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Zinc(II) phthalocyanine fused in peripheral positions octa-substituted with alkyl linked carbazole: Synthesis, electropolymerization and its electro-optic and biosensor applications

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ABSTRACT

Zinc(II) phthalocyanine fused in peripheral positions octa-substituted with alkyl linked carbazole has been prepared by cyclomerization reaction of 4,5-bis(6-carbazole-9-yl-hexylsulfanil)phthalonitrile in the presence of anhydro Zn(II) acetate and a strong organic base (DBU). Synthesis steps were optimized and higher efficiency synthesis was achieved. The purpose of combining of carbazole moieties with phthalocyanine on the peripheral position is to enhance some properties such as photo and electrochemical properties because of strong electron-donating properties of carbazole group. This molecule has been electrochemically polymerized and the electrical and optical properties of the resulting conductive polymer have been investigated. Amperometric detection was carried out following oxygen consumption at −0.7 V vs. the Ag reference electrode in phosphate buffer (50 mM, pH 6.0). The novel biosensor showed a linear amperometric response for glucose within a concentration range of 0.05 mM to 1.5 mM (LOD: 0.024 mM). This result shows that modification of the proposed biosensor by copolymerization have provided to give perfect response to different glucose concentrations. Because of its superior spectral and electrochemical properties and contained zinc metal which can act as a mediator during biochemical reactions, this material has been used as a glucose biosensor platform to detection for real samples.

1. Introduction

Phthalocyanines (Pc) as tetrapyrrolic macrocycle have been the important research topics over 75 years. This great interest is because of their exceptional chemical and thermal stability, unique unexpected photophysical, photochemical and electrochemical properties (Bekaroglu, 1996; Dumoulin et al., 2010). These extra-ordinary properties give opportunities for their applications in different areas such as chemical sensors (Valli, 2005; Sizun et al., 2011), nonlinear optics (de la Torre et al., 2004; Germa et al., 1997; Mensing et al., 2013), electrochromic materials (Gümrükçü et al., 2011), liquid crystals (Swarts et al., 2001; Nolte et al., 2006; Özmen et al., 2012) second generation photosensitizers in photodynamic theraphy (Ali and van Lier, 1999), optical limiting devices (Calvete et al., 2004) and solar cell (Hagfeldt et al., 2010; Ragoussi et al., 2013). A disadvantage of phthalocyanines is their limited solubility in common organic solvents. The solubility of phthalocyanines in solvents is improved by making suitable substitutions on periheral or non-peripheral positions of aromatic rings (Brewis et al., 2000; Ogunbayo and Nyokong, 2009). Metal free or metallo phthalo-cyanines containing alkyl thio groups on peripheral or non-peripheral positions have been less studied (Ogunbayo and Nyokong, 2009; Gurek and Bekaroglu, 1994; Karimi and Khodadadi, 2012; Bıyıklıoğlu et al., 2010). In addition to that thioalkyl linked carbazole derivatized phthalocyanines have not been investigated.

Electroactive conducting polymers (ECPs) are a part of a new generation of smart materials that allow the direct delivery of electrical, optical, electrochemical and electromechanical stimulation. Additionally, these properties can be altered and controlled through stimulation (e.g. electricity, light, pH) even after synthesis. These and a number of other unique characteristics of ECPs that make them well-suited for integration with many technological applications such as OLED, fuel cell, biosensor, gas sensor, smart windows, displays etc (Soganci et al., 2016, 2014; Tekbaşoğlu et al., 2017; Akbulut et al., 2015; Guler et al., 2016; Ureta-Zañartu and Gutiérrez, 2016; Acar et al., 2014). Carbazole and its derivatives are one of the most studied conductive polymers. They have a strong interest due to their valuable properties by chemists, biologists and medicinal chemists (Knölker and Reddy, 2002; Zhang et al., 2010). Also, carbazole derivatives draw much attention because of their importance to understand the relation-

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ship between photophysical properties and a large scale areas such as solar cells, organic light-emitting devices (OLED), non-linear optical materials, hole-transport materials, organic photoconductors and phosphorescence applications (Hagfeldt et al., 2010; Tang et al., 2007; Chang et al., 2017; Sizun et al., 2011; Xia and Advincula, 2001).

Therefore, introduction of phthalocyanine moieties to the polymer architectures imparts a variety of functions to the conducting polymers. Up to now, the incorporation of some Pc, especially metallo phthalocyanines (MPc), to the conducting polymers has been successfully achieved by electrochemical polymerization of electroactive monomers in aqueous media using sodium salt of MPc as the supporting electrolyte (Skotheim et al., 1985; Al-Sagur et al., 2017). Limited literature is available regarding hybrid conducting polymers synthesized by electropolymerization of electroactive monomers substituted metallo phthalocyanines (Cogal et al., 2014; Galal et al., 2007; Gökçeören et al., 2014; Göksel et al., 2016; İpsiz et al., 2016; Muto et al., 2000; Özçeşmeci et al., 2013).

