



Novel ball-type homo- and hetero-dinuclear phthalocyanines with four 1,1'-methylenedipthalen-2-ol bridges: Synthesis and characterization, electrical and gas sensing properties and electrocatalytic performance towards oxygen reduction

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ABSTRACT

The new mono-nuclear Fe(II) phthalocyanine **2** and ball-type homo-dinuclear Fe(II)–Fe(II) phthalocyanine **3** were synthesized from the corresponding 4,4'-[1,1'-methylenebis-(naphthalene-2,1-diyl)]bis(oxy)diphthalonitrile **1**, and then ball-type hetero-dinuclear Fe(II)–Co(II) phthalocyanine **4** was synthesized from **2**. The novel compounds have been characterized by elemental analysis, UV/vis, IR and MALDI-TOF mass spectroscopies. Electrocatalytic activity of the high-surface area carbon, Vulcan XC-72R (VC) and Nafion® (Nf) supported complexes towards oxygen reduction was investigated and compared by surface cyclic voltammetry and rotating ring-disk electrode experiments in acidic medium. The VC/Nf/**2** and especially VC/Nf/**3** modified glassy carbon electrodes showed high catalytic performance, producing water as the main product through the direct four-electron path. A.c. and d.c. measurements were performed on spin coated **2–4** films as a function of temperature (290–436 K). The d.c. results showed an activated conductivity dependence on temperature. The a.c. results gave a temperature dependent frequency exponent *s*. Gas sensing properties of the films for the volatile organic compounds (VOCs) (toluene, chloroform, ethanol and carbontetrachloride) were also investigated in the temperature range from 290 to 436 K. It was observed that the operating temperature had a considerable effect on sensing characteristics of **3** but not **4**.

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1. Introduction

The synthesis and study of metallophthalocyanine (MPc) dimers and multimers are among the priorities of modern Pc chemistry since this type of complexes have attracted special interest in areas such as semiconductors [1], nonlinear optics, optical limiting [2], liquid crystals [3], electrochromism [4], and photovoltaic, solar and fuel cells [5,6]. However, the studies on the synthesis of ball-type bis MPcs and especially the investigation of their electrical, electrochemical [7,8], electrochromic [9], gas sensing [10] and nonlinear optic properties [11] have been rarely reported in the literature. The first synthesis of ball-type bis MPcs was reported by Zefirov group [12,13]. However, these studies did not include the investigation of their mentioned properties, and did not continue until we

have reported for the last 6 years on the synthesis and properties of this type of Pcs with various linkages and metal centers, usually including zinc and cobalt. These novel compounds showed interesting electrical [14–16], electrochemical [17], gas sensing [18–20] and optical properties [21,22], usually due to strong interaction between the face-to-face Pc rings or two metal centers. The fact that the nature of the metal centers leads to important changes in Pc characteristics and our continuing efforts in the design of novel macrocycles with potential applicability in various technological areas prompted us to synthesize new examples of ball-type bis MPcs with iron–iron and iron–cobalt centers.

Cofacial Fe–Fe bis Pcs are considered as suitable complexes for homogeneous and heterogeneous catalyses under harsh conditions which include the presence of reactive species such as singlet oxygen and free radicals. By using these catalysts, some researchers have tried to convert CO₂ to CH₃OH. As it is well known, carbon dioxide contributes to the green-house effect and, possibly, respiratory organ diseases. Therefore, detection and the control of CO₂ concentration are extremely important. In literature, cofacial

