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Triazole substituted phthalocyanines and their electrochemical properties

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ABSTRACT

New cobalt (II), zinc (II), tin (II) and metal free phthaloyanines having peripherally triazole and Schiff's base groups on were synthesized and their electrochemical properties were studied. In the first step of the synthetic procedure, triazole moiety, in the second step Shiff base moiety and in the third step key compound substituted phthalonitrile have been synthesized successfully in high yield. At the final stage target phthalocyanines have been obtained and characterized by combination of spectral analysis. The electrochemical measurements showed that while Free- and Sn-Pc give irreversible oxidation process, Co- and Zn- phthalocyanines give quasi-reversible electron transfer reaction in dichloromethane solution.

Keywords:
Phthalocyanine; Metallophthalocyanine; Triazole; Schiff base; Electrochemistry.

INTRODUCTION

Phthalocyanines (Pcs) can be used many different applications such as gas sensors, electrochromic devices, photovoltaic cells and photodynamic therapy (PDT), due to their 18-π planar conjugate electron system [1-4]. Therefore synthesizing Pcs having different groups play a vital role in promoting these high technologies.

These macrocyclic compounds are ideal building blocks for applications when they are modified with groups in the desired properties. For this reason, substitution of Pcs either on peripheral/non-peripheral or axial positions has vital importance for their utilizations. Furthermore, the solubility of Pc derivatives plays a critical role in order to use in all those applications. Phthalocyanines that unsubstituted are not soluble in common organic solvents due to the aggregation. These compounds can be made soluble in organic solvents by integration of substituents in the periphery/non-periphery of Pc core, thus increasing their electrochemical and catalysis applications. [5].

1,2,4-Triazole derivatives are one of the key organic compound class have an important functions in biological applications. It's known that some of 1,2,4-triazoles exhibit biological trenchancy e.g. antifungal, anti microbial, anti viral, anti tubercular, antidepressant, anti inflammatory, anti oxidant anti convulsant and anticancer [6-8]. Furthermore, Schiff base derivatives of [1,2,4] triazoles have been identified having diverse pharmacological properties, like antifungal, antimicrobial, anticancer, antioxidant, anticonvulsant and anti-tubercular activities [9-12]. Moreover, Schiff bases bearing 1,2,4-triazole ring play important roles in coordination chemistry as they easily stable complexes with most transition metal ions [13, 14].

Recently, Tanyeli and co-workers drew attention the promising results for photochromic applications of triazole substituted zinc(II) Pc [15]. Kantekin et al. studied on the singlet oxygen quantum yield of phthalocyanine complexes substituted with tetra triazole groups on periphery and they have studied the electrochemical properties of 1,2,4-triazole substituted Pcs [16, 17]. Bayır and co-workers have recently investigated the electrochemical properties of Pcs that have thiazole substituents containing Cobalt, Zinc and manganese as metal centers [5].

As mentioned above, to the best of our knowledge, there are few studies concerning about the electrochemical applications of triazole containing Pcs. For this purpose, the main goal of this work is to prepare new metal free and metallo Pcs (cobalt(II), Zinc(II) and tin(II)) containing triazole and Schiff base moieties with long alkyl chain and to investigate the electrochemical properties of them. Long alkyl chain and bulky heterocyclic moieties were purposely chosen and adapted the structure to overcome the insolubility and aggregation drawback of Pcs.

EXPERIMENTAL

Material and equipment used in this study and experimental studies were explained in supplementary information.

RESULTS AND DISCUSSION

Synthesis and characterization

The synthesis step of new compounds is shown in Figure 1. The starting material was synthesized the reaction which was used sodium ethoxide as basic catalyst, initial triazole and 1-bromoheptane in absolute ethanol [21], Compound **(2)** was obtained from the reaction between compound (**1**) and 4-hydroxybenzaldehyde at 160-165 °C. The phthalonitrile compound **(3)** was synthesized by using compound **(2)**, 4-nitrophthalonitrile and K_2CO_3 in DMF. In the last step, the intended compounds **(4-7)** were obtained by the cyclotetramerization of the compound **(3)** in n-pentanol at reflux temperature and by the catalyst of DBU.