So far there have been two studies on biosensor applications of phthalocyanine-containing conductive polymers in the literature. But in both studies, phthalocyanine is not tied to the conducting polymer backbone with a covalent bond (Buber et al., 2017a; Al-Sagur et al., 2017). Although the crucial effect of the metal-based hybrid materials on biochemical reactions is known, there is no study available on the use of metallo phthalocyanine substituted hybrid-conducting polymer for biosensor applications.

In this work, Zinc (II) phthalocyanine fused in peripheral positions octa-substituted with alkyl linked carbazole has been prepared. The purpose of combining of carbazole moieties with phthalocyanine on the peripheral position is to enhance some properties such as photo and electrochemical properties, photo-sensitizer activity, electro-polymerization and organic dyes ability because of strong electron-donating properties of carbazole group (Khoza et al., 2013; Liu et al., 2014; Lv et al., 2011). As the electrical and optical properties of this molecule are superior, the electrochromic, optical and electrical properties of the conductive polymer obtained by electrochemical polymerization have been investigated. This molecule has been electrochemically polymerized and the electrical and optical properties of the resulting conductive polymer have been investigated. Because of its superior spectral and electrochemical properties and contained zinc metal which can act as a mediator during biochemical reactions, this material has been used as a glucose biosensor platform.

2. Results and discussion

2.1. Synthesis and characterization

The reaction sequence to the novel peripherally alkyl linked carbazole substituted phthalonitrile and its zinc phthalocyanine (ZnPc) derivative has been shown in Scheme 1. The precursor compound namely 6-(9H-carbazol-9-yl)hexane-1-thiol (**3**) has been synthesized a known route that contains a little different strategy. This compound was prepared previously a good yield (Lv et al., 2011). 9-(6-bromohexyl)−9H-carbazole (**1**) (Liu et al., 2015) and potassium thioacetate should be sufficient to achieve quantitative conversion of esterification reaction in 96% yield. The hydrolyze reaction of this compound was investigated in the presence of KOH/*i*-PrOH-THF-H_2O at 60 °C for 5 h. The choice of proposed route [(H_2SO_4/H_2O)(1/1) to obtain 6-(9-carbazol-9-yl)hexane-1-thiol (**5**) was essentially easier, advantage in terms of yield (92%), short reaction time (3 h), easy work-up and cheap starting materials. Detailed information on the all synthesis scheme is given Supporting Information.

2.2. Cyclic voltammetry

The cyclic voltammetry technique was used to study both the redox behavior of ZnPc and its capacity to produce polymer electrochemically.

Fig. 1 shows the repeated cyclic voltammetry graph of electropolymerization of ZnPc in 0.1 M TBAP/DCM. There is no any current increase was observed until potential increase about the 1.0 V in first anodic scan of CV. From this potential value, which is referred to as the onset monomer oxidation potential, ZnPc macrocycles are polymerized according to the ECE mechanism. Oxidation of the macrocycle continued to give a peak maximum at 1.5 V. In the first cathodic scan, two reduction peaks were observed at 0.88 V and 0.43 V correspond to the reduction of the oxidized polymer formed during the anodic scan. In the second anodic scan, new oxidation peak has been observed at 0.98 V, which has been a proof that ZnPc forms a conducting polymer on the electrode surface. The oxidation peak of the monomer in this cycle is a more positive value than that of the first cycle. This can be explained by the depleting of the monomer in the double layer of the electrode as the polymerization continues. Another proof of the deposition electroactive conductive film on the electrode surface is the continuous increase in the oxidation and reduction peak current values in the subsequent cycles. In addition, it has been observed that the oxidation peak potential value increased in each cycle, while a decrease in the reduction peak potential value as the number of cycles increased. For example, the polymer cathodic peak potentials in the first and third cycles decreased from 0.43 and 0.88 V to 0.36 and 0.77 V, respectively, while anodic peak values of second and third cycles increased from 0.98 V to 1.07 V. This observation is due to the fact that the resistance of the coated polymer film over the working electrode has been increased as its thickness has been increased in each cycle (Cihaner and Önal, 2005).

