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Piperazin Türevi İçeren Yeni Çinko (II) ve Kobalt (II) Ftalosiyaninlerin Sentezi, Spektroskopik ve Elektrokimyasal Özelliklerinin İncelenmesi

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Öz: Bu çalışmada, ter-butil4-(4-(3,4-disiyanofenoksi)fenil)piperazin-1-karboksilat grubu ihtiva eden yeni Zn(II) ve kobalt(II) ftalosiyanin kompleksleri elde edilerek, yapıları karakterize edilmiştir. Her iki kompleks te, DMF, DMSO, THF ve $CHCl_3$ gibi polar çözücülerde çözünmektedir. Komplekslerin farklı çözücü ve konsantrasyonlarda agregasyon özellikleri de incelenmiştir. DMF, DMSO ve THF çözücülerinde 1.10^{-5} M konsantrasyona kadar her iki kompleksinde agregasyona uğramadığı, fakat $CHCl_3$ çözücüsünde agregasyona uğradıkları gözlenmiştir. Ayrıca komplekslerin elektrokimyasal özellikleri dönüşümlü voltametri ve kare dalga voltametri teknikleriyle incelenmiştir.

Anahtar kelimeler: Ftalosiyanin, Agregasyon, Zn(II) kompleks, Co(II) kompleks, Elektrokimya

Novel Zinc(II) and Cobalt(II) Phthalocyanines Bearing Piperazine Derivative: Spectroscopic and Electrochemical Properties

Abstract: In this manuscript, novel zinc (II) and cobalt (II) phthalocyanine complexes (ZnPc and CoPc) modified with tert-butyl 4-(4-(3,4-dicyanophenoxy)phenyl)piperazine-1-carboxylate substituents have been prepared and characterized. These complexes are solouble in many organic solvents such as DMF, DMSO, THF and $CHCl_3$. Aggregation properties of complexes were examined in different solvents and different concentrations. Spectroscopic evaluation of the Pcs showed a monomeric behaviour evidenced by a single Q band for ZnPc and CoPc up to $1 .10^{-5}$ mol dm^{-3} in DMF, DMSO and THF as typical of metallo Pcs. In all studied organic solvents except $CHCl_3$, ZnPc and CoPc complexes were non-aggregated. Cyclic and square wave voltammetries were used to evaluate the electrochemical properties of the synthesized complexes. Cyclic voltammetry showed two reduction couples and one oxidation peak for the two phthalocyanine complexes.

Keywords: Phthalocyanine, Aggregation, Zn(II) complex, Co(II) complex, Electrochemistry

1. Introduction

The study of Phthalocyanine compounds is one of the growing areas in macrocyclic chemistry (Arul et al., 2016; Shumba and Nyokong, 2016; Yanık et al., 2016) owing to their increased stability, improved spectroscopic characteristics and diverse coordination properties. They can form different types of coordination compounds with metal ions due to several electron rich donor centers with unique structural and chemical properties. Considerable efforts have been devoted to the rational design and synthesis of functional phthalocyanines (Pcs) and their complexes, which are widely employed in the catalysis (Karaca, 2016; Medyouni et al., 2016) biological and environmental applications (Abramczyk et al., 2017; Wu et al., 2016), sensors (Klyamer et al., 2016;

Kumar et al., 2015), medicine (Cong et al., 2015), dyes (Belekoukia et al., 2016; Sokolov et al., 2016), organic solar cells (Fukui et al., 2014; Williams et al., 2014) and photosensitizer for photodynamic therapy (PDT) (Duchi et al., 2016; Goksel, 2016; Oluwole et al., 2016; Pucelik et al., 2016). The low solubility and aggregation tendency of phthalocyanine molecules, has hindered the study of their structures and reactions (Shivashimpi et al., 2014). The attachments of the different functional groups to the Pcs increases the solubility and hinder the aggregation tendency, leading to significant advances in research.

In this study, two new Zn(II) and Co(II) complexes (ZnPc and CoPc) were obtained, and they were structurally and spectrally characterized, in detail for the first time to confirm the proposed structure using NMR (^{1}H, ^{13}C), FT-IR, UV–Vis, and elemental analysis. Electrochemical properties of the metal complexes were investigated in DMSO solution containing 0.1 M tetrabutylammonium tetrafluoroborate (TBATFB) as supporting electrolyte by cyclic and square wave voltammetry. Within our knowledge, this is the first paper which contains the synthesis, characterization, and redox properties of ZnPc and CoPc compounds.

2. Materials and methods

All chemicals were purchased from commercial suppliers unless otherwise specified. 4-Nitrophthalonitrile (Young and Onyebuagu, 1988) and *tert*-Butyl 4-(4-hydroxyphenyl)piperazine-l-carboxylate was prepared according to the literature procedures (Franc et al., 2009) and purified according to well-known literatures. The elemental analyses (C, H and N) were performed using a LECO-932 CHNSO model analyzer. NMR experiments were performed with a Varian Unity INOVA 500 spectrometer using a 5 mm ID-PFG probe at 298.15 K. Samples were dissolved in DMSO. Chemical shifts were reported in ppm relative to TMS for ^{1}H NMR and ^{13}C NMR spectra. The FT-IR spectra of solid samples were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer (Universal/ATR Sampling Accessary). UV-Vis spectra were obtained using Shimadzu UV-1700 visible recording spectrophotometers. Melting points were determined with an electrothermal apparatus and were not corrected.

2.1. Synthesis of Boc-Pip

tert-Butyl4-(4-(3,4-dicyanophenoxy) phenyl) piperazine-1-carboxylate (Boc-Pip) was synthesized modification of the literature procedures (Zheng et al., 2013). A mixture of *tert*-Butyl 4-(4- hydroxyphenyl) piperazine-l-carboxylate (1.39 g, 5.0 mmol), 4-nitrophthalonitrile (0.87 g, 5.0 mmol), and anhydrous K_2CO_3 (1.38 g, 10 mmol) in DMF (20 mL) was stirred at 40 °C for 48 h. The reaction mixture was poured into ice water (200 mL) to give light red precipitate, which was collected by filtration, washed with water until pH 7 and dried in vacuum.

FT-IR (ν/cm^{-1}): 3073 (Ar-H); 2976, 2863, 2827 (CH_3, CH_2); 2228 (CN); 1689 (C=O); 1597, 1566, 1504, 1485 (C=C); 1230 (C-N); 1170 (C-O).

^{1}H NMR (400 MHz, DMSO-d_6, ppm, δ): 8.04 (d, 1H); 7.67 (d, 1H); 7.25-7.28 (dd, 1H); 7.02-7.07 (m, 4H); 3.44 (t, 4H); 3.09 t, 4H); 1.40 (s, 9H).

^{13}C NMR (125 MHz, DMSO-d_6, δ): 28.49, 48.90, 79.46, 107.81, 115.90, 116.43, 116.97, 118.02, 121.48, 121.71, 122.31, 136.67, 146.31, 149.36, 154.27, 162.48.

2.2. Synthesis of ZnPc

A mixture of compound Boc-Pip (0.55 g, 1.5 mmol), anhydrous $Zn(CH_3COO)_2$ (0.23 g, 1.5 mmol) and a catalytic amount of 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) in dry DMF (1 mL) was refluxed for 48 h. After cooling to room temperature, the reaction mixture was precipitated by adding methanol. The product was separated by filtration as a green solid which was washed several times with methanol and water. The residue was purified by a silica gel column chromatography using $CHCl_3/CH_3OH$ (14:1, v/v) as eluent. The obtained green solid was further purified by chromatography again using CH_2Cl_2/CH_3OH (10:1, v/v) as eluent to give a dark-green solid ZnPc (0.155 g, 7.36%).

FT-IR (ν/cm^{-1}): 3043 (Ar-H); 2972, 2917, 2850, 2816 (CH_3, CH_2); 1691 (C=O); 1610 (C=N); 1505, 1466 (C=C); 1220 (C-N); 1161 (C-O).