The IR spectrum of compound (**1**) displayed absorption bands at 3305, 3260 cm^{-1} corresponding to the NH_2 and at 1713 cm^{-1} corresponding to triazole C=O groups, respectively. In the ^1H NMR spectrum of compound (**1**), the aliphatic CH_2, CH_3 and CH_2-N protons were observed at between 0.83-3.64 ppm. The ^{13}C NMR signals for aliphatic carbons were recorded at between 11-46 ppm.

In the FT-IR spectrum of compound (**2**), the -NH_2 stretching vibration of the compound (**1**) at 3305 cm^{-1} disappeared and new –OH stretching at 3171 cm^{-1} appeared and in ^1H-NMR spectrum of the same compound the signals of the protons for the –NH_2 group of the compound **(1)** at 4.22 ppm disappeared and new signals at 6.73 and 9.62 ppm that belong to the protons of –OH and –CH=N groups, respectively, came along after the reaction and verifies the propounded structure. ^{13}C-NMR and mass spectral data promotes the framework of the compound **(2)**.

For compound **(3)**, in the FT-IR spectral data, evidence of the nascency of the phthalonitrile compound is the disappearence of the –OH stretching of compound **(2)** and the appearence of a novel vibration at 2234 cm^{-1} that belongs to C≡N group. From the ^1H NMR and ^{13}C NMR measurements, the absence of signal of the –OH proton of compound **(2)** and the new carbon signals at 116.84 and 116.33 ppm that belong to nitrile carbons verifies the formation of the anticipated product. Mass spectral values confirmed the desired structure.

Cyclotetramerization of a substituted phthalonitrile is a general way to synthesize of modified Pcs. It is necessary to use high boiling solvents (Dimethylaminoethanol, n-pentanol etc.) and catalysts (DBU) [3, 22]. During the preparation of Pc compounds **(4-7)** n-pentanol and DBU were used and obtained isomeric mixtures were not

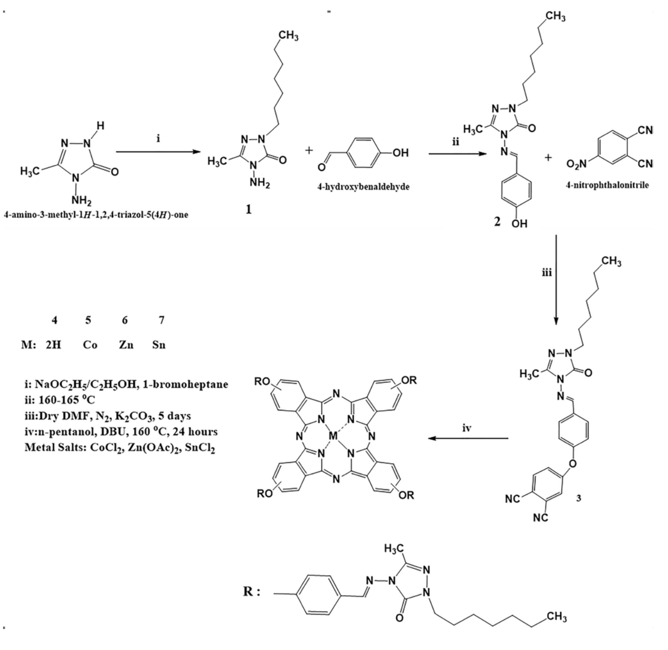

Figure 1. Reaction scheme of new compouds (**1-7**).

separated [23]. In the FT-IR spectra of Pcs **(4-7)**, the case of the achievement of the reactions is the disappearence of the vibration of the nitrile group of compound **(3)** at 2234 cm^{-1} in their spectra. Differently form metallophthalocyanines **(5-7)**, in the IR spectrum of metal-free phthalocyanine **(4)** the vibration of inner –NH group was also monitored at 3288 cm^{-1}. The rest of the spectrums of the compound **(3)** and Pcs **(4-7)** were similar. ^{1}H NMR measurement of compound **(5)** could not be carried out because of the paramagnetic central metal ion and the spectra of compounds **(4, 6, 7)** were similar to the spectrum of their starting material (compound **(3)**). Some signals were broad because of their isomeric mixture and probable aggregation at measured concentrations. However, the inner core –NH proton signal were also could not be determined because of aggregation of metal-free Pc molecule **(4)** at NMR measurement concentration [24]. Moreover, mass spectral data supported the proposed structures of the novel Pcs **(4-7)**.

