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# TEMPO-functionalized zinc phthalocyanine: synthesis, magnetic properties, and its utility for electrochemical sensing of ascorbic acid

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Zinc(II) phthalocyanine (**TEMPO-ZnPc**), peripherally functionalized with 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) radicals is synthesized and its magneto structural and electrochemical behaviors are investigated. **TEMPO-ZnPc** shows multi-electron ring based reduction reactions and a TEMPO based oxidation reaction. Spectroelectrochemical measurements support these peak assignments. **TEMPO-ZnPc** is tested as homogeneous and heterogeneous ascorbic acid (AA) sensor. Disappearance of **TEMPO-ZnPc** based reduction processes and observation of new waves at around 0 and 1.20 V with respect to increasing AA concentration indicate interaction of **TEMPO-ZnPc** with AA and usability of the complex as electrochemical AA sensor. For practical usage as heterogeneous electrocatalysts for AA sensing, glassy carbon electrode (GCE) is coated with **TEMPO-ZnPc** (GCE/**TEMPO-ZnPc**) and this modified electrode is tested as heterogeneous AA sensor. Redox peak of

GCE/**TEMPO-ZnPc** at 0.81 V decrease in peak current while a new wave is observed at 0.65 V during titration of the electrolyte with AA. GCE/**TEMPO-ZnPc** sense AA with  $1.1 \times 10^{-9}$  mol.dm<sup>-3</sup> LOD with a sensitivity of  $1.1 \times 10^{-9}$  A.cm.mol<sup>-1</sup>.

## Introduction

Metallophthalocyanines (MPcs) are used as active electrocatalysts and electrochemical sensors due to their rich redox properties and chemical and thermal stabilities.<sup>1,2</sup> Although redox activity of the central metal ions and phthalocyanine ring play important role for their electrocatalytic and electro-sensing activities,<sup>3-7</sup> the redox activity of substituents on phthalocyanine is also very important for these applications.<sup>8,9</sup> TEMPO is a stable free radical and covalently attached to other organic compounds and biomolecules to yield nitroxyl bearing molecules (spin-labeled compounds) and making them particularly suitable for many applications.<sup>10</sup> Functional materials containing TEMPO radical are used as active electrocatalyst for different target molecules, oxidation of alcohols,<sup>11,12</sup> radical polymerizations,<sup>13</sup> and also used as cathode active materials in Li ion cells.<sup>14-16</sup> It is well known that TEMPO radical is redox active and capable of being oxidized electrochemically and reversibly through the loss of one electron to yield the corresponding oxoammonium cation.<sup>17</sup> Another important feature of TEMPO is the ability to readily react with ascorbic acid with the gain of a proton and an electron, generating ascorbic acid radicals and TEMPOH which shows possible usage of TEMPO bearing compounds as ascorbic acid sensors.<sup>18</sup> The literature contains only a few studies on the synthesis and sensing activities of phthalocyanines containing nitroxide free-radical moieties.<sup>19-21</sup> More recently, Ishii and co-workers have applied phthalocyaninatosilicon (SiPc) covalently linked to one or two TEMPO radicals as fluorescence probes for detecting ascorbic acid.<sup>21</sup> Herein we show, the synthesis, preliminary EPR investigations and possible usage of **TEMPO-ZnPc** as active AA sensor. To

the best of our knowledge, peripherally TEMPO substituted metallo phthalocyanine is the first example in the literature.

## Results and Discussion

### Synthesis

Scheme 1 shows the synthesis of TEMPO-functionalized phthalocyanine derivative **TEMPO-ZnPc**. The starting compound **TEMPO-Pht** was prepared by a base catalyzed nucleophilic aromatic displacement of 4-nitrophthalonitrile with TEMPOL. The reaction was carried out at room temperature in dry dimethylformamide with  $K_2CO_3$ . Cyclotetramerization of the dinitrile compound **TEMPO-Pht** in the presence of anhydrous  $Zn(CH_3COO)_2$  gave the desired metallophthalocyanine **TEMPO-ZnPc**. The blue product was isolated by column chromatography on silica gel. This compound was soluble in acetone, tetrahydrofuran, dimethyl sulfoxide, and dimethylformamide. As a natural consequence of the single substituent on each benzo group, the zinc phthalocyanine is all a mixture of four constitutional isomers. Due to the paramagnetic nature of nitroxide, the use of NMR precludes structural characterization. Thus, the structures of the novel compounds were confirmed by FT-IR, UV-Vis, EPR and MS spectroscopic techniques.

IR spectrum of **TEMPO-Pht** indicated the presence of aromatic, aliphatic and  $C\equiv N$  groups by the intense stretching bands at 3068, 2980 and 2232  $cm^{-1}$ , respectively. In the LC-MS spectrum of **TEMPO-Pht**, we observed the  $[M+2H]^+$  peak at  $m/z$  300.2 amu. The IR spectra of zinc phthalocyanine confirmed the formation of the macrocycle, due to disappearance of the sharp triple bond signal seen in **TEMPO-Pht** at 2232  $cm^{-1}$ . In the MALDI-TOF and LC-MS spectrum, we observed a  $[M+H]^+$  peak at 1259.7 amu for **TEMPO-ZnPc**. The phthalocyanines display typical steady-state electronic absorption spectra with two strong absorption regions, one of them in the UV region at about 300-350

nm (B band) and the other one in the visible region at 600-700 nm (Q band). The steady-state absorption spectra of **TEMPO-ZnPc** in tetrahydrofuran exhibit intense Q band at 678 nm and the B band in the near UV region, at 349 nm, both correlated to  $\pi$ - $\pi^*$  transitions.