^{1}H NMR (400 MHz, DMSO-d_6, ppm, δ): 7.54-7.10 (m, 28H); 3.50 (t, 14H); 3.13 (t, 16H); 1.42 (s, 36H).

^{13}C NMR (125 MHz, DMSO-d_6, ppm, δ): 28.68, 49.55, 79.61, 109.99, 117.96, 118.48, 118.81, 121.47, 121.65, 121.92, 123.68, 139.61, 148.71, 151.29, 154.47, 161.45.

2.3. Synthesis of CoPc

A mixture of compound Boc-Pip (0.55 g, 1.5 mmol), anhydrous $CoCl_2$ (0.195 g, 1.5 mmol) and a catalytic amount of 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) in dry DMF (1 mL) was refluxed for 24 h. After cooling to room temperature, the reaction mixture was precipitated by adding water. The product was separated by filtration as a green solid which was washed several times with water. The residue was purified by a silica gel column chromatography using $CHCl_3/CH_3OH$ (10:1, v/v) as eluent. A green band was collected and concentrated to give a crude product, which was purified by chromatography again using CH_2Cl_2/CH_3OH (10:1, v/v) as eluent.

FT-IR (ν/cm^{-1}): 3042 (Ar-H); 2971, 2919, 2885, 2816 (CH_3, CH_2); 1689 (C=O); 1610 (C=N); 1505, 1463 (C=C); 1221 (C-N); 1162 (C-O).

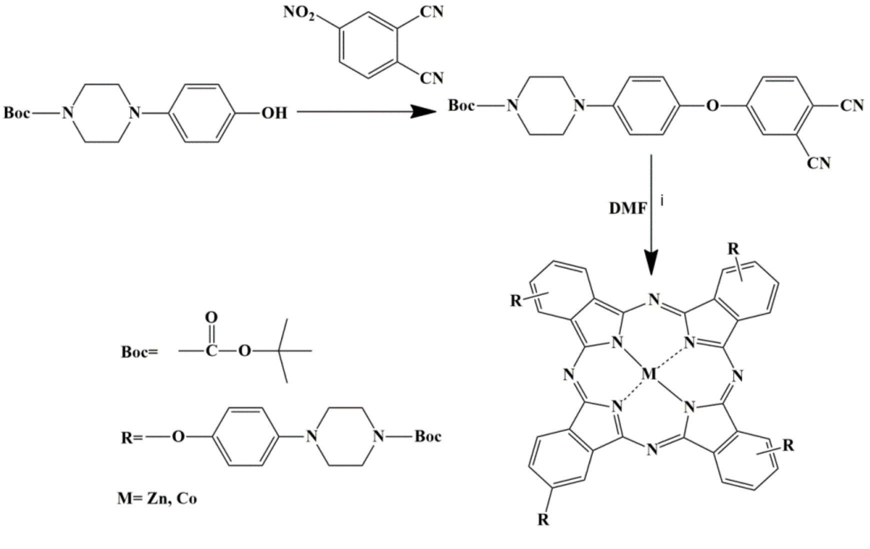
2.4. Electrochemical measurements

All electrochemical experiments were performed using a Gamry Reference 600 workstations (Gamry, Pennsylvania, USA) electrochemical analyzer (Model 600C series) equipped with BAS C3 cell stand. The working electrode was a bare, glassy carbon disk (BAS Model MF-2012) with a geometric area of 0.027 cm^2. The reference electrode was Ag/Ag$^+$ (0.01 M) in nonaqueous media, and the counter electrode was a Pt wire. The glassy carbon electrodes were prepared by first polishing them first with fine, wet emery papers (grain size 4000) (Buehler, Lake Bluff, IL, USA) and then 0.1 µm and 0.05 µm alumina slurry on polishing pads (Buehler, Lake Bluff, IL, USA) in order to give them a mirror-like appearance. The electrodes were sonicated for 5 min in water and in a 50:50 (v/v) isopropyl alcohol and acetonitrile (IPA+MeCN) solution purified over activated carbon. Prior to the electrochemical experiments, the electrodes were dried with an argon gas stream, and the solutions were purged with pure argon gas (i.e., 99.999%) for at least 10 minutes; additionally, an argon atmosphere was maintained over the solution during the experiments.

3. Results and discussion

3.1. Synthesis and Characterization

The *tert*-Butyl 4-(4-hydroxyphenyl) piperazine-l-carboxylate substituted phthalonitrile derivative (Boc-Pip) was obtained by reaction of tert-Butyl 4-(4-hydroxyphenyl) piperazine-l-carboxylate with 4-nitrophthalonitrile in the presence of K_2CO_3 (Scheme 1). The reaction was carried out in DMF.



Scheme 1. Synthesis of ZnPc and CoPc; i: DBU, $Zn(CH_3COO)_2$ or $CoCl_2$

Phthalonitrile derivative (Boc-Pip) was respectively treated with the zinc(II) acetate or cobalt (II) chloride in DMF in the presence of DBU to afford corresponding tetra-substituted phthalocyanine derivatives (ZnPc and CoPc) (Scheme 1). The ZnPc and CoPc were washed with methanol, water and ethanol and then were purified by column chromatography by using chloroform / methanol or dichloromethane / methanol as eluent. ZnPc and CoPc have good solubility in many polar organic solvents, such as DMSO, DMF, THF and $CHCl_3$. Their chemical structures were fully characterized by elemental analysis, FT-IR, ^{1}H NMR, ^{13}C NMR. The FT-IR spectrum of Boc-Pip, CN stretching peak was seen at 2228 cm^{-1}. This peak disappeared in the case of ZnPc and CoPc, indicative of phthalocyanine formation. The $C–H_{arom}$ and $C–H_{aliph}$ vibrations were observed at about 3043-3073 cm^{-1} and 2976-2816 cm^{-1}, respectively.

The ^{1}H NMR spectra of Boc-Pip (Fig. S1) and ZnPc (Fig. S2) were recorded in DMSO-d_6. In the ^{1}H-NMR spectra of Boc-Pip, a singlet signal at 8.89 ppm concerning the -OH group disappeared, and new chemical shifts at about 7.25-8.04 ppm was observed that could be assigned to the new aromatic ring. The chemical shifts of $N–CH_2$ protons were observed at about 3.44-3.50 and 3.09-3.13 ppm as triplets for Boc-Pip and ZnPc.

The ^{1}H NMR and ^{13}C NMR spectra of ZnPc are broader than the corresponding NMR signals in the starting dinitrile because of the aggregation of phthalocyanine cores (Bilgin et al., 2007; Kantar et al., 2015)

The ^{13}C-NMR spectra of Boc-Pip (Fig. S3) and ZnPc (Fig. S4) show 16 different carbon atoms. In other respects, ^{1}H NMR spectra and ^{13}C NMR of CoPc could not be measured due to the paramagnetic cobalt(II) center (Saka et al., 2013). The detailed information belonging to the chemicals shifts was given in the experimental section.

Spectroscopic evaluation was performed in several solvents such as, DMSO, DMF, THF and $CHCl_3$. In the UV-vis spectra, ZnPc (Fig. 1) and CoPc (Fig. 2) show an intense single Q band absorption of π-π* transition at around 678-683 nm and 664-673 nm respectively in the pure solvents. B (Soret) bands of the complexes were observed in the UV region at about 350 nm. The two complexes showed similar absorption features in solutions.

