/2}(\text{V})$	(V)	
5	-2.24	-1.64	-0.68	-	0.58	2.22	Tw
8	-2.25	-1.64	-0.69	-	0.57	2.21	Tw
CoPcOR	-	-1.45	-0.38	0.49	0.97	2.42	[34]
Co[(Et) ₄ Pc]	-	-1.45	-0.32	0.49	0.94	2.39	[35]

^a $E_{1/2}(\text{V}) = (E_{\text{pa}} + E_{\text{pc}})/2$

^b $\Delta E = E_{1/2}(\text{Pc}^{-2}/\text{Pc}^{-1}) - E_{1/2}(\text{Pc}^{-2}/\text{Pc}^{-3})$; tw: this work

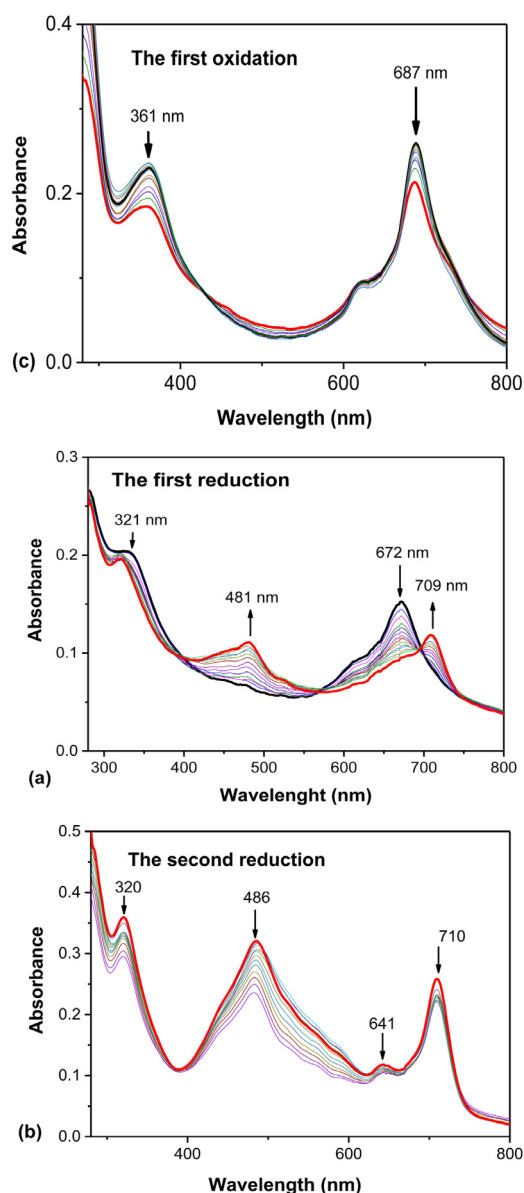


Fig. 7. Time-resolved UV-vis spectral changes of **8** during the oxidation ($E_{app} = 1.00$ V) (a), the first reduction ($E_{app} = -1.00$ V) (b), and the second reduction ($E_{app} = -1.80$ V) (c) in DMF solution containing 0.2 M TBAP in a thin-layer cell at a scan rate of 0.100 V s^{-1} .

their corresponding starting compounds (**3a** and **3b**) [22], however $^1\text{H-NMR}$ measurements of CoPcs (**5** and **8**) and MnPcs (**6**, **9**) could not be performed because of paramagnetic nature of these metal complexes [26]. On the other hand, mass spectral data of these complexes are satisfactory and supports the proposed structures (Fig. 2).

UV-Vis absorption spectroscopy is the most effective technique for proving the formation Pcs. Commonly Pcs display two strong absorption bands in their ground-state absorption spectra. They are designated as Q band (at around 600–750 nm) and B-band (at around 300–350 nm) [27]. The Q-bands of these MPc derivatives (**4**–**9**) were observed at 691, 671, 634, 686, 670 and 634 nm and B-bands were observed at 363, 335, 351, 370, 340 and 353 nm, respectively in DMF solutions at 1×10^{-5} M concentrations. It can be seen that the problem of aggregation is prevented by the connection of the triazole groups to the Pc skeleton in their spectra (Fig. 3).