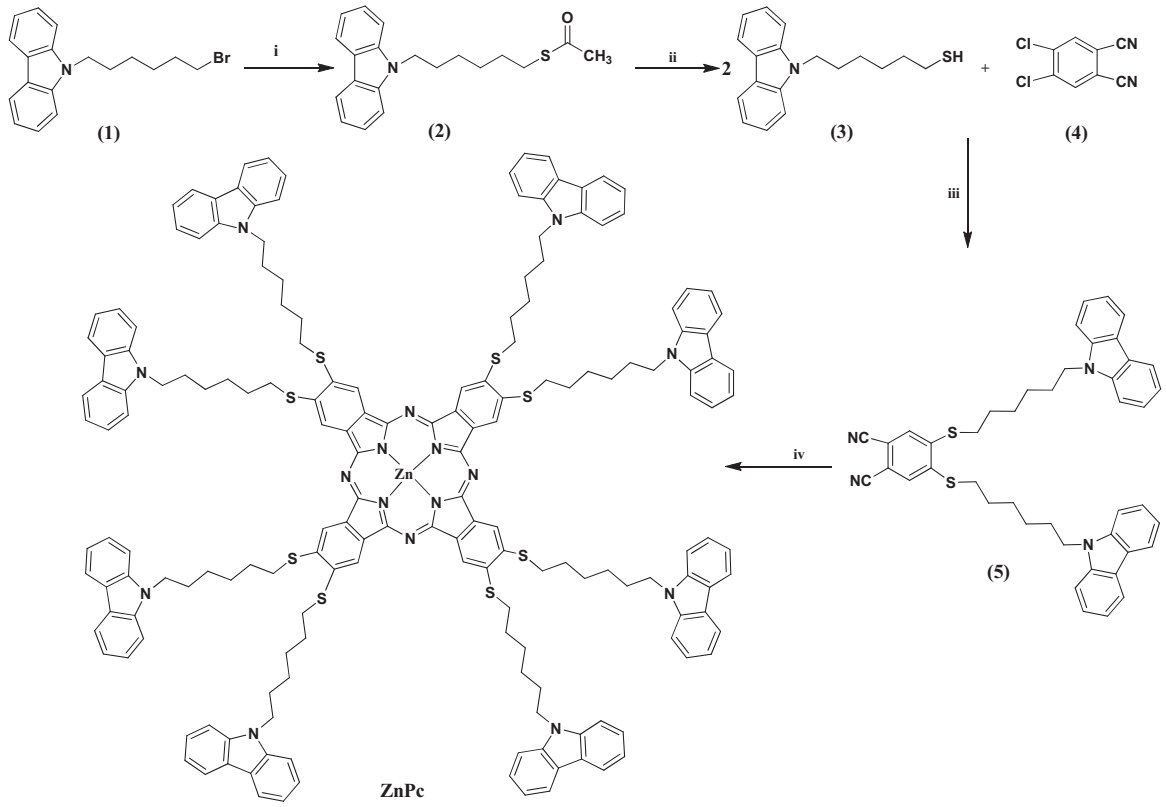
After cleaning the obtained polymer film from monomer residues, cyclic voltammetry technique has been used at varying scan rates in the monomer-free solution to investigate redox behavior of the polymer. Cyclic voltammetry graph of the polymer at a scan rate of 10 mV/s showed two reversible oxidation peaks at 1.03 and 1.40 V and corresponding reduction peaks at 0.75 and 1.09 V (Fig. 1b).

Cyclic voltammetry graph of polymer at scan rates ranging from 50 to 300 mV/s are given in Fig. 1c. When obtained redox peak potential values using this graph have been plotted versus corresponding scan rate values, a linear graph has not been obtained unexpectedly (Fig. 1c). Usually this graph has been obtained linearly because the redox process is not diffusion controlled for conducting polymers films on the electrode surface. This difference for P(ZnPc**)** indicates that the redox process is diffusion controlled. This claim has been verified by the linearity obtained when the same graph is plotted against the square root of scan rate. When the polymer film oxidized, dopant anions have to balance the positive charge created on the polymer backbone in order to maintain electroneutrality. It is thought that, diffusion of dopant anions is predominant step in the process due to the compact structure of P(ZnPc) and therefore diffusion controlled process is realized. Beside this, electron transfer coefficiency (α) of polymeric film was calculated as 0.191 s^{-1} described in the literature (Laviron, 1979).

2.3. Spectroelectrochemistry

Absorption spectrum of ZnPc was measured in dichloromethane to compare with its polymer absorption (Fig. 1e inset). ZnPc showed the intense Q-band with two maximum in the region of 600–750 nm and present a band at around 345 nm which is assigned to the phthalocyanine B band which are characteristic of the metallophthalocyanine derivatives.

In situ UV–vis spectroelectrochemical experiment seems to be the most appropriate technique to investigate electronic transitions between fundamental levels and polaronic or bipolaronic levels involve the energy of photons from the visible region of the spectrum. Spectroelectrochemical measurements were realized for the P(ZnPc) film coated onto ITO glass electrode in the 0.1 M TBAP/DCM solution.