3.2. Aggregation studies

The aggregation properties of the phthalocyanines ZnPc and CoPc were investigated at different concentrations ranging from 1.10^{-6}-16.10^{-6} M in DMSO, DMF, THF and $CHCl_3$. The results are given in Table 1. The UV-Vis spectra of ZnPc and CoPc compounds in DMSO, DMF, THF (Fig. 1,2) exhibit an intense and sharp Q-band at about 673-683 nm. But in

$CHCl_3$ solvent, the splitting of Q band was observed at 720 and 692 nm for ZnPc, 604, 667 and 720 nm for CoPc indicating the structure with non-degenerate D_{2h} symmetry of metal free. The results in DMF solutions investigated at different concentrations is given as an example in Fig. 3 and 4. The Q-band strictly obeys the Lambert-Beer law. The results in DMSO and THF solutions is given in Fig. S5-S8.

Table 1. UV–Vis results in various solvents

Compound	Solvent	Q-Band λ_{max},(nm)	log ε	B-Band λ_{max},(nm)	log ε
ZnPc	DMSO	683	5.05	353	4.67
ZnPc	DMF	681	4.83	353	4.38
ZnPc	THF	678	5.04	348	4.68
ZnPc	$CHCl_3$	692, 720	3.65, 3.67	370	3.80
CoPc	DMSO	664	4.68	333	4.48
CoPc	DMF	667	4.64	327	4.54
CoPc	THF	673	4.19	353	3.98
CoPc	$CHCl_3$	604, 667,720	4.55	350	4.23

3.3. Electrochemical studies

Cyclic voltammetry (CV) is a powerful method for investigating the electrochemical properties. The electrochemical properties of metallophthalocyanines have been studied extensively for their possible applications, including organic conductors, chemical sensors, electrocatalysts, and electrochromic materials (Prakash Singh et al., 2010). CV and Square Wave Voltammetry (SWV) experiments were performed for ZnPc and CoPc in DMSO using a GCE, a Pt gauze counter electrode and an Ag/AgCl reference electrode at ambient temperature. The cyclic and square wave voltammograms of ZnPc and CoPc are given in Figs. 5-6 and Figs. 7-8, respectively. The experimental results of electrochemical analyses and assignments are given in Table 2. The voltammograms given in Fig. 5 and Fig 7 were recorded at 100 mV s^{-1} with in the 0 V to -1.5 V potential window, and demonstrated two pair of symmetric peaks,

According to the ΔE_p values, ZnPc gives two quasi-reversible reduction (R_1 at -0.78 V, ΔE_p = 130 mV and R_2 at -1.18 V, ΔE_p = 140 mV), and one irreversible oxidation reactions (Fig. S9, Fig. S10) (O_1 at 0.74 V). The other complex, CoPc, behaved similarly. These two reduction couples are connected with the ring reduction processes, namely $[M(II)Pc(-2)]$ / $[M(II)Pc(-3)]^-$ and $[M(II)Pc(-3)]^-$/ $[M(II)Pc(-4)]^{2-}$ (M: Zn, Co) respectively (Acar et al., 2014; Çakır et al., 2015; Ömeroğlu et al., 2014). Also, the peak currents increased linearly with the square root of the scan rates for ZnPc (Fig. 10) and CoPc (Fig. 11).

Table 2. Voltammetric results in DMSO–TBATFB

Compound	Redox couple	Label	E_{pa} (V)	E_{pc} (V)	ΔE_p (mV)	$E_{1/2}$ (V)^a
ZnPc	$[Zn(II)Pc(-2)]$ / $[Zn(II)Pc(-3)]^-$	R_1	-0.84	-0.71	130	-0.78
ZnPc	$[Zn(II)Pc(-3)]^-$/ $[Zn(II)Pc(-4)]^{2-}$	R_2	-1.11	-1,25	140	-1.18
CoPc	$Co(II)Pc(-2)$ / $[Co(II)Pc(-3)]^-$	R_1	-0.50	-0.22	280	-0.36
CoPc	$[Co(II)Pc(-3)]^-$/ $[Zn(II)Pc(-4)]^{2-}$	R_2	-1.32	-1.23	90	-1.28

E_{pa} (anodic peak potential), E_{pc} (cathodic peak potential),

^{a} $E_{1/2} = (E_{pa}+E_{pc})/2$ for reversible or quasi-reversible processes.

4. Conclusion

We have described the preparation, spectroscopic and electrochemical studies of novel zinc (II) and cobalt (II) phthalocyanine compounds (ZnPc and CoPc) modified with four tert-butyl 4-(4-(3,4-dicyanophenoxy)phenyl)piperazine-1-carboxylate moieties. Spectroscopic evaluation of the Pcs showed a monomeric behaviour in DMF, DMSO and THF. In all studied organic solvents except $CHCl_3$, ZnPc and CoPc complexes were non-aggregated. The redox behaviour was showed on the ring centered reduction processes for all complexes.

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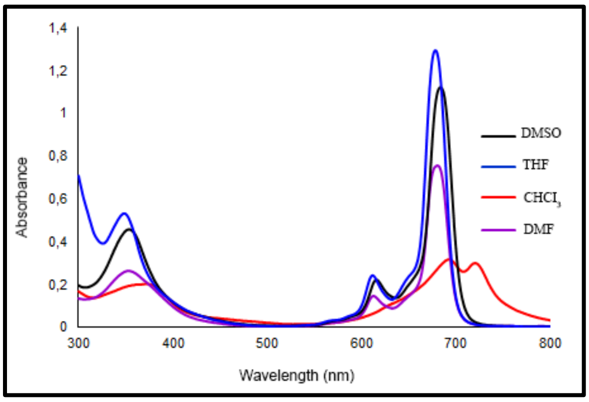