### EPR studies

The X-band EPR (Electron Paramagnetic Resonance) measurements at ambient temperature were carried out on the **TEMPO-Pht** and **TEMPO-ZnPc**. Fig. 1 shows the EPR spectrum of **TEMPO-Pht** in chloroform and its computer simulation. They are in a good agreement. The spectrum consists of three hyperfine lines of equal intensity. The hyperfine splitting is due to interaction of the unpaired electron with one nitrogen nucleus ( $^{14}\text{N}$ ,  $I = 1$ ). The number of lines is determined according to the relation of  $2nI + 1$ , where  $n$  is the number of equivalent nitrogen nucleus. This spectrum clearly belongs to free **TEMPO-Pht** mono radical ( $S = 1/2$ ,  $I = 1$ ,  $n=1$ ) in solution media. The spectra were simulated with the values of  $g$ ,  $a\text{N}$  (isotropic hyperfine coupling constant in gauss) and linewidth ( $\Delta\text{Hp-p}$ ) extracted from the solution spectrum, using WinEPR computer program. The best simulation parameters were determined as  $g = 2.0073$ ,  $a\text{N} = 15.51$  G and  $\Delta\text{Hp-p} = 2.75$  G. The powder EPR spectrum of **TEMPO-Pht** has a single signal with  $g = 2.012$  and  $\Delta\text{Hp-p} = 14.6$  G, as indicated in fig. 2. The cause of this is that, at high concentrations the exchange interaction time quite shortens, this also decreases the interaction time between nuclear spin and states of electron spin so that the time-averaged hyperfine field goes to zero. Therefore, hyperfine lines coalesce to a single and narrowed signal.

**TEMPO-ZnPc** also shows the similar hyperfine structure in solution media (Fig. 3). The best simulation parameters were determined as  $g = 2.0065$ ,  $a\text{N} = 15.51$  G and  $\Delta\text{Hp-p} = 4$  G. Line width of this is slightly greater than that of TEMPO.<sup>22,23</sup> In this compound TEMPO is bound to ZnPc, so free rotation correlation time of TEMPO becomes longer, that is, the

motion of radical is restricted. This case leads to changes of the amplitudes of EPR signals and anisotropic interactions, so broadening of hyperfine lines. Fig. 4 shows powder EPR spectrum of **TEMPO-ZnPc** and its simulation. It has a broad signal with  $g = 2.012$  and  $\Delta H_{pp} = 32$  G. The broadness of signal arises due to dipolar interactions and spin-exchange interactions. So, hyperfine splitting could not be resolved.

### Electrochemistry and in situ spectroelectrochemistry of **TEMPO-ZnPc**

Redox properties of functional species should be known in order to decide their usage as electrocatalysts or electro-sensors. For usage as an active electrocatalyst or electro-sensor, functional materials having reversible redox processes at small potentials generally show better electrocatalytic activities. In order to decide the possible usage of **TEMPO-ZnPc** as an electrochemically functional material, its electrochemical responses were determined in solution and in solid state.

Figure 5 shows CV and SWV responses of **TEMPO-ZnPc** recorded in DMSO/TBAP electrolyte system. **TEMPO-ZnPc** shows three quasi-reversible reduction processes,  $[\text{Zn}^{\text{II}}\text{Pc}^2] / [\text{Zn}^{\text{II}}\text{Pc}^{3-}]^{1-}$  couple at -0.83 V,  $[\text{Zn}^{\text{II}}\text{Pc}^{3-}]^{1-} / [\text{Zn}^{\text{II}}\text{Pc}^{4-}]^{2-}$  couple at -1.28 V, and  $[\text{Zn}^{\text{II}}\text{Pc}^{4-}]^{2-} / [\text{Zn}^{\text{II}}\text{Pc}^{5-}]^{3-}$  couple at -1.98 V. First two reduction couples are electrochemically quasi-reversible with respect to  $\Delta E_p$  and  $I_{pa}/I_{pc}$  values. Unity of  $I_{pa}/I_{pc}$  ratios at all scan rates and linear variation of the peak currents with square root of the scan rates indicate purely diffusion controlled characters of the redox processes. During the anodic potential scans an irreversible huge oxidation wave is observed at 0.83 V. While the reduction processes are in harmony with the redox responses of the reported ZnPc complexes.<sup>24-26</sup> The oxidation process is different than the Pc passed redox processes of ZnPcs. Peak assignments were performed with in situ spectroelectrochemical measurements (Fig. 6) in order to clarify the electrochemical mechanism of the complex. Fig. 6a illustrates Pc ring-based electron transfer

characters of the first reduction process of **TEMPO-ZnPc**. Change of the intensity of the Q band without a shift and observation of new bands in metal to ligand charge transfer (LMCT) region indicated Pc based characters of the first reduction process of **TEMPO-ZnPc**.<sup>25-28</sup> In situ spectroelectrochemical measurements indicated that second (Fig. 6b) and third reduction processes are also ring-based processes. Decreasing of the Q band without shift and observation of new bands between 550-650 nm indicate ring based character of these processes. Fig. 6c illustrates different spectral changes than Pc based processes.<sup>25-28</sup> All bands decrease in intensity at 0.90 V potential application. These spectral changes could not be attributed to Pc ring and/or metal center. Thus, this process should be a TEMPO based oxidation reaction. Fig. 6d shows the color changes recorded during the electron transfer processes. While distinct color change was observed during the reduction processes. Color change during oxidation process is trivial. Cyan color of the neutral **TEMPO-ZnPc** turns to light blue during the first reduction and turns to dark blue during the second reduction process.