Scheme 1. (i) KSAc, THF, reflux, (ii) H_2SO_4/H_2O, methanol, reflux, (iii) Na_2CO_3, dry DMF, 50 °C, (iv) $Zn(CH_3COO)_2$, DBU, dry n-pentanol, reflux.

Fig. 1e shows the UV–vis absorption profile correlated with the applied potentials for P(ZnPc).

Spectroelectrochemistry of P(ZnPc) at 0.3 V (its neutral state) exhibited strong absorption below 400 nm assigned to π–π* transitions in carbazole moiety but it was almost transparent in the visible and NIR regions. In this neutral state, only Q band absorption of phthalocyanine between 600 and 800 nm was observed. The optical band gap of polymer was calculated by the onset of the absorption peak determined from the UV–Vis spectra as 3.42 eV. During the electro oxidation of P(ZnPc) the band at 300 nm gradually lost its intensity with the applied potential. At moderate potential values, a new peak emerged at 400 nm and its intensity increased with a maximum at 1.2 V. At the further applied potentials, a decrease in intensity of this peak, which is thought to be the absorption of the polaron bands, were observed due to the conversion of polaron to bipolaron bands. Besides Q band absorption of phthalocyanine, absorption of polycarbazole between 600 and 800 nm were observed in the fully oxidized state of P(ZnPc).

A repeated potential stepping method coupled with UV–vis spectroscopy was used to investigated spectroelectrochemical switching properties of P(ZnPc). Spectroelectrochemical switching experiments were performed at regular intervals of 15 s in a monomer free 0.1 M TBAP/DCM solution. Several parameters such as response time which is the time needed for the realization of the 95% of the full optical contrasts and percentage of optical contrast (ΔT%) at a fixed wavelength, were calculated. Response time is defined as the time required for a conducting polymer to change from colored state to bleached state at a given wavelength. Fig. 1f displays the switching properties of P(ZnPc) between 0.3 and 1.6 V at 665 nm. From this graph, the optical contrast was calculated as 53% and the response time was 6.8 s. P(ZnPc) has high response time when compared with the relevant literature. It is thought that dopant anions are difficult to intercalate into the compact P(ZnPc) backbone which is confirmed by SEM analysis.

2.4. Biosensor investigations

2.4.1. Electrochemical characterization of the P(ZnPc-co-TP)

The detailed copolymerization studies is given Supporting Information (Fig. S4). To address the analytical applicability of the ZnPc-*co*-TP, the electrochemical deposition of ZnPc-*co*-TP was operated via CV by sweeping the potential between −0.9 and 1.6 V. At first, the electrochemistry of different copolymerization ratios was studied on the cleaned bare graphite electrode (Preparation of enzyme electrode is given Supporting Information). Fig. 2a and b shows the typical cyclic voltammograms of the 0.6 ZnPc/0.4 TP and 0.04 ZnPc/0.096 TP in the presence of 0.1 M TBAP/DCM at a scanrate of 100 mV s^{-1}. When the analyzing CVs of ZnPc-*co*-TP and TP (Guler et al., 2014), it has been confirmed that the copolymerization was achieved successfully. When the comparing of 0.6 ZnPc/0.4 TP and 0.04 ZnPc/0.096 TP, the increase in oxidation and reduction peak currents of 0.6 ZnPc/0.4 TP and 0.04 ZnPc/0.096 TP.

On the other hand, to get the best biosensor performance, the effect of copolymerization ratios on the sensor performance were investigated. Firstly, copolymers were polymerized on the graphite electrode surfaces with different amounts (0.6 ZnPc/0.4 TP and 0.04 ZnPc/0.096 TP each of them 1 mM) to investigate the effect of the copolymerization ratio. After copolymerization, a proper amount of GOx solution and 1.0% of 10 μL GA were dropped on the electrode which have different copolymer ratio. The bioensor responses were monitored while the enyzme amount was kept constant. The highest signal was monitored for the biosensor constructed using 0.6 ZnPc/0.4 TP (Fig. 2c), which was chosen as the optimum copolymerization ratio and used for the ensuing experiments.