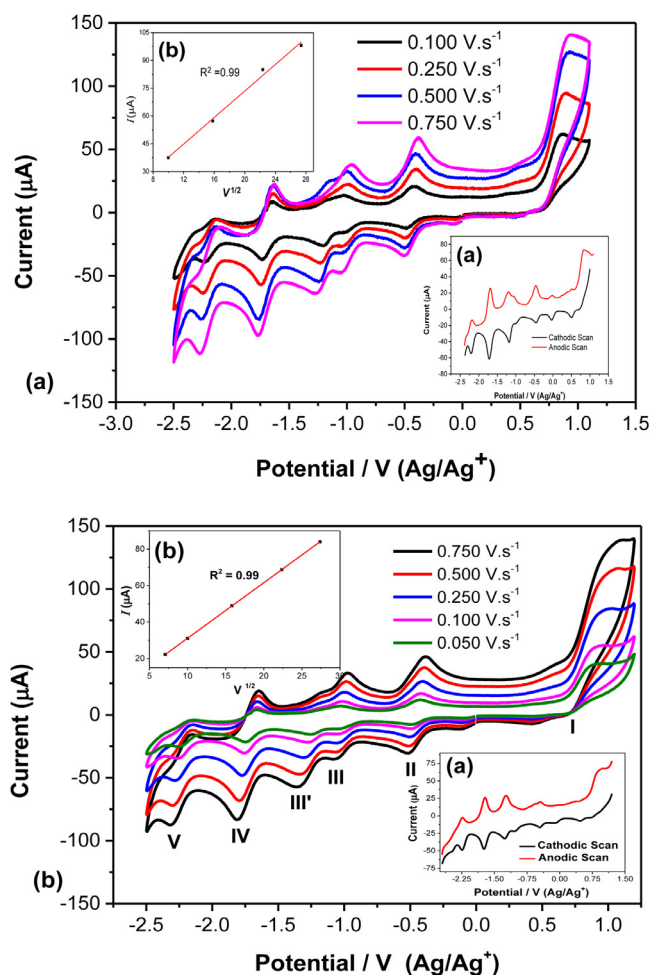


Fig. 8. CVs of **6** (a) and **9** (b) in DMF solution containing 0.2 M TBAP at scan rates between 0.050 and 0.750 V.s^{-1} . Inset a: SWVs of MnPcs (**6** and **9**). Inset b: the plots of I_p vs. scan rate v for the first reduction process. Conditions for SWV: pulse PH/PW 0.025 V for 0.01 s; step height 2.00 mV; scan rate 0.100 V.s^{-1} .

3.2. Evaluation of electrochemical measurements

The routine electrochemical behaviors of ZnPcs (**4** and **7**) were investigated by CV and SWV in the presence of 0.2 M tetra-*n*-butylammonium perchlorate ($n\text{-Bu}_4\text{NClO}_4$) as a supporting electrolyte in DMF (Fig. 4). Fig. 4 shows the CVs of **4** and **7** in the scan rates between 0.025 and 0.500 V.s^{-1} , where SWVs of **4** and **7** and the plots of I_p vs. square root of scan rate ($v^{1/2}$) for the first reduction process are represented as insets a and b, respectively.

As seen from Fig. 4, ZnPcs **4** displayed three well-defined reductions and two oxidations waves in DMF containing an Ag/Ag^+ electrode system, all of which are based on the Pc ring only because of the electroinactive nature of the Zn metal coordinated to the macrocycle [28–30]. All of the redox waves can be also seen from SWVs (inset a in Fig. 4). These waves (Red1, Red2, Red3, Oxd1 and Oxd2) are indicated as $\text{Pc}^{2-}/\text{Pc}^{3-}$, $\text{Pc}^{3-}/\text{Pc}^{4-}$, $\text{Pc}^{4-}/\text{Pc}^{5-}$, $\text{Pc}^{2-}/\text{Pc}^-$ and Pc^-/Pc^0 couples, respectively in Table 1. The differences between peak potentials of the first reduction and the first oxidation processes, the first reduction and the second reduction, and the first oxidation and second oxidation processes (ΔE) for **4** and **7** are in accord with those of the some substituted ZnPcs (Table 1).