Fig.1. UV–Vis spectrum of 1.10^{-5} M ZnPc in DMSO, THF, $CHCl_3$ and DMF

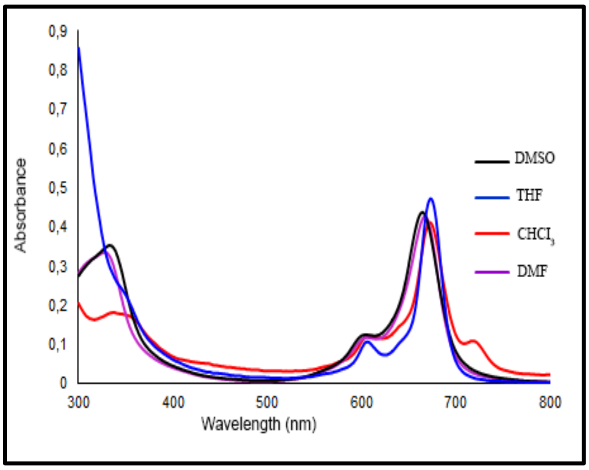

Fig.2. UV–Vis spectrum of 1.10^{-5} M CoPc in DMSO, THF, $CHCl_3$ and DMF

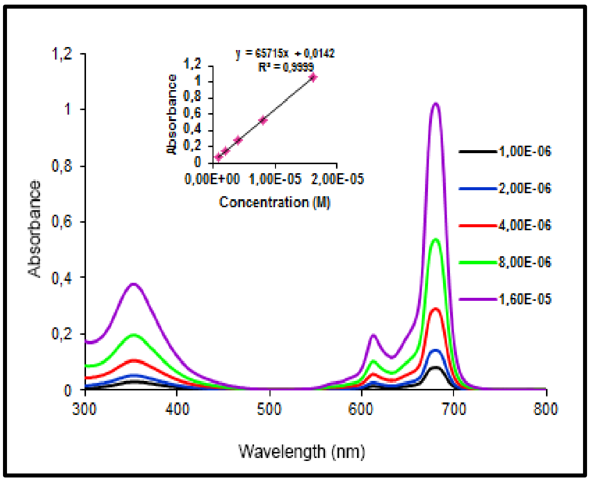

Fig. 3. UV-Vis spectrum of ZnPc in DMF

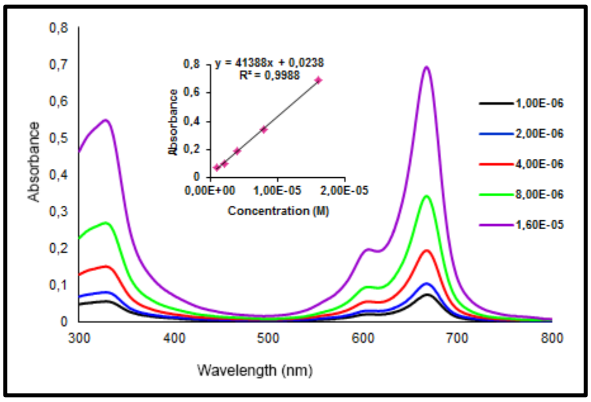

Fig. 4. UV-Vis spectrum of CoPc in DMF

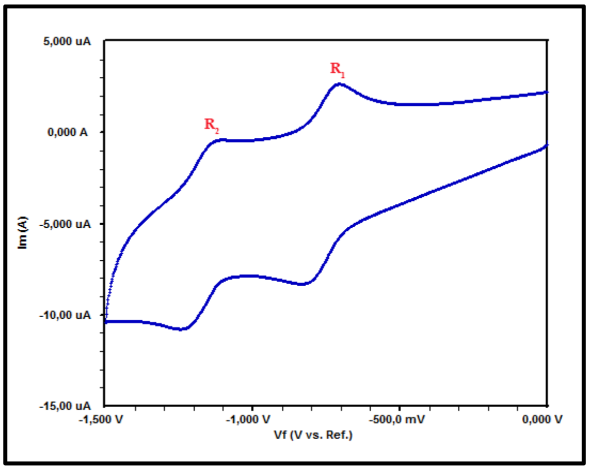

Fig. 5. Cyclic voltammograms of ZnPc in DMSO