#### **Electrochemical homogeneous ascorbic acid sensing measurements of TEMPO-ZnPc**

Homogeneous electro-sensing studies of **TEMPO-ZnPc** were performed in DMSO solution, which was titrated with AA. Before sensing measurements, blank tests GCE was carried out in AA free DMSO solution with SWV. When the responses of blank measurements were reached to a steady state, AA solutions were gradually added with increasing amounts. These studies show that **TEMPO-ZnPc** successfully senses AA in solution as shown in Fig. 7. During titration, the reduction peaks of **TEMPO-ZnPc** at -0.83 V and -1.28 V gradually decrease and the TEMPO based peak at 0.83 V increases, while two new peaks increase at 0.04 V and 1.02 V with respect to increasing AA concentration. These SWV responses

indicate the interaction of **TEMPO-ZnPc** with AA and the products of this interaction give redox responses at 0.04 V and 1.02 V.

It is well known that for practical application, a functional molecule should be coated on an electrode, and this modified electrode should behave as heterogeneous active electro-sensor for target molecules.<sup>29-31</sup> Here, we have examined heterogeneous sensing activities of **TEMPO-ZnPc** coated on GCE and this electrode has been tested as an electro-sensor for AA, uric acid (UA) and dopamine (DA). Before sensing measurements, blank test of GCE/**TEMPO-ZnPc** working electrode is carried out in AA free DMSO solution with SWV techniques in order to investigate the redox activity and stability of the modified electrode. When the responses of blank measurements were reached to a steady state, AA solutions were gradually added with increasing amounts. Before AA addition, GCE/**TEMPO-ZnPc** gives a sharp oxidation peak ( $T_{\text{oxd}}$ ) at 0.81 V. When AA is gradually added, while  $T_{\text{oxd}}$  peak decreases in current intensity, a new wave, AA at 0.65 V increases in the current intensity. As shown in the Fig. 8a, decrease in the intensity of TEMPO based peak and observation of a new wave indicates there is an interaction reaction between **TEMPO-ZnPc** and AA and this interaction cause the decreasing of the TEMPO based peak and observation of a new peak. In order to investigate selectivity of the electrode, sensing measurements of the electrode were also performed for UA and DA. While only the TEMPO based peak decreases in intensity during UA titration, DA titration give a new peak at 0.20 V (Fig. S7). Mixture of AA and DA is also tested and GCE/**TEMPO-ZnPc** electrode sense these molecules selectively as shown in Fig. 8b. When AA is added only the peak at 0.65 V increases, and DA addition cause the increasing of the peak at 0.20 V. Basic sensor parameters, calibration lines, and detection limits (LOD) of GCE/**TEMPO-ZnPc** electrode were derived from SWV analyses. SWV amperometric sensing analysis gives a linear range between 2.50 and 100.0  $\mu\text{mol}\cdot\text{dm}^{-3}$  AA with a sensitivity of  $1.89 \cdot 10^3 \text{ A}\cdot\text{cm}^{-1}\cdot\text{mol}^{-1}$  and LOD of  $1.75 \cdot 10^{-6} \mu\text{mol}\cdot\text{dm}^{-3}$ . Although, there



are many AA sensors reported in the literature,<sup>32-34</sup> the main problems of these studies are reported as the difficulties of the selectivity of AA from the mixture of AA, UA and DA. These three molecules may be present in the same media and they generally give redox peaks between 0 and 0.5 V.<sup>35-37</sup> On most sensor electrodes the redox processes of this molecule were overlapped with each other, which obstruct detection of AA selectively. Differently the sensor electrode, GCE/**TEMPO-ZnPc** detects AA with the redox peak (AA) at 0.65 V and DA with the redox peak (DA) at 0.20 V, which may solve the selectivity problem of AA sensing measurements.

### Conclusions

Zinc(II) phthalocyanine bearing stable free radical TEMPO moieties was synthesized and its magneto structural and electrochemical behaviors are investigated. Multi-electron and reversible reduction reactions and TEMPO based oxidation process of **TEMPO-ZnPc** showed the usability of the complex as reasonable electro-sensor. Especially, redox responses beyond 0.65 V for AA indicate usability of GCE/**TEMPO-ZnPc** electrode as selective AA sensor with reasonable low detection limit.

### Experimental section

#### Chemicals and reagents

The experimental studies were carried on with high purity chemicals. Extra pure dimethyl sulfoxide (DMSO), and ultra-pure water ( $\geq 18$  M, Milli-Q, Millipore) were used as solvents. Electrochemical grade tetrabutylammonium perchlorate (TBAP), LiClO<sub>4</sub> and other reagents were purchased from Aldrich and used without further purification. GC working electrodes were modified with **TEMPO-ZnPc** by using cast film coating technique. During this

modification processes, 100 mL of  $5.0 \times 10^{-4} \text{ mol.dm}^{-3}$  **TEMPO-ZnPc** solution was dropped on GCE surface then dried under vacuum at 25 °C.

### **EPR measurements**

The EPR solution and powder spectra were recorded with a Bruker EMX X-band (9.8 GHz) spectrometer, with 100 kHz magnetic field modulation and about 20 mW microwave power. The amplitude of modulation was set below of the estimated peak-to-peak width for all spectra. The magnetization measurements in the temperature range of 10–300 K were performed on a Quantum Design PPMS system, using the constant magnetic field of 1kOe.