The cathodic and anodic currents for the reduction couples in DMF each increased in direct proportion to the square root of scan rate between 0.025 and 0.500 V.s^{-1} , suggesting that the redox re-

Table 3

Electrochemical half-wave potentials of MnPcs (6 and 9) and some selected phthalocyanines from literature

MnPcs	Pc ⁻⁴ /Pc ⁻⁵	Reductions Pc ⁻³ /Pc ⁻⁴	Oxidations Pc ⁻² /Pc ⁻³	Mn ⁺² /Mn ⁺³	Pc ⁻² /Pc ⁻¹	^a ΔE	^b ΔE	Reference
6	-2.18	-1.69	-1.03 (-1.19)*	-0.45	0.77	1.80	0.66	tw
9	-2.20	-1.69	-1.03 (-1.17)*	-0.46	0.80	1.83	0.66	tw
(Phthalocyaninato)Mn(II)	-	-1.46	-0.69	-0.14	0.87	1.66	0.77	[40]
[NhtMnPc]	-	-1.31	-0.67	-0.055	-	-	0.64	[28]

$$E_{1/2}(V) = (E_{pa} + E_{pc})/2$$

$$^a \Delta E = E_{1/2}(\text{Pc}^{-2}/\text{Pc}^{-1}) - E_{1/2}(\text{Pc}^{-2}/\text{Pc}^{-3})$$

$$^b \Delta E = E_{1/2}(\text{Pc}^{-2}/\text{Pc}^{-3}) - E_{1/2}(\text{Pc}^{-3}/\text{Pc}^{-4})$$

* aggregated/disaggregated form; tw: this work

actions in solution are controlled by diffusion (inset b in Fig. 4) [31–34].

To further confirm the electrochemical processes of **4** illustrated by CV and SWV, UV–vis spectral changes of the electro-reduced species were also recorded using *in situ* spectroelectrochemical techniques in a thin-layer cell at applied potentials ($E_{app} = -1.40$, -1.89 V, and -2.40 V) in DMF solution containing 0.2 M TBAP (Fig. 5).

The UV–vis spectral changes upon the first reduction of **4** showed that the main Q-band at 685 nm disappeared in the course of reduction process and some new bands appeared at 430 nm, 580 nm, and 969 nm in the region of MLCT, illustrating the reduction of the neutral **4** [$\text{Zn}^{2+}\text{Pc}^{2-}$] to [$\text{Zn}^{2+}\text{Pc}^{3-}$] species (Fig. 5a). It is clear that there are no aggregated species in the case of neutral and reduced species in DMF solution. The band observed at 969 nm indicates that the reduced species upon the first reduction of [$\text{Zn}^{2+}\text{Pc}^{3-}$] exist as a monoanionic form in DMF [28]. The decrease in the bands at 670 and 969 nm and observation of a new band at 551 nm are assigned to the formation of dianionic [$\text{Zn}^{2+}\text{Pc}^{4-}$]²⁻ species (Fig. 5b). These spectral changes observed for [$\text{Zn}^{2+}\text{Pc}^{3-}$] and [$\text{Zn}^{2+}\text{Pc}^{4-}$]²⁻ are also typical of singly and doubly reduced monophthalocyanines based on a macrocyclic ring [28,35–37]. We could also observe clear spectral changes corresponding to the third reduction process ([$\text{Zn}^{2+}\text{Pc}^{5-}$]²⁻) at the applied potential ($E_{app} = -2.40$ V), which shows stability of thirdly reduced species during the electrolysis. However, in the *in situ* spectroelectrochemistry study, the oxidation product ($E_{app} = 1.00$ V) was degraded during electrolysis.

