Electrochemical pesticide sensors based on electropolymerized metallophthalocyanines

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ABSTRACT

New metallophthalocyanines (MPcs) were designed with redox active Co(II) (CoPc(ma)), Cl-Mn(III) (Cl-MnPc (ma)), and Ti(IV)O (TiOPc(ma)) metal centers and morpholin and amino bearing substituents (ma). While redox active metal centers enhanced redox activity of the complexes, redox active and electropolymerizable [2-(4-{[(1E)-(4-morpholin-4-ylphenyl)methylene]amino}phenyl)ethoxy] substituents triggered the coating of MPcs with the oxidative electropolymerizations. Voltammetry and in situ spectroelectrochemistry techniques were used for the electrochemical characterizations of MPcs. All complexes gave metal based reduction processes in addition to the Pc based processes. Moreover, all complexes were coated on GCE with the oxidations of morpholin and amino moieties of the substituents, thus redox active and conductive GCE/MPc(ma) electrodes were constructed. Modified electrodes were investigated as the potential pesticide sensors. Changing the metal center of the complexes significantly altered their sensing activities. While all complexes showed interaction abilities for chlorophyros, fenitrothion, and methomyl. GCE/CoPc(ma) electrode sensed fenitrothion with good selectivity and sensitivity. A linear range for the fenitrothion sensing with GCE/CoPc(ma) electrode was observed between $1.20\ \mu moldm^{-3}$ and $42.0\ \mu moldm^{-3}$ concentrations. Moreover, sensitivity and LOD of the electrode were found as $0.26\ Acm^{-2}M^{-1}$ and $0.46\ \mu moldm^{-3}$ respectively. Although GCE/TiOPc(ma) electrode also sensed fenitrothion with a good selectivity, the linear range of this sensing was very narrow. GCE/Cl-MnPc(ma) electrode sensed all pesticides with similar voltammetric responses, thus its selectivity is poorer than the others, although it has good sensitivity for the pesticides.

1. Introduction

Due to the highly toxic effects of pesticides on human nervous system, there has been growing interest to develop new pesticide sensors with high sensitivity, ease preparation, low cost, reliability and selectivity [1–3]. The rapid detection of these toxic agents in the environment, public places, or workplaces and the monitoring of individual exposures to chemical warfare agents is crucial for human health. For these purposes, numerous pesticide sensors working with different techniques were published [2,4–6]. Among the techniques such as gas chromatography–mass spectrometry (GC–MS) [7,8], high-performance liquid chromatography (HPLC) [9], optical [10] approaches, and etc., the electrochemical methods were extensively preferred due to the one of the solution for disadvantages of the analyses at centralized laboratories, requiring extensive labor and analytical resources, and often results in a lengthy turnaround time. With the electrochemical methods, long analysis time and extensive sample

handling could be resolved with portability, rapid turnaround time, and cost-effectiveness. In many of pesticide sensing systems, enzymes, such as acetylcholinesterase enzyme (AChE) is the most studied functional material [5,11–13]. However, AChE based biosensors have especially low stability, difficulties of immobilization, leakage from the substrate surface, and low chemical and thermal stabilities [5,11–13]. Low selectivity is the main drawback of AChE based biosensors. Similar interaction reactions of AChE with the pesticides show very similar electrochemical responses for every pesticides [12,14,15]. In order to solve these mentioned limitations, the studies have been focused on new functional materials, which can be used as instead of enzyme-based sensors. Metal oxides and transition metal's organic compounds were investigated as the sensitive and selective enzymeless pesticide sensors [2,3,16,17]. For example, Kang J.F. et al. reported a parathion sensor based on electrodeposition of gold nanoparticles on a multi-walled carbon nanotubes modified glassy carbon electrode [18]. They reported a linear response to parathion in the concentration range from