### **Electrochemical measurements**

The electrochemical applications and measurements were performed with a potentiostat (GAMRY Instruments, Reference 600 Potentiostat/Galvanostat/ZRA) utilizing a three-electrode cell configuration at 25 °C. For cyclic voltammetry (CV) and square wave voltammetry (SWV) measurements, the working electrode was a bare or modified glassy carbon electrode (GCE) with a surface area of  $0.071 \text{ cm}^2$  (diameter of the electrodes are 3 mm). A Pt wire was used as the counter electrode. Ag/AgCl electrode was employed as the reference electrode and separated from bulk of the solution by a double bridge. High purity  $\text{N}_2$  was used to remove dissolved  $\text{O}_2$  for at least 15 min prior to each run and to maintain a nitrogen atmosphere over the solution during the measurements. Electro-sensing measurements were performed by using SWV. During homogeneous electro-sensing measurements, SWV responses of bare GCE were recorded in **TEMPO-ZnPc** dissolved DMSO solution during titration with AA. For homogeneous electro-sensing measurements, SWV responses of bare GCE/ **TEMPO-ZnPc** were recorded in DMSO solution during titration with AA. UV-Vis absorption spectra and chromaticity diagrams were measured with

an OceanOptics QE65000 diode array spectrophotometer. In situ spectroelectrochemical measurements were carried out by utilizing a three-electrode configuration of thin-layer quartz thin-layer spectroelectrochemical cell at 25 °C. The working electrode was a Pt gauze electrode. A Pt wire counter electrode separated by a glass bridge and a SCE reference electrode separated from the bulk of the solution by a double bridge were used. In situ electrocolorimetric measurements, under potentiostatic control, were obtained using an OceanOptics QE65000 diode array spectrophotometer at color measurement mode by utilizing a three-electrode configuration of thin-layer quartz spectroelectrochemical cell. The standard illuminant A with 2 degree observer at constant temperature in a light booth designed to exclude external light was used. Prior to each set of measurements, background color coordinates (x, y, and z values) were taken at open-circuit, using the electrolyte solution without the complexes under study. During the measurements, readings were taken as a function of time under kinetic control, however only the color coordinates at the beginning and final of each redox processes were reported.

**Synthesis of TEMPO-Pht.** 4-nitrophthalonitrile (0.500 g, 2.9 mmol), TEMPOL (0.497 g, 2.9 mmol) and K<sub>2</sub>CO<sub>3</sub> (1 g, 7.3 mmol) were stirred in dry dimethylformamide (50 mL) at room temperature for 48 h. The mixture was poured into ice water and the resulting precipitates were filtered off. The crude product was recrystallized from n-hexane. This compound was soluble in acetone, chloroform, methanol, ethanol, dichloromethane. Yield 0.170 g (46%). Mp: 155 °C. FT-IR:  $\nu_{\max}$  3068.57 (CH, aromatic), 2980.18 (CH, aliphatic), 2232.39 (C≡N), 1364.80 (N–O, radical). MS (LC-MS): m/z 300.20 [M+2H]<sup>+</sup>, 284.00 [M-methyl]<sup>+</sup> (theoretical m/z value = 298.36).

**Synthesis of TEMPO-ZnPc.** A mixture of dinitrile **TEMPO-Pht** (0.100 g, 0.335 mmol), and  $\text{Zn}(\text{CH}_3\text{COO})_2$  (0.015 g, 0.084 mmol) in 2-(dimethylaminoethanol) (4 mL) was refluxed under Ar for 24 h. After it was cooled to room temperature, the crude product was precipitated with n-hexane. The blue product was filtered off and washed with water and methanol. Finally, pure zinc phthalocyanine derivative was obtained by chromatography on silica gel (first with tetrahydrofuran then with hexane:ethylacetate (7:3) mixture as eluents). This compound was soluble in acetone, tetrahydrofuran, dimethyl sulfoxide, and dimethylformamide. Yield 0.016 g (32%). FT-IR:  $\nu_{\text{max}}$  3062.89 (CH, aromatic), 2934.21 (CH, aliphatic), 1332.51 (N -O, radical). UV-Vis (tetrahydrofuran):  $\lambda_{\text{max}}$  678, 349. MS (LC-MS and MALDI-TOF):  $m/z$  1259.71  $[\text{M}+\text{H}]^+$  (theoretical  $m/z$  value = 1258.83).