2.4.2. Characterization of the P(ZnPc-co-TP)/GOx enzyme electrode surface

To identify the surface of the electrode was utilized by scanning electron microscopy. For these reason, ZnPc, ZnPc-*co*-TP were poly-

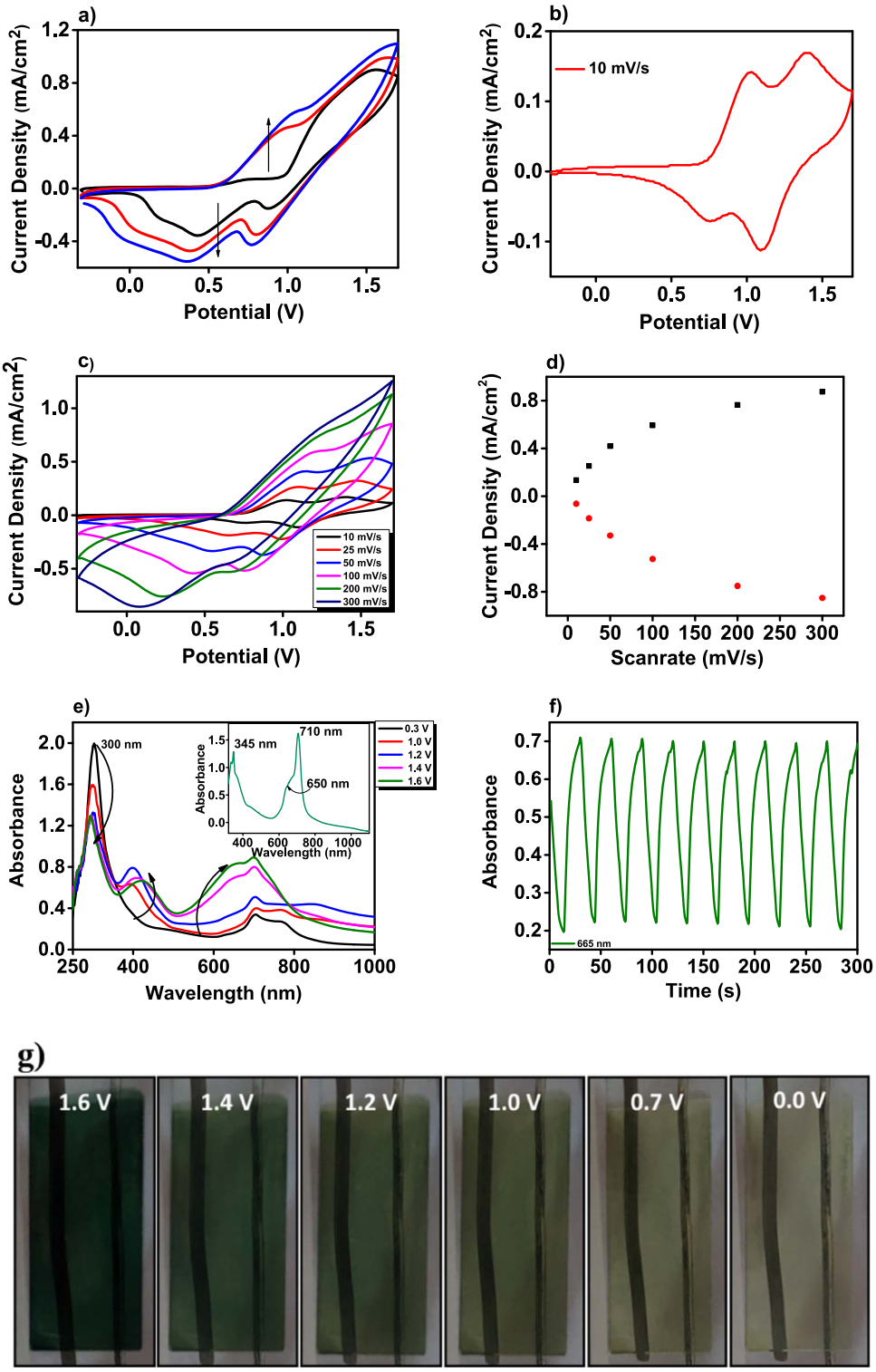


Fig. 1. Typical cyclic voltammetric graph of a) ZnPc (Scan rate = 100 mVs^{-1}) and b) P(ZnPc) Scan rate = 10 mVs^{-1} in 0.1 M TBAP/DCM, c) CVs of ZnPc recorded at various scan rates on a ITO working electrode in 0.1 M TBAP/DCM and d) A plot of scan rates against current density during cyclic voltammetry of P(ZnPc) thin film, e) Optoelectrochemical spectrum of P(ZnPc) film in TBAP/DCM and f) Optical absorbance change monitored for P(ZnPc) between +0.3 and +1.6 V, g) The colors of P(ZnPc) films at their neutral and various oxidized states.

merized on the surface of the graphite rods by an electrochemically and it was coated onto the electrode surface. After a drop of the GOx, GOx was immobilized onto electrode surface. The SEM images of graphide rode, ZnPc, ZnPc-*co*-TP and ZnPc-*co*-TP/GOx are shown in Fig. 3. The surface of graphite rode displays a lettuce morpohology (Fig. 3a). When analyzing surface of polymer coating graphite rode, the ZnPc shows a homogeneus spherical form while the copolymer coated surface displays a non-homogeneus structure (Fig. 3b, c). The none-homogeneus spherical surface of ZnPc-*co*-TP has tightly covered with enzyme which this means immobilization of enzyme has been executed succesfully (Fig. 3d). All these result shows that surface of the electrodes has distinctly different morphologies.