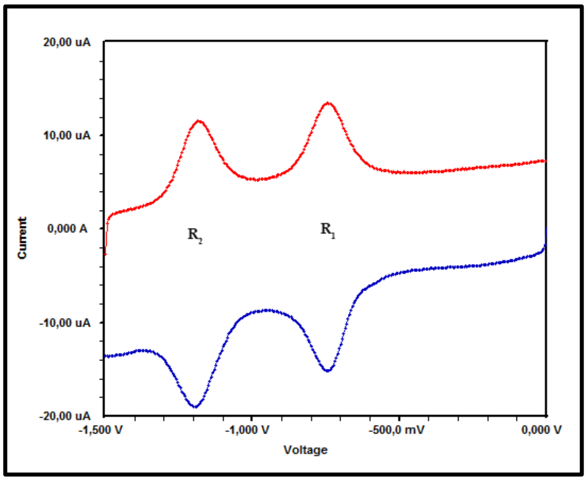

Fig. 6. SWV of ZnPc for cathodic scan

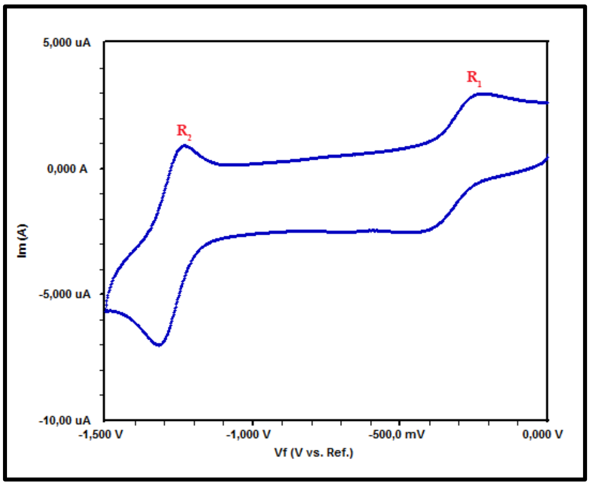

Fig. 7. Cyclic voltammograms of CoPc in DMSO

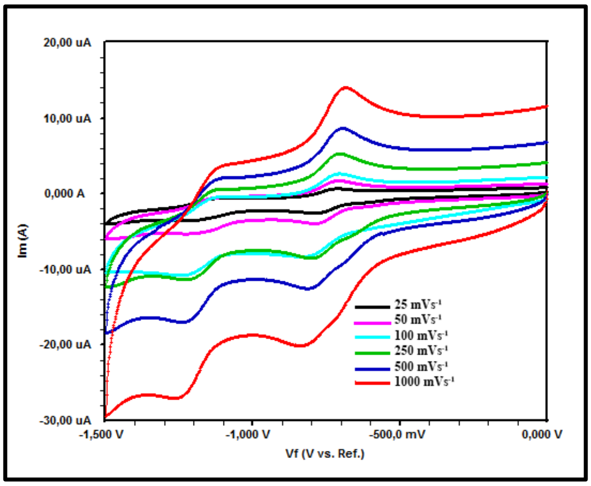

Fig. 9. CV of ZnPc at different scan rates

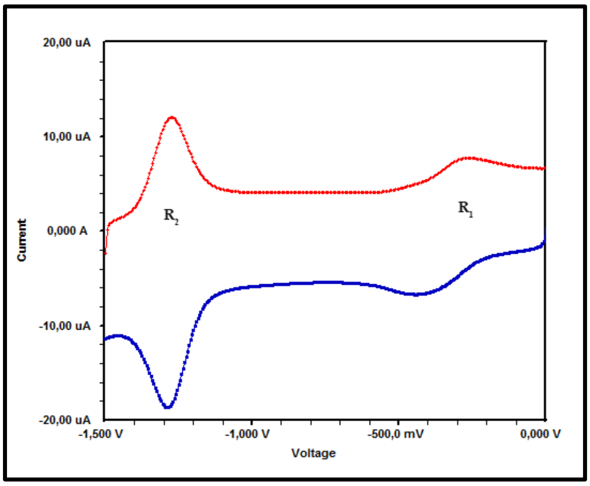

Fig. 8. SWV of CoPc for cathodic scan

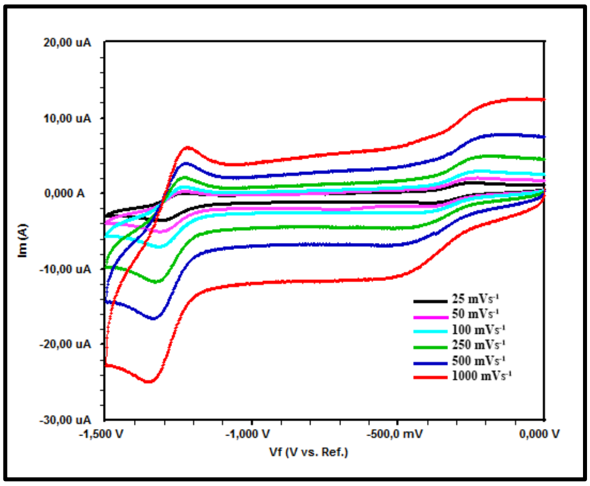

Fig. 10. CV of CoPc at different scan rates