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Fe–Fe bis Pcs synthesized from mono iron Pcs by using oxygen [23] and nitrogen [24] bridges [(PcFe)₂O, (PcFe)₂N], and these complexes were also used as catalysts for the reaction producing CH₃OH from CH₄. Another application area for cofacial Fe–Fe bis Pcs is fuel cells. The first priority for fuel cell catalyst development, at present is to explore new non-noble catalysts and enhance catalytic activity through some innovative ways of preparation and synthesis. It is well known that N₄-chelates of transition metals such as iron and cobalt Pcs and porphyrins are the most popular catalysts for oxygen reduction (OR). OR reaction has a special importance [25–27] due to its application in proton exchange membrane fuel cells which convert chemical energy directly to electrical energy with a minimum energy loss. Accordingly, a significant amount of work has been done in the field of transition metal macrocyclic-catalyzed OR [28–30]. The most common macrocycles studied are iron and cobalt Pcs and porphyrins. In the presence of these complexes, OR occurs at significantly less negative potentials, which is attributed to the formation of suitable intermediates including metal [28–30]. It appears that MPcs are generally easier to synthesize and more cost effective to produce when compared to metal porphyrins. In addition, the added tetraaza nitrogens give them higher stability, relative to metal porphyrins. The cofacial complexes involving two metal centers are much more efficient in catalyzing OR, due to the possibility of peroxide intermediate formation. Although the catalytic activity of cofacial porphyrin dimers towards OR was investigated widely in previous literature [31–36], there has been no report on that of ball-type Pc dimers, except the recent ones reported by our group [5,6].

The d.c. and a.c. electrical properties of Pc thin films have a vital importance for the fabrication of practical devices. For example, we need to know the effect of the temperature on the electrical properties of the film to achieve the accurate design of any device. It is also well known that the detection of VOC is highly interesting for a number of applications, e.g. sensing indoor air quality, breath monitoring, fire detection, as well as safety application [37]. A number of materials including phthalocyanine [38,39] have been used as sensitive coating for the recognition of the organic solvent molecules.

In this study, we synthesized and characterized tetra-1-((2-(3,4-dicyanobenzyl)-1,8a-dihydronaphthalen-1-yl)methyl)naphthalen-2-olate substituted Fe(II) mono-nuclear Pc **2** and ball-type 1,1'-methylenediphenyl-2-ol-linkaged Fe(II)–Fe(II) **3** and Fe(II)–Co(II) **4** Pcs. The complexes **3** and **4** are the first examples of ball-type iron–iron homo- and iron–cobalt heterodinuclear MPcs. We also studied the electrocatalytic performances of the complexes for OR in a fuel cell-similar acidic reaction medium involving a proton conductive polymer, Nafion® (NF) and a high-surface area conducting nanocarbon like commercial Vulcan XC-72R (VC), and discussed the outcomes in relation with their surface redox properties. In addition, the electrical and gas sensing properties of the complexes were examined.

2. Experimental

The starting material **1** was synthesized by the method described previously in the literature [14]. IR spectra were recorded on a Shimadzu FTIR-8300 spectrophotometer as KBr pellets. Electronic spectra were recorded on a Shimadzu UV-1601 spectrophotometer. Elemental analyses were performed by the Instrumental Analysis Laboratory of Tubitak–Ankara. Mass spectra were acquired on a Voyager-DETM PRO MALDI-TOF mass spectrometer (Applied Biosystems, USA) equipped with a nitrogen UV-Laser operating at 337 nm. Spectra were recorded reflectron modes with average of 50 shots.