The routine electrochemical behaviors of CoPcs (**5** and **8**) were also investigated by CV and SWV in the presence of 0.2 M tetra-*n*-butylammonium perchlorate ($n\text{-Bu}_4\text{NClO}_4$) as a supporting electrolyte in DMF (Fig. 6). Fig. 6 shows the CVs of **5** and **8** in the scan rates between 0.025 and 0.500 V.s⁻¹, where SWVs and the plots of I_c vs. square root of scan rate ($v^{1/2}$) for the first reduction process are represented as insets a and b, respectively. The cathodic and anodic currents for the reduction couples in DMF each increased in direct proportion to the square root of scan rate between 0.025 and 0.500 V.s⁻¹, suggesting that the redox reactions in solution are controlled by diffusion.

As seen from Figs. 6a and 6b, compounds **5** and **8** displayed three reductions and one oxidation waves in DMF containing an Ag/Ag⁺ electrode system. These redox waves are based on both the Pc ring and electroactive nature of the Co metal. All of which can be also seen from SWV (inset a). In a coordinating solvent like DMF, the first oxidation process occurs at the central metal in CoPc complexes. However, in this study, metal-based oxidation peak was not observed. The process Oxd (at 0.58 V versus Ag/Ag⁺) is in the range for the oxidation of the ring in CoPc complexes and is thus assigned to [$\text{Co}^{2+}\text{Pc}^{2-}$] / [$\text{Co}^{2+}\text{Pc}^{-}$]⁺ process. The data obtained in this work and some selected data from literature are tabulated in Table 2. The differences between peak potentials of the second reduction ([$\text{Co}^{2+}\text{Pc}^{2-}$] / [$\text{Co}^{2+}\text{Pc}^{3-}$]²⁻) and the oxidation

([$\text{Co}^{2+}\text{Pc}^{2-}$] / [$\text{Co}^{2+}\text{Pc}^{-}$]⁺) processes (ΔE) for **5** and **8** are in accord with those some substituted CoPcs (Table 2) [37,38]. Red1 at -0.68 V versus Ag/Ag⁺ may thus be assigned to metal reduction [$\text{Co}^{2+}\text{Pc}^{2-}$] / [$\text{Co}^{2+}\text{Pc}^{2-}$]⁻ process [36,39]. The remaining redox processes are assigned as follows: Red2 ([$\text{Co}^{2+}\text{Pc}^{2-}$] / [$\text{Co}^{2+}\text{Pc}^{3-}$]²⁻) (-1.64 V) and Red3 ([$\text{Co}^{2+}\text{Pc}^{3-}$]²⁻ / [$\text{Co}^{2+}\text{Pc}^{4-}$]³⁻) (-2.24 V). The redox processes of compound **8** are assigned as follows: the Oxd process at 0.57 V, Red1 at -0.68 V, Red2 at -1.64 V and Red3 at -2.25 V (Table 2).

The spectroelectrochemical studies of the phthalocyanines facilitate the understanding of the nature of the redox processes which may occur at either the central metal atom or the phthalocyanine ring, but this cannot usually be distinguished by using electrochemistry alone [39]. To further confirm the electrochemical processes of compound **8** illustrated by CV and SWV, UV–vis spectral changes of the electro-oxidized and the electro-reduced species were also recorded using *in situ* spectroelectrochemical techniques in a thin-layer cell at applied potentials ($E_{app} = 1.00$, -1.00 , and -1.80 V) in DMF solution containing 0.2 M TBAP (Fig. 7).

UV–vis spectral changes upon the oxidation **8** in DMF are shown in Fig. 7a. The decreases in the intensity of the Q (687 nm) and B bands (361 nm) are observed. The broad, low-intensity spectrum is very similar in appearance to those reported for the ring oxidations of phthalocyanines and metalloporphyrins to form the phthalocyanine and porphyrin cation radical species [36]. Fig. 7b represents *in situ* UV–vis spectral changes during the first reduction of **8** at -0.69 V versus Ag/Ag⁺. The Q band at 672 nm decreases and shifts 709 nm, while a new band at 481 nm appears. The band at 481 nm and shifting of the Q band indicate the formation of [$\text{Co}^{2+}\text{Pc}^{2-}$]⁻ species, confirming the CV assignment of the Red1 to [$\text{Co}^{2+}\text{Pc}^{2-}$] / [$\text{Co}^{2+}\text{Pc}^{2-}$]⁻ process [39]. The spectrum is typical of a [$\text{Co}^{2+}\text{Pc}^{2-}$]⁻ species, characterized by the appearance of strong band at 481 nm, assigned as a metal-to-ligand charge transfer from $\text{Co}^{2+}\text{Pc}^{2-}$ [$d(xz; yz) \rightarrow \pi(1b1u) \text{Pc}^{2-}$], a red shift, and an decrease in intensity of the Q band centered at 672 nm. The well-defined UV–Vis spectral changes during the second reduction of **8** are shown in Fig. 7c where it was observed a decrease in intensity of the Q and B bands relative to that of the first reduction product [39].