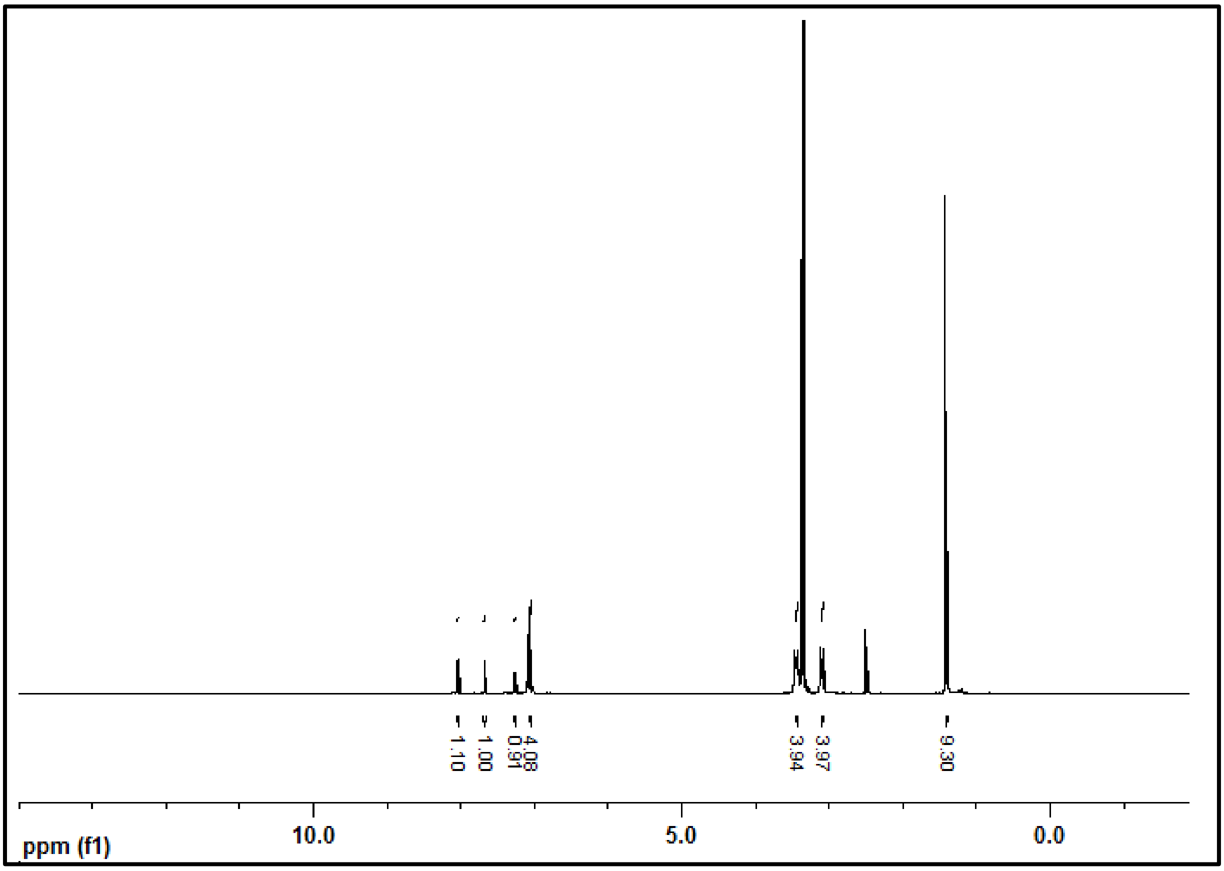

Fig. S1. ^{1}H NMR spectra of Boc-Pip

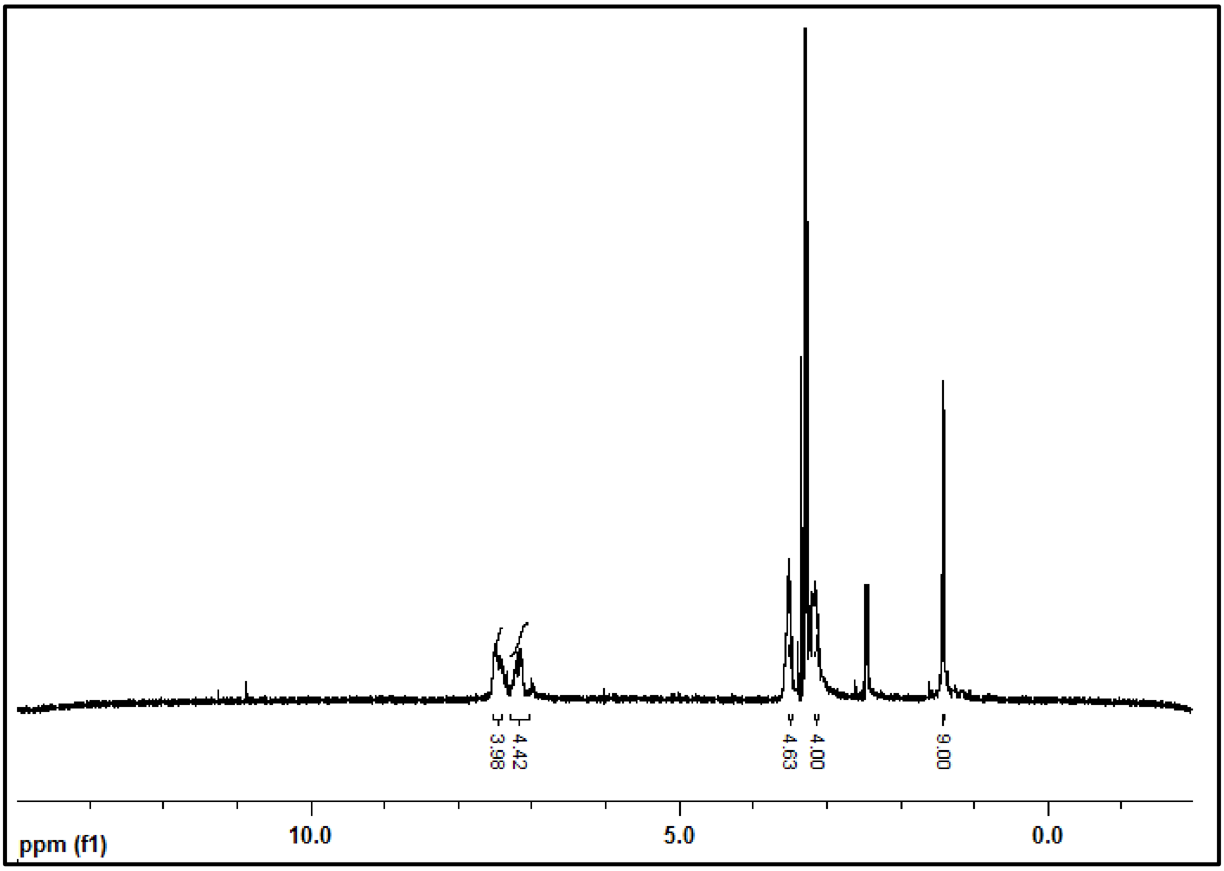

Fig. S2. ^{1}H NMR spectra of ZnPc

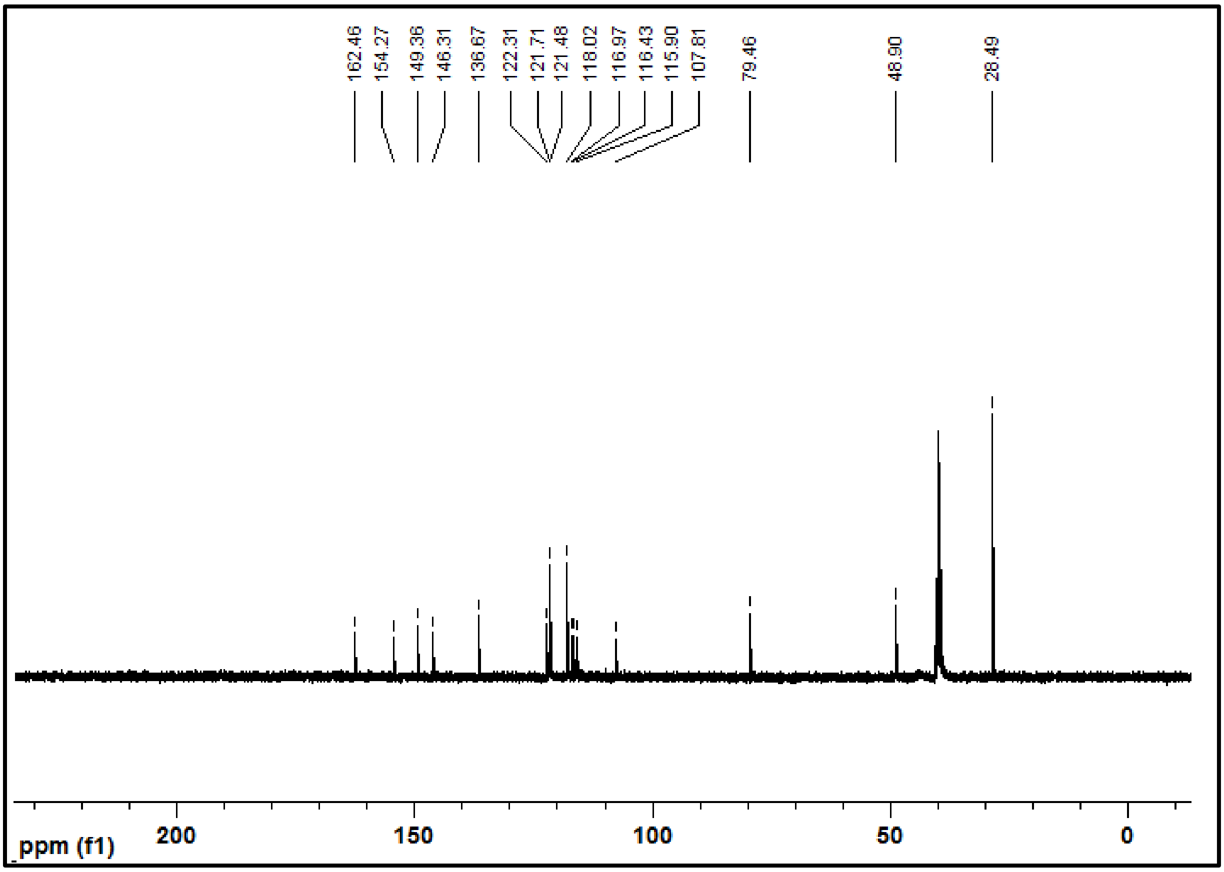

Fig. S3. ^{13}C NMR spectra of Boc-Pip

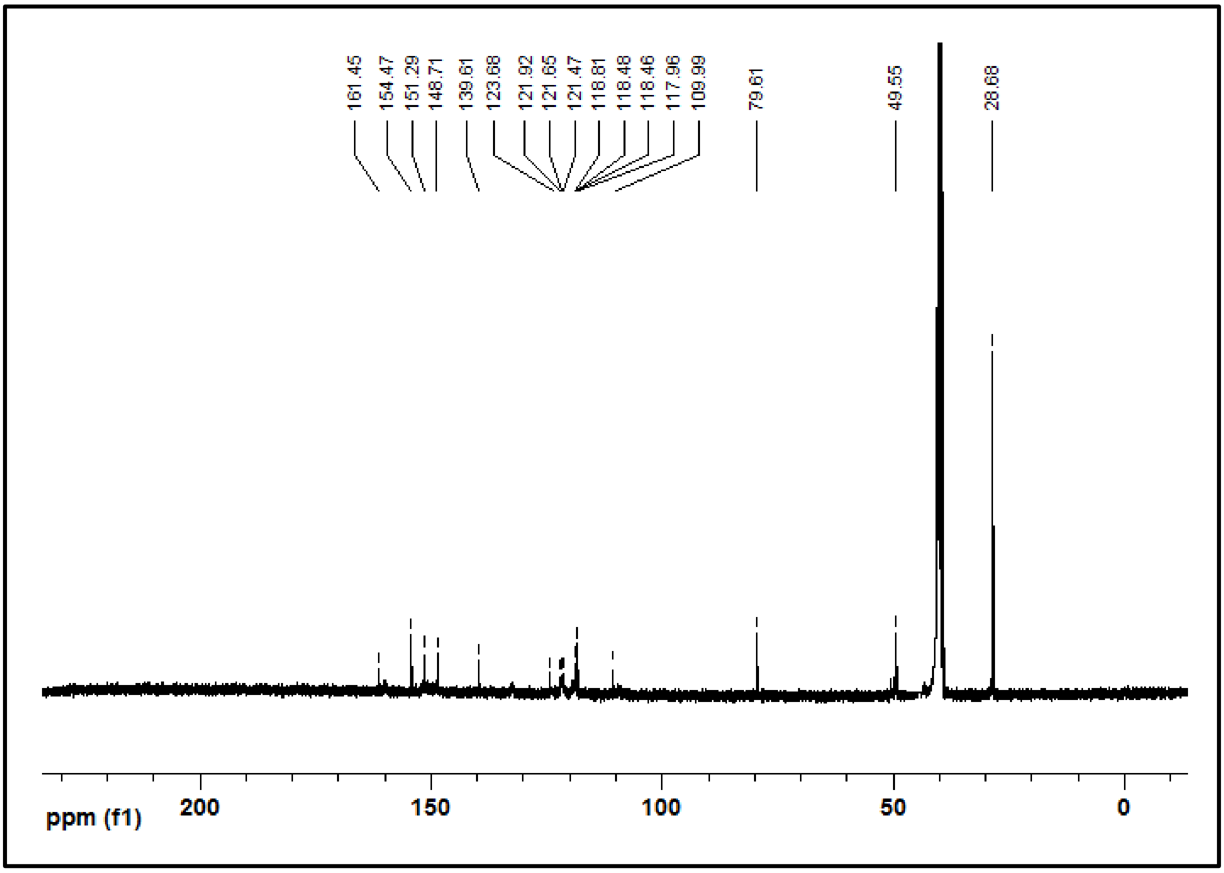

Fig. S4. ^{13}C NMR spectra of ZnPc

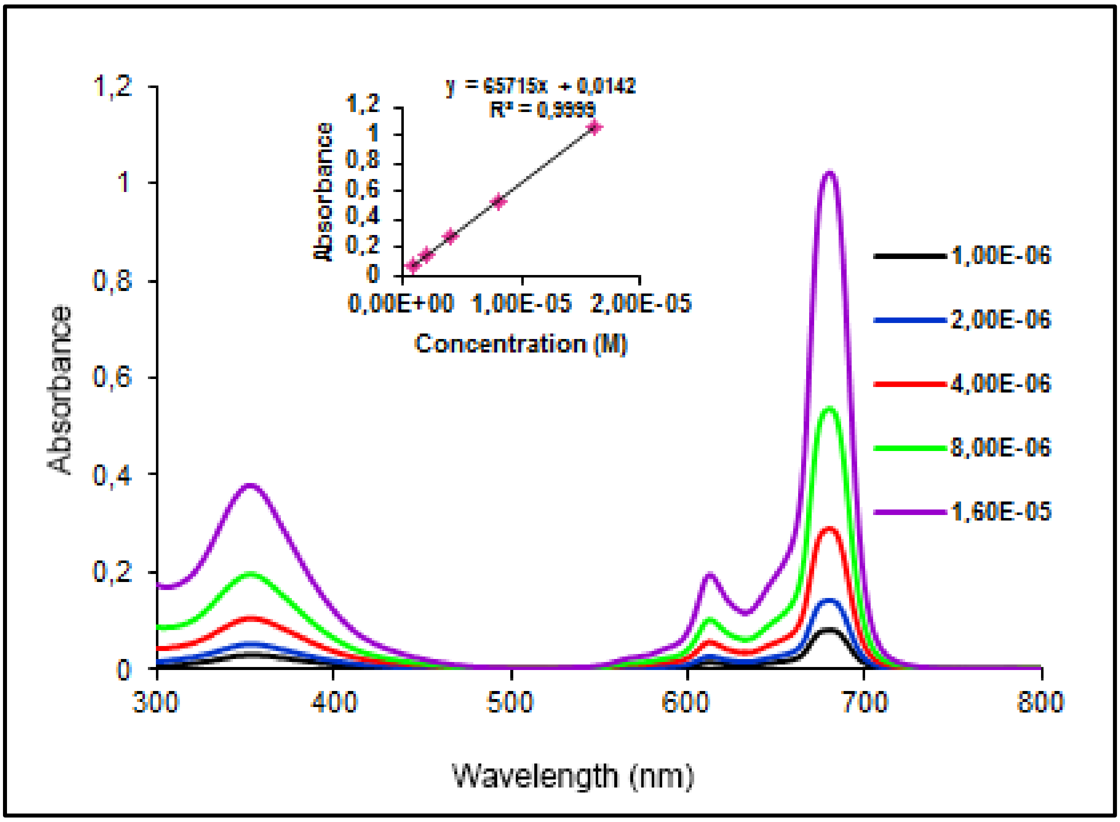

Fig. S5. UV-Vis Spectra of ZnPC (DMF)