### Acknowledgements

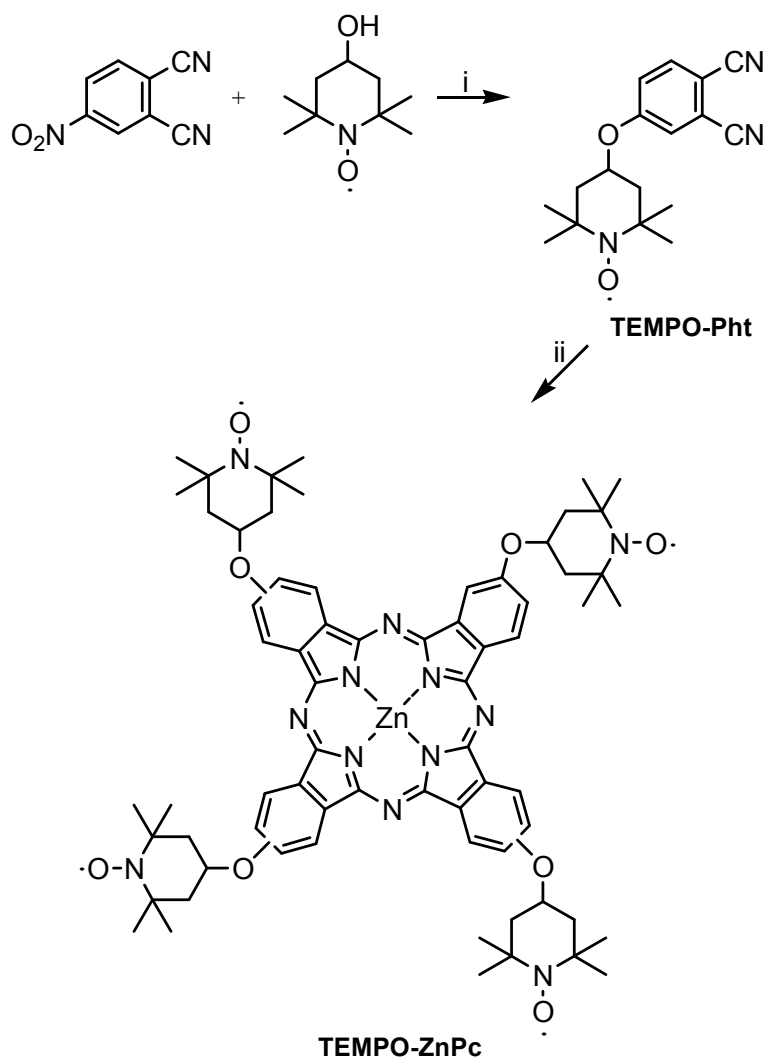
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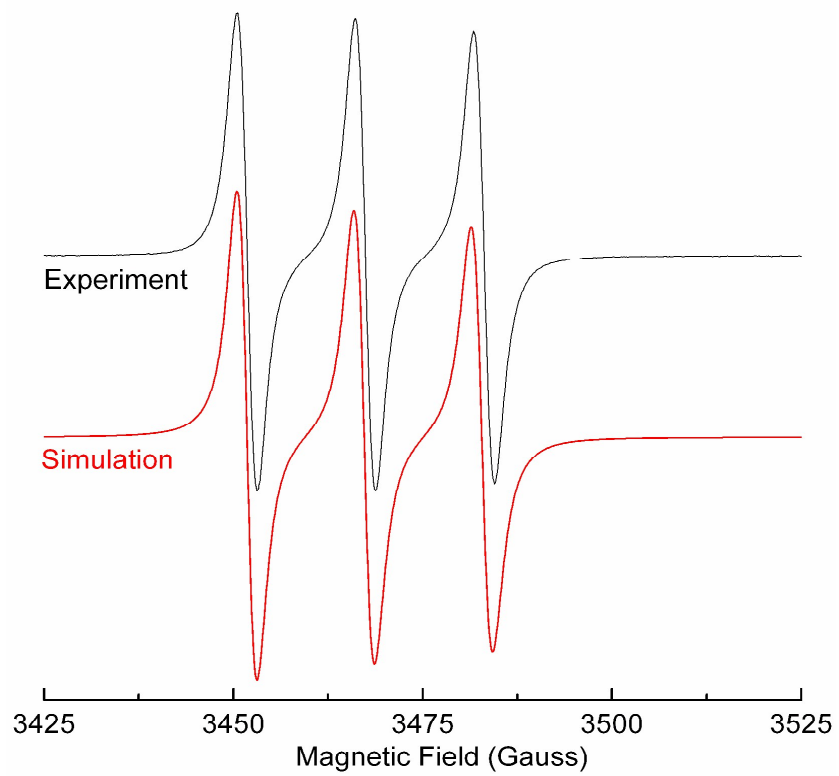
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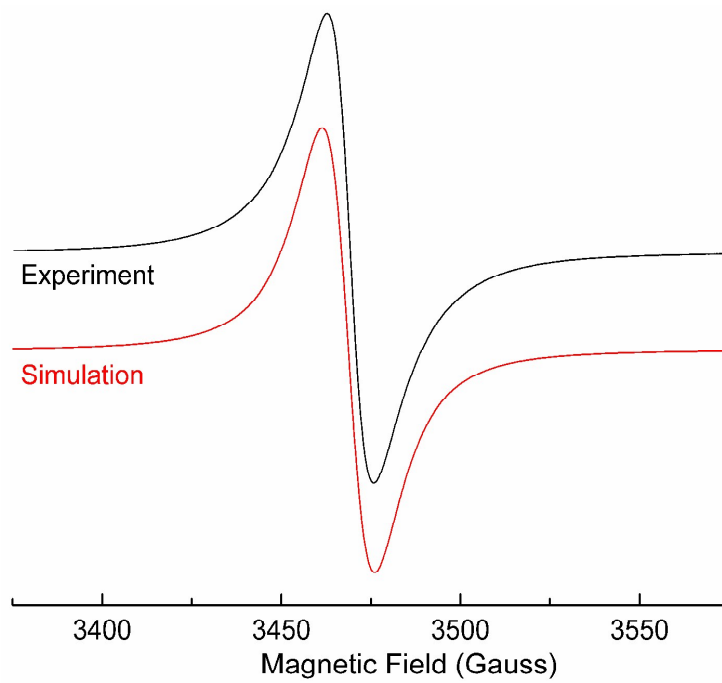


**Scheme 1:** Synthesis of **TEMPO-ZnPc** and its precursor, where i)  $\text{K}_2\text{CO}_3$ , dry DMF, 48 h; ii)  $\text{Zn}(\text{CH}_3\text{COO})_2$ , DMAE, 24 h.