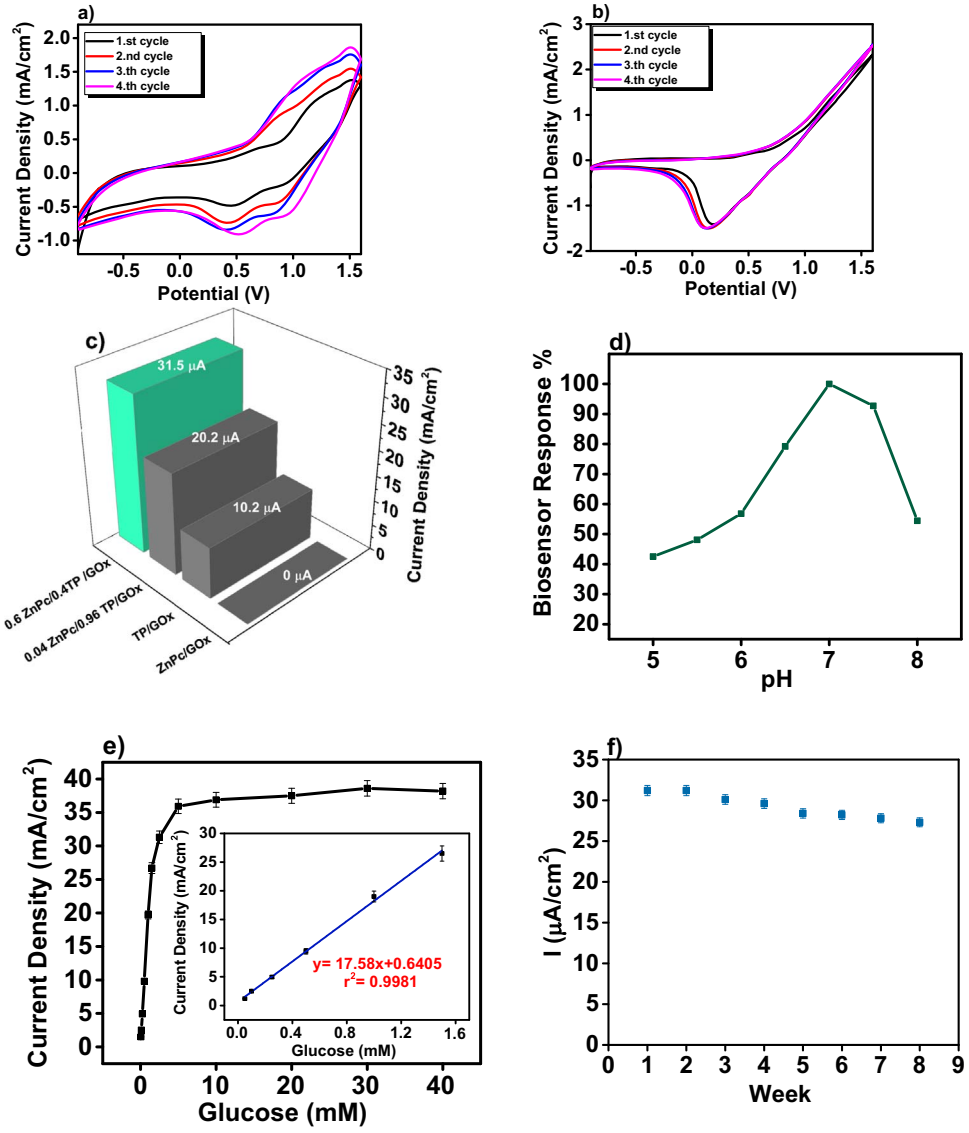


Fig. 2. CVs of a) 0.6 ZnPc /0.4 TP (0.1 M), b) 0.04 ZnPc (0.1 M) /0.096 TP (in DCM containing 0.1 M TBAP as the supporting electrolyte. Scanrate 100 mV/s, c) Amperometric biosensor responses of P(ZnPc-*co*-TP)/GOx at different copolymerization ratio (0.6 ZnPc/0.4 TP and 0.04 ZnPc/0.096 TP) in sodium phosphate buffer, pH 7.0, −0.7 V, [Glc]:2.5 mM, P(TP)/GOx in sodium acetate buffer,50 mM, pH4.5, −0.7 V,[Glc]:2.5 mM, P(ZnPc)/GOx in sodium phosphate buffer,50 mM, pH6.5, −0.7 V,[Glc]:2.5 mM, d) Effect of pH P(ZnPc-*co*-TP)/GOx. (in Na-acetate buffer, 50 mM, at pH 5.0–5.5 and in Na-phosphate buffer 50 mM, at pH 6.0–8.0; −0.7 V, [Glc]: 2.5 mM), e) Calibration curve for glucose (in pH 7.0, 50 mM PBS, −0.7 V). Error bars show the standard deviation of three measurements, f) Stability of the P(ZnPc-*co*-TP)/GOx enzyme sensor.

2.4.3. *Effect of pH*

The influence of pH was investigated to obtain the optimum conditions for the determine the electrocalytic activity of the developed ZnPc-*co*-TP/GOx enzyme sensor. The pH was varied between 5.0 and 8.0 using the 50 mM Na-phosphate buffer (PBS) at −0.7 V. The measured currents were plotted as a function of pH. As can be seen from Fig. 2.d the response increases significantly from pH 5.0–7.0. After this value, current value was decreased. For this reason, the optimal enzyme sensor electrocatalytic activity was obtained at pH 7.0 of PBS.

2.4.4. *Calibration of enzyme electrode*