Generally Pcs possess absorptions nearby 650-750 nm due to the $\pi \rightarrow \pi^*$ transitions and named as Q-band and 300-350 nm -deeper π-levels to π^* transitions are named as B band. Entire recent Pcs **(4-7)** were solvable in polar non aqueous solvents and their Electronic spectra were evaluated in trichloromethane (Fig. 2). Unlike the strong single absorption of Q-band of metallophthalocyanines, metal free phthalocyanines show as doublet in their electronic spectra [25]. The Q bands of the compounds **4-7** were observed at 700-665, 665, 676 and 705 nm, respectively (Fig. 2). The B bands of the substituted Pcs **(4-7)** were monitored at 324, 327, 315 and 315 nm, respectively. Furthermore the aggregation behavior of Pcs can be identified from their absorption spectra at measurement concentration and all Pcs did not show aggregation in chloroform 1x10^{-5} M concentration.

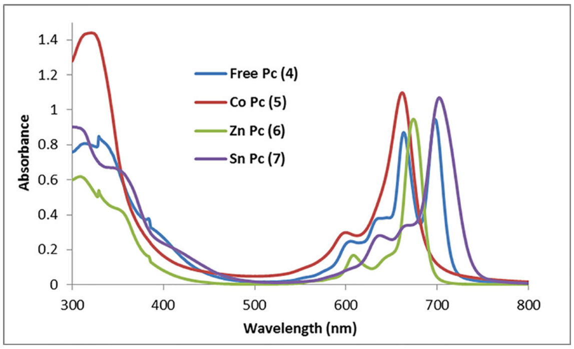

Figure 2. Electronic spectra of Pcs **(4-7)** in trichloromethane at 1x10^{-5} M concentration.

The fluorescence spectra of the Pcs were investigated in CH_2Cl_2 at 1×10^{-6} M concentration. The investigated compounds, except for Co-Pc, exhibited Stokes shift ranges from 19–42 nm in CH_2Cl_2. Fluorescence excitation and emission spectra of Sn- and Zn-Pc in CH_2Cl_2 were shown in Figure 3 and Figure S1 and data tabulated in Table 1. Fluorescence emission spectrum of Zn-Pc was of typical character for similar phthalocyanines – they mirrored

Table 1. Fluorescence data for compounds.

Compound	*Q-band wavelength (nm)*	*Excitation wavelength (nm)*	*Emission wavelength (nm)*
Free-Pc	*700, 655, 642, 609*	*703, 664, 637, 604*	*787, 723*
Zn-Pc	*676, 614*	*694, 677, 614*	*760, 699*
Co-Pc	*665, 608*	-	-
Sn-Pc	*705, 643, 670*	*699, 665, 638, 606*	*784, 738, 706, 666*

Table 2. Electrochemical data for Fc and Pcs

Compound	E_{pa} (V)^a	E_{pc} (V)^a	$E^{o'}$ (V)^b	ΔE (V)^c	I_c/I_a	Egap(eV)^d	Egap(eV)^e
Free-Pc	*0.445*^{f} *-1.129*	— *-1.262*	— *-1.196*	— *0.133*	— *2.22*	*1.65*	*1.65*
Co-Pc	*0.317* *-0.563* *-1.025*	*0.225* *-0.758* *-1.191*	*0.271* *0.661* *1.108*	*0.092* *0.195* *0.166*	*0.67* *2.59* *3.17*	*1.50*	*1.58*
Zn-Pc	*0.302* *-1.342*	*0.185* —	*0.244* —	*0.117* —	*0.72* —	*1.65*	*1.72*
Sn-Pc	*0.689*^{g} *-1.007* *-1.335*	— *-0.864* *-1.178*	— *0.936* *-1.257*	— *0.143* *0.157*	— *1.51* *4.10*	*1.70*	*1.59*

a: Potential (V) ***vs.*** Fc/Fc$^+$.