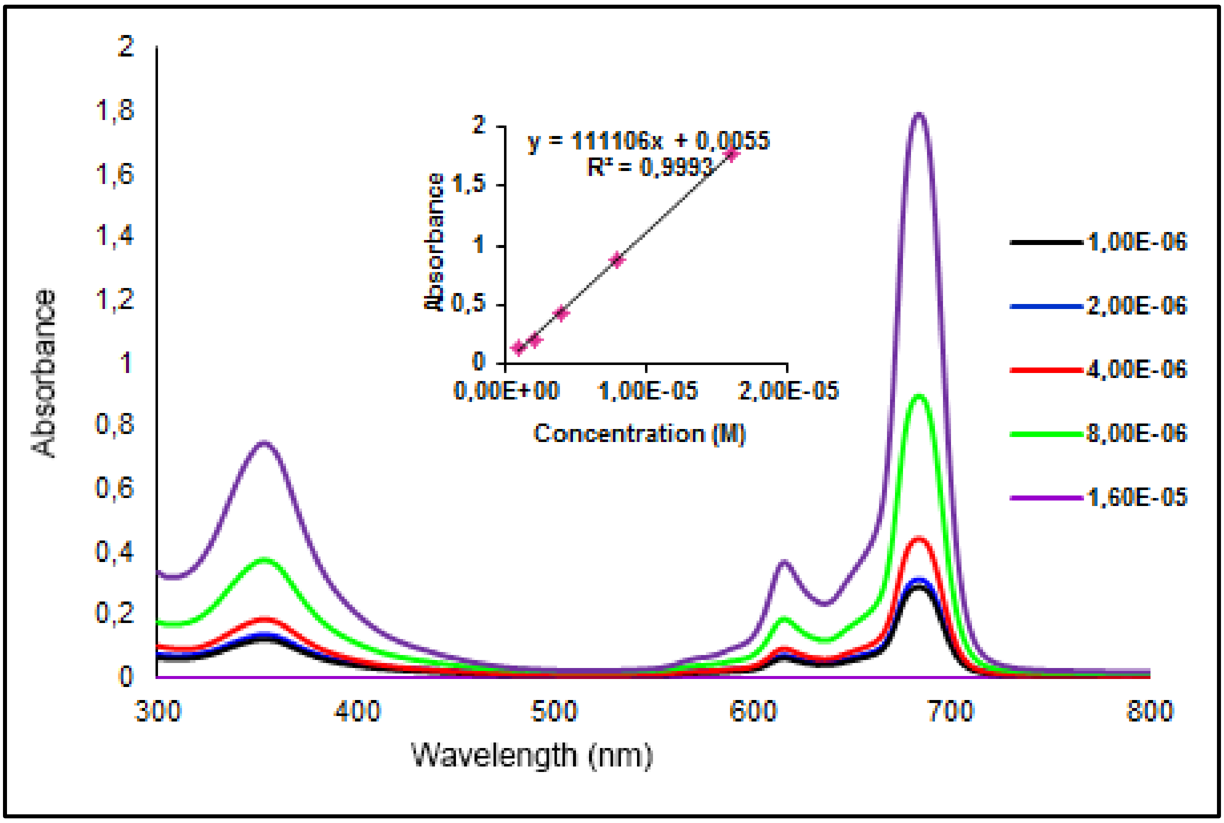

Fig. S6. UV-Vis Spectra of ZnPC (DMSO)

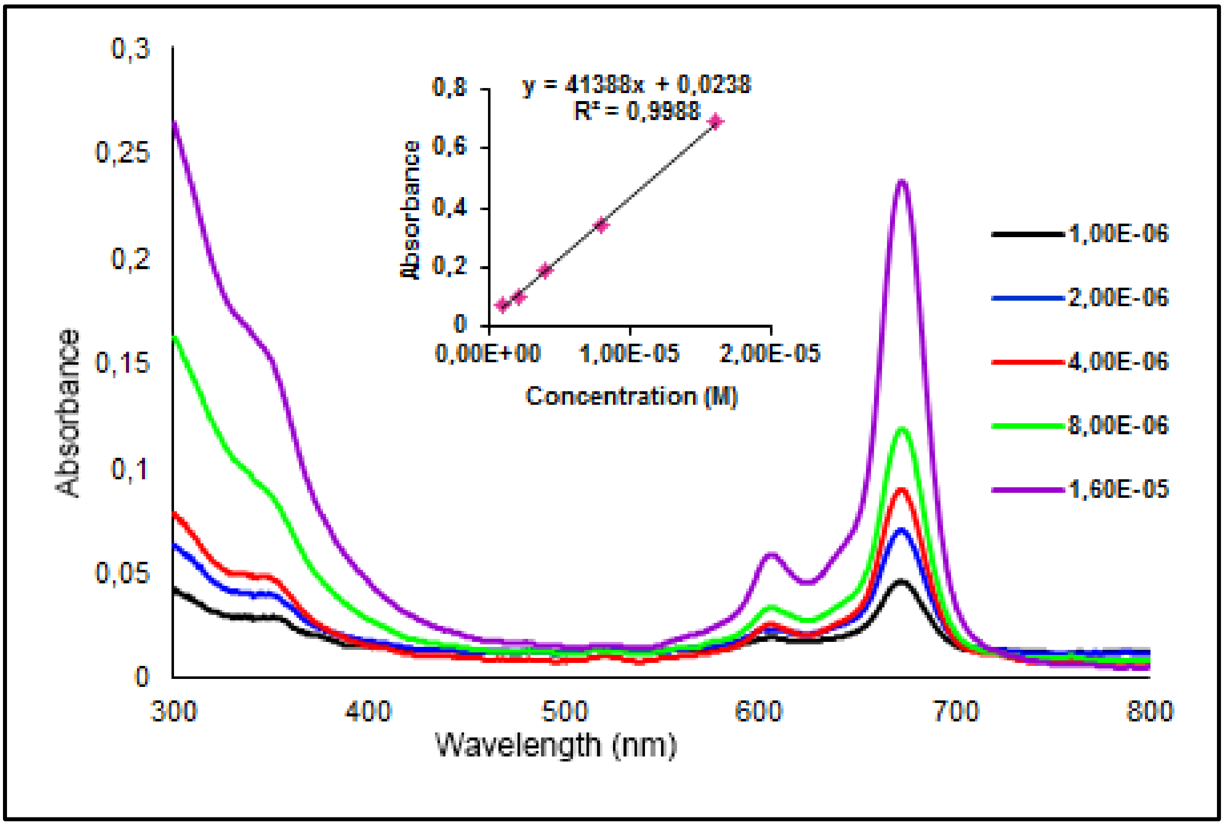

Fig. S7. UV-Vis Spectra of CoPC (THF)