6.0×10^{-5} to 5.0×10^{-7} M and a detection limit of 1.0×10^{-7} M. Although they reported reasonable sensitivity, an selectivity analysis was not performed. Similarly Gong J. et al. developed a biosensor based on zirconia nanoparticles decorated graphene nano-sheets (labelled as ZrO$_2$NPs-GNs) for the detection of methyl parathion [19]. The detection limit of 0.6 ng mL^{-1} was reported for methyl parathion (MP) in aqueous solutions. Although they reported reasonable sensitivity, selectivity phenomena were not mentioned. To increase the selectivity of the biosensors, molecularly imprinted sensors (MIPs) were generally developed [20–23]. Marx S. and his coworkers developed a molecularly imprinted sol–gel polymer and selectively detect the parathion [24]. Although MIPs sensors were studied as the mimic function of biological receptors with high selectivity, preparation difficulties and stability of the sensors are still important problems for these electrodes. Therefore, the studies based on stable, selective and sensitive pesticide biosensors are still take great attention. One of the functional materials presently studied as the selective and stable sensors are metallophthalocyanines (MPcs) [3,25,26]. Due to the high thermal and chemical stabilities and excellent redox activities, MPcs have been extensively studied in various technological fields as well as sensor applications. Tailoring of MPc with different metal cations in the cavity of Pc and various substituents ensure synthesizing MPcs having desired properties for the target applications [3,27–33]. Various MPcs were reported as pesticide sensors [34–38]. For instance, the formetanate hydrochloride was detected with 9.7×10^{-8} mol dm^{-3} LOD value with a CoPc-fMWCNT/GCE sensor [37]. Similarly, Sibulelo Vilakazi and co-workers constructed CoPc based electrode and sensed dicrotophos pesticide with the LOD value of 1.25×10^{-7} mol dm^{-3} [38]. It was clearly indicated that the metal center and substituents of MPcs and the electrode modification techniques considerably influence the sensing properties of these complexes. In our previous studies, we have reported different MPcs as selective and sensitive pesticide sensors [3,32,35]. Various sensor electrodes based on MPcs by using different modification techniques, such as, Langmuir-Blodgett, self-assembled monolayer thin films, electropolymerization, spin coating and click electrochemistry methods were reported. Here we have constructed new electrodes with the electropolymerization of MPcs having redox active Co^{II} (CoPc(ma)), Mn^{III} (Cl-MnPc(ma)), and Ti^{IV}O (TiOPc(ma)), and redox active and electropolymerizable [2-(4-{[(1E)-(4-morpholin-4-ylphenyl)methylene] amino}phenyl)ethoxy] containing substituents. MPcs having morpholin containing substituents was previously reported. Here MPcs having two polymerizable groups (morpholin and amino moieties) have been investigated to alter the redox activity of the electropolymerized films and to increase the selectivity and sensitivity of the sensors.

2. Experimental

2.1. Materials and equipment

The experimental measurements were carried on with high purity chemicals. Dimethylsulfoxide (DMSO) (Merck, K38436331 807, 99.9% purity), dichlorometane (DCM) and ultra-pure water ($\geq$ 18 MΩ, Milli-Q, Millipore) were used as solvents. Tetrabutylammonium perchlorate (TBAP) (Fluka Analytical, 86893, $\geq$ 99% purity) and LiClO$_4$ (Aldrich, 431567-50G) were used as supporting electrolytes in the solutions. Chlorophyros, fenitrothion, and methomyl were purchased from Sigma-Aldrich and they were used as received. 2-(4-Aminophenyl)ethanol, 4-morpholin-4-ylbenzaldehyde, and 4-nitrophthalonitrile were purchased from Aldrich.

The IR spectra were recorded on a Perkin Elmer 1600 FT-IR Spectrophotometer, using KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometers in CDCl$_3$, DMSO-d_6 and chemical shifts were reported (δ) relative to Me$_4$Si as internal standard. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC-MS/MS spectrometer. MALDI-MS of complexes were obtained in dihydroxybenzoic acid as MALDI matrix using nitrogen

laser accumulating 50 laser shots using Bruker Microflex LT MALDI-TOF mass spectrometer Bremen, Germany). Optical spectra in the UV–Vis region were recorded with a Perkin Elmer Lambda 25 spectrophotometer. Melting points were measured on an electrothermal apparatus and are uncorrected. The elemental analyses were performed on a Costech ECS 4010 instrument.

2.2. Synthesis

2.2.1. 2-(4-{[(1E)-(4-Morpholin-4-ylphenyl)methylene]amino}phenyl) ethanol (1)

A mixture of 2-(4-aminophenyl)ethanol (1.40 g, 10.4 mmol), 4-morpholin-4-ylbenzaldehyde (2.00 g, 10.4 mmol) and six drops of acetic acid were added to ethanol (120.0 mL) and the reaction mixture was stirred at 80 °C under an nitrogen atmosphere for 1 day. Then, the solvent was evaporated under reduced pressure to near dryness. The crude product was purified by recrystallization from ethanol. Yield: 2.60 g (81.0%), m.p. 267–269 °C. IR (ATR), ν/cm^{-1}: 3213 (OH), 3028 (Ar–H), 2969–2829 (Alif. C–H), 1609, 1594, 1560, 1517, 1504, 1438, 1383, 1347, 1263, 1234, 1220, 1177, 1112, 1065, 1050, 938, 921, 890, 820, 802. ^{1}H NMR (DMSO-d_6), (δ:ppm): 8.43 (s, 1H, =CH), 7.75 (d, 2H, Ar–H), 7.13 (d, 2H, Ar–H), 7.01 (d, 2H, Ar–H), 6.79 (d, 2H, Ar–H), 3.73 (t, 4H, CH$_2$–O), 3.51 (t, 2H, CH$_2$–O), 3.22 (t, 4H, CH$_2$–N), 2.91 (t, 2H, Ar–CH$_2$), 2.25 (s, 1H, OH). ^{13}C NMR (DMSO-d_6), (δ:ppm): 157.16, 156.08, 153.18, 143.76, 130.05, 127.52, 122.58, 116.10, 114.50, 66.40, 63.22, 47.83, 38.45. MS (ES$^+$), (m/z): 311 [M + H]$^+$. Elemental analysis: (found: C 73.80, H 6.90, N 9.28%, C$_{19}$H$_{22}$N$_2$O$_2$ (310) requires C 73.52, H 7.14, N 9.03%).