b: Formal standard potential ($E^{0'}$) = E_{pc} + E_{pa}/2.

c: ←E = E_{pa} - E_{pc}

d: HOMO-LUMO gap from electrochemical measurement

e: HOMO-LUMO gap from UV/vis spectroscopy

f: Potential (V) ***vs.*** Ag/AgCl.

g: Anodic peak potential for irreversible process.

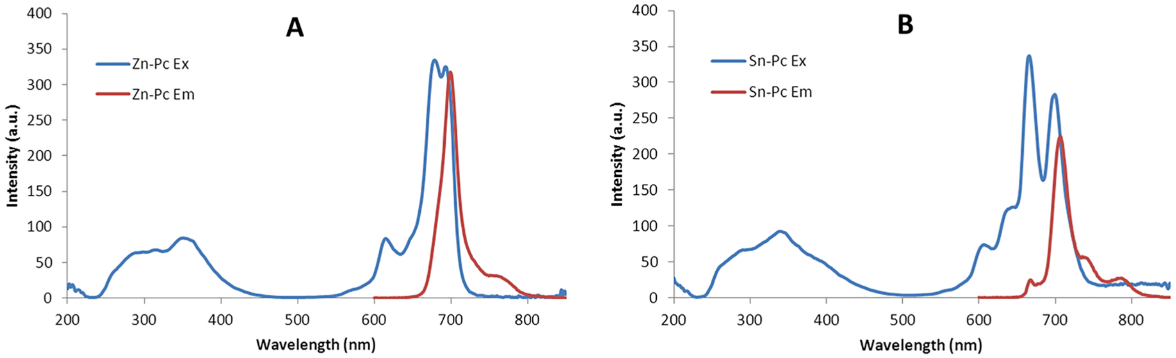

Figure 3. Fluorescence excitation and emission spectra of ZnPc (A) and SnPc (B); excitation wavelengths are 677 nm for ZnPc and 665 nm for SnPc.

the absorption Q-band with only small Stokes shift (20 nm). Because of the loss of symmetry and size of the Sn^{2+} ion coordinated to Pc ring, there was a characteristic disagreement of the absorption, excitation and emission spectra of Sn-Pc complex (Figure 3) [26]. Excitation spectra of Sn-Pc was not accordance with the absorption spectra proved that the compound was present exclusively in its aggregated state in electronic spectra [27]. Because of the enhanced spin–orbital coupling, or an energy or electron transfer mechanism properties of the paramagnetic transition metals, almost no fluorescence signal has been detected for Co-Pc (see Supplementary Fig. S1) [28, 29].

Electrochemical Studies

Electrochemical properties of compounds were investigated by using cyclic voltammetry technique in dichloromethane solution containing 0.1 M tetra-n-butylammonium perchlorate (TBAP, $n\text{-}Bu_4NClO_4$). The obtained electrochemical data were listed in Table 2 and voltammograms of compounds were given in Fig. 4. In order to establish electrochemical stability and reversibility criteria, cyclic voltammograms (CVs) of ferrocene were recorded in the same experimental conditions using Pt working electrodes (Figure S2). The formal standard potential ($E^{0\prime}$) of Fc^+/Fc under experimental conditions was calculated as 0.487 V vs. Ag/AgCl [ΔE_p (the anodic to cathodic peak-to-peak separation) = 0.082 V, I_{pc}/I_{pa} (the cathodic-anodic peak ratio) = 1.06].