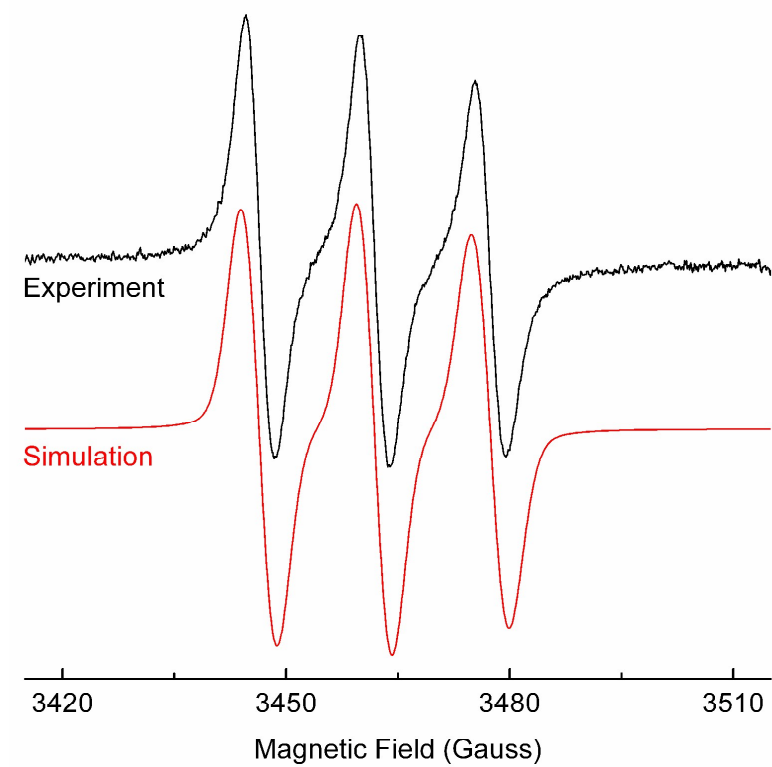


**Fig. 1:** The EPR spectrum of **TEMPO-Pht** in chloroform solution at ambient temperature and its simulation.

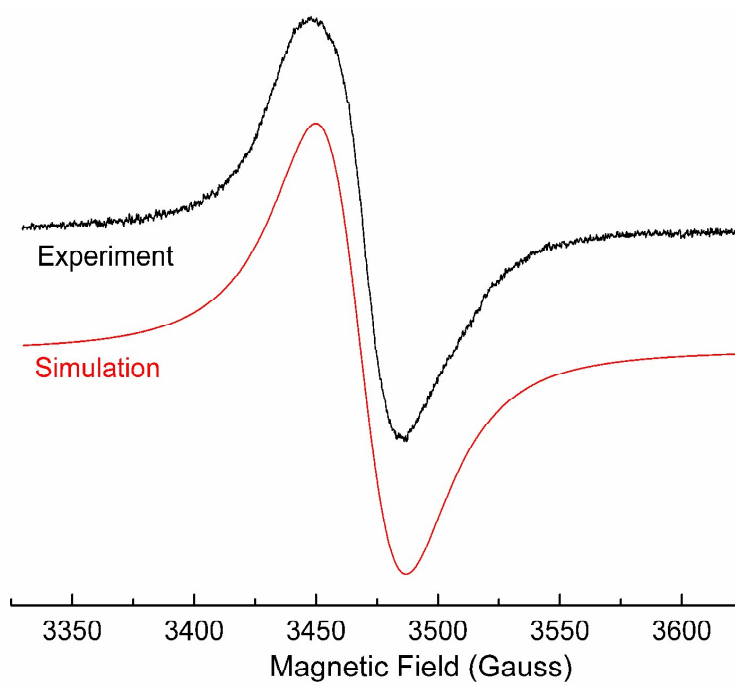




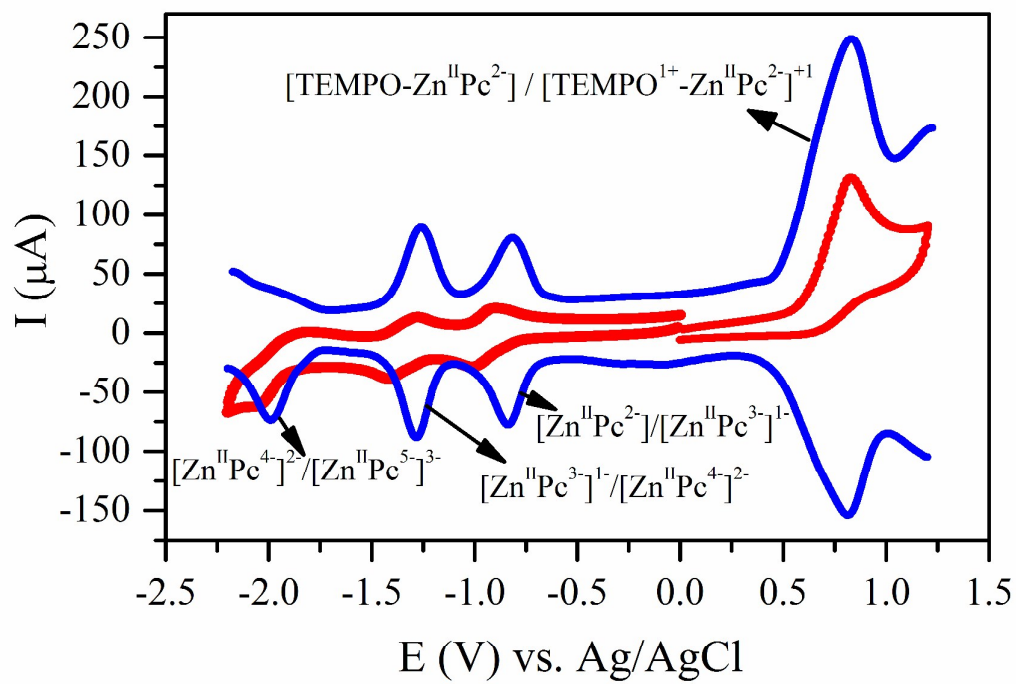
**Fig. 2:** The powder EPR spectrum of **TEMPO-Pht** at ambient temperature and its simulation.