2.2.2. 4-[2-(4-{[(1E)-(4-Morpholin-4-ylphenyl)methylene]amino}phenyl) ethoxyl] phthalonitrile (3)

4-Nitrophthalonitrile 2 (0.660 g, 3.87 mmol) was dissolved in 20.0 mL dry DMF under N$_2$ 4-atmosphere and of 2-(4-{[(1E)-(4-morpholin-4-ylphenyl)methylene]amino}phenyl)ethanol 1 (1.20 g, 3.87 mmol) was added to this mixture. After stirring for 10 min at 50 °C, finely ground anhydrous K$_2$CO$_3$ (1.600 g, 11.61 mmol) was added portion within 2 h. The reaction mixture was stirred under N$_2$ at 50 °C for 4 days. Then, the reaction mixture was poured into water. The crude product was crystallized from ethanol. Yield: 1.31 g (78.0%), m.p. 216–218 °C. IR (ATR), ν/cm^{-1}: 3074 (Ar–H), 2969–2849 (Alif. C–H), 2231 (C≡N), 1624, 1594, 1563, 1514, 1484, 1447, 1380, 1340, 1307, 1246, 1232, 1192, 1122, 1051, 1030, 952, 923, 838, 803, 722, 651. ^{1}H NMR (DMSO-d_6), (δ:ppm): 8.49 (s, 1H, =CH), 8.11 (d, 1H, Ar–H), 7.80 (d, 3H, Ar–H), 7.40 (d, 1H, Ar–H), 7.38 (d, 2H, Ar–H), 7.22 (d, 2H, Ar–H), 7.05 (d, 2H, Ar–H), 4.12 (t, 2H, CH$_2$–O), 3.75 (t, 4H, CH$_2$–O), 3.25 (t, 4H, CH$_2$–N), 3.17 (t, 2H, Ar–CH$_2$). ^{13}C NMR (DMSO-d_6), (δ:ppm): 161.87, 160.69, 153.67, 151.59, 150.12, 136.76, 130.63, 126.82, 123.39, 122.88, 122.18, 121.66, 117.13, 116.40, 115.88, 114.38, 108.43, 71.12, 66.36, 47.66, 38.44. MS (ES$^+$), (m/z): 437 [M + H]$^+$. Elemental analysis: (found: C 74.42, H 5.40, N 12.98%, C$_{27}$H$_{24}$N$_4$O$_2$ (436) requires C 74.29, H 5.54, N 12.84%).

2.2.3. 2(3),9(10),16(17),23(24)-Tetrakis-[2-(4-{[(1E)-(4-morpholin-4-ylphenyl)methylene]amino}phenyl)ethoxy]phthalocyaninato cobalt(II) [CoPc(ma)], (3a)

4-[2-(4-{[(1E)-(4-Morpholin-4-ylphenyl)methylene]amino}phenyl) ethoxy]phthalonitrile 3 (0.150 g, 0.340 mmol), anhydrous cobalt(II) chloride (0.023 g, 0.170 mmol), n-pentanol (2.7 mL) and 1,8-diazabycyclo[5.4.0]undec-7-ene (DBU) (6 drops) was refluxed with stirring for 24 h under N$_2$ at 160 °C. After cooling to room temperature, 50 mL ethanol was added to precipitate the product. The precipitate was filtered and dried in vacuo. The crude product was purified by passing through an aluminum oxide column using CHCl$_3$:CH$_3$OH (100:2) as solvent system. Yield: 0.038 g (25.0%), m.p. > 300 °C. IR (ATR), ν/cm^{-1}: 3032 (Ar–H), 2918–2850 (Alif. C–H), 1601, 1515, 1494, 1466, 1406, 1378, 1332, 1262, 1228, 1196, 1171, 1112, 1093, 1051, 956,