As shown in Fig. 4, metal free Pc **(4)** gives ill-defined oxidation peak located in the positive area due to the aggregation of compound in working electrolyte system. According to literature data, this peak could be assigned to the irreversible oxidation of the Pc ring. On the other hand metal free Pc **(4)** exhibited diffusion-controlled quasi-reversible reduction features at -1.196 V. While coordination to Sn(II) center caused to shift higher potential, the broad oxidation wave of Pc ring shifted to negative potential values by coordination of Zn(II) and Co(II) metals due to the charge of the electron transfer center. Because the orbital energy level of first-row transition metal ions may be positioned between HOMO—LUMO levels of Pc ligand, coordination of metal ion to ring cavity could alter electrochemical properties of compounds. As a result of coordination through N atom of the Pc ring, CoPc **(5)** and ZnPc **(6)** compounds exhibited quasi-reversible oxidation processes at 0.271 (I_c/I_a= 0.67) and 0.244 V (I_c/I_a=0.72) vs. Fc/Fc^+, respectively (for the detailed electrochemical analysis see Supplementary Fig. S3) [30].

ZnPc **(6)** shows a totally irreversible reduction character at -1.342 V vs. Fc/Fc^+. On the other hand, reduction processes for CoPc **(5)** and SnPc **(7)** are not completely reversible in terms of both ΔE and the ratio of anodic to cathodic peak currents (Table 2). Ground state of the CoPc **(5)** corresponds to electronic configuration $(a_{1g})^2$ $(a_{1u})^2$ $(1_{eg})^3$, which yield ^2E_g state and one-electron oxidation occurs from the Pc a_{1u} orbital, the first reduction involves addition of an electron to the partially filled $1e_g$ corresponding Co-based d-orbitals [31]. Thus potential gap of the first oxidation and second reduction in cyclic voltammetry directly related to HOMO-LUMO gap. When the central metal atom is Zn or Sn, the 3d subshell is filled and removal of an electron from HOMO and addition of electron to LUMO corresponds the first oxidation and reduction couples [17]. For all the redox processes, the plots of square root of scan rate versus current were linear confirming diffusion control. The onset values of the absorption spectrum of compounds were used

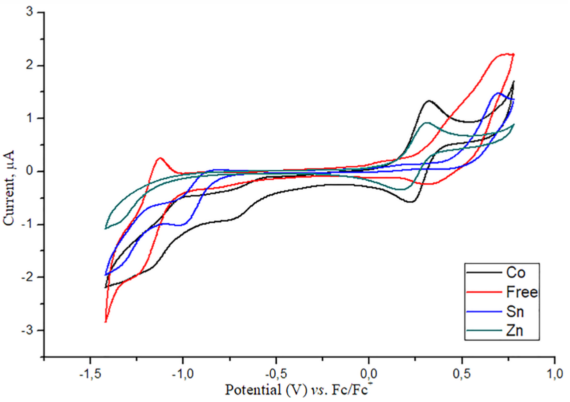

Figure 4. Cyclic voltammograms of compounds **(4-7)** at 100 mV s^{-1} scan rate in CH_2Cl_2 solution containing 0.1 M TBAP.

as an approach to estimate HOMO-LUMO gap energy of molecules and a correlation with electrochemical data have been established in Table 2 [32].

CONCLUSION

In conclusion, the preparation of metal free Co(II), Zn(II) and Sn(II) Pcs complexes bearing [1,2,4] triazole and Schiff base parts have been synthetized and electrochemical properties of these compounds have been investigated. The yields of the reactions pretty high and final obtained phthalocyanines have high solubility and did not show aggregation in organic solvents as intended. The electrochemical studies of novel compounds show that metal free Pc **(4)** exhibited diffusion-controlled quasi-reversible reduction features at -1.196 V and CoPc **(5)** and ZnPc **(6)** compounds exhibited quasi-reversible oxidation processes at 0.271 (I_c/I_a= 0.67) and 0.244 V (I_c/I_a=0.72) vs. Fc/Fc$^+$, respectively. ZnPc **(6)** shows a totally irreversible reduction character at -1.342 V vs. Fc/Fc$^+$. On the other hand, reduction processes for CoPc **(5)** and SnPc **(7)** are not completely reversible in terms of both ΔE and the ratio of anodic to cathodic peak currents.

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