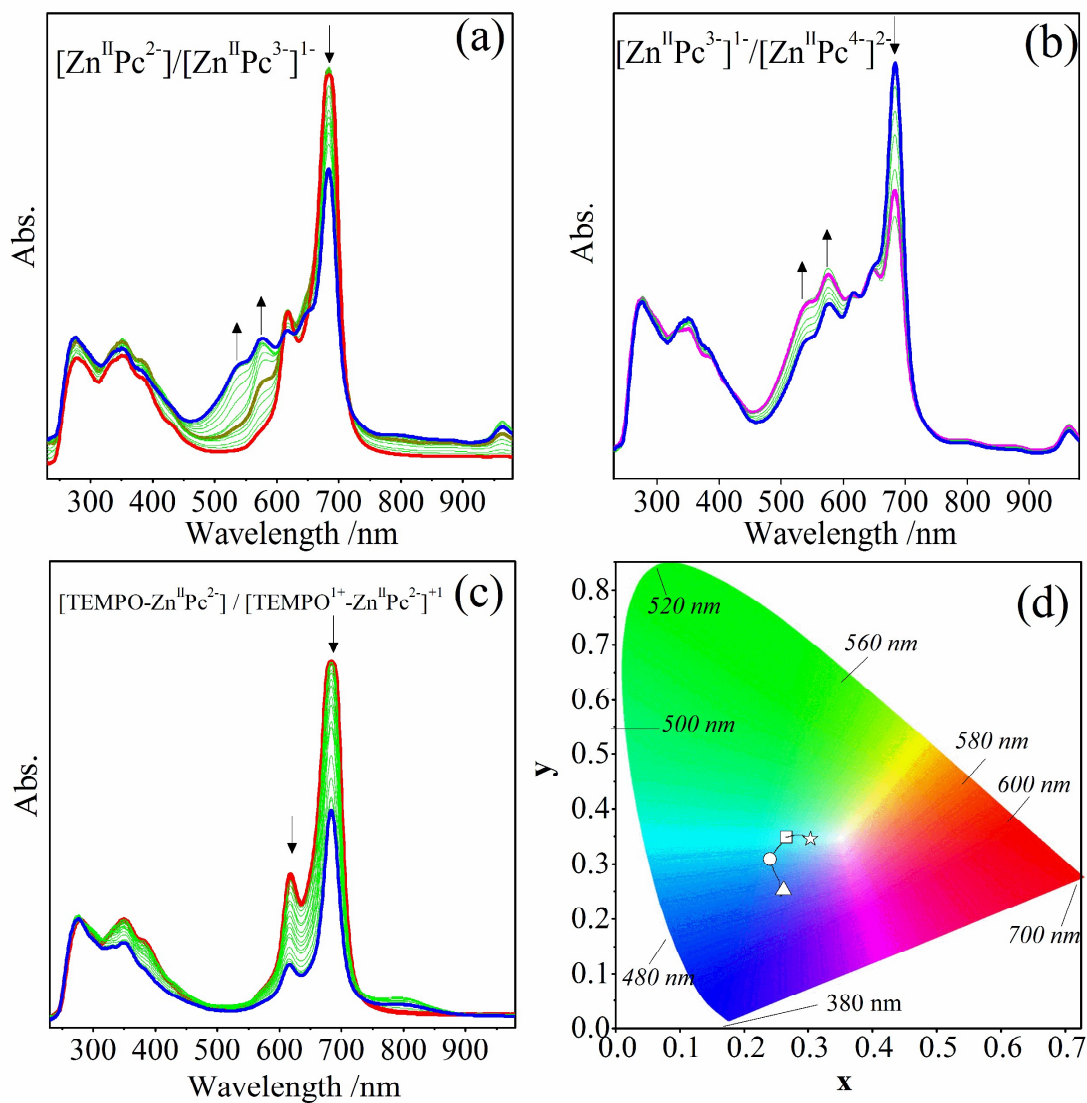
**Fig. 3:** The EPR spectrum of **TEMPO-ZnPc** in THF solution at ambient temperature and its simulation.



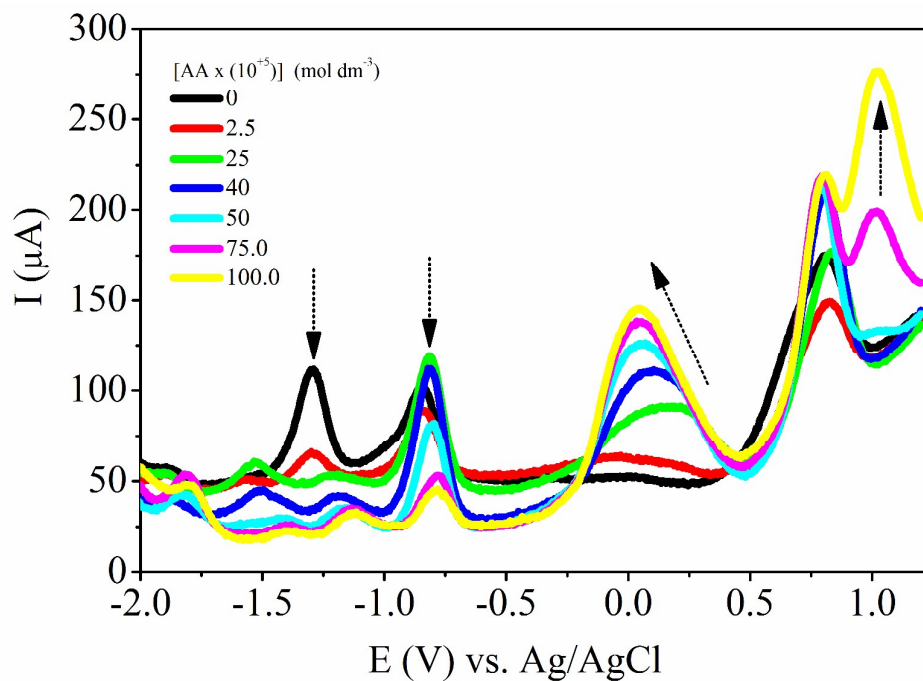
**Fig. 4:** The powder EPR spectrum of **TEMPO-ZnPc** at ambient temperature and its simulation.