After the optimization of experimental conditions, a calibration curve for glucose was plotted (Fig. 2e). The current change was observed for the substrate over a concentration range of 0.05–40 mM. The ZnPc-*co*-TP/GOx enzyme sensor has showed a sensitive response towards the different concentrations of glucose and the current response increased as the glucose concentration was increased upto 5 mM after which it became constant upto 40 mM. A linear relationship of P(ZnPc-*co*-TP)/GOx was observed between 0.05 and 1.5 mM glucose concentration satisfying the equation y = 17.58x + 0.6465 and R^2 = 0.998. The analytical characterization parameters of the glucose enzyme sensor can be summarized as follows. Limit of detection (LOD) and sensitivity were specified 0.064 µM and 30.681 µA/mM cm^2 for glucose with S/N = 3 criteria.

In order to certify the repeatability of the fabricated enzyme sensor, the P(ZnPc-*co*-TP)/GOx responses corresponding to 2.5 mM glucose solution were saved for fifteen times. The standard deviation (SD) and variation efficiency for these measurements were calculated as ± 0.12% and 0.40% respectively. On the other hand, the life-time of the P(ZnPc-*co*-TP)/GOx was also measured by taking amperometric measurements for 60 days with a once a week. The electrode was stored in the refrigerator in pH: 7 buffer that was most suitable for the enzyme activity. Only 12.5% of activity loss was observed at the end of this time (Fig. 2f). Comparison of analytical parameters of the present biosensor with the previously reported studies is summarized in Table 1.

Beside this, the practical possibility of the enzyme sensor and various interfering substances in the real samples has been evaluated.