Manganese phthalocyanine (MnPc) complexes have very interesting electrochemistry due to the fact that Mn exhibits variable oxidation states ranging from Mn⁺ to Mn⁴⁺ in MnPc complexes [40–43]. MnPcs have three forms of namely manganese(2+) phthalocyanine ([Mn²⁺Pc]), manganese(3+) phthalocyanine ([Mn³⁺Pc]) and μ -oxo-manganese(3+) phthalocyanines ([Mn³⁺Pc-O-PcMn³⁺]), can be formed depending on the reaction conditions [31]. Fig. 8 shows CV and SWV responses of **6** and **9** in DMF containing an Ag/Ag⁺ electrode system, which displays three well-defined reductions and two oxidations waves based on either the Pc ring or electroactive Mn center. The oxidation waves (II and I) of **6** and **9** are assigned to metal-based oxidation process (II) corresponding to [$\text{Mn}^{2+}\text{Pc}^{2-}$] / [$\text{Mn}^{3+}\text{Pc}^{2-}$]⁺ couples (at -0.45

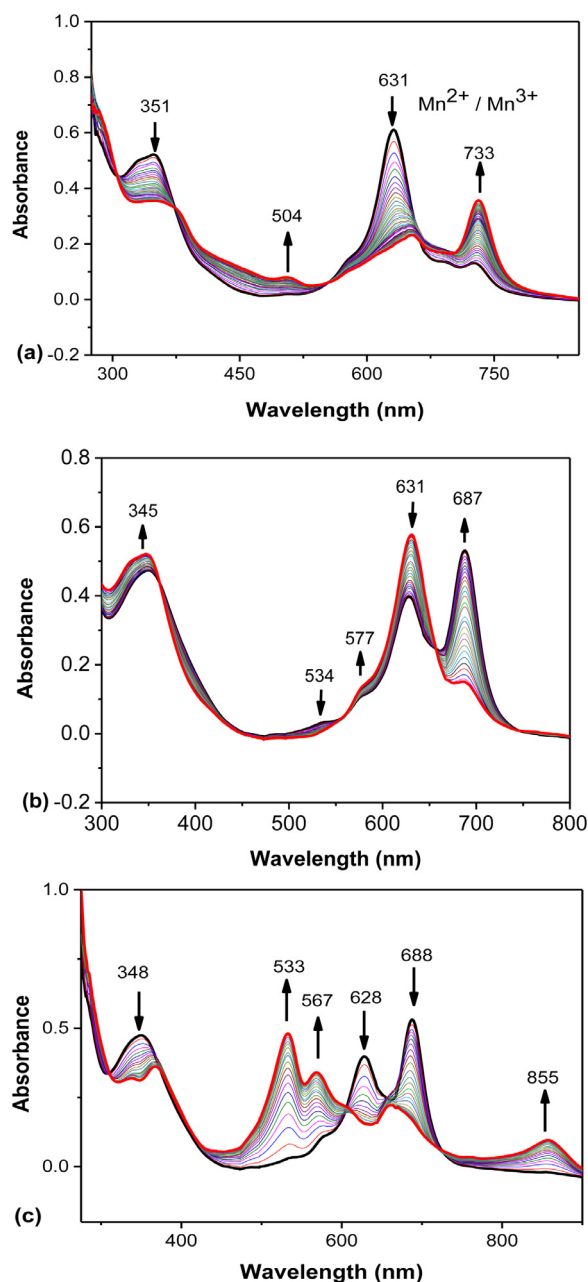


Fig. 9. Time-resolved UV-vis spectral changes of **6** and **9** during the first oxidation ($E_{app} = 0.14$ V) (a), the first reduction ($E_{app} = -1.50$ V) (b), and the second reduction ($E_{app} = -2.10$ V) (c) in DMF solution containing 0.2 M TBAP in a thin-layer cell at a scan rate of 0.100 V s^{-1} .