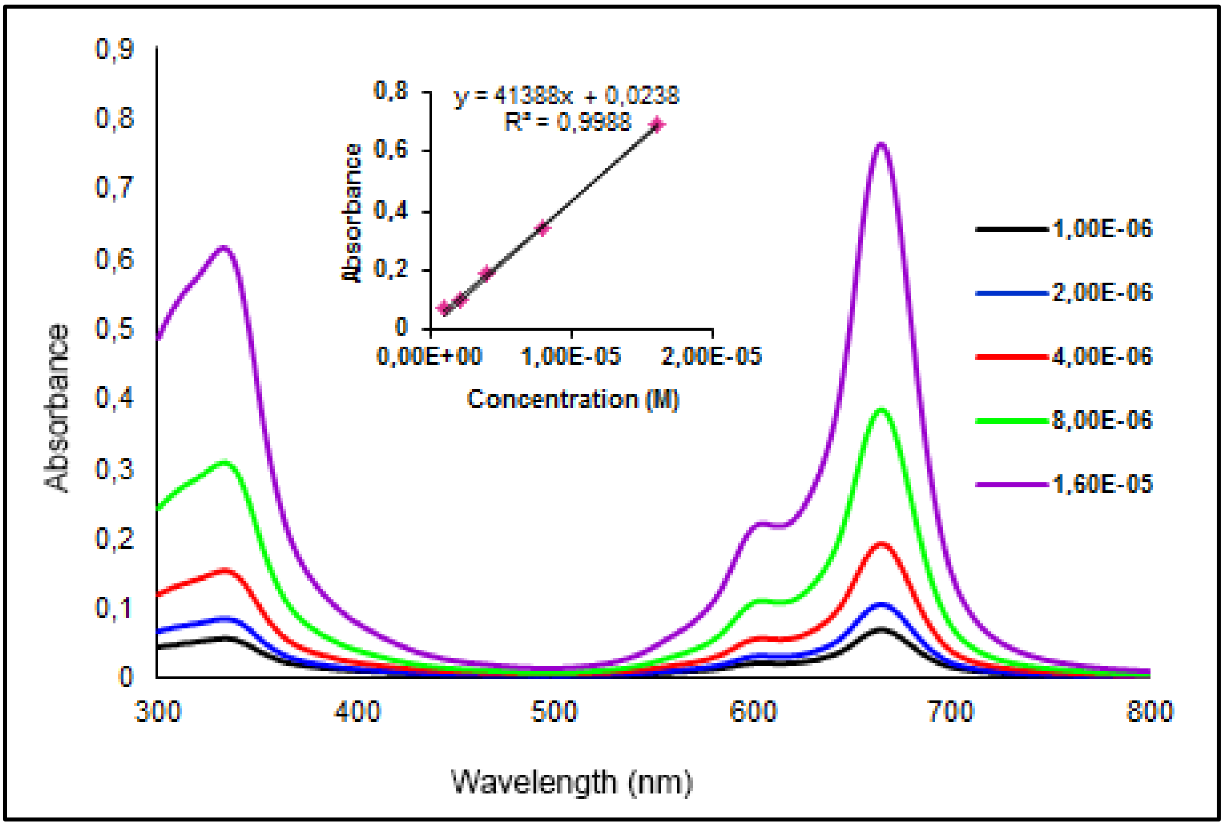

Fig. S8. UV-Vis Spectra of CoPC (DMSO)

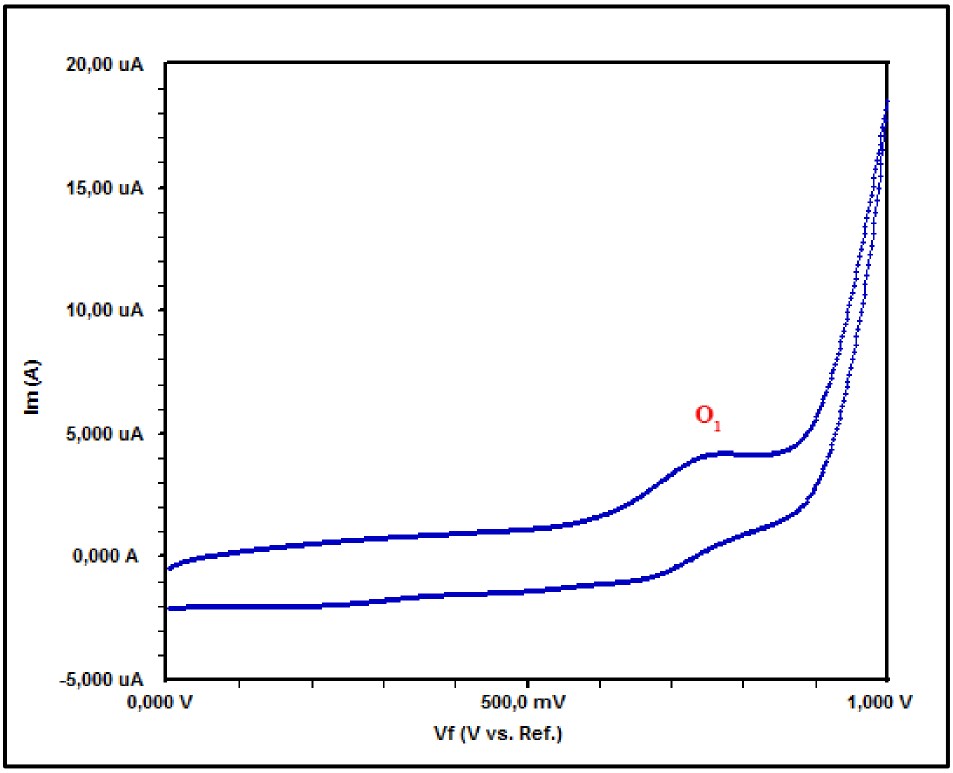

Fig. S9. Cyclic voltammograms of ZnPc in DMSO

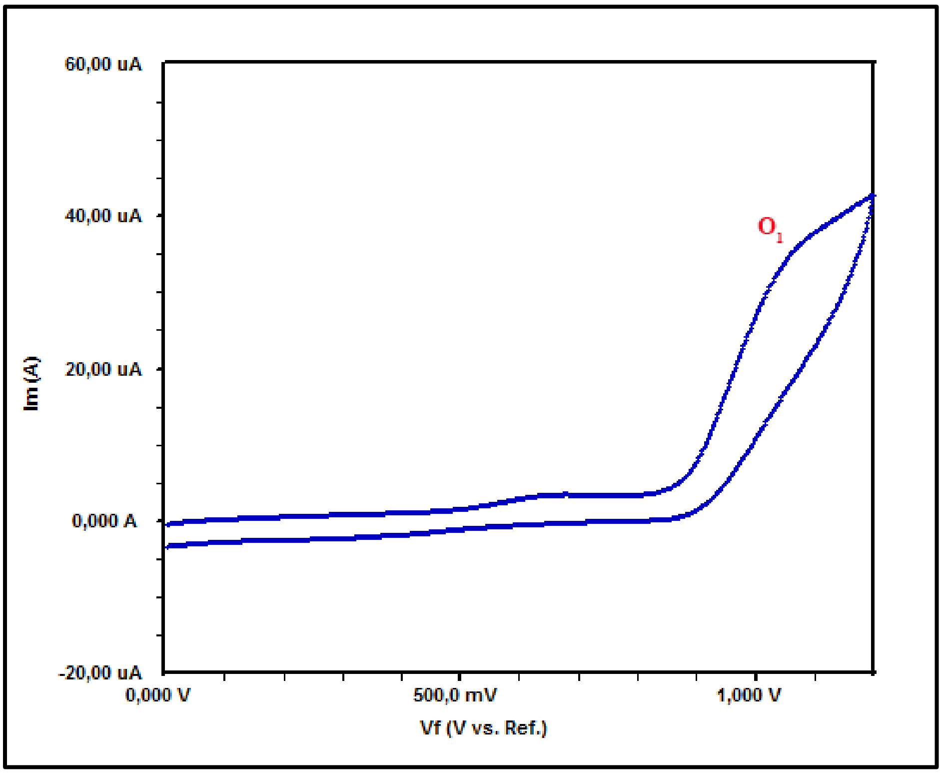

Fig. S10. Cyclic voltammograms of CoPc in DMSO