2.1. Synthesis and characterization of compounds

2.1.1. Synthesis of [2,10,16,24-tetrakis(3,4-dicyanobenzylmethylenedioxy-naphthalenyl)phthalocyaninato iron(II)] (**2**)

The mixture of compound **1** (0.2 g, 0.365×10^{-3} mol) and Fe(OAc)₂ (0.016 g, 0.091×10^{-3} mol) was powdered in quartz crucible and taken the powder mixture in reaction tube. Then 0.3 ml DMF was added to the reaction mixture and heated in the sealed glass tube for 10 min under dry N₂ atmosphere at 400 °C. After cooling to room temperature, 3 ml of DMF was added to the residue to solve the product. The reaction mixture was precipitated by adding acetic acid. The precipitate was filtered and washed with acetic acid, ethanol and acetonitrile for 12 h, respectively in the soxhlet apparatus. The crude product was purified by column chromatography with silica gel eluting with chloroform a gradient of chloroform–THF up to 5% THF. This compound is soluble in chloroform (slightly), THF, DMF and DMSO, *M_p* > 350 °C. Yield: 75 mg (36%). IR (KBr pellet) $\nu_{\max}/\text{cm}^{-1}$: 523, 749, 816, 995, 1086, 1120, 1232, 1335, 1394, 1402, 1452, 1510, 1592, 1722, 2231, 2815, 2830, 3066. Anal calculated for C₁₄₈H₈₀FeN₁₆O₈: C 78.44%, H 3.56%, N 9.89%, found C 78.32%, H 3.67%, N 9.71%. MS (MALDI-TOF): *m/z* 2265 (M+H).

2.1.2. Synthesis of [8,8'-tetrakisbis-(2',10',16',24'-phthalocyaninato)diiron(II)-methylenedioxy-naphthalene] (**3**)

The mixture of compound **1** (0.2 g, 0.365×10^{-3} mol), Fe(OAc)₂ (0.128 g, 0.728×10^{-3} mol) and 0.5 ml DMF was taken in a sealed tube. Reaction mixture was heated for 10 min under dry N₂ atmosphere at 400 °C. The dark green reaction product was obtained, isolated and purified with using the same procedure explained above for **2**. This compound is soluble in THF, DMF and DMSO. Yield: 82 mg (39%). *M_p* > 350 °C. IR (KBr pellet) $\nu_{\max}/\text{cm}^{-1}$: 524, 748, 815, 965, 994, 1085, 1120, 1232, 1308, 1334, 1401, 1462, 1510, 1592, 1604, 1721, 2955, 3059. Anal calculated for C₁₄₈H₈₀Fe₂N₁₆O₈: C 76.55%, H 3.47%, N 9.65%, found C 76.37%, H 3.77%, N 9.69%. MS (MALDI-TOF): *m/z* 2321 (M+H).

2.1.3. Synthesis of [8,8'-tetrakisbis-(2',10',16',24'-phthalocyaninato)iron(II)cobalt(II)-methylenedioxy-naphthalene] (**4**)

The compound **2** (0.04 g, 1.76×10^{-5} mol), Co(OAc)₂·4H₂O (0.013 g, 5.22×10^{-5} mol) and 1 ml DMF were taken in a sealed glass tube and then heated for 12 h under dry N₂ atmosphere at 200 °C. After cooling to room temperature, the reaction mixture was precipitated by adding acetic acid. The precipitate was filtered and washed with acetic acid, ethanol and acetonitrile for 12 h respectively in the soxhlet apparatus. The crude product was purified by column chromatography with silica gel eluting with chloroform a gradient of chloroform–THF up to 5% THF. This compound is soluble in THF, DMF and DMSO, *M_p* > 350 °C. Yield: 25 mg (63%). IR (KBr pellet) $\nu_{\max}/\text{cm}^{-1}$: 748, 814, 995, 1061, 1095, 1232, 1335, 1408, 1461, 1511, 1593, 1607, 1720, 2953, 3057. Anal calculated for C₁₄₈H₈₀CoFeN₁₆O₈: C 76.45%, H 3.47%, N 9.64%, found C 76.32%, H 3.56%, N 9.55%. MS (MALDI-TOF): *m/z* 2332 (M+H).

2.1.4. MALDI sample preparation

MALDI matrix, α-cyano-4-hydroxycinnamic acid (ACCA) was prepared in tetrahydrofuran at a concentration of 10 mg/ml. MALDI samples were prepared by mixing sample solutions (2 mg/ml in tetrahydrofuran) with the matrix solution (1:10, v/v) in a 0.5 ml eppendorf® microtube. Finally 0.5 μl of this mixture was deposited on the sample plate, dried at room temperature and then analyzed.

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