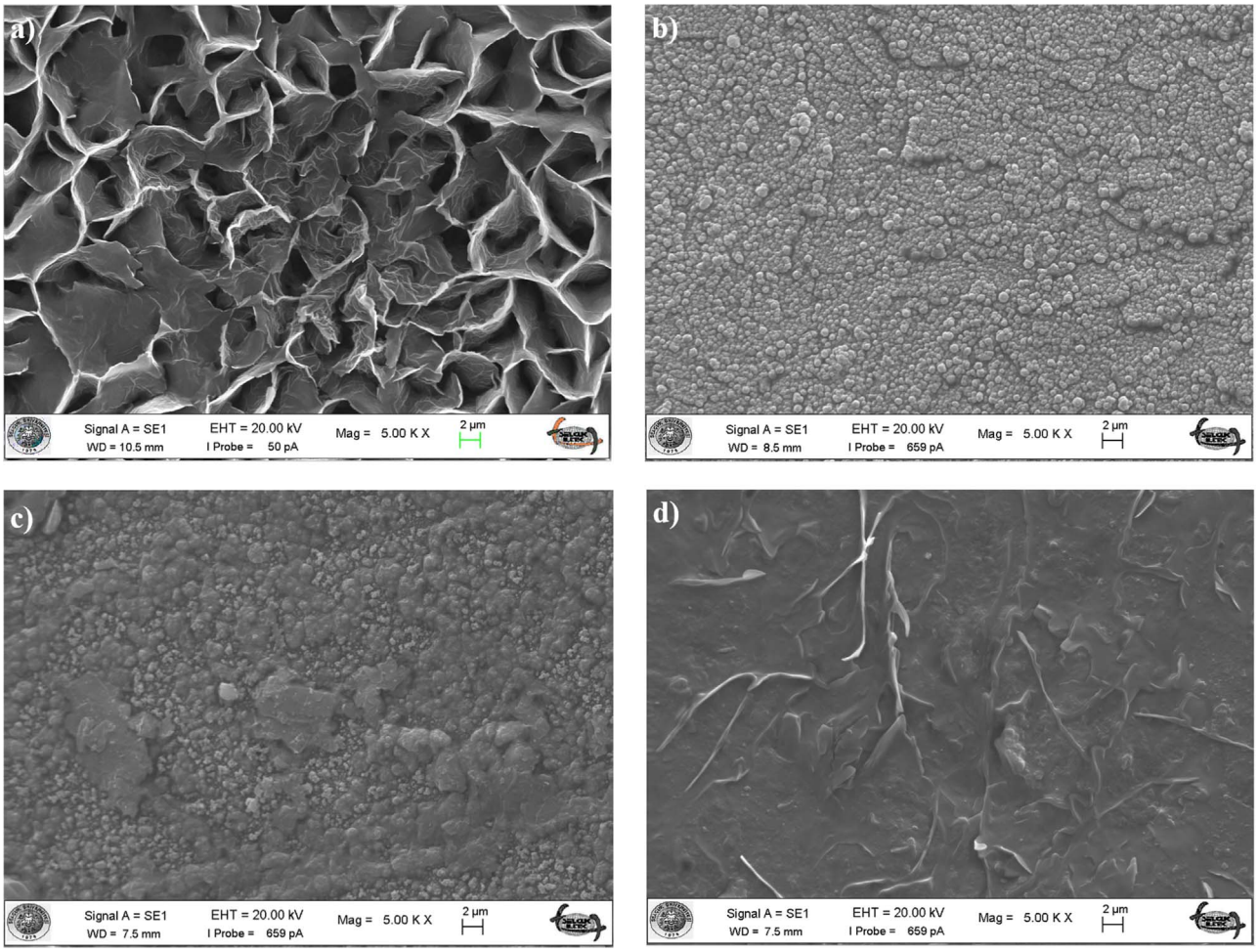


Fig. 3. SEM images of a) graphite rode, b) ZnPc, c) ZnPc-*co*-TP and d) ZnPc-*co*-TP/GOx.

The current values for two different commercial examples has been signified in Table S2. As seen in Table S3 the proposed enzyme sensor did not give any significant response to interfering substances. Detailed information is given Supporting Information.

3. Conclusion

In summary, the peripherally substituted zinc(II) phthalocyanine containing octa alkyl linked carbazole moieties and the optimized conditions for some reaction steps such as esterification (**2**), ester hydrolyses (**3**) and substituted dicyano compound (**4**) were significantly achieved in good yields. The structures of these compounds were confirmed with elemental analysis and several spectroscopic methods. The conductive polymer obtained by electrochemical polymerization of this octa-substituted novel zinc(II) phthalocyanines bearing carbazole groups is characterized in terms of optical, electrical and surface properties. The novel conductive polymer showed superior properties in terms of stability, optical contrast, and other electrochromic properties. Since it is known that metals can catalyze biochemical reactions as mediators, the obtained zinc-containing material has been tested for its utility as a biosensor platform. After determining optimum conditions, the prepared glucose biosensor platform was applied to the real samples.

Table 1
Comparison of analytical performance of phatalocyanine derivatives based enzyme sensor.

Immobilization Matrix	Biological Material	Linear Range for Glucose (mM L^{-1})	LOD (mM)	Sensitivity (µA $mM^{-1}cm^{-2}$)	Stability	Reference
SNS-NH_2	GOx	1–10	0.903	6.3	NR	Ayranci et al., 2015
GR-CoPc/GOx	GOx	0.01–14.8	1.6	5.09	NR	Mani et al., 2014
GCE–CoPc–$(CoTPP)_4$	GOx	up to 11 mM	0.01	24.20	Longer than 2 weeks	Ozoemena and Nyokong, 2006
Poly/MWCNT/ZnPc/GOx	GOx	0.025–1.0	0.018	82.18	Longer than 4 weeks	Buber et al., 2017b
GOD/Nafion/$(LbL)_{3.5}$/ABS	GOx	0.1–8	0.05	17.5	Longer than 4 weeks	Zhang et al., 2013
P(ZnPc-*co*-TP)	**GOx**	**0.05–1.5**	**0.024**	**30.68**	**Longer than 8 weeks**	**This Work**

NR: Not Reported.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.bios.2017.06.028.

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