V for **6** and -0.46 V for **9**) and Pc ring-based oxidation process (I) belonging to $[Mn^{3+}Pc^{-2+}]/[Mn^{3+}Pc^{-2+}]^{2+}$ couples (at 0.77 V for **6** and 0.80 V for **9**). The others are assigned to the Pc ring-based reduction processes related with $[Mn^{2+}Pc^{2-}]/[Mn^{2+}Pc^{3-}]^{-}$, $[Mn^{2+}Pc^{3-}]/[Mn^{2+}Pc^{4-}]^{2-}$ and $[Mn^{2+}Pc^{4-}]^{2-}/[Mn^{2+}Pc^{5-}]^{3-}$ couples, the redox potentials of which are presented and compared with some selected MnPcs [30,43] along with their potential differences ($\Delta E: E_{1/2}(Pc^{-2}/Pc^{-1}) - E_{1/2}(Pc^{-2}/Pc^{-3})$ and $E_{1/2}(Pc^{-2}/Pc^{-3}) - E_{1/2}(Pc^{-3}/Pc^{-4})$) in Table 3. It is seen that the redox processes of compounds **6** and **9** are in accordance well with those of the selected MnPcs. All of the redox waves can be also seen from SWVs (inset a in Fig. 8). As observed in ZnPcs and CoPcs, the cathodic and anodic currents for the reduction couples in DMF each increased in direct proportion to the square root of scan

rate between 0.050 and 0.750 V s^{-1} , suggesting that the redox reactions in solution are controlled by diffusion (inset b in Fig. 8).

Fig. 9a shows *in situ* UV-vis spectral changes observed upon controlled potential oxidation of **6** ($E_{app} = 0.14$ V for the first oxidation process) in DMF/TBAP electrolyte system. As shown in Fig. 9a, the Q band at 631 nm considerably decreases in intensity, while the bands at 733 nm and 504 nm increase in intensity, which are clearly assign to formation of the metal-based oxidation species $[Mn^{3+}Pc^{-2+}]^{+}$ [31]. Figs. 9b and 9c show *in situ* UV-vis spectral changes observed upon controlled potential reductions of **6** ($E_{app} = -1.50$ and -2.50 V for the first and the second reduction processes, respectively). The observed spectral changes were similar to what were observed for MnPcs [31].

4. Conclusions

In this study, new Zn^{2+} , Co^{2+} and Mn^{2+} phthalocyanine complexes containing substituted 1,2,4-triazole groups on peripheral positions have been synthesized. The structural characterizations of these complexes have been succeeded with the help of FT-IR NMR, MALDI-TOF, UV-Vis methods. The use of triethylamine and acetone combination in the synthesis of nitrile structures **3a** and **3b** was applied and both increased yield of products and shortened reaction time compared to classical synthesis of nitrile structures. The electrochemical characteristics of new phthalocyanines complexes were also investigated by cyclic voltammetry (CV), square wave voltammetry (SWV) and *in situ* UV-vis spectroelectrochemistry to understand electron transfer mechanism of the complexes in DMF, thereby revealing their possible applications.

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.

CRediT authorship contribution statement

Rıza Bayrak: Investigation, Methodology, Writing - review & editing. **Seçil Kırılancık Ataşen:** Investigation, Methodology, Writing - original draft. **İsmail Yılmaz:** Investigation, Methodology, Writing - review & editing. **İzzet Yalçın:** Investigation, Methodology, Writing - original draft. **Murat Erman:** Investigation, Methodology, Writing - original draft. **Yasemin Ünver:** Investigation, Methodology, Writing - original draft. **İsmail Değirmencioglu:** Investigation, Methodology, Writing - review & editing.

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