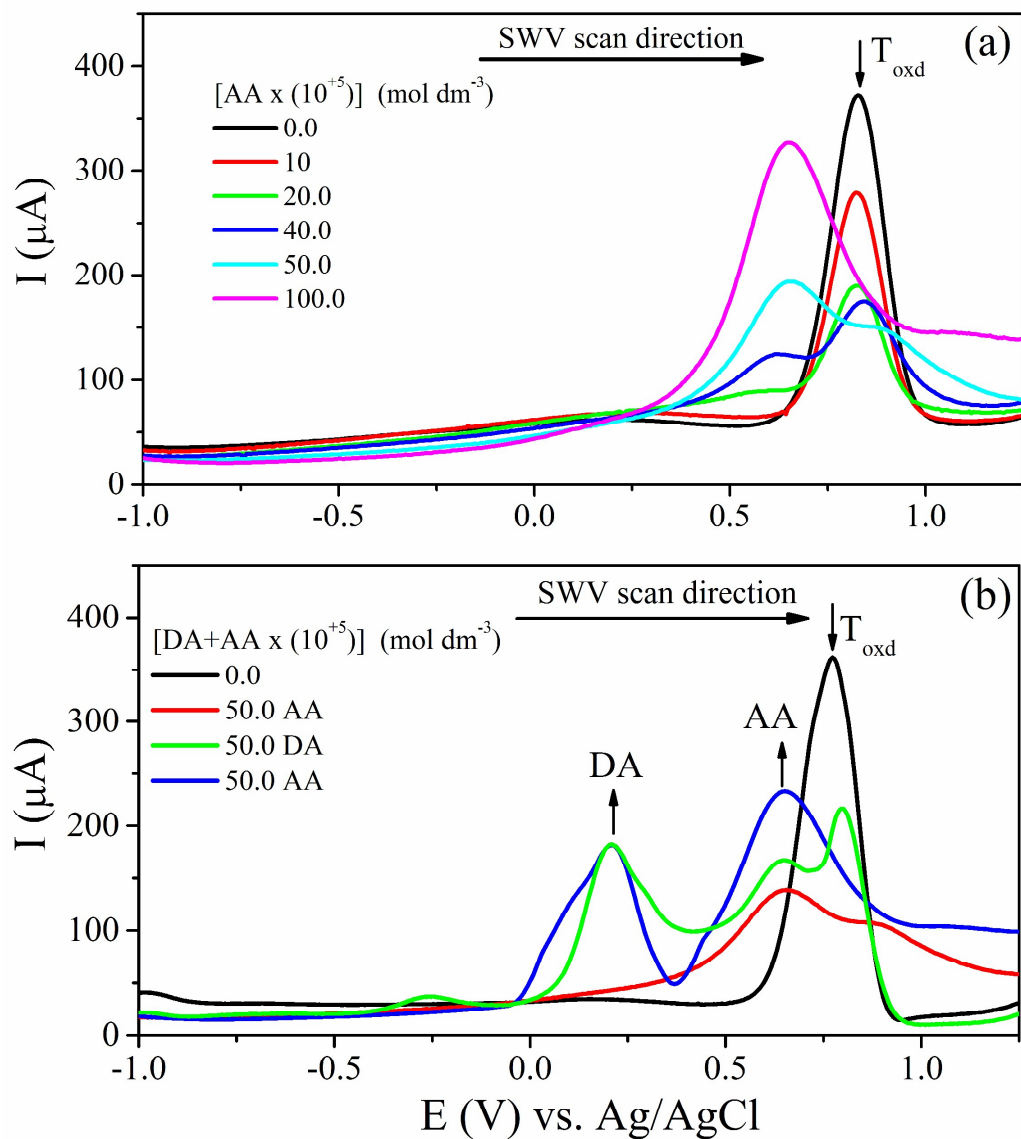
**Fig. 5:** CV and SWV of TEMPO-ZnPc ( $5.0 \times 10^{-4} \text{ mol.dm}^{-3}$ ) at various scan rates on GCE in DMSO/TBAP electrolyte system.



**Fig. 6:** In situ UV-Vis spectral changes of **TEMPO-ZnPc** in DMSO/TBAP. **a)**  $E_{app} = -0.90$  V. **b)**  $E_{app} = -1.40$  V. **c)**  $E_{app} = 0.90$  V. **d)** Chromaticity diagram (each symbol represents the color of electro-generated species;  $\square$ :  $[TEMPO-Zn^{II}Pc^{2-}]$ ,  $\circ$ :  $[TEMPO-Zn^{III}Pc^{3-}]^{1-}$ ,  $\triangle$ :  $[TEMPO-Zn^{III}Pc^{4-}]^{2-}$ ;  $\star$ :  $[TEMPO^{1+}-Zn^{II}Pc^{2-}]^{1+}$ ).



**Fig. 7:** SWVs of **TEMPO-ZnPc** dissolved in DMSO/TBAP during titration with AA (SWV parameters: Pulse size = 100 mV; Step size = 5 mV; Frequency = 25 Hz,  $E_i = -2.00$  V;  $E_f = 1.25$  V).



**Fig. 8:** a) SWVs of GCE/TEMPO-ZnPc in H<sub>2</sub>O/LiClO<sub>4</sub> during titration with AA. b) SWVs of GCE/TEMPO-ZnPc in H<sub>2</sub>O/LiClO<sub>4</sub> during titration with the mixture of AA and DA. (SWV parameters: Pulse size = 100 mV; Step size = 5 mV; Frequency = 25 Hz, E<sub>i</sub> = -1.00 V; E<sub>f</sub> = 